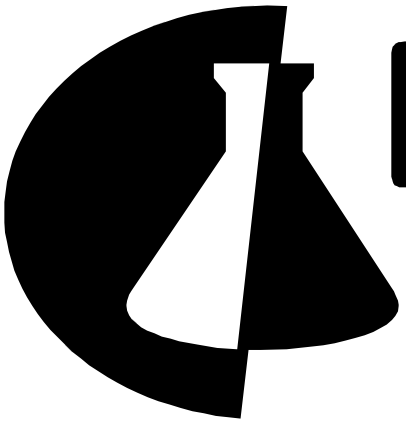

44. International Chemistry Olympiad USA 2012

National German Competition

Volume 18

Preface

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

The problems to be solved in the 1st round are sent to all high schools. To solve the problems the students may use all resources available, e.g. 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 their solutions are collected. Future participants should use this booklet to become acquainted with the problems of the competition. Therefore the solutions to the problems given in this booklet are more detailed than the answers we expect from the students in the competition.

In the appendix you find tables of historical interest.

Wolfgang Hampe

This booklet including the problems of the 44rd IchO and the latest statistics is available as of September 2012 from
http://www.icho.de (chapter:"Aufgaben")

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Part 1: The problems of the four rounds

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

Part 3: Appendix

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Part 1

The problem set of the four rounds

First Round

Problem 1–1 Air –In the Beginning there was Soup

Today's atmosphere is a mixture of different gases which underwent severe changes in the evolutionary history of the earth.

a) *Write down the composition of today's atmosphere (free of water) at sea level in percentage of volume. Consider the components nitrogen, oxygen, argon and carbon dioxide. Give the major natural sources of these gases.*

An additional fifth component of waterless air varies strongly depending on season, position and height. On the one hand it protects life on earth, on the other hand it leads to damages indirect exposition.

b) *Give the name of this molecule and draw, if possible, the Lewis structures of the five gases as they exist in the air.*

The names of some components of the air refer to their chemical reactivity.

c) *Explain the correlation between the name and the chemical reactivity of at least two of the components.*

The evolution of the atmosphere of the earth can be divided into three stages: a reducing first atmosphere probably free of oxygen, a second nitrogen containing one and a third one which reacts oxidizing.

d) *State the name giving components of the first and the third atmosphere and elucidate the terms reducing and oxidizing atmosphere with the help of an equation of a probable reaction at that time.*
Determine the oxidation numbers of all atoms of the compounds involved in these reactions.
Hint: In the scientific literature you find contradictory information about the composition of the first atmosphere. Assume those components which are in best accord with the reaction equation of part e).

The theory of the primordial soup provides a possible explanation of the formation of today's air with the main component nitrogen.
The main component **A** of the first atmosphere and the compounds ammonia and water react to form the second atmosphere with its gaseous main product **B** and two gaseous side products **C** and **D**:

$$A + NH_3 + H_2O \longrightarrow B + C + D$$

e) *Find **A**, **B**, **C** and **D** and balance the reaction equation.*

The main components of today's atmosphere are nitrogen and oxygen with a percentage of volume of 78.08% and 20.94%, respectively. If you consider the masses of these components you get another percentage.

f) Calculate the mass percentage of these elements at 20 °C.
$d(air_{20°C}) = 1.204\ kg/m^3$, $p = 1.013 \cdot 10^5\ Pa$

Many elements react when exposed to air. If for example magnesium is burned in air it reacts in a vigorous and light-emitting reaction to form a grey-yellow powder (experiment A).
If water is added to this grey-yellow powder (experiment B) moistened pH-paper turns blue if held over the mixture.
The mixture is heated to boiling for some minutes and pH-paper is held into the solution. The pH-paper turns blue, too.

g) Explain the reactions and write down the reaction equations for the experiments A and B.

h) Describe the function of boiling. Explain why the pH-paper turns blue even after boiling.

Problem 1-2 A Sparkling Drink

In order to illustrate problem 1-3 the solubility of carbon dioxide in water shall be examined in a practical experiment. This experiment can be performed in school as well as at home.

Equipment: six fizzy tablets from the food store, a pneumatic bowl (crystallizing dish), a measuring cylinder.
If the experiment is performed at home you may take a plastic bowl instead of the crystallizing dish and a bottle instead of the measuring cylinder. The bottle can be gauged with a measuring device of the household and a waterproof pen.

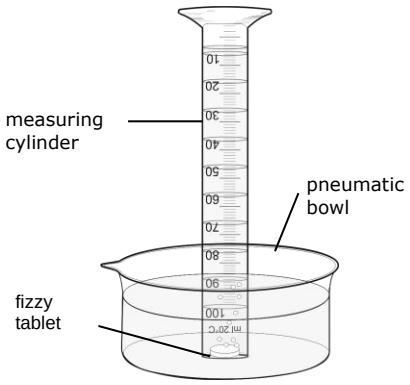

Fig. 1

Preparation: The measuring cylinder is filled with cold tap water and positioned top down in the pneumatic bowl (fig 1).
Procedure: A fizzy tablet is put under the cylinder as quickly as possible. Take care that the cylinder cannot turn over. Look at the bubbles when rising. Read the volume of the generated gas (V_1) when the tablet has dissolved totally.

Then the second tablet is put under the cylinder and the volume (V_2) of the newly generated gas is read.
The same experiment is repeated with ice-cold and with lukewarm water.

a) State the behavior of the bubbles when rising and explain your observations. Account for the difference of V_1 and V_2.
Write down the equations of the equilibria which exist between water and carbon dioxide and indicate which of them is the most important with respect to the solubility of carbon dioxide.

b) What is the influence of the variably tempered water on the solubility of carbon dioxide and what conclusions do you derive?

Problem 1-3 Water on Mars?

A lake is an open system in equilibrium with the surrounding atmosphere.
Besides other parameters the pH value of the lake is controlled by the amount of dissolved carbon dioxide. The solubility of carbon dioxide obeys approximately Henry's law[1,2]:

$$K_H = \frac{c(CO_2\,(aq)) + c(H_2CO_3\,(aq))}{p(CO_2\,(g))}$$

$$K_H = 7.5 \cdot 10^{-4}\ \text{mol} \cdot \text{m}^{-3} \cdot \text{Pa}^{-1} \text{ at O °C}$$

The atmospheres of Earth and Mars differ significantly. While there is a normal pressure of 1013 mbar with a CO_2 percentage (V/V) of 0.038 % on Earth the atmosphere of Mars has only a pressure of 6.36 mbar with a CO_2 percentage of 95.32 % (V/V).

a) Calculate the pH value of a hypothetical lake on Mars at 0 °C which is exclusively controlled by the CO_2 content of the atmosphere.

The pH value of waters is influenced by many factors. Mostly our inshore waters show a basic reaction rather than an acidic one.

b) Calculate the percentage (V/V) of CO_2 in the atmosphere of the Earth which would lead to an acidic reaction in our waters (pH = 6). (Do not consider other factors which influence the pH value.)

c) Which pH value do you expect if a water sample which was sealed on Mars is opened on Earth, intensely stirred and then the pH is measured at 0 °C?
The calculation should be carried out on the one hand with and on the other hand without considering the autoprotolysis of water.

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1 Henry's law should only be used for pressures up to $5 \cdot 10^5$ Pa. It's valid for diluted solutions and small partial pressures.

2 You have to consider the sum of the concentrations of both CO_2 species in the numerator as if you apply Henry's law the particles dissolved should not really react with the solvent.

Constants at 273.15 K:
Ionic product of water: $K_w = 0.12 \cdot 10^{-14}$
$pK_{a1}(CO_2 + H_2CO_3) = 6.59$, $pK_{a2}(HCO_3^-) = 10.27$

Problem 1-4 Ozone as Reagent

Ozone adds to molecules with C=C double bonds.
Ozone is an electrophilic agent and adds in a first step to the double bond to form the so called molozonide. Once formed, the molozonide then spontaneously rearranges to form an ozonide. Treated with a reducing agent the ozonide converts to the respective carbonyl compounds, aldehydes and ketones.

a) Draw the different steps of the reaction of ozone with 1-butene: formation of the molozonide, the ozonide and at least the formation of two aldehydes.

b) Draw the structure of all products which could form in the total reaction of Lycopene $C_{40}H_{56}$ with ozone followed by a treatment with a reducing agent.
What is the ratio of the amounts of these products supposing a total reaction?

An aromatic compound **A** reacts with ozone followed by a reduction which leads to two compounds, **B** and **C**.

- **B** has the empirical formula C_7H_6O
- **C** has the empirical formula C_3H_6O
- **B** reacts with Tollens‘ reagent as well as with Fehling’s reagent
- **C** does not react with one of these reagents
- In the presence of a catalyst 1 mol of **A** reacts with 1 mol of H_2 to form **D**
- 1 mol of **A** reacts with 1 mol of bromine to form compound **E**

*c) Draw the structural formulae of **A** to **E** and the schemes of ozonolysis, hydrogenation and brominating (don’t take stereochemical aspects into account).*

Second Round (homework)

Problem 2-1 A Riddle

i) The sought-after element is prepared from its oxides and sulphides.

ii) It burns in air it to form an oxide.

iii) It is insoluble in not oxidizing acids. It expands as it freezes.

iv) If an aqueous solution of iodide is added to a solution of ions of the unknown element, a precipitate forms. The precipitate dissolves in an excess of the iodide solution.

v) If a clear solution of its ions in hydrochloric or in nitric acid is treated with water, the solution becomes opaque.

vi) If a binary compound with a mass percentage of 85.15% of the sought-after element is treated with hydrochloric acid, a gas forms. Thermal decomposition of this gas followed by cooling gives a black precipitate.

vii) A nail of iron colours black if it is put in an aqueous solution of ions of the element.

a) Find out which element is sought after.
b) Write a balanced equation for the preparation of this element (to i)).
c) What is the colour of the oxide formed in ii)? Can its colour arise from a d-d transition? Give a short explanation!
d) Give three examples of substances which expand on freezing, too.
e) Write down the balanced equations of iv). Which structure of the compound formed in an excess of the iodide solution do you expect using the VSEPR concept? Justify by using a Lewis formula.
f) Write down the reaction equation to illustrate v).
g) Which is the binary compound? Write down the equations for the reactions described in vi)!
h) Give an equation for the reaction in vii).

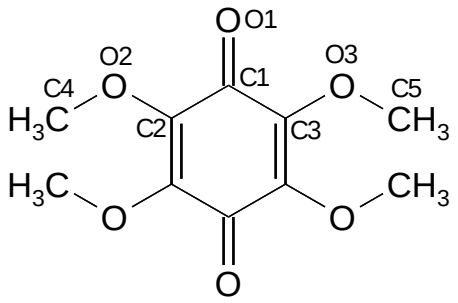
Problem 2-2 Looking for a Structure!

The compound tetramethoxy-p-benzochinone crystallizes in the space group $P2_1/n$.

The lattice parameters of the unit cell are:

a = 4.021 Å b = 7.778 Å c = 16.792 Å

α = 90.0° β = 94.1° γ = 90.0°



The position of atoms and ions in a unit cell can be described by their relative locations xyz (fractional coordinates). Their values lie normally between 0 and 1. For the compound mentioned on the previous page the following fractional coordinates were found:

	x_c	y_c	z_c
O1	0.8626	-0.1766	0.6089
O2	0.7315	-0.3311	0.4746
O3	0.6714	0.1432	0.6519
C1	0.6890	-0.0953	0.5593
C2	0.6062	-0.1720	0.4781
C3	0.5703	0.0786	0.5778
C4	0.7038	-0.4314	0.4031
C5	0.5224	0.0631	0.7182

a) Sketch the unit cell and state to which crystal system it belongs. Calculate the volume of the unit cell in Å³.

b) Which symmetry operations are possible in this space group?

c) Which of these symmetry operations matches/match with the molecular symmetry?

The volume of a non-hydrogen atom is supposed to be about 18 Å³.

d) How many molecules (number Z) will you find in the unit cell? (If you could not solve a) take 525 Å³ as the volume of the unit cell.)

e) Indicate the remaining non-hydrogen atoms of the molecule with an additional " ' ", e.g. O1', and their coordinates with x_c', y_c' und z_c'.
Calculate the fractional coordinates of O1' and C3' using the inversion through the symmetry centre (x_i=0.5; y_i=0; z_i=0.5).

In order to determine bond lengths and the bond angles from the *fractional coordinates* (x_c, y_c, z_c), they have to be transformed into orthogonal co-ordinates (x_o, y_o, z_o). In this case the transformation can be performed in the following way:

$$\begin{pmatrix} x_o \\ y_o \\ z_o \end{pmatrix} = \begin{pmatrix} a & b\cdot\cos\gamma & c\cdot\cos\beta \\ 0 & b\cdot\sin\gamma & \dfrac{c(\cos\alpha - \cos\beta\cdot\cos\gamma)}{\sin\gamma} \\ 0 & 0 & \dfrac{c\cdot\sin\beta}{\sin\gamma} \end{pmatrix} \cdot \begin{pmatrix} x_c \\ y_c \\ z_c \end{pmatrix}$$

The multiplication of matrices follows the rule $c_{ij} = \sum_{k=1}^{m} a_{ik} \cdot b_{kj}$,

e.g.

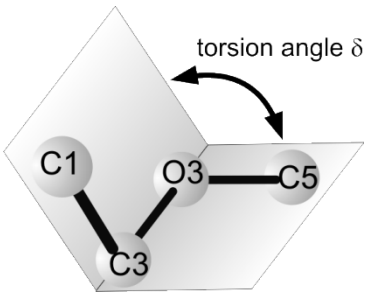
$$\begin{pmatrix} c_{11} \\ c_{21} \\ c_{31} \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \cdot \begin{pmatrix} b_{11} \\ b_{21} \\ b_{31} \end{pmatrix} = \begin{pmatrix} a_{11}\cdot b_{11} + a_{12}\cdot b_{21} + a_{13}\cdot b_{31} \\ a_{21}\cdot b_{11} + a_{22}\cdot b_{21} + a_{23}\cdot b_{31} \\ a_{31}\cdot b_{11} + a_{32}\cdot b_{21} + a_{33}\cdot b_{31} \end{pmatrix}.$$

f) Calculate the orthogonal coordinates of C1, C3, C5 and O3. From these results calculate the length of the bonds (in Å) d(C1-C3), d(C3-O3), d(O3-C5).

g) Determine the angles θ =∠C1-C3-O3 and ω =∠C3-O3-C5.

For steric reasons the atoms C1, C3, C5 und O3 will not lie in one plane. The C5 atom will unscrew from the plane formed by C1, C3 and O3.

h) Calculate the angle δ (angle of torsion).



For the total problem 2-2: Angles and volume should be shown with 1, other numbers with 4 decimal places.

Problem 2-3 Kinetics

The reactions (1), (2), (3) and (5) are elementary reactions, reaction (4) is more complex and not elementary.

$CH_3NC \longrightarrow CH_3CN$	k_1	(1)
$(E)\text{-}C_2H_2I_2 \longrightarrow (Z)\text{-}C_2H_2I_2$	k_2	(2)
$(Z)\text{-}C_2H_2I_2 \longrightarrow (E)\text{-}C_2H_2I_2$	k_{-2}	(3)
$H_3AsO_3(aq) + I_3^-(aq) + H_2O(aq) \longrightarrow 2\ H^+(aq) + 3\ I^-(aq) + H_3AsO_4(aq)$	k_3	(4)
$2\ NOCl(g) \longrightarrow Cl_2(g) + 2\ NO(g)$	k_4	(5)

a) Form if possible theoretically based rate laws for the reactions (1) to (5). What are the molecularities and the reaction orders (with regard to single substances and to the total reaction)?

Hint: Besides the reaction equations shown above there is no further data to your disposal to form the rate law.

The following data is available for the isomeration reaction (1) at 202 °C:

Tab. 1. Concentration of CH_3NC as a function of time (ϑ = 202 °C)

t/min	0	50	75	100	125	150	200	300
$c(CH_3NC)/mol \cdot L^{-1}$	0.5000	0.4145	0.3774	0.3436	0.3129	0.2849	0.2362	0.1623

b) Determine the rate law constant k_1 for reaction (1) in s^{-1}.Calculate the half-life.

Rate law constants at other temperatures were determined in the same way:

Tab. 2. Temperature dependence of the rate constant of reaction (1)

ϑ /°C	227	252	277	302
k_1 /s^{-1}	$4.71 \cdot 10^{-4}$	$2.93 \cdot 10^{-3}$	$1.55 \cdot 10^{-2}$	$7.06 \cdot 10^{-2}$

c) Determine the Arrhenius parameters A and E_A.

The combination of the elementary reactions (2) und (3) shows an equilibrium reaction. For further considerations reaction (3) shall be looked at as back reaction of reaction (2).

d) Determine the equilibrium constant K at 806 K.
(The change of Gibbs energy of this reaction is $\Delta_R G(806\ K) = -2.167\ kJ/mol$).

e) Find the combined rate law for the total reaction (E)-$C_2H_2I_2$ $\rightleftharpoons$ (Z)-$C_2H_2I_2$. Derive a formula which links the equilibrium constant to the rate law constants k_2 und k_{-2}.

Rate law constants can be determined by the method of relaxation. Thereby the system which is already in equilibrium is disturbed e.g. by a sudden change of temperature. Then rate constants can be determined by the observation of the adjustment of the new equilibrium.

The deflection from the equilibrium is defined as $\Delta x = c_E - c_E^{eq} = c_Z^{eq} - c_Z$ where c is the concentration at time t and c^{eq} the concentration in the equilibrium (for the (E) and the (Z) isomer, respectively). For smaller deflections a good approximation is

$$\Delta x = \Delta x_0 \cdot e^{-(k_2 + k_{-2}) \cdot (t - t_0)}$$

where Δx_0 is the deflection shortly after the disturbance at the time t_0.

The relaxation time $\tau = t - t_0$ is the time in which the deflection Δx has fallen to 1/e (~ 37%) of the deflection at the beginning Δx_0.

f) Find a term for the relaxation time τ.

In an experiment the relaxation time at 806 K was determined: τ = 115.3 s.

g) Determine the rate constants k_2 und k_{-2}. Hint: Use in this case K = 1.400.

Another possibility to find reaction orders and rate constants is the so called method of isolation combined with the method of initial rates.
The data in Tab. 3 is measured for reaction (4) at room temperature.

Tab 3. Test series of initial rates and concentrations or reaction (4)

	$c(H_3AsO_3)$ /mol · L^{-1}	$c(I_3^-)$ / mol · L^{-1}	$c(I^-)$ / mol · L^{-1}	$c(H^+)$ / mol · L^{-1}	v_0 / mol · L^{-1} · min^{-1}
1	0.150	$3.45 \cdot 10^{-5}$	0.0250	0.150	1.882
2	0.113	$2.08 \cdot 10^{-5}$	0.0450	0.150	0.2639
3	0.0750	$6.90 \cdot 10^{-5}$	0.0250	0.150	1.882
4	0.150	$1.04 \cdot 10^{-4}$	0.0250	0.150	5.674
5	0.100	$3.00 \cdot 10^{-5}$	0.0200	0.100	2.558

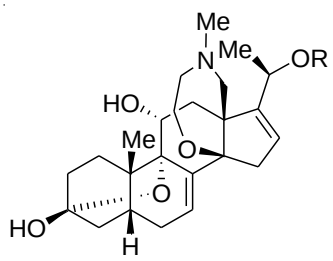
Assumption: The order of the reaction is 0 with reference to $c(H_3AsO_4)$.

h) Determine the rate law for the reaction.

i) Calculate the rate law constant at room temperature.

Problem 2-4 Synthesis of a Natural Compound

The compound represented by its structure shown on the right is part of a natural compound and interesting as a pharmaceutical lead.



a) This molecule contains a structural segment which occurs frequently in nature. Which one is it (name)?

b) Mark the stereogenic centres of the natural compound. Choose two of these centres and assign R or S configuration (Cahn-Ingold-Prelog rules). Account for your decision!

c) How many stereo isomers may theoretically exist?

An intermediate of this compound can be synthesized in 12 steps which are shown in the reaction scheme below.

*d) i) Draw the structural formulae of the compounds **A, B, C** and **D.** Take account of the correct stereochemical configuration.*

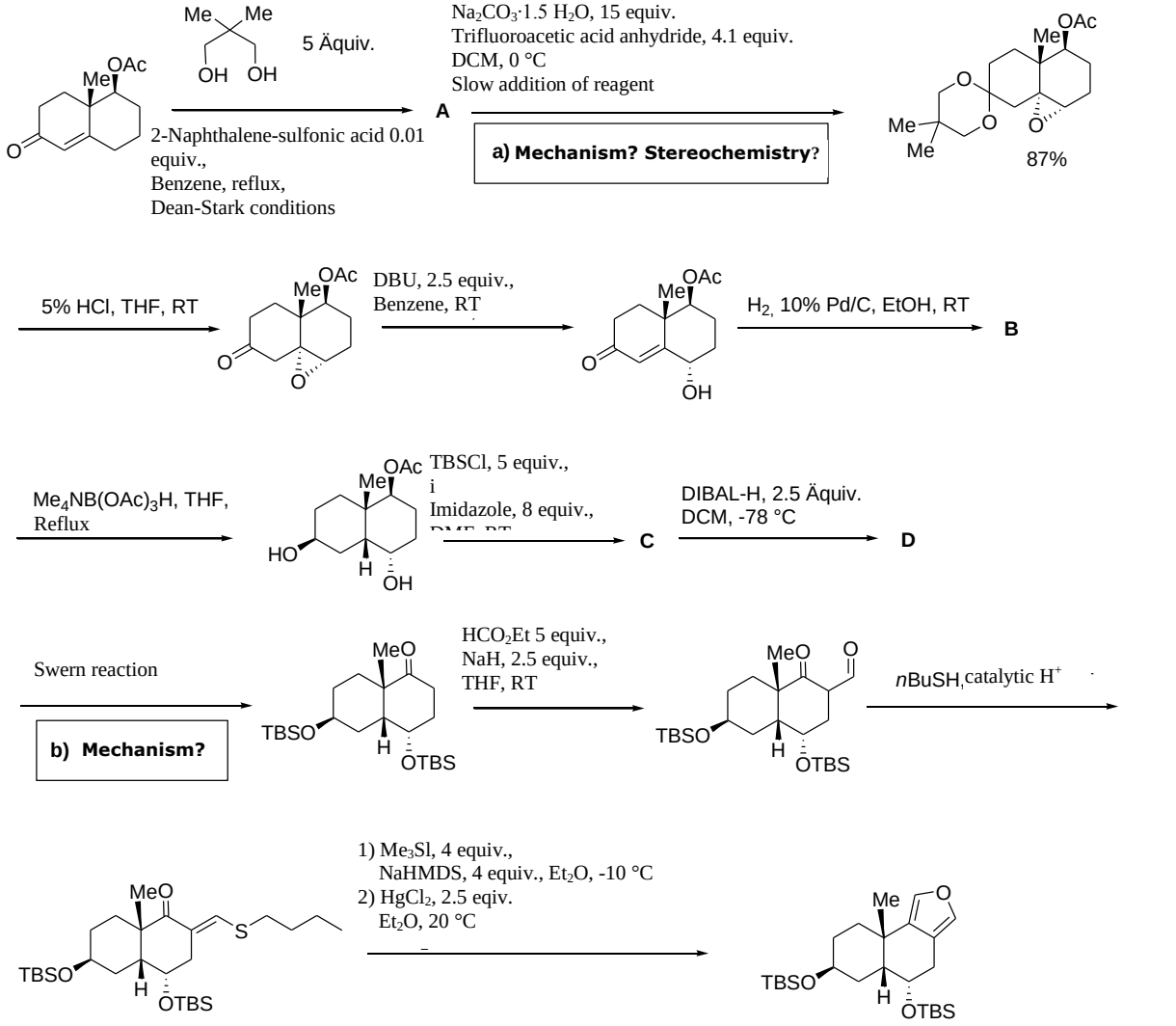
*ii) Two of the three signals in the ^{1}H-NMR spectrum of compound **A** at 1.14 (3H, s), 1.02 (3H, s) and 0.88 (3H, s) are assigned to the methyl groups of the protective group. Why are the signals of the methyl groups different?*

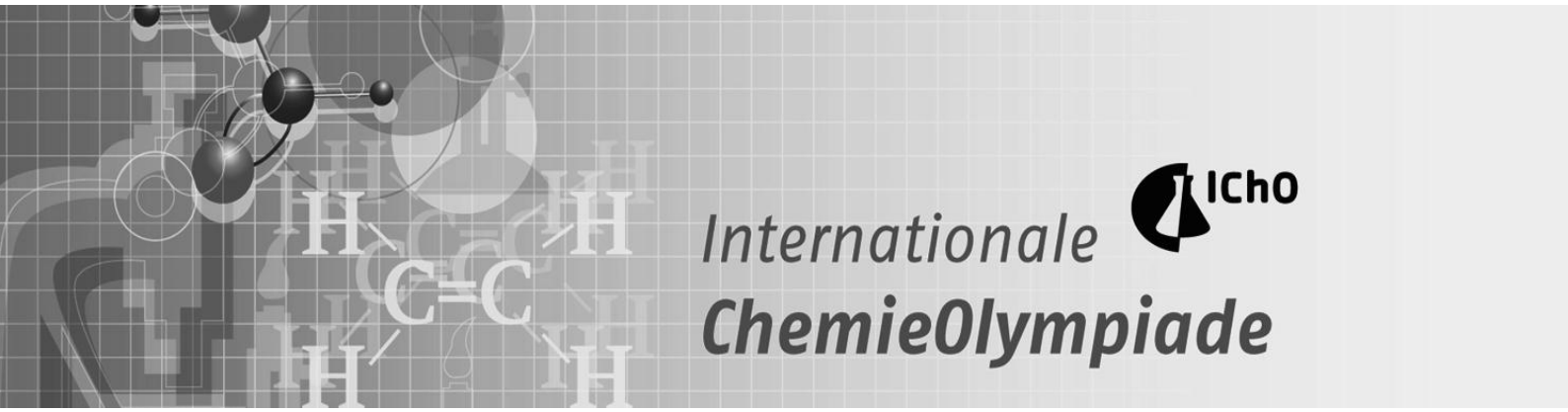
*iii) Give a reasonable mechanism for the reactions **a)** and **b)** in the scheme below. (The fragment of the molecule which in not involved in reaction b) may be written as R.)*

iv) To form a double bond in the left six membered carbon ring a large non-nucleophilic base is used. Why? Give a short explanation.

Hint to i): the ^{1}H-NMR spectrum (500 MHz, $CDCl_3$) of **A** shows the following signals in ppm (signals of particular importance are printed in bold):

5.33	(1H, m)	2.32-2.20	(2H, m)	1.50	(1H, dd)
4.78	**(1H, dd)**	2.07-2.03	(1H, m)	1.42-1.35	(1H, m)
3.53	(2H, q)	2.06	(3H, s)	1.14	(3H, s)
3.43	(2H, s)	1.76-1.70	(2H, m)	1.02	(3H, s)
2.58	(1H)	1.60-1.55	(2H, m)	0.88	(3H, s)





Problems Round 3

Test 1 Göttingen 2012: Problems 3-01 to 3-10

Test 2 Göttingen 2012: Problems 3-11 to 3-20

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

Good Luck

Useful formulas and data

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

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

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

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

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

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

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

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

rate laws

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

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

A	pre-exponential factor.
E_a	activation energy

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

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

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

Speed of light	$c = 3.000 \cdot 10^8$ ms^{-1}
Gas constant	$R = 8.314$ JK^{-1}mol^{-1}
Faraday constant	$F = 96485$ Cmol^{-1}
Avogadro constant	$N_A = 6.022 \cdot 10^{23}$ mol^{-1}
Planck constant	$h = 6.6261 \cdot 10^{-34}$ Js

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

1 Å $= 10^{-10}$ m

A periodic table was provided

Third Round Test 1

Problem 3-01 Multiple Choice

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

a) Which of the following bonds has the most ionic properties?

A Br-Br	**B** Be-F	**C** C-F	**D** Mg-F	**E** Na-F

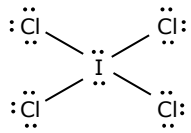
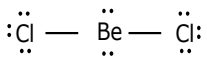
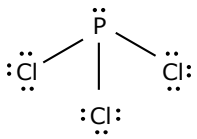
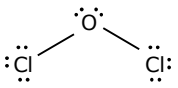
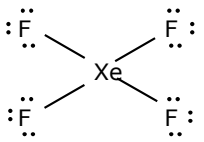
b) Which of the following sets of ions can coexist at large in an aqueous solution?

A Ag^+, Pb^{2+}, H_3O^+	**B** I^-, IO_3^-, H_3O^+	**C** NH_4^+, HCO_3^-, OH^-	**D** Fe^{3+}, Cu^{2+}, SO_4^{2-}	**E** Na^+, Ca^{2+}, CO_3^{2-}

c) Which of the following solutions has a pH value larger than 7?

A NaF (1 mol/L)	**B** NH_3(1 mol/L) + NH_4Cl(2 mol/L)	**C** HCl ($1\cdot10^{-4}$mol/L)	**D** Na_2S (1 mol/L)	**E** CH_3COOH (1 mol/L)

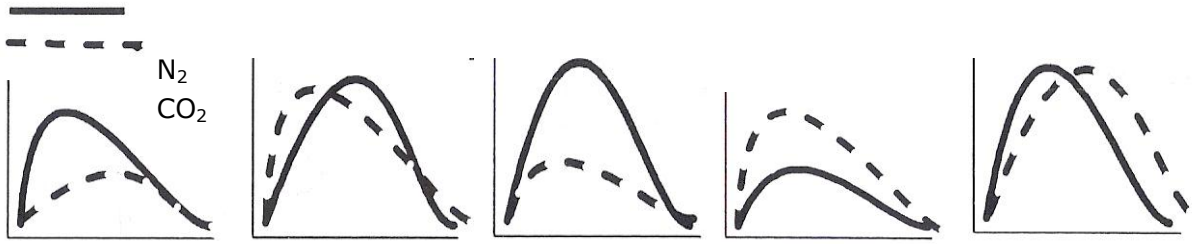
d) Which of the following Lewis structures is correct?

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

e) Which solution would have the greatest electric conductivity?

A HCl (0.1 mol/L)	**B** NH_3 (0.1 mol/L)	**C** H_3BO_3 (0.1 mol/L)	**D** CH_3COOH (0.5 mol/L)	**E** NaOH (0.05 mol/L)

f) A flask contains a mixture of N_2 and CO_2. The partial pressure of CO_2 is 130 hPa and the total pressure is 450 hPa. Which graph below would present the distribution of molecular speed best? (x-coordinate: speed, y-coordinate: amount of molecules)



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

g) Which of the following statements on the reactions of copper is **<u>wrong</u>**?

- **A** Reaction with concentrated sulphuric acid gives O_2.
- **B** Reaction with diluted sulphuric acid gives H_2.
- **C** Reaction with concentrated nitric acid gives NO_2.
- **D** Reaction with diluted nitric acid gives NO.
- **E** Copper does not react with diluted hydrochloric acid.

Problem 3-02 „Once upon a Time …"

The first International Chemistry Olympiad started in Prague in1968. Three countries participated: Hungary, Poland and Czechoslovakia. In the following the first and the second problem of the two hours test of that event are slightly changed and combined:

A mixture of hydrogen and chlorine kept in a closed flask at constant temperature was irradiated with scattered light.
After a certain time the resulting mixture had a composition as follows: 60 % (by volume) of chlorine, 10 % (by volume) of hydrogen and 30 % (by volume) of hydrogen chloride. At this time the chlorine content decreased by 20% compared with the starting mixture.

a) Determine the composition of the initial mixture.

b) Which of the given detail(s) is (are) unnecessary?

Write down equations for the following reactions:

c) Oxidation of chromium(III) chloride with bromine in alkaline solution (KOH).

d) Oxidation of potassium nitrite with potassium permanganate in acidic solution (H_2SO_4).

e) Reaction of chlorine with limewater (suspension of calcium hydroxide in water) at 0 °C.

Problem 3-03 Nitrogen up and down

Nitrogen occurs in all oxidation states from –III up to +V.

a) Give an example for each oxidation state.
Write the empirical formula, the name and the Lewis structure of the respective species. (If there are resonance structures it is sufficient to sketch only one of them)

Nitrogen may show oxidation states which are not represented by whole numbers.

b) Give an example for a compound or ion of nitrogen with an oxidation state which is not a whole number.

Problem 3-04 An Alloy

An alloy prepared for experimental reasons contains aluminium, zinc, silicon and copper.

If 1000 mg of this alloy react with an excess of hydrochloric acid 899 mL of hydrogen form (21°C, 102.25 kPa). However, there remains an insoluble residue of 170 mg.

If 500 mg of this alloy react with an excess of an aqueous solution of sodium hydroxide 552 mL of hydrogen form (21°C, 102.25 kPa). Here, too, a residue remains.

a) Name the elements of the alloy which react with hydrochloric acid by writing the reaction equations. What is the residue?

b) Name the elements of the alloy which react with sodium hydroxide solution by writing the reactions equations. What is the residue?

c) Calculate the composition of the alloy in percentage of mass with 2 decimals.

Problem 3-05

The following data concerning the dehydrogenation of ethene is given:

$\Delta G°_{900}$	= 22.39 kJ/mol
$S°_{900}(H_2)$	= 163.0 J/(mol·K)
$S°_{900}$(Ethan)	= 319.7 J/(mol·K)
$S°_{900}$(Ethen)	= 291.7 J/(mol·K)

a) Write the equation for the dehydrogenation of ethene.

b) Calculate K_p for this reaction at 900 K.

c) Determine ΔH° for the hydrogenation of ethene at 900 K.

d) What is the composition (in percentage of volume) of the reaction mixture in equilibrium over a hydrogenation catalyst at 900 K?
The total pressure in equilibrium amounts to 1020 hPa.
(If you could not solve b) take $K_p = 50{,}0 \cdot 10^{-3}$)

e) Find the value of K_p at 600 K. Assume that enthalpy and entropy are independent of temperature.
(If you could not solve c) take $|\Delta H°| = 150$ kJ/mol. (You have to decide on the algebraic sign for yourself.)

f) Compare K_{p600} and K_{p900} and interpret the difference briefly.

Problem 3-06

In 1808 boron was identified as an element for the first time. It took until 1909 that an American scientist, E. Weintraub, could prepare it in pure crystal shape.

A branch of modern inorganic chemistry research is concerned with boranes, compounds of boron with hydrogen.

The simplest boron hydride is, according to the number of valence electrons of boron, BH_3.

However, it was found in inspections that the monomer form of BH_3 is not stable und does not match the molecular mass found in analysis. Instead the dimer $(BH_3)_2 = B_2H_6$ was observed.

a) Account for the dimerisation.

b) Sketch the spatial structure of diborane.

c) Which coordination of the nearest neighbours around the two boron centres in the dimer do you find using the VSEPR model?

Besides boron and hydrogen borazine (1,3,5,2,4,6-Triazatriborinane, M = 80.5 g/mol) is composed of the element nitrogen. Borazine was first synthesized by the German Noble Prize Laureate Alfred Stock in 1926.

d) What is the empirical formula of borazine and with which carbon hydrate is it isoelectronic?
(Hint: Isoelectronic = isosteric, which are atoms, molecules or ions with the same number of atoms and the same number of valence electrons)

e) Draw all resonance forms of borazine.

f) Which factors favour the delocalisation of electrons described by the resonance structures of borazine? More than one correct answer is possible.

A	**B**	**C**	**D**	**E**
differences in electronegativity of the ring atoms	Inductive effect of the hydrogen atoms	Free electron pair of the nitrogen atom	Hydrogen bridges	Electron deficit of the boron atom

g) Give three reasons why borazine could be said to be an aromate.

Problem 3-07 Spectroscopy

Manganese and chromium in steel can be determined simultaneously by photoelectron spectroscopy. Permanganate and dichromate ions in sulphuric acid (c = 1 mol/L) absorb at 440 nm and 545 nm. At these wavelengths, the molar extinction coefficient of MnO_4^- is ε_1 = 95 $L \cdot mol^{-1} \cdot cm^{-1}$ and ε_2 =2350 $L \cdot mol^{-1} \cdot cm^{-1}$, respectively and that of $Cr_2O_7^{2-}$ is ε_3 =370 $L \cdot mol^{-1} \cdot cm^{-1}$ and ε_4 =11 $L \cdot mol^{-1} \cdot cm^{-1}$ respectively.
A sample of 1.374 g of steel was dissolved and manganese and chromium in the resulting solution oxidized to MnO_4^- und $Cr_2O_7^{2-}$. The solution was diluted with sulphuric acid

(c = 1 mol/L) to 100.0 mL.
The transmittances of this solution were measured with a cell of 1.0 cm path length and with sulphuric acid (c = 1 mol/L) as blanc. The observed transmittances at 440 nm and 545 nm were 0.355 (or 35.5 %), and 0.166 (or 16.6 %), respectively.
Assume that Beer's law is valid for each ion and that the absorption, due to one ion is unaffected by the presence of the other ion. Fe^{3+} ions were treated in a way that they do not interfere with the measurement.

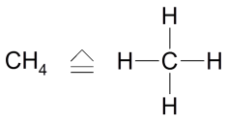
a) Calculate the mass percentage of manganese and chromium in the steel sample from these data. (Give the result with 2 significant figures.)

Cobalt(II) forms a single complex [CoL_3^{2+}] with an organic ligand L. The complex absorbs strongly at 560 nm. Neither Co(II) nor L absorb at this wavelength.
Two solutions of the following composition were prepared:
Solution 1 c(Co(II)) = $1.00 \cdot 10^{-5}$ mol/L and c(L) = $5.00 \cdot 10^{-5}$ mol/L
Solution 2 c(Co(II)) = $3.00 \cdot 10^{-5}$ mol/L and c(L) = $8.00 \cdot 10^{-5}$ mol/L.
The absorption of solution 1 and solution 2 at 560 nm, measured with a cell of 1 cm path length, were 0,305 and 0,630, respectively. It may be assumed that in solution 1 all Co(II) is consumed in the formation of the complex.

b) Calculate the constant for the formation of [CoL_3^{2+}].

Problem 3-8 Fundamental Organic Chemistry

a) Draw all possible line-bond structures of the six empirical formulae given below

C_3H_8		
CH_5N		
C_2H_6O	*(2 Isomers),*	Example 
C_2H_4O	*(3 Isomers),*	
C_3H_7Br	*(2 Isomers),*	
C_3H_9N	*(4 Isomers).*	

b) Draw the line-bond structure of 2,6-dimethyloctane and 3-isopropyl-2-methylhexane, respectively.

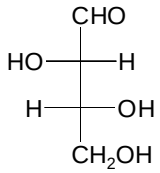
c) The names given below are not correct. Write down the correct IUPAC names and draw the respective line-bond structures.
i) 3-Meythyl-2-propylhexane
ii) 4,4-Dimethyl-3-ethylpentane

d) Draw line-bond structures of R- and S-lactic acid ($CH_3CH(OH)COOH$) which indicate the overall shape of the molecules
(Instructions: Bond receding into page  ,
bond coming out of paper plane )

e) Which kind of stereoisomerism do these molecules show?

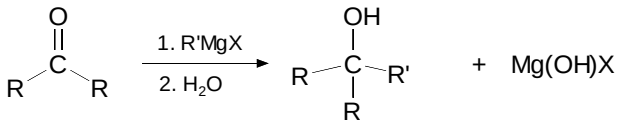
f) Convert the given Fisher projection into a line-bond structure which indicates the overall shape of the molecules.

g) Give the complete name of this compound (use the CIP convention).

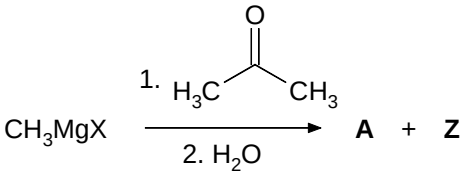


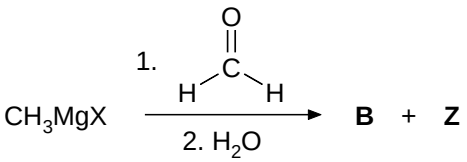
Problem 3-9 Grignard Reactions

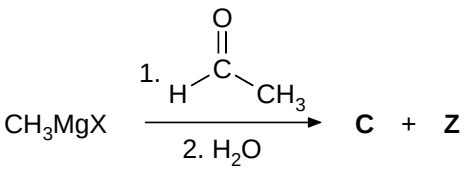
Alkyl halides, RX, react with magnesium metal in ether or tetrahydrofuran solvent to yield alkylmagnesium halides, RMgX, called Grignard reagents.
Grignard reagents are very reactive. With carbonyl compounds they form alcohols:

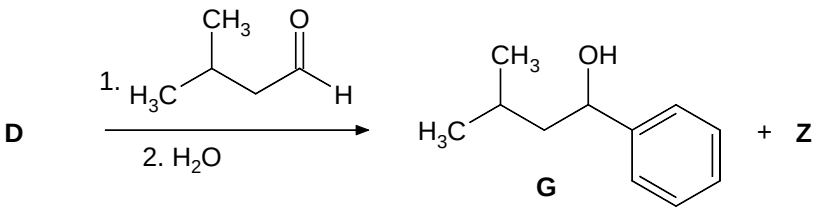


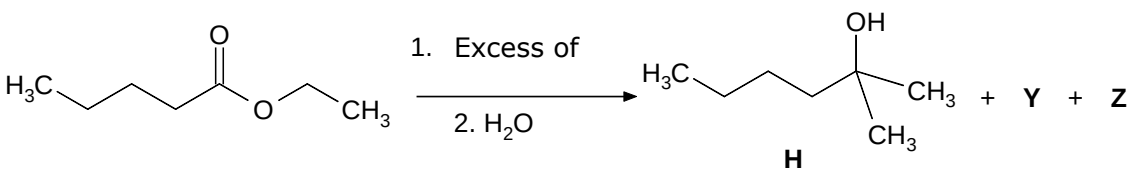
*a) Determine the compounds **A** to **E**, **Y** and **Z** in the reaction schemes below.*







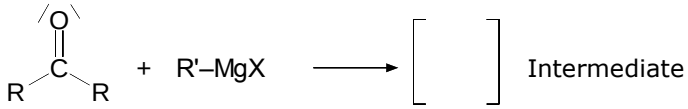




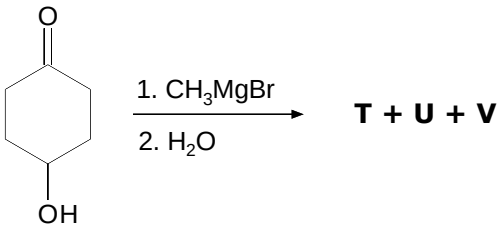
b) How many different primary, secondary and tertiary alcohols do you find in part a)? Assign the letters to the different alcohols.

The mechanism of a Grignard reaction is regarded as a nucleophilic reaction.

c) Assign the charge distribution of the reactants in the following reaction scheme by using δ+/δ–. Give the mechanism of the nucleophilic step to the formation of the intermediate.

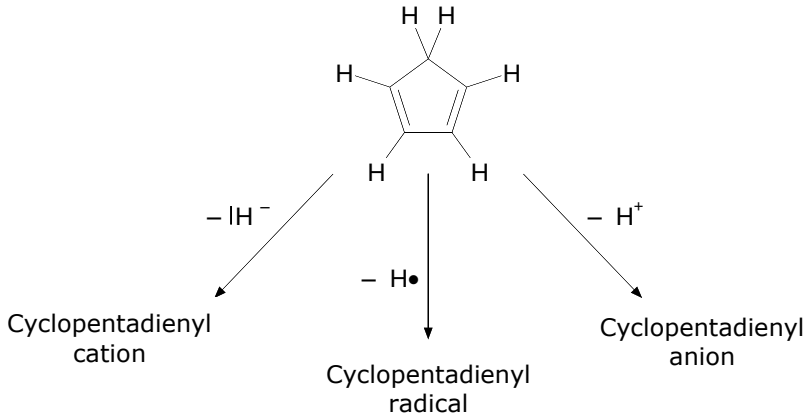


*d) Complete the reaction scheme below by determining the compounds **T** to **V**.*



Problem 3-10 Stability of 5 and 7 Membered Rings

You may assume the following reactions of cyclopenta-1,3-diene C_5H_6:

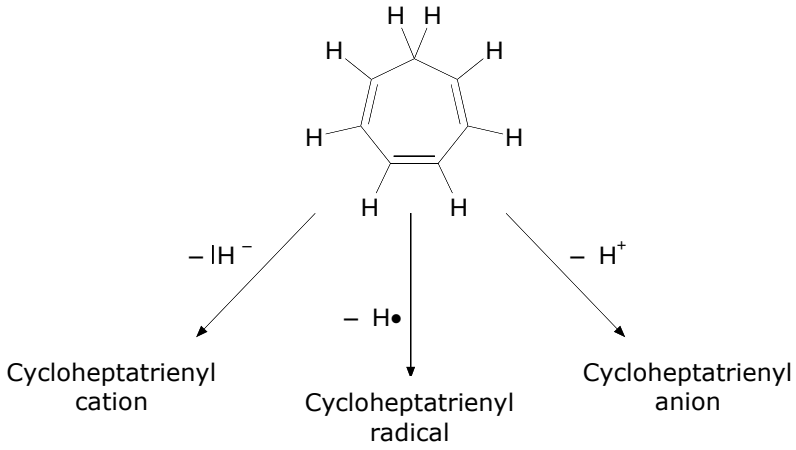


The cyclopentadienyl cation as well as the cyclopentadienyl radical is very unstable and highly reactive. The cyclopentadienyl anion in contrast is extremely stable.

a) Account for the stability of the cyclopentadienyl anion. To do so sketch the carbon skeleton of the ring and mark the sp^2 orbitals, the p_z orbitals and the free electron pairs (orbital view). What is the reason for the stability of the anion?

b) Propose a way to synthesize the cyclopentadienyl anion.

You may assume the following reactions of cycloheptatriene:



c) How stable are the cycloheptatrienyl cation, the cycloheptatrienyl radical and the cycloheptatrienyl anion, respectively? Account for your suggestion of a stable species by sketching an image of the orbitals and the electrons in the ring, similar to that of a).

Third Round Test 2

Problem 3-11 Multiple Choice

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

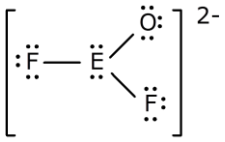
a) Which of the following compounds are likely to be soluble in water: $Ni(OH)_2$, $ZnCl_2$, CuS, $BaSO_4$, AgCl and $Pb(NO_3)_2$?

A $ZnCl_2$ only	**B** $ZnCl_2$ and $Pb(NO_3)_2$	**C** CuS and AgCl	**D** $BaSO_4$ and $Ni(OH)_2$	**E** $BaSO_4$ only

b) A mixture of gas contains NO_2, NH_3 and O_2. These three gases react completely to form N_2 and H_2O. What is the volume ratio $V(NO_2):V(NH_3):V(O_2)$ of the original mixture?

A 2 : 4 : 1	**B** 2 : 1 : 2	**C** 1 : 2 : 1	**D** 1 : 4 : 3	**E** 1 : 3 : 4

c) The Lewis structure of an anion is shown in the image on the right. What is the central atom E?



A B	**B** Si	**C** P	**D** Se	**E** I

d) How many electrons are collected by 1 mol of $Cr_2O_7^{2-}$ if it reacts completely with a primary alcohol in an acidic solution?

A 1 mol	**B** 3 mol	**C** 6 mol	**D** $6.022 \cdot 10^{23}$	**E** $36.132 \cdot 10^{46}$

e) Xenon is a noble gas. Which of the following statements is correct?

A Xe does not participate in any reaction.

B Since the Hindenburg disaster in 1937 Xe has replaced hydrogen as a lifting gas in blimps and balloons.

C Xe forms compounds with highly electronegative atoms.

D Xe reacts with superacids (acids with an acidity greater than 100 % pure sulphuric acid).

E Xe shows the largest 1. ionization energy of its period.

f) Consider following equilibrium system: $XYZ_2(g) \rightleftarrows XY(g) + Z_2(g) \quad \Delta H>0$.
Which of the following statements on the equilibrium constant K is correct?

A Decreasing of c(XY) will increase K.

B increasing of $c(Z_2)$ will increase K.

C Increasing of temperature will decrease K.

D Decreasing of temperature will decrease K.

g) The solubility of Ag_2CrO_4 is $3.00 \cdot 10^{-4}$ mol/L.
How large is the solubility product?

A $3.00 \cdot 10^{-4}$	**B** $1.80 \cdot 10^{-7}$	**C** $9.00 \cdot 10^{-8}$	**D** $1.08 \cdot 10^{-10}$	**E** $27.0 \cdot 10^{-12}$

Problem 3-12 Different Acids

a) Give the pH-value of hydrochloric acid with c(HCl) = 0.0200 mol/L.

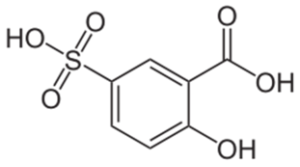
b) Give the pH-value of sulphuric acid with c(H_2SO_4) = 0.0200 mol/L. (pK_{a2} = 1.92)

1 L of sulphuric acid (c = 0.0500 mol/L) and 1 L of hydrochloric acid (c = 0.0250 mol/L are mixed.

c) Give the pH-value of this mixture of these two acids.

Write your results of a), b) and c) with 3 significant figures.

Sulphosalicylic acid is a threeprotic acid.
In the first step of protolysis it is a strong acid. The values of the 2. and 3. step are pK_{a2} = 2.60 and 11.70, respectively.



d) Attach hydrogen atoms to the different steps of hydrolysis.

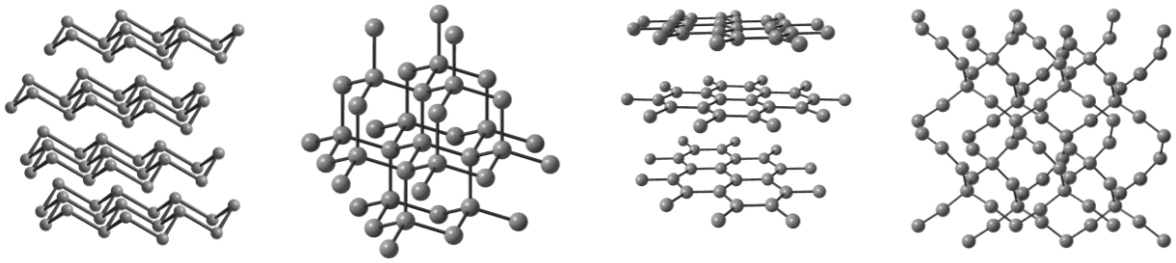
Problem 3-13 Tin and its Compounds

Tin is of importance as a metal as well as in compounds. You find the metal as coating material on cans and in alloys. Its salts are used in analytical chemistry to detect other metals.

a) Write down the electron configuration of tin.

Tin is a semimetal. It exists in a metallic form (β-tin) and in a non-metallic form as a dull- grey powdery material (α-tin) which has a diamond cubic crystal structure.

b) Which of the images shown below shows the structure of α-tin? What is the coordination number of the tin atoms in α-tin?



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

Elementary tin does not react with groceries. Thus it is often used to protect iron cans. A film as this as about 0.3 µm of tin (that are about 2 g/m²) is a sufficient to protect steel from corrosion. A further method to protect steel is a cover coat of zinc ("hot zinc dipped steel").

Source:http://www.gemeinde.ritten.bz.it/u/pictures/Umweltmappe/dosen.jpg

An excerpt from the electrochemical series:

$Zn^{2+} + 2\ e^-$	$\rightleftharpoons$ Zn	E° = -0.76 V
$Fe^{2+} + 2\ e^-$	$\rightleftharpoons$ Fe	E° = -0.41 V
$Sn^{2+} + 2\ e^-$	$\rightleftharpoons$ Sn	E° = -0.14 V
$2\ H^+ + 2\ e^-$	$\rightleftharpoons$ H_2	E° = 0.00 V

c) What happens if the respective protecting film is violated and iron is in contact with the surrounding? Write reaction equations which illustrate the proceeding redox processes. Which of the two materials protects iron better? Account for your statement.

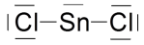
If tin shavings are dissolved in hydrochloric acid crystals of $SnCl_2 \cdot 2\ H_2O$, the so called tin salt, form.

d) Write down the equation for this dissolving reaction.

Tin salt dissolves in water very well. But if you add water to a clear concentrated solution of this salt, clouding occurs caused by the formation of a basic salt with the exact empirical formula $Sn_{21}Cl_{16}O_6(OH)_{14}$. Formally it consists of three components. (In comparison Fe_3O_4 can be written as $FeO \cdot Fe_2O_3$.)

e) Which are the components of the basic salt and in which ratio are they contained in the empirical formula?

At temperatures above 1100 °C anhydrous tin chloride exists of single molecules. The Lewis formula indicates an electron deficient compound. Therefore solid tin chloride has a chain structure.



f) What does this chain structure look like? Draw a line-bond structure.

Being a Lewis acid tin chloride may attach a chloride ion to form $SnCl_3$ ions.

g) Draw the Lewis formula of $SnCl_3^-$. Which kind of structure should this anion have applying the VSEPR model?

A mediocre student of chemistry has to analyse a sample of salts containing $Fe(OH)_3$, $SnCl_2 \cdot 2\ H_2O$, NaCl, and $BaCO_3$. This sample is sparsely soluble in hydrochloric acid and he tries to dissolve it by adding concentrated nitric acid followed by heating, as it is described in text books. Some insoluble precipitate remains in the test tube. He complains to the assistant because his sample should not contain insoluble substances. "There have not been any of them" the assistant told him.

h) Which insoluble compound did the student see in the test tube? Which fact did he not take into account? Write a reaction equation.

If a solution of sodium hydroxide is added to an aqueous solution of $SnCl_2$ a white precipitate (1) is formed which dissolves in an excess of the same solution (2, see part g)). In the presence of cationic bismuth ions this alkaline solution produces a black precipitate (3) if cooled down. When the alkaline solution is heated to boiling this test will also show a positive result even if there is no bismuth compound present (4).

i) Write reaction equations which explain the observations (1) to (4).

Problem 3-14: Kinetics of the Peroxodisulphate Ion

The peroxodisulphate ion is one of the strongest oxidants that are known, although the oxidation reaction is relatively slow.
Peroxodisulphate ions are able to oxidize all halides, except fluoride, to halogens.
The initial rate (r_0) of the iodine-formation according to

$$u\ S_2O_8^{2-} + v\ I^- \longrightarrow w\ SO_4^{2-} + x\ I_2$$

was determined as a function of the initial concentrations (c_0) of the reactants at 25°C:

	$c_0(S_2O_8^{2-})$ [mol·L^{-1}]	$c_0(I^-)$ [mol·L^{-1}]	r_0 [10^{-8} mol·L^{-1}·s^{-1}]
(1)	0.00010	0.010	1.10
(2)	0.00014	0.010	1.54
(3)	0.00018	0.015	2.97

a) Draw the line-bond structure of the peroxodisulphate ion and determine the oxidation states of all atoms and the integers u, v, w and x.

b) Write down the rate equation for the reaction shown above. Determine the order of the reaction and the rate constant.

The activation energy of the reaction mentioned above is 42 kJ·mol^{-1}.

c) What temperature (in °C) has to be chosen to decuple the rate constant?

Iodine reacts rapidly with thiosulfate ions ($S_2O_3^{2-}$) forming iodide ions.

d) Write down the reaction scheme of this reaction.

e) Write down the rate equation for the reaction

$$u\ S_2O_8^{2-} + v\ I^- \rightarrow w\ SO_4^{2-} + x\ I_2$$

assuming that there is an excess of thiosulfate ions relative to the peroxodisulphate ions and the iodide ions in the solution.

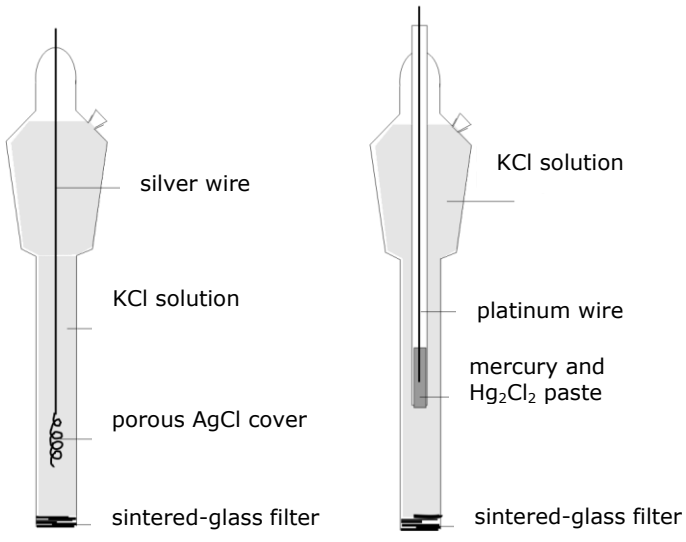
Problem 3-15 Metal/Insoluble Salt Electrodes

These electrodes consist of a layer of an insoluble salt (MX) coated onto the outside of a metal (M) electrode. The whole thing is immersed in a solution containing X^- ions.
The most common example is the silver/silver chloride electrode (Ag, AgCl/Cl^-) another important one is the one involving mercury and (insoluble) mercury(I)chloride traditionally known as calomel electrode (Hg, Hg_2Cl_2/Cl^-).
The standard potential of a cell constructed of these two half cells

(-) Ag, AgCl/KCl(aq) / Hg_2Cl_2, Hg (+)

is E° = 0.0452 V at 298 K.

(In parts a) to f) use concentrations instead of activities for simplification)



a) State at which of the electrodes of such a standard cell an oxidation, at which a reduction takes place. Write down the equations for the reactions at the electrodes. Give an equation for the overall reaction of the cell.
Which of the standard potentials E°(Ag, AgCl/Cl^-) and E°(Hg, Hg_2Cl_2/Cl^-) is greater? Account for your decision.

b) Calculate ΔG° for the process in the cell at t = 298 K.
Which relevance does the algebraic sign of ΔG° have?

The temperature coefficient of this cell is reported to be $\frac{dE^0}{dT}$ = 3.38·10^{-4} VK^{-1}.

Consider n·F·$\frac{dE^0}{dT}$ = ΔS°.

c) What is the meaning of the temperature coefficient?

d) Calculate the changes of entropy and enthalpy for the process proceeding in the cell at 298 K. (If you could not solve b) take ΔG° = - 4.40 kJmol^{-1})

e) Give an equation for the relation between E°(Ag$^+$/Ag) and E°(Ag, AgCl/Cl$^-$). Calculate the standard potential of an (Ag, AgCl/Cl$^-$) electrode.

f) Calculate E°(Hg, Hg_2Cl_2/Cl$^-$). (If you could not solve e) take E°(Ag, AgCl/Cl$^-$) = 0.219 V.)

Being correct you have to use the activity of an ion instead of its concentration c in the logarithmical part when applying the Nernst equation.

g) Give the activity a(Cl$^-$) in a calomel electrode with E = E°.
(If you could not solve f) take E°(Hg, Hg_2Cl_2/Cl$^-$) = 0.2682 V.)

The potential of a calomel electrode with c(Cl$^-$) = 0.1 mol/L is 0.3337 V at 298 K.

h) Determine the activity a(Cl$^-$) in a solution of KCl with c(Cl$^-$) = 0,1 mol/L.

Standard potentials E°(Ag$^+$/Ag) = 0.7996 V E°(Hg_2^{2+}/Hg) = 0.7986 V
Solubility product K_{sp}(AgCl) = 1.78·10^{-10} (at 298 K)

Problem 3-16 A Substance to find

Substance A is free of water. It may take up water of crystallisation to form Z which is used in analytical chemistry. 0.392 g of Z was dissolved in water. The solution was treated with an excess of barium chloride solution after which 0.466 g of a white precipitate formed which was not soluble in acids. The precipitate was filtered off, an excess of alkaline was added to the filtrate and heated up to boiling. As a result 46.7 mL of a gas C (25 °C and 104.3 kPa) and a grey green residue of a hydroxide of the metal X was formed. The light green colour of the hydroxide turned brown when the hydroxide was kept on the air. The gas C has a typical pungent smell. It is totally absorbed by sulphuric acid.

Student Manfred prepared a sample of Z and for whatever reason decided to dry it in vacuum before use. This resulted in partial water loss. In order to determine the composition of the dried substance a sample of 0.3796 g of it was dissolved in sulphuric acid (c = 0.5 mol/L) and a potentiometric titration with cerium(IV) sulphate (c = 0.0500 mol/L) was performed:

V/mL	10.00	18.00	19.80	20.00	20.20	22.00	30.00
E/mV	771	830	889	1110	1332	1391	1453

V: added volume of a solution of cerium(IV) sulphate

E: measured potential of the galvanic cell

During this titration only the metal ions of X are oxidized.

a) Determine the formulae of A, B, C, X and Z.
Write down equations for the five mentioned reactions.

b) How can the endpoint of a redox titration be recognized?

c) Plot the graph E = f(V) and mark the endpoint of the titration. Find the volume V_{eq} which is needed to oxidize all the ions of X. Write down the equation of the oxidizing reaction.

d) Determine the composition of the substance after drying.

Problem 3-17 Knowledge about Substances

Six diluted solutions of the following substances were given:

Chromium(III) chloride, iron(III) chloride, hydrogen peroxide, sodium hydroxide and ammonia.

Reactions were carried out between all solutions. The results can be found in the table below.

Added \ Received	A	B	C	D	E	F
A		-	-	grey green pr. diss.	grey green pr. diss.	-
B			-	green pr.	green pr. diss.	-
C				gas f.	gas f	-
D					-	brown pr.
E						brown pr.
F						

pr: precipitate dis.: the precipitate dissolves in an excess of the added solution

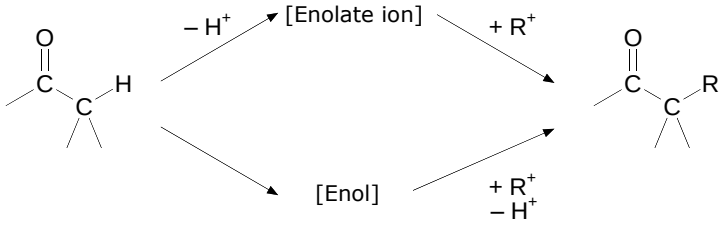
gas f.: formation of a gas

Attach the substances to the letters.

For each substance identified write the equation of each reaction.

Problem 3-18 α-Substitution Reactions

α-Substitution reactions allow a lot of important organic syntheses. They occur next to the position to the carbonyl group – the α position – and involve the substitution of an α hydrogen atom through either an enol or an enolate ion intermediate. The reaction is base-catalysed as well as acid-catalysed:

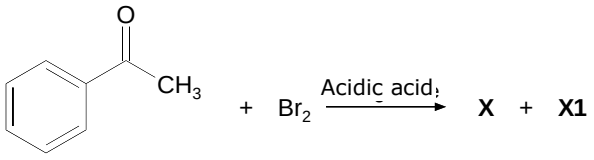


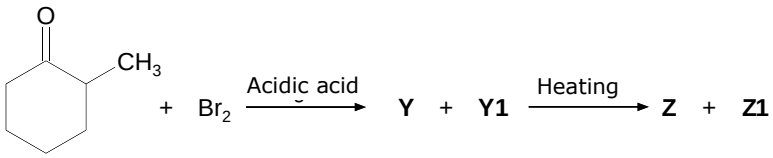
a) Draw structures of the enolate ion and of the enol for the scheme above. Be aware of possible resonance structures.

b) Mark the reactivity of the α hydrogen atoms in the compounds given below by using the terms "very reactive" and "weakly reactive".

CH_3COOH; CH_3CH_2CHO; $CH_3CON(CH_3)_2$; 1,3-Cyclohexandione

c) Determine the compounds X, X1, Y, Y1, Z and Z1 in the following schemes of a double halogenation.

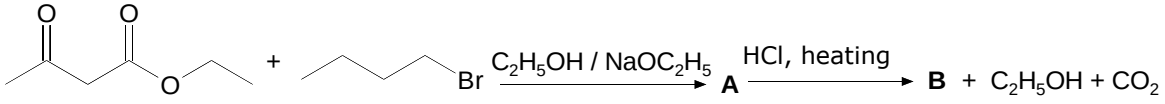




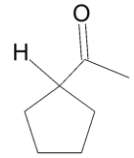
d) Write down the names of the compounds X, Y and Z.

e) Formally Br_2 can be split into Br^+ and Br^-. Which of these species reacts with the enol? Which intermediate forms? Sketch the reaction mechanism.

f) Which product forms when acetoacetic ester reacts with 1-bromobutane? Complete the following reaction scheme.



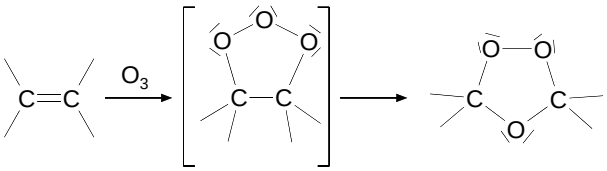
g) Propose a way to synthesize methyl-cyclopentyl-ketone.



Use *acetoacetic ester as reactant. A five membered ring component is not available.*

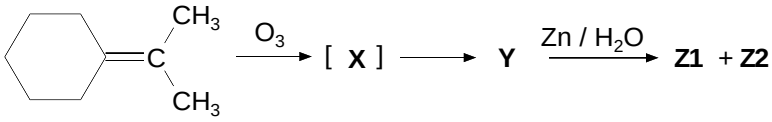
Problem 3-19 Alkene Cycloaddition Reactions

The best known cycloaddition is the reaction of ozone (O_3) with a carbon-carbon double bond:

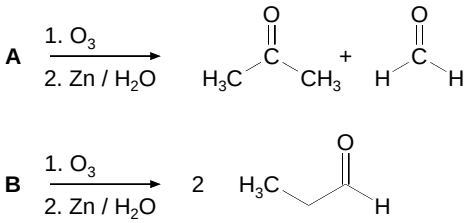


These rings are explosive and unstable and are therefore not isolated. Instead, the ozonide is treated with a reducing agent to convert it to a ketones and aldehydes (ozonolysis).

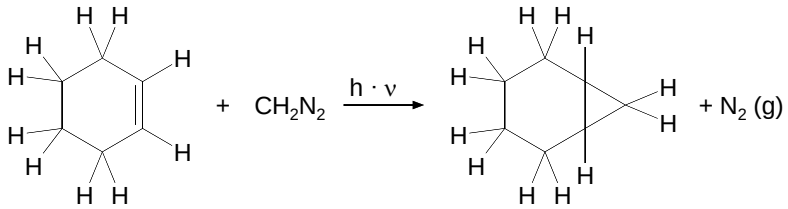
*a) Complete the following the reaction scheme by drawing the structures of **X**, **Y**, **Z1** and **Z2**. Write down the names of **Z1** and **Z2**.*



*b) Which compounds lead to the following products of an ozonolysis. Give the structures and the names of **A** and **B**.*



The following reactions provide in contrast more stable cycloaddition products.



In this reaction diazomethane is cleaved and nitrogen and an extremely reactive gas **M** form. The gas **M** in the example above reacts immediately with the double bond of cyclohexene.

c) *Draw the structure of compound **M**. Draw the orbital structure of **M** (hybridisation, free orbitals, charges and electrons).*

d) *Characterise the addition of **M** to the double bond. Is this reaction a nucleophilic or an electrophilic addition?*

The following conversion is base-catalysed and leads to compound **D**.

e) *Draw the structure of **D**.*

f) *Draw the structure and the orbital structure of the reactive intermediate.*

The reaction of 2-pentene with chloroform shown above is performed with cis-2-Penten.

g) *Draw the structure of cis 2-pentene and the spatial structure(s) of the product(s) using the instructions below.*
(Instructions: Bond receding into page  ,
bond coming out of paper plane )

Problem 3-20 Peptide Synthesis

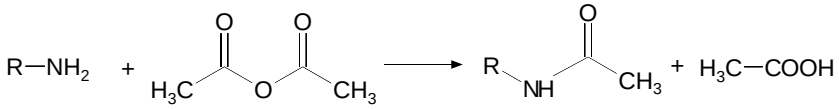
Reactions of acids, amines and amino acids.

a) *Which product do you expect if butanoic acid reacts with methyl alcohol in the presence of hydrochloric acid? Write down the reaction equation and the name of the product.*

b) *Show where the alcohol attacks in the decisive step. Is it a nucleophilic or an electrophilic attack? Draw the instable intermediate.*

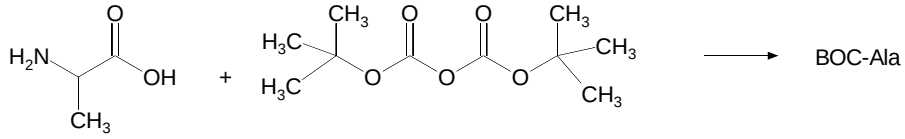
c) *Which (main) product do you expect if 5-hydroxypentanoic acid is acidified?*

The conversion of amines RNH_2 into amides $RCONH_2$ can be carried out with acetic anhydride:



In the synthesis of peptides di-tert-butyl dicarbonate is often used. Tert-butoxycarbonyl-amid, or BOC-Amid, is formed.

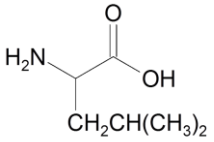
d) Draw the line-bond structure of BOC-Ala.



Alanin

The BOC group can be removed by treatment with a strong organic acid such as CF_3COOH.

e) Develop a plan to synthesize the peptide H-Leu-Ala-OH.
Write down the different steps in words without using reaction equations.
Regard that only the protection of the active groups of the amino acids leads to a high specific yield.



Leucine

f) Give the reaction equations of your proposed steps.

Fourth Round (theoretical problems)

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

Problem 4-01 Solubility and Equilibria

Mercury(II)-sulfide is one of the least soluble salts with the solubility product of $K_{sp} = 1.58 \cdot 10^{-52}$.

a) Calculate the solubility L of HgS in mol/L. You may assume that no hydrolysis of Hg^{2+} and S^{2-} takes place.

The solubility L calculated in a) differs severely from the solubility found in experiments. If you take hydrolysis into account you get (after some work of calculation) the following correlation between the concentrations of H_3O^+ und S^{2-}:

$$c(S^{2-})^2 \cdot \left(1 + \frac{c(H_3O^+)}{K_{a2}} + \frac{c(H_3O^+)^2}{K_{a1} \cdot K_{a2}}\right) = K_L \cdot \left(1 + \beta_1 \cdot \frac{K_W}{c(H_3O^+)} + \beta_2 \cdot \frac{K_W^2}{c(H_3O^+)^2}\right) \qquad (1)$$

Furthermore given:

· acid constants of H_2S: $K_{a1} = 7.94 \cdot 10^{-8}$ $K_{a2} = 1.26 \cdot 10^{-13}$

· constants for the forming of complexes from Hg^{2+} and OH^-:

for $[Hg(OH)]^+$: $\beta_1 = 2.00 \cdot 10^{10}$

for $[Hg(OH)_2]$: $\beta_2 = 5.01 \times 10^{21}$

· $K_W = 1.00 \cdot 10^{-14}$

· solubility product of HgS $K_{sp} = 1.58 \cdot 10^{-52}$

b) Write a set of equations which determines the concentrations of all ions and molecules present in the solution.

From this set equation (1) can be derived but you shall not do this in this test.

In a solution of HgS you find pH = 7.

c) Calculate the concentrations of Hg^{2+} and S^{2-} ions.

d) Calculate the solubility L of HgS in water starting with the equations of b) and the results of c). How much differs this result from that of a)? Give a factor.

e) Explain by calculating the changes of OH^- and H_3O^+ concentrations why the hydrolysis of Hg^{2+} and S^{2-} does not influence the pH value of pure water.

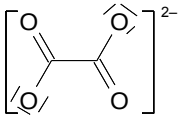
Problem 4-02 Isomerism of Complex Compounds

Complex compounds show different kinds of isomerism, especially stereoisomerism when atoms (or ions) are connected in the same order but with a different geometry. An important role plays the coordination number of the center and the ligands themselves.

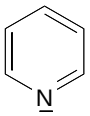
a) Draw all stereoisomers of the complexes on the answer sheet. If there are enantiomers draw only one of them.

b) How many stereoisomers of the complex compounds below do you expect? Complete the table on the answer sheet.

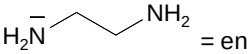
$[Cr(ox)_2(H_2O)_2]^-$, $Co(py)_3Cl_3$, $Co(en)(NH_3)_2Cl_2$, $(C_9H_6NO)_3Al$



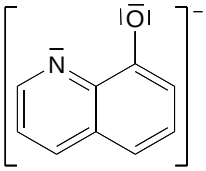
= ox



= py



= en



= C_9H_6NO

Problem 4-03 Thermodynamics

In the presence of certain catalysts hydrazine (N_2H_4) may decompose forming ammonia and nitrogen gas.

a) Write a balanced equation for the decomposition reaction.

Given the following data at 298 K:

	N_2H_4 (l)	N_2H_4 (g)
$\Delta_f H°$ in kJ/mol	50.6	95.4

	N-N
average bond energies B in kJ/mol	159

During the decomposition of 1 mol of N_2H_4 (l) 112.2 kJ/mol are set free.

b) Calculate the average bond energy B(N≡N) and the standard enthalpy of formation of ammonia $\Delta_f H°(NH_3)$.

A sample of 5.00g of N_2O_4 is introduced into an evacuated container at 90.0 °C.
Data for the reaction $N_2O_4 \rightleftharpoons 2\ NO_2$ at this temperature:

$\Delta_R H$ = 57.7 kJ/mol $\Delta_R S$ = 177 $J \cdot K^{-1} \cdot mol^{-1}$.

(These values are considered to be constant in the range of 293 K < T < 393 K.)

c) To how many significant figures should the results of the following calculations be quoted?

d) Calculate the pressure after the equilibrium is installed.

e) Determine the degree of decomposition (α) of N_2O_4.

If there are 5.00 g of N_2O_4 at 70.0 °C in a 2.00 L container, 60.6 % of the N_2O_4 are decomposed to NO_2 (α = 0,606). The conversion shall be halved at the same temperature by changing the volume of the container.

f) Calculate the volume of the container.

Problem 4-04 Electron Deficiency - Help?

There are 3 valence electrons in boron as well as in aluminum. Their compounds belong to electron deficient compounds. Boron and aluminum compensate this deficiency in their compounds in different ways.
The analysis of the bonds in boron trifluoride shows bond lengths $d_{B\text{-}F}$ = 130 pm for all bonds. A single bond B-F and a double bond B=F have a length of 145 pm and 125 pm, respectively.

a) Take BF_3 in order to explain how the electron deficiency at the boron center is evened out.

Besides orthoboric acid (H_3BO_3 or $B(OH)_3$), found in nature, α-boric acid (HBO_2) exists. It forms a trimeric oligomer.
In an aqueous solution of boric acid the following species (among others) are found:
i) $[B(OH)_4]^-$ ii) $[B_3O_3(OH)_4]^-$ iii) $[B_4O_5(OH)_4]^{2-}$.

b) Which reaction is responsible for the acidic reaction of orthoboric acid? Give a reaction equation.

c) Draw the Lewis structures of α-boric acid and of the species i), ii) und iii).

The melting points of $AlCl_3$ and $AlBr_3$ are 192 °C and 98 °C, respectively, while AlF_3 is a high melting (1291 °C) insoluble solid.

d) Account for these differences with the help of the structures of the solids.

$AlCl_3$(l) exists as dimer.

e) Draw the Lewis structure of this dimer.

Dimers of associated monomers are found in aluminum alkyl compounds, too. These associations are approved by NMR measurements.
Trimethyl aluminum shows in the ^{1}H NMR spectrum at a temperature of – 50 °C two signals (0.50 ppm and 0.65 ppm) in the proportion 1 : 2. If the temperature is raised to – 25°C these two signals start to combine, at 20 °C only one sharp signal is found (-0,30 ppm).

f) Account for this observation!

g) What is the reason that no pure aluminum alkyls AlRR'R'' with different substituents R, R', R'' can be isolated.

Many compounds of boron and aluminum are Lewis acids. The strength of Lewis acids and Lewis bases is influenced by electronic and steric effects.

h) Arrange the three bases and the three acids in the order of increasing strength (>) and account for your decision.

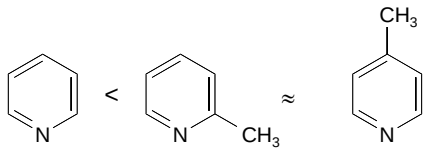
i) NH_3, NF_3, $N(CH_3)_3$

ii) BH_3, BF_3, $B(CH_3)_3$

Using the values of electronegativity you could predict the following order of Lewis acids: $BF_3 > BCl_3 > BBr_3$. The order found experimentally is just the opposite.

i) Explain why boron trichloride is a harder Lewis acid than boron trifluoride.

In regard to protons pyridine and its methyl derivates show the following Lewis base strength:



1 2 3

In regard to $B(CH_3)_3$ the base strength of compound 1 and 3 are approximately the same and much higher than that of compound 2.

j) Rationalize shortly!

k) Account for the following observation:
More space demanding substituents lead to a decrease of the Lewis acidity of BR_3 compounds (R = alkyl).

Problem 4-05 Kinetics

The so-called iodine clock reaction is a classical demonstration experiment to display chemical kinetics in action. Two clear solutions are mixed and after a short time delay, the colorless liquid suddenly turns to dark blue. This experiment has several variations. One of them involves the following reaction:

$S_2O_8^{2-} + 3\ I^- \longrightarrow 2\ SO_4^{2-} + I_3^-$ (All species are aqueous.)

The following mechanism is proposed for this reaction:

$$
\begin{array}{lcl}
S_2O_8^{2-} + I^- & \xrightarrow{k_1} & IS_2O_8^{3-} \\
IS_2O_8^{3-} & \longrightarrow & 2\ SO_4^{2-} + I^+ \\
I^+ + I^- & \xrightarrow{k_2} & I_2 \\
I_2 + I^- & \underset{k_4}{\overset{k_3}{\rightarrow}} & I_3^-.
\end{array}
$$

a) Derive an equation for the rate of formation of I_3^-. Apply the steady-state approximation to all intermediates.

Consider two sequential first-order reactions:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Starting with A it is relatively straightforward how the concentrations of A, B and C vary with time for given values of the rate constants k_1 and k_2. Look at these reactions under the following conditions:

i) $k_1 > k_2$ perhaps $k_1 \approx 10 \cdot k_2$
ii) $k_1 \approx k_2$
iii) $k_1 < k_2$ perhaps $\approx 0.1 \cdot k_2$

b) Draw graphs carefully which show how the concentrations of A, B and C change for the three different combinations of the rate constants. Account for your graphs i) and iii).[3]

In water from a lake, the rate of radioactivity decay of dissolved ^{222}Rn has the value of 4.2 $\frac{atoms}{\text{min} \cdot 100\ L}$. All of this ^{222}Rn is produced by decay of dissolved ^{226}Ra, which has an activity of 6.7 $\frac{atoms}{\text{min} \cdot 100\ L}$. These activities do not change measurably with time. Because every atom of ^{226}Ra that decays produces an atom of ^{222}Rn, the deficit in ^{222}Rn activity implies that ^{222}Rn is being lost from the lake by an unknown process.
Half-life: $t_{½}(^{222}Rn)$= 3.8 days $t_{½}(^{226}Ra)$= 1600 years.

c) Calculate the concentration of ^{222}Rn in atoms/100L as well as in mol/L. Be aware of significant figures in the result.

Suppose that the unknown process obeys a first order rate law.

d) Calculate the rate constant for this process in min^{-1}.

^{222}Rn decays exclusively by α emission.

e) Identify its radioactive decay product including the mass.

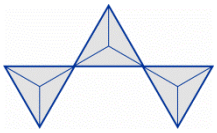
Problem 4-06 Silicon

You can deduce silicates from the anhydride SiO_2 of the silicic acids m $SiO_2 \cdot$ n H_2O.
Silicic acids show a great tendency to split off intermolecular water to form oligo- or polysilicic acids and in the end silicon dioxide.

a) Write the equation for the condensation reaction of two molecules of silicic acid H_4SiO_4 to form disilicic acid. Use structural formulae of the reactant and the product.

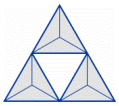
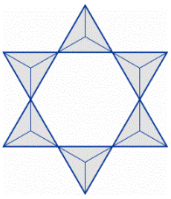
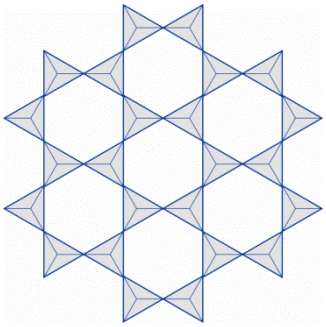
[3] Idea and solution from J. Keeler and P. Wothers, Chemical Structure and Reactivity, 2008, page 423

Further condensation reactions may lead to cyclosilicates (rings), inosilicates (single and double chains), phyllosilicates (sheets), tectosilicates (3 D framework). In all of them you find SiO_4 tetrahedrons knitted together at the corners:

 = $[SiO_4]^{4-}$  = $[Si_3O_{10}]^{8-}$

b) Find the empirical formulae of the silicate anions i) – iii).

i) ii) iii)

If you melt down silica and alkali carbonates, alkali silicates $M_2O \cdot n\ SiO_2$ are formed which are soluble in water. You can buy aqueous solutions as soluble glass. They are used as mineral adhesives and harden in contact with air. Addition of acid leads to immediate solidification.

c) Account for the solidification of liquid glass $Na_2SiO_3(aq)$ when acid is added. Write a reaction equation for the process of hardening at air.

If partly alkylated silicic acids undergo a condensation reaction silicones form. Depending on the kind of the reactants you can get different degrees of condensation and thus generate characteristic properties of the product.

Reactants are methyl silanes which are generated by the process of Müller-Rochow from methyl chloride (CH_3Cl) and silicon with a copper catalyst.

d) Write the reaction equation for the formation of dimethyl chlorosilane from methyl chloride and silicon.

Besides dimethyl silane you find more main products such as trimethyl silane and methyl trichlorosilane.

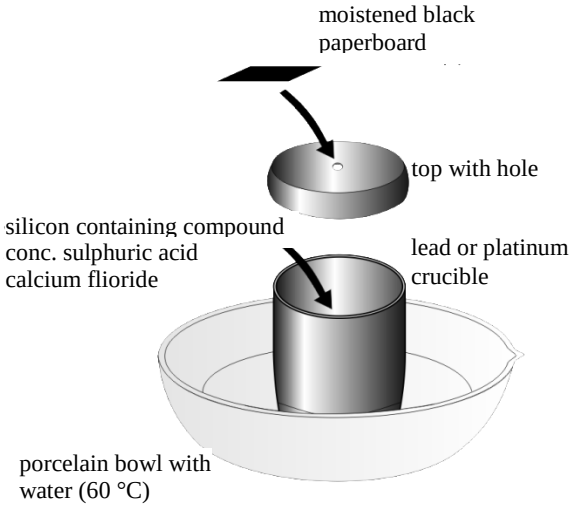
e) Write reaction equation(s)!

f) Draw the structure of a silicone which is formed by the hydrolysis of dimethyl silane.

It is easy to detect silicates with the water droplet probe.

The sample to analyze is mixed in a lead crucible with calcium fluoride and concentrated sulphuric acid and heated in a water bath. A cover plate with a small hole is placed on top. A moistened black piece of paperboard is put over the small hole.

If there is a silicate in the sample a white spot forms on the paperboard.



g) Which reactions take place? Write the necessary equations. Use SiO_2 as silicate content of the sample.

Problem 4-07 Calculations in the World of Atoms and Molecules

A Again and again: The electron in the 1-D box

In quantum mechanics the model of a particle in a one dimensional box describes a particle constrained to move between two impenetrable walls with the distance L. The allowed energy levels of such a particle are

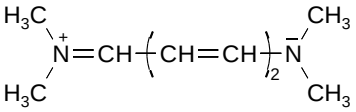
$E = \frac{h^2 n^2}{8 m L^2}$,

h = Planck's constant, n = quantum number, m = mass of the particle,

L = length of the box.

In order to apply the model of a particle in a box to conjugated linear molecules the delocalized π-electrons are treated as particles moving freely along the central chain of the molecule.

The molecule with the formula below has a conjugated chain between the two ends.



a) Draw the resonance forms of this molecule and determine the number of delocalized electrons in this molecule.

b) Derive a formula for the transition energy from one energy state to the next one ($n \rightarrow n+1$).

The wave length of the light absorbed by this molecule was experimentally determined and recorded at λ = 605 nm.

c) Predict the chain length where the electrons can move freely in this molecule.

The average carbon-carbon bond length in a hydrocarbon chain of alternating single and double bonds can be approximated to 140 pm.

d) Estimate the wave length of the lowest electronic transition for 1,3-penta-diene.

B Structure of wustite

Iron is the most important metall. During the production of pig iron in a blast furnace oxidic iron ore is reduced by carbon monoxide generated in the lower part of the furnace. Carbon monoxide reduces in the so-called reduction zone iron ores which in this region consist partly of hematite and magnetite but mainly of wustite (Fe_xO).

The structure of ideal stoichiometric iron(II)-oxide corresponds to the structure of NaCl: cubic close-packed O^2 ions (cubic-F) with Fe^{2+} ions in the octahedral interstices.

e) Draw an image of this structure and mark one octahedral interstice.

There are tetrahedral interstices in this structure, too.

f) Mark one tetrahedral interstice and give the number of such interstices in an elementary cell.

Pure iron(II) oxide does not exist under normal conditions. At the reduction of iron(III) oxide a black product (Fe_xO), wustite, forms. It crystallizes in a lattice of the NaCl type. The density of wustite is ρ = 5.71 g·cm^{-3}.
To determine the structure by X-ray diffraction radiation emitted by molybdenum (λ = 71.41) is used. The first-order diffraction of wustite gives $2\cdot\Theta$ = 19.42°.

g) Calculate the lattice constant of a wustite elementary cell.

h) Determine x.

The charge equalization in wustite is explained in the way that not only Fe^{2+} ions but also Fe^{3+} ions are existent.

i) Calculate the theoretical percentage of Fe^{2+} and Fe^{3+}, respectively, in wustite and write a formula of the type $Fe(II)_uFe(III)_vO$.

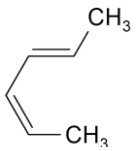
Problem 4-08 Stereochemistry of Electrocyclic Reactions

The cyclisation of 2,4,6-octatrien yields dimethylcyclohexatrienes when heated.

a) Write the equation for the reaction of 2,4,6-octatrien to give dimethylcyclohexatriene without disregarding the stereochemistry. Give the correct IUPAC name.

The cyclisation to form dimethylcyclohexatriene results in a certain stereospecific compound. For example, (2E,4Z,6E)-octatrien yields only the cis-product when heated.

Example for the E/Z naming:



(2E,4Z)-Hexadien

b) Draw for the reaction equation below the structural formulae of (2E,4Z,6E)-octatrien and of the product. Visualize the stereochemical situation in the cis-product.

(2E,4Z,6E)-octatrien ⇌ *cis-compound*

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

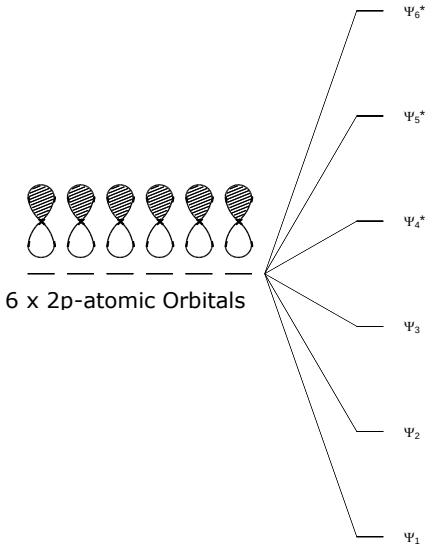
In the following the stereoselective reaction is explained using the symmetry of the molecular orbitals (MOs) of the reactant.

Following the MO theory a bond forms by overlapping of two atomic orbitals to form an MO. These MOs contain 2 electrons. The overlapping of two atomic orbitals leads to 2 molecular orbitals, a bonding MO(Ψ) and an antibonding MO(Ψ^*).

It is known from quantum mechanical calculations that by combination of atomic orbitals algebraic signs, (+) and (-), for the orbital lobes of the MO orbitals have to be assigned. Bonds result from the overlapping of orbital lobes with the same sign.

c) Draw the molecular orbitals Ψ_1 to Ψ_6^* of 2,4,6-octatrien into the scheme below. Mark the existing nodes on the different levels and give their number.

(Hint: Ψ_1 has no node, the algebraic signs (+,–) of the lobes may be indicated by different colouring.)



π-Molecular orbitals of 2,4,6-octatrien

d) Complete the π MO schemes of 2,4,6-octatrien on the answer sheet with the available number of π electrons in the

i) ground state

ii) 1. excited state.

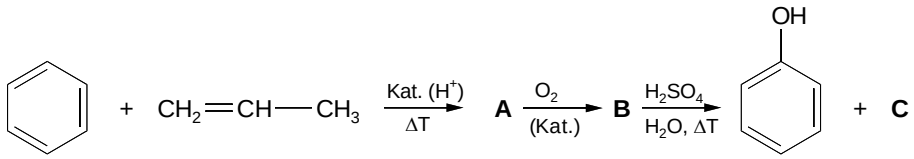
The stereoselectivity of the cyclisation of polyenes is determined by the highest occupied molecular orbital (HOMO) in the MO scheme. The two outer lobes of the HOMO with their algebraic signs are crucial for the formation of a bond.

e) Show with the help of an image the thermal cyclisation of (2E,4Z,6E)-octatrien. Draw the responsible outer lobes of the HOMO with their signs.
In which direction do the lobes have to rotate in order to make the cyclisation possible?

Problem 4-09 Phenol and Derivatives

Nowadays phenol is produced industrially from benzene, propene and oxygen. In this process a ketone is formed as a side product.

a) Complete the reaction scheme of the industrial phenol production by giving the structural formulae and the names of A, B and C. What kind of reaction is the formation of A?



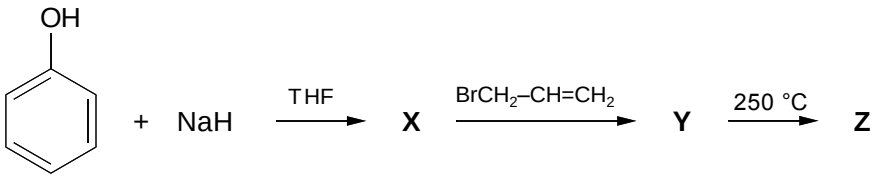
b) Compare the acidity of phenol and ethanol. Account for your decision.

c) How does the acidity of phenol change if it is substituted with a nitro group in ortho or para position? Account for your decision.

Oxidation of phenol with a strong oxidation reagent leads to p-benzoquinone (2,5-cyclohexadiene-1,4-dione) which can easily be reduced to hydroquinone.
The redox potentials of quinones are crucial to the functioning of living cells, where compounds called ubiquinones act as biochemical agents to mediate the electron-transfer processes in energy production in the NADH/NAD^+ process . Ubiquinone consists of a benzoquinone ring which is substituted in 2, 3, 5, 6 positions by different groups R^1, R^2, R^3 and R^4.

d) Give a reaction equation for the oxidation of NADH with the help of ubiquinone.
Write a second equation for the recovering of ubiquinone with oxygen.

e) Complete the following reaction scheme by giving the structures of X, Y and Z.



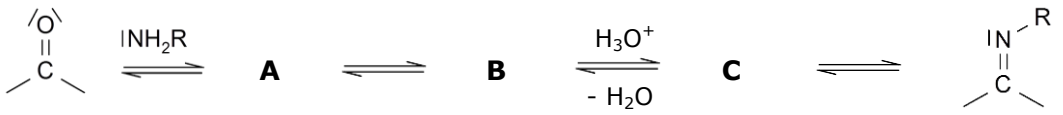
(Hint: Contrary to compound Y compound Z shows acidic properties.)

f) Give the mechanism of the reaction Y ⟶ Z.

Problem 4-10 Imines and Imine Reactions

Primary amines add to aldehydes and ketones to yield imines. Secondary amines add similarly to yield enamines.

a) Give the intermediate stages A to C of the reaction mechanism for the formation of an imine:

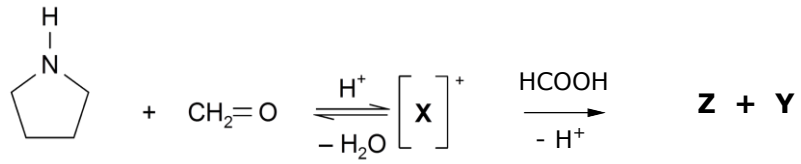


Ketone/Aldehyde | tetrahedral intermediate stage | Carbinolamine | Iminium ion | Imine

b) Write the equation for the reaction of acetone with 2,4-dinitrophenylhydrazine. What can this reaction of 2,4-dinitrophenylhydrazine with aldehydes and ketone be used for?

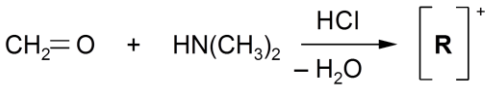
The methylation of a primary or a secondary amine is performed with a mixture of formaldehyde and formic acid.

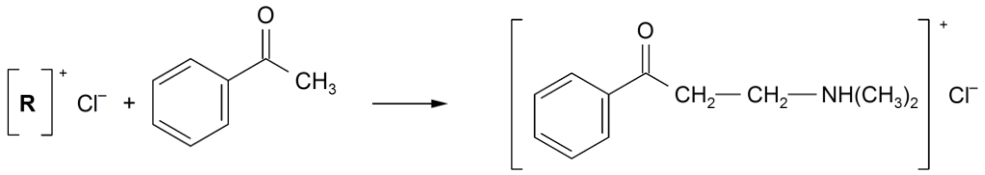
*c) Complete the following reaction scheme. Write the structural formulae of **X**, **Y** and **Z**. Name the pyrrolidine compound.*



Pyrrolidine

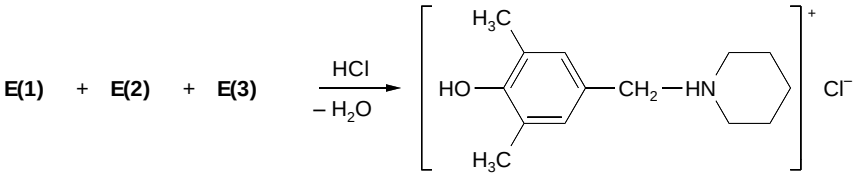
The Mannich reaction is a special kind of an imine reaction. It can be described as an addition of a nucleophilic C atom to an intermediate iminium ion. The aldehyde and amine components formaldehyde and dimethylamine are particularly reactive.

1. Step 

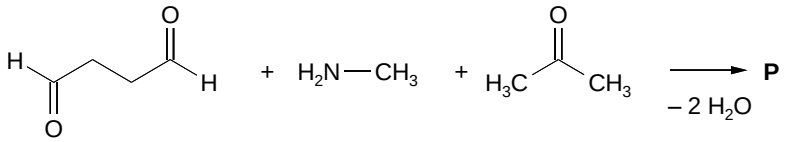
2. Step 

*d) Write the structural formula of the intermediate iminium ion **R**⁺.*
Propose a mechanism how the iminium cation reacts with acetophenone.

*e) Which are the reactants **E(1)** to E**(3**) employed to yield the following compound by a Mannich reaction?*



*f) Which compound **P** do you expect in the following Mannich reaction?*
(Hint: **P** is a bicyclic compound which is a precursor of cocaine.)



Fourth Round (practical problems)

Safety precautions for all laboratory work:

Wear eye protection and protective clothing.

Problem 4-11 Synthesis and Analysis of a Copper Compound

In this experiment a diammonium tetrachlorocuprate compound will be prepared. This compound is used for finding its composition by determining its copper content:

$$2\ NR_3 \cdot HCl + CuCl_2 \rightleftharpoons (NR_3H)_2CuCl_4$$

Only these three possible compounds have to be considered as reagents:

$(CH_3)_2NH_2Cl$ bzw. $(CH_3)_2NH \cdot HCl$

$((CH_3)_2CH)NH_3Cl$ bzw. $((CH_3)_2CH)NH_2 \cdot HCl$

$(CH_3CH_2)_2NH_2Cl$ bzw. $(CH_3CH_2)_2NH \cdot HCl$

Equipment and Glassware:

2 Erlenmeyer flasks (100mL), magnetic stirrer plate with stirring bar, graduated cylinder (25 mL), volumetric pipette (5 mL), volumetric pipette (10 mL), glass rod, suction pump, suction flask, Büchner funnel with rubber seal, filter paper (2x) for Büchner funnel, desiccator for drying, 2 beakers (50 mL), volumetric flask (100 mL) with stopper, volumetric pipette (100 mL), pipette control, 2 conical beakers (300 mL, wide mouth),spatula, burette (25 mL) with funnel and clamp, stand with boss and clamps, icewater bath.

Chemicals:

unknown ammonium chloride (already weighed in an Erlenmeyer flask labeled with 1 and A – F)	
1.70 g of dry copper(II) chloride · n H_2O (n ≤ 2), (already weighed in an Erlenmeyer flask labeled with 2)	
Ethanol	
2-Propanol	
Ethyl acetate	
Acetone	
Dil. sulfuric acid, c(H_2SO_4) = 1 mol/L	
Potassium iodide	
Standard solution of sodium thiosulfate, c($Na_2S_2O_3$) = 0.1 mol/L	
Solution of starch	
Demineralized water	

Procedure:

Part 1: Preparation of the copper compound

15 mL of 2-propanol are added to ammonium chloride which then is dissolved by heating gently on the heat plate of the stirrer.

A stirring bar and 3 mL of ethanol are added to the flask with the copper chloride which then is dissolved by stirring and gently heating.

The solution of ammonium chloride is given to the solution of copper chloride. A mixture of 2 mL of 2-propanol and 8 mL of ethyl acetate is added.

This mixture is gently heated for 3 to 4 minutes followed by cooling to room temperature. For crystallizing, the flask is put into the icewater bath.

The precipitated solid is filtered off with a Büchner funnel, washed three times with maximal 10 mL of ethyl acetate until the solid looks passably homogeneously.

In case of a yellow product the solid can be washed with a small (!) amount of acetone.

Attention: The green product dissolves readily in acetone and must not be washed with acetone.

The upper part of the Büchner funnel together with the product is put into the desiccator for drying.

The yield is not asked.

Part 2: Iodometric determination of the copper contend of the synthesized copper compound

Approximately 1g of the copper compound is accurately weighed (with the help of a small beaker) and transferred quantitatively to a 100 mL volumetric flask. The copper compound dissolves readily in water.

The flask has to be filled up to 100 mL. The solution is mixed well to form the test solution.

20 mL of this solution are transferred with a pipette to a conical beaker (wide mouth). 25 mL of diluted sulfuric acid and water are added to yield about 100 mL.

About 2 g of potassium iodide (heaped spatula) are added, the solution swung and immediately titrated with the standard solution of sodium thiosulfate until a light yellow color occurs.

Approximately 2 mL of starch solution is added shortly before the end and then titrated until the end point of the dark solution.

Disposal: All solutions have to be poured into the provided disposal.

Problems:

a) *Write down the label code of the Erlenmeyer flask with ammonium chloride on the answer sheet.*

b) On which reactions is the iodometric determination of copper based? Write all relevant reaction equations.

c) Record the mass of the weighed sample and the consumption of the standard solution of $Na_2S_2O_3$.
Calculate the mass concentration β of copper in your test solution (in mg/L).

d) Identify which of the three ammonium chloride compounds was used for the preparation.

Problem 4-12 Complexometric Determination of Nickel

Equipment and Glassware:
Volumetric flask (100 mL) with stopper with test solution, volumetric pipette (20 mL), pipettes control, 2 burettes (25 and 50 mL) with funnel, stand and clamp, spatula, 2 conical beakers (300 mL, wide mouth).

Chemicals:

Test solution containing nickel a volumetric flask  for $NiSO_4$(s)

Dil. solution of ammonia, c(NH_3) = 2 mol/L
Solution of murexide indicator
Standard solution of $Na_2EDTA \cdot 2\ H_2O$, c(Na_2EDTA) = 0.1 mol/L
Demineralized water

Procedure:
The flask with the test solution has to be filled up to 100 mL. The solution has to be mixed well.
20 mL of this solution are transferred with a pipette to a conical beaker (300 mL, wide mouth) and 15 mL of the solution of ammonia are added.
Drops of the indicator solution are added until intense yellow color occurs (approximately 8 drops). If the solution in orange the pH value is not high enough and additional solution of ammonia has to be added.
The mixture is filled up with demineralized water to about 100 mL and then titrated with the standard solution of Na_2EDTA.
There will be a sharp change of colors from yellow to violet. This color has to persist.

Disposal: All solutions have to be poured into the provided disposal.

Problems:

a) Write down the label code of your volumetric flask on the answer sheet.

b) Record the consumption of the standard solution of Na_2EDTA.
Calculate the mass concentration β of nickel in your tested solution (in mg/L).

Problem 4-13 Qualitative Analysis

There are pure substances or mixtures of two substances in 8 test tubes. The following ions are contained:

Cations: Ag^+, Ba^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, K^+, NH_4^+, Pb^{2+},
Anions: Cl^-, I^-, IO_3^-, NO_3^-, OAc^-, SCN^-, SO_4^{2-}.

Equipment and Glassware:
10 test tubes, test tube holder, 3 Pasteur pipettes, pipette control, bars of magnesia, cobalt glass, pH paper, spatula, Bunsen burner.

Chemicals:

8 Test tubes with salts or mixtures of salts (labeled 1 to 8)	
Dil. solution of ammonia, c(NH_3) = 2 mol/L	
Dil. hydrochloric acid, c(HCl) = 2 mol/L	
Conc. hydrochloric acid, w(HCl) = 36 % (in the hood)	
Dil. solution of sodium hydroxide, c(NaOH) = 2 mol/L	
Solution of potassium permanganate, c($KMnO_4$) ≈ 0.02 mol/L	
Sodium sulfite, Na_2SO_3	
Demineralized water	

The following means are available for your support:
Diluted solution of ammonia, dil. hydrochloric acid, dil. solution of sodium hydroxide, solution of potassium permanganate, sodium sulfite, pH paper, cobalt glass.

Problems:

a) *Find out which substances are in which test tubes by reactions between the test solutions and reactions of the test solutions with the means for support.*
Write your results on the answer sheet.

b) *For each ion found write the reaction equation of its detection or how the detection was performed.*

Hints:
The substances to analyze contain poisonous heavy metals such as lead and barium. Handle them carefully and do not dispose them into the sink in any case.

Disposal: All solutions have to be poured into the provided disposal.

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

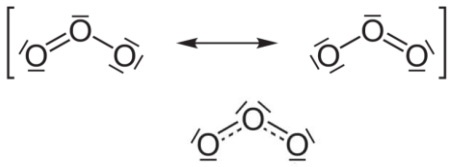
Solution to problem 1-1

a)

Component of earth atmosphere	Percentage of volume	Natural Sources
nitrogen	78.08	volcanism
oxygen	20.94	Photo synthesis
argon	0.93	decay of ^{40}K
carbon dioxide	~ 4×10^{-2}	combustion, cellular respiration

or other main sources which are reasonable.

b) Fifth component: ozone

Component	Lewis formula
nitrogen	|N≡N|
oxygen	⟨O÷O⟩ ⟨O=O⟩ is not accurate as it shows the excited singlet oxygen
argon	nothing or |$\overline{\underline{Ar}}$|
carbon dioxide	⟨O=C=O⟩
ozone	 * *or a diagram with charge distribution

c) Part of the answer is related to the German language and therefore difficult to translate. The explanation for nitrogen and oxygen won't work in English, but the origin of the name Argon is Greek (agros) meaning inactive referring to its chemical inertness and the term noble gases uses noble in the sense of chemical inactivity as well.

d)

	Component	Possible Reactions
First atmosphere (reducing)	methane	Condition: absence of oxygen, reductions e.g.: $\overset{-IV\ +I}{CH_4} + \overset{0}{\frac{1}{2}\ S_8} \longrightarrow \overset{+IV\ -II}{CS_2} + \overset{+I\ -II}{H_2S}$ $\overset{-IV\ +I}{CH_4} + \overset{0}{X_2} \longrightarrow \overset{-II\ +I\ -I}{CH_3X} + \overset{+I\ -I}{HX}$ X = halogen $\overset{-IV\ +I}{CH_4} + 2\ \overset{0}{Cl_2} \longrightarrow \overset{0\ +I\ -I}{CH_2Cl_2} + \overset{+I\ -I}{2\ HCl}$
	Component	**Possible Reactions**

Third atmosphere (oxidizing)	oxygen	Condition: oxygen offering, oxidations, e.g.: $\overset{+II\ -II}{4\ FeS} + 7\ \overset{0}{O_2} \longrightarrow \overset{+III\ -II}{2\ Fe_2O_3} + 4\ \overset{+IV\ -}{SO_2}$ $\overset{+II\ -I}{4\ FeS_2} + 11\ \overset{0}{O_2} \longrightarrow \overset{+III\ -II}{2\ Fe_2O_3} + 8\ \overset{+IV\ -}{SO_2}$ Oxidations of Mn^{2+} to form MnO_2 and S^{2-} to form SO_4^{2-}, too

e) $CH_4 + 2\ NH_3 + 2\ H_2O \longrightarrow CO_2 + N_2 + 7\ H_2$

f) $V(100\ g\ air) = 0.1\ kg / 1.204\ kg \cdot m^{-3} = 0.08306\ m^3$

$\Rightarrow$ $N_2 = 0.7808 \cdot 0.08306\ m^3 = 0.06485\ m^3$

$O_2 = 0.2094 \cdot 0.08306\ m^3 = 0.01739\ m^3$

with $p \cdot V = n \cdot R \cdot T$ you get the respective amount:

$m(N_2) = \frac{1.013 \cdot 10^5\ Pa \cdot 0.6845\ m^3}{8.314\ JK^{-1}mol^{-1} \cdot 293.15\ K} \cdot 2 \cdot 14.01\ g \cdot mol^{-1} = 75.52\ g$

that is 75.52 % (m/m) of nitrogen

$m(O_2) = \frac{1.013 \cdot 10^5\ Pa \cdot 0.1739\ m^3}{8.314\ JK^{-1}mol^{-1} \cdot 293.15\ K} \cdot 2 \cdot 16.00\ g \cdot mol^{-1} = 23.13\ g$

that is 23.13 % (m/m) of oxygen

g) Experiment A:

By burning magnesium oxide and magnesium nitride form

$2\ Mg + O_2 \longrightarrow 2\ MgO$

$3\ Mg + N_2 \longrightarrow Mg_3N_2$

Experiment B:

With water magnesium hydroxide and ammonia form

$MgO + H_2O \longrightarrow Mg(OH)_2$

$Mg_3N_2 + 6\ H_2O \longrightarrow 3\ Mg(OH)_2 + 2\ NH_3$

(or $Mg_3N_2 + 3\ H_2O \longrightarrow 3\ MgO + 2\ NH_3$)

Ammonia is discharged and turns the pH paper blue because of its basic impact.

h) Boiling removes ammonia totally from the solution because of the presence of MgO. The alkaline reaction after boiling is due to the presence of magnesium hydroxide.

Solution to problem 1-2

a) When ascending the bubbles become smaller because a part of the carbon dioxide dissolves when ascending.

V2 > V1. Both tablets form the same volume of carbon dioxide when reacting with water. While a lot of the gas formed of the first tablet dissolves in water, the gas of the second tablet bubbles through a nearly saturated solution which can only dissolve a small amount of carbon dioxide.

Equilibrium reactions:

$$CO_2(g) \rightleftharpoons CO_2(aq) \quad (1)$$

$$CO_2(aq) + 2\,H_2O \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq) \quad (2)$$

$$HCO_3^-(aq) + H_2O \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq) \quad (3)$$

Equilibrium (1) is most important. The latter reactions (2) und (3) do not play a decisive role as 99.8% of the carbon dioxide exists in water as CO_2 molecules.

b) The higher the temperature of the water used the larger the volume of the gas in the measuring cylinder. You may deduce that the colder the water the better carbon dioxide dissolves.

Solution to problem 1-3

In this solution H^+ is used instead of H_3O^+ in order to represent it more clearly.

a) Partial pressure of CO_2 on the Mars: $p(CO_2) = 636\ Pa \cdot 0.9532 = 606.2\ Pa$
with $K_H = 7.5 \cdot 10^{-4}\ mol \cdot m^{-3} \cdot Pa^{-1}$ follows:
$c(CO_2(aq)) + c(H_2CO_3(aq)) = c_{total} = 7.5 \cdot 10^{-4}\ mol \cdot m^{-3} \cdot Pa^{-1} \cdot 606.2\ Pa$
$c_{total} = 0.4547 \cdot 10^{-3}\ mol \cdot L^{-1}$
As K_{a1} is considerable higher than K_{a2} only the first step of hydrolysis is important for the pH value.
$K_{a1} = \frac{c^2(H^+)}{c_{ges}}$ with $pK_a(CO_2 + H_2CO_3) = 6.59$: $c(H^+) = \sqrt{K_{a1} \cdot c_{total}}$
$\Rightarrow c(H^+) = \sqrt{10^{-6.59} \cdot 0.4547 \cdot 10^{-3}}\ mol \cdot L^{-1} = 1.081 \cdot 10^{-5}\ mol \cdot L^{-1} \quad \Rightarrow pH = 4.97$

b) $p(Earth_{atm}) = 101300\ Pa$
$c_{total} = \frac{c^2(H^+)}{K_{S1}} \Rightarrow c_{total} = \frac{(10^{-6}\ mol \cdot L^{-1})^2}{10^{-6.59}\ mol \cdot L^{-1}} = 3.89 \cdot 10^{-6}\ mol \cdot L^{-1} = 3.89 \cdot 10^{-3}\ mol \cdot m^{-3}$

$p(CO_2) = \frac{c_{total}}{K_H} \Rightarrow p(CO_2) = \frac{3.89 \cdot 10^{-3}\ mol \cdot m^{-3}}{7.5 \cdot 10^{-4}\ mol \cdot m^{-3} \cdot Pa^{-1}} = 5.19\ Pa$

percentage of $CO_2 = \frac{p(CO_2)}{101300\ Pa} \cdot 100\ \% = 0.0051\ \%$

c) Partial pressure of CO_2 on the Earth:
$p(CO_2) = 1.013 \cdot 10^5\ Pa \cdot 3.8 \cdot 10^{-4} = 38.49\ Pa$
After opening and stirring an equilibrium with the atmosphere of the Earth is established. Then with Henry's law:
$c(CO_2(aq)) + c(H_2CO_3(aq)) = c_{total} = 7.5 \cdot 10^{-4}\ mol \cdot m^{-3} \cdot Pa^{-1} \cdot 38.49\ Pa$
$c_{total} = 0.029\ mol \cdot m^{-3} = 2.9 \cdot 10^{-5}\ mol \cdot L^{-1}$

- without considering the autoprotolysis of water (analog to a)):
  $c(H^+) = \sqrt{K_{a1} \cdot c_{total}} \Rightarrow c(H^+) = \sqrt{10^{-6.59} \cdot 2.9 \cdot 10^{-5}}\ mol \cdot L^{-1} \Rightarrow pH = 5.56_{38}$
- considering the autoprotolysis of water:
  Let be $HA = H_2CO_3$
  There are the following equilibriums in the solution:
  $HA \rightleftharpoons H^+ + A^-$ and $H_2O \rightleftharpoons H^+ + OH^-$
  $\Rightarrow c(H^+) = c(H^+_{acid}) + c(H^+_{water}) = c(A^-) + c(OH^-)$

$K_{a1} = \frac{c(H^+)\cdot c(A^-)}{c(CO_2)+c(HCO_3)} = \frac{c(H^+)\cdot (c(H^+ - c(OH^-))}{c(CO_2)+c(HCO_3)} = = \frac{c(H^+)^2 - K_w}{c(CO_2)+c(HCO_3)}$

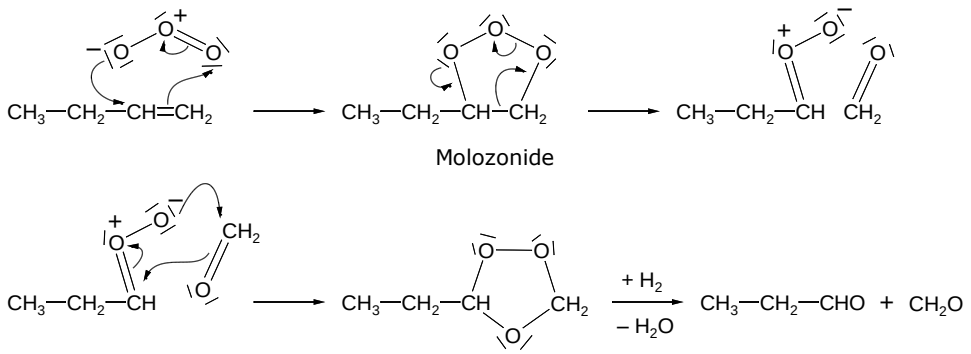
$c(H^+)^2 = K_w + K_{a1} \cdot c_{total} \Rightarrow c(H^+) = \sqrt{0.12 \cdot 10^{-14} + 10^{-6.39} \cdot 2.9 \cdot 10^{-5}}$ mol·L^{-1}

$c(H^+) = 2.73 \cdot 10^{-6}$ mol·L^{-1} $\Rightarrow$ pH = 5.56_{37}

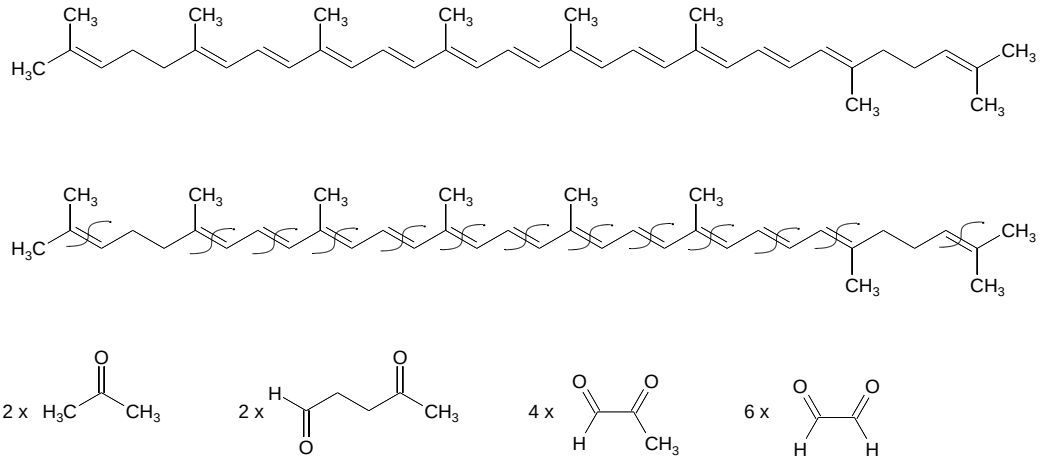
The difference is negligible. Autoprotolysis does not have to be taken into consideration.

Solution to problem 1-4

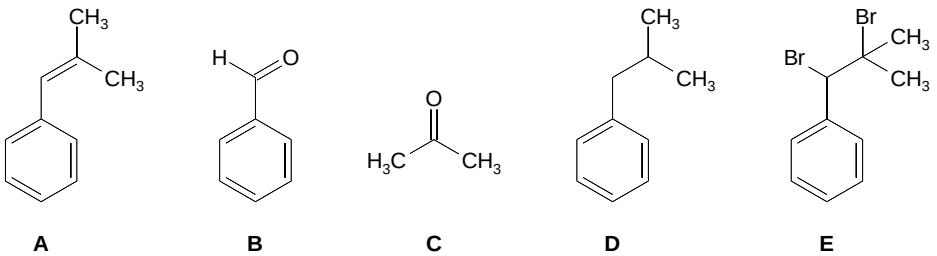
a)



b)



c)



Ozonolysis: A + O_3 $\xrightarrow{Zn(HCl)}$ B + C

Hydrogenation A + H_2 $\xrightarrow{Ni, Pd\ etc.}$ D

Brominating A + Br_2 $\longrightarrow$ E

Answers Round 2

Solution to problem 2-1

a) Bismuth

b) At least one of the following equations:

Bi_2S_3 (s) + 3 Fe (s) $\rightleftharpoons$ 2 Bi (s) + 3 FeS (s)

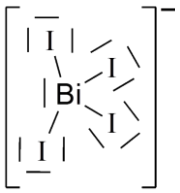
Bi_2S_3 (s) + 4.5 O_2 (g) $\rightleftharpoons$ Bi_2O_3 (s) + 3 SO_2 (g)

2 Bi_2O_3 (s) + 3 C (s) $\rightleftharpoons$ 3 CO_2 (g) + 4 Bi (s)

c) The oxide B_2O_3 is (light) yellow coloured. The colour cannot arise for a d-d transition as the Bi^{3+} cation possesses no unoccupied orbitals which are energetically relevant.

d) E.g. water, antimony, silicon, germanium, gallium

e) Bi^{3+}(aq) + 3 I^- (aq) $\rightleftharpoons$ BiI_3 (s) BiI_3 (s) + I^- (aq) $\rightleftharpoons$ $[BiI_4]^-$ (aq)



4 bonds, 1 free electron pair: expected structure is a distorted tetrahedron (derived from a trigonal dipyramid).

f) Bi^{3+} (aq) + H_2O (aq) + Cl^- (aq) $\rightleftharpoons$ BiOCl (s) + 2 H^+ (aq) or

Bi^{3+} (aq) + H_2O (aq) + NO_3^- (aq) $\rightleftharpoons$ $BiONO_3$ (s) + 2 H^+ (aq)

g) Binary compound: M(Mg_3Bi_2) = 490,88 g/mol

Mg_3Bi_2 (s) + 6 HCl (aq) $\rightleftharpoons$ 3 $MgCl_2$ (aq) + 3 BiH_3 (g)

BiH_3 (g) $\rightleftharpoons$ Bi (g) + 1.5 H_2 (g)

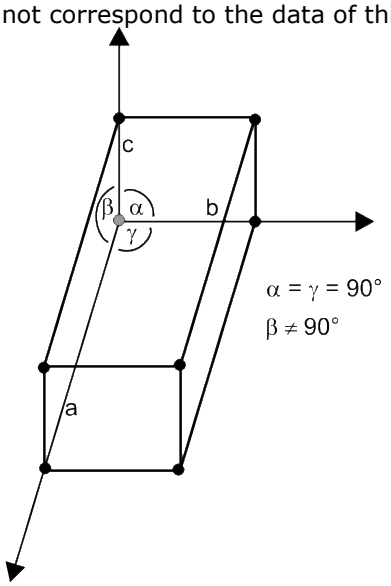
Gaseous Bi will precipitate immediately on a cool surface.

h) Bi^{3+} (aq) + Fe (s) $\rightleftharpoons$ Fe^{3+} (aq) + Bi (s)

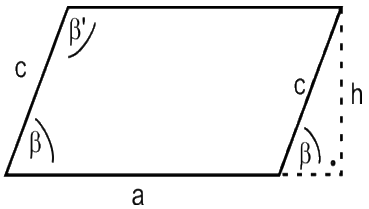
Solution to problem 2-2

a) Monoclinic crystal system

A general monoclinic unit the data of which does not correspond to the data of this problem:



Calculation of h:



β + β' = 180°

h = c · sin β

V = a · b · h

V = 4.01 Å·7.778 Å·16.792 Å·sin 94.1°

V = 523.8 Å³

In textbooks of crystallography you find the following formula which leads to the same result.

$$V = a \cdot b \cdot c \cdot \sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2 \cdot \cos\alpha \cdot \cos\beta \cdot \cos\gamma}$$

b) 2_1 Screw axis, n-glide plane, inversion centre, identity.

c) Inversion through a centre, identity.

d) 523.8 Å^3 : 18 Å^3 = 29.1 non-hydrogen atoms,
there are 16 not-hydrogen atoms in a molecule $\Rightarrow$ **Z = 2.**

e) The distances of x_c and x_c', y_c and y_c' as well as of z_c and z_c' to the centre of inversion have to be identical. For the co-ordinates x_i, y_i und z_i of the inversion centre the following equations

are valid: $x_i = \frac{x_c + x_c'}{2}$ $y_i = \frac{y_c + y_c'}{2}$ $z_i = \frac{z_c + z_c'}{2}$

and thus:

	x_c'	y_c'	z_c'
O1'	0.1374	0.1766	0.3911
C3'	0.4297	-0.0786	0.4222

f) Example: Calculation of the co-ordinates of C1:

$$\begin{pmatrix} x_{C1} \\ y_{C1} \\ z_{C1} \end{pmatrix} = \begin{pmatrix} 4.021 & 0 & -1.204 \\ 0 & 7.778 & 0 \\ 0 & 0 & 16.749 \end{pmatrix} \cdot \begin{pmatrix} 0.6890 \\ -0.0953 \\ 0.5593 \end{pmatrix} = \begin{pmatrix} 2.0971 \\ -0.7412 \\ 9.3677 \end{pmatrix}$$

In the same way you get the other orthogonal co-ordinates:

	x_o	y_o	z_o
C1	2.0971	-0.7412	9.3677
C3	1.5975	0.6114	9.6776
C5	1.2359	0.4908	12.0291
O3	1.9148	1.1138	10.9187

Calculation of the bond lengths d:

d(bond) = $\sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}$

Example for the bond length between C1 und C3:

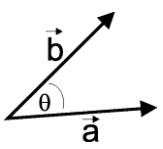
$$d(C1 - C3) = \sqrt{(2.0971 - 1.5975)^2 + ((-0.7412) - 0.6114)^2 + (9.3677 - 9.6776)^2} = 1.4748$$

In the same way you get the other values:

d(C1-C3) 1.4748 Å
d(C3-O3) 1.3760 Å
d(O3-C5) 1.4430 Å

g) If you describe the bonds as vectors the bond angle can be calculated as follows:

$$\cos\theta = \frac{\vec{a} \cdot \vec{b}}{|\vec{a}| \cdot |\vec{b}|}$$



bond(C3-C1): d(C1-C3) = 1.4748 Å (from f))

$$\vec{a}=\overrightarrow{C3\text{-}C1}=\begin{pmatrix}1.5975 - 2.0971\\0.6114 + 0.7412\\9.6776 - 9.3677\end{pmatrix}=\begin{pmatrix}-0.4996\\1.3526\\0.3099\end{pmatrix}$$

bond(C3-O3):d(C3-O3) = 1.3760 Å (from f))

$$\vec{b}=\overrightarrow{C3\text{-}O3}=\begin{pmatrix}1.5975 - 1.9148\\0.6114 - 1.1138\\9.6776 - 10.9187\end{pmatrix}=\begin{pmatrix}-0.3173\\-0.5024\\-1.2411\end{pmatrix}$$

angle θ between the vectors $\vec{a}$ and $\vec{b}$: $\cos\theta = \frac{a_x \cdot b_x + a_y \cdot b_y + a_z \cdot b_z}{\sqrt{(a_x^2 + a_y^2 + a_z^2)} \cdot \sqrt{(b_x^2 + b_y^2 + b_z^2)}}$

angle θ (C1-C3-O3) between the vectors $\overrightarrow{C3-C1}$ und $\overrightarrow{C3-O3}$:

$$\cos\theta = \frac{-0.4996 \cdot (-0.3173) + (1.3526) \cdot (-0.5024) + 0.3099 \cdot (-1.2411)}{\sqrt{(-0.4996)^2 + 1.3526^2 + 0.3099^2)} \cdot \sqrt{(-0.3173)^2 + (-0.5024)^2 + (-1.2411)^2}} = -0.4463$$

θ = 116.5°

ω(C3-O3-C5) can be calculated in the same way:

bond(O3-C3):d(O3-C3) = 1.3760 Å (from f))

$$\vec{a}=\overrightarrow{O3\text{-}C3}=\begin{pmatrix}1.9148 - 1.5975\\1.1138 - 0.6114\\10.9187 - 9.6776\end{pmatrix}=\begin{pmatrix}0.3173\\0.5024\\1.2411\end{pmatrix}$$

bond(O3-C5):d(O3-C5) = 1.4430 Å (from f))

$$\vec{b}=\overrightarrow{O3\text{-}C5}=\begin{pmatrix}1.9148 - 1.2359\\1.1138 - 0.4908\\10.9187 - 12.0291\end{pmatrix}=\begin{pmatrix}0.6789\\0.6230\\-1.1104\end{pmatrix}$$

angle ω between the vectors $\overrightarrow{O3-C3}$ and $\overrightarrow{O3-C5}$:

$$\cos\omega = \frac{0.3173 \cdot 0.6789 + 0.5024 \cdot 0.6230 + 1.2411 \cdot (-1.1104)}{\sqrt{0.3173^2 + 0.5024^2 + 1.2411^2)} \cdot \sqrt{0.6789^2 + 0.6230^2 + (-1.1104)^2}} = -0.4280$$

***ω*= 115.3°**

h) The wanted angle of torsion lδ is the angle between the two planes shown in the problem. These planes are determined by their directional vectors $\overrightarrow{C3-C1}$, $\overrightarrow{C3-O3}$ and $\overrightarrow{O3-C3}$, $\overrightarrow{O3-C5}$ respectively.

The angle between two planes can be determined by calculating the angle between the vectors which are perpendicular to these planes.

You can get a perpendicular vector to a plane with the directional vectors $\vec{a}$ and $\vec{b}$ by the vector product (cross product) of $\vec{a}$ and $\vec{b}$.

$$\vec{a} \times \vec{b} = \begin{pmatrix}a_1\\a_2\\a_3\end{pmatrix} \times \begin{pmatrix}b_1\\b_2\\b_3\end{pmatrix} = \begin{pmatrix}a_2 b_3 - a_3 b_2\\a_3 b_1 - a_1 b_3\\a_1 b_2 - a_2 b_1\end{pmatrix}$$ (the result is a vector)

length of $\vec{a} \times \vec{b}$ = (length($\vec{a}$) · length($\vec{b}$) · sin(smaller angle between $\vec{a}$ and $\vec{b}$))

The angles and length you need are already calculated in the course of this problem.

$$\overrightarrow{C3-C1} \text{ x } \overrightarrow{C3-O3} = \vec{u} = \begin{pmatrix} -0.4996 \\ 1.3526 \\ 0.3099 \end{pmatrix} \text{x} \begin{pmatrix} -0.3173 \\ -0.5024 \\ -1.2411 \end{pmatrix} =$$

$$\begin{pmatrix} 1.3526 \cdot (-1.2411) - 0.3099 \cdot (-0.5024) \\ 0.3099 \cdot (-0.3173) - (-0.4996) \cdot (-1.2411) \\ -0.4996 \cdot (-0.5024) - 1.3526 \cdot (-0.3173) \end{pmatrix} = \begin{pmatrix} -1.5230 \\ -0.7184 \\ 0.6802 \end{pmatrix}$$

length of $\vec{u}$ = u = d(C3-C1) · d(C3-O3) · sin θ / Å = 1.4748· 1.3760 Å · sin 116.5° = 1.8161 Å

You get the result for the second plane in the same way:

$$\overrightarrow{O3-C3} \text{ x } \overrightarrow{O3-C5} = \vec{v} = \begin{pmatrix} 0.3173 \\ 0.5024 \\ 1.2411 \end{pmatrix} \text{x} \begin{pmatrix} 0.6789 \\ 0.6230 \\ -1.1104 \end{pmatrix} =$$

$$\begin{pmatrix} 0.5024 \cdot (-1.1104) - 1.2411 \cdot 0.6230 \\ 1.2411 \cdot 0.6789 - 0.3173 \cdot (-1.1104) \\ 0.3173 \cdot 0.6230 - 0.5024 \cdot 0.6789 \end{pmatrix} = \begin{pmatrix} -1.3311 \\ 1.1950 \\ -0.1434 \end{pmatrix}$$

length of $\vec{v}$ = v = d(O3-C3) · d(O3-C5) · sin ω / Å = 1.3760 ·1.4430 Å· sin115.3° = 1.7952 Å

Thus the angle of torsion δ is

$$\cos\delta = \frac{\vec{u} \cdot \vec{v}}{u \cdot v} = \frac{\begin{pmatrix} -1.5230 \\ -0.7184 \\ 0.6802 \end{pmatrix} \cdot \begin{pmatrix} -1.3311 \\ 1.1950 \\ -0.1434 \end{pmatrix}}{1.8161 \cdot 1.7952} =$$

$$\frac{(-1.5230 \cdot (-1.3311)) + ((-0.7184) \cdot 1.1950) + (0.6802 \cdot (-0.1434))}{1.8161 \cdot 1.7952} = \frac{1.0713}{3.2603} = 0.3286$$

δ = 70.8°

(An angle of torsion of 180°-70.8° = 109.2° will be graded as correct, too.)

Solution to problem 2-3

a)

	Rate law	**Molecularity**	**Reaction order**
(1)	$v_c = k_1\ c(CH_3NC)$	unimolecular	1
(2)	$v_c = k_2\ c((E)\text{-}CH_2Cl_2)$	unimolecular	1
(3)	$v_c = k_{-2}\ c((Z)\text{-}CH_2Cl_2)$	unimolecular	1
(4)	Not possible as it is not an elementary reaction		
(5)	$v_c = k_4\ c(NOCl)^2$	bimolecular	2

b) The integrated rate law for unimolecular reactions is

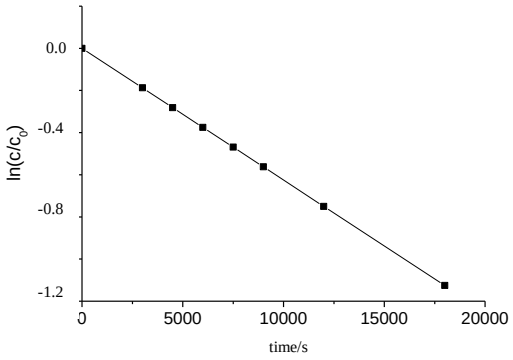
$$\int_{c_0}^{c} \frac{dc}{c} = -k_1 \int_{t_0=0}^{t} dt \Rightarrow \ln\frac{c}{c_0} = -k_1 t$$

The plot of $\ln(c/c_0)$ versus t gives the reaction constant as negative slope of the straight line

$\ln(0.1623/0.5) = -k_1 \cdot 300 \cdot 60$ s $\quad \Rightarrow \quad k_1 = 6.25 \cdot 10^5\ s^{-1}$

Half-life $t_{1/2} = \ln 2 / k_1 = 11090$ s ≅ 185 min

(This result can be found without any plot because the reaction order of 1 is given)



c) Arrhenius equation: $k(T) = A \cdot e^{-E_A/(R \cdot T)} \Rightarrow \ln k(T) = \ln A - E_A/(R \cdot T)$

Inserting two pairs of values:

$\ln 4.71 \cdot 10^{-4}\ s^{-1} = \ln A - E_A/(R \cdot 500\ K)$

$\ln 7.06 \cdot 10^{-2}\ s^{-1} = \ln A - E_A/(R \cdot 575\ K)$

$\Rightarrow \quad R \cdot \ln \frac{7.06 \cdot 10^{-2}}{4.71 \cdot 10^{-4}} = E_A \cdot (500^{-1} - 575^{-1})\ K^{-1}$

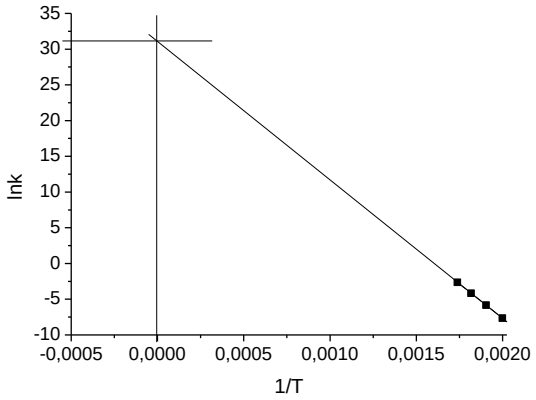
$\Rightarrow \quad E_A = -159.668\ kJ/mol \cong 160\ kJ/mol$

Insertion of other pairs of values leads to very similar results.

$A = k(T) / e^{-E_A/(R \cdot T)} \quad \Rightarrow \quad A = \frac{4.71 \cdot 10^{-4}\ s^{-1}}{e^{-160000/(8.314 \cdot 500)}} = 2.45 \cdot 10^{13}\ s^{-1}$

There is a graphic solution, too:

If you plot lnk(T) versus 1/T you get E_A from the slope and A from the intersection with the lnk(T) axis.



$E_A = 160\ kJ/mol$ and $A = 2.29 \cdot 10^{13}\ s^{-1}$

d) $\Delta_R G = -RT \cdot \ln K \qquad K = e^{2167/(8.314 \cdot 806)} = 1.382$

e) $\vec{v} = \overleftarrow{v} \quad \Rightarrow \quad k_2 \cdot c(E) - k_{-2} \cdot c(Z) = 0 \Rightarrow K = \frac{k_2}{k_{-2}} = \frac{c(Z)}{c(E)}$

or

$v_c = -\frac{dc(E)}{dt} = \frac{dc(Z)}{dt} = k_2 c(E) - k_{-2} c(Z) = 0 \quad \Rightarrow \quad K = \frac{k_2}{k_{-2}} = \frac{c(Z)}{c(E)}$

f) After the period of time τ the deflection from the equilibrium is $\Delta x(t - t_0) = \Delta x \cdot \tau = \frac{\Delta x_0}{e}$

You insert this term in the given formula (in the same way as to determine the half-life of the radioactive decay).

$$\frac{1}{e} = e^{-(k_2+k_{-2})\cdot\tau} \Rightarrow \ln\frac{1}{e} = -1 = -(k_2+k_{-2})\cdot\tau \Rightarrow \ln e = 1 = (k_2+k_{-2})\cdot\tau \Rightarrow \tau = \frac{1}{k_2+k_{-2}}$$

g) $115.3\ s = (k_2 + k_{-2})^{-1}$ $115.3\ s \cdot (k_2 + k_{-2}) = 1\ (k_{-2})^{-1} = 115.3\ s + 115.3\ s \cdot K$

$k_{-2} = (115.3\ s + 115.3\ s \cdot 1.4)^{-1}\ k_{-2} = 3.61\cdot10^{-3}\ s^{-1}$

$k_2 = K \cdot k_{-2}$ $k_2 = 1.4 \cdot 3.61\ s^{-1}\ k_2 = 5.06\cdot10^{-3}\ s^{-1}$

h) Approach for the rate: $v = k_4 \cdot c(H_3AsO_3)^a \cdot c(I_3^-)^b \cdot c(H^+)^c \cdot c(I^-)^d$

($c(H_3AsO_4)$ does not occur as $c(H_3AsO_4)^0 = 1$)

Test series 1 and 4: $b = 1$

Test series 1 und 3: $a = b$ and thus $a = 1$

$\Rightarrow v = k_4 \cdot c(H_3AsO_3)^1 \cdot c(I_3^-)^1 \cdot c(H^+)^c \cdot (I^-)^d$

Test series 1: $1.882\ min^{-1} = k_4 \cdot 0.150 \cdot 3.45\cdot10^{-5} \cdot 0.150^c \cdot 0.025^d$

$1.882\ min^{-1}/(0.150 \cdot 3.45 \cdot 10^{-5}) = k_4 \cdot 0.150^c \cdot 0.025^d$ (1)

Test series 2: $0.2639\ min^{-1}/(0.113 \cdot 2.08 \cdot 10^{-5}) = k_4 \cdot 0.150^c \cdot 0.045^d$ (2)

(1) / (2): $\frac{1.882\ min^{-1}/(0.150 \cdot 3.45\cdot10^{-5})}{0.2639\ min^{-1}/(0.113 \cdot 2.08\cdot10^{-5})} = (0.25/0.45)^d$

$\ln 3.329 = d \cdot \ln (0.25/0.45) \Rightarrow d = -2$

By combination of any test series with (5) you get in the same way $c = -1$.

$\Rightarrow v = k_4 \cdot c(H_3AsO_3) \cdot c(I_3^-) \cdot c(H^+)^{-1} \cdot c(I^-)^{-2}$

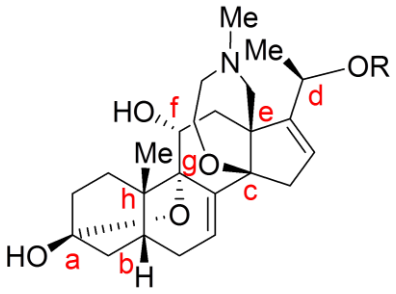
i) You calculate k for each test series and then form the mean value.

Nr.	1	2	3	4	5	Ø
k /(mol²·L⁻²·min⁻¹)	34.1	34.1	34.1	34.1	34.1	34.1

Solution to problem 2-4

a) Steroid

b) Stereogenic centres



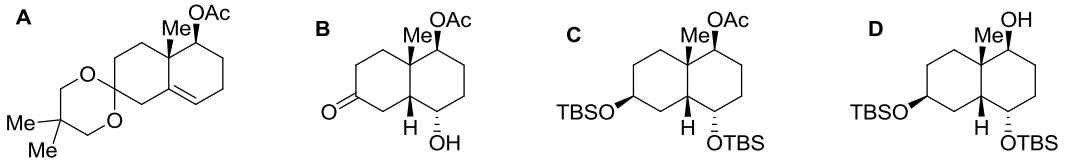
Stereogenic centre	CIP	Justification
a	R	[**C**H_2-CH_2]: O_{Ether} > $O_{Hydroxyl}$ > CH_2CHCC
b	R	[H]: **C**(Me)(CH_2)(CH_2) > (CH_2)**C**(CH_2)(O)(O) > (CH_2)**C**H(=C)
c	S	[CH_2]: O > C_e > $C_{double\ bond}$
d	R	[H]: **O**CO > **C**(C)(=C) > **C**H_3

e	S	[**C**H_2-CHOH]: **C**(O)(C)(C) > C(C)(C)(C) > CH_2-CH_2N
f	R	[H]: **O** > **C**(O)(C)(C) > **C**H_2
g	R	[C-C=C]: O > CHO > C(C)(C)(C) = C(C)(C)(C) As there are empty places in the 3. belt according to the double bond this substituent has the lowest priority.
h	S	[**C**H_3]: C(OCC) > C(CCH) > CH_2

In rectangular brackets: lowest-priority group; in bold: crucial atom

c) No symmetry plane, thus $2^n = 2^8 = 256$.

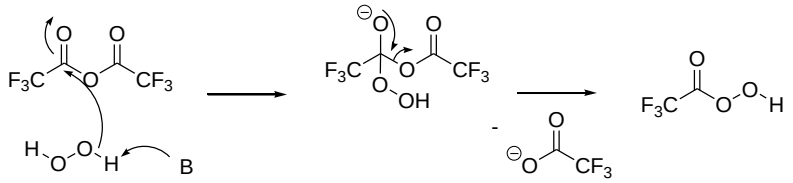
d) i)



Hint: The position of the double bond in **A** can be deduced from the data of the ^{1}H-NMR spectrum and from the consecutive compound.

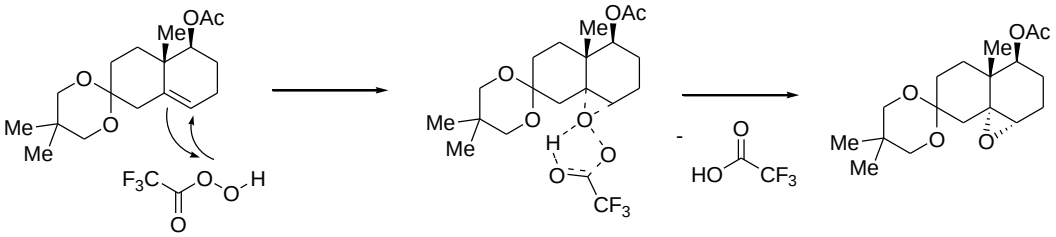
ii) There is no free rotation at the acetal carbon atom of the spiro group thus the methyl groups are fixed and differ in their magnetic characteristics.

iii) a) Mechanism und stereochemistry of the peroxide formation:



pK_s = 11.6

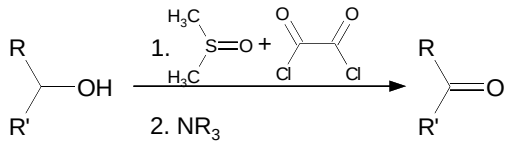
Only slightly acidic but considerably stronger than water



Attack from the less hindered side "Butterfly" intermediate

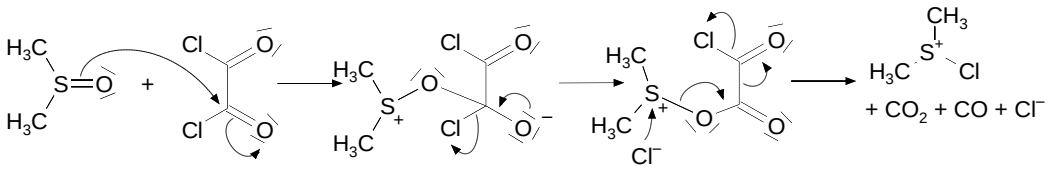
b) Mechanism of the Swern oxidation

Information: The Swern oxidation is used to form aldehydes and ketones from primary and secondary alcohols without further oxidation to carboxylic acids. The Swern oxidation is an environmental-friendly alternative to an oxidation with chromium containing reagents.

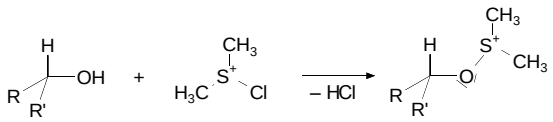


Mechanism:

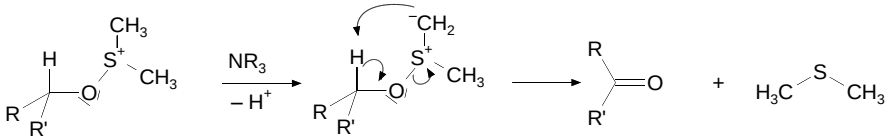
At first an adduct forms from dimethyl sulfoxide and oxalylchloride, which decomposes to form a dimethylchlorosulfonic-acid salt, carbon dioxide and carbon monoxide:



The dimethylchlorosulfonic-acid cation reacts at –78°C to form an alkoxysulfonium cation:



Using a base (tert. amine. solution of sodium hydroxide) this cation can be deprotonated to form a zwitterion (ylide). This rearranges to dimethylsulfide and the wanted carbonyl compound:



iv) You need a large non nucleophilic base (e.g. DBU) so that the epoxide is not attacked.

Answers Round 3 Test 1

Solution to problem 3-01

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

Solution to problem 3-02

a) $H_2 + Cl_2 \longrightarrow 2\ HCl$

30 parts by volume of HCl are formed from 15 parts by volume H_2 and Cl_2 each

$\Rightarrow$ content of $(Cl_2)_0$ = 60% + 15% = 75%

content of $(H_2)_0$ = 10% + 15% = 25%

b) One of the two following statements: the chlorine content decreased by 20% or 30 % (by volume) of hydrogen in the resulting mixture.

c) $2\ CrCl_3 + 3\ Br_2 + 16\ KOH \longrightarrow 2\ K_2CrO_4 + 6\ KBr + 6\ KCl + 8\ H_2O$ or

$2\ Cr^{3+} + 3\ Br_2(aq) + 16\ OH^- \longrightarrow 2\ CrO_4^{2-} + 6\ Br^- + 8\ H_2O$

d) $5\ KNO_2 + 2\ KMnO_4 + 3\ H_2SO_4 \longrightarrow 2\ MnSO_4 + K_2SO_4 + 5\ KNO_3 + 3\ H_2O$ or

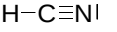
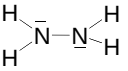
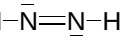
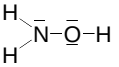
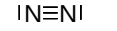
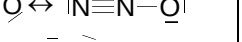
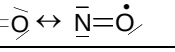
$5\ NO_2^- + 2\ MnO_4^- + 6\ H_3O^+ \longrightarrow 2\ Mn^{2+} + 5\ NO_3^- + 9\ H_2O$

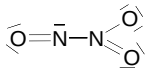
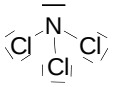
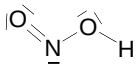
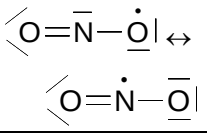
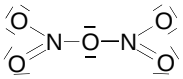
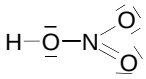
e) $2\ Cl_2 + 2\ Ca(OH)_2 \longrightarrow Ca(OCl)_2 + CaCl_2 + 2\ H_2O$

or $Cl_2 + Ca(OH)_2 \longrightarrow CaCl(OCl) + H_2O$

Solution to problem 3-03

a)

Oxidation state	Empirical formula	Name	Lewis formula
-III	NH_3	ammonia	
	Li_3N	lithium nitride	
	HCN	hydrogen cyanide	
-II	N_2H_4	hydrazine	
-I	N_2H_2	diazene	
	H_3NO	hydroxylamine	
0	N_2	nitrogen	
+I	N_2O	dinitrogen mono-oxide	
	HNO	nitrosohydrogen	
+II	NO	nitrogen mono-oxide	

Oxidation state	Empirical formula	Name	Lewis formula
+III	N_2O_3	dinitrogen trioxide	
	NCl_3	nitrogen trichloride	
	HNO_2	nitrous acid	
+IV	NO_2	nitrogen dioxide	
+V	N_2O_5	dinitrogen pentaoxide	
	HNO_3	nitric acid	

b) E.g. HN_3: hydrazoic acid, N_3^-: azide ion oxidation state of N: $-^1/_3$

Solution to problem 3-04

a) $6\ HCl + 2\ Al + 12\ H_2O \longrightarrow 3\ H_2 + 2\ [Al(H_2O)_6]Cl_3$

$2\ HCl + Zn \longrightarrow H_2 + ZnCl_2$

Residue Si and Cu

b) $2\ NaOH + 2\ Al + 10\ H_2O \longrightarrow 2\ Na[Al(OH)_4(H_2O)_2] + 3\ H_2$

$2\ NaOH + Zn + 2\ H_2O \longrightarrow Na_2[Zn(OH)_4] + H_2$

$2\ NaOH + Si + H_2O \longrightarrow Na_2SiO_3 + 2\ H_2$

Residue Cu

(Reaction equations with ions and without complex bounded water in a) und b) will be regarded as correct).

c) 899 mL H_2 $\triangleq$ $n_a = \frac{102.25 \cdot 10^3 \cdot 899 \cdot 10^{-6}}{8.314 \cdot 294}$ mol = 37.61 mmol

2·552 mL H_2 $\triangleq$ $n_b = \frac{102.25 \cdot 10^3 \cdot 1104 \cdot 10^{-6}}{8.314 \cdot 294}$ mol = 46.18 mmol

Silicon: ½ · ($n_a - n_b$) = n(Si) $n_a - n_b$ = 8.57 mmol ⇒ n(Si) = 4.285 mmol

m(Si) = n(Si)·M(Si) m(Si) = 4.285 mmol·28.09 g/mol = 120.4 mg

that are 12.04 %

Copper: m(Si) + m(Cu) = 170 mg ⇒ m(Cu) = 49.6 mg that are 4.96 %

Aluminium: m(Al) + m(Zn) = 1000 mg – 170 mg = 830 mg

x mg Al give 3/2 · x mg/M(Al) = 3/2 · x/26.98 mmol H_2

(830-x) mg Zn give (830 – x) mg/M(Zn) = (830 –x)/65.41 mmol H_2

3/2 · x/26.98 + (830 –x)/65.41 = 37.61 ⇒ x = 618.3 618.3 mg $\triangleq$ 61.83 %

Zinc : m(Zn) = (830 – 618.3) mg m(Zn) = 211.7 mg that are 21.17 %

Solution to problem 3-05

a) $C_2H_6 \rightleftharpoons C_2H_4 + H_2$

b) $K_{p900} = e^{\frac{-\Delta G^\circ}{R \cdot T}}$ $K_{p900} = e^{\frac{-22390\ J \cdot mol^{-1}}{8.314\ J \cdot (mol \cdot K)^{-1} \cdot 900\ K}}$ $K_{p900} = 50.2 \cdot 10^{-3}$

c) $C_2H_4 + H_2 \rightleftharpoons C_2H_6$

$\Delta H^\circ = \Delta G^\circ + T \cdot \Delta S^\circ$ $\Delta S^\circ = [319.7 - (291.7 + 163.0)]\ J/(mol \cdot K)$

$\Delta H^\circ = -22390\ kJ/mol + 900\ K \cdot (-135.0\ J/(mol \cdot K))$ $\Delta H^\circ = -143.9\ kJ/mol$

d)

	C_2H_6	$\rightleftharpoons$	C_2H_4	+	H_2	
Initial amount n in mol	1		0		0	
Amount n in equilibrium in mol	1 – x		x		x	$\Sigma = 1 + x$
Partial pressure in equilibrium	$\frac{1-x}{1+x} \cdot p_{total}$		$\frac{x}{1+x} \cdot p_{total}$		$\frac{x}{1+x} \cdot p_{total}$	

$\Rightarrow$ $K_{p900} = (\frac{x}{1+x} \cdot p_{ges}/p_0)^2 \ / \ (\frac{1-x}{1+x} \cdot p_{ges}/p_0) = \frac{x^2}{(1+x)\cdot(1-x)} \cdot p_{total}/p^\circ = \frac{x^2}{1-x^2} \cdot p_{total}/p^\circ$

$K_{p900} = 50.2 \cdot 10^{-3}$. $p_{total} = 1.020 \cdot 10^5$ Pa and $p^\circ = 1.000 \cdot 10^5$ Pa

$\Rightarrow$ $50.2 \cdot 10^{-3} = \frac{x^2}{1-x^2} \cdot 1.02$ $x^2 = 0.0469$ $x = 0.217$

hydrogen $\frac{x}{1+x} \cdot 100\ \% = 17.8\ \%$

ethene $\frac{x}{1+x} \cdot 100\ \% = 17.8\ \%$

ethane $\frac{1-x}{1+x} \cdot 100\ \% = 64.4\ \%$

e) $\ln \frac{K_{p1}}{K_{p2}} = -\frac{\Delta H^\circ}{R} \cdot (\frac{1}{T_1} - \frac{1}{T_2})$ $\ln K_{p600} = \ln K_{p900} + \frac{143900 \frac{J}{mol}}{8.314 \frac{J}{mol \cdot K}} \cdot (\frac{1}{600\ K} - \frac{1}{900\ K})$

$\ln K_{p600} = -12.61$ $K_{p600} = 3.338 \cdot 10^{-6}$

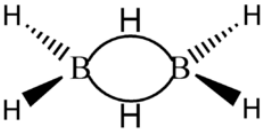
f) $K_{p600} = 3.338 \cdot 10^{-6} < K_{p900} = 50.2 \cdot 10^{-3}$

The dehydrogenation is endothermic thus the equilibrium counteracts the imposed change in temperature (900 K $\rightarrow$ 600 K) by shifting in the direction of releasing energy i.e. to the left which means that K_p becomes smaller (Le Chatelier's principle) .

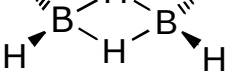
Solution to problem 3-06

a) By dimerisation the boron atom gets an electron octet.

b)



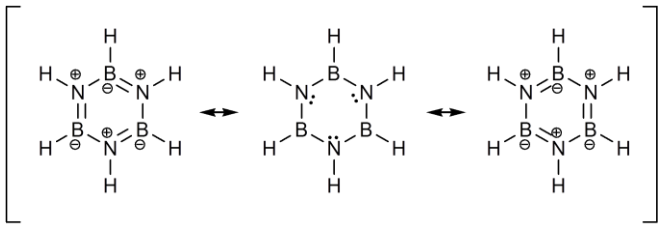
or



Three-centre two-electron bond

c) Tetrahedral

d) $B_3H_6N_3$, isosteric with benzene

e) 

f) C, E

g) Planar ring system conjugated and delocalized system of double bonds, matching the Hückel rule.

Solution to problem 3-07

a) $T = \frac{I}{I_0} \Rightarrow A = \lg \frac{I_0}{I} = -\lg T$ $\quad A = -\lg T$

$A_{440\ nm} = -\lg 0.355 = 0.45$ $\quad A_{545\ nm} = -\lg 0.166 = 0.78$

$A_{440\ nm} = 0.45 = \varepsilon_1 \cdot c(MnO_4^-) + \varepsilon_3 \cdot c(Cr_2O_7^{2-})$

$A_{545\ nm} = 0.78 = \varepsilon_2 \cdot c(MnO_4^-) + \varepsilon_4 \cdot c(Cr_2O_7^{2-})$

$\Rightarrow$ $c(MnO_4^-) = 3.27 \cdot 10^{-4}$ mol/L $= 3.27 \cdot 10^{-5}$ mol/100 mL

$c(Cr_2O_7^{2-}) = 11.3 \cdot 10^{-4}$ mol/L $= 11.3 \cdot 10^{-5}$ mol/100 mL

that are $(3.27 \cdot 10^{-5}$ mol $\cdot$ 54.94 g/mol)/1.374 g $\cdot$ 100 % = 0.13 % (m/m) of manganese

and $(11.3 \cdot 10^{-5}$ mol $\cdot$ 2 $\cdot$ 52.00 g/mol)/1.374 g $\cdot$ 100 % = 0.86 % (m/m) of chromium.

b) From the absorbance of solution 1 the molar absorption coefficient can be determined:

$c([CoL_3^{2+}]) = c_0(Co(II)) = 1.00 \cdot 10^{-5}$ mol/L

$\varepsilon = \frac{0.305}{1.00 \cdot 10^{-5} \frac{mol}{L} \cdot 1\ cm} = 3.05 \cdot 10^4\ Lmol^{-1}cm^{-1}$

From the absorbance of solution 2 you get

$c([CoL_3^{2+}]) = \frac{0.630}{3.05 \cdot 10^4\ Lmol^{-1}cm^{-1} \cdot 1\ cm} = 2.07 \cdot 10^{-5}$ mol/L

$c(Co^{2+}) = c(Co^{2+})_0 - c([CoL_3]^{2+})$ $\quad c(Co^{2+}) = (3.00 \cdot 10^{-5} - 2.07 \cdot 10^{-5})$ mol/L

$c(Co^{2+}) = 0.93 \cdot 10^{-5}$ mol/L

$c(L) = c(L)_0 - 3 \cdot c([CoL_3]^{2+})$ $\quad c(L) = (8.00 \cdot 10^{-5} - 3 \cdot 2.07 \cdot 10^{-5})$ mol/L

$c(L) = 1.79 \cdot 10^{-5}$ mol/L

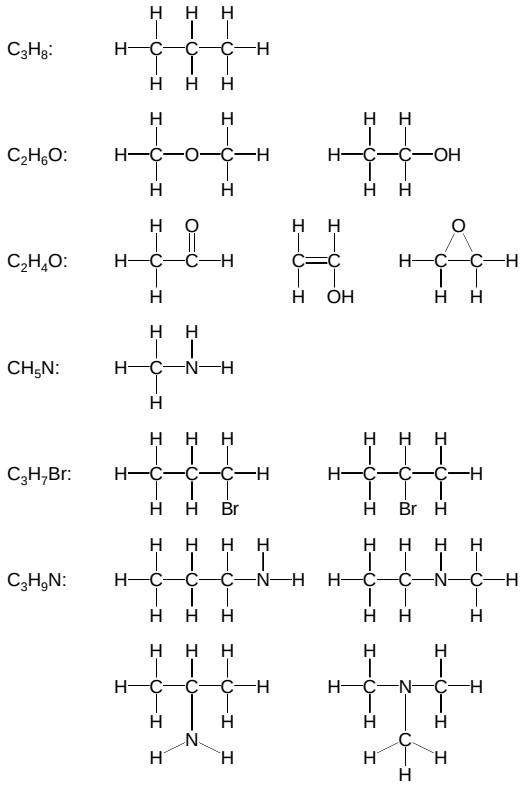
$$Co^{2+} + 3\ L \rightleftharpoons [CoL_3]^{2+}$$

$K = \frac{c([CoL_3]^{2+}) \cdot (mol/L)^3}{c(Co^{2+}) \cdot c(L)^3}$ $\quad K = \frac{2.07 \cdot 10^{-5}}{0.93 \cdot 10^{-5} \cdot (1.79 \cdot 10^{-5})^3}$ $\quad K = 3.88 \cdot 10^{14}$

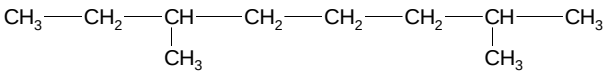
(A calculation with another amount of sign. figures leads to a slightly different result.)

Solution to problem 3-8

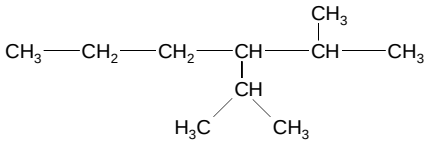
a)



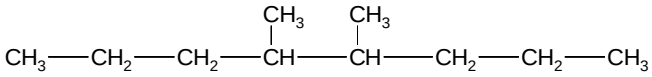
b) 2,6-Dimethyloctane:



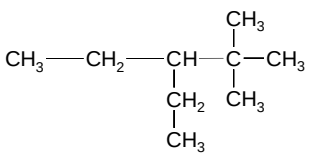
3-Isopropyl-2-methylhexane:



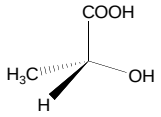
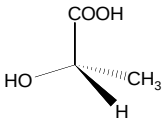
c) i) 3-Methyl-2-propylhexane, correct: 4,5-Dimethyloctane



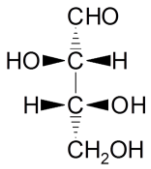
ii) 4,4-Dimethyl-3-ethylpentane, correct: 2,2-Dimethyl-3-ethylpentane



d) and e)

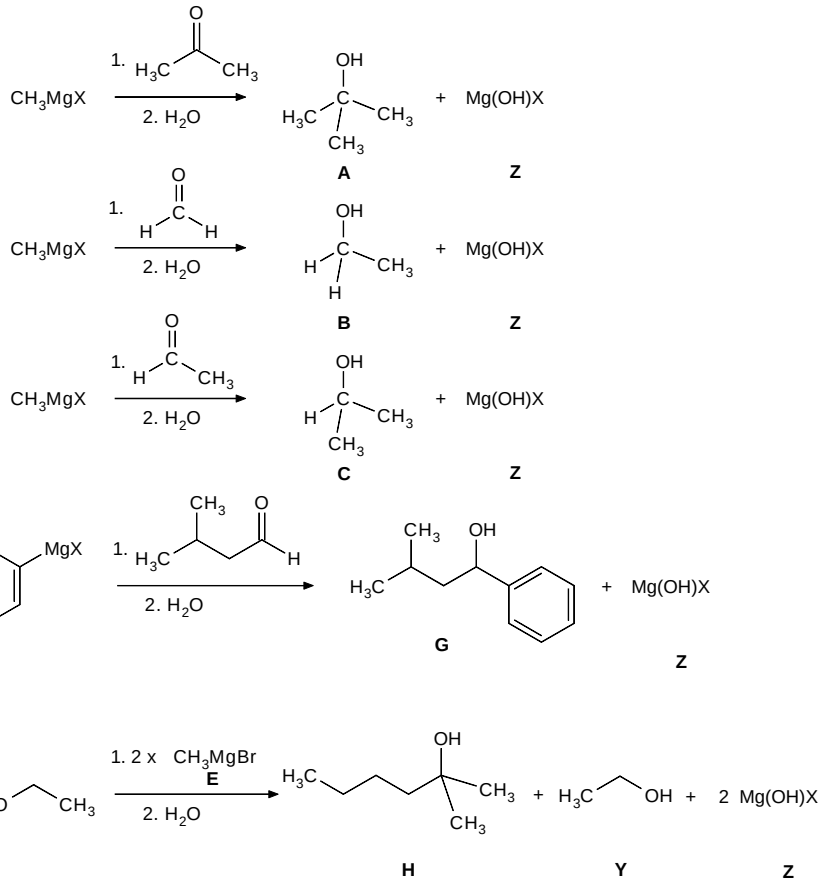
R-lactic acid  enantiomers  S-lactic acid

f) and g)

2S,3R-2,3,4-Trihydroxybutanal 

Solution to problem 3-9

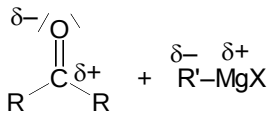
a)



b)

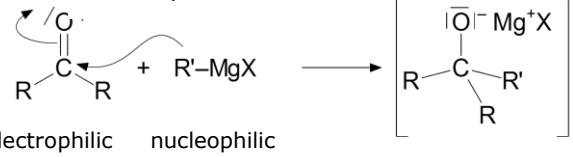
Primary alcohols	Secondary alcohols	Tertiary alcohols
B, Y	**C, G**	**A, H**

c) Charge distribution:



Mechanism:

Nucleophilic Addition

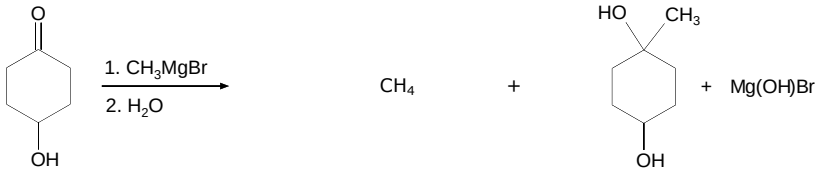


Electrophilic C atom

nucleophilic rest R'

Intermediate

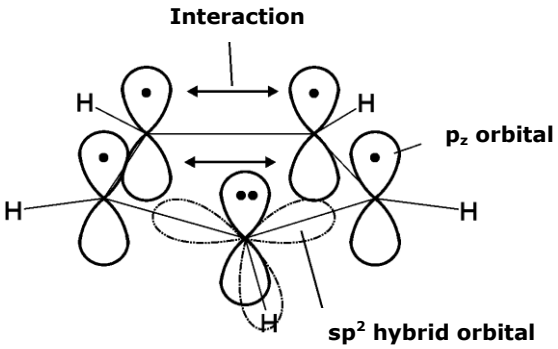
d)



T U V

Solution to problem 3-10

a) Stability of the cyclopentadienyl anion



- 5 sp^2 hybrid orbitals, planar ring
- 5 equivalent p_z orbitals, overlapping above and below the ring, formation of a delocalized π system
- 6 π electrons showing cyclic conjugation (Hackel's 4n+2 rule works and predicts aromaticity.)

$\Rightarrow$ The five membered ring of the anion $C_5H_5^-$ is stable.

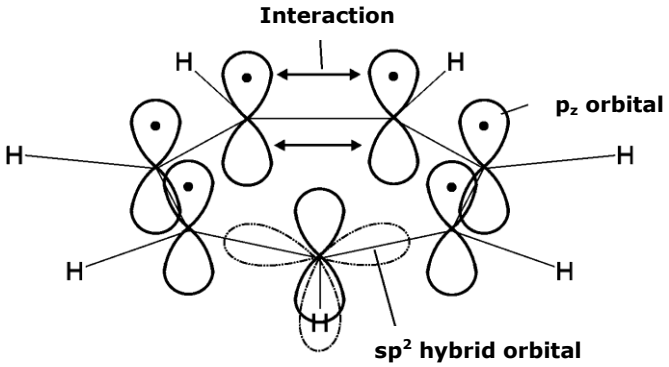
b) For example: $2\ C_5H_6 + 2\ Na \longrightarrow 2\ NaC_5H_5 + H_2\ (g)$

c) Cycloheptatrienyl cation: very stable
Cylcoheptatrienyl radical: reactive, very unstable
Cycloheptatrienyl-Anion: reactive, very unstable
Reasons for stability:

- 7 sp^2 hybrid orbitals, planar ring
- 7 equivalent p_z orbitals, overlapping above and below the ring, formation of a delocalized π system

- 6 π electrons showing cyclic conjugation (Hückel's 4 n+2 rule works and predicts aromaticity.)

$\Rightarrow$ The seven membered ring of the cation $C_7H_7^+$ is stable.



Answers of Round 3 Test 2

Solution to problem 3-11

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

Solution to problem 3-12

a) HCl protolyses completely. pH = - lg (c(HCl)/c^0) pH = - lg 0.0200 pH = 1.670

b) H_2SO_4 protolyses completely to form H_3O^+ and HSO_4^-.

	HSO_4^- + H_2O ⇌	H_3O^+ +	SO_4^{2-}
c in mol/L at the begin	0.0200	0.0200	0
c in mol/L in equilibrium	0.0200 – x	0.0200 + x	x

$K_a = \frac{(0.0200+x)\cdot x}{0.0200-x}$ ⇒ $x^2 + x\cdot(0.0200 + 10^{-1.92}) - 0.0200\cdot 10^{-1.92} = 0$

$x_1 = 6.278\cdot10^{-3}$. ($x_2 < 0$) $c(H_3O^+) = (0.02 + x_1)$ mol/L pH = 1.58

c) In the first step both acids protolyse totally. The concentration of H_3O^+ from these steps is (0.0250 + 0.0125) mol/L = 0.0375 mol/L.

	HSO_4^- + H_2O ⇌	H_3O^+ +	SO_4^{2-}
c in mol/L at the begin	0.0250	0.0375	0
c in mol/L in equilibrium	0.0250 - x	0.0379 + x	x

$K_{a2} = \frac{(0.0375+x)\cdot x}{0.0250-x}$ ⇒ $x^2 + x\cdot(0.0375 + 10^{-1.92}) - 0.0250\cdot 10^{-1.92} = 0$

$x_1 = 5.47\cdot10^{-3}$, ($x_2 < 0$) $c(H_3O^+) = (0.0375 + x_1)$ mol/L = 0.0430 mol/L

pH = 1.37

d) 1. Step: R-SO_3**H** 2. step R`-COO**H** 3. step R"-O**H**

Solution to problem 3-13

a) In short: $[Kr]4d^{10}5s^25p^2$

or in detail: $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^2$

b) Structure B, the coordination number is 4.

c) <u>Tin coating:</u>

$Fe \longrightarrow Fe^{2+} + 2\ e^-$

$2\ H_2O + 2\ e^- \longrightarrow 2\ OH^- + H_2$

<u>Zinc coating:</u>

$Zn \longrightarrow Zn^{2+} + 2\ e^-$

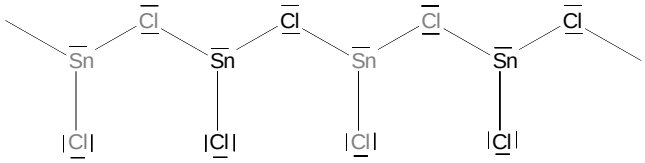
$2\ H_2O + 2\ e^- \longrightarrow 2\ OH^- + H_2$

Zinc is the better anti-corrosive material. In this case the iron does not corrode and zinc is oxidized because of the position in the electrochemical series If a tin film is violated iron will oxidize for the same reason.

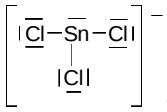
d) Sn (s) + 2 HCl (aq) $\longrightarrow$ $SnCl_2 \cdot 2\ H_2O$ (s) + H_2 (g)

e) 8 $SnCl_2$, 6 SnO, 7 $Sn(OH)_2$

f)



g)



trigonal pyramidal shape of the molecule

h) It is tin dioxide SnO_2 which forms after heating with the oxidising nitric acid.

$SnCl_2 + 2\ HNO_3 \longrightarrow SnO_2 + 2\ NO_2 + 2\ HCl$

or $3\ SnCl_2 + 2\ HNO_3 + 2\ H_2O \longrightarrow 3\ SnO_2 + 2\ NO + 6\ HCl$

i) 1. $SnCl_2 + 2NaOH \longrightarrow Sn(OH)_2 + 2\ NaCl$

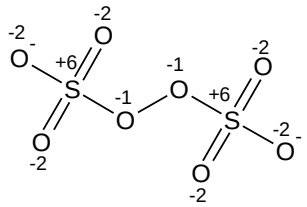
2. $Sn(OH)_2 + NaOH \longrightarrow Na[Sn(OH)_3]$

3. $9\ OH^- + 3\ Na[Sn(OH)_3] + 2\ Bi^{3+} \longrightarrow 2\ Bi + 3\ [Sn(OH)_6]^{2-} + 3\ Na^+$

4. $2\ Na[Sn(OH)_3] \longrightarrow Sn + Na_2[Sn(OH)_6]$ disproportionation

Solution problem 3-14

6.1



u = 1 v = 2 w = 2 x = 1

$1\ S_2O_8^{2-} + 2\ I^- \longrightarrow 2\ SO_4^{2-} + 1\ I_2$

b) $r = k \cdot c(S_2O_8^{2-})^a \cdot c(I^-)^b$

Test (1) and (2): $c_0(S_2O_8^{2-})_{(2)} / c_0(S_2O_8^{2-})_{(1)} = 1.4$ $c_0(I^-)_{(2)} = c_0(I^-)_{(1)}$

$v_{0(2)} / v_{0(1)} = 1.40$ $\Rightarrow$ a = 1

Test (1) and (3): $c_0(S_2O_8^{2-})_{(3)} / c_0(S_2O_8^{2-})_{(1)} = 1.8$ $c_0(I^-)_{(3)} / c_0(I^-)_{(1)} = 1.5$

$v_{0(3)} / v_{0(1)} = 2.70 = 1.8 \cdot 1.5$ $\Rightarrow$ b = 1

$r = k \cdot c(S_2O_8^{2-}) \cdot c(I^-)$ reaction order: 2

$$k = \frac{r}{c(S_2O_8^{2-}) \cdot c(I^-)} = \frac{1.1 \cdot 10^{-8}\ mol \cdot L^{-1} \cdot s^{-1}}{1 \cdot 10^{-4} \cdot 1 \cdot 10^{-2}\ mol^2 \cdot L^{-2}} = 0.011\ \ L \cdot mol^{-1} \cdot s^{-1}$$

c) Using the Arrhenius equation we may write

$$k_1 = A \cdot e^{-\frac{E_a}{RT_1}} \qquad k_2 = A \cdot e^{-\frac{E_a}{RT_2}} \qquad \Rightarrow \qquad \frac{k_1}{k_2} = e^{\frac{E_a}{R}} \cdot \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

because $k_1/k_2 = 1/10$, it follows that

$$ln\frac{1}{10} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \Leftrightarrow \frac{1}{T_2} = \frac{R}{E_a} \cdot \ln\frac{1}{10} + \frac{1}{T_1} \qquad \Rightarrow T_2 = 345\ K \approx 72°C$$

d) $2\ S_2O_3^{2-} + I_2 \rightarrow 2\ I^- + S_4O_6^{2-}$

e) It has to be noticed that the concentration of the iodide ions does not vary any longer, because the iodine formed reacts quickly with thiosulfate ions (which are available in excess according to the precondition) forming iodide ions again.
Therefore the reaction is of pseudo-1st -order and the rate equation is given by $r = k' \cdot c(S_2O_8^{2-})$
(It is important to note that the rate constant k' is different from k of the parts 6.2 - 6.5 of this problem, because it includes the pseudo-constant concentration of the iodide ions.)

Solution to problem 3-15

a) Oxidation: $Ag + Cl^- \longrightarrow AgCl + e^-$
Reduction: $Hg_2Cl_2 + 2e^- \longrightarrow 2\ Hg + 2\ Cl^-$ or $½\ Hg_2Cl_2 + e^- \longrightarrow Hg + Cl^-$
in total: $Ag + ½\ Hg_2Cl_2 \longrightarrow AgCl + Hg$
Electrons flow form (-) to (+) and from the electrode with lower to that of higher potential.
$\Rightarrow$ E°(Ag, AgCl/Cl-) < E°(Hg, Hg_2Cl_2/Cl^-).

b) $\Delta G° = - n \cdot F \cdot E°$ $\Delta G° = -1 \cdot 96485\ C \cdot mol^{-1} \cdot 0{,}0452\ V = -4.36\ kJmol^{-1}$
$\Delta G° < 0$ $\Rightarrow$ the process is spontaneous.

c) $\frac{dE^0}{dT}$ gives the variation of the standard potential with the temperature.
(If you plot E° as a function of T, you get a straight line with the slope $\frac{dE^0}{dT}$).

d) $\Delta S° = n \cdot F \cdot \frac{dE^0}{dT}$ $\Delta S° = 96485\ C \cdot mol^{-1}\ 3.38 \cdot 10^{-4}\ VK^{-1}$ $\Delta S° = 32.6\ Jmol^{-1}K^{-1}$
$\Delta G° = \Delta H° - T \cdot \Delta S°$ $\Delta H° = -4.36\ kJmol^{-1} + 298\ K \cdot 32.6\ Jmol^{-1}K^{-1} = 5.35\ kJmol^{-1}$

e) $E(Ag^+/Ag) = E°(Ag^+/Ag) + R \cdot T/F \cdot \ln c(Ag^+)/c°$
The potential of such a half cell over a precipitate of AgCl is determined by the solubility product: $c(Ag^+) = \frac{K_{sp}}{c(Cl^-)/(mol \cdot L^{-1})} \cdot (c°)^2$.
Thus $E(Ag, AgCl/Cl^-) = E°(Ag^+/Ag) + RT/F \cdot \ln \frac{K_L}{c(Cl^-)/(mol \cdot L^{-1})}$,
$E(Ag, AgCl/Cl^-) = E°(Ag^+/Ag) + RT/F \cdot \ln K_{sp} - RT/F \cdot \ln [c(Cl^-)/c°)]$
thereby is $E°(Ag^+/Ag) + RT/F \cdot \ln K_{sp} = E°(Ag, AgCl/Cl^-)$

$E°(Ag, AgCl/Cl^-) = 0.7996\ V + 8.314\ JK^{-1} \cdot mol^{-1} \cdot 298\ K/96485\ Cmol^{-1} \cdot \ln 1.78 \cdot 10^{-10}$
$E°(Ag, AgCl/Cl^-) = 0.223\ V$

f) $E°(Hg, Hg_2Cl_2/Cl^-) - E°(Ag, AgCl/Cl^-)$ = standard potential of the cell
$E°(Hg, Hg_2Cl_2/Cl^-) = 0.0455\ V + 0.223\ V$ $E°(Hg, Hg_2Cl_2/Cl^-) = 0.268\ V$

g) $E = E°$ $\Rightarrow RT/(2 \cdot F) \cdot \ln \frac{1}{a(Cl^-)^2} = 0$ $\Rightarrow - \ln a(Cl^-) = 0$ $\Rightarrow a(Cl^-) = 1$

h) $E = E° - RT/F \cdot \ln a(Cl^-)$
$0.3337\ V = 0.2682\ V - RT/F \cdot \ln a(Cl^-)$
$\ln a(Cl^-) = (0.2682\ V - 0.3337\ V) \cdot F/RT$
$\ln a(Cl^-) = - 2.55$ $a(Cl^-) = 0.0780$

Solution to problem 3-16

a) B: $BaSO_4$ C: NH_3 X: Fe

$n(BaSO_4) = m/M = 0.466\ g/(233.37\ g/mol) = 0.00200\ mol$

$n(NH_3) = p \cdot V/(R \cdot T) = 104.3 \cdot 10^3\ Pa \cdot 46.7 \cdot 10^{-6}\ m^3/(8.314\ JK^{-1}mol^{-1} \cdot 298\ K) = 0.00196\ mol$

$n(NH_3) \approx 0.00200\ mol$

$\Rightarrow$ A: $Fe(NH_4)_2(SO_4)_2$ Z: $Fe(NH_4)_2(SO_4)_2 \cdot x\ H_2O$

$M(Fe(NH_4)_2(SO_4)_2) = 284.07\ g/mol$

$M(Fe(NH_4)_2(SO_4)_2) \cdot x\ H_2O) = 0.392\ g/(0.001\ mol) = 392\ g/mol$

$284.07 + x \cdot 18.016 = 392$ $\Rightarrow x = 6.0$ $\Rightarrow$ Z: $Fe(NH_4)_2(SO_4)_2 \cdot 6\ H_2O$

$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O(aq) + 2\ BaCl_2(aq) \longrightarrow 2\ BaSO_4(s) + FeCl_2(aq) + 2\ NH_4Cl(aq) + 6\ H_2O(l)$

$NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$

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

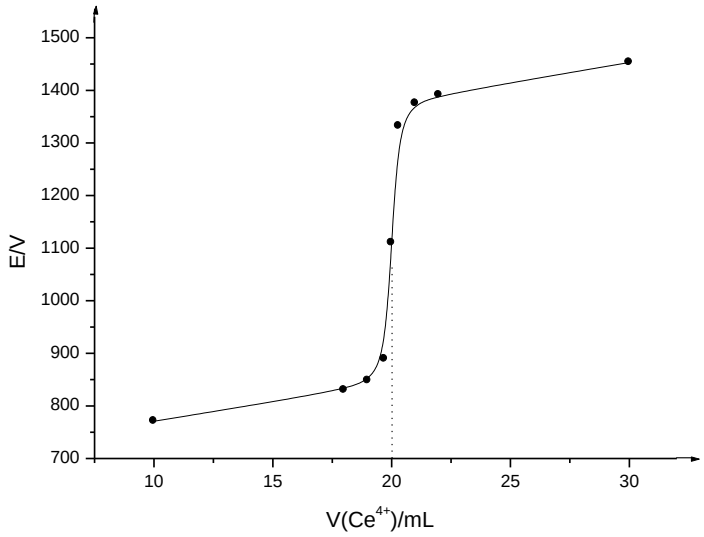
$4\ Fe(OH)_2 + O_2 + 2\ H_2O \longrightarrow 4\ Fe(OH)_3$

$NH_3 + H_2SO_4 \longrightarrow NH_4HSO_4$ ($2\ NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$, too)

Equations of ions are accepted, too.

b) The endpoint of a redox reaction can be recognised by potentiometric methods or by using redox indicators such as ferroine and diphenylamine.

c) $Fe^{2+} + Ce^{4+} \longrightarrow Fe^{3+} + Ce^{3+}$



$V_{eq} = 20\ mL$

d) mass fraction of iron in the substance after drying:

$w(Fe) = M(Fe) \cdot V_{eq} \cdot c(Ce^{4+})\ /m(dried\ substance)$

$w(Fe) = 55.85\ g/mol \cdot 20\ mL \cdot 0.05\ mol/L\ /0.3796\ g = 0.1471$

$w(Fe) = 55.85\ g/mol\ /\ (284.07\ g/mol) + y \cdot 18.02\ g/mol)$

$\Rightarrow$ $0.1471 = 55.85/(284.07 + y \cdot 18.02)$ $\Rightarrow y \approx 5.3$

$\Rightarrow$ Composition of the dried substance: $Fe(NH_4)_2(SO_4)_2 \cdot 5.3\ H_2O$

Solution to problem 3-17

A: $CrCl_3$ D: $Cr^{3+}(aq) + 3\ OH^-(aq) \longrightarrow Cr(OH)_3(s)$

$Cr(OH)_3(s) + 3\ OH^-(aq) \longrightarrow [Cr(OH)_6]^{3-}(aq)$

E: $Cr^{3+}(aq) + 3\ NH_3(aq) + 3\ H_2O \longrightarrow Cr(OH)_3(s)\downarrow + 3\ NH_4^+(aq)$

$Cr(OH)_3(s) + 6\ NH_3(aq) \longrightarrow [Cr(NH_3)_6]^{3+}(aq) + 3\ OH^-(aq)$

B: $NiCl_2$ D: $Ni^{2+}(aq) + 2\ OH^-(aq) \longrightarrow Ni(OH)_2(s)$

E: $Ni^{2+}(aq) + 2\ NH_3(aq) + 2\ H_2O(l) \longrightarrow Ni(OH)_2(s)\downarrow + 2\ NH_4^+(aq)$

$Ni(OH)_2(s) + 6\ NH_3(aq) \longrightarrow [Ni(NH_3)_6]^{2+}(aq) + 2\ OH^-(aq)$

C: H_2O_2 D, E: $2\ H_2O_2(aq) \xrightarrow{OH^-} 2\ H_2O(l) + O_2(g)$

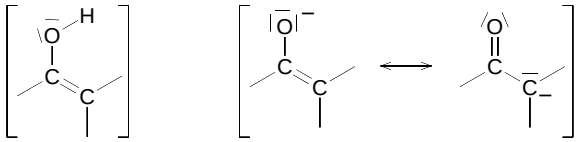
D: NaOH F: $3\ OH^-(aq) + Fe^{3+}(aq) \longrightarrow Fe(OH)_3(s)$

E: NH_3 F: $3\ NH_3(aq) + 3\ H_2O(l) + Fe^{3+}(aq) \longrightarrow Fe(OH)_3(s)\ (s) + 3\ NH_4^+(aq)$

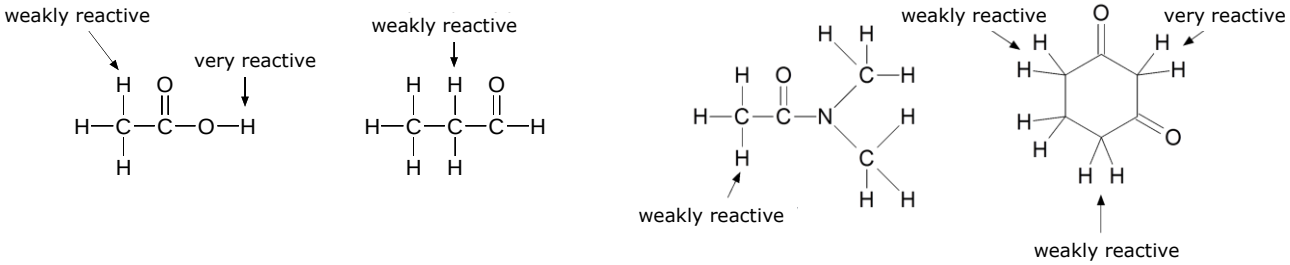
F: $FeCl_3$

Solution to problem 3-18

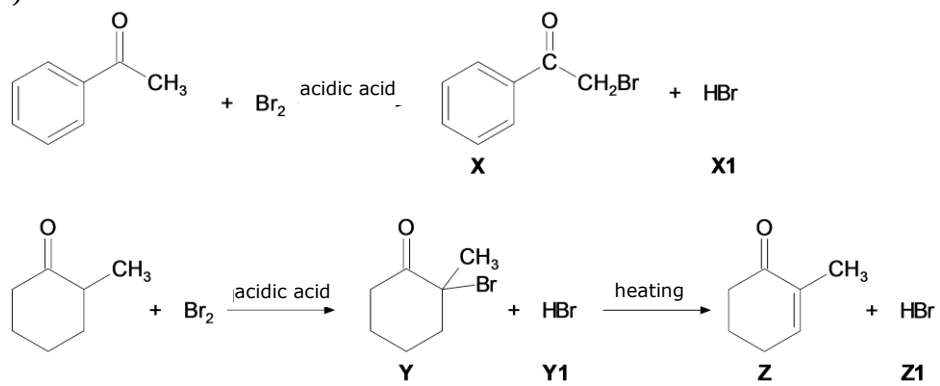
a)



b)



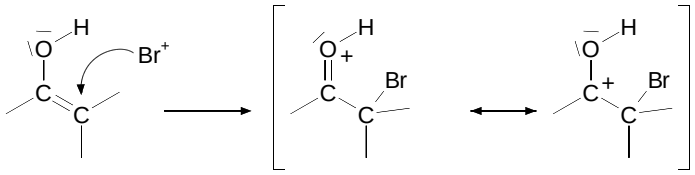
c)



d) X: α-Bromoacetophenone, 1-Bromoacetophenone

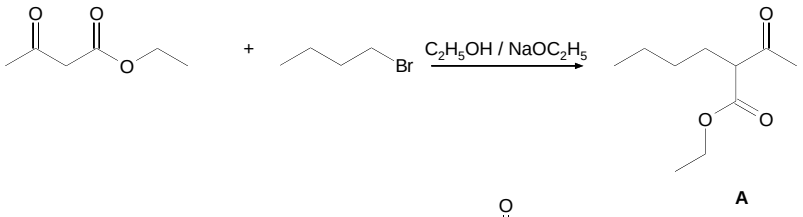
Y: 2-Bromo-2-methylcyclohexanone Z: 2-Methyl-2-cyclohexene-1-on

e) Br^+ is electrophilic. The enol reacts in an initial addition with an electrophile to give an intermediate cation

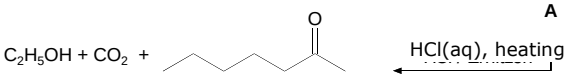


Carbocation

f)

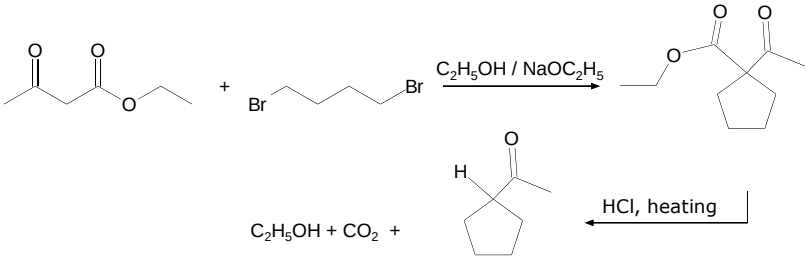


A



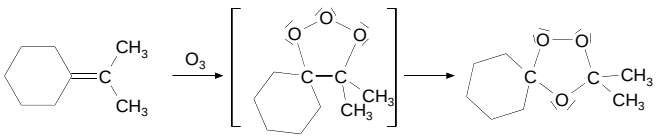
B

g)

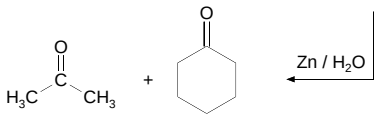


Solution to problem 3-19:

a)



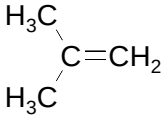
X Y



Z1/Z2 Z2/Z1

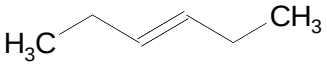
Acetone Cyclohexanone

b) Compound A



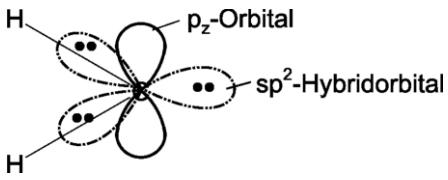
2-Methylpropene

Compound B:



Hex-3-ene

c) M methylene, the simplest carben:



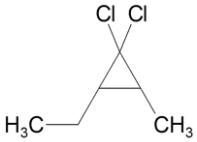
Additional information:

sp^2 Hybrid orbital, 6 electrons in sp^2 orbitals, p_z orbital vacant,

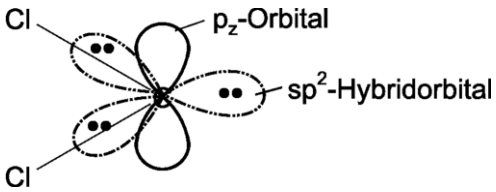
planar with the angle ∢ HCH = 120°, positive charge, electron sextet.

d) Methylene is a very reactive electron-deficient compound which adds electrophilic.

e) Compound D:



f) The intermediate is Cl_2C (dichlorocarben):

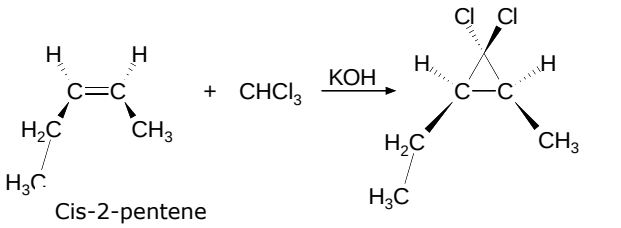


Additional information:

sp^2 Hybrid-Orbital, 6 elections in sp^2 orbitals, p_z orbital vacant,

planar with the angle ∢ HCH = 120°, positive charge, electron sextet.

g)

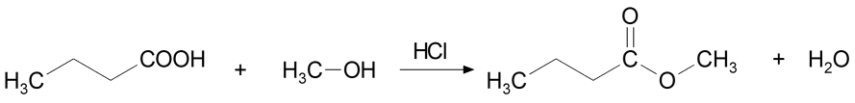


Cis-2-pentene

Cis structure is conserved

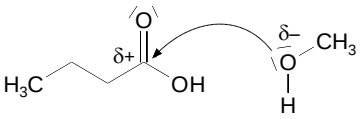
Solution to problem 3-20:

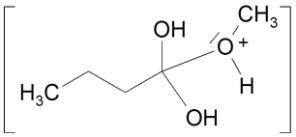
a)



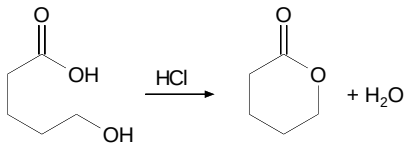
Methyl butanoate

b) Nucleophilic attack of the alcohol: Intermediate:



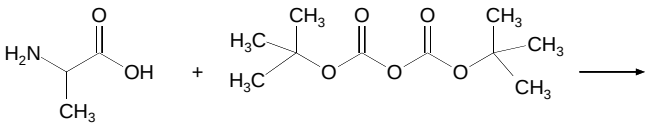


c) Preferential intramolecular reaction of *5-hydroxypentanoic acid*

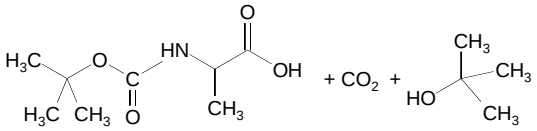


Lactone ring

d)



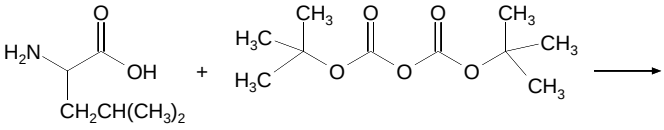
Alanin



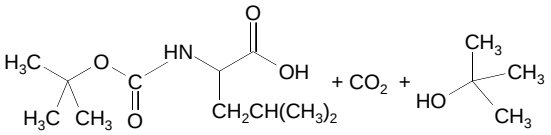
e) Plan to synthesize H-Leu-Ala-OH:

1. Introduce protecting groups for leucine (NH_2 group) and alanine (COOH group)
2. Coupling of the two protected amino acids leucine and alanine
3. Remove the protecting groups from the peptide formed.

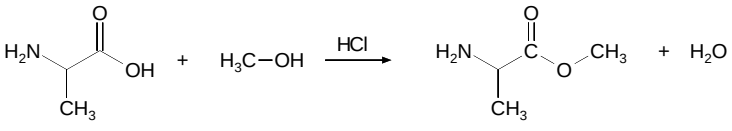
f) 1. Introduction of the protecting groups



Leucine

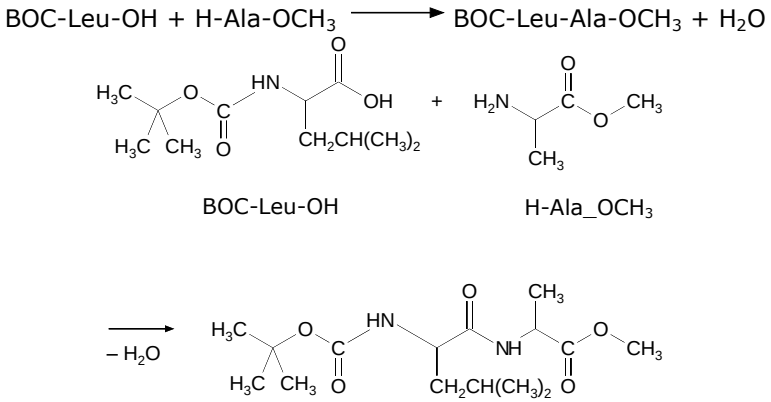


BOC-Leu-OH

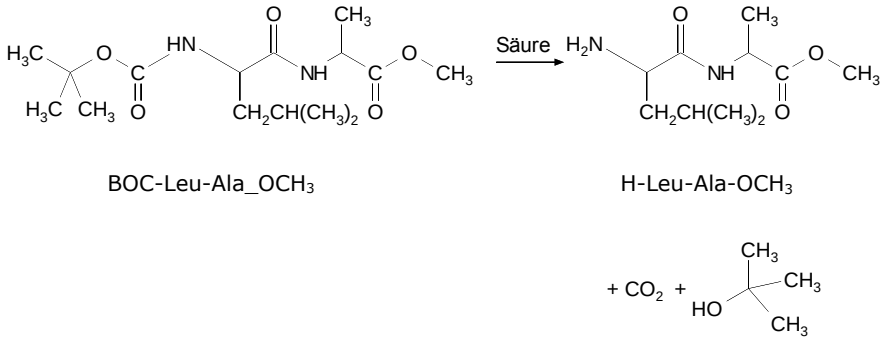


Alanine H-Ala_OCH3

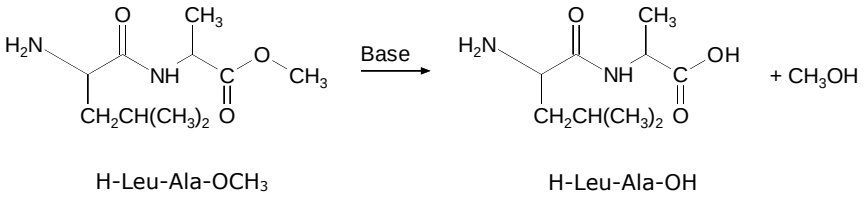
2. Coupling of the protected amino acids:



3. Removal of the protecting groups from the formed peptide.
   Acidic hydrolysis:



   Basic hydrolysis:



Answers Round 4 (theoretical)

Solution to problem 4-01

a) L = $c(Hg^{2+}) = \sqrt{K_{sp}}$ mol/L = $\sqrt{1.58 \cdot 10^{-52}}$ mol/L L = $1.26 \cdot 10^{-26}$ mol/L

b) There are 8 kinds of ions and molecules besides H_2O in the solution:
H_2S. HS^-, S^{2-}, H_3O^+, OH^-, $[Hg(OH)_2](aq)$, $[HgOH]^+(aq)$, Hg^{2+}.
Thus 8 equations are needed:

(1) $\frac{c(H_3O^+) \cdot c(HS^-)}{c(H_2S)} = K_{a1} \cdot c^\circ$ with $c^\circ = 1$ mol/L

(2) $\frac{c(H_3O^+) \cdot c(S^{2-})}{c(HS^-)} = K_{a2} \cdot c^\circ$

(3) $c(H_3O^+) \cdot c(OH^-) = K_W \cdot c^{\circ 2}$

(4) $\frac{c([Hg(OH)]^+(aq))}{c(Hg^{2+}) \cdot c(OH)^-} = \beta_1 \cdot c^{\circ -1}$

(5) $\frac{c([Hg(OH)_2](aq))}{c(Hg^{2+}) \cdot c^2(OH)^-} = \beta_2 \cdot c^{\circ -2}$

(6) $c(Hg^{2+}) \cdot c(S^{2-}) = K_L \cdot c^{\circ 2}$

(7) Balance of charge:
$c(HS^-) + 2 \cdot c(S^{2-}) + c(OH^-) = c(H_3O^+) + 2 \cdot c(Hg^{2+}) + c([Hg(OH)]^+(aq))$

(8) Total concentration of all Hg species = total concentration of all S species:
$c(H_2S) + c(HS^-) + c(S^{2-}) = c([Hg(OH)_2](aq)) + c([Hg(OH)^+](aq)) + c(Hg^{2+})$

c) As $c(H_3O^+)$ is known $c(S^{2-})$ can be calculated with equation 1) from problem part a):
$c(S^{2-}) = 6.64 \cdot 10^{-26}$ mol/L

$c(Hg^{2+}) = \frac{K_L \cdot c^{\circ 2}}{c(S^{2-})} = \frac{1.58 \cdot 10^{-52}}{6.64 \cdot 10^{-26}} \cdot c^\circ$ $c(Hg^{2+}) = 2.38 \cdot 10^{-27}$ mol/L

d) The solubility L is equal to the sum of all concentrations of S species and all concentrations of Hg species, respectively.
Sulfur containing species:
$c(S^{2-}) = 6.64 \cdot 10^{-26}$ mol/L
$c(HS^-) = c(H_3O^+) \cdot c(S^{2-})/(K_{S2} \cdot c^\circ)$ $c(HS^-) = (10^{-7} \cdot 6.64 \cdot 10^{-26} / 1.26 \cdot 10^{-13})$ mol/L
$c(HS^-) = 5.27 \cdot 10^{-20}$ mol/L
$c(H_2S) = c(H_3O^+) \cdot c(HS^-)/(K_{S1} \cdot c^\circ)$ $c(H_2S) = (10^{-7} \cdot 5.27 \cdot 10^{-20} / 7.94 \cdot 10^{-8})$ mol/L
$c(H_2S) = 6.64 \cdot 10^{-20}$ mol/L
L = $(6.64 \cdot 10^{-26} + 5.27 \cdot 10^{-20} + 6.64 \cdot 10^{-20})$ mol/L L = $1.19 \cdot 10^{-19}$ mol/L

Mercury containing species:
$c(Hg^{2+}) = 2.38 \cdot 10^{-27}$ mol/L
$c([Hg(OH)]^+(aq)) = c(Hg^{2+}) \cdot c(OH^-) \cdot \beta_1 \cdot c^{\circ -1}$
$c([Hg(OH)]^+(aq)) = (2.38 \cdot 10^{-27} \cdot 10^{-7} \cdot 2.00 \cdot 10^{10})$ mol/L
$c([Hg(OH)]^+) = 4.76 \cdot 10^{-24}$ mol/L
$c([Hg(OH)_2](aq)) = c(Hg^{2+}) \cdot c^2(OH^-) \cdot \beta_2$
$c([Hg(OH)_2](aq)) = (2.38 \cdot 10^{-27} \cdot 10^{-14} + 5.01 \times 10^{21})$ mol/L

c([$Hg(OH)_2$](aq)) = = $1.19 \cdot 10^{-19}$ mol/L

L = ($2.38 \cdot 10^{-27}$ + $4.76 \cdot 10^{-24}$ + $1.19 \cdot 10^{-19}$) mol/L L = $1.19 \cdot 10^{-19}$ mol/L

The results from a) and d) differ with the factor $1.19 \cdot 10^{-19}$ / $1.26 \cdot 10^{-26}$ = $1.06 \cdot 10^{-7}$.

e) $2 \cdot c([Hg(OH)_2](aq)) + c([HgOH]^+(aq)) \approx 2.380 \cdot 10^{-19}$ mol/L of OH^- ions are used for the hydrolysis of Hg^{2+}. That does not change the pH just as the consumption of H_30^+ because of the hydrolysis of S^{2-} of $2 \cdot c(H_2S) + c(HS-) \approx 1.855 \cdot 10^{-19}$ mol/L.

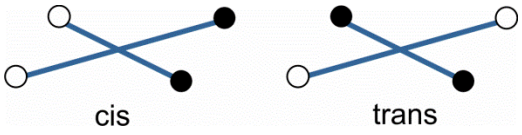
Solution to problem 4-02

(There were 4 crosses for quadratic planar or octahedral structures given in each box of the answer sheet)

a)

quadratic planar complex with ● ○ ✕ ▲ (4 different ligands):

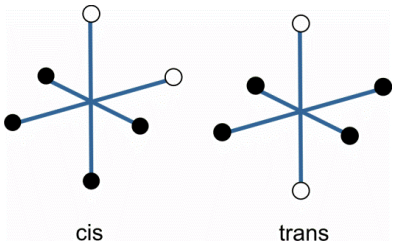
quadratic planar complex with 2 x ●, 2 x ○ (two pairs of identical ligands):



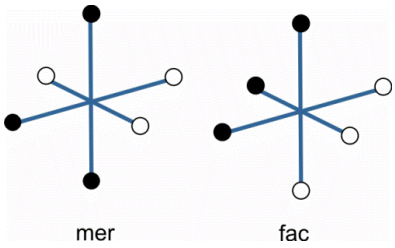
quadratic planar complex with 2 x ●, 1 x ⌒ (2 identical ligands, 1 chelate ligand)

Note: The relatively small ligand en is not able to bind to two opposite positions.

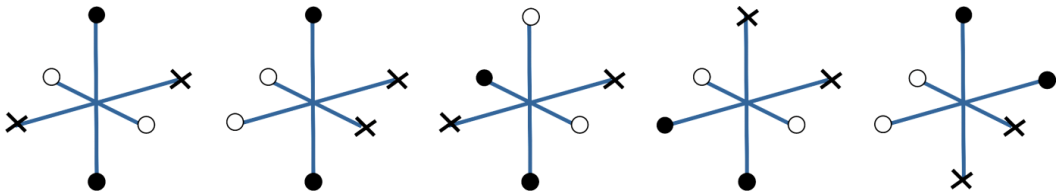
octahedral complex with 4 x ●, 2 x ○ (4 identical and 2 identical ligands):



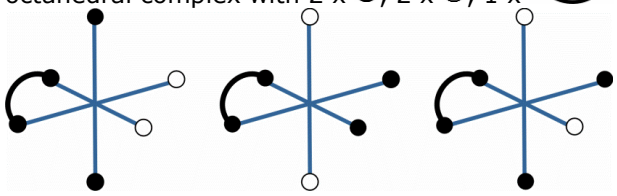
octahedral complex with 3 x ●, 3 x ○ (2 pairs of 3 identical ligands):



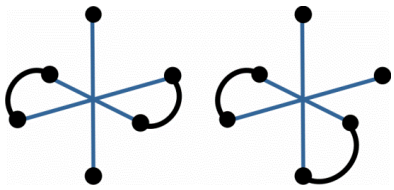
octahedral complex with 2 x ●, 2 x ○, 2 x ✕ (3 pairs of identical ligands):



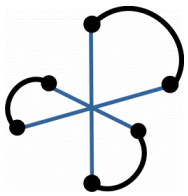
octahedral complex with 2 x ●, 2 x ○, 1 x ⌒ (2 pairs of identical ligands, 1 chelate ligand):



octahedral complex with 2 x ●, 2 x ⌒ (2 identical ligands, 2 identical chelate ligands)



octahedral complex with 3 x ⌒ (3 identical chelate ligands):



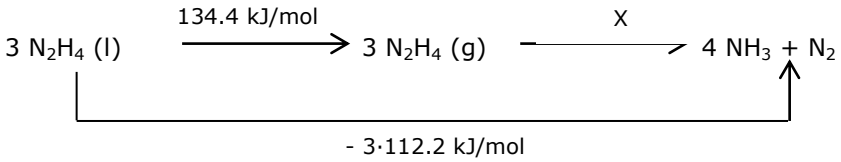
b) Stereoisomers

Complex compound	Number of stereoisomers	Pairs of enantiomers among them
$[Cr(ox)_2(H_2O)_2]^-$	3	1
$Co(py)_3Cl_3$	2	0
$Co(en)(NH_3)_2Cl_2$	4	1
$(C_9H_6NO)_3Al$	4	2

Solution to problem 4-03

a) $3\ N_2H_4 \longrightarrow 4\ NH_3 + N_2$

b) $3\ N_2H_4\ (l) \longrightarrow 3\ N_2H_4\ (g)$ $\quad \Delta_R H° = 3\cdot(95.4 - 50.6)\ kJ/mol = 134.4\ kJ/mol$



X = - 134.4 kJ/mol – 336.6 kJ/mol = - 471.0 kJ/mol

$X = -B(N\equiv N) - 4\cdot3\cdot B(N\text{-}H) + 3\cdot4\cdot B(N\text{-}H) + 3\cdot B(N\text{-}N)$

$\Rightarrow$ $B(N\equiv N) = 471.0\ kJ/mol + 3\cdot159\ kJ/mol$ $\quad B(N\equiv N) \approx 948\ kJ/mol$

$4\cdot\Delta_fH°(NH_3) = 3\cdot\Delta_fH°(N_2H_4\ (l)) - 3\cdot112.2\ kJ/mol$

$\Rightarrow$ $\Delta_fH°(NH_3) = ¾\ (50.6 - 112.2)\ kJ/mol$ $\quad \Delta_fH°(NH_3) = -46.2\ kJ/mol$

c) 3 significant figures in the results, intermediate results may have more.

d) $\Delta G = \Delta H - T\cdot\Delta S$ $\quad \Delta G = 57.7\ kJ - 363\ K \cdot 177\ J\cdot K^{-1}\cdot mol^{-1} = -6551\ J/mol$

$\Delta G = -R\cdot T\cdot \ln K_p$ $\quad \ln K_p = 2.171$ $\quad K_p = 8.764$

	N_2O_4 ⇌	$2\ NO_2$
before equilibrium	p_0	0 bar
in equilibrium	$p_0 - p_z$	$2 \cdot p_z$

amount in the beginning $n_0(N_2O_4) = 5/92\ mol$

$p_0\cdot V = n_o\cdot R\cdot T$ $\quad p_0 = \frac{5\cdot8.314\cdot363}{92.02\cdot4\cdot10^{-3}}\cdot10^{-5}\ bar$ $\quad p_0 = 0.4100\ bar$

$K_p = \frac{(2\cdot x)^2}{0.4100 - x}$ with $x = p_z/bar$

$8.764 \cdot (0.4100 - x) = 4\ x^2$ $\quad x^2 + 2.191\cdot x - 0.8983 = 0$

$x_1 = 0.3531$ $\quad (x_2 = -2.544)$ $\quad \Rightarrow$ $p_z = 0.3531\ bar$

$p_{total} = p_0 + p_z = (0.4100 + 0.3531)\ bar$ $\quad p_{total} \approx 0.763\ bar$

e) $\alpha = \frac{p_z}{p_0} = \frac{0.3531}{0.4100}$ $\quad \alpha = 0.861 \triangleq 86.1\ \%$

f) You may find $K_p(343\ K)$ by using $\Delta H - T\cdot\Delta S = -R\cdot T\cdot \ln K_p$ or with the help of van t'Hoff isochore. In both cases: $\ln K_p = 1.056$. $K_p = 2.875$

	N_2O_4 ⇌	$2\ NO_2$
before equilibrium	p_0	0 bar
in equilibrium	$p_0 - p_z$	$2 \cdot p_z$

$\alpha = \frac{p_z}{p_0}$ $\quad \Rightarrow p_z = 0.303\cdot p_0$

$p(NO_2) = 2\cdot p_z = 0.606\cdot p_0$ $\quad p(N_2O_4) = p_0 - p_z = p_0 - 0.303\cdot p_0 = 0.697\cdot p_0$

$K_p = \frac{(0.606\cdot p_o/1bar)^2}{0.697\cdot p_0/1bar}$ $\quad p_0 = 2.875\cdot\frac{0.697}{0.606^2}\ bar$ $\quad p_0 = 5.457\ bar$

amount in the beginning $n_0(N_2O_4) = 5.00/92.02\ mol$

$p_0\cdot V = n_o\cdot R\cdot T$ $\quad V = \frac{\frac{5}{92,02}mol\cdot8,314\ Jmol^{-1}K^{-1}\cdot343\ K}{5,457\cdot10^5\ Pa}$ $\quad V = 284\ mL$

Solution to problem 4-04

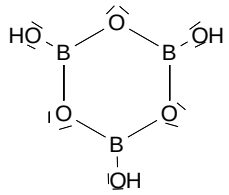
a) The result of the analysis shows a trend to a double bond. There is a pπ-pπ back bonding from fluorine towards boron. Thus an electron octet at the boron center is formally created.

b) $B(OH)_3 + 2\ H_2O \rightleftharpoons [B(OH)_4]^- + H_3O^+$

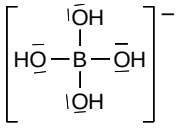
or $B(OH)_3 + H_2O \rightleftharpoons [B(OH)_4]^- + H^+$

c)

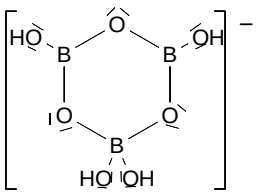
α-boric acid



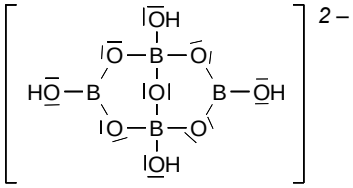
i) $[B(OH)_4]^-$



ii) $[B_3O_3(OH)_4]^-$

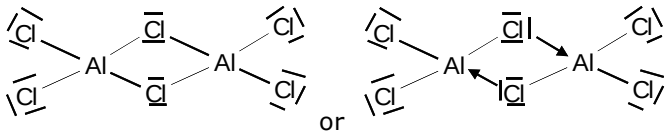


iii) $[B_4O_5(OH)_4]^{2-}$

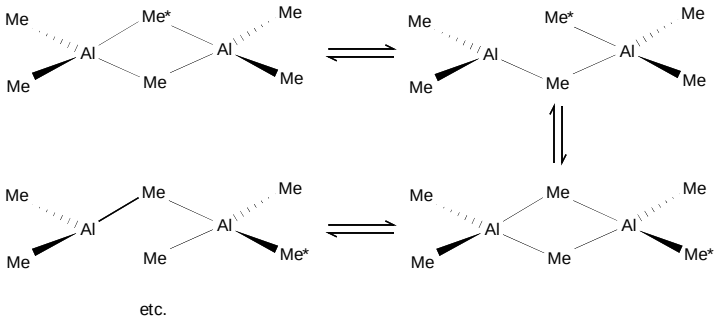


d) Solid AlF_3 shows a three-dimensional highly polymeric structure. Each Al is surrounded by six F atoms in a distorted octahedron. AlF_3 has significantly ionic character. The high coordination number and the small size of the fluoride anions lead to a very high lattice energy. Both facts are responsible for the high melting point and the insolubility.
$AlCl_3$ crystallizes in a highly polymeric layer structure indicative of greater covalence. In the solid Al has the coordination number 6. When melting this number changes to 4.
Solid $AlBr_3$ has predominantly covalent bonds; in the solid Al has already the coordination number 4.

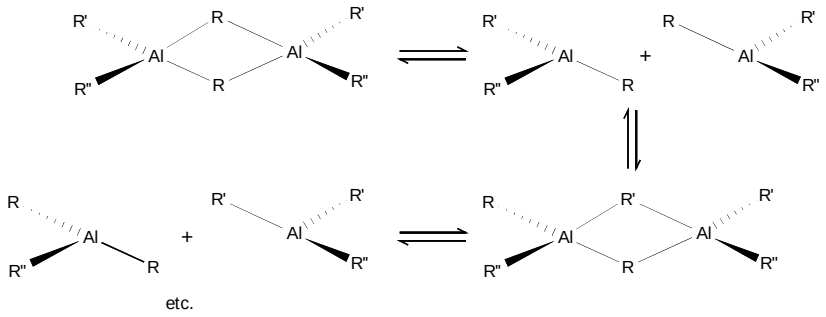
e)



f) The NMR spectrum at low temperature (-50 °C) indicates that there are two different kinds of H atoms, at the terminal and at the bridging CH_3 group. At higher temperature (starting at 20 °C) the CH_3 groups are switching between bridging and terminal environment on a scale faster than the NMR experiment. This is indicated by one sharp line in the ^1H NMR spectrum at 25 °C:



g) Besides the intramolecular process of exchange you find intermolecular processes of exchange between the different dimers. This results in an uncontrolled mixture of substituents:



h) The better substituents withdraw electrons the softer is the Lewis base and the harder the Lewis acid:

i) $N(CH_3)_3 > NH_3 > NF_3$ ii) $BF_3 > BH_3 > B(CH_3)_3$

i) Boron trihalogenides have a planar molecule structure where B-Xπ- interaction is possible. If boron trihalogenide combines with a Lewis base the planar molecule is pyramidal distorted and the B-Xπ- interaction is lost. This interaction is especially high with fluorine and thus the formation of an adduct is not much favoured. Bromine and chlorine have a smaller B-Xπ- interaction and thus a higher Lewis acidity.

j) The methyl group in position 2 of compound 2 has a steric interaction with the methyl groups of $B(CH_3)_3$. Thus the formation of an adduct of $B(CH_3)_3$ with compound 2 is less favoured than the formation of an adduct with the compounds 1 and 3.

k) When $B(CH_3)_3$ forms an adduct the planar molecule structure changes to a distorted pyramid. Then more space demanding substitutes disturb each other.

Solution to problem 4-05

a) $v = \frac{d[I_3^-]}{dt} = k_4 \cdot [I_2] \cdot [I^-]$

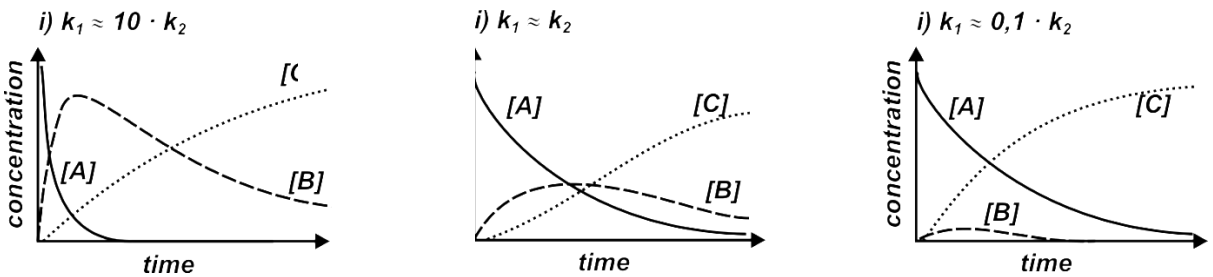
$\frac{d[I_2]}{dt} = k_3 \cdot [I^+] \cdot [I^-] - k_4 \cdot [I_2] \cdot [I^-] = 0 \quad \Rightarrow \quad v = k_4 \cdot [I_2] \cdot [I^-] = k_3 \cdot [I^+] \cdot [I^-]$

$\frac{d[I^+]}{dt} = k_2 \cdot [IS_2O_8^{3-}] - k_3 \cdot [I^+] \cdot [I^-] = 0 \quad \Rightarrow \quad v = k_3 \cdot [I^+] \cdot [I^-] = k_2 \cdot [IS_2O_8^{3-}]$

$\frac{d[IS_2O_8^{3-}]}{dt} = k_1 \cdot [S_2O_8^{2-}] \cdot [I^-] - k_2 \cdot [IS_2O_8^{3-}] = 0 \Rightarrow v = k_2 \cdot [IS_2O_8^{3-}] = k_1 \cdot [S_2O_8^{2-}] \cdot [I^-]$

$\frac{d[I_3^-]}{dt} = k_1 \cdot [S_2O_8^{2-}] \cdot [I^-]$

b)



i) Since step 1 has a much larger rate constant than step B, A is more or less completely converted to B before there is time for much of B to be converted to C. The fall of A is mirrored by the rise of B. Once the initial phase is over we have only the slower conversion of B to C.

iii) In graph iii) we have the opposite situation in which the rate constant for step 2 is much larger than for step 1. At the moment any of the intermediate B is formed, it rapidly reacts to give the final product C. As a result, little B accumulates and the fall of A is mirrored by the rise of C.

c) For a reaction of first order is $\lambda = \ln 2/t_{½}$.

$\lambda(^{222}Rn) = \ln 2/3.8\ d = 0.182\ d^{-1} = 1.26\cdot10^{-4}\ min^{-1}$

Number of decays = $\lambda \cdot$ c(decaying species) $\Rightarrow$

$4.2\ \frac{atoms}{min\cdot 100\ L} = \lambda(^{222}Rn)\cdot c(^{222}Rn) = 1.26\cdot10^{-4}\ min^{-1}\cdot c(^{222}Rn)$ $\quad c(^{222}Rn) = 3.3\cdot10^{4}\ \frac{atoms}{100\ L}$

$c(^{222}Rn) = 3.33\cdot10^{4}\ \frac{atoms}{100\ L}\ /(6.022\cdot10^{23}\ mol^{-1})$ $\quad c(^{222}Rn) = 5.5\cdot10^{-22}\ mol/L$

d) Since the activity of ^{222}Rn does not change with time, its addition to the lake by ^{226}Ra decay must be exactly balanced by its loss through radioactive decay and the unknown first order process:

$6.7\ \frac{atoms}{min\cdot 100\ L} = (\lambda(^{222}Rn) + k)\cdot c(^{222}Rn) = (1.26\cdot10^{-4}\ min^{-1} + k)\cdot 3.3\cdot10^{4}\ \frac{atoms}{100\ L}$

where k = rate constant for the unknown process.

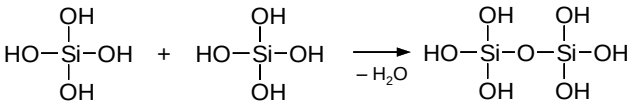
$k = 7.7\cdot10^{-5}\ min^{-1}$

(The unknown process is the diffusion of Rn through the water/air interface and escape to the atmosphere.)

e) α Emission reduces the atomic number by 2 and the atomic mass by 4, the product is ^{218}Po.

Solution to problem 4-06

a)



b) i) $[Si_3O_9]^{6-}$ bzw. $([SiO_3]^{2-})_3$

ii) $[Si_6O_{18}]^{12-}$ bzw. $([SiO_3]^{2-})_6$

iii) $[Si_{24}O_{66}]^{36-}$ bzw. $([Si_4O_{11}]^{6-})_6$

c) Liquid glass shows a strong alkaline reaction. At addition of acid the silicate anions are protonated. Then they can condensate (see part a)).

In the reaction with air carbon dioxide is responsible for the hardening:

$2\ CO_2 + 2\ H_2O + SiO_3^{2-} \rightleftharpoons H_2SiO_3 + 2\ HCO_3^-$ or

$CO_2 + H_2O + SiO_3^{2-} \rightleftharpoons H_2SiO_3 + CO_3^{2-}$ or

$4\ CO_2 + 4\ H_2O + SiO_4^{4-} \rightleftharpoons H_4SiO_4 + 4\ HCO_3^-$ or

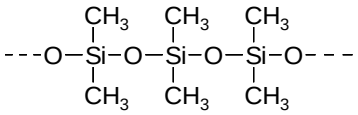
$2\ CO_2 + 2\ H_2O + SiO_4^{4-} \rightleftharpoons H_4SiO_4 + 2\ CO_3^{2-}$

H_2SiO_3 and H_4SiO_4 do not split off water under these conditions.

d) $2\ CH_3Cl + 2\ Si \rightleftharpoons 2\ (CH_3)_2SiCl_2$

e) $2\ (CH_3)_2SiCl_2 \rightleftharpoons (CH_3)_3SiCl + (CH_3)SiCl_3$

f) You can expect a chain:



g) $CaF_2 + H_2SO_4 \rightleftharpoons CaSO_4 + 2\ HF$

$4\ HF + SiO_2 \rightleftharpoons SiF_4 + 2\ H_2O$

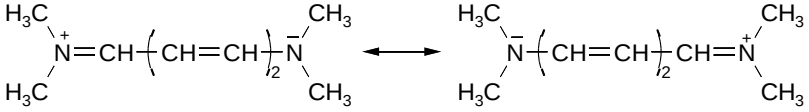
$3\ SiF_4 + 3\ H_2O \rightleftharpoons H_2SiO_3 + 2\ H_2[SiF_6]$ or

$SiF_4 + 2\ H_2O \rightleftharpoons SiO_2(s)\cdot aq + 4\ HF$

Solution to problem 4-07

A

a)



N = 8 delocalized electrons

b) $\Delta E = \frac{h^2}{8\,m\,L^2}\ ((n+1)^2 - n^2) = \frac{(2n+1)\,h^2}{8\,m\,L^2}$

c) Number of occupied orbitals in ground state n = N/2 = 4.

$\Delta E = \frac{9\,h^2}{8\,m\,L^2}$ und $\Delta E = \frac{h\,c}{\lambda}$

$\Rightarrow L = \sqrt{\frac{9\,h\,\lambda}{8\,m\,c}}$ with λ = 605 nm:

$\Rightarrow L = \sqrt{\frac{9\cdot 6.6261\cdot 10^{-34}\,Js\cdot 605\cdot 10^{-9}\,m}{8\cdot 9.1094\cdot 10^{-31} kg\cdot 3.00\cdot 10^{8}\,ms^{-1}}}$ $L = 1.28\cdot 10^{-9}$ m = 1.28 nm

d) There are 4π-electrons in 1,3-pentadiene ⇒ n(homo) = 2. L = 4·140 pm = 560 pm

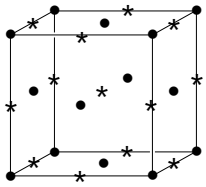
$\Delta E = \frac{5\,h^2}{8\,m\,L^2}$ und $\lambda = \frac{h\,c}{\Delta E}$

$\Rightarrow \lambda = \frac{8\cdot c\cdot m\cdot L^2}{5\,h}$ $\lambda = \frac{8\cdot 3\cdot 10^8\,\frac{m}{s}\cdot 9.1094\cdot 10^{-31}\,kg\cdot (560\cdot 10^{-12}\,m)^2}{5\cdot 6.6261\cdot 10^{-34}\,Js}$

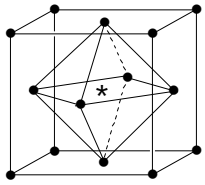
λ = 207 nm

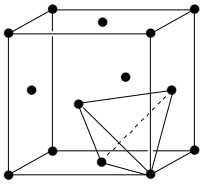
B

e) and f)



• Oxygen ions
* Iron(II) ions





(To give a better view the iron ions on the edges are left out)

1 octahedral interstice 8 tetrahedral interstices

g) The diffraction planes of the elementary cell are the planes at the right and the left hand site of the cell and one parallel to them exactly in the middle,

$\Rightarrow$ edge length a of the crystal = 2·distance d of the planes.

λ = 2·d·sin Θ (Bragg condition) 2·d = 71.41 pm /sin $\frac{19.42^\circ}{2}$ 2·d = a = 423.4 pm

h) There are 4 formula units per elementary cell.

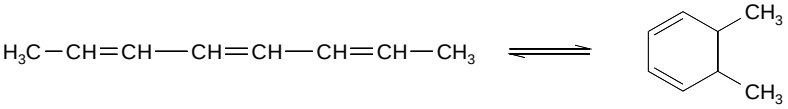
$\rho = \frac{m(cell)}{V(cell)} = \frac{4 \cdot M}{N_A \cdot a^3}$ 5.71 g/cm^3 = $\frac{4 \cdot (55.85 \cdot x + 16.00)\ g \cdot mol^{-1}}{6.022 \cdot 10^{23}\ mol^{-1} \cdot (423.4 \cdot 10^{-10}\ cm)^3}$ x = 0.882

i) u + v = 0.882 (mass balance) 2·u + 3·v = 2 (charge balance)

$\Rightarrow$ u = 0.646 und v = 0.236 $Fe(II)_{0.646}Fe(III)_{0.236}$

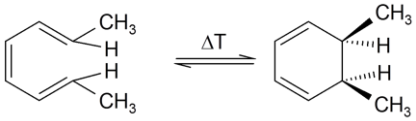
Solution to problem 4-08

a) Reaction equation of 2,4,6-Octatrien $\longrightarrow$ Dimethylhexadien:

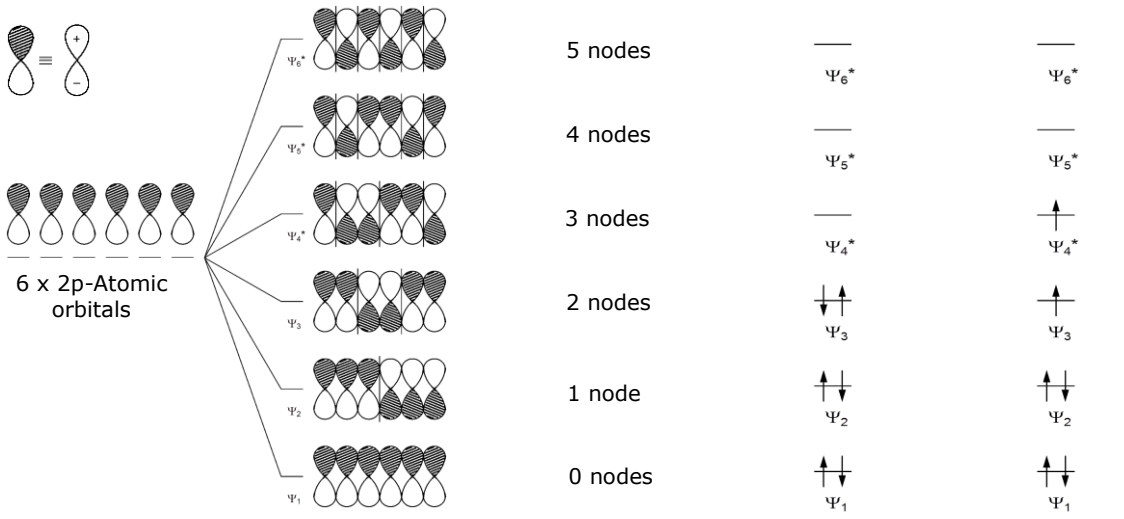


5,6-Dimethyl-1,3-cyclohexadien

b) Formation of cis-5,6-dimethyl-1,3-cyclohexadien:



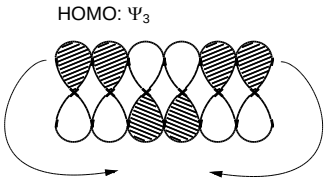
c)



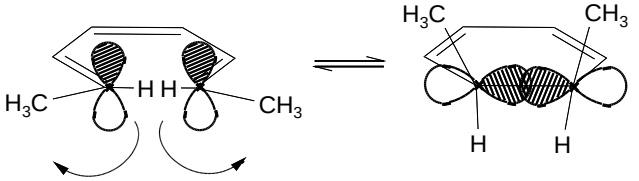
π-Molecular orbitals of 2,4,6-octatrien

d) 6 π electrons are available:

e) For thermal reactions, the ground-state electronic configuration is used to identify the HOMO. Decisive orbital:

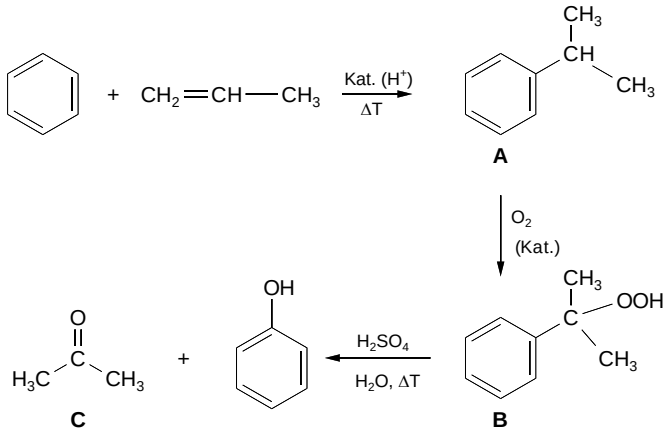


The disrotatory direction of rotation leads to a bond (ring closure) and formation of the cis compound.



Solution of problem 4-09

a)



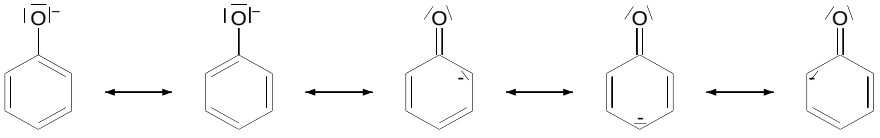
A: (1-Methylethyl) benzene or cumene or isopropylbenzene

B: cumene hydroperoxide

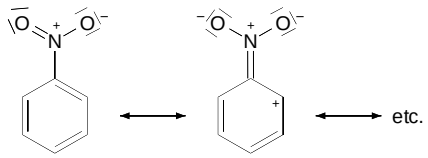
C: Acetone or propanone or dimethylketone

Formation of A: Friedel-Crafts alkylation

b) Ethanol (pK_a = 16) is less acidic than phenol (pK_a = 10).
Phenol is more acidic than ethanol because the phenoxide anion is resonance-stabilized. The negative charge is delocalized over the ortho and para positions:

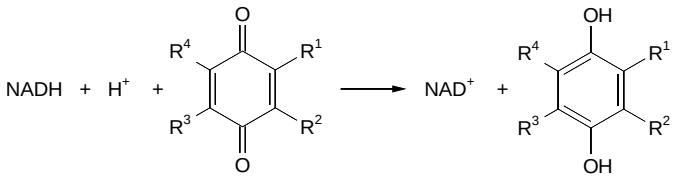


c) NO_2 is an electron-withdrawing group. The negative charge of the substituted phenol is more delocalized and thus the phenoxide anion stabilized.

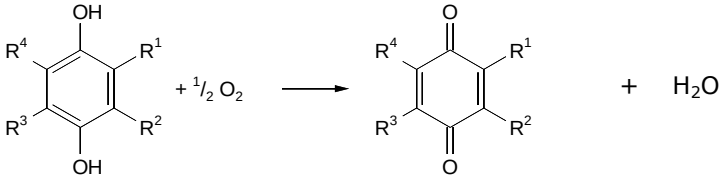


This results in a higher acidity of these substituted phenols.

d) Oxidation:

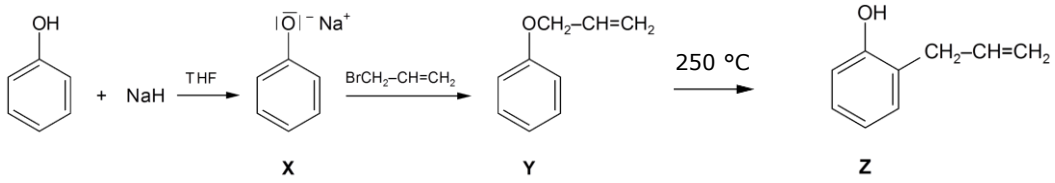


Recovering of ubiquinone:

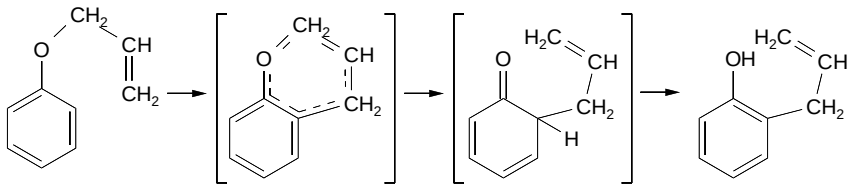


Net change (not asked): $NADH + ½\ O_2 + H^+ \longrightarrow NAH^+ + H_2O + energy$

e) Reaction to form o-allylphenol

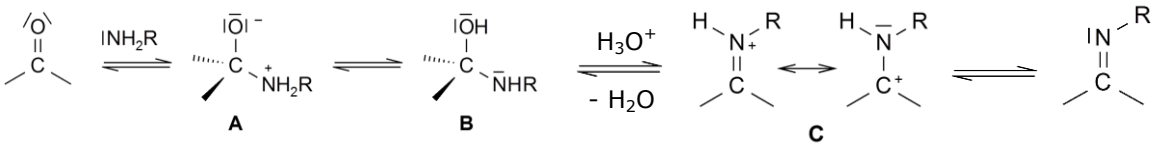


f) Mechanism of the Claisen rearrangement:

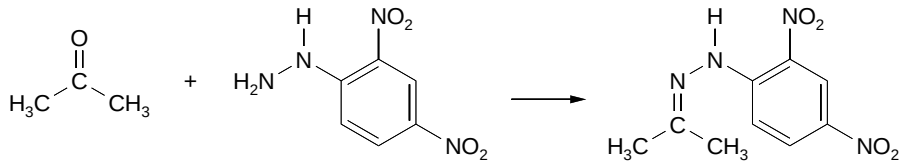


Solution to problem 4-10

a)

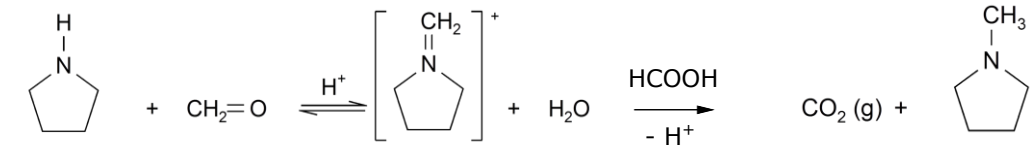


b)



The reaction of 2,4-dinitrophenylhydrazine is (or was) used to identify aldehydes and ketones by the specific melting points of the products.

c)



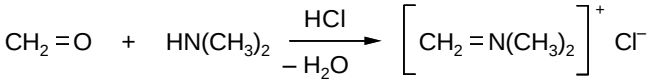
Pyrrolidine

X

Y

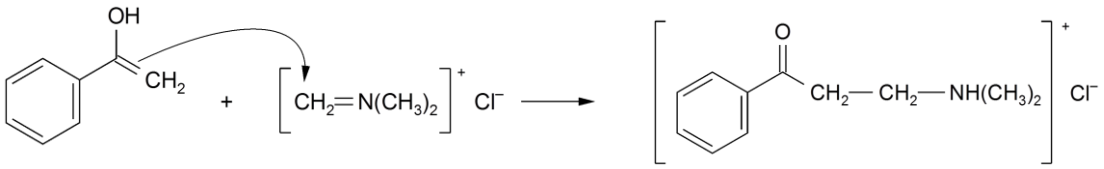
Z

d)



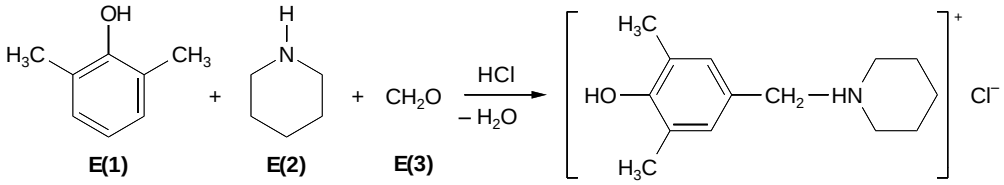
R

Nucleophilic attack of acetophenone at N,N-dimethylmethyleniminiumchloride



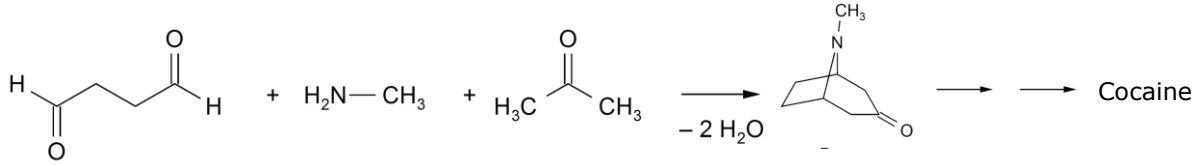
Enole

e)



E(1) **E(2)** **E(3)**

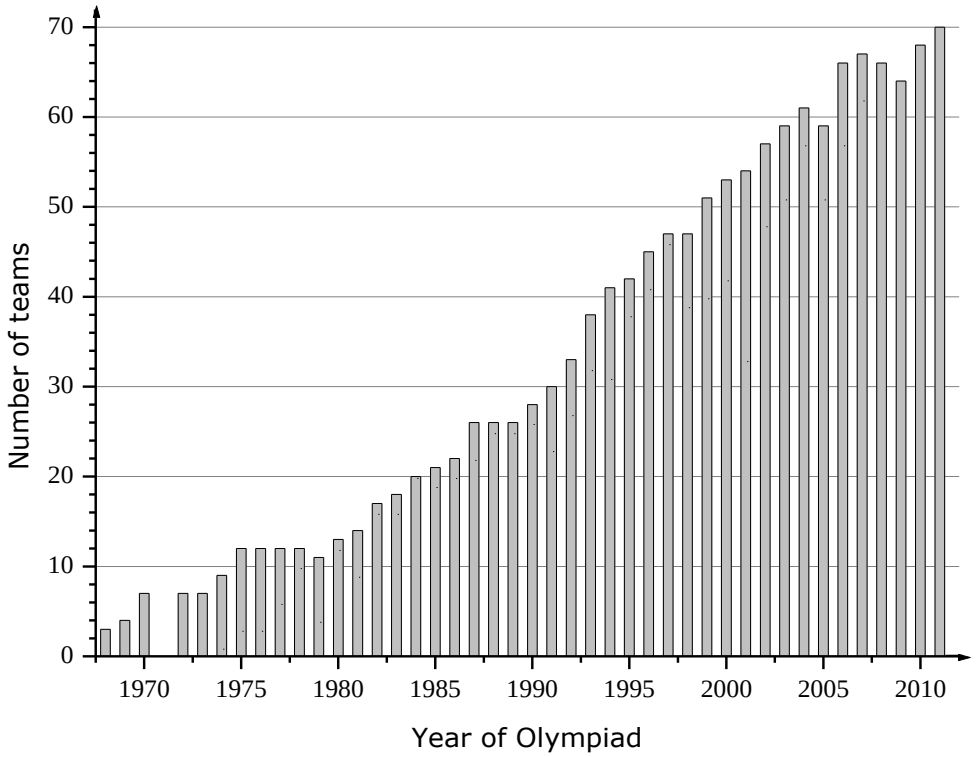
f)



About the history of the International Chemistry-Olympiads

The idea of chemistry olympiads was born 1968 during an Czechoslovakian national olympiad that was attended by observers from Poland and Hungary. These three countries participated in the first IChO 1968 in Prague. The number of teams attentding the IChO in the following years are shown in the plot below.

Number of teams attending the IChO



The participating countries are shown in the following table.

Participating Delegations

in alphabetical order

+ = host. + = participant. o = observer

Country ↓ / Year →	68	69	70	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99
Argentina																											+	+	+	+	+
Armenia																															
Australien																			o	+	+	+	+	+	+	+	+	+	+	+	+
Austria							+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Azerbaijan																													o	o	
Belarus																												+	+	+	+
Belgium							+	+	+			+				+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Brasil																													o	o	+
Bulgaria		+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Canada																o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+
China																			+	+	+	+	+	+	+	+	+	+	+	+	+
Chinese Taipei																								+	+	+	+	+	+	+	+
Costa Rica																															
Croatia																														o	o
Cuba																	+	o	+	+	+	+	+		+	+	+	+	+		+
Cyprus																						o	+	+	+	+	+	+	+	+	+
Czech Rep.																									+	+	+	+	+	+	+
Czechoslovakia	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+							
Denmark														+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
DDR		o	+	+	+	+	+	+	+	+	+	+	+	+	+		+	+	+	+	+	+									
Egypt																															
El Salvador																															
Estonia																										+	+	+	+	+	+
Finland								o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
France												o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
fYROM (Macedonia)																															
Germany						o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Greece																+	+	+	+		+	+	+	+	+	+	+	+	+	+	+
Hungary	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Iceland																															
India																													o	o	+
Indonesia																												o	+	+	+
Iran																									+	+	+	+	+	+	+
Ireland																												o	o	+	+
Israel																															
Italy												+	+	+	+	+	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

Participating Delegations

in alphabetical order

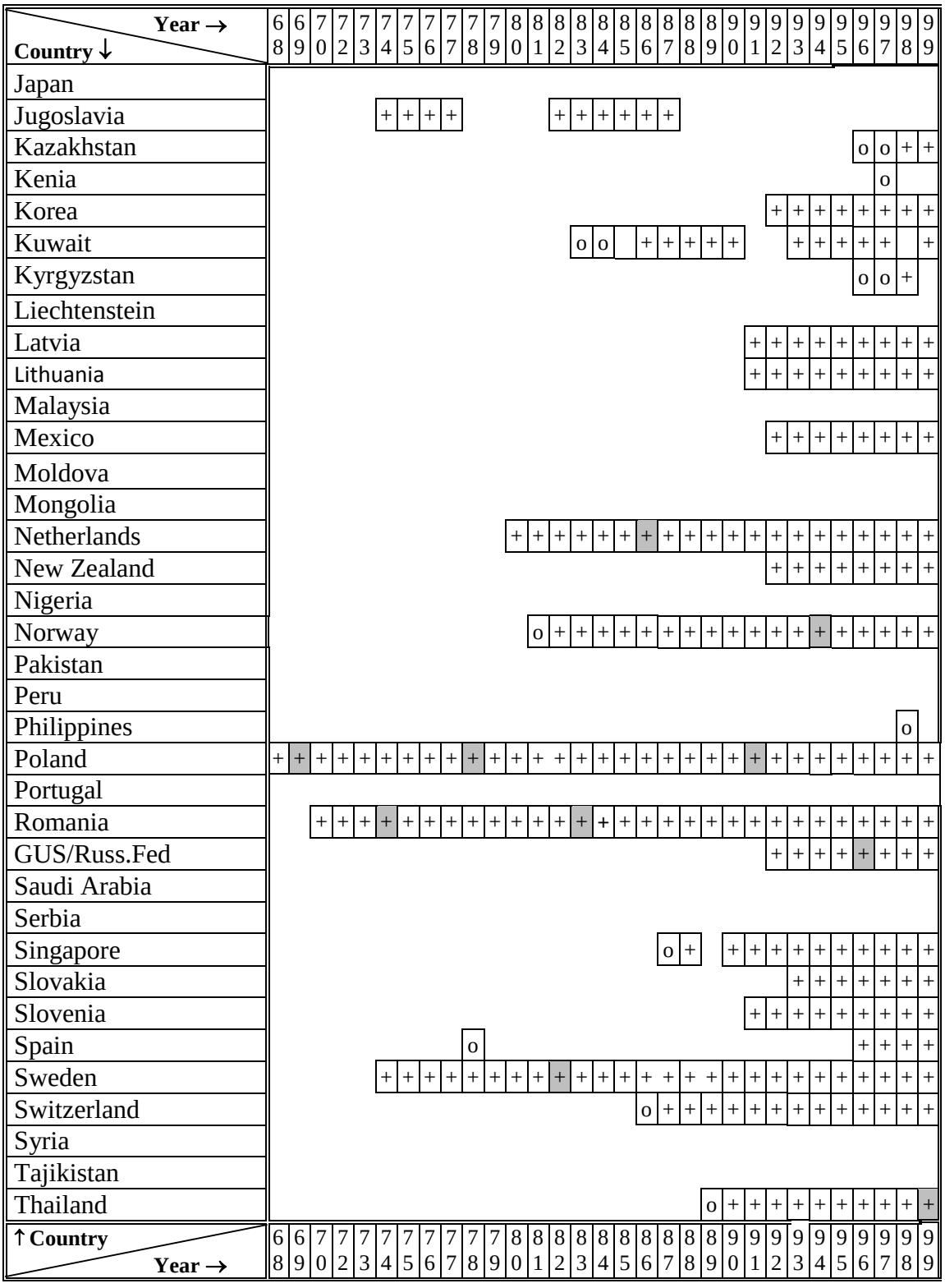
+ = host. + = participant. o = observer

Country ↓ \ Year →	00	01	02	03	04	05	06	07	08	09	10	11	12
Argentina	+	+	+	+	+	+	+	+	+	+	+	+	
Armenia					o	o	+	+	+	+	+	+	
Australien	+	+	+	+	+	+	+	+	+	+	+	+	
Austria	+	+	+	+	+	+	+	+	+	+	+	+	
Azerbaijan	+	+	+	+	+	+	+	+	+	+	+	+	
Belarus	+	+	+	+	+	+	+	+	+	+	+	+	
Belgium	+	+	+	+	+	+	+	+	+	+	+	+	
Brasil	+	+	+	+	+	+	+	+	+	+	+	+	
Bulgaria	+	+	+	+	+	+	+	+	+	+	+	+	
Canada	+	+	+	+	+	+	+	+	+	+	+	+	
China	+	+	+	+	+		+	+	+	+	+	+	
Chinese Taipei	+	+	+	+	+	+	+	+	+	+	+	+	
Costa Rica									o	o	+	+	
Croatia	+	+	+	+	+	+	+	+	+	+	+	+	
Cuba		+	+	+	+	+	+	+	+	+	+	+	
Cyprus	+	+	+	+	+	+	+	+	+	+	+	+	
Czech Rep.	+	+	+	+	+	+	+	+	+	+	+	+	
Czechoslovakia													
Denmark	+	+	+	+	+	+	+	+	+	+	+	+	
DDR													
Egypt	o	o	+	+	+	+	+					+	
El Salvador												o	
Estonia	+	+	+	+	+	+	+	+	+	+	+	+	
Finland	+	+	+	+	+	+	+	+	+	+	+	+	
France	+	+	+	+	+	+	+	+	+	+	+	+	
fYROM (Macedonia)												o	
Germany	+	+	+	+	+	+	+	+	+	+	+	+	
Greece	+	+	+	+	+	+	+	+	+	+	+	+	
Hungary	+	+	+	+	+	+	+	+	+	+	+	+	
Iceland	o	o	+	+	+	+	+	+	+	+	+	+	
India	+	+	+	+	+	+	+	+	+	+	+	+	
Indonesia	+	+	+	+	+	+	+	+	+	+	+	+	
Iran	+	+	+	+	+	+	+	+	+	+	+	+	
Ireland	+	+	+	+	+	+	+	+	+	+	+	+	
Israel					o	o	+	+	+	+	+	+	
Italy	+	+	+	+	+	+	+	+	+	+	+	+	
↑ Land / Year →	00	01	02	03	04	05	06	07	08	09	10	11	12

Participating Delegations

in alphabetical order

+ = host. + = participant. o = observer



Participating Delegations

in alphabetical order

+ = host. + = participant. o = observer

Year → / Country ↓	00	01	02	03	04	05	06	07	08	09	10	11	12
Japan			o	+	+	+	+	+	+	+	+	+	
Jugoslavia			o										
Kazakhstan	+	+	+	+	+	+	+	+	+	+	+	+	
Kenia		o											
Korea	+	+	+	+	+	+	+	+	+	+	+	+	
Kuwait	+	+	+	+	+	+	+	+	+	+	+	+	
Kyrgyzstan	+	+	+	+	+	+	+	+	+	+	+	+	
Liechtenstein										o	o	o	
Latvia	+	+	+	+	+	+	+	+	+	+	+	+	
Lithuania	+	+	+	+	+	+	+	+	+	+	+	+	
Malaysia					o	+	+	+	+		+	+	
Mexico	+	+	+	+	+	+	+	+	+	+	+	+	
Moldova					o		o	+	+	+	+	+	
Mongolia		o			o	o	+	+	+	+	+	+	
Netherlands	+	+	+	+	+	+	+	+	+	+	+	+	
New Zealand	+	+	+	+	+	+	+	+	+	+	+	+	
Nigeria								o			o	o	
Norway	+	+	+	+	+	+	+	+	+	+	+	+	
Pakistan					o	o	+	+	+	+	+	+	
Peru			o	o	+	+		+	+	+	+	+	
Philippines													
Poland	+	+	+	+	+	+	+	+	+	+	+	+	
Portugal		o	o	+	+	+	+	+	+	+	+	+	
Romania	+	+	+	+	+	+	+	+	+	+	+	+	
GUS/Russ.Fed	+	+	+	+	+	+	+	+	+	+	+	+	
Saudi Arabia					o	o	+	+		o	o	+	
Serbia											o	o	
Singapore	+	+	+	+	+	+	+	+	+	+	+	+	
Slovakia	+	+	+	+	+	+	+	+	+	+	+	+	
Slovenia	+	+	+	+	+	+	+	+	+	+	+	+	
Spain	+	+	+	+	+	+	+	+	+	+	+	+	
Sweden	+	+	+	+	+	+	+	+	+	+	+	+	
Switzerland	+	+	+	+	+	+	+	+	+	+	+	+	
Syria									o	o	+	+	
Tajikistan			o	o	+	+	+	+	+		+	+	
Thailand	+	+	+	+	+	+	+	+	+	+	+	+	
↑ Country / Year →	00	01	02	03	04	05	06	07	08	09	10	11	12

Participating Delegations

in alphabetical order

+ = host. + = participant. o = observer

Year → / Country ↓	68	69	70	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99
Turkey									o	+															o	+	+	+	+	+	+
Turkmenistan																															o
UdSSR			+	+	+	+	+	+	+	+	+		+	+	+	+	+	+	+	+	+		+								
Ukraine																										+	+	+	+	+	+
United Kingdom												o		o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
United States													o		o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Uruguay																													o	o	+
Usbekistan																															
Venezuela														o		o									+	+	+	+	+	+	+
Vietnam																												+	+	+	+
↑ Country / Year →	68	69	70	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99

Participating Delegations

in alphabetical order

+ = host. + = participant. o = observer

Country ↓ / Year →	00	01	02	03	04	05	06	07	08	09	10	11	12
Turkey	+	+	+	+	+	+	+	+	+	+	+	+	
Turkmenistan	o	o	+	+	+		+	+	+	+	+	+	
UdSSR													
Ukraine	+	+	+	+	+	+	+	+	+	+	+	+	
United Kingdom	+	+	+	+	+	+	+	+	+	+	+	+	
United States	+	+	+	+	+	+	+	+	+	+	+	+	
Uruguay	+	+	+	+	+	+	+	+	+	+	+	+	
Usbekistan												o	
Venezuela	+	+	+	+	+	+	+	+	+	+	+	+	
Vietnam	+	+	+	+	+	+	+	+	+	+	+	+	
↑ Country / Year →	00	01	02	03	04	05	06	07	08	09	10	11	12

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 105)

	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 105)

	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
IChO held in	**IND**	**NL**	**GR**	**D**	**TPE**	**ROK**	**RUS**	**H**	**GB**	**J**	**TR**	**USA**
1	RC	RC	RC	RC	ROK	RC	RC	RC	TPE	RC	RC	
.	ROK	T	IR	ROK	VN	TPE	RUS	RUS	RC	T	ROK	
.	USA	TPE	ROK	RUS	IR	ROK	TPE	UA	ROK	ROK	RUS	
.	RUS	ROK	T	UA	RUS	RUS	PL	ROK	RUS	J	RI	
5	IR	A	BY	D	AZ	VN	ROK	T	SGP	TPE	USA	
.	TR	UA	RUS	PL	TPE	T	D	BY	J	H	T	
.	IND	USA	IND	TPE	T	J	T	VN	USA	CZ	SGP	
.	AUS	PL	SGP	H	RA	Pl	IND	TPE	H	SGP	CDN	
.	TPE	IND	D	TR	D	IND	H	H	IR	**USA**	H	
10	T	D	TPE	VN	IND	D	SK	SGP	GB	IR	IR	
.	SGP	IR	UA	IND	A	SK	LT	KZ	RO	RUS	TR	
.	PL	H	PL	IR	CZ	DK	USA	A	T	TR	IND	
.	RO	RUS	CDN	RO	UA	SGP	VN	PL	D	LT	CZ	
.	F	CDN	CZ	LT	PL	BR	GB	IR	IND	D	F	
15	SK	TR	RO	CZ	AUS	CDN	BY	IND	PL	PL	J	
.	H	AUS	KZ	USA	TR	AZ	EST	RO	AUS	GB	TPE	
.	VN	GB	VN	SGP	H	UA	UA	AUS	A	IND	**D**	
.	CZ	SGP	EST	CDN	SK	USA	RI	D	BY	RI	SK	
.	RA	E	GB	AZ	USA	H	IR	SK	VN	RO	KZ	
20	BY	SK	AUS	AUS	GB	CZ	RO	TR	F	A	AUS	
.	C	BY	H	KZ	RO	AUS	AUS	LT	RI	VN	VN	
.	D	VN	SK	GB	BY	IRL	A	EST	TR	SK	RO	
.	GB	FIN	USA	J	SGP	F	KZ	I	LT	CDN	GB	
.	UA	F	YV	A	J	IR	SGP	GB	UA	EST	BY	
25	A	LT	IND	BY	RI	A	NZ	CDN	EST	AUS	PL	
.	MEX	CZ	F	SK	LV	TR	CZ	NZ	CZ	UA	A	
.	DK	KZ	A	T	BG	RI	F	BR	SK	F	LT	
.	CDN	LV	I	RA	HR	GB	TR	USA	CDN	RA	EST	
.	EST	NL	TR	EST	MEX	RO	J	LV	I	NZ	RA	
30	RI	RO	AZ	F	KZ	NL	ARM	RI	RA	BY	UA	
.	HR	RA	MEX	NZ	LT	HR	SLO	F	NZ	KZ	FIN	
.	I	EST	LT	SLO	F	LT	RA	CZ	TM	BR	SLO	
.	N	HR	NL	HR	EST	KZ	BR	J	MEX	IL	I	
.	BG	BG	FIN	LV	CDN	SLO	CDN	DK	KZ	HR	BR	
35	CY	NZ	HR	NL	I	EST	I	RA	IL	SLO	HR	
.	KZ	I	J	I	DK	RA	MAL	MEX	BR	FIN	NZ	
.	B	DK	DK	CH	SLO	BR	IL	SLO	HR	DK	TM	
.	LT	SLO	RA	FIN	FIN	TJ	IRL	IL	AZ	NL	LV	
.	NZ	N	GR	RI	NL	LV	NL	AZ	DK	E	S	
40	CH	YV	LT	S	IRL	MAL	CH	HR	S	I	NL	
.	E	MEX	E	BG	GR	S	S	TM	LV	LV	PE	
.	FIN	BR	TM	KS	NZ	IRL	LV	BG	IRL	BG	PK	
.	SLO	S	BR	E	KS	IL	DK	MGL	FIN	CR	TJ	
.	NL	RI	BG	GR	S	FIN	MD	IRL	N	CH	E	
45	LV	TM	CH	BR	B	IS	E	MAL	E	IRL	MEX	
.	BR	B	NZ	TM	BR	I	BG	E	NL	MEX	CH	
.	S	IRL	IS	CY	CH	CY	TM	S	MGL	MGL	MGL	
.	YV	CH	IRL	YVA	P	N	HR	NL	PE	MAL	IL	
.	IRL	C	CY	IRL	IS	TM	PK	CH	PK	N	CY	
50	GR	CY	KS	IS	N	CH	N	ROU	SLO	S	BG	

(List of abbreviations see 105)

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