

2nd BChO, 1994, Vilnius, Lithuania

Problem 1 – INORG – Famous for not just the wine

The Burgundy mixture is prepared from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and Na_2CO_3 (soda) and is used to protect plants from fungal diseases. In agriculture, 1% of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (by mass) is prepared and dissolved in an equivalent soda solution to produce 1% Burgundy mixture. To prepare the Burgundy mixture, a gardener took soda with 50% excess. Then, he added CuSO_4 solution to the soda solution. The mixing was carried out in a zinc-coated vessel. Due to carelessness, instead of soda ash (Na_2CO_3), the gardener took crystalline soda ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), assuming it is an anhydrous salt.

- Write equations of the described reactions.
- Estimate the mass percentage of soluble substances in the resulting solution.

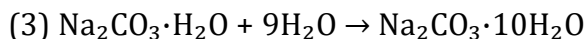
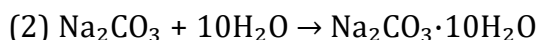
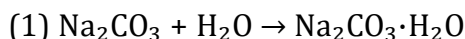
Problem 2 – KINETICS – Unstable chemical

Substance **A** decomposes spontaneously. The half-life of substance **A** at 30 °C is 318 seconds, and at 24.7 °C – 460 seconds. How much time is needed for substance **A** to decay 99% at 35 °C.

Problem 3 – EQUIL, THERMO – All the kinds of soda

The enthalpies of dissolution of Na_2CO_3 , $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ and $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ are $-24.6 \text{ kJ mol}^{-1}$, $-10.5 \text{ kJ mol}^{-1}$, and 66.6 kJ mol^{-1} , respectively.

- Calculate the enthalpies of hydration of the following reactions.



10.0 grams of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ was dissolved in 10.0 grams of water.

- Calculate the molar fraction of Na_2CO_3 in the solution.
- Calculate the pH of the solution ($K_{a1} = 4.45 \cdot 10^{-7}$, $K_{a2} = 4.69 \cdot 10^{-11}$; $\rho = 1.2 \text{ g cm}^{-3}$).

Problem 4 – INORG – Copper nitrate

19.1 grams of copper was dissolved in 189 cm^3 of 40.0% nitric acid ($\rho = 1.25 \text{ g cm}^{-3}$) which gave off 6.72 dm^3 of gases (STP) with a density of 1.93 relative to air.

- Which gases were released and in what ratio?
- Write equations of the described reactions.
- How much unreacted nitric acid remained in the solution?

Problem 5 – ELECTRO, EQUIL – A simple lead battery

Hydrogen and $\text{Pb}/\text{Pb}(\text{OH})_2$ electrodes were used to make a galvanic cell with KOH electrolyte.

- Write the reactions occurring at the electrodes (the hydrogen electrode, in this element, is the negative electrode).
- Write an equation to calculate the EMF and show that the EMF does not depend on the concentration of the solution.
- Calculate the solubility product value of $\text{Pb}(\text{OH})_2$ at 25 °C, knowing that $\text{EMF} = 0.261 \text{ V}$, the standard potential of lead with respect to $[\text{Pb}^{2+}]$ is $E^\circ(\text{Pb}^{2+}/\text{Pb}) = -0.126 \text{ V}$, and $K_w = 10^{-14}$.

Problem 6 – MECH, STEREO – Three children of cyclohexane

Three cyclohexane derivatives, **A**, **B**, and **C**, contain the same percentage of chlorine – 73.20%. In a $4.70 \cdot 10^{-3}$ molar sodium hydroxide solution in ethanol, the reaction rates of **A**, **B**, and **C** were measured at the same concentration ($8 \cdot 10^{-4}$ M). Substance **B** did not react. The reaction rate constants for compounds **A** and **C** were 0.167 and $0.0435 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively. In both reactions, only one product (a diene) was formed.

- Explain why the reaction rate constants are different.
- Draw structural formulas of **A–C**. Label the absolute configurations for **A–C**.
- Write the reaction equations.

Problem 7 – ABC, BIO – The smell of Baltics

Terpenoids consist of isoprene (2-methyl-1,3-butadiene) fragments and contain different functional groups (hydroxyl, etc.). These compounds have a pleasant odor and are found in the essential oils of plants. Terpene **A** is a cyclohexane derivative, which is oxidized to ketone **B** with chromic acid. Dehydration of **A** produces compound **C**, which contains 86.96% carbon and 13.04% hydrogen. When **C** is hydrogenated, compound **D** is formed. Ozonolysis of product **C** with water yields substance **E**. Oxidation of substance **E** under severe conditions yields a mixture of various acids and CO_2 . It is possible to isolate 3-methylpropane-1,3-dicarboxylic acid (β -methyl- glutaric acid) from the mixture.

- Draw the structures of **A–E**.
- Write all the described reaction equations.
- Which plant essential oils contain substances **A–C**.

Problem 8 – ABC, SPECTRA – Another fossil fuel

0.10 grams of a hydrocarbon was burned, and the gaseous products were passed through 300 cm^3 of 0.0200 molar $\text{Ba}(\text{OH})_2$ solution, resulting in 0.850 g of precipitate. The ^1H NMR spectrum of this carbohydrate consists of one quartet. X-ray structural analysis showed that the lengths of C–C bonds between all carbon atoms in the hydrocarbon are the same. Write the structural formulas of three hydrocarbons that meet the conditions.