

4th BChO, 1996, Riga, Latvia

Problem 1 – ABC – An unknown alloy

1.0000 g of powder of a mixture of two metals was heated at 300 °C in a stream of NO₂. As a result, 0.6683 g of light yellow substance **A** ($w_0 = 25.18\%$) was distilled off, and 0.7149 g of red powder remained in the reaction vessel. The reaction of **A** with concentrated hydrochloric acid produced 129.9 cm³ of gas at 25 °C and 100.2 kPa. The density of this gas under these conditions is 2.8689 g dm⁻³. After the excess hydrochloric acid was neutralized with KOH, a compound with a chlorine content of 44.21% was isolated. This compound was dissolved in hydrochloric acid, and upon the addition of zinc, one of the parent metals was obtained.

- Identify two metals in the original mixture.
- Write equations for all reactions.

Problem 2 – APPLIED, THERMO – Old-school hydrogen

One industrial method of hydrogen production is the Mark-1 thermodynamic cycle:

- $\text{CaBr}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + 2\text{HBr}$
- $2\text{HBr} + \text{Hg} \rightarrow \text{HgBr}_2 + \text{H}_2$
- $\text{HgBr}_2 + \text{Ca(OH)}_2 \rightarrow \text{CaBr}_2 + \text{HgO} + \text{H}_2\text{O}$
- $2\text{HgO} \rightarrow 2\text{Hg} + \text{O}_2$

A second purely thermodynamic hydrogen production cycle, Mark-8, was developed by the author of Mark-1 two years later. The Mark-8 cycle, like the Mark-1 cycle, utilizes water and thermal energy. The Mark-8 cycle involves the manganese compounds MnCl₂, Mn₃O₄, and MnO₂, as well as HCl, H₂O, H₂, and O₂. Oxygen is released at 1170 K from manganese dioxide; the other two reactions occur at 970 K and 370 K.

- Write the reaction equations occurring in the Mark-8 cycle.
- Explain the advantages of each of the cycles.

Problem 3 – ELECTRO – On cobalt and ammonia

For the determination of the ligand molecule number in complex cation $\text{Co(NH}_3)_n^{2+}$, the EMF of the following electrochemical cell $\text{Co} \mid 0.05 \text{ M CoCl}_2 + x \text{ M NH}_3 \cdot \text{H}_2\text{O} \mid 1.00 \text{ M NaOH} \mid \text{HgO} \mid \text{Hg}$ at 25 °C was determined at various concentration of dissolved ammonia. The gas phase was, in all cases, in equilibrium with the solution. Calculate the n value using data given in the table assuming that in all solutions $[\text{Co}^{2+}] \ll [\text{Co(NH}_3)_n^{2+}]$, thus $[\text{Co(NH}_3)_n^{2+}] \approx \text{const.}$

EMF [V]	0.619	0.659	0.683	0.715
$p(\text{NH}_3)$ mmHg	27.8	44.7	63.4	107.7

Problem 4 – EQUIL, THERMO – Combustion of acid vapors

At 1000 K and pressure 10⁵ Pa, the degrees of dissociation of water vapor and hydrogen chloride are $2.48 \cdot 10^{-7}$ and $1.10 \cdot 10^{-3}$, correspondingly. Calculate the value of equilibrium constant and Gibbs free energy change for the reaction $4\text{HCl} + \text{O}_2 \rightleftharpoons 2\text{Cl}_2 + 2\text{H}_2\text{O}$.

Problem 5 – ABC, SPECTRA – Determining molecular mass without a mass spectrometer

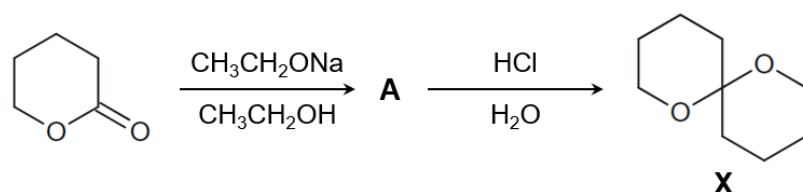
Organic compound **A** (melting point 167 °C) consists of two elements. The mass fraction of element **X** is 88.8%. In the ¹H-NMR spectrum of compound **A**, there is only one signal (singlet, $\delta = 2.34$ m.d.). To determine the molecular weight by cryoscopy, 0.040 g of compound **A** was fused with 0.50 g of camphor – the melting point of the mixture was 159 °C (melting point of

pure camphor is 178 °C, cryoscopic constant $K = 39.7 \text{ K kg mol}^{-1}$). Heating substance **A** in potassium permanganate solution, substance **B** ($w_x = 42.1\%$). Heating **B** in excess of acetic anhydride yielded substance **C**, which also consists of two elements and the mass fraction of element **X** in the substance is 50.0%.

- Write the chemical formulas of **A–C**.
- Write the equations for all reactions.

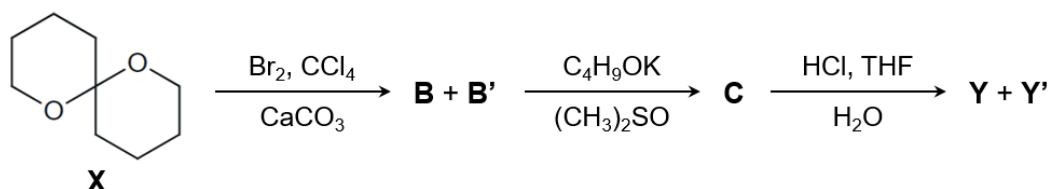
Problem 6 – STEREO, SYNTH – Chemical hormones

The widespread use of insecticides causes a disturbance of the ecological balance, which makes it relevant to use pheromones to monitor this insect and to keep it under control. The main active substance of pheromone is 1,7-dioxaspiro(5,5)undecane – compound **X**. It is synthesized from δ -valerolactone.



- Identify the intermediate compound **A**.
- Compound **X** exists in a single configuration. Draw the structure of this configuration and note the stereoelectronic effects that make it stable.
- Identify peaks in the ^1H NMR spectrum of compound **X** at 3.52 (2H) and 3.65 (2H).

Feramon also contains compound **Y**. The scheme of its production is as follows:



- The halogenation of a carbonyl compound occurs via an enolic intermediate **X** (acetal). Write the mechanism of bromination of **X**.

Upon treatment of brominated **X** with potassium *tert*-butoxide in dimethyl sulfoxide at 110 °C, compound **B'** reacted completely. On further heating for 6 hours, compound **B** reacts completely as well. In both cases, compound **C** is formed.

- Write the structural formulas of **B** and **B'**. Explain the reactivity of compounds **B** and **B'** in terms of the reaction mechanism.

Compound **C** is converted into diastereoisomers **Y** and **Y'** ($M = 172 \text{ g mol}^{-1}$) by stereospecific hydration in THF (tetrahydrofuran). The ratio of the stereoisomers **Y** : **Y'** = 18 : 1.

- Write their structural formulas and write reaction equations for each stage. Identify the structural effects that cause the preferential formation of compound **Y**.
- Write the absolute configurations of all chiral atoms in compounds **Y** and **Y'**.