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# 55 Chemistry Olympiad

## Final competitions (28.03.2009)

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### *Theoretical tasks and solutions*

#### TASK I:

##### **Enzymatic biosensors**

Modern analytical chemistry often faces the need of assessment of biologically important compounds. Among possible procedures, methods using enzymes, specific for the analyte, are especially useful. In course of enzymatic reaction a product (of amount dependent on the concentration of reaction substrate) is obtained which can be easily detected or quantitatively determined.

A model of enzymatic reaction is taken into consideration, where  $\text{OH}^-$  ions are released, according to the scheme:  $\text{S} \xrightarrow{\text{enzyme}} \text{P} + \text{OH}^-$ , where S is the substrate – analyte, P is product (*generally, S and P can be ions or neutral molecules*).

The reaction occurs in the presence of a buffer, necessary to maintain the proper functioning of the enzyme. The assessment is based on monitoring of pH increase resulting from enzymatic reaction and consumption of S.

Measurements were carried out in solution of volume 1 mL, containing phosphoric buffer ( $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$  of equal concentrations) and enzyme. The substrate, S, of concentration in the range from 0.001 do 0.005 M was subsequently added to the solution. Assuming that the substrate and enzyme concentrations are constant, the following dependence is fulfilled:  $\eta = k [\text{S}] t$ , where  $\eta$  is number of moles of  $\text{OH}^-$  ions, produced in a time unit,  $t$  is time from substrate addition and  $k$  is a constant, characteristic for a given enzyme concentration.

##### **Problems:**

- Under applied experimental conditions  $k = 0,004 \text{ min}^{-1}$ . Specify the concentration of the buffer which should be chosen to obtain maximal pH changes (but not exceeding one unit) after 10 minutes and for the given concentration range of the substrate. Explain your suggestion. You can use buffers of the following concentrations (both acidic and basic form): 0.05, 0.005, 0.0005, 0.0001 M.
- For the selected buffer calculate the initial pH (before substrate addition) and pH recorded after 10 minutes for two separate additions of substrate to yield concentration in the studied solution: 0.001 and 0.005 M.
- Indicate the direction of changes and calculate the changes of potential of a pH-metric electrode ( $\Delta E$ ) resulting from above (point **b**) described additions of the substrate to the buffer (i.e. of concentrations in the studied solution: 0.001 and 0.005 M). Potential of the electrode,  $E$  (expressed in mV) is described by equation:  $E = \text{const} - 59 \cdot \text{pH}$ .
- Calculate the concentration of substrate S in the sample, if the recorded potential change was equal to 10 mV. Assuming that the lowest measurable potential change is 1 mV, calculate the minimal concentration of S, which can be determined using his method.
- Propose two ways to decrease the minimal concentration, measurable using his method.

Dissociation constants for phosphoric acid:

$$K_{a1} = 6 \cdot 10^{-3}; \quad K_{a2} = 6 \cdot 10^{-8}; \quad K_{a3} = 5 \cdot 10^{-13}$$

## TASK 2

### **Boron compounds**

Salt **A** was crystallized from the water solution obtained by neutralization of 40 % solution of tetrafluoroboric acid with lithium hydroxide. Then, 11.25 g ( $m_1$ ) of **A** was heated to 350 °C, resulting in evolution of gas (compound **B**), which was absorbed in diethyl ether. The weight of the solid product of thermal decomposition (compound **C**) was equal to 3.1128 g ( $m_2$ ). The ether solution of compound **B** was used in subsequent reactions under dry nitrogen.

In the reaction I the reagents were used in 3:4 molar ratio (LiH: **B**) leading to the formation of gaseous compound **D**. As the result of ethyl ether evaporation from the resulting solution, compound **A** was crystallized. Compound **D** is a very reactive and toxic gas of density equal to 1.23 kg/m<sup>3</sup> (standard conditions), oxidizing in air and reacting readily with water.

0.763 g of LiH and 1/5 of the obtained ether solution of **B** were used in reaction II. During reaction no gaseous products were observed, but among others the ionic compound **E** was formed. Then ether solution containing 1.90 g of trimethylamine hydrofluoride was added to the post-reaction mixture. Evaporation of ethyl ether resulted in formation of mixture of products. White crystalline compound **F** was further isolated by sublimation, while compound **C** was identified as the only remaining product. Elemental analysis of compound **F** revealed the following composition: 14.8 % B, 49.4 % C and 19.2 % N.

In the reaction III, 1.182 g of trimethylamine was added to 1/6 of ethyl ether solution of **B**. As a result of solvent evaporation compound **G** was obtained and subsequently purified by vacuum sublimation. 2.31 g of **G** was isolated as hexagonal crystals isotypic with crystals of compound **F**.

### Problems:

- Provide a chemical equation for the thermal decomposition reaction of **A** and give the chemical formulas of compounds **B** and **C**.
- Provide a chemical formula of compound **D** and equation representing its synthesis (reaction I). Draw a molecular structure and describe bonds in compound **D**.
- Provide a chemical equation for the reaction of compound **D** with water.
- Provide a chemical formula of compound **E** and equation representing its synthesis (reaction II). Propose the structure of anion present in this compound. Provide the explanation along with appropriate calculations.
- Provide a chemical formula of compound **F** and equation representing its synthesis. Give an explanation supported by appropriate calculations.
- Provide a chemical formula of compound **G** and its molecular structure. Calculate the yield of synthesis reaction of compound **G**.

For calculations use the following molar masses:

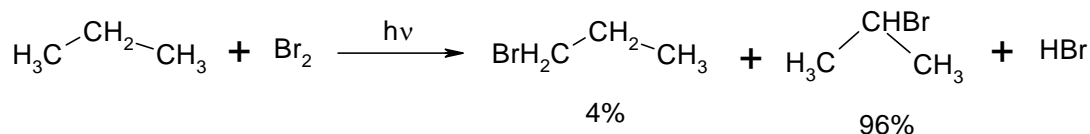
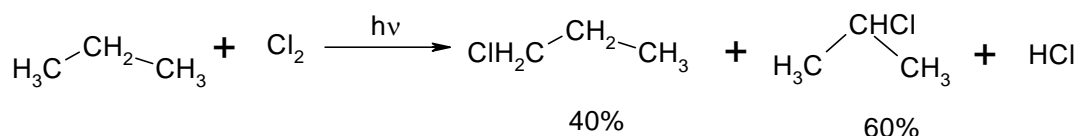
H – 1.008 g/mol; B – 10.81 g/mol; N – 14.01 g/mol; C – 12.01 g/mol; F – 19.00 g/mol; Li – 6.94 g/mol;

and the molar gas volume at normal conditions equal to  $V_m=22,41 \cdot 10^{-3} \text{ m}^3/\text{mol}$ .

## TASK 3

### **Selectivity of the radical chain reaction**

Reactions of alkanes with halogens proceed according to the radical chain mechanism consisting of the following general steps: initiation, propagation and termination. The selectivity is determined by the relative rates of formation of different alkyl radicals from a starting alkane. It depends strongly on the kind of halogen, as illustrated by reactions of propane with dichlorine and dibromine, which result in the formation of mixtures of corresponding monohalogenated propane derivatives in different proportions (reactions conditions were optimized to minimize the formation of polyhalogenated products):



The useful thermochemical data, i.e. enthalpies of bond dissociation  $\Delta H_d$ , are given below:

Bond	$\Delta H_d$ , kJ mol <sup>-1</sup>
Cl-Cl	+242
Br-Br	+193
H-Cl	+431
H-Br	+366
H-(1-propyl)	+410
H-(2-propyl)	+395

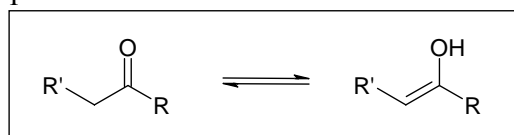
### Problems:

- Calculate the relative reactivities of primary and secondary hydrogen atoms in reactions of propane with dichlorine and dibromine.
- Write the mechanism of the reaction of propane with dichlorine yielding 2-chloropropane consisting of initiation (1 step), propagation (2 steps) and termination (1 of several possible reactions).
- Based on the proper thermochemical data calculate enthalpies of elemental parallel reactions of chlorine-induced formation of 1- and 2-propyl radicals ( $\Delta H_I$ ,  $\Delta H_{II}$ ), as well as analogous reactions with bromine ( $\Delta H_{III}$ ,  $\Delta H_{IV}$ ). Compare results of calculations. What is the difference of enthalpies of parallel reactions of formation of 1- and 2-propyl radicals?
- Draw the reaction-energy diagram illustrating the course of parallel reactions of chlorine-induced formation of 1- and 2-propyl radicals (with energy maxima for corresponding transition states). Notice that the energy difference changes monotonically. The diagram should be correctly drawn to scale and properly described. Draw lines related to activation energies and enthalpies of both reactions. Draw the analogous diagram for the reaction with bromine.
- Compare both diagrams from the point of view of difference of activation energies. Which diagram exhibits the bigger difference of activation energies? Is it in agreement with experimental results concerning the selectivities of propane halogenation? Give the explanation.
- Calculate the difference of activation energies for both parallel reactions ( $\Delta E_{a(I,II)}$  and  $\Delta E_{a(III,IV)}$ ) using Arrhenius' equation and results obtained in *a*. Assume that the preexponential factor *A* is equal for both reactions and that the temperature is  $T = 298$  K.

### TASK 4

#### Enols and enolates in organic chemistry

Scheme 1 depicts a phenomenon, which on the one hand is a basis of many important organic reactions, but on the other hand often causes unfavorable side reactions. Below, several problems related to this phenomenon are presented.

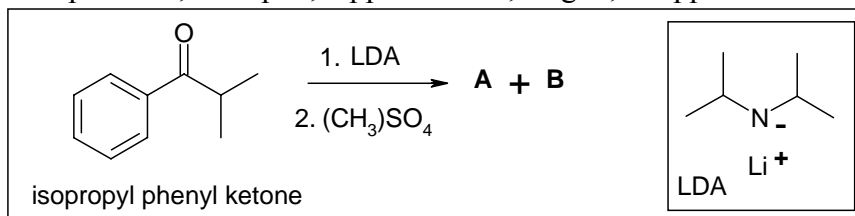


Scheme 1

1. Isopropyl phenyl ketone was treated with LDA (Lithium diisopropylamide), and then alkylated with dimethyl sulphate (see scheme 2). As a result of the reaction two products were obtained, **A** and **B**. The ratio of these products could be changed by modifying reaction conditions. Polar, aprotic solvents (e.g. HMPA, hexamethylphosphoramide) would increase amount of product **A**, whereas tert-butyl alcohol, in opposite, would increase amount of product **B**.

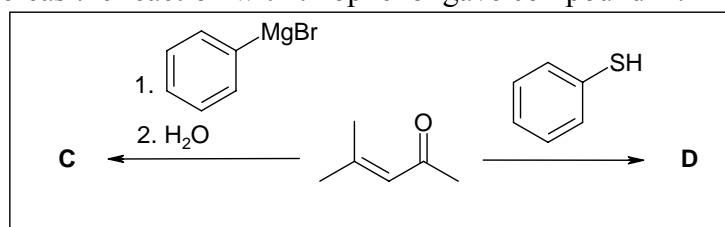
$^1\text{H}$  NMR data of comp. **A**: 5H, multiplet, 7 ppm; 3H, singlet, 3.3 ppm; 3H, singlet, 1.8 ppm; 3H, singlet, 1.7 ppm

$^1\text{H}$  NMR data of comp. **B**: 5H, multiplet, 7 ppm and 9H, singlet, 1.2 ppm



Scheme 2

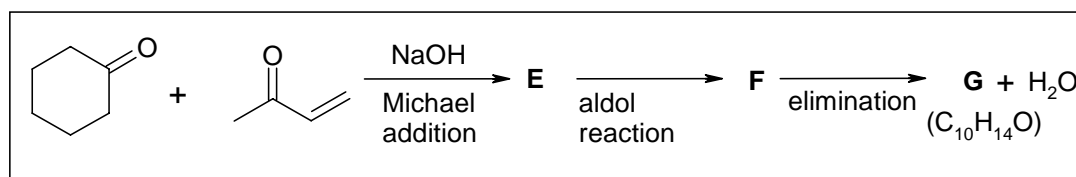
2. An alpha-beta unsaturated ketone, depicted in scheme 3, undergoes 1,2- or 1,4- addition reaction (Michael addition) depending on the used nucleophile. The reaction with Grignard reagent gave compound **C**, whereas the reaction with thiophenol gave compound **D**.



Scheme 3

3. Cyclohexanone and methyl vinyl ketone treated with base undergo Robinson annulation (scheme 4). This is a process, which includes three steps. The first of them is the above-mentioned Michael addition, subsequently intermediate **E** obtained during this reaction undergoes intramolecular aldol reaction leading to compound **F**, which finally undergoes elimination giving the product of Robinson annulation (**G**) with formula  $\text{C}_{10}\text{H}_{14}\text{O}$ .

The most important  $^1\text{H}$  NMR and IR data of comp. **G**: In IR spectrum an intensive band at  $1705\text{ cm}^{-1}$  is observed. In  $^1\text{H}$  NMR spectrum a number of signals characteristic for protons bound to  $\text{sp}^3$ -hybridized carbon atoms are observed and one signal characteristic to proton bound to  $\text{sp}^2$ -hybridized carbon atom.



Scheme 4

**Note:** an interpretation of spectroscopic data plays supporting role and is not required in solution of the problem

**Problems:**

- Name the phenomenon depicted in scheme 1.
- Draw structural formulas of the compounds **A** and **B**.
- Explain the effect of solvent on the distribution of alkylation products described in sub-item 1.
- In sentence: "LDA is a strong/weak Brønsted base and a strong/weak nucleophile" cross out two words, to make this sentence true. Explain your choice shortly.
- Draw structural formulas of the compounds **C** and **D**.

- f. Using theory of soft and hard acids and bases (HSAB) explain the structures of the formed products **C** and **D**.
- g. Draw structural formulas of the intermediates **C**, **D** and the final product of Robinson annulation **G**.

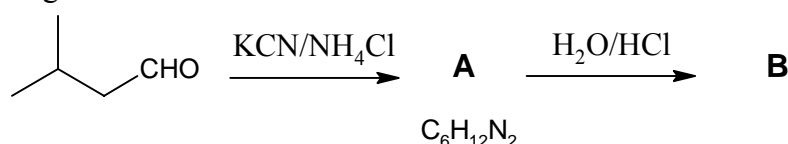
### TASK 5

#### *Peptides and peptidomimetics*

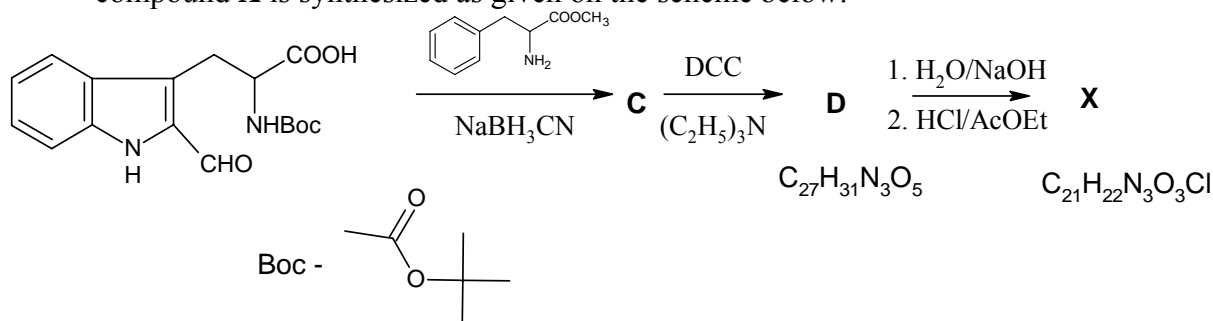
In the studies of peptides structure activity relationship (SAR) analogs of parent peptides are used. Such analogs contain so-called “constrained amino acids” (with restricted rotation of side chains). Those analogs (peptidomimetics) are useful in the conformation analysis of parent peptide. It may be helpful in the determination of position of amino acids’ side chains essential for biological activity.

Give the structure of a **peptidomimetic P** knowing that:

- a peptidomimetic **P** is formed by 2 amino acids residues and the **X** residue ;
- the molar mass of **P** is 533 g/mol;
- in the reaction of **P** with 1-fluoro-2,4-dinitrobenzene (DNFB) the derivative with the molar mass 241 g/mol is obtained
- after digestion with carboxypeptidase the amino acid is isolated; that amino acid is synthesized as given on the scheme below:



- compound **X** is synthesized as given on the scheme below:



(DCC – dicyclohexyl carbodiimide, coupling reagent)

#### Problems:

- a. What is the *N*-terminus amino acid? Explain briefly your choice.
- b. Draw the structural formulas of compounds **A**, **B**, **C**, **D** (without stereochemistry determination).
- c. Draw the structural formula of peptidomimetic **P** (without stereochemistry determination) and explain briefly your choice.
- d. Peptidomimetic **P** was designed to determine the conformation of some side chains in parent linear peptide **I** (molar mass 521 g/mol). Give the sequence of peptide **I** and draw its structural formula. Use the following molar masses: H-1 g/mol, C-12 g/mol, N-14 g/mol, O-16g/mol.

## SOLUTIONS

### SOLUTION OF TASK 1

- a.** From equation  $\eta = 0,004[S] t$ , it follows that for time  $t = 10$  minutes and maximal concentration  $[S] = 0.005$  M, the reaction results in release of  $0.0002 \text{ mol}\cdot\text{L}^{-1} \text{ OH}^-$  ions, i.e. 0.0002 millimoles in 1 mL of reaction medium. Therefore, the buffer with concentrations of both acidic and basic forms 0.0005 M should be chosen. Under such conditions pH changes of the buffer will be sufficiently high due to low buffer capacity, but not all acidic form ( $\text{H}_2\text{PO}_4^-$ ) will be consumed in reaction with  $\text{OH}^-$  ions (which would result in large pH increase).
- b.** Following  $\text{OH}^-$  ions release (resulting from enzymatic reaction) into the phosphoric buffer solution, the following reaction occurs:  $\text{H}_2\text{PO}_4^- + \text{OH}^- \rightarrow \text{HPO}_4^{2-} + \text{H}_2\text{O}$ , i.e. the acidic form of the buffer is transformed into the basic one.

pH value of phosphoric buffer can be described by equation:

$$\text{pH} = \text{p}K_{a2} + \log \frac{n(\text{HPO}_4^{2-})}{n(\text{H}_2\text{PO}_4^-)}, \text{ where } n \text{ denotes number of millimoles of the form given in}$$

parentheses.

Before substrate addition, numbers of moles of acidic and basic forms were equal, i.e.  $\text{pH} = \text{p}K_{a2} = -\log(6 \cdot 10^{-8}) = 7,22$ .

Following substrate addition and  $\text{OH}^-$  release, number of moles of acidic and basic forms changes:  $n(\text{HPO}_4^{2-}) = n^0(\text{HPO}_4^{2-}) + n(\text{OH}^-)$  and  $n(\text{H}_2\text{PO}_4^-) = n^0(\text{H}_2\text{PO}_4^-) - n(\text{OH}^-)$ , where  $n^0$  denotes initial number of millimoles,  $n(\text{OH}^-)$  is number of millimoles of produced  $\text{OH}^-$  ions.

For S concentrations equal to 0.001 and 0.005 M, number of millimoles of produced  $\text{OH}^-$  ions is  $4 \cdot 10^{-5}$  and  $2 \cdot 10^{-4}$  millimoles, respectively.

Assuming that  $n^0(\text{H}_2\text{PO}_4^-) = n^0(\text{HPO}_4^{2-}) = 0.0005$  millimoles and using equation given in the text, the following results can be obtained (see Table below).

Concentration S / M	pH	$\Delta E$ / mV
0	7.22	0
0.001	7.29	-4
0.005	7.59	-22

- c.** Increasing pH results in decrease of potential. Using equation describing the electrode potential,  $\Delta E$  values can be calculated, i.e. decrease in potential in relation to the substrate free buffer; these data were also included in the Table.
- d.** Potential decrease 10 mV corresponds to pH increase equal to  $10/59 = 0.17$  units. After inserting into equation:

$$\log \frac{0.0005 + x}{0.0005 - x} = 0.17, \text{ where } x \text{ is number of millimoles of produced } \text{OH}^- \text{ ions, after solution one obtains } x = 9.6 \cdot 10^{-5} \text{ millimoles } \text{OH}^-. \text{ This corresponds to substrate concentration } [S] = 2.4 \cdot 10^{-3} \text{ mol/dm}^3.$$

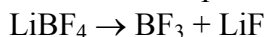
After analogous calculations, 1 mV potential decrease corresponds to pH increase equal to  $1/59 = 0.017$  units. After inserting into equation:

$$\log \frac{0.0005 + x}{0.0005 - x} = 0.017, \text{ and after solution one obtains } x = 9.8 \cdot 10^{-6} \text{ millimoles } \text{OH}^-. \text{ This corresponds to substrate concentration } [S] = 2.5 \cdot 10^{-4} \text{ mol/dm}^3.$$

- e.** Both methods are related to increase of number of produced  $\text{OH}^-$  ions. The first method is enzyme concentration increase, resulting in higher  $k$ , the second method is reaction time increase. However, in both cases excessive increase (of concentration or reaction time) can result in violation of conditions necessary to obtain the equation  $\eta = k[S] t$ , because substrate concentration changes in course of reaction would be significant.

## SOLUTION OF TASK 2

- a. As a result of neutralization of fluoroboric acid with lithium hydroxide,  $\text{LiBF}_4$  is formed. Thermal decomposition reaction of  $\text{LiBF}_4$  is described by the following reaction:



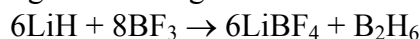
Such course of reaction is confirmed by the compound **A** mass changes:

$$n_{\text{LiBF}_4} = \frac{m_1}{M_{\text{LiBF}_4}} = \frac{11,25}{93,75} = 0,1200 \text{ mole}$$

$$M_{\text{LiF}} = \frac{m_2}{n_{\text{LiF}}} = \frac{3,1128}{0,1200} = 25,94 \text{ g/mole which corresponds to LiF molar mass.}$$

Thus the compound **B** is  $\text{BF}_3$  and compound **C** is  $\text{LiF}$ .

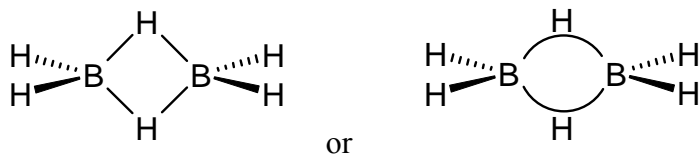
- b. Reaction stoichiometry as well as the formation of product  $\text{LiBF}_4$  (compound **A**) proves that the ligand exchange from  $\text{F}^-$  to  $\text{H}^-$  occurs according to the following reaction:



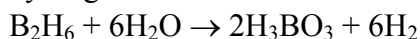
The gas density value indicates that the above boron compound (**D**) occurs in a form of a dimer, that is  $\text{B}_2\text{H}_6$ .

$$M_D = \rho_D \cdot V_m = 1,235 \text{ kg/m}^3 \cdot 22,41 \cdot 10^{-3} \text{ m}^3/\text{mol} = 27,68 \text{ g/mol} \approx M_{\text{B}_2\text{H}_6} = 27,668 \text{ g/mol}$$

Dimeric structure of  $\text{B}_2\text{H}_6$  is formed by two bridged 3c-2e bonds B-H-B, called as electron deficiency bonds, which are characteristic for boron compounds. The remaining B-H bonds are typical  $\sigma$  bonds formed by valence electron pairs (2c-2e). The structure of  $\text{B}_2\text{H}_6$  may be described as a two deformed tetrahedral  $\text{BH}_4$  units linked via a common edge:



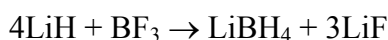
- c. Diborane  $\text{B}_2\text{H}_6$  exhibit strong reducing properties and reacts readily with water to form hydrogen and boric acid:



- d. For reaction II the substrates were taken in the following amounts:

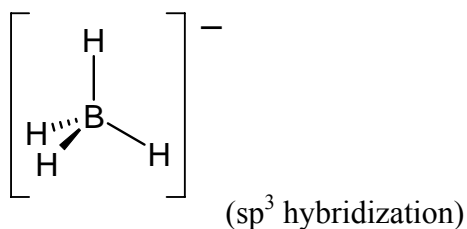
$$n_{\text{LiH}} = \frac{0,763 \text{ g}}{7,948 \text{ g/mol}} = 0,0960 \text{ moles of LiH and } \frac{1}{5} \cdot 0,120 = 0,0240 \text{ moles of BF}_3, \text{ thus in 4:1}$$

molar ratio. The complete exchange of  $\text{F}^-$  ligands for  $\text{H}^-$  ligands takes place, and the excess of  $\text{LiH}$  leads to formation of lithium salt containing  $\text{BH}_4^-$  anions, according to the following reaction:



Thus the compound **E** is a lithium borohydride,  $\text{LiBH}_4$ .

In the structure of this ionic compound there are tetrahedral  $\text{BH}_4^-$  anions, since  $\text{B}^{3+}$  is a coordination center interacting with four equivalent  $\text{H}^-$  ligands:

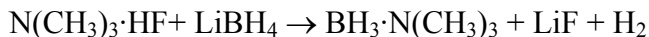


- e.  $\frac{1,90 \text{ g}}{79,12 \text{ g/mol}} = 0,0240$  moles of trimethylamine hydrofluoride was used for the reaction. The molar ratio of substrates was 1:1. Reducing properties of  $\text{LiBH}_4$  leads to the formation of hydrogen and  $\text{BH}_3$  when reacting with amine hydrofluoride.  $\text{BH}_3$  being a Lewis acid forms a

donor-acceptor complex with amine. Compound **F** consists of the boron, nitrogen and carbon atoms in the following molar ratio:

$$\frac{14,8 \text{ g}}{10,81 \text{ g/mol}} : \frac{19,2 \text{ g}}{14,01 \text{ g/mol}} : \frac{49,4 \text{ g}}{12,01 \text{ g/mol}} = 1,37 : 1,37 : 4,11 = 1 : 1 : 3.$$

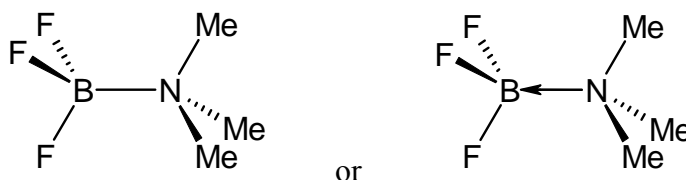
This corresponds to  $\text{BH}_3 \cdot \text{N}(\text{CH}_3)_3$  complex (compound **F**) formed according to the following reaction:



- f.* Compound **B** ( $\text{BF}_3$ ) has the Lewis acidic properties and reacts with bases like *eg* amines forming donor-acceptor complexes. The molar ratio of trimethylamine :  $\text{BF}_3$  is equal

$$\frac{1,182 \text{ g}}{59,112 \text{ g/mol}} : \frac{1}{6} \cdot 0,120 \text{ mol} = 0,0200 : 0,0200 = 1 : 1, \text{ thus the } \text{BF}_3 \cdot \text{N}(\text{CH}_3)_3 \text{ complex is formed}$$

(compound **G**) exhibiting structure analogous to the structure of compound **F**. There are a donor-accepting bonding between the boron and nitrogen atoms, and the molecule exists in an anti-periplanar conformation due to the interaction between the fluorine atoms and the methyl groups.



Molar mass of  $\text{BF}_3 \cdot \text{N}(\text{CH}_3)_3$  is equal to 126.922 g/mol, and thus the reaction yield is equal to:

$$\frac{2,31 \text{ g}}{126,922 \text{ g/mol} \cdot 0,0200 \text{ mol}} \cdot 100\% = 91,0\%$$

### SOLUTION OF THE TASK 3

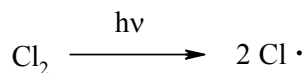
- a.* The relative reactivities of primary and secondary hydrogen atoms in the molecule of propane can be calculated on the basis of relative proportions of isomeric halopropanes. The unequal number of primary and secondary hydrogen atoms should be taken into account.

The reactivity ratio for the chlorination of propane  $\text{H}(1^\circ)/\text{H}(2^\circ)$  is as follows:

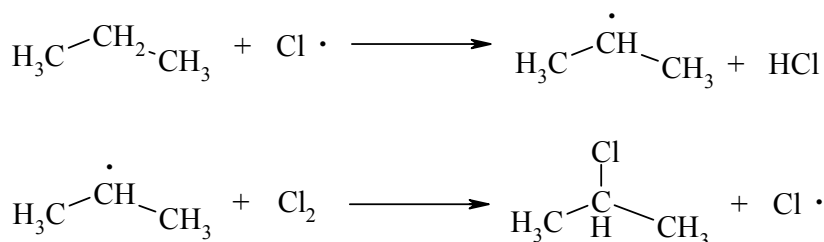
$$(40/6) : (60/2) = 1 : 4,5.$$

The reactivity ratio for the bromination of propane is  $(4/6) : (96/2) = 1 : 72$ .

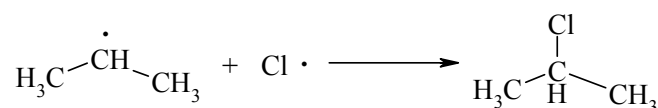
- b.* The initiation step involves the photolytic cleavage of the relatively weak bond in the molecule of chlorine:



The sequence of propagation steps is started with an attack of a chlorine atom on a molecule of propane. The radical thus formed can react with a molecule of chlorine:



Termination steps involve recombinations of two radical species, e.g.:



c. Enthalpies of reactions of chlorine-induced formation of 1- and 2-propyl radicals:

$$\Delta H_{\text{I}} = \Delta H_{\text{dys}}[\text{H}-(1\text{-propyl})] - \Delta H_{\text{dys}}[\text{H-Cl}] = 410 - 431 = -21 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{II}} = \Delta H_{\text{dys}}[\text{H}-(2\text{-propyl})] - \Delta H_{\text{dys}}[\text{H-Cl}] = 395 - 431 = -36 \text{ kJ mol}^{-1}$$

Analogous calculations can be performed for reactions with bromine:

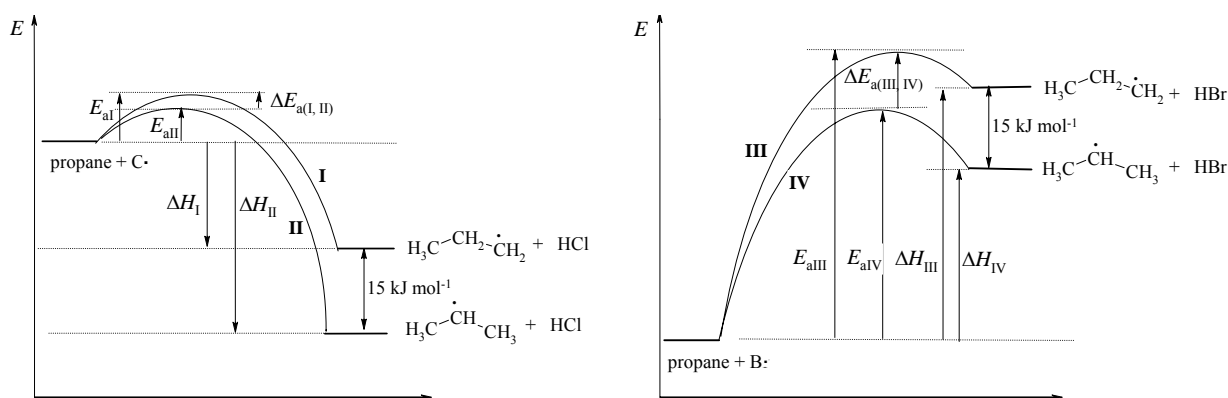
$$\Delta H_{\text{III}} = \Delta H_{\text{dys}}[\text{H}-(1\text{-propyl})] - \Delta H_{\text{dys}}[\text{H-Br}] = 410 - 366 = +44 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{IV}} = \Delta H_{\text{dys}}[\text{H}-(2\text{-propyl})] - \Delta H_{\text{dys}}[\text{H-Br}] = 395 - 366 = +29 \text{ kJ mol}^{-1}$$

Chlorinations are exothermic whereas brominations – endothermic.

The difference of enthalpies of parallel reactions of formation of 1- and 2-propyl radicals is  $15 \text{ kJ mol}^{-1}$  – of course it does not depend on the kind of halogen.

d.



e. The difference of activation energies is bigger for the bromination reactions (the 2nd diagram).

These reactions are endothermic. Corresponding transition states are similar to the products (in other words, they have a significant radical character). Hence, the difference of their energies is only slightly smaller than the difference of energies of corresponding radical products. For the chlorination reactions the difference of activation energies is much smaller. The bigger difference of activation energies imposes the bigger difference of rate constants of parallel reactions, which improves the selectivity of halogenation. In fact, the bromination of propane is much more selective than the chlorination.

f. The reactivity ratio of primary and secondary hydrogen atoms is equal to the ratio of rate constants of corresponding parallel reactions statistically corrected due to the unequal number of primary and secondary hydrogen atoms in the molecule of propane. For the reactions with chlorine we obtain:

$$\frac{k_{\text{I}}}{k_{\text{II}}} = \frac{Ae^{-E_{\text{aI}}/RT}}{Ae^{-E_{\text{aII}}/RT}} = e^{-\Delta E_{\text{a(I,II)}/RT}} = \frac{1}{4,5}$$

$$\Delta E_{\text{a(I,II)}} = -RT \ln(1/4,5) = -8,314 \cdot 298 \cdot \ln(1/4,5) = 3,7 \text{ kJ mol}^{-1}$$

We make similar calculations for the reactions with bromine:

$$\frac{k_{\text{III}}}{k_{\text{IV}}} = \frac{Ae^{-E_{\text{aIII}}/RT}}{Ae^{-E_{\text{aIV}}/RT}} = e^{-\Delta E_{\text{a(III,IV)}/RT}} = \frac{1}{72}$$

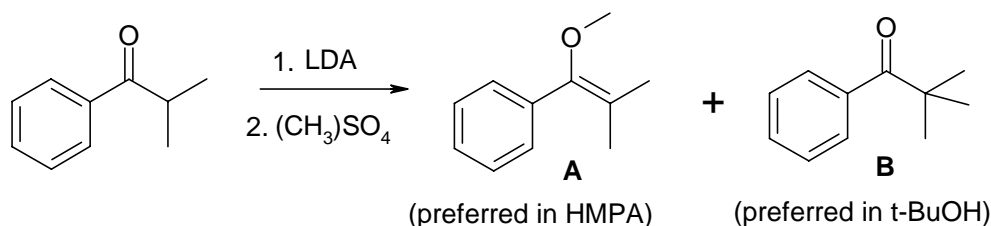
$$\Delta E_{\text{a(III,IV)}} = -RT \ln(1/72) = -8,314 \cdot 298 \cdot \ln(1/72) = 10,6 \text{ kJ mol}^{-1}$$

Qualitatively, this is in agreement with results obtained from the comparison of energy profile diagrams as  $\Delta E_{\text{a(I,II)}} < \Delta E_{\text{a(III,IV)}} < 15 \text{ kJ mol}^{-1}$ .

### Solution of Task 4

a. Keto-enol tautomerism is presented in scheme 1

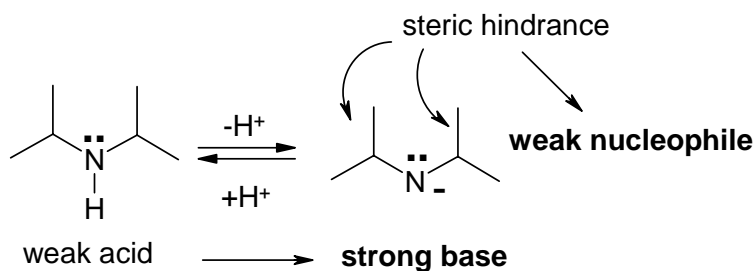
b.



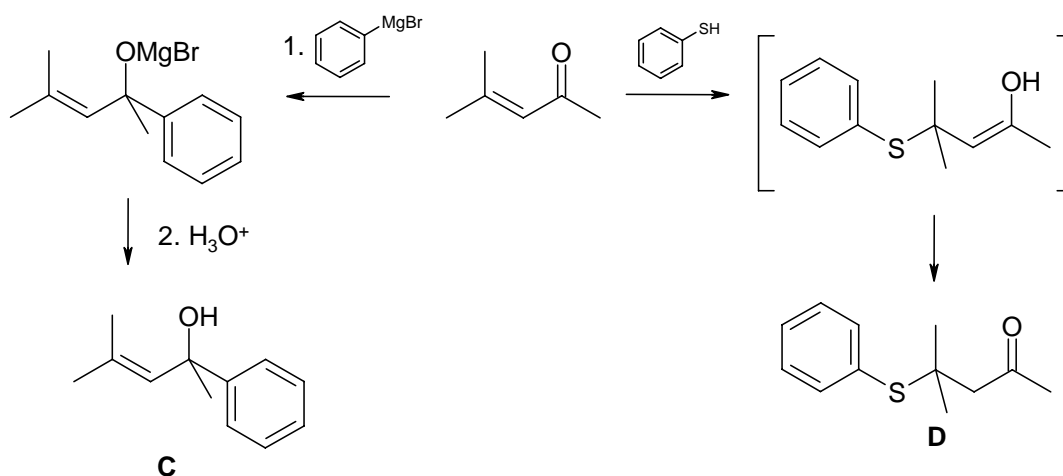
c. O-alkylation is preferred in the case, when enolate is dissociated, what is facilitated by HMPA, which is able, as a polar, aprotic solvent, to form complexes with lithium ion. Tert-butyl alcohol is able to form hydrogen bonds with oxygen atom in enolate, which inhibits O-alkylation reaction and prefers C-alkylation.

d. LDA is a strong base, because it is coupled with weak acid (diisopropylamine), and weak nucleophile because of steric hindrance caused by two isopropyl substituents. "LDA is a strong Brønsted base and a weak nucleophile."

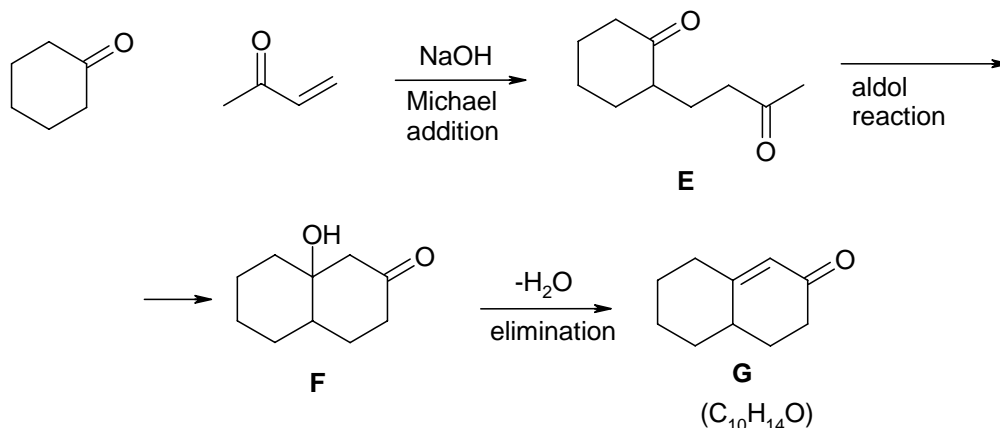
e.



f. Grignard reagents are hard nucleophiles, then according to HSAB theory prefer attack on hard electrophilic centre, which is the carbonyl carbon atom. Thiophenol is a soft nucleophile, then it prefers the soft electrophilic centre - vinyl carbon atom (beta).

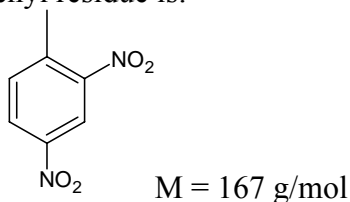


g.

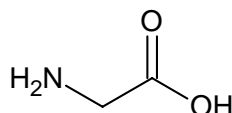


### SOLUTION OF TASK 5

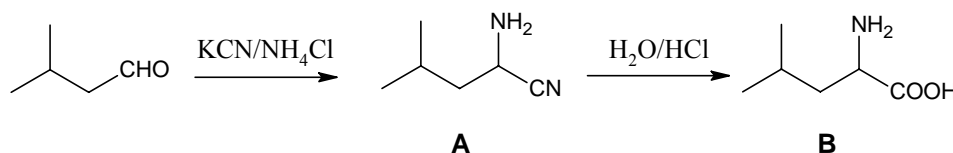
- a. *N*-terminus amino acid is identified in the reaction with 1-fluoro-2,4-dinitrobenzene (DNFB). The molar mass of 2,4-dinitrophenyl residue is:



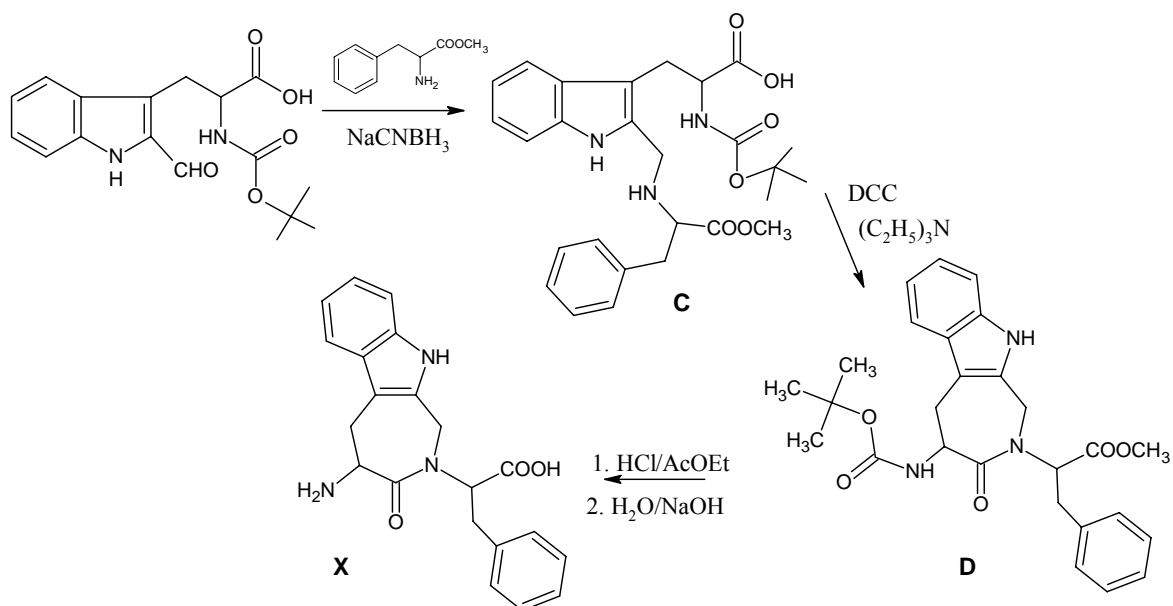
So the molar mass of *N*-terminus amino acid is as follow:  $241 - 167 + 1 = 75$  g/mol. It is the molar mass of glycine (Gly)



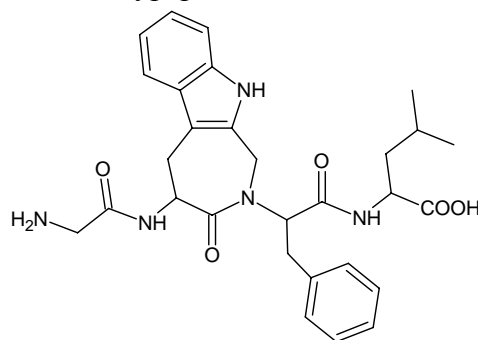
- b. The first scheme presents Stercker synthesis of amino acids. Compound A is  $\alpha$ -aminonitrile, compound B is *C*-terminus amino acid. It is leucine (Leu).



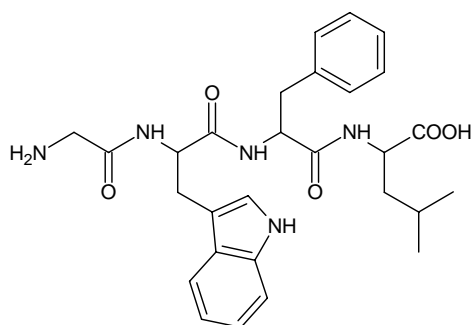
Compound X is formed in reaction of formyl derivative of Trp; amino group in Trp is blocked by Boc (t-butyloxycarbonyl) group. The first step is reductive amination (the reaction between aldehyde and amine with reduction of imine intermediate) and the compound C is obtained. The next step is the reaction in the presence of DCC. It is the coupling reagent to enable the reaction between amine and carboxyl groups. Compound C contains COOH and secondary amino groups and that is why reaction between those groups leads to the 7-membered ring in compound D. The next steps are deprotections of amino and carboxyl groups. Compound X can be incorporate into the peptide chain, because contains NH<sub>2</sub> and COOH groups.



- c. It is known that peptidomimetic **P** is formed by 2 amino acids residues. The *N*-terminus amino acid is determined in reaction with 1-fluoro-2,4-dinitrobenzene (DNFB) and the *C*-terminus after enzymatic digestion with carboxypeptidase. The structural formula of **P** is given below:



- d. Parent linear peptide **I** must contain the same side chains as presented in peptidomimetic **P**. Compound **X** can be considered as constrained dipeptide Trp-Phe. Thus the sequence of peptide **I** is as follow: Gly-Trp-Phe-Leu. The structural formula is given below:





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# 55 Chemistry Olympiad

## Final competitions (27<sup>th</sup> Mar 2009)

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### *Practical tasks and solutions*

#### TASK I:

##### *Investigating purity of medicines*

Technical acetylsalicylic acid (Aspirin) which is contaminated with acetic acid will be investigated. A sample of such a mixture weighing  $x$  (from now on called sample X) was divided into three equal parts:

- two of them were dissolved in alcohol and were transferred into a 100mL volumetric flask labelled with letter A

- third part of the sample was dissolved in sodium hydroxide solution and was heated in boiling water bath for 15 minutes. After cooling down, the solution was transferred into a 200 mL volumetric flask labelled with the letter B and filled up to a volume of 200.0 mL.

The aim of the analysis is the determination of sample X's composition. It may be useful to know that salicylic acid reacts with bromine in acidic medium, producing gaseous  $\text{CO}_2$ .

#### Solutions at your disposal:

<b>Chemicals:</b>	<b>Concentration:</b>
sodium hydroxide	$0,1000 \text{ mol L}^{-1}$
potassium bromate(V)	$0,0200 \text{ mol L}^{-1}$
sodium thiosulphate	$0,0500 \text{ mol L}^{-1}$

#### Apparatus for every student:

burette	2 ~300 mL Erlenmeyer flask with ST
small funnel	25 mL volumetric pipette
100 mL beaker	pissette with distilled water
25 mL graduated cylinder or pipette	

#### Chemicals for all the students:

<b>Chemicals:</b>	<b>Concentration:</b>
potassium bromide	10% aqueous solution
hydrochloric acid	$2 \text{ mol L}^{-1}$ , aqueous solution
potassium iodide	20% aqueous solution
starch (indicator)	1% aqueous solution
phenolphthalein (indicator)	0,5% ethanol solution

## **Problems:**

- a.** What chemical process took place during heating of the analysed sample in the NaOH solution (before transferring of the sample to the flask **B**)? Write the equation of this chemical reaction.
- b.** Read the procedures given below, consider which ones will be necessary and present the analysis plan which will lead to the determination of sample X's composition in a form of a list.
- c.** Write equations of all the chemical reactions taking place during your analysis.
- d.** Taking into account the volumes and concentrations of appropriate titrants and the relative volumes of volumetric apparatus, derive formulae which will be used in calculations in points **e.-g.**
- e.** Carry out necessary titration, calculate and give the total number of moles of acids in sample X.
- f.** (Carry out necessary titration, calculate and give the mass of acetylsalicylic acid in sample X.
- g.** Carry out necessary titration, calculate and give the mass of acetic acid in sample X.
- h.** Propose, how to modify the way of analysis, if the tested sample (marked as Y) were a ternary mixture, containing salicylic acid beside acetylsalicylic and acetic acid. Give the formulae for the number of millimoles of every acid in sample Y, taking into account the number of millimoles and the kind of acids in flasks **A** and **B**.

When deriving formulae, use symbols that are analogous to the ones given in the table below:

$n_{(1)kw}$	total number of moles of acids in the titrated sample
$n_{(A)kw}$	total number of moles of acids in flask A
$n_{(X)kw}$	total number of moles of acids in sample X
$m_{(B)acsal}$	mass of acetylsalicylic acid in flask B
$m_{(X)oct}$	mass of acetic acid in sample X
$n_{(... )acsal,sal}$	total number of moles of acetylsalicylic and salicylic acid in flask ...

## **Procedures**

### ***Direct determination of carboxylic acids***

Transfer 25,0 mL of the solution containing determined acids into an Erlenmeyer flask. Add a few drops of phenolphthalein and titrate with NaOH solution with known concentration until pink colour appears.

### ***Bromate-iodometric determination of salicylic acid***

Transfer a sample of acetylsalicylic-acid solution (e.g. 25,0 mL) into an Erlenmeyer flask with ST. Add precisely 25,0 mL of potassium-bromate(V) solution and 5 mL of potassium-bromide solution. Add quickly 15 mL of hydrochloric-acid solution and immediately close the flask. Shake it vigorously for 2 minutes and put into a dark place for 15 minutes, mixing its contents from time to time. Lift the stopper a little and add 10 mL of potassium-iodide solution. Wash the stopper with water from the pisette. Titrate the produced iodine with sodium-thiosulphate solution, until the brown colour turns into yellowish. Add approximately 2 mL of starch solution as indicator and continue titration until the solution turns colourless

### ***Determination of acetylsalicylic acid***

Transfer the tested solution containing determined esters into an Erlenmeyer flask. Add a certain amount of NaOH solution with a known concentration. Put funnel into the flask and place in a beaker filled with water. Heat the beaker and let the water boil for 15 minutes. Cool down the solution, add a few drops of phenolphthalein and titrate with a HCl solution with a known concentration until the pink colour disappears.

## TASK 2

### *Yellow solution of metal salts*

There are solutions of metal salts in four test tubes labelled with letters **A-D**:

- one of the test tubes contains a mixture of palladium(II) and platinum(IV) salts the mass ratio Pd:Pt in the mixture is not constant, but is enclosed between 1:2 and 2:1
- the rest of the test tubes contain single salts of chromium(VI), gold(III) and vanadium(V)

The concentration of metal ions is not greater than  $100 \mu\text{g mL}^{-1}$  and the solutions are acidified with hydrochloric acid

There are solutions of reagents producing coloured compounds with metal ions in test tubes labelled **1-4**. They are described in the table below:

Reagent	Form	Effects
$\alpha$ -furyl dioxime	1% solution in acetone	combined with Pd(II) produces internal chelate, soluble in chloroform giving yellow solution
1,5-diphenylcarbazide	0,25% solution in acetone	characteristic reaction with chromium(VI)
hydrogen peroxide	3% aqueous solution	helpful in detecting vanadium(V)
Tin(II) chloride*	5% solution in HCl of conc. $2 \text{ mol L}^{-1}$	produces coloured complexes with the platinum group metals (see the graph and table of colours)

\* when small amount of  $\text{SnCl}_2$  mixed with tin(IV) chloride is combined with gold(III) in a diluted solution of hydrochloric acid, solution of colloidal gold results which is red

There is a graph on your desk where the relationship between molar absorptivity ( $\epsilon$ ) of coloured palladium(II) and platinum(IV) complexes with tin(II) chloride and wavelength of absorbed light is shown. The given relationship was obtained for a 0,5% concentration of  $\text{SnCl}_2$  in solution and the concentration of HCl of  $2 \text{ mol L}^{-1}$ .

The ratio of absorbance measured for a few wavelengths to the absorbance measured for the wavelength of 635 nm is given in the table under the figure. The ratio is given for a solution resulting from mixing 2 mL of your mixture, 1 mL of  $\text{SnCl}_2$  solution and adding  $2 \text{ mol L}^{-1}$  HCl solution so that the volume of the resulting solution is 10 mL. The measurement was carried out 20 minutes after preparation of the 10-mL solution. Absorbance is stable within 3 hours after preparation of the solution.

At the bottom of the page with the graph there is a table with information about the principal and complementary colours corresponding to the given wavelengths. This will allow you to determine the colour of palladium and platinum complexes with  $\text{SnCl}_2$ .

This is at your disposal:

- six empty test tubes
- polyethylene Pasteur pipettes
- graduated pipette
- graduated cylinder with a stopper
- pH indicator paper

Chemicals for all the students:

- chloroform
- hydrochloric acid (conc.  $2 \text{ mol L}^{-1}$ )
- 20% tin(IV) chloride solution in  $1 \text{ mol L}^{-1}$  solution of hydrochloric acid

You may also use chemicals prepared for problem 1.

On a separated desk there is a spectrophotometer working with wavelength from 490 nm to 700 nm that allows one to measure absorbance up to the value of 0,6. The cuvette width is given next to the device. You may measure absorbance for one, chosen wavelength.

## Procedure

### ***Producing colloidal gold***

Add 1 mL of tested sample to 2-3 mL of water. In another test tube mix 1 mL of SnCl<sub>4</sub> solution with one drop of SnCl<sub>2</sub> solution. Add a drop of the prepared mixture to the diluted solution of your sample. After a while, crimson (red) colour appears which means that gold is present in the sample.

### **Problems:**

- a.** (12 points) Identify solutions in all the test tubes. Present short justification of the identification (remember to give at least two reactions confirming your identification)
- b.** (2 points) Confirm that the mixture is made up of palladium(II) and platinum(IV), knowing that Pt(IV) does not react with  $\alpha$ -furyl dioxime in room temperature.
- c.** (5 points) Present in the form of a list the way to determine concentrations [ $\mu\text{g}/\text{cm}^3$ ] in the mixture. Take into account the way of preparing the sample for spectrophotometric measurement. Give the principle of determining the quantities of compounds in the mixture. Give the derived formulae for the palladium and platinum concentrations in the solution prepared for spectrophotometric measurement.
- d.** (0-5 points) Give the concentrations of both components in the analysed mixture.

Attention!

USE YOUR SOLUTIONS ECONOMICALLY. DO NOT USE GREATER AMOUNTS OF YOUR SOLUTIONS THAN 1 mL FOR THE TESTS.

### **Points:**

**problem 1 - 36 points**

**problem 2 - 24 points**

**SUM 60 points**

**Important! The answers for the questions have to be placed in the right fields in the table on the answer sheet. Anything placed beyond those fields will no be marked!**

**Write your answers neatly and legibly. Illegible answers may be the reason for lower marks and will not be considered in the appeals.**

**Remember to work safely when carrying out analysis**

**Duration of the examination: 300 min**

## SOLUTIONS

### SOLUTION OF TASK 1

<i>Problem a.</i>	points
Chemical process that took place upon heating is: hydrolysis of sodium acetylsalicylate yielding sodium salicylate and sodium acetate. Chemical reaction equation	2 pts
$\text{CH}_3\text{COOC}_6\text{H}_4\text{COO}^- + \text{OH}^- \xrightarrow{\text{heat}} \text{CH}_3\text{COO}^- + \text{HOC}_6\text{H}_4\text{COO}^-$	1 pts
<b>Sum</b>	<b>3 pts</b>

<i>Problem b.</i>	points
Plan of analysis:	
1. Determination of the sum of acids in flask <b>A</b> in direct titration with a NaOH solution, having known concentration, in the presence of phenolphthalein.	2 pts
2. Determination of salicylic acid in flask <b>B</b> with a bromate-iodometric method (back titration) using a sodium thiosulphate solution with a known concentration in the presence of starch.	2 pts
<b>Sum</b>	<b>4 pts</b>

<i>Problem c.</i>	points
The reactions that took place during the analysis:	
$\text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$	0,5 pts
$\text{CH}_3\text{COOC}_6\text{H}_4\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COOC}_6\text{H}_4\text{COO}^- + \text{H}_2\text{O}$	0,5 pts
$\text{BrO}_3^- + 5\text{Br}^- + 6\text{H}^+ \rightarrow 3\text{Br}_2 + 3\text{H}_2\text{O}$	0,5 pts
$\text{HOC}_6\text{H}_4\text{COOH} + 3\text{Br}_2 \rightarrow \text{HOC}_6\text{H}_2\text{Br}_3 + 3\text{Br}^- + 3\text{H}^+ + \text{CO}_2$	0,5 pts
$\text{Br}_2 + 2\text{I}^- \rightarrow 2\text{Br}^- + \text{I}_2$	0,5 pts
$\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$	0,5 pts
<b>Sum</b>	<b>3 pts</b>

<i>Problem d.</i>	points
Ad. 5. Total number of moles of acids in the sample [mmol]	
$n_{(\text{A})\text{kw}} = V_{\text{NaOH}} \cdot c_{\text{NaOH}} \cdot \frac{100}{25}$	$n_{(\text{X})\text{kw}} = 1,5 \cdot n_{(\text{A})\text{kw}}$
	2 pts

Ad. 6. Acetylsalicylic acid mass [mg]		3 pts
$m_{(B)acsal} = \frac{200}{25} \cdot (V_{KBrO_3} \cdot c_{KBrO_3} - \frac{1}{6} V_{tios} \cdot c_{tios}) \cdot M_{acsal} \quad m_{(X)acsal} = 3 \cdot m_{(B)acsal}$		
Ad.7. Acetic acid mass [mg]		3 pts
$m_{(A)oct} = [V_{NaOH} \cdot c_{NaOH} \cdot \frac{100}{25} - (V_{KBrO_3} \cdot c_{KBrO_3} - \frac{1}{6} c_{tios} \cdot V_{tios}) \cdot \frac{400}{25}] \cdot M_{oct} \quad m_{(X)oct} = 1,5 \cdot$		
<b>Sum</b>		<b>8 pts</b>

<b>Problems e.-g.</b>			<b>points</b>
Titration, used titrant	V[mL]	V <sub>mean</sub> [mL]	Total number of millimoles of acids <b>n<sub>(X)kw</sub> = 8,98</b>
Direct titration of acids, NaOH solution	15,3	14,97	
	14,9		
	14,95		
Titration of iodine, thiosulphate solution	26,0	25,80	Acetylsalicylic acid mass[mg] <b>m<sub>(X)acsal</sub> = 1232,6</b>
	25,8		
	25,8		
			Acetic acid mass [mg] <b>m<sub>(X)oct</sub> = 128,4</b>
<b>Sum</b>			<b>12 pts</b>

<b>Problem h.</b>	<b>points</b>
<p>1. Dissolving 2/3 of the analyzed sample Y in alcohol, solution in flask <b>A</b>. Determination of the sum of all acids in flask <b>A</b> with direct titration, using a solution of NaOH with a known concentration in the presence of phenolphthalein, <math>n_{(A)kw} = n_{(A)acsal} + n_{(A)sal} + n_{(A)}</math></p> <p>2. Dissolving 1/3 of the analyzed sample in a known quantity of NaOH solution, hydrolysis of sodium acetylsalicylate, solution in flask <b>B</b>. Determination of the sum of acids in flask <b>B</b> with back titration with an HCl solution in the presence of phenolphthalein until the solution turn colourless, <math>n_{(B)kw} = 2 \cdot n_{(B)acsal} + n_{(B)sal} + n_{(B)oct}</math></p> <p>3. Determination of salicylic acid (present in the sample and produced as a result of sodium acetylsalicylate hydrolysis) in flask <b>B</b> with the bromate-iodometric method,</p> $n_{(B)acsal,sal} = n_{(B)acsal} + n_{(B)sal}$ $n_{(Y)acsal} = 3 \cdot n_{(B)kw} - 1,5 \cdot n_{(A)kw};$ $n_{(Y)sal} = 3 \cdot n_{(B)acsal,sal} - (3 \cdot n_{(B)kw} - 1,5 \cdot n_{(A)kw});$ $n_{(Y)oct} = 1,5 \cdot n_{(A)kw} - 3 \cdot n_{(B)acsal,sal}$	
<b>Sum</b>	<b>6 pts</b>

### Comments to the solution of task 1

#### Problems d.-g.

Acetylsalicylic acid is an acid and ester at the same time. Direct titration of the sample containing acetylsalicylic acid and acetic acid with sodium hydroxide solution with a known

concentration, in the presence of phenolphthalein allows to determine number of moles of acids ( $n_{(1)kw}$ ) in the titrated solution:  $n_{(1)kw} = n_{oct} + n_{acsal}$ .

Taking into account relative volumes of the flask and pipette one can calculate the total number of moles of acids in flask **A**, and then in the sample X, according to the formulae presented in the table.

In order to determine the amount of acetylsalicylic acid in the sample, one has to determine sodium salicylate amount which was produced during hydrolysis of this acid. Salicylic acid, which has to be brominated, is produced upon acidification of the solution. The amount of bromine produced in the system depends on the amount of added bromate (in the symproportionation reaction with bromides in the acidic solution). Unreacted (in the bromination reaction) bromine oxidises added iodide ions to iodine, which is in turn titrated with a sodium thiosulphate solution.

One gets the number of moles of acetylsalicylic acid in flask **B** from the difference between the amount of added bromine (produced from  $KBrO_3$ ) and the amount of titrated iodine. One may calculate the number of moles of bromine, which reacted with salicylic acid, using the result  $V_{tios}$  [mL] of the titration with the sodium thiosulphate solution.

According to the reaction equations, 3 moles of bromine are produced from one mole of bromate. Then 3 moles of bromine react with one mole of salicylic acid, so 1 mole of bromate corresponds to one mole of salicylic acid. Upon reacting with iodide ions, one mole of bromine which was not used during bromination gives one mole of iodine (one mole of  $KBrO_3$  produces 3 moles of iodine) which reacts with thiosulphate (1 mole of iodine with two moles of thiosulphate), so 1 mole of bromate corresponds to 6 moles of thiosulphate.

$$n_{acsal} = (n_{KBrO_3} - \frac{1}{6} n_{tios}) \text{ [mmol]}$$

$$n_{(B)acsal} = (V_{KBrO_3} \cdot c_{KBrO_3} - \frac{1}{6} c_{tios} \cdot V_{tios}) \cdot \frac{200}{25} \text{ [mmol]}$$

In the whole sample X there is three times as much acid, so:

$$n_{(X)acsal} = 3 \cdot n_{(B)acsal} = (V_{KBrO_3} \cdot c_{KBrO_3} - \frac{1}{6} c_{tios} \cdot V_{tios}) \cdot \frac{600}{25}$$

One finds the number of moles of acetic acid present in flask **A** taking into account the titration with NaOH, the titration with thiosulphate and remembering that the portion of sample X in flask **A** is twice as big as the portion in flask **B**.

$$n_{(A)acsal} = 2 \cdot n_{(B)acsal} \text{ [mmol]}$$

$$n_{(A)oct} = n_{(A)kwas} - 2 \cdot n_{(B)acsal} \text{ [mmol]}$$

$$n_{(A)oct} = V_{NaOH} \cdot c_{NaOH} \cdot \frac{100}{25} - 2 \cdot (V_{KBrO_3} \cdot c_{KBrO_3} - \frac{1}{6} c_{tios} \cdot V_{tios}) \cdot \frac{200}{25}$$

There is 1.5 times as much acid in the whole sample, so:

$$n_{(X)oct} = 1,5 \cdot n_{(A)oct} = V_{NaOH} \cdot c_{NaOH} \cdot \frac{150}{25} - \left( V_{KBrO_3} \cdot c_{KBrO_3} - \frac{1}{6} c_{tios} \cdot V_{tios} \right) \cdot \frac{600}{25}$$

In order to calculate the mass of each acid, one has to multiply the number of millimoles times the mass of one millimole of the acid

$$m_{(X)oct} \text{ [mg]} = n_{(X)oct} \cdot M_{oct} = n_{(X)oct} \text{ [mmol]} \cdot 60,05 \text{ [mg/mmol]}$$

$$m_{(X)acsal} \text{ [mg]} = n_{(X)acsal} \cdot M_{acsal} = n_{(X)acsal} \text{ [mmol]} \cdot 180,16 \text{ [mg/mmol]}$$

**SOLUTION OF TASK 2**

Exemplary arrangement of samples for analysis:

Test tube	Metal ions solution	Test tube	Substance
<b>A</b>	Au(III)	<b>1</b>	$\alpha$ -furyl dioxime
<b>B</b>	Pd(II) i Pt(IV)	<b>2</b>	1,5-diphenylcarbazide
<b>C</b>	V(V)	<b>3</b>	SnCl <sub>2</sub>
<b>D</b>	Cr(VI)	<b>4</b>	hydrogen peroxide

Exemplary composition of the mixture solution:  $c_{Pd} = 60 \mu\text{g/mL}$ ;  $c_{Pt} = 56 \mu\text{g/mL}$ 

<b>Problem a.</b>				
Sample number	substance (name or formula)	Pts for identification	Justification	Pts for justification
<b>1</b>	$\alpha$ -furyl dioxime	0,75	<ul style="list-style-type: none"> <li>◇ insoluble in water(acetone solution);</li> <li>◇ gives yellow, floccular precipitate with Pd(II) in acidic solution;</li> <li>◇ gives colloidal Au with Au(III) solution upon heating;</li> </ul>	0,75
<b>2</b>	1,5–diphenylcarbazide	0,75	<ul style="list-style-type: none"> <li>❖ insoluble in water(acetone solution);</li> <li>❖ gives violet complex with Cr(VI) in acidic solution</li> <li>❖ gives brown colour with vanadium;</li> </ul>	0,75
<b>3</b>	SnCl <sub>2</sub>	0,75	<ul style="list-style-type: none"> <li>◇ aqueous solution, strongly acidic, hydrolyses easily, has reducing properties;</li> <li>◇ gives green complex with Pd(II);</li> <li>◇ gives yellow complex with Pt(IV);</li> </ul>	0,75
<b>4</b>	Hydrogen peroxide	0,75	<ul style="list-style-type: none"> <li>❖ aqueous solution, nearly neutral;</li> <li>❖ oxidizing properties (KI to I<sub>2</sub>);</li> <li>❖ gives red-brown complex with V(V);</li> <li>❖ gives pale, blue colour with Cr(VI);</li> </ul>	0,75
<b>A</b>	Au(III)	0,75	<ul style="list-style-type: none"> <li>◇ gives crimson colour (colloidal gold; see procedure);</li> <li>◇ gives olive-coloured sol of gold with SnCl<sub>2</sub>;</li> <li>◇ gives precipitate of colloidal gold with <math>\alpha</math>-furyl dioxime upon heating;</li> </ul>	0,75
<b>B</b>	Pd(II) and Pt(IV)	0,75	<ul style="list-style-type: none"> <li>❖ gives green complex with SnCl<sub>2</sub>;</li> <li>❖ gives yellow, floccular precipitate with Pd(II) in acidic solution;</li> <li>❖ gives red-brown complex with iodide ions (KI);</li> </ul>	0,75
<b>C</b>	V(V)	0,75	<ul style="list-style-type: none"> <li>◇ upon addition of SnCl<sub>2</sub> yellow colour disappears and faint blue colour appears;</li> <li>◇ gives red-brown complex with hydrogen peroxide;</li> </ul>	0,75
<b>D</b>	Cr(VI)	0,75	<ul style="list-style-type: none"> <li>❖ the yellow colour disappears upon addition of SnCl<sub>2</sub>;</li> <li>❖ gives violet complex with 1,5-diphenylcarbazide in acidic solution;</li> <li>❖ upon addition of H<sub>2</sub>O<sub>2</sub> faint, waning, blue colour appears;</li> </ul>	0,75
<b>Sum</b>		<b>6 pts</b>	<b>Sum</b>	<b>6 pts</b>

<b>Problem b.</b>	<b>Points</b>
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<p>Platinum(IV) reacts with <math>\alpha</math>-furyl dioxime in room temperature, whereas palladium gives a chelate complex. The produced palladium compound can be extracted with chloroform. The presence of palladium is shown by the yellow colour of the chloroform layer. Colourless, aqueous layer turns yellow upon addition of <math>\text{SnCl}_2</math>, if platinum is present in the solution.</p> <p><i>or:</i></p> <p>Molar extinction coefficient of the palladium complex has the same value at the wavelengths 432 nm and 635 nm (<math>\epsilon_{\text{Pd},635} = \epsilon_{\text{Pd},432}</math>). If the sample contained only palladium, upon addition of <math>\text{SnCl}_2</math> a green solution would be formed which would have the same absorbance at 432nm and 635 nm. One can read from the table below the graph that the ratio of the absorbance at 432 nm to the absorbance at 635 nm is greater than 1, which indicates that the sample contains platinum.</p>	2 pts
<b>Sum</b>	<b>2 pts</b>

<b>Problem c.</b>	<b>Points</b>
<p><b>Preparation of the solution for spectrophotometric measurement</b></p> <p>Mixing 2 mL of the analysed mixture, 1 mL of <math>\text{SnCl}</math> solution and adding 2 mol/L HCl solution so that the volume of the resulting solution is 10 mL. Waiting for 20 minutes.</p> <p><b>The principle of the composition of the analysed mixture determination</b></p> <p>The platinum complex does not absorb light at <math>\lambda_{\text{max}}</math> of palladium complex (635 nm). The absorbance measurement at this wavelength, knowledge of <math>\epsilon_{\text{Pd},635}</math> and path length <math>l</math> allows one to calculate palladium concentration.</p> <p>At 432nm <math>\epsilon_{\text{Pd},635}</math> equals <math>\epsilon_{\text{Pd},432}</math>. One has to read from the table under the graph that the ratio of absorbance at 432nm to absorbance at 635 nm equals 2,216 which allows one to calculate the sum of absorbance of palladium and platinum complexes. One gets the absorbance of platinum complex by subtracting from this sum the absorbance of palladium complex, which equals the absorbance of the analysed solution measured at 635 nm. One can compute platinum concentration, taking into account the value of <math>\epsilon_{\text{Pt},432}</math> and path length <math>l</math>.</p>	1 pts
<p><b>Formulae:</b> <math>A_{\text{Pd+Pt},432} = 2,216 \cdot A_{\text{Pd},635}</math>      <math>A_{\text{Pt},432} = A_{\text{Pd+Pt},432} - A_{\text{Pd},635} = (2,216-1) A_{\text{Pd},635}</math></p> $c_{\text{Pd}} [\mu\text{g/mL}] = \frac{A_{635}}{\epsilon_{\text{Pd},635} \cdot l} \cdot M_{\text{Pd}} \cdot 1000$ $c_{\text{Pt}} [\mu\text{g/mL}] = \frac{(2,354-1) \cdot A_{635}}{\epsilon_{\text{Pt},432} \cdot l} \cdot M_{\text{Pt}} \cdot 1000$	2 pts
<b>Sum</b>	<b>5 pts</b>

<b>Problem d.</b>				<b>Points</b>
Sample volume [mL]	2	Analyte	Absorbance (wavelength)	Conc. $\mu\text{g/mL}$
Solution volume [mL]	10	Pd(II)	0,290 (635 nm)	59,8
Path length [cm]	1,00	Pt(IV)	0,353 (432 nm)	55,5
<b>Sum</b>				<b>5 pts</b>

## *Comments to the solution of problem 2*

### *Problem a.*

Identification should be started with finding  $\text{SnCl}_2$  solution. It is one of the aqueous solutions with a clearly acid reaction (litmus). Upon dilution with water the solution becomes opaque as a result of hydrolysis. Upon reaction with Pd(II) a green complex is formed and upon reaction with Pt(IV) – a yellow complex. This takes place with test tube **3**.

Upon addition of  $\text{SnCl}_2$  to solutions from test tubes **A-D** ( ca. 0,5 mL of  $\text{SnCl}_2$  solution should be added to 1mL of the analysed solutions) one can observe effects described in the table.

Such results allow one to conclude that the test tube **A** contains Au(III), test tube **B** – mixture of Pd(II) and Pt(IV), test tube **C** – V(V) or Cr(VI) and test tube **D** – Cr(VI) or V(V).

Forming of the crimson, colloidal precipitate of gold is a confirmation of the presence of gold in test tube **A**.

The presence of vanadium in test tube **C** is confirmed by the appearance of brown-red complex upon addition of the solution from test tube **4**, which also indicates that there is hydrogen peroxide there. Addition of hydrogen peroxide solution to test tube **D** causes the appearance of bluish, waning colour coming from the formed chromium peroxide.

Mixing the contents of test tube **D** with acetone solution from test tube **2** leads to the appearance of violet colour which indicates the presence of Cr(VI) in test tube **D** and 1,5-diphenylcarbazide in test tube **2**. The presence of 1,5-diphenylcarbazide is confirmed by the brown colour after mixing solutions from test tube **2** and **C**, as vanadium(V) forms a brown compound with 1,5-diphenylcarbazide (extractable to the chloroform layer).

Detection of  $\alpha$ -furyl dioxime in test tube **1** is possible thanks to the reaction with solution from test tube **B**, leading to the formation of yellow, floccular precipitate of palladium  $\alpha$ -furyl dioximate, which is extractable with chloroform.

### *Problem d.*

When computing the Pd(II) and Pt(IV) concentrations in the sample one has to take into account the volume of the sample  $V_P$  taken to prepare the solution and the solution volume  $V_R$  prepared for the spectrophotometric measurement.

Having a graduated cylinder and a graduated pipette one has to take, for instance, 2 mL (absorbance of the prepared solutions should not exceed 0,5) of the analysed mixture, add 1 mL of Pd(II) chloride and add hydrochloric acid to 10 mL (the volume of the whole solution). The absorbance should be measured at 635 nm after 20 minutes. It amounts to **0,290**.

The concentration of metals in the prepared solution has to be calculated from the above derived formulae, having read the values of molar extinction coefficients from the graph.  $\epsilon_{\text{Pd},635}$  amounts 2580, and  $\epsilon_{\text{Pt},432}$  equals 6200 [ $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ].

The path length should be written down from the spectrophotometer which has been used for the measurement. Calculating the concentrations in the sample, the obtained concentrations have to be multiplied by  $V_R$  and divided by  $V_P$ , which equal 10 and 2 mL, respectively.