

7th BChO, 1999, Kaunas, Lithuania

Problem 1 – ABC – Haloalkane redox magic

Compound **A** ($C_8H_{15}Cl$) is a racemate. It does not discolor bromine in carbon tetrachloride or potassium permanganate solution. If **A** is treated with zinc and acetic acid and the resulting mixture is separated by chromatography, two fractions, **B** and **C**, with identical molecular formulas, are obtained. Fraction **B** is a racemate.

The reaction of **A** with sodium methoxide (CH_3ONa) in ethanol yields compound **D**. Hydrogenation of **D** over a platinum catalyst gives the product **C**. Ozonolysis of **D** followed by the addition of zinc and water produces the dione **E**. From compound **E**, iodoform is formed by reaction with iodine in NaOH solution. After isolation of iodoform and acidification, adipic acid (1,4-butanedicarboxylic acid) is obtained.

- Write the structural formulas of **A**, **B**, **C**, **D**, and **E**.
- Show the stereoisomerism of the compounds.
- Write the reaction equations.
- Write the reaction mechanism for the preparation of compound **D** from compound **A**.

Problem 2 – BIO, CALC – The ones that hide inside potatoes

Hydrolysis of starch in dilute aqueous acid solution yields only "sweet" products – saccharides: glucose, maltose, etc. Hydrolysis of 30-40% starch suspension in dilute HCl solution at 130-140 °C gives bittersweet saccharide **X**. Substance **X** was separated and purified for analysis. A series of experiments were carried out to identify it.

(1) Hydrolysis of starch in acidic solution. One of the products is glucose.

(2) Reducing properties.

25 mg of substance **X** was diluted in 25.0 cm³ of 0.0100 M $K_3[Fe(CN)_6]$ solution, 5 cm³ of 0.1 M KOH solution was added and the mixture was heated at 100 °C for 15 minutes. The concentration of $K_3[Fe(CN)_6]$ was determined using the iodometry method. KI and CH_3COOH were added; 10.5 cm³ of 0.0100 M $Na_2S_2O_3$ solution was required to titrate I_2 .

(3) Methylation and oxidation.

Substance **X** was methylated with excess CH_3I in the presence of Ag_2O . The product was heated in a 30% nitric acid solution. Two acids were detected in the reaction mixture: 2,3,4-trimethoxy-5-hydroxyadipic acid, $HOOC-CH(OH)-[CH(OCH_3)]_3-COOH$ and 2,3,4,6-tetramethoxy-5-hydroxycaproic acid $H_3COCH_2CH(OH)-[CH(OCH_3)]_3COOH$.

- Draw the structure of substance **X**.
- Write the reaction equations for the identification of substance **X**.

Problem 3 – ELECTRO, EQUIL – A way to dissolve silver

The potential E_1 of the silver electrode was determined in a solution of $AgNO_3$ with a concentration of 0.0100 M. After that, 0.0170 g of NH_3 was added to 10.0 cm³ of the solution. In the resulting solution, the potential of the Ag electrode was different from E_1 by 0.285 V. The temperature of the solution was 25 °C.

NH_3 forms a complex in $AgNO_3$ solution according to the reaction $Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$. Calculate the equilibrium constant of the above reaction.

Problem 4 – EQUIL – Hydrazine

25 cm³ of 0.0160 M Zn(NO₃)₂ solution and 75 cm³ of 0.133 M hydrazine solution were mixed. $K_{sp}[\text{Zn}(\text{OH})_2] = 1.20 \cdot 10^{-17}$, $K_b(\text{H}_4\text{N}_2) = 1.3 \cdot 10^{-6}$ (proton addition).

- Write all the reaction equations and give expressions for the equilibrium constants.
- Calculate the equilibrium concentration for each component of the solution.
- Calculate the pH of the solution.

Problem 5 – CALC – Carbon tet

2.000 g of unknown metal oxide with an oxygen content of 31.58% was heated at 750 °C in a quartz tube. Gaseous CCl₄ was passed through the tube. The gases exiting the tube were passed through lime water. 1.974 g of a white substance precipitated, which dissolved in a hydrochloric acid solution. A red-purple powder remained in the tube. At a reduced temperature, chlorine was passed through the tube. At a reduced temperature, the solid turned into a gas which, in reaction with solid CO₂, turned into a brown solid with a chlorine content of 73.1%. The reaction of this compound with water produced an acidic solution and a mixture of gases that changed the color of the KI solution to brown when passed through it.

- Write all the reaction equations and support them with calculations.
- What are the processes involved in the reaction of brown solid with water?

Problem 6 – STRUCT – A colorful manganese complex

KSCN solution was added to Mn(NO₃)₂ solution and a crystalline substance with a molar mass of 445.8 g mol⁻¹ was obtained. The experimentally determined magnetic moment of this compound was equal to $\mu = 6.1$ Bohr magneton. $\mu = \sqrt{n(n+2)}$. Write the formula of the obtained substance, draw its structure, and explain what information the value of the magnetic moment provides.

Problem 7 – ABC – Four seasons

At 500 °C, 8.000 g of substance **B** and 2.469 dm³ of gaseous substance **C** (20 °C and 740 mm Hg) are formed from salt **A** in water vapor. The gas **C** reacts completely with the original amount of substance **A** in an aqueous solution to form 16.800 g of substance **D**. When the resulting solution is boiled and then dried, the original amount of substance **A** is released.

Determine the compounds **A**, **B**, **C**, and **D** (all are water-soluble) and write and prove the reaction of **A** with water vapor.