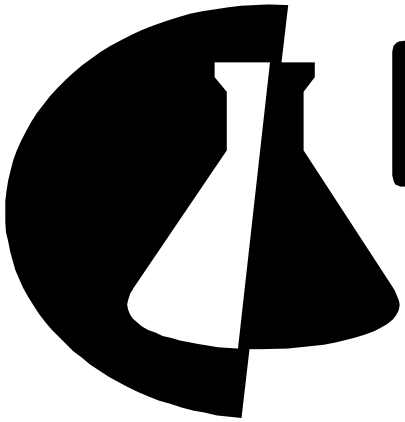

40. International Chemistry Olympiad Hungary 2008

National German Competition and Problems of the IChO

Volume 14

Preface

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

The problems to be solved in the 1st round are sent to all highschools. To solve the problems the students may use all resources available, e.g. textbooks etc.

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

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

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

In this booklet all problems of the selection procedure and the solutions are collected.

In the appendix you find tables of historical interest.

Acknowledgements

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

Wolfgang Hampe

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Part 1: The problems of the four rounds

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

Part 3: The IChO in Budapest

Part 4: Appendix

You will find these problems including the problems of the 40. IChO as pdf-file as of September 2008 in the internet:
http://www.ipn.uni-kiel.de/abt_chemie/icho/icho.html

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

Part 1

The problem set of the four rounds

First Round

Problem 1-1 Where does the water come from?

As soon as the family of Eileen got their new pool they filled it up with water. Eileen is interested in the quality of the water and calls the water supply com-pany to obtain a list of all the ingredients of the provided water. This is not a problem but there are four different water supply stations which provide the residential area of Eileens family with water and they do not know which one was on duty the day the basin was filled. So she gets the test reports of each of the four stations and considers how to find out where the water came from.

	Station 1	Station 2	Station 3	Station 4
Calcium (Ca)	74.6	112	114	95.7
Magnesium (Mg)	12.9	14.5	10.8	9.91
Sodium (Na)	29.7	67.7	19.7	16.6
Potassium (K)	3.54	4.87	3.16	2.87
Ammonium (NH_4)	0.18	0.03	0.12	0.07
Chloride (Cl)	144	146	45	21
Nitrate (NO_3)	1.2	2.0	2.3	2.0
Nitrite (NO_2)	0.08	<0.02	0.03	0.02
Phosphate (PO_4)	0.22	<0.06	0.09	0.10

all informations in mg/L

At first Eileen determines the mass concentration of chloride by applying a precipitation titration (method of Mohr).

a) *Write the reaction equation of this determination of chloride!*
How do you identify the end of the reaction? Give the reaction equation!

b) *Account for the reason why the pH value in this determination must not fall below a value of pH = 6!*

Eileen titrates three samples of 100 mL of water each with a solution of silver nitrate (c = 0.01 mol/L) and finds the following consumptions:
Sample 1: 40.4 mL Sample 2: 41.5 mL Sample 3: 40.9 mL

c) *Calculate the mass concentration of chloride in mg/L!*

Eileen determines the amount of calcium by complexiometric titration with a solution of Na_2EDTA (c = 0.01 mol/L) using calconcarboxylic acid as indicator. She titrates three samples of 100 mL of water each and finds the following consumptions of the Na_2EDTA solution:
Sample 1: 27.9 mL Sample 2: 28.4 mL Sample 3: 28.0 mL.

d) Calculate the mass concentration of calcium in mg/L!

e) Which water supply station delivered the water?

From hearsay Eileen knows that salty water is particularly healthy. She wants to raise the mass content of chloride in the pool water to 1%. 1 kg of pure salt costs € 1.24. The pool has a base area of 5 m x 6 m and is filled up to 1.6 m. The density of the water delivered by the company amounts to 1 g /cm^3.

e) Calculate the expense to reach the wanted mass concentration by adding pure salt (assume in your calculation an original mass content of 20 mg of chloride/100 mL of water. This is not the result of question c)).

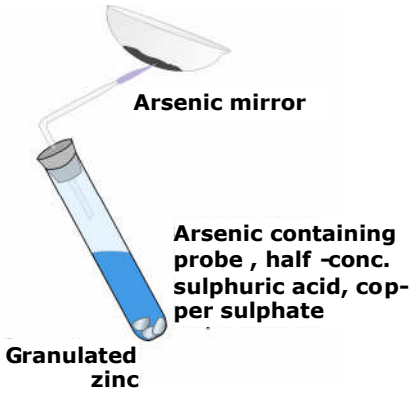
Problem 1-2 Arsenic and old lace

Arsenic-oxygen compounds are strong poisons, for example arsenic(III) oxide (As_2O_3, white arsenic), which was used in criminal cases of poisoning in former times. An easily accessible source of arsenic(III) oxide was the so called fly-paper, which consisted of pulp slices which were impregnated with arsenious acid.

a) Give the formula of arsenious acid and draw the Lewis structure.

b) How is it possible to get arsenic(III) oxide using fly-paper as source? Give a reaction equation!

Arsenic accumulates in hair and nails. It is possible to detect it in exhumed dead bodies even after decades. The qualitative identification may be done by Marsh's test. The substance to be analised is heated with granulated zinc, half-concentrated sulphuric acid and a small amount of copper sulphate. Arsenic is identified in elemental form.



c) Which reactions proceed during Mash's test? Write reaction equations starting with arsenic(III) oxide.

d) What is the function of copper sulphate?

The quantitative analysis of arsenic(III) can be performed using bromatometry.

e) How does this method work? Give the reaction equation.
Which indicator is used?

In old expertises of forensic medicine you often find that poisenors used glass-works as source of white arsenic.

f) What is the reason to use white arsenic in the production of glass?

Besides arsenic(III) oxide there exist two more anhydrides of arsenic-oxygen acids.

g) Which are they? How can you gain them? Give appropriate reaction equations.

Important oxygen acids of phosphorus, the lighter homolog of arsenic, are phosphinic acid (H_3PO_2), phosphorous acid (H_3PO_3) and phosphoric acid (H_3PO_4).

h) How many protons can these acids give off in a Brønsted acid-base reaction? Rationalize your answer by using Lewis structures of these acids.

Problem 1-3 Properties and derivates of 1,3-cyclopentadiene

1,3-Cyclopentadiene is a cyclic hydrocarbon with an unusually low pK_a value of pK_a=16 in comparison to other hydrocarbons with pK_a values of about 40. Thus the reaction of 1,3-cyclopentadiene with strong bases e.g. sodium amide ($NaNH_2$) leads to the salt sodium 1,3-cyclopentadienide.

a) Write the equation of this reaction.

b) Draw five equivalent resonance structures of the cyclopentadienyl anion.

c) Rationalize the great stability of the cyclopentadienyl anions using the Hückel rule.

d) Draw one resonance structure of a cyclopentadienyl cation. Compare its stability with that of the cyclopentadienyl anion and account for your opinion.

e) Compare the acidity of the 1,4-dicyano derivate of 1,3-cyclopentadiene with that of unsubstituted 1,3-cyclopentadiene. Give reasons!

Sodium 1,3-cyclopentadienide reacts with iron(II) salts in the molar ratio of 2:1. An orange and diamagnetic compound X forms which does not decompose in air.

f) Write the reaction equation of the formation of compound X.

g) Draw a 3D-structure of compound X.

Compound X reacts with different substances in a characteristic way, e.g.

(1) with ethyl chloride in the presence of aluminium chloride
or
(2) with concentrated sulphuric acid.

h) Write the equations of the reactions (1) and (2) of compound X. Draw 3D-structures of each product.

i) Give the general mechanisms of these reactions. Which kind of reaction mechanism is present in both cases?

Compound X can be protonated by strong acids to yield an addition compound.

j) Draw a 3D-structure of this addition compound!

Second Round (homework)

Problem 2-1: Colour and Solvents

The intensity of colour of the elements of group 17 of the PSE increases from fluorine to iodine. While fluorine is an almost colourless gas chlorine shows yellow colour if in high concentration, bromine is a brown fluid and iodine forms black-violet cristals.

a) *Explain this feature with the help of a qualitative MO-diagram of the halogen molecules X_2 ((X = Cl, Br, I).*

(Account only for the atom orbitals of the valence electrons.)

If iodine is dissolved in different solvents the solutions show different colours. Iodine as an electron-pair acceptor forms Lewis acid-base adducts with the molecules of many solvents. These adducts show charge transfer. You can examine the formation of such adducts by photometrical methods. These are equivalent reactions described as follows (D = donator):

$$I_2 + D \rightleftharpoons I_2 \cdot D \qquad (I_2 \cdot D = \text{adduct})$$

with the equilibrium constant

$$K = \frac{c(I_2 \cdot D)}{c(I_2) \cdot c(D)}$$

Assuming the concentration of the donator being much larger than of the adduct this equation can be simplified to

$$K = \frac{c(I_2 \cdot D)}{[c_0(I_2) - c(I_2 \cdot D)] \cdot c_0(D)} \qquad (c_0 = \text{inital concentrations})$$

Using the law of Lambert and Beer the absorption coefficient ε_0 arises to

$$\varepsilon_0 = \frac{\log \frac{I_0}{I}}{c(I_2 \cdot D) \cdot d} \qquad (d = \text{pathlength})$$

The Lewis acid-base adducts of iodine with benzene and mesitylene in a solution of tetrachloromethane show the following photometrical data:

$c_0(I_2)\cdot 10^5$ in mol/L	$c_{i,0}$(benzene) in mol/L	$\frac{c_0(I_2)\cdot d}{\log\frac{I_0}{I}}\cdot 10^5$ in cm · mol/L
3.26	1.0000	10.29
6.96	0.9240	10.58
10.42	0.8120	10.98
10.42	0.6190	12.59
17.40	0.2130	24.90
43.5	0.0862	51.00
21.8	0.0433	93.00

$c_0(I_2)\cdot 10^5$ in mol/L	$c_{i,0}$(mesitylene) in mol/L	$\frac{c_0(I_2)\cdot d}{\log\frac{I_0}{I}}\cdot 10^5$ in cm · mol/L
9.20	1,0000	12,02
49.5	0,0281	62,9
1597	0,0281	63,5
99.0	0,01398	121,6

b) Determine the average equilibrium constant K of the adducts of iodine with benzene and mesitylene.

The formation of which complex will be favoured?

Similar to iodine other substances show strong solvation chromism. You can use this property to find an empirical parameter for the polarity of solvents.
You have to look for the absorption maximum with the longest wavelength.
Using this wavelength you can calculate the molar excitation energy E_T of a chosen compound:

$$E_T = h\cdot\nu_{max}\cdot N_A$$

($h = 6.63\cdot 10^{-34}$ J·s . $N_A = 6.022\cdot 10^{23}$ mol^{-1}, ν_{max} = frequency in the absorption maximum with the longest wavelength)

Two compounds A and B show their absorption maxima in a UV/VIS-spectrum at the following wavelengths:

Solvent	λ_{max} of compound A in nm	λ_{max} of compound B in nm
Dimethyl formamide	653	526
Methylene chloride	695	541
Acetonitrile	622	518

c) Determine for both compounds the respective values of E_T(A) and E_T(B) in kJ · mol^{-1} (give your results in integers!).

d) Plot a diagram of the pairs (E_T(A) / E_T(B)) of the same solvent and draw the best fit straight line.

Find its equation.

Compound B is dissolved in other solvents and provides the following wavelengths λ_{max} of their absoprtion maxima:

Solvent	λ_{max} (in nm)
Acetone	538
Benzene	578
n-Butyl ether	592
Trichloromethane	553
Dichloroethane	546
Diethyl ether	571
Dimethoxyethane	550
Dioxan	568
Tetrachloromethane	599
Tetrahydrofuran	555

e) Find standard values of E_T(A) in kJ · mol^{-1} using your linear equation of the best fit straight line (your results in integers again).
Find an order of increasing polarity of all 13 solvents.

f) Give a reason for the fact that different compounds are employed to find the empirical data of polarity of solvents.

The polariaty of a solvent has great influence on the solubility of substances. Polar compounds dissolve better in polar, unpolar better in unpolar solvents.

Compound C may serve as a solutizing agent. It can be synthesized in the following way:

The reaction of oxirane (ethylene oxide) with ethylene glycol (1,2-ethane diol) leads under catalytic influence of an acid to compound A (among others) with a molecular peak $M^{\cdot+}$ at 150 in the mass spectrum.
Compound A reacts with thionyl chloride in the presence of a catalytic amount of quarternary ammonium salt to form compound B with a molecular peak $M^{\cdot+}$ at 186.
At first 750 mmol of compound A der Verbindung A react with potassium-hydroxide solution (w(KOH) = 60 %) and then with a solution of 750 mmol of B. After recovery you get a compound C with a singlet at δ = 3.691 in its ^{1}H-NMR-spectrum in $CDCl_3$.

g) Give the empirical and the structural formulas of the compounds A, B and C. What is the systematic and the trivial name of compound C?

Compound C is dissolved in benzene, then potassium chloride is added.

h) Which unexpected observation can be made? Account for it.

Problem 2-2 Kinetics in Technical Chemistry

If you want to transfer a chemical reaction to a large-scale technical process it is among other things important to know the exact kinetics of the reaction exactly and furthermore the heat that has to be supplied or dissipated. All this is necessary to hold the process unter control.

As an example we want to use the synthesis and the saponification of ethyl acetate.

Ethyl acetate can be produced directly from ethanol and acetic acid using an acid as catalyzer:

$$CH_3COOH + C_2H_5OH \rightleftarrows CH_3COOC_2H_5 + H_2O$$

As the equilibrium lies not totally on the side of the products you have to take the reverse reaction into your considerations. From investigations it is known that the rate laws of the reaction and of the reverse reaction are of first order with respect to acetic acid (c(AcOH)) and ethanol (c(EtOH)) as well as ethyl acetate (c(AcOEt)) and water (c(H_2O) respectively:

$$-\frac{dc(AcOH)}{dt} = k \cdot c(AcOH) \cdot c(EtOH) - k' \cdot c(AcOEt) \cdot c(H_2O)$$

The influence of temperature and concentration of the catalytic acid is already incorporated in the values of the reaction rate constants.

The reaction shall be carried out in a batch reactor. In the beginning the reactor is filled with the reactants. After the reaction it is discharged.

For the synthesis of ethyl acetate the reaction shall be interrupted in a state of conversion of 37.5 %. The reaction mixture at the beginning contains 4.17 mol L^{-1} of acetic acid, 10.9 mol L^{-1} of ethanol and 16,1 mol $L^{-}1$ of water.

The reaction rate constants are:

k = $4{,}76 \cdot 10^{-4}$ L mol^{-1} min^{-1} for the reaction

k' = $1{,}63 \cdot 10^{-4}$ L mol^{-1} min^{-1} for the reverse reaction

a) Calculate the maximum conversion under the given conditions.
(Proposal: Use in your calculations c(AcOEt) = $x \cdot c_0$(AcOH))

b) Of which volume does the reactor have to be if 29 t of ethyl acetate shall be produced during one day. Between two production cycles additional 25 minutes are needed for discharging, cleaning and refilling the reactor.

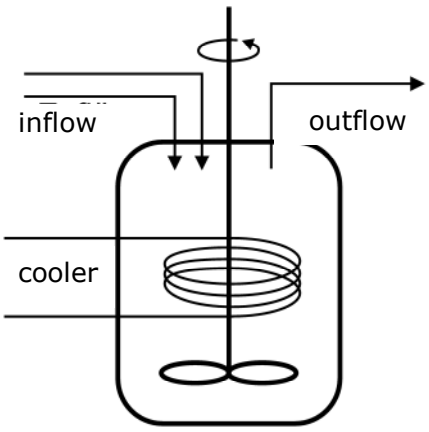
Note to b):

1. To solve the problem the solution of the integral below is needed. You get it by means of partial fraction expansion. Therefore you need the roots of the denominator (x_{01} und x_{02}) which must not not be equal.

$$\int \frac{dx}{x^2 + bx + c} = \frac{1}{x_{01} - x_{02}} \cdot (\ln|x - x_{01}| - \ln|x - x_{02}|) + C$$

2. If you cannot determine the time of one reaction cycle use t = 115 min. This value is identical to the value calculated in b).
3. Round the number of cycles per day to an integer.

A continuously operating stirred-tank reactor is an alternative to the batch reactor. A permanent stream of reactants flows into it while the content of the reactor persists in stady state. To simplify the handling of kinetics you may assume that the reactor is perfectly stirred and the concentrations are equal at each part of the vessel.



The alkaline hydrolysis of ethyl acetate can be performed in such a reactor (V = 40 L). The inlet of the reactor consists of two equal streams of aquous solutions of sodium hydroxide (1 mol L^{-1}, 20 °C) and ethyl acetate (0,8 mol L^{-1}, 25 °C) respectively.
The temperature in the reactor is constantly 25 °.
Under these conditions the rate law of the reaction is of first order with respect to both reactants (rate law constant k = 4,738 L mol^{-1} min^{-1})

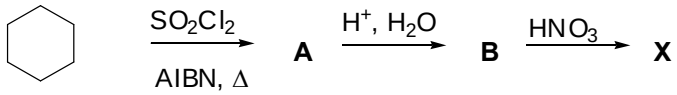
c) 80 % of the ethyl acetate shall be hydrolysed. Calculate the volume of the streams (in L min^{-1}).
Assume that the reaction proceeds isochorely.

Q = -24,92 kJ of the heat released at the reaction have to be dissipated by a cooler with the thermal conductivity of W = 35,65 kJ m^{-2}. The cooling water passes with a mean temperature of 18 °C through the cooler.

d) Calculate the appropriate surface of the cooler.

Problem 2-3 Organic Syntheses

The synthesis of compound **X** follows the scheme below:



X is a colourless oil with a boiling point of 156 °C. It is used as starting material to produce different synthetic fibres such as Perlon or Dederon.
Compound **X** consists of 73,43 % of carbon and 10,27 % of hyxdrogen.

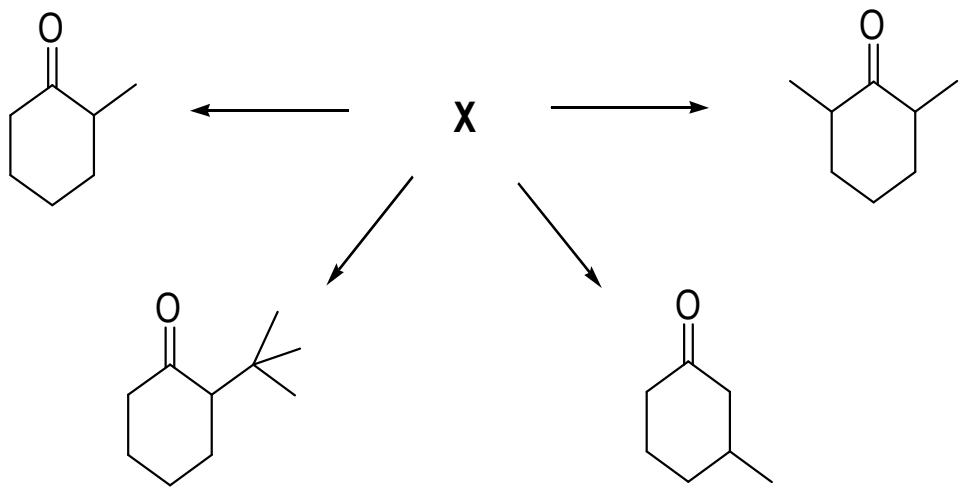
*a) Complete the structural formulas of the intermediates A, B and the product **X** in the reaction scheme above. What is the name and the empirical formula of **X**?*

b) Show the different steps of the mechanism of the formation of A starting with cyclohexane.

What happens if **X** is treated with methyl iodide in the presence of a base such as NaOMe?

c) Give the mechanism of this reaction. Explain which product(s) may be obtained. Does this kind of preparation make sense?

Several compounds can be prepared with **X** as reactant:



d) *Give a reaction equation of the formation of each compound.*
Take into your considerations that the products should be formed extensively selective i.e. without byproducts.
It is not necessary that the formation is performed in a one step reaction, in some cases you may need several steps. Write in these cases all intermediates.

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Problems Round 3

Test 1 Göttingen 2008: Problems 3-01 to 3-10

Test 2 Göttingen 2008: Problems 3-11 to 3-20

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

Good Luck

Useful formulas and data

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

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

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

$K_{th} = K_p \cdot p_o^{-\Delta n}$; $K_{th} = K_c\ (mol/l)^{-\Delta n}$ $\ln (Kp_1/Kp_2) = \frac{-H^0}{R} \cdot (T_1^{-1} - T_2^{-1})$

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

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

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

rate laws

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

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

A pre-exponential factor,
E_a activation energy

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

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

ε molar absorption coefficient
d length of the cuvette
c concentration

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

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

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

$p_o = 1{,}000 \cdot 10^5$ Pa 1 atm $= 1{,}013 \cdot 10^5$ Pa 1 bar $= 1 \cdot 10^5$ Pa

1 Å $= 10^{-10}$ m

A periodic table was provided

Third Round, Test 1

Problem 3-1 Multiple Choice (with one or more correct answers)

a) During the formation of ice out of liquid water ...

A) energy is set free **B)** the surrounding cools down **C)** the pressure in the surounding decreases
D) the mass of water increases **E)** the volume of the total portion of ice and water decreases

b) 10 cm^3 of diluted hydrochloric acid with a pH-value of 4 have to be neutralised. Which volume of a sodium hydroxid solution with a pOH-value of 5 has to be added?

A) 10 cm^3 **B)** 20 cm^3 **C)** 40 cm^3 **D)** 80 cm^3 **E)** 100 cm^3

c) Both of the given substances are dissoluted in water in a molar ratio of 1:1. Which of the solution(s) does (do) not form a buffer solution?

A) HCl/KCl **B)** Na_2HPO_4/Na_3PO_4 **C)** CH_3COOH/CH_3COOK **D)** $NaNO_3$/HNO_3 **E)** $KHCO_3$/Na_2CO_3

d) To electrolyse 1 mol of water completely you need the following amount of charge (F represents the Faraday constant):

A) F **B)** (4/3)·F **C)** (3/2)·F **D)** 2·F **E)** 3·F

e) A sick person has to ingest an antibiotic in a way that he takes an amount of 12 mg/kg weight evenly distributed in 2 doses per day.
How many drops with a content of 60 mg of active ingridient does a patient with a mass of 60 kg have to take in the morning?

A) 6 **B)** 12 **C)** 30 **D)** 36 **E)** 72

f) What is the total sum of concentrations of all ions in a solution of 2 mmol of magnesium chloride in 6 ml of water?

A) 111 mmol/L **B)** 222 mmol/L **C)** 333 mmol/L **D)** 667 mmol/L **E)** 1000 mmol/L

g) Catalysts ...

A) are consumed in spontaneous reactions.
B) reduce the activation energy of chemical reactions
C) change the difference in energy between reactant and product.
D) increase the amount of thermal energy which is released in a reaction.
E) move the equilibrium towards the products of a reaction.

Problem 3-2

1.004 g of a metal chloride (MCl_y , $1 \leq y \leq 4$) are slowly heated in air until it is red hot. 0.594 g of a solid is formed which does no longer contain any chlorine but the same mass of metal as the original chloride.

a) *Identify these substances and write a balanced equation of the reaction that occured during the heating. Examine whether there is more than one possible solution.*

Besides the composition of a substance the structure of its molecule or ion is of interest. To predict the structure you may use the electron repulsion theory (VSEPR).

The following sulphur compounds are choosen as examples

SO_2, $SO_3(g)$ SOF_2, SO_4^{2-}, SF_4, SOF_4, SF_6 .

b) *Draw the structure of these species. Insert the free electron pairs of S. Give the name of the geometrical shape of these compounds or ions.*

Problem 3-3 Storage of Hydrogen I

Metal hydrides are suitable to store great amounts of hydrogen safely (e.g. to run fuel cells). An example for such a metal hydride is Mg_2NiH_4, which is formed by ball milling of magnesium hydride and elemental nickel. In the unit cell of Mg_2NiH_4 the nickel atoms are placed cubic face centered and the magnesium ions occupy tetrahedral holes. Four hydrogen atoms are coordinated to a single nickel atom.

a) *Write a blanced reaction equation for the formation of Mg_2NiH_4. Give the oxidation numbers of the occuring elements.*

b) *Determine the mass content (in %) of hydrogen in this compound.*

c) *Draw the unit cell with all nickel atoms and two magnesium ions of your choice. Show that these magnesium ions are placed in a tetrahedral hole. How many tetrahedral and how many octahedral holes exist in a unit cell?*

d) How many Mg_2NiH_4 units are there in a unit cell?

e) Which geometrical configuration does the $[NiH_4]^{4-}$ polyhedron show? Answer this question by drawing the electron distribution of the complex anion in Pauling notation.

This metal hydride was analyzed by X-ray diffraction. The diffraction of first order was performed with CuKα radiation (λ = 1,542 Å) and gave rise to diffracted intensity at an angle of 11.92°. The planes associated with this reflection are perpendicular to the solid diagonal of the unit cell. They divide the diagonal into three parts of same length.

f) Determine the edge length of the unit cell, a_0.

g) Determine the density of the powder (in g/cm^3).

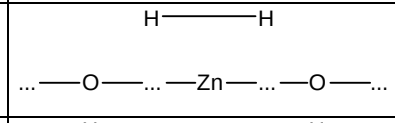
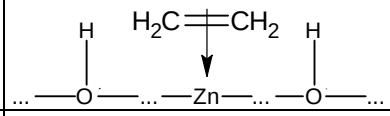
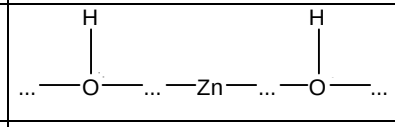
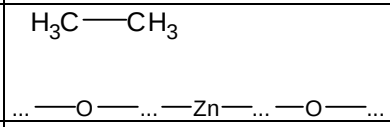
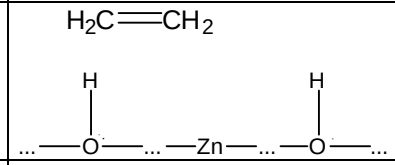
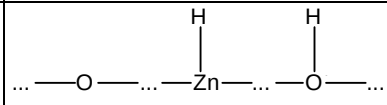
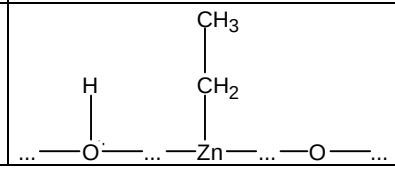
h) Calculate the rate of (mass of hydrogen stored in Mg_2NiH_4)/(mass of hydrogen in fluid hydrogen (density : 70,8 kg/m^3 at 20 K)).

i) Calculate the pressure which has to be held in a hydrogen tank of 20°C, which contains the same amount of hydrogen as a portion of Mg_2NiH_4 with the same volume.

Problem 3-4 Catalytic Hydrogenation of Ethylene

At the beginning of the last century, ethylene, which is a colourless gas, was considered to be a chemical curiosity without any practical importance.
Today, large amounts of ethylene are produced: in Germany, 60 kg per capita in 2001. There are even ethylene pipelines between different locations of the chemical industry.
Ethylene can be converted into ethane with the help of various catalysts. Using a zinc oxide catalyst the reaction is so slow that the reaction mechanism can be analyzed.
The pictures on the next page show the reaction steps of the hydrogenation of ethylene (charges and stoichiometric coefficients are neglected in all the following tasks).

a) Write down the correct order of the steps by numbering them consecutively.

No.		No.	
			
			
			
			

θ(H) describes the fraction of surface sites that are occupied by hydrogen atoms, $\theta(C_2H_4)$ describes the fraction of surface sites that are occupied by ethylene molecules and $\theta(C_2H_5)$ describes the fraction of surface sites that are occupied by the adsorbed intermediate.

b) Which of the following rate equations is correct, if the hydrogenation of the adsorbed intermediate is the slowest step of the reaction?

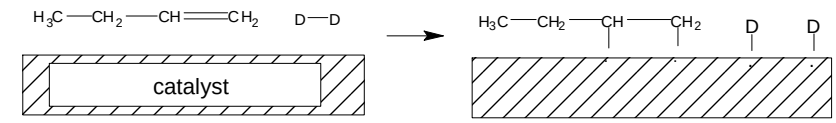
(1) $r = k \cdot \theta(H)$ (2) $r = k \cdot \theta(C_2H_4)$
(3) $r = k \cdot \theta(H) \cdot \theta(C_2H_4)$ (4) $r = k \cdot \theta(H) \cdot \theta(C_2H_5)$

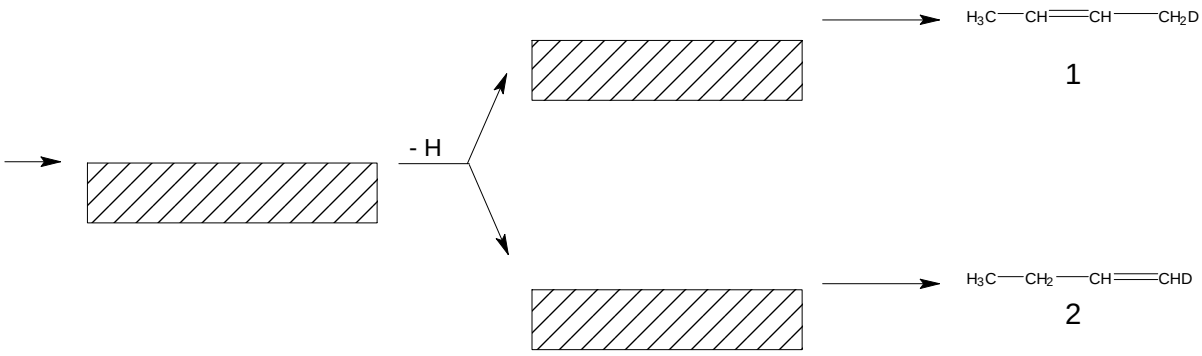
When zinc oxide is used as a catalyst, the hydrogenation of ethylene is blocked by water.

c) Explain this blocking by drawing the interaction between water and the catalyst analogous to that of task 1 of this problem.

If a metal catalyzes the hydrogenation of alkenes, isomer alkenes are formed in a side reaction. When D_2 (deuterium) reacts with 1-butene the side products **1** and **2** will form.

d) Complete the reaction scheme on the next page and write down the structures of the intermediates.





Problem 3-5 Equilibria

Pink flourishing hydrangea thrive in soil with a pH-value below 6 with blue blossoms when absorbing aluminium compounds.
To achieve this colour of the flowers you have to water the plants several times with a solution of 40 to 50 g of alum ($KAl(SO_4)_2 \cdot 12H_2O$) in 10 dm^3 of water.

a) Write the equation of the protolysis causing the solution to react acidic.

b) Determine the ph-value of a solution of 40 g of alum in 10 dm^3 of water.

($pK_a(Al^{3+}) = 4.85$)

You may regard an acid/base - indicator as a weak base or a weak acid.
The acid constant can be obtained by using spectrometrical methods.
A certain indicator, HIn, absorbs strongly at 520 nm.
Three aqueous solutions of the indicator, all of them having the same concentration, are adjusted by buffer solutions to certain pH-values.
Their absorbance at 520 nm was determined:

pH - value	2.0	7.4	12.0
absorbance	0.9	0.64	0.1

c) Find the acid constant of this indicator.

Problem 3-6

A mixture containing oxalic acid, $(COOH)_2$, ammonium oxalate, $Na_2(COO)_2$, and a water soluble impurity reacts neither with a solution of sodium hydroxide nor with a solution of potassium permanganate. In this mixture the mass of the ingredients had to be determined.

Therefore the following aqueous solutions were placed at the disposal:

solution of $Fe(NH_4)_2(SO_4)_2$	c = 0.1100 mol/dm^3
hydrochloric acid	c = 0.1000 mol/dm^3
solution of sodium hydroxide	c ≈ 2 mol/dm^3
solution of $KMnO_4$	c ≈ 0.02 mol/dm^3

2.500 g of the mixture were dissolved in water to give 100.00 cm^3 of a solution. The following dterminations were executed:

(1) 50 cm^3 of the solution of sodium hydroxide were diluted to 1.000 dm^3 . 20.00 cm^3 of this diluted solution were titrated with hydrochloric acid using phenolphthalein as indicator.
Consumption: 20.80 cm^3 of hydrochloric acid.

(2) 10.00 cm^3 of the solution of $Fe(NH_4)_2(SO_4)_2$ were titrated with the solution of potassium permanganate in an acidic medium.
Consumption: 12.20 cm^3 of solution of potassium permanganate.

(3) 10.00 cm^3 of the solution of the mixture were titrated with the diluted solution of sodium hydroxide (of (1)) using phenolphthalein as indicator.
Consumption: 17.30 cm^3 of the solution of sodium hydroxide.

(4) 5.00 cm^3 of the solution of the mixture were titrated with the solution of potassium permanganate in an acidic medium.
Consumption: 23.35 cm^3 of the solution of potassim permanganate.

Determine the mass fractions (in %) of oxalic acid, sodium oxalate and the impurity in the mixture.
Write the reaction equations of the titrations (1) to (4). Specify the aim of each particular determination.

Oxalic acid	pK_1 = 1.23	pK_2 = 4.19
Transition intervals	phenolphthalein:	pH = 8.2 to 10

Problem 3-7

A concentration cell is made, using Ag electrodes immersed in $AgNO_3$ solutions of different concentrations. When the two cell compartments have an $AgNO_3$-concentration of 1 mol/dm^3 and 0.1 mol/dm^3,respectively, the measured voltage is 0.065 V ($T \neq 298.15$ K).

a) What is the voltage if the two compartments have $AgNO_3$-concentrations of 1 mol/dm^3 *and 0.01* mol/dm^3*, respectively?*

Nanometer-sized metal clusters have properties other than bulk materials. To investigate the electrochemical behaviour of silver nanoclusters, the following electrochemical cells are considered:
(on the right-hand side: half-cell where reduction takes place)

(I) Ag(s)/AgCl (saturated)//Ag^+ (aq, c = 0.01 mol/dm^3)/Ag(s)
U_4 = 0.170 V

(II) Pt/ Ag_n(s, nanoclusters), Ag^+ (aq, c = 0.01 mol/dm^3)
//AgCl (saturated)/Ag(s)
U_5 = 0.430 V for Ag_{10} nanoclusters
U_6 = 1.030 V for Ag_5 nanoclusters

b) Calculate the solubility product of AgCl.

Ag_5- and Ag_{10}-nanoclusters consist of metallic silver but nevertheless have standard potentials different from the potential of metallic bulk silver.

c) Calculate the standard potentials of the Ag_5 and Ag_{10} nanoclusters.
(Use in this case $K_{sp}(AgCl) = 1.800 \cdot 10^{-5}$ as solubility product. This value does not agree with the value calculated in b))

d) What happens if you put the Ag_{10} nanoclusters and – in a second experiment – the Ag_5 nanoclusters into an aqueous solution of pH = 5?
Estimate by using the potentials.

$E^0(Ag/Ag^+) = 0.800$ V for b), c) and d): T= 298.15 K

Problem 3-8 Isomers

a) Sketch the structures of all isomers with the empirical formula $C_4H_{10}O$.
b) Write down their full IUPAC names.

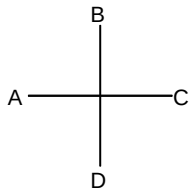
Problem 3-9 Preparations of Alcohols

Two alcohols have to be prepared (possibly as racemate):
Alcohol A: Butane-1-ol
Alcohol B: Butane-2-ol
The following chemicals are at your disposal:
Boron hydride (in THF), aqueous solution of hydrogen chloride, but-1-ene, potassium permanganate, solution of sodium hydroxide, water, hydrogen peroxide.

a) Note down a (non stoichiometric) scheme to prepare alcohol A using only the given choice of substances.
b) Show the essential steps of the reaction mechanism.
c) Note down a (non stoichiometric) scheme to prepare alcohol B using only the given choice of substances.
d) Show the essential steps of the reaction mechanism.

Problem 3-10 Fischer Projections

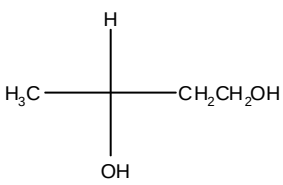
The structure of enantiomers is easily shown by using Fischer projections.
In such a projection a carbon atom is represented by two crossed lines. By convention, the horizontal lines represent bonds coming out of the page, and the vertical lines represent bonds going into the page.



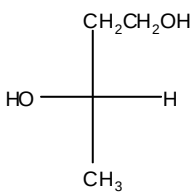
A and C lie in front of the paper plane
B and D lie behind it

Given the following Fischer projections:

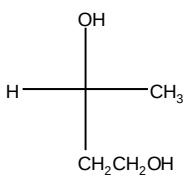
Compound A



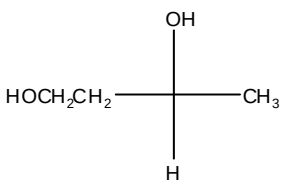
Compound B



Compound C



Compound D



a) Draw the configurational (space) formula of A using the following instructions
(-----) bond lies behind the paper plane,
() bond lies infront of it.
b) Give the full name of compound A (in R,S nomenclature).
c) Which of the compounds B to D is identical, which is different from A?
d) Give the full name(s) of the non identical compound(s) of A. Determine the stereochemical relation of A to this (these) compound(s).

Third Round, Test 2

Problem 3-1 Multiple Choice (with one or more correct answers)

a) In a medical lab 1 cm^3 of urine of Mrs. B. was mixed with 19 cm^3 of water. 3 cm^3 of an reagent were transferred to 3 cm^3 of this mixture. In the resulting solution the concentration of urea was measured 5 $mmol/dm^3$. Which value did the concentration of urea have in the original urine of Mrs. B.?

A) 67 $mmol/dm^3$ **B)** 90 $mmol/dm^3$ **C)** 100$mmol/dm^3$ **D)** 180$mmol/dm^3$ **E)** 200$mmol/dm^3$

b) Which of the following nitrogen compounds contains nitrogen with the lowest oxidation number?

A) NO **B)** N_2O **C)** N_2O_2 **D)** N_2O_3 **E)** N_2O_5

c) Which of the following pair(s) is (are) **not** a corresponding acid/base pair?

A) HCO_3^-/CO_3^{2-} **B)** H_3O^+/H_2O **C)** H_3PO_4/HPO_4^{2-} **D)** NH_4^+/NH_3 **E)** HCl/Cl^-

d) Which reaction does an aqueous solution of (Na_2HPO_4) show?

A) alkaline independent of concentration
B) acidic independent of concentration
C) neutral independent of concentration
D) alkaline only if the concentration is low (c< 0,1 mol/dm^3) otherwise neutral
E) acidic only if the concentration is low (c< 0,1 mol/dm^3) otherwise neutral

e) The molar solubility *C* (mol/dm^3) of $Th(IO_3)_4$, a poorly soluble salt of thorium, can be expressed as a function of the solubility product K_{sp} by one of the followng equations. Which one?

A) $C = (K_{sp}/128)^{1/4}$ **B)** $C = (K_{sp}/256)^{1/5}$ **C)** $C = 256\ K_{sp}^{1/4}$

D) $C = (128\ K_{sp})^{1/4}$ **E)** $C = (256\ K_{sp})^{1/5}$ **F)** $C = ½ \cdot (K_{SP}/128)^{1/5}$

f) 10,0 cm^3 of HCl (c = 0.50 mol/dm^3) and 10.0 cm^3 of an NaOH solution (c = 0.50 mol/dm^3), both of the same temperature, were mixied in a calorimeter resulting in an increase of temperature of ΔT.
Estimate the increase of temperature in case of using only 5.0 cm^3 NaOH solution (c = 0.50 mol/dm^3) instead of 10 cm^3. Let us assume that the loss of heat is negligible and that the heat capacity of both solution is the same.

A) ΔT **B)** $(1/2)\cdot\Delta T$ **C)** $(2/3)\cdot\Delta T$ **D)** $(3/4)\cdot\Delta T$ **E)** $(4/3)\cdot\Delta T$

g) The structure of which of the following compounds turns out to be planar?

A) methane **B)** ethene **C)** ethanol **D)** propanal **E)** 1-propene-3-ol

Problem 3-12 Inorganic Chemistry I

a) Write balanced equations for each of the reactions described below.
All reactions occur in aqueous solutions.

A) A piece of calcium is added to water.
B) A solution of lead acetate and dilute sulfuric acid are mixed.
C) Concentrated hydrochloric acid is added to manganese(IV) oxide.
D) Sodium cyanide is added to water.
E) A piece of silver is placed in dilute nitric acid.
F) An excess of sodium hydroxide is added to aqueous aluminium nitrate.

b) The conductivity of several aqueous solutions was tested producing these results:

Solution	(concentration)	Relative Conductivity
$CoCl_2$ (aq)	(0.10 mol/dm^3)	high
$Co(CH_3COO)_2$ (aq)	(0.10 mol/dm^3)	high
H_2S (aq)	(0,10 mol/dm^3)	low

(i) Account for these results.

Two additional tests are to be performed, this time on mixtures of solutions:

Solution	(concentration)	Relative Conductivity
1. $CoCl_2$ (aq) + H_2S (aq)	(je 0.10 mol/dm^3)	?
2. $Co(CH_3COO)_2$ (aq) + H_2S (aq)	(je 0.10 mol/dm^3)	?

For each of these mixtures answer the following questions.

(ii) Write an ionic equation of the process happening during the mixing process. Give state symbols for all species such as (aq), (s) et.
(iii) Describe any visual changes expected while mixing the solutions.
(iv) Predict the relative conductivity expected for the final solution. Explain your predictions.

Problem 3-13 Unknown Substances

A

A certain amount of vapour of compound X and some oxygen reacted completely. Both gaseous substances were provided at the same pressure (< 1 bar) and temperature (> 100°C).

After the reaction the system was brought back to the starting conditions concerning pressure and temperature. At this point the volume turned out to be the same as before the reaction.
The products consisted of water vapor and carbon dioxide each making up 50% of the volume.

a) Identify X! Write the reaction equation. If there is more than one possibility report it too.

B

Cleaning up a laboratory an unlabeled vessel was found containing pale greyish tablets covered with paraffin oil.
When a tablet was dropped into water a violent reaction took place with the tablet zigzagging on the surface of the water emitting gas and smoke which caused a tickle in one's throat.
The gas around the tablet burned when ingnited with a beautiful scarlet flame.
Finally the tablet was totally gone and the solution turned purple when phenolphthaleine was added.
An quantitative experiment brought an astonishing result. When 10.00 g of the unknown substance reacted with an excess of water 29.20 dm^3 of a gas (δ = 20°C, p = 1.050 bar) were formed.
The aqueous solution formed in this experiment was neutralized with hydrogen fluoride and evaporated to dryness. The remaining white substance had a mass of 32.64 g.

b) Which substance did the tablet consist of? Account for your decision. Show your calculations and write the equation of the reaction with water!

Problem 3-14 Acid/Base/Buffer

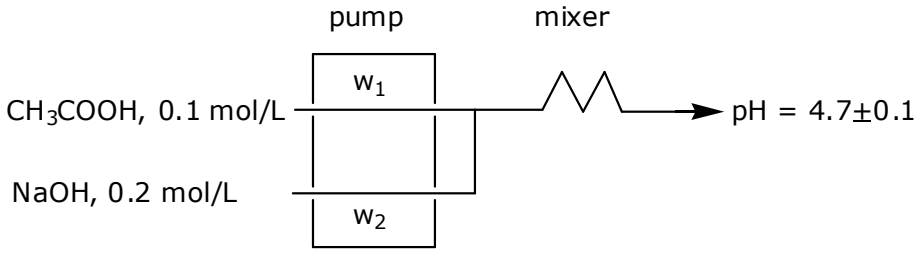
3.00 g of an unknown monocarboxylic acid is dissolved in water to give a solution of 1.00 dm^3.
From the freezing point depression it can be concluded that the total amount of dissolved molecules and ions was 37.6 mmol.
By measuring the electric conductivity of the solution it was shown that 18.5 % of the acid molecules underwent protolysis.
The combustion products of the compound caused a white precipitate when induced into a silver-nitrate solution acidified with nitric acid.

a) Calculate the molar mass and the acid constant K_a. Which acid could it be?

The flow chart shown in the figure below shall provide a buffer solution of pH = 4.7 ± 0.1. To install it, it is necessary to find the flow rates of the given solutions. The flow rates are determined by the diameters of the pump tubings. Available are the tubings which provide the following flow rates w:

116, 165, 330, 348, 490, 580, 660, 710, 780 µL/min.

pK_a(acetic acid) = 4.76

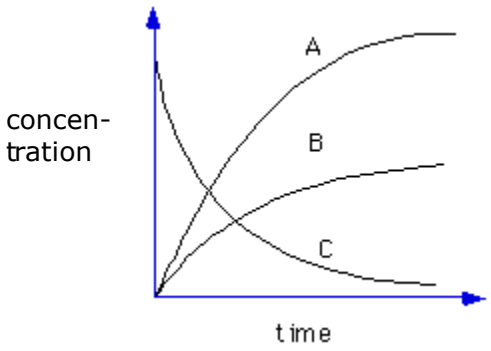


b) Calculate the flow rates (w_1 und w_2) needed.

Problem 3-15 Kinetics

Given is the reaction $2\ NO_2(g) \longrightarrow 2\ NO(g) + O_2(g)$.
Each of the following curves represents the concentration of one of the three species.

a) Which of them characterises the time dependence of the concentration of oxygen? Give a short explanation!



Studying the kinetics of the reaction

$$2\ [Fe(CN)_6]^{3-} + 2\ I^- \rightleftharpoons 2\ [Fe(CN)_6]^{4-} + I_2$$

the initial rates of formation of iodine depending on different starting mixtures were measured. None of the mixtures contained iodine in the beginning.

	$c([Fe(CN)_6]^{3-})$ in mol/dm^3	$c(I^-)$ in mol/ dm^3	$c([Fe(CN)_6]^{4-})$ in mol/ dm^3	initial rate in mmol·L$^-$1·h^{-1}
1. test	1	1	1	1
2. test	2	1	1	4
3. test	1	2	2	2
4. test	2	2	1	16

The rate law depends on the concentrations as follows

$$\frac{dc(I_2)}{dt} = k \cdot c^a([Fe(CN)_6]^{3-}) \cdot c^b(I^-) \cdot c^d([Fe(CN)_6]^{4-}) \cdot c^e(I_2)$$

b) Determine the values of a, b, d, e and the rate constant k.

The molar Gibbs function of the transition state $\Delta G^{\#}$ has the values of 75.240 kJ/mol at 25°C and 76.100 kJ/mol at 35°C.

c) Calculate the activation enthalpy and the activation entropy.

As mechanism for the reaction above two elementary reactions are proposed:

$$[Fe(CN)_6]^{3-} + 2\ I^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe[(CN)_6]^{4-} + I_2^-$$

$$[Fe(CN)_6]^{3-} + I_2^- \xrightarrow{k_2} [Fe(CN)_6]^{4-} + I_2\ .$$

One of these reaction runs fast, the other one slowly.

d) Specify which of the reactions is slow, which one is fast.
Show that the mechanism is compatible to the rate law found in b).

Problem 3-16

Lithium cobalt oxide and carbon (graphite) are active ingredients of the positive and negative electrodes, respectively, of a rechargeable lithium battery.
During the charge/recharge cycles, lithium is built into the crystalline lattice of both electrode materials, a process called intercalation.
The following reversible half-reactions occur:

(1) $C_6 + Li^+ + e^- \rightleftharpoons LiC_6$

(2) $2\ Li_{0,5}CoO_2 + Li^+ + e^- \rightleftharpoons 2\ LiCoO_2$

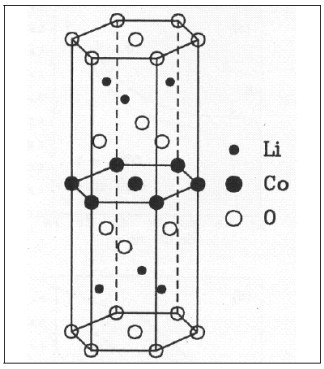
a) Calculate the potential of the battery. Give the equation of the reactions at the electrodes during discharging of the battery and account for your equation.

The total amount of energy a battery can store is rated in mAh. A battery rated at 1500 mAh can power a device drawing 100 mA for 15 hours.

Graphite has lithium intercalation sites between its layers. Assume a maximum 6:1 carbon-to-lithium intercalation stoichiometry.

b) Calculate the theoretical charge capacity of 1.00 g of graphite to intercalate lithium. (Answer in mAh/g)

The structure of lithium cobalt oxide is derived from a cubic close packed structure of O^{2-} ions. Li and Co occupy the octahedral holes and form an alternating layer structure. Part of the $LiCoO_2$ lattice (not the unit cell) is shown in the figure.



c) Draw the unit cell of cubic close packed O^{2-} ions and mark the centres of all relevant octahedral holes.
Determine the ratio (amount of O^{2-} ions) : (number of octahedral holes).

A producer supplies batteries which contain 1.00 cm^3 of graphite (ρ = 2.25 g/cm^3) and 1.30 cm^3 of $LiCoO_2$ (ρ = 4.8 g/cm^3).

d) Calculate the total energy (in kJ) that this battery can theoretically supply.

To decrease mass and size of batteries the possibility is considered to replace graphite by metallic lithium. In a test 0.5 cm^3 of lithium (and 1.30 cm^3 of $LiCoO_2$ again) is used. Lithium crystillizes in a body-centred cubic structure. The length of the edges of the unit cell amounts to a = 3.51 Å.

e) Calculate the density of metallic lithium!

f) Calculate the total energy (in kJ) that this battery can theoretically supply.

(Use ρ(Li) = 0,5 g/cm^3 independent of the result of e).)

Thermodynamical data:

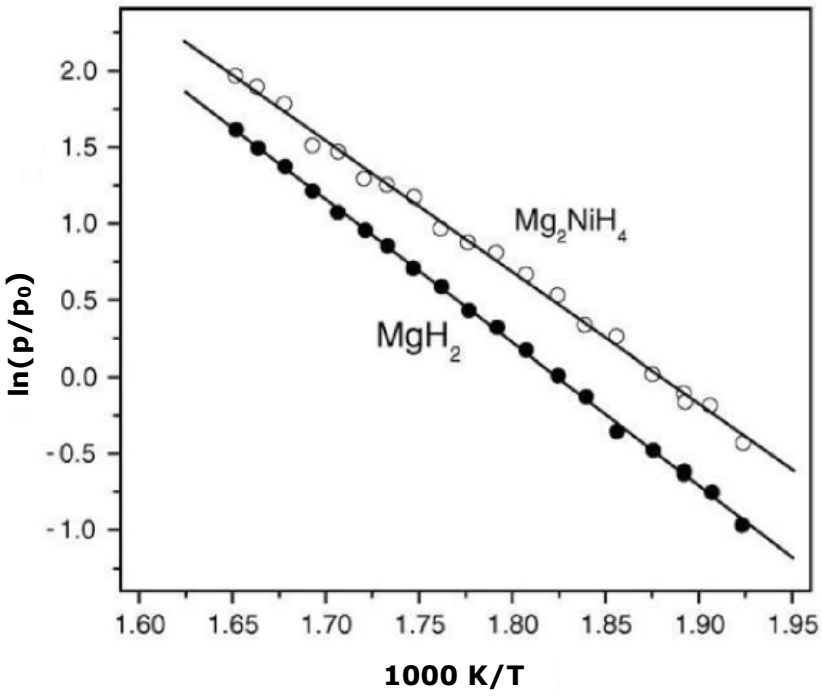
Compound	$Li_{0.5}CoO_2$	$LiCoO_2$	LiC_6
ΔG_f^0 in kJ/mol	- 424	-614	-4

Problem 3-17 Storage of Hydrogen II

If you want to use metal hydrides as „hydrogen tanks" the absorption and the release of hydrogen have to be reversible reactions. Especially temperature and pressure play an important part. Therefore we have to look at the thermodynamics of these reactions.

a) *Write balanced reaction equations of the release of hydrogen from magnesium hydride, MgH_2, and from dimagnesium-nickel tetrahydride, Mg_2NiH_4. The latter one forms an intermetallic phase with the ratio n(Ni):n(Mg) = 1:2. Give the oxidation numbers of the occuring elements.*

The release reaction was studied at different temperatures by measuring the partial pressure of hydrogen (p_0 = standard pressure).



b) *Determine the reaction enthalpy of both release reactions using values from the diagram. Let us assume that these reaction enthalpies are independent of temperature. Plot the pairs of values you used on the answer sheet!*

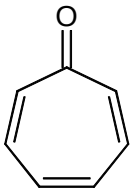
c) *Determine the enthalpy of formation of the intermetallic Ni:Mg (1:2)-phase.*

(If you could not solve b) assume $\Delta H_f° = 163.4$ kJ/mol as enthalpy of decomposition of Mg_2NiH_4 an. This is not the true value calculated in b).)

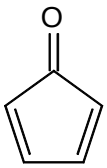
Thermodynamic data: $\Delta H_f°\ (Mg_2NiH_4) = -176.0$ kJ/mol

Problem 3-18 Stability of two Oxides

The oxides A and B differ in stability



Oxide A



Oxide B

One of them can be isolated as a stable compound, the other one can not be synthezised.

a) Write down the names of both oxides.

b) Which of them is stable?
Account for your decision with the help of resonance structures.

Problem 3-19 Changes in Solutions of Sugars

X-ray structure analysis of a cristal of β-D-glucose shows a chair-like geometry of a six–membered ring. All OH-groups at the ring are equatorial. The infrared spectrum does not show any corbonyl band.
If a sample of β-D-glucose is dissolved in water the optical rotation slowly changes. At first you find a specific rotation of about +18 to +20° which is slowly changing and ultimately converges to a constant value of + 52°.
From this solution a new product A can be isolated. Its melting point and its specific rotation is diffrent to the values of β-D-glucose.

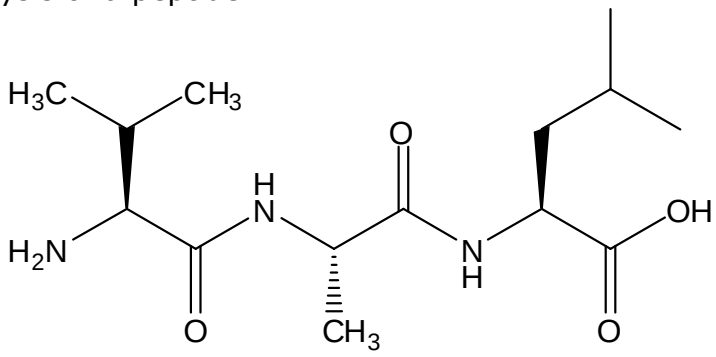
a) Write the reactions which take place in the aqueous solution and give the products.
Show the sugar molecules in chair conformation.

A solution of a sugar X with a concentration of 0.1 mol/L is added to a freshly prepared aqueous solution of β-D-glucose. In the mixture you find a rotation of 0°.

b) Write down the name of X. Draw this sugar in chair conformation and in Fischer projection.

Problem 3-20 Analysis of Peptides

Peptides are polymers of amino acids. You can get all amino acids involved by a complete hydrolysis of a peptide.

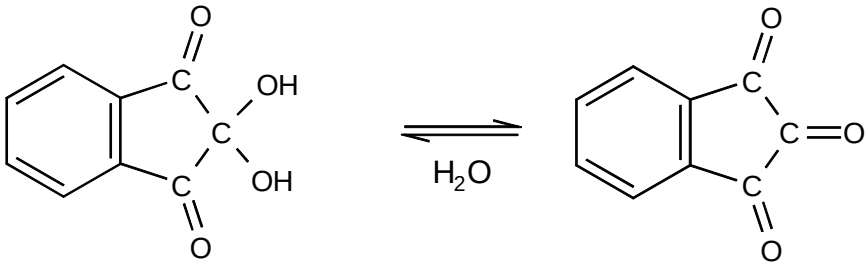


a) *Which amino acids do you get by complete hydrolysis of this peptide? Write down their IUPAC names (in R, S-nomenclature).*

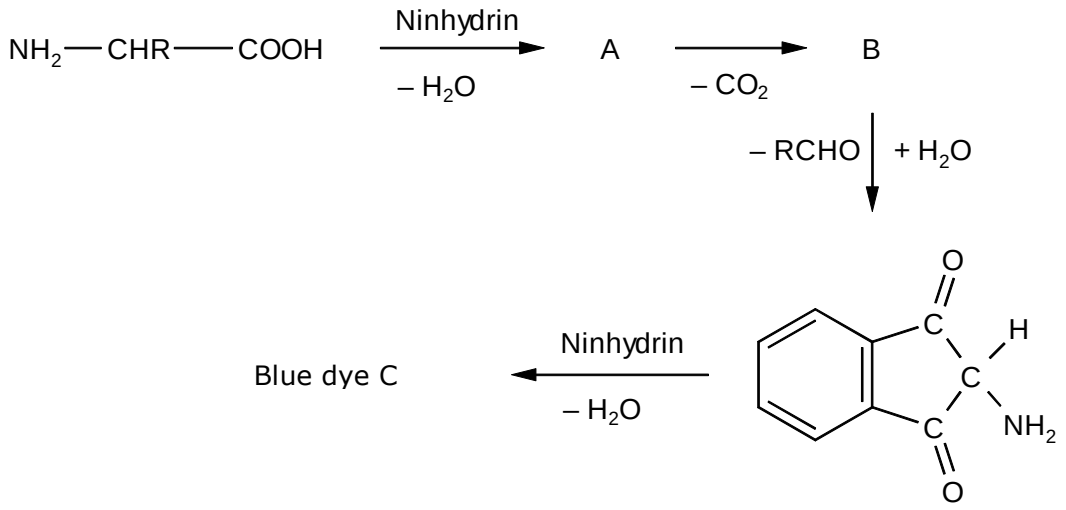
b) *Draw the spacial configuration of one of these amino acids.*

To determine individual amino acids automatically operating analysers are used. After hydolysis the amino acids are seperated within these analysers by columns. Each eluated amino acid is detected with a ninhydrin reaction test. Ninhydrin forms a blue dye in aqueous solutions with all amino acids. The dye is gauged by a spectrophotometer.

In aqueous solutions ninhydrin establishes the following equilibrium:



The reaction scheme below shows the reaction of an amino acid with ninhydrin to form a blue dye.



c) Complete this reaction scheme.

d) Make a proposal of a procedure to analyse an amino acid qualitatively and quantitatively in an amino-acid analyser.

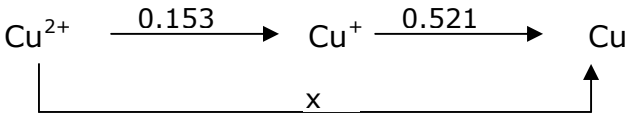
Fourth round (theoretical problems)

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

Problem 4-1 Electrochemistry and Equilibria

A

Copper may form Cu^+ and Cu^{2+} ions with the standard potentials
$E°(Cu^{2+}/Cu^+) = 0.153$ V $E°(Cu^+/Cu) = 0.521$ V .
These potentials can be presented by a so called Latimer diagram:



a) Use this diagram to calculate x.

b) Is Cu^+ stable towards disproportionation?
Rationalize by a calculation.
Give a simple criterion based on the Latimer diagram whereby you are able to recognize whether disproportionation takes place or not.

Whether Cu^+ is stable towards disproportionation or not you may calculate an equilibirium constant even if a reaction does not happen spontaneously.

c) Calculate the equilibirium constant of the disproportionation of Cu^+.

Using CuI (with $c(I^-) = 1$ mol/L) instead of Cu^+ in the Latimer diagram you find

$$CuI \xrightarrow[-\ 0.147]{} Cu\ .$$

d) Calculate the solubility product K_{sp} of CuI.

For the reaction $CuI \longrightarrow Cu^+ + I^-$ you may evaluate $\Delta G° = -R\cdot T\cdot \ln K_{sp}$.

e) Find $\Delta G°$ of the reduction of Cu^{2+} by I^- to form CuI:

$$Cu^2 + I^- + e^- \longrightarrow CuI$$

(Use in this case $K_{sp} = 4\cdot 10^{-12}$)

f) Determine the equilibrium constant of the reaction

$$2\ Cu^{2+} + 4\ I^- \longrightarrow 2\ CuI + I_2\ .$$

$E°(I_2/2I^-) = 0.535$ V

B

Uranium, too, is able to form ions with different oxidation numbers:

$UO_2^{2+} + 4\ H^+ + 2\ e^- \longrightarrow U^{4+} + 2\ H_2O \qquad E^0_1 = + 0{,}32\ V$

$UO_2^{2+} + 4\ H^+ + 6\ e^- \longrightarrow U + 2\ H_2O \qquad E^0_2 = - 0{,}82\ V$

$UO_2^{2+} + e^- \longrightarrow UO_2^{+} \qquad E^0_3 = + 0{,}06\ V$

$U^{4+} + e^- \longrightarrow U^{3+} \qquad E^0_5 = - 0{,}63\ V$

g) Sketch a Latimer diagram and use it to determine $E°(U^{3+}/U)$. Which of these species will disproportionate? To find the answer you may use the criterion of b). Write the reaction equation(s).

h) Calculate the equlibrium constant of the disproportionation of U^{3+}.

Problem 4-2 Analysis and Equilibria

The separation process of cations is based on sparingly soluble salts and readily soluble complex compounds.

Many cations of metals form sulfides are showing poor solubility. They precipitate by passing-in hydrogen sulfide. Hydrogen sulfide is a weak acid which can donate two protons (pK_{a1} = 6.9; pK_{a2} = 12.9). The concentration of the sulfide ions can be fixed by the pH value.

Passing H_2S in water or a solution of an acid a saturated solution of H_2S forms with $c(H_2S)$ = 0.10 mol/L.

a) Determine $c(S^{2-})$ at pH = 2.0.

Sulfides of the formula MeS and Me_2S, respectively, shall be seperated completely by passing-in H_2S at pH = 2. A precipitation is concidered to be complete if the concentration of the cations remaining in the solution is smaller than 10^{-5} mol/L.

b) Calculate $K_{sp(max)}$ of sulfides of these types.

Cd^{2+} and Cu^+ form with cyanide ions complexes such as $[Cu(CN)_4]^{3-}$ and $[Cd(CN)_4]^{2-}$, respectively.

c) Is it possible to separate a precipitate of CdS and Cu_2S by a solution of KCN (c = 1.0 mol/L)?

(Protonation of S^{2-} by the solvent should be neglected.)

Solubility products: $K_{sp}(Cu_2S) = 2{,}0.10^{-47}$ $K_{sp}(CdS) = 1{,}0.10^{-27}$

Constants of complex formation: $\beta([Cu(CN)_4]^{3-}) = 2{,}0.10^{27}$

$\beta([Cd(CN)_4]^{2-}) = 7{,}0.10^{16}$

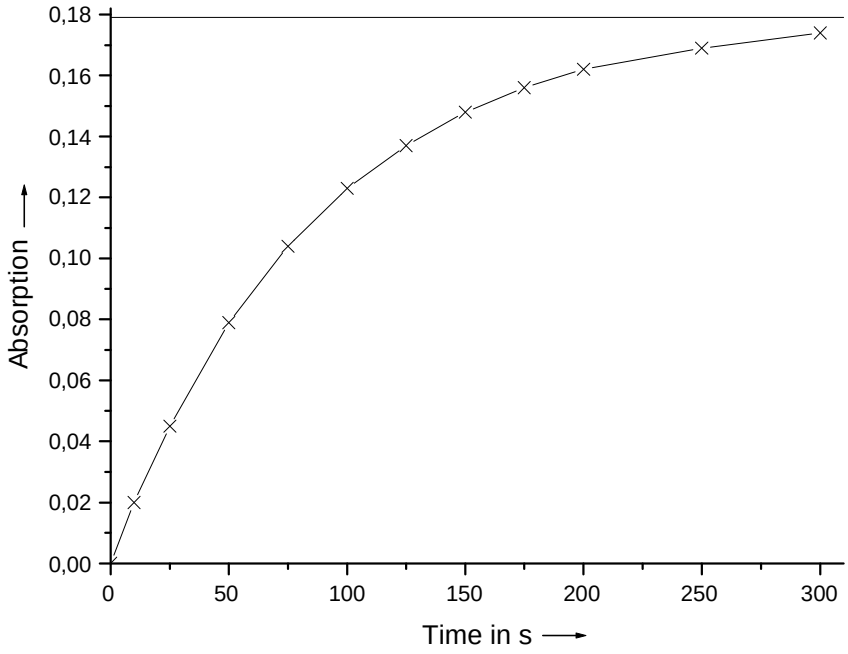
Problem 4-3 A Lot of Kinetics

A

The decay $E \longrightarrow P + Q$ is of first order. The process was spectrometrically analyzed.

A solution of E (c(E) = 0.020 mol/L) was filled into a cuvette (length 0.95 cm). The absorption was measured at a wavelength at which only compound P absorbes (fig. below).

(The upper limit of absorption is plotted as a straight line.)



a) Determine the molar extinction coefficient.

b) Estimate the initial rate of the decay and determine the rate constant.

c) Ascertain the half life of the decay by approximation.

d) Verify whether the approximate half life matches the plot above.

e) How much time does it take until 95% of E have decayed?

The initial rate does not change if the temperature is beeing increased from 300°C to 450°C, while the initial concentration of E at 450°C amounts only to 1/3 of that at 300°C.

f) Find the activation energy.

B

For the reaction $2\ O_2^- + 2\ H^+ + E \longrightarrow O_2 + H_2O_2 + E$

the rate law $v = k \cdot c(O_2^-)$ with $k = 501\ L/(mol \cdot s)$

has been derived experimentally.

E refers to an enzyme, superoxiddismutase, which was used in this case. The initial concentration amounted to $c_0(E) = 0.400 \cdot 10^{-6}$ mol/L.

The following mechanism was proposed for this reaction:

$$O_2^- + E \xrightarrow{k_1} O_2 + E^-$$

$$O_2^- + E^- \xrightarrow{k_2} O_2^{2-} + E \xrightarrow[2\ H^+]{\text{fast}} E + H_2O_2$$

Assume $k_2 > k_1$. E^- is not very stable, therefore $c(E^-)$ remains constant after a short initial phase.

g) Propose a rate law for this mechanism. Find out whether this law matches the experimentally found law.

Asume that k_2 is twice as big as k_1.

h) Calculate both rate constants k_1 und k_2 using the steady state approximation.

Problem 4-4 Acids, Bases and so on

A

There are different acid/base theories and definitions. One of them is refers to solvents which show self-dissociation:

$$2\ HSol \rightleftharpoons H_2Sol^+ + Sol^- .$$

Following this theory a substance is called an acid if it increases the fraction of the cationic part of the solvent, a substance that decreases this part (respectively increases the anionic part) is called a base.

E.g. in water you find $2\ H_2O \rightleftharpoons H_3O^+ + OH^-$.

Acids are substances that raise $c(H_3O^+)$, bases raise $c(OH^-)$.

In ethanol you find $2\ C_2H_5OH \rightleftharpoons C_2H_5OH_2^+ + C_2H_5O^-$,

Acids are substances that raise $c(C_2H_5OH_2^+)$, bases raise $c(C_2H_5O^-)$.

Then a neutralization is a reaction of an acid with a base forming a salt and the solvent.

Relating to this theory the definition of pH is $pH = -\log c(H_2Sol^+)$.

a) Give an example of an acid and a base in liquid ammonia as solvent.

b) The ion product of ammonia amounts to $1.0 \cdot 10^{-29}$ $(mol/L)^2$. What is the pH of liquid ammonia?
(In this case H means the cationic part of the solvent)

c) Explain whether water is an acid or a base in liquid ammonia.

d) Rationalize why CH_3COOH is an acid in liquid ammonia. Is it a stronger or a weaker acid than in water as solvent?

e) Is it possible that a compound exists that is a strong acid in water and a weak base in liquid ammonia? If you agree give an example, if you deny account for your answer.

f) Show that NaOH is a salt in liquid ammonia. Give an example of a reaction in which NaOH is formed in liquid ammonia.

g) Is there a compound which is a base in water but an acid in liquid ammonia? Give an example or explain your denial.

h) Is there a solvent in which water is a base?
Give an example or explain your denial.

i) Are there acids and bases in tetrachloromethane?
Give an example or explain your denial.

(Please keep in mind: All terms in section **A** refer to the acid/base theory explained above!)

B

The following problems refer to aqueous solutions of acids!

j) Calculate the pH value and the protolysis degree α_1 of diluted methanoic acid (c = 0.5 mol/L).
Calculate the pH value and the protolysis degree α_2 of diluted acetic acid (c = 0.5 mol/L).

1.5 L of a mixture of acids contain 0.75 mol acetic acid and 34,5 g methanoic acid.

k) Calculate the protolysis degree of both acids and the pH value of the solution.

21.42 g of a monoprotoic acid with the molar mass of 102 g/mol are dissolved in water to form 1.4 L of solution at pH = 2.82.

l) Calculate pK_a of the acid!

K_a(methanoic acid) $= 1.77 \cdot 10^{-4}$ K_a(acetic acid) $= 1.76 \cdot 10^{-5}$

Problem 4-5

A

Silver reacts with an aqueous solution of sodium cyanide in contact with air in the following way:

$$4\ Ag + O_2 + 2\ H_2O + 16\ CN^- \longrightarrow 4\ Ag(CN)_4^{3-} + 4\ OH^- .$$

In order to suppress the formation of hydrocyanic acid, which is very volatile and toxic, the pH of such a solution must be kept above 10.

a) Which concentration of a solution of sodium cyanide has to be chosen to adjust the pH-value to 10.7?

A solution contains silver(I) ions and 0.020 mol/L sodium cyanide. Compared with Ag^+ there is a great excess of sodium cyanide. The pH-value of this solution amounts to 10.8. The following equilibrium exists in this solution:

$$Ag^+ + 4\ CN^- \rightleftharpoons Ag(CN)_4^{3-} \qquad \beta_1 = 5.00 \cdot 10^{20}$$

b) Determine the ratio of $c([Ag(CN)_4]^{3-})/c(Ag^+)$ in this solution.

The concentration of free, non-complex silver ions shall be increased by adding sodium hydroxide or perchloric acid.

c) Justify your selection.

The Ag^+ concentration shall be increased tenfold in comparison to the concentration of the solution in b) by adding acid/base.

d) Calculate $c(CN^-)$ in this new solution.

(Use in this case $c(CN^-) = 0.0196$ mol/L in the solution of b), do not use your solution of question b). Furthermore assume that the volume of the solution increases only negligible by adding acid/base.)

pK_a(HCN) = 9.31

Problem 4-6 Structures and Species of Oxygen

The density of barium amounts to ρ = 3.65 g/cm^3, its atomic radius is 2.174 Å. Barium cristallizes in a regular cubic lattice, simple, body-centered or face-centered.

a) Determine the kind of cubic lattice barium cristallizes in.

Barium oxide cristallizes in the same way as sodium chloride.

b) Which are the cristallisation numbers of barium and oxygen ions in this type of lattice?

Barium peroxide, too, cristallizes in a sodium-chloride structure, but slightly distorted in direction of one axis. Thus a tetragonal cell of calcium-carbide type occurs.

c) What could the reason be for this distortion from cubic to tetragonal? Sketch he unit cells of barium oxide and barium peroxide together with the position and (if possible) the orientation of the ions. (in barium oxide the barium cations are situated on the corners of the elementary cell, in barium peroxide they occupy the other position!).

Barium forms different oxides e.g. BaO, BaO_2 and $Ba(O_2)_2$.

d) Write equations of reaction which lead to the formation of these three barium oxides.

The energy released at the formation of a cristal can be estimated by the Kapustinskii equation. Its simplest form is

$$\Delta U_{Gitter} = -107000 \frac{\nu |z_+||z_-|}{r_+ + r_-}$$

where ν is the total number of ions in the empirical formula, z_+ and z_- are the charges in the individual ions, r_+ and r_- are the ionic radii in pm and the result is given in kJ/mol.

e) Calculate the molar lattice energies of barium oxide, barium peroxide and barium hyperoxide (the diatomic ions are regarded to be spherically) by using the Kapustinskii equation.

f) Calculate the energy released at the formation of the three barium oxides. The formation of which of these oxides should be favoured using this very simple estimate?

Anion	O^{2-}	O_2^{2-}	O_2^-
ΔH_f (kJ/mol)	904	553	-43
Ionic radius	140	173	158

Barium: Enthalpie of atomisation ΔH_{atom} = 180 kJ/mol, ionization energy IE_1 = 503 kJ/mol, IE_2 = 965 kJ/mol, ionic radius of Ba^{2+}= 135 pm)

Another diatomic species of oxygen is the dioxygenyl cation O_2^+.

g) Complete the qualitative MO diagrams of the dioxygenyl cation, of dioxygen, of the hyperoxide anion and of the peroxide dianion and determine the respective bond order. Which behaviour do you expect in a magnetic field?

Another species of oxygen is the ozonide anion which forms salt-like compounds with potassium and rubidium. These two compounds cristillize in a caesium-chloride structure in which you find isolated ozonide anions.

h) Draw the Lewis formula(e) of the ozonide anion. Which geometrical structure do you expect referring to the VSEPR model?

i) Write two isoelectronic systems of his anion.

j) What is special about these systems? What kind of reactions of these species can you expect?

Ozonide react extremely vehemently with water to form oxygen. The resulting solution shows basic reaction.

k) Write the reaction equation. Assign in all cases oxidation numbers (you may use fractions as oxidation numbers). Which kind of reaction is it about?

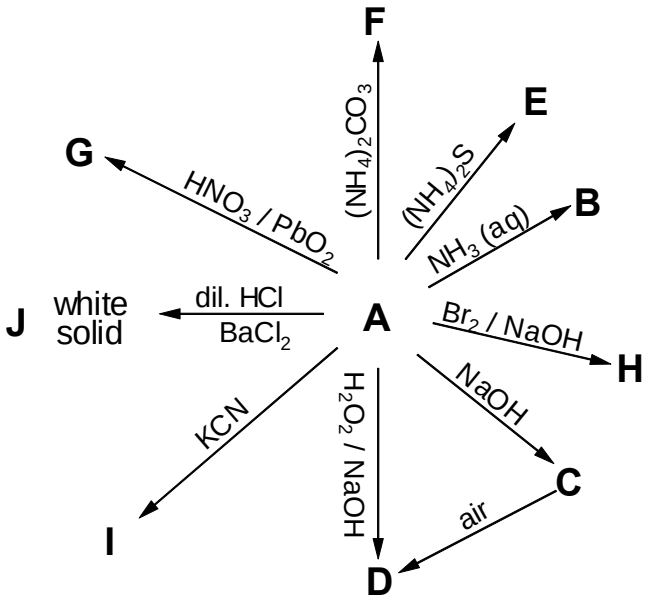
Problem 4-7 A Lot of Chemistry

The elemental analysis of a purchasable salt A of a metal X provides the following data:

Kind of atoms	chlorine	carbon	oxygen	sulfur	nitrogen	hydrogen
Mass fraction in %	0.00	0.00	57.38	14.38	0.00	3.62

Thermogravimetrical inspection of A shows that before the begin of total decomposition 30% of the starting mass is lost.

An aqueous solution of A shows the following reactions (except with air all other reactants are aqueous solutions):



a) Determine metal X and give the empirical formula of compound A.

b) Give the name of the compound A and account for it.

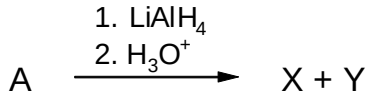
c) What are the compounds B to J? Write down the equations of the reactions given in the scheme above.

d) Calculate the expected magnetic moment of all X containing species A to J in aqueous solutions μ ($\mu = \sqrt{n \cdot (n+2)}$, n = number of unpaired electrons, result in BM, in complex ions assume octahedral complexes).

Problem 4-8 Reactions with Lithium Aluminium Hydride

The reaction of ethyl 3-pentenoate (compound A) with lithium aluminium hydride provides two products (compound X and compound Y).
In the infrared spectrum of compound X you find a broad band at 3500 cm^{-1} and a sharp band in the region of 1630 cm^{-1} (see table next page). Compound X discolours a soltution of bromine in water. The second comound Y shows a peak at 28 m/z in the mass spectrogram.

a) Complete the reaction scheme



Note down the structures and the names of the compounds.

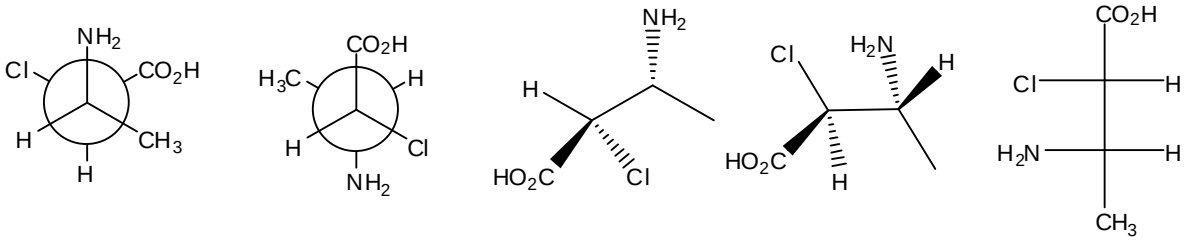
b) Show the mechanism of this reaction. Keep in mind that first a reaction with $LiAlH_4$ takes place followed by a reaction with the acid.

c) Identify the peak at 28m/z in the mass sprectrogram of compound Y.

You find "Regions of wave numbers of characteristic stretching vibrations of organic compounds" at the end of the test.

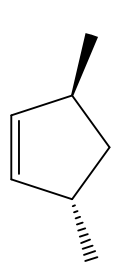
Problem 4-9 Stereochemistry and Stereoselective Reactions

a) Determine for each of the following figures of 2-chloro-3-aminobutanoic acid the ablolute configuration of both asymmetric C-atoms following the CIP-rules (due to the form (2S, 3R)). Clarify the numeration of the carbon chain. Which compounds are enantiomers?

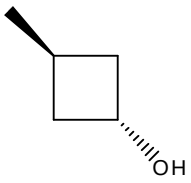


1 2 3 4 5

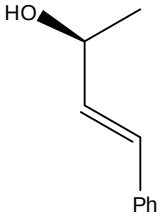
Given are the following compounds



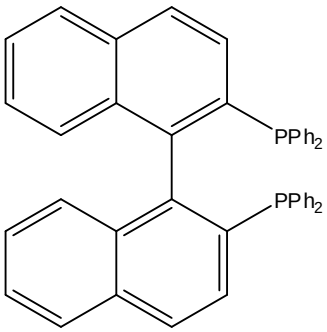
A



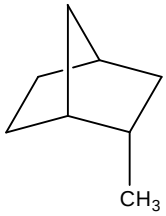
B



C



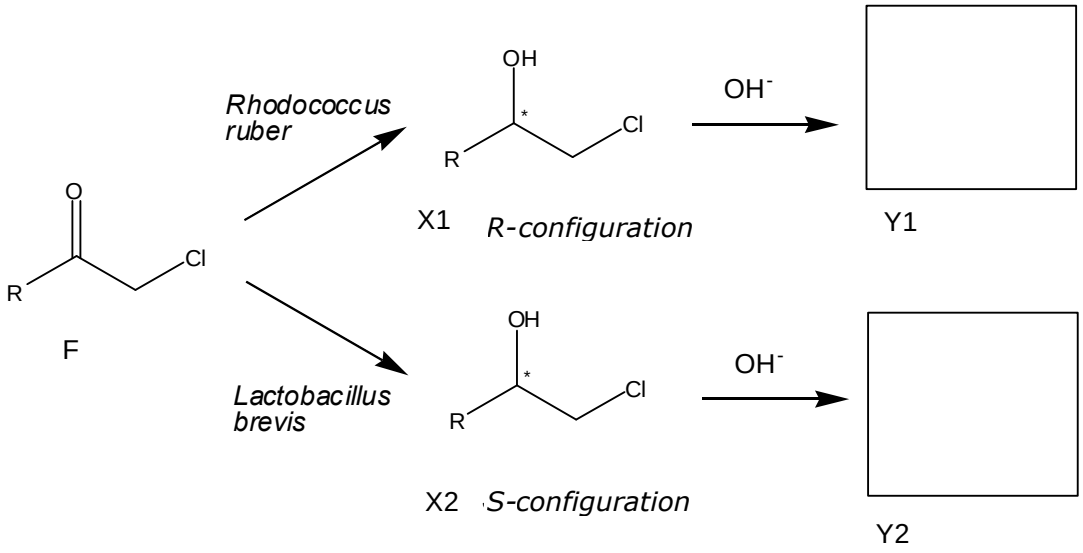
D



E

b) How many stereoisomers of the compounds A to E do exist? Draw these isomers in a way that the spacial structure can be recognized easily.

Compound F is converted stereoselectively with biochemical methods to form two alcohols X(1) und X(2) (R = Alkyl). Then a reaction to the specific epoxides follows.

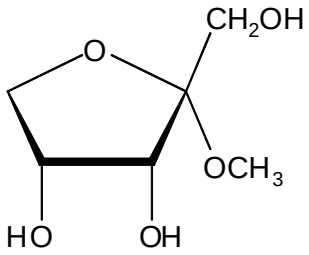


c) Draw the spatial structures of X(1) and X(2).

d) Draw the spatial structures of both epoxides Y(1) and Y(2) as R- or S-compound which are formed from the alcohols X(1) and X(2). Write down whether these epoxides are R- or S-compounds.
Account for your decision by demonstrating the proceding of the formation of the epoxides by arrows which show the path of the electrons.

Problem 4-10 Reaction of sugars

The starting material of a reaction is 1-O-methyl-α-D-ribulose (compound A).



A

Compound A reacts with an acetone/H^+ solution to form two products:

$$\text{A} \xrightarrow{\text{acetone}} \text{B(1)} + \text{B(2)}$$

a) Draw the structures of both compounds B(1) and B(2). Which of them is the main product? Account for your opinion.

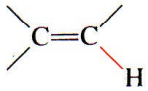
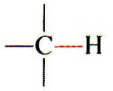
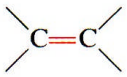
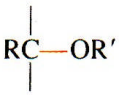
The following synthesis starts with the main product B(1). It reacts with acetic anhydride to form compound C. On careful heating of C in a diluted acid, D is formed together with two more products. 1 mol of D reacts with 1 mol of methanol to form E. In E it is no longer ascertainable whether it is an α- or a β-sugar.

$$\text{B(1)} \xrightarrow{\text{acetic anhydride}} \text{C} \xrightarrow{H_2O\,/\,H_3O^+} \text{D} \xrightarrow{H_3COH\,/\,H_3O^+} \text{E}$$

b) Draw the structure of the compounds C to E.

c) Rationalize why it is no longer ascertainalble whether compound E is an α- or a β-sugar.

Regions of wave numbers of characteristic stretching vibrations of organic compounds

bond or functional group		
RO–H	(alcohols)	3200–3650
RCO–H	(carboxylic acids)	2500–3300
R_2N–H	(amines)	3300–3500
RC≡C–H	(alkines)	3260–3330
	(alkenes)	3050–3150
	(alkanes)	2840–3000
RC≡CH	(alkines)	2100–2260
RC≡N	(nitriles)	2220–2260
RCH, RCR′	(aldehydes, ketones)	1690–1750
RCOR′	(ester groups)	1735–1750
RCOH	(carboxylic acids)	1710–1760
	(alkenes)	1620–1680
	(alcohols, ethers)	1000–1260

Fourth round (practical problems)

Problem 4-11 Gravimetric Determination of Zinc as $Zn(NH_4)PO_4$

Equipment:

2 x 400 mL beaker 25 mL pipette with pipette control 50 mL graduated cylinder
100 mL narrow-necked bottle Bunsen burner with tripod and tile glass rod
2 glass filter crucibles suction flask with rubber ring pressure tubing
vacuum attachment desiccator with drying agent precision balance pen

Chemicals:

test solution (100 mL volumetric flask)
diluted hydrochloric acid, c(HCl) = 2 mol/L
ammonium chloride, NH_4Cl(s), (Xn), R22-36, S22
solution of diammonium hydrogen phosphate $w((NH_4)_2HPO_4) = 10$ %
indicator solution of methyl red in Ethanol $w(C_{15}H_{15}N_3O_2) = 0{,}05$ %
Ethanol (F), R11, S7-16
solution of ammonia $c(NH_3) = 2$ mol/L (PE-bottle)
demineralized water (l)

Safety precautions: Wear eye protection.

Procedure:

The test solution has to be filled up with demineralized water to the calibration mark and mixed well. 25 mL of this solution are pipetted into a 400 mL beaker. Approximately 150 mL of demineralized water are added.
Then 25 mL of diluted hydrochloric acid, 2-3 full spatulas of ammonium chloride, 25 mL of a solution of diammonium hydrogen phosphate and some drops of methyl-red indicator solution are added.
Heat to boiling and add dropwise diluted ammonia until a colour change to yellow-orange can be observed. Then stir with the glass rod until the precipitate has formed crystals or is well sedimented.
While the solution cools down to room temperature the glass filter crucibles are marked with the pen, weighed and the values are listed.
The precipitate is sucked through a glass filter crucible, washed with a small portion of cold demineralized water and then dried at 130°C for one hour in a drying oven.
The crucible is cooled down to room temperature for about 20 to 30 minutes in an exsiccator and then weighed again.

Repeat the whole procedure.

a) Calculate the mass concentration of zinc in mg/L in your test solution.

b) What kind of compound is zinc ammonium phosphate, a mixed crystal, a mixture of crystals, a double salt or an alloy? Account for your decision.

c) Why does the colour change of methyl red indicate the optimum of precipitation? Give the rough value of the transition interval of methyl red. Show interfering side reactions which occur at considerably higher or lower pH values and may distort the result of the analysis.

d) What happens if you anneal the precipitate? Write down the reaction equation.

Problem 4-12 Komplexometric Determination of Aluminium, Calcium and Magnesium

At first the mass concentration β of aluminium is determined by a back titration of Na_2EDTA standard solution with zinc-sulfate standard solution and xylenyl-orange as indicator.
To find out the mass concentration β of magnesium and calcium, aluminium is masked with triethanol amine and the content of calcium is determined with Na_2EDTA standard solution and calcon carboxylic acid as indicator.
At least the sum of the contents of calcium and magensium in the solution after aluminum is masked is determined with Na_2EDTA standard solution and indicator buffer pills as indicator.
By forming the difference you find the mass concentration β of magnesium.

Procedure for A, B and C

The test solution (250 mL volumetric flask) has to be filled up with demineralized water to the calibration mark and mixed well.

A Determination of Aluminium

Equipment

25 mL pipette with pipette control 300 mL Erlenmeyer flask 25 mL burette
stand with funnel and clamp Bunsen burner with tripod and tile
indicator paper spatula microspatula glass rod

Chemicals:

Test solution (250 mL volumetric flask)
standard solution of $Na_2EDTA \cdot 2\ H_2O$ $c(Na_2EDTA) = 0.1$ mol/L
sodium acetate (CH_3COONa) (s)
xylenolorange (s), trituration with sodium chloride $w(C_{31}H_{32}N_2O_{13}S) = 1$ %
standard solution of zink sulfate $c(ZnSO_4) = 0.1$ mol/L, (N), R 52/53, S61
demineralized water (l)

Safety precautions: Wear eye protection

Procedure:

Use the pipette to transfer exactly 25 mL of the test solution into an Erlenmeyer flask and fill up with demineralized water to approximately 100 mL. Add exactly 25 mL of the standard solution of Na_2EDTA by using a pipette and heat it shortly to boiling.

After the solution has cooled down to room termperature add 2 to 3 full spatulas of sodium acetate to yield a pH value of 5 and the solution of 2 microspatula tips of xylenolorange indicator trituration.

Titrate with standard solution of zink sulfate until the colour changes from yellow to red-violet.

Waste disposal:

The titrated solution is given into the container of heavy metall waste.
Remains of Na_2EDTA solution can be given into the sink directly.

a) *Calculate the mass concentration β in mg/L of aluminium in your test solution.*
b) *What is the reason for short boiling?*
c) *Give an order of the ions Al^{3+}, Ca^{2+}, Mg^{2+}, Zn^{2+} following increasing stability of the complex [cation · EDTA]!*

B Determination of Calcium

Equipment

25 mL pipette with pipette control	300 mL Erlenmeyer flask
25 mL graduated cylinder	10 mL measuring pipette
25 mL burette	stand with funnel and clamp
glass rod spatula microspatula	universal indicator paper

Chemicals:

Test solution (250 mL volumetric flask)
triethanol amine $C_6H_{15}NO_3$ (l)
solution of potassium hydroxide, w(KOH) = 25 %, (C), R22-35, S26-36/37/39-45
calcon carboxylic acid (s), trituration with sodium chloride, $w(C_{21}H_{14}N_2O_7S) = 0.2$ %
standard solution of $Na_2EDTA \cdot 2\ H_2O$ $c(Na_2EDTA) = 0.1$ mol/L
demineralized water (l)

Safety precautions: Wear eye protection.

Procedure:

Use the pipette to transfer exactly 25 mL of the test solution into an Erlenmeyer flask and fill up with demineralized water to approximately 100 mL. Add 10 mL of triethanol amine, 10 mL of the solution of potassium hydroxide and two microspatula tips of calcon carboxylic acid trituration as indicator.
Titrate with standard solution of Na_2EDTA until the colour changes from pink to azure.

Waste disposal:

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

d) Calculate the mass concentration β in mg/L of calcium in your test solution.

C Determination of the sum of the contents of calcium and magnesium

Equipment:

25 mL pipette with pipette control	300 mL Erlenmeyer flask
25 mL graduated cylinder	10 mL measuring pipette
25 mL burette	stand with funnel and clamp
glass rod spatula microspatula	universal indicator paper

Chemicals:

Test solution (250 mL volumetric flask)
triethanolamin $C_6H_{15}NO_3$ (l)
ammonium chloride NH_4Cl(s), (Xn), R22-36, S22
solution of ammonia , $w(NH_3) = 25$ %, (C, N), R 34-50, S 26-36/37/39-45-61
standard solution of $Na_2EDTA \cdot 2\ H_2O$ $c(Na_2EDTA) = 0.01$ mol/L
indicator buffer pills (Merck), (Xn), R 22-36-42/43 S 22-24-37-45
demineralized water (l)

Safety precautions: Wear eye protection.
Use concentrated ammonia solution under the hood only.

Procedure:

Use the pipette to transfer exactly 25 mL of the test solution into an Erlenmeyer flask and fill up with demineralized water to approximately 100 mL. Add 3 to 4 full spatulas of ammonium chloride, 10 mL of triethanol amine, 5 mL of conc. solution of ammonia and 1 indicator buffer pill. The pH should reach the range of 10 to 11.
Titrate with standard solution of Na_2EDTA until the colour changes from red to green.

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

e) Calculate the mass concentration β in mg/L of calcium and magnesium in your test solution.

f) Calculate the mass concentration β in mg/L of magnesium in your test solution.

Part 2

The answers to the problems of the four rounds

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

Answers Round 1

Solution to problem 1-1

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

At the end of the titration brown silver chromate forms from the excess of silver cations and added solution of potassium chromate.

$2\ Ag^+ + CrO_4^{2-} \longrightarrow Ag_2CrO_4$

b) Because of the chromate-dichromate equilibrium at lower pH values nearly all of the chromate exists as dichromate ions. Silver dichromate has a higher solubility product than silver chromate and thus the consumption of silver nitrate solution would be too high.

c) Average consumption V = 40.93 mL

$m(Cl^-)$/1000 mL of water = $10 \cdot c(AgCl) \cdot V \cdot M(Cl^-)$

= 10 · 0.01 mol/L · 40.93 mL · 35.45 g/mol = 145.10 mg

d) Average consumption V = 28.10 mL

$m(Ca^{2+})$/1000 mL of water = $10 \cdot c(Na_2EDTA) \cdot V \cdot M(Ca)$

= 10 · 0.01 mol/L · 28.10 mL · 40.08 g/mol = 112.62 mg

e) The water came from station 2.

f) In the basin there are 5 m x 6 m x 1.6 m = 48 m^3 = 48000 L of water with a mass of 48000 kg.

Existing concentration of chloride: 20 mg in 100 mL of water.

Then 48000 kg of tap water contain 0.2 g/L · 48000 L = 9.6 kg of chloride.

You have to add x kg of sodium chloride.

Total mass after adding of sodium chloride: (48000 + x) kg of solution.

x kg of NaCl contain $x \cdot \frac{35{,}45}{58{,}45}$ kg of Cl^- - ions.

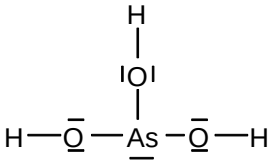
[$x \cdot \frac{35{,}45}{58{,}45}$ kg + 9.6 kg] Cl^-- ions shall be 1 % (m/m) of (48000 + x) kg of the salt solution.

$\Rightarrow \quad x \cdot \frac{35{,}45}{58{,}45} + 9.6 = 0.01 \cdot (48000 + x) \qquad \Rightarrow \quad x = 788.60$

You need 788.6 kg of sodium chloride which cost € 977.86.

Solution to problem 1-2

a) H_3AsO_3



b) Dissolving in water and concentration by evaporation

$2\ H_3AsO_3 \rightleftharpoons As_2O_3 + 3\ H_2O$

c) Formation of arsenic(III) hydride (arsane)

$As_2O_3 + 6\ Zn + 12\ H^+ \rightleftharpoons 2\ AsH_3 + 6\ Zn^{2+} + 3\ H_2O$

thermal decomposition of arsane: $2\ AsH_3 \rightleftharpoons 2\ As + 3\ H_2$

or if hydrogen reacts immediately with oxygen of the air

$4\ AsH_3 + 3\ O_2 \rightleftharpoons 4\ As + 6\ H_2O$

d) Copper sulphate activates the surface of zinc by forming a local cell.

e) Bromate reacts strongly oxidizing and therefore is reduced to bromine:

$BrO_3^- + 3\ As^{3+} + 6\ H^+ \rightleftharpoons Br^- + 3\ As^{5+} + 3\ H_2O$

$BrO_3^- + 5\ Br^- + 6\ H^+ \rightleftharpoons 3\ Br_2 + 3\ H_2O$

The colour of bromine is not suitable for identyfying the end of the titration. Therefore organic dyes such as methyl red or methyl orange are added. They are destroyed by bromine and the solution turns colourless.

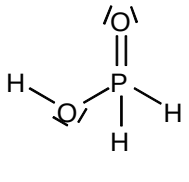
f) Arsenic(III) oxide is used as clarifying substance to remove remaining gases from the glass melt.

g) Diarsenic pentoxide (As_2O_5) and diarsenic tetraoxide (As_2O_4). They are available from the appropriate acids:

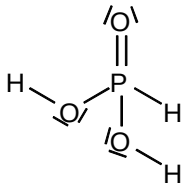
$2\ H_3AsO_4 \rightleftharpoons As_2O_5 + 3\ H_2O$

$H_3AsO_4 + H_3AsO_3 \rightleftharpoons As_2O_4 + 3\ H_2O$

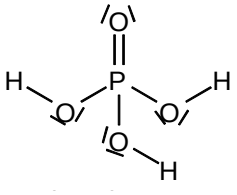
h) Phosphinic acid (H_3PO_2) may give off one, phosphorous acid (H_3PO_3) two and phosphoric acid three protons. In phosphinic acid and in phosphorous acid some of the hydrogen atoms are directly bonded to phosphorus and thus do not undergo an acidic reaction.



Phosphinic acid



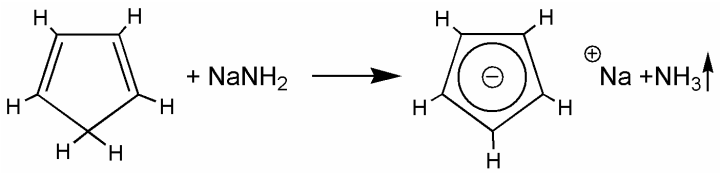
Phosphorous acid



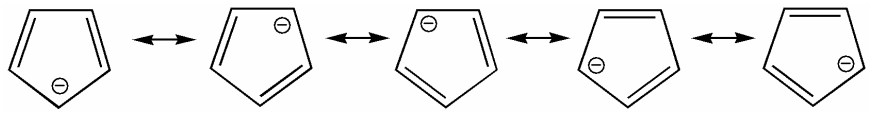
Phosphoric acid

Solution to problem 1-3

a)

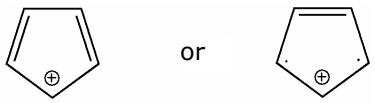


b)



c) The anion is planar and has a cyclic conjugated π-electron system with 4n+2 electrons (n = 1 following Hückel). It is aromatic and thus especially stable.
Note: There's nothing in the definition that says the number of atoms or the charge of the compound have any influence on aromaticity.

d)



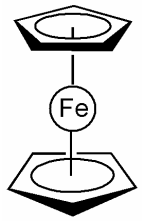
(Spektra show a diradical)

The cyclopentadienyl cation is very reactive. The anion is more stable.
Reason: With 4 π-electrons the cation is antiaromatic.

e) The acidity of the dicyano compound is higher.
Reason: The substituents withdraw electons from the ring (-I and –M effect respectively); the C-H bond is weakened and the resulting anion is stabilised.

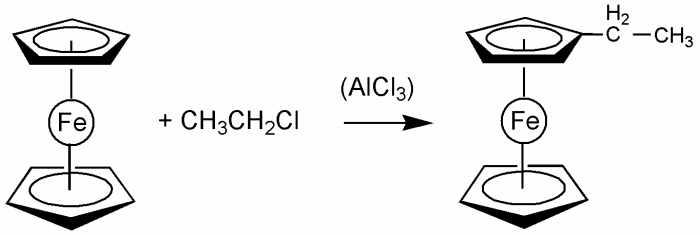
f) $FeX_2 + 2\ NaC_5H_5 \rightarrow (C_5H_5)_2Fe + 2\ NaX$ (X = halogen)

g) Ferrocene (analog to benzene)



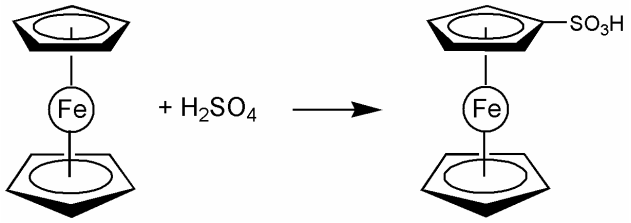
Sandwich structure

h) (1)



(Substitution is also possible at both Cp^- rings)

(2)



(Substitution is also possible at both Cp^- rings)

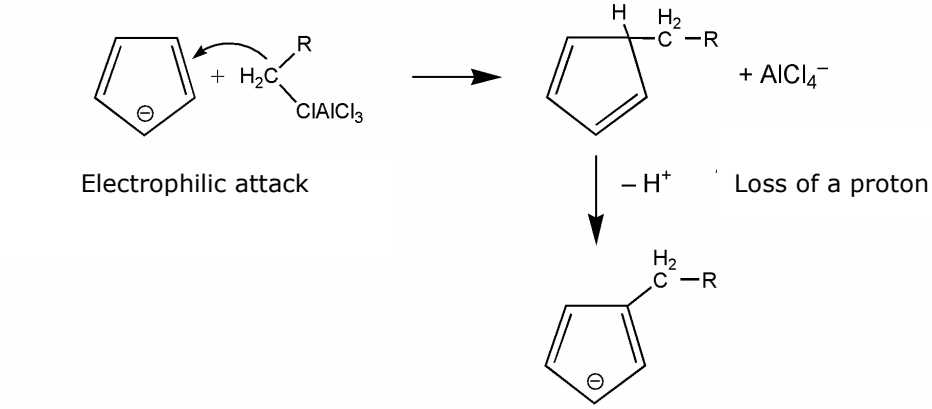
i) Type of reactions: elektrophilic aromatic substitution

(1) in this case: in accordance with Friedel-Crafts alkylation of benzene (R = CH_3)

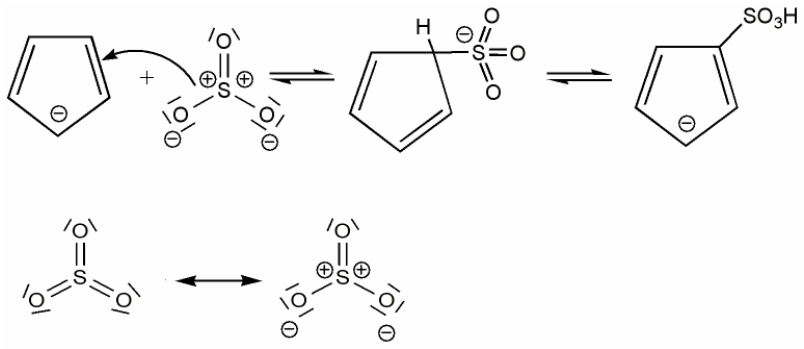
First step : Activation of the carbon atom of the alkyl halide

$RCH_2Cl + AlCl_3 \rightarrow RCH_2ClAlCl_3$ (or $RCH_2^+AlCl_4^-$)

Second step :



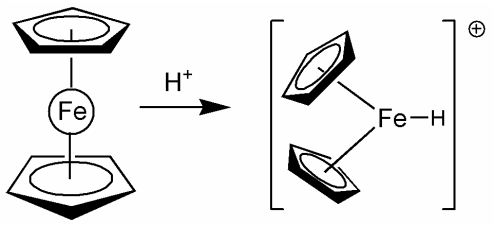
(2) in this case: in accordance with sulfonation of benzene:



The reactive electrophile is SO_3 from concentrated sulphuric acid.

The sulphur atom is strongly electrophil caused by the great electron-attracting effect of three oxygen atoms. It attacks the electron rich Cp ring directly.
Then the sulphonic-acid derivate forms by tranfer of a proton.

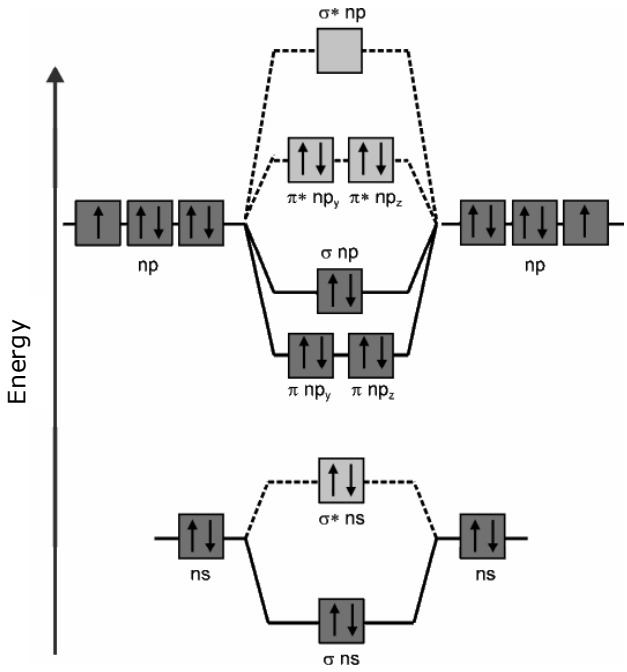
j) Protonation of ferrocene:



Answers Round 2

Solution to problem 2-1

a) The colour of the halogen molecules is the consequence of the electronic transition from the highest occupied molecular orbital (σp und πp*) to the lowest unoccupied one (σ*p). The difference in energy of these occupied and unoccupied orbitals decreases from fluorine to iodine. The result is a batho-chromic shift (shift to the red). The colour becomes more intensive.



b) At first the given equations are combined by elimination of $c(I_2 \cdot D)$ to form equation (3):

$$c(I_2 \cdot D) = \frac{\log \frac{I_0}{I}}{\varepsilon_0 \cdot d} \qquad (1)$$

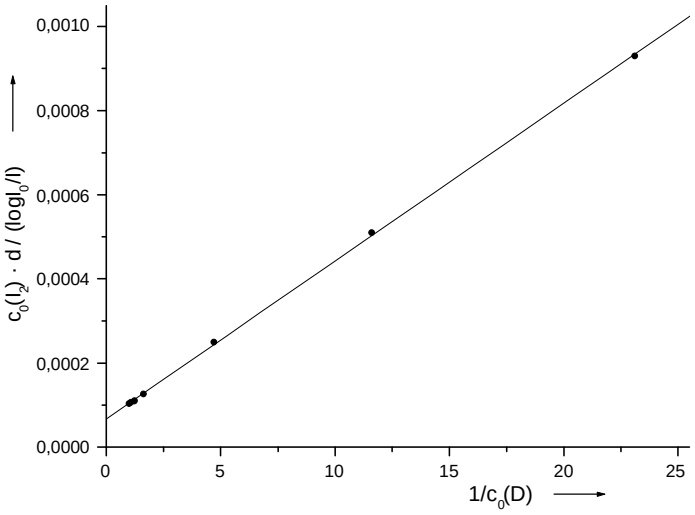
$$c(I_2 \cdot D) = \frac{c_0(D) \cdot K \cdot c_0(I_2)}{1 + c_0(D) \cdot K} \qquad (2)$$

$$\frac{\log \frac{I_0}{I}}{\varepsilon_0 \cdot d} = \frac{c_0(D) \cdot K \cdot c_0(I_2)}{1 + c_0(D) \cdot K} \qquad (3)$$

Thus the following equation can be derived: $\frac{c_0(I_2) \cdot d}{\log \frac{I_0}{I}} = \frac{1}{K \cdot \varepsilon_0} \cdot \frac{1}{c_0(D)} + \frac{1}{\varepsilon_0}$

If you plot $1/c_0(D)$ against the left expression of the equation above you get a straight line, the slope and intercept of which can be determined.

Benzene:

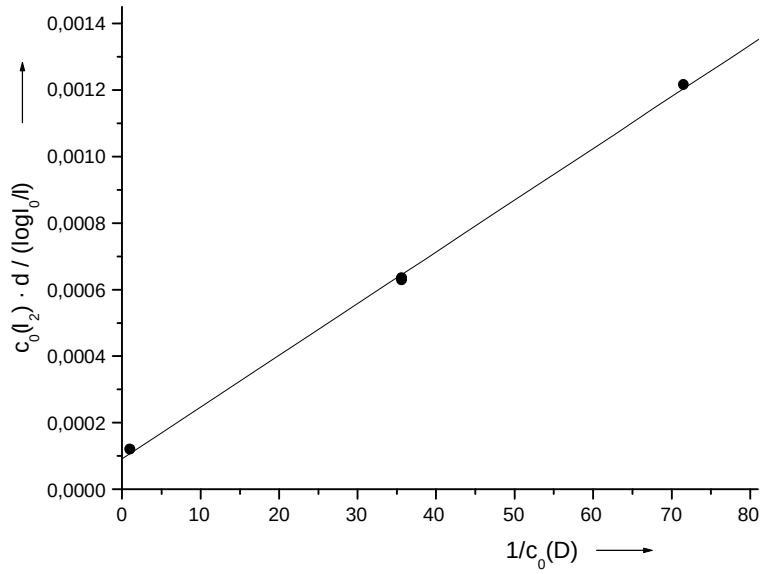


$$\frac{c_0(I_2)\cdot d}{\log\frac{I_0}{I}} = 3.76\cdot10^{-5}\cdot\frac{1}{c_0(D)} + 6.70\cdot10^{-5}$$

$$\Rightarrow \quad \frac{1}{\varepsilon_0} = 6.70\cdot10^{-5} \qquad \varepsilon_0 = 14925\ L\cdot mol^{-1}\cdot cm^{-1}$$

$$\text{and} \qquad \frac{1}{K\cdot\varepsilon_0} = \frac{1\cdot6.7\cdot10^{-5}}{K} = 3.76\cdot10^{-5} \qquad K = 1.78\ L\cdot mol^{-1}$$

Mesitylene:



$$\frac{c_0(I_2)\cdot d}{\log\frac{I_0}{I}} = 1.55\cdot10^{-5}\ \cdot\frac{1}{c_0(D)} + 9.14\cdot10^{-5}$$

$\Rightarrow \quad \frac{1}{\varepsilon_0} = 9.14\cdot10^{-5}$ $\qquad\qquad \varepsilon_0 = 10940\ L\cdot mol^{-1}\cdot cm^{-1}$

and $\frac{1}{K\cdot\varepsilon_0} = \frac{1\cdot 9.14\cdot10^{-5}}{K} = 1.55\cdot10^{-5}$ $\qquad\qquad K = 5.90\ L\cdot mol^{-1}$

The formation of the adduct of mesitylene should be favoured.

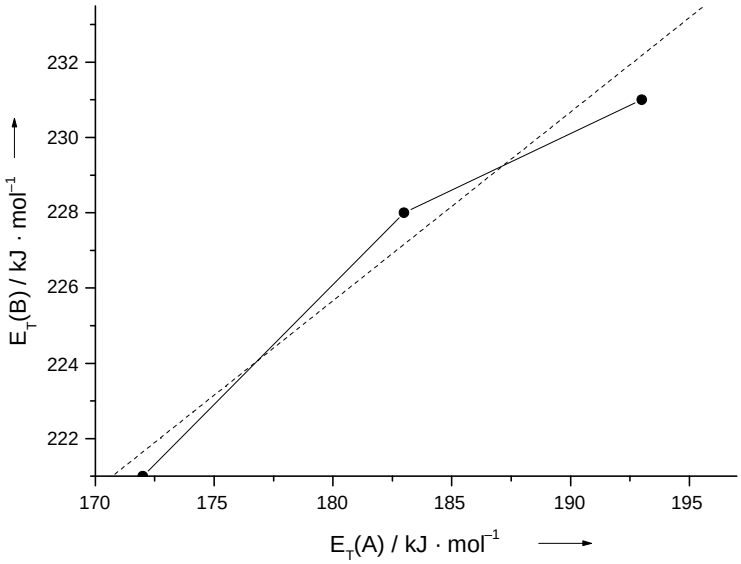
c) $E_T = h\cdot\nu_{max}\cdot N_A \qquad E_T = h\frac{c}{\lambda_{max}}\cdot N_A \qquad$ with $c = 3.00\cdot10^8\ ms^{-1}$

$E_T = 6.63\cdot10^{-34}\ J\cdot s\cdot\frac{3.00\cdot10^8\ ms^{-1}}{653\cdot10^{-9}\ m}\cdot\cdot 6.022\cdot10^{23}\ mol^{-1} \qquad \approx 183\ kJ\cdot mol^{-1}$

analogue:

Solvent	**E_T(A) in kJ·mol^{-1}**	**E_T(B) kJ·mol^{-1}**
Dimethyl formamide	183	228
Methylene chloride	172	221
Acetonitrile	193	231

d)



$E_T(B) = 139.2\ kJ\ mol^{-1} + 0.48\cdot E_T(A)$

e)

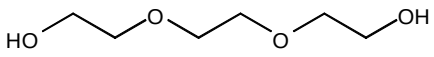
Solvent	λ_{max} in nm	$E_T(B)$ in kJ mol^{-1}	$E_T(A)$ in kJ mol^{-1}
Acetone	538	223	175
Benzene	578	207	141
n-Butyl ether	592	202	131
Trichloromethane	553	217	162
Dichloroethane	546	219	166
Diethyl ether	571	210	148
Dimethoxyethane	550	218	164
Dioxan	568	211	150
Tetrachloromethane	599	200	127
Tetrahydrofuran	555	216	160
Dimethyl formamide			183
Methylene chloride			172
Acetonitrile			193

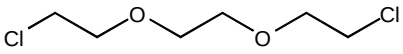
Solvents in order of increasing polarity:

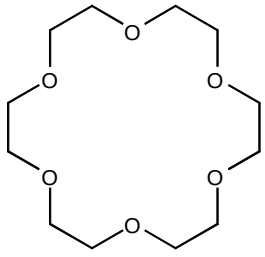
Tetrachloromethane - n-butyl ether – benzene – diethyl ether – dioxan – tetrahydro-furan – trichloromethane – dimethoxyethane – dichloroethane - methylene chloride – acetone – dimethyl formamide – acetonitrile

f) In different solvents the solubility of a substance may vary in a large range. Not all chemicals are soluble in all solvents. Thus you need to use different compounds.

g)

A  $C_6H_{14}O_4$, Triethylenglycol

B  $C_6H_{12}Cl_2O_2$, 1,2-bis(2-chloroethoxy)ethane

C  $C_{12}H_{24}O_6$, 1,4,7,10,13,16-Hexaoxacyclooctadecane

18-crown-6

h) The ionic compound potassium chloride dissolves in the unpolar solvent benzene. The crown ether complexes the potassium cation and enables the solution of the salt.

(The diameter of the cavity of the crown ether can be estimated to be 260 to 320 nm. That matches perfectly the ionic diameter of 266 nm.)

Solution to problem 2-2

a) The maximum conversion is obtained when the thermodynamical equilibrium is reached.

$$K = \frac{c(AcOEt)\cdot c(H_2O)}{c(AcOH)\cdot c(EtOH)} = \frac{k}{k'} \qquad K = 2.92$$

You can express all concentrations as functions of the conversion x of acetic acid:

$c(AcOEt) = x\cdot c_0(AcOH)$

$c(H_2O) = c_0(H_2O) + x\cdot c_0(AcOH)$

$c(AcOH) = (1 - x)\cdot c_0(AcOH)$

$c(EtOH) = c_0(EtOH) - x\cdot c_0(AcOH)$

$$K = \frac{x\cdot c_0(AcOH)\cdot [c_0H_2O) + x\cdot c_0(AcOH)]}{[c_0(AcOH) - x\cdot c_0(AcOH)]\cdot [c_0(EtOH) - x\cdot c_0(AcOH)]}$$

$$2.92 = \frac{x\cdot 4.17[16.1 + x\cdot 4.17]}{[4.17 - x\cdot 4.17]\cdot [10.9 - x\cdot 4.17]}$$

$$\Rightarrow \quad x^2 - 7.51\cdot x + 3.98 = 0$$

$(x_1 = 6.94) \qquad x_2 = 0.574$

Maximum conversion = 57.4 %

b) You have to calculate at first how long it will take to reach conversion of 37.5 % and how many production cycles are possible during one day.

To accomplish this the rate law has to be integrated. As in part a) all concentrations are expressed as functions of conversion x.

$$-\frac{dc(AcOH)}{dt} = \frac{dc(AcOEt)}{dt}$$

$$\frac{dc(AcOEt)}{dt} = \frac{d[x\cdot c_0(AcOH)]}{dt} = c_0(AcOH)\cdot \frac{dx}{dt}$$

$$-\frac{dc(AcOH)}{dt} = k\cdot c(AcOH)\cdot c(EtOH) - k'\cdot c(AcOEt)\cdot c(H_2O)$$

then

$$c_0(AcOH)\cdot \frac{dx}{dt} = k\cdot [c_0(AcOH) - x\cdot c_0(AcOH)]\cdot [c_0(EtOH) - x\cdot c_0(AcOH)]$$

$$- k'\cdot x\cdot c_0(AcOH)\cdot [c_0(H_2O) + x\cdot c_0(AcOH)]$$

$$\frac{dx}{dt} = k\cdot [1 - x]\cdot [c_0(EtOH) - x\cdot c_0(AcOH)] - k'\cdot x\cdot [c_0(H_2O) + x\cdot c_0(AcOH)]$$

$$\frac{dx}{dt} = 4.76\cdot 10^{-4}\ min^{-1}\cdot [1-x][10.9 - x\cdot 4.17] - 1.63\cdot 10^{-4}\ min^{-1}\cdot x\cdot [16.1 + x\cdot 4.17]$$

$$\Rightarrow \quad \frac{dx}{dt} = 1.31\cdot 10^{-3}\ min^{-1}\cdot (x^2 - 7.51x + 4.00)$$

$$\int_0^{0.375} \frac{dx}{x^2 - 7.51x + 4.00} = \int_0^{t} 1.31 \cdot 10^{-3}\ \text{min}^{-1}\ dt$$

The roots of the denominator are x_{01} = 6.93 und x_{02} = 0.577

$$\left| \frac{1}{6.93 - 0.577} \cdot (\ln|x - 6.93| - \ln|x - 0.577| \right|_0^{0.375} = 1.31 \cdot 10^{-3}\ \text{min}^{-1}\ t$$

$$0.548 - 0.391 = 1.31 \cdot 10^{-3}\ \text{min}^{-1}\ t$$

$$t = 120\ \text{min}$$

Time to reach a conversion of 37.5 % t = 120 min.

Together with discharging, cleaning and refilling the reactor you need approximately 145 minutes for one production cycle, so you can carry out (rounded) 10 cycles a day.

(The same number (rounded) is achieved for t = 115 min.)

In one cycle 2900 kg of ethyl acetate have to be produced, that are 32915 mol. As only 37.5% are converted you have to insert 87773 mol with a given concentration of 4.17 mol L^{-1}. This corresponds to 21.048 m^3.

The volume of the reactor has to be 21.05 m^3 at least.

c) As this reactor operates uninterrupted the concentrations of substances do not change in the course of time. Thus the input of AcOEt corresponds exactly to the amount of AcOEt that reacts, plus the output of AcOEt that leaves without reacting.

The incoming amount comes up to the stream of incoming volume (q_e) multiplied with the initial concentration c_e(AcOEt). The analogue is valid for the output. The amount that reacts can be calculated as the product of the volume of the reacting mixture (V) and the reaction rate (r).

$$q_e \cdot c_0 = r \cdot V + q_a \cdot c_a$$

As the reactor operates almost isochore the volume of incoming and outgoing streams are equal.

$$q = \frac{r \cdot V}{c_e - c_a}$$

c_e(AcOEt) = ½ ·0.8 mol/L = 0.4 mol L^{-1}

(Dilution by sodium-hydroxide solution!)

c_a(AcOEt) = c_e(AcOEt)·(1–x)

c_a(AcOEt) = 0.4 mol/L·(1 - 0.8) = 0.08 mol L^{-1}

c_e(NaOH) = ½ · 1 mol/L = 0.5 mol/L (Dilution by ester)

c_a(NaOH) = c_e(NaOH) – c_e(AcOEt)·x

c_a(NaOH) = 0.5 mo./L - 0.4 mol/L·0.8 = 0.18 mol L^{-1}

$r = k \cdot c(AcOEt) \cdot c(NaOH)$ $\quad r = 4.738 \cdot 0.08 \cdot 0.18$ mol L^{-1} min^{-1}

$r = 0.0682$ mol L^{-1} min^{-1}

$\Rightarrow \quad q = \frac{r \cdot V}{c_e - c_a}$ $\qquad q = \frac{0.0682 \cdot 40\ L min^{-1}}{0.4 - 0.08}$ $\qquad q = 8.525$ L min^{-1}

q stand for the total stream. For the special streams of ethyl acetate and sodium-hydroxide solution you get 4.26 L min^{-1} each.

d) The necessary surface (O) of the immersion cooler depends on its thermal conductivity (W) and the difference between the temperatures of cooling water and reactor content.

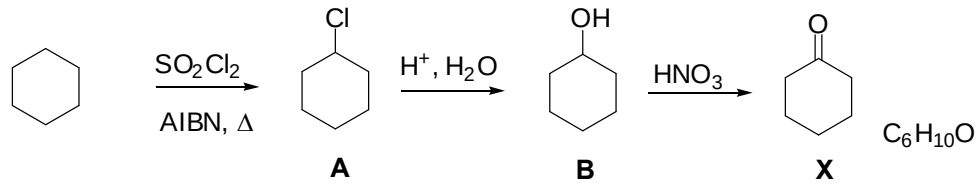
$$O = \frac{Q}{W(T_{reactor\ \ content} - T_{cooling\ \ water})}$$

$$O = \frac{24.92\ kJ\ min^{-1}}{35.65\ kJ\ m^{-2}\ min^{-1} K^{-1}\ (298\ K - 291\ K)} = 0.100\ m^2$$

The surface of the cooler has to be 0.100 m^2.

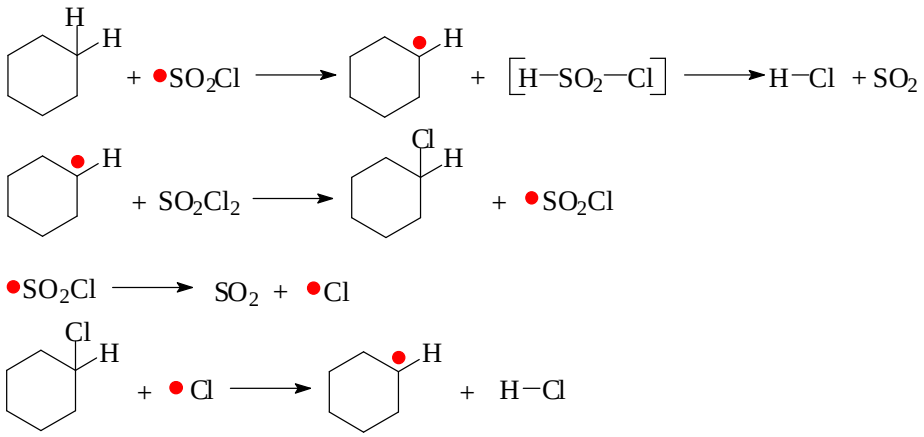
Solution to problem 2-3

a) 1. step: radical chlorination to chlorocyclohexane **A**
2. step : hydrolysis in water to cyclohexanol **B**
3. step: oxidation with diluted nitric acid to cyclohexanone **X**



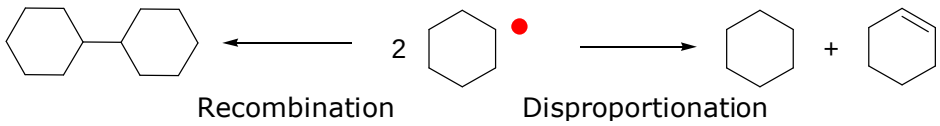
b) Mechanism of radical chlorination:

- Initation reaction: Decompositon of AIBN into two radicals, reaction with SO_2Cl_2 (Cl cleaves off) leads to $\bullet SO_2Cl$, which is the cyc lohexane attacking radical.
- Chain propagation:

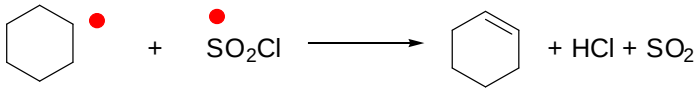


Note: In this reaction chlorine atoms are **not** attacking radicals.

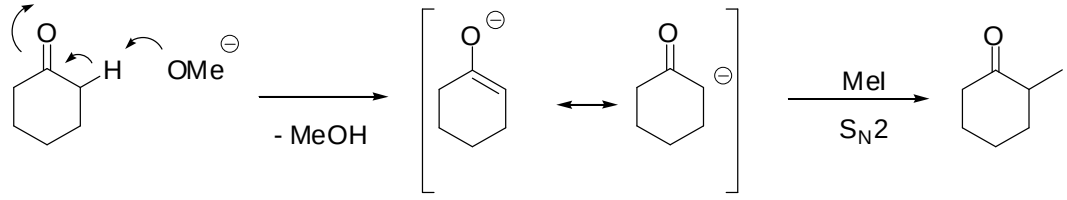
- Chain termination by recombination or by disproportionation of radicals
  e.g.



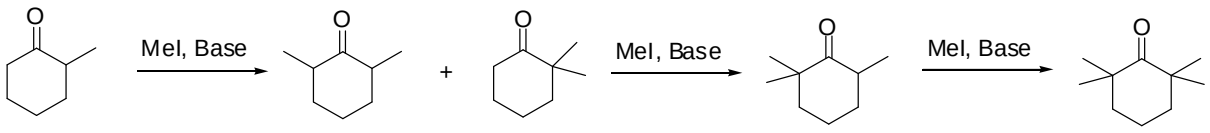
or



c) If cyclohexanone reacts with alkylating agents (MeI) in the presence of a base alkylation in α-position takes place. This reaction proceeds forming a resonace-stabilized anion (enolate anion) in between. It is a good nucleophile and reacts with MeI in a classical S_N2-reaction to form the product.



Problem: polyalkylation will take place as the product itself may undergo deprotonation and alkylation again to get a mixture of mono- and polyalkylated products. Thus the reaction of ketones with an alkylating agent in the presence of bases makes no sense if you want to get a monoalkylated derivate.

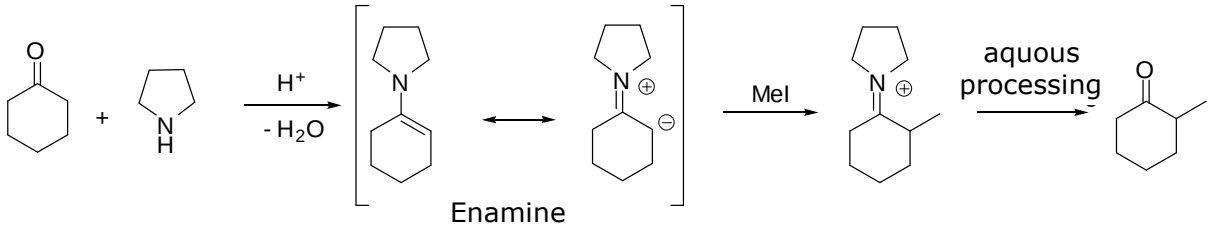


d) In order to prepare the shown derivates of cyclohexanone you have to find reaction conditions which lead selectively to the main product.

D1: 2-Methyl cyclohexanone: Selective monomethylation using enamine synthesis.

A methyl group shall be introduced in α-position in a way that anew methylation of the product is not possible. In this case enamines proved to be applicable.

The conversion of a ketone with a secondary amine, e.g. pyrrolidine, leads to the formation of an enamine. This is similar to the enolate anion (but a little bit weaker) a good nucleophile, that reacts with alkylating agents as MeI in a S_N2-reaction.
The product itself, an iminium ion, is no longer a nucleophile, thus no polyalkylation happens. In the following aqueous processing the imidium ion is hydrolized and you get the monoalkylated ketone.

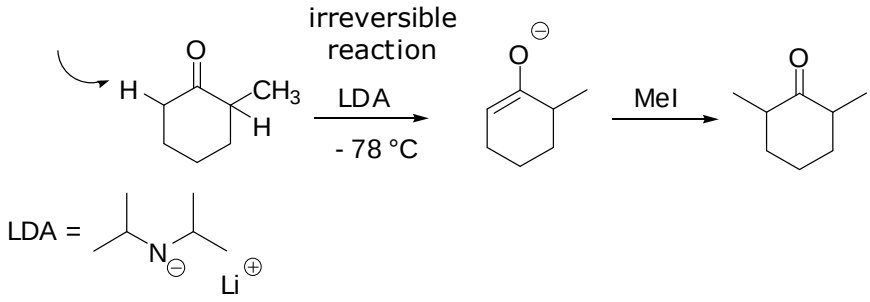


Enamine

Instead of pyrrolidine you may also use other secondary amines, such as piperidine and morpholine.

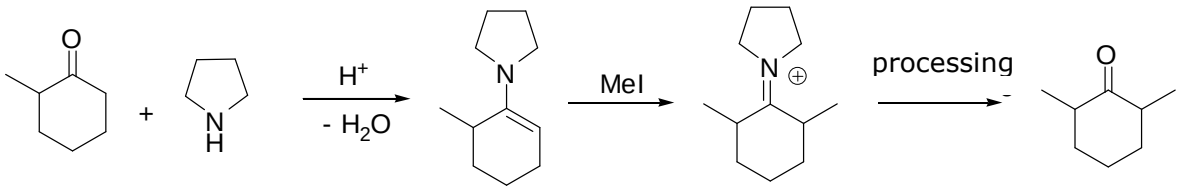
D2: Selective α,α'-dimethylation: kinetic favoured formation of enolate.

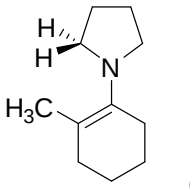
Starting with monomethyl cyclohexanone (D 1) you may prepare α,α'-dimethyl cyclohexanone. Therefore you have to take care that the formation of the enolate occurs on the less substituted side. This can be obtained under so called kinetic conditions by using a strong, bulky base (such as LDA) at deep temperatures.



bulky, sterically demanding base
preferably deprotonizing at the most accessible place

There is an alternative which is for the reactant to form an enamine again and then to alkylate it. It is easier to remove the hydrogen from the carbon which has not have the methyl group attached simply because these protons are less sterically hindered.

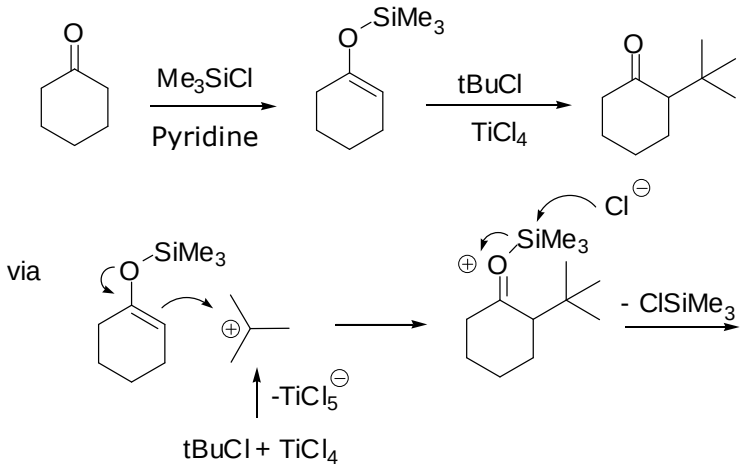




does not form because of steric hindrance

D3: Preparation of tert.-butylcyclohexanone:
Alkylation of a silylenol ether

In the reactions above the alkylation of enolates and enamines takes place in an S_N2 reaction. It is not possible to introduce a t-butyl group in this way because the large methyl groups prevent the nucleophile approaching.
To insert a t-alkyl halide you have to provide reaction conditions which allow an S_N1 mechanism, what cannot be done by the formation of enolates and enamines or other strongly nucleophilic compounds. It can be done by using R_3SiCl to form a silylenol ether (as an equivalent to the enolate) shown below for example with an $SiMe_3$ ether but other SiR_3 groups are also possible.
At first the ketone is transformed into a silenyl ether, which reacts with t-butyl bromide in the presence of a Lewis acid.



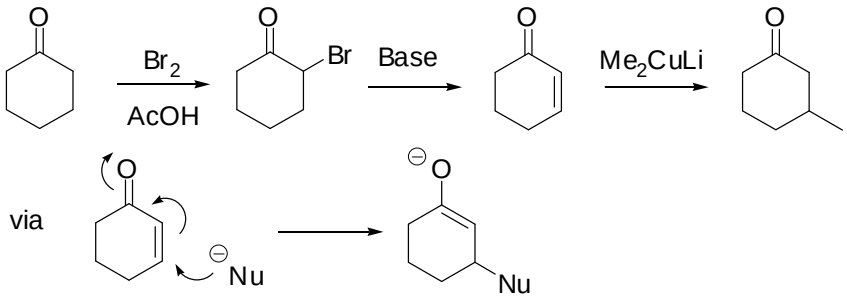
Note: There exist more alternatives, e.g. $FeCl_3$ and $AlCl_3$ as Lewis acids as well as other alkylating agents t-BuX. However, a reaction in an aqueous solution with t-BuOH in the presence of mineral acids does not lead to the requested result as silylenol ether hydrolizes. You have to work in a medium free from water.

D4: Preparation of 3-Methyl cyclohexanone: Michael-Addition

You cannot prepare 3-methyl cyclohexanone by direct alkylation of cyclohexanone. None of the ways shown above will be sucessfull, as only the hydrogen atoms in α position are acidic.

Alkyl groups in β position to a carbonyl group may be introduced by Michael-addition. At first cyclohexanone has to be transformed into cyclohexenone, a Michael system. This can be done by halogenating in α position followed by elimination. In a Michael-addition you have to aware that have to apply „soft" nucleophiles in order to avoid a 1,2-addition to the carbonyl group. Best suited are cuprates.

Example:



Answers Round 2

Notes: Other halogenating agents (NBS, NCS etc.) are usefull too, but you have to halogenate in an acidic medium. Under basic conditions the halogenation can not be established as you do not get the mono- but the dibromide. Because of the -I effect the acidity of the remaining hydrogen atom is increased in such an extend that the following bromation is even faster and more easy going.

Reactions with Grignard agents instead of cuprates lead to a mixture of 1,2 -and 1,4 - addition but are principally possible.

The reaction with lithium compounds such as MeLi are not suitable, they react exclusively with the carbonyl group (1,2-addition).

Answers Round 3 Test 1

Solution to problem 3-1

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

Solution to problem 3-2

a) M = metal, X = M(M), n = n(MCl_y)

$MCl_y + \frac{y}{4} O_2 \longrightarrow MO_{y/2} + \frac{y}{2} Cl_2$

(i) $n \cdot X + n \cdot y \cdot 35.45$ g/mol $= 1.004$ g

(ii) $n \cdot X + n \cdot y \cdot 0.5 \cdot 16.00$ g/mol $= 0.594$ g /-

$n \cdot y \cdot 27.45$ g/mol $= 0.410$ g $n = \frac{0{,}410}{27.45 \cdot y}$ mol

(i) $\Rightarrow$ $X = 1.004 \text{ g}/n - y \cdot 35.45$ g/mol

$X = y \cdot (1.004 \cdot \frac{27.45}{0.410} - 35.45)$ g/mol

y	1	2	3	4
X in g/mol	31.77	63.54	95.31	127.08
M	-	Cu	Mo	Te

y = 2 $\Rightarrow$ M = Cu $2\,CuCl_2 + O_2 \longrightarrow 2\,CuO + 2\,Cl_2$

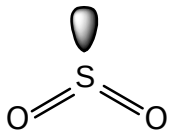
(y = 3 $\Rightarrow$ M = Mo $4\,MoCl_3 + 3\,O_2 \longrightarrow 2\,Mo_2O_3 + 6\,Cl_2$

but under these conditions the persistent MoO_3 is formed thus molybdenum does not have to be considered. This knowledge is not expected.)

y = 4 $\Rightarrow$ M = Te $TeCl_4 + O_2 \longrightarrow TeO_2 + 2\,Cl_2$

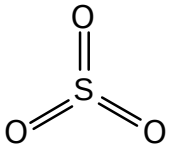
b) **SO_2:**

bent



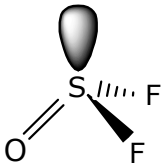
SO_3:

trigonal planar



SOF_2:

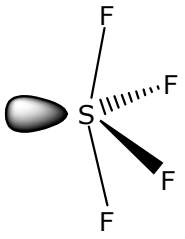
trigonal pyramidal



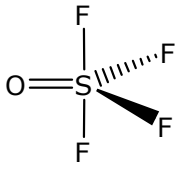
SO_4^{2-}:

tetrahedral with S in the centre and oxygen with a double bond at the corners

SF_4:
irregular tetrahedron (angle FSF equatorial 101°, axial 173°)



SOF_4:
irregular trigonal bipyramidal (angle FSF equatorial 110°, axial 178.4°)



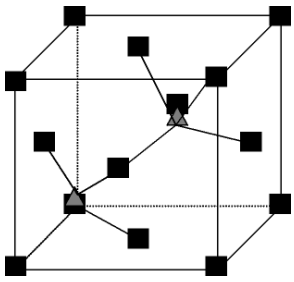
SF_6: octahedral with S in the centre and fluorine at the corners.

Solution to problem 3-3

a) $2\ MgH_2 + Ni \longrightarrow Mg_2NiH_4$ Mg: +II Ni: 0 H: -I

b) mass content = $\frac{4 \cdot 1.008\ g/mol}{(2 \cdot 24.31 + 58.69 + 4 \cdot 1.008)\ g/mol} \cdot 100\% =$ 3.621%

c)



Ni: ■

Mg: ▲

8 tetrahedral holes and 1 + ¼ · 12 = 4 octahedreal holes

d) number of nickel atoms per unit cell = 8· ⅛ + 6· ½ = 4

⇒ 4 Mg_2NiH_4 units per unit cell

e) Ni(0): 10 e^- as well as 4 ligands H^- with 2 e^- each (dyed grey)

[Ar] ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓

3d 4s 4p

sp^3-hybridization ⇒ tetraedral arrangement

f) Bragg condition: $n \cdot \lambda = 2d \cdot \sin(\vartheta)$

with n = 1, λ = 1.542 Å, ϑ = 11.92°

$d = \frac{1 \cdot 1.542 \cdot 10^{-10} m}{2 \cdot \sin(11.92°)}$ $d = 3.733 \cdot 10^{-10}$ m

d is the layer spacing, 3·d the length of the solid diagonal of the cell.

$a_0 \cdot \sqrt{3} = 3 \cdot d$ $a_0 = \sqrt{3} \cdot 3.733 \cdot 10^{-10}$ m $a_0 = 6.465 \cdot 10^{-10}$ m

g) $\rho = m/V = \frac{4 \cdot M(Mg_2NiH_4)}{N_A \cdot a_0^3}$ $\qquad \rho = \frac{4 \cdot 111.34\ g/mol}{6.022 \cdot 10^{23} mol^{-1} \cdot (6.465 \cdot 10^{-8} cm)^3}$

$\rho = 2.737\ g/cm^3$

h) $f = \frac{\text{mass of hydrogen in } 1\ cm^3 \text{ of hydride}}{\text{masse of hydrogen in } 1\ cm^3 \text{ of fluid hydrogen}} = \frac{2.737\ g/cm^3 \cdot 3.622/100}{0.0708 g/cm^3} = 1.40$

In the same volume (e.g. 1 cm^3) the metal hydride stores the 1.4 fold mass of hydrogen.

i) m(hydrogen in hydride)= $\rho \cdot$(mass content) = 2.737 $g/cm^3 \cdot 0.03622 = 0.0991\ g/cm^3$

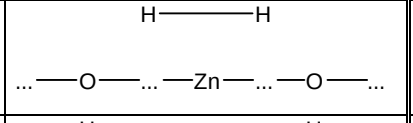
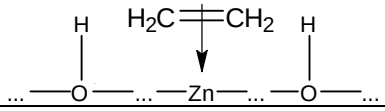
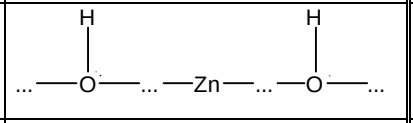
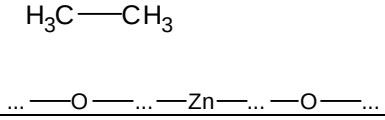
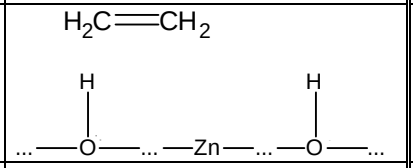
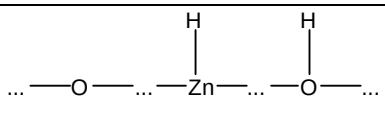
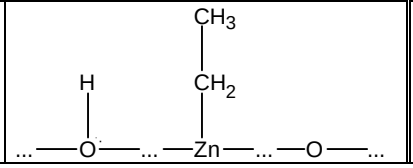
$n(H_2 \text{ im hydride}) = m/M = \frac{0.0991\ g/cm^3}{2 \cdot 1.008\ g/mol} = 0.0492\ mol/cm^3$

$p = nRT/V \qquad p = \frac{0.0492\ mol \cdot 8.314\ Jmol^{-1}K^{-1} \cdot 293\ K}{10^{-6}\ m^3}$

$p = 1199 \cdot 10^5\ Pa$

Solution to problem 3-4

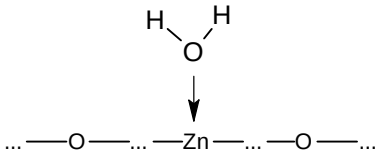
a)

No.		No.	
1		5	
3		7	
4		2	
6			

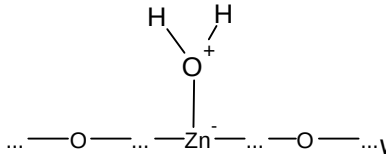
b) The hydrogenation of the adsorbed intermediate is the slowest step of the reaction. This is the reason why the concentration of the intermediate, or in this case the fraction of surface sites that are occupied by it, has to be part of the rate equation

$\Rightarrow$ (4) .

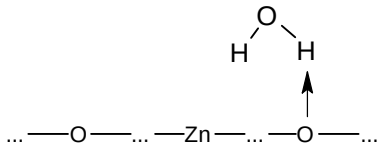
c) Four answers can be accepted:



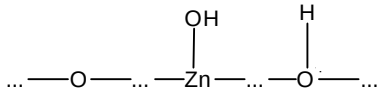
showing some kind of complex, or



with a bond between the zinc and the oxygen atoms

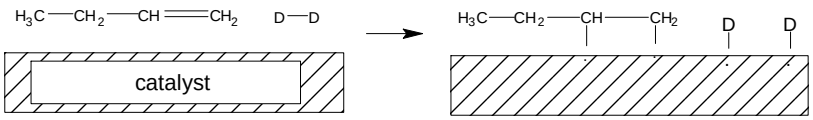


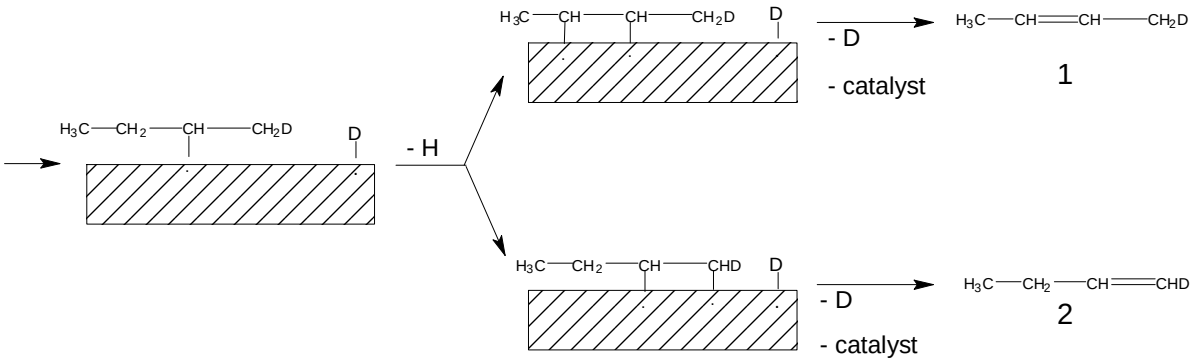
showing a hydrogen bond



showing the formation of "zinc hydroxide" and OH-groups on the catalyst surface.

d)





Solution to problem 3-5

a) Dissolving alum hydrated Al^{3+} ions are formed:

$$\underset{c_0 - x}{Al(H_2O)_6^{3+}} + H_2O \rightleftharpoons \underset{x}{[Al(H_2O)_5(OH)]^{2+}} + \underset{x}{H_3O^+}$$

b) 4 g/dm³ of $KAl(SO_4)_2 \cdot 12H_2O$ (M = 474.4 g/mol) $\triangleq$ $c_0 = 8.43 \cdot 10^{-3}$ mol/dm³ Al^{3+}

$K_a = \frac{x^2}{c_0 - x}$ $\qquad 10^{-4.85} = \frac{x^2}{8.432 \cdot 10^{-3} - x}$

$x^2 + x \cdot 1.41 \cdot 10^{-5} - 1.19 \cdot 10^{-7} = 0$

$x_{01} = 3.38 \cdot 10^{-4}$ $\qquad (x_{02} = -3.52 \cdot 10^{-4})$

$pH = - \lg 3.38 \cdot 10^{-4}$ $\qquad pH = 3.47$

c) $HIn + H_2O \rightleftharpoons In^- + H_3O^+$ $\qquad K_a = \frac{c(In^-) \cdot c(H_3O^+)}{c(HIn)}$

You may take for granted that at pH = 2 only HIn, at pH = 12 only In^- are present. At pH = 7.4 let x and y be the fractions of HIn and In^-, respectively, of c_0, the original concentration of the indicator:

$c(HIn) = x \cdot c_0$ $\quad c(In^-) = y \cdot c_0$ $\qquad$ with $\quad x + y = 1$

$0.64 = c(HIn) \cdot 0.9 + c(In^-) \cdot 0.1$ $\qquad 0{,}64 = x \cdot c_0 \cdot 0.9 + y \cdot c_0 \cdot 0.1$

$\Rightarrow x = 0.675 c(HIn) = 0.675 \cdot c_o$ $\qquad y = 0.325$ $\quad c(In^-) = 0.325 \cdot c_0$

$K_a = \frac{0.325\, c_0 \cdot 10^{-7.4}}{0.675\, c_0}$ $\qquad K_a = 1.92 \cdot 10^{-8}$

Solution to problem 3-6

(1) Aim: Determination of the concentration of the sodium hydroxid solution.

$H_3O^+ + OH^- \longrightarrow 2\ H_2O$ $\qquad (HCl + NaOH) \longrightarrow NaCl + H_2O)$

$c(HCl) \cdot V(HCl) = c(NaOH) \cdot V(NaOH)$ $\qquad 0.1000$ mol/dm³ $\cdot 20.80 = c(NaOH) \cdot 20.00$

$c(NaOH) = 0.1040$ mol/dm³

(2) Aim: Determination of the concentration of the potassium permanganate solution.

$5\ Fe^{2+} + MnO_4^- + 8\ H_3O^+ \longrightarrow 5\ Fe^{3+} + Mn^{2+} + 12\ H_2O$

$c(Fe(NH_4)_2(SO_4)_2 \cdot V(Fe(NH_4)_2(SO_4)_2 = 5 \cdot c(KMnO_4) \cdot V(KMnO_4)$

0.1100 mol/dm³ $\cdot 10.00 = 12.20 \cdot 5 \cdot c(KMnO_4)$ $\qquad c(KMnO_4) = 0.01803$ mol/dm³

(3) Aim: Determination of the concentration of oxalic acid.

At this specific transition interval oxalate ions are existent.

$(COOH)_2 + 2\ OH^- \longrightarrow {}^-OOC\text{-}COO^- + 2\ H_2O$

$2 \cdot c((COOH)_2) \cdot V(mixture) = c(NaOH) \cdot V(NaOH)$

$2 \cdot c((COOH)_2) \cdot 10.00 = 0.1040$ mol/dm³ $\cdot 17.30$ $\qquad c((COOH)_2) = 0.08996$ mol/dm³

(4) Aim: Determination of the total amount of oxalate ($c((COOH)_2)$ + $c(^-OOC\text{-}COO^-)$)

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

$5 \cdot c(MnO_4^-) \cdot V(MnO_4^-) = 2 \cdot c(C_2O_4^{2-}) \cdot V(\text{mixture})$

$5 \cdot 0.01803\ mol/dm^3 \cdot 23.35 = 2 \cdot c(C_2O_4^{2-}) \cdot 5.00$ $\quad c(C_2O_4^{2-}) = 0.2105\ mol/dm^3$

m(oxalic acid) = n(oxalic acid)·M(oxalic acid) = c(oxalic acid)·V(total)·M(oxalic acid)

$m(\text{oxalic acid}) = 0.08996\ mol/dm^3 \cdot 0.1\ dm^3 \cdot 90.04\ g/mol = 0.810\ g$ 32.4%

c(sodium oxalate) = c(total oxalate) - c(Oxalic acid) = (0.2105 - 0.08996) mol/dm^3

$m(\text{sodium oxalate}) = 0.12054 \cdot 0.1 \cdot 134.02\ g = 1.615\ g$ 64.6%

$m(\text{impurity}) = (2.500 - 0.810 - 1.615)\ g = 0.075\ g$ 3.0 %

Solution to problem 3-7

a) $U_1 = 0.8\ V - (0.8\ V + \frac{RT}{nF} \cdot \ln 0{,}1) - \frac{RT}{nF} \cdot \ln 0{,}1 = 0.065\ V$

$U_2 = -\frac{RT}{nF} \cdot \ln 0{,}01 = -\frac{RT}{nF} \cdot \ln (0{,}1)^2 = 2 \cdot (-\frac{RT}{nF} \cdot \ln 0{,}1) = 2 \cdot 0.065\ V = 0.130\ V$

b) The potential of a half-cell is described by the Nernst equation:

$E = E^0 + \frac{RT}{nF} \cdot \ln \frac{c(Ox)}{c(Red)}$

$U = E(\text{Kathode}) - E(\text{Anode})$ $\quad E = E^0 + R \cdot T \cdot F^{-1} \cdot \ln[(c(Ag^+)/(1\ mol/dm^3)]$

$U_1 = 0.800\ V + R \cdot T \cdot F^{-1} \cdot \ln 0.01 - 0.800\ V - R \cdot T \cdot F^{-1} \cdot \ln x$

$U_1 = \frac{RT}{F} \cdot \ln \frac{0.01}{x}$ $\quad 0.170\ V = \frac{8.314 \cdot 298.15}{96485} V \cdot \ln \frac{0.01}{x}$

$x = 1.337 \cdot 10^{-5}$ $\quad c(Ag^+ \text{ in the saturated solution}) = 1.337 \cdot 10^{-5}\ mol/L$

with $c(Ag^+) = c(Cl^-)$

$K_{sp} = (1.337 \cdot 10^{-5})^2$ $\quad K_{sp} = 1.788 \cdot 10^{-10}$

c) For the right cell of (II): $\quad E(AgCl) = 0.8\ V + R \cdot T \cdot F^{-1} \cdot \ln \sqrt{1.800 \cdot 10^{-10}}$

$E(AgCl) = 0.512\ V$

Es ist $U = E(AgCl) - E(Ag_n . Ag^+)$ and

$E(Ag_n/Ag^+) = E^0(Ag_n/Ag^+) + R \cdot T \cdot F^{-1} \cdot \ln(0.01)$

<u>Ag_{10}:</u> $\quad E(Ag_{10}/Ag^+) = 0.512\ V - 0.430\ V = 0.082\ V$

$E^0(Ag_{10}/Ag^+) = 0.082\ V - R \cdot T \cdot F^{-1} \cdot \ln 0.01$ $\quad E^0(Ag_{10}/Ag^+) = 0.200\ V$

<u>Ag_5:</u> $\quad E(Ag_5/Ag^+) = 0.512\ V - 1.030V = -0.518\ V$

$E^0(Ag_5/Ag^+)) = -0.518\ V - R \cdot T \cdot F^{-1} \cdot \ln 0.01$ $\quad E^0(Ag_5/Ag^+) = -0.400\ V$

d) $E(H_2/2H^+) = R \cdot T \cdot F^{-1} \cdot \ln(10^{-5})$ $\quad E(H_2/2H^+) = -0.269\ V$

$E^0(Ag_{10}/Ag^+)$= 0.200 V > $E(H_2/2H^+)$ = - 0.269 V > $E^0(Ag_5/Ag^+)$)=-0.400 V

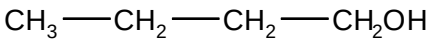
Ag_{10} clusters: no reaction takes place.

The standard potential of the Ag_5 clusters is lower than the standard potential of hydrogen. Thus, hydronium ions will be reduced to hydrogen while Ag_5 clusters (metallic silver) are oxidized into silver ions: The Ag-clusters dissolve.
After some time, silver ions present in the solution can also be reduced to metallic bulk silver. Under this condition, this reduction will preferably take place, because the electrochemical potential is even higher than that of the hydronium ion reduction.

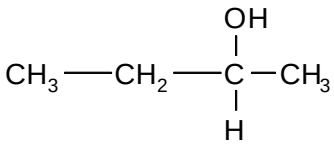
Solution to problem 3-8

a) b)

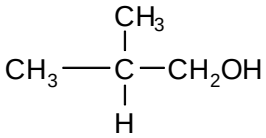
Alcohol



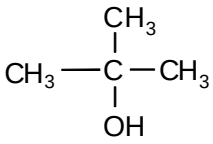
Butane-1-ol



Enantiomers:
2-R-Butanole
2-S-Butanole

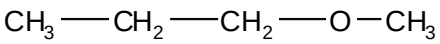


2-Methyl-1-propanole

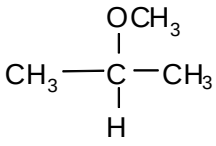


2-Methyl-2-propanole

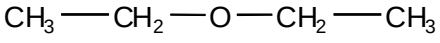
Ether



Methylpropyl ether



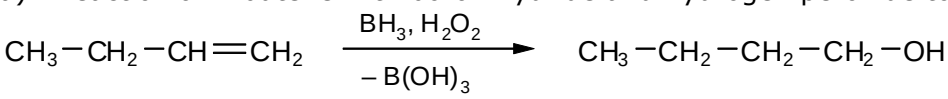
Methylisopropyl ether



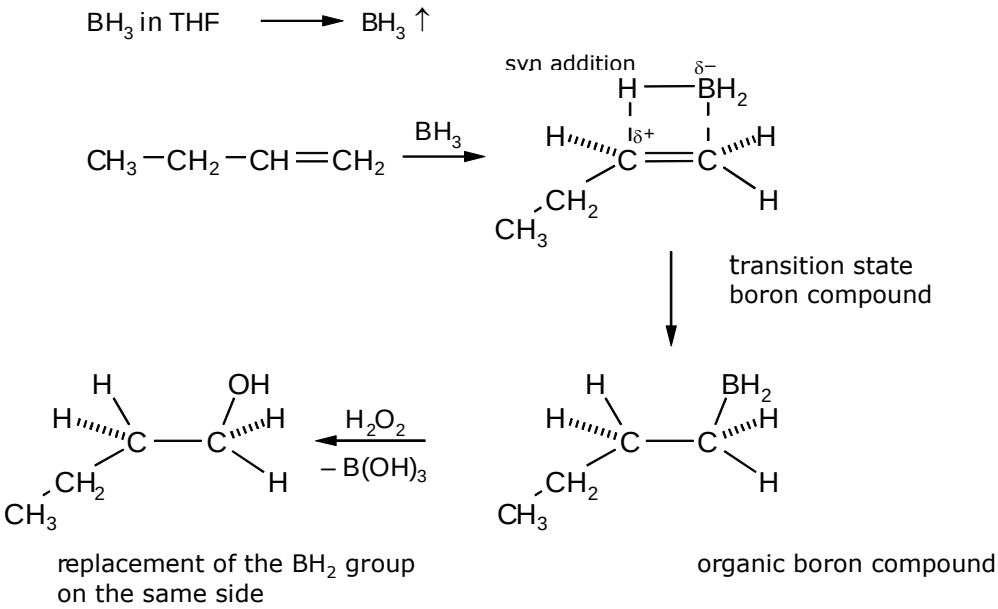
Diethyl ether

Solution to problem 3-9

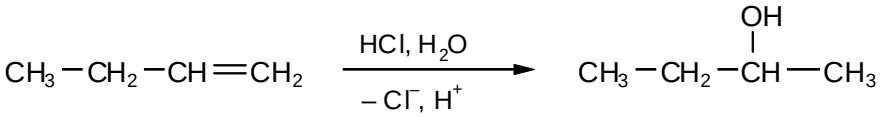
a) Reaction of 1-butene with boron hydride and hydrogen peroxide to form butane-1-ol



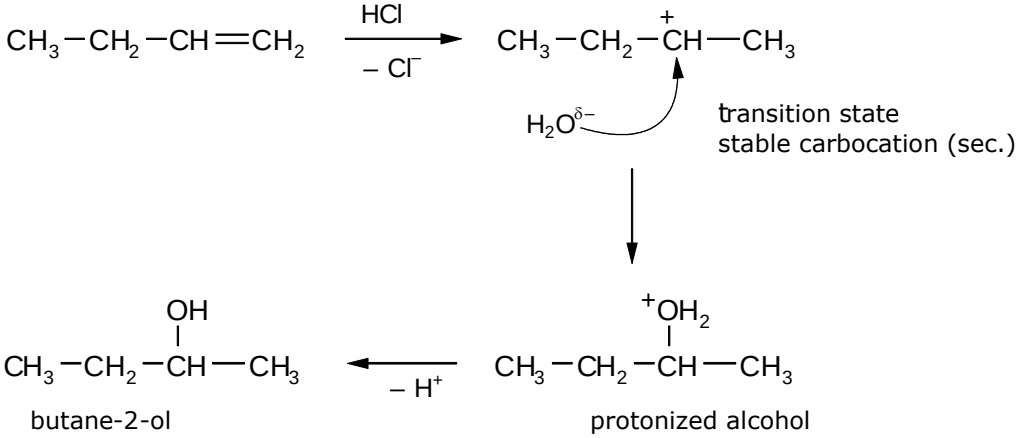
b) Reachtion mechanism: Anti-Markownikoff-addition of water by addtion of boron hydrogen first followed by oxidation.



c)



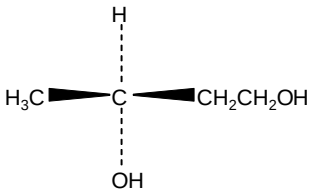
d) Markownikoff-addition of HCl and water



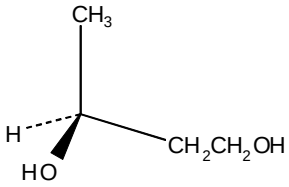
Remark: Using potassium permangante as an oxidizing agent leads to 1,2-diols.

Solution to problem 3-10

a)



or



b) S-3-Hydroxybutane-1-ol or S-1,3-Dihydroxybutane

c) B and D are identical to A, C is not.

d) Name of C: R-3-Hydroxybutane-1-ol. A and C are enantiomers.

Answers Round 3 test 2

Solution to problem 3-11

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

Solution to problem 3-12

a) A) $Ca(s) + 2\ H_2O(l) \longrightarrow Ca^{2+}(aq) + 2\ OH^-(aq) + H_2(g)$

B) $Pb^{2+}(aq) + 2\ Ch_3COO^-(aq) + 2\ H^+(aq) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2\ CH_3COOH(aq)$

C) $MnO_2(s) + 4\ H^+(aq) + 2\ Cl^-(aq) \longrightarrow Mn^{2+}(aq) + 2\ H_2O(l) + Cl_2(g)$

D) $NaCN(s) + H_2O(l) \longrightarrow Na^+(aq) + HCN(aq) + OH^-(aq)$

E) $3\ Ag(s) + 4\ H^+(aq) + NO_3^-(aq) \longrightarrow 3\ Ag^+(aq) + NO(g) + 2\ H_2O(l)$

F) $[Al(H_2O)_6]^{3+}(aq) + 6\ OH^-(aq) \longrightarrow [Al(OH)_6]^{3-}(aq) + 6\ H_2O(l)$

b)

(i) In an aqueous solution $CoCl_2$ and $Co(CH_3COO)_2$ form ions almost to the entire extend. Co^{2+} and Cl^- do not react further, even CH_3COO^- reacts only in very small amounts to form CH_3COOH ($\approx 7{,}6 \cdot 10^{-3}$ %). In doing so OH^- ions are generated $\Rightarrow$ high conductivity.

In an aqueous solution H_2S exists mainly as molecules which are not protolysed and do not give reason to conductivity.

(ii)-(iv) <u>1. solution:</u>

$Co^{2+}(aq) + S^{2-}(aq) \longrightarrow CoS(s)$

and $HS^-(aq) + H_2O(l) \longrightarrow S^{2-}(aq) + H_3O^+(aq)$

$H_2S(aq) + H_2O(l) \longrightarrow HS^-(aq) + H_3O^+(aq)$,

Colour change: sligthly pink [$Co^{2+}(aq)$] to black [$CoS(s)$].

The precipitation of one Co^{2+} ion leads to the formation of 2 H_3O^+ ions which lead to a relatively high conductivity.

<u>2. solution:</u>

$Co^{2+}(aq) + S^{2-}(aq) \longrightarrow CoS(s)$

and $HS^-(aq) + H_2O(l) \longrightarrow S^{2-}(aq) + H_3O^+(aq)$

$H_2S(aq) + H_2O(l) \longrightarrow HS^-(aq) + H_3O^+(aq)$ (see solution 1)

Colour change: sligthly pink [$Co^{2+}(aq)$] to black [$CoS(s)$].

The precipitation of one Co^{2+} ion leads to the formation of 2 H_3O^+ ions but the react with CH_3COO^- ions to form uncharged molecules:

$CH_3COO^-(aq) + H_3O^+(aq) \longrightarrow CH_3COOH(aq) + H_2O(l)$

$\Rightarrow$ relatively small conductivity.

Solution to problem 3-13

a) $V(H_2O) = V(CO_2)$ $\Rightarrow$ $n(H_2O) = n(CO_2)$ etwa $n(H_2O) = 1$ mol

n(products) = 2 mol $\Rightarrow$ n(reactants) = 2 mol, existing of

<u>possibility 1:</u> 1 mol of O_2 and 1 mol of a compound containng 1 mol of C, 2 mol of H and 1 mol of O. $\Rightarrow$ **X = CH_2O**, formaldehyde (methanal)

$$O_2 + CH_2O \longrightarrow 2\ H_2O + 2\ CO_2$$

<u>possibility 2:</u> 1.5 mol of O_2 and 0.5 mol of a compound with 2 mol Of C and 4 mol of H per mol $\Rightarrow$ X = C_2H_4, ethene

$$3\ O_2 + C_2H_4 \longrightarrow 2\ H_2O + 2\ CO_2$$

b) As the solution reacts alkaline and there is a scarlet flame you may suppose that a compound of an alkali or alkaline earth metal is concerned which reacts with water to form hydrogen and hydroxide ions.

$n = p \cdot V/(R \cdot T)$ $\quad n = \dfrac{1.05 \cdot 10^5 \text{Pa} \cdot 29.2 \cdot 10^{-3}\ \text{m}^3}{8.314 \text{JK}^{-1}\text{mol}^{-1} \cdot 293 \text{K}}$ $\quad n = 1.259$ mol

that is 1 mol of the gas is formed by 10.00 g/1.259 = 7.94 g of the unknown substance $\Rightarrow$ metal = Li (M = 6,94 g/mol),

in addition 7.94 g of the substance generate 25.93 g of fluorid. That leads with M(F) = 19 g/mol to lithium as cation, too.

The unknown substance is lithium hydride, **LiH**.

$$LiH + H_2O \longrightarrow Li^+ + OH^- + H_2$$

Solution to problem 3-14

a) $HA + H_2O \rightleftharpoons A^- + H_3O^+$

$n(HA) + n(A^-) + n(H_3O^+) = 37.6 \cdot 10^{-3}$ mol

$n_0(HA) + 0.185 \cdot n_0(HA) = 37.6 \cdot 10^{-3}$ mol $\quad n_0(HA) = 31.73 \cdot 10^{-3}$ mol

$M = 3.00\ \text{g} / 31.73 \cdot 10^{-3}$ mol $\quad$ **M = 94.55 g/mol**

$K_a = \dfrac{(31.73 \cdot 10^{-3} \cdot 0.185)^2}{0.815 \cdot 31.73 \cdot 10^{-3}}$ $\quad$ **$K_a = 1.33 \cdot 10^{-3}$**

The white precipitate is silver chloride thus one molecule contains at least 1 Cl.

94.55 g/mol - 35.45 g/mol = 59.10 g/mol, that is M(CH_2COOH).

The acid could be monochloro-acetic acid, **$CH_2ClCOOH$**.

b) $c(Na^+) = c(CH_3COO^-)$ and $c_0(CH_3COOH) = c(CH_3COO^-) + c(CH_3COOH)$

$$pH = pK_a + \lg \frac{c(CH_3COO^-)}{c(CH_3COOH)} \qquad 4.7 = 4.76 + \lg \frac{c(Na^+)}{c_0(CH_3COOH) - c(Na^+)}$$

$\lg \dfrac{c(Na^+)}{c_0(CH_3COOH) - c(Na^+)} = 0$ meets the conditon of the problem (pH = 4.7 $\pm$ 0.1)*

$\Rightarrow \quad \frac{c(Na^+)}{c_0(CH_3COOH) - c(Na^+)} = 1 \qquad 2 \cdot c(Na^+) = c_0(CH_3COOH)$

To fulfil this condition the flow rate of acetic acid has to be four times the flow rate of the sodium-hydroxide solution: **w_1 = 660 µL/min** **w_2 = 165 µL/min**

(*If you calculate precisely you get

$\lg \frac{c(Na^+)}{c_0(CH_3COOH) - c(Na^+)} = -0.06 \qquad \frac{c(Na^+)}{c_0(CH_3COOH) - c(Na^+)} = 0.871$

$1.871 \cdot c(Na^+) = 0.871 \cdot c_0(CH_3COOH) \qquad 2.15 \cdot c(Na^+) = c_0(CH_3COOH)$

The flow rate of acetic acid has to be 4.13 times the flow rate of the sodium-hydroxide solution: w'_1 = 710 µL/min w_2 = 165 µL/min)

Solution to problem 3-15

a) The concentrations of NO and O_2 increase with time (curve Kurve A and B), twice as much NO as O_2, is formed $\Rightarrow$ $c(O_2)$ is represented by curve **B**.

b) test 1. and 2. $\Rightarrow$ **a = 2** test 1. und 4. $\Rightarrow$ **b = 2**
test 1. und 3. $\Rightarrow$ **d = -1** **e = 0**

$\frac{dc(I_2)}{dt} = k \cdot c^2([Fe(CN)_6]^{3-}) \cdot c^2(I^-) \cdot c^{-1}([Fe(CN)_6]^{4-})$

1. test: $1 \cdot 10^{-3}\ mol \cdot dm^{-3} \cdot h^{-1} = k \cdot 1\ mol^2 \cdot L^2 \cdot 1\ mol^2 \cdot dm^{-6} \cdot (1\ mol \cdot dm^{-3})^{-1}$

$k = 1 \cdot 10^{-3}\ mol^{-2} \cdot dm^6 \cdot h^{-1}$

c) $\Delta G°^{\#} = \Delta H°^{\#} - T \cdot \Delta S°^{\#}$

whereas $\Delta H°^{\#}$ and $\Delta S°^{\#}$ are supposed to be independent of temperature.

$\Delta S°^{\#} = \frac{\Delta G_1^{0\#} - \Delta G_2^{0\#}}{T_2 - T_1} \qquad \Delta S°^{\#} = \frac{75240 - 76100}{10}\ JK^{-1}mol^{-1}$

$\Delta S°^{\#}$ = - 86 $JK^{-1}mol^{-1}$ **$\Delta H°^{\#}$ = 49.612 $kJmol^{-1}$**

d) The equilibrium (1. reaction) settles very quickly:

$\frac{k_1}{k_{-1}} = \frac{c([Fe(CN)_6]^{4-}) \cdot c(I_2^-)}{c([Fe(CN)_6]^{3-}) \cdot c^2(I^-)} \qquad \Rightarrow \qquad c(I_2^-) = \frac{k_1}{k_{-1}} \cdot \frac{c([Fe(CN)_6]^{3-}) \cdot c^2(I^-)}{c([Fe(CN)_6]^{4-})} \qquad (1)$

2. reaction slow: $\frac{dc(I_2)}{dt} = k_2 \cdot c([Fe(CN)_6]^{3-}) \cdot c(I_2^-) \qquad (2)$

combining (1) and (2): $\frac{dc(I_2)}{dt} = \frac{k_1}{k_{-1}} \cdot k_2 \cdot \frac{c([Fe(CN)_6]^{3-})^2 \cdot c^2(I^-)}{c([Fe(CN)_6]^{4-})}$ q.e.d.

(2. reaction fast and 1. reaction slow: $\frac{d\,c(I_2)}{dt} = k_2 \cdot c([Fe(CN)_6]^{3-}) \cdot c(I_2^-)$ (2)

and $c(I_2^-) = k_1 \cdot c([Fe(CN)_6]^{3-}) \cdot c^2(I^-)$ (1') $\Rightarrow \frac{d\,c(I_2)}{dt} = k_1 \cdot k_2 \cdot c([Fe(CN)_6]^{3-})^2 \cdot c^2(I^-)$,

that does not match the rate law found in b))

Solution to problem 3-16

a) $C_6 + Li^+ + e^- \rightleftharpoons LiC_6$

$2\,LiCoO_2 \rightleftharpoons 2\,Li_{0,5}CoO_2 + Li^+ + e^-$

ΔG for the reaction $2\,LiCoO_2 + C_6 \rightleftharpoons LiC_6 + 2\,Li_{0,5}CoO_2$

has to be determined.

$\Delta G = 2 \cdot (-424\ kJ/mol) - 4\ kJ/mol - 2 \cdot (-614\ kJ/mol) = +376\ kJ/mol$

that is on discharging the reaction runs spontaneously from the right hand side to the left ($\Delta G = -376\ kJ/mol$).

$\Delta G = -n \cdot F \cdot \Delta E$ $\quad \Delta E = \frac{376000}{96485} V$ $\quad$ **$\Delta E = 3.9\ V$**

At discharging ΔG has to be negative. Thus the following reactions occur:

(1') $LiC_6 \rightleftharpoons C_6 + Li^+ + e^-$

(2) $2\,Li_{0,5}CoO_2 + Li^+ + e^- \rightleftharpoons 2\,LiCoO_2$

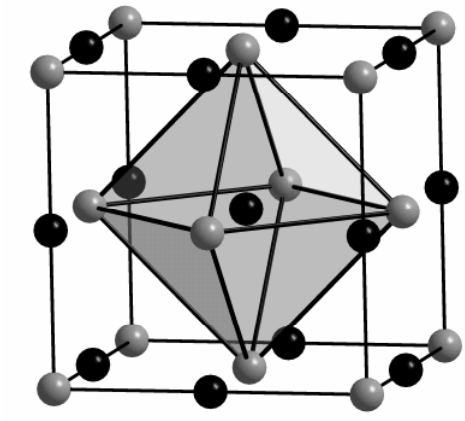
b) 1.00 g of graphite corresponds to 0.0833 (1/12) mol of carbon,

0.0833 mol carbon incorporate 0.0833/6 mol = 0.0139 mol of Li,

to insert 0.0139 mol of Li you need 0.0139 mol · F = 1340 C,

1340 C/g = 1340 As/g = $1340 \cdot 10^3$ mA · 3600^{-1}h/g = **372 mAh/g**

c)



O^{2-} ions

centres of cubic holes

Besides the octahedral hole in the centre of the cube there are 12 additional holes in the middle of the edges of the cube, each shared of 4 cubes.

$n(O^{2-}) = 8 \cdot ⅛ + 6 \cdot ½ = 4$

n(octahedral holes) $= 1 + 12 \cdot ¼ = 4$

$n(O^{2-})$: n(octahedral holes) = 1 : 1

Note:
The incorporation of the metal ions leads to a hexagonal distortion. Thus $LiCoO_2$ has a hexagonal unit cell with a = 2.86 Å and c = 14.080 Å.

d) 1 cm^3 of graphite correspond to 2.25 mol12 = 0.1875 mol C.
that corresponds to 0.1875 mol/6 $= 31.25 \cdot 10^{-3}$ mol of C_6Li

1.3 cm^3 of $LiCoO_2$ correspond to 1.3·4.8 mol/97.87 = $63.76\cdot10^{-3}$ mol of $LiCoO_2$
that corresponds to $63.76\cdot10^{-3}$ mol of $Li_{0.5}CoO_2$.

As the cell reaction $n(C_6Li) : n(Li_{0.5}CoO_2)$ is equal to 1 : 2 theoretically
$31.25\cdot10^{-3}$ mol of C_6Li are converted (there is a small excess of $Li_{0.5}CoO_2$).
So in the process $31.25\cdot10^{-3}$ mol·376 kJ/mol = **11.75 kJ** are supplied theoretically.

e) A body-centred cell containes 1 + 8·⅛ = 2 atoms of Li

$m = 2 \cdot M(Li) / N_A$ $\quad m = (2\cdot6.94\ g\cdot mol^{-1})/(6.022\cdot10^{23}mol^{-1})$

$V = (3.51\ Å)^3$ $\quad V = (3.51\cdot10^{-8}\ cm)^3$

$\rho = m/V$ $\quad \rho = \dfrac{2\cdot6.94\ g}{(3.51\cdot10^{-8}\ cm)^3\cdot6.022\cdot10^{23}}$ **$\rho = 0.533\ g/cm^3$**

f) The occuring reactions would be

(1'') $\quad Li \rightleftharpoons Li^+ + e^-$

(2) $\quad 2\ Li_{0.5}CoO_2 + Li^+ + e^- \rightleftharpoons 2\ LiCoO_2$

ΔG for the reaction $\quad 2\ Li_{0.5}CoO_2 + Li \rightleftharpoons 2\ LiCoO_2$
has to be determined.

ΔG = 2·(-614 kJ/mol) - 2·(- 424 kJ/mol) = - 380 kJ/mol

0.5 cm^3 of Li correspond to (0.5 cm^3 · 0.5 g/cm^3)/(6.94 g/mol) = $36\cdot10^{-3}$ mol of Li, furthermore there exist $63.76\cdot10^{-3}$ mol of $Li_{0.5}CoO_2$ (see d)) in charged state.

⇒ at discharging a maximum of $63.76\cdot10^{-3}$ mol of $Li_{0.5}CoO_2$ can be converted (there is a small excess of Li).

Theoretically ½ · $63.76\cdot10^{-3}$ mol·380 kJ/mol = **12.11 kJ** are supplied.

Solution to problem 3-17

a) $\overset{+2\ -1}{MgH_2} \longrightarrow \overset{0}{Mg} + \overset{0}{H_2}$ $\qquad$ $\overset{+2\ 0\ -1}{Mg_2NiH_4} \longrightarrow \overset{0\ \ 0}{Mg_2Ni} + \overset{0}{2\ H_2}$

b) $\ln\left(\dfrac{K_{p1}}{K_{p2}}\right) = \dfrac{\Delta_R H}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$ $\quad \Rightarrow \quad$ $\Delta_R H = R \cdot \left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)^{-1} \cdot \ln\left(\dfrac{K_{p1}}{K_{p2}}\right)$

decomposition of MgH_2: $K_p = p/p_0$ $\qquad$ decomposition of Mg_2NiH_4: $K_p = p^2/p_0^2$

p: equilibrium pressure of hydrogen $\qquad$ p_0: standard pressure

Read from the diagram:

MgH_2 (1000 K/T ; $\ln(p/p_0)$):	(1.65 ; 1.60)	(1.875 ; - 0.5)
converted to (T ; p/p_0):	(606 K; 4.95)	(533 K ; 0.607)
Mg_2NiH_4 (1000 K/T ; $\ln(p/p_0)$):	(1.65 ; 1.95)	(1.875 ; 0.05)
converted to (T ; p/p_0):	(606 K; 7.03)	(533 K; 1.05)

MgH_2: $\quad \Delta_R H = 8.314 \cdot \ln\left(\dfrac{4{,}95}{0{,}607}\right)\cdot\left(\dfrac{1}{533} - \dfrac{1}{606}\right)^{-1}$ J/mol $\quad$ **$\Delta_R H \approx 77.2$ kJ/mol**

Mg_2NiH_4: $\quad \Delta_R H = 8.314 \cdot \ln\left(\dfrac{7{,}03^2}{1{,}05^2}\right)\cdot\left(\dfrac{1}{533} - \dfrac{1}{606}\right)^{-1}$ J/mol $\quad$ **$\Delta_R H \approx 139.9$kJ/mol**

c) $Mg_2NiH_4 \longrightarrow Mg_2Ni + 2\ H_2$ $\quad \Delta_R H_1 = 139.9$ kJ/mol

$2\ Mg + Ni + 2\ H_2 \longrightarrow Mg_2NiH_4$ $\quad \Delta_R H_2 = -176.0$ kJ/mol

$2\ Mg + Ni \longrightarrow Mg_2Ni$ $\quad \Delta_R H_3 = \Delta_R H_1 + \Delta_R H_2$

$\Delta H^0_f(Mg_2Ni) = (139.9 - 176.0)$ kJ/mol $\quad$ **$\Delta H^0_f(Mg_2Ni) = -36.1$ kJ/mol**

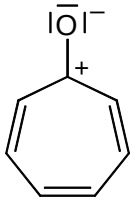
(alternatively $= (163.4 - 176.0)$ kJ/mol $= -12.6$ kJ/mol)

Solution to problem 3-18

a) Oxide A: 2,4,6-Cycloheptatriene-1-one, Oxide B: 2,4-Cyclopentadiene-1-one

b) Oxide A is stable.

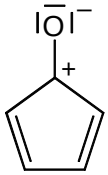
Reason: There is a resonance structure with the following electron distribution



Thus the π-electron system with 6 electrons fullfills the Hückel (4n + 2) rule to form a cyclic and planar aromatic system.

On the other hand cyclopentadienone (oxide B) is extremely instable.

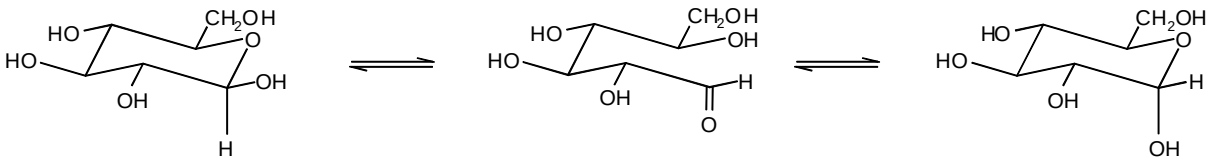
Reason: There is a correspondent electron structure



The cyclopentadiene ring contains 4 π-elektrons which leads to high instability.

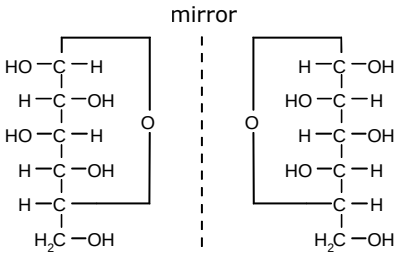
Solution to problem 3-19

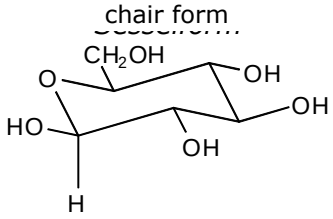
a)



β-D-glucose aldehyde form α-D-glucose

b) Added sugar: You need to look for the mirror image (enantiomer) of β-D-glucose. This is β-L-glucose (but not the α-compound).

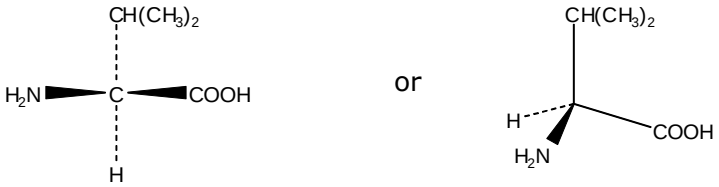




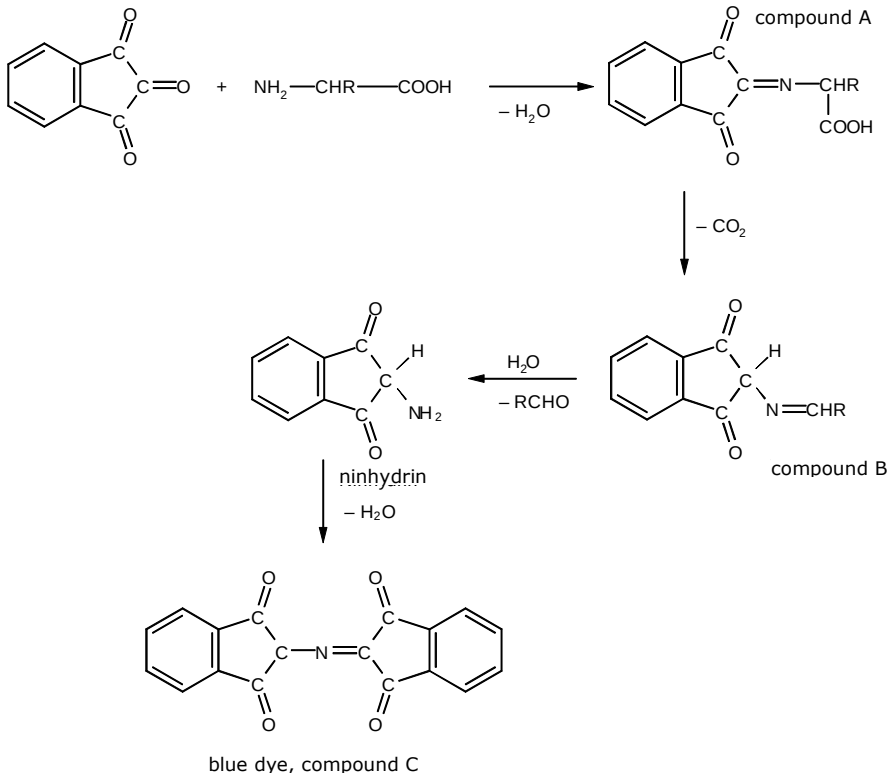
Solution to problem 3-20

a) S-2-amino-3-methylbutanoic acid (L-valine) S-2-aminopropionic acid (L-alanine) S-2-amino-4-methylpentanoic acid (L-leucine)

b) Configuration of an amino acid (S-2-amino-3-methylbutanoic acid):



c)



d) Qualitative determination:

After breaking down the peptide into its constituent amino acids the resulting amino acid mixture is seperated by a column as described in the problem. Using a series of aquous buffers as the mobile phase then effects a seperation into component amino acids. As each amino acid elutes from the end of the chromatogrphy column, it mixes with a solution of ninhydrin to form an intense purple (blue) color. The purple color is detected by a spectrometer, and a plot of elution time versus spectrometer absorbance is obtained. Since the amount of time required for a given amino acid to elute from the column is reproducable the identity of all amino acids can be determined simply by noting the various elution times.

Quantitative determination:

The area below an absoprtion maximum of a dye complex shows the amount of this complex and thus the amount of the amino acid. Here, too, a calibration with a comparative solution of known content of amino acid has to go ahead.

Answers Round 4 (theoretical)

Solution to problem 4-1

A

a) $2 \cdot x = 0.153 + 0.521$ $\quad x = 0.337$

b) $2\ Cu^+ \longrightarrow Cu^{2+} + Cu$ [0]

is broken down into two reactions:

[1'] $Cu^{2+} + e^- \longrightarrow Cu^+$ $\quad \Delta G_1'° = -1 \cdot F \cdot 0.153$ V

[1] $Cu^+ \longrightarrow Cu^{2+} + e^-$ $\quad \Delta G_1° = -1 \cdot F \cdot (-0.153$ V) oxidation

[2] $Cu^+ + e^- \longrightarrow Cu$ $\quad \Delta G_2° = -1 \cdot F \cdot 0.521$ V reduction

[0] = [1] + [2] $\quad \Delta G° = -1 \cdot F \cdot (0.521\ V - 0.153\ V)$ $\quad \Delta G° = -35506$ J/mol

$\Delta G° < 0$ $\quad \Rightarrow$ **Disproportionation is a spontaneous reaction**.

If you generalize the equation to find $\Delta G°$ with respect to the Latimer diagram you find $\quad \Delta G° = -n \cdot F \cdot (E°(right) - E°(left))$. $\quad \Rightarrow$

$\Delta G° < 0$ that is to say disproportionation is spontaneous $\quad \Leftrightarrow$ **$E°(ox.) < E°(red.)$**.

c) $\Delta G° = -35506$ J/mol $\quad K = e^{35506/(8.314 \cdot 298.15)}$ $\quad$ **$K = 1.66 \cdot 10^6$**

d) In a solution above CuI(s) with $c(I^-) = 1$ mol/L you find $c(Cu^+) = K_{sp}$ mol/L.
Comparing the Latimer diagrams you get

$-0.147\ V = 0.521\ V + R \cdot T/F \cdot \ln K_{sp}$ $\quad \ln K_{sp} = \dfrac{-0{,}668 \cdot 96485}{8{,}314 \cdot 298{,}15}$

$\ln K_{sp} = -26.001$ $\quad$ **$K_{sp} = 5.10 \cdot 10^{-12}$**

e) $Cu^{2+} + e^- \longrightarrow Cu^+$ $\quad E° = 0.153$ V $\quad \Delta G = -F \cdot 0.153$ V

$Cu^+ + I^- \longrightarrow CuI$ $\quad \Delta G_4 = +R \cdot T \cdot \ln K_{sp}$ $\quad \Delta G = -64452$ J/mol

$Cu^{2+} + I^- + e^- \longrightarrow CuI$ $\quad \Delta G = -F \cdot 0.153$ V $- 64452$ J/mol $=$ **-79214 J/mol**

f) $2\ Cu^{2+} + 2\ I^- + 2\ e^- \longrightarrow 2\ CuI$ $\quad \Delta G = -2 \cdot 79214$ J/mol

$2\ I^- \longrightarrow I_2$ $\quad \Delta G = -2 \cdot F \cdot (-0.535\ V) = 103239$ J/mol

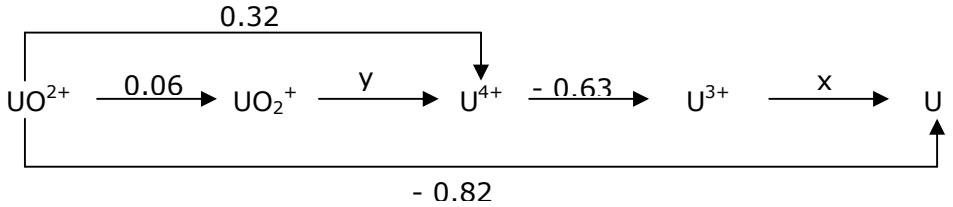
$2\ Cu^{2+} + 4\ I^- \longrightarrow 2\ CuI + I_2$ $\quad \Delta G = (-158428 + 103239)$ J/mol

$\Delta G = -55189$ J/mol $\quad \Delta G = -R \cdot T \cdot \ln K$ $\quad$ **$K = 4.67 \cdot 10^9$**

(Note: The equilibrium lies on the side of the products in such a way that the disproportionation of Cu^+ doesn't play any role and this reaction can be used for the iodometric determination of Cu^{2+}.)

B

g)



$2\cdot0.32 + (-0.63) + 3\cdot x = 6\cdot(-0.82)$ $x = -1.64$ $E°(U^{3+}/U) = -1.64$ V

$0.06 + y = 2\cdot0.32$ $y = 0.58$

Using the criterion of b) only UO_2^+ (0.06 < 0.58) disproportionates:

$$2\ UO_2^+ + 4\ H^+ \longrightarrow U^{4+} + UO_2^{2+} + 2\ H_2O$$

h) $4\ U^{3+} \rightleftharpoons 3\ U^{4+} + U$

$\Delta G° = -3\cdot F\cdot(-1.64\ V + 0.63\ V)$ $\Delta G° = 292350$ J/mol

$K = e^{-\Delta G°/(R\cdot T)}$ **$K = 6.02\cdot10^{-52}$**

Solution to problem 4-2

a) $H_2S + 2\ H_2O \rightleftharpoons 2\ H_3O^+ + S^{2-}$ $K = \dfrac{c^2(H_3O^+)\cdot c(S^{2-})}{c(H_2S)} = K_{a1}\cdot K_{a2}$

$c(S^{2-}) = 10^{-6.9}\cdot10^{-12.9}\cdot 0.1/0.01^2$ $c(S^{2-}) = 1.58\cdot10^{-17}$ mol/L

b) MeS: $K_{sp(max)} = 10^{-5}\cdot1.58\cdot10^{-17}$ $K_{sp(max)} = 1.58\cdot10^{-22}$

Me_2S: $K_{sp(max)} = (10^{-5})^2\cdot1.58\cdot10^{-17}$ $K_{sp(max)} = 1.58\cdot10^{-27}$

c) You have to check, whether the sulfides dissolute in a solution with $c(CN^-) = 1$. The solubility is recognizable from the concentration of S^{2-} ions in this solution.

$CdS \rightleftharpoons Cd^{2+} + S^{2-}$

$Cd^{2+} + 4\ CN^- \rightleftharpoons [Cd(CN)_4]^{2-}$

Using $c(Cd^{2+}) = x$ $c(S^{2-}) = y$ $c([Cd(CN)_4]^{2-}) = z$ you get

$K_{sp} = x\cdot y$ $\beta = z/(x\cdot1^4)$ $y = x + z$ $\Rightarrow$ $y = 8.37\cdot10^{-6}$

$c(S^{2-}) = 8.37\cdot10^{-6}$ mol/L this is the solubility of CdS in the solution of KCN.

$Cu_2S \rightleftharpoons 2\ Cu^+ + S^{2-}$

$Cu^+ + 4\ CN^- \rightleftharpoons [Cu(CN)_4]^{3-}$

Using $c(Cu^+) = x$ $c(S^{2-}) = y$ $c([Cu(CN)_4]^{3-}) = z$ you get

$K_{sp} = x^2\cdot y$ $\beta = z/(x\cdot1^4)$ $y = ½\cdot x + ½\cdot z$ $\Rightarrow$ $y = 271$

$c(S^{2-}) = 271$ mol/L this is the solubility of Cu_2S in the solution of KCN.

Comparing the solubilities you find that Cu_2S dissolves completely in the solution of cyanide, CdS, however, does not. Thus a speration is possible.

Solution to problem 4-3
A

a) $A_\infty(P) = 0.179$ $\varepsilon = A/(c\cdot d)$ $c = 0.020$ mol/L $d = 0.95$ cm

$\varepsilon = 0.179/(0.020\ mol/L\cdot 0.95\ cm)$ $\varepsilon = 9.421\ L\cdot mol^{-1}\cdot cm^{-1}$

b) $v = \dfrac{c_0(E) - c_t(E)}{t} = \dfrac{c_t(P)}{t}$ e.g. t = 50 s with A = 0.079

$c_t(P) = A/\varepsilon\cdot d$; $c_{50}(P) = 0.079/(9.421\cdot0.95\ L\cdot mol^{-1})$; $c_{50}(P) = 8.837\cdot10^{-3}$ mol/L

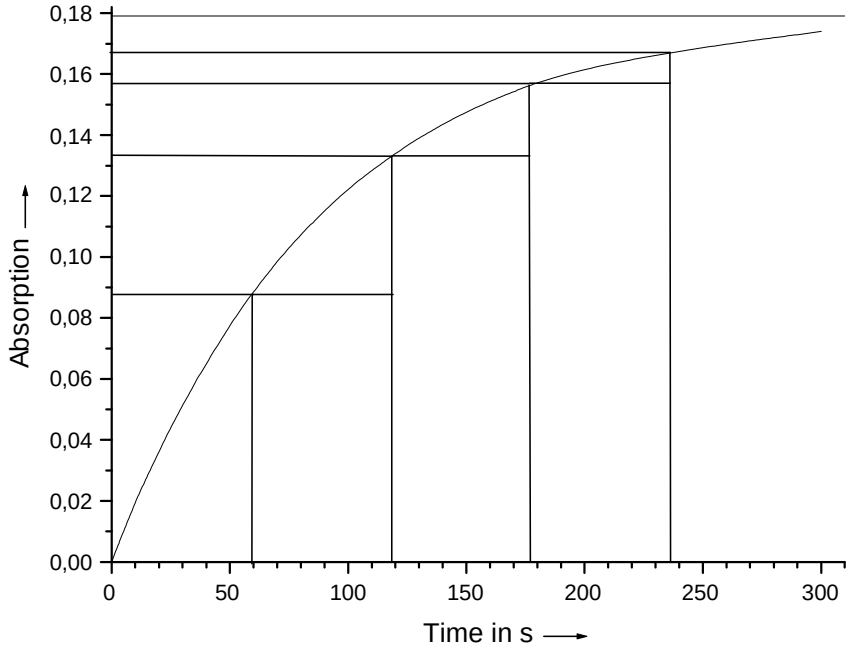
$v = 8.837\cdot10^{-3}\ mol\cdot L^{-1}/50s$ $v = 1.765\cdot10^{-4}\ mol\cdot L^{-1}\cdot s^{-1}$

$c_t(E) = c_0(E)\cdot e^{-k\cdot t}$ $\quad k = -\frac{1}{50\ s}\cdot \ln\frac{c_{50}(E)}{c_0(E)}$ $\quad c_{50}(E) = c_0(E) - c_{50}(P)$

$c_{50}(E) = 0.01116$ mol/L $\quad k = 0.0117\ s^{-1}$

c) $t_{½} = \ln 2/k$ $\quad t_{½} = 59$ s

d) At 59 s you find c(E) = c(P) = 0.010 mol/L according to A = 0.090.
At 118 s you should find A = 0.090 + 0.045 = 0.135,
and in each of the following time intervals of 59 s the increase in the plot should be half of the increase of the precedent increase.
This is approximately correct:



e) $t_{95\%} = -k^{-1}\cdot\ln(1-0.95)$ $\quad t_{95\%} = 256$ s

f) $v_{573} = k_{573}\cdot c_{573}(E)$ $\quad v_{723} = k_{723}\cdot c_{723}(E)$
$v_{573} = v_{723}$ and $c_{723}(E) = 3\cdot c_{573}(E)$ $\Rightarrow$ $k_{723}/k_{573} = 3/1$
$k = e^{-(Ea/R\cdot T)}$
$\ln\frac{k_{723}}{k_{573}} = -\frac{Ea}{R}\cdot(723^{-1} - 573^{-1})$ $\quad Ea = -8.314\cdot\ln 3\cdot(723^{-1} - 573^{-1})^{-1}$ J/mol
Ea = 25.2 kJ/mol

B

g) The first step is rate determining: $v = k_1\cdot c(O_2^-)\cdot c(E)$.
$c(E_0)$ is constant likewise $c(E^-)$ after a short time of starting-up and thus $c(E) = c_0(E) - c(E^-)$ is constant too: $v = k\cdot c(O_2^-)$ with $k = k_1\cdot c(E)$.
This is consistant with the experimetally found law.

h) Steady state of E^-: $0 = k_1 \cdot c(O_2^-) \cdot c(E) - k_2 \cdot c(O_2^-) \cdot c(E^-) \quad \Rightarrow \quad k_1 \cdot c(E) = k_2 \cdot c(E^-)$

$c(E) = c_0(E) - c(E^-) \quad \Rightarrow \quad k_1 \cdot (c_0(E) - c(E^-)) = k_2 \cdot c(E^-)$

$$\Rightarrow \quad c(E^-) = \frac{k_1 \cdot c(E_0)}{k_1 + k_2}$$

with $k_2 = 2 \cdot k_1$ $\quad c(E^-) = \frac{c(E_0)}{3} \quad \Rightarrow \quad c(E) = \frac{2 \cdot c(E_0)}{3}$

Following g): $\quad k = k_1 \cdot c(E) \quad k = k_1 \cdot \frac{2 \cdot c(E_0)}{3}$

given are $\quad k = 501\ L/(mol \cdot s)$ and $\quad c_0(E) = 0.400 \cdot 10^{-6}\ mol/L$:

$$k_1 = \frac{3 \cdot 501\,L/(mol \cdot s)}{2 \cdot 0.4 \cdot 10^{-6} mol/L} \qquad k_1 = 1.88 \cdot 10^9\ (mol/L)^{-2} s^{-1} \qquad k_2 = 3.76 \cdot 10^9\ (mol/L)^{-2} s^{-1}$$

Solution to problem 4-4

A

a) Self-dissociation $\quad 2\ NH_3 \rightleftharpoons NH_4^+ + NH_2^-$.

Acids increase the concentration of NH_4^+ $\quad$ e.g. NH_4Cl

bases increase the concentration of NH_2^- $\quad$ e.g. KNH_2.

b) $pH = -\lg c(NH_4^+) \qquad K = c(NH_4^+) \cdot c(NH_2^-)$ mit $K = 1.0 \cdot 10^{-29}\ (mol/L)^2$

$c(NH_4^+) = c(NH_2^-) \quad \Rightarrow \quad c(NH_4^+) = 1.0 \cdot 10^{-14.5} mol/\ell. \qquad pH = 14.5.$

c) Water reacts as an acid because in increases the concentration of NH_4^+:

$$H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-\ .$$

d) $CH_3COOH + NH_3 \rightleftharpoons NH_4^+ + CH_3COO^- \quad \Rightarrow$ CH_3COOH reacts as an acid.
As NH_3 is a better electron donator as water the solvolysis of acetic acid in ammonia is more extended than in water and thus it is a stronger acid in ammonia.

e) The sizing of ammonia to react as electron-pair donator is more extended than that of water (NH_4^+ is easier formed than H_3O^+). Thus the solvolysis of any acid will be stronger in ammonia than in water and so an acid in water can never be a base in ammonia.

f) It is sufficient to show that NaOH forms at a neutralization:

$$H_2O + NaNH_2 \rightleftharpoons NaOH + NH_3$$
$$(\text{ acid} + \text{ base} \rightleftharpoons \text{salt} + \text{solvent})$$

g) Such a compound should form OH^- in water and NH_4^+ in ammonia. It could be a bi-functional compound with a basic function that is weaker than that of ammonia in water and an acid function that is weaker than the conjugated acid of the basic function in water. Such an example is hydroxylamine, NH_2OH.
In water the following equilibrium forms

$$H_2NOH + H_2O \rightleftharpoons {}^{+}H_3NOH + OH^-.$$

In liquid amonia the following equilibrium prevails

$$H_2NOH + NH_3 \rightleftharpoons H_2NO^- + NH_4^+.$$

h) Yes, e.g. sulfuric acid: $2\ H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$.

Reaction with water: $H_2SO_4 + H_2O \rightleftharpoons HSO_4^- + H_3O^+$,

water increases the concentration of the anionic part of the solvent $\Rightarrow$ it is a base.

i) No, there is no self-dissociation of CCl_4.

B

For all of the following problems you need the equation of protolysis:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-, \qquad K_a = \frac{c(H_3O^+)\cdot c(A^-)}{c(HA)}, \qquad \alpha = \frac{c(H_3O^+)}{c_0(HA)}.$$

j) $c(H_3O^+) = c(HCOO^-) = x$ und $c(HCOOH) = c_o - x$

$1.77\cdot10^{-4} = \frac{x^2}{0.5-x}$ $\quad x = 9.32\cdot10^{-3}$ $\quad pH = 2.0$

$\alpha_1 = x/0.5$ $\quad \alpha_1 = 1.9\cdot10^{-2}$

Calculating in the same way for acetic acid leads to

$x = 2.96\cdot10^{-3}$ $\quad pH = 2.5$ $\quad \alpha_2 = 5.9\cdot10^{-3}$

k) 34.5 g of methanoic acid are 34.5 g/(46 g/mol) = 0.75 mol.

c_o(methanoic acid) = c_o(acetic acid) =0.5 mol/L.

The hydrogen ions are formed by both acids.

Let α_1 be the protolysis degree of methanoic acid, α_2 that of acetic acid.

$c(H_3O^+) = \alpha_1\cdot c_o + \alpha_2\cdot c_o$

$c(HCOO^-) = c_o\cdot\alpha_1$ $\quad c(HCOOH) = c_o\cdot(1-\alpha_1)$

$c(CH_3COO^-) = c_o\cdot\alpha_2$ $\quad c(CH_3COOH) = c_o\cdot(1-\alpha_2)$

K_a(methanoic acid) $= \frac{(0.5\alpha_1+0.5\alpha_2)\cdot0.5\alpha_1}{0.5\cdot(1-\alpha_1)}$ (*)

K_a(acetic acid) $= \frac{(0.5\alpha_1+0.5\alpha_2)\cdot0.5\alpha_2}{0.5\cdot(1-\alpha_2)}$

As shown in j) at these concentrations you may set $1 - \alpha \approx 1$.

$\frac{1.77\cdot10^{-4}}{1.76\cdot10^{-5}} = \frac{\alpha_1}{\alpha_2}$ $\quad \alpha_2 = 0.0994\cdot\alpha_1$ $\quad$ bzw. $\alpha_1 = 10.06\cdot\alpha_2$.

Inserted in (*) you find $\quad \alpha_1 = 1.78\cdot10^{-2}$ $\quad \alpha_2 = 1.77\cdot10^{-3}$.

$c(H_3O^+) = (\alpha_1 + \alpha_2)\cdot c_0$ $\quad c(H_3O^+) = 9.79\cdot10^{-3}$ mol/L $\quad pH = 2.0$

l) 21.42 g are 0.21 mol $\Rightarrow$ c_o(acid) = 0.15 mol/L

$c(H_3O^+) = c(A^-) = 10^{-pH}$ mol/L and $c(HA) = (0.15 - 10^{-pH})$mol/L

$K_a = \frac{(10^{-2.82})^2}{0.15-10^{-2.82}}$ $\quad K_a = 1.54\cdot10^{-5}$ $\quad pK_a = 4.81$

Solution to problem 4-5

A

a) $CN^- + H_2O \rightleftharpoons HCN + OH^-$ $\quad K_B = \frac{c(HCN)\cdot c(OH^-)}{c(CN^-)\cdot 1mol/L}$ $\quad K_B = K_w/ K_s = 10^{-4.69}$

$c_0 = c(HCN) + c(CN^-)$ und $c(HCN) \approx c(OH^-) = 10^{-3.3}$ mol/L

$10^{-4.69} = \frac{(10^{-3.3})^2}{c_0 - 10^{-3.3}}$ $\Rightarrow$ **c_0 = 0.0128 mol/L**

b) $Ag^+ + 4\ CN^- \rightleftharpoons [Ag(CN)_4]^{3-}$ $\quad \beta_1 = \frac{c([Ag(CN)_4]^{3-})}{c(Ag^+)\cdot c(CN^-)^4} = 5.00\cdot 10^{20}$

$\frac{c([Ag(CN)_4]^{3-})}{c(Ag^+)} = \beta_1 \cdot c(CN^-)^4$

Due to excess CN^- follows $c(CN^-) \approx c(NaCN) - c(OH^-)$

$c(CN^-) \approx (0.020 - 10^{-3.2})$ mol/L = 0.0194 mol/L

$\frac{c([Ag(CN)_4]^{3-})}{c(Ag^+)} = 5.00\cdot 10^{20} \cdot 0.0194^4 =$ **$7.04\cdot 10^{13}$**

c) $c(Ag^+)$ increases if $c(CN^-)$ decreases and $c(CN^-)$ decreases if $c(OH^-)$ decreases. Thus you need an acid, $HClO_4$.

d) v and n indicate the concentrations before and after increasing $c(Ag^+)$, respectively.

$c(Ag^+)_n / c(Ag^+)_v = 10$ und $c([Ag(CN)_4]^{3-}) = c(Ag^+) \cdot \beta_1 \cdot c(CN^-)^4$

$c([Ag(CN)_4]^{3-})_v + c(Ag^+)_v = c([Ag(CN)_4]^{3-})_n + c(Ag^+)_n$

$\Rightarrow$ $c(Ag^+)_v \cdot \beta_1 \cdot c(CN^-)^4_v + c(Ag^+)_v = c(Ag^+)_n \cdot \beta_1 \cdot c(CN^-)^4_n + c(Ag^+)_n$

$\frac{c(Ag^+)_n}{c(Ag^+)_v} = \frac{\beta_1 \cdot c(CN^-)_v^4 + 1}{\beta_1 \cdot c(CN^-)_n^4 + 1} = 10$

$c(CN^-)^4_n = \frac{\beta_1 \cdot c(CN^-)_v^4}{10\cdot\beta_1} - \frac{9}{10\cdot\beta_1} \approx \frac{\beta_1 \cdot c(CN^-)_v^4}{10\cdot\beta_1}$ because of $\beta_1 = 5.00\cdot 10^{20}$

$c(CN^-)_n = c(CN^-)_v \cdot (\sqrt[4]{10})^{-1} = 0.0196 \cdot (\sqrt[4]{10})^{-1}$ **$c(CN^-)_n$ = 0.0110 mol/L**

Solution to problem 4-6

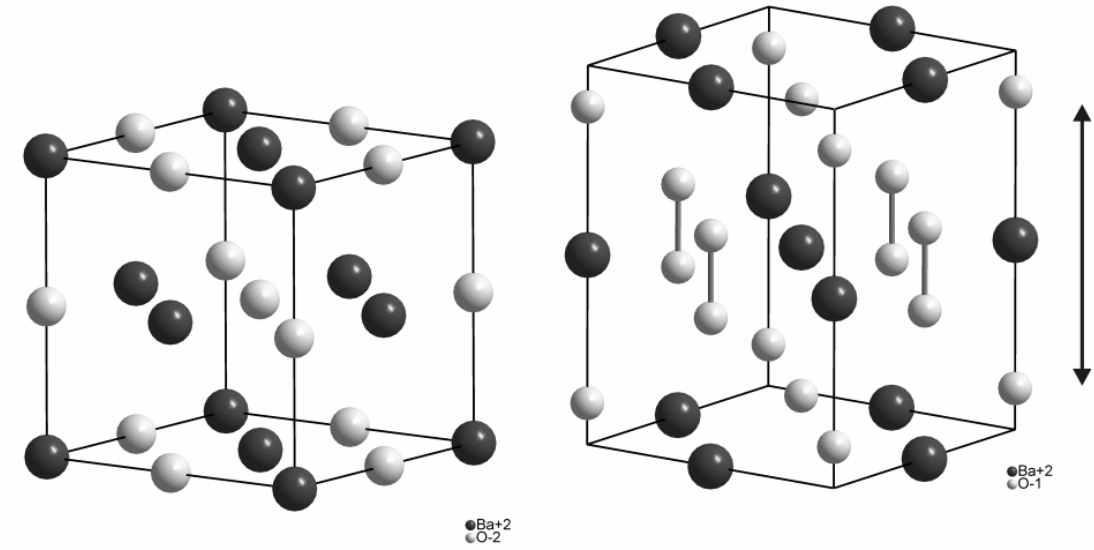
a) With M(Ba) = 137.3 g/mol, atomic radius r = $217.4 \cdot 10^{-10}$ cm, edge length a and the number n of atoms/cell you find $\rho = m/V = \frac{n \cdot 137.3\ g/mol}{N_A \cdot a^3}$.

	simple cubic	cubic body-centered	cubic face-centered
Edge length a of the elementary cell	$2 \cdot r$ $= 434.8 \cdot 10^{-10}$ cm	$2 \cdot 2 \cdot r / \sqrt{3}$ $= 502.1 \cdot 10^{-10}$ cm	$2 \cdot \sqrt{2} \cdot r$ $= 614.9 \cdot 10^{-10}$ cm
Number of Ba atoms/cell	1	2	4
calculated density	2.77 g/cm^3	3.60 g/cm^3	3.92 g/cm^3

Barium cristallizes cubic body-centered.

b) Coordination numbers 6.6.

c) In barium peroxide the sperically shaped O^{2-} anions of barium oxide are replaced by dumbbell-shaped O_2^{2-} anions which arrange themselfes parallel to one of the axes.



d) $Ba + O_2 \longrightarrow BaO_2$

$Ba + ½\ O_2 \longrightarrow BaO$

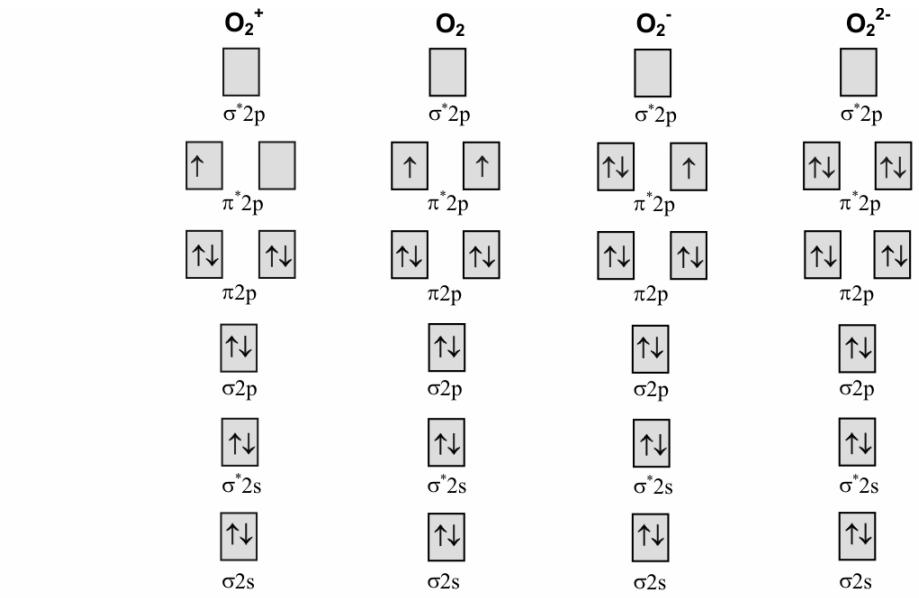
$Ba + 2\ O_2 \longrightarrow Ba(O_2)_2$

e + f) Formation of Ba^{2+} ions: (180 + 503 + 965) kJ/mol = 1648 kJ/mol

Compound	**BaO**	**BaO_2**	**$Ba(O_2)_2$**
$\Delta U_{lattice}$ (kJ/mol)	-3113	-2779	-2191
$\Sigma\ \Delta H_{reactions}$ (kJ/mol)	2100	2201	1562
$\Delta H_{Reaktion}$ (kJ/mol)	-1013	-578	-629

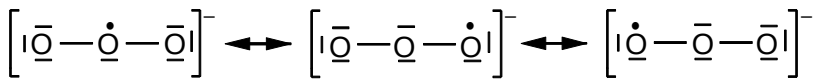
Barium oxide BaO should be formed preferentially.

g)



bond order	2,5	2	1,5	1
behaviour in a magn. field	paramagnetic	paramagnetic	paramagnetic	diamagnetic

h)



You may expect a puckered structure which is indeed found.

i) Examples NF_2. SO_2^-. S_3^-. ClO_2. P_3^{4-}. PO_2^{2-}

j) These systems possess 19 electrons and are radicalic. Dimerisation could be expected which is found in some cases (e.g. S_6^{2-}. N_2F_4. Cl_2O_4).

k)

$$2\,O_3^{-\,1/3} + H_2^{+I}O^{-II} \longrightarrow 2\,\tfrac{1}{2}\,O_2^{\pm 0} + 2\,OH^{-II+I}$$

$$5\,O^{-1/3} \longrightarrow 5\,O^0 + {}^5/_3\,e^-$$

$$1\,O^{-1/3} + {}^5/_3\,e^- \longrightarrow 1\,O^{-II}$$

Disproportionation.

Solution to problem 4-7

a) $n(H) : n(O) : n(S) = \frac{3{,}62}{1{,}008} : \frac{57{,}38}{16} \; \frac{14{,}38}{32{,}07} = 3.59 : 3.59 : 0.448$

$n(H) : n(O) : n(S) = 8 : 8 : 1$ empirical formula $(H_8O_8S)_n$

mass fraction of X = 100% - (3.62 + 57.38 + 14.38)% = 24.62%

n=1: M(X) = 24.62/0.448 g/mol = 54.95 g/mol X = manganese

n=2: M(x) = 109.9 there is no metal with this molar mass.

n=3: M(X) = 164.9 X = holmium. But it does'nt show the reactions mentioned in the scheme.

empirical formula of compound A: MnH_8O_8S

b) In the scheme you find the reaction A ⟶ J. Compound A has to be a sulfate: $MnH_8O_4SO_4$. Still H_8O_4 has to be assigned. The thermogravimetric inspections showed a decrease of mass of about 30 % of the initial mass (M(A)=223.074). This is consistent with four molecules of water.

The compound is manganese(II)-sulfate-tetrahydrate $MnSO_4 \cdot 4\ H_2O$.

c) The X containing compound is printed in bold letters, crystal water is omitted.

B: $MnSO_4 + 6\ NH_3 \longrightarrow \mathbf{[Mn(NH_3)_6]^{2+}} + SO_4^{2-}$

C: $MnSO_4 + 2\ NaOH \longrightarrow \mathbf{Mn(OH)_2} + Na_2SO_4$

D: $Mn(OH)_2 + ½\ O_2 \longrightarrow \mathbf{MnO(OH)_2}$ bzw.

$MnSO_4 + H_2O_2 + 2\ OH^- \longrightarrow \mathbf{MnO(OH)_2} + SO_4^{2-} + H_2O$

E: $MnSO_4 + (NH_4)_2S \longrightarrow \mathbf{MnS} + (NH_4)_2SO_4$

F: $MnSO_4 + (NH_4)_2CO_3 \longrightarrow \mathbf{MnCO_3} + (NH_4)_2SO_4$

G: $2\ MnSO_4 + 5\ PbO_2 + 4\ H^+ \longrightarrow 2\ \mathbf{MnO_4^-} + 5\ Pb^{2+} + 2\ SO_4^{2-} + 2\ H_2O$

H: $2\ MnSO_4 + 5\ Br_2 + 16\ OH^- \longrightarrow 2\ \mathbf{MnO_4^-} + 10\ Br^- + 2\ SO_4^{2-} + 8\ H_2O$

I: $MnSO_4 + 6\ KCN \longrightarrow \mathbf{[Mn(CN)_6]^{4-}} + SO_4^{2-} + 6\ K^+$

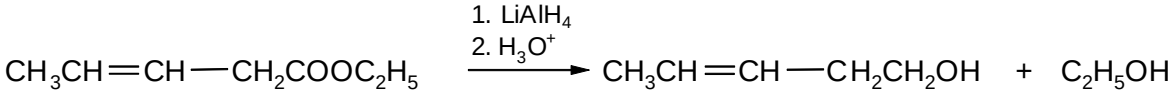
J: $MnSO_4 + BaCl_2 \longrightarrow BaSO_4 + \mathbf{MnCl_2}$

d)

	X containing species	unpaired electrons	μ in BM
A	$\mathbf{[Mn(H_2O)_6]^{2+}}$	5	5.92
B	$\mathbf{[Mn(NH_3)_6]^{2+}}$	5	5.92
C	$\mathbf{Mn(OH)_2}$	5	5.92
D	$\mathbf{MnO(OH)_2}$	3	3.87
E	**MnS**	5	5.92
F	$\mathbf{MnCO_3}$	5	5.92
G	$\mathbf{MnO_4^-}$	0	0
H	$\mathbf{MnO_4^-}$	0	0
I	$\mathbf{[Mn(CN)_6]^{4-}}$	1 (low-spin)	1.73
J	$\mathbf{MnCl_2}$	5	5.92

Solution to problem 4-8

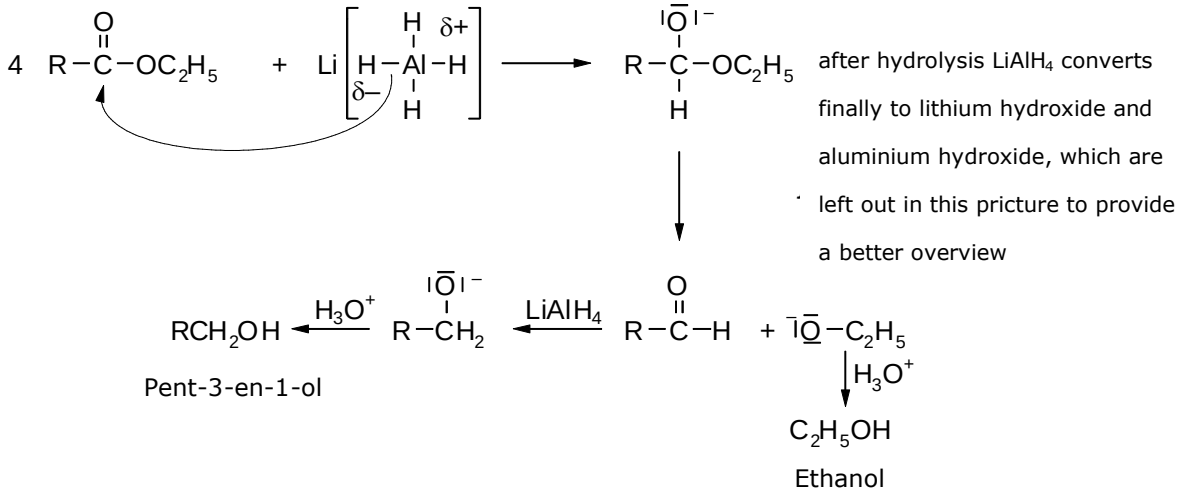
a)



Pent-3-en-1-ol Ethanol

b)

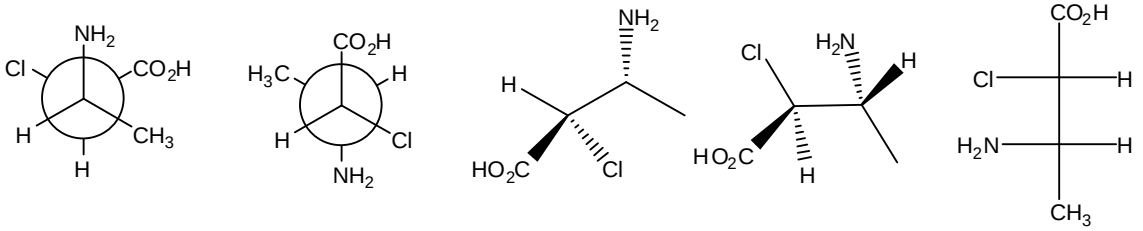
R: $CH_3CH{=}CH{-}CH_2-$ *does not change*



c) The peak = 28 m/z is the result of cleavage of water ($M(H_2O)$ = 18 g/mol) from ethanol ($M(C_2H_5OH)$ = 46 g/mol)

Solution to problem 4-9

a)



1 2 3 4 5

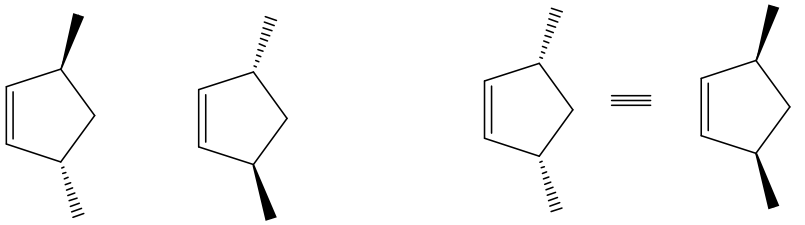
2-Chloro-3-aminobutanoic acid

compound 1: (2R. 3R) compound 2: (2R. 3S) compound 3: (2R. 3R)

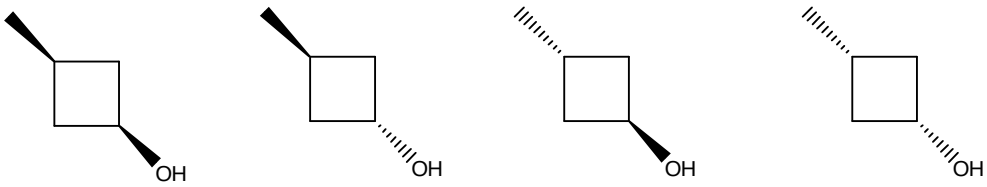
compound 4: (2S. 3R) compound 5: (2S. 3S)

1 = 3 and 5 are enantiomers 2 and 4 are enantiomers

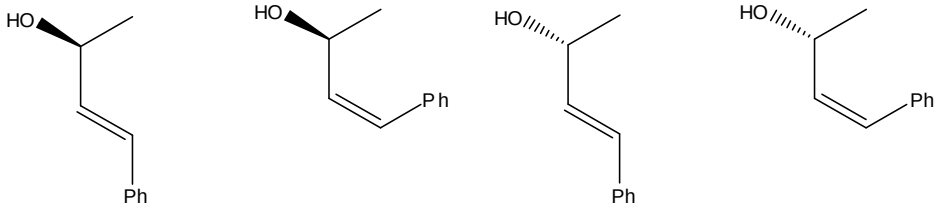
b) compound A: 3 stereoisomers



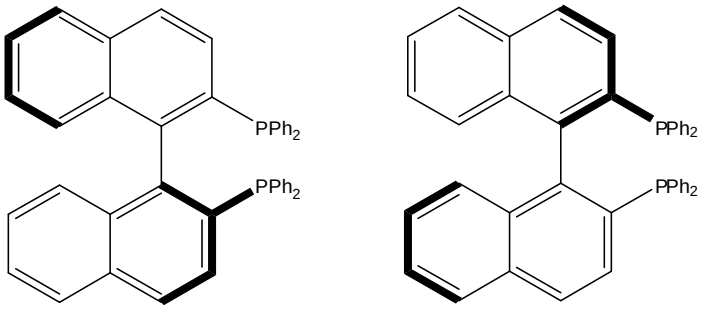
compound B: 3 stereoisomers



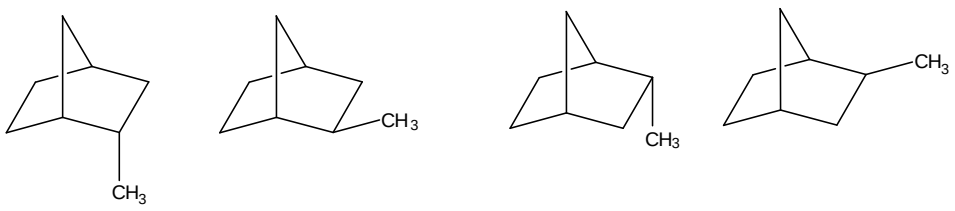
compound C: 4 stereoisomers



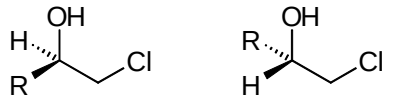
compound D: 2 stereoisomers



compound E: 4 stereoisomers



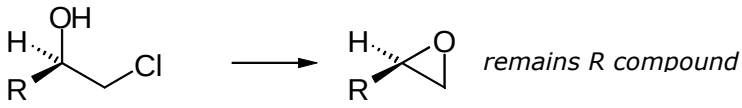
c) Structures of X(1) and X(2):



R compound *S compound*

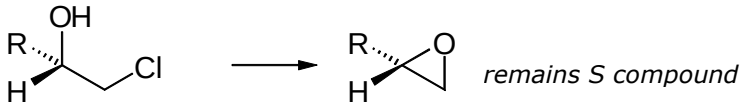
d) Structures of epoxides Y(1) and Y(2):

R compound

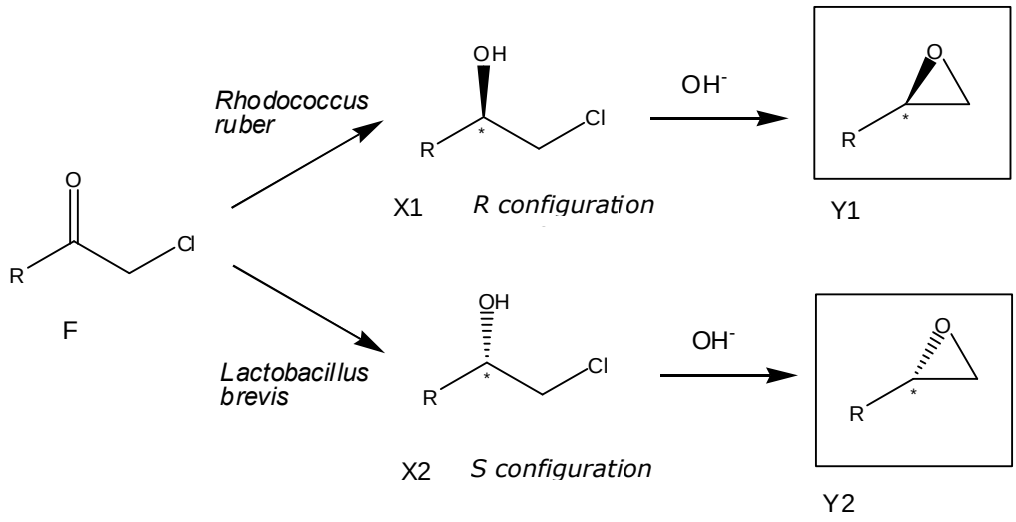


remains R compound

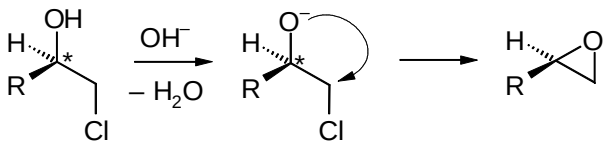
S compound



remains S compound

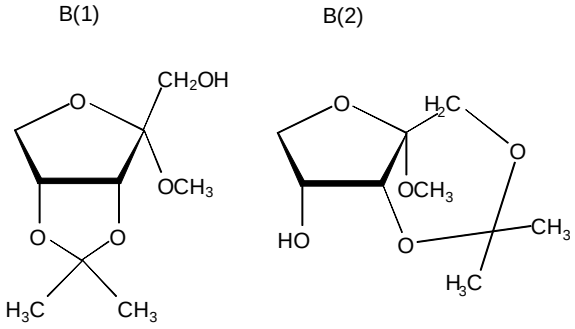


Reason: the mechanism of forming the ring has no influence on the central chiral carbon atom. Example:



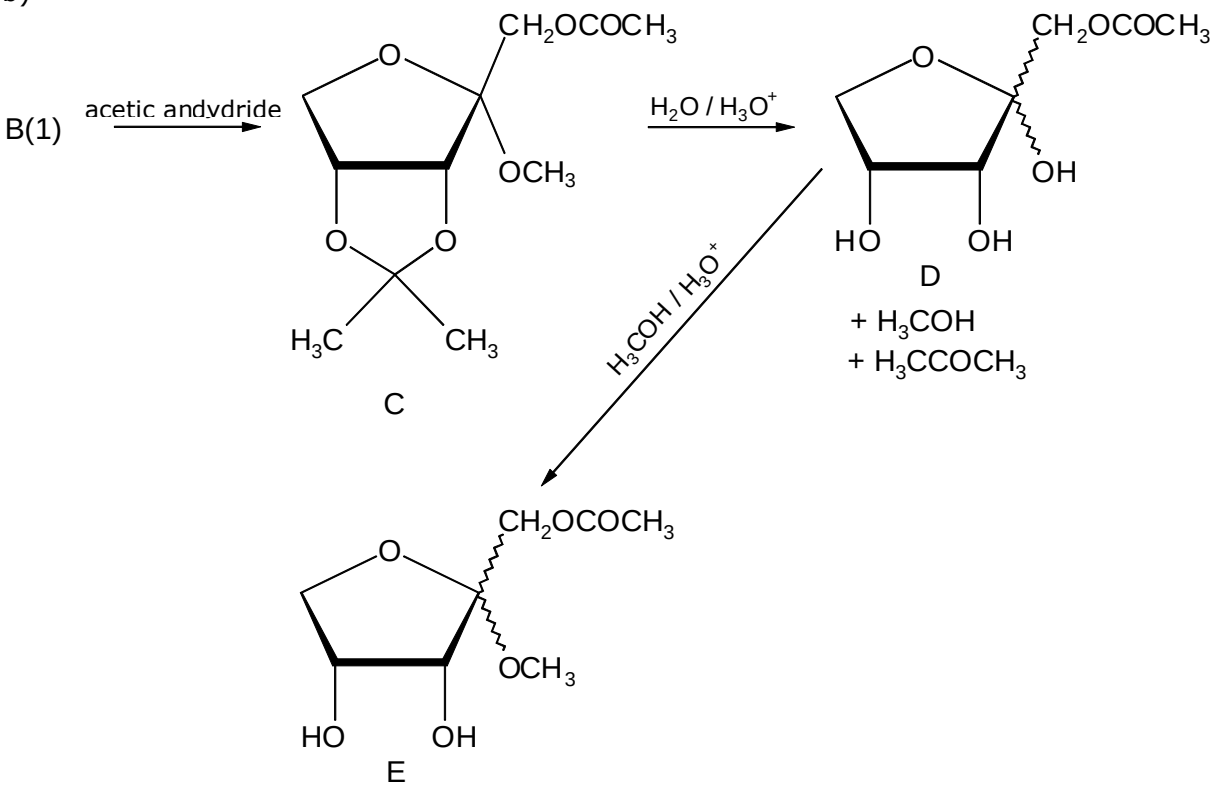
Solution to problem 4-10

a)



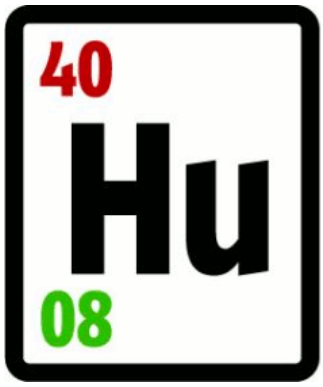
B(1) is the main product. Reason: steric hindrance during the formation of B(2).

b)



c) Sugar D does not any longer possess a fixed glycosidic OH-group after saponification. Hence it depends on the reaction conditions during the formation of compound E which sugar is formed preferentially.

Part 3



40th International Chemistry Olympiad

Theoretical and Practical Problems

17 + 15 July 2008

Budapest, Hungary

Avogadro constant:	$N_A = 6.022 \cdot 10^{23}$ mol^{-1}	Ideal gas equation:	$pV = nRT$
Gas constant:	$R = 8.314$ J K^{-1} mol^{-1}	Gibbs energy:	$G = H - TS$
Faraday constant:	$F = 96485$ C mol^{-1}		$\Delta_r G^o = -RT \ln K = -nFE^o_{cell}$
Planck constant:	$h = 6.626 \cdot 10^{-34}$ J s	Nernst equation:	$E = E^o + \frac{RT}{zF} \ln \frac{c_{ox}}{c_{red}}$
Speed of light:	$c = 3.000 \cdot 10^8$ m s^{-1}	Energy of a photon:	$E = \frac{hc}{\lambda}$
Zero of the Celsius scale:	273.15 K	Lambert-Beer law:	$A = \log \frac{I_0}{I} = \varepsilon c l$

In equilibrium constant calculations all concentrations are referenced to a standard concentration of 1 mol/dm^3. Consider all gases ideal throughout the exam.

Periodic table with relative atomic masses

1																	18
1 H 1.008	2											13	14	15	16	17	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.30	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.96	43 Tc -	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57-71	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -							

57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm -	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
89 Ac -	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

Problem 1

The label on a bottle containing a dilute aqueous solution of an acid became damaged. Only its concentration was readable. A pH meter was nearby, and a quick measurement showed that the hydrogen ion concentration is equal to the value on the label.

a) *Give the formulae of four acids that could have been in the solution if the pH changed one unit after a tenfold dilution.*

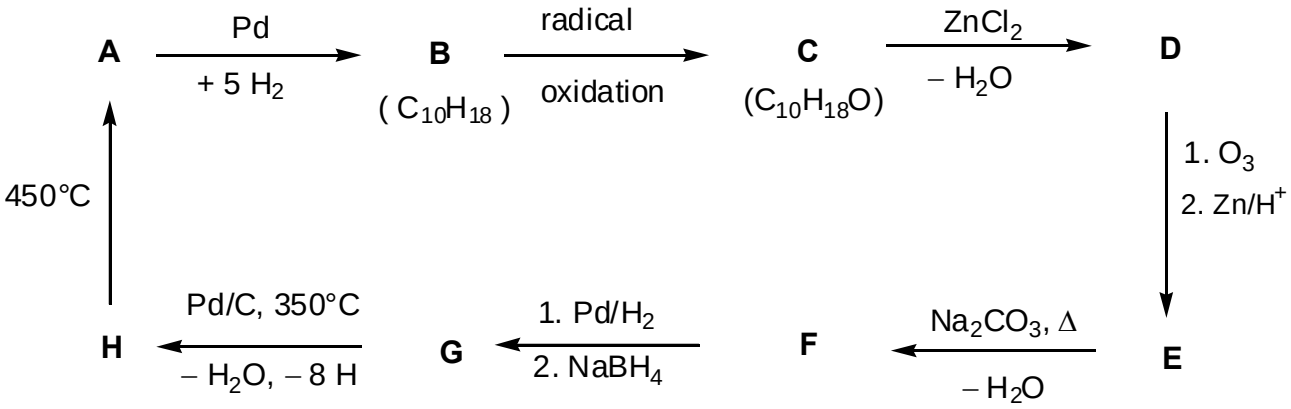
b) *Could it be possible that the dilute solution contained sulfuric acid?*
Sulfuric acid: $pK_{a2} = 1.99$
If yes, calculate the pH (or at least try to estimate it) and show your work.

c) *Could it be possible that the solution contained acetic acid?*
Acetic acid: $pK_a = 4.76$
If yes, calculate the pH (or at least try to estimate it) and show your work.

d) *Could it be possible that the solution contained EDTA (ethylene diamino tetraacetic acid)? You may use reasonable approximations.*
EDTA: $pK_{a1} = 1.70$, $pK_{a2} = 2.60$, $pK_{a3} = 6.30$, $pK_{a4} = 10.60$
If yes, calculate *the concentration.*

Problem 2

Determine the structure of the compounds **A**-**H** (stereochemistry is not expected), based on the information given in the following reaction scheme:

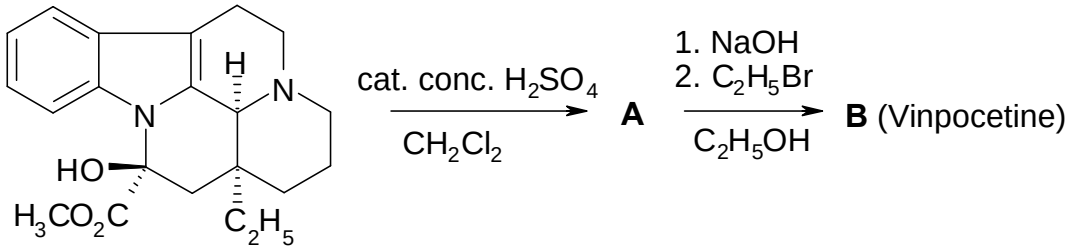


Hints:

- **A** is a well-known aromatic hydrocarbon.
- A hexane solution of **C** reacts with sodium (gas evolution can be observed), but **C** does not react with chromic acid.
- ^{13}C NMR spectroscopy shows that **D** and **E** contain only two kinds of CH_2 groups.
- When a solution of **E** is heated with sodium carbonate an unstable intermediate forms at first, which gives **F** on dehydration.

Problem 3

Vinpocetine (Cavinton®, Calan®) is one of the best selling original drugs developed in Hungary. Its preparation relies on a natural precursor, (+)-vincamine ($C_{21}H_{26}N_2O_3$), which is isolated from the vine plant, *vinca minor*. The transformation of (+)-vincamine to vinpocetine is achieved in two steps depicted below.



Vincamine

All compounds (**A** to **F**) are enantiomerically pure compounds.

- The elementary composition of **A** is: C 74.97%, H 7.19%, N 8.33%, O 9.55%.
- **B** has 3 other stereoisomers.

*a) Propose structures for the intermediate **A** and vinpocetine (**B**).*

A study of the metabolism of any drug forms a substantial part of its documentation. There are four major metabolites each formed from vinpocetine (**B**): **C** and **D** are formed in hydrolysis or hydration reactions, while **E** and **F** are oxidation products.

Hints:

- The acidity of the metabolites decreases in the order **C** >> **E** >> **D**. **F** does not contain an acidic hydrogen.
- **C** and **E** each have 3 other stereoisomers, while **D** and **F** each have 7 other stereoisomers.
- **F** is a pentacyclic zwitterion and it has the same elementary analysis as **E**: C 72.11%, H 7.15%, N 7.64%, O 13.10%.
- The formation of **E** from **B** follows an electrophilic pattern.
- The formation of **D** from **B** is both regio- and stereoselective.

*b) Propose one **possible** structure for each of the metabolites **C**, **D**, **E** and **F**!*

*c) Draw a resonance structure for **B** that explains the regioselective formation of **D** and the absence of the alternate regioisomer in particular.*

Problem 4

A major transformation route for oxiranes (epoxides) is ring opening. This may be accomplished in various ways.

On acid catalysis the reactions proceed through cation-like (carbenium ion-like) species. For substituted oxiranes the direction of ring opening (which C–O bond is cleaved) depends on the stability of the intermediate carbenium ion. The more stable the intermediate carbenium ion the more probable its formation. However, an open carbenium ion (with a planar structure) only forms if it is tertiary, benzylic or allylic.

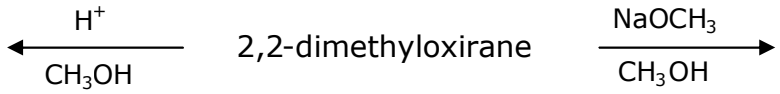
On base catalysis the sterically less hindered C–O bond is cleaved predominantly.

Keep stereochemistry in mind throughout the whole problem. To depict stereochemistry use only the  bond symbols and nothing else where necessary.

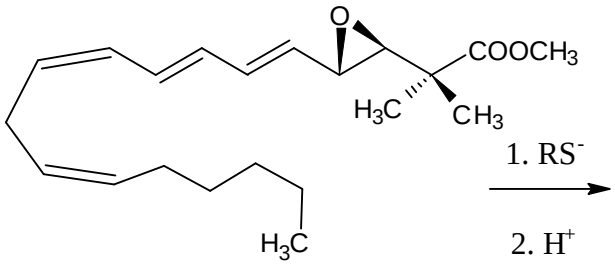
a) Draw the structure of the reactant and the predominant products when 2,2-dimethyl-oxirane (1,2-epoxy-2-methylpropane) reacts with methanol at low temperatures, catalysed by

(i) sulfuric acid

(ii) $NaOCH_3$.



b) Draw the structure of the predominant product when the epoxide ring of the following leukotriene derivative is opened with a thiolate (RS^-).



Different porous **acidic** aluminosilicates can also be used to catalyse the transformation of alkyl oxiranes. In addition to ring opening, cyclic dimerisation is found to be the main reaction pathway producing mainly 1,4-dioxane derivatives (six-membered saturated rings with two oxygen atoms in positions 1,4).

c) *Draw the structure(s) of the most probable 1,4-dioxane derivative(s) when the starting compound is (S)-2-methyloxirane ((S)-1,2-epoxypropane). Give the structure of the reactant as well.*

d) *Draw the structure(s) of the substituted 1,4-dioxane(s) when the epoxide reacting is (R)-1,2-epoxy-2-methylbutane ((R)-2-ethyl-2-methyloxirane). Give the structure of the reactant as well.*

e) *Give the structure(s) of the substituted 1,4-dioxane(s) when this reaction is carried out with racemic 1,2-epoxy-2-methylbutane (2-ethyl-2-methyloxirane).*

Problem 5

A and **B** are white crystalline substances. Both are highly soluble in water and can be moderately heated (up to 200 °C) without change but both decompose at higher temperatures. If an aqueous solution of 20.00 g **A** (which is slightly basic, pH ≈ 8.5-9) is added to an aqueous solution of 11.52 g **B** (which is slightly acidic, pH ≈ 4.5-5) a white precipitate **C** forms that weighs 20.35 g after filtering, washing and drying. The filtrate is essentially neutral and gives a brown

colour reaction with an acidified KI solution. When boiled, the filtrate evaporates without the appearance of any residue.

The white solid **D** can be prepared by the heating of **A** in the absence of air. The exothermic reaction of **D** with water gives a colourless solution. This solution, if kept in an open container, slowly precipitates a white solid **E** and leaves water. Upon prolonged exposure to air at room temperature, solid **D** is transformed into **E** as well. However, heating **D** in air at 500 °C produces a different white substance **F**, which is barely soluble in water and has a mass of only 85.8% of the **E** formed from the same amount of **D**. **F** gives a brown colour reaction with an acidified solution of KI.

E can be converted back into **D** but ignition above 1400 °C is required for this purpose. The reaction of **B** and **D** in water forms the precipitate **C** and is accompanied by a characteristic odour.

*a) Give the formulae of the substances **A** - **F***

*b) Write balanced equations for all the reactions mentioned. (The equation for the thermal decomposition of **B** is not required.)*

Problem 6

A feathery, greenish solid precipitate can be observed if chlorine gas is bubbled into water close to its freezing point. Similar precipitates form with other gases such as methane and noble gases. These materials are interesting because vast quantities of the so-called methane-hydrates are supposed to exist in nature (comparable in quantity with other natural gas deposits).

These precipitates all have related structures. The molecules of water just above its freezing point form a hydrogen-bonded structure. The gas molecules stabilize this framework by filling in the rather large cavities in the water structure forming clathrates.

The crystals of chlorine and methane clathrates have the same structure. Their main characteristics are dodecahedra formed from 20 water molecules. The unit cell of the crystal can be thought as a body-centered cubic arrangement built from these dodecahedra which are almost spherical objects. The dodecahedra are connected via additional water molecules located on the faces of the unit cell. Two water molecules can be found on each face of the unit cell. The unit cell has an edge dimension of 1.182 nm.

There are two types of cavities in this structure. One is the internal space in the dodecahedra (**A**). These are somewhat smaller than the other type of voids (**B**), of which there are 6 for each unit cell.

*a) How many type **A** cavities can be found in a unit cell?*

b) How many water molecules are there in a unit cell?

c) If all cavities contain a guest molecule, what is the ratio of the number of water to the number of guest molecules?

*d) Methane hydrate is formed with the structure in **c)** at temperatures between 0-10 °C. What is the density of the clathrate?*

e) The density of chlorine hydrate is 1.26 g/cm^3. What is the ratio of the number of water and guest molecules in the crystal?
Which cavities are likely to be filled in a perfect chlorine hydrate crystal? Mark one or more.

Covalent radii reflect atomic distances when the atoms are covalently bonded. Nonbonded or van der Waals radii give a measure of the atomic size when they are not bonded covalently (modeled as hard spheres).

Atom	Covalent radius (pm)	Nonbonded radius (pm)
H	37	120
C	77	185
O	73	140
Cl	99	180

f) Based on the covalent and nonbonded radii of these atoms estimate lower and upper bounds for the average radii of the cavities where possible. Show your reasoning.

Let us consider the following processes

$H_2O(l) \rightarrow H_2O(s)$ (1)

$x\ CH_4(g) + H_2O\ (l) \rightarrow xCH_4.1H_2O(clathrate)$ (2)

g) What are the signs of the following molar quantities referring to these reactions in the given direction at 4 °C? Mark with a –, 0 or +.

	sign		sign		sign
$\Delta G_m(1)$		$\Delta H_m(2)$		$\Delta S_m(2) - \Delta S_m(1)$	
$\Delta G_m(2)$		$\Delta S_m(1)$		$\Delta H_m(2) - \Delta H_m(1)$	
$\Delta H_m(1)$		$\Delta S_m(2)$			

Problem 7

The dithionate ion ($S_2O_6^{2-}$) is a rather inert inorganic ion. It can be prepared by bubbling sulphur-dioxide continously into ice-cooled water to which manganese dioxide is added in small increments. Dithionate and sulphate ions are formed under these circumstances.

a) Write the balanced chemical equations for the two reactions.

After the reaction is complete, $Ba(OH)_2$ is added to the mixture until the sulphate ions are fully precipitated. This is followed by the addition of Na_2CO_3.

b) Write the balanced equation for the reaction that takes place upon addition of Na_2CO_3.

Sodium dithionate is then crystallized by evaporating some of the solvent. The prepared crystals dissolve readily in water and do not give a precipitate with $BaCl_2$ solution. When the solid is heated and maintained at 130 °C, 14.88 % weight loss is observed. The resulting white powder dissolves in water and does not give a precipitate with $BaCl_2$ solution. When another sample of the original crystals is kept at 300 °C for a few hours, 41.34 % weight loss occurs. The resulting white powder dissolves in water and gives a white precipitate with $BaCl_2$ solution.

c) Give the composition of the prepared crystals and <u>write</u> balanced equations for the two processes that occur during heating.

Although dithionate ion is a fairly good reducing agent thermodynamically, it does not react with oxidants in solution at room temperature. At 75 °C, however, it can be oxidized in acidic solutions. A series of kinetic experiments were carried out with bromine as an oxidant.

d) Write the balanced chemical equation for the reaction between bromine and dithionate ion.

The initial rates (v_0) of the reaction were determined in a number of experiments at 75 °C:

$[Br_2]_0$ (mmol/dm^3)	$[Na_2S_2O_6]_0$ (mol/dm^3)	$[H^+]_0$ (mol/dm^3)	v_0 (nmol dm^{-3}s^{-1})
0.500	0.0500	0.500	640
0.500	0.0400	0.500	511
0.500	0.0300	0.500	387
0.500	0.0200	0.500	252
0.500	0.0100	0.500	129
0.400	0.0500	0.500	642
0.300	0.0500	0.500	635
0.200	0.0500	0.500	639
0.100	0.0500	0.500	641
0.500	0.0500	0.400	511
0.500	0.0500	0.300	383
0.500	0.0500	0.200	257
0.500	0.0500	0.100	128

e) Determine the order of the reaction with respect to Br_2, H^+ and $S_2O_6^{2-}$, the experimental rate equation, and the value and unit of the rate constant.

In similar experiments, chlorine, bromate ion, hydrogen peroxide and chromate ion have all been used as oxidizing agents at 75 °C. The rate equations for these processes are analogous to the one observed with bromine, the units of all rate constants are the same, the values are $2.53 \cdot 10^{-5}$ (Cl_2), $2.60 \cdot 10^{-5}$ (BrO_3^-), $2.56 \cdot 10^{-5}$ (H_2O_2), and $2.54 \cdot 10^{-5}$ ($Cr_2O_7^{2-}$).

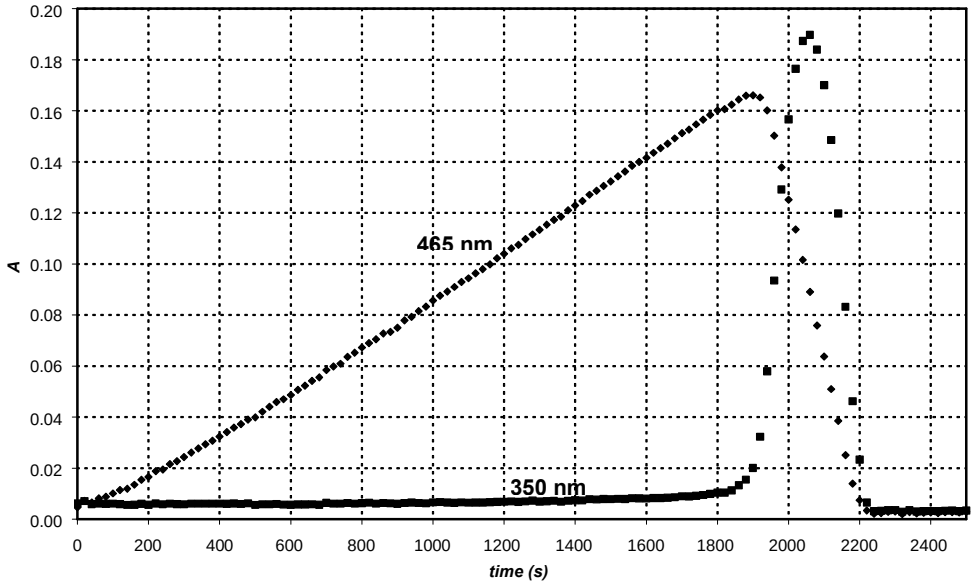
Experiments were also carried out in acidic sodium dithionate solution without any oxidizing agent. When following the processes by UV spectrophotometry, the slow appearance of a new absorption band around 275 nm was observed. Although hydrogen sulphate ion is a detectable product of the reaction, it does not absorb any light above 200 nm.

f) Give the formula of the major species causing the new absorption band and write the balanced equation of the chemical reaction occurring in the absence of oxidants.

An experiment was carried out to follow the absorbance at 275 nm with initial concentrations: $[Na_2S_2O_6]$ = 0.0022 mol/dm^3, $[HClO_4]$ = 0.70 mol/dm^3, and the temperature was 75 °C. A pseudo first-order kinetic curve was found with a half-life of 10 hours and 45 minutes.

g) Calculate the rate constant of the reaction.
Suggest a balanced chemical equation for the rate determining step of the reactions that used an oxidizing agent.

When periodate ion (which is present as $H_4IO_6^-$ in aqueous solution) was used as an oxidant for dithionate ion, the two kinetic curves depicted in the graph were detected at 75 °C in the same experiment at two different wavelengths. The initial concentrations were $[H_4IO_6^-] = 5.3 \cdot 10^{-4}$ mol/dm^3, $[Na_2S_2O_6] = 0.0519$ mol/dm^3, $[HClO_4] = 0.728$ mol/dm^3 At 465 nm, only I_2 absorbs and its molar absorption coefficient is 715 dm^{3}mol^{-1}cm^{-1}. At 350 nm, only I_3^- absorbs and its molar absorption coefficient is 11000 dm^{3}mol^{-1}cm^{-1}. The optical path length was 0.874 cm.



h) Write balanced chemical equations for the reactions that occur in the region where the absorbance increases at 465 nm, and in the region where the absorbance decreases at 465 nm.
Calculate the expected time for the maximum absorbance of the kinetic curve measured at 465 nm.
Estimate the expected ratio of the slopes of the increasing and decreasing regions in the kinetic curve measured at 465 nm

Problem 8

Ms. Z was a bright student, whose research project was to measure the complexation of all lanthanide(III) ions with newly designed complexing ligands. One

day she monitored the UV-vis absorption with Ce(III) and a particularly poor complexing ligand in a spectrophotometer. She noticed that some small bubbles had formed in the closed cell by the end of the 12-hour experiment. Soon she realized that the presence of the ligand is not necessary to see the bubble formation, and continued her experiments with an acidified $CeCl_3$ solution. Bubble formation never occurred when she just kept the solution in the spectrophotometer without turning on the instrument. Next, Ms. Z used a small quartz flask, in which she dipped a chloride ion selective electrode and could also withdraw samples regularly for spectrophotometric measurements. She calibrated the chloride ion selective electrode using two different NaCl solutions and obtained the following results:

c_{NaCl} (mol/dm^3)	E (mV)
0.1000	26.9
1.000	−32.2

*a) Give a formula to calculate the chloride ion concentration of an unknown sample based on the electrode voltage reading (*E*).*

Ms. Z also determined the molar absorption coefficient for Ce^{3+} (ε = 35.2 dm^{3}mol^{-1}cm^{-1}) at 295 nm, and, as a precaution, also for Ce^{4+} (ε = 3967 dm^{3}mol^{-1}cm^{-1}).

*b) Give a formula to calculate the Ce^{3+} concentration from an absorbance reading at 295 nm (*A*) measured in a solution containing $CeCl_3$ (cuvette path length: 1.000 cm).*

Ms. Z prepared a solution which contained 0.0100 mol/dm^3 $CeCl_3$ and 0.1050 mol/dm^3 HCl, and began her experiment by turning on a quartz lamp. HCl does not absorb at 295 nm.

c) What were the expected initial absorbance and voltage readings?

Before the quantitative experiment Ms. Z collected the gas formed into a carefully neutralized solution of methyl orange (acid-base and redox indicator). Although she saw bubbles going through the solution, the colour did not change or fade even after a day.

d) Give the formula of two gases, comprised of elements in the illuminated sample, which could not be present given the results of this experiment.

During her quantitative experiment she recorded the absorbance and voltage values regularly. The uncertainty of the spectophotometric measurements is ±0.002 and the accuracy of the voltage measurements is ±0.3 mV.

time (min)	0	120	240	360	480
$A_{295\ nm}$	0.3496	0.3488	0.3504	0.3489	0.3499
E (mV)	19.0	18.8	18.8	19.1	19.2

e) Estimate the average rate of change in the concentrations of Ce^{3+}, Cl^-, H^+.

The following day, Ms. Z used an intense monochromatic light beam (254 nm) with an intensity of 0.0500 W. She passed this light through a 5-cm long quartz photoreactor filled with the same acidic $CeCl_3$ solution she had used before. She measured the molar absorption coefficient for Ce^{3+} (ε = 2400 $dm^3mol^{-1}cm^{-1}$) at 254 nm.

f) What percentage of the light is absorbed in this experimental setup?

The equipment allowed her to lead the gas first through a drying tube that removed traces of water vapour and then into a closed chamber, whose volume was 68 cm^3. The chamber was equipped with a high-precision manometer and an igniter. She first filled the chamber with dry argon to a pressure of 102165 Pa and then she turned on the lamp. In 18.00 hours, the pressure reached 114075 Pa. The temperature of the equipment was 22.0 °C.

g) Estimate the amount of substance of the gas collected in the chamber.

At this point, Ms. Z turned off the light and pressed the ignition button. When the chamber cooled down to the initial temperature, the final pressure was 104740 Pa.

Suggest the formula(s) of the gas(es) formed and collected, and <u>give</u> the balanced equation for the original chemical reaction taking place under illumination.

h) What would be the final pressure after the ignition if the chamber was being filled for 24 hours before ignition?

i) Estimate the quantum yield of product formation in the Ce(III) solution.

Problem 9

Thallium exists in two different oxidation states: Tl^+ and Tl^{3+}. Iodide ions can combine with iodine to form tri-iodide ions (I_3^-) in aquous solutions.

The standard redox potentials for some relevant reactions are:

$Tl^+(aq) + e^-$	$\longrightarrow$	$Tl(s)$	$E^o_1 = -0.336$ V
$Tl^{3+}(aq) + 3e^-$	$\longrightarrow$	$Tl(s)$	$E^o_2 = +0.728$ V
$I_2(s) + 2e^-$	$\longrightarrow$	$2I^-(aq)$	$E^o_3 = +0.540$ V

The equilibrium constant for the reaction $I_2(s) + I^-(aq) \rightarrow I_3^-(aq)$: $K_1 = 0.459$.
Use T=25 °C throughout this problem.

a) Calculate the redox potential for the following reactions:

$Tl^{3+}(aq) + 2\ e^- \rightarrow Tl^+(aq)$ E^o_4

$I_3^-(aq) + 2\ e^- \rightarrow 3\ I^-(aq)$ E^o_5

b) Write empirical formulae for all theoretically possible neutral compounds that contain one thallium ion and any number of iodide and/or tri-iodide ion(s) as anion(s).

There is an empirical formula that could belong to two different compounds. Which one?

Based on the standard redox potentials, which of the two isomers mentioned above is the stable one at standard conditions? Write the chemical reaction for the isomerisation of the other isomer of thallium iodide.

Complex formation can shift this equilibrium. The cumulative complex formation constant for the reaction $Tl^{3+} + 4I^- \rightarrow TlI_4^-$ is $\beta_4 = 10^{35.7}$

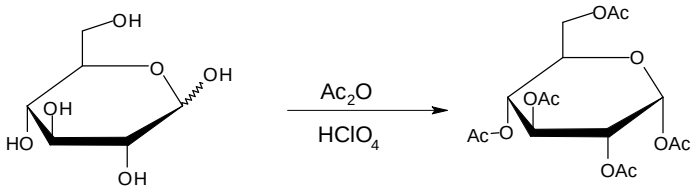
c) Write the reaction that takes place when a solution of the more stable isomer of thallium iodide is treated with an excess of KI. Calculate the equilibrium constant for this reaction.

If the solution of the more stable isomer is treated with a strong basic reagent precipitation of a black substance can be observed. After the water content of the precipitate is removed, the remaining material contains 89.5% thallium (by mass).

d) What is the empirical formula of this compound? Show your calculations. Write a balanced equation for its formation.

Practical Problems

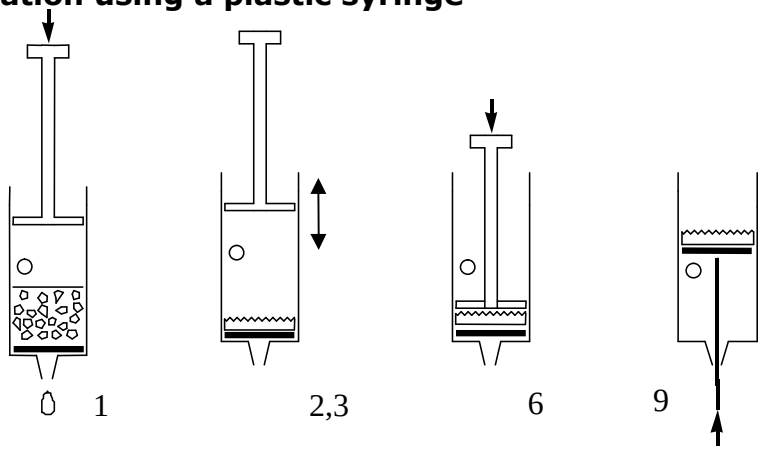
Task 1 Synthesis of α-D-glucopyranose pentaacetate



Caution: Use gloves while manipulating acetic acid and acetic anhydride. Let the lab supervisors know if any is spilled.

Add and mix 12 cm^3 of pure acetic acid to 12 cm^3 of acetic anhydride (provided in an Erlenmeyer flask) and add 3.00 g glucose (acetic anhydride is in excess). Add with a Pasteur-pipette 5 drops of 30% $HClO_4$ dissolved in acetic acid. After the addition of the catalyst the solution might warm up considerably.
Let the mixture rest covered for 10 minutes and swirl it from time to time. Pour the reaction mixture into 100 cm^3 of water in a beaker. Scratch the wall of the beaker with a glass rod to initiate crystallization, and let it crystallize for 10 minutes. Filter and wash the product two times with 10 cm^3 of water using the syringe and the porous polypropylene filter disc.

Filtration using a plastic syringe



1. Pull out the piston. Fill the syringe from above with the suspension to be filtered. The syringe can be filled to the level of the hole. Replace piston.
2. Cover the hole with your finger and press in the piston as far as the hole.
3. Open the hole and draw the piston back. Do not draw in air through the filter.
4. Repeat steps 2-3 a few times to expel the liquid.

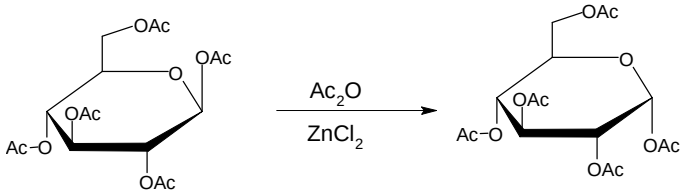
5. Repeat steps 1-4 until all solids are on the filter.
6. Press the piston against the filter cake and squeeze out the liquid.
7. Wash the product twice with 10 cm^3 of water repeating steps 1-4.
8. Press the piston against the filter cake and squeeze out the water.
9. Pull the piston out with the hole closed to lift out the filter cake. (Pushing with the end of the spatula can help.)

a) Place your product in the open Petri dish marked with your code. Leave it on your table. The organizers will dry it, weigh it and check it for purity.

*b) Calculate the theoretical yield (mass) of your product in g. (*M*(C) = 12 g/mol,* M*(O) = 16 g/mol,* M*(H)= 1.0 g/mol*

Synthesis of α-D-glucopyranose pentaacetate from β-D-glucopyranose pentaacetate

An alternative synthesis of α-D-glucopyranose pentaacetate starts from readily available β-D-glucopyranose pentaacetate. In this experiment we will study the kinetics of this reaction with thin layer chromatography.



Add 1.5 cm^3 acetic anhydride to 50 mg of anhydrous $ZnCl_2$ (preweighed in a test tube). Add 100 mg of pure β-D-glucopyranose pentaacetate (BPAG) and swirl until dissolved. Take three drops from this mixture into an Eppendorf tube, add 0.5 cm^3 methanol and save it.

Place the test tube in the heating apparatus under the hood closest to your desk. Place the test tube in the heating block preadjusted to 70ºC. Mix the contents of the test tube from time to time. During the reaction take three drops of sample from the mixture with a Pasteur pipet after 2, 5, 10, and 30 minutes. Mix immediately each sample with 0.5 cm^3 of methanol to stop the reaction in an Eppendorf tube.

Prepare a silica TLC plate with the collected samples to study the reaction kinetics. Apply the necessary reference compounds as well to help identification of the spots on the plate. Mark the spots with a pencil, and develop the plate in isobutyl acetate/ isoamyl acetate (1:1) eluent. Heat the plates with a heat-gun

(under the hood!) to visualise the spots (the colour is stable). You can ask for a second plate without penalty points if needed for proper evaluation.

c) *Copy your plate on the answer sheet and place your plate in the labeled zip-lock bag.*

d) *Interpret your experimental findings answering the questions on the answer sheet.*

The acetylation reaction of glucose is exothermic.
☐ a) Yes ✓
☐ b) No
☐ c) Cannot be decided based on these experiments

The isomerisation reaction of β-D-glucopyranose pentaacetate can be used for the preparation of pure α-D-glucopyranose pentaacetate.
☐ a) Yes ✓
☐ b) No
☐ c) Cannot be decided based on these experiments

Task 2

Insert this remark in your translation if your students do not know this kind of pipette.

Hint: The pipette has two graduation marks. Stop at the second mark to measure out exact volumes. Do not let all the solution to run out.

When potassium hexacyanoferrate(II), $K_4[Fe(CN)_6]$ is added to a solution containing zinc ions, an insoluble precipitate forms immediately. Your task is to find out the composition of the stoichiometric precipitate that contains no water of crystallization.

The precipitation reaction is quantitative and so quick that it can be used in a titration. The end point can be detected using redox indication, but first the concentration of the potassium hexacyanoferrate(II) solution has to be determined.

Preparation of $K_4[Fe(CN)_6]$ solution and determination of its exact concen-tration

Dissolve the solid $K_4[Fe(CN)_6].3H_2O$ (M = 422.41 g/mol) sample in the small Erlenmeyer flask and quantitatively transfer it into the 100.00 cm^3 volumetric flask. Take 10.00 cm^3 portions of the hexacyanoferrate(II) solution. Add 20 cm^3 1 mol/dm^3 sulfuric acid and two drops of the ferroin indicator solution to each

sample before titration. Titrate with the 0.05136 mol/dm^3 Ce^{4+} solution. Repeat titration as necessary. Cerium(IV) is a strong oxidant under acidic conditions forming Ce(III).

a) Report the Ce^{4+} solution volumes consumed.

b) Give the equation for the titration reaction. What was the mass of your $K_4[Fe(CN)_6].3H_2O$ sample?

The reaction between zinc ions and potassium hexacyanoferrate(II)

Take 10.00 cm^3 of the hexacyanoferrate(II) solution and add 20 cm^3 1 mol/dm^3 sulfuric acid. Add three drops of indicator solution (diphenyl amine) and two drops of $K_3[Fe(CN)_6]$ solution. The indicator only works if the sample contains some hexacyanoferrate(III), $[Fe(CN)_6]^{3-}$. Titrate slowly with the zinc solution. Continue until a bluish violet colour appears. Repeat titration as necessary.

c) Report the zinc solution volumes consumed.

d) Interpret the titration answering the questions on the answer sheet.

The diphenyl amine indicator changes in colour at the end point
- ☐ a) because the concentration of the Zn^{2+} ions increases.
- ☐ b) because the concentration of the $[Fe(CN)_6]^{4-}$ ions decreases. ✓
- ☐ c) because the concentration of the $[Fe(CN)_6]^{3-}$ ions increases.
- ☐ d) because the indicator is liberated from its complex.

Which form of the indicator is present before the end point?
- ☐ a) Oxidized
- ☐ b) Reduced ✓
- ☐ c) Complexed to a metal ion

At the beginning of the titration the redox potential for the hexacyanoferrate(II) - hexacyanoferrate(III) system is lower than the redox potential of the diphenyl amine indicator.
- ☐ a) True ✓
- ☐ b) False

e) Determine the formula of the precipitate.

Caveat: Best marks are not necessarily awarded to measurements reproducing theoretically expected values.

Task 3

Caution: Handle all unknown solutions as if they were toxic and corrosive. Discard them only in the appropriate waste container.
The heat gun heats the expelled air up to 500 °C. Do not direct the stream towards combustible materials or body parts. Be careful with the hot nozzle.
Always place a single piece of pumice into liquids before heating to avoid bumping. Never point the mouth of a heated test tube towards a person.

You have eight unknown aqueous solutions. Each solution contains only one compound. The same ion may appear in more than one solution. Every compound formally consists of one type of cation and one type of anion from the following list:

Cations: H^+, NH_4^+, Li^+, Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Sr^{2+}, Ag^+, Sn^{2+}, Sn^{4+}, Sb^{3+}, Ba^{2+}, Pb^{2+}, Bi^{3+}

Anions: OH^-, CO_3^{2-}, HCO_3^-, CH_3COO^-, $C_2O_4^{2-}$, NO_2^-, NO_3^-, F^-, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, SO_4^{2-}, HSO_4^-, S^{2-}, HS^-, Cl^-, ClO_4^-, MnO_4^-, Br^-, I^-

You have test tubes and heating but no additional reagents apart from distilled water and pH paper.

*Identify the compounds in the solutions **1**-**8**. You can use the solubility table for some of the anions on the next page. If you are unable to identify an ion exactly, give the narrowest selection possible.*

Remarks:
The unknown solutions may contain minor impurities arising from their exposure to air. The concentration of all solutions is around 5 % by mass so you can expect clearly observable precipitates from the main components. In some cases, precipitation does not occur instantaneously; some substances may remain in an oversaturated solution for a while. Don't draw negative conclusions too hastily, wait 1-2 minutes where necessary. Always look carefully for all signs of a reaction.
Keep in mind that heating accelerates all processes, increases the solubility of most substances, and may start reactions that do not take place at room temperature.

Solutions used in the test: $AgNO_3$, $KHCO_3$, NH_4ClO_4, NaOH, NaHS, $Pb(OAc)_2$, BaI_2, $MgSO_4$

Solubility Table at 25 °C

	NH_4^+	Li^+	Na^+	Mg^{2+}	Al^{3+}	K^+	Ca^{2+}	Cr^{3+}	Mn^{2+}	Fe^{2+}	Fe^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Sr^{2+}	Ag^+	Sn^{2+}	Sn^{4+}	Sb^{3+}	Ba^{2+}	Pb^{2+}	Bi^{3+}
CH_3COO^-														HR			1.0	↓	↓	↓			↓
$C_2O_4^{2-}$			3.6	↓			↓		↓	↓ (Y)	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
NO_2^-	HR				HR			HR		↓ R				HR	↓		0.41 ((Y))	↓ R	↓	↓			↓
NO_3^-																							
F^-		0.13		↓	0.5		↓	4.0	1.0	↓ (W)	↓ (W)	1.4	2.6	↓	1.6	↓			↓		0.16	↓	↓
SO_4^{2-}							0.21									↓	0.84		↓		↓	↓	
PO_4^{3-}	HR	↓		↓	↓		↓	↓	↓	↓ (W)	↓	↓ (P)	↓	↓	↓	↓	↓ (Y)	↓	↓	↓	↓	↓	↓
HPO_4^{2-}		↓		↓	↓		↓	↓	↓	↓ (W)	↓ (W)	↓ (P)	↓	↓	↓	↓	↓ (Y)	↓	↓	↓	↓	↓	↓
$H_2PO_4^-$					HR		1.0	HR	HR		↓ (W)	HR		↓	↓	HR	↓ (Y)	↓	↓	↓	HR	↓	↓
ClO_4^-						2.1																	
MnO_4^-	HR							HR	↓ R	R		HR					0.91	R		R		↓ R	
Br^-																	↓ ((Y))					0.98	
I^-											R			↓ R			↓ (Y)	1.0				↓ (Y)	↓ (B)

No entry: Soluble compound ↓: Insoluble compound **R**: Redox reaction at room temperature
HR: Soluble at room temperature. In hot solution a reaction with an observable effect (not necessarily a precipitate) takes place.
Solubilities in g (substance) / 100 g water. Accurately known values between 0.1 and 4 are shown only.
Precipitates whose colour significantly differs from that of their hydrated ions: (**B**) = black, (**P**) = purple, (**W**) = white, ((**Y**)) = pale yellow, (**Y**) = yellow.

Answers to the Theoretical Problems

Solution to problem 1

a) HCl, HI, HNO_3, $HClO_4$, any univalent stron g acid but not HF

b) no

c) yes, but only in quite dilute solutions this can happen.

$c = c(HA) + c(A^-) = c(H^+)$ und $c(H^+) = c(A^-) + c(OH^-)$

$\Rightarrow \quad c(HA) = c(OH^-)$

$$K_s = \frac{c(H^+)\cdot c(A^-)}{c(HA)} = \frac{c(H^+)\cdot (c(H^+)\cdot c(OH^-))}{c(HA)} = \frac{c(H^+)^3}{K_w} - c(H^+)$$

Solution by iteration: pH = 6.25.

You get the same solution using the approximation $c(H^+) = \sqrt[3]{K_s \cdot K_w}$.

d) Yes. You may suppose that this solution would be quite acidic, so that the 3rd and 4th protolysation step can be disregarded.

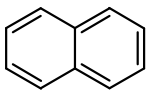
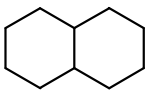
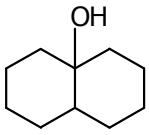
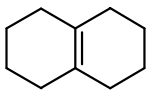
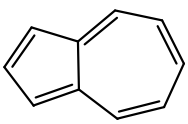
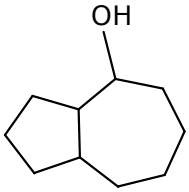
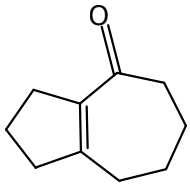
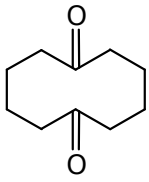
$c = c(H_4A) + c(H_3A^-) + c(H_2A^-) = c(H^+)$

$c(H^+) = c(H_3A^-) + 2\cdot c(H_2A^-) \quad \Rightarrow \quad c(H_4A) = c(H_2A^-)$

$$K_{s1} \cdot K_{s2} = \frac{c(H^+)^2 \cdot c(H_2A^-)}{c(H_4A)} = c(H^+)^2 \quad \Leftrightarrow \quad pH = ½ \cdot (pK_{s1} + pk_{S2})$$

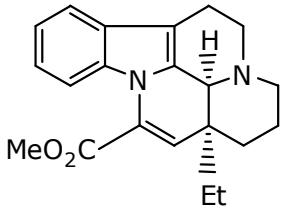
pH = 2.15 $\quad c = 10^{-2.15}$ mol/L $\quad c = 0.0071$ mol/L

Solution to problem 2

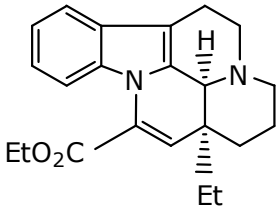
A 	**B** 	**C** 	**D** 
E 	**F** 	**G** 	**H** 

Solution to problem 3

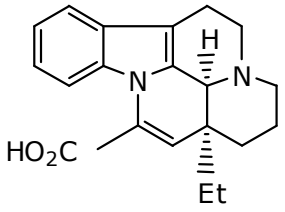
a) **A**



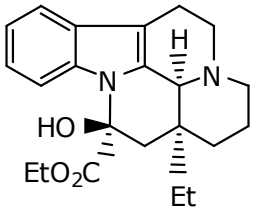
B



b) **C**

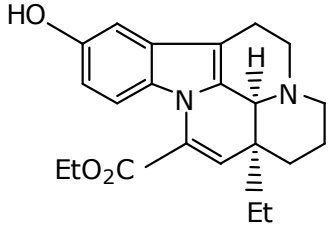


D

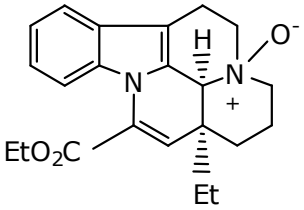


both stereoisomers around the new chiral center are acceptable.

E

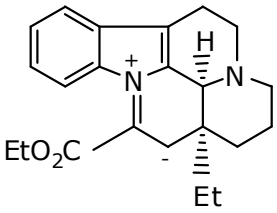


F



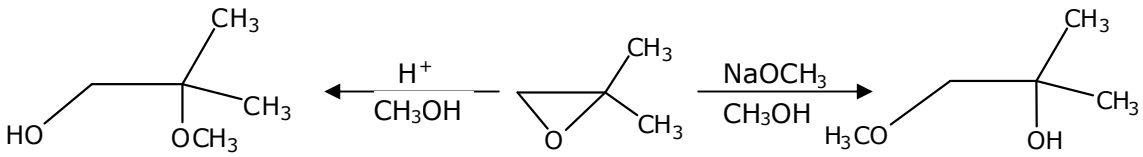
All aromatic posittions for OH in **E** are acceptable.

c)

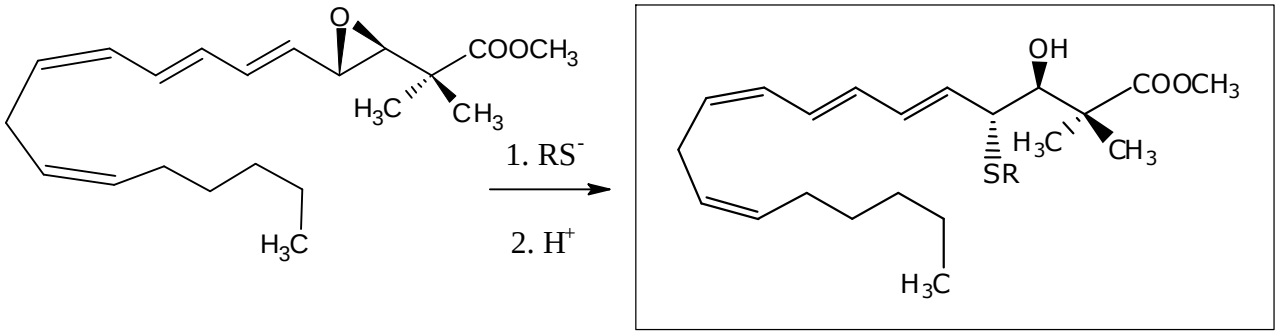


Solution to problem 4

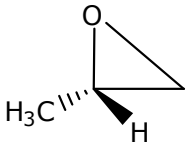
a) 2,2-dimethyloxirane



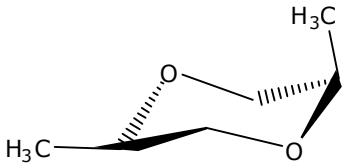
b)



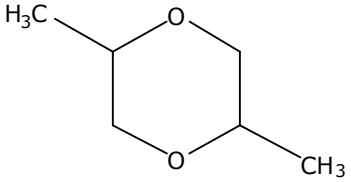
c)



(S)-2-methyloxirane

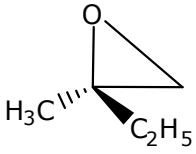


or

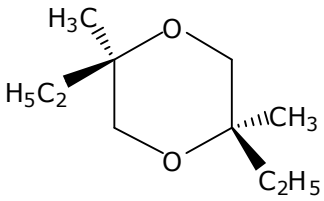


produkt

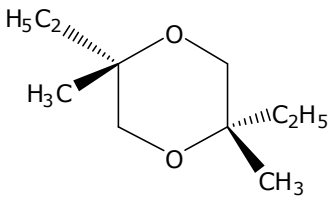
d)



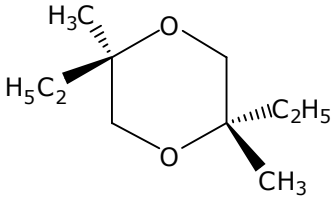
(R)-1,2-epoxy-2-methylbutane



R,R

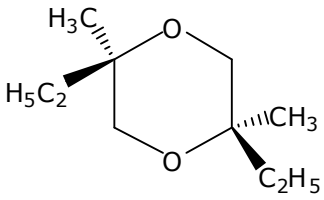


S,S

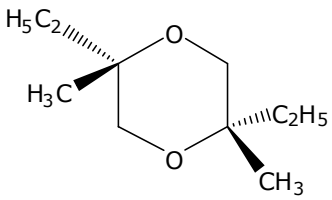


R,S

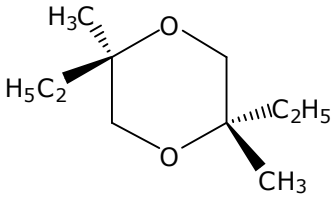
e)



R,R



S,S



R,S

Solution to problem 5

a)

A	$Ba(NO_3)$	**B**	$(NH_4)_2SO_4$	**C**	$BaSO_4$
D	BaO	**E**	$BaCO_3$	**F**	BaO_2

b)

$Ba(NO_3)_2 \longrightarrow BaO + NO + NO_2$

$(NH_4)_2SO_4 \longrightarrow NH_4HSO_4 + NH_3$

$Ba^{2+} + SO_4^{2-} \longrightarrow BaSO_4$

$2\ NO_2^- + 2\ I^- + 4\ H^+ \longrightarrow 2\ NO + I_2 + 2\ H_2O$

$NH_4^+ + NO_2^- \longrightarrow N_2 + 2\ H_2O$

$BaO + H_2O \longrightarrow Ba^{2+} + 2\ OH^-$

$Ba^{2+} + 2\ OH^- + CO_2 \longrightarrow BaCO_3 + H_2O$

$BaO + CO_2 \longrightarrow BaCO_3$

$2\ BaO + O_2 \longrightarrow 2\ BaO_2$

$BaO_2 + 2\ I^- + 4\ H^+ \longrightarrow Ba^{2+} + I_2 + 2\ H_2O$

$BaCO_3 \longrightarrow BaO + CO_2$

$NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$

Solution to problem 6

a) 2 b) 20·2 (dodecahedra) + 6·2 /2 (faces) c) 46 : 8 = 5.75

d) V(unit cell) = 1.183^3 nm^3 = 1.651 nm^3
the unit cell contains 8 methane and 46 water molecules with the mass of
m = 957 g mol^{-1} / N_A = $1.589 \cdot 10^{-21}$ g
ρ = 1.589/1.651 g/cm^3 = 0.962 g/cm^3

e) m(unit cell) = 1.651 nm^3 · 1.26 g/cm^3 = $2.081 \cdot 10^{-21}$ g.
M(unit cell) = $2.081 \cdot 10^{-21}$ g · N_A = 1253 g/mol
M(unit cell) – 46 · $M(H_2O)$ = 424.3 g/mol.
according to 11.97 chlorine atoms/unit cell (6 Cl_2 molecules)
ratio = 46 : 6 = 7.68
it is expected that only the 6 larger B type cavities contain chlorine.

f) Methan mit einem ungefähren Radius von (37 + 77 + 120) pm = 234 pm passt in alle Lücken, das Chlormolekül mit dem Radius von (180 + 99) pm = 279 pm nur in B passt.
$\Rightarrow$ 234 < r(A) < 279 pm < r(B)

g)

	sign
$\Delta G_m(1)$	+
$\Delta G_m(2)$	-
$\Delta H_m(1)$	-
$\Delta H_m(2)$	-
$\Delta S_m(1)$	-
$\Delta S_m(2)$	-
$\Delta S_m(2) - \Delta S_m(1)$	-
$\Delta H_m(2) - \Delta H_m(1)$	-

Solution to problem 7

a) $MnO_2 + 2\ SO_2 \longrightarrow Mn^{2+} + S_2O_6^{2-}$
$MnO_2 + SO_2 \longrightarrow SO_4^{2-}$

b) $MnS_2O_6 + Na_2CO_3 \longrightarrow Na_2S_2O_6 + MnCO_3$

c) Formela: $Na_2S_2O_6 \cdot 2H_2O$
at 130 °C: $Na_2S_2O_6 \cdot 2H_2O \longrightarrow Na_2S_2O_6 + 2\ H_2O$
at 300 °C $Na_2S_2O_6 \longrightarrow Na_2SO_4 + SO_2$

d) $S_2O_6^{2-} + Br_2 + 2\ H_2O \longrightarrow 2\ SO_2^{2-} + 2\ Br^- + 4\ H^+$

e) Reaction order of Br_2: 0 H^+: 1 $S_2O_6^{2-}$: 1
experimental rate equation: $v = k \cdot c(S_2O_6^{2-}) \cdot c(H^+)$
$k = 2.56 \cdot 10^{-5}\ dm^3 mol^{-1} s^{-1}$

f) Species: SO_2 or H_2SO_3
$S_2O_6^{2-} + H^+ \longrightarrow HSO_4^- + SO_2$

g) $t_{½} = 10\ h\ 45\ min = 3.87 \cdot 10^4\ s$
$k_{beob.} = \ln 2 / t_{½} = 1.79 \cdot 10\text{-}5\ s^{-1}$
$k = k_{beob.}/c(H^+) = 2.56 \cdot 10^{-5}\ dm^3 mol^{-1} s^{-1}$
Rate determining step: $S_2O_6^{2-} + H^+ \longrightarrow HSO_4^- + SO_2$

h) Increase: $2\ H_4IO_6^- + 7\ S_2O_6^{2-} + 2\ H_2O + 2\ H^+ \longrightarrow 14\ HSO_4^- + I_2$
Decrease: $I_2 + S_2O_6^{2-} + 2\ H_2O \longrightarrow 2\ HSO_4^- + 2\ I^- + 2^+$

$v = k \cdot c(S_2O_6^{2-}) \cdot c(H^+) = 2.56 \cdot 10^{-5}\ dm^3 mol^{-1} s^{-1} \cdot 0.0519\ mol/dm^3 \cdot 0.728\ mol/dm^3$
$v = 967\ nmol/L \cdot s^{-1}$
$\Delta n(S_2O_6^{2-}) = v \cdot \Delta t \qquad \Delta n(H_4IO_6^-) = 2/7 \cdot n(S_2O_6^{2-})$
$\Rightarrow \quad t_{max} = \dfrac{7 \cdot n_0(H_4IO_6^-)}{2 \cdot v} = 1{,}92 \cdot 10^3\ s$

slope ratio = 1:(-7) (it reflects the stoichiometry).

Solution to problem 8

a) $c(Cl^-) = 10^{-(E + 32.2\ mV)/59.1\ mV}$ b) $c(Ce^{3+}) = \frac{A_{295\ nm}}{35.2\ dm^3mol^{-1}}$

c) $c(Ce^{3+}) = 0.0100\ mol/dm^3 \Rightarrow A_{295\ nm} = 0.352$
$c(Cl^-) = (3\cdot0.0100 + 0.1050)\ mol/dm^3 = 0.1350\ mol/dm^3 \Rightarrow E = 19.2\ mV$

d) HCl. Cl_2 (O_3. ClO_2)

e) $dc(Ce^{3+})/dt = 0$ $dc(Cl^-)/dt = 0$ $dc(H^+)/dt = 0$

f) $A = 2400\ dm^3mol^{-1}cm^{-1} \cdot 5\ cm \cdot 0.0100\ moldm^{-3} = 120$
$\Rightarrow (100 - 10^{118})\ \% = 100\ \%$

g) $p_{partial} = p_{final} - p_{initial} = 114075\ Pa - 102165\ Pa = 11910\ Pa$
$n = p_{partial}\cdot V/(R\cdot T) = 11910\ Pa \cdot 6.8\cdot10^{-5}\ m^3/(8.314\ JK^{-1}mol^{-1}\cdot295.15\ K)$
$n = 3.3\cdot10^{-4}\ mol$
H_2, O_2 $2\ H_2O \longrightarrow 2\ H_2 + O_2$

h) $p_{final} = 104740\ Pa$ (saturated water vapor)

i) $3.3\cdot10^{-4}$ mol Gas = $2.2\cdot10^{-4}$ mol H_2 + $1.1\cdot10^{-4}$ mol O_2
Light beam intensity $0.0500 Js^{-1} \Rightarrow \frac{0.0500\ J/s\,\lambda}{hcN_A} = 1.06\cdot10^{-7}\ mols^{-1}$ photons

Total tiöme 18 h = 64800 s
absorbed photons 64800 s $\cdot$ $1.06\cdot10^{-7}\ mols^{-1} = 6.87\cdot10^{-3}$ mol
Quantum yield for H_2 production: $\Phi = 2.2\cdot10^{-4}$ mol/ $6.87\cdot10^{-3}$ mol = 0.032
Quantum yield for O_2 production: $\Phi = 0.016$

Solution to problem 9

a) $E^0_4 = \frac{3\cdot E^0_2 - E^1_0}{2} = 1.26\ V$ $E^0_5 = E^0_3 + 0.050/2 \cdot lg(1/K_1) = 0.550\ V$

b) TlI. TlI_3. TlI_5. TlI_7. TlI_9 TlI_3 can be either $Tl^{3+}(I^-)_3$ or $Tl^+(I_3^-)$
more stable: $Tl^+(I_3^-)$. da $E^0_4 > E^0_5$ bzw. E^0_3 ist
Isomeration $Tl^{3+} + 3\ I^- \longrightarrow Tl^+ + I_3^-$

c) $Tl^+ + I_3^- + I^- \longrightarrow TlI_4^-$ thought as addition of
$Tl^+(aq) \longrightarrow Tl^{3+}(aq) + 2e^-$ $-E^0_4 = -1.26\ V$ $\Delta G^0_4 = nF\,E^0_4$
$\Delta G^0_4 = 243.1\ kJ/mol$
$I_3^-(aq) + 2e^- \longrightarrow 3\ I^-(aq)$ $E^0_5 = 0.550\ V$ $\Delta G^0_5 = -106.1\ kJ/mol$
$Tl^{3+} + 4\ I^- \longrightarrow TlI_4^-$ $\beta_4 = 10^{35.7} \Rightarrow \Delta G^0_6 = -RTln\beta_4$
$\Delta G^0_6 = -203.8\ kJ/mol$

$\Delta G^0_7 = \Delta G^0_4 + \Delta G^0_5 + \Delta G^0_6 = -66.8\ kJ/mol$
$K_2 = e^{-\Delta G_7/RT} = 4.96\cdot10^{11}$

d) Supposing that the substance contains Tl and an anion: Tl_aX_b

$$\Rightarrow \quad \frac{a \cdot 204,4}{a \cdot 204,4 + b \cdot M_X} = 0.895$$

From the values a = 1. 2. 3 and b = 1.3 only a = 2 and b = 3 give a realistic M_X:

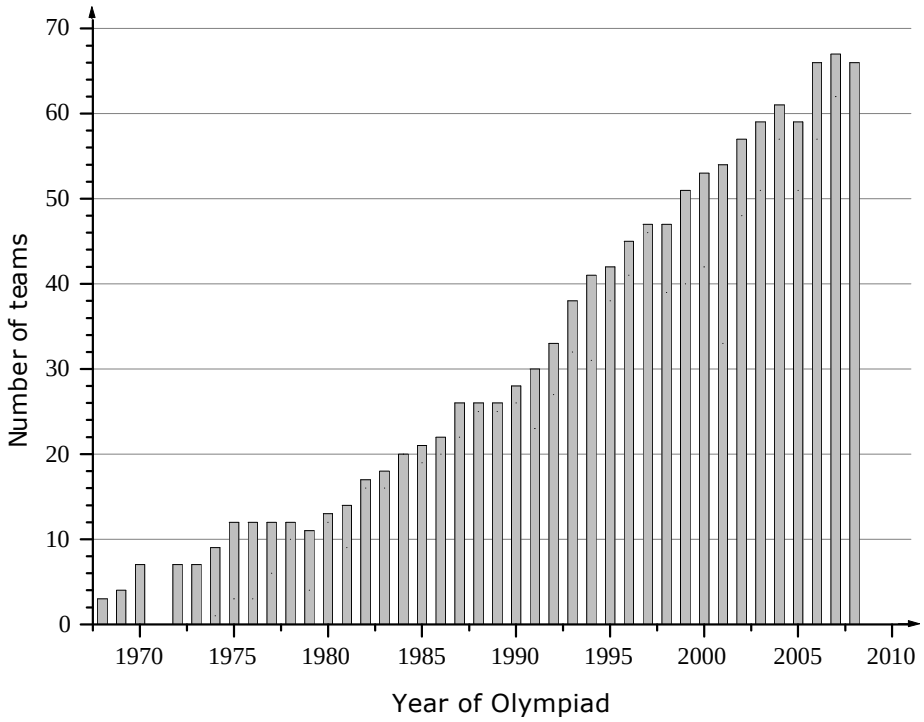
M_x = 16.0 g/mol X = oxygen

Tl_2O_3. $2\ TlI_3 + 6\ OH^- \longrightarrow Tl_2O_3 + 6\ I^- + 3\ H_2O$

About the history of the International Chemistry-Olympiads

The idea of chemistry olympiads was born 1968 during an Czechoslovakian national olympiad that was attended by observers from Poland and Hungary. These three countries participated in the first IChO 1968 in Prague. The number of teams attending the IChO in the following years are shown in the plot below.

Number of teams attending the IChO



The participating countries are shown in the following table.

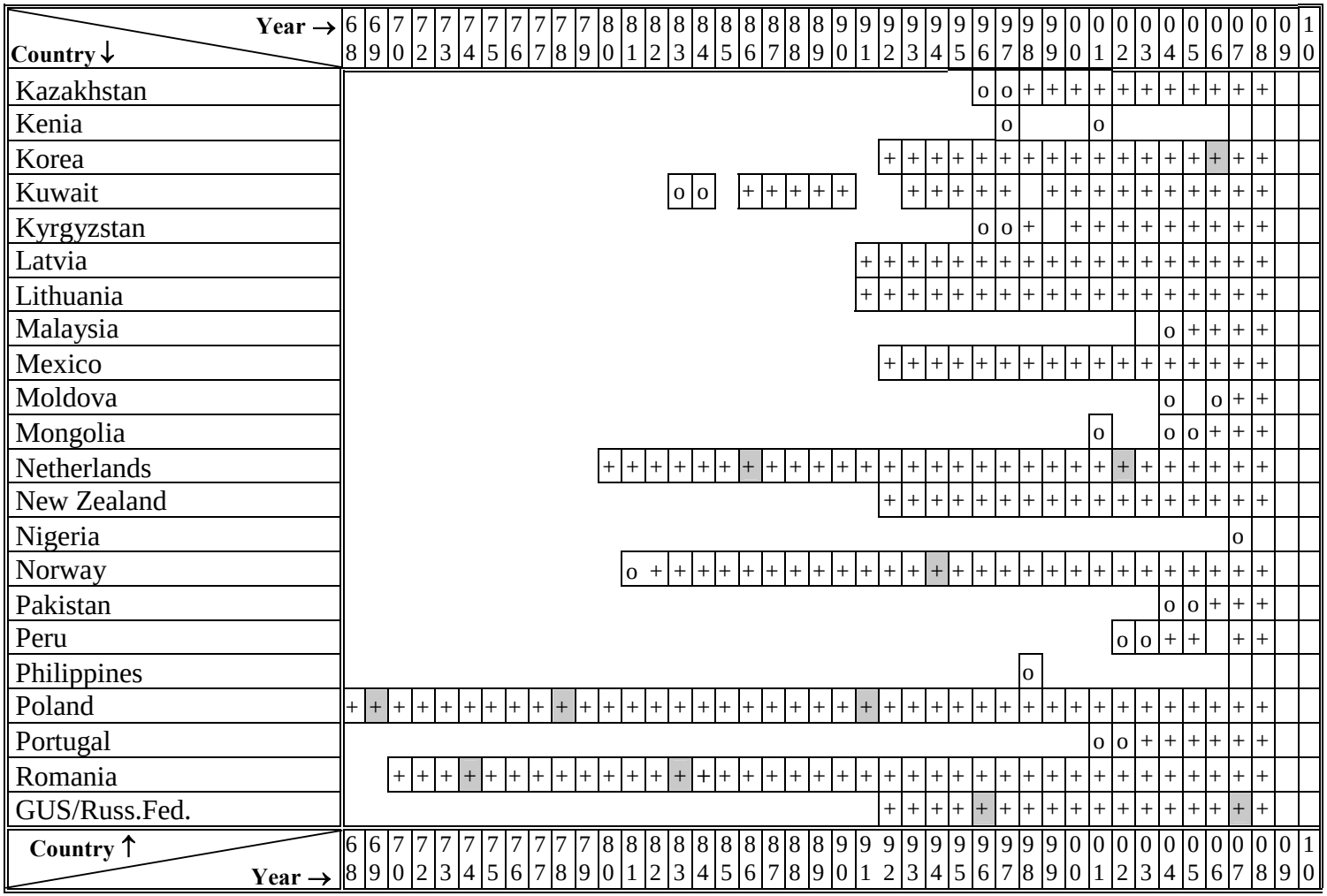
Participating Delegations

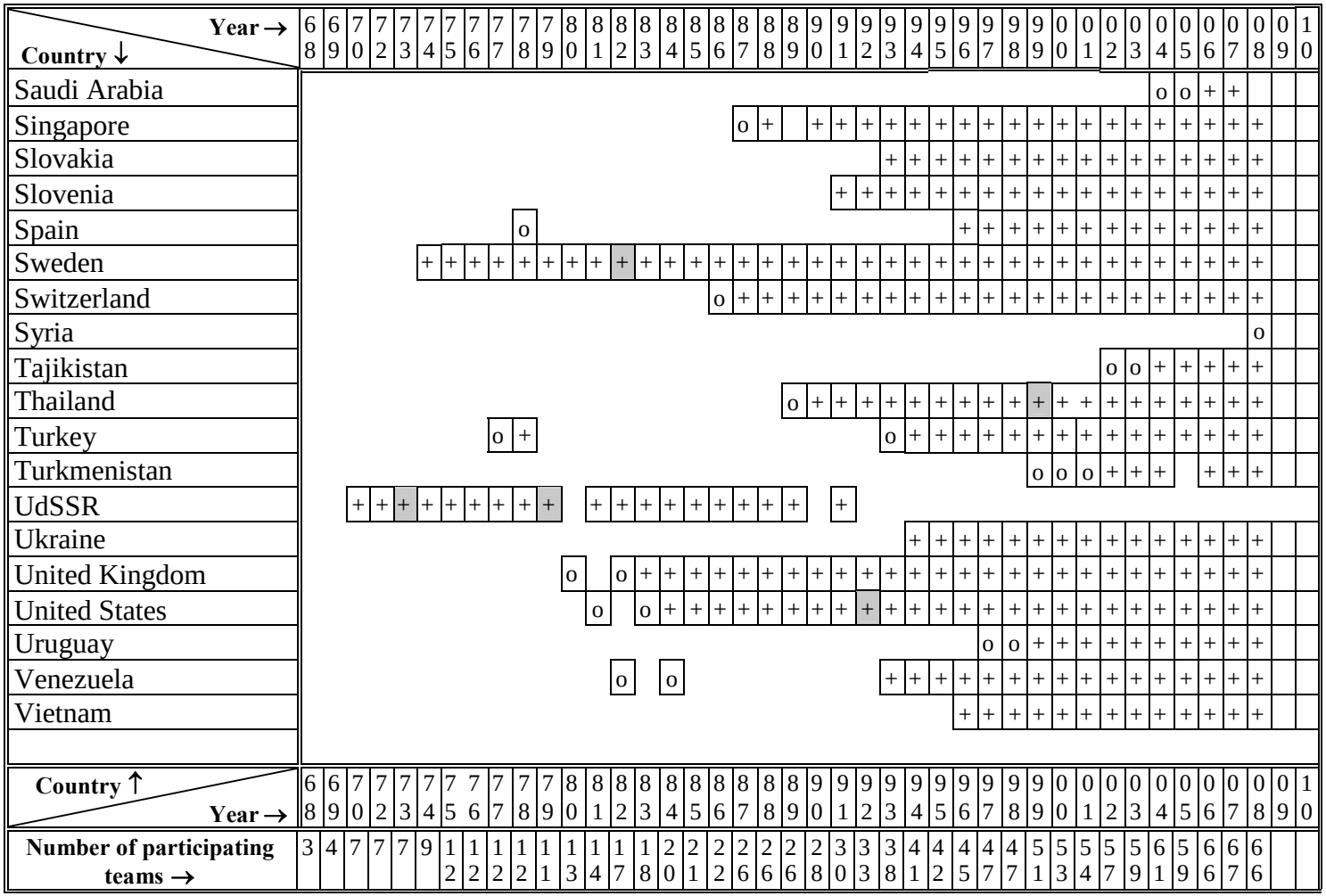
in alphabetical order

+ = 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	06	07	08	09	10
Argentina																											+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+		
Armenia																																				o	o	+	+	+		
Australien																			o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+		
Austria							+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+		
Azerbaijan																													o	o		+	+	+	+	+	+	+	+	+		
Belarus																												+	+	+	+	+	+	+	+	+	+	+	+	+		
Belgium							+	+	+			+				+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+		
Brasil																													o	o	+	+	+	+	+	+	+	+	+	+		
Bulgaria		+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+		
Canada																	o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+		
China																			+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+		
Chinese Taipei																								+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+		
Costa Rica																																								o		
Croatia																														o	o	+	+	+	+	+	+	+	+	+		
↑ Country / Year →	68	69	70	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	00	01	02	03	04	05	06	07	08	09	10

Country ↓ \ Year →	68	69	70	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	00	01	02	03	04	05	06	07	08	09	10
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	+	+	+	+	+	+	+	+	+	+	+		
Indonesia																												o	+	+	+	+	+	+	+	+	+	+	+	+		
Iran																									+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+		
Ireland																												o	o	+	+	+	+	+	+	+	+	+	+	+		
Israel																																				o	o	+	+	+		
Italy												+	+	+	+	+	o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+		
Japan																																o	+	+	+	+	+	+	+		
Jugoslavia						+	+	+	+					+	+	+	+	+	+													o										
Country ↑ \ Year →	68	69	70	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	00	01	02	03	04	05	06	07	08	09	10


Year →
Country ↓
68 69 70 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 00 01 02 03 04 05 06 07 08 09 10
Kazakhstan
Kenia
Korea
Kuwait
Kyrgyzstan
Latvia
Lithuania
Malaysia
Mexico
Moldova
Mongolia
Netherlands
New Zealand
Nigeria
Norway
Pakistan
Peru
Philippines
Poland
Portugal
Romania
GUS/Russ.Fed.
Country ↑
Year →


Year →
Country ↓
68 69 70 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 00 01 02 03 04 05 06 07 08 09 10
Saudi Arabia
Singapore
Slovakia
Slovenia
Spain
Sweden
Switzerland
Syria
Tajikistan
Thailand
Turkey
Turkmenistan
UdSSR
Ukraine
United Kingdom
United States
Uruguay
Venezuela
Vietnam
Country ↑
Year →
Number of participating teams →
3 4 7 7 7 9 12 12 12 12 11 13 14 17 18 20 21 22 26 26 26 28 30 33 38 41 42 45 47 47 51 53 54 57 59 61 59 66 67 66

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 139)

	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 139)

	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
IChO held in	**IND**	**NL**	**GR**	**D**	**TPE**	**ROK**	**RUS**	**H**	**GB**	**J**		
1	RC	RC	RC	RC	ROK	RC	RC	RC				
.	ROK	T	IR	ROK	VN	TPE	RUS	RUS				
.	USA	TPE	ROK	RUS	IR	ROK	TPE	UA				
.	RUS	ROK	T	UA	RUS	RUS	PL	ROK				
5	IR	A	BY	D	AZ	VN	ROK	T				
.	TR	UA	RUS	PL	TPE	T	D	BY				
.	IND	USA	IND	TPE	T	J	T	VN				
.	AUS	PL	SGP	H	RA	Pl	IND	TPE				
.	TPE	IND	D	TR	D	IND	H	H				
10	T	D	TPE	VN	IND	**D**	SK	SGP				
.	SGP	IR	UA	IND	A	SK	LT	KZ				
.	PL	H	PL	IR	CZ	DK	USA	A				
.	RO	RUS	CDN	RO	UA	CDN	VN	PL				
.	F	CDN	CZ	LT	PL	SGP	GB	IR				
15	SK	TR	RO	CZ	AUS	BY	BY	IND				
.	H	AUS	KZ	USA	TR	AZ	EST	RO				
.	VN	GB	VN	SGP	H	UA	UA	AUS				
.	CZ	SGP	EST	CDN	SK	USA	RI	D				
.	RA	E	GB	AZ	USA	H	IR	SK				
20	BY	SK	AUS	AUS	GB	CZ	RO	TR				
.	C	BY	H	KZ	RO	AUS	AUS	LT				
.	D	VN	SK	GB	BY	NZ	A	EST				
.	GB	FIN	USA	J	SGP	F	KZ	I				
.	UA	F	YV	A	J	IR	SGP	GB				
25	A	LT	IND	BY	RI	A	NZ	CDN				
.	MEX	CZ	F	SK	LV	TR	CZ	NZ				
.	DK	KZ	A	T	BG	RI	F	BR				
.	CDN	LV	I	RA	HR	GB	TR	USA				
.	EST	NL	TR	EST	MEX	RO	J	LV				
30	RI	RO	AZ	F	KZ	NL	ARM	RI				
.	HR	RA	MEX	NZ	LT	HR	SLO	F				
.	I	EST	LT	SLO	F	LT	RA	CZ				
.	N	HR	NL	HR	EST	KZ	BR	J				
.	BG	BG	FIN	LV	CDN	SLO	CDN	DK				
35	CY	NZ	HR	NL	I	EST	I	RA				
.	KZ	I	J	I	DK	RA	MAL	MEX				
.	B	DK	DK	CH	SLO	BR	IL	SLO				
.	LT	SLO	RA	FIN	FIN	TJ	IRL	IL				
.	NZ	N	GR	RI	NL	LV	NL	AZ				
40	CH	YV	LT	S	IRL	MAL	CH	HR				
.	E	MEX	E	BG	GR	S	S	TM				
.	FIN	BR	TM	KS	NZ	IRL	LV	BG				
.	SLO	S	BR	E	KS	IL	DK	MGL				
.	NL	RI	BG	GR	S	FIN	MD	IRL				
45	LV	TM	CH	BR	B	IS	E	MAL				
.	BR	B	NZ	TM	BR	I	BG	E				
.	S	IRL	IS	CY	CH	CY	TM	S				
.	YV	CH	IRL	YVA	P	N	HR	NL				
.	IRL	C	CY	IRL	IS	TM	PK	CH				
50	GR	CY	KS	IS	N	CH	N	ROU				

(List of abbreviations see page 139)

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
IL	Israel
IND	India
IR	Iran
IRL	Ireland
IS	Iceland
J	Japan
KS	Kyrgistan
KWT	Kuwait
KZ	Kasakhstan
LV	Latvia
LT	Lithuania
MAL	Malaysia
MD	Moldova
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