# PART II.c – Analytical chemistry

## Problem 1

During the decay of radon isotopes $^{210}$Pb, $^{210}$Bi and $^{210}$Po are formed in steady-state concentrations. These isotopes were separated and dissolved to form a solution. When copper plate was put into the solution, α-radioactive isotope X precipitated. Then remaining solution was evaporated and the remaining solid was dissolved in hydrochloric acid. To the solution which formed 2 mg of isotope **Z** chloride were added. After nickel plate was put into the solution, β-radioactive isotope **Y** precipitated. Isotope **Z** remained in the solution.

1. Which isotope of radon forms the named isotopes $^{210}$Pb, $^{210}$Bi and $^{210}$Po?
2. Calculate conventration of isotopes in 0,1 M HCl solution, which emits 500 β decays per minute per dm$^3$.
3. Calculate which form of $\mathrm{BiCl}_n^{m+}$ is in excess in 0,1 M Hcl solution. $\mathrm{p}K_{\mathrm{Bi^{3+}/BiCl^{2+}}} = 2,44$, $\mathrm{p}K_{\mathrm{BiCl^{2+}/BiCl_2^+}} = 0,66$, $\mathrm{p}K_{\mathrm{BiCl_2^+/BiCl_3}} = 0,64$, $\mathrm{p}K_{\mathrm{BiCl_3/BiCl_4^-}} = 0,03$.
4. Draw molecular structure of $\mathrm{MeCl}_n^{m\pm}$ ions (determine the metal), which may be presented in solutions with the named geometry: i) seesaw, ii) trigonal pyramidal, iii) tetrahedral pyramidal, iv) octahedral.
5. Determine isotopes **X**, **Y**, **Z**. $E^0_{\mathrm{Pb^{2+}/Pb}} = -0,13\,\mathrm{B}$, $E^0_{\mathrm{Bi^{3+}/Bi}} = +0,23\,\mathrm{B}$, $E^0_{\mathrm{Po^{4+}/Po}} = +0,77\,\mathrm{B}$.

## Problem 2

### Analyzing minerals with methods from 19th century

A mineral from a copper mine was brought to chemist because copper could not be extracted from it despite its metallic luster. Chemist suspected this to be a different sulphide mineral because copper is mined as a copper sulphide. He carried out the following experiments:

A sample was crushed and then was heated in air for a long time. After heating its metallic luster had disappeared, its mass had increased by 9,7% and there was a smell of burning sulphur in the lab. 10g of the resulting orange powder (X) were mixed with 100g of water. It seemed not to dissolve and was still orange, but when it was filtrated and weighted its mass had decreased by 5%. Filtrate (Y) was concentrated by evaporation and white solid particles formed. The solution itself showed no change when either sulphuric acid or sodium hydroxide were added, however, when zinc granules were dropped into the mixture of the solution, white participate and sulphuric acid a gas was released and it had a slight smell of garlic. At this point the chemist was confident that he knew what kind of mineral that was. However, just to be sure he carried out two more experiments. He prepared another solution A and this time he added hydrochloric acid to it. Then he bubbled hydrogen sulphide through it. He predicted that yellow participate will be formed and he was right, form 100 g of filtrate Y 1.8-1.9g of yellow solid was formed. Then he took the powder X produced by heating and heated it in a glass pipe under a flow of hydrogen. A black powder at the same place and a black shiny residue slightly downstream the pipe was formed. The black powder unlike the orange one was attracted by a magnet.

1. What was the composition of the mineral (you can give the name as well if you know it)?

2. Give balanced equations for all reactions, including those that are not obvious.

## Problem 3

Radioactive element X was discovered in 1898 by Pierre and Marie Curie, when they were looking for a source of strong radioactivity of several minerals. Marie Curie dissolved mineral containing U, Th, Pb, Bi, Cu, As, Sb, X and some other elements in nitric acid. Then evaporated the solution, dissolved the dry residue in water and treated with gaseous hydrogen sulfide. Black radioactive precipitate formed which she treated with ammonium sulfide to separate arsenic and antimony, which form tiosalts **A** ($\omega_{As}$ = 29.1%, $\omega_N$ = 16.3%) and **B** ($\omega_{Sb}$ = 44.7%, $\omega_N$ = 15.4%). Undissolved part of the

precipitate Curie dissolved in nitric acid, then added sulfuric acid and evaporated solution on the burner flame until dense white fumes of $SO_3$ formed. After cooling down the participate it was found to contain only a nonradioactive sulfate **C**. Then to the filtered solution a concentrated solution of ammonia was added. This time a white precipitate formed containing basic suflate **D** and hydroxide **E** of the same element, and color of the solution turned deep-blue. Unlike the filtrate the white precipitate was radioactive. Curie once again modified white precipitate to dark-brown sulfide **F**, dryed it and heated in an evacuated ampoule. Solid emitted some fumes, which condensed in a form of a black film **G** ($\omega_S$ = 13.2%) at a cold glass. The film was radioactive and obviosly contained a new radioactive element.

1. Determine the compounds **A**–**G.**
2. In which order do the sulfides of the following cations precipitate: $Pb^{2+}$, $Bi^{3+}$, $Cu^{2+}$ and $X^{2+}$, if solubility products are: SP(PbS) = $10^{-26.6}$, SP($Bi_2S_3$) = $10^{-97}$, SP(CuS) = $10^{-35.1}$, SP(XS) = $10^{-29.7}$.
3. At which pH value does $Bi(OH)_3$ start precipitating from 0.01 M solution of $Bi^{3+}$ and at which pH value pH $Bi^{3+}$ is precipitates (by 99.99%), SP($Bi(OH)_3$) = $10^{-39.5}$.

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