

6th BChO, 1998, Tartu, Estonia

Problem 1 – ABC, CALC – Another white powder in the lab

The analysis laboratory received a white crystalline material for analysis. The analyst weighed out two samples of the material. Sample 1, with a mass of 1.084 g, was dissolved in water. As the material dissolved, 26.17 cm³ of gas, having a mass of 37.39 mg, was released. The resulting solution was found to be very acidic. Addition of hydrochloric acid caused a precipitate to form. After the addition of 47.5 cm³ 0.0983 molar HCl, no more precipitate was formed. The precipitate was recovered, dried, and weighed. The mass of the precipitate was 0.6693 g.

Sample 2, with a mass of 1.120 g, was heated to above 300 °C. During heating, 324.6 cm³ of gas was collected with a mass of 599.0 mg. After heating, a light-colored metal with a mass of 0.521 g remained. The gas was dissolved in 100 cm³ of water. Not all the gas dissolved, 54.10 cm³, with a mass of 77.2 mg, remained. The pH of the solution was found to be 1.015.

- Determine the compound in the sample with calculations.
- What reactions took place during the analysis?

Problem 2 – CALC – Analysis of gas mixture

A sample of a compound was heated at 600 °C. A solid with a mass of 4.51 g remained after heating and 21.48 dm³ of gas was liberated at 600 °C. The solid contains 21.25% oxygen. After cooling to room temperature, the gas occupies 2.69 dm³ and has a density of 1.61 g dm⁻³. After passing the gas through an alkaline solution, there remained 1.34 dm³ of a combustible gas having a density of 1.25 g dm⁻³.

- Determine the compound in the sample.
- Write all appropriate equations.

Problem 3 – STEREO, SYNTH – Recreating a natural biosynthesis in a lab

R-(+)-glycerol aldehyde can be transformed to (-)-malic acid (2-hydroxybutanedioic acid) according to the following scheme. *R*-(+)-glycerol aldehyde was treated with hydrogen cyanide and two isomeric compounds were formed, namely **A** and **B**. Those compounds were separated by fractional crystallization. Only isomer **B** was used for further transformations. This compound was converted to **C** (C₄H₈O₅) upon hydrolysis and then oxidized by conc. nitric acid to produce compound **D** (C₄H₆O₆). Further, compound **D** was treated with phosphorus tribromide, thus, compound **E** (C₄H₅BrO₅) was formed. Finally, compound **E** was converted to (-)-malic acid after the reaction of zinc with an acid.

- Write the equations of all reactions using stereochemical (Fisher projections) formulas.
- Explain why only one isomer **E** was formed from **D**.
- How many isomers of **E** can be formed starting the synthesis from an isomer **A**?

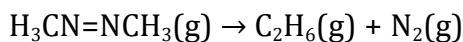
Problem 4 – MECH – Lethally spicy

Mustard gas (2,2'-dichloro sulfide) can be used as a chemical weapon via releasing HCl in hydrolysis reaction. In comparison, 1,5-dichloropentane is hydrolyzed much more slowly.

- Write the mechanism of the above-described reaction for both compounds.
- Which well-known compound might be used to destroy this gas?
- Write a synthetic pathway to produce the mustard gas.

Problem 5 – KINETICS – A rapid synthesis of ethane

The thermal decomposition of azomethane (compound **A**) follows the equation:



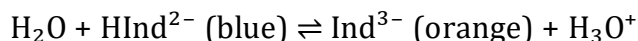
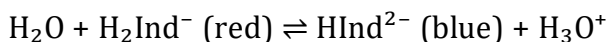
The half-life of compound **A** at 320.6 °C is 9.5 min. The total pressure of the mixture of gases at the temperature of 298.0 °C was measured at different time periods:

t [min]	10.0	21.0	35.0	∞
p [Torr]	491.9	548.0	609.7	861.6

- Prove that the process is a first-order reaction.
- Calculate the average value of the rate constant at 298.0 °C.
- Determine the activation energy of the reaction.

Problem 6 – EQUIL – pH-dependent titration

Eriochrome Black T (H_3Ind) is a typical metal ion indicator used in complex-formation titrations with EDTA ($\text{Na}_2\text{H}_2\text{Y}$). This compound contains a sulfonic acid group, which is completely dissociated in water, and two phenolic groups that dissociate only partially ($K_{a1} = 5.0 \cdot 10^{-7}$ and $K_{a2} = 2.8 \cdot 10^{-12}$).



- The metal complexes of Eriochrome Black T are generally red. Calculate the minimum pH at which Eriochrome Black T can be used as an indicator in complex-formation titrations (assume that the detectable color change requires a tenfold excess of one or other colored species).
- Determine the transition range for Eriochrome Black T in titrations of Mg^{2+} and Ca^{2+} at pH 10.0, given that the (thermodynamic) formation constant for MgInd^- is $1.0 \cdot 10^7$ and for CaInd^- is $2.58 \cdot 10^5$.

50.00 cm³ of 0.00500 M Mg^{2+} and Ca^{2+} solutions were both titrated with 0.0100 M EDTA solution at pH 10. Conditional formation constants (Instead of the equilibrium concentration of Y^{4-} the total concentration of all forms of EDTA is used) at that pH are $1.72 \cdot 10^8$ for MgY^{2-} and $1.75 \cdot 10^{10}$ for CaY^{2-} .

- Calculate the equilibrium concentrations of the metal cations at the equivalence point.
- Determine the sign of the relative error, connected with assuming that the stoichiometric point is judged to be approached at the first change of color of the solution.