

19th BChO, 2011, Vilnius, Lithuania

Problem 1 – EQUIL, STRUCT – Aluminum

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

- a) 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.
- b) The most important aluminum ore is bauxite, which contains Al_2O_3 and impurities. Bauxite can be purified by dissolving in a concentrated NaOH solution. Write a molecular equation that shows what happens when Al_2O_3 reacts with NaOH solution.
- c) After removing insoluble impurities, a 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 the mass of pure $\text{Al}(\text{OH})_3$ that can be dissolved in 10.0 dm^3 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 the direct determination of aluminum ions because EDTA reacts with aluminum ions too slowly. The problem can be solved by applying the back titration method. In the beginning, EDTA and aluminum compound solution are allowed to react in the hot solution for several minutes, and then excess EDTA can be fast and easily titrated with $\text{Zn}^{2+}(\text{aq})$. The analysis is performed in the presence of a buffer solution. Reactions taking place in this method can be represented as $\text{Al}^{3+} + \text{EDTA}^{4-} \rightarrow \text{AlEDTA}^-$ and $\text{Zn}^{2+} + \text{EDTA}^{4-} \rightarrow \text{ZnEDTA}^{2-}$.

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

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

- e) Assuming that L is a monodentate ligand, draw all possible geometrical isomers of AlCl_3L_2 .
- f) In the gas phase, aluminum trichloride is an Al_2Cl_6 molecule with two bridging Cl atoms. Make a drawing that represents the spatial structure of the Al_2Cl_6 molecule.

Problem 2 – ABC, KINETICS – Beware of light!

Students found in a laboratory a bottle with a little bit of wet reagent **A**, which had the 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 had happened to the content of the bottle. There were three compounds formed: **B**, **C** and **D**. Compound **A** is also used to increase the 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 is 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 consists of only two elements, the reaction leads to **C**, **F** and two other products.

- Write the chemical formulas of compounds **A–G**.
- Write reaction equations for all mentioned processes.
- Why is compound **A** sensitive to light but nothing happens if it is stored in the dark?
 - ☐ Light is a form of activation energy provided.
 - ☐ Light initiates electrolytic dissociation.
 - ☐ Light initiates the formation of radicals.
 - ☐ Light is an oxidizing agent.
 - ☐ Light is a reducing agent.
- Why does the solubility of **C** in water increase if compound **A** is added?
- Draw the Lewis structure of anion **E**.
- Calculate the maximum pH at which a reaction between **A** and **G** still proceeds at 25 °C, if $[G] = 0.25 \text{ M}$ and $[A] = 0.10 \text{ M}$. $E^\circ(A) = 0.536 \text{ V}$, $E^\circ(G) = 1.195 \text{ V}$.

Before the summer holidays started, students used compound **A** to investigate reaction kinetics. It is known that compound **A** reacts with persulfate ions ($S_2O_8^{2-}$) forming compound **C** and sulfate ions. Investigating kinetics at 25 °C temperature, they obtained data of initial reaction rate v_0 depending on reactant concentrations c_0 . The data are shown in the table.

$c_0(S_2O_8^{2-}), \text{ mM}$	$c_0(A), \text{ mM}$	$v_0 \times 10^8, \text{ mol dm}^{-3} \text{ s}^{-1}$
0.10	10	1.1
0.20	10	2.2
0.20	5.0	1.1

- Write the chemical equation for the reaction of persulfate ions with compound **A**.
- Determine reaction partial orders, write a kinetic expression and calculate reaction rate constant at 25 °C.
- They found in literature that activation energy for this reaction is 42 kJ mol^{-1} . Calculate the temperature (in °C) needed to increase the reaction rate 10 times if reactant concentrations remain the same.
- Calculate what time (in hours) is necessary to decrease reactant concentrations 10 times if initial concentrations for both reactants are equal to 1.0 mmol dm^{-3} at 25 °C.

Problem 3 – EQUILIB – Ordinary Physical Chemistry

Part I.

Initial conditions of the reaction $H_2 + N_2 \rightarrow NH_3$ is $n_0(H_2) = n_0(N_2)$, $n_0(NH_3) = 0$. At 400 °C, the equilibrium constant K_p of the reaction is $1.60 \cdot 10^{-14} \text{ Pa}^{-2}$.

- Write the reaction equation.
- Express analytically the mole fraction $x(NH_3)$ 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, $y = n_\infty(NH_3)/2n_0$ or $n_\infty(NH_3) = 2yn_0$.
- Calculate the pressure (Pa) under which the partial pressure of NH_3 is 11.11% of the total.

Part II.

A mixture of gases containing CO, H₂, and CH₃OH 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:

$$p_{\text{CO}} = 9p_{\text{H}_2} = 99p_{\text{CH}_3\text{OH}}, p_{\text{CH}_3\text{OH}} = 9900 \text{ Pa, and } \Delta G_r^\circ = 21.21 \text{ kJ mol}^{-1}.$$

e) Calculate the value of Q when $\Delta G_r = 0 = \Delta G_r^\circ + RT \ln Q$. Is it the minimal or maximal value above or below which the equilibrium is shifted towards methanol production?

Problem 4 – ABC, INORG – Smart robot

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**. The robot divided this sample into two halves of equal masses. With the help of the gas diffusion method, it quickly separated the first half into two parts. It obtained two equal volumes of gases (under appropriate conditions) whose weights were 4.92 and 5.08 mg; activities equaled $5.19 \cdot 10^{13}$ and $2.94 \cdot 10^{13}$ decays per second, respectively. 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.

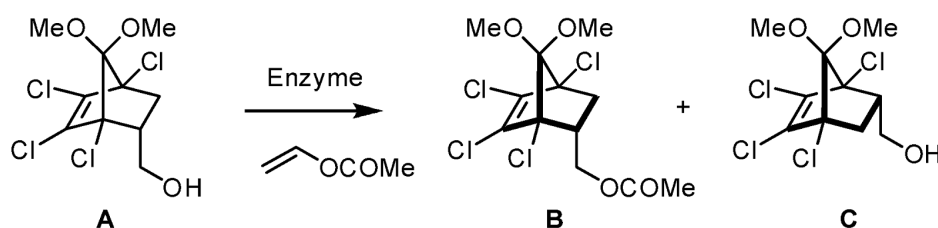
- Write the chemical symbols for element **A** and formulas for compounds **B–D**.
- Write four equations for the reactions mentioned above.
- Provide calculations to confirm the validity of your solution.
- By what time will all the samples have almost completely decayed, i.e. would the total remaining activity 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, it obtained yellow substance **F**. When hydrolyzed in water, substance **F** formed diprotic weak acid **G**, diprotic oxyacid **H**, and acid **D**. This solution was titrated with 2.136 cm³ of 0.4321 M NaOH solution.

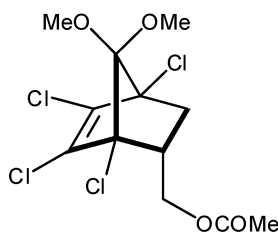
- Write the chemical symbols for element **E** and formulas for compounds **F–H**.
- Write five equations for chemical reactions and two reactions of radioactive decay of isotopes of element **A**.
- Provide calculations to confirm the validity of your solution. *Hint: Assume that the molar mass of an isotope is an integer number.*

Problem 5 – BIO, STEREO – Chiral polyhydroxylated cyclohexanoids

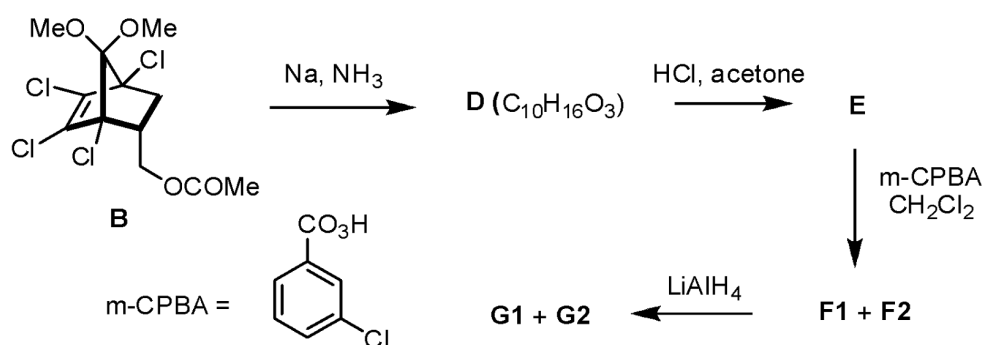
Enantiomerically pure polyhydroxylated cyclohexanoids could be useful for treating diabetes, viral infections, and cancers. The scheme shows the enzyme-catalyzed kinetic enantiomeric separation of compound **B**:



- a) Which class of enzymes will catalyze this reaction: **i)** oxidoreductase, **ii)** isomerase, **iii)** lipase, **iv)** ligase?
- b) What is the maximum yield of compound **B**: **i)** 100%, **ii)** 90%, **iii)** 75%, **iv)** 50%?
- c) Identify chiral centers of compound **B** and indicate their configurations.



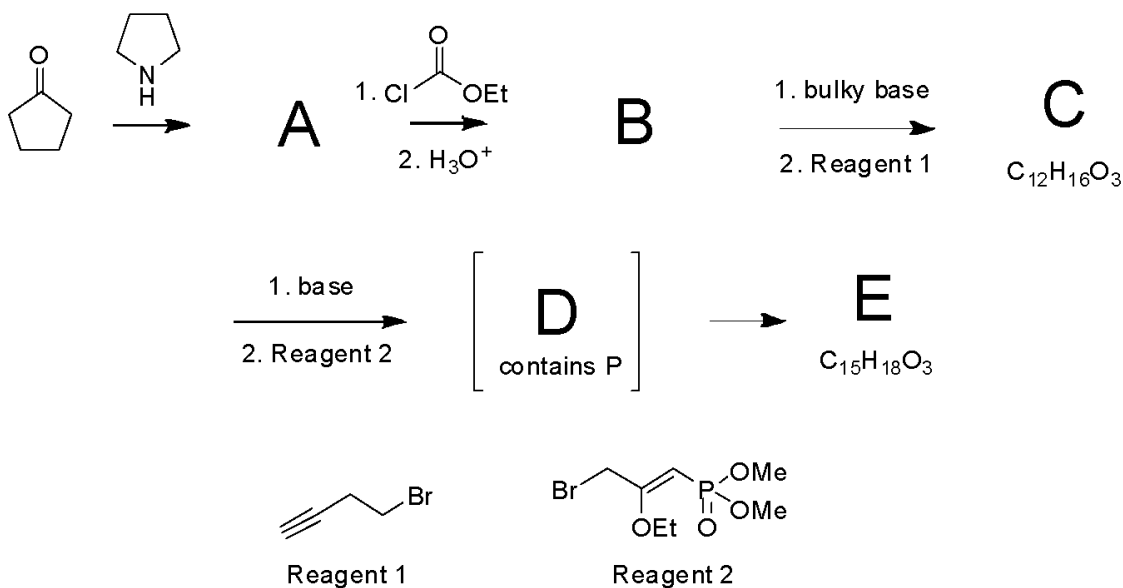
Compound **B** is a starting compound for the synthesis of enantiomerically pure polyhydroxylated compounds **G1** and **G2**:



- d) Draw the structural formulas of compounds **D–G**.
- e) With respect to each other, compounds **G1** and **G2** are: **i)** enantiomers, **ii)** structural isomers, **iii)** diastereomers, **iv)** conformers.

Problem 6 – SYNTH – The hunt for the flat carbon

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

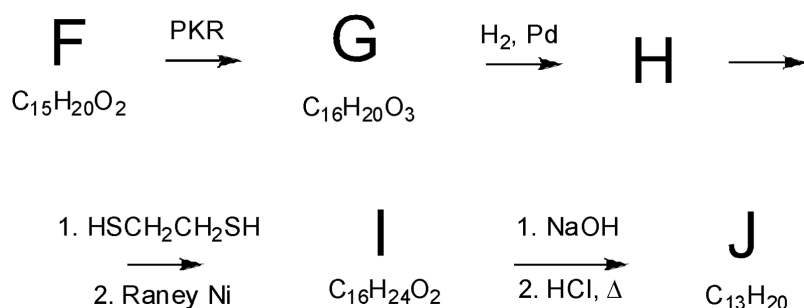


A special class of compounds – fenestranes, could as well be an answer to this scientific challenge. However, it must be noted that the most desirable symmetrical C_9 fenestrane, which could have planar symmetry, has not yet been synthesized.

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 the carbon atom is not achieved.

- Bulky base means 2 equivalents of sterically hindered (bulky) base like LDA.
- The theoretical amount of base needed to obtain **D** is one mole.
- The base used in the 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 unstable and converts into **E**.
- **E** is a 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 a cobalt catalyst, PKR leads to the formation of a cyclopentenone ring. Note: In order to apply PKR in the present synthesis, the carbonyl group in **E** was removed to give **F**.



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

- Draw the structural formulas of compounds **A–J**.
- Suggest a mechanism for transformation **D** $\rightarrow$ **E**.