

5th BChO, 1997, Vilnius, Lithuania

Problem 1 – INORG – Simple electrolysis

The CuSO_4 solution was subjected to electrolysis for 30.0 hours with very intense stirring. During electrolysis, the current density was 1.00 A, and all the copper (31.75 g) from the solution precipitated.

- Which newly formed compound remains in solution?
- What amount (in moles) of this substance was formed?
- What volume of gas (under normal conditions) is released at the anode and cathode?
- Write reaction equations for all the processes.

Problem 2 – INORG – Mercury from a gemstone

One of the methods for obtaining mercury is the calcination of mercury(II) sulfide cinnabar with calcium oxide at 600-700 °C. 500.00 g of cinnabar containing iron(II) sulfide was heated with 170.00 g of calcium oxide. 393.16 g of mercury was distilled off, the reducing agent was oxidized to the maximum. The gray residue was extracted in a Soxhlet extractor for a long time. From the original gray residue, 43.98 g of black powder **A** remained. The solution in the distillation flask and the precipitate formed therein were saturated by boiling with carbon dioxide. The resulting precipitate was filtered and dried; the resulting mass of the precipitate was 443.68 g. An excess of hydrochloric acid was added to the precipitate. After the reaction, precipitate **B** remained, the mass of which, after calcination at 400 °C, was 58.88 g.

- Write equations of all the reactions taking place.
- What mass of CaO is needed to react completely with this ore?
- Write the reaction equations if the reaction mixture was heated with calcium oxide in a current of air.
- What is the % of both FeS and HgS in the ore?
- Why was the solution boiled while being saturated with carbon dioxide?

Problem 3 – EQUIL – Carbon monoxide conversion

Carbon dioxide formed during the combustion of solid fuel takes part in the equilibrium reaction (1) $\text{C(s)} + \text{CO}_2\text{(g)} \rightleftharpoons 2\text{CO(g)}$. The logarithms of the equilibrium constants at 1000 K of the following reactions are given: (2) $\text{C(s)} + \frac{1}{2}\text{O}_2\text{(g)} \rightleftharpoons \text{CO(g)}$ $\log K_2 = 10.477$ and (3) $\text{C(s)} + \text{O}_2\text{(g)} \rightleftharpoons \text{CO}_2\text{(g)}$ $\log K_3 = 20.675$.

- Calculate the equilibrium constant of reaction (1) at 1000 K and 1 atm pressure.
- Find the content of gases (CO_2 , CO, N_2) in vol. % if the temperature in the furnace is 1000 K. The fuel burns in the air, the composition of which is assumed to be 80% N_2 and 20% O_2 .

Problem 4 – ELECTRO – A simple galvanic cell

At 20 °C, the standard EMF of the cell $\text{Pt, H}_2 \mid \text{HCl, HgCl}_2 \mid \text{Hg}$ is 0.2692 V; at 30 °C, it is equal to 0.2660 V. The calomel electrode is the positive pole.

- Write the total reaction equation of the cell.
- Determine ΔG° , ΔH° , ΔS° and the equilibrium constant of the reaction at 25 °C.

Problem 5 – ABC – A funny ketone

Compound **A** ($C_{13}H_{15}NO$) can react with iodine in an alkaline aqueous solution. As a result of the reaction, yellow precipitate **B** ($w_1 = 96.70\%$) and acid **C** ($C_{12}H_{13}NO_2$) are formed. Compound **C** undergoes hydrolysis giving products **D** and **E** ($C_7H_7NO_2$). The original compound **A** undergoes hydrolysis giving products **D** and **F**. When substance **F** reacts with iodine and sodium hydroxide, compounds **E** and **B** are formed after acidification of the reaction mixture with hydrochloric acid.

Compound **E** decomposes if heated with NaOH. In this case, it is possible to isolate the basic compound **G** (C_6H_7N). This compound reacts with an aqueous solution of Br_2 to form a precipitate. Compound **D** (C_5H_8O) does not decolorize the solution of $KMnO_4$. It does not react with metallic sodium or silver oxide in ammonia. It can be oxidized under harsh conditions to acid $C_5H_8O_4$.

Draw the structural formulas of compounds **A–G**.

Problem 6 – ABC, BIO – Sweet toxins

Many marine mollusks contain the toxic substance holothurin, which has the structure **R–O–TS**, in which **R** is a polycyclic alcohol residue, and **TS** is a tetrasaccharide composed of four different monosaccharides **A**, **B**, **C**, and **D**.

After complete acid hydrolysis, two monosaccharides are readily identifiable by paper chromatography. These monosaccharides are glucose (**A**) and xylose (**B**). The molecular mass of saccharide **C** is 164 g mol^{-1} and monosaccharide **D** is 194 g mol^{-1} . According to the NMR spectrum, monosaccharides **C** and **D** contain one methyl group. Both monosaccharides can be obtained from glucose: monosaccharide **C** is obtained by selective reduction; monosaccharide **D** is obtained by methylation at the third position.

By partial enzyme hydrolysis of the tetrasaccharide, the oligosaccharides **DA–OH**, **CD–OH**, and **DAB–OH** can be isolated (–OH represents the oligosaccharide's free reducing group).

a) Draw the structural formulas of **C** and **D**.

b) Draw the structural formula of a tetrasaccharide, assuming that all monosaccharides are in pyranose form and that all monosaccharides are joined by a $\beta(1 \rightarrow 4)$ glycosidic bond.

The structures of glucose and xylose are as follows:

