

### 3rd BChO, 1995, Tartu, Estonia

#### Problem 1 – ABC, MECH, SPECTRA – Shapeshifting organics

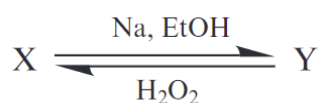
Compound **X** turns into hydrocarbon **Y** via reduction and rearrangement in the presence of  $\text{HBF}_4$ . The reverse intermolecular rearrangement occurs by heating the potassium salt of the oxidation product of the compound **Y** in  $\text{CO}_2$  atmosphere. After treatment with  $\text{D}_2\text{O}$ , the NMR spectrum of compound **X** presents a singlet at  $\delta = 8.1$  (DMSO). 1.4 times less oxygen is needed for the complete burning of 1 mole of compound **X** compared to the same amount of **Y**.

- Write the chemical equations for all the reactions.
- Write the mechanisms of the rearrangements.

#### Problem 2 – CALC, INORG – Oxidation of rhenium

Compound **X** [ $w(\text{Re}) = 68.16\%$ ] turns into compound **Y** according to the following scheme:

| $c_x [\text{M}]$ | $A(346 \text{ nm})$ | $A(330 \text{ nm})$ |
|------------------|---------------------|---------------------|
| 8.4422           | 0.1815              | 0.291               |
| 8.5924           | 0.1847              | 0.295               |
| 8.7989           | 0.1883              | 0.302               |



The results of absorption spectroscopic measurements of standard solutions of **X** are in the Table. Two more measurements were made as follows. 1.0360 g of compound **Y** was treated with hydrogen peroxide. The excess of the reagent was removed by boiling.

- The solution was quantitatively transferred into a  $500.34 \text{ cm}^3$  volumetric flask,  $2.50 \text{ cm}^3$  of concentrated  $\text{H}_2\text{SO}_4$  was added, and the flask was filled to the line. Result: at  $A(346 \text{ nm}) = 0.1844$ .
- $50.0 \text{ cm}^3$  of the solution a was pipetted into a  $100 \text{ cm}^3$  volumetric flask,  $0.250 \text{ cm}^3$  of concentrated  $\text{H}_2\text{SO}_4$  was added, and the flask filled to the line. Result: at  $A(330 \text{ nm}) = 0.294$ .

Write the chemical formulas of **X** and **Y**. Show your calculations.

#### Problem 3 – ELECTRO – Silver energy

The EMF of a silver-zinc cell  $\text{Zn} | \text{ZnSO}_4(\text{l}) || \text{AgNO}_3(\text{l}) | \text{Ag}$  is 1.562 V if the concentrations of the solutions are 1 M at  $T = 25^\circ\text{C}$ .

- Write the equations of the reactions in the whole cell and at single electrodes if current is taken from the cell.
- Calculate the EMF of the cell after 20 days of running at 0.050 A.

#### Problem 4 – KINETICS – The kinetics of March test

The kinetics of the decomposition of  $\text{AsH}_3$  was studied by measuring pressure in a closed glass tube. The initial pressure of gaseous  $\text{AsH}_3$  in the tube was 86.1 kPa. After 2 hours, the pressure in the tube was 112.6 kPa. The formed As condensed on the walls of the glass tube.

- Write the chemical equation of the decomposition reaction.
- Calculate the pressure in the glass tube after the reaction is completed.
- Calculate the rate constant and the rate of the reaction.
- Calculate the time necessary to decompose 99.9% of  $\text{AsH}_3$ .

### Problem 5 – ABC – A lot of heating

5.5541 g of a crystalline hydrate was heated at 100 °C. Its mass decreased to 4.1128 grams. The remnant was heated at 150 °C to obtain 2.0818 g of a gas with a volume of 7.044 dm<sup>3</sup> at 150 °C and 100000 Pa. The remnant of the other heating (2.0310 g) was treated with overheated steam to obtain 1.5910 g of a solid oxide containing 20.11% oxygen. All the mentioned heatings were carried out to constant weight.

- Write the chemical formula of the crystalline hydrate. Show your calculations.
- Write the chemical equations of all the reactions.

### Problem 6 – BIO – Don't starve

The oxidation of glucose is the human organism's primary energy source. However, while starving, the reserve of hydrocarbons is diminishing, and the oxidation of two monocarbonic acids, **A** and **B**, becomes the main energy source. The acids **A** and **B** turn easily into one another due to an enzymatic redox reaction. Acid **A** contains 47.06% C and 5.88% H; **B** contains 46.15% C and 7.70% H. Acid **A** decomposes slowly and spontaneously in blood, giving a volatile compound **C** that can be smelled in the air exhaled by a starving person. The density of the vapors of the compound **C** is 2.00 with respect to the air, and there is only one peak in its <sup>1</sup>H NMR spectrum. Write the structural formulas of **A**, **B**, and **C**.

### Problem 7 – ABC – Organic riddle

Compound **A** (C<sub>16</sub>H<sub>15</sub>NO<sub>2</sub>) dissolves only in concentrated sulfuric acid and reacts with hydrazine to form a precipitate. Compound **A** was hydrolyzed in an alkaline solution. Compound **B** was separated from the solution by extracting it with ether. The remnant was acidified to separate a solid compound **C** with a molar mass of 164 g mol<sup>-1</sup>. Compounds **A** and **C** react with an alkaline solution of iodine to give a precipitate **D**. The other product that formed in the reaction from compound **C** was turned into acid **E** by the agency of an acid. One mole of NaOH reacts with 83 g of the acid **E**. Heating the acid **E** results in compound **F**, which does not react with sodium hydrogen carbonate. Boiling compound **F** in water for a long time returns it to compound **E**.

Compound **B** has an unpleasant smell, and it dissolves in a 5% solution of HCl. It reacts with an acidified solution of sodium nitrite to liberate a gas and form compound **G**, which is insoluble in water but reacts with sodium. Compound **G** is oxidized with chromosulfuric acid to give compound **H**. Melting **H** with NaOH gives benzene.

- Write the structural formulas of compounds **A**–**H**.

### Problem 8 – EQUIL – Removal of iron from water

At what pH of the solution does FeS begin to precipitate if the initial concentration of the cation is 0.01 M, the total concentration of all the forms of sulfide ions in the solution is also 0.01 M, the dissociation constants for dihydrogen sulfide are  $K_1 = 1 \cdot 10^{-7}$  and  $K_2 = 1 \cdot 10^{-13}$  and the solubility product for FeS is  $K_{sp} = 1 \cdot 10^{-18}$ ? At what pH of the solution could the precipitation of FeS be considered complete (i.e. 99.9% of the initial amount of the cation has precipitated)?