
# National German competition 2004

**Volume 10**

# Preface

To become a member of the German IChO-team you have to be successful in 4 rounds.
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 the students who solve about 70% 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 members 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 elected.

## Contact addresses:


IPN z.H. Dr.Bünder
Olshausenstraße 62
24098 Kiel
tel: +431-880-5013 (3168)
fax: +431-880-5468
email: buender@ipn.uni-kiel.de

StD.Wolfgang Hampe
Habichtweg 11
24147 Klausdorf
tel: +431-79433
email: Hampe@t-online.de

Association to promote the IChO
(Association of former participants and friends of the IChO)
Christoph Jacob
Erlenweg 4
61138 Niederdorfelden
tel. +6101-33100
email: chjacob@web.de


**Internet address :** **www.fcho.de**

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# Part 1

## The problem set of the four rounds

# First Round (homework)

## Problem 1-1: Gases in cakes or elsewhere

Salt of hartshorn can be found in recipes for ginger bread as baking-powder - a remedy to rise dough. It is a mixture of ammonium hydrogencarbonate and ammonium carbamate.
In books you often find other compositions.

*a) Give other specifications of the composition of salt of hartshorn and the place you found it.*

Upon heating at 180°C both compounds decompose. Consider salt of hartshorn as a mixture of equal amounts of ammonium hydrogencarbonate and ammonium carbamate.

*b) Write a balanced reaction equation of the decomposition. Calculate the maximum increase of volume of dough when 1 g of salt of hartshorn decomposes at 180° C (p=1.013 bar).*

The temperature is a bit higher in the next question. At very high temperatures molecular hydrogen decomposes into atoms. The equilibrium constant for the reaction $H_2 \rightleftarrows 2\,H$ at 3000 K has the value $Kp = 2.51 \cdot 10^{-2}$ bar.
Imagine a system containing hydrogen only with a total pressure of p = 980 hPa.

*c) Calculate the partial pressure of the atomic hydrogen in equilibrium.*

*d) Calculate the density of the gas (kg/m$^3$) in equilbrium under the conditions given.*

## Problem 1-2: Sea water

Students have to investigate sea water. They have to determine the concentrations of calcium-, magnesium-, sodium-, chloride- and sulfate ions.

To simplify the question assume that the amount of carbonate ions is neglectible and that there are no other ions in sea water.

The following investigations are made:

1. 10 mL of see water pass a cation exchanger. Afterwards the solution is titrated with a solution of sodium hydroxide (c = 0.500 mol/L).
   Mean value of consumption: 11.76 mL.
2. 10 mL of see water are diluted to give 100 mL. 10 mL of this diluted solution are titrated with a solution of silver nitrate (c = 0.086 mol/L).
   Mean value of consumption: 6.21 mL.
3. An indicator buffer tablet is added to 10 mL of sea water. The solution is titrated with a solution of EDTA (c = 0.05 mol/L).
   Mean value of consumption: 12.60 mL.
4. An excess of ammonium oxalate is added to 100 mL of sea water. The precipitate is filtered off and dissolved in hot diluted sulfuric acid. The resulting solution is titrated with potassium permanganate (c = 0.02 mol/L).

Mean value of consumption: 24.00 mL.

a) *Calculate the concentration of the ions mentioned above (g/L). Show your way of reasoning.*
*Give balanced equations for the reactions performed. Use „RH" as a symbol for the cation exchanger loaded with acid, „$H_4Y$" for EDTA or $Y^{4-}$ for its anion.*

b) *In performing the titration with silver nitrate (investigation 2.) some droplets of potassium chromate are used as an indicator. Explain how it works.*

c) *How can the students recover the silver from the silver chloride precipitate (investigation 2.)? What is the value of the silver gained from treatment of 5 L solution of a silver salt (c = 0.2 mol/L)? Price of silver: see newspapers.*

d) *Draw a line-bond formula of the anion of EDTA ($Y^{4-}$) and a structural formula of the calcium-EDTA complex.*
*Explain the colour change at the equivalence point in investigation 3.*

e) *In the inland it's not always possible to get sea water. The following salts are available for a teacher: NaCl, $Na_2SO_4 \cdot 10\ H_2O$, $CaCl_2 \cdot 6\ H_2O$, $MgCl_2 \cdot 6\ H_2O$, $MgSO_4 \cdot 7\ H_2O$.*
*Calculate how to compose a portion of „sea water" of the composition you found above using all or some of the salts available.*

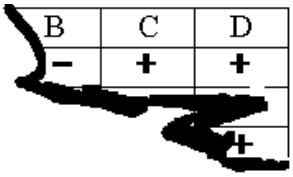
## Problem 1-3: A present

Eight substances were given to a school as a gift: Ag, Fe, Cu, Mg, $AgNO_3$, $Fe(SO_4)_2$, $Cu(NO_3)_2$ and $Mg(NO_3)_2$. Unfortunately the labels on the bottles could not be read.

A student had to investigate the content of the bottles by preparing solutions of the salts (marked 1, 2, 3 ,4) and adding the metals (marked A, B, C, D) to each solution. In case of reaction he wrote „+" otherwise „-" in his table.

| | A | B | C | D |
|---|---|---|---|---|
| 1 | | | | |
| 2 | | | | |
| 3 | | | | |
| 4 | | | | |

After finishing his task he was happy until he turned a bottle with concentrated sulfuric acid over.
Only two pieces of his table shown beside remained.
Other students laughed at him but the next day he came, showed the right result and said there were even two pieces of information he did not need.





a) *Assign the name of the compounds to A, B, C, D, 1, 2, 3 ,4 and show your way of arguing.*

*b) Which are the two pieces of information the student did not need?*

## Problem 1-4 Dangerous food

Stones of fruit and bitter almonds contain a compound A that decomposes upon acidic hydrolysis into hydrocyanic acid among other compounds. When this fact became evident in the 19$^{th}$ century it caused great surprise - and was frightening too.
Compound A has the molecular formula $C_{20}H_{27}O_{11}N$.
An precise analysis of the hydrolysis products showed that besides hydrocyanic acid glucose and benzaldehyde are formed.

*a) Write a balanced reaction equation of the acidic hydrolysis of compound A.*

Further investigation showed A to be a glycoside. Glycosides are compounds widespread in plants consisting of a sugar component and a non sugar component. These two component are connected by a glycosidic bond - similar to an ether bond.

*b) Draw the structural formula of A. Don't specify the sugar component, write it as molecular formula [$C_xH_yO_z$]. Thus stereochemistry can be ignored.*

# Second Round (homework)

## Problem 2-1

Willi Wusel is used to keep his nails and screws in glasses. One day, he discovers a forgotten glass with a rusty nail where rain has got in in his garden. When he takes out the nail, a reddish brown layer of $Fe(OH)_3$ can be found at the glass. In order to clean the glass, he continuously adds hydrochloric acid (that he has found in his shed) to the water in the glass until the layer has dissolved completely. Three quarters of the glass (0.2 L) are filled with a yellow liquid then.

He determines the pH of the solution with pH paper. The pH is 2.0. The concentration of the hydrochloric acid that he has found in the shed is 0.5 mol/L. He puts a paper clip of copper into the yellow solution. After some time, the colour of the solution has changed.

*a) What is the pH of hydrochloric acid found in the shed?*

*b) Show that the following equation is approximately valid for the concentration of chloride ions in the solution after the dissolution of the layer:*

$$c(Cl^-) = 3 \cdot \frac{K_L}{K_W^3} \cdot c(H^+)^3 + c(H^+)$$

*c) Calculate the concentrations of chloride and iron(III) in the yellow solution. What was the amount of rust (in mmol and mg) that the reddish brown layer consisted of?*

*d) How much hydrochloric acid (in mL) did Willy need to dissolve the layer?*

*e) How does the colour of the solution change? Give reasons for your answert. Determine the concentrations of the iron- and copper ions.*

**Useful formalas and values:**

solubility product of $Fe(OH)_3$: $K_L = 2.0 \cdot 10^{-39}\ mol^4 \cdot L^{-4}$

ionic product of water: $K_W = 1.0 \cdot 10^{-14}\ mol^2 \cdot L^{-2}$

$E_0\,(Fe^{3+}/Fe^{2+}) = 0.771$ V $\quad E_0\,(Cu^{2+}/Cu) = 0.345$ V

The temperature is summer-like (27 °C).

## Problem 2-2

In a nitrogen atmosphere, 85.0 mg of an unknown reddish brown metal iodide are put into a cylindrical metal tube having a diameter of 12.0 mm and a length of 18.3 cm. The following values for temperature and pressure are measured: $\vartheta$ = 25.0 °C, p = 1.013 bar. Afterwards, the tube is closed and heated to a constant temperature of 450 °C. There is a continuous pressure change in the tube until there is a constant pressure value of 3.346 bar. After opening the metal tube that is still hot, a violet vapour escapes; the initial substance has disappeared.

*a) Determine the original metal iodide assuming that all gaseous substances show an ideal behaviour.*

One of the gas-phase reactions that have been investigated the best is the reaction of hydrogen with iodine:

$$H_2 + I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,HI$$

The following rate constants result from kinetic measurements at different temperatures:

| temperature [K] | $k_1$ [L·mol$^{-1}$·s$^{-1}$] | $k_{-1}$ [L·mol$^{-1}$·s$^{-1}$] |
|---|---|---|
| 400 | $8.37\cdot10^{-12}$ | $3.25\cdot10^{-14}$ |
| 500 | $2.48\cdot10^{-7}$ | $1.95\cdot10^{-9}$ |
| 600 | $2.38\cdot10^{-4}$ | $2.97\cdot10^{-6}$ |
| 700 | $3.22\cdot10^{-2}$ | $5.61\cdot10^{-4}$ |
| 800 | 1.27 | $2.85\cdot10^{-2}$ |

b) *Is the reaction exothermal or endothermal? Give reasons. What principle has been applied?*

c) *Calculate the reaction enthalpy and the reaction entropy of the formation of HI assuming that these values are independent of temperature in the investigated range .*

d) *Caulate the degree of dissociation of HI at 6 K. How does it change with pressure assuming the validity of the ideal gas law?*

Elemental iodine is only poorly soluble in water. In the presence of iodide ions, however, the solubility in water increases considerably. This can be attributed to the formation of triiodide anions $I_3^-$ :

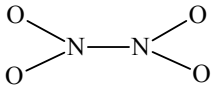
$$I_2 + I^- \rightleftharpoons I_3^-$$

A certain amount of $I_2$ is shaken together with $CS_2$ and an aqueous KI-solution of the concentration $c_0(KI) = 31.25\cdot10^{-3}$ mol/L until there is an establishment of equilibrium. Then, the concentration of $I_2$ is determined by titration with $Na_2S_2O_3$. In the $CS_2$-phase, it is 32.33 g/L and in the aqueous solution, it is 1.145 g/L. The coefficient od distribution for $I_2$ between $CS_2$ and water is 585.

e) *Calculate the equilibrium constant for the formation of triiodide anions.*

## Problem 2-3

a) *Draw the three-dimensional structure of the complex ions that can be found in the compounds* **A – H** and *find out which of them are chiral*. *To increase clarity and facilitate drawing, you can use abbreviations for the chelate ligands*, N——N *for 2,2'-bipyridine ,* O——O *for oxalate,* N——O *for glycinate and*



*for EDTA.*

*[please write down, however, the complete structural formula of complex* **H** ]
*The coordination geometry of the metal must be clearly readable .*

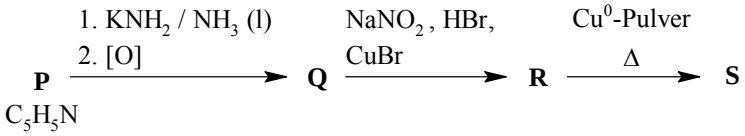
**A**: *trans*-$[Cu^{II}(gly)_2]$ **B**: $[Zn(gly)_2]$ **C**: $[Ca(EDTA)]^{2-}$
**D**: $[Cu(bpy)_2]ClO_4$ **E**: $K_3[Fe(C_2O_4)_3]$ **F**: $K_2[Cu(C_2O_4)_2]$
**G**: $[Co^{III}\{cis\text{-}Co^{III}(NH_3)_4(\mu\text{-}OH)_2\}_3]^{6+}$ **H**: $[Pt(meso\text{-}1,2\text{-}(NH_2)_2C_6H_{10})BrCl]$

**Explanations:**
gly = glycinate bpy: 2,2'-bipyridine 1,2-$(NH_2)_2C_6H_{10}$ 1,2-diaminocyclohexane; concern*i*ng **G**: the μ-OH-groups bind the outer Co-ions to the central ones.

*b) How many different types of achiral monodentate ligands ($L^1$, $L^2$,…) are needed at least to obtain a chiral complex with an octahedrally coordinated metal ion (M)?*

*c) What is the composition of the complex in problem b)? Draw all possible structures of this complex. Please write down which complexes are chiral and which are not chiral.*

The following equation describes the synthesis of a ligand and a derived complex:




*d) Complete the synthesis scheme. **P** is a toxic, weak base that has an unpleasant smell and can be mixed with water.*

*e) A surplus of* **S** *reacts with iron(II)-sulfate; complex* **T** forms*. What is the composition of this complex? Draw the structure(s) of all isomers. Draw as well the orbital scheme for the d-orbitals.*

The investigation of the gradual formation of complex **T** shows that the equilibrium constant for the last step of complex formation is higher than the equilibrium constant for the penultimate step.

*f) Write down a possible explanation that considerates the electronic situation of the complexes.*

## Problem 2-4

Silicon dioxide occurs in nature in its crystalline (e.g. mountain crystal) as well as in its amorphous (e.g. opal) form. $SiO_2$-resources can be used for the production of water glasses. $SiO_2$ (quartz sand) is molten with much $Na_2CO_3$. The glass that has formed is dissolved in water at 160°C under pressure. If such a water glass is analyzed by $^{29}$Si-NMR-spectroscopy, mostly 5 groups of signals can be found in the spectrum.

*a) Why does gaseous $SiO_2$ that is analogous to* $CO_2$ *not exist under normal conditions?*

*b) Give examples for the appplication of water glasses.*

*c) Which 5 principal* Si*-environments can be assigned to the $^{29}$*Si*-NMR-signals of water glasses?*

Another possibility of using $SiO_2$ is its reduction to Si that is used e.g. for the production of solar cells in its purified form. It can as well be processed to important basic chemicals. Elemental Si reacts with chloromethane at about 300°C in the presence of catalysts. The main products that form are methylchlorosilanes $(CH_3)_nSiCl_{4-n}$ (n = 1, 2, 3).

*d) Write down coordinated reaction equations for the reactions of these 3 chlorosilanes with an excess of water.*

*e) What are the hydrolysis products of* $(CH_3)_2SiCl_2$ *and what is their technical sifnificance?*

Silicon that is an element of the fourth main group is mostly tetravalent. Its oxidation number is +4 in compounds. There are only a few examples of stable compounds with bivalent Si having the oxidation number +2. Compound **E** is an example of such a compound. **E** is produced by the condensation of 1,2-ethanedial with 2 equivalents of **A** (**A** = primary amine, $C_4H_{11}N$, 2 signals in the $^{13}C$-NMR-spectrum) to **B**. **B** reacts with 2 equivalents of Li to form **C**. Then, C reacts with $SiCl_4$ to form **D** and 2 LiCl. The reduction of **D** with potassium results in **E**.

*f) Write down the equations for all the mentioned reactions. Write down the structural formulas of the compounds* **A**, **B**, **C**, **D**,*and* **E**. *Conclude from the electronic structure of* **E** *the reason for the extraordinary stability of the compound.*

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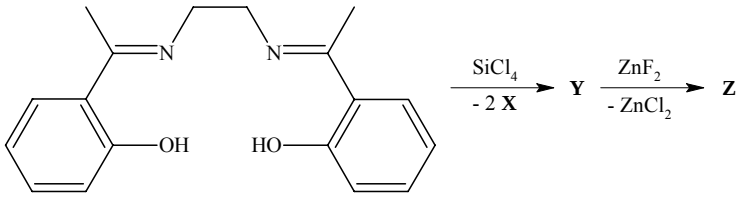
It is true that the oxidation number of Si is +4 in a different group of interesting Si-compounds, but the Si-atom has additional coordinated donor atoms and reaches the coordination number 6 (compounds in which the coordination number that is to be expected according to the octet rule is exceeded are called hypercoordinated compounds). The compounds **Y** and **Z** are such compounds and can be obtained by the following reaction:




**Z** crystallizes from acetonitrile as monoclinic crystals. 1 mol of acetonitrile crystallizes as well in 1 mol of **Z**. The unit cell of **Z** has the following dimensions: a = 12.3826 Å, b = 10.8405 Å, c = 13.8507 Å, $\beta$ = 98.800°, $\alpha = \gamma$ = 90°.

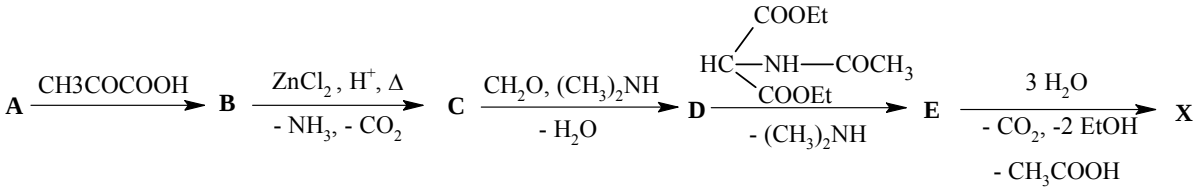
*g) Write down the structural formulas of* **Y** *and* **Z** *. What is* **X***?*

*h) Why can Si exceed the octet rule in contrast to carbon?*

*i) Write down the value of n (n = number of molecules of* **Z** *and acetonitrile that are in the unit cell, n = even whole number, assuming that every non hydrogen atom requires a space of 15 to 19* $Å^3$ *. Calculate the density of* **Z***.*

## Problem 2-5

The natural substance **X** that is extremely important for human beings can synthesized the following way:



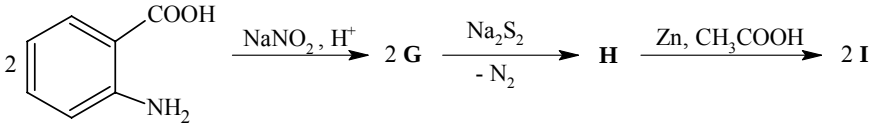

Substance **C** that is a byproduct of this reaction (total formula: $C_8H_7N$) and **E** are natural degradation products of **X** and can be found in human faeces. If **C** is oxidized in the body it will form the product **Cox** that can be found in urine and is an important reactive intermediate in an industrial process: The important dye **F** forms in an alkaline medium from two molecules of **Cox**.

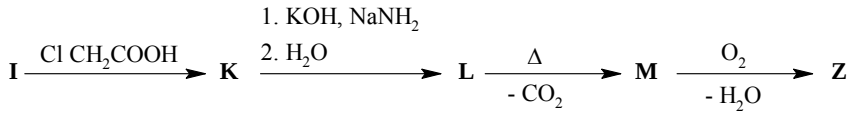
The results of the elemental analysis of the initial compound **A** are the following values: 66.62% of carbon, 7.47% of hydrogen and 25.91% of nitrogen; The molecular peak is at *m/z* =108 in the mass spectrum..

*a) Write down the structural formulas of the compounds* **A – E***,* **X***,* **Cox** and **F***.*

*b) What is the reaction mechanism of the reaction from* **B** *to* **C***?*

The red dye **Z** has a structure that is analogous to that of **F**. Its total formula $C_{16}H_8O_2S_2$ can be obtained synthetically from anthranilic acid:




*c) Write down the structural formulas of the substances* **G – M** *and* **Z***.*

# Third Round, Test 1

A formulary and a periodic table were made available for the two tests of the third round.

## Problem 3-1

A) Concentrated sulfuric acid was added to the following salts.
*In which case can a redox reaction not be expected?*

| a) $NaNO_3$ | b) $Na_2S_2O_3$ | c) NaI | d) $Na_3PO_4$ | e) $Na_2C_2O_4$ | f) $NaClO_3$ |
|---|---|---|---|---|---|

B) *Which of the following elements has the lowest second ionization energy?*

| a) Be | b) K | c) Cs | d) S | e) Ba |
|---|---|---|---|---|

C) *Which of the following ions has the smallest ionic radius?*

| a): $Ag^+$ | b) $F^-$ | c) $H^-$ | d) $Al^{3+}$ | e) $Na^+$ |
|---|---|---|---|---|

D) *Which of the following particles has the most negative redox potential?*

| a): $F_2$ | b): Ag | c): Na | d): $Li^+$ | e): C |
|---|---|---|---|---|

E) *Which of the following empirical formulas represents exactly 5 isomers?:*

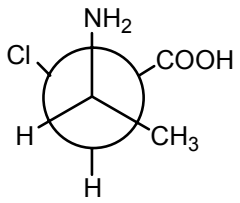
| a): $C_4H_9Cl$ | b): $C_7H_{16}$ | c): $C_6H_6$ | d): $C_3H_7Br$ |
|---|---|---|---|

F) *Which of the following empirical formulas represents the highest number of isomers?*

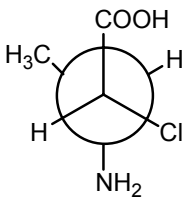
| a): $C_4H_9Cl$ | b): $C_7H_{16}$ | c): $C_6H_6$ | d): $C_3H_7Br$ |
|---|---|---|---|

G) *Which of the following* images does not represent *(R,R)-2-chlorine-3-aminobutanoic acid?*

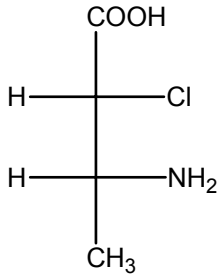
*a)*



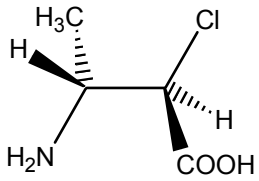

*b)*



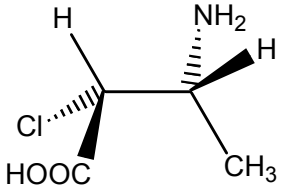

*e)*




*c)*



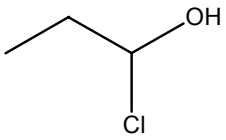

*d)*



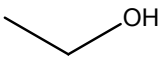

H) *Which of the following molecules has the smallest dipole moment?*

| a) $CO_2$ | b) $SiO_2$ | c) $SO_3$ | d) $SF_6$ | e) $UF_6$ | f) $XeF_6$ |
|---|---|---|---|---|---|

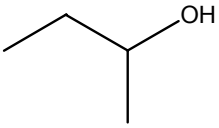
I) *In which of the following alcohols is the hydroxyl group oxidized to the aldehyde group the fastest (e.g. with dichromate)?*



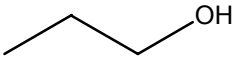
a)



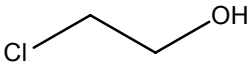
b)



c)

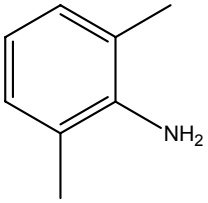


d)

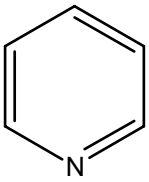


e)

J) *Which of the following compounds is the strongest base?*



a)



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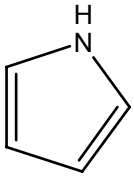
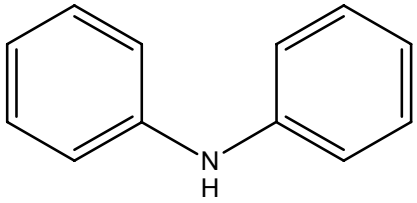


c)



d)

## Problem 3-2 Unknown solutions

In 7 test tubes with numbers from 1 to 7, there are dilute aqueous solutions of the following substances:

$CuSO_4$ $AgNO_3$ NaCl $Na_2CO_3$ NaOH HI $H_2SO_4$

In the test tubes **X** and **Y**, there are dilute aqueous solutions of an unknown substance each. The following reactions could be observed each time two of the nine solutions were mixed:

| | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **X** | **Y** |
|---|---|---|---|---|---|---|---|---|---|
| **1** | * | / | / | / | p(b) | p(bl) | p(bl) | p(b) | / |
| **2** | | * | p(w) | / | / | / | / | / | / |
| **3** | | | * | / | p(y) | p(b) | p(wy) | p(y) | p(w) |
| **4** | | | | * | / | / | gas | / | / |
| **5** | | | | | * | / | gas | / | p(b) |
| **6** | | | | | | * | / | pun. smell | p(bl) |
| **7** | | | | | | | * | / | p(bl) |
| **X** | | | | | | | | * | p(b) |
| **Y** | | | | | | | | | * |

Meanings of the abbreviations:

| | | | |
|---|---|---|---|
| p(w) | = white precipitate | p(wy) | = white-yellow precipitate |
| p(y) | = yellow precipitate | p(b) | = brown precipitate |
| p(bl) | = light blueprecipitate | gas | = gas development |
| pun. sm | = pungent smell | / | = no reaction observed |

*a) Write down which substance can be found in which test tube.*

*b) Which kinds of substances are X and Y?*

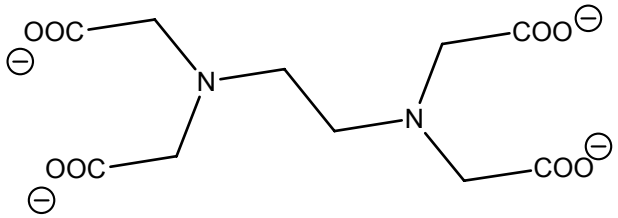
*c) Write down the reaction equations and ionic notations that are the beses of all the observations that are expected to happen.*

## Problem 3-3 Iron-EDTA complexes

In an aqueous solution, iron(III)-ions react with EDTA (ethylenediaminetetraacetic acid = Y) almost quantitatively. **A** $[FeY]^-$ forms primarily. This complex is sterically tense and continues reacting with $OH^-$ to form the complexes **B** $[FeY(OH)]^{2-}$ (lg $K_1$ = 6,45) and **C** $[FeY(OH)_2]^{3-}$ (lg $K_2$ = 4.53). It comes to a steric relaxation. The coordination number of iron is 6 in all these complexes.

$$[FeY]^- + OH^- \rightleftharpoons [FeY(OH)]^{2-} \qquad \lg K_1 = 6.45$$

$$[FeY(OH)]^{2-} + OH^- \rightleftharpoons [FeY(OH)_2]^{3-} \qquad \lg K_2 = 4.53$$




EDTA (**Y**)

*a) Calculate the content of $[FeY(OH)]^{2-}$ and $[FeY(OH)_2]^{3-}$ ions in a solution still containing 0.001 mol/dm³ $[FeY]^-$ . The pH-value of the solution is 8.*
*Why is the complex-formation constant $K_2$ considerably lower than $K_1$?*

Instead of $[FeY(OH)_2]^{3-}$, Ph-OH complexes of the type $[FeY(OH)(PhO)]^{3-}$ form in the presence of phenols. Almost no $[FeY(PhO)_2]^{3-}$ forms, however, in an excess of phenol. Ligands like 8-hydroxychinoline or 1,2-dihydroxybenzene-derivates, however, can as well displace the second hydroxo ligand from the initial compound **C**.

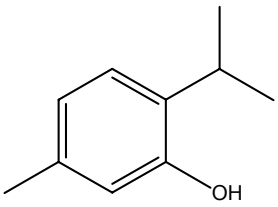
*b) Sketch a complex $[FeY(OH)(PhO)]^{3-}$, having the reaction behaviour described.*

*c) Why is $[FeY(OH)_2]^{3-}$ much more paramagnetic than $[Fe(CN)_6]^{3-}$?*

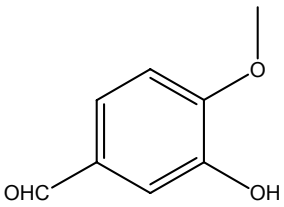
The exchange of a hydroxo ligand of **C** by a ligand like phenolate, thioalcoholate or thiocyanate results in the formation of intensively coloured (red or blue) complexes. In contrast to that, **C** is coloured only very weakly (orange-yellow).

*d) What is the reason for the intensive colours of the phenolato-, thioalcoholato- und thiocyanato-complexes?*

This intensive colour of the complexes of the type $[FeY(OH)(PhO)]^{3-}$ can be used for UV/VIS-spectroscopic determination of phenol contents.
In an instruction for the preparation of such a photometry solution you can read the following:
„ 25 mL of 0.4 M EDTA-solution and 2 mL of 1.0 M $Fe(ClO_4)_3$-solution are mixed and analyte-solution is added to this mixture. The pH-value has to become 8 with $NH_3$ and $HClO_4$. Then, the mixture is filled up to 50 ml and the extinction is measured in a 1 cm cuvette.
The results of the measurements are analyzed the following way: The amount of phenol in the added analyte is calculated from the extinction (E) according to the equation
$E = b \cdot c + a$ (c in mg)
The values of the factors a and b are the following: for thymol: a = 0.013, b = 0.0048 $mg^{-1}$
for vanillin: a = 0.008, b = 0.0245 $mg^{-1}$




thymol




vanillin

According to the method mentioned above, thymol is determined in an extract of a natural substance. 1 g of a raw substance is dissolved in methanol and filled up to 5 mL. 1 mL of this solution is added as an analyte to the photometry solution described above. The measurement of the extinction (at $\lambda_{max}$ = 540 nm), however, is carried out in a 5 cm cuvette. The extinction is: E = 1.505.

e) *Determine the content of thymol (mass fraction and mole fraction) in the extract of a natural substance that has been analyzed.*

f) *Write down the apparently molar coefficient of extinction $\varepsilon'$ for the complex $[FeY(OH)(Thymolat)]^{3-}$. Why is this an "apparent" coefficient of extinction and not the real molar coefficient of extinction of this complex?*
*Why is the value b for vanillin considerably higher than that for thymol, when it can be assumed that the real molar coefficients of extinction of the phenolato-complexes scarcely differ?*

## Problem 3-4 Niobium-Sulfur-Clusters

When niobium(V)ethoxide ($Nb(OCH_2CH_3)_5$ = $Nb(OEt)_5$ ) reacts with hexamethyldisilathiane ( $(CH_3)_3Si\text{-}S\text{-}Si(CH_3)_3$ = $(Me_3Si)_2S$ ) and tetraethylammoniumchloride in acetonitrile ($CH_3CN$) as a solvent, an interesting niobium-sulfur compound **(1)** forms in the form of black crystals according to the following reaction equation:

$$Nb(OEt)_5 + (Me_3Si)_2S + NEt_4Cl \xrightarrow{CH_3CN} (NEt_4)_4[Nb_6S_{17}] \bullet 3\ CH_3CN + Me_3SiOEt + Me_3SiCl$$

**(1)**

hexamethyldisilathiane: $\rho$ = 0.846 g/ml niobium(V)ethoxide**:** $\rho$ = 1.268 g/ml

a) *Balance the reaction equation.*

b) *What is the driving force for this reaction ?*

c) *Calculate an experimental assay, if 5.000 g of the compound (**1**) should be obtained at a yield of 75%. Take into consideration that there is 1.4 times the amount of the components $(Me_3Si)_2S$ and $NEt_4Cl$ with regard to $Nb(OEt)_5$. What are the necessary amounts of substances in gram (for $NEt_4Cl$) or rather in millilitre (for $Nb(OEt)_5$ and $(Me_3Si)_2S$).*

d) *What are the oxidation numbers of niobium and sulfur in the initial compounds and in compound (**1**) ?*

Compounds like e.g. **(1)** can be of use as a brilliant initial compound for the production of clusters. A cluster is a compound with metal-metal bonds in addition to metal-nonmetal bonds. In a simple representation of clusters, mostly only the metal atoms are considered. $M_3M'_3$ is such a cluster compound in which M and M' are two different metals. In this $M_3M'_3$-cluster the metal atoms should be octahedrally arranged.

*e) Draw all possible isomers of the $M_3M'_3$ -cluster*

## Problem 3-5 Products of Electrolysis

A potassium-chloride solution is being electrolyzed for two hours at 80°C in a primitive electrolytic cell. The voltage is 6 V and the intensity of the electric current is 2 A. The cathode consists of a rectangular iron plate having the size of 20 cm · 30 cm. A spiral titanium wire (diameter: 2 mm) having a length of 20 m is used as an anode.

*a) What is the power of the electrolytic cell? What is the curent density (electric current per electrode surface)?*

After electrolysis, $CO_2$ is led through the solution until it is saturated. Afterwards, water is carefully being evaporated. A white residue remains. The test for chlorate is positive. According to powder diffractometry, the residue consists altogether of three salts..

*b) What substances have to be reckoned on as well in this residue?*

Analysis 1: 1 g of this residue is being dissolved in water, acidified with nitric acid that produces a slight gas formation and titrated with a 0.1 molar $AgNO_3$-solution. consumption: 18.80 ml.

Analysis 2: 1 g of this residue is heated to 600 °C (the substance mixture melts), cooled down again and the mass is determined once again: 0.95 g.

Analysis 3: A powder diffractogram of this melting residue shows that one component of the initial substance is still present and that the other two components, however, have been transformed into two new salts.

Analysis 4: The 0.95 g of the melting residue are as well being dissolved in water and acidified with nitric acid. A slight gas formation can as well be observed. Then, it is being titrated with a 0,1-molar $AgNO_3$-solution. consumption: 33.05 mL.

*c) Write down all reaction equations that are important for these analyses. Which two salts have disappeared and which two salts have newly formed?*

*d) Determine the mass fractions of the three salts of the initial solid and those of the three salts of the melting residue.*

## Problem 3-6 Saponification

Skrabal investigated the saponification of an ethylidene diacetate as an aqueous 0.1 M solution and catalyzed by protons (HCl-concentration = 0.05 mol/L) at 25 °C.

$$(CH_3COO)_2CHCH_3 + H_2O \longrightarrow 2\ CH_3COOH + CH_3CHO$$

He obtained the following series of measurements:

| t [min] | 0 | 240 | 660 | 1400 | 2093 | 3403 | 6369 |
|---|---|---|---|---|---|---|---|
| c($CH_3COOH$) [mol/L] | 0.02160 | 0.04570 | 0.06495 | 0.09395 | 0.11520 | 0.14475 | 0.17915 |

All values of the calculation have to be provided with SI-units!

a) *Find out by a diagram if it is a zero- or first-order reaction (note: both reaction orders have to be checked for!).*

b) *Give a classic example of a zero- as well as a first-order reaction.*

c) *Determine the values of the rate constant and the half life.*

Let`s have a look at the ester saponificationof ethyl acetate in the presence of alkali.
A 0.02 N solution of ethyl acetate has been saponificated with a 0.02 N caustic soda solution. After 25 minutes, 73 % of it has been saponificated. The second-order rate law for equal initial concentrations of the reactants can be applied to this reaction.

d) *Write down the reaction equation of the ester saponification. How would you determine the turnover of the reaction?*

e) *Determine the rate constant of this ethyl-acetate saponification.*

f) *Determine the half life of this saponification. When is a turnover of 99% obtained?*

## Problem 3-7 Redox equilibria

Solid iron(III)-bromide smells of bromine. Thus, it decomposes according to the following equation whereat an equilibrium establishes:

$$2\ FeBr_3 \rightleftharpoons 2\ FeBr_2 + \tfrac{1}{2}\ Br_2$$

In an aqueous solution as well, $Fe^{3+}$-ions react with halide ions. 0.01 mol sodium halide per litre of solution is dissolved in an acid, aqueous solution of 1 mol/L iron(III)-perchlorate at 25°C and without air. In addition to that, the following values are given:

$E^0(Fe^{3+} + e^- \longrightarrow Fe^{2+})$ = 0.77 V
$E^0(X_2 + 2e^- \longrightarrow 2\ X^-)$ = 1.36 V for chlorine/chloride, 1.07 V for bromine/bromide and 0.54 V for iodine/iodide.

The solubilities of the halides in water should be regarded as negligibly low and thus, their concentrations should be regarded as being constant.

a) *Calculate for all three reactions (addition of chloride, bromide and iodide to the $Fe^{3+}$ -solution) the concentration of free $Fe^{2+}$ and write down the $pFe^{2+}$-value for every reaction.*

*b) In which form can the $Fe^{3+}$- and. $Fe^{2+}$-ions be obtained in a dilute acid, aqueous solution?*

*c) Why is the pH-value for the reaction above so important, although neither $H^+$ nor $OH^-$ or $H_2O$ take part in the reaction? Give a reason for this importance and write down 2 reaction equations at least proving a pH-Wert-dependence of these redox systems.*

The influence of the pH-value has to be noticed especially when iron is to be transformed into the oxidation number +VI. Thus, iron(III)hydroxide can be oxidized with chlorine to ferrate(VI) having a structure that is similar to that of chromate in highly concentrated cold caustic soda lye. If potassium ferrate(VI) is dissolved in pure water, it will decompose again, however, into iron(III)-hydroxide.

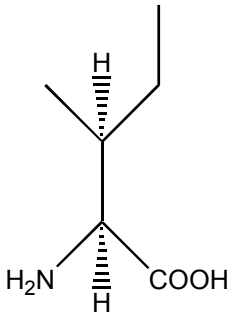
*d) Write down balanced reaction equations for these reactions.*

## Problem 3-8 Peptide chain

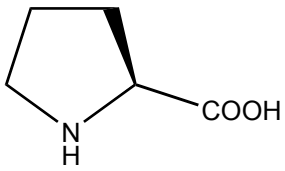
*a) What is the stereochemical configuration (according to Fischer) of almost all natural amino acids ?*

*b) There is a peptide consisting of 50 molecules of alanine. Both stereoisomers of alanine are possible. How many stereoisomers of the peptide are possible?*

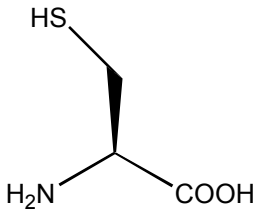
*c) Determine the absolute configuration (according to the Cahn-Ingold-Prelog-nomenclature) of every stereocentre of the following amino acids:*




isoleucine

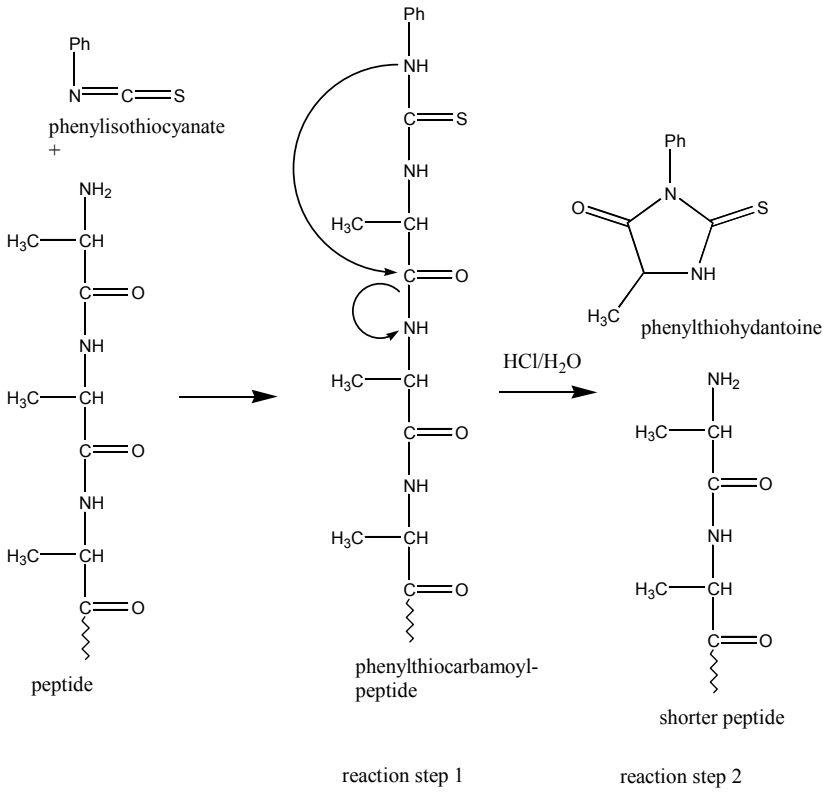



proline




cysteine

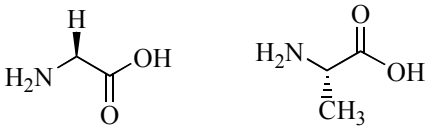
The "Edman degradation", e.g., is used for the analysis of the amino-acid sequence of a peptide. It has the following mechanism:




The result of the two reaction steps is a one amino acid shorter peptide. The chromatographic analysis of phenylthiohydantoine shows which amino acid is found in phenylthiohydantoine. The amino-acid sequence of an unknown peptide can be determined by several repititions of this process.

In a modified process **1**, a little (!) isocyanate (R-N=C=O) is used as well, apart from isothiocyanate. Isocyanate, however, stops reacting at reaction step 1. Both reaction steps are repeated a lot of times in a reaction vessel, so that the peptide is (sometimes completely) degradated. Afterwards, a mass-spectrometric analysis of the reaction solution is carried out.

Chromatographic methods have shown that an unknown peptide X only contains the amino acids glycine and alanine:



glycine (Gly) alanine (Ala)

The analysis of the unknown peptide X according to process **1** resulted in mass peaks at the following m/z-values in the mass spectrum:

| | | | | | |
|---|---|---|---|---|---|
| 521.5 | 450.5 | 402.4 | 393.4 | 336.3 | 331.3 |
| 279.3 | 274.3 | 217.2 | 208.2 | 160.2 | 89.1 |

It could be found out that the compounds belonging to the m/z-conditions did not contain s-atoms.

*d) Identify the compounds belonging to the m/z-conditions listed up above. (The explicit structural formula needn`t be drawn, amino acids can be abbreviated by their three-letter-code, e.g. $NH_2$-ala-ala-COOH for the dipeptide alanine-alanine)*

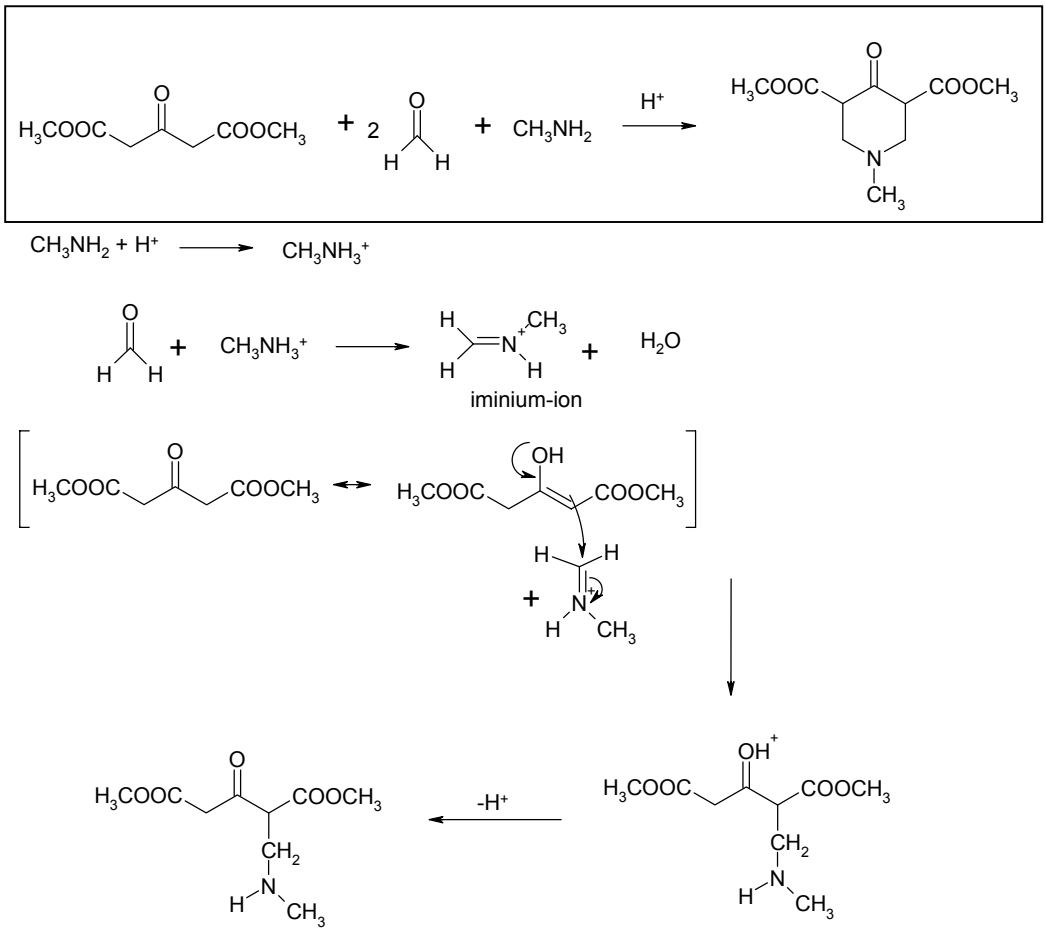
*e) Determine the sequence of the unknown peptide X.*

## Problem 3-9 Mannich-reaction

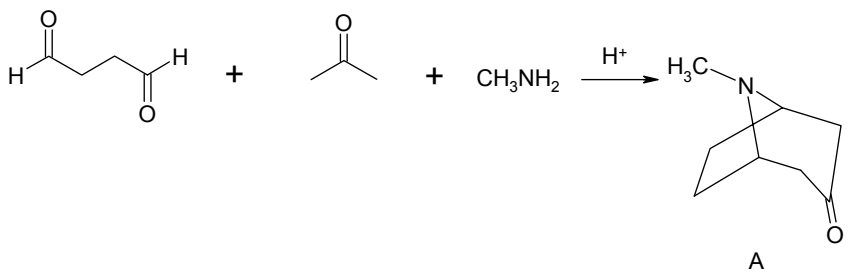
In the following, the mechanism of the Mannich-reaction is explained by an example.

In the first step, an amine reacts with an **aldehyde** to form an iminium ion that reacts with a **ketone**.

Then the nitrogen atom is protonated again. The reaction with an additional formaldehyde molecule results in the formation of a further iminium ion leading to the product in an intramolecular cyclization:



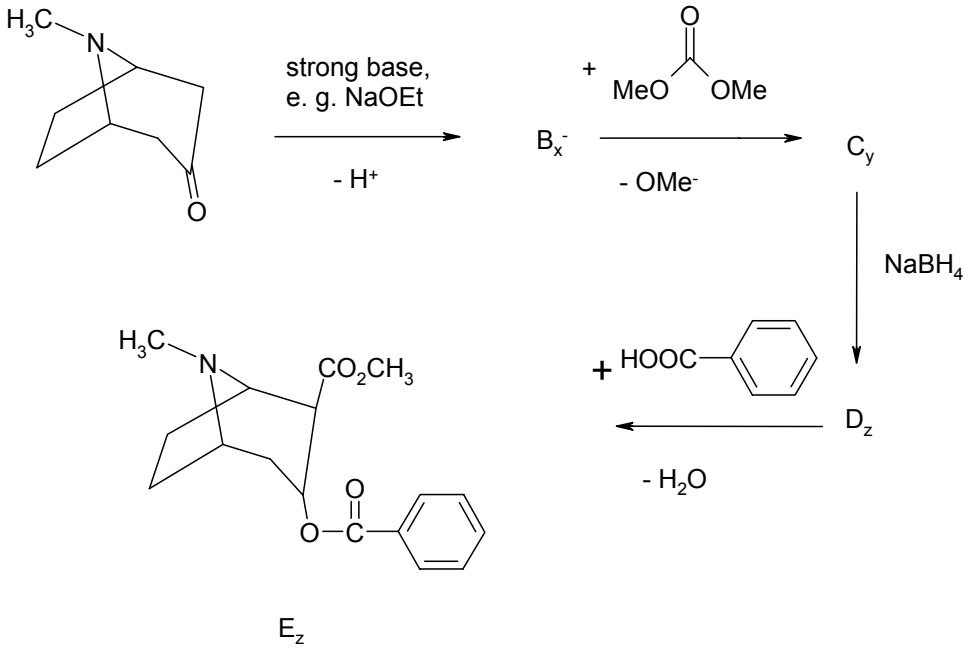

A Mannich-reaction can as well be carried out with the following initial products:




A

*a) Draw the reaction mechanism with all intermediates (see above) leading to product **A**.*

In the following, product **A** takes part in further reactions:



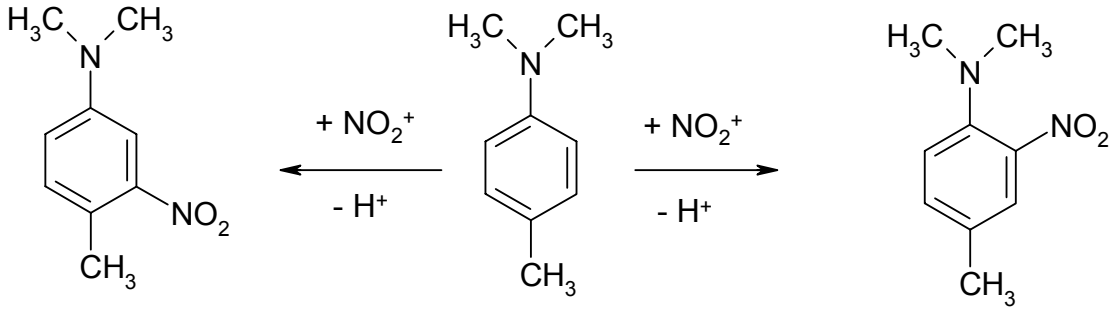

$E_z$

*b) Draw the structural formulas of the compounds* $\boldsymbol{B_x^-}$, $\boldsymbol{C_y}$, $\boldsymbol{D_z}$ *and* $\boldsymbol{E_z}$
*It's enough if you draw one possible isomer of every* $\boldsymbol{B_x^-}$, $\boldsymbol{C_y}$, $\boldsymbol{D_z}$ *and* $\boldsymbol{E_z}$.

*c) How many isomers can be obtained in this synthesis from the compound* $\boldsymbol{E_z}$ *? Which types of isomers appear in this synthesis?*

## Problem 3-10 Nitro compounds

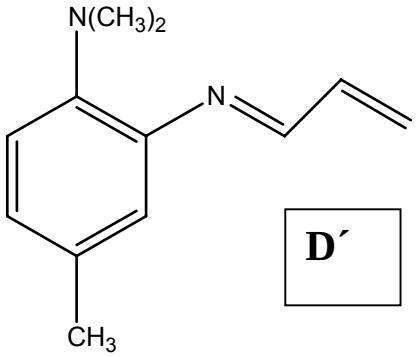
According to the pH-value, the nitration of **A** results in compound **B** or **C**.




C A B

*a) Which of the two products forms in a weakly acid solution and which forms in a strongly acid solution ?*
*Explain this reactive behaviour with the resonance formulas of the* $\sigma$*-complexes appearing as transient states in the formation process of the two processes.*

Compound **B** reacts with zinc powder in dilute hydrochloric acid to form **D**. Compound **D** reacts with acrolein (propenal) in a strongly sulfuric medium and is oxidized (e.g. with $Fe^{3+}$) to form **E** (**E** = $C_{12}H_{14}N_2$). **E** has two condensed aromatic ring systems. This reaction has the reactive intermediate **D´** (see illustration).




*b) Write down a balanced reaction equation for the reaction from **B** to **D**.*

*c) Draw the structural formulas of **D** and **E**.*

# Third round, test 2

## Problem 3-11

*1) Which of the following mixtures of substances is not a buffer mixture?*

| | | |
|---|---|---|
| a) $KH_2PO_4/H_3PO_4$ 2:1 | b) $CH_3COOH/NaOH$ 2:1 | c) $NaH_2PO_4/Na_2HPO_4$ 1:1 |
| d) $CH_3COONa/CH_3COOH$ 3:1 | | e) $CH_3COOH/KOH$ 1:2 |

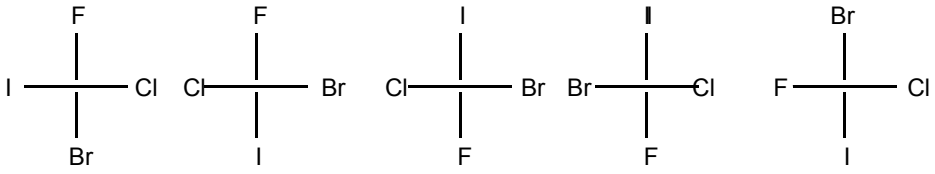
*2) Which of the following buffer solutions ($CH_3COOH$ / $CH_3COONa$) is the most acid one?*

| | | |
|---|---|---|
| a) 1-molar / 1-molar | b) 1-molar / 0,1-molar | c) 0,1-molar / 0,1-molar |
| d) $10^{-9}$ -molar / $10^{-12}$ -molar | e) $10^{-10}$ -molar / $10^{-20}$-molar | |

*3) 100 mL of destilled $H_2O$ are mixed with 1 l of ethanol (96 vol-%). The volume contraction is 1%. What is the concentration of water in the mixture?*

| | | |
|---|---|---|
| a) 14.8 mol/L | b) 7.78 mol/L | c) 7.14 mol/L |
| d) 0.09 mol/L | e) 0.1 mol/L | f) 16.5 mol/L |

*4) Which of the following formulas of the Fischer-projection shows the enantiomer that can be found only once?*

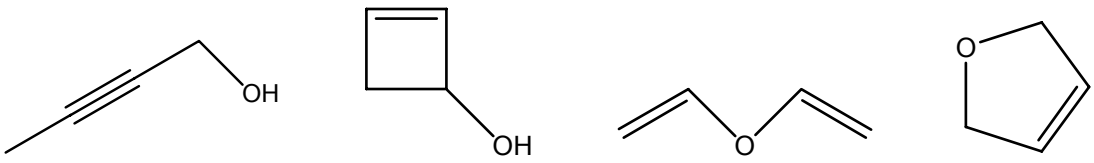



a) b) c) d) e)

*5) How many cis/trans-isomers can the compound 1,3,5,7-nonatetraene form?:*

| | | | | | |
|---|---|---|---|---|---|
| a) 2 | b) 4 | d) 8 | c) 5 | e) 10 | f) über 10 |

*6) Which of the following compounds of $C_4H_6O$ has the highest steam pressure at 25°C?*

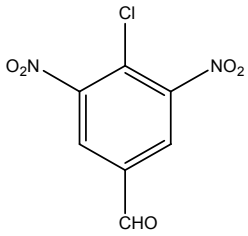



a) b) c) d)

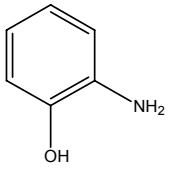
*7) Which of the following elements has several modifications at 25°C?*

| | | | | |
|---|---|---|---|---|
| a) bromine | b) argon | c) phosphorus | d) nitrogen | e) sodium |

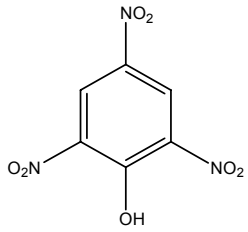
*8) Which of the following compounds is the strongest acid?*



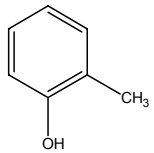
a)



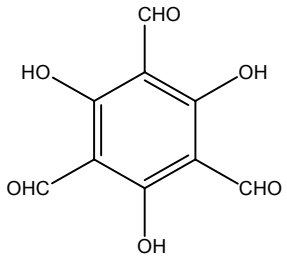
b)



c)



d)



e)

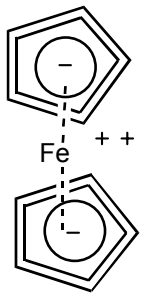
## Problem 3-12 Hybridization

a) *Draw the Lewis formula of the* allene molecule *(propadiene) and give the hybridization of the single C-atoms.*

*b) How does the hybridization of the borine atom change in the following reaction?*

$$BF_3 + F^- \longrightarrow [BF_4]^-$$

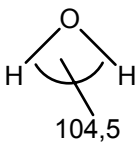
*c) Give the hybridization of the Fe-atom in the following diamagnetic compounds: [Fe(CO)$_5$], [Fe(cyclopentadienide)$_2$] = ferrocene (illustration) Explain your decision with the electron configuration of the Fe-atoms of the compounds.*



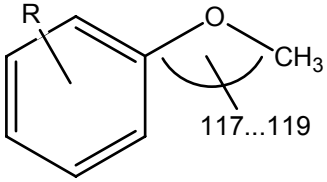

*d) The degree of hybridization of C, N, O in the compounds methane, ammonia and water is sp$^3$. Give reasons for the following different bond angles: in $CH_4$: H-C-H = 109.4°, in $NH_3$: H-N-H = 106.8°, in $H_2O$: H-O-H = 104.5°.*

*e) Explain the following bond angles with the hybridization concept:*

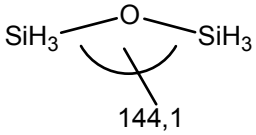
**A**




**B**




**C**




*Why do the hybridization states in the compounds **A, B** and **C** differ?*

## Problem 3-13 The "adamantane diamond“

Adamantane ($C_{10}H_{16}$), see illustration 1, is a hydrocarbon with a very high symmetry. Assuming that only the bridgehead C-Atome take part in further reactions, adamantane can be called as well "inflated $sp^3$-hybridized C-atom". This molecule containing 2 such "inflated C-atoms", 1,1´-biadamantane, more or less a "di-adamantane-ethane" would have the structure shown in illustration 2.

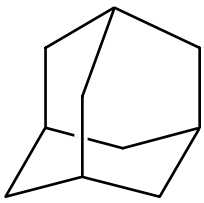


illustration 1: adamantane

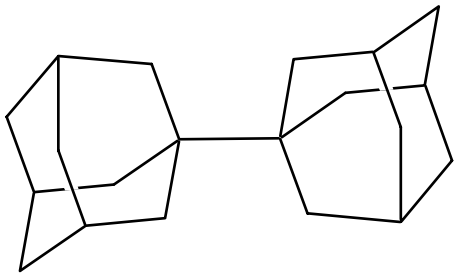


illustration 2: "di-adamantane-ethane"

a) *Calculate the "atomic radius" of the "inflated C-atom" assuming that all carbon atoms of adamantane are ideally $sp^3$-hybridized and thus have bond angles of 109.4°.The C-C-bond distances in the adamantane backbone are 154.0 pm. These distances are 157.8 pm between the adamantane units.*

Carbon, in the modification of diamond, crystallizes in a cubic lattice. Every C-atom is tetrahedrally surrounded by 4 further C-atoms (see illustration 3).

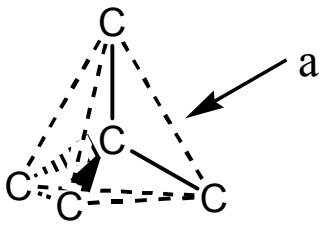
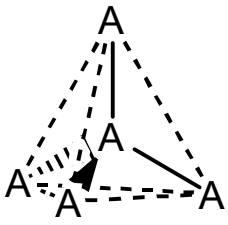



illustration 3: binding conditions of the C-atoms in diamond; the tetrahedral edge length a is 252.22 pm

illustration 4: part of the "adamantane-diamond".




b) *Calculate the atomic radius of the C-atom in the diamond lattice.*

According to the idea of an "inflated C-atom", all the real C-atoms of the diamond have to be substituted by adamantane units (illustration 4, atom A corresponds to the adamantane-backbone). The density of a real diamond is 3.514 g/cm$^3$

c) *Calculate the density of the "adamantane diamond".*

d) *Make a qualitative statement on the solidity of the "adamantane diamond" in contrast to the real diamond.*

e) *Why does cubic boron nitride $(BN)_x$ have physical properties that are similar to those of the real diamond?*

## Problem 3-14 Catalysis

Many subgroup elements react with carbon monoxide to form complexes. There is, e.g., the binuclear cobalt complex $[Co_2(CO)_8]$ having a Co-Co single bond that can be cleaved by hydrogenation so that $[CoH(CO)_4]$ forms.

$[CoH(CO)_4]$ is a very strong acid (pKs = 1) forming the ion $[Co(CO)_4]^-$ in an aqueous solution.

*a) How many ligands (CO, $H^-$) are bound to the Co-atom in these 3 complex compounds. Give reasons for your answer.*

*b) What is the difference between the ionic dissociation of $[CoH(CO)_4]$ and that of nitric acid?*

$[CoH(CO)_4]$ can be used as a catalyzer for so-called "hydroformylation". An alkene reacts with $H_2$ and CO to form an aldehyde in the presence of a catalyzer. At an increased temperature (90°C - 250°C), the complex $[CoH(CO)_4]$ is mostly decomposed into carbon monoxide and **A**. (M(**A**) = 144 g/mol). **A** can form the $\pi$-complex **B** by coordination to ethene. **B** transposes to the alkyl complex **C**. The next step is the coordination of further CO to the Co-atom. **D** forms and transposes to the alkyl complex **E** that is cleaved by hydrogen into **A** and an aldehyde **F**.

*c) Write down the structural formulas of the compounds **A** to **F**. (It can be assumed that the complexes **B** and **D** obey to the same "coordination rules" as $[Co_2(CO)_8]$ and $[CoH(CO)_4]$ do.)*

*d) How do you think can the cleavage by hydrogenation of **C** be stpped in order to obtain a maximum yield of the aldehyde **F**?*

$[CoH(CO)_4]$ can be used as well as a catalyst for the isomerisation of alkenes. 3-methyl-1-butene, e.g., transforms into 2-methyl-2-butene in the presence of $[CoH(CO)_4]$.

*e) Propose a mechanism for such an isomerisation reaction.*

*f) Give the isomerisation product(s) of 2-ethyl-1-butene as well of propene-3-ol.*

## Problem 3-15 Nuclear reactions

Radioactive decay reactions always take place according to a first-order rate law: $N(t) = N_0e^{-kt}$. $N_0$ is the number of atoms at the point of time t = 0 and k is the radioactive decay constant. The half life $t_{½}$ is the time needed for half the initial number of nuclei to desintegrate.

*a) Write down a decay law not containing any longer k but $t_{½}$.*

When the elements came into being, many radionuclides came into being as well. Some of them like certain uranium- and thorium isotopes can still be found on earth because of their longevity. Natural uranium consists of several isotopes. The most long-life ones 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 uranium isotopes have considerably shorter half lifes. Thorium consists exclusively of the long-life isotope $^{232}Th$ ($t_{½} = 1.405 \cdot 10^{10}$ a). $^{237}Np$ ($t_{½} = 2.14 \cdot 10^6$ a) was an additional, relatively long-life isotope. It has, however, already decayed. All these isotopes undergo $\alpha$-decay.

*b) At what point of time in the past were the fractions of both uranium isotopes the same?*

A further isotope $^{234}U$ with a fraction of about 0.005% can be found in natural uranium. It has not remained since the date of origin of the earth, but is formed continuously by the decay of

one of the four isotopes mentioned above. A radioactive equilibrium has established at which the concentration of $^{234}U$ is constant, that means that the formation- and decay rates are the same.

c) *Which of the isotopes mentioned above is $^{234}U$ produced of by a series of $\alpha$- and $\beta^-$-decays? Write down the path of formation.*

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

The recovery of the noble gas radon is difficult because of its short half life ($t_{½}$=3.825 d). It is recovered from he radon isotope $^{226}Ra$ ($t_{½}$ = 1598 a).

$$^{226}Ra \xrightarrow{K_1} {}^{222}Rn \xrightarrow{k_2} 218Po$$

A certain amount of $RaCl_2$ is dissolved in water. After the concentration of radon has reached 99% of the concentration in the radioactive equilibrium, radon is drained by pumping. Because the half life of $^{226}Ra$ is much longer than that of $^{222}Rn$, the concentration of radon can be assumed as being constant. The following relation can be applied:

$$[^{222}Rn] = [^{226}Ra]\ \frac{k_1}{k_2}\ (1-e^{-k2t})$$

e) *After what period of time can radon be drained by pumping?*

f) Why is insoluble $RaSO_4$ not taken as a basis?

## Problem 3-16 Silicon monoxide

Silicon dioxide ($SiO_2$) is the most frequent mineral of the earth`s crust. If it is heated in a high vacuum to high temperatures (>1000 °C), it will decompose into gaseous silicon monoxide (SiO) and oxygen according to the following reaction equation:

$$2\ SiO_2\ (s) \rightleftharpoons 2\ SiO\ (g) + O_2\ (g)$$

At a temperature of 1300 °C, the equilibrium constant $K_p$ for this reaction is $K_p = 3.9 \cdot 10^{-15}$ $mbar^3$.

The thermodynamic data for $SiO_2$ (s), SiO (g) and $O_2$ (g) at different temperatures can be found in the following table:

| T [°C] | $SiO_2$ (s) | | SiO (g) | | $O_2$ (g) | |
|---|---|---|---|---|---|---|
| | $\Delta H_f$ [kJ $mol^{-1}$ ] | S [J $mol^{-1}K^{-1}$] | $\Delta H_f$ [kJ $mol^{-1}$ ] | S [J $mol^{-1}K^{-1}$] | $\Delta H_f$ [kJ $mol^{-1}$ ] | S [J $mol^{-1}K^{-1}$] |
| 800 | - 860.3 | 122.1 | - 74.3 | 253.8 | 25.2 | 246.1 |
| 1000 | - 846.4 | 134.2 | - 67.1 | 260.0 | 32.3 | 252.1 |
| 1200 | - 832.0 | 144.8 | - 59.7 | 265.4 | 39.5 | 257.3 |

(The values refer to a standard pressure $p^0$ of 1.013 bar)

a) *Why is the formation enthalpy $\Delta H_f$ indicated for oxygen not zero, although oxygen is a chemical element?*

*b) Calculate $\Delta H_R$, $\Delta S_R$ and $\Delta G_R$ for this reaction at temperatures of 800 °C, 1000 °C and 1200 °C. Is the reaction exothermal or endothermal?*

*c) Write down the equilibrium constant $K_p$ for this reaction at 800 °C, 1000° C and 1200 °C .*

*d) Calculate the partial pressure of SiO that will result from the equilibrium, if solid $SiO_2$ is heated to 1300 °C in a high vacuum.*

*e) How can gaseous SiO be produced without oxygen being formed as well? Write down the reaction equation supporting your proposal!*

## Problem 3-17 Solubility product

The solubility product $K_L$ of iron(II)-hydroxide is to be determined by potentiometry. A galvanic cell is set up. One half cell consists of a slightly acid 0.01 molar $Fe^{2+}$-solution in which an iron rod is placed. A copper half cell with a 0,5-molar $Cu^{2+}$-solution is used as a reference half cell. A voltage of 0.830V can be read.
Then, the pH-value in the iron half cell is made exactlly 12 with caustic soda lye. But watch out! No air must get into the half cell. A white precipitate can be observed in the solution. The voltage changes to 1.090 V.
The experiment is carried out under standard conditions.
Standard redox potential: $Cu/Cu^{2+}$: +0.340V

*a) Write down the reaction equations for the processes in the reduction- as well as the oxidation half cells and the total equation.*

*b) Calculate the standard redox potential of $Fe/Fe^{2+}$.*

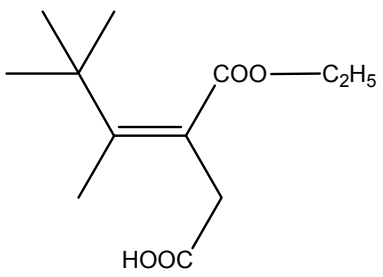
*c) What will happen if caustic sodium lye is added to the iron half cell? Write down the reaction equation.*

*d) What would happen if caustic sodium lye was added to an open iron half cell? Write down the reaction equation.*

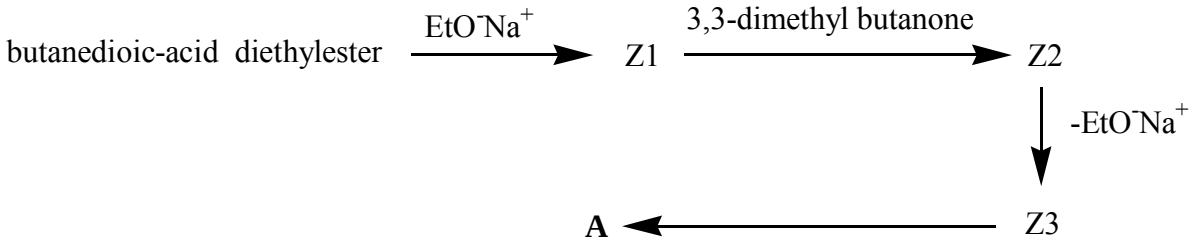
*e) Calculate the solubility product $K_L$ of iron(II)-hydroxide. Write down as well the $pK_L$-value of $Fe(OH)_2$.*

## Problem 3-18

Ester **A** (see illustration) forms by a mixture of 3,3-dimethyl butanone, butanedioic acid diethylester and sodium ethanolate ($CH_3CH_2O^-Na^+$). The mole ratio is 1 : 1 : 1.

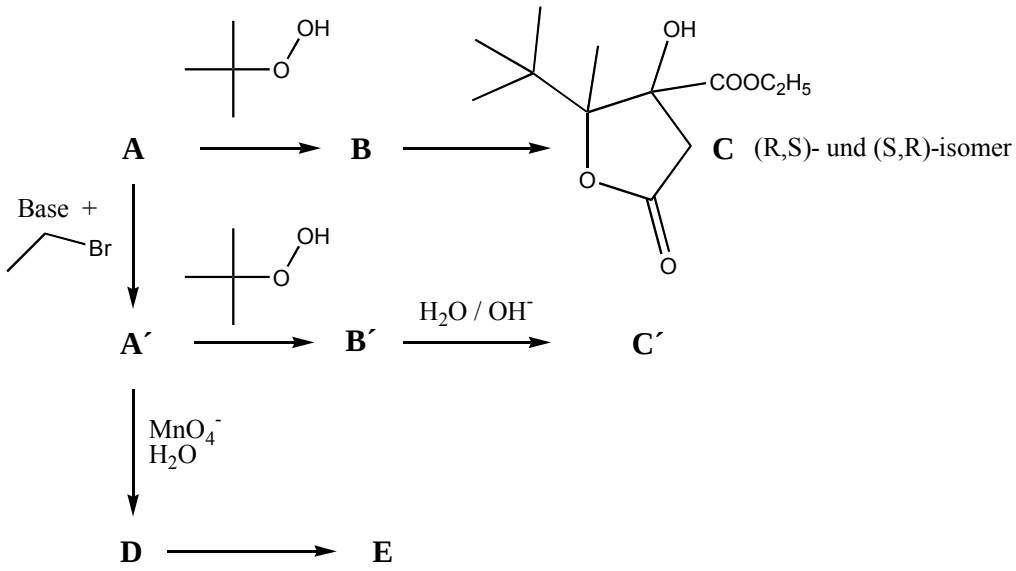



**A**




*a) Write down the reaction mechanism of the formation of **A** from the initial substances mentioned above (see scheme). Give the intermediate stages Z1, Z2 and Z3. Why is a stoichiometric amount of the catalyst sodium ethanolate added?*

**A** undergoes the following reactions:

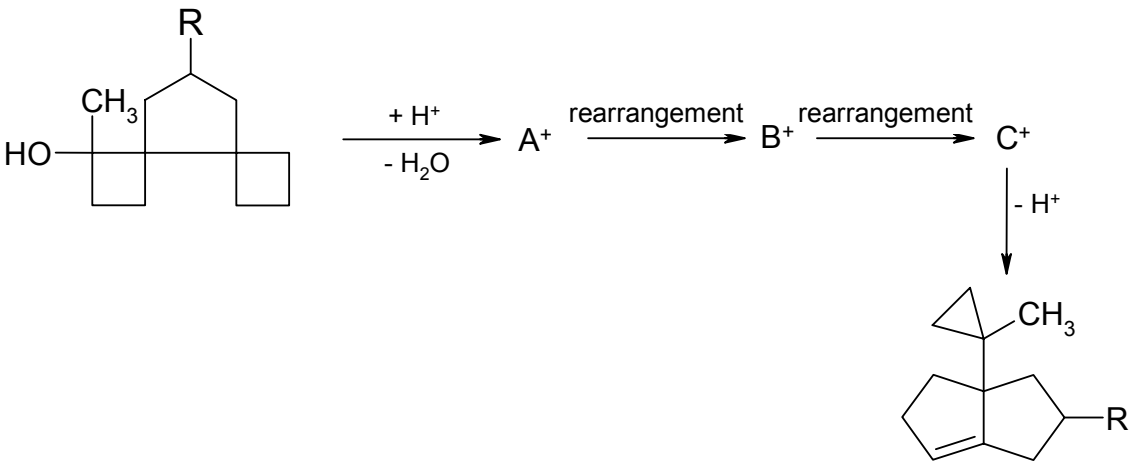



**B** is very reactive and transforms very quickly into **C**. If **A** is transformed into **A´**, the more stable product **B´** will form. **B´** can only transform into **C´** after alkali reprocessing.
The oxidation of **A´**with dilute alkali permanganate solution, however, does not lead to **C** but to **D** and finally to **E**.

*b) Draw the structural formulas of the compounds **B**, **A´**, **B´**, **C´**, **D** and **E**. Please write down if and which stereoisomers can occur.*

## Problem 3-19

The following illustration shows a skeletal rearrangement::




R = phenyl

a) *Draw the structural formulas of the compounds **A**$^+$, **B**$^+$ as well as **C**$^+$ and indicate with an arrow in the structure the migration direction of the compounds (each rearrangement results in only one compound wandering! )*

   *Note: compound **B**$^+$ already contains a three-membered ring*

b) *What is the driving force for the rearrangement ?*

If **C**$^+$ does not immediately separate a proton, but first reacts with the water molecule separated in the first step, **D** will form.

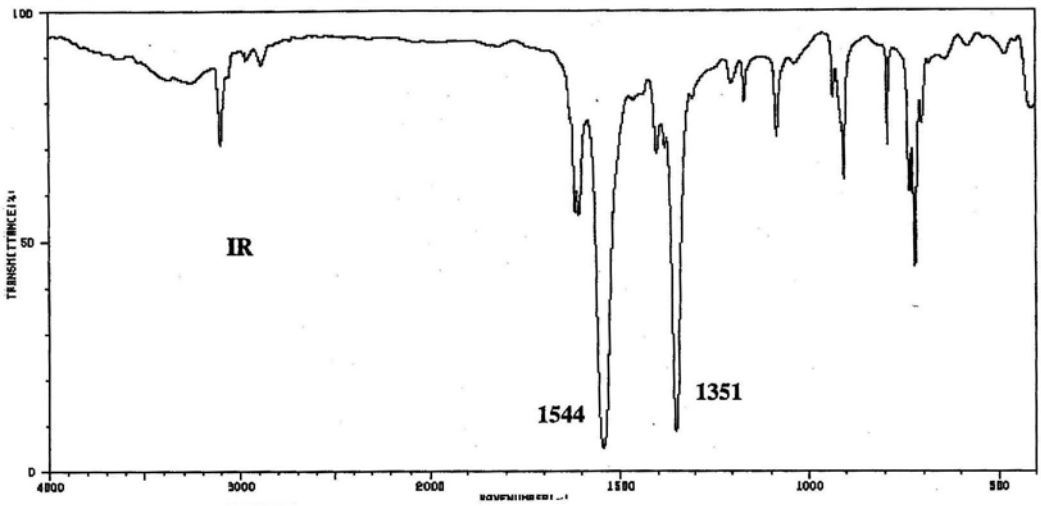
c) *Draw **D**, mark all asymmetric C-atoms in **D**. How many stereoisomers does **D** have?*

## Problem 3-20

The composition of an organic compound consisting of C, H, O and N was determined by quantitative elemental analysis resulted in the following values: 37.02% C; 2.22% H; 18.50% N. The peak in the mass spectrum of the compound is m/Z = 227.

*a) Determine the total formula of the compound that has to be found out.*

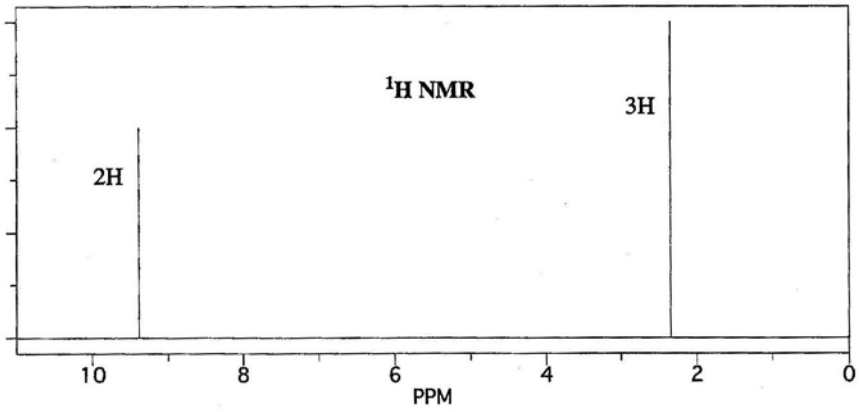
The following illustration shows the IR-spectrum of the compound:




There are two strong absorption bands at 1544cm$^{-1}$ and 1351cm$^{-1}$.

*b) Which group(s) in the molecule do these signals refer to? (Use the added IR-table.)*

In addition to that, the $^{1}$H-NMR spectrum of the compound is shown in the following diagram:




*c) Use the complete information to determine the structure of the compound. Draw the Lewis formula.*

*d) What is the usual name of the compound and what particular physical property is it famous for?*

# Fourth round (theoretical problems)

(The same formulary as in the third round and a periodic table were made available to the students)

## Problem 4-1 Copper(I)-bromide

Copper(I)-bromide is a poorly soluble salt ($pK_L$ = 7.4).

*a) How much water is needed to dissolve 1 gram of CuBr completely?*

Copper(I)-ions react with ammonia to form diamminecopper(I)-ions :

$$Cu^+ \underset{-NH_3}{\overset{+NH_3}{\rightleftharpoons}} [Cu(NH_3)]^+ \underset{-NH_3}{\overset{+NH_3}{\rightleftharpoons}} [Cu(NH_3)_2]^+ \qquad (1)$$

The equilibrium constants for the two steps of complex formation are $lgK_1$ = 6.18 and $lgK_2$ = 4.69.

An ammonia solution (c = 0.1 mol/L $NH_3$) can be used for the dissolution of 1 g of CuBr.

*b) What is the volume of this $NH_3$-solution needed for dissolving CuBr?*

*c) Give the conditional solubility product of CuBr in the resulting solution.*
*$K_{L(kond)} = \{c(Cu^+) + c([Cu(NH_3)]^+) + c([Cu(NH_3)_2]^+)\} \cdot c(Br^-)$*

## Problem 4-2: Thermodynamics of Xylenes

Xylenes (dimethylbenzenes) are obtained from naphtha, the medium petroleum fraction. They are very precious initial products for the production of plastics. Because the natural content of xylenes is only about a few percent, naphta fractions are submitted to the so-called reforming process in which aromatic hydrocarbons form by cyclization and dehydrogenation.

When 1 mol of liquid p-xelene is combusted, 4551.4 kJ/mol are liberated at constant pressure and standard conditions.

*a) Write down a balanced reaction equation for this combustion reaction.*

*b) Calculate the free standard heat of formation $\Delta H_f^0$ of liquid p-xylene by means of the heat of combustion.*
*(The result does not correspond to the value indicated in the table)*

The industrial needs for different xylene isomers are very different. The needed amounts are largest for p-xylene, followed by o-xylene amd m-xylene. The isomerization reactions of xylenes that take place in the gas phase with Lewis acids as catalysts are of great technical importance.

*c) Calculate the free standard heat of formation $\Delta H_f^0$ and free standard reaction entropy $\Delta S_f^0$ for the transformation of o-xylene into p-xylene in the gas phase at T = 500 K, assuming that the heat capacities are independent of temperature. Use the thermodynamic data indicated below.*

*d) Calculate the percentages of the three xylene isomers in the equilibrium mixture at T = 500 K.*

In industrial processes, acid zeolite catalysts are used for isomerization reactions. They contain long channels that have diameters chosen in a way that para-isomers can diffuse quickly into and out of these catalysts while the other isomers have to remain in the catalyst. In this way, a fraction of p-xylene of about 80% can be reached.

*e) Which principle was made use of in the upper process?*

**necessary values:**

| | $\Delta H_f^0$ [kJ/mol] | $S^0$ [J/(molK)] | $C_p$(l) [J/(molK)] | $C_p$ (g) [J/(molK)] | $T_s$ [K] | $\Delta H_{evap}$ [kJ/mol] |
|---|---|---|---|---|---|---|
| o-Xylol | -24.4 | 246.0 | 187.7 | 171.6 | 417.0 | 36.2 |
| m-Xylol | -25.4 | 253.8 | 184.6 | 167.1 | 412.3 | 35.7 |
| p-Xylol | -24.4 | 247.2 | 182.2 | 167.4 | 411.4 | 35.7 |
| $CO_2$ | -393.5 | | | | | |
| $H_2O$ | -285.8 | | | | | |

## Problem 4-3: Kinetics of ethyl iodide

*a) Calculate the solubility product of AgI at 25°C from the values in table.*

*b) Calculate the solubility product at 75°C. Could the result be expected?*

The thermal decay of ethyl iodide into hydrogen iodide and ethene is to be investigated – that means that the rate constant is to be determined. A sample of ethyl iodide is heated to 600 K for a certain period of time. HI that has formed is absorbed by a substance binding HI selectively. Ethyl iodide that is left is acidified with 200 mL of 1M nitric acid at 25 °C and 50 ml of 1M NaOH are added to it. Then, 0.1 g of $AgNO_3$ is added to this mixture. A silver electrode is put into the solution and the potential is measured against a calomel electrode ($\varepsilon_{Kalomel}$ = 0.283 V). The values of the emf depending on time at bei 600 K can be found in table 2.

*c) Calculate the equilibrium constant of the decay reaction at 600 K and give reasons for the selective absorption of HI being necessary.*

*d) Give the potential of the silver electrode in dependence on the iodide concentration.*

*e) Which reaction order does the decay have? Give the iodide concentration in dependence on time.*

*f) Insert the result of e) into the result of d) and calculate the emf ($\varepsilon_{Kalomel}$ - $\varepsilon_{Ag}$) in dependence on time. Simplefy this expression. Determine the rate constant and the initial amount of ethyl iodide in g on the basis of an appropiate plotting of the values of table 2. Note: Determine gradient and axis intercept graphically!*

table 1

| | $\Delta H^o_f$ [kJ/mol] | $\Delta G^o_f$ [kJ/mol] | $E^0$ [V] |
|---|---|---|---|
| $Ag^+ + e^- \rightarrow Ag$ | | | 0.799 |
| $½\ I_2 + e^- \rightarrow I^-$ | | | 0.535 |
| $AgI_{(s)}$ | -61.84 | -66.19 | |
| $Ag^+_{(aq)}$ | 105.79 | | |
| $I^-_{(aq)}$ | -56.78 | | |
| $Ag_{(s)}$ | | 0.0 | |
| $I_{2(s)}$ | | 0.0 | |
| $HI_{(g)}$ | 26.5 | 1.7 | |
| $C_2H_{4(g)}$ | 52.5 | 68.4 | |
| $C_2H_5I_{(g)}$ | -8.1 | 19.2 | |

table 2

| t [h] | emf [mV] |
|---|---|
| 2 | 365 |
| 5 | 361 |
| 8 | 356 |
| 14 | 347 |
| 19 | 340 |

## Problem 4-4 Free molecule spectroscopy

Biological cells as well as subcellular units (organelles) are separated from each other by lipid bilayers. In the recent years, fluorescence-free molecule spectroscopy has made important contributions to the information about their structures and functions. This method contains the integration of lipid-like fluorescent dye molecules (fluorophores like e.g. "DiO" (3,3'-dioctadecyloxacarbocyanine perchlorate, structure: see next page) as markers in membranes and the observation of their movements by the emitted fluorescence of the single molecules by means of high-sensitive CCD-cameras. The membranes are mostly lighted with intensive (kW/cm²) laser pulses of a duration of some ms.
50 μL of a 10 mM solution of DOPC (1,2-dioleoyl-sn-glycero-3-phosphocholine) in chloroform are used for the modelling of natural membranes. After the addition of methanolic DiOsolution, the mixture is filled up to100 μL with chloroform.

*a) How many μL of a methanolic DiO-solution (10 μg/L) have to be added, so that 50 DiO-molecules can be found per 100 μm² of lipid bilayer (free of chloroform)?*
*(note: every DOPC-molecule demands 0,64 nm² in the lipid membrane)*

Within DOPC-bilayers, lipid molecules diffuse with a diffusion coefficient of $D = 6 \cdot 10^{-8}$ cm²/s at room temperature. 10 ms are neded for the exposure and 25 ms are needed for the selection process per photo. The averaged square of the covered distance Δx can be described by the formula $\left\langle (\Delta x)^2 \right\rangle_T = 2\, fD\Delta t$. *f* is the degree of freedom (dimension) of the movement and $\Delta t$ is the time distance between two photos. ($\langle A \rangle_T$ is the time average of *A*.)

*b) How long is the average distance (in μm) of the movement of a molecule between two sequential photos?*

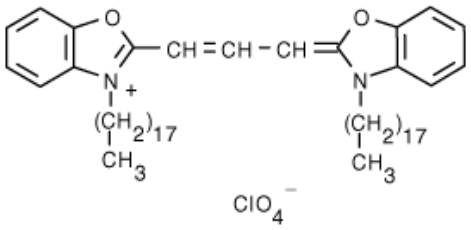
*c) How long is the distance after 4 photos?*

*d) How long does it take on average until a lipid molecule has "hiked through" the extentions of a cell (10 μm) within the model membrane that has been investigated?*

After the absorption of a photon, a molecule can fluoresce while returning to the basic state. It can, however, as well change into a longer-life excited state (triplet state). Within this state, it can irreversibly chemically react and decoulourize. It is assumed that DiO decolourizes exponentially under the selected conditions of excitation with a half life of 75 ms.

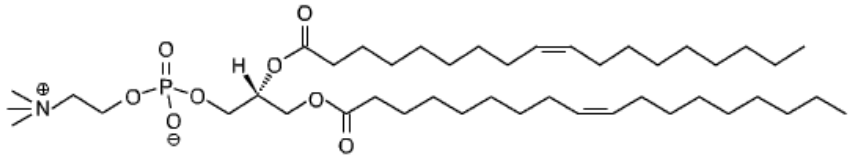
*e) After how many photos are 10% of all DiO molecules that have initially been present in an investigated part of a membrane still fluorescent?*

**Structure and molecular mass of DiO**



M = 882 g/mol

**Structure of DOPC**



## Problem 4-5 Solid-state chemistry: spinels

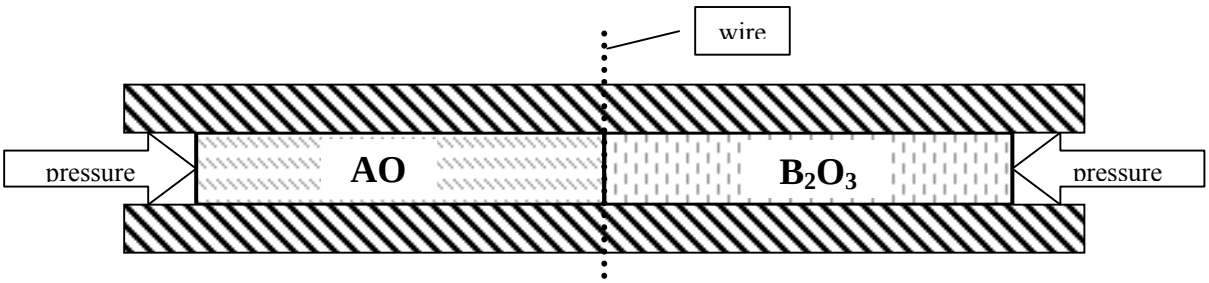
Spinels are a large group of compounds having the general formula $AB_2O_4$. The parent compound, the mineral spinel, has the composition $MgAl_2O_4$. Its noble varieties are used as precious stones.

The simplest way of producing spinels is the direct reaction of the single oxides:

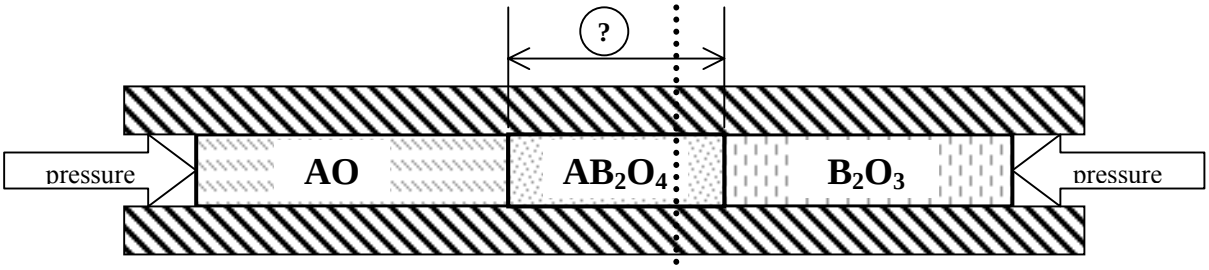
$$MgO + Al_2O_3 \longrightarrow MgAl_2O_4$$

The reaction proceeds with noticeable speed only at very high temperatures (> 1800 °C), because it is only then that the mobility of the particles in the solid becomes sufficiently high.

Two blocks of the metal oxides AO andd $B_2O_3$ are compressed and heated for the determination of the reaction mechanism of spinel formation.




The interphase is marked e.g. by a thin wire. The reaction starts by ions diffusing through the interphase. After some time, some spinels have formed. Conclusions about the reaction mechanism can be drawn from the position of the wire.




In principle, three basic mechanisms are possible: (i) only the cations $A^{2+}$ and $B^{3+}$ diffus (ii) only the ions of AO diffuse ($A^{2+}$ und $O^{2-}$) (iii) only the ions of $B_2O_3$ diffuse ($B^{3+}$ and $O^{2-}$)

*a) Decide for each of the three cases in which ratio the ions have to diffuse to keep electroneutrality.*

*b) Decide for each of the three cases where in the $AB_2O_4$-layer the wire that has marked the initial interphase can be found after the reaction has finished.*

*c) Why can the wire nevertheless be found sometimes at positions different from those predicted in (b)?*

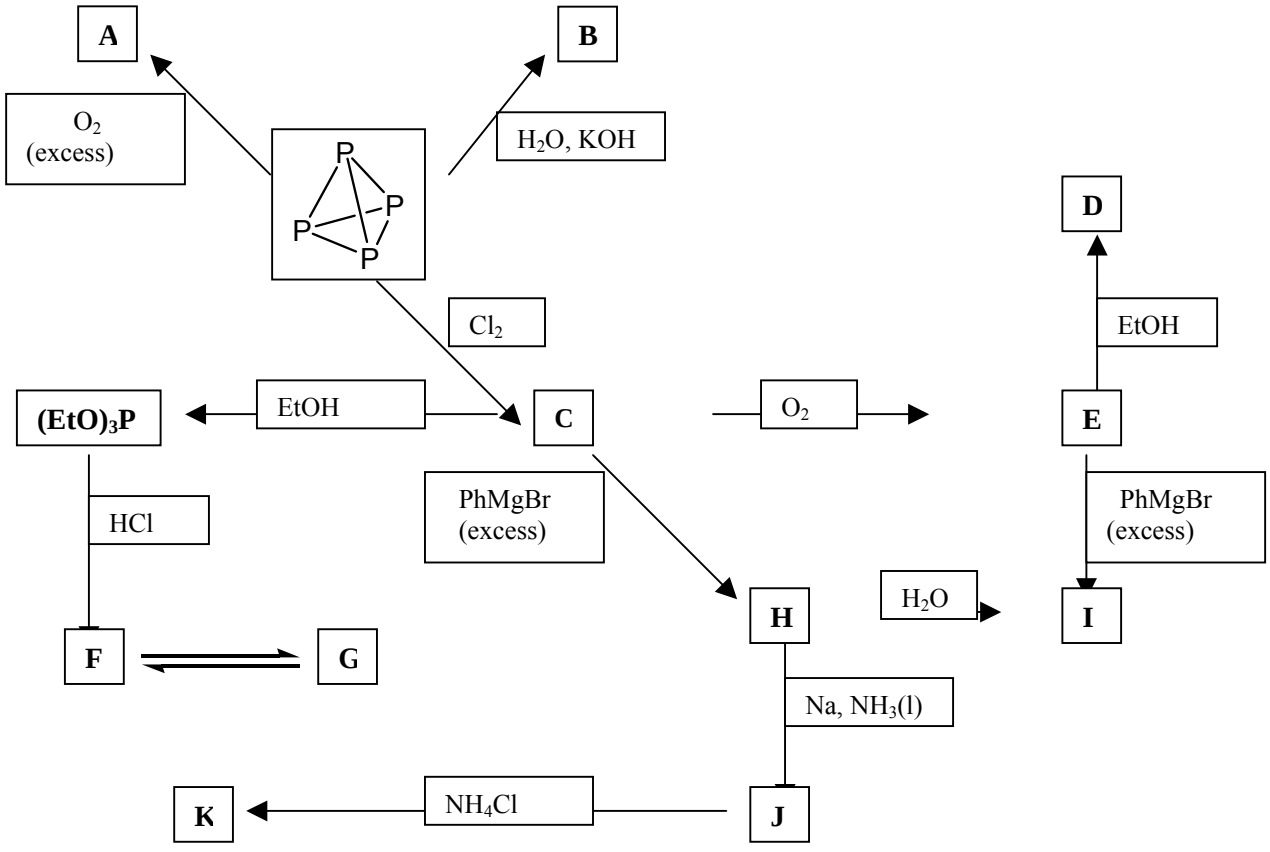
## Problem 4-6: Chemistry of phosphorus

*Determine the compounds from A to K.*

notes: the stoichiometric ratios are not indicated.

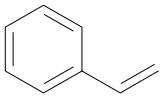
F: one equivalent of chloroalkane forms as a byproduct

J: J is a salt



## Problem 4-7 Anionic polymerization

High degrees of polymerization can be obtained already in the beginning of free radical polymerization. The degree of polymerization, however, ideally increases linearly with the monomer turnover in the anionic-polymerization process (no termination reaction during polymerization). In addition to that, the fast initiation reaction with carbanionic combounds like sec-butyllithium guarantees a closed molecular-weight distribution. The (numerically averaged) degree of polymerization $P_n$ indicates the number of minomer units per polymer molecule.
Different polysterene samples are to be synthsized by anionic polymerization by means of a single solution, so that a monomer turnover of 25 %, 50 % and und 75 % can be obtained.


styrene

a) *A reaction with 100 g of sterene and 1,54 g of sec-butyllithium is prepared. Calculate the average degrees of polymerization (numerical average) of the samples for monomer turnovers of 25, 50 und 75 %.*

b) *What is aimed at with polymerization is getting samples of polysterene that have the same masses but different degrees of polymerization. Calculate the volume fractions of the solutions at 25, 50 and 75 % of turnover, so that the masses of pure polymer (without monomer or any solvent) are the same for all three degrees of polymerization. Ignore changes in volume as a result of polymerization. Assign the volume fractions to the initial solution (solution before the start of the reaction). Consider that the total residual solution has to be taken and processed at the last sampling at 75 %.*

### Polymer analytics

The distribution of the molar mass of a synthesized polymer is analyzed by mass spectrometry (matrix assisted laser desorption ionization, time-of-flight, MALDI-TOF-MS). TheMALDI-TOF-method guarantees a minimal fragmentation of the polymer molecules. After the substraction of the charge carrier ($Ag^+$), the following frequency distribution can be obtained:

| molar mass *M* [g/mol] | 890 | 994 | 1098 | 1202 | 1306 |
|---|---|---|---|---|---|
| frequency of the molecules in the mixture *h* [mol-%] | 2.5 | 25 | 45 | 25 | 2.5 |

c) *What will bethe name of the monomer of the polymer and which terminal group does the polymer have, if sec-butyllithium is used as an initiator? Calculate the degree of polymerization of each species.*

d) *Calculate from the table above two two average values of the molecular weight,*

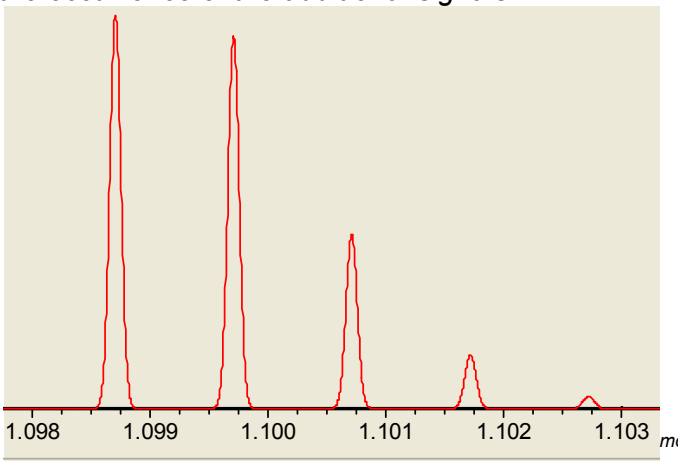
*the numerical average $M_n$ ,* *defined as* $M_n = \dfrac{\sum_{i=1}^{\infty} h_i \cdot M_i}{\sum_{i=1}^{\infty} h_i}$

*and the weight average $M_w$ , defined as* $M_w = \dfrac{\sum_{i=1}^{\infty} w_i \cdot M_i}{\sum_{i=1}^{\infty} w_i} = \dfrac{\sum_{i=1}^{\infty} h_i \cdot M_i^2}{\sum_{i=1}^{\infty} h_i \cdot M_i}$

*(w is the weight fraction of the single molecules in the mixture).*

*Calculate the quotient from $M_w$ and $M_n$. Calculate as well the quotient from $M_n$ and $M_w$ for monodisperse beef insulin (single species at 5733,5 g/mol). So what does the quotient $M_w/M_n$ mean now ?*

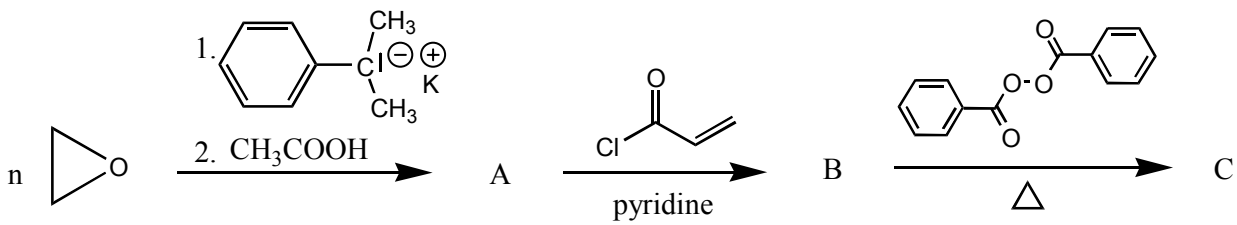
e) *If the MALDI-TOF-spectrum is expanded, there will be a finer structuring of the single peaks, like e.g. the simulation for the peak at 1098 g/mol (see illustration below). Give reasons for the occurrence of the additional signals.*




**Synthesis scheme**

Apart from the usual linear polymers, other polymer structures are of great interest as well. New structures can be synthesized by the combination of different methods.

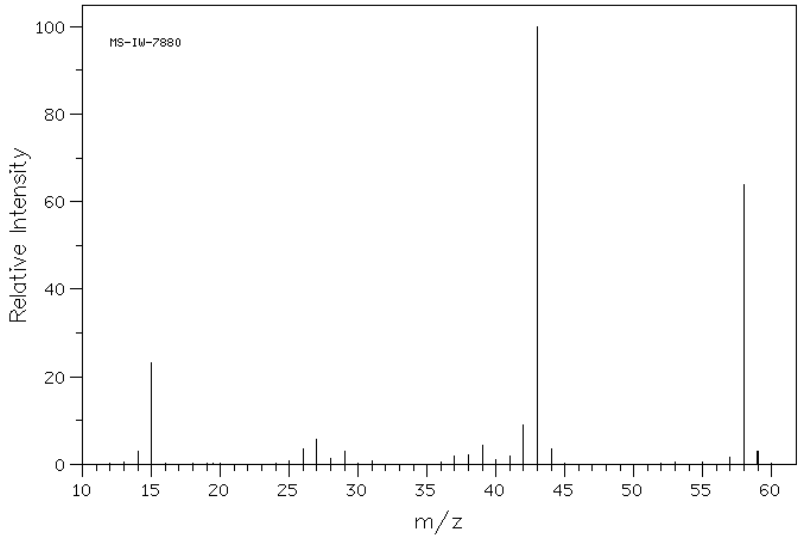
f) *Give the formulas of A, B and C. Make a rough sketch of C. Which current names does product A have? Which complications that could be negative for the planned architecture could appear in the last step?*



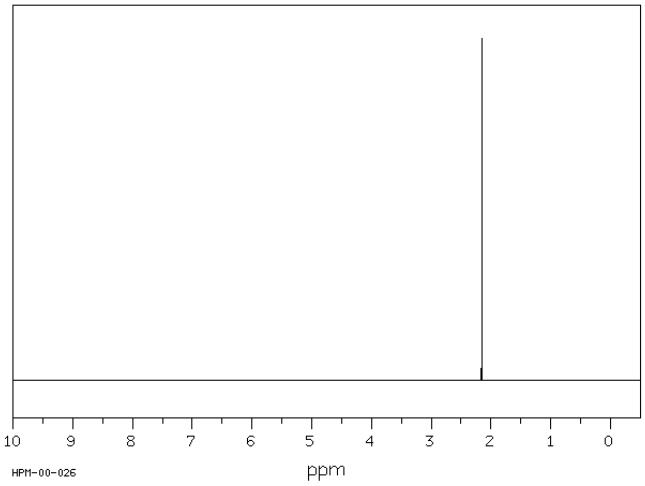
## Problem 4-8 Organic structural analysis

*a) Which organic compound A that consists of three elements (chemical formula and name) produces the following spectra?*

**mass spectrum**




$^1$H- NMR- spectrum




*b) Assign a cationic molecular fragment to each quite high peak (mass numbers 15, 27, 42, 43, 58) in the mass spectrum . Why is there only one peak in the $^1$H- NMR- spectrum?*

If compound A reacts with itself in an acid medium, pinacol will mainly form in a reductive coupling.

*c) Write down the reaction equation and give the name of pinacol according to the IUPAC-rules!*

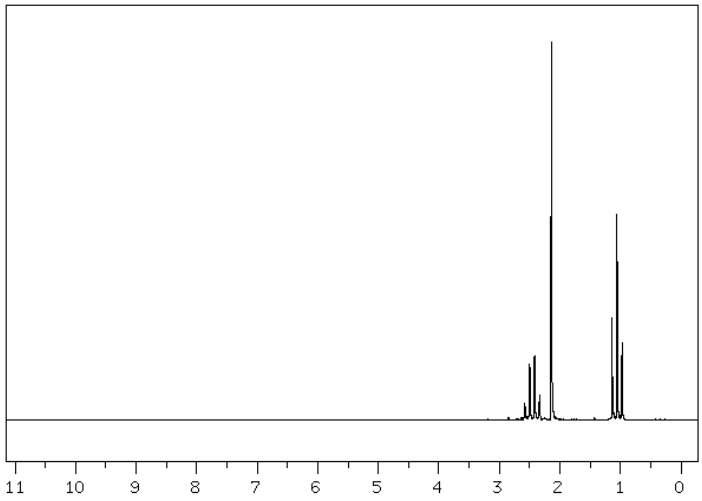
Pinacol - pinacolone - rearrangement

If pinacol is distilled with highly concentrated sulfuric acid, pinacolon (2,2- Dimethyl-butan-3-on) will form, water will be cleaved and there will be an intramolecular rearrangement.

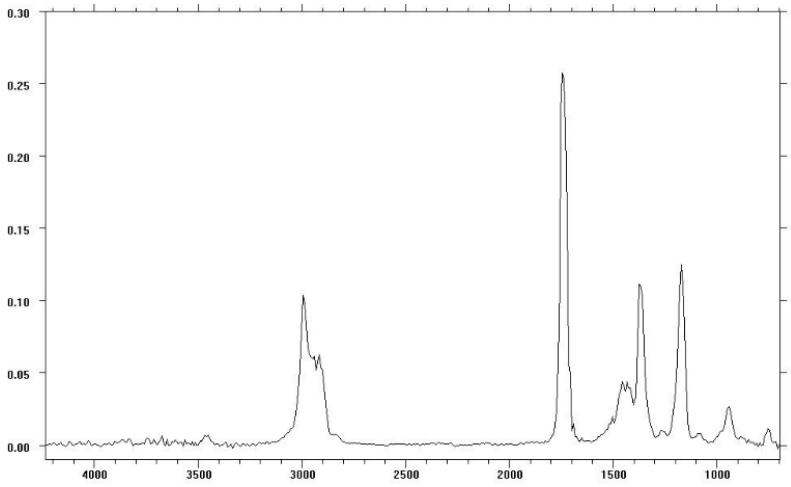
*d) Formulate the reaction equation as well as the reaction mechanism of the rearrangement.*

*e) A compound that is homologous to A produces the two spectra shown below. What kind of compound is that?*

$^1$H- NMR- spectrum

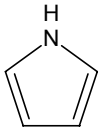



IR- spectrum



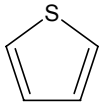

## Problem 4-9 Heteroaromatics

The following molecules are examples of heteroaromatics. Heteroaromatics are aromatic systems in which one or more carbon atoms are substituted by heteroatoms.




pyrrole


furan




thiophene

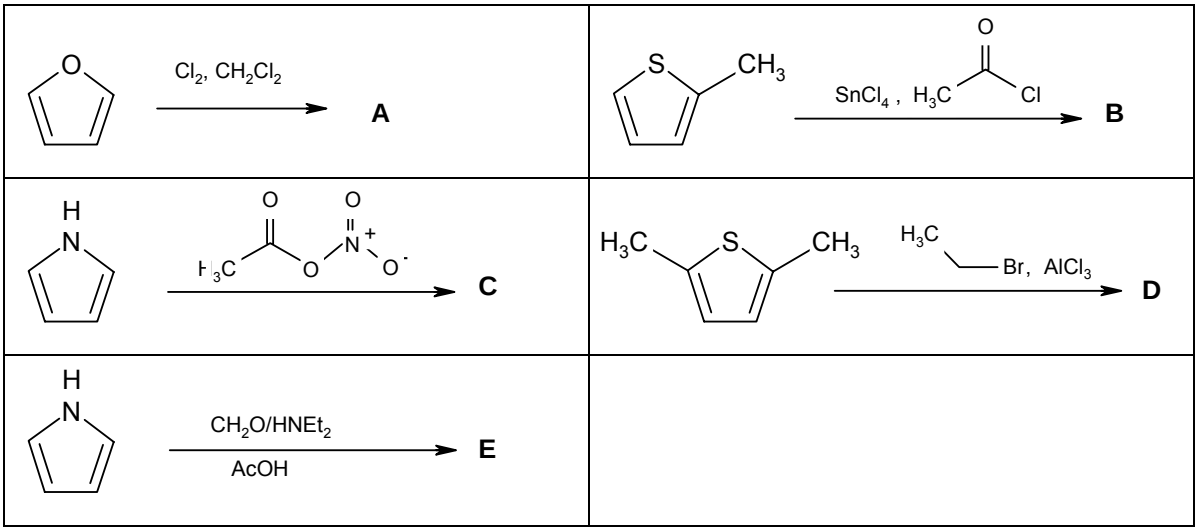
*a) When is a pi-electron system aromatic? Give four conditions.*

*b) Draw resonance structures of pyrrole emphasising its aromatic property.*

*c) Order the given molecules according to increasing aromaticity. Give reasons for this order.*

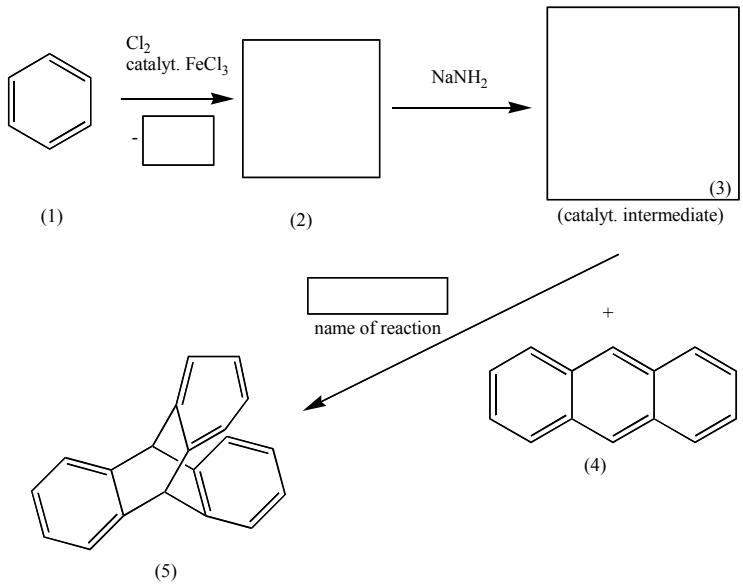
*d) In which position do you expect an electrophilic aromatic substitution of pyrrole? Give reasons.*

*e) Give the products of the following reactions:*




## Problem 4-10 Organic synthesis

*a) Complete the following reaction scheme:*

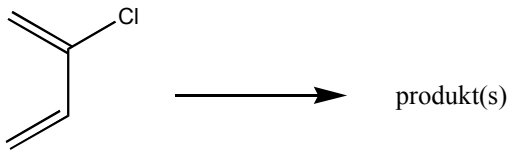



*b) Give the name of the compound (2)*

*c) What is the name of the reactive intermediate (3) ?*

*d) What is the name reaction of (3) with (4) to (5) called? What is the name of compound (5)?*

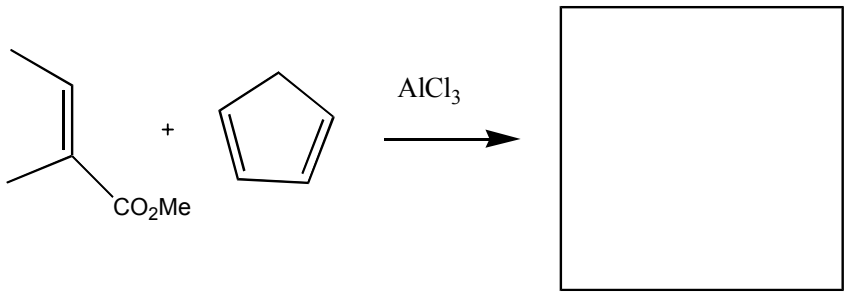
Iin the following, two molecules of the compound (6) react with each other in the name reaction of d) to form one or several possible product(s).




(6)

*e) Draw the structural formula(s) of the possible product(s).*

*f) Complete the reaction scheme of the following reaction with endo-selectivity:*




2 isomers

*g) What is the stereochemical relation of the two isomers ?*

# Fourth round (theoretical problems)

## Practical problem 4-11 Synthesis

**Procedure:**

0.30 g of NaOH globules are added to 1.0 g of 2,3-dihydroxynaphthalene in 10 ml of water at about 60°C, so that this mixture is a clear liquid.
This mixture is cooled down to room temperature (20...25°C) (e.g. with a cool water bath ).
0.65 mL of acetic anhydride are added (by injection) drop by drop while shaking the solution softly. After some drops already, the product precipitates as a solid. After each further addition of acetic anhydide, the cream has to be mixed well by powerful shaking. If necessary, a glass rod can be used for shaking.
Then, 10 ml of distilled water are added to the mixture. 5 minutes later, it is kept in a warm water bath at 60°C for about 10 minutes, until it shows a neutral or weakly acid reaction.
Afterwards, it is cooled down to 15°C (water bath) and kept at this temperature for about 10 minutes.
The product is sucked off, washed several times with a small amount of cold distilled water and pressed dry on filter paper. About 10 mg (= sample 1) are withdrawn from the raw product and dried in air.
The rest of the raw product is stirred in maximally 10 mL of about 50%- ethanol (that has to be produced by yourself) in the heat and, if necessary, dissolved completely in the heat by the addition of some 96%-ethanol. When it is cooled down, the product crystallizes in the form of glittering placelets. For completion of the crystallization, an ice bath can be used for cooling.
The purified product is sucked off, washed with a small amount of cold 50%-ethanol, pressed dry on filter paper and dried in air (= sample 2).
Mass and melting point of sample two have to be determined.
A TLC is made for 2,3-dihydroxynaphthalene, sample 1 and sample 2 (the solvent acetone/n-hexane 1:2 has to be produced by yourself). After drying, the thin-layer chromatogram is contemplated under ultraviolet light. The substance stains are marked with a pencil and wetted with dilute $FeCl_3$-solution with a capillary.
The $R_f$-values have to be determined.

*a) Give the reaction equation as well as the mechanism of the reaction.*

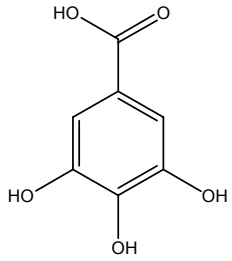
*b) Which compounds may form as by-products?*

*c) Illustration 1 (annexe) shows the $^{1}$H-NMR-spectrum and the $^{13}$C-NMR-spectrum of the product that is to be synthesized. Draw the structure of the compound and assign the marked signals of the $^{1}$H-NMR-spectrums to the hydrogen atoms.*

*d) In the past, ink was produced from iron salts and gallic acid (see illustration 2). How could gallic acid be obtained at that time?*

*e) Which analogy is there between the production of this gallic ink and the qualitative reaction with $FeCl_3$ that has been carried out by you?*

illustration 2: gallic acid




*f) Phenols like e.g. gallic acid were and are used in pyrotechnics for the production of whistling device. What is the mixing ratio of gallic acid and potassium chlorate ($KClO_3$) to obtain only water, carbon dioxide and KCl?*

## Practical problem 4-12 Analysis

**Procedure:**

The content of ammonium chloride of a sample has to be determined by acid-base titration.

1) The NaOH-solution for the titration has to be produced by yourself. A certain amount of solid NaOH has to be dissolved in about 100 mL of water (in a 250 mL gratuated flask) and filled up to 250 mL, so that a 0.1-molar NaOH-solution forms. By at least two titrations of a sample of about 100 to 150 mg of oxalic acid dihydrate HOOC-COOH · 2 $H_2O$ (oxalic acid dihydrate has to be weighed accurately to 0.1 mg, transformed into an Erlenmeyer flask and dissolved in about 50 mL of distilled water) against phenolphthalein, the factor (titer) of caustic soda solution has to be determined.

   Afterwards, a sample of ammonium chloride with an unknown concentration has to be titrated with this caustic soda solution.

2) **AT YOUR PLACE:** Fill up the ammonium-chloride solution (in the second graduated flask, marked as "analysis") to the mark.

   **IN THE HOOD:** 10 mL of the formaldehyde solution have to be put into the Erlenmeyer flask, filled up with about 50 to 100 mL of distilled water and 3 drops of phenolphthalein solution have to be added to this mixture.

   **AT YOUR PLACE:** The dilute formaldehyde solution has to be neutralized exactly with caustic soda solution. Then, an aliquot (20 or 25 mL) of the ammonium-chloride solution is added to this mixture. The mixture is titrated until there is a new change in colour (the colour should remain at the equivalence point for one minute at least).

   The titration will be repeated to obtain a reproduceable analytical result.

*a) Give the ammonium-chloride content of your sample (in mg).*

*b) Give all reaction equations that are important for this analysis.*

c) *Sketch the titration curve for i) the titration of ammonium chloride with caustic soda solution ($pK_S(NH_4^+)$ = 9.25) and ii) the titration of ammonium chloride with caustic soda solution in the presence of formaldehyde.*

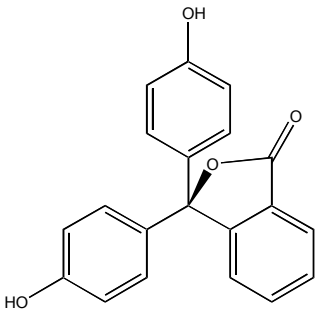
d) *Which preconditions does an acid-base indicator has to fulfill to be appropiate for this titration?*

e) *Oxalic-acid dihydrate is an original titer in this problem. Which properties must a substance have to be used as an original titer?*

f) *Which of the following compounds can not be used as original titers?:*
*$NH_4SCN$, $KIO_3$, Zn, $Mg(NO_3)_2$, $K_2Cr_2O_7$, NaCl*

g) *Illustration 3 shows the formula of phenolphthalein as a colourless compound in an acid solsution. Draw the structural formula of phenolphthalein as a red compound in a basic solution.*

illustration 3: phenolphthalein, colourless form



# Part 2

## Answers

# Answers Round 1

## Solution to problem 1-1

a) You find (i) ammonium hydrogencarbonate $NH_4HCO_3$
(ii) ammonium carbonate $(NH_4)_2CO_2$
*(iii) a mixture of (i) and (ii).*

b) $NH_4HCO_3 \longrightarrow NH_3 + CO_2 + H_2O$
$NH_4CO_2NH_2 \longrightarrow 2\,NH_3 + CO_2$

A mixture of 1 mol of ammonium hydrogencarbonate (M = 79.06 g/mol) and 1 mol of ammoniumcarbamate (M = 78.08 g/mol) weighs 157.14 g and releases upon heating 6 mol of gases.

1 g of salt of hartshorn provides n = 6·(1/157.14) mol of gases upon heating.

Using $p \cdot V = n \cdot R \cdot T$ : $V = \frac{6 \cdot 1 \cdot 8.314 \cdot (180 + 273)}{157.14 \cdot 1.013 \cdot 10^5}\,m^3 = 1.42 \cdot 10^{-3}\,m^3$

**V = 1.42 dm³**

c) $p(H) + p(H_2) = 0.98$ bar and $\frac{p^2(H)}{p(H_2)} = 2.51 \cdot 10^{-2}$ bar

$\Leftarrow p^2(H) - 2.51 \cdot 10^{-2}\,\text{bar} \cdot (0.980\,\text{bar} - p(H)) = 0$ **p(H) = 0.145 bar**

d) From c) you get $p(H_2) = 0.835$ bar.
1 mol of the mixture contains 0,145/0.98 mol of H and 0.835/0.98 mol of $H_2$.
Mean value of the molar mass:

$\overline{M}$ (Wasserstoff, 3000 K, 0.98 bar) = $\frac{(0.145 \cdot 1.008 + 0.835 \cdot 2.016) \cdot 10^{-3}\ kg \cdot mol^{-1}}{0.98}$

$\overline{M}$ (Wasserstoff, 3000 K, 0.98 bar) = $1.87 \cdot 10^{-3}$ kg·mol$^{-1}$.

With $p \cdot V = n \cdot R \cdot T$, $n = m/M$ and $\rho = m/V$ you get

$m/V = \rho = \frac{p \cdot \overline{M}}{R \cdot T}$, $\rho = \frac{10^5\,Pa \cdot 1.87 \cdot 10^{-3}\,kg \cdot mol^{-1}}{8.314\,JK^{-1}mol^{-1} \cdot 3000K}$, **$\rho = 7.35 \cdot 10^{-3}$ kg/m³** .

## Solution to problem 1-2

a)

| investigation 2: concentration of $Cl^-$ ions | investigation 1: total concentration of cations | investigation 3: total concentration of $Ca^{2+}$ and $Mg^{2+}$ ions | investigation 4: concentration of $Ca^{2+}$ ions |
|---|---|---|---|
| ⇩ | ⇩ | ⇩ | |
| concentration of $SO_4^{2-}$ | concentration of $Na^+$ | concentration of $Mg^{2+}$ | |

investigation 1:

$RH + Na^+ + H_2O \longrightarrow RNa + H_3O^+$
$2\ RH + Ca^{2+}\ (Mg^{2+}) + 2\ H_2O \longrightarrow R_2Ca\ (R_2Mg) + 2\ H_3O^+$
$n(H^+) = n(Na^+) + 2\cdot n(Ca^{2+}) + 2\cdot n(Mg^{2+})$
$n(H^+) = V(NaOH)\cdot c(NaOH)$ in 10 mL of sea water $n(H^+) = 0.500\cdot 11.76\cdot 10^{-3}$ mol
for 1 L of sea water: $c(Na^+) + 2\cdot c(Ca^{2+}) + 2\cdot c(Mg^{2+}) = 0.588$ mol/L

<u>investigation 2:</u>
$Ag^+ + Cl^- \longrightarrow AgCl$
for 1 L of sea water: $n(Cl^-) = 0{,}086 \cdot 6{,}21 \cdot 10^{-3}$ mol $= 0.534\cdot 10^{-3}$ mol
$c(Cl^-) = 0.534$ mol/L

<u>investigation 3:</u>
$Y^{4-} + Ca^{2+} \longrightarrow CaY^{2-}$ and $Y^{4-} + Mg^{2+} \longrightarrow MgY^{2-}$
in 10 mL of sea water: $n(Ca^{2+}) + n(Mg^{2+}) = 0.05\cdot 12.60\cdot 10^{-3}$ mol $= 0.63\cdot 10^{-3}$mol
$c(Ca^{2+}) + c(Mg^{2+}) = 0.063$ mol/L

<u>investigation 4:</u>
$Ca^{2+} + (COO^-)_2 \longrightarrow Ca(COO)_2$
$Ca(COO)_2 + 2\ H_3O^+ \longrightarrow Ca^{2+} + (COOH)_2 + 2\ H_2O$
$5\ (COOH)_2 + 2\ MnO_4^- + 6\ H_3O^+ \longrightarrow 2\ Mn^{2+} + 10\ CO_2 + 14\ H_2O$
$n(Ca^{2+}) = n((COO^-)_2) = \frac{5}{2}\cdot n(MnO_4^-)$
in 100 mL of sea water $n(Ca^{2+}) = \frac{5}{2}\cdot 0.02\cdot 24.00\cdot 10^{-3}$ mol
$c(Ca^{2+}) = 0.012$ mol/L

Calculation
investigation 2: $c(Cl^-) = 0.534$ mol/L, with $M(Cl^-) = 35.45$ g/mol **18.93 g/L $Cl^-$**

investigation 1: $0.588\ mol/L = c(Na^+) + 2\cdot c(Ca^{2+}) + 2\cdot c(Mg^{2+}) = c(Cl^-) + 2\cdot c(SO_4^{2-})$
$2\cdot c(SO_4^{2-}) = (0.588 - 0.534)\ mol/L = 0.054\ mol/L$
$c(SO_4^{2-}) = 0.027$ mol/L, with $M(SO_4^{2-}) = 96.07$ g/mol **2.59 g/L $SO_4^{2-}$**

investigation 4: $c(Ca^{2+}) = 0.012$ mol/L, with $M(Ca^{2+}) = 40.08$ g/mol **0.48 g/L $Ca^{2+}$**

investigation 3: $c(Ca^{2+}) + c(Mg^{2+}) = 0.063$ mol/L und $c(Ca^{2+}) = 0.012$ mol/L
$c(Mg^{2+}) = 0.063 mol/L - 0.012\ mol/L = 0.051\ mol/L$
with $M(Mg^{2+}) = 24.31$ g/mol **1.24 g/L $Mg^{2+}$**
$c(Na^+) + 2\cdot c(Ca^{2+}) + 2\cdot c(Mg^{2+}) = 0.588$ mol/L and
$2\cdot c(Ca^{2+}) + 2\cdot c(Mg^{2+}) = 2\cdot 0.063$ mol/L $c(Na^+) = 0.462$ mol/L
with $M(Na^+) = 22.99$ g/mol **10.62 g/L $Na^+$**

b) Silver chloride (white) and silver chromate (reddish brown) are sparingly soluble salts. However, the solubility of silver chloride is smaller than that of silver chromate. So,

during investigation 2 silver chloride precipitates first. The reddish brown silver chromate does not precipitate till silver chloride has precipitated nearly completely. This is the reason silver chromate can serve as an indicator for the end of the precipitation of silver chloride.

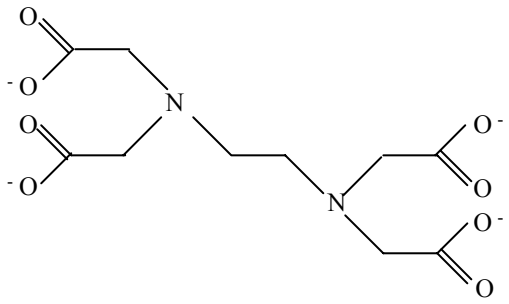
c) Additon of other less noble metals:

$$2\ AgCl(s) + Zn(s) \xrightarrow{H_2O} 2\ Ag(s) + Zn^{2+}(aq) + 2\ Cl^-(aq)$$

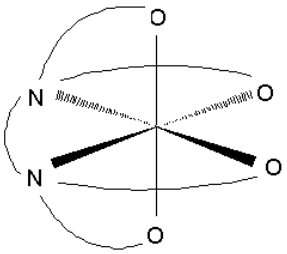
m(Ag) = 107,9 g/mol · 5 L · 0,2 mol/L = 107.9 g

Price of silver on March 3rd 2003: 124 €/kg, value of 107.9 g of silber = **13.4 €**

d) The anion of EDTA
$(^-OOC\text{-}CH_2)_2\ N\text{-}CH_2\text{-}CH_2\text{-}N\ (CH_2\text{-}COO^-)_2$
is hexacoordinated.
The structure of the complex shown in the second figure has the metal ion in the middle.



Upon reacting with the indicator ions of$Mg^{2+}$ and $Ca^{2+}$ form a red complex while the free indicator is blue.
If indicator is added to a solution of ions of $Ca^{2+}$ and $Mg^{2+}$ a red solution forms. The red complex disappears upon adding a solution of EDTA. That's why at the equivalence point a clear change of colour from red to blue is visible.



e) *To prove other proposals for the composition the molar masse shown:*

| salt | NaCl | $Na_2SO_4 \cdot 10\ H_2O$ | $CaCl_2 \cdot 6\ H_2O$ | $MgCl_2 \cdot 6\ H_2O$ | $MgSO_4 \cdot 7\ H_2O$ |
|---|---|---|---|---|---|
| mol. mass | 58.44 g/mol | 322.05 g/mol | 218.98 g/mol | 203.21 g/mol | 246.38 g/mol |

$c(Na^+)$ = 0.462 mol/L **27.00 g/L NaCl**
$c(Ca^{2+})$ = 0.012 mol/L **2.63 g/L $CaCl_2 \cdot 6\ H_2O$**
$c(SO_4^{2-})$ = 0.027 mol/L **6.65 g/L $MgSO_4 \cdot 7\ H_2O$**
$c(MgCl_2 \cdot 6\ H_2O) = c(Mg^{2+}) - c(MgSO_4 \cdot 7\ H_2O)$ = 0.051 mol/L – 0.027 mol/L
$c(MgCl_2 \cdot 6\ H_2O)$ = 0.024 Mol/L **4.88 g/L $MgCl_2 \cdot 6\ H_2O$**

$Na_2SO_4 \cdot 10\ H_2O$ is not used for this solution.

## Solution to problem 1-3

a) The key to the solution of this problem is the different number of reactions the metals and the salts undergo. You need to know the standard electrode potentials.
Silver does not react with any of the given salts, copper with one of them ($AgNO_3$), iron with two ($AgNO_3$, $Cu(NO_3)_2$) and magnesium with three ($AgNO_3$, $Cu(NO_3)_2$, $Fe(NO_3)_3$) .
Magnesium nitrate reacts with none of the given metals, iron nitrate with one (Mg), copper with two (Fe und Mg) and silver nitrate with three (Fe, Mg, Cu).
On the remaining pieces of paper you realize:

| | |
|---|---|
| B, C, D react at least once | ⇐ A = silver, |
| 1, 3, 4 react at least once | ⇐ 2 = magnesium nitrate, |
| 1 does not react with silver (A) but twice otherwise | ⇐ 1 = copper nitrate, |
| $Cu(NO_3)_2$ does not react with silver (A) nor with copper | ⇐ B = copper, |
| copper (B) reacts with silver nitrate only | ⇐ 4 = silver nitrate, |
| that leaves | 3 = iron nitrate |
| $Fe(NO_3)_3$ (3) reacts with magnesium only | ⇐ D = magnesium |
| that leaves | C = iron . |

b) Results not used: A/3 and A/4 .

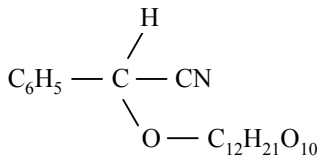
## Solution to problem 1-4

a) Reaction equation for the hydrolysis of A:

$$C_{20}H_{27}O_{11}N + 2\,H_2O \longrightarrow 2\,C_6H_{12}O_6 + C_6H_5CHO + HCN$$

glucose benzaldehyde hydrocyanic acid

b) Structural formela of compound A



glycosidic bond

sugar component consisting of two glucose moieties

# Answers round 2

## Solution to problem 2-1

a) $pH = - \lg \frac{c(H^+)}{c_0}$ with $c_o = 1\ mol \cdot L^{-1}$ , $pH = - \lg 0.5$ $pH = 0.30$

b) $c(Cl^-) + c(OH^-) = 3 \cdot c(Fe^{3+}) + c(H^+)$

At pH = 2 $c(OH^-) = \frac{K_W}{c(H^+)} = 10^{-12}\ mol \cdot L^{-1}$.

As the concentration of $Cl^-$ is at least as large as the concentration of $H^+$ ( $= 10^{-2}\ mol \cdot L^{-1}$) the concentration of $OH^-$ can be neglected.

$c(Cl^-) = 3 \cdot \frac{K_L}{c(OH^-)^3} + c(H^+)$ and $c(OH^-) = \frac{K_W}{c(H^+)}$

$\Leftarrow c(Cl^-) = 3 \cdot \frac{K_L}{K_W^3} \cdot c(H^+)^3 + c(H^+)$

c) Chloride:

$c(Cl^-) = 3 \cdot \frac{2 \cdot 10^{-39} mol^4 \cdot L^{-4}}{(10^{-14} mol^2 \cdot L^{-2})^3} \cdot (10^{-2}\ mol \cdot L^{-1})^3 + 10^{-2}\ mol \cdot L^{-1}$

$c(Cl^-) = 1{,}6 \cdot 10^{-2}\ mol \cdot L^{-1}$ .

Iron:

$c(Fe^{3+}) = \frac{K_L}{c(OH^-)^3} = \frac{2 \cdot 10^{-39} mol^4 \cdot L^{-4}}{(10^{-12} mol^2 \cdot L^{-2})^3} = 2 \cdot 10^{-3}\ mol \cdot L^{-1}$.

Rust ($Fe(OH)_3$):

$n(Fe(OH)_3) = n(Fe^{3+}) = c(Fe^{3+}) \cdot V$

$= 2 \cdot 10^{-3}\ mol \cdot L^{-1} \cdot ¾ \cdot 0.2\ L = 0.3\ mmol$ .

$M(Fe(OH)_3) = 106.88\ g/mol$

$m(Fe(OH)_3) = n(Fe^{3+}) \cdot M(Fe(OH)_3 = 0.3\ mmol \cdot 106.88\ g/mol \approx 32\ mg$

d) Amount of $Cl^-$ in the yellow solution:

$n(Cl^-) = n(Cl^-) \cdot V = 1.6 \cdot 10^{-2}\ mol \cdot L^{-1} \cdot 0.15\ L = 2.4\ mmol$

The same amount must have been in the hydrochloric acid ($c_0 = 0{,}5\ mol \cdot L^-1$) added before.

$\Delta V(HCl) = \frac{n(HCl)}{c(HCl)} = 4{,}8\ mL$

e) $2\ Fe^{3+} + Cu \longrightarrow 2\ Fe^{2+} + Cu^{2+}$

yellow bluish green

Assuming the reaction is complete:

$c_{bluish\ green}(Fe^{2+}) = c_{yellow}(Fe^{3+}) = 2 \cdot 10^{-3}\ mol \cdot L^{-1}$

$c_{bluish\ green}(Cu^{2+}) = ½ \cdot c_{yellow}(Fe^{3+}) = 1 \cdot 10^{-3}\ mol \cdot L^{-1}$

In the bluish green solution: $E(Fe^{3+}/Fe^{2+}) = E(Cu^{2+}/Cu)$

$$E = E^0(Cu^{2+}/Cu) + \frac{R \cdot T}{2 \cdot F} \cdot \ln \frac{c(Cu^{2+})}{c_0}$$

$$E = 0.345\ V + \frac{8.314 \cdot 300}{2 \cdot 96487} V \cdot \ln 1 \cdot 10^{-3} \qquad E = 0.256\ V$$

$$E = E^0(Fe^{3+}/Fe^{2+}) + \frac{R \cdot T}{F} \cdot \ln \frac{c(Fe^{3+})}{c(Fe^{2+})}$$

$$0.256\ V = 0.771\ V + 0.0259\ V \cdot \ln \frac{c(Fe^{3+})}{c(Fe^{2+})}$$

$c(Fe^{3+}) = 2.31 \cdot 10^{-9} \cdot c(Fe^{2+})$

$c(Fe^{3+}) = 4.63 \cdot 10^{-12}$

## Solution to problem 2-2

**a)**

$$AI_x \longrightarrow A + \frac{x}{2} I_2$$

$p_2 = p_2(N_2) + p_2(I_2)$.

$$p_2(N_2) = p_1(N_2)\frac{T_2}{T_1} = 1{,}013 \cdot 10^5 Pa \frac{723.15 K}{298.15 K} = 2{,}457 \cdot 10^5 Pa,$$

$p_2(I_2) = p_2 - p_2(N_2) = 3.346 \cdot 10^5$ Pa $- 2.457 \cdot 10^5$ Pa $= 8.89 \cdot 10^4$ Pa.

$$n(I_2) = \frac{pV}{RT} = \frac{8.89 \cdot 10^4 Pa \cdot 2.070 \cdot 10^{-5} m^3}{8.314 J \cdot K^{-1} mol^{-1} \cdot 723.15 K} = 3.061 \cdot 10^{-4} mol.$$

$m(I_2) = n(I_2) \cdot M(I_2) = 77{,}7$ mg,

$m(A) = m(AI_x) - m(I_2) = 7{,}3$ mg

$$n(A) = \frac{2}{x} n(I_2)$$

$\Leftarrow$

$$M(A) = \frac{m(A)}{n(A)} = \frac{x}{2} \cdot \frac{m(A)}{n(I_2)} = x \cdot \frac{7.3 \cdot 10^{-3} g}{2 \cdot 3.061 \cdot 10^{-4} mol} = 11.9 \cdot x\ g/mol.$$

| | | |
|---|---|---|
| x = 1 | M(A) =11.9 g/mol (C) | $\Rightarrow$ C isn't a metal |
| x = 2 | M(A) =23.9 g/mol (Mg) | $\Rightarrow$ $MgI_2$ is not volatile |
| x = 3 | M(A) = 35.8 g/mol (Cl) | $\Rightarrow$ Cl isn't a metal |
| x = 4 | M(A) = 47.7 g/mol (Ti) | $\Rightarrow$ $TiI_4$ is volatile and decomposes into the elements |
| x = 5 | M(A) = 59.5 g/mol | $\Rightarrow$ there is no suitable element. |

Metal iodides with more than 5 iod atoms are currently not to be known.

Solution: $TiI_4$.

b) Für die Änderung der Konzentration von HI in der (kurzen) Zeit $\Delta t$ gilt:

$$\Delta c(HI) = (2k_1 c(H_2)c(I_2) - 2k_{-1} c^2(HI))\Delta t.$$

In equilibrium $\Delta c(HI) = 0 \quad \Leftarrow \quad k_1 c(H_2)c(I_2) - k_{-1} c^2(HI) = 0$

$$K = \frac{c^2(HI)}{c(H_2)c(I_2)} = \frac{k_1}{k_{-1}}.$$

| T, K | 400 | 500 | 600 | 700 | 800 |
|---|---|---|---|---|---|
| K | 258 | 127 | 80.1 | 57.4 | 44.6 |

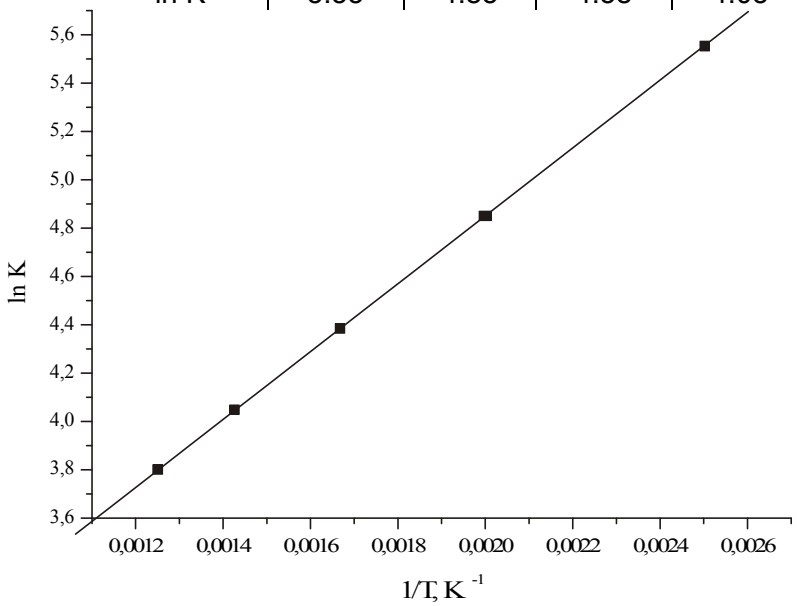
The higher the temperature the lower die equilibrium constant $\Rightarrow$ the reaction is exothermic (prinziple of Le Chatelier).

c) Die Temperaturabhängigkeit der Gleichgewichtskonstante ist durch die van't Hoffsche Reaktionsisobare gegeben:

$$ln\frac{K_2}{K_1} = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

so dass aus der Steigung der Geraden ln K = f (1/T) die Reaktionsenthalpie abgelesen werden kann.

| T, K | 400 | 500 | 600 | 700 | 800 |
|---|---|---|---|---|---|
| 1/T, $K^{-1}$ | $2.50\cdot10^{-3}$ | $2.00\cdot10^{-3}$ | $1.67\cdot10^{-3}$ | $1.43\cdot10^{-3}$ | $1.25\cdot10^{-3}$ |
| ln K | 5.55 | 4.85 | 4.38 | 4.05 | 3.80 |




From values at 400 K and 800 K $\quad \Delta H_r = -11.7$ kJ/mol.

$\Delta G_r = -RT \ln K$

$\Delta S_r = (\Delta H_r - \Delta G_r)/T.$

| T, K | 400 | 500 | 600 | 700 | 800 |
|---|---|---|---|---|---|
| $\Delta G_r$, kJ/mol | –18.5 | –20.1 | –21.9 | –23.6 | –25.3 |
| $\Delta S_r$, $J\cdot K^{-1}\cdot mol^{-1}$ | 16.9 | 16.9 | 16.9 | 17.0 | 16.9 |

$\Delta S_r = 16.9\ J\cdot K^{-1}\cdot mol^{-1}.$

d) Degree of dissociation of HI at 600 K = $\alpha$. $c(H_2) = c(I_2) = ½\ \alpha c_0$, $c(HI) = (1-\alpha)\ c_0$,

$$K = \frac{c^2(HI)}{c(H_2)\,c(I_2)} = \frac{4\alpha^2}{1-\alpha}$$

K = 80,1 $\Leftarrow$ $\alpha$ = 0.955.

The number of particles does not change $\Leftarrow$ the equivalent constant does not depend on the pressure.

e)
$$K = \frac{c(I_2\ in\ CS_2)}{c(I_2\ in\ H_2O)} = 585.$$

$$c(I_2\ in\ CS_2) = \frac{32.33\ g/L}{253.8\ g/mol} = 0.127\ mol/L,$$

$$c(I_2\ in\ H_2O) = \frac{0.127\ mol/L}{585} = 2.18\cdot10^{-4}\ mol/L.$$

$$c(I_3^-\ in\ H_2O) = \frac{1.145\ g/L}{253.8\ g/mol} - 2.18\cdot10^{-4}\ mol/L = 4.29\cdot10^{-3}\ mol/L,$$

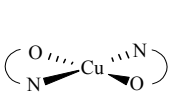
$$c(I^-\ in\ H_2O) = c_0(KI) - c(I_3^-\ in\ H_2O) = 3.125\cdot10^{-2}\ mol/L \cdot 4.29\cdot10^{-3}\ mol/L$$
$$= 2.70\cdot10^{-2}\ mol/L.$$

$$K = \frac{c(I_3^-\ in\ H_2O)}{c(I_2\ in\ H_2O)\,c(I^-\ in\ H_2O)} = 7.3\cdot10^2\ L/mol.$$

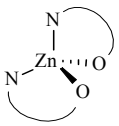
## Solution to problem 2-3

a)

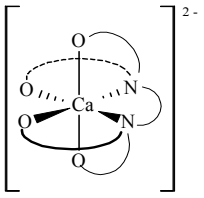
(C: the five-times coordinated structure is also taken as correct, it is chiral too)



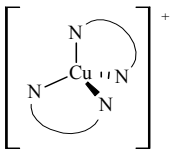
**A** achiral



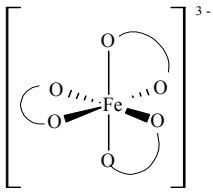
**B** chiral



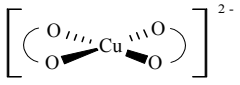
**C** chiral



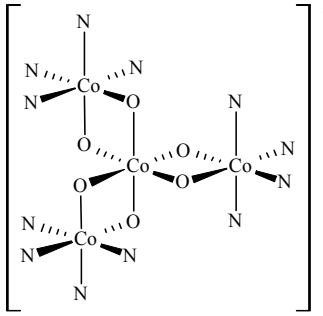
**D** achiral



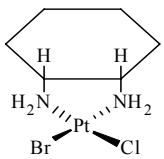
**E** chiral



**F** achiral



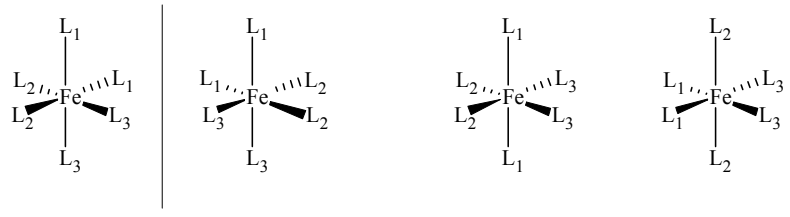
**G** chiral



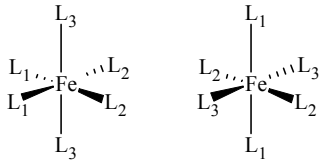
**H** chiral

b) 3

c) $M(L^1)_2(L^2)_2(L^3)_2$. with 6 stereoisomeres

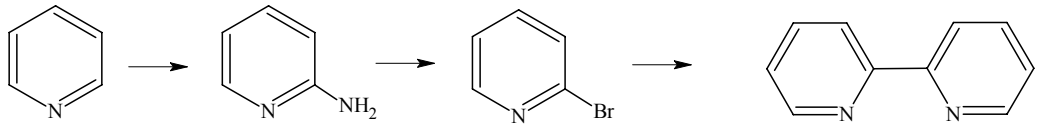


chiral achiral achiral



achiral achiral

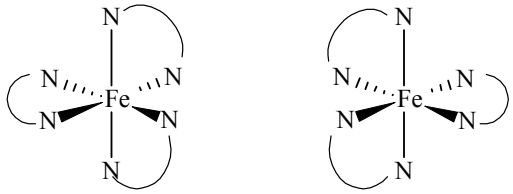
d)

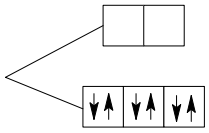


**P** **Q** **R** **S**

2,2'-Bipyridin

e) T = $[Fe(bpy)_3]\ SO_4$.





f) The formation of $[Fe(bpy)_3]^{2+}$ in an aquous solution is a three step process:

$$[Fe(H_2O)_6]^{2+} \xrightarrow[-\ 2\ H_2O]{bpy} [Fe(H_2O)_4(bpy)]^{2+} \xrightarrow[-\ 2\ H_2O]{bpy} [Fe(H_2O)_2(bpy)_2]^{2+} \xrightarrow[-\ 2\ H_2O]{bpy} [Fe(bpy)_3]^{2+}$$

high-spin high-spin high-spin low-spin

In the third step a transition from high-spin- to low-spin takes place. The stabilisation energy of the ligand field connected with this step favors the complexation and draws attention to the equivalent constant.

## Solution to problem 2-4

a) The Si atom is larger than the C atom, so a higher coordination number is preferred. Si belongs to the 3rd period of the PSE so overlapping of $\pi$ orbitals does hardly contribute to a gain of bonding energy. Forming of 4 $\sigma$ bondings with O is favored.

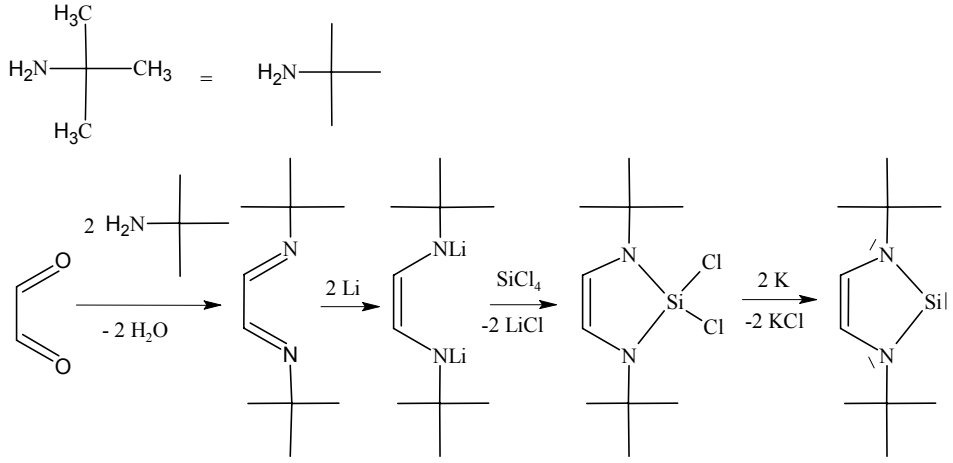
b) Hardening agent and impregnant in construction industry, paper manufacturing, ...

c) Q-Gruppen von Q0 bis Q4, also $SiO_4^{4-}$,(Si-O-)$SiO_3^{3-}$,(Si-O-)$_2SiO_2^{2-}$, Si-O-)$_3SiO^-$,(Si-O-)$_4$Si

d)
$$2\ (CH_3)_3SiCl + H_2O \longrightarrow (CH_3)_3SiOSi(CH_3)_3 + 2\ HCl$$
$$m\ (CH_3)_2SiCl_2 + m\ H_2O \longrightarrow [(CH_3)_2SiO]_m + 2m\ HCl$$
$$n\ CH_3SiCl_3 + 1{,}5n\ H_2O \longrightarrow [CH_3SiO_{1,5}]_n + 3n\ HCl$$

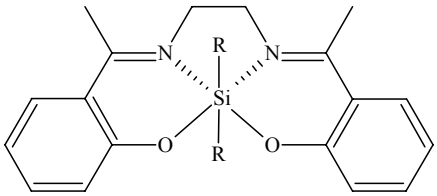
e) Silicones

f) **A** ist tert-Butylamin:




Compund **E** is aromatic

g) **Y**, **Z** = (R = Cl bei **Y**, R = F bei **Z**) **X** = HCl.



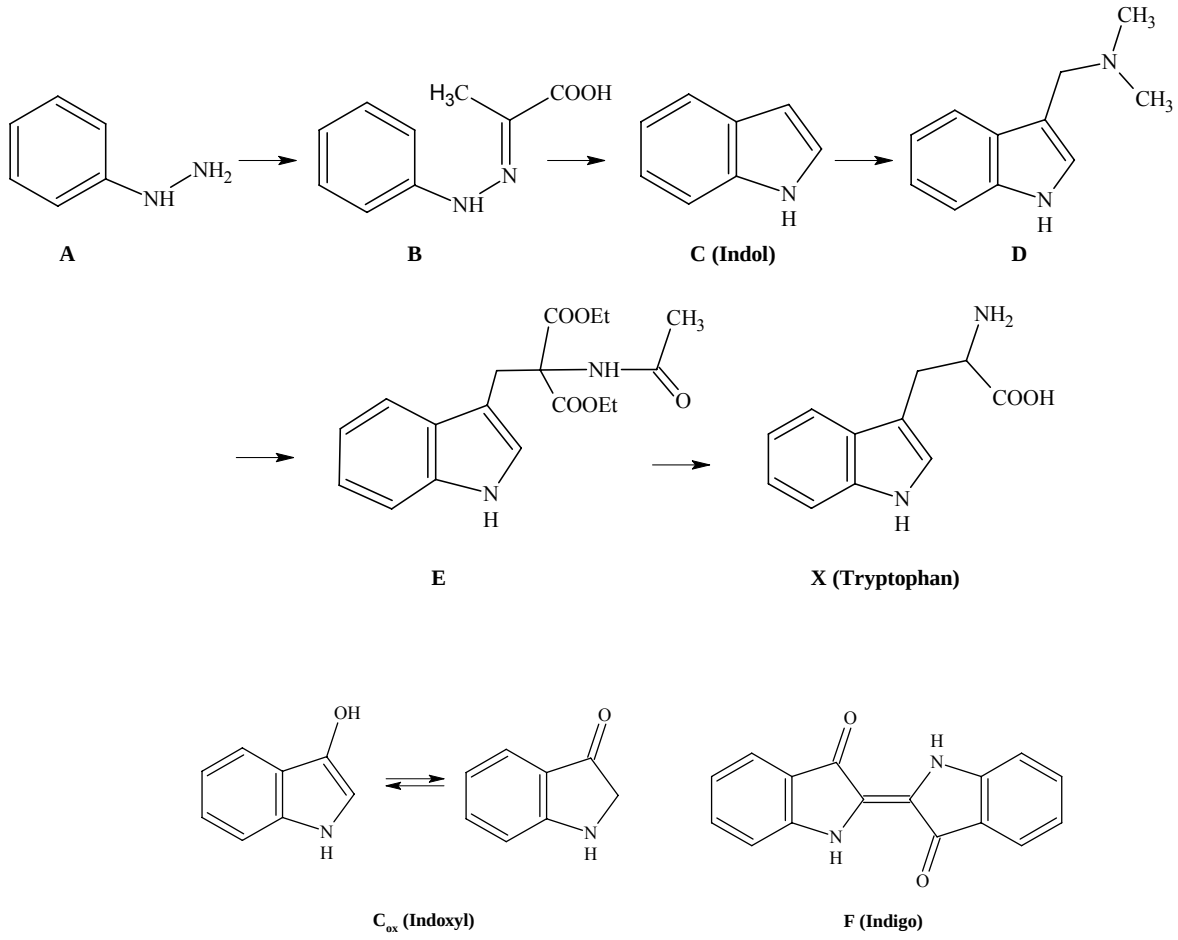

h) The octet rule is strictly valid only in the 2nd period. As Si belongs to the 3rd period there are d orbitals with a capacity of 18 electrons (principally). The Si atom provides empty orbitals for further ligands/donor atoms.

i) Volume of a monoclinic unit cell: $V(EZ) = a \cdot b \cdot c \cdot \sin\beta = 1837\ Å^3$,
$C_{20}H_{21}F_2N_3O_2Si$, has 28 non-hydrogen atoms.
With n = 4 : 16.4 $Å^3$ for a non-hydrogen atom (n = 2 is to small, n = 6 is to large).
The unit cell consists of 4 complex molecules Z and 4 molecules acetonitrile.

$$\rho = \frac{m(EZ)}{V(EZ)} = \frac{n \cdot (M(Z) + M(CH_3CN))}{V(EZ)} = \frac{4 \cdot 401.5 \cdot 1.66 \cdot 10^{-27} g}{1.873 \cdot 10^{-24} cm^3} = 1.42 g / cm^3$$

## Solution to problem 2-5

a)

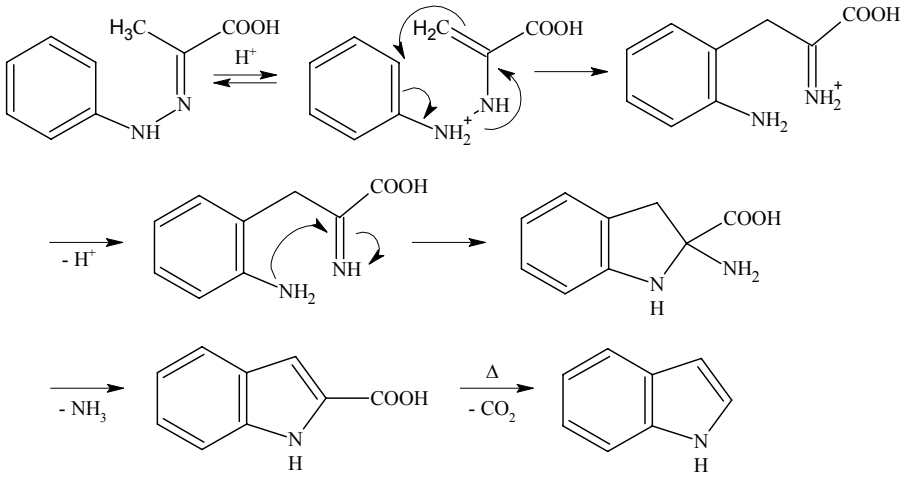



**A** **B** **C (Indol)** **D**

**E** **X (Tryptophan)**

**$C_{ox}$ (Indoxyl)** **F (Indigo)**

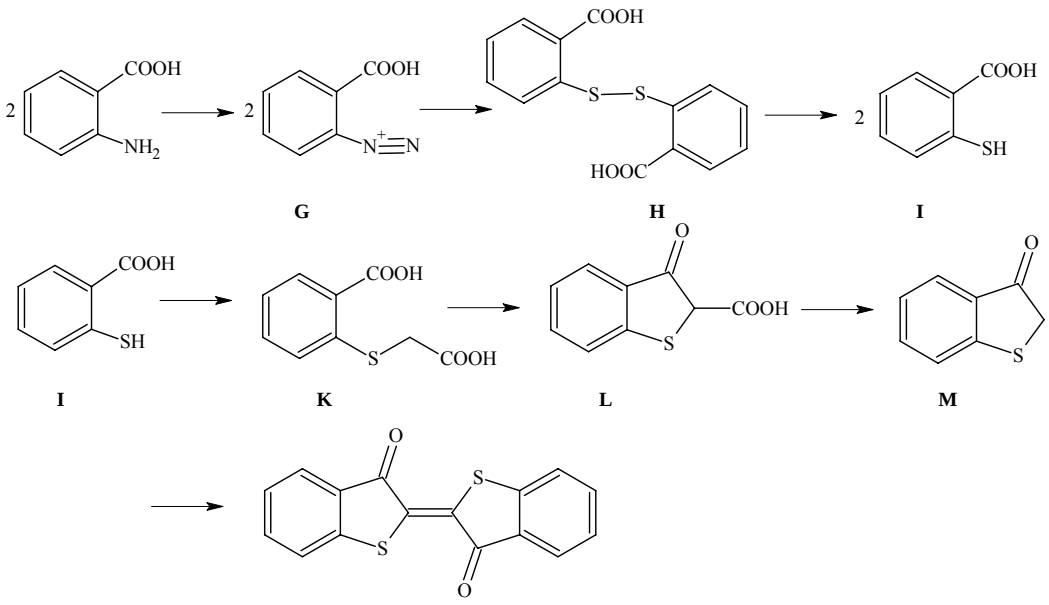
b) Mechanismus der Fischer-Indolsynthese:




**C (Indol)**

c)

a)




**G** **H** **I**

**I** **K** **L** **M**

**Z (Thioindigo)**

# Answers round 3 test 1

(They are explained in a more detailed way than expected from the pupils)

## Solution to problem 3-1

A) d  B) e  C) d  D) c  E) a  F) c  G) b  H) f  I) d  J) b

## Solution to problem 3-2

a)

| | | | | | | |
|---|---|---|---|---|---|---|
| 1 $CuSO_4$ | 2 NaCl | 3 $AgNO_3$ | 4 $H_2SO_4$ | 5 HI | 6 NaOH | 7 $Na_2CO_3$ |

b) X = $NH_4I$  Y = $CuCl_2$

c)

| | | | |
|---|---|---|---|
| $Cu^{2+} + 2I^-$ | ⟶ | $CuI + 1/2\ I_2$ | N(b) [$CuI_2^-$ is correct as well] |
| $Cu^{2+} + CO_3^{2-}$ | ⟶ | $CuCO_3$ | N(bl) [$Cu(OH)_2 \cdot CuCO_3$ is correct as well] |
| $Cu^{2+} + 2\ OH^-$ | ⟶ | $Cu(OH)_2$ | N(bl) |
| $Ag^+ + Cl^-$ | ⟶ | AgCl | N(w) |
| $Ag^+ + I^-$ | ⟶ | AgI | N(y) |
| $2Ag^+ + CO_3^{2-}$ | ⟶ | $Ag_2CO_3$ | N(wy) |
| $2Ag^+ + 2OH^-$ | ⟶ | $Ag_2O + H_2O$ | N(b) [AgOH is correct as well] |
| $NH_4^+ + OH^-$ | ⟶ | $NH_3 + H_2O$ | pungent smell |
| $2H_3O^+ + CO_3^{2-}$ | ⟶ | $CO_2 + 3H_2O$ | gas |

## Solution to problem 3-3

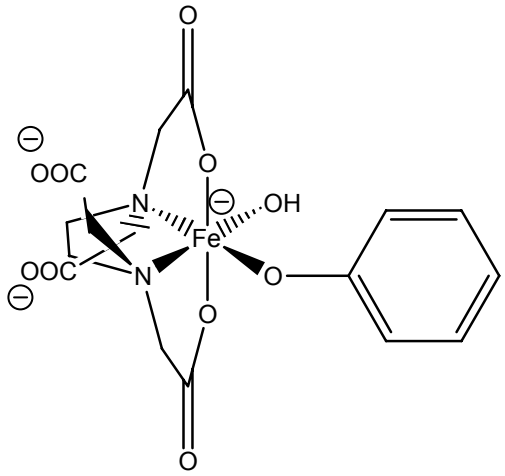
a) $K_1 = c(\mathbf{B})/[c(\mathbf{A}) \cdot c(OH)]$

$c(\mathbf{B}) = K_1 \cdot c(\mathbf{A}) \cdot c(OH) = 10^{6.45} \cdot 0.001 \cdot 10^{-6}$ = 0.002818 mol/L

$c(\mathbf{C}) = K_2 \cdot c(\mathbf{B}) \cdot c(OH) = 10^{4.53} \cdot 0.002818 \cdot 10^{-6}$ = 0.000095 mol/L

The major part of steric expansion already occurs at the formation of **B** from **A**.

b)




It must be a complex with cis-monodentate ligands.

c) Cyanide is a very strong ligand, this is the reason why there is a high ligand-field splitting of the d-orbitals in the octahedral field of hexacyanoferrate(III). Hexacyanoferrate(III) occurs as a low-spin-complex (1 unpaired electron). The iron-EDTA-complexes are high-spin-complexes (5 unpaired electrons). Thus, the O-donor-ligands produce a much weaker ligand field than cyanide.

d) Iron(III) is a weak oxidizing agent; thiolates and phenolates are weak reducing agents. They make possible a charge-transfer (partial redox process between ligand and central ion). This process can easily be excited by light. This is the reason for the intensive colour of CT-complexes.

e) E = 1.505 (5cm-cuvette) corresponds to E = 0.301, according to the original prescription with a 1 cm-cuvette. $E = b \cdot c + a$, $c = (E-a)/b = (0.301-0.013)/0.0048\ mg^{-1} = 60$ mg of thymol in the analyte. However, only 1 mL of 5 mL of the analyte-solution was added. Thus, the sample (1 g) contained altogether 300 mg of thymol. The mass fraction is 30 %. M(thymol) = 150,23 g/mol. 0,3 g = $2 \cdot 10^{-3}$ mol (per gram of raw substance) or rather 0,002 mol per gram of raw substance.

f) $E = c \cdot d \cdot \varepsilon'$ $\varepsilon' = E/(c \cdot d)$ The concentration of thymol in the photometry-solution was: ($2 \cdot 10^{-3}$ mol/g and one fifth of it ( $4 \cdot 10^{-4}$ mol) in 50 $cm^3$ of photometry solution) $c = 8 \cdot 10^{-6}$ mol/$cm^3$. d = 5 cm, E = 1,505. The result is $\varepsilon' = 37625\ cm^2$/mol.
$\varepsilon'$ is the apparent coefficient of extinction, because the real concentration of $[FeY(OH)(thymolate)]^{3-}$ is not known.
The OH-group of vanillin is sterically less hindered than that of thymol. Thus, there is a higher fraction of CT-complex in the photometry-solution and a higher relative extinction b.

## Solution to problem 3-4

a)

$$6\ Nb(OEt)_5 + 17\ (Me_3Si)_2S + 4\ NEt_4Cl \xrightarrow{CH_3CN} (NEt_4)_4[Nb_6S_{17}] \bullet 3\ CH_3CN + 30\ Me_3SiOEt + 4\ Me_3SiCl \quad \textbf{(1)}$$

b) In the course of the reaction 35 particles form from 27 particles (30 particles, if the solvent molecules $CH_3CN$ are taken into consideration as well). That means that the numer of particles and the disorder increase. A higher disorder corresponds to a higher entropy that is energetically more favourable, that means that it favours the reaction.

The nascent Si-O and Si-Cl-bonds are more stable than the S-Si-bond in the initial compound.

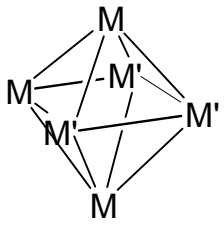
c) At first, the relative molar masses of the compounds $Nb(OEt)_5$, $(Me_3Si)_2S$, $NEt_4Cl$ and $(NEt_4)_4[Nb_6S_{17}]*3CH_3CN$ have to be calculated:
$M(Nb(OEt)_5)$ = 318.21 g/mol $M((Me_3Si)_2S)$ = 178.45 g/mol
$M(NEt_4Cl)$ = 165.45 g/mol $M((NEt_4)_4[Nb_6S_{17}] \cdot 3CH_3CN)$ = 1745.7 g/mol
5g of (**1**) should be obtained from a yield of 75%.
The following calculation has to be made at first: $\frac{100\%}{75\%} \cdot 5.000g = 6.667g$.
6,667g of (**1**) correspond to $\frac{6.667g}{1745.7g/mol} = 3.819 \cdot 10^{-3} mol$.
Thus, the following amounts are needed from the initial substances:

| | n in mol | n in mol | m in g | V in mL |
|---|---|---|---|---|
| $Nb(OEt)_5$ | $6 \cdot 3.819 \cdot 10^{-3}$ mol | 0.02291 mol | 7.291 | 5.750 |
| $(Me_3Si)_2S$ | $1.4 \cdot 17 \cdot 3.819 \cdot 10^{-3}$ mol | 0.09089 mol | 16.220 | 19.173 |
| $NEt_4Cl$ | $1.4 \cdot 4 \cdot 3.819 \cdot 10^{-3}$ mol | 0.02139 mol | 3.538 | |

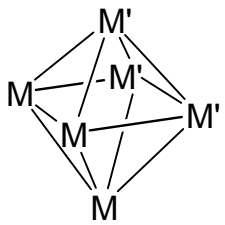
(The volumes can be determined from the indicated densities.)

d) Nb has the oxidation number +V in the initial substance as well as in **(1)**.
S has the oxidation number – II in the initial substance as well as in **(1)**.

e) There are two isomers:




mer-isomer




fac-isomer

## Solution to problem 3-5

a) P = 6 V · 2 A = 12 W,
Cathode: surface = 2 · 0.2 m · 0.3 m = 0.12 $m^2$; that results in a current density (cathode) of 16.67 $A/m^2$
Anode: surface = 20 m · 0.002 m · $\pi$ = 0.1257 $m^2$, current density (anode) = 15.91 $A/m^2$

b) Unconverted KCl will probably form. In addition to that, KOH forms during the electrolysis. It reacts with an excess of $CO_2$ to form $KHCO_3$.

c) $KClO_3$ and $KHCO_3$ are decomposed; $KClO_4$ and $K_2CO_3$ form

| | | | |
|---|---|---|---|
| acidification: | $H^+ + HCO_3^-$ | $\longrightarrow$ | $H_2O + CO_2$ |
| | $2\ H^+ + CO_3^{2-}$ | $\longrightarrow$ | $H_2O + CO_2$ |
| titration: | $Ag^+ + Cl^-$ | $\longrightarrow$ | $AgCl$ |
| in the melt: | $2\ KHCO_3$ | $\longrightarrow$ | $H_2O + CO_2 + K_2CO_3$ |
| | $4\ KClO_3$ | $\longrightarrow$ | $3\ KClO_4 + KCl$ |

d) $M(KCl) = 74.55$ g/mol; $M(KClO_3) = 122.50$ g/mol; $M(KClO_4) = 138.50$ g/mol; $M(CO_2) = 44.01$ g/mol; $M(KHCO_3) = 100.10$ g/mol; $M(K_2CO_3) = 138.20$ g/mol; $M(H_2O) = 18.01$ g/mol.

Melting results in a decrease of mass of 0.05 g. ($H_2O$ and $CO_2$ escape in the molar ratio of 1:1) $M(H_2O)+ M(CO_2) = 62.02$ g/mol.

0.05 g correspond to $8.061 \cdot 10^{-4}$ mol ($H_2O + CO_2$). They have formed from 0.0016122 mol of (0.161 g of) $KHCO_3$, thus $8.061 \cdot 10^{-4}$ mol (0.111 g of) of $K_2CO_3$ have formed.

0.0188 L · 0.1 mol/L = 0.00188 mol of silver nitrate were consumed in the first titration. This corresponds to 0.00188 mol of (0.140 g of) KCl.

Finally, the melting mixture contains 0.003305 mol of (0.246 g of) KCl.

The mass difference of the initial substance (1 g - 0.161 g - 0.140 g) = 0.699 g corresponds to 0.0057061 mol of $KClO_3$. That is 0.0042795 mol of (0.593 g of) $KClO_4$ in the melt. This mass corresponds to the mass difference as well (0.95 g - 0.111 g- 0.246 g) = 0.593 g.

| | | | | |
|---|---|---|---|---|
| initial substance: | 0.161 g of $KHCO_3$ | 0.140 g of KCl | 0.699 gof $KClO_3$ | $\Sigma$ = 1.00 g |
| melt: | 0.111 g of $K_2CO_3$ | 0.246 g of KCl | 0.593 g of $KClO_4$ | $\Sigma$ = 0.95 g |

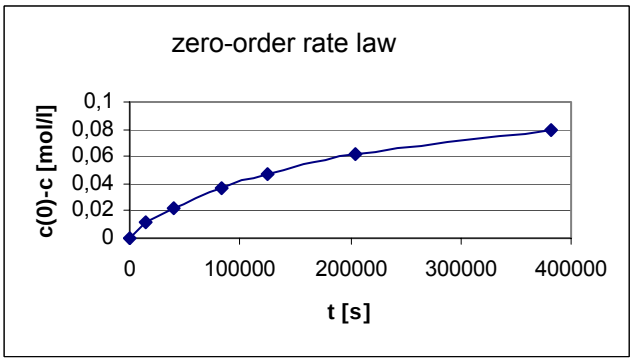
## Solution to problem 3-6

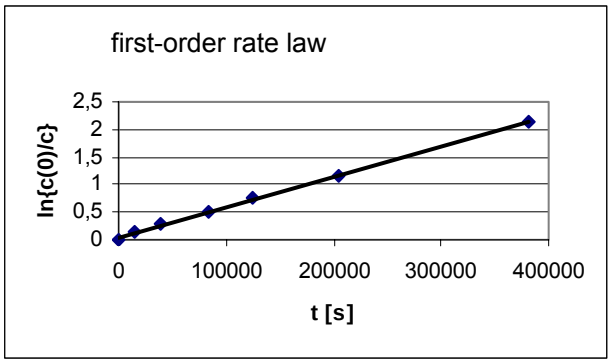
a) The concentration of ethylen diacetate is:
$c((CH_3COO)_2CHCH_3) = c_0((CH_3COO)_2CHCH_3) - 0{,}5 \cdot c(CH_3COOH)$

In order to check for a zero-order reaction, $c - c_0$ is plotted against the time t in a diagram, according to the rate law $c = c_0 - k_0 \cdot t$.

In order to check for a first-order reaction, $c = c_0 - k_0 \cdot t$ is plotted against the time t in a diagram, according to the rate law $c = c_0 \cdot e^{-k_1 t}$.

| t [min.] | 0 | 240 | 660 | 1400 | 2093 | 3403 | 6369 |
|---|---|---|---|---|---|---|---|
| t [s] | 0 | 14400 | 39600 | 84000 | 125580 | 204180 | 382140 |
| c (acid) [mol/L ] | 0.0216 | 0.0457 | 0.06495 | 0.09395 | 0.1152 | 0.14475 | 0.17915 |
| c(ethylen diacetate)[mol/L ] | 0.0892 | 0.0772 | 0.0675 | 0.0530 | 0.0424 | 0.0276 | 0.0104 |
| $c_0$-c [mol/L ] | 0 | 0.01205 | 0.021675 | 0.036175 | 0.0468 | 0.061575 | 0.078775 |
| ln ($c_0$/c) | 0 | 0.145 | 0.278 | 0.520 | 0.7437 | 1.172 | 2.147 |




Only the diagram for the first-order rate law corresponds to a straight line. Thus, the reaction is a first-order or rather a pseudo first-order reaction (because of the high excess of water).

b) zero-order reaction: heterogeously catalyzed reactions at surfaces; the absorbed amount of substance is constant
first-order reactions: radioactive decay

c) The rate constants are calculated and the mean values are determined from the data of the table above for $\ln(c_0/c)$ and t by means of $k_1 = \ln(t^{-1} \cdot c_0/c)$:

| t [s] | 14400 | 39600 | 84000 | 125580 | 204180 | 382140 |
|---|---|---|---|---|---|---|
| $\ln (c_0/c)$ | 0.145 | 0.278 | 0.520 | 0.7437 | 1.172 | 2.147 |
| $k_1$ [$s^{-1}$] | $1.0078 \cdot 10^{-5}$ | $7.0299 \cdot 10^{-6}$ | $6.1919 \cdot 10^{-6}$ | $5.9224 \cdot 10^{-6}$ | $5.7408 \cdot 10^{-6}$ | $5.6175 \cdot 10^{-6}$ |

The first value at t = 14400 s is not considered for the calculation of the mean value, because this value has a deviation that is too high. Thus, $\bar{k}_1 = 6.1 \cdot 10^{-6}\ s^{-1}$, so that $t_{1/2} = k_1^{-1} \cdot \ln 2$. This results in $t_{1/2} = 113.6 \cdot 10^3\ s \approx 31.56\ h$

d) $CH_3COOCH_2CH_3 + OH^- \longrightarrow CH_3COO^- + C_2H_5OH$.
For the determination of the reaction turnover the reaction is stopped by the addition of destilled water or rather strongly slowed down. Afterwards, the amount of still remaining caustic sodium lye is quickly determined by titration.

e) After t = 25 min, 73 % of the ester were saponificated with $c_0 = 0.02$ mol/l.
$\Leftarrow$ c(ester, 25 min) = $c_0 \cdot (100\text{-}73)/100 = 5.4 \cdot 10^{-3}$ mol/L
The second-order rate law is valid for equal initial concentrations of the educts:
$c^{-1} = k_2 \cdot t + c_0^{-1}$.
$k_2 = 0.090$ L/(mol·s) can be obtained by insertion.

f) The half lifet $t_{1/2}$ results from the insertion of $c = ½ \cdot c_0$ into the rate law:
$(0.5 \cdot c_0)^{-1} = k_2 \cdot t_{1/2} + c_0^{-1} \quad \Leftarrow \quad t_{1/2} = (c_0 \cdot k_2)^{-1}$ $\qquad t_{1/2} = 555\ s \qquad = 9.25\ min$
$(0.01 \cdot c_0)^{-1} = k_2 \cdot t_{99\%} + c_0^{-1} \quad \Leftarrow \quad t_{99\%} = 99 \cdot (c_0 \cdot k_2)^{-1}$ $\qquad t_{99\%} = 54.9 \cdot 10^3\ s \qquad = 15.3\ h.$

## Solution to problem 3-7

a) $E = E^0 + \frac{R \cdot T}{n \cdot F} ln \frac{c(Ox)}{c(Red)}$

iron half cell: $E = 0.77\ V + \frac{R \cdot T}{F} ln \frac{c(Fe^{3+})}{c(Fe^{2+})}$

halogen-halide half cell: $E = E^0_{(halogen)} + \frac{R \cdot T}{2 \cdot F} ln \frac{1}{c(X^-)^2 / (1\ mol/L)^2}$

$c(Fe^{2+}) = 0.01$ mol/L - $c(X^-)$, $c(Fe^{2+}) = 1$ mol/L - $c(Fe^{3+})$.
Because of the standard redox potentials, the equilibrium is strongly on the left side ⇐
$c(Fe^{3+}) = 1$ mol/L or rather $c(Cl^-) = 0.01$ mol/L
E(Fe) = E(Cl) results in the following:
0,77 V + RT/F · ln [(1 mol/L)/$c(Fe^{2+})$] = 1,36 V + RT/F · ln (1/0.01)
⇐ $c(Fe^{2+}) = 10^{-12}$ mol/L $pFe^{2+} = 12$

The calculation for the system with bromide results in the following:
⇐ $c(Fe^{2+}) = 8.23 \cdot 10^{-8}$ mol/L $pFe^{2+} = 7.08$

Because of the standard potentials of the system with iodide, the equilibrium is strongly on the right side:
$c(Fe^{2+}) = 0.01$ mol/L - $c(I^-)$, $c(Fe^{2+}) = 1$ mol/L - $c(Fe^{3+})$.
0,77 V + RT/F · ln ((1 mol/L -$c(Fe^{2+})$/$c(Fe^{2+})$) = 0.54 V+ RT/F · ln (1/(0.01 mol/L - $c(Fe^{2+})$
⇐ $c(Fe^{2+}) = 9.99 \cdot 10^{-3}$ mol/L $pFe^{2+} = 2$

b) These cations are hydrated; at simplest, they can be found as complexes: $[Fe(H_2O)_6]^{2+}$ or rather $[Fe(H_2O)_6]^{3+}$.

c) The hydrated cations have an acidic effect. The different hydroxo-complexes have different redox potentials. The redox potentials of the halogens as well depend very strongly on the pH-value, because with an increasing pH, chlorine, bromine and iodine undergo always more and more disproportionation reactions like e.g.
$Cl_2 + 2\ OH^- \longrightarrow Cl^- + ClO^- + H_2O$.

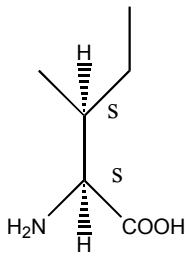
d) $2\ Fe(OH)_3 + 3\ Cl_2 + 10\ OH^- \longrightarrow 2\ FeO_4^{2-} + 6\ Cl^- + 8\ H_2O$
$4\ K_2FeO_4 + 10\ H_2O \longrightarrow 4\ Fe(OH)_3 + 8\ K^+ + 8\ OH^- + 3\ O_2$.

## Solution to problem 3-8

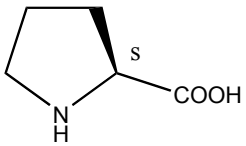
a) L-configuration (Fischer projection)

b) Every amino acid can have either a D- or an L-configuration. Thus, there are $2^{50}$ stereoisomers of a peptide consisting of 50 molecules of alanine.

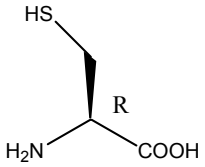
c)




isoleucine



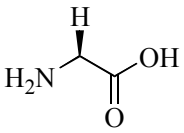

proline




cysteine

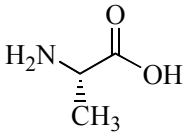
The S-atom has a higher priority than the O-atom of the COOH group

d)




75.07 gmol$^{-1}$

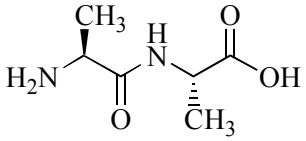
glycine (Gly)




89.09 gmol$^{-1}$

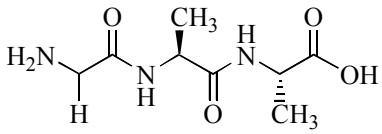
alanine (Ala)

The peak at m/z = 89.1 can be attributed to alanine. Concerning polypeptide fragments, notice that every formation of a peptide bond results in a cleavage of water (M = 18.02 g/mol ). The addition of the molar mass of a second amino acid (glycine or alanine) -18.02 g/mol -(water) shows that there is only the mass peak for the dipeptide ala-ala. By further trying out the following peptides form. Their masses appear in the mass spectrum:



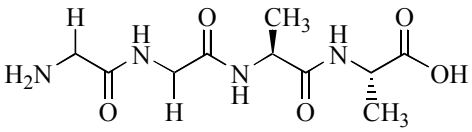

alanine alanine

molar mass: 160.17 gmol$^{-1}$



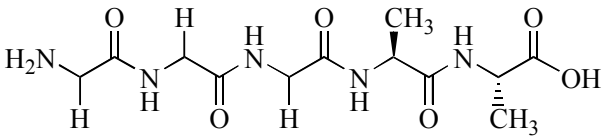

glycine alanine alanine

molar mass: 217.22 gmol$^{-1}$



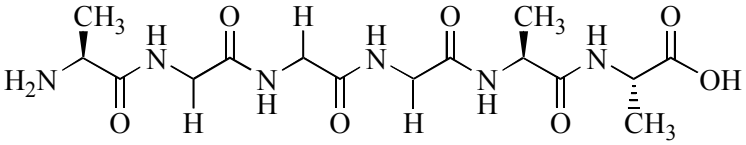

glycine glycine alanine alanine

molar mass: 274.27 gmol$^{-1}$




glycine glycine glycine alanine alanine

molar mass: 331.33 gmol$^{-1}$




alanine glycine glycine glycine alanine alanine

molar mass: 402.40 gmol$^{-1}$

The remaining mass peaks can be obtained from the phenyl carbamoyls of the peptides:

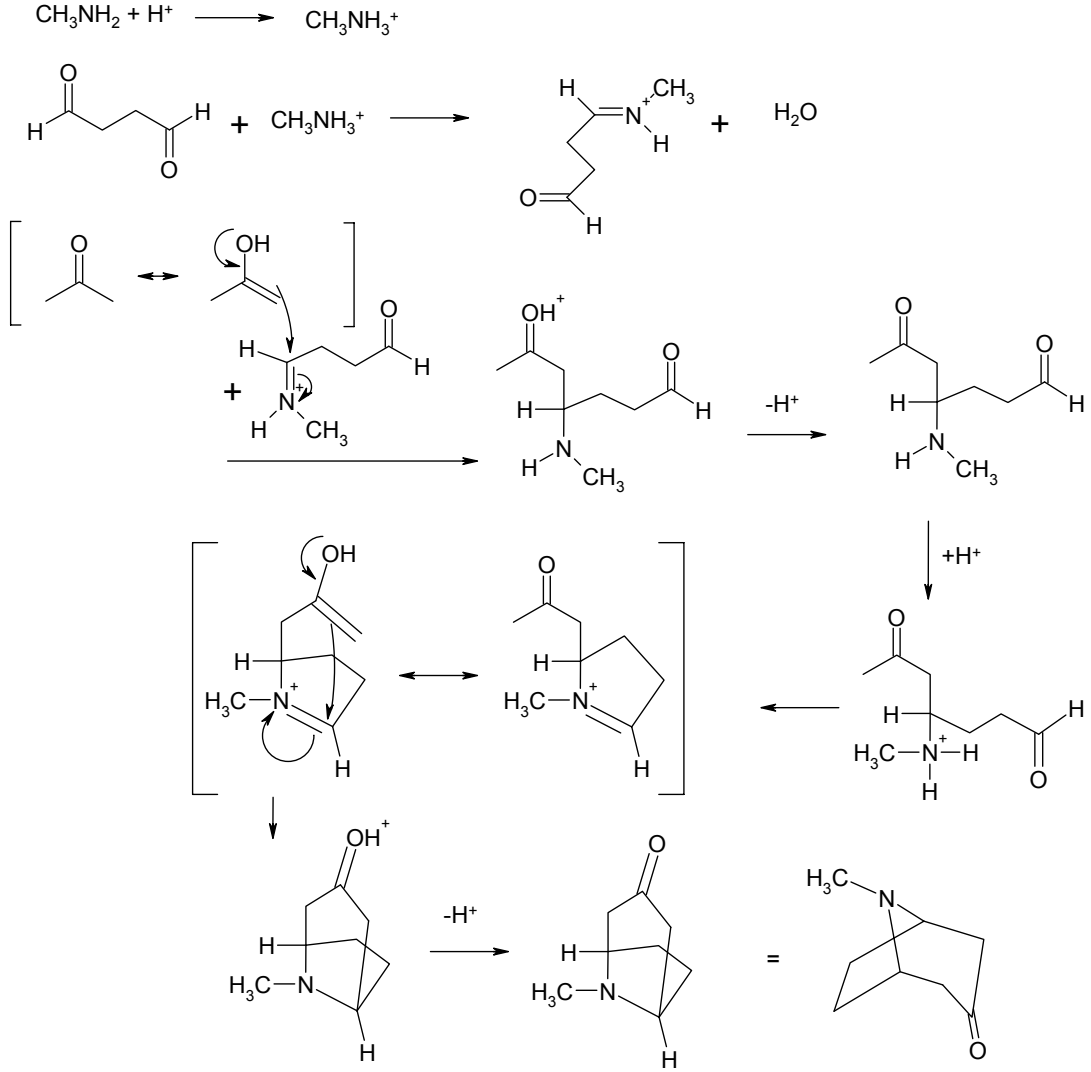
Ph-NH-CO-NH-ala-COOH 208.2 g/mol

| | |
|---|---|
| Ph-NH-CO-NH-ala-ala-COOH | 279.3 g/mol |
| Ph-NH-CO-NH-gly-ala-ala-COOH | 336.3 g/mol |
| Ph-NH-CO-NH-gly-gly-ala-ala-COOH | 393.4 g/mol |
| Ph-NH-CO-NH-gly-gly-gyl-ala-ala-COOH | 450.5 g/mol |
| Ph-NH-CO-NH-ala-gly-gly-gly-ala-ala-COOH | 521.5 g/mol |

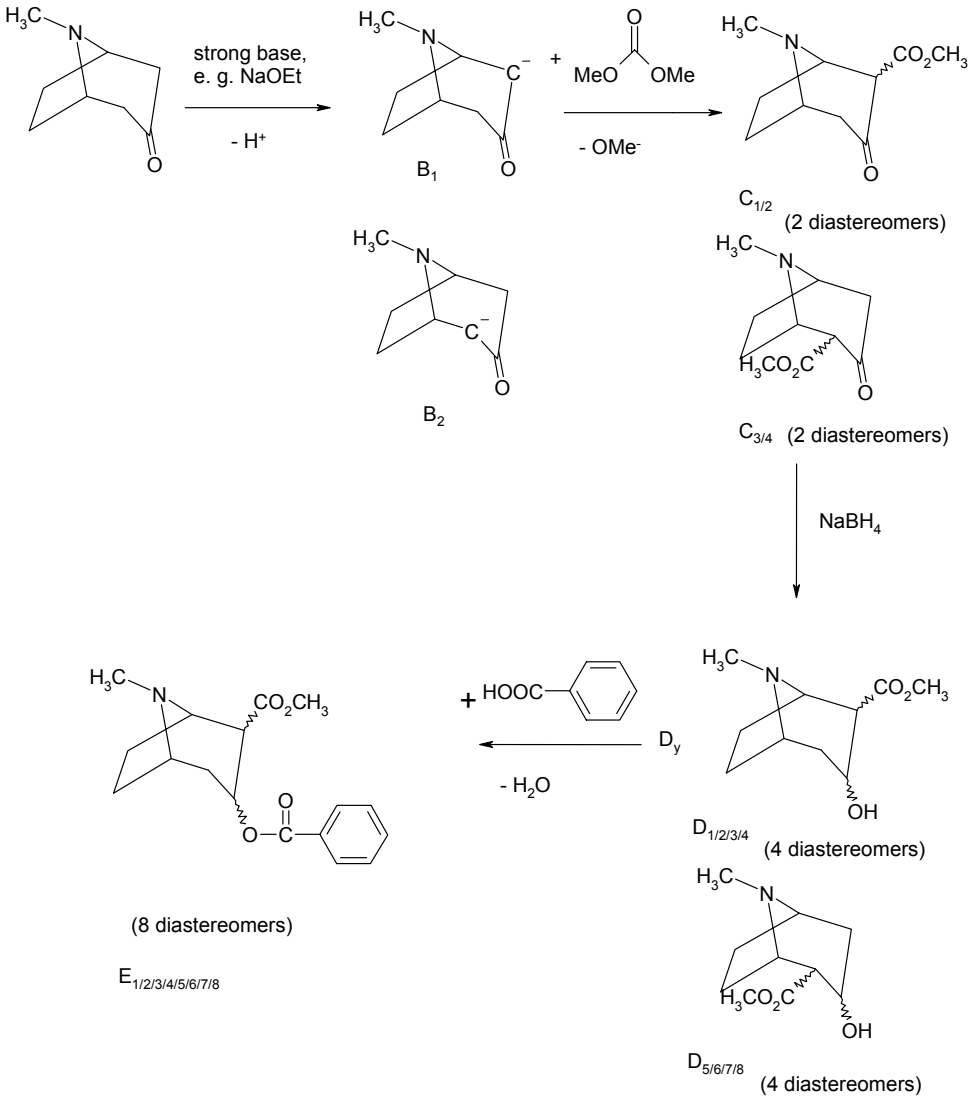
e) X = $NH_2$-ala-gly-gly-gly-ala-ala-COOH

## Solution to problem 3-9

a)



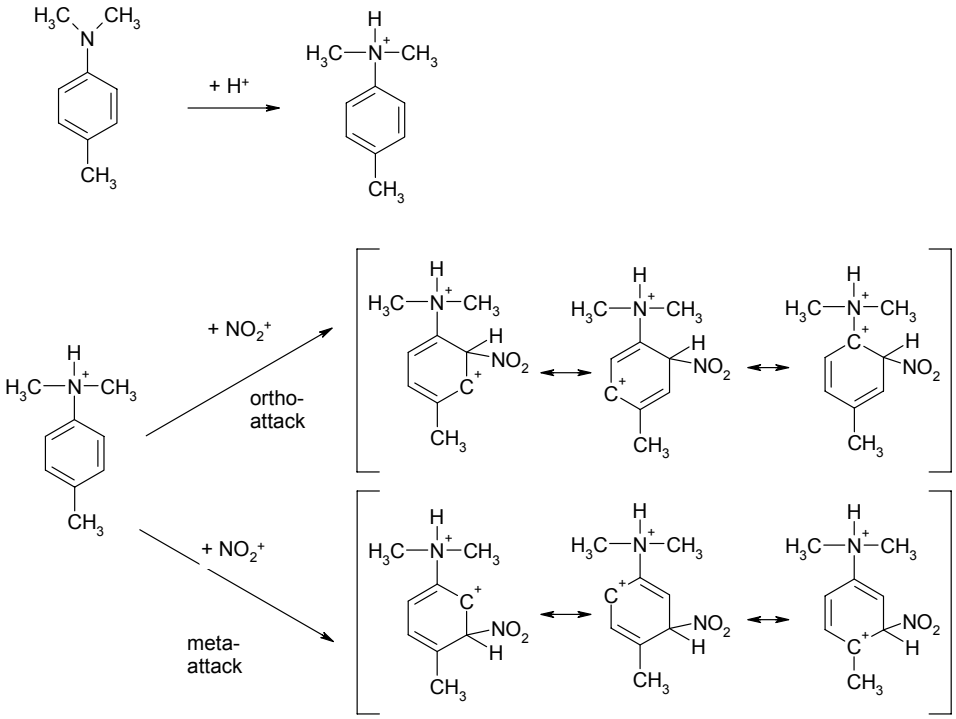
b)




c) Altogether 8 isomers can be obtained. There are two enantiomers of compound $B_x^-$ ; compound $C_y$ has four isomers (2 diastereomeric pairs of enantiomers). There are eight isomers each of compound $D_z$ and $E_z$ (4 diastereomeric pairs of enantiomers). Thus, the different types of isomerism are stereoisomers, strictly speaking enantiomers and diastereomers.

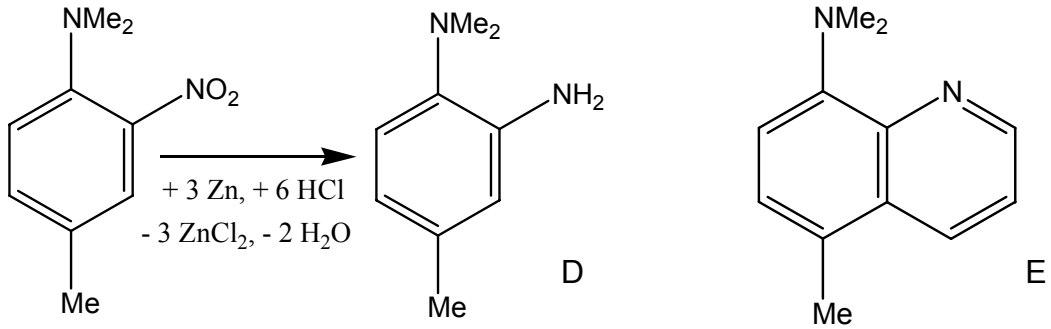
## Solution to problem 3-10

a) weakly acid: B, strongly acid ($NMe_2$-group protonated): A




The ortho attack (concerning the dimethylammonia group) results in an extremely unfavourable resonance structure in which the C-atom has a further positive formal charge apart from the nitrogen atom that is already positively charged anyway. This resonance structure is so unfavourable, that exclusively the meta product forms in a strongly acid solution. Such a resonance structure does not appear in the formation of such a product.

b), c)



# Answers round 3 test 2

## Solution to problem 3-11

1) e  2) b  3) c  4) c  5) d  6) c  7) c  8)c

## Solution problem 3-12

a) $H_2C{=}C{=}CH_2$

$sp^2$ $sp$ $sp^2$

b) $sp^2 \longrightarrow sp^3$

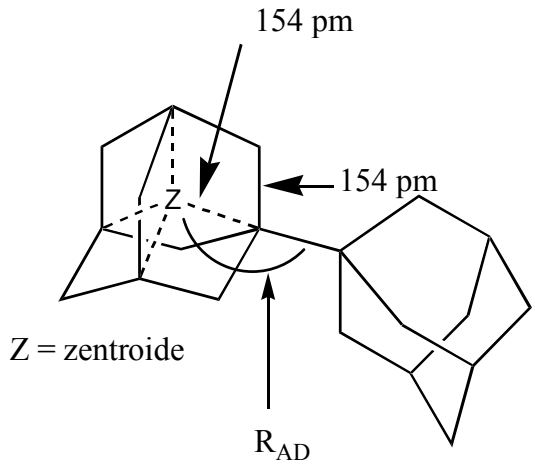
c) $[Fe(CO)_5]$: **$dsp^3$** (Fe(0) has 8 valence electrons, diamagnetic: only paired valence electrons. It follows: 1 free 3d-orbital, free 4s-orbital, 3 free 4p-orbitals. These orbitals are occupied with 5 electron pairs of the ligands.)
$[Fe(Cp)_2]$: **$d^2sp^3$** (Fe(+II), diamagnetic, has 2 free 3d-orbitals, free 4s-orbital as well as 3 free 4p-orbitals accepting 12 electrons from the ligands.)

d) A free electron pair needs more space than a single bond to a (H-) atom. Thus, with an increasing number of free electron pairs at the atom X, the H-X-H bond angles become smaller.

e) **A**: angles almost tetrahedral angles, $sp^3$-hybridized at the O-atom because of 4 electron pairs (2 free electron pairs + 2 single bonds)
**B**: angles approximately 120°, $sp^2$-hybridization at the O-atom, because one of the free electron pairs occupies a p-orbital to be in conjugation with the $\pi$-electron system of the aromatic.
**C**: angle between 120° and 180° indicates a partial double-bond property of the two Si-O-bonds; hybridization between $sp^2$ and sp.

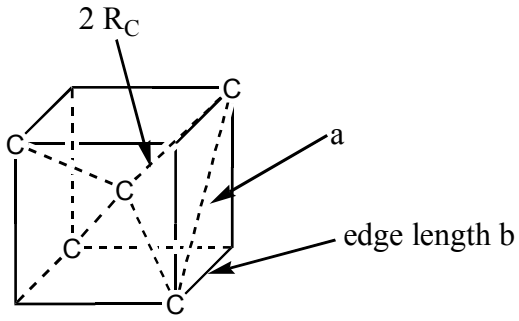
## Solution to problem 3-13

a)




The radius of the "inflated C-atom" is composed of half the distance between the units and the distance between the bridgehead C-atoms and the centre of the adamantane cage (this distance is the same as the C-C bond length in the adamantane backbone because of the symmetry of the cage). $R_{AD}$ = ½ ·157.8 pm + 154.0 pm = 232.9 pm.
$R_{AD}$ = 232.9 pm

b) The edge length a of the tetrahedron is the same as the plane diagonal of the auxiliary construction "cube". In this cube, the atomic radius $R_C$ is a quarter of the space diagonal.




$4\ R_C = (3b^2)^{1/2}$, $a = (2b^2)^{1/2}$, $b^2 = a^2/2$
$4\ R_C = (3a^2/2)^{1/2}$, $R_C = (3a^2/2)^{1/2} / 4$
$R_C = (3 \cdot (252.22\ pm)^2/2)^{1/2} / 4$
$R_C = 77.2263$ pm

c) The ratio of the volumes of the adamantane unit to the C-atom is $V_{AD} / V_C = R_{AD}^3/R_C^3 = 27.429$. The ratio of the masses (adamantane unit to C-atom) is $M_{AD} / M_C = (10 \cdot M_C + 12 \cdot M_H) / M_C = 11.007$.
$\rho_{AD} = M_{AD} / V_{AD}$, $\rho_C = M_C / V_C$ results from $\rho = m/V$
The following equation results from the transposition of the formula: $\rho_{AD} = \rho_C \cdot (M_{AD} / M_C) / (V_{AD} / V_C)$
If the ratios of the masses of the units as well as those of the unit volumes are inserted, $\boldsymbol{\rho_{AD}} = 1.41\ g/cm^3$ will be obtained.

d) The adamantane diamond should have a considerably lower hardness than the real diamond because of the smaller "bond density" (C-C bonds per volume unit) between the units.

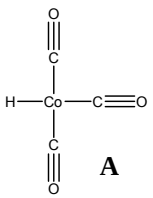
e) isomorphic, isoelectronic

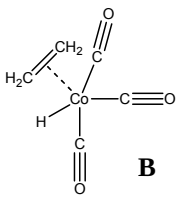
## Solution to problem 3-14

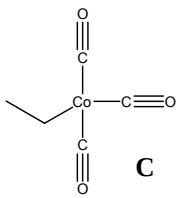
a) Co(0) with 4 ligands and a Co-Co bond as well as Co(+I) with 5 ligands and Co(-I) with 4 ligands fulfill the 18-electrons rule; thus they have a noble-gas shell.

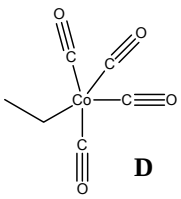
b) When $[CoH(CO)_4]$ dissociates, the oxidation number of the hydrido-ligand (-I) increases to + I (proton), that of the Co-central particle decreases from +I to -I. This is a redox reaction.

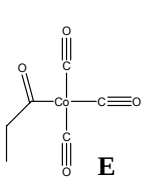
c)

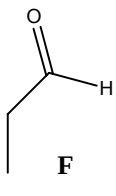

**A**


**B**


**C**

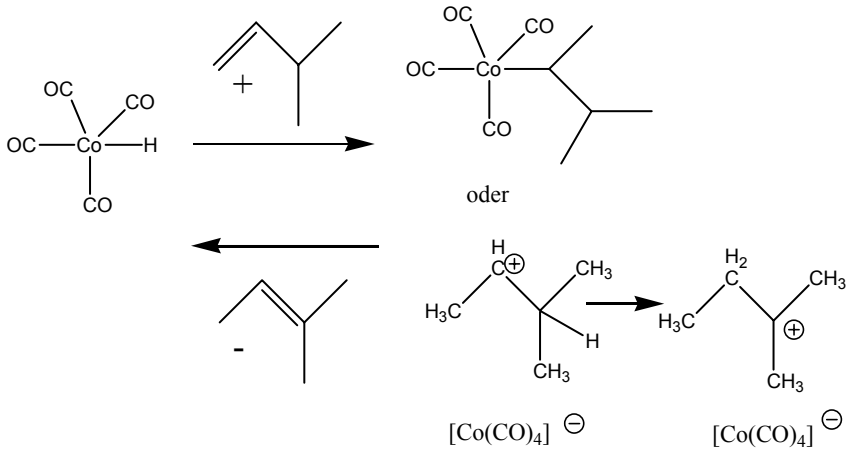

**D**


**E**

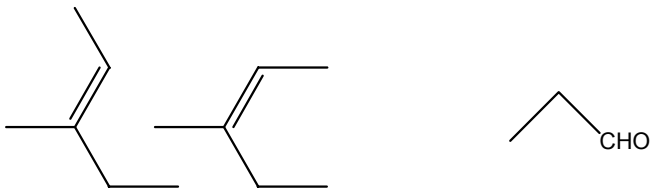

**F**

d) The formation of **D** and the transformation to **E** are more likely to take place by the use of a high excess of CO.

e)




f)




from 2-ethyl-1-butene  from propene-3-ol

## Solution to problem 3-15

a) $N(t) = N_0 2^{-t/t_{½}}$

b)

$$N_{0(238)} \cdot 2^{-t/T_{238}} = N_{0(235)} \cdot 2^{-t/T_{235}}$$

$$2^{-t/T_{238}+t/T_{235}} = {N_{0(235)}}/{N_{0(238)}}$$

$$t\left({1}/{T_{235}} - {1}/{T_{238}}\right) = log_2 {N_{0(235)}}/{N_{0(238)}}$$

$$t = \frac{log_2 {N_{0(235)}}/{N_{0(238)}}}{{1}/{T_{235}} - {1}/{T_{238}}} = \frac{ln {N_{0(235)}}/{N_{0(238)}}}{ln 2\left({1}/{T_{235}} - {1}/{T_{238}}\right)}$$

$$\underline{\underline{t = -5.9 \cdot 10^9\ a}}$$

c) Mass numbers only change by alpha-decay, namely by 4 units.
The decay path is the following:.

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

d) The formation rate of $^{234}U$ from $^{238}U$ is the same as the decay rate of $^{234}U$: (all intermediate steps cancel each other out!)

$$N_{234} k_{234} = N_{238} k_{238}$$

$$N_{234} \frac{\ln 2}{T_{234}} = N_{238} \frac{\ln 2}{T_{238}}$$

$$T_{234} = T_{238} \frac{N_{234}}{N_{238}}$$

$$\underline{\underline{T_{234} = 2.3 \cdot 10^5 \text{ a}}}$$

e) In the radioactive equilibrium, ($t$ >> 0) the term in brackets equals 1. The time $t$ results from the following:

$$1 - 2^{-t/T_{\text{Rn}}} = 0.99$$

$$\ln 0.01 = -\frac{t \cdot \ln 2}{T_{\text{Rn}}}$$

$$\underline{\underline{t = 25.4 \text{ d}}}$$

f) In insoluble $RaSO_4$, nascent radon would be trapped in the solid. In an aqueous system, Rn is dissolved in water and evaporates slowly. It can be just simply drained by pumping.

## Solution to problem 3-16

a) The standard formation enthalpies $\Delta H^0_f$ (at a temperature of 298.15 K and a pressure of 1013 mbar) of the elements are zero by definition. The formation enthalpy of oxygen, however, is indicated at a different temperature.

b) The following formulas are valid for the different temperatures:

$\Delta H_R = 2\ \Delta H_f (SiO) + \Delta H_f (O_2) - 2\ \Delta H_f (SiO_2)$

$\Delta S_R = 2\ S (SiO) + S (O_2) - 2\ S (SiO_2)$

$\Delta G_R = \Delta H_R - T\ \Delta S_R$

The following values are obtained (notice the units, convert the temperatures into Kelvinin!):

| | $\Delta H_R$[kJ mol$^{-1}$] | $\Delta S_R$ [J mol$^{-1}$K$^{-1}$] | $\Delta G_R$ [kJ mol$^{-1}$] |
|---|---|---|---|
| T = 800 °C | 1597,2 | 509,5 | 1050,4 |
| T = 1000 °C | 1590,9 | 503,7 | 949,7 |
| T = 1200 °C | 1584,1 | 498,5 | 849,8 |

The reaction is (strongly) endothermal at all temperatures (because $\Delta H_R > 0$)

c) The dimensionless, thermodynamic equilibrium constant $K_{th}$ can be calculated for the single temperatures according to $\Delta G = -RT\ln K_{th}$

The equilibrium constant $K_p$ for the given reaction results from the following:

$$K_p = K_p \cdot p_0^{\Delta n} = K_{th} \cdot p_0^3 = K_{th} \cdot (1013 \text{ mbar})^3$$

with $\Delta n = 3$, because only gaseous species are taken into consideration.
The following numerical values are obtained:

$K_{th}$ (800 °C) = $7.3 \cdot 10^{-52}$ $K_p$ (800 °C) = $7.6 \cdot 10^{-43}$ mbar $^{-3}$
$K_{th}$ (1000 °C) = $1.1 \cdot 10^{-39}$ $K_p$ (1000 °C) = $1.1 \cdot 10^{-30}$ mbar $^{-3}$
$K_{th}$ (1200 °C) = $7.4 \cdot 10^{-31}$ $K_p$ (1200 °C) = $7.7 \cdot 10^{-22}$ mbar $^{-3}$

d) According to the reaction equation, $p(SiO) = 2 \cdot p(O_2)$. The following can be determined:
$p(O_2) = x$ and $p(SiO) = 2x$
Thus, $K_p = p(SiO)^2 \cdot p(O_2) = (2x)^2 \cdot x = 4\,x^3$
so: $x = \sqrt[3]{\frac{K_p}{4}}$ = $9.9 \cdot 10^{-6}$ mbar $p(SiO) = 2x = 2.0 \cdot 10^{-5}$ mbar
(note: the pressure is quite low, thus the reaction has to be carried out under high-vacuum conditions, so that as few other gases as possible are present as impurities)

e) Gaseous SiO can be produced in a comproportionation reaction by heating a mixture of solid Si and solid $SiO_2$:

$Si_{(solid)} + SiO_{2\,(solid)} \longrightarrow 2\,SiO_{(g)}$ $O_{2\,(g)}$ (temperature > 1100 °C)

Gaseous SiO can as well produced by leading gaseous oxygen above solid Si at high temperatures:

$2\,Si_{(solid)}) + O_{2\,(g)} \longrightarrow 2\,SiO_{(g)}$ (temperature > 1100 °C)

(this method, however, needs a very careful dosing of oxygen)

## Solution to problem 3-17

a) iron is oxidized: $Fe \longrightarrow Fe^{2+} + 2\,e^-$
copper is reduced : $Cu^{2+} + 2\,e^- \longrightarrow Cu$
$Fe + Cu^{2+} \longrightarrow Fe^{2+} + Cu$

b) Nernst equation:

$$0.830V = \Delta E_0 + \frac{R \cdot T}{2 \cdot F} \cdot ln \frac{c(Cu^{2+})}{c(Fe^{2+})} \qquad \Delta E_0 = 0{,}830V - \frac{R \cdot T}{2 \cdot F} \cdot ln \frac{0.5}{0.01} = 0.780V$$

$$\Delta E_0 = E_0^{red} - E_0^{ox} \qquad E_0^{ox} = E_0^{red} - \Delta E_0 = 0.340V - 0.780V = -0.440V$$

c) By the addition of caustic soda solution the concentration of $OH^-$-ions increases in the solution. $Fe(OH)_2$ is a poorly soluble salt, so that it starts to appear as a white precipitate

when the concentration of $OH^-$-ions is increased. So, the concentration of $Fe^{2+}$ is highly decreased.

$$Fe^{2+}(aq) + 2\ OH^-(aq) \longrightarrow Fe(OH)_2(s)$$

d) If air was added, iron(II)-hydroxide would immediately be oxidized to iron(III)-hydroxide.

$$4\ Fe(OH)_2 + O_2 + 2\ H_2O \longrightarrow 4\ Fe(OH)_3$$

e) potential of the copper half cell: $E^{red} = +0.340\ V + \frac{R \cdot T}{2 \cdot F} \cdot ln\,0.5 = 0.331\ V$

potential of the iron half cell: $E^{ox} = E^{red} - \Delta E = 0.331\ V - 1.09\ V = -0.759\ V$

concentration of $Fe^{2+}$:

$$-0.759\ V = -0.440\ V + \frac{R \cdot T}{2 \cdot F} \cdot ln[c(Fe^{2+})/(1mol/L)]$$

$$c(Fe^{2+}) = 1.58 \cdot 10^{-11} molL^{-1}$$

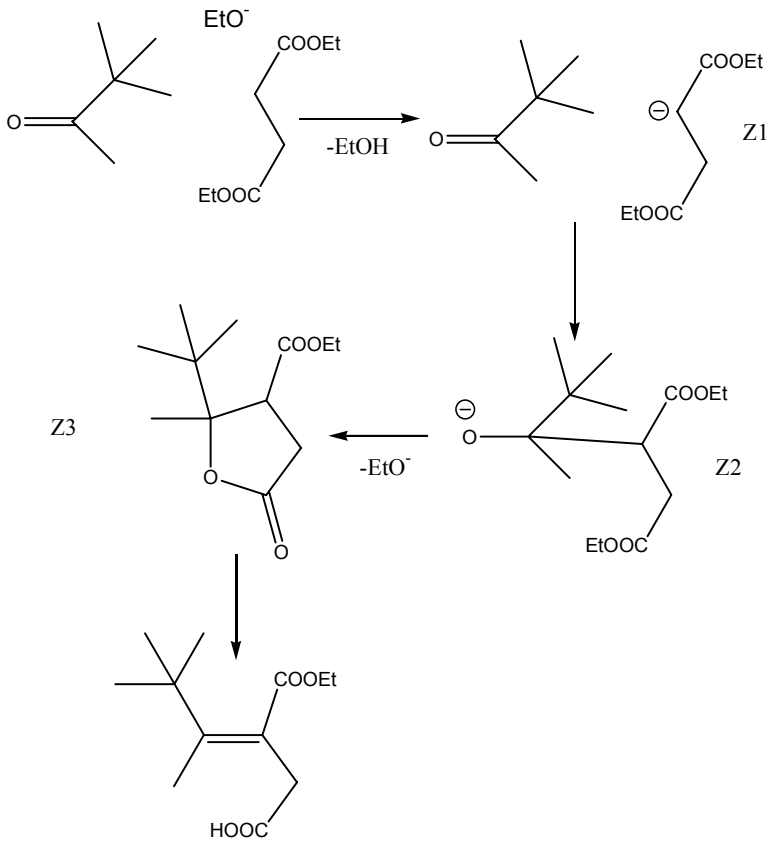
solubility product:

$$K_L = c(Fe^{2+}) \cdot c^2(OH^-) = 1.58 \cdot 10^{-11} molL^{-1} \cdot (10^{-2} molL^{-1})^2 = 1.58 \cdot 10^{-15} mol^3L^{-3}$$

$pK_L$ = 14.8

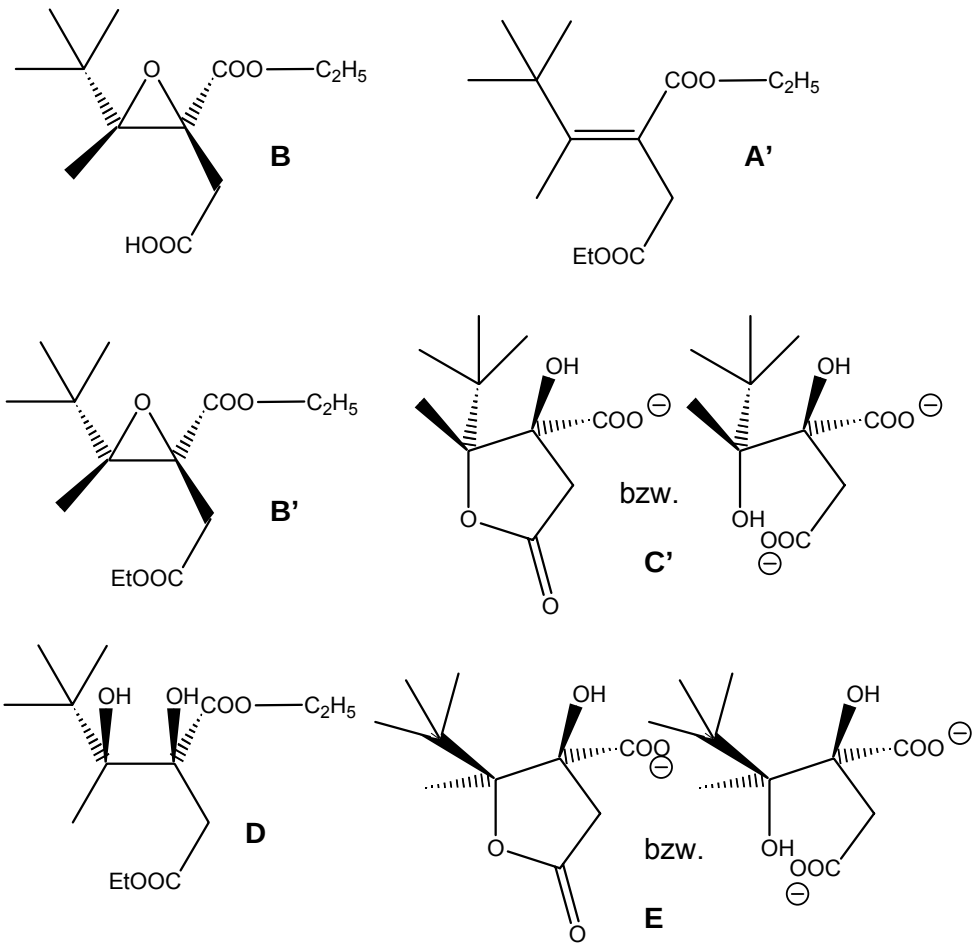
## Solution to problem 3-18

a)




Carboxylic acid that has formed reacts with ethanolate to form ethanol and the carboxylic-acid anion. The elimination reaction (lactonic cleavage), that is an equilibrium reaction, is shifted to the side of the products.

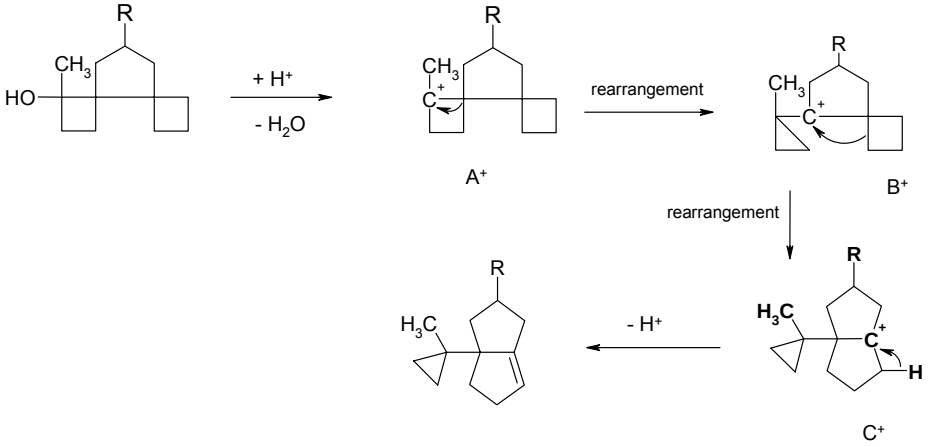
b)




**B**: enantiomers: (R,R); (S,S)
**B´**: enantiomers: (R,R); (S,S)
**D**: enantiomers: (R,R); (S,S)
**A´**: trans-isomer remains
**C´**: enantiomers: (R,S); (S,R)
**E**: enantiomers: (R,R); (S,S)

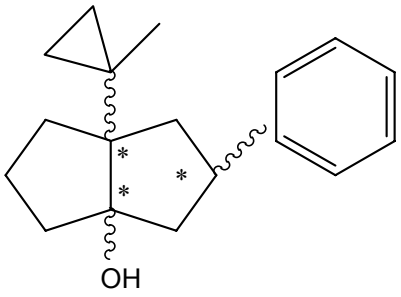
## Solution to problem 3-19

a) In the first step, water is eliminated. The carbenium ion that has formed undergoes two [1,2]-Wagner-Meerwein-rearrangements. In the last step, $H^+$ is eliminated:



b) The steric relaxation of the initial compound that contains two highly tightened four-membered rings is the driving force for the rearrangement.

c)




**D** has 8 stereoisomers.

4 pairs of enantiomers: (R,R,R) (S,S,S) (R,R,S) (S,S,R)
(R,S,S) (S,R,R) (R,S,R) (S,R,S)

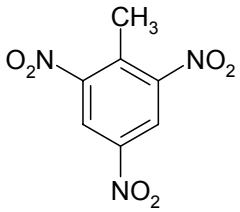
## Solution to problem 3-20

a) oxygen: 100% - 37.02% - 2.22% - 18.50% = 42.26%

total formula: $C_{37.02/12}H_{2.22/1}O_{42.26/16}N_{18.50/14}$ $C_{3.08}H_{2.22}O_{2.64}N_{1.32}$
$C_7H_5O_6N_3$

b) The two strong bands in the range around 1540cm$^{-1}$ and 1350cm$^{-1}$ indicate one or several nitro groups (-$NO_2$). Because there is no indication of other functional groups with oxygen or nitrogen in the IR-spectrum, three nitro groups have to be found in the molecule according to the total formula.

c) The 3H-singlet in the H-NMR indicates an isolated methyl group that is only weakly screened. The further 2 H-atoms are still in the aromatic range, but they are badly screened as well by the neighbouring $NO_2$-groups and thus shifted to a lower level. The two aromatic H-atoms are chemically equivalent. That indicates a symmetric arrangement of the nitro groups and the methyl group at the aromatic ring.




d) The compound is: TNT (2,4,6-trinitrotoluene). It is highly explosive.

# Answers round 4

## Solution to problem 4-1

a) $pK_L = 7.4$ $K_L = 3.98 \cdot 10^{-8}$ mol$^2$/L$^2$ $L_n = (K_L)^{1/2} = 2.00 \cdot 10^{-4}$ mol/L
M(CuBr) = 143.45 g/mol $L_m = 0.0286$ g/L $V(H_2O) = 34.9$ L

b) $lgK_1 = 6.18$ $K_1 = 1513561$ L/mol $lgK_2 = 4.69$ $K_1 = 48978$ L/mol
assumption: because of the high numerical values for $K_1$ and $K_2$, $Cu^+$ can be found in an ammoniacal solutions nearly exclusively as $[Cu(NH_3)_2]^+$.
The following equations can be applied:
1) $K_1K_2 = c([Cu(NH_3)_2]^+)/ c(Cu^+)c(NH_3)^2$
2) $K_L = c([Cu(NH_3)_2]^+) \cdot c(Cu^+)$, because $c(Br^-) = c([Cu(NH_3)_2]^+)$
3) $c(NH_3) = 0.1$ mol/L $- 2c([Cu(NH_3)_2]^+)$
The insertion of 2) and 3) into 1) results in the following equations:
$c(NH_3)^2 - \{0.05/(0.25 - K_1K_2K_L)\} \cdot c(NH_3) + 0.0025/(0.25 - K_1K_2K_L) = 0$
$c(NH_3) = 9.12 \cdot 10^{-4}$ mol/L
Without any simplification the following equations can be applied:
1) $K_1K_2 = c([Cu(NH_3)_2]^+)/ c(Cu^+)c(NH_3)^2$ $K_1 = c([Cu(NH_3)]^+)/ c(Cu^+)c([NH_3)$
2) $K_L = \{c([Cu(NH_3)_2]^+) + c([Cu(NH_3)]^+) + c(Cu^+)\} \cdot c(Cu^+)$
3) $c(NH_3) = 0.1$ mol/L $- c([Cu(NH_3)]^+) - 2c([Cu(NH_3)_2]^+)$
Insertion and rearrangement lead to the following equation:
$(K_1K_2 - 4 \cdot K_1^2K_2^2K_L) \cdot c(NH_3)^4 + (K_1 - 0.2 \cdot K_1K_2 + 4 \cdot K_1^2K_2K_L) \cdot c(NH_3)^3 + (1 - 0.2 \cdot K_1 + 0.01 \cdot K_1K_2 - K_LK_1) \cdot c(NH_3)^2 + (0.01 \cdot K_1 - 0.2) \cdot c(NH_3) + 0.01 = 0$ (term 1 = 0)

The insertion of the approximate result $c(NH_3) = 9.12 \cdot 10^{-4}$ mol/L as an initial value results in the following:
term 1 = 27.09

| approximation: | | |
|---|---|---|
| $c(NH_3)_{1st\ experiment}$ | $= 9.20 \cdot 10^{-4}$ mol/L | term 1 = 16.61 |
| $c(NH_3)_{second\ experiment}$ | $= 9.30 \cdot 10^{-4}$ mol/L | term 1 = 2.84 |
| $c(NH_3)_{third\ experiment}$ | $= 9.32 \cdot 10^{-4}$ mol/L | term 1 = 0.0004 |

The following values can be obtained from $c(NH_3) = 9.32 \cdot 10^{-4}$ mol/L:
$c(Cu^+) = 7.61 \cdot 10^{-7}$ mol/L
$c(Br^-) = 0.052$ mol/L. that is 7.50 g/L of CuBr.
133.3 ml of 0.1-molar $NH_3$-solution are needed for dissolving 1 g of CuBr.

c) $K_{L(cond)} = c(Br^-)^2 = c(\text{dissolved CuBr})^2$ $K_{L(cond)} = (0.0523 \text{ mol/L})^2 = 2.74 \cdot 10^{-3}$ mol$^2$/L$^2$

## Solution to problem 4-2

a) $C_8H_{10} + 10{,}5\ O_2 \longrightarrow 8\ CO_2 + 5\ H_2O$.

b) According to a), the combustion enthalpy is:
$\Delta H_c = 8\ \Delta H_f^0(CO_2) + 5\ \Delta H_f^0(H_2O) - \Delta H_f^0(p\text{-Xylol})$
$\Delta H_f^0(p\text{-Xylol}) = 8\ \Delta H_f^\circ(CO_2) + 5\ \Delta H_f^\circ(H_2O) - \Delta H_c$
$= 8 \cdot (-393.5\ kJ/mol) + 5 \cdot (-285.8\ kJ/mol) + 4551\ kJ/mol$
$= -25.6\ kJ/mol$

c) The formation enthalpies of the gaseous xylenes at T = 500 K can be calculated from the standard values according to the following scheme:
$\Delta H_f(g.500\ K) = \Delta H^0_f + C_p(l) \cdot (T_s - 298.15\ K) + \Delta H_{dil} + C_p(g) \cdot (500\ K - T_s)$.
Analogous to the upper equation. the following equation can be applied to the entropies of the gaseous xylenes:
$S(g,500\ K) = S^0 + C_p(l) \cdot \ln(T_s/298.15\ K) + \Delta H_{dil}/T_s + C_p(g) \cdot \ln(500\ K/T_s)$.

| | $\Delta H_f$(g. 500 K). [kJ/mol] | S(g. 500 K). [$JK^{-1}mol^{-1}$] |
|---|---|---|
| o-Xylol: | 48.4 | 426.9 |
| m-Xylol | 46.0 | 432.6 |
| p-Xylol | 46.8 | 425.3 |

The reaction enthalpy of the isomerization reaction can be calculated the following way :
ortho-xylene $\longrightarrow$ para-xylene
$\Delta H_r(500\ K)$ = 46.8 kJ/mol - 48.4 kJ/mol = -1.6 kJ/mol
$\Delta S_r(500\ K)$ = 425.3 $JK^{-1}mol^{-1}$ - 426.9 $JK^{-1}mol^{-1}$ = -1.6 $JK^{-1}mol^{-1}$

d) The reaction enthalpies for meta-Xylol $\longrightarrow$ para-Xylol can be obtained according to the same way:
$\Delta H_r(500\ K)$ = 46.8 kJ/mol - 46.0 kJ/mol = 0.8 kJ/mol
$\Delta S_r(500\ K)$ = 425.3 $JK^{-1}mol^{-1}$ - 432.6 $JK^{-1}mol^{-1}$ = -7.3 $JK^{-1}mol^{-1}$
The following values are the changes in free enthalpy for the two reactions:
ortho-xylene $\rightarrow$ para-xylene $\Delta G_r(500\ K) = \Delta H_r(500\ K) - 500\ K \cdot \Delta S_r(500\ K) = -0.8\ kJ/mol$
meta-xylene $\rightarrow$ para-xylene $\Delta G_r(500\ K) = \Delta H_r(500\ K) - 500\ K \cdot \Delta S_r(500\ K) = 4.5\ kJ/mol$

The equilibrium constants for the isomerizations can be calculated from the upper values:

$$K(ortho \rightarrow para) = \frac{c(para)}{c(ortho)} = e^{-\Delta G_R / (RT)} = 1.21$$

$$K(meta \rightarrow para) = \frac{c(para)}{c(meta)} = e^{-\Delta G_R / (RT)} = 0.34$$

The composition of the equilibrium mixture at 500 K is:
para-xylene: 21 % meta-xylene: 62 % ortho-xylene: 17 %.

e) Because the product p-xylene is faster removed, the equilibrium is shifted to the side of p-xylene. This is the result of the mass action law.

## Solution to problem 4-3

a) Division of the total reaction into two parts:
$AgI \longrightarrow Ag + ½\ I_2$ $(K_1)$ $Ag + ½\ I_2 \longrightarrow Ag^+ + I^-$ $(K_2)$
$AgI \longrightarrow Ag^+ + I^-$ $(K_L)$ $K_L = K_1 \cdot K_2$
$K_1$ is calculated from thermodynamic data, $K_2$ is calculated from electrochemical data:
$K_1 = e^{-\Delta G(AgI)/(R \cdot 298\ K)}$
$\Delta G_2 = (\varepsilon_{Ag+/Ag} - \varepsilon_{I2/I-}) \cdot F$ $K_2 = e^{-\Delta G2/(R \cdot 298\ K)}$
$K_L = 8.56 \cdot 10^{-17}\ (mol/L)^2$

b) Application of van't Hoff`s equation:
$\ln K(75) = \ln K(25) - \Delta_r H_1/R \cdot (1/(348\ K) - 1/(298\ K))$
mit $\Delta_r H_1 = \Delta H(I^-) + \Delta H(Ag^+) - \Delta H(AgI) = 110.88\ kJ/mol$
$K(75) = 5.31 \cdot 10^{-14}\ (mol/L)^2$
Explanation with Le Chatellier: the solubilization process is endothermal.

c) $\Delta_r G_2(298) = \Delta G(C_2H_4) + \Delta G(HI) - \Delta G(C_2H_5I) = 50.9\ kJ/mol$
$\Delta_r H_2(298) = \Delta H(C_2H_4) + \Delta H(HI) - \Delta H(C_2H_5I) = 87.1\ kJ/mol$
Van't Hoff`s equation (reaction at 600 K):
$\ln K(600) = -\Delta_r G_2(298)/(R \cdot 298K) - \Delta_r H_2 / R\ (1/(600\ K) - 1/(298\ K)) = 0.06$
HI has to be removed to prevent a back reaction.

d) $\varepsilon = \varepsilon^o + RT/F \ln [Ag^+] = \varepsilon^o + RT/F \ln K_L - RT/F \ln [I^-]$

e) It is a first-order reaction. $c(I^-) = c_0I^- \cdot e^{-kt}$ $c_0(I^-)$ is as well the initial concentration of $C_2H_5I$.

f) The insertion results in the following:
$\varepsilon = \varepsilon_{Kalomel} - \varepsilon^o - RT/F \ln K_L + RT/F \ln [I]_0 - RT/F\ kt$
If emf is plotted against t. the gradient is $k = 1.6 \cdot 10^{-5}\ s^{-1}$
The axis intercept results in $c_0(I-) = 0.077\ M$
$m(C_2H_5I) = 0.25\ L \cdot 0.077\ mol/L \cdot M(C_2H_5I) = 3\ g$

## Solution to problem 4-4

a) 100µm² of lipid bilayer contain $N_{DOPC} = 2 \cdot 100\mu m^2 / 0{,}64 nm^2 = 3.13 \cdot 10^8$ DOPC-molecules. (it must be factor 2 because it is a bilayer). Thus, for every DiO-molecule, there are $A = n_{DOPC}/n_{DiO} = 3.13 \cdot 10^8 / 50 = 6.25 \cdot 10^6$ DOPC –molecules.
$\Leftarrow \quad n_{DiO} = n_{DOPC}/A = V_{DOPC} \cdot c_{DOPC}/A = 50\mu l \cdot 10mM / 6{,}25 \cdot 10^6 = 8.0 \cdot 10^{-14} mol$.

$$V_{DiO} = n_{DiO}/c_{DiO} = n_{DiO} \Big/ \left(c^w_{DiO}/M_{DiO}\right) = 8{,}0 \cdot 10^{-14}\,\text{mol} \Big/ \left(10\,\frac{\mu g}{l} \Big/ 882\,g\right) = 7{,}1\,\mu l$$

b) The following formula is needed for the calculation of the distance: $\left\langle (\Delta x)^2 \right\rangle_T^{\Delta t'} = 2fD\Delta t' = 2 \cdot 2 \cdot 6 \cdot 10^{-8}\,\mathrm{cm^2/s} \cdot (25+10)\,\mathrm{ms} = 0{,}84\,\mu\mathrm{m}^2$ (*f* = 2)

Thus, $\Delta x_{\Delta t'} = \sqrt{\left\langle (\Delta x)^2 \right\rangle_T^{\Delta t'}} = 0.91 \mu m$ (mit $\Delta t' = 35 ms$).

c) The lenght of the distance is:

$$\overline{\Delta x_{4\Delta t'}} = \sqrt{\left\langle (\Delta x)^2 \right\rangle_T^{4\Delta t'}} = \sqrt{2fD \cdot 4\Delta t'} = 2\sqrt{\left\langle (\Delta x)^2 \right\rangle_T^{\Delta t'}} = 1{,}82\,\mu\mathrm{m}\,.$$

d) The time needed by the lipid molecule is:

$$\Delta t' = \left\langle (\Delta x)^2 \right\rangle_T^{\Delta t'} \Big/ 2fD = (10\,\mu\mathrm{m})^2 \Big/ \left(2 \cdot 2 \cdot 6 \cdot 10^{-8}\,\mathrm{cm^2/s}\right) = 4{,}2\,\mathrm{s}$$

e) The concentration of the molecules decreases exponentionally with time, that means according to first order:

$$N(t) = N_0 \cdot 2^{-t/\tau_{1/2}} = N_0 \cdot \left(e^{\ln 2}\right)^{-t/\tau_{1/2}} = N_0 \cdot e^{-t \cdot \ln 2/\tau_{1/2}}\,.$$

Thus, it follows: $N(t)/N_0 = 0{,}1$: $\quad \dfrac{t}{\tau_{1/2}} = -\dfrac{ln(N(t)/N_0)}{ln\,2} = -\dfrac{ln\,0.1}{ln\,2} = 3.3$

After $t = 3.3 \cdot \tau_{1/2} = 3.3 \cdot 75ms = 250ms$ of exposure time, 10% of all molecules are still fluorescent, that means after maximally $250ms/10ms = 25$ photos.

## Solution to problem 4-5

a) (i) 3 ions $A^{2+}$ to the right, 2 ions $B^{3+}$ to the left; (ii) one ion $A^{2+}$ to the right and one ion $O^{2-}$ to the right; (iii) two ions $B^{3+}$ and three ions $O^{2-}$ to the left.

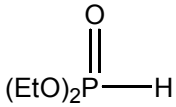
b) (i) 3 $A^{2+}$ move to the right, these are three formula units $AB_2O_4$, two $B^{3+}$ move to the left, this is one formular unit $AB_2O_4$. The wire would divide the $AB_2O_4$-layer in the ratio of 3:1 and would be on the right side at 75%; (ii) $AB_2O_4$ forms only at the right side of the wire, the wire would be situated extremely on the the left side; (iii) $AB_2O_4$ only forms on the left side of the wire, the wire would be situated extremely on the right side.

c) 1. Several of the basic mechanisms can take place simultaneously ; 2. the metals can possibly change their oxidation numbers because of diffusion – electrons and metal will diffuse separately then.

## Solution to problem 4-6

A = $P_4O_{10}$ B = $PH_3$ C = $PCl_3$ D = $(EtO)_3PO$

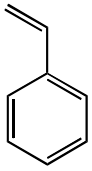
E = $POCl_3$ F = $(EtO)_2POH$ H = $PPh_3$

I = $Ph_3PO$ J = $NaPPh_2$ G = 

K = $Ph_2PH$

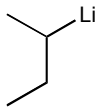
## Solution to problem 4-7

a)



$C_8H_8$
M = 104.15 g/mol

styrene




$C_4H_9Li$
M = 64.06 g/mol

sec-butyllithium

$$\frac{c(Styrol)}{c(sec-Butyllitium} = 40$$

$\Rightarrow$ degree of polymerization $P_n$ at a turnover of 25%: $P_n = 10$

at a turnover of 50%: $P_n = 20$

at a turnover of 75%: $P_n = 30$

b) $v_x$ is the volume fraction of the umpteenth sampling

$0.25 \cdot v_1 = 0.5 \cdot v_2 = 0.75 \cdot v_3$ mit $v_3 = 1 - v_1 - v_2$

$0.25 \cdot v_1 = 0.75 - 0.75 \cdot v_1 - 0.75 \cdot v_2$ $v_1 = 0.75 - 0.75 \cdot v_2$

$0.5 \cdot v_2 = 0.75 - 0.75 \cdot v_1 - 0.75 \cdot v_2$ $0.75 \cdot v_1 = 0.75 - 1.25 \cdot v_2$

$\Leftarrow$ $v_1 = 0.55$ $v_2 = 0.27$ $v_3 = 0.18$

**Polymer analytics**

c) difference of the molar masses of two neighbouring polymer molecules:
e.g. 994 g/mol – 890 g/mol = 104 g/mol
$\Leftarrow$ sterene is the most common monomer with the calculated molecular weight

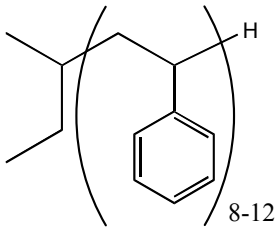
calculation of the degree of polymerization e.g. for the species at 1098 g/mol:
1098 g/mol : 104 g/mol = 10,56

| species [g/mol] | 890 | 994 | 1098 | 1202 | 1306 |
|---|---|---|---|---|---|
| $P_n$ | 8 | 9 | 10 | 11 | 12 |

Concerning a degree of polymerization of 10, there are the following masses per mole for the initial- and final groups of the polymer:

1098 g/mol – 1040 g/mol = 58 g/mol

only one proton remains as a final group of the polymer while sec-butyllithum is an initiator-entity grouping (sec-Butyl ~ 57 g/mol).




d) $\sum_{i=1}^{\infty} h_i \cdot M_i$ = 1098 g/mol; $\sum_{i=1}^{\infty} h_i$ = 1; $\sum_{i=1}^{\infty} h_i \cdot M_i^2$ = 1213175.2 g$^2$/mol$^2$

$M_n$ = 1098 g/mol; $M_w$ = 1104.9 g/mol ⇐ $M_w / M_n$ = 1.00

the quotient for beef insulin is: $M_n = M_w$ = 5733.5 g/mol ⇐ $M_w / M_n$ = 1

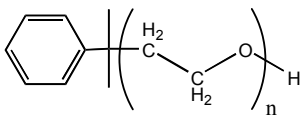
$M_w / M_n$ is a measure for the range of a molecular-weight distribution.

(The sample is monodisperse for $M_w / M_n$ = 1; usually, the $M_w / M_n$ – values of radical polymerizations are around 2, while values around 1.01 are not seldom for anionic polymerization)

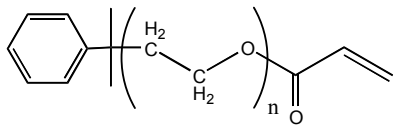
e) Large molecules are more likely to contain one or more rather heavy isotopes of carbon ($^{13}$C) or hydrogen ($^{2}$H). There are as well heavy polymer molecules in the mixture.

(The shifting of the lightest peak from 1098 to almost 1099 is caused by the proton mass that is a little bit higher than 1 g/mol, because $M(^{1}H)$ = 1,008 g/mol and $M(^{12}C)$ = 12,000 g/mol.)

f)

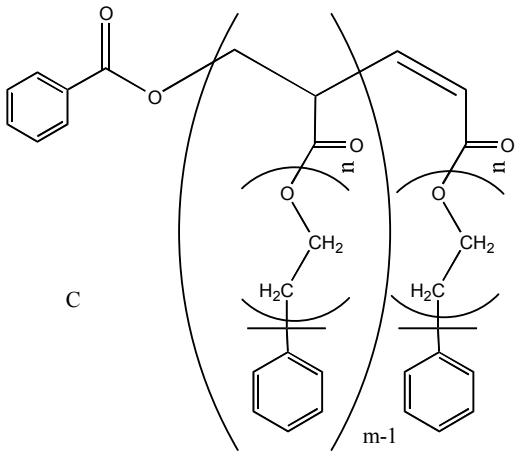



A = polyethylene oxid (or polyethylene glycol, polyoxirane ...)



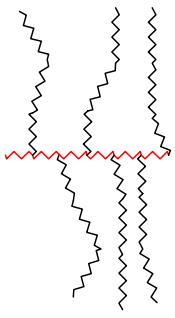

B

e.g.




C

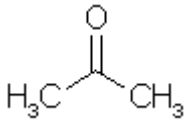
brush-like structure



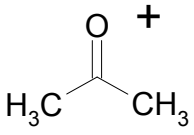
Hydrogen transports from the polyethylene-oxide chain to the growing polymer radical are possible by the radical course of the reaction. In this way, undesirable crosslinkings may form.

## Solution to problem 4-8

a) It is acetone

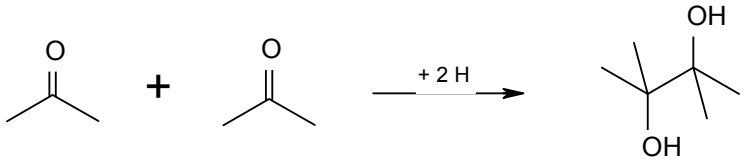


b)

| mass number | 15 | 27 | 42 | 43 | 58 |
|---|---|---|---|---|---|
| species | $^{+}CH_3$ | $^{+}CH_3 - C$ | $^{+}CH_3 - C - CH_3$ , $^{+}CH_2 - C = O$ | $^{+}CH_3 - C = O$ |  |

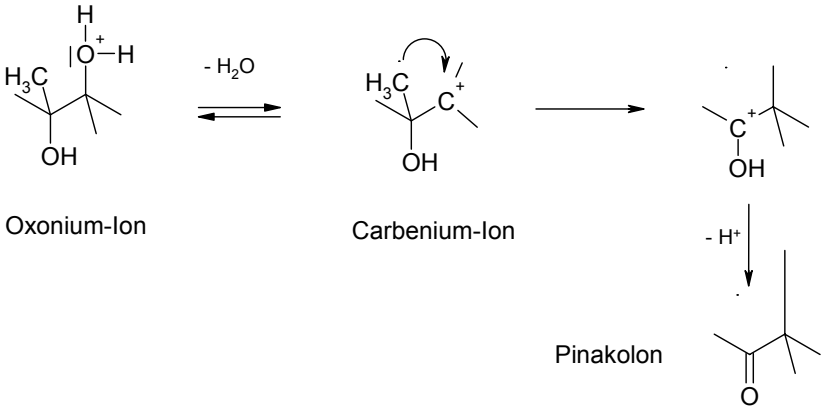
There is only one signal in the $^{1}H$- NMR-spectrum, because all hydrogen atoms are chemically equivalent in A.

c)




The systematic name of pinacolone is 2,3-dimethylbutane-2,3-diol.

d) An oxonium ion forms by the protonation of a OH-group. This ion transforms into a carbenium-ion and water is cleaved. By 1,2-shifting of an alkyl-anion, a resonance-stabilized carbenium-ion forms that transforms into pinacolone by release of a proton.




Oxonium-Ion

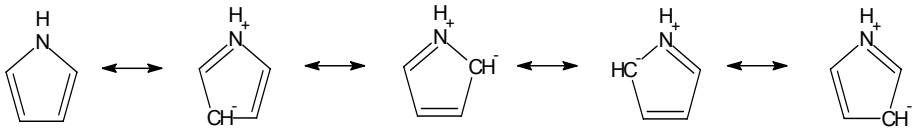
Carbenium-Ion

e) butanone

## Solution problem 4-9

a) cyclic, conjugated, planar, 4n+2 electrons

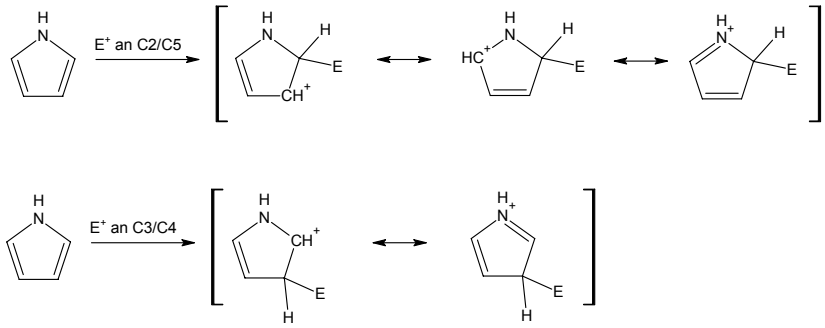
b)



c) first variant: furan < pyrrole < thiophene
(decreasing electronegativity of the heteroatom favours the delocation of a free electron pair)

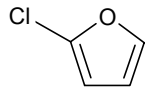
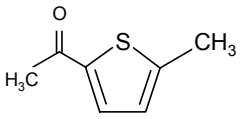
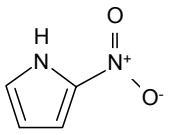
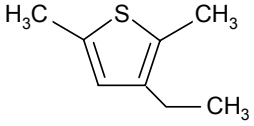
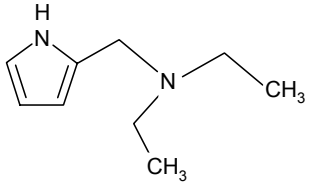
second variant: thiophene < furan < pyrrole
(a different orbital size of the S-atom could be unfavourable for the conjugation)

d)



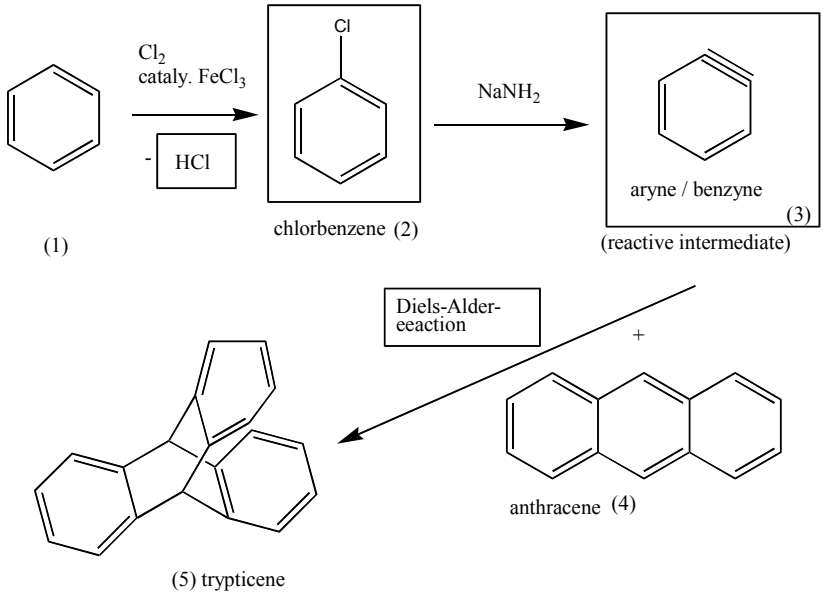

➔ electrophilic aromatic substitution at C2/C5 is favoured, because of a higher delocation of the positive charge

e)

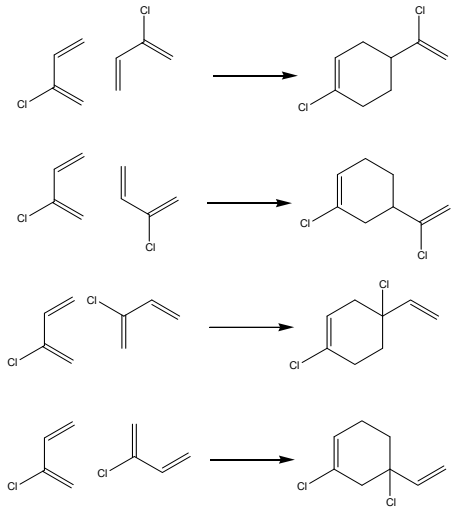
| | | |
|---|---|---|
| **A**  | **B**  | **C**  |
| **D**  | **E**  | |

## Solution problem 4-10

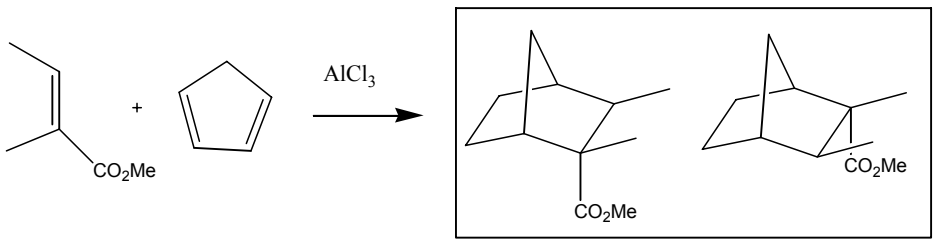
a) - d)




e) 2-chlorobutadiene reacts with itself in a Diels-Alder reaction. Altogether four different products can form:



f) and g)




The two compounds are enantiomers.

# Part 3

# 36. International Chemistry Olymmpiad

**Kiel, Friday 29. July**

# Theoretical Test

## Problem 1: Thermodynamics

For his 18th birthday party in February Peter plans to turn a hut in the garden of his parents into a swimming pool with an artificial beach. In order to estimate the costs for heating the water and the house, Peter obtains the data for the natural gas composition and its price.

*1.1 Write down the chemical equations for the complete combustion of the main components of natural gas, methane and ethane, given in Table 1. Assume that nitrogen is inert under the chosen conditions.*

*Calculate the reaction enthalpy, the reaction entropy, and the Gibbs energy under standard conditions ($1.013 \cdot 10^5$ Pa, 25.0°C) for the combustion of methane and ethane according to the equations above assuming that all products are gaseous.*

The thermodynamic properties and the composition of natural gas can be found in Table 1.

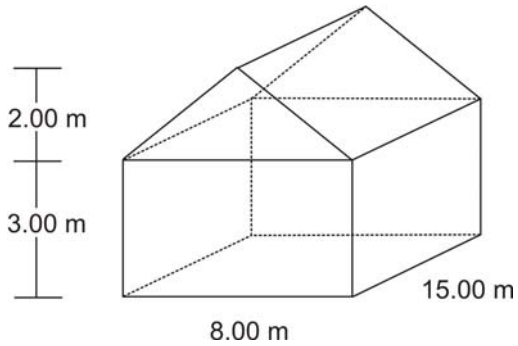
*1.2 The density of natural gas is 0.740 g $L^{-1}$ ($1.013 \cdot 10^5$ Pa, 25.0°C) specified by PUC, the public utility company.*

*a) Calculate the amount of methane and ethane (in moles) in 1.00 $m^3$ of natural gas (natural gas, methane, and ethane are not ideal gases!).*

*b) Calculate the combustion energy which is released as thermal energy during the burning of 1.00 $m^3$ of natural gas under standard conditions assuming that all products are gaseous. (If you do not have the amount from 1.2a) assume that 1.00 $m^3$ natural gas corresponds to 40.00 mol natural gas.)*

*According to the PUC the combustion energy will be 9.981 kWh per $m^3$ of natural gas if all products are gaseous. How large is the deviation (in percent) from the value you obtained in b)?*

The swimming pool inside the house is 3.00 m wide, 5.00 m long and 1.50 m deep (below the floor). The tap water temperature is 8.00°C and the air temperature in the house (dimensions given in the figure below) is 10.0°C. Assume a water density of $\rho$ = 1.00 kg $L^{-1}$ and air behaving like an ideal gas.




*1.3 Calculate the energy (in MJ) which is required to heat the water in the pool to 22.0°C and the energy which is required to heat the initial amount of air (21.0% of $O_2$, 79.0% of $N_2$) to 30.0°C at a pressure of $1.013 \cdot 10^5$ Pa.*

In February, the outside temperature is about 5°C in Northern Germany. Since the concrete walls and the roof of the house are relatively thin (20.0 cm) there will be a loss of energy. This energy is released to the surroundings (heat loss released to water and/or ground should be neglected). The heat conductivity of the wall and roof is 1.00 W $K^{-1}$ $m^{-1}$.

*1.4 Calculate the energy (in MJ) which is needed to maintain the temperature inside the house at 30.0°C during the party (12 hours).*

1.00 $m^3$ of natural gas as delivered by PUC costs 0.40 € and 1.00 kWh of electricity costs 0.137 €. The rent for the equipment for gas heating will cost him about 150.00 € while the corresponding electrical heaters will only cost 100.00 €.

*1.5 What is the total energy (in MJ) needed for Peter's "winter swimming pool" calculated in 1.3 and 1.4? How much natural gas will he need, if the gas heater has an efficiency of 90.0%?*
*What are the different costs for the use of either natural gas or electricity? Use the values given by PUC for your calculations and assume 100% efficiency for the electric heater.*

Table 1: Composition of natural gas

| Chemical Substance | mol fraction $x$ | $\Delta_f H^0 \cdot$( kJ $mol^{-1})^{-1}$ | $S^0 \cdot$(J $mol^{-1}$ $K^{-1})^{-1}$ | $C_p{}^0 \cdot$(J $mol^{-1}$ $K^{-1})^{-1}$ |
|---|---|---|---|---|
| $CO_2$ (g) | 0.0024 | -393.5 | 213.8 | 37.1 |
| $N_2$ (g) | 0.0134 | 0.0 | 191.6 | 29.1 |
| $CH_4$ (g) | 0.9732 | -74.6 | 186.3 | 35.7 |
| $C_2H_6$ (g) | 0.0110 | -84.0 | 229.2 | 52.5 |
| $H_2O$ (l) | - | -285.8 | 70.0 | 75.3 |
| $H_2O$ (g) | - | -241.8 | 188.8 | 33.6 |
| $O_2$ (g) | - | 0.0 | 205.2 | 29.4 |

Equation:

$J = E \cdot (A \cdot \Delta t)^{-1} = \lambda_{wall} \cdot \Delta T \cdot d^{-1}$

| | |
|---|---|
| $J$ | energy flow $E$ along a temperature gradient (wall direction z) per area $A$ and time $\Delta t$ |
| $d$ | wall thickness |
| $\lambda_{wall}$ | heat conductivity |
| $\Delta T$ | difference in temperature between the inside and the outside of the house |

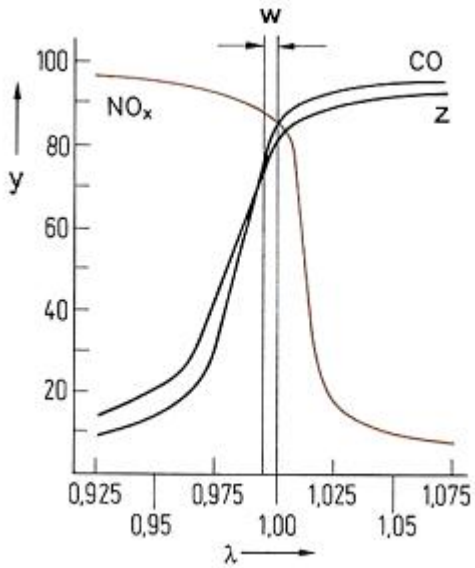
## Problem 2: Kinetics at catalyst surfaces

Apart from other compounds the exhaust gases of an Otto engine are the main pollutants carbon monoxide, nitrogen monoxide and uncombusted hydrocarbons, as, for example, octane. To minimize them they are converted to carbon dioxide, nitrogen and water in a regulated three-way catalytic converter.

*2.1 Complete the chemical reaction equations for the reactions of the main pollutants in the catalyst.*

To remove the main pollutants from the exhaust gas of an Otto engine optimally, the □-value is determined by an electro-chemical element, the so called lambda probe. It is located in the exhaust gas stream between engine and the three-way catalytic converter.
The lambda value is defined as

$$\lambda = \frac{\textit{amount of air at the inlet}}{\textit{amount of air necessary for complete combustion}}.$$




w: $\lambda$-window
y: conversion efficiency (%)
z: Hydrocarbons

*2.2 Decide the questions on the answer sheet concerning the λ probe.*

The adsorption of gas molecules on a solid surface can be described in a simple model by using the Langmuir isotherm:

$$\theta = \frac{K \cdot p}{1 + K \cdot p}$$

where θ is the fraction of surface sites that are occupied by the gas molecules, p is the gas pressure and K is a constant.
The adsorption of a gas at 25 °C may be described by using the Langmuir isotherm with $K = 0.85\ kPa^{-1}$.

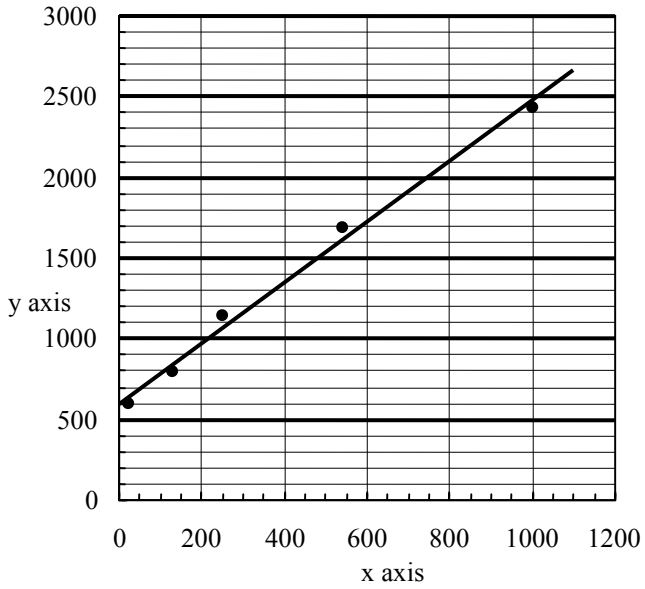
*2.3 a) Determine the surface coverage θ at a pressure of 0.65 kPa.*

*2.3 b) Determine the pressure p at which 15 % of the surface is covered.*

2.3 c) The rate r of the decomposition of gas molecules at a solid surface depends on the surface coverage □(reverse reaction neglected): $r = k \cdot \theta$

*Give the order of the decomposition reaction at low and at high gas pressures assuming the validity of the Langmuir isotherm given above (products to be neglected).*

2.3 d) Data for the adsorption of another gas on a metal surface (at 25°C)




x axis: $p \cdot (Pa)^{-1}$
y axis: $p \cdot V_a^{-1} \cdot (Pa\ cm^{-3})^{-1}$

$V_a$ is the gas volume that has been adsorbed.

*If the Langmuir isotherm can be applied, determine the gas volume $V_{a,max}$ needed for a complete coverage of the metal surface and the product $K \cdot V_{a,max}$.*

*Hint: Set $\theta = V_a / V_{a,max}$ .*

Assume that the catalytic oxidation of CO on a Pd surface with equal surface sites proceeds in the following way:
In a first step adsorbed CO and adsorbed $O_2$ form adsorbed $CO_2$ in a fast equilibrium,

$$CO\ (ads.) + 0.5\ O_2\ (ads.) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CO_2\ (ads.)$$

In a slow second step, $CO_2$ is then desorbed from the surface:

$$CO_2\ (ads.) \xrightarrow{k_2} CO_2\ (g)$$

*2.4 Derive the formula for the reaction rate of the $CO_2$(g) - formation as a function of the partial pressures of the reaction components.*
Hint: Use the Langmuir isotherm with the proper number of gas components

$$\theta(i) = \frac{K_i \cdot p_i}{1 + \sum_j K_j \cdot p_j}$$ j: relevant gas components

## Problem 3: Monovalent alkaline earth compounds?

In the past there have been several reports on compounds of monovalent calcium. Until recently the nature of these "compounds" was not known but they are still of great interest to solid state chemists.
Attempts to reduce $CaCl_2$ to CaCl have been made with
(a) Calcium (b) Hydrogen (c) Carbon

*3.1 Give the corresponding reaction equations that could potentially lead to the formation of CaCl.*

After an attempt to reduce $CaCl_2$ with the stoichiometric 1:1 molar amount of Ca one obtains an inhomogeneous grey substance. A closer look under the microscope reveals silvery metallic particles and colorless crystals.

*3.2 What substance are the metallic particles and the colorless crystals?*

When $CaCl_2$ is attempted to be reduced with elemental hydrogen a white product forms. Elemental analysis shows that the sample contains 52.36 m/m% of calcium and 46.32 m/m% of chlorine.

*3.3 Determine the empirical formula of the compound formed!*

When $CaCl_2$ is attempted to be reduced with elemental carbon a red crystalline product forms. The molar ratio of Ca and Cl determined by elemental analysis is $n$(Ca):$n$(Cl)=1.5:1. During the hydrolysis of the red crystalline substance the same gas is evolved as during the hydrolysis of $Mg_2C_3$.

*3.4 a) Show the two acyclic constitutional isomers of the gas that is formed by hydrolysis.*

*b) What compound is formed by the reaction of $CaCl_2$ with carbon?*

*(Provided that monovalent calcium does not exist.)*

As none of these attempts lead to the formation of CaCl more consideration has to be given as to the hypothetical structure of CaCl. One can assume that CaCl is likely to crystallize in a simple crystal structure.
It is the radius ratio of cation $r(M^{m+})$ and anion $r(X^{x-})$ of salts that often determines the crystal structure of a particular compound as shown for MX compounds in the table below.

| Coordination number of M | Surrounding of X | Radius ratio $r_M/r_X$ | Structure type | estimated $\Delta_L H^0$ for CaCl |
|---|---|---|---|---|
| 3 | Triangular | 0.155-0.225 | BN | - 663.8 kJ mol$^{-1}$ |
| 4 | Tetrahedral | 0.225-0.414 | ZnS | - 704.8 kJ mol$^{-1}$ |
| 6 | Octahedral | 0.414-0.732 | NaCl | - 751.9 kJ mol$^{-1}$ |
| 8 | Cubic | 0.732-1.000 | CsCl | - 758.4 kJ mol$^{-1}$ |

$\Delta_L H^0$(CaCl) is defined for the reaction $Ca^+(g) + Cl^-(g) \longrightarrow CaCl(s)$

*3.5a) What type of structure is CaCl likely to have?*
[$r(Ca^+) \approx 120$ pm (estimated), $r(Cl^-) \approx 167$ pm)]

Not only the lattice energy $\Delta_L H^0$ for CaCl is important for the decision whether CaCl is thermodynamically stable or not. In order to decide whether it is stable to decompositon into its elements, the standard enthalpy of formation $\Delta_f H^0$ of CaCl has to be known.

*3.5b) Calculate the value of $\Delta_f H^0$ (CaCl) with the aid of a Born-Haber-cycle.*

| | | | |
|---|---|---|---|
| heat of fusion | $\Delta_{fusion} H^0$(Ca) | | 9.3 kJ mol$^{-1}$ |
| ionization enthalpy | $\Delta_{1.\ IE} H$(Ca) | $Ca \longrightarrow Ca^+$ | 589.7 kJ mol$^{-1}$ |
| ionization enthalpy | $\Delta_{2.\ IE} H$(Ca) | $Ca^+ \longrightarrow Ca^{2+}$ | 1145.0 kJ mol$^{-1}$ |
| heat of vaporization | $\Delta_{vap} H^0$(Ca) | | 150.0 kJ mol$^{-1}$ |
| dissociation energy | $\Delta_{diss} H(Cl_2)$ | $Cl_2 \longrightarrow 2\ Cl$ | 240.0 kJ mol$^{-1}$ |
| enthalpy of format. | $\Delta_f H^0(CaCl_2)$ | | -796.0 kJ mol$^{-1}$ |
| electron affinity | $\Delta_{EA} H$(Cl) | $Cl + e^- \longrightarrow Cl^-$ | - 349.0 kJ mol$^{-1}$ |

To decide whether CaCl is thermodynamically stable to disproportionation into Ca and $CaCl_2$ the standard enthalpy of this process has to be calculated. (The change of the entropy $\Delta S$ is very small in this case, so its influence is negligible.)

*3.6 Does the disproportionation of CaCl take place from a thermodynamic point of view? Base your decision on a calculation!*

## Problem 4: Determining atomic masses

The reaction of the element X with hydrogen leads to a class of compounds that is analogous to hydrocarbons. 5.000 g of X form 5.628 g of a molar 2:1 mixture of the stoichiometric X-analogues of methane and ethane, respectively.

*4.1 Determine the molar mass of X from this information. Give the chemical symbol of X, and the 3D-structure of the two products.*

The following more complex case is of great historical interest.
The mineral Argyrodite is a stoichiometric compound that contains silver (oxidation state +1), sulphur (oxidation state -2) and an unknown element Y (oxidation state +4). The ratio between the masses of silver and Y in Argyrodite is m(Ag) : m(Y) = 11.88 : 1. Y forms a reddish brown lower sulfide (oxidation state of Y is +2) and a higher white sulfide (oxidation state of Y is +4). The coloured lower sulfide is the sublimate obtained by heating Argyrodite in a flow of hydrogen. The residues are $Ag_2S$ and $H_2S$. To convert 10.0 g of Argyrodite completely, 0.295 L of hydrogen are needed at 400 K and 100 kPa.

*4.2 Determine the molar mass of Y from this information. Give the chemical symbol of Y, and the empirical formula of Argyrodite.*

The atomic masses are correlated with spectroscopic properties.

To determine the vibrational frequency $\tilde{\nu}$ expressed in wave numbers of chemical bonds in IR spectra chemists use Hooke's law which focuses on the frequency of the vibration (attention to units!):

$$\tilde{\nu} = \frac{1}{2\pi c} \cdot \sqrt{\frac{k}{\mu}}$$

| | |
|---|---|
| $\tilde{\nu}$ | vibrational frequency of the bond, in wavenumbers ($cm^{-1}$) |
| c | speed of light |
| k | force constant, indicating the strength of the bond ($N\ m^{-1} = kg\ s^{-2}$) |
| $\mu$ | reduced mass in $AB_4$, which is given by $\mu = \frac{3m(A)m(B)}{3m(A)+4m(B)}$ |
| m(A), m(B) | the masses of the two bond atoms |

The vibrational frequency of the C-H bond of methane is known to be 3030.00 $cm^{-1}$. The vibrational frequency of the Z-analogue of methane is known to be 2938.45 $cm^{-1}$. The bond enthalpy of a C-H bond in methane is 438.4 kJ $mol^{-1}$. The bond enthalpy of a Z-H bond in the Z-analogue of methane is known to be 450.2 kJ $mol^{-1}$.

*4.3 Determine the force constant k of a C-H bond using Hooke's law.*

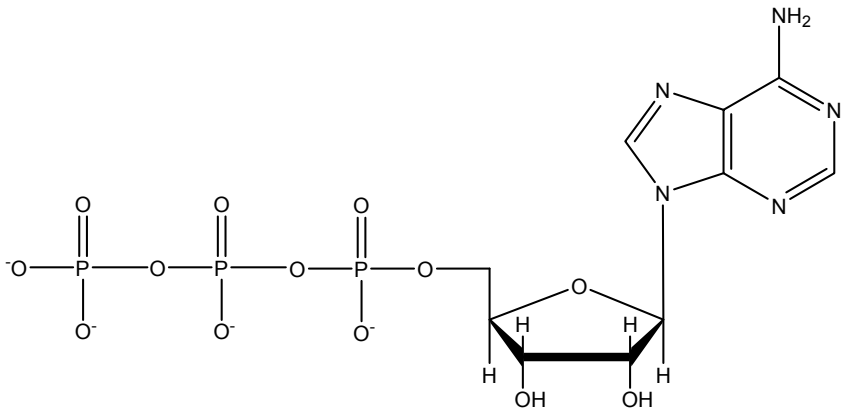
*Estimate the force constant k of a Z-H bond, assuming that there is a linear proportionality between force constant and bond enthalpy.*

*Determine the atomic mass of Z from this information.*

*Give the chemical symbol of Z.*

## Problem 5: Biochemistry with Thermodynamics

**Structure of $ATP^{4-}$**




**Shifting chemical equilibria with ATP:**

Animals use free energy from the oxidation of their food to maintain concentrations of ATP, ADP, and phosphate far from equilibrium. In red blood cells the following concentrations have been measured:

$c(ATP^{4-})$ = 2.25 mmol $L^{-1}$ $c(ADP^{3-})$ = 0.25 mmol $L^{-1}$
$c(HPO_4^{2-})$ = 1.65 mmol $L^{-1}$

Free energy stored in ATP can be released according to the following reaction:

$ATP^{4-} + H_2O \rightleftarrows ADP^{3-} + HPO_4^{2-} + H^+$ $\Delta G°' = -30.5$ kJ $mol^{-1}$ (1)

As the pH is close to 7 in most living cells, biochemists use $\Delta G°'$ instead of $\Delta G°$. The standard state of $\Delta G°'$ is defined as having a constant pH of 7. In equations with $\Delta G°'$ and K' for reactions at pH=7 the concentration of $H^+$ is therefore omitted. Standard concentration is 1 mol $L^{-1}$.

*5.1 Calculate the actual $\Delta G'$ of reaction (1) in the red blood cell at 25°C and pH = 7.*

In living cells many so-called "anabolic" reactions take place, which are at first sight thermodynamically unfavourable because of a positive $\Delta G$. The phosphorylation of glucose is an example:

glucose + $HPO_4^{2-} \rightleftarrows$ glucose 6-phosphate$^{2-}$ + $H_2O$ $\Delta G°' = +13.8$ kJ $mol^{-1}$ (2)

*5.2 Calculate first the equilibrium constant K' of reaction (2) and then the ratio c(glucose 6-phosphate) / c(glucose) in the red blood cell in chemical equilibrium at 25°C and pH = 7.*

To shift the equilibrium to a higher concentration of glucose 6-phosphate, reaction (2) is coupled with hydrolysis of ATP:

glucose + $ATP^{4-} \xrightleftarrows{\text{hexokinase}}$ glucose 6-phosphate$^{2-}$ + $ADP^{3-}$ + $H^+$ (3)

*5.3 Calculate $\Delta G°'$ and K' of reaction (3). What is now the ratio c(glucose 6-phosphate) / c(glucose) in the red blood cell in chemical equilibrium at 25°C and pH = 7?*

**ATP synthesis:**

An adult person ingests about 8000 kJ of energy ($\Delta G'$) per day with the food.

*5.4 a) What will be the mass of ATP that is produced per day if half of this energy is used for ATP synthesis? Assume a $\Delta G'$ of -52 kJ $mol^{-1}$ for reaction (1), and a molecular weight of 503 g $mol^{-1}$ for ATP.*

*b) What mass of ATP does the human body contain on average if the mean lifetime of an ATP molecule until its hydrolysis is 1 min?*

*c) What happens to the rest of the free energy, which is not used for ATP synthesis? Mark on the answer sheet.*

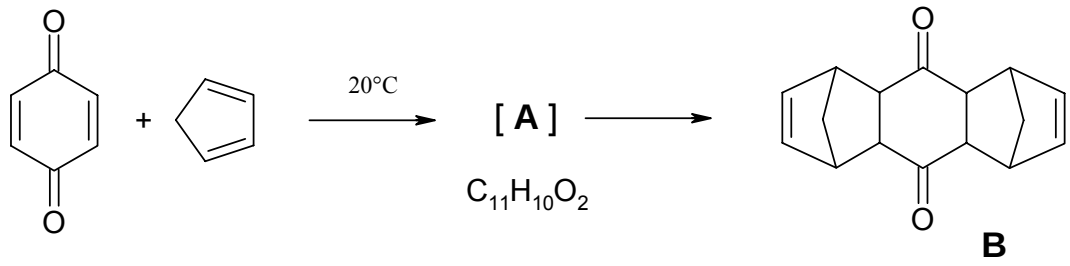
In animals the energy obtained by the oxidation of food is used to pump protons out of specialized membrane vesicles, the mitochondria. ATP-synthase, an enzyme, will allow protons to re-enter the mitochondria if ATP is simultaneously synthesized from ADP and phosphate.

*5.5 a) How many protons ($H^+$) are in a spherical mitochondrium with a diameter of 1 $\mu$m at pH = 7?*

*b) How many protons have to enter into each of the 1000 mitochondria of a liver cell via the ATP-synthase to allow the production of a mass of 0.2 fg of ATP per cell? Assume that 3 protons have to enter for the synthesis of 1 molecule of ATP.*

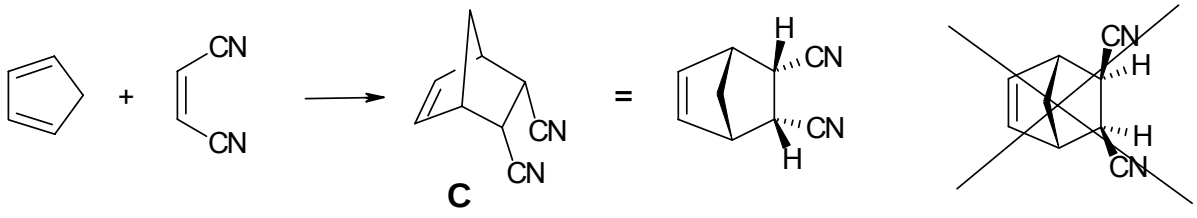
## Problem 6: Diels-Alder Reactions

The Diels-Alder reaction, a concerted [4+2]-cycloaddition between a diene and an olefin to yield a cyclohexene, was discovered in 1928 here in Kiel. Prof. Otto Diels and his coworker Kurt Alder mixed *p*-benzoquinone with an excess of cyclopentadiene and obtained the following result:




*6.1 Draw the structure of A (without stereochemical information).*

The Diels-Alder reaction is a concerted, one-step reaction that proceeds with high stereospecificity. For example, only a single stereoisomer **C** is formed in the following reaction



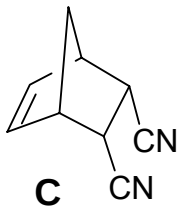

Not formed

If you use the *E*-isomer of the alkene instead, you will obtain two other stereoisomers **D1** and **D2**.

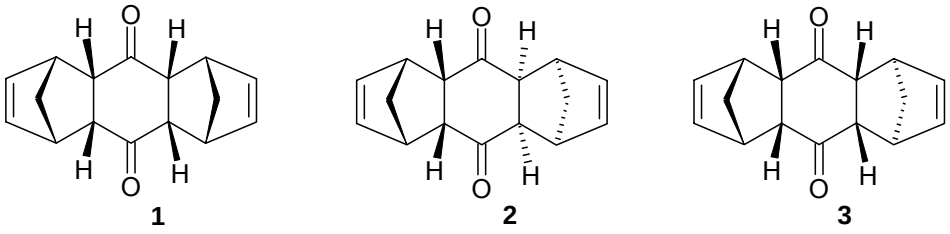
*6.2 Give the structures of D1 and D2.*

Accordingly, in the original reaction (formation of **B** from cyclopentadiene and benzoquinone) Diels and Alder found only one of the following six conceivable stereoisomers of **B** (see next page).

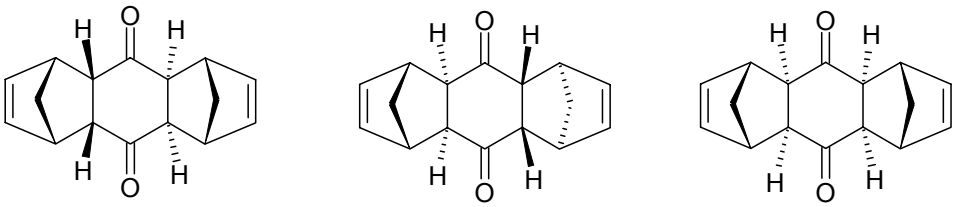
Hints:
- keep the stereospecific formation of **C** in mind
and
- the sterically less hindered isomer forms.




**C**



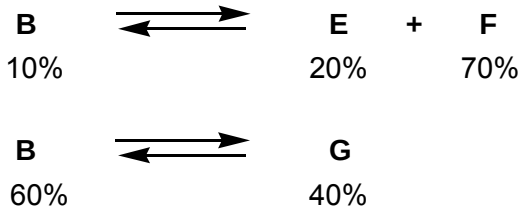

**1** **2** **3**




**4** **5** **6**

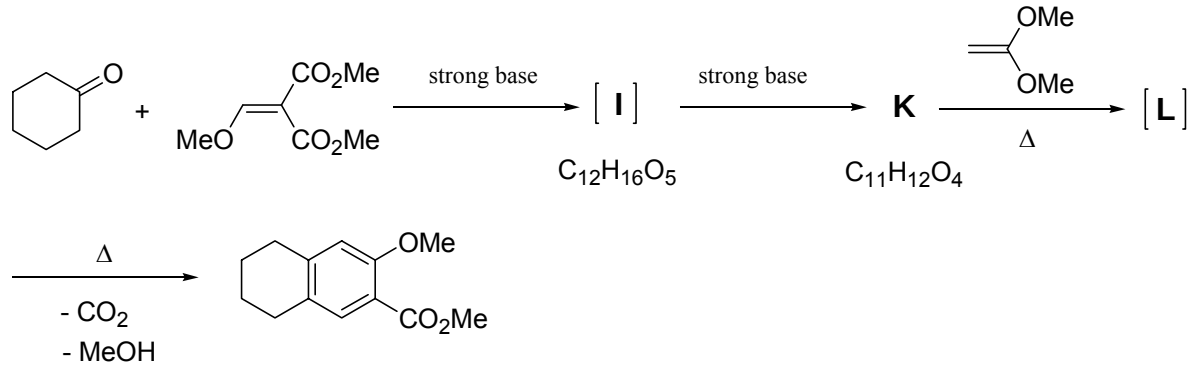
*6.3 Which single isomer of the six stereoisomers 1-6 of B shown above did they isolate?*

After prolonged heating (15h, 120°C) of the originally isolated stereoisomer **B** (melting point mp: 157°C), Diels and Alder obtained two new stereoisomers **E** (mp: 153°C) and **F** (mp: 163°C). Equilibration of **B** with a catalytic amount of a strong base at 25°C gave a further stereoisomer **G** (mp: 184°C).




*6.4 Decide the questions on the answer sheet concerning the Diels-Alder reaction.*
Hint: You do not need to know, which of the six stereoisomers 1 - 6 (shown above) corresponds to either E, F or G in order to anwer this question.

The Diels-Alder reaction plays also an important role in the following reaction sequence.




*6.5 Draw the structures for I, K and L.*

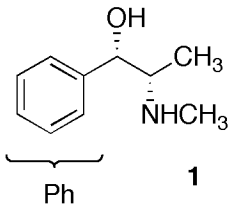
Hints: - **K** has only one methyl group.
- **L** is the Diels-Alder adduct of **K** and the alkene shown.

## Problem 7: Stereochemistry in Drugs

The Cahn-Ingold-Prelog rules are used to specify the stereochemistry of molecules.

*7.1 Order the groups on the answer sheet according to their priority in the Cahn-Ingold-Prelog (CIP)-system*.

Pseudoephedrine **1** is a constituent in many common drugs against colds, e.g. in nasal sprays.

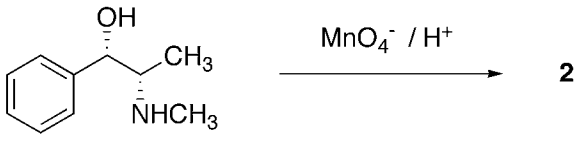



**1**

*7.2 Mark the stereocenters in 1 with an * on the answer sheet.*
*Order the substituents on each stereocenter in 1 according to their priority and determine their absolute configuration (R or S).*

*7.3 Draw a Newman or a sawhorse representation of 1.*
*Draw a Fischer representation of 1.*

Treatment of **1** with acidic permanganate solutions under mild conditions yields the stimulant Methcathinone **2**:




**1**

*7.4 Draw the stereochemically correct structure of 2 and a balanced redox equation of the reaction. Indicate in your equation the particular oxidation number on <u>all</u> atoms which undergo a change in their formal oxidation numbers.*

The treatment of **2** with $LiAlH_4$ results exclusively in compound **3**, which differs from **1** in its melting point.


*7.5 a) Draw the stereochemically correct structure of 3.*
*7.5 b) Decide the statements on the answer sheet concerning isomers.*
*7.5 c) Draw a structural model to rationalize the exclusive formation of 3 from 2.*

## Problem 8: Colloids

The combination of an inorganic and an organic component on a nanometer scale yields materials with excellent properties. Thus the synthesis of hybrid nanoparticles is of interest. (T = 298.15 K throughout whole problem)

Solution A is an aqueous solution of $CaCl_2$ with a concentration of 1.780 g $L^{-1}$.
Solution B is an aqueous solution of $Na_2CO_3$ with a concentration of 1.700 g $L^{-1}$.

$pK_{a1}(H_2CO_3) = 6.37$ $pK_{a2}(HCO_3^-) = 10.33$

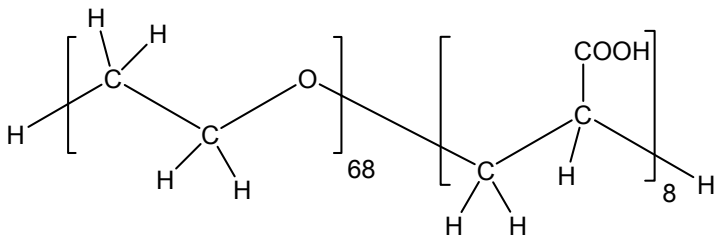
*8.1 Calculate the pH of solution B using reasonable assumptions.*

100 mL of solution **A** and 100 mL of solution **B** are mixed to form solution **C**. Solution **C** is adjusted to pH 10. A precipitate forms.

$K_{sp}(Ca(OH)_2) = 6.46 \cdot 10^{-6}\ mol^3\ L^{-3}$ $K_{sp}(CaCO_3) = 3.31 \cdot 10^{-9}\ mol^2\ L^{-2}$

*8.2 Show by calculation for each of the compounds $Ca(OH)_2$ and $CaCO_3$ whether it can be found in the precipitate or not.*

In a similar experiment 100 mL of solution **A** additionally contain 2 g of a copolymer consisting of two water soluble blocks: a poly(ethylene oxide) block and a poly(acrylic acid) block:



The polymer does not undergo any chemical reaction (except protolysis of the acid) and yet has a strong effect: after mixing of the two solutions (A+B) no precipitate can be observed. Small calcium carbonate particles with the polymer chains attached to their surface form. The attached polymers prevent further crystal growth and the hybrid particles remain in solution.

*8.3. Circle the block of the polymer (on the answer sheet) that attaches to the surface of the growing calcium carbonate crystal.*

To characterize the hybrid particles they are separated from the preparation solution and transferred into 50 mL of an aqueous NaOH solution (c(NaOH) = 0.19 mol $L^{-1}$). The solution is diluted by the addition of 200 mL of water. Assume that the new solution contains only the hybrid particles and no additional calcium or carbonate ions. All acidic groups participate in the acid-base equilibrium.

- For the new solution, a pH of 12.30 is measured.
- In electron microscopy you only can see the inorganic particles (not the polymer): Spherical particles of 100 nm diameter are observed.
- The molar mass of the hybrid particles (inorganic and organic part together) is determined to be M = $8.01 \cdot 10^8$ g $moL^{-1}$
- The charge of the particles is found to be Z = - 800 (number of unit charges).

($pK_a$(COOH, copolymer) = 4.88)

*8.4 How much of the initial amount of polymer (2 g) can still be found in the hybrid particles?*

*8.5. Calculate which modification of calcium carbonate has been formed.*

| *Modification* | *density* |
|---|---|
| Calcite | 2.71 g $cm^{-3}$ |
| Vaterite | 2.54 g $cm^{-3}$ |
| Aragonite | 2.95 g $cm^{-3}$ |

A periodical system and the following list of constants and useful formulas were provided.

## Constants and useful formulas

| f | p | n | μ | m | k | M | G | T |
|---|---|---|---|---|---|---|---|---|
| femto | pico | nano | micro | milli | kilo | mega | giga | tera |
| $10^{-15}$ | $10^{-12}$ | $10^{-9}$ | $10^{-6}$ | $10^{-3}$ | $10^{3}$ | $10^{6}$ | $10^{9}$ | $10^{12}$ |

Gas constant R = 8.314 J $K^{-1}$ $mol^{-1}$ Faraday constant F = 96485 C $mol^{-1}$

Use as standard pressure: p = $1.013 \cdot 10^5$ Pa

Use as standard temperature: T = 25°C = 298.15 K

Avogadro's number $N_A = 6.022 \cdot 10^{23}$ $mol^{-1}$ Planck constant h = $6.626 \cdot 10^{-34}$ J s

Speed of light c = $3.00 \cdot 10^8$ m $s^{-1}$

$\Delta G = \Delta H - T\Delta S$ $\Delta G = -nEF$

$\Delta G^0 = -RT \cdot lnK$ $\Delta G = \Delta G^0 + RT \cdot lnQ$ *with* $Q = \frac{product\ of\ c(products)}{product\ of\ c(reactands)}$

$\Delta H(T_1) = \Delta H^0 + (T_1 - 298.15\ K) \cdot C_p$ ($C_p$ = constant)

Arrhenius equation $k = A \cdot e^{-\frac{E_a}{R \cdot T}}$

Ideal gas law $pV = nRT$

Nernst equation $E = E^0 + \frac{RT}{nF} \cdot ln\frac{c_{ox}}{c_{red}}$

Bragg's law $n\lambda = 2d \cdot \sin\theta$

Beer- Lambert Law $A = \log\frac{P_0}{P} = \varepsilon \cdot c \cdot d$

$p = \frac{F}{A}$ $F = ma$

V(cylinder) = $\pi r^2 h$ A(sphere) = $4\pi r^2$ V(sphere) = $\frac{4}{3}\pi r^3$

1 J = 1 N m 1 N = 1 kg m $s^{-2}$ 1 Pa = 1 N $m^{-2}$ 1 W = 1 J $s^{-1}$

1 C = 1 A s

# Solutions to the Theoretical Test

## Solution to problem 1

**1.1** **a) methane:** $CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O$

**b) ethane:** $2\ C_2H_6 + 7\ O_2 \longrightarrow 4\ CO_2 + 6\ H_2O$

**Thermodynamic data for the equations:**

$\Delta H^0 = [2 \cdot (-241.8) - 393.5 - (-74.6)]$ kJ mol$^{-1}$ = -802.5 kJ mol$^{-1}$

$\Delta S^0 = [2 \cdot (188.8) + 213.8 - 186.3 - 2 \cdot 205.2]$ J mol$^{-1}$ K$^{-1}$ = -5.3 J mol$^{-1}$ K$^{-1}$

$\Delta G^0 = -802.5$ kJ mol$^{-1}$ – 298.15 K · (-5.3 J mol$^{-1}$ K$^{-1}$) = -800.9 kJ mol$^{-1}$

**Methane:** $\Delta H^0 = -802.5$ kJ mol$^{-1}$ $\Delta S^0 = -5.3$ J mol$^{-1}$ K$^{-1}$ $\Delta G^0$ = -800.9 kJ mol$^{-1}$

$\Delta H^0 = [6 \cdot (-241.8) - 4 \cdot 393.5 - 2 \cdot (-84.0)]$ kJ mol$^{-1}$ = -2856.8 kJ mol$^{-1}$

$\Delta S^0 = [6 \cdot 188.8 + 4 \cdot 213.8 - 2 \cdot 229.2 - 7 \cdot 205.2]$ J mol$^{-1}$ K$^{-1}$ = +93.2 J mol$^{-1}$ K$^{-1}$

$\Delta G^0 = -2856.8$ kJ mol$^{-1}$ – 298.15 K · (93.2 J mol$^{-1}$ K$^{-1}$) = -2884.6 kJ mol$^{-1}$

**Ethane:** $\Delta H^0 = -2856.8$ kJ mol$^{-1}$ $\Delta S^0 = +93.2$ J mol$^{-1}$ K$^{-1}$ $\Delta G^0$ = -2884.6 kJmol$^{-1}$

**1.2 a)** $m = \rho \cdot V = 0.740$ g L$^{-1}$ · 1000 L = 740 g

$M_{av} = \sum_i x(i)M(i) = 0.0024 \cdot 44.01$ g mol$^{-1}$ + 0.0134 · 28.02 g mol$^{-1}$

+ 0.9732 · 16.05 g mol$^{-1}$ + 0.011 · 30.08 g mol$^{-1}$

= 16.43 g mol$^{-1}$

$n_{tot} = m\ (M_{av})^{-1} = 740$ g · (16.43 g/mol)$^{-1}$ = 45.04 mol

$n(i) = x(i) \cdot n_{tot}$ $n(CH_4) = x(CH_4) \cdot n_{tot} = 0.9732 \cdot 45.04$ mol = 43.83 mol

$n(C_2H_6) = x(C_2H_6) \cdot n_{tot} = 0.0110 \cdot 45.04$ mol = 0.495 mol

**1.2 b) Energy of combustion, deviation:**

$E_{comb.}(H_2O(g)) = \sum_i n(i)\Delta_c H°(i) = 43.83$ mol · (-802.5 kJ mol$^{-1}$) + 0.495 mol · 0.5 · (-2856.8 kJ mol$^{-1}$)

= -35881 kJ

$E_{comb.}$ = -35881 kJ

*Deviation from PUC*

$E_{PUC}(H_2O(g)) = 9.981$ kWh m$^{-3}$ · 1 m3 · 3600 kJ (kWh)$^{-1}$ = 35932 kJ

deviation: $\Delta E = (E_{comb.}(H_2O(g)) - E_{PUC}(H_2O(g)) \cdot 100\% \cdot [E_{comb.}(H_2O(g))]^{-1}$

$= (35881$ kJ - 35932 kJ$) \cdot 100\% \cdot (35881$ kJ$)^{-1} = -0.14\%$

**deviation = -0.14 %**

**1.3 Energy for heating the water:**

Volume of water: $V_{water} = 22.5$ m$^3$

$n_{water} = V_{water}\ \rho_{water}\ (M_{water})^{-1} = 22.5$ m$^3$ · 10$^6$ g m$^{-3}$ · (18.02 g mol$^{-1}$)$^{-1}$ =1.249·10$^6$ mol

$E_{water} = n_{water} \cdot C_p \cdot \Delta T = 1.249 \cdot 10^6$ mol · 75.30 JK$^{-1}$ mol$^{-1}$ · 14 K = 1316 MJ $E_{water}$ = 1316 MJ

**Energy for heating the air**

Volume of the house is: $V_{air} = 15$ m · 8 m · 3 m + 0.5 · 15 m · 8 m · 2 m = 480 m$^3$

$n_{air} = pV \cdot (RT)^{-1} = 1.013 \cdot 10^5$ Pa · 480 m$^3$ · (8.314 J (K mol)$^{-1}$ · 283.15 K)$^{-1}$ = 2.065·10$^4$ mol $C_p$(air)

= 0.21 · 29.4 J (K mol)$^{-1}$ + 0.79 · 29.1 J (K mol)$^{-1}$ = 29.16 J (K mol)$^{-1}$

$E_{air} = n_{air} \cdot C_p(air) \cdot \Delta T = 2.065 \cdot 10^4$ mol · 29.17 J (K mol)$^{-1}$ · 20 K = 12.05 MJ $E_{air}$ = 12.05 MJ

**1.4 Energy for maintaining the temperature:**

surface area of the house:

$A_{house}$ = 3 m · 46 m + 8 m · 2 m + ((2 m)$^2$ + (4 m)$^2$)$^{1/2}$ · 2 · 15 m = 288.16 m$^2$

Heat conductivity: $\lambda_{wall}$ = 1 J (s K m)$^{-1}$

Energy flux along a temperature gradient (wall thickness d = 0.2 m)

$J = E_{loss}\ (A \cdot \Delta t)^{-1} = \lambda_{wall} \cdot \Delta T \cdot d^{-1}$

$E_{loss}$ = 288.16 m$^2$ · (12·60·60 s) · 1 J (s K m)$^{-1}$ · 25 K · (0.2 m)$^{-1}$ = 1556 MJ **$E_{loss}$ = 1556 MJ**

**1.5 Total energy and costs:**

total energy: $E_{tot} = E_{water} + E_{air} + E_{loss}$ = 1316 MJ + 12 MJ + 1556 MJ = 2884 MJ

total energy $E_{tot}$ = 2884 MJ

2884 MJ corresponds to 2.884·10$^6$ kJ · (3600 s h$^{-1}$ · 9.981 kJ s$^{-1}$ m$^{-3}$ · 0.9)$^{-1}$ = 89.18 m$^3$

volume of gas $V$ = 89.18 m$^3$

2884 MJ correspond to a cost of: 0.40 €m$^{-3}$ · 89.18 m$^3$ = 35.67 €

rent for equipment: 150.00 €

total cost of gas heating = 185.67 €

2884 MJ correspond to a cost of

2.884·10$^6$ kJ · 0.137 € · (3600 s h$^{-1}$·1 kJ s$^{-1}$ h)$^{-1}$ = 109.75 €

rent for equipment: 100.00 €

total cost of electric heating = 209.75 €

## Solution to problem 2

**2.1 Reaction equations:**

$$2\ CO + O_2 \longrightarrow 2\ CO_2$$

$$2\ NO + 2\ CO \longrightarrow N_2 + 2\ CO_2$$

$$2\ C_8H_{18} + 25\ O_2 \longrightarrow 16\ CO_2 + 18\ H_2O$$

**2.2 Questions concerning the λ probe:**

| | true | false | no decision possible |
|---|---|---|---|
| If the λ-value is in the range of the λ-window, carbon monoxide and hydrocarbons can be oxidised at the three-way catalytic converter. | x | ☐ | ☐ |
| With λ > 1, carbon monoxide and hydrocarbons can be oxidised at the three-way catalytic converter. | x | ☐ | ☐ |
| With λ < 0.975, nitrogen oxides can be reduced poorly | ☐ | x | ☐ |

**2.3 a) Surface coverage:** $\theta = \dfrac{0.85kPa^{-1} \cdot 0.65kPa}{1 + 0.85 \cdot 0.65}$ $\theta$ = 0.356 or 35.6 %

**2.3 b) Pressure at which 15% of the surface is covered:**

$$\theta = \frac{K \cdot p}{1 + K \cdot p} \quad \Leftrightarrow \quad K{\cdot}p = \theta + \theta \cdot K{\cdot}p \quad \Leftrightarrow \quad p \cdot (K - \theta \cdot K) = \theta \quad \Leftrightarrow \quad p = \frac{\theta}{K - \theta \cdot K}$$

$\theta$ = 0.15 p = 0.21 kPa

**2.3 c) Orders of decomposition:**

order of the decomposition reaction at low gas pressures 1

order of the decomposition reaction at high gas pressures 0

*notes:*

$r = k \cdot \theta = k \cdot \frac{K \cdot p}{1 + K \cdot p}$, *p low* $\Rightarrow p << \frac{1}{K} \Rightarrow r = k \cdot K \cdot p$ *reaction order 1.*

*p high* $\Rightarrow p >> \frac{1}{K} \Rightarrow r = k$ *reaction order 0*

**2.3 d) Gas volume $V_{a,max}$ and product $K \cdot V_{a,max}$:**

$\frac{1}{\theta} = \frac{1}{K \cdot p} + 1 = \frac{V_{a,max}}{V_a} \quad \Rightarrow \quad \frac{1}{K \cdot V_{a,max}} + \frac{p}{V_{a,max}} = \frac{p}{V_a}$

slope: $\frac{1}{V_{a,max}} = 1.9\ cm^{-3} \quad \Rightarrow \quad V_{a,max} = 0.53\ cm^3$

intercept: $\frac{1}{K \cdot V_{a,max}} = 6 \cdot 10^2\ Pa\ cm^{-3} \quad \Rightarrow \quad K \cdot V_{a,max} = 1.7 \cdot 10^{-3}\ Pa^{-1}\ cm^3$

**2.4 Equation for reaction rate:**

The information given in the text leads directly to $r = k_2 \cdot \theta_{CO_2}$

The law of mass action for the first step of the mechanism is given by

$\theta_{CO_2} = \frac{k_1}{k_{-1}} \cdot \theta_{CO} \cdot \theta_{O_2}^{\frac{1}{2}}$, (2) $\Rightarrow \quad r = k_2 \cdot \frac{k_1}{k_{-1}} \cdot \theta_{CO} \cdot \theta_{O_2}^{\frac{1}{2}}$.

The Langmuir isotherm gives:

$$\theta_{CO} = \frac{K_{CO} \cdot p_{CO}}{1 + K_{CO_2} \cdot p_{CO_2} + K_{CO} \cdot p_{CO} + K_{O_2} \cdot p_{O_2}} \text{ and } \theta_{O_2} = \frac{K_{O_2} \cdot p_{O_2}}{1 + K_{CO_2} \cdot p_{CO_2} + K_{CO} \cdot p_{CO} + K_{O_2} \cdot p_{O_2}}$$

$$r = k_2 \frac{k_1}{k_{-1}} \frac{K_{CO} \cdot p_{CO} \cdot \left(K_{O_2} \cdot p_{O_2}\right)^{\frac{1}{2}}}{\left(1 + K_{CO_2} \cdot p_{CO_2} + K_{CO} \cdot p_{CO} + K_{O_2} \cdot p_{O_2}\right)^{\frac{3}{2}}}.$$

## Solution to problem 3

**3.1 Chemical equations:**

(a) $CaCl_2 + Ca \longrightarrow 2\ CaCl$

(b) $2\ CaCl_2 + H_2 \longrightarrow 2\ CaCl + 2\ HCl$

(c) $4\ CaCl_2 + C \longrightarrow 4\ CaCl + CCl_4$

**3.2** silvery metallic particles: Ca

colorless crystals: $CaCl_2$

*Note: CaCl cannot be obtained by a conventional solid state reaction of Ca and $CaCl_2$*

**3.3 Empirical formula:**

100 % –(m/m% Ca + m/m% Cl) = m/m% X

100 % –(52.36% + 46.32%) = 1.32% X

mol% of Ca = 52.36 m/m% / M(Ca)

= 52.36 m/m% / 40.08 g mol-1 = 1.31 mol%

mol% of Cl = 46.32 m/m% / M (Cl)

= 46.32 m/m% / 35.45 g $mol^{-1}$

= 1.31 mol%

mol% of X = 1.32 % X / M (H)

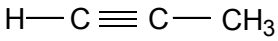
= 1.32 % X / 1.01 g $mol^{-1}$

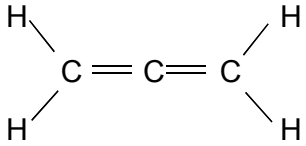
= 1.31 mol%

*n*(Ca) : *n*(Cl) : *n*(H) = 1 : 1 : 1 empirical formula CaClH

Notes: The reaction of $CaCl_2$ with hydrogen does not lead to CaCl. The hydride CaClH is formed instead. The structure of this compound was determined by X-ray structure analysis which is not a suitable method to determine the position of light elements like hydrogen. Thus, the presence of hydrogen was missed and CaClH was thought to be CaCl for quite a long time

**3.4 a) Structures only:**





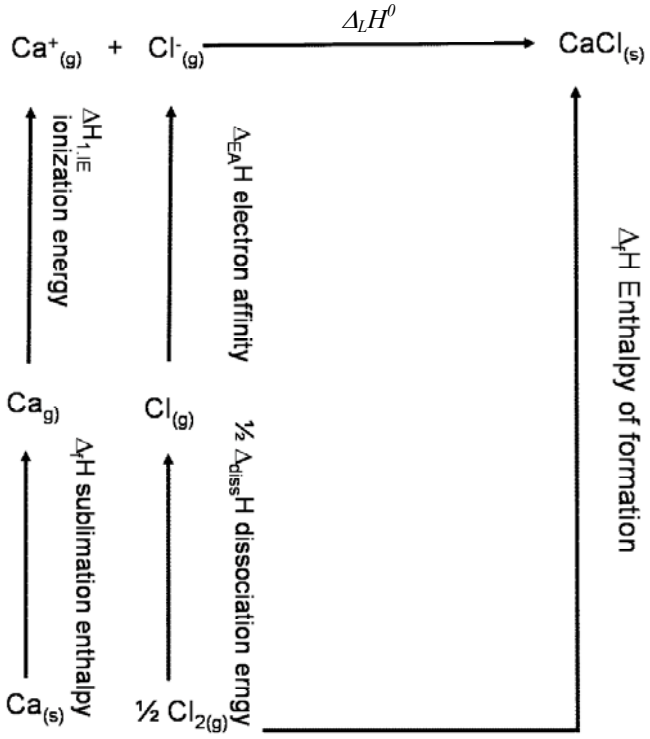
**3.4 b) Empirical formula of the compound formed:** $Ca_3C_3Cl_2$

Notes: If the ratio of n(Ca):n(Cl) = 1.5 : 1 [or better = 3 : 2 which can be rewritten as $CaCl_2 \cdot 2Ca^{2+} = Ca_3Cl_2^{4+}$ ] is given and the reduction product must contain a $C_3^{4-}$ anion which needs two $Ca^{2+}$ cations for electroneutrality, the composition $Ca_3C_3Cl_2$ will follow.

**3.5 a) Structure type CaCl likely to have:** $r(Ca^+)/r(Cl^-)$ = 120 pm/167 pm = 0.719

| NaCl | CsCl | ZnS | BN | no decision possible |
|---|---|---|---|---|
| x | ☐ | ☐ | ☐ | ☐ |

**3.5 b) $\Delta_f H^0$(CaCl) with a Born-Haber-cycle:**




Summing up of all the single steps of the Born-Haber-cycle:

$\Delta_f H^0$ (CaCl) = $\Delta_{subl}H^0$(Ca) + $\Delta_{1.\,IE}H$(Ca) + ½ $\Delta_{diss}H$($Cl_2$) + $\Delta_{EA}H$(Cl) + $\Delta_L H$(CaCl)

= (159.3 + 589.7 + 120 - 349.0 - 751.9) kJ $mol^{-1}$

$\Delta_f H^0$(CaCl) = -231.9 kJ$mol^{-1}$

**3.6 Stability to disproportionation:**

2 CaCl ⟶ $CaCl_2$ + Ca

$\Delta H = \Delta_f H^0(CaCl_2) - 2\,\Delta_f H^0(CaCl)$ = -796.0 kJ $mol^{-1}$ + 463.8 kJ $mol^{-1}$ = -332.2 kJ $mol^{-1}$

| disproportionation | yes | no | no decision possible, more information needed |
|---|---|---|---|
| | ☐ | x | ☐ |

## Solution to problem 4

**4.1 Atomic mass of X, symbol of X, structures:**

1) $X + 2\,H_2 \longrightarrow XH_4$

2) $2\,X + 3\,H_2 \longrightarrow X_2H_6$

I) $5.0\text{ g} = [n_1(X) + n_2(X)] \cdot M(X)$

II) $5.628\text{ g} = n_1(XH_4) \cdot [M(X) + 4 \cdot 1.01\text{ g mol}^{-1}] + n_2(X_2H_6) \cdot [2M(X) + 6 \cdot 1.01\text{ g mol}^{-1}]$

III) $n_1(XH_4) = 2n_2(X_2H_6)$

III,I) $\rightarrow$ I') $2n_1(X) \cdot M(X) = 5.0\text{ g}$

III,II) $\rightarrow$ II') $n_1(X) \cdot [2M(X) + 7.07\text{ g mol}^{-1}] = 5.628\text{ g}$

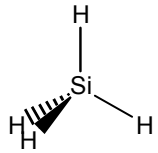
I',II') $\rightarrow$ VI) $(5.0\text{ g}) \cdot [2M(X)]^{-1} = (5.628\text{ g}) \cdot [2M(X) + 7.07\text{ g mol}^{-1}]^{-1}$

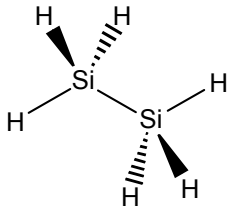
$M(X) = 3.535\text{ g mol}^{-1} \cdot (5.628\text{ g})^{-1} \cdot [(5.0\text{ g})^{-1} - (5.628\text{ g})^{-1}]^{-1}$

$M(X) = 28.14\text{ g mol}^{-1}$

atomic mass of X $M(X) = 28.14\text{ g mol}^{-1}$ chemical symbol of X: Si

3D structures of the two products:




**4.2 Atomic mass of Y and empirical formula of Argyrodite:**

$Ag_aY_bS_{0.5\cdot a + 2\cdot b} + b\,H_2 \longrightarrow 0.5a\,Ag_2S + b\,YS + b\,H_2S$

I) $10\text{ g} = n(Ag_aY_bS_{0.5\cdot a + 2\cdot b}) \cdot [a \cdot 107.87\text{ g mol}^{-1} + b \cdot M(Y) + (0.5 \cdot a + 2 \cdot b) \cdot 32.07\text{ g mol}^{-1}]$

II) $n(H_2) = \dfrac{p \cdot V(H_2)}{RT}$ $\qquad n(H_2) = \dfrac{100kPa \cdot 0.295 \cdot 10^{-3} m^3}{8.314 JK^{-1}mol^{-1} \cdot 400K}$

$n(H_2) = 8.871 \cdot 10^{-3}\text{ mol}$ $\qquad n(Ag_aY_bS_{0.5\cdot a + 2\cdot b}) = b^{-1} \cdot 8.871 \cdot 10^{-3}\text{ mol}$

III) $11.88 = \dfrac{a \cdot 107.87 gmol^{-1}}{b \cdot M(Y)}$ $\qquad a \cdot 107.87\text{ gmol}^{-1} = 11.88 \cdot b \cdot M(Y)$

II,I) $\rightarrow$ II') $b \cdot 10\text{ g} \cdot (8.871 \cdot 10^{-3}\text{ mol})^{-1} = a \cdot 107.87\text{ g mol}^{-1} + b \cdot M(Y) + (0.5 \cdot a + 2b) \cdot 32.07\text{ g mol}^{-1}$

$b \cdot 1127\text{ g mol}^{-1} = a \cdot 107.87\text{ g mol}^{-1} + b \cdot M(Y) + (0.5 \cdot a + 2b) \cdot 32.07\text{ g mol}^{-1}$

III,II') $\rightarrow$ IV) $b \cdot 1127\text{ g mol}^{-1} = 11.88 \cdot b \cdot M(Y) + b \cdot M(Y) + (0.5 \cdot a + 2b) \cdot 32.07\text{ g mol}^{-1}$

$b \cdot 1127\text{ g mol}^{-1} = 11.88 \cdot b \cdot M(Y) + b \cdot M(Y) + \left(0.5 \cdot \dfrac{11.88 \cdot b \cdot M(Y)}{107.87 gmol^{-1}} + 2b\right) \cdot 32.07\text{ g mol}^{-1}$

$M(Y) = 72.57\text{ g mol}^{-1}$

molar mass $M(Y) = 72{,}57\text{ g mol}^{-1}$

$M(Y) = 72.57\text{ g mol}^{-1} \rightarrow$ III a:b = 8:1

chemical symbol of Y: Ge empirical formula of Argyrodite: $Ag_8Ge$

**4.3 The force constants of a C-H bond:**

$$k(\text{C-H}) = [2\pi \cdot c \cdot \tilde{\nu}\,(\text{C-H})]^2 \cdot \frac{1}{N_A} \cdot \frac{3M(C) \cdot M(H)}{3M(C) + 4M(H)}$$

$$= [2\pi \cdot 3 \cdot 10^{10}\text{ cm} \cdot \text{s}^{-1} \cdot 3030\text{ cm}^{-1}]^2 \cdot \frac{1}{6.022 \cdot 10^{23} mol^{-1}} \cdot \frac{3 \cdot 12.01 \cdot 1.01}{3 \cdot 12.01 + 4 \cdot 1.01} gmol^{-1}$$

$k(\text{C-H}) = 491.94\text{ N m}^{-1}$

**The force constants of a Z-H bond:**

$$k(\text{Z-H}) = k(\text{C-H}) \cdot \frac{\Delta_b H(Z-H)}{\Delta_b H(C-H)}$$

$$= 491.94 \text{ N m}^{-1} \cdot 450.2 \text{ kJ mol}^{-1} \cdot [438.4 \text{ kJ mol}^{-1}]^{-1}$$

$$k(\text{Z-H}) = 505.18 \text{ N m}^{-1}$$

**The molar mass and symbol of Z:**

$$\frac{3M(Z) \cdot M(H)}{3M(Z) + 4M(H)} = \frac{k(Z-H) \cdot N_A}{[2\pi \cdot c \cdot \tilde{\nu}(Z-H)]^2}$$

$$\text{M(Z)} = \frac{4}{3} \cdot \left( \frac{[2\pi \cdot c \cdot \tilde{\nu}(Z-H)]^2}{k(Z-H) \cdot N_A} - \frac{1}{M(H)} \right)^{-1}$$

$$M(\text{Z}) = \frac{4}{3} \cdot \left( \frac{[2\pi \cdot 3 \cdot 10^{10} \cdot 2938.45]^2}{505180 \cdot 6.022 \cdot 10^{23}} - \frac{1}{1.01} \right)^{-1} \text{ g mol}^{-1}$$

molar mass of Z $M(\text{Z}) = 72.68 \text{ g mol}^{-1}$

**chemical symbol of Z** Ge

Note: Even if the students find different values (± 2) due to different ways of rounding, they will be able to find Ge as Z has to be an analogue of carbon.

## Solution to problem 5

**5.1 Actual *ΔG'* of reaction (1):**

$$\Delta G' = \Delta G^{o\prime} + RT \ln \frac{c(\text{ADP}^{3-})/(1 \text{ mol L}^{-1}) \cdot c(\text{HPO}_4^{2-})/(1 \text{ mol L}^{-1})}{c(\text{ATP}^{4-})/(1 \text{ mol L}^{-1})}$$

$$= -30500 \text{ J mol}^{-1} + 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \cdot 298.15 \text{ K} \cdot \ln (0.00025 \cdot 0.00165 / 0.00225)$$

$$= -30.5 \text{ kJ mol}^{-1} - 21.3 \text{ kJ mol}^{-1} = -51.8 \text{ kJ mol}^{-1}$$

$$\Delta G' = -51.8 \text{ kJ mol}^{-1}$$

**5.2 Equilibrium constant *K'* of reaction (2), ratio *c*(glucose 6-phosphate) / *c*(glucose):**

$\Delta G^{o\prime} = -RT \cdot \ln K'$ $\quad K' = e^{-\Delta G^{\circ\prime}/RT}$

$$= e^{-13800 \text{ J/mol} / (8.314 \text{ J/(mol K)} \cdot 298.15 \text{ K})}$$

$$= 0.0038$$

$$K' = \frac{c(\text{glucose 6-phosphate})/(1 \text{ mol L}^{-1})}{c(\text{glucose})/(1 \text{ mol L}^{-1}) \cdot c(\text{HPO}_4^{2-})/(1 \text{ mol L}^{-1})}$$

$$\frac{c(\text{glucose 6-phosphate})}{c(\text{glucose})} = K' \cdot c(HPO_4^{2-}) \cdot (1 \text{ mol L}^{-1})^{-1}$$

$$= 0.0038 \cdot 0.00165 = 6.3 \cdot 10^{-6}$$

K' = 0.0038 $\quad \frac{\underline{c(\text{glucose 6-phosphate})}}{c(\text{glucose})} = 6.3 \cdot 10^{-6}$

**5.3 *ΔG°'* and *K'* of reaction (3), ratio c(glucose 6-phosphate) / c(glucose):**

$$\Delta G^{\circ\prime}(3) = \Delta G^{\circ\prime}(1) + \Delta G^{\circ\prime}(2)$$

$$= -30.5 \text{ kJ mol}^{-1} + 13.8 \text{ kJ mol}^{-1} = -16.7 \text{ kJ mol}^{-1}$$

$\Delta G°' = -RT \cdot \ln K'$

$K' = e^{-\Delta G°'/RT} = e^{16700\ J/mol\ /\ (8.314\ J/(mol\ K) \cdot 298.15\ K)} = 843$

$$K' = \frac{c(\text{glucose 6-phosphate}) \cdot c(ADP^{3-})}{c(\text{glucose}) \cdot c(ATP^{4-})}$$

$$\frac{c(\text{glucose 6-phosphate})}{c(\text{glucose})} = K' \cdot \frac{c(ATP^{4-})}{c(ADP^{3-})}$$

$= 843 \cdot 2.25\ mmol\ L^{-1} / 0.25\ mmol\ L^{-1} = 7587$

**5.4 a) Mass of ATP produced per day:**

Energy available for ATP synthesis: $8000\ kJ\ day^{-1} \cdot 0.5 = 4000\ kJ\ day^{-1}$

Energy required for synthesis of ATP: $52\ kJ\ mol^{-1}$

Amount of ATP produced: $4000\ kJ\ day^{-1} / 52\ kJ\ mol^{-1} = 76.9\ mol\ day^{-1}$

Mass of ATP produced: $76.9\ mol\ day^{-1} \cdot 503\ g\ mol^{-1} = 38700\ g\ day^{-1} = 38.7\ kg\ day^{-1}$

$m_{day-1} = 38.7\ kg\ day^{-1}$

**5.4 b) Mass of ATP in the human body:**

Average lifetime: $1\ day = 1440\ min \quad 1\ min = 1440^{-1}\ day$

Mass of ATP in the body: $38.7\ kg\ day^{-1} / (1440\ min\ day^{-1}) \cdot 1\ min = 26.9\ g$ $m_{body} = 26.9\ g$

**5.4 c) What happens to the rest of the free energy? Mark one correct answer:**

It is used to reduce the entropy of the body. ☐

It is released from the body in the O-H bonds of the water molecule and the C=O bonds of the carbon dioxide molecule. ☐

It is used to regenerate the state of the enzymes which act as catalysts in the production of ATP. ☐

It heats the body of the person. x

**5.5 a) How many protons are in a spherical mitochondrium with a diameter of 1 m at pH=7?**

$V = 4/3\ \pi \cdot r^3 = 4/3\ \pi\ (0.5 \cdot 10^{-6}\ m)^3 = 5.2 \cdot 10^{-19}\ m^3 = 5.2 \cdot 10^{-16}\ L$

$c = 10^{-7}\ mol\ L^{-1}$

$n = V \cdot c \cdot N_A = 5.2 \cdot 10^{-16}\ L \cdot 10^{-7}\ mol\ L^{-1} \cdot 6.022 \cdot 10^{23}\ mol^{-1}$ $n = 31$

**5.5 b) How many protons have to enter a mitochondrium?**

Number of ATP molecules:

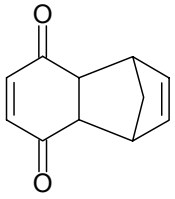
$$n(ATP) = \frac{m(ATP) \cdot N_A}{M(ATP)} = \frac{0.2 \cdot 10^{-15} g \cdot 6.022 \cdot 10^{23} mol^{-1}}{503\ g\ mol^{-1}} = 239400$$

Number of $H^+$ per cell $n(H^+_{per\ cell}) = n(ATP) \cdot 3 = 718300$

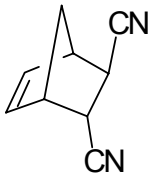
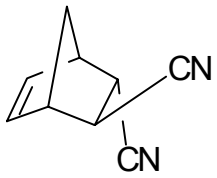
Number of $H^+$ per mitochondrium: $n(H^+_{mit}) = n(H^+_{per\ cell}) / 1000 = 718$ $n(H^+_{mit}) = 718$

## Solution to problem 6

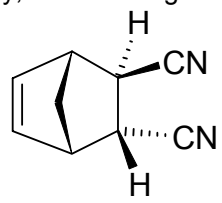
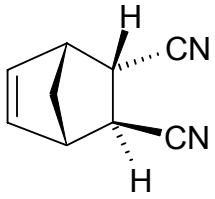
**6.1 Structure of A:**

[ **A** ] : 

**6.2 Structures of D1, D2 only:**

**D1:**  (1) **D2:**  (1)

alternatively, the following structures are also correct:

Note: The two compounds are enantiomers

**6.3 Correct structure of B** (circle only one):

**1** **2** **3** **4** **5** **6**

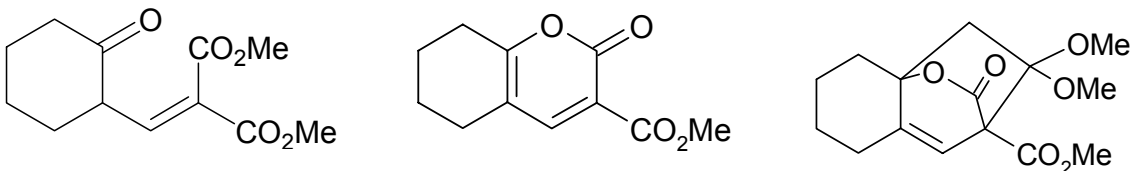
Notes: The Diels-Alder reaction gives products with an endo-stereochemistry. The preference of this configuration was outlined in problem 6.2, structure **C**. As shown in structure **C** this endo-configuration is characterized by the two H atoms and the $CH_2$-bridge of the bicyclic system being on the same side of the ring. Only structures **1** and **2** of the six stereoisomers have an endo,endo stereochemistry. All other isomers have at least one exo configuration. In structure **1** the three rings form a U-shaped molecule which is sterically more hindered than structure **2** which has a zig-zag structure

**6.4 Decide the questions concerning the Diels-Alder reaction.**

| | true | false | no decision possible |
|---|---|---|---|
| The Diels-Alder reaction is reversible | x | ☐ | ☐ |
| The formation of B in the original reaction is thermodynamically controlled | ☐ | x | ☐ |
| B is thermodynamically more stable than E | ☐ | x | ☐ |
| E is thermodynamically less stable than F | | x ☐ | ☐ |
| G is an enantiomer of B | ☐ | x | ☐ |
| G is thermodynamically more stable than F | ☐ | ☐ | x |

**6.5 Structures of I, K, L only:**

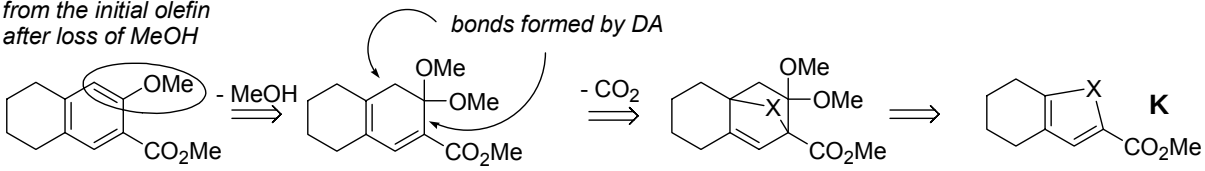
**I** **K** **L**




*Notes next page*

*from the initial olefin after loss of MeOH*

*bonds formed by DA*

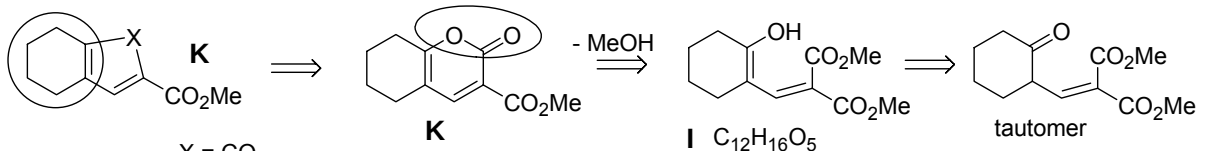



$C_{13}H_{16}O_3$
**product**

*diene must result from los s of $CO_2$ from the initial DA cyclohexene adduct*

**L** X = $CO_2$
$C_{15}H_{20}O_6$

X = $CO_2$
$C_{11}H_{12}O_4$
*must be a 1,3-diene*




*from the initial cyclohexenone*

X = $CO_2$

**K**

*lactone = transesterification with loss of MeOH*

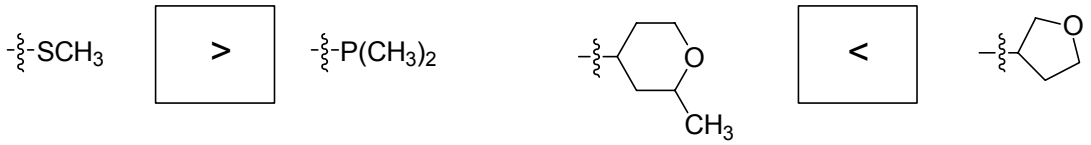
**I** $C_{12}H_{16}O_5$

tautomer

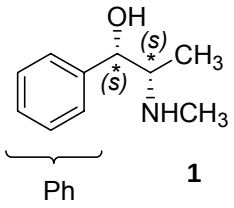
*from Michael Addition with subsequent loss of MeOH*

## Solution to problem 7

**7.1 Fill in < or > (A < B means A has a priority lower than B) :**




**7.2**

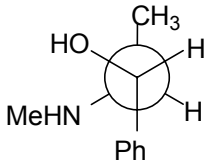



**1**

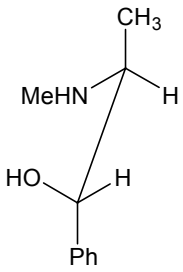
highest priority → lowest priority

| | | | |
|---|---|---|---|
| OH | $CH(NHCH_3)CH_3$ | Ph | H |
| $NHCH_3$ | CH(OH)Ph | $CH_3$ | H |

**7.3 Newman projection or sawhorse projection of 1:**

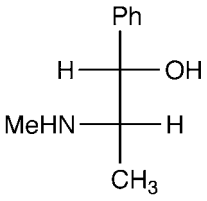



or

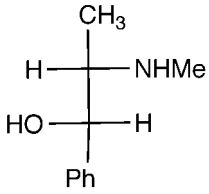



(Me = $CH_3$)

**Fischer projection of 1:**




or

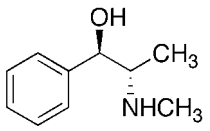



(Me = $CH_3$)

**7.4 Equation with oxidation numbers and stereochemically correct structure of 2:**


**1** **2**

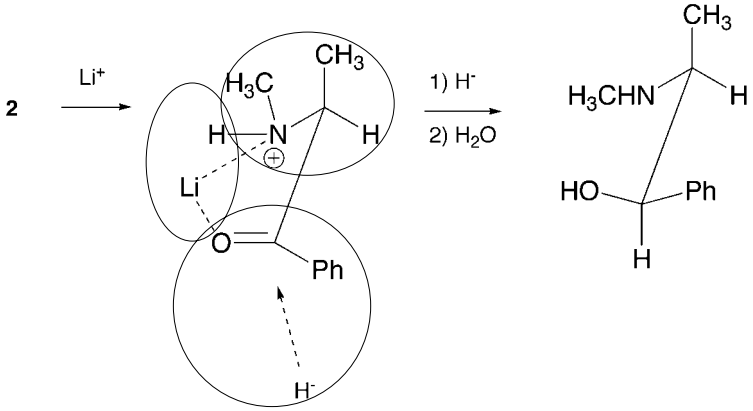
**7.5a) Structure of 3 (correct stereochemistry):**



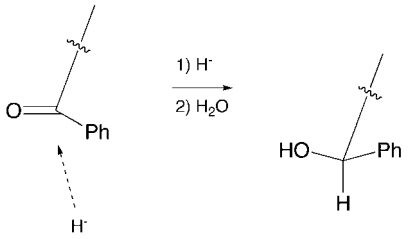

**7.5b) Statements concerning isomers:**

| | true | false |
|---|---|---|
| 1 and 3 are stereo-isomers | x | ☐ |
| 1 and 3 are enantiomers | ☐ | x |
| 1 and 3 are diastereomers | x | ☐ |
| 1 and 3 are conformational isomers | ☐ | x |

**7.5c) Draw a structural model to rationalize the exclusive formation of 3 from 2**




Notes: Attack of hydride occurs from the sterically least hindered side.
Full points will also be given for an explanation using the formation of a hydrogen bond.
1 point will be given for any representation indicating the attack of hydride on the correct face of the carbonyl group, i.e.




## Solution to problem 8

### 8.1 pH of solution B:

$$K_{b2} = \frac{c(HCO_3^-)/(1\ mol\ L^{-1}) \cdot c(OH^-)/(1\ mol\ L^{-1})}{c(CO_3^{2-})/(1\ mol\ L^{-1})} \quad (1) \qquad K_{b2} = \frac{10^{-14}}{10^{-10.33}}$$

$K_{b2} = 2.14 \cdot 10^{-4}$ $\qquad$ $K_{b1} = 2.34 \cdot 10^{-8}$

Since $K_{b2} >> K_{b1}$, only one protonation step of the $CO_3^{2-}$ has to be considered.

$c(HCO_3^-) = c(OH^-) = x$ $\qquad$ and $\qquad$ $c(CO_3^{2-}) = c_0(CO_3^{2-}) - x$

$$c_0(Na_2CO_3) = \frac{1.700\ g\ L^{-1}}{105.99\ g\ mol^{-1}} \qquad c_0(Na_2CO_3) = c_0(CO_3^{2-}) = 0.016\ mol\ L^{-1}$$

$$K_{b2} = \frac{x^2/(1\ mol\ L^{-1})}{(c_0(CO_3^{2-}) - x)} \quad (1) \qquad x = c(OH^-) = 1.75 \cdot 10^{-3}\ mol\ L^{-1}$$

pH = 11.2

### 8.2 $Ca(OH)_2$ , $CaCO_3$ in the precipitate?

$M(CaCl_2) = 110.98\ g\ mol^{-1}$ $\qquad$ pH = 10 , $c(OH^-) = 10^{-4}\ mol\ L^{-1}$

$$c_0(Na_2CO_3) = \frac{1.700\ g\ L^{-1}}{105.99\ g\ mol^{-1} \cdot 2} \qquad c(CaCl_2) = \frac{1.780\ g\ L^{-1}}{110.98\ g\ mol^{-1} \cdot 2}$$

$c_0(Na_2CO_3) = 8.0 \cdot 10^{-3}\ mol\ L^{-1}$ (0.5) $\qquad$ $c(CaCl_2) = c_0(Ca^{2+}) = 8.0 \cdot 10^{-3}\ mol\ L^{-1}$

Calculations for $Ca(OH)_2$:

$c(OH^-)^2 \cdot c_0(Ca^{2+}) = 8 \cdot 10^{-11}\ mol^3\ L^{-3} < 6.46 \cdot 10^{-6}\ mol^3\ L^{-3} = K_{sp}(Ca(OH)_2)$ $\qquad$ no precipitate

Calculations for $CaCO_3$:

(regarding proteolysis: 1 point)

$$K_{b2} = \frac{c(HCO_3^-) \cdot c(OH^-)}{c(CO_3^{2-})}, \qquad c(HCO_3^-) = \frac{K_{b2}}{c(OH^-)} \cdot c(CO_3^{2-})$$

$c(HCO_3^-) = 2.14 \cdot c(CO_3^{2-})$ $\qquad$ and $\qquad$ $c(HCO_3^-) + c(CO_3^{2-}) = c_0(Na_2CO_3)$

$2.14 \cdot c(CO_3^{2-}) + c(CO_3^{2-}) = 8.0 \cdot 10^{-3}\ mol\ L^{-1}$

Initial concentration of $CO_3^{2-}$ in solution C: $\quad c(CO_3^{2-}) = 2.55 \cdot 10^{-3}\ mol\ L^{-1}$

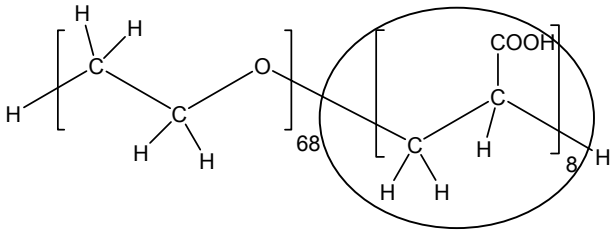
Initial concentration of $Ca^{2+}$ in solution C: $\quad c(Ca^{2+}) = 8.0 \cdot 10^{-3}\ mol\ L^{-1}$

hence $c(CO_3^{2-}) \cdot c(Ca^{2+}) = 2.04 \cdot 10^{-5}\ mol^2\ L^{-2} > 3.31 \cdot 10^{-9}\ mol^2\ L^{-2} = K_{sp}(CaCO_3)$ $\qquad$ precipitate

$Ca(OH)_2$ will be found in the precipitate $\qquad$ yes ☐ $\qquad$ no x

$CaCO_3$ will be found in the precipitate $\qquad$ yes x $\qquad$ no ☐

**8.3 Circle the <u>block</u> that attaches to the $CaCO_3$ crystal:**




Notes: Both polymer blocks are hydrophilic. The acrylic acid block will preferably bind to the crystal since it is more polarized and additionally charged. The polymer binds to the surface at positions where there is an excess of calcium ions on the surface of the ionic crystal.

**8.4 How much of the initial amount of polymer (2 g) can still be found in the hybrid particles?**

$RCOOH + OH^- \rightleftarrows RCOO^- + H_2O$ $\quad pK_b = 9.12$

pH and $pK_a$ lead to the total concentration of COOH groups in the solution:

$c(COO^-) = x$ $\quad c(COOH) = c_0(COOH) - x$ $\quad x = c_0(OH^-) - c(OH^-)$

$c_0(OH^-) = \frac{50\,mL}{250\,mL} 0.19\,mol\,L^{-1}$ $\quad c_0(OH^-) = 0.038\ mol\ L^{-1}$

$c(OH^-) = 10^{-1.7}\ mol\ L^{-1} = 0.02\ mol\ L^{-1}$ (0.5) $\quad x = 0.018\ mol\ L^{-1}$

$$K_b = \frac{(c_0(COOH) - x)/(1\ mol\ L^{-1}) \cdot c(OH^-)/(1\ mol\ L^{-1})}{x/(1\ mol\ L^{-1})}$$

$$c_0(COOH) = \frac{K_b x \cdot (1\ mol\ L^{-1})}{c(OH^-)} + x \quad (1) \qquad c_0(COOH) = \left( \frac{0.018 \cdot 10^{-9.12}}{0.02} + 0.018 \right) mol \cdot L^{-1}$$

$c_0(COOH) = 0.018\ mol \cdot L^{-1}$

(Or as pH >> $pK_a$: $c_0(COOH) = c(COOH) + x \approx x$)

*Total concentration of polymer chains* $c(polymer) = \frac{c_0(COOH)}{8}$

$M(polymer) = M(C_{160}O_{84}H_{306}) = 3574.66\ g\ mol^{-1}$

(0.5) (0.5)

$m(polymer) = c(polymer) \cdot V \cdot M(polymer)$

$$m(polymer) = \frac{c_0(COOH) \cdot V \cdot M(polymer)}{8} = \frac{0.018 \cdot 0.250 \cdot 3574.66}{8} g = 2.0\ g$$

**8.5 Modification of $CaCO_3$:**

The charge of the particles is caused by the number of protolized COOH groups per particle.

$c(COO^-) \approx c_0(COOH)$, $\alpha \approx 1$

Number of COOH groups per particle: $N_{COOH} = \frac{|Z|}{\alpha}$ $\quad N_{COOH} = 800$

Number of polymer chains per particle: : $N_{polymer} = \frac{N_{COOH}}{8} = 100$

The number of polymers per particle indicates the mass of polymer per particle. Thus, the mass of the calcium carbonate particle can be calculated:

$M(CaCO_3\ particle) = M(total\ particle) - N_{polymer} \cdot M(polymer)$

$M(CaCO_3\ particle) = 8.01 \cdot 10^8\ g\ mol^{-1} - 100 \cdot 3574.66\ g\ mol^{-1}$

$M(CaCO_3\ particle) = 8.01 \cdot 10^8\ g\ mol^{-1}$

Mass of one $CaCO_3$ particle: $m(CaCO_3 particle) = M(CaCO_3\ particle) \cdot N_A^{-1}$

and with the volume of the spherical particle ($V = \frac{4}{3} \cdot \pi \cdot r^3$) the density can be calculated:

$$\rho(CaCO_3) = \frac{m(CaCO_3\ particle)}{V(CaCO_3\ particle)} = \frac{3 \cdot m(CaCO_3\ particle)}{4\pi \cdot r^3}$$

$$= \frac{3(M\ (total\ particle) - N_{polymer} \cdot M(polymer))}{N_a \cdot 4\pi \cdot r^3}$$

$$= \frac{3 \cdot 8.01 \cdot 10^8\ g\ mol^{-1}}{N_A \cdot 4\pi\ (5 \cdot 10^{-6} cm)^3} = 2.54\ g\ cm^{-3}$$

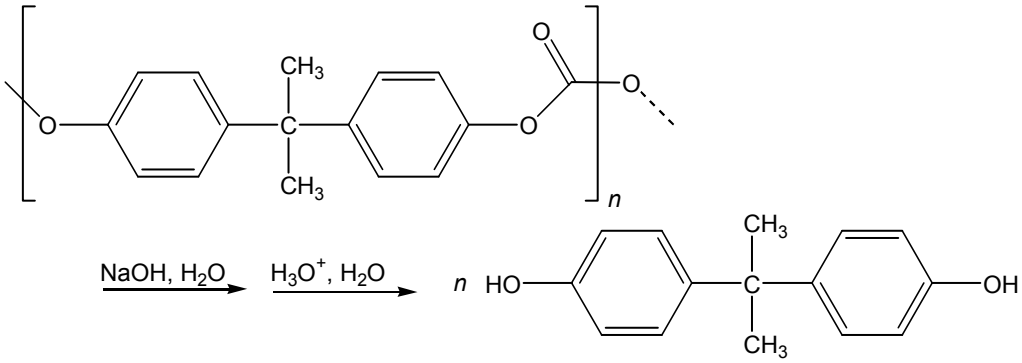
The modification of calcium carbonate is Calcite ☐ Vaterite x Aragonite ☐

# 36th IChO Practical Problems

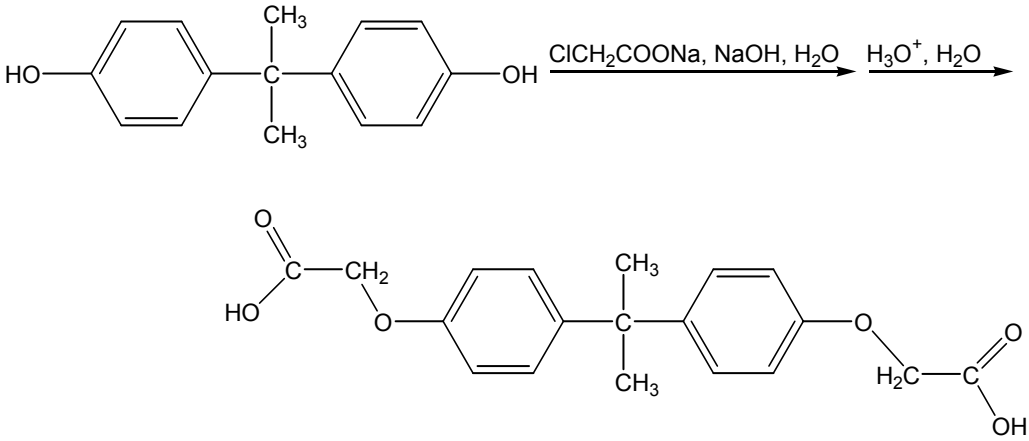
## Problem 1. Two-Step Organic Synthesis of 2,2-Bis(*p*-phenyleneoxyacetic acid)propane (Bisphenol A bis(carboxymethyl)ether)

Introduction

In the first step the sodium salt of bisphenol A results as an intermediate from the alkaline hydrolysis of a polycarbonate. By adding an acid this salt is converted into the free 2,2-bis(4-hydroxyphenyl)propane (bisphenol A).




In the second step bisphenol A reacts with sodium chloroacetate to form the phenolic ether, bisphenol A bis(carboxymethyl)ether.




- In each step the product has to be isolated. (Drying and weighing will be done by the organizer.)
- For the product of step 2 three melting point tubes have to be filled. (Filling of the melting point tubes in step 1 will be done by the organizer.The melting points will be determined by the organizer.)
- When the organizer receives your labelled beaker A of step 1 you will get 2.00 g of bisphenol A as starting material for the second step.
- Answer the additional questions on the answer sheet **P1**.
- Do not remove the Ceran plate from the magnetic stirrer.

## Procedures

**Step 1 Preparation of bisphenol A by alkaline hydrolysis of a polycarbonate**

**Preparation:**

- Put the pre-weighed 2.54 g of polycarbonate (No. **1**), 4.0 g of sodium hydroxide (No. **5**) and 3 mL of demineralized water into a 100 mL Erlenmeyer flask with ground-glass joint.
- Close the flask with a plastic plug and swirl it gently so that the solution does not contact the ground-glass joint. For aeration open the plastic plug occasionally. Strong heating can be observed, as the sodium hydroxide partially dissolves.
- Remove the plastic plug after swirling for about 4 minutes, add a magnetic stirring bar and put the flask onto a heating plate. Put a reflux condenser above the neck of the flask. Use a Teflon coupling as a connection between flask and condenser. Fix the apparatus tightly to a stand.
- Finally, add 20 mL of ethanol (No. **2**) through the condenser while stirring the reaction mixture.
- Heat the reaction mixture under reflux for 60 minutes. In the beginning adjust the thermostat of the heating plate to maximum. When the mixture starts boiling reduce the heat carefully, so that the mixture is kept under gentle reflux.
- A white precipitate is formed on heating.

**During this waiting period you are highly advised to start working on the analytical chemistry experiment.**

**Isolation:**

- Stop heating after one hour, allow the reaction mixture to cool down to ambient temperature, remove the condenser, add 25 mL of demineralized water and transfer the reaction mixture into a 400 mL beaker. Rinse the Erlenmeyer flask with 25 mL of demineralized water and add this to the contents of the beaker.
- Finally, fill up to 150 mL with demineralized water.
- If the reaction mixture is not clear, the mixture has to be filtered over fibre glass into an Erlenmeyer flask.
- Add slowly 15 mL of hydrochloric acid (No. **3**) stirring the mixture simultaneously with a glass rod. A rather oily or sometimes crystalline precipitate is formed.
- Ask your instructor for some seed crystals of bisphenol A (No. **27**) in order to accelerate the crystallization.
- Stir the reaction mixture thoroughly with the glass rod. For a quantitative crystallisation continue stirring from time to time till the supernatant aqueous solution is nearly clear.
- Collect the crude product by vacuum filtration, wash it twice with 10 mL portions of demineralized water and transfer it quantitatively into the tared and labelled beaker A.
- **For drying and weighing deliver your labelled beaker A into the instructor room.**
- Afterwards you will get a small jar filled with 2.00 g of bisphenol A (No. **28**), your starting material of the second step.

- On delivery of your product and on receipt of the starting material you have to sign. Even if you do not have any bisphenol A, please bring the empty beaker A to the instructors' room in order to get the starting material for step 2.

**Step 2 Reaction of Bisphenol A with Chloroacetic Acid forming 2,2-Bis(*p*-phenyleneoxyacetic acid)propane (Bisphenol A bis(carboxymethyl)ether)**

**Preparation:**

- Pour all the bisphenol A (No. **28**) you have received from the organizer when you had finished step 1 into a 100 mL Erlenmeyer flask with ground-glass joint.
- Add 10 mL of an aqueous sodium-hydroxide solution (No. **6**), 1 mL of demineralized water and a magnetic stirring bar.
- Put the flask onto a heating plate. Put a reflux condenser above the neck of the flask. Use a Teflon coupling as a connection between flask and condenser. Fix the apparatus tightly to a stand.
- Heat the reaction mixture with gentle stirring until a clear solution is formed.
- Remove the heating plate and the condenser and add 5.0 g of the sodium salt of chloroacetic acid (No. **4**) to the reaction mixture.
- After reconnecting the flask with the reflux condenser, heat the mixture to reflux with vigorous stirring for 30 min.
- Initially a clear solution is formed on heating. In some cases a colorless solid precipitates. If the complete mixture becomes solid in the course of the reaction, heating **must** be stopped.
- After that, 50 mL of ethanol (No. **2**) are added carefully through the condenser (beware of sudden boiling!). The mixture is stirred and heated under reflux for 5 minutes. A colourless solid precipitates, or the crystallisation which has already started is completed.

**Isolation:**

- After leaving it to cool down for 5 minutes, transfer the reaction mixture with another 50 mL of ethanol (No. **2**) quantitatively to a beaker. The reaction mixture should be stirred vigorously.
- The magnetic stirring bar is removed and the reaction mixture is filtered through a suction filter. Solids which separate in the filtrate are rejected. Rinse the beaker with 10 mL of ethanol (No. **2**). The precipitate is washed twice with 10 mL portions of ethanol (No. **2**). (The filtrate must be disposed of in the organic solvent waste!)
- Transfer the precipitate quantitatively into a beaker, add a stirring bar and dissolve it in 150 mL of demineralized water. The mixture must be stirred vigorously. Larger lumps of the solid must be crushed with the spatula.
- If the solution is not clear, it has to be filtered over a folded filter paper into an Erlenmeyer flask.
- The slow addition of 5 mL of hydrochloric acid (No. **3**) to the stirred reaction mixture results in the formation of a white precipitate.
- Collect the crude product by vacuum filtration, wash it twice with 10 mL portions of demineralized water and transfer it quantitatively into the tared and labelled beaker B.
- Take a small sample of the product with a micro spatula, crush it and dry it on a shard. Fill three melting point tubes with the homogenized, dried sample. For a close-packed and 5 mm high filling use the 75 cm glass tube and the measure.
- **Put all three melting point tubes into the test tube B, which is labelled with your student code, and give it together with your labelled beaker B with the product to the instructor. On delivery you have to sign.**

## Problem 2. Qualitative and Quantitative Analysis of a Superconductor

### Introduction

Superconductors based on lanthanum cuprate ($La_2CuO_4$) have the general composition of $La_xM_{(2-x)}CuO_4$ (M = Ca, Sr, Ba).

This problem consists of two parts:
- the qualitative determination of the alkaline earth metal(s)
- the quantitative determination of lanthanum and copper.

Read the burette as accurately as possible. Report your results on the answer sheets.
**Answer the additional questions and write the results with adequate accuracy.**
The qualitative and quantitative parts of this experiment may be done in any order.

Procedures

**2.1 Qualitative determination of the alkaline earth metal(s)** (If the hood is occupied start with the titration 2.2)

In this experiment you have to use the superconductor as a solid ($La_xM_{(2-x)}CuO_4$; No. **14**).
At the beginning, lanthanum has to be separated as an insoluble residue.
**All steps must be carried out in the hood!**

Dissolve the complete sample in a beaker in about 5 mL of perchloric acid (No. **22**) by heating the mixture. Add 5 mL of demineralized water afterwards.
Cool down the solution until it is lukewarm.

Add about 5 mL of demineralized water and then ammonia solution (No. **17**), until the reaction mixture shows a basic reaction. Lanthanum precipitates as hydroxide and copper forms an intense blue-coloured tetraammine complex. The precipitate is filtered off and washed with a small amount of demineralized water.

An excess of ammonium-carbonate solution (No. **18**) is added to the filtrate and the mixture is being boiled for some minutes. The alkaline earth metal(s) will precipitate as carbonate(s). The precipitate is filtered off and washed a few times with a small amount of demineralized water.

Then, the precipitate is dissolved in acetic acid (No. **16**). Add sodium acetate (No. **9**) and an excess of potassium-dichromate solution (No. **23**). In the presence of barium, yellow $BaCrO_4$ precipitates. After boiling the mixture for one minute barium chromate is filtered off and washed with demineralized water.
(If there is no barium chromate precipitation, proceed in a way as if there were precipitation.)

Ammonia solution (No. **17**) is added to the clear filtrate until it is basic. Add an excess of ammonium-carbonate solution (No. **18**) and boil the mixture for some minutes. In the presence of strontium and/or calcium, white carbonate(s) precipitate(s).

The precipitate is filtered off and washed a few times with demineralized water.

Then it is dissolved in a mixture of about 2 mL of demineralized water and a few drops of hydrochloric acid (No. **3**). This solution is devided between two test tubes:

- Saturated calcium-sulfate solution (No. **21**) is added to one of the test tubes. In the presence of strontium a small amount of white strontium sulfate precipitates. To accelerate the precipitation, you can grind the inner surface of the test tube with a glass rod for a few minutes.
- Ammonium-sulfate solution (No. **20**) is added to the second test tube. In the presence of strontium and/or calcium, white sulfate(s) precipitate(s). The precipitate is filtered off and washed with a very small amount of demineralized water.
  1 mL of ammonium-oxalate solution (No. **19**) is added to the filtrate. In the presence of calcium, white calcium oxalate precipitates after a few minutes.

**Preparation of the superconductor parent solution**

**There is a superconductor solution ($La_xM_{(2-x)}CuO_4$ in perchloric acid; No.** 13**) in a volumetric flask.**

**Fill it up with demineralized water to a volume of 250.0 mL. From now on this solution is called "parent solution".**

**2.2 Quantitative determination of the total content of lanthanum and copper**

Transfer 25.00 mL of the parent solution into an Erlenmeyer flask.

Add about 5-6 piled spatula of sodium acetate ($CH_3COONa$; No. **8**) and 2 micro spatula of xylenol orange indicator (No. **15**) to this solution and make up with demineralized water to a volume of about 75 mL.

The pH-value has to be about **pH 6** before the determination, otherwise add more sodium acetate.

Titrate the solution with $Na_2$-EDTA solution (No. **7**). The color of the solution changes from light violet to intensely light-green. (In between, the color changes a few times.)

Repeat this procedure as many times as necessary.

**2.3 Quantitative determination of the copper content**

Transfer 25.00 mL of your parent solution (No. **13**) into the 100 mL volumetric flask and fill up with demineralized water to a volume of 100.0 mL.

For each titration, transfer 25.00 mL of this solution into an Erlenmeyer flask and add sodium hydroxide solution (No. **6**), until the solution shows an alkaline reaction. During this procedure, a blue precipitate for

# About the history of the International Chemistry-Olympiads

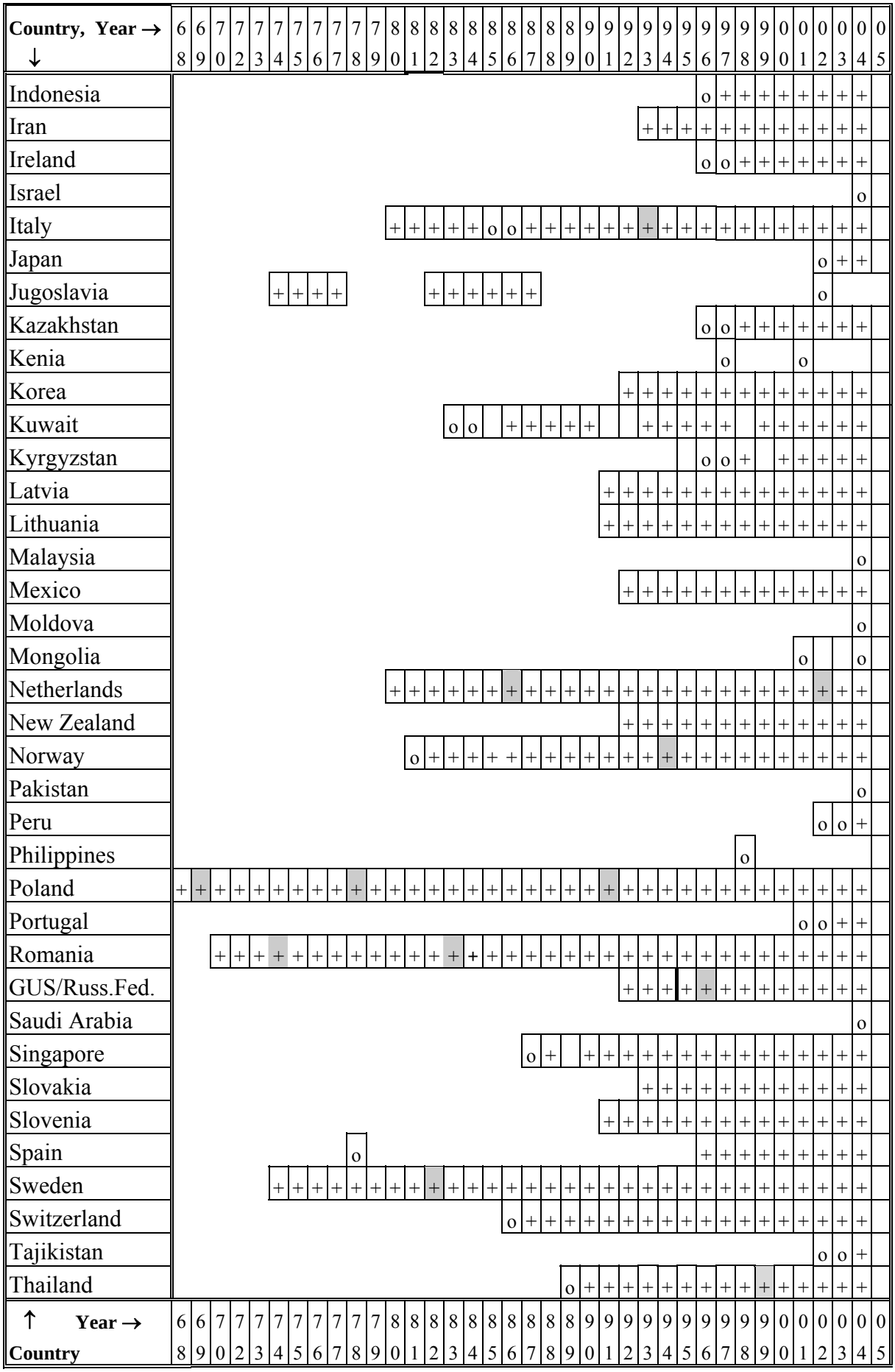
The idea of chemistry olympiads was born 1968 during an Czechoslovakian national olympiad that was attended by observers from Poland and Hungary. These three countries participated in the first IChO 1968 in Prague. The participating countries of the following years are shown in the table.

**Participating Delegations**

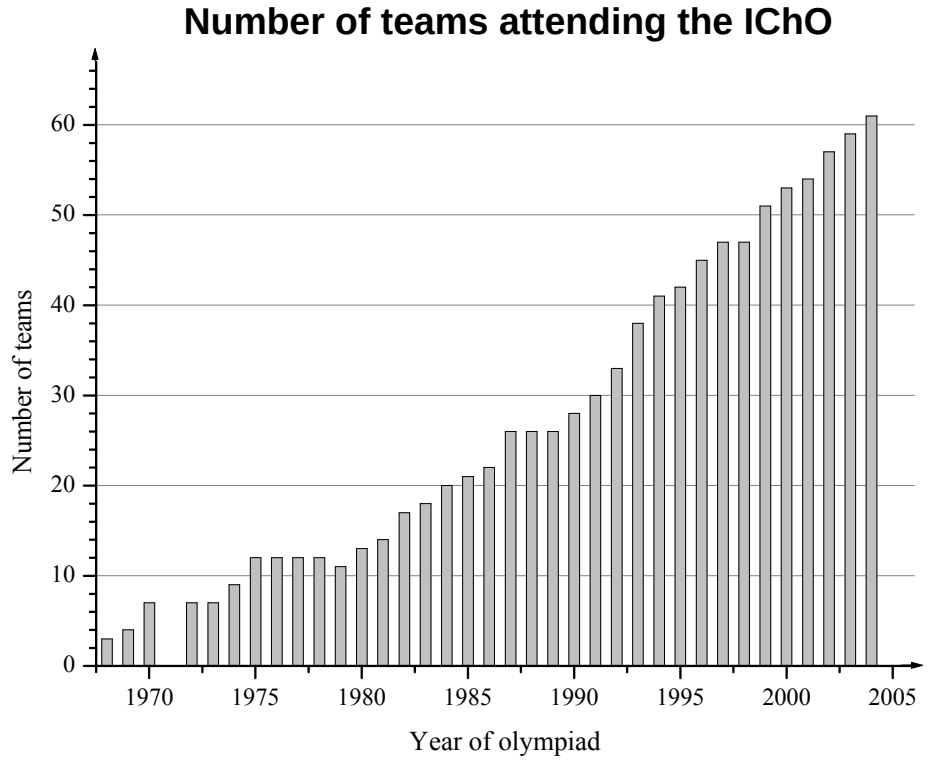
(in the alphabetical order of the German names)

(+ = host, + = participant, o = observer)

| Country, Year → ↓ | 68 | 69 | 70 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 | 87 | 88 | 89 | 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 00 | 01 | 02 | 03 | 04 | 05 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Argentina | | | | | | | | | | | | | | | | | | | | | | | | | | | + | + | + | + | + | + | + | + | + | + | | |
| Armenia | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | o | |
| Australien | | | | | | | | | | | | | | | | | | | o | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | |
| Austria | | | | | | | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | |
| Azerbaijan | | | | | | | | | | | | | | | | | | | | | | | | | | | | | o | o | | + | + | + | + | + | |
| Belarus | | | | | | | | | | | | | | | | | | | | | | | | | | | | + | + | + | + | + | + | + | + | + | |
| Belgium | | | | | | | + | + | + | | | + | | | | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | |
| Brasil | | | | | | | | | | | | | | | | | | | | | | | | | | | | | o | o | + | + | + | + | + | + | |
| Bulgaria | | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | |
| Canada | | | | | | | | | | | | | | | | o | o | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | |
| China | | | | | | | | | | | | | | | | | | | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | |
| Chinese Taipei | | | | | | | | | | | | | | | | | | | | | | | + | + | + | + | + | + | + | + | + | + | + | + | + | + | |
| Croatia | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | o | o | + | + | + | + | + | |
| Cuba | | | | | | | | | | | | | | | | | + | o | + | + | + | + | | + | + | + | + | + | | + | | + | + | + | + | |
| Cyprus | | | | | | | | | | | | | | | | | | | | | | o | + | + | + | + | + | + | + | + | + | + | + | + | + | + | |
| Czech Rep. | | | | | | | | | | | | | | | | | | | | | | | | | + | + | + | + | + | + | + | + | + | + | + | + | |
| Czechoslovakia | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | | | | | | | | | | | |
| Denmark | | | | | | | | | | | | | | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | |
| DDR | | o | + | + | + | + | + | + | + | + | + | + | + | + | + | | + | + | + | + | + | + | | | | | | | | | | | | | | | |
| Egypt | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | o | o | + | + | + | |
| Estonia | | | | | | | | | | | | | | | | | | | | | | | | | | | + | + | + | + | + | + | + | + | + | + | |
| Finland | | | | | | | | | o | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | |
| France | | | | | | | | | | | | o | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | |
| Germany | | | | | | | | o | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | |
| Greece | | | | | | | | | | | | | | | | + | + | + | + | | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | |
| Hungary | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | |
| Iceland | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | o | o | + | + | + | |
| India | | | | | | | | | | | | | | | | | | | | | | | | | | | | | o | o | + | + | + | + | + | + | |
| ↑ 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 |


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
Indonesia
Iran
Ireland
Israel
Italy
Japan
Jugoslavia
Kazakhstan
Kenia
Korea
Kuwait
Kyrgyzstan
Latvia
Lithuania
Malaysia
Mexico
Moldova
Mongolia
Netherlands
New Zealand
Norway
Pakistan
Peru
Philippines
Poland
Portugal
Romania
GUS/Russ.Fed.
Saudi Arabia
Singapore
Slovakia
Slovenia
Spain
Sweden
Switzerland
Tajikistan
Thailand
↑ Year →
Country

| **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 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Turkey | | | | | | | | | o | + | | | | | | | | | | | | | | | o | + | + | + | + | + | + | + | + | + | + | + | |
| Turkmenistan | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | o | o | o | + | + | + | |
| UdSSR | | | + | + | + | + | + | + | + | + | + | | + | + | + | + | + | + | + | + | + | | + | | | | | | | | | | | | | | |
| Ukraine | | | | | | | | | | | | | | | | | | | | | | | | | | + | + | + | + | + | + | + | + | + | + | + | + | |
| United Kingdom | | | | | | | | | | | | o | | o | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | |
| United States | | | | | | | | | | | | | o | | o | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | + | |
| Uruguay | | | | | | | | | | | | | | | | | | | | | | | | | | | | | o | o | + | + | + | + | + | + | |
| Venezuela | | | | | | | | | | | | | | o | | o | | | | | | | | | + | + | + | + | + | + | + | + | + | + | + | + | |
| Vietnam | | | | | | | | | | | | | | | | | | | | | | | | | | | | + | + | + | + | + | + | + | + | + | |
| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| ↑ **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 |
| **Number of 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 | |



# 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 |

(List of abbreviations see page 127)

| | 1989 | 1990 | 1991 | 1992 | 1993 | 1994 | 1995 | 1996 | 1997 | 1998 | 1999 | 2000 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **IChO held in** | **DDR** | **F** | **PL** | **USA** | **I** | **N** | **RC** | **RUS** | **CDN** | **AUS** | **T** | **DK** |
| 1 | DDR | RC | RC | RC | RC | RC | RC | IR | H | SGP | USA | RC |
| . | D | PL | RO | H | TPE | GB | IR | RC | D | USA | ROK | RUS |
| . | RC | D | H | PL | USA | USA | RO | RUS | TR | ROK | RC | USA |
| . | BG | USA | PL | USA | I | A | A | A | TPE | RC | IR | H |
| 5 | SU | CS | NL | A | GUS | SGP | D | D | IR | H | RO | TPE |
| . | H | RO | USA | GUS | H | ROK | GB | USA | RUS | RA | H | A |
| . | PL | F | I | D | D | TPE | SK | UA | ROK | RUS | TPE | SK |
| . | RO | A | D | RO | CDN | CZ | TPE | CZ | RC | AUS | UA | BY |
| . | CS | DDR | N | F | SGP | GUS | I | H | SGP | D | PL | VN |
| 10 | I | H | GB | I | CZ | IR | CZ | RO | PL | GB | AUS | TR |
| . | NL | GB | CS | SGP | A | D | RUS | GB | USA | PL | VN | SGP |
| . | GB | I | SU | CS | RO | H | H | TPE | UA | A | D | D |
| . | A | AUS | A | AUS | P | RO | AUS | BY | AUS | RO | RA | ROK |
| . | USA | SGP | AUS | NL | NZ | DK | SGP | SGP | CDN | TPE | BY | IR |
| 15 | S | NL | DK | DK | ROK | I | F | RA | RO | SK | T | CZ |
| . | F | N | SGP | ROK | LV | T | TR | TR | A | NL | F | FIN |
| . | N | DK | CDN | GB | IR | NZ | PL | F | T | IR | TR | T |
| . | AUS | T | BG | CH | DK | UA | USA | I | EST | UA | SGP | MEX |
| . | CDN | FIN | F | T | AUS | AUS | DK | AUS | CZ | VN | IND | GB |
| 20 | DK | CDN | S | LV | NL | F | RA | ROK | VN | LT | GB | AUS |
| . | FIN | BG | T | NZ | LT | PL | ROK | EST | F | TR | RUS | IND |
| . | B | C | CH | S | SK | NL | UA | CDN | S | BY | MEX | CDN |
| . | C | S | LV | LT | F | SK | LT | T | BY | F | A | RA |
| . | GR | CH | LT | N | C | CDN | T | VN | NZ | I | IRL | UA |
| 25 | CH | B | FIN | CDN | GB | LT | NL | SK | LV | T | NZ | PL |
| . | KWT | GR | C | SLO | T | S | CH | CH | RA | FIN | I | NZ |
| . | | KWT | GR | BG | BG | N | BG | NL | SLO | CZ | CDN | BG |
| . | | CY | B | TPE | B | BG | S | NZ | GB | CDN | LT | F |
| . | | | CY | B | S | FIN | NZ | DK | SK | S | NL | DK |
| 30 | | | SLO | FIN | FIN | EST | EST | PL | LT | BG | SK | NL |
| . | | | | GR | SLO | LV | CDN | SLO | I | N | BG | B |
| . | | | | CY | GR | CH | MEX | MEX | DK | MEX | KZ | RO |
| . | | | | MEX | MEX | MEX | N | LV | NL | CH | DK | KZ |
| . | | | | | N | SLO | SLO | N | IRL | SLO | CH | LT |
| 35 | | | | | CH | B | LV | CY | N | EST | CZ | CH |
| . | | | | | YV | CY | CY | BG | MEX | CY | FIN | SLO |
| . | | | | | CY | GR | B | S | CH | LV | B | EST |
| . | | | | | KWT | TR | GR | LT | CY | DK | S | S |
| . | | | | | | YV | FIN | E | E | NZ | CY | YV |
| 40 | | | | | | C | YV | B | FIN | GR | EST | CY |
| . | | | | | | KWT | KWT | GR | BG | KZ | LV | HR |
| . | | | | | | | C | FIN | YV | E | SLO | I |
| . | | | | | | | | YV | GR | IRL | YV | RI |
| . | | | | | | | | C | B | B | BR | N |
| 45 | | | | | | | | KWT | RI | KS | E | AZ |
| . | | | | | | | | | KWT | YV | N | IRL |
| . | | | | | | | | | C | RI | RI | E |
| . | | | | | | | | | | | GR | LV |
| . | | | | | | | | | | | ROU | GR |
| 50 | | | | | | | | | | | C | BR |

(List of abbreviations see page 127)

| | 2001 | 2002 | 2003 | 2004 | 2005 | 2006 | 2007 | 2008 | 2009 | 2010 | 2011 | 2012 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **IChO held in** | **IND** | **NL** | **GR** | **D** | **TPE** | **ROK** | | | | | | |
| 1 | RC | RC | RC | RC | | | | | | | | |
| . | ROK | T | IR | ROK | | | | | | | | |
| . | USA | TPE | ROK | RUS | | | | | | | | |
| . | RUS | ROK | T | UA | | | | | | | | |
| 5 | IR | A | BY | D | | | | | | | | |
| . | TR | UA | RUS | PL | | | | | | | | |
| . | IND | USA | IND | TPE | | | | | | | | |
| . | AUS | PL | SGP | H | | | | | | | | |
| . | TPE | IND | D | TR | | | | | | | | |
| 10 | T | D | TPE | VN | | | | | | | | |
| . | SGP | IR | UA | IND | | | | | | | | |
| . | PL | H | PL | IR | | | | | | | | |
| . | RO | RUS | CDN | RO | | | | | | | | |
| . | F | CDN | CZ | LT | | | | | | | | |
| 15 | SK | TR | RO | CZ | | | | | | | | |
| . | H | AUS | KZ | USA | | | | | | | | |
| . | VN | GB | VN | SGP | | | | | | | | |
| . | CZ | SGP | EST | CDN | | | | | | | | |
| . | RA | E | GB | AZ | | | | | | | | |
| 20 | BY | SK | AUS | AUS | | | | | | | | |
| . | C | BY | H | KZ | | | | | | | | |
| . | D | VN | SK | GB | | | | | | | | |
| . | GB | FIN | USA | J | | | | | | | | |
| . | UA | F | YV | A | | | | | | | | |
| 25 | A | LT | IND | BLR | | | | | | | | |
| . | MEX | CZ | F | SK | | | | | | | | |
| . | DK | KZ | A | T | | | | | | | | |
| . | CDN | LV | I | RA | | | | | | | | |
| . | EST | NL | TR | EST | | | | | | | | |
| 30 | RI | RO | AZ | F | | | | | | | | |
| . | HR | RA | MEX | NZ | | | | | | | | |
| . | I | EST | LT | SLO | | | | | | | | |
| . | N | HR | NL | HR | | | | | | | | |
| . | BG | BG | FIN | LV | | | | | | | | |
| 35 | CY | NZ | HR | NL | | | | | | | | |
| . | KZ | I | J | I | | | | | | | | |
| . | B | DK | DK | CH | | | | | | | | |
| . | LT | SLO | RA | FIN | | | | | | | | |
| . | NZ | N | GR | RI | | | | | | | | |
| 40 | CH | YV | LT | S | | | | | | | | |
| . | E | MEX | E | BG | | | | | | | | |
| . | FIN | BR | TM | KS | | | | | | | | |
| . | SLO | S | BR | E | | | | | | | | |
| . | NL | RI | BG | GR | | | | | | | | |
| 45 | LV | TM | CH | BR | | | | | | | | |
| . | BR | B | NZ | TM | | | | | | | | |
| . | S | IRL | IS | CY | | | | | | | | |
| . | YV | CH | IRL | YVA | | | | | | | | |
| . | IRL | C | CY | IRL | | | | | | | | |
| 50 | GR | CY | KS | IS | | | | | | | | |

(List of abbreviations see page 127)

# List of abbreviations

| | |
|---|---|
| A | Austria |
| 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 Independent States |
| H | Hungary |
| HR | Croatia |
| I | Italy |
| IND | India |
| IR | Iran |
| IRL | Ireland |
| IS | Iceland |
| J | Japan |
| KS | Kyrgistan |
| KWT | Kuwait |
| KZ | Kasakhstan |
| LV | Latvia |
| LT | Lithuania |
| MEX | Mexico |
| MGL | Mongolei |
| N | Norway |
| NL | Netherlands |
| NZ | New Zealand |
| P | Portugal |
| PE | Peru |
| 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 |