SECTION I. LIFE SCIENCES AND POLYMERS

Problem 1

Both industrial and home cooking can lead to substances potentially harmful to man. The reasons include high temperatures, extreme pH and non-natural compounds (e.g. preservation agents).

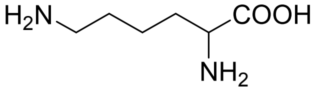
A non-canonical α-amino acid **A** (40.44% C, 7.92% H, 15.72% N, and 35.92% O by mass) is formed from a canonical amino acid **B**, for example as a result of soya bean processing into its hydrolysate.

1. Draw the structures of the amino acids **A** and **B** with stereochemical details, if no other initial compounds but **B** are needed in the reaction of **A** formation.

A is one of substrates in the enzymatic synthesis of a dipeptide **C** (26.1% C, 52.2 % H, and 13.0% O by moles) occurring in bacteria. **C** is found in the cell wall peptidoglycan as a terminal residue, and is vitally important for the bacteria stability. Alkaline hydrolysis of **C** under extreme conditions leads to the formation of an optically inactive substance **D** as the only product.

2. Deduce **C** and **D**.

The amino acid **X** causes high nephrotoxicity in mice. The **X** residue can be formed upon heat treatment of protein containing food in alkaline medium (e.g., upon milk sterilization). The **X** residue is formed due to a modification of the side chain of the canonical amino acid *L*-lysine.



lysine

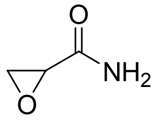
It is worth mentioning that there is a stable intermediate interacting non-enzymatically with the lysine residue at the stage of **X** formation. The intermediate is the residue of a non-canonical α-amino acid **Y** (41.38% C, 5.79% H, 16.09% N, and 36.74% O by mass), which cannot be isolated in a free form because of its low stability.

3. Draw the structures of **X** and **Y** with stereochemical details.

4. Write down the reaction equations explaining extreme instability of **Y** in an aqueous solution.

5. Propose the structural formulae of two canonical amino acids (without stereochemical details), residues of which in a protein can form the **Y** residue in one stage at pH≥10.

Acrylamide is another toxic substance formed during cooking. It is transformed into glycidamide in a process catalyzed by the cytochrome P450 dependent monooxygenase. Glycidamide interacts with DNA nitrogenous bases (a nitrogen atom in the cycle is being attacked), which is behind mutagenic action of the substance.

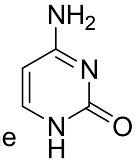


glycidamide

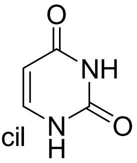
It was demonstrated that **Z** reacts with 2'-deoxycytidine in a buffer solution with the formation of two products **Z1** (45.71% C, 35.53% O, and 13.33% N by mass) and **Z2** (45.57% C, 40.47% O, and 8.86% N by mass).

6. Draw the structural formulae of **Z1** and **Z2**, if it is known that **Z2** (by contrast to **Z1**) is a 2'-deoxyuridine derivative.

The structures of nitrogenous bases are:



cytosine



uracil

Problem 2

Reactions of carbohydrates are important in living things. However, even in the absence of additional reactants, various reactions can occur in aqueous solutions of sugars.

1. Based on the Fischer projection of D-glucose given in the Answers Sheet, draw all its cyclic forms coexisting in its aqueous solution.

Microwave treatment of a glucose solution in aqueous sulfuric acid leads to the formation of valuable products. One of these, **A** (^{1}H NMR, ppm: 9.59 s, 1H; 7.22 d, 1H; 6.52 d, 1H; 4.73 s, 2H; 3.73 broad s, ex. with D_2O) is a product of elimination of three water molecules from glucose. It is the formation of **A** in acidic medium that determines the sample coloration in the Molisch's test for carbohydrates (the reaction with phenols). Reduction of **A** affords **B** which is used in the synthesis of polyurethanes. The ^{1}H NMR spectra of **B** posess 3 signals, one of these exchange with D_2O.

2. Draw the structures of **A**, **B**, copolymer of **B** with hexamethylene-1,6-diisocyanate, and the product of interaction of **A** with two molecules of α-naphthol.

Heating of an aqueous solution of carbohydrates leads to its transformation into dark viscous mass (this is the way to caramel). The selectivity of the process being poor due to high temperature, the product mixture contains hundreds of compounds formed via isomerization, dehydration, condensation, and disproportionation. The overall process can be illustrated by the van Krevelen diagram (with the H/C and O/C ratios in the products at the axes, each product being represented by a point).

3. a) At the van Krevelen diagram of the products of glucose caramelization (see the Answers Sheet), draw an arrow showing the exact direction corresponding to the intramolecular dehydration. Calculate the slope of the arrow referred to the horizontal axis.

b) From the list given there, choose the type of reactions leading to the group III products.

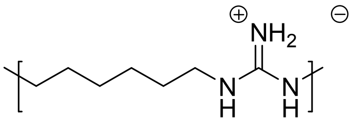
Caramelization of glucose occurs at 160°C, therefore heating of the aqueous solution leads first to evaporation of the major fraction of water, and the reactions take place practically in the glucose melt. Heating in a sealed vessel (autoclaving) allows attaining high temperature even of dilute solutions. Autoclaving brings water to the subcritical state with significantly decreased dielectric constant, making possible reactions atypical for aqueous solutions. Autoclaving of aqueous solutions of glucose affords nanoparticles with the graphite core and the surface bearing different oxygen-containing functional groups.

4. A small fraction of similar products is formed during caramelization at atmospheric pressure. Which group number at the van Krevelen diagram such products belong to?

Composition of the autoclaving products is described by the content of the functional groups per substance mass rather than by conventional formulas. The Boehm titration described below is a convenient method of analysis of carbonaceous particles. Two portions of the particles (0.5000 g each) were incubated in aqueous solutions of sodium hydrocarbonate and sodium hydroxide (concentration of each 0.1000 M, volume of each 50.00 mL). The precipitates were then discarded, and 10.00 mL aliquots of 1.000 M hydrochloric acid were added to each filtrate. The filtrates were boiled and titrated with 1.000 M of sodium hydroxide solution. 7.10 and 8.35 mL of the titrant were consumed, respectively.

5. Suppose that only carboxylic and phenolic oxygen-containing groups are found at the particles surface. Determine the quantities of these groups per 1.000 g of the particles.

Since acidic groups are found at the surface of the prepared particles, the latter can be used for removal of basic pollutants (e.g. bactericide agent Biopag) from an aqueous solution.



Biopag

The interaction of equal volumes (1 L each) of aqueous solutions (both at pH 4) of Biopag (44.43 g/L) and polyacrylic acid (18.00 g/L) resulted in the release of additional 0.22 mol of protons into the solution. The insoluble product did not contain chloride ions, and polyacrylic acid was not found in the solution.

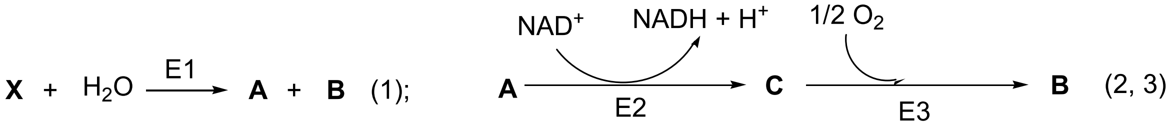
6. Calculate the fraction of Biopag left over in the solution after the interaction with polyacrylic acid and the mass fraction of Biopag in the dried precipitate.

7. Calculate the maximum mass of Biopag which can be removed from its aqueous solution using 1.000 g of nanoparticles described in i. 5. Suppose equal efficiency of Biopag interaction with the acidic groups of polyacrylic acid and the carbonaceous nanoparticles.

Problem 3

In 2017, the HVMN Company commercialized Ketone, a novel energy drink based on the compound **X** and designed to improve the athletes' results.

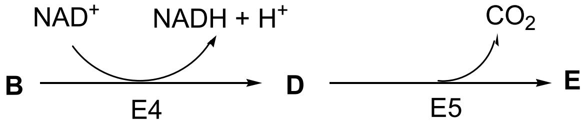
If taken, **X** (54.53% C, 9.15% H, 36.32% O by mass) is hydrolyzed in small intestine affording the compounds **A** and **B**. **A** is absorbed into blood, which is followed by its metabolic transformation into **B** in liver. The corresponding reaction equations are given hereunder (E1 – E3 are enzymes):



1. Deduce the molecular and all possible structural formulae of **X** meeting the above conditions including **A** transformation into **B** and having the minimum possible molecular mass.

2. How would your previous answer change if you get to know that the molar fraction of C is higher by 6.7% than that of O in **B**. Be sure to support your new answer by calculations.

B can be enzymatically oxidized in blood into the compound **D**, which decomposes either enzymatically or non-enzymatically to the compound **E** containing hydrogen atoms of only one type. The corresponding reaction equations are given hereunder (E4 and E5 are enzymes):



3. Deduce the structural formulae of **A** and **X**.

Let us suppose you have decided to use Ketone to run marathon (42.2 km) having in mind to demonstrate a very good time of 2 hours 20 minutes (neglect energy consumption on all other process but running). It is known that:

- The derivative of **D** with co-enzyme A reacts with free co-enzyme A affording the sole product **J**. Complete oxidation of **J** in mitochondria leads to energy elaboration of 360 kJ/mol;
- The efficiency of **J** oxidation in man approaches two thirds of the theoretical maximum;
- Running on a plane road requires 40 kJ/min at the speed of 8 km/h, 65 kJ/min at 11 km/h, and 95 kJ/min at 19 km/h.

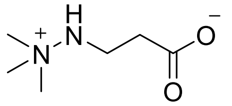
4. Calculate the number of the Ketone bottles (shown on the picture) you will need provided **X** is your only energy source when running. If you have failed to deduce the structure of **X**, show your work in general form.

Some bacteria (e.g. *Ralstonia eutrophus*) produce a biopolymer using **B** as the only starting substance.

5. Draw the structural formula of the biopolymer.

6. In the Answer Sheet, choose only one correct statement explaining the reason behind the biopolymer synthesis by microorganisms.

It is quite probable that **X** will be once included in the list of the World Anti-Doping Agency (WADA), similarly to what has happened to the pharmaceutical Meldonium in 2015.



meldonium

High-performance liquid chromatography-mass selective detection assay with electrospray ionization used for Meldonium determination in an athlete's urine requires the compound **Y** (a zwitter-ion; 25.0% C, 8,3% O, and 8.3% N by moles) as an internal standard. The molar mass of **Y** is within the range of 100 to 200 g/mol. The mass-spectrum of the solution prepared by mixing aliquots of **Y** solution and urine containing Meldonium is characterized by five pronounced peaks with *m/z* 58, 59, 60, 61, and 62 (other peaks are also found in the spectrum).

7. Deduce possible structures of **Y**, show calculations supporting your answer.

The mixed doubled curling team representing Olympic Athletes from Russia had to return the bronze medal won at the Olympic Games in PyeongChang, since 8.1 mcg/mL (probe A dated 02.02.2018) and 5.7 mcg/mL (probe B dated 03.02.2018) were found in urine of one curler. It is also known that no Meldonium was detected in his urine in the probe dated 22.01.2018. According to the WADA database, the absolute maximum Meldonium content ever found in an athlete's urine is 1428 mcg/mL.

8. Based on the above information, choose only one correct statement in the Answer Sheet.

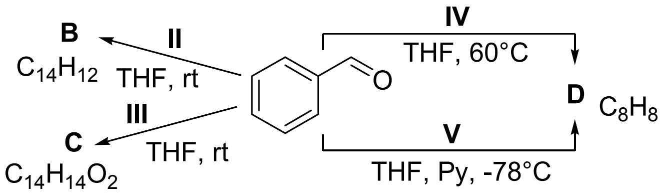
SECTION II. ORGANIC CHEMISTRY

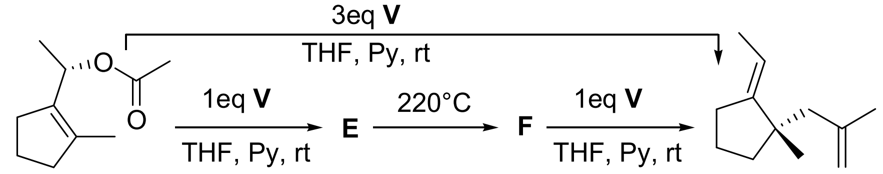
Problem 1

Organometallic reagents. Organometallic compounds **I**–**V** based on the element **X** are important reagents in organic chemistry. Most of them are derivatives of **X**, containing cyclopentadienyl (Cp or C_5H_5) ligand, which can be obtained from binary compound **A**. Thus, by treating the liquid chloride **A**, which intensively emits fumes when exposed to air, with sodium cyclopentadienide in tetrahydrofuran (THF), the bright red crystals of compound **I** (w(**X**) = 19.23%) are formed. **I** is the starting compound for other cyclopentadienyl complexes of **X** synthesis. When **I** is reduced with magnesium in the atmosphere of CO, the maroon complex **II** (w(**X**) = 20.45%) is formed. But if **I** is reduced with zinc in tetrahydrofuran, the green crystals of compound **III** (w(**X**) = 22.42%) can be extracted, which exists in free form as a dimer. The treatment of **I** with the excess of MeLi leads to the formation of **IV** (w(**X**) = 23.00%), and if **I** is reacted with 2 equivalents of Me_3Al in toluene, the binuclear complex **V** (w(**X**) = 16.82%) is formed, which has 2 tetrahedral metallic centers connected to each other with two bridging ligands. In this reaction the compound **Y** (w(Al) = 29.17%) is also formed and methane releases. The compounds **IV** and **V** are precursors of highly reactive molecule **Z**, what is more, it can be generated from **IV** by heating or from **V** by pyridine treatment.

1. Determine the element **X** and compound **A**. Draw structural formulae of complex compounds **I**–**V**, molecule **Z** and compound **Y**. In complexes **I**–**V** and compounds **A** and **Z** indicate the formal oxidation state of element **X**.

The diversity of mentioned reagents possibilities can be illustrated with the following schemes:

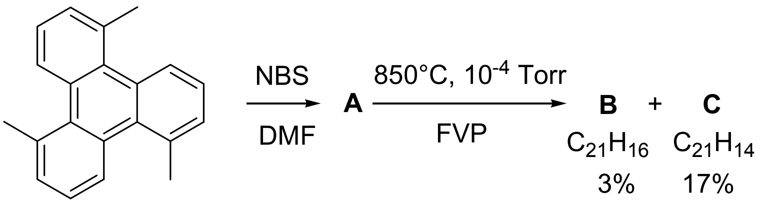


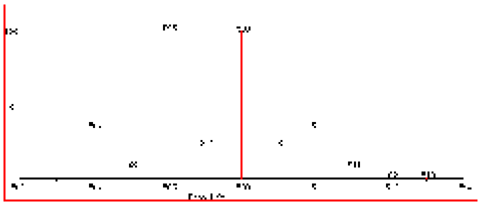


2. Draw the structural formulae of compounds **B** – **F**, if it is known, that compound **B** is thermodynamically more stable isomer, and **C** is chiral. Correlate the reagents **II** – **V** with their role in organic transformations (olefinating reagent, deoxygenative reagent, one-electron reductant).

Problem 2

Sumanene (from Hindi "flower") is a conjugated hydrocarbon **X** ($C_{21}H_{12}$), which can be considered as a fullerene fragment. Attempts to synthesize **X** began in 1993 with the pyrolysis of the corresponding substance **A**. However, during this sythesis, only compounds **B** and **C** were isolated with a low yield.

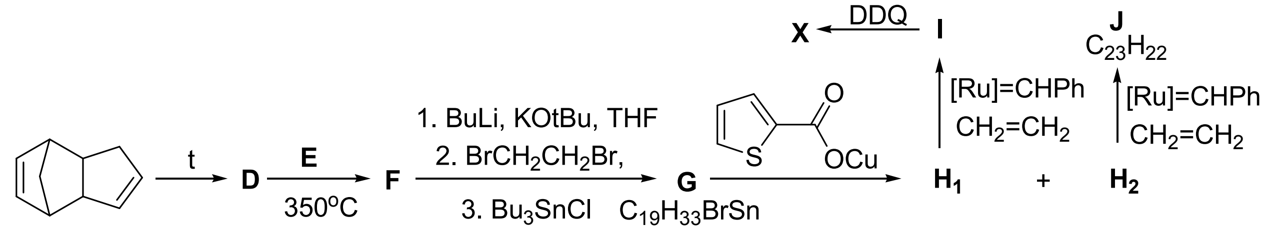




Mass Spectrum of **A** in the Molecular Ion Region

1. Give the structures of sumanene **X** and compounds **A** – **C**

Successful synthesis of Sumanene **X** was realized only 10 years later, in 2003. The synthesis began from hydrocarbon **F**, which has 3 signals in the ^1H NMR spectrum (int 2:1:1) and 3 signals in the ^{13}C NMR spectrum. In his turn, hydrocarbon **F** is obtained by the reaction of equimolar addition of hydrocarbon **D** and gas **E** (w_C = 92.3%). A further step was the modification of **F** to form a bifunctional compound **G**, which, under the action of copper (I) salts, gives a mixture of hydrocarbons **H1** and **H2** in a ratio of 1:3 with the brute formula $C_{21}H_{18}$. The major **H2** isomer under olefin metathesis conditions leads to hydrocarbon **J**. At the same time, the minor isomer of **H1** under similar conditions leads to compound **I**, which during oxidation gave the desired sumanene **X**.



2. Give the structural formulae of compounds **D** – **J**.

The sumanene which was synthetized, possesses a number of interesting properties. Thus, there are two doublets in the ^1H NMR spectrum of sumanene at 25°C at 3.42 and 4.71 ppm, which, when heated to 140°C, merge into a wide signal. For a more detailed study of this phenomenon, a deuterated derivative of **Y** was obtained according to the scheme given below. Compound **Y** at room temperature in the NMR spectrum gave two singlets at 3.42 and 4.71 ppm. with equal intensities, which indicated the existence of **Y** in two forms. In addition, it was found that the transition frequency between these two forms was 0.066 s^{-1} and 0.007 s^{-1} at 318 K and 298 K, respectively.

$$\mathbf{X} \xrightarrow{\substack{\text{excess of } t\text{-BuLi} \\ \text{- 100 °C, THF}}} \mathbf{Z} \xrightarrow{CD_3OD} \mathbf{Y}$$

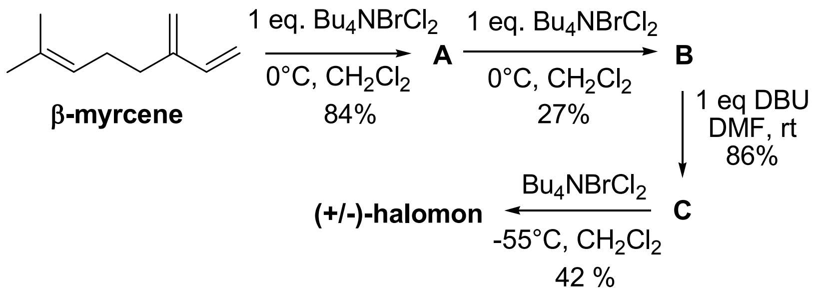
3. Draw the structural formulae of **Y** and anion **Z**.

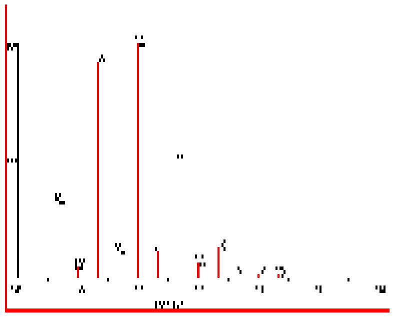
4. Show the structures of two forms of **Y**, which has the corresponding signals in NMR: 3.42 and 4.71 ppm

5. Calculate the activation energy to pass from one form of **Y** to another.

Problem 3

Halomon: chemist vs algae. In 1992, substance **X** later called **halomon**, was isolated from the red alga *Portieria hornemannii.* The compounds surprisingly possessed a unique ability of selective toxicity to certain cancer cells lines. Combustion of 1.00 g of halomon leads to formation of 24.9 mmol of CO_2, 12.5 mmol of water and a mixture of hydrogen halides, which under $AgNO_3$ treatment gave 2.01 g of precipitate. In the mass spectrum of halomon there is a bizarre signal in the region with an unusual distribution of isotopic peaks. In addition, it was found that halomon in nature is synthesized from β-myrcene –– an acyclic monoterpene and has a 3-S, 6-R-configuration. However, despite the preliminary success of the compound testing, its low natural concentration and difficulties with the breeding of *Portieria hornemannii*, forced the project to stop. He was rescued by synthetic chemists in 2000 by the synthesis of racemic halomon from β-myrcene according to the scheme presented below. But the synthesis did not solved the problem due to its low selectivity and accessibility only to the racemic compound. On the step of compound **B** formation, the main product was compound **B1** with a terminal double bond, as well as impurity **B2** as a mixture of *cis* / *trans* isomers. At the final step of halomon formation, the byproduct **D** was isolated, which appears halomon diastereomer.





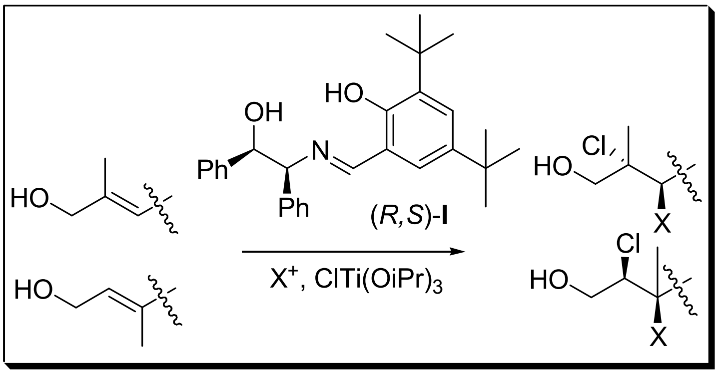
The molecular peak of halomon

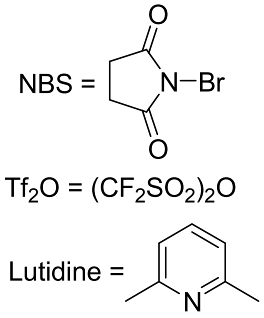
1. Determine the empirical formula of halomon, the answer is confirmed by calculation.

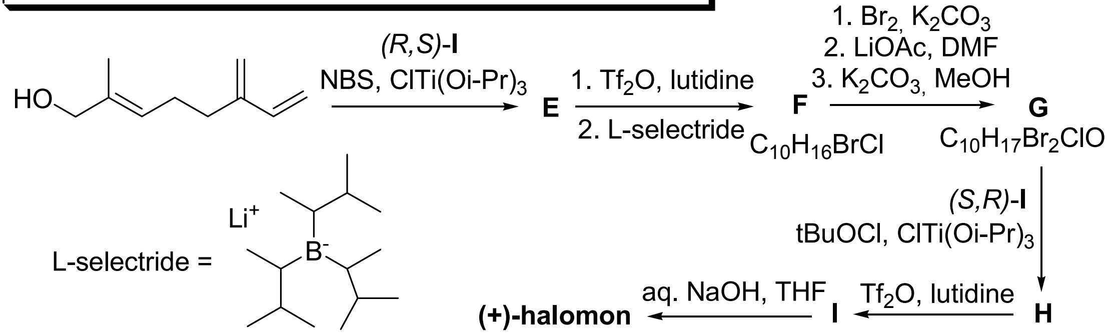
2. Give the structural formula of the natural enantiomer of halomon.

3. Decipher compounds **A** – **C**, **B1**, **B2** and **D**.

The final synthetic victory over halomon chemists celebrated in 2015, developing a preparative method for the synthesis of the natural enantiomer. The method was based on the enantioselective halogenation of allylic alcohols according to the general scheme given below. Thus, the dual use of this method using different enantiomers of the catalyst starting from hydroxylated β-myrcene in 6 preparative steps with high yield and optical purity.







4. Decipher compounds **E** – **I**.

SECTION III. ANALYTICAL CHEMISTRY

Problem 1

Salts of ethylenediaminetetraacetic acid (EDTA, H_4Y) form very stable $MetY^{(4-x)-}$ complexes with many Met^{x+} metal ions. EDTA is used in textile, paper, paint, and other industries to soften industrial water, as well as in analytical chemistry. EDTA is a weak acid, its dissociation constants are as follows: $K_1 = 1.0\cdot10^{-2}$; $K_2 = 2.1\cdot10^{-3}$; $K_3 = 6.9\cdot10^{-7}$; $K_4 = 5.5\cdot10^{-11}$.

1. There is water of medium hardness without precipitate (calcium concentration: 2.9 mM, magnesium: 2.0 mM, total concentration of all forms of carbonic acid: 1.8 mM).

a. Calculate the volume of a 1 M solution of EDTA disodium salt Na_2H_2Y, which should be added to 1 m^3 of such water to reduce its hardness (Ca + Mg) to 1.5 mM.

b. What are the concentrations of forms of carbonic acid in such water, if its pH equals 6.3? Dissociation constants of carbonic acid: $K_1 = 4.5\cdot10^{-7}$, $K_2 = 4.8\cdot10^{-11}$.

c. The maximum possible pH of the water described in the problem situation is determined by the precipitation of insoluble carbonates. Calculate this value, assuming the system is in equilibrium. Solubility products: $K_S(CaCO_3) = 3.8\cdot10^{-9}$, $K_S(MgCO_3) = 2.1\cdot10^{-5}$.

2. To 1 m^3 of the same water as in item **1**, 30.0 L of a 1.00 M solution of EDTA disodium salt were added.

a. In which reactions will ions Ca^{2+} and Mg^{2+} and the salts of carbonic acid enter upon the addition of the softening agent? Write down the reaction equations.

b. Let the initial pH of the water be equal to 6.3. Estimate the pH value of this water after the addition of EDTA, considering complexation complete.

c. Complete complexation of magnesium and calcium with EDTA occurs at pH ≥ 8.0. What amount of 1M alkali solution should be added to 1 m^3 of the softened water, so that its pH reaches this value? Consider that CO_2 does not evaporate from the solution.

Problem 2

At the beginning of the 20th century, the ability of glass membranes to selectively react to hydrogen ions was discovered, which triggered the development of ion-selective electrodes. A combined glass ion-selective electrode measures the potential difference between the inner solution with a known pH value and the test solution. This difference in potentials is given by formula (1), where *S* is the angle of inclination of the electrode function, theoretically equal to 2.3RT/F (in practice this value may be different):

$$\Delta E = S\cdot\log\frac{[H^+]_{test}}{[H^+]_{inner}} \qquad (1)$$

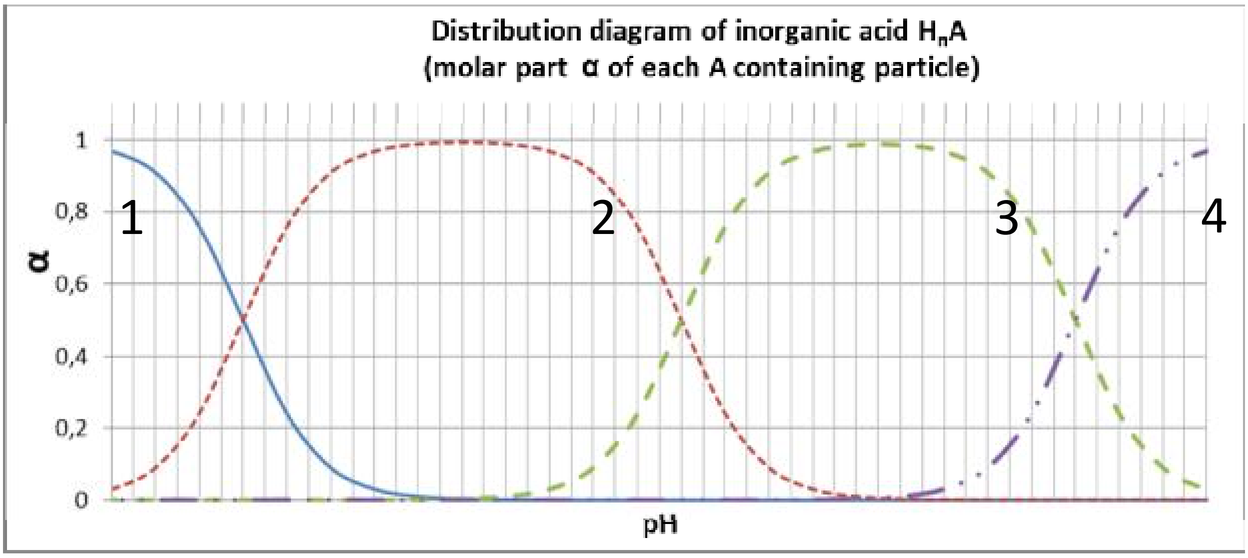
1. The electrode potential was measured in two buffer solutions with pH 4.00 and 7.00, obtaining the potential differences of 0.2094 V and 0.0352 V, respectively. Calculate the pH of the inner electrode solution and parameter S.

Under real-world conditions, the alkali metals cations can interfere with the measurement of the proton concentration, since the electrode glass is partially selective to these cations. This selectivity is determined by the selectivity constant $k_{H/M}$, and the potential difference is determined by formula (2):

$$\Delta E = S \cdot \log \frac{[H^+]_{test} + k_{H/M} \cdot [M^+]}{[H^+]_{inner}} \qquad (2)$$

2. Determine the selectivity constant $k_{H/Na}$ of the electrode, knowing that the error in measuring the concentration of H^+ ions for 0.2018 M solution of NaOH is 2018%.

Below is given a distribution diagram of all forms of inorganic acid H_nA. This electrode was used to measure the pH value of two solutions: 0.100 M Na_nA and an acid salt 0.100 M $Na_mH_{n-m}A$. The obtained potential values are –0.2376 and 0.1803 V respectively.



3. According to the diagram, what is the basicity of the acid?

4. What forms of acid does correspond to each of four curves?

5. Find all acidity constants for H_nA acid.

Quantitatively, the A ions were determined by precipitation of a silver salt: 20.0 mL of a solution prepared by dissolving 1.53 g of $H_nA \cdot 0.5H_2O$ in a 100 mL flask was titrated with 0.500 M $AgNO_3$ solution in the presence of chromate and sodium acetate. The volumes spent in the titration were as follows: 12.15; 12.20; 12.75 mL.

6. What is the role of chromate and acetate during the titration? Write the corresponding chemical reactions.

7. Find the molecular mass of H_nA and it formula, if A consists of two elements.

Problem 3

The systematic qualitative analysis of the mixture of four chlorides is described below. All salts are white crystalline solids with no crystallization water. To an aqueous solution of this sample the solution of complex acid **A**, containing 47.60 wt% of a platinum group metal, was added. *Precipitate 1* thus obtained was then separated. To remaining *solution 1,* the solution of double acetate **B**, containing 41.64 wt% uranium and some amount of zinc, was added. A yellow precipitate of triple salt hexahydrate **C** was formed, with mass percentages of metals of 1.49%, 46.43% and 4.25%. This confirmed the presence of metal **X1** salt in the sample.

Precipitate 1 was washed, dried, calcined and dissolved in water. The resulting *solution 2* was separated from metallic *precipitate 2,* and the solution (in hydroiodic acid) of complex acid **D**, containing bismuth and 70.74 wt% of iodine, was added to it. The obtained precipitate of compound **E** confirms the presence of metal **X2** salt in the sample. Mass fractions of **X2** and iodine in **E** are related as 1:2.865, and the anion has a structure of two octahedra sharing a common face with an atom of bismuth in the center of each octahedron.

The remained *solution 3* was several times evaporated with HNO_3, the residue was dissolved in water, and $NaNO_2$, $Bi(NO_3)_3$ and $AgNO_3$ were added to resulting *solution 4*. The formation of yellow precipitate **F** indicated the presence of **X3** in the sample. **F** contains an ion of bismuth coordinated with six equal ligands, and mass fractions of nitrogen and oxygen in **F** are 11.00 and 25.14%, respectively.

Finally, after separation of precipitate **F,** the reagent for cations of metal **X4** was added to resulting *solution 5*. This reagent is a sodium salt **G** containing 14.59 wt% of cobalt as a part of complex anion. Herewith in the presence of remaining silver nitrate in the solution, a yellow precipitate of compound **H** with mass percentage of **X4** 15.01% was formed.

Note: use all the relative atomic masses of elements accurate to a hundredth.

1. Determine the composition of the initial mixture of salts, metals **X1**–**X4** and write down the formulae of compounds **A**–**H**. Confirm the answers with calculations.

2. Draw the structural formulae of complex anions of **A**, **D** and **E**.

3. Write down the equations of all reactions mentioned.

SECTION IV. PHYSICAL CHEMISTRY

Problem 1

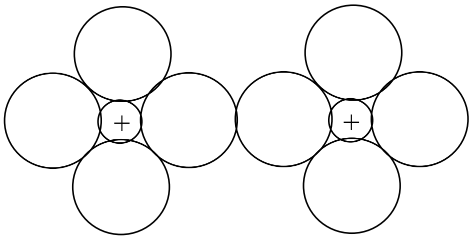
The binding energy (E) can be calculated in a direct way, using the $\Delta H°_x$ for the reaction $M(g) + aL(g) = ML_a(g)$ if enough data is available for the thermodynamic cycle. This is possible when calculating the affinity for the proton (A_p).

1. Calculate the A_p $NH_3(g) + H^+(g) = NH_4^+(g)$ and E_{av} of the N–H bond in NH_4^+ if $\Delta_f H^0$ are as follows (kJ/mol): –46.0 (NH_3), 664 (NH_4^+), 218 (H), 473 (N), and the ionization potential $H = H^+ + e^-$ is equal to $I = 13.6$ eV.

The data are also sufficient for **Me**(g) + aCO(g) = **Me**(CO)$_a$(g), since $\Delta_f H^0$(kJ/mol) are known: –110 (CO), –732 (**Me**(CO)$_a$), 424 (**Me**). For the carbonyl $W_C = 30.6\%$ by weight.

2. Determine **Me** and carbonyl. Describe the structure of carbonyl by the valence bond method (VB).

3. Calculate the E_{av} of the **Me**–CO bond and explain its difference from the real (251 kJ/mol), indicating the process included in the VB method and that was not taken into account during the calculation. Calculate its $(\Delta H^0)^*$.



In the case of **Me**$^{2+}$(g) cations, the data for the direct method are insufficient. Therefore, first $\Delta H°_x$ of hydration is calculated, and from this value $\Delta H°_x$ for other ligands is obtained. To calculate the $\Delta H°_x$ of hydration from the standpoint of the electrostatic theory, it is considered that it is equal to the potential energy (U) of a system containing $6H_2O$ at the vertices of octahedron and **Me**$^{2+}$ at the center of it. This energy (kJ/mol) includes the cation-dipole attraction (–1395), the cation-induced dipole attraction (–897), as well as the dipole-dipole (513) and the cation-dipole (407) repulsions.

4. Calculate the value of U and the average bond energy E_{av} for **Me**–H_2O

A more accurate calculation of E_{av} can be performed in a semi-empirical way using the experimental enthalpies (kJ/mol): $H_2O(l) = H_2O(g)$ ($\Delta H^0_v = 44.0$); **Me**$^{2+}$(g) + $6H_2O(l)$ = **Me**$(H_2O)_6^{2+}$(aq) ($\Delta H^0_g = -1958.1$) and the calculated Born heat of hydration **Me**$(H_2O)_6^{2+}$(g) = **Me**$(H_2O)_6^{2+}$(aq): $\Delta H^0_B = -N_A e^2 z^2(1 - 1/\varepsilon - T(\partial \ln\varepsilon/\partial T)_P/\varepsilon^2)/4\pi\varepsilon_0 r = -kz^2(1 - 1/\varepsilon + 0.356T/\varepsilon^2)/r$, where $e = 1.602\cdot10^{-19}$ C; $\varepsilon_0 = 8.854\cdot10^{-12}$ F/m; $N_A = 6.02\cdot10^{23}$; z – cation charge; r – the distance between the cations. The entropy is $\Delta S^0_B = -0.356kz^2/\varepsilon^2 r$.

5. Calculate ΔH^0_B, ΔS^0_B, ΔG^0_B, if $\varepsilon = 78$ at 298 K, r(**Me**$^{2+}$) = 0.83 Å, diameter H_2O $D = 2.76$ Å

6. Calculate ΔH^0_x for **Me**$^{2+}$(g) + $6H_2O(g)$ = **Me**$(H_2O)_6^{2+}$(g) and E_{av} for the bond **Me**–H_2O.

There are noticeable differences in the values of E_{av} obtained from the electrostatic model and the semi-empirical method for all electronic configurations except d^0, d^{10}, d^5 (weak field).

7. Specify the name of the energy, which is not included in the calculation of the electrostatic model.

Problem 2

Electron spin resonance (ESR) spectroscopy is a powerful method to study paramagnetic species (these containing one or several unpaired electrons), widely used in physics, chemistry, and biology. Intensity of the ESR signal is proportional to the number of unpaired electrons in the sample, therefore quantitative measurements using ESR method are possible without additional data on the substance, in contrast to other spectroscopy methods.

1. Which of the species listed in the Answer Sheet (OH, H, H_2, $TiCl_3$, $H[CuCl_2]$, $VOSO_4$, $ZnCl_2$), can be observed by means of ESR?

ESR is of special importance in radiation chemistry (a branch of science studying the processes occurring under the action of ionizing radiation). The irradiation induces the formation of radicals, structure and concentration of which can be determined by means of ESR. *To answer this and following questions, use the definitions and reference data given in the end of the task.*

2. Calculate the steady-state concentration of radicals formed upon irradiation and indicate whether they can be detected by means of ESR. Assume that the radicals disappear only via bimolecular reaction between them. Radiation-chemical yield G = 2 radicals/100 eV, dose rate I = 10 J/kg·s, sample volume 10 μL, sample density ρ = 1 g/mL, rate constant of radicals recombination $k = 10^{10}$ L/mol·s, temperature 298 K, sensitivity of the ESR spectrometer 10^{11} spins in a sample.

To study the short-living radicals, the measurements are performed on cooling, and the radicals recombination can be neglected for.

3. Estimate the radiation-chemical yield of radicals at 77 K if the measured intensity of the ESR signal is 0.0366, dose rate 10 J/(kg·s), irradiation duration 20 min, sample density ρ = 0.98 g/mL, intensity of ESR signal of the reference sample (150 mg of $CuCl_2 \cdot 2H_2O$) 52.4. The ampoule with the sample is a cylinder with diameter d = 4 mm and height l = 1.5 cm.

4. UV absorption spectrum of the irradiated sample (see i. 3) was recorded. The detected absorbance in the absorption maximum was A = 1.33. Calculate the molar absorptivity ε if only a single type of radicals is stabilized in the sample, and the absorption is due to the presence of these radicals. Optical path goes along the ampoule diameter. *If you have failed to solve i. 3, take the number of radicals in the sample equal to* $5 \cdot 10^{17}$.

5. Calculate the minimum concentration of the radicals described in ii. 3–4 that can be detected by means of a) UV spectroscopy (the lowest reliably measurable absorbance $A = 0.01$) and b) ESR spectroscopy (detector sensitivity10^{11} spins in a sample). *If you have failed to solve i. 4, take ε = 1500* L/mol·cm.

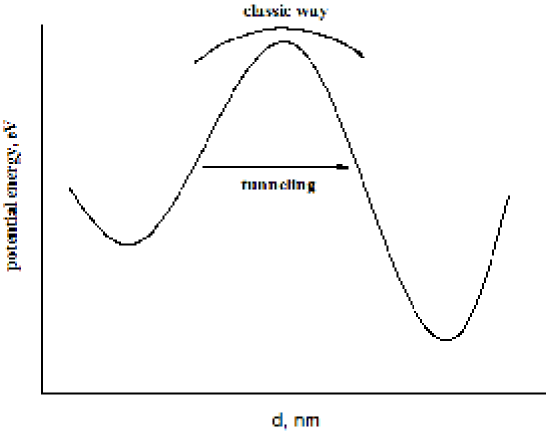
The radicals formation is important in view of radiation-chemical transformations of polymers. For polymers prone to crosslinking under irradiation, the gel dose term is used; this is a minimum dose of the radiation sufficient for the transformation of the sample in a single cross-linked macromolecule.

6. Calculate the gel dose for polyethylene (M = 100000 g/mol). Radiation-chemical yield of radicals $G = 3$ radicals/100 eV. Account for the processes of the radicals formation under irradiation and their recombination.

Absorbed dose (unit J/kg) is the energy of radiation absorbed per a mass unit. Dose rate is the dose absorbed by the substance per a time unit. Radiation-chemical yield is the number of species appeared or decayed in the sample upon absorption of 100 eV of radiation. 1 eV = $1.6\cdot10^{-19}$ J. $A = \varepsilon\cdot d\cdot c$ (d is the optical path length, c is the concentration of the absorbing species).

Problem 3

«I will never be as cold now as I will in the future.
The future of cold is infinite. The future of heat is the future of cold».
From the movie «Proof». Dedicated to the dear city N.



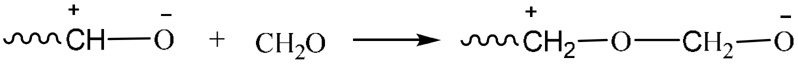
At extremely low temperatures (4–100 K), the reaction rate constants can't be no more described by the Arrhenius law, and the quantum tunnel effect – transition under the potential barrier – becomes the dominant mechanism of the reactions. For the manifestation of the wave properties of particles with mass and velocity v, it is necessary for the de Broglie wavelength $\lambda = h/mv$ to exceed the width d of the potential barrier. In addition, classical transitions through the barrier are slow when the barrier height E is greater than k_BT. According to Gol'danskii, tunnel effect dominates under the condition $\lambda/d > k_BT/E$

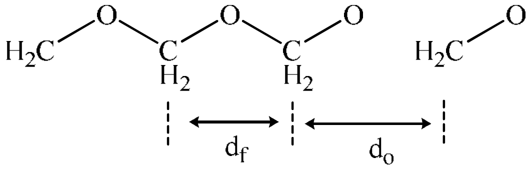
The temperature T_K, below which the quantum description of chemical processes becomes necessary, is called the low temperature limit of the reactions.

1. Arrange the particles e^-, C, D, H, Cl in the order of increasing the probability of tunneling. Assume that all particles have the same kinetic energy.

2. Obtain an expression for the temperature T_K through the parameters m, d and E, assuming the kinetic energy of the tunneling particle to be E.

Tunneling can be exposed not only to electrons and protons, but also heavy atoms and even entire molecules. An example is the reaction of low temperature polymerization of formaldehyde: $H(OCH_2)_n + OCH_2 \rightarrow H(OCH_2)_nOCH_2$.





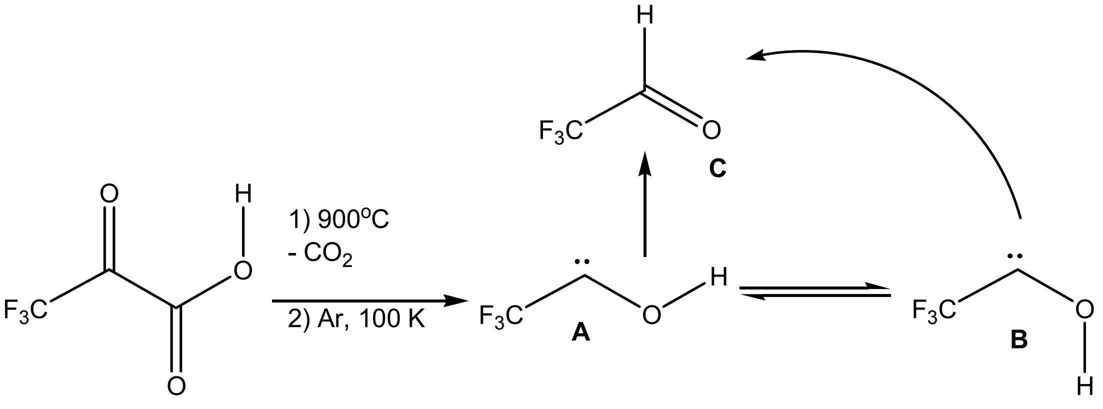
3. Knowing that $d_0 = 0.320$ nm, $E = 0.1$ eV and taking into account the distance $d_f = 0.0155$ nm between the adjacent carbon atoms in the final polymer chain, calculate the low temperature limit (T_K) of the formaldehyde polymerization reaction.

At $T_1 = 80$ K average time of linkage to the polymer chain $\tau_{01} = 10^{-5}$ s, at lower temperatures it reaches a stationary value $\tau_{02} = 10^{-2}$ s.

4. Determine τ_{02} for the case of absence of tunneling and the validity of the Arrhenius law. Accept $T_2 = 10$ K and the activation energy of the polymerization reaction to be 8.4 kJ/mol.

Tunneling is a conformationally specific process. An example – the reaction of trifluoromethylhydroxycarbene conversion formed during vacuum pyrolysis of 3,3,3-trifluoro-2-oxopropanoic acid to trifluoroacetaldehyde at 100 K (reactions **2** and **3**). This carbene can be isomerized upon irradiation with wavelength of 465 nm (reaction **1**). The energies of the ground state of the two isomers have sufficiently close values differing by 3.34 kJ/mol only.

№	reaction	d, nm	$\Delta H^{\neq}$, eV
1	**A↔B**	?	1.14
2	**A→C**	0.13	?
3	**B→C**	0.20	1.18



The O–H bond length is of 0.096 nm.

5. Determine for which reactions (**1**, **2** or **3**) the transport of the hydrogen atom can occur via the tunnel mechanism. Fill the blanks in the table. Assume that the O–H bond position in the *cis*- and *trans*- isomers differs by an angle of 111°. According to the classical theory of transition state, the rate constant $k = \frac{k_B T}{h}\exp\left(-\Delta G^{\neq}/RT\right)$, where $\Delta G^{\neq}$ – Gibbs energy of the transition state. For reaction **2**: $\Delta S^{\neq} = 856$ J/mol·K, $\tau_{1/2} = 72$ days.

6. a) Draw the energy profile of the reactions, labeling the reagents and products with **A**, **B**, **C**; b) Which isomer, *cis*- or *trans*-, is more stable?

Reference data: Planck constant $h = 6.63 \cdot 10^{-34}$ J·s, Boltzmann constant $k_B = 1.38 \cdot 10^{-23}$ J/K, 1 a.m.u. = $1.66 \cdot 10^{-27}$ kg, gas constant $R = 8.314$ J/mol·K, 1 eV = $1.6 \cdot 10^{-19}$ J, proton mass $m_p = 1.675 \cdot 10^{-27}$ kg.

SECTION V. INORGANIC CHEMISTRY

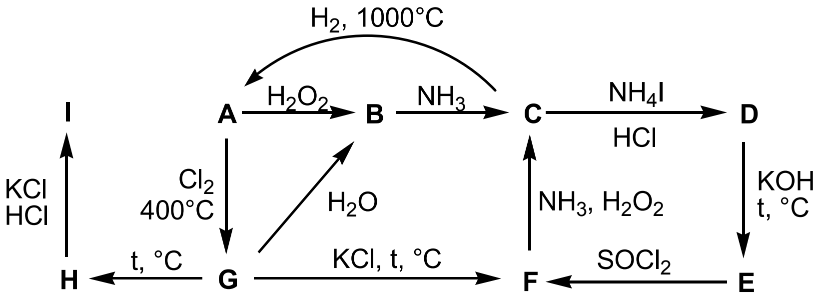
Problem 1

The silver-white **A** transition metal reacts with an excess of 30% hydrogen peroxide forming a solution of **B** substance. The solution of **B** absorbs ammonia easily forming **C** compound. In industry **A** is produced from **C** substance by hydrogen reduction at 1000°C. **A** metal refers to rare and trace elements, it is used mainly as a catalyst and a component of heat resistant and refractory alloys.

C refers to the compounds where **A** presents at the highest oxidation state, but exhibits oxidizing properties only in acidic medium. Thus, the interaction with ammonium iodide in a hydrochloric acid solution leads to the **C** reduction with forming of **D** and the appearance of a complex color of the solution obtained by mixing of green and brown colors. Melting of **D** substance with potassium hydroxide leads to the gas evolution with a sharp odor and **E** formation, which reacts with liquid $SOCl_2$ forming **F** stable chloride complex, the solution of which is green. By the reaction between **F** solution, ammonia and an oxidizing agent, for example hydrogen peroxide, it is easily to obtain **C** once again.

A forms the range of chlorides, many of them are clusters with different multiplicity of metal-metal bonds. Thus, chlorination of **A** at 400°C leads to the formation of red-brown crystals of **G** substance. The structure of **G** consists of $Cl_4A(\mu\text{-}Cl)_2ACl_4$ dimers, in which two octahedra $[ACl_6]$ are connected by two bridging chlorine atoms. **F** can be obtained by fusion of **G** with potassium chloride, and in water **G** disproportionates to **B** and other precipitate product containing **A** in its composition. Heating up to ~150°C leads to the beginning of **G** sublimation, accompanied by decomposition with the formation of chlorine and **H** dark red crystals. **H** is a diamagnetic substance, what is explained by the presence of multiple metal-metal bonds, and the distance of such bond is less than the one in a simple compound. The interaction of **H** with a potassium chloride solution in a concentrated hydrochloric acid gives red crystals of **I** compound, which contains **A**, potassium (ω = 10.65%) and chlorine (ω = 38.63%), and the molar mass of **I** is 1101.33 g/mol.

1. Determine **A** – **I** substances. Write down all the mentioned chemical reactions, according to the given scheme. In the **B**, **G**, {**F** and **D**}, **H** range the oxidation state of **A** metal decreases.



2. Figure the fragments of the crystal structure of **H** compound and **I** anion part, if it is known that in both compounds there are a threefold axis and a mirror plane perpendicular to it. In addition, in both compounds there are two types of chlorine atoms, with their ratio in **H** – 2:1, and in **I** – 3:1.

3. The polymerization isomer of **I** compound of blue color with a molar mass of 734.22 g/mol is known. Determine the composition of this isomer and depict the structure of its symmetrical diamagnetic anionic part.

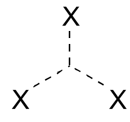
Problem 2

The complex **A**, one of the first stable in air metal complexes of **Me** (I) with ligand $\mathbf{X_n}H_{n+3}^-$, was synthesized in the mid-1970s by N. Greenwood's group. To obtain the ligand, 0.138 g of $\mathbf{X_m}H_{m+4}$ were pyrolysed (225°C; 0.2 atm), and 0.0315 g of $\mathbf{X_nH_{n+4}}$ were obtained (yield of 25%), which were added to potassium hydride (KH) solution in THF and stirred at –60°C until K$[\mathbf{X_nH_{n+3}}]$ was formed.

1. Decode hydrides, if $\mathbf{X_m}H_{m+4}$ contains 78.3 wt.% of **X**.

2. Represent the structural formula of $\mathbf{X_m}H_{m+4}$ and complete the diagram of the MO fragment of **XHX**.

In the structure $\mathbf{X_n}H_{n+4}$: the **X** atoms are located in the vertices of a pyramid; the number of the skeleton bonds is **n** + 2 or **s** + **t** + **y** (**s** – number of the bonds **X**---H---**X**, **t** – number of the three-center bonds



, **y** – number of bonds **X–X**); each **X** gives 4 bonds; **X** in the vertex of a pyramid is bonded to all the **X** atoms in the base with the two- (**XX**) and the three-center (**XXX**) bonds; electron density on H in **XHX** is higher than in **X**H.

3. Calculate **s**, **t**, and **y** (**y** > **t**) and represent the structural formulae $\mathbf{X_n}H_{n+4}$ and $\mathbf{X_n}H_{n+3}^-$.

4. Write down the equation of the reaction of K$[\mathbf{X_n}H_{n+3}]$ synthesis and calculate ΔH^0 of pyrolysis reaction, if the bond energies (kJ/mol) are: 436 (HH); 332 (**XX**); 380 (**XXX**); 441 (**XHX**); 381 (**X**H).

The compound **B**, which contains **Me** (I) (Vaska's complex), was obtained by the reaction of $P(C_6H_5)_3$, hereinafter PPh_3, with $\mathbf{MeCl_3}$ (64.3 wt.% of **Me**) in methoxyethanol as solvent, CO source and reductant.

5. Decode the Vaska's complex formula (**B**) (67.2 wt.% of PPh_3; 3.57 wt.% of CO) and represent its structural formula, if it is a trans-isomer containing Cl^-.

To obtain **A**, 0.390 g of **B** were dissolved in 20 mL of CH_2Cl_2, and all the obtained solution of K$[\mathbf{X_n}H_{n+3}]$ in THF was added at –70°C, the mixture was heated to –20°C, stirred for 3 hours until changing of color from red to yellow, and forming of KCl and 0.0720 g of **A**. With the **A** formation, the number of atoms in the base of a pyramid $\mathbf{X_n}H_{n+3}^-$ increased due to cleavage of the **XHX** bond and formation of the **X**H**Me** and **MeX** bonds, and the three-center **XHX** remain at different **X**.

6. Decode **A**, write down the equation of the reaction of its obtaining and calculate its yield.

7. Represent the structural formula **A**.

Problem 3

Some transition metals are formed coordination complexes in which the role of the ligand is performed by O_2^{2-} peroxide ion. These are the so-called peroxy-compounds. To obtain many of which is possible by simple reaction with hydrogen peroxide.

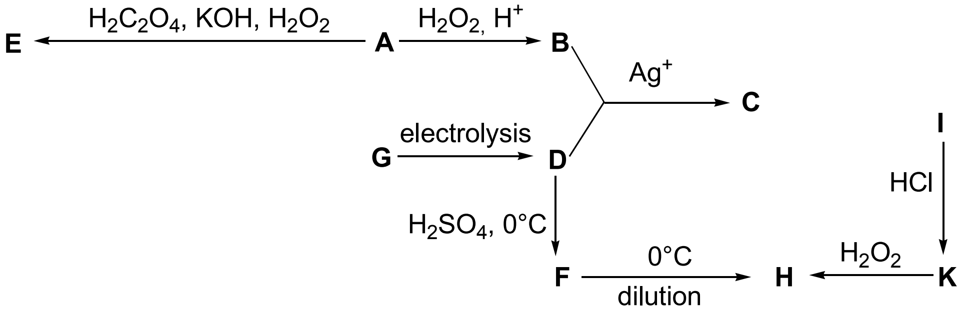
Thus, when hydrogen peroxide is added to **A**, freshly precipitated metal oxide of pale orange color ($\omega(O) = 43.99\%$), an intense red color is observed in the sulfuric medium resulting from the formation of **B** complex in which the metal ion coordinates one peroxide ion and the charge of the complex particle is +1. When oxalic acid reacts with a solution obtained by **A** and potassium hydroxide dissolving in 3% hydrogen peroxide, an orange color, caused by **E** compound, in which the complex anion contains two ion peroxide, is appeared.

In strongly acidic media the reduction of **B** to **C** occurs. The same process occurs when adding **D** oxidizing agent to the **B** solution only in the presence of Ag^+ silver ions.

D is a popular substance as an oxidizer in the analytical practice, as a pesticide, food additive, bleach, a component of explosive mixtures, etc. in industry, **D** is a potassium salt of **F** acid. **D** is obtained by electrolysis of **G**, acid salt of potassium solution. In this process, the formation of **F** acid at the anode occurs, which is neutralized by potassium hydroxide formed in the cathode area. Due to its poor solubility, **D** precipitates.

The dissolution of **D** in concentrated sulfuric acid upon cooling leads to the formation of **F** acid, which decomposes to the other **H** acid in the diluted solution upon cooling. This **H** acid is very unstable in water, explosive in the crystalline state, it is obtained in two stages. Firstly, **I**, nonmetal oxide ($\omega(O) = 59.95\%$), reacts with hydrogen chloride forming **K** compound, which further reacts with anhydrous hydrogen peroxide forming **H**.

1. Determine all unknown substances and write the mentioned equations of chemical reactions according to the given scheme, confirm the data by calculations.

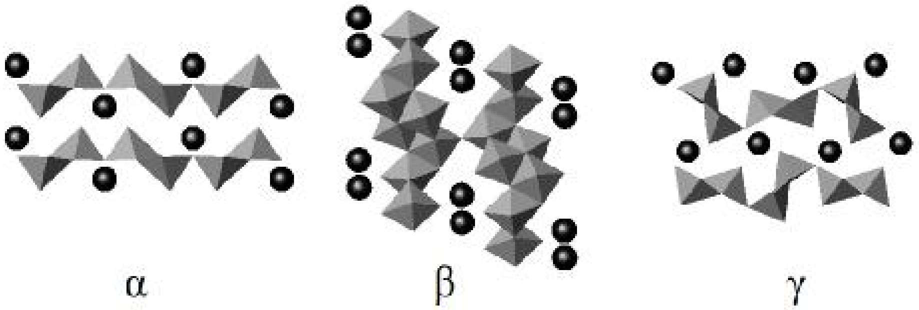


2. Write down the reaction mechanism of the **B** and **D** interaction, catalyzed by Ag^+ silver ions.

3. Figure the structure of the anionic part of **E** complex and indicate the coordination number of the metal atom in it.

4. **F** and **H** acids belong to a special class of acids. Figure the structure of the anions of these acids and circle the functional group that determines their specificity.

When alloying **A** with alkali metal oxides, oxide bronzes are formed. In this process oxygen is lost, and the obtained phases are blue-black colored and possess an electronic conductivity. Depending on the number of embedded atoms, various structural types of bronzes are realized, as shown in the figure (the metal-oxygen framework is shown by polyhedrons, alkali metal atoms are shown in black, the relative amount of alkali metal increases in the α-β-γ bronze range). The simplest α-type is a solid solution with the introduced alkali metal atoms into the metal-oxygen framework of the starting oxide **A**.



5. Determine the composition of α-type lithium bronze, if heating in the air, the sample mass increased by 1.733% due to complete metal oxidation.