

XIX Baltic Chemistry Olympiad



Theoretical Problems

**15-17 April 2011
Vilnius, Lithuania**

Instructions

- Write your code in the top of each page of the answer sheets.
- You have 5 hours to work on the problems. Begin only when the START command is given.
- All results must be written in the appropriate boxes. Anything written elsewhere will not be graded. Use the reverse of the sheets if you need scratch paper.
- Write relevant calculations in the appropriate boxes when necessary. If you provide only correct end results for complicated problems, you receive no score.
- If answer does not fit into space provided, you should ask for additional answer sheets.
- You must stop your work immediately when the STOP command is given. A delay in doing this by 5 minutes may lead to cancellation of your exam.
- Do not leave your seat until permitted by the supervisors.
- This examination has 12 pages in tasks booklet and 12 pages in answer sheets.
- The official English version of this examination is available on request only for clarification.

Constants and Formulae

Avogadro constant:	$N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1}$	Ideal gas equation:	$pV = nRT$
Gas constant:	$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$	Gibbs energy:	$G = H - TS$
Faraday constant:	$F = 96485 \text{ C mol}^{-1}$	$\Delta_r G^\circ = -RT \ln K = -nFE_{\text{cell}}^\circ$	
Planck constant:	$h = 6.626 \cdot 10^{-34} \text{ J s}$	Nernst equation:	$E = E^\circ + \frac{RT}{zF} \ln \frac{P_{\text{ox}}}{P_{\text{red}}}$
Speed of light:	$c = 3.000 \cdot 10^8 \text{ m s}^{-1}$	activity	$a = \lambda N$
Arrhenius eq.	$k = A \cdot \exp(-E_A/RT)$	decay	$N = N_0 \cdot \exp(-\lambda t)$

In equilibrium constant calculations all concentrations are referenced to a standard concentration of 1 mol/dm^3 . Consider all gases ideal throughout the exam.

Periodic table with relative atomic masses

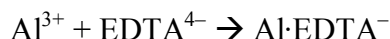
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Problem 1. Aluminium**6 points**

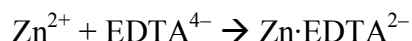
Aluminium is the most abundant metal in the Earth's crust. Some compounds of aluminium, like alum (the double sulphate $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) were in use since ancient Greece time.

- The freezing point depression constant for water is $K_f = 1.86 \text{ }^\circ\text{C kg mol}^{-1}$. Calculate the freezing point of the solution prepared by dissolving 9.48 g of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ in 100.0 g of water.
- The most important ore of aluminium is bauxite, which consists from Al_2O_3 and impurities. Bauxite can be purified by dissolving in concentrated NaOH solution. Write molecular equation that shows what is happening when Al_2O_3 reacts with NaOH solution.
- After removal of insoluble impurities, weak acid is added to the solution obtained in part b and $\text{Al}(\text{OH})_3$ is precipitating. Solubility product K_{sp} for $\text{Al}(\text{OH})_3$ is $1.3 \cdot 10^{-33}$ (at $25 \text{ }^\circ\text{C}$). Calculate mass of pure $\text{Al}(\text{OH})_3$ that can be dissolved in 10.0 L of pure water at $25 \text{ }^\circ\text{C}$.

EDTA (ethylenediaminetetraacetic acid or its salts) is among the most important and widely used reagents in titrimetry. Unfortunately, this reagent is not good for direct determination of aluminium ions, because EDTA reacts with aluminium ions too slowly. Problem can be solved by applying back titration method. In the beginning EDTA and aluminium compound solution are allowed to react in the hot solution for several minutes, and then excess EDTA can be fast and easily titrated with $\text{Zn}^{2+}(\text{aq})$. Analysis is performed in presence of buffer solution. Reactions taking place in this method can be represented as:



and



- 20.00 mL of solution, that contains Al^{3+} , was transferred into flask that contains 50.00 mL 0.0500 M EDTA solution. Mixture was boiled for several minutes. For titration of the resulting mixture 23.25 mL of 0.0500 M Zn^{2+} solution was necessary. Calculate molar concentration of Al^{3+} in the initial solution.

Trihalides of aluminium (like AlCl_3) are very strong Lewis acids and finds extensive use as catalysts. With some ligands L aluminium trichloride may form four-coordinated AlCl_3L or even five-coordinated AlCl_3L_2 .

- Assuming that L is a monodentate ligand, draw all possible geometrical isomers of AlCl_3L_2 .
- In gas phase aluminium trichloride exists as Al_2Cl_6 molecules with two bridging Cl atoms. Make a drawing that represents spatial structure of Al_2Cl_6 molecule.

Problem 2

Beware of light!

10 pointys

Students found in a laboratory a bottle with little bit wet reagent **A**, which had label „light sensitive”. Students have not paid attention to this label, and left the bottle on the bench over the summer break. As a result, the bottle was in direct sunlight for several hours a day. After the summer break students noticed that some changes happened to the content of the bottle. There were three compounds formed: **B**, **C** and **D**.

Compound **A** is also used to increase solubility of **C** in aqueous solutions. In this process anion **E** is formed, which is also a part of compound **D**. If concentrated solutions of **A** are mixed with concentrated solution **B** and then the obtained solution are allowed to react with some yellow-green gas **F**, two new compounds are formed. Of this mixture, compound **G** in acidic media reacts with **A**, which leads to **C** as one of the products. Oxygen content in compound **G** is 22.4% (by mass). If compound **G** reacts with the acid derived from **F**, which consist of only two elements, the reaction leads to **C**, **F** and two other products.

1. Provide formulae for compounds **A** - **G** and reaction equations for all mentioned processes.
2. Why **A** is light sensitive and nothing happens if it is stored in the dark?
Mark correct answer(-s).

- a. light is form of activation energy provided
- b. light initiates electrolytic dissociation
- c. light initiates formation of radicals
- d. light is oxidizing agent
- e. light is reducing agent

3. Why the solubility of **C** in water increases if compound **A** is added?
4. Draw the Lewis structure of anion **E**.
5. Calculate maximum pH, at which a reaction between **A** and **G** still proceeds at 25 °C, if $[G] = 0.25\text{M}$ and $[A] = 0.10\text{M}$. $E^\circ(\text{A}) = 0.536\text{ V}$, $E^\circ(\text{G}) = 1.195\text{ V}$.

Before summer holidays started students used compound **A** for investigation of reaction kinetics. It is known that compound **A** reacts with persulphate ions ($\text{S}_2\text{O}_8^{2-}$) forming compound **C** and sulphate ions. Investigating kinetics at 25°C temperature

they obtained data of initial reaction rate v_0 depending on reactant concentrations C_0 . These data are shown in table 1.

Table 1

$C_0(\text{S}_2\text{O}_8^{2-})$, mmol/L	$C_0(\text{A})$, mmol/L	$v_0 \times 10^8$ mol/(L×s)
0.10	10	1.1
0.20	10	2.2
0.20	5.0	1.1

6. Write balanced chemical equation for reaction of persulphate ions with compound **A** (net ionic equation is also acceptable).
7. Determine reaction partial orders, write kinetic expression and calculate reaction rate constant at 25°C.
8. They found in literature that activation energy for this reaction is 42kJ/mol. Calculate temperature (in °C) needed to increase reaction rate 10 times if reactant concentrations remains the same.
9. Calculate what time (in hours) is necessary to decrease reactant concentrations 10 times if initial concentrations for both reactants are equal with 1.0 mmol/L at 25°C temperature.

Problem 3. Ordinary Physical Chemistry**7 points**

Part I. Initial conditions of the reaction $\text{H}_2 + \text{N}_2 \rightarrow \text{NH}_3$ is $n_0(\text{H}_2) = n_0(\text{N}_2)$, $n_0(\text{NH}_3) = 0$. At 400 °C equilibrium constant K_p of the reaction is $1,60 \cdot 10^{-4} \text{ bar}^{-2}$.

a) Write the equation of the reaction.

b) Express analytically the mole fraction $x(\text{NH}_3)$ and K_p in terms of a ratio y , which is a fraction of the amount of produced ammonia to twice the initial amount of reagents, $y = n_\infty(\text{NH}_3)/2n_0$ or $n_\infty(\text{NH}_3) = 2yn_0$.

c) Calculate the pressure (bar), under which the partial pressure of NH_3 equals 11.11% of total pressure.

Part II. Mixture of gases containing CO , H_2 , and CH_3OH is blown over a catalyst at 500 K.

d) Would methanol form in the reaction $\text{CO} + \text{H}_2 \rightarrow \text{CH}_3\text{OH}$ under the given conditions: $p_{\text{CO}} = 9p_{\text{H}_2} = 99p_{\text{CH}_3\text{OH}}$, $p_{\text{CH}_3\text{OH}} = 0.099 \text{ bar}$, and $\Delta_r G^\circ = 21.21 \text{ kJ/mol}$.

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q$$

e) Calculate the value of Q when $\Delta_r G = 0$. Is it the minimal or maximal value above or below which the equilibrium is shifted towards methanol production?

Problem 4. Smart robot**13 points**

The hero of the movie “Star Wars” – a very intelligent robot R2-D2 received 20.0 mg of radioactive sample **P** known to contain only element **A**. Robot divided this sample into two halves of equal masses. With the help of gas diffusion method he quickly separated the first half into two parts. He obtained two equal volumes of gasses (under appropriate conditions) which weights were 4.92 and 5.08 mg; activities equaled $5.19 \cdot 10^{13}$ and $2.94 \cdot 10^{13}$ decays per second, correspondingly. These two were isotopes of element **A**. R2-D2 chlorinated the second half of the sample yielding higher chloride **B** which after hydrolysis in water gave a solution of triprotic acid **C** and strong acid **D**. This solution was titrated with 19.95 cm³ of 0.1234 M NaOH solution.

a) Write the chemical symbols for element **A** and formulas for compounds **B–D**.

b) Write four equations for the reactions mentioned above.

c) Provide calculations to confirm the validity of your solution.

d) By what time all the sample will have almost completely decayed, i.e. total remaining activity would be less than 0.1% of the initial one.

R2-D2 found that after this time the remaining 10.0 mg of sample **P** consisted of two isotopes of element **E**. Robot could not resist the delight of chlorinating them. As a result he obtained yellow substance **F**. When hydrolysed in water substance **F** formed diprotic weak acid **G**, diprotic oxoacid **H**, and acid **D**. This solution was titrated with 2.136 cm³ of 0.4321 M NaOH solution.

e) Write the chemical symbols for element **E** and formulas for compounds **F–H**.

f) Write five equations for chemical reactions and two reactions of radioactive decay of isotopes of element **A**.

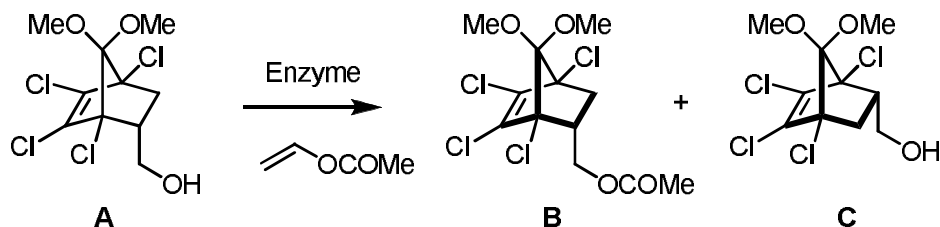
g) Provide calculations to confirm the validity of your solution.

Hint: Assume that molar mass of an isotope is an integer number.

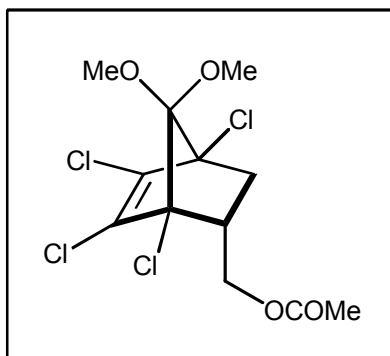
Problem 5. Chiral polyhydroxylated cyclohexanoids. 11 points

It is supposed that enantiomerically pure polyhydroxylated cyclohexanoids could be useful for the treatment of diabetes, viral infections and cancers.

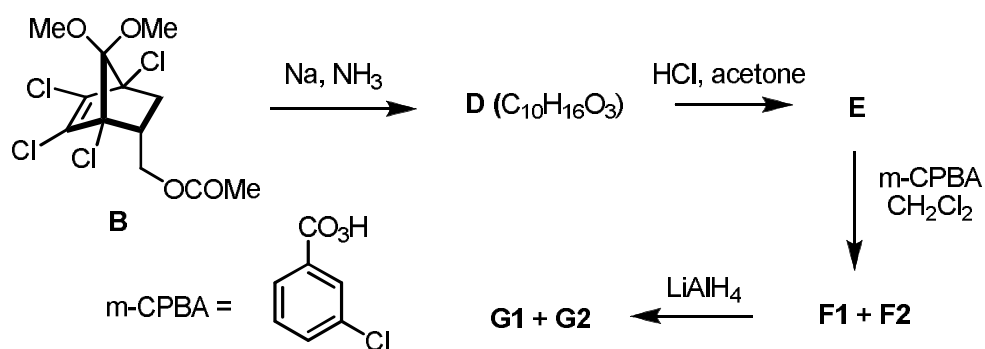
The scheme shows enzyme-catalyzed kinetic enantiomeric separation of compound **B**:



1. Which class of enzymes will catalyze this reaction? (select the appropriate class of enzymes)
 - a) oxidoreductase
 - b) isomerase
 - c) lipase
 - d) ligase
2. What is the maximum yield of compound **B**?
 - a) 100 %
 - b) 90 %
 - c) 75 %
 - d) 50 %
3. Find chiral centers of compound **B** and indicate their configurations.



One of the ICHO'43 organizers C. Tanyeli from Turkey Ankara Middle East Technical University used **B** as a starting compound for synthesis of enantiomerically pure polyhydroxylated compounds **G1** and **G2**:



4. Draw the entire structures of compounds **D-G**.

5. In respect to each other compounds **G1** and **G2** are:

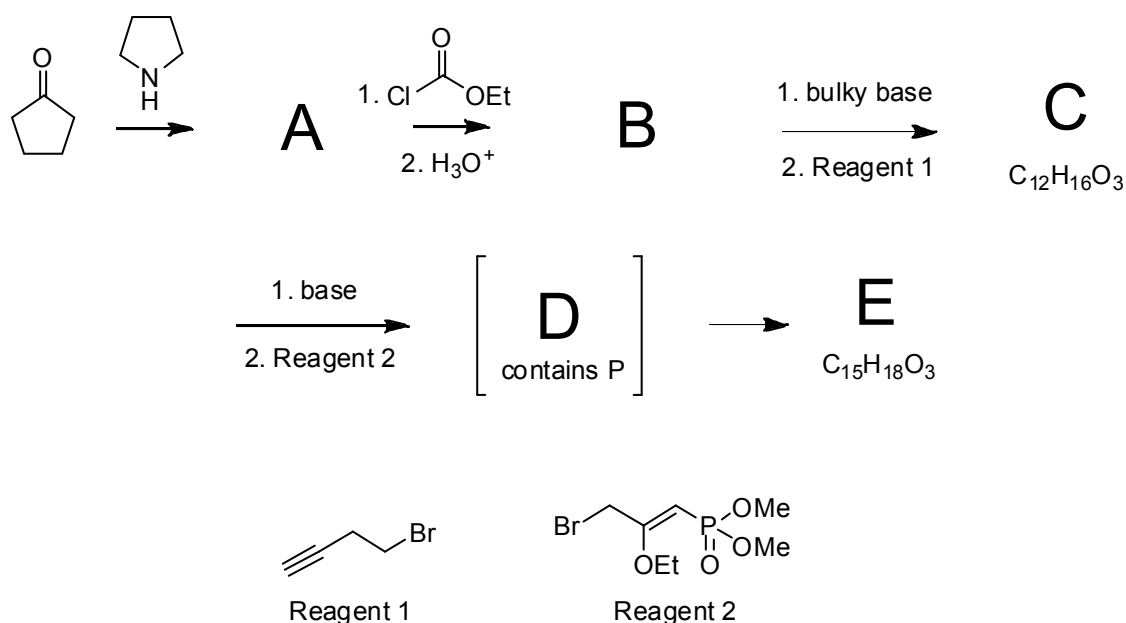
- a) enantiomers
- b) structural isomers
- c) diastereomers
- d) conformers.

Problem 6. The hunt for the flat carbon. 13 points

Incorporating a “flat” carbon atom in sp^3 hybridization in a molecule would be very exciting achievement from theoretical point of view. Such geometry is associated with enormous amount of strain and it is a huge challenge to incorporate such element in a “stable” molecule.

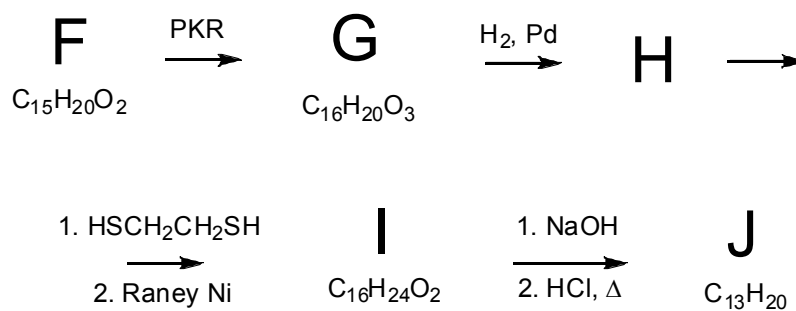
A special class of compounds – fenestranes, could as well be an answer to this scientific challenge, although it must be noted that the most desirable symmetrical C_9 fenestrane, which could planar symmetry, is not yet synthesized.

The problem outlined below shows the synthesis of C_{13} symmetrical fenestrane, even though bond angles in this molecule are distorted to a large extent, the planar symmetry around carbon atom is not achieved.



- Bulky base = 2 equivalents of sterically crowded base like LDA (lithium diisopropylamide)
- Theoretical amount of base needed to obtain **D** is one mole
- The base used in deprotonation of **C** does not react with terminal alkyne
- **D** is formed in the initial S_N2 reaction and contains phosphorus, under acidic workup conditions this compound is not stable and it converts into **E**
- **E** is C_8 bicyclic compound.

Further carbon skeleton construction required the *Pauson-Khand reaction* (PKR). In general PKR involves alkyne, alkene and carbon monoxide. In the presence of cobalt catalyst PKR leads to a formation of cyclopentenone ring. **Note!** In order to apply PKR in the present synthesis, carbonyl group in **E** was removed to give **F**.



- **G** already possesses the carbon skeleton found in **J**.
- **J** is very symmetrical.

1. Give structure of compounds **A-J**
2. Suggest a mechanism for transformation **D** \rightarrow **E**