

Problem 1 – CALC, CRYSTAL, SPECTRA – European Union

Two chemists received for analysis two samples of a metal ($\rho = 5.245 \text{ g}\cdot\text{cm}^{-3}$) with equal mass. Both chemists used X-ray analysis to determine that the metal crystallized in the BCC arrangement with the elementary cell edge length of $4.582 \text{ \AA}$.

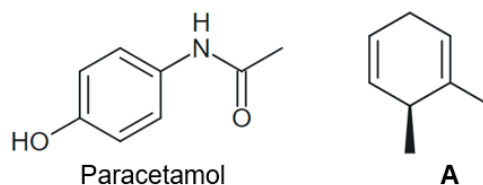
The more careless chemist left the sample in the air, where its surface quickly lost metallic shine. When he crushed the sample and put it into a beaker with water, a vigorous reaction gave a white precipitate. The obtained solution was strongly basic. The solution containing the precipitate was acidified with hydrochloric acid and carefully evaporated to obtain 363.7 mg of colorless crystals. Sulfur(IV) oxychloride was added to the crystals and refluxed until the evolution of gases had ceased to give 340.0 mg of white deliquescent crystals. Their IR spectrum was obtained at low temperatures, in high dilution, in the matrix of an inert gas, and displayed four bands. The compound was put into a beaker and dissolved in water. Dilute sulfuric acid was added to the solution until no more precipitate formed. 166.9 mg of colorless crystals were obtained. On heating, the mass of the crystals reduced to 134.2 mg and did not change anymore.

The other chemist never liked to go to the beaten path. So, he dissolved his sample in liquid ammonia to obtain, under an inert atmosphere, a blue solution. As he added ammonium chloride to the solution, the solution became colorless, a gas evolved, and some precipitate formed. The precipitate was gently heated *in vacuo* to yield 293.3 mg of a white crystalline solid. Its IR spectrum displayed three bands. The compound was put into a beaker and dissolved in water. Dilute sulfuric acid was added to the solution until no more precipitate formed. Some excess acid was added, and the solution was set aside to ensure complete precipitation. Yet, contrary to expectations, the mass of the colorless, crystalline precipitate significantly decreased on standing. By pure coincidence, the second chemist also obtained 166.9 mg of precipitate. On heating, the mass of the precipitate reduced further to 134.2 mg and did not change anymore.

- Using the X-ray data, determine the analyzed metal.
- Draw structural formulas for both compounds analyzed by IR spectroscopy. Identify vibrations corresponding to the observed bands.
- Write equations for all the mentioned reactions.

Problem 2 – ABC, SYNTH – After the fever is gone

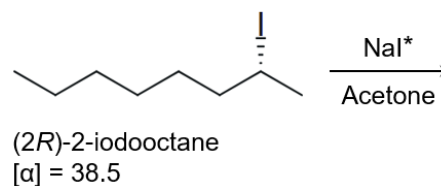
When **A** reacts with O_3 in water, compounds **B** and **C** are formed. Both compounds react with PCl_5 yielding **D** and **E**. Compound **D** can react with paracetamol to yield **F** and **G**. Compound **E** reacts with paracetamol yielding compound **H**. Vapor of **F** over anhydrous AlCl_3 leads to compound **I**. In the presence of $\text{HF} + \text{SbF}_5$ mixture, compound **H** isomerizes to **J** and **K**. When **I** is heated in attenuated sulfuric acid, compound **L** is formed. Under the same conditions, both **J** and **K** yield to **M**.



- Draw the structures for compounds **A–M**.
- Describe the function of anhydrous AlCl_3 .
- Describe the function of $\text{HF} + \text{SbF}_5$ for **H** isomerization.

Problem 3 – KINETICS, MECH – Nucleophilic substitution

Nucleophilic substitution plays a prominent role in functional group transformations. We distinguish between two limiting mechanisms for nucleophilic substitution: S_N1 (unimolecular) and S_N2 (bimolecular). For some reactions, it is possible to determine the mechanism using chiral reagents. The reaction of (2*R*)-2-iodooctane with radioactive iodide ions was investigated.



Assuming that only nucleophilic substitution reactions take place and radioactive iodine isotope has the same chemical and physical properties as non-radioactive isotope, explain the experimental data:

t [s]	0	633	1523	1945	2718	4214	5378	7163	9231	13332
α [°]	2.36	2.29	2.19	2.14	2.05	1.92	1.80	1.65	1.51	1.18

- Specific rotation of reaction mixture changes during the reaction. Which mechanism can be used to explain such results?
- The rate of non-radioactive iodine substitution with radioactive isotope is two times less than the racemization rate. How could you explain this phenomenon?
- What will the specific rotation of the reaction be after the reaction has ended?
i) +38.5°; ii) -38.5°; iii) 0°; iv) +77°; v) -77°.
- To determine the radioactive isotope substitution rate, the reaction is stopped with the addition of cold water and extraction with CCl_4 . What substance(s) are found in the water phase? Why is it better to use cold water?
- When the reaction is performed in methanol, the relation between the racemization rate and radioactivity of organic extract is not observed. How can this phenomenon be explained?
- Calculate the racemization if $[2\text{-iodooctane}]_0 = 0.118\text{ M}$ and $[NaI^*]_0 = 0.0163\text{ M}$.

Problem 4 – INORG, SPECTRA – Pharaoh's Compliment

To the cobalt(II) chloride solution, a white solid **A** (18.1% C, 7.52% H, and 53.3% Cl), NaOH and 30% H_2O_2 were added separately. Orange compound **B** (19.8% C, 7.16% H, and 29.3% Cl) was obtained. In small amounts, concentrated ammonia and excess aqueous formaldehyde were added to the solution of **B** at pH 10, and a yellow solid **C** (31.9% C, 6.65% H, and 23.6% Cl) was isolated. ^{13}C NMR spectra show one signal for **A** (43 ppm) and **B** (45 ppm) and two signals of equal intensity for **C** (54 and 67 ppm). ^1H NMR spectra in D_2O show a singlet for **A** (2.65 ppm) and a broad singlet for **B** (2.85 ppm).

- Identify compounds **A**, **B**, and **C**.
- B** is an equimolar mixture of two enantiomers: **B1** and **B2**. Draw structural formulas for **B1** and **B2**. Propose how they can be isolated separately.
- Compound **C** was given the trivial name sepulchrates ("sepulchrum" means "grave or sarcophagus" in Latin). Write a structural formula for **C** and propose the reaction $B \rightarrow C$ mechanism.

Problem 5 – EQUIL – Chemical equilibrium

The vessel with a volume of 1200 cm^3 was vacuumed and filled with nitrogen monoxide up to pressure 180.0 mm Hg at 297 K . Then the gas was frozen, and 720.0 mg bromine was added to the vessel. The temperature was raised to 335 K . After the equilibrium was reached, the pressure in the vessel was 230.0 mm Hg .

- a) Write the equation for the chemical reaction.
- b) Calculate the equilibrium constant K_p for the nitrosyl bromide decomposition (the vessel volume does not change with the temperature).
- c) How does the pressure influence the equilibrium state?
- d) Calculate the amount of nitrogen oxide moles in the equilibrium mixture.

Problem 6 – ELECTRO, EQUIL – Electrolysis

The aqueous solution containing ethanoic acid and sodium ethanoate was electrolyzed. The gases deliberated on Pt-electrodes were collected and purged through a concentrated KOH solution. It was established that during the electrolysis at STP, the mass of the KOH solution was increased by 5.213 g .

- a) Write the equations for electrode reactions.
- b) Calculate the amounts (mol dm^{-3}) of gases evolved at the anode and reacting and not reacting with KOH solution. The relative density of non-reacting gas against hydrogen is 15.0 .
- c) Calculate the consumed electrical energy (A h) if the yield of anodic reaction products by current was 100% .
- d) What was the electrolysis duration if the current was 706 mA ? Calculate the mass of Cu deposited in a copper coulometer serially connected with an electrolyzer.
- e) Calculate the equilibrium potential when the ratio of ethanate concentrations is $1 : 3$ and the hydrogen partial solution is $1.0 \cdot 10^5\text{ Pa}$. $K_a(\text{CH}_3\text{COOH}) = 1.85 \cdot 10^{-5}$.