

## SECTION I. PHYSICAL CHEMISTRY

## Problem 1

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One of the topical areas of energy is thermonuclear fusion. In 2007, the development of a thermonuclear reactor was launched in France, the goal of which is to show by 2025 the possibility of controlling thermonuclear reactions and creating a thermonuclear station for generating energy. Artificial nuclear fusion is based on the interaction of a stable nucleus X with a radioactive nucleus Y with the formation of a stable nucleus Z and one neutron. The nuclei X and Y are isotopes. Synthesis takes place at high temperatures ( $T \sim 10^8$  K) in plasma, which is held by a magnetic field in the shape of a toroid (see Fig. 1).

The content of Y nuclei on our planet is very low, they are formed under the action of cosmic radiation on  $^{14}\text{N}$  atoms (interaction with a neutron), but are not able to accumulate due to the short half-life  $t_{1/2} \sim 10\text{--}16$  years. Artificially, Y nuclei are synthesized by irradiating a stable target A with neutrons (one neutron bombards one A nucleus). In addition to the Y nucleus, only Z nuclei are formed.

The specific activity of the Y nuclei is 9650 Ci/g. A sample containing  $2.82 \cdot 10^{21}$  nuclei loses 14.475 Ci of activity in 2 years. The cost of producing Y nuclei is quite high: \$30 million/kg. Keep in mind that all stable nuclei have the same number of protons and neutrons.

1. Calculate the exact half-life of the nuclei Y.
2. Calculate the financial losses for 2 months of storage of 600 g of Y nuclei.
3. a) Decipher the nuclei X, Y, Z and A; b) Write three nuclear reactions: fusion of Y nuclei from  $^{14}\text{N}$ , artificial synthesis of Y and reaction in a thermonuclear reactor.

The energy released during the effective collision of X and Y nuclei is  $3 \cdot 10^{-12}$  J.

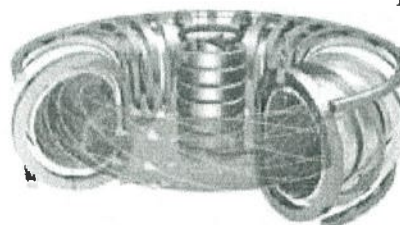
4. What quantity (mol) of the propane-butane (1:1) mixture burned is energetically equivalent to the reaction of the same number of X and Y nuclei with a total concentration of  $10^{16}$  particles/L?

$$\Delta_f H(\text{CO}_2) = -393.5 \text{ kJ/mol}, \quad \Delta_f H(\text{H}_2\text{O}) = -285.8 \text{ kJ/mol},$$
$$\Delta_f H(\text{C}_3\text{H}_8) = -103.9 \text{ kJ/mol}, \quad \Delta_f H(\text{C}_4\text{H}_{10}) = -126.2 \text{ kJ/mol},$$

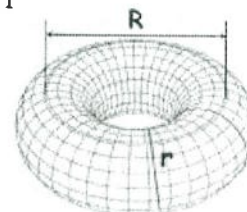
Toroid volume  $V = 2\pi^2 R^2 r$ . Assume  $R = 9$  m,  $r = 52$  cm.

The high temperature of the reaction medium is necessary to overcome the electrostatic repulsion between the nuclei. One of the main problems is the thermal stability of the reactor walls, for which two materials are tested – metal M and its binary compound  $\text{N} = \text{AM}$ . Metal M has a cubic lattice (without specifying which of the three) with a parameter of  $3.16 \text{ \AA}$  and an atomic mass of more than  $140 \text{ g/mol}$ . The lattice of the N compound is hexagonal (see Fig. 2). The mass fraction of metal M is more than 50%. The compound density N is 1.23 times less than the density of pure metal M. Cell parameters:  $a = b = 2.92 \text{ \AA}$ ,  $c = 2.82 \text{ \AA}$ .

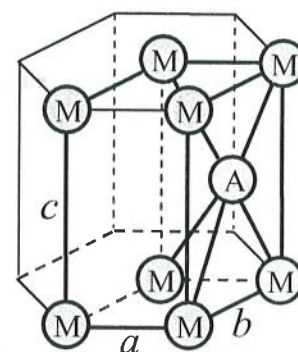
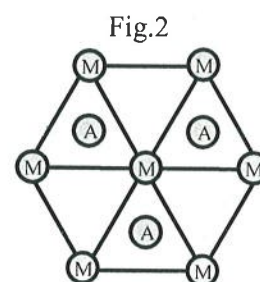
5. Using the given data, decipher M and N.



ITER reactor



Toroid



## Problem 2

Anation reactions (substitution of  $\text{H}_2\text{O}$  by  $\text{X}^-$ ) in easily hydrolyzed complexes  $[\text{Me}(\text{H}_2\text{O})_6]^{3+} \rightleftharpoons [\text{Me}(\text{H}_2\text{O})_5\text{OH}]^{2+} + \text{H}^+$  ( $K_a$ ) proceed along two routes ( $k_1$  and  $k_2$ ) at a rate of  $r = (k_1[\text{Me}^{3+}] + k_2[\text{MeOH}^{2+}]) \cdot C(\text{X}^-)$ .

1. For  $[\text{Me}(\text{H}_2\text{O})_6]^{3+} + \text{X}^- \rightarrow$ , using its short form ( $\text{Me}^{3+} + \text{X}^- \rightarrow$ ), write down the reaction equations for the indicated two routes.

Connick and Coppel showed that if  $\text{X}^-$  is an anion of strong acid, then  $k_{\text{obs}} = (k_1[\text{H}^+] + k_2 K_a)/([\text{H}^+] + K_a)$  and the rate increases with decrease of  $[\text{X}^-]$ . Pouli and Smith established that for the weak acids HX

$k'_{\text{obs}} = (k_3[\text{H}^+] + k_4K_a)/K$ , rate decreases with reducing  $[\text{X}^-]$  and there action proceeds *via* two routes:  $\text{Fe}^{3+} + \text{HX} \rightleftharpoons \text{FeX}^{2+} + \text{X}^-$  ( $k_3, k_{-3}, K = k_3/k_{-3}$ ) and  $\text{FeOH}^{2+} + \text{HX} \rightleftharpoons \text{FeX}^{2+} + \text{H}_2\text{O}$  ( $k_4, k_{-4}$ ). For the anation reactions of  $\text{Fe}^{3+}$  with participation of  $\text{Cl}^-$  and  $\text{HN}_3$  at 25 °C it was obtained:

$[\text{H}^+]$ , mol/L	1.0	0.5	0.1	0.05	0.01
$k_{\text{obs}}$ , L/mol·s	83.60	156.9	709.2	1325.2	4458.0
$k'_{\text{obs}}$ , L/mol·s	85.15	81.76	79.05	78.71	78.44

2. Derive the kinetic equation for the reaction rate of  $\text{Fe}^{3+} + \text{Cl}^- \rightarrow$ , assuming that the ions  $\text{Fe}^{3+}$  and  $\text{FeOH}^{2+}$  are in equilibrium. The concentrations of chloride complexes can be neglected ( $[\text{Fe}^{3+}]$  and  $[\text{FeOH}^{2+}] \gg [\text{FeCl}^{2+}]$  and  $[\text{FeOHCl}^+]$ ), and  $C(\text{Fe}) = [\text{Fe}^{3+}] + [\text{FeOH}^{2+}]$ . Calculate  $k_1, k_2$  and  $K_a$  for  $[\text{H}^+] < 0.5$  mol/L, using the table data.

3. Derive the kinetic equation for the reaction rate of  $\text{Fe}(\text{H}_2\text{O})_6^{3+} + \text{HN}_3 \rightleftharpoons$  and the expression for  $k'_{\text{obs}}$ , if the rate of the forward reaction is the same as in the case of  $[\text{Cl}^-]$ , and the sum  $k_{-3}[\text{H}^+] + k_{-4}$  for the reverse reaction can be obtained from the equilibrium condition ( $r = 0$ ). Consider the concentrations  $C(\text{HN}_3) = [\text{HN}_3]$  and  $C(\text{Fe}) \gg C(\text{FeN}_3)$  and  $C(\text{FeOHN}_3)$ . Calculate  $k_3, k_4$  and  $k_{-3}$  for  $[\text{H}^+] < 0.5$  mol/L.

It was established that in the case of anions of weak acids, the anation mechanism  $\text{Fe}(\text{H}_2\text{O})_6^{3+} + \text{N}_3^-$  includes two stages: reversible with formation of  $\text{HN}_3$  and constant of  $K_x$  and irreversible with  $k_4$ , and  $k''_{\text{obs}}$  does not depend on pH.

4. Give the reaction mechanism and expression for  $k''_{\text{obs}}$ . Calculate  $K_x$  and  $k''_{\text{obs}}$ , if the dissociation constant of  $\text{HN}_3$   $K_{a1} = 1.9 \cdot 10^{-5}$ . For the reaction  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$  with  $\text{Cl}^-$  at 40 °C and pH = 0,  $k_1 = 275.9$ .

5. Calculate the activation energy ( $E_a$ ) for  $\text{Fe}(\text{H}_2\text{O})_6^{3+} + \text{Cl}^- \rightarrow \text{Fe}(\text{H}_2\text{O})_5\text{Cl}^{2+} + \text{H}_2\text{O}$ .

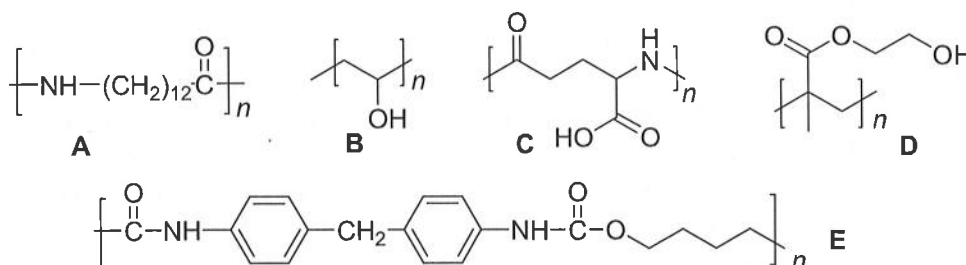
In the reaction mechanism of  $\text{Fe}(\text{H}_2\text{O})_6^{3+} + \text{X}^-$  the first stage depends on the strength of the acid  $\text{HX}$  and can proceed in two ways: either with the formation of a trigonal bipyramid (C. N. = 5), or an ion pair in the form of an octahedral wedge (C.N. = 7).

6. Describe a two-stage mechanism in the case of  $\text{Cl}^-$  and  $\text{N}_3^-$ .

## Problem 3

Smart materials can significantly increase the effectiveness of athletes. At the 2008 Olympiad games, some swimmers used swimming suits created with participation of NASA. As a result, 94% of gold medals were received by athletes in this sportswear. The key to success was the cross-linking of polymer fibers with a unique composition that reduces water resistance, which increased the speed of swimmers by 4%.

1. From the structures below, select two examples of polymers that could be used in such effective swimsuits.



Sewing microcapsules from materials with a reversible phase transition coated with a hydrophobic shell into the fibers of the fabric allows for the body's thermoregulation during intensive training, both indoors and outdoors. Such materials are capable of absorbing heat with its subsequent release upon returning to the initial temperature and phase state. One of example of such materials is polymer **F** ( $t_{\text{melt}} = 38^\circ\text{C}$ ) obtained by cationic polymerization of **G** at low temperatures. **G** is released in the composition of an equimolar gas mixture with  $M_{\text{av}} = 44$  g/mol during the thermal decomposition of ethylene carbonate. Cationic polymerization of **G** is carried out according to the scheme:

- |                   |  |   |
|-------------------|--|---|
| 1) initiation     | $\text{H}^+\text{A}^- + \text{G} \rightarrow \text{M}^+\text{A}^-$       | $k_i = 9.5 \cdot 10^{-3}$ L/mol·s,                      |
| 2) propagation    | $\text{M}^+\text{A}^- + \text{G} \rightarrow \text{F}_{i+1}^+\text{A}^-$ | $k_p = 0.94$ L/mol·s,                                   |
| 3) chain transfer | $\text{M}^+\text{A}^- + \text{G} \rightarrow \text{P}$                   | $k_{\text{tr}} = 8.0 \cdot 10^{-3}$ L/mol·s,            |
| 4) termination    | $\text{M}^+\text{A}^- \rightarrow \text{M}_i + \text{H}^+\text{A}^-$     | $k_{\text{term}} = 7.5 \cdot 10^{-2}$ s <sup>-1</sup> , |

where  $H^+A^-$  – polymerization initiator,  $M^+A^-$  – active site of the growing chain,  $k_j$  – the rate constants of the corresponding stages.

2. a) Determine **F** and **G**; b) Using the approximation  $V_i = V_{\text{term}}$  get the expression for the rate of cationic polymerization; c) Get an expression for the average degree of polymerization  $X_{\text{av}} = V_p/(V_{\text{term}} + V_{\text{tr}})$ .

3. a) Calculate the value of heat a runner releases into the surrounding space, exercising on a treadmill for 1 hour, if the change in internal energy is  $-3.38$  MJ and the power generated is  $235$  W. b) By how many degrees does a runner raise the temperature of the surrounding air while exercising in a room with area of  $2500$  m<sup>2</sup> and a ceiling height of  $5$  m?  $\rho_{\text{air}} = 1.165$  kg/m<sup>3</sup>, heat capacity  $c_{\text{air}} = 1.005$  kJ/kg·K.

4. a) What amount of microcapsules of polymer **F** with a diameter of  $40$   $\mu\text{m}$  can be obtained by polymerization of  $2.15$  mol of **G** in  $1$  L of the reaction mixture if the reaction yield is  $95\%$ ? Take  $\rho_F = 1200$  kg/m<sup>3</sup>.

*If You didn't determine the degree of polymerization, accept  $M(F) = 500$  g/mol.*

b) What proportion of the heat generated by a runner can be absorbed by sportswear containing all the obtained microcapsules of polymer **F**? A runner's skin temperature is  $34^\circ\text{C}$  at the start of a workout and  $40^\circ\text{C}$  at the end.

$c(F, s) = 8.48 \cdot 10^{-11}$  kJ/microsphere·K,  $c(F, l) = 6.28 \cdot 10^{-11}$  kJ/microsphere·K,

$\Delta_{\text{melt}}H(F) = 6.11 \cdot 10^{-9}$  kJ/microsphere.

Assume that heat is distributed evenly from all area and clothing covers  $80\%$  of the body.

The implementation of tribo-, piezo- and thermoelectric materials into clothing allows sports to use mechanical energy and heat generated to operate vital signs sensors or more complex wearable electronics. For example, a  $30$   $\mu\text{m}$  thick film of piezoelectric polymer **K**, placed in a runner's sneakers, is capable of generating power  $W = 1$  mW. Output voltage  $U = \gamma Ph / \epsilon \epsilon_0$ , where  $\gamma$  – piezoelectric coefficient,  $P$  – applied pressure,  $h$  – film thickness,  $\epsilon$  – the dielectric constant,  $\epsilon_0$  – electrical constant.

5. a) Determine the current that can be generated while running if the mass of the runner is  $55$  kg, and the area of the sneakers is  $189$  cm<sup>2</sup>. Accept  $\gamma(K) = 49.6 \cdot 10^{-12}$  C/N,  $\epsilon(K) = 10$ ; b) How many percent can runner charge a heart rate sensor with a  $130$  mA·h battery in  $1$  hour of running? c) Identify polymer **K** and monomer **L** if the last one is known to be an unsaturated halogenated hydrocarbon containing  $37.5\%$  C and  $3.1\%$  H. The electron impact ionization mass spectrum of **L** (containing both molecular and fragment positive ions) contains intense peaks with the ratio masses of ions to their charge  $m/z = 64, 63, 50$  and  $14$ .

Physical constants: electrical constant  $\epsilon_0 = 8.85 \cdot 10^{-12}$  F/m, gravitational acceleration  $g = 9.8$  m/s<sup>2</sup>.

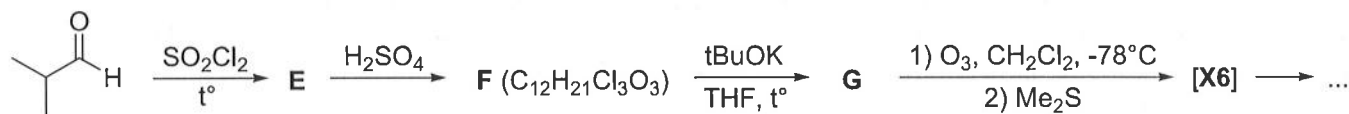
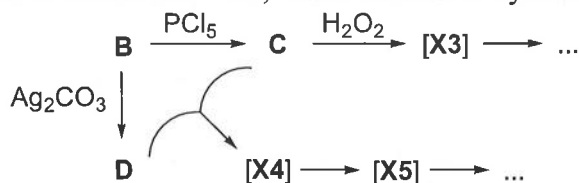
## SECTION II. ORGANIC CHEMISTRY

## Problem 1

Some carbon compounds, in particular, CO and CO<sub>2</sub> oxides, are considered in the framework of inorganic chemistry. However, there are quite a lot of oxygen compounds of carbon related to organic substances. Such “carbon oxides” **X1** – **X11** will be considered in the present problem. In the mild ozonolysis of a elementary substance **A**, a compound **X1** with an oxygen mass fraction of 6.24% is formed. When heated or photolyzed, it loses the oxygen molecule and forms the compound **X2**.

1. Give the molecular formulas of **A**, **X1**, and **X2**. Support the answer with calculations.

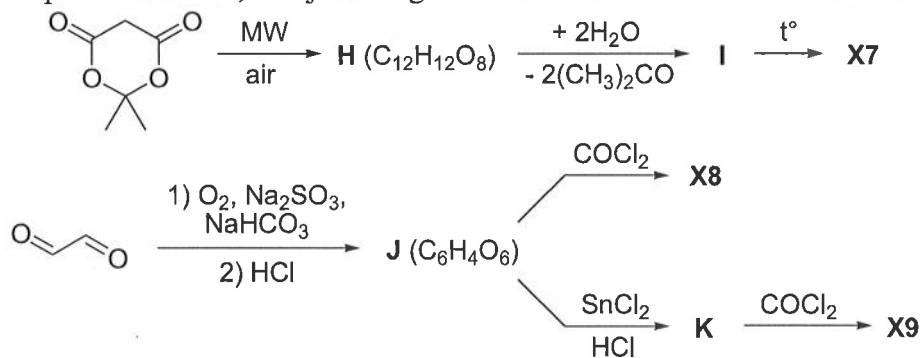
Oxygen-containing carbon compounds **X3** – **X6** are unstable substances of the cyclic structure. **X3** and **X6** decompose to form the same gas with a higher density than air. Substance **X4** is formally a dimer of compound **X5**. When **X4** decomposes, an equimolar mixture of two gases and substance **X5** is first formed, which then decomposes to form a mixture of gases of the same density. The simplest dicarboxylic acid **B** can be used to obtain **X3** – **X5**, while **X6** can be synthesized from isobutyraldehyde:



2. Give the structural formulas of **B** – **G** and **X3** – **X6**.

3. The adjacent homolog of substance **B** also forms a “carbon oxide” when heated with phosphorus(V) oxide. Give a reaction equation providing the structural formulas of organic substances.

Oxygen compounds **X7** – **X9** have the same empirical formula, corresponding to the lightest carbon oxide, containing two, three, and four cycles in their structures, respectively. All the substances **H** – **K** have 1 signal each in <sup>1</sup>H NMR spectra, and in <sup>13</sup>C NMR spectra there are 4 signals for substance **H**, 2 signals each for compounds **I** and **J**, and just 1 signal for **K**.

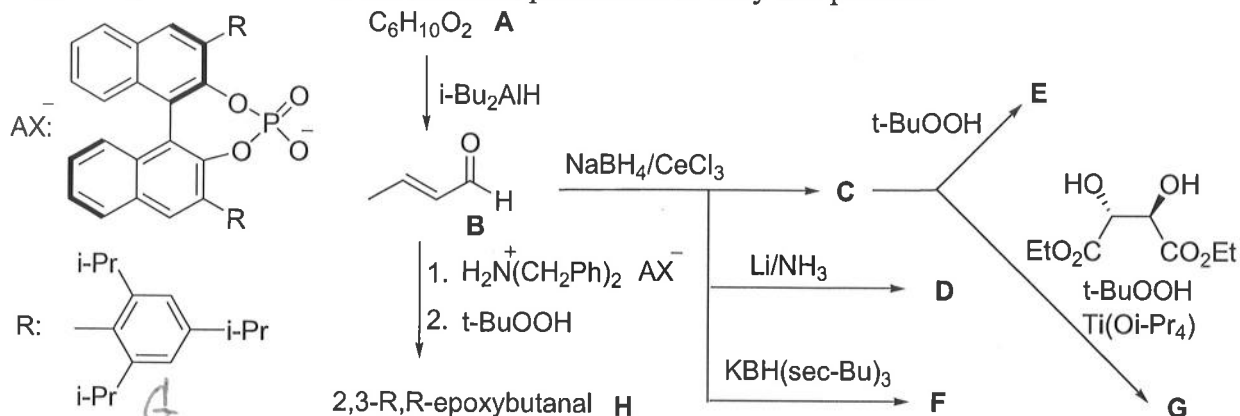


4. Give the structural formulas of **H** – **K** and **X7** – **X9**.

5. Adding substance **C** to **J** and **K**, two more “carbon oxides” **X10** and **X11** can be obtained. They have the same empirical formula as **X7** – **X9** and contain 10 and 12 carbon atoms, respectively. Give the structural formulas of **X10** and **X11**.

## Problem 2

Ideal organic synthesis involves the selective production of only one product.

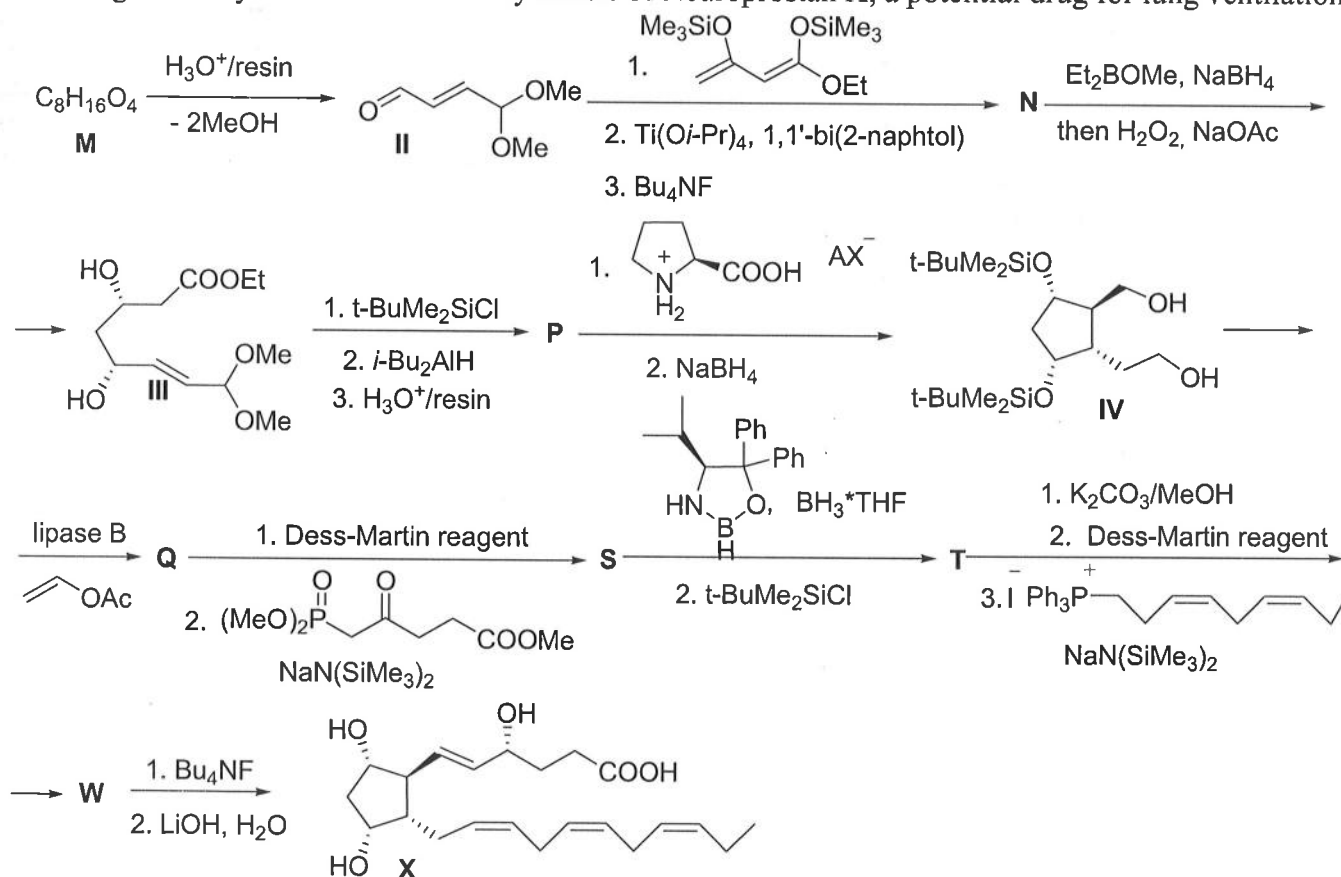


1. Decode **A**, **J** if  $^1\text{H}$  NMR spectra of **A** and **B** differ in the absence of a doublet ( $\delta \approx 10$  ppm) and the presence of a triplet and a quadruplet. In the IR spectrum of **C**, **F**, **E** and **J** there is a broad band ( $3500\text{ cm}^{-1}$ ); **B** and **D** are isomers.

2. Give spatial structures of **H** and **G** (S,S-isomer).

3. Which reactions in the above scheme are chemoselective (preferably proceed through one functional group of the substrate); regioselective (selectively proceed according to a certain position); stereoselective (preferably one of the diastereomers is formed), enantioselective (preferably one enantiomer is formed)?

For their achievements in the field of organocatalysis, List and MacMillan received the Nobel Prize in 2021. Organocatalysis was used in the synthesis of Neuroprostan **X**, a potential drug for lung ventilation.



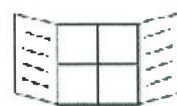
4. Decode **M**, **N**, **P**, **Q**, **S**, **T**, **W**.

5. For the oxidation of **Q** to **S**, the Dess-Martin reagent is used, which is obtained in two stages from *ortho*-iodobenzoic acid. The first stage of its synthesis is the oxidation with the  $\text{KBrO}_3\text{-H}_2\text{SO}_4$  system, the second stage of the synthesis is the interaction of the product, obtained at the first stage, with acetic anhydride. Give the structure of the Dess-Martin reagent and its precursor.

**Problem 3**

In 1972, the structures of polycyclic compounds were proposed, where the  $sp^3$  carbon atom should be flattened for steric reasons.

Such compounds are called fenestranes (from Latin window) because its representative [4,4,4]-fenestrane ( $C_9H_{12}$ ) resembles a window (in the case of a completely flat central carbon atom). Due to strong steric hindrance [4,4,4]-fenestrane has not been synthesized, although its analog [4,4,4]-fenestrane ( $C_8H_{12}$ ) – “broken window” exists.



"fenestra"

(a)



(b)



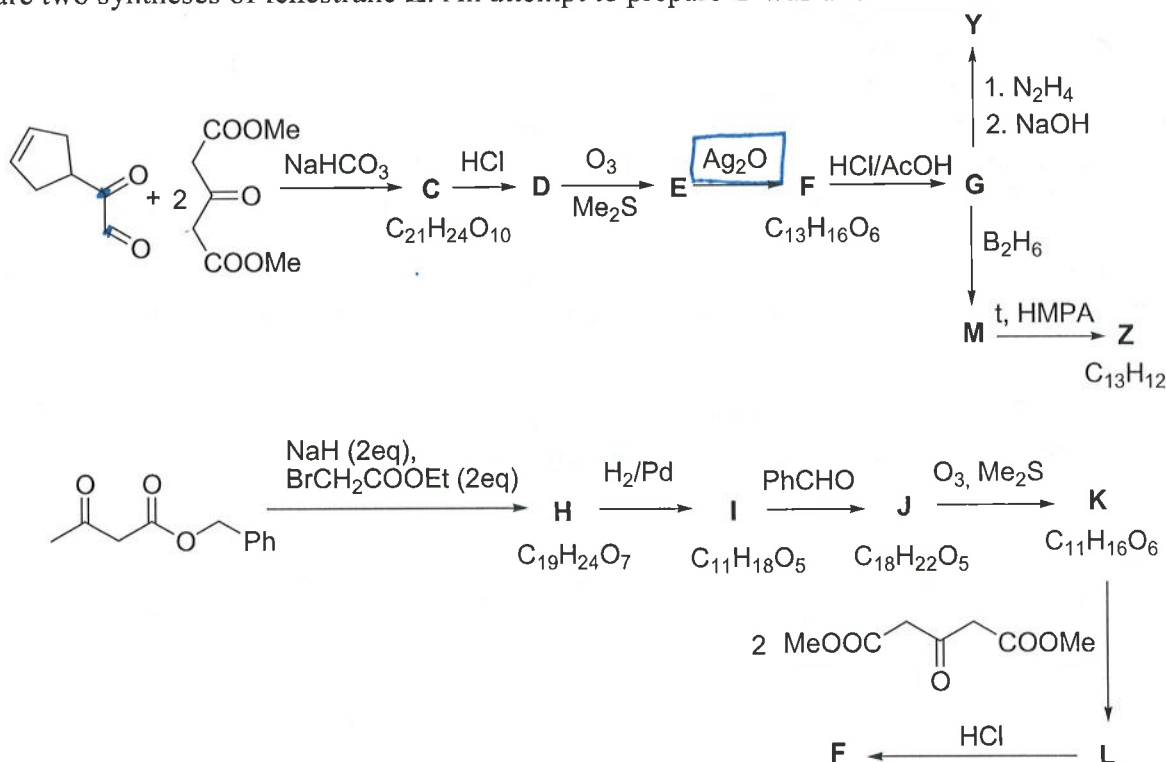
(c)

1. Draw the structures of [4,4,4]-fenestrane, [4,5,4,5]-fenestrane and [4,4,5,5]-fenestrane.

[2+2]-Cycloaddition **A** ( $C_{12}H_{16}O$ ) followed by Kizhner-Wolf reduction of cycloadduct **B** is used in the synthesis of fenestrane **X**.

2. Suggest the structures of substances **A**, **B**, **X**, if there are double bonds in structure **A**.

Below are two syntheses of fenestrane **Z**. An attempt to prepare **Y** was unsuccessful.



3. Decode **C** – **K**, **Z**.

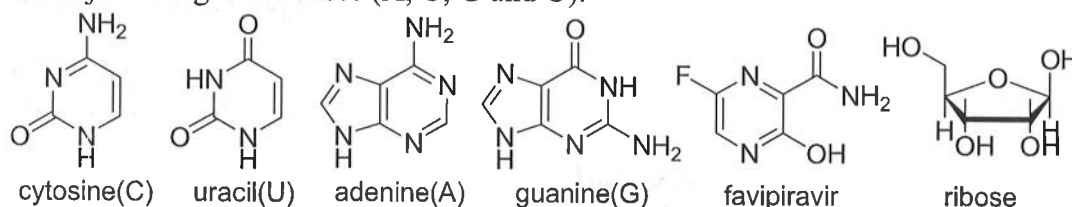


## SECTION III. LIFE SCIENCES AND POLYMERS

## Problem 1

SARS-CoV-2, a member of the family of coronaviruses (RNA viruses), was behind the COVID-19 pandemic. Several treatment patterns have been elaborated as the pandemic response, and other (initially developed to cure different virus diseases) were redesigned. Most approaches are based on the nucleosides with the structures so similar to those of the natural compounds that they and their derivatives act as substrates of the enzymes involved into the virus replication.

1. Correlate the potential anti-COVID-19 drugs given in the Answer sheet with the nucleoside analogs formed by the major nitrogenous bases (A, C, G and U).



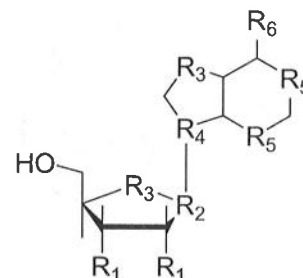
The drug Favipiravir is capable of complementary overlapping with A, C, G, and U with the same number of hydrogen bonds as in the native pairs. The energies and lengths of the hydrogen bonds in all the artificial pairs are comparable.

2. Indicate potential donors (D) and acceptors (A) of hydrogen bonds in the Favipiravir molecule given in the Answer sheet.

3. Draw complementary pairs between Favipiravir and pyrimidine bases (use dashed lines to show the hydrogen bonds).

The skeleton of the compound **X** ( $C_{11}H_{15}N_5O_3$ ), previously used in therapy for viral hepatitis C and later implemented in treatment of COVID-19, is given on the fig. Some atoms or group of atoms are encoded as  $R_1 - R_6$ , and the multiple bonds in the heterocycle are omitted. The molar masses of  $R_1 - R_6$ , if rounded to integers, are the terms of an arithmetic sequence with the initial term of 12.

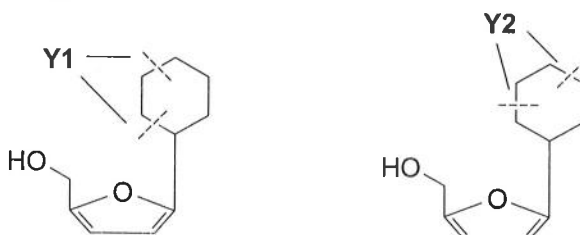
4. Decipher  $R_1 - R_6$ . Draw the structure of **X**.



Molnupiravir causes mutations in the RNA virus during its amplification without preterm termination of replication due to the formation of complimentary pairs with both A and G depending on the tautomeric form. The (-)RNA is synthesized at replication using a coronavirus single strain (+)RNA as the matrix. In turn, the (-)RNA becomes the matrix affording new copies of (+)RNA. Only (+)RNA can be the matrix RNA for biosynthesis of viral proteins.

5. Consider the fragment ...AGAACUU... of a single strain (+)RNA, which undergoes several cycles of replication from the initial RNA towards daughter (+)RNAs in a cell in the presence of Molnupiravir. Propose the sequences of all possible secondary (+)RNA fragments.

Nucleoside **Y** is an isomer of one of the major nucleosides. **Y** is the key component of some mRNA vaccines used for the preventive care of COVID-19. Analysis of **Y** using liquid chromatography-mass spectrometry (LC-MS) reveals a characteristic signal  $m/z$  of 164, which is due to the ionic forms ( $M^+$ ) of two isomeric products (**Y1** and **Y2**) of the destruction of **Y**. The common formula of the immediate precursor of **Y1** and **Y2** (the MS intermediate; the detailed image of the nitrogenous base missing) with the schemes of its fragmentation is:

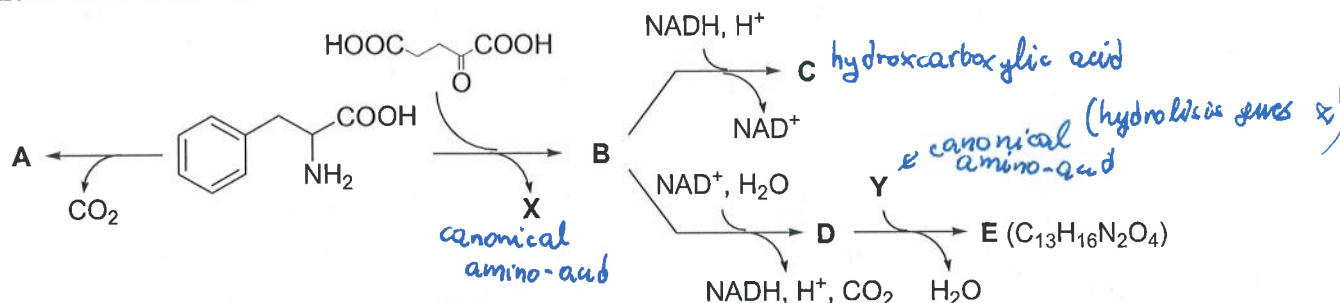


6. Deduce the structure of **Y**, if the residues of the nitrogenous base in **Y1** and **Y2** are formed by seven atoms each.

7. In the Answer sheet, choose one correct statement explaining why **Y** is widely used for the development of mRNA vaccines instead of its native analog.

## Problem 2

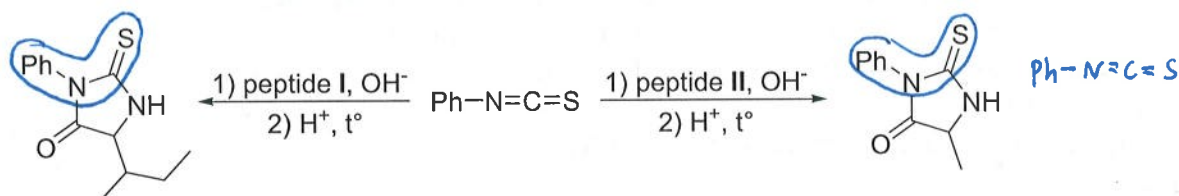
Phenylketonuria is a genetic disease that leads to phenylalanine (Phe) metabolism abnormalities caused by mutations in the gene encoding the enzyme phenylalanine-4-hydroxylase (PAH). As a result of the disease, Phe and toxic products of its transformations accumulate in the body. The biosynthesis of some of the metabolites is shown in the scheme.



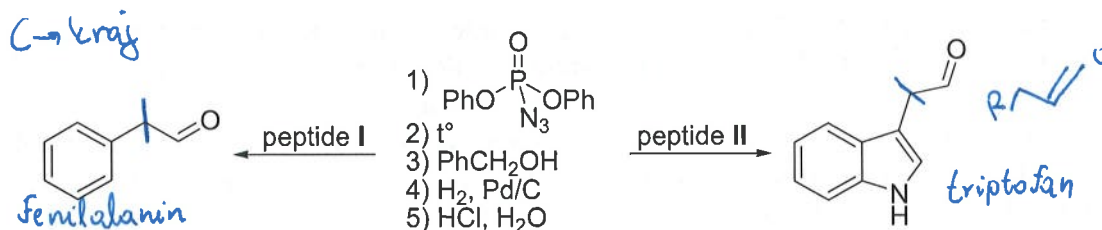
1. Draw the structures of **A** – **E**, **X** and **Y**, if **C** is a hydroxycarboxylic acid, **X** and **Y** are canonical amino acids with 5 carbon atoms each, and the hydrolysis of **Y** gives **X**.

One of the mutations in the gene (R408W) responsible for phenylketonuria is associated with a single nucleotide substitution. This leads to a change in the triplet and synthesis of PAH with another amino acid. To determine which amino acid has been substituted, two pentapeptides were isolated and sequenced (determination of the amino acid sequence). The pentapeptides were the fragments of healthy (peptide **I**) and diseased (peptide **II**) human proteins.

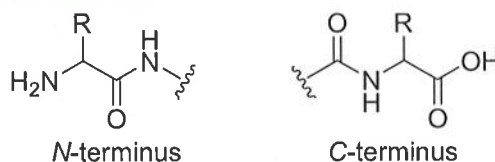
a) The action of phenylisothiocyanate (PhNCS) resulted in the following products (the Edman degradation):



6) The Bergmann degradation is a multi-step process. First, the peptides are treated with diphenyl phosphoryl azide (DPPA), affording acyl azides. The latter undergo the Curtius rearrangement. Subsequent treatment with benzyl alcohol gives carbamates, and the hydrogenolysis removes the benzyl protecting group. Finally, acid hydrolysis leads to aldehydes containing the side chain of a terminal amino acid:



2. Which of the above methods allows determination of the *N*-terminal, and which one of the *C*-terminal amino acids? Draw the structures of the intermediates at each step and the final products, denoting the *N*- and *C*-terminuses as follows:



3. Determine the *N*- and *C*-terminal amino acids of the peptides **I** and **II**.

After the cleavage of the *N*- and *C*-terminal amino acids in the peptides **I** and **II** according to the above methods, the tripeptides **I'** and **II'** formed were partially hydrolyzed. The resulting mixtures were analyzed by soft ionization mass spectrometry (ESI-MS). The *m/z* values (the mass to charge ratio of an



ion) of the protonated molecular ions for the mixtures obtained after hydrolysis of **I'** were 136.5 and 185; and those of **II'** were 229, 233, and 330. Consider that all the analyzed oligopeptides contain a free amino group at the *N*-terminus and a free carboxyl group at the *C*-terminus.

4. Based on the mass spectrometric data, propose all possible variants of the amino acid sequences in **I'** and **II'** (use designations).

5. Decipher the structures of **I** and **II** by writing the designations of the amino acids from *N*- to *C*-terminus. Indicate which amino acid substitution occurs as a result of the R408W mutation.

Reference data:

Name	Designation	Molecular mass ( $M_r$ )
Glycine	Gly	75
Alanine	Ala	89
Serine	Ser	105
Proline	Pro	115
Valine	Val	117
Threonine	Thr	119
Cysteine	Cys	121
Isoleucine	Ile	131
Leucine	Leu	131
Asparagine	Asn	132

Name	Designation	Molecular mass ( $M_r$ )
Aspartic acid	Asp	133
Glutamine	Gln	146
Lysine	Lys	146
Glutamic acid	Glu	147
Methionine	Met	149
Histidine	His	155
Phenylalanine	Phe	165
Arginine	Arg	174
Tyrosine	Tyr	181
Tryptophan	Trp	204

### Problem 3

The interaction of poly(methyl acrylate) (see the Answer Sheet; assume the head-to-tail connection of the repeat units) with methylamine at heating leads to the formation of units **X** (10.07 wt% of N) in the polymer.

1. Draw the reaction scheme leading to **X**. Calculate the degree of polymerization (the number of the repeat units) of the sample prepared by the above reaction from poly(methyl acrylate) with the molar mass of 25000 g/mol, if the conversion of the methyl acrylate units equals 40%. Calculate the resulting loss of mass.

Alkaline hydrolysis of the units **A** (26.40 wt% of N) of some polymer leads to the formation of copolymers containing additionally units **B** and **C** (19.71 and 0 wt% of N, respectively). One of such hydrolysis products (polymer **P**) contains 7.35 wt% of N, 28.29 wt% of O, and 15.98 wt% of Na.

2. Elucidate the structures of **A**, **B**, and **C**.

3. Determine the molar fractions of **A**, **B**, and **C** in **P**.

Heating of **P** after its treatment with dilute hydrochloric acid, washing with water, and drying leads to the formation of the units **Y** homologous to **X**. The transformation occurs stepwise: first at 90°C without a mass loss and then at 160°C with a mass loss.

4. Elucidate the structure of **Y**. Draw the schemes of the described reactions (use the **A**, **B**, **C**, **Y** to denote the repeat units). Calculate the mass loss of the sample (%) at the second step assuming the maximum conversion at both steps of the process. *If you have failed to answer the previous question, give the answer in the general form denoting the molar fractions of **A**, **B**, and **C** in **P** as  $a$ ,  $b$ , and  $c$ , respectively.*

5. A copolymer similar to **P**, still of arbitrary composition has been prepared. Let us denote the molar fractions of **A**, **B**, and **C** in this copolymer as  $a$ ,  $b$ , and  $c$ , respectively. At which ratios between  $a$ ,  $b$ , and  $c$  the second step is still possible, if the first step has been conducted to the maximum possible conversion.

6. The compositions of several copolymers analogous to **P** are given in the Answer Sheet. Arrange those in the order of increasing the content of **Y** in the products of their thermal treatment (heating) assuming that the reactions described in this task are conducted to the maximum possible conversion.

## SECTION IV. INORGANIC CHEMISTRY

## Problem 1

«I often think that the night is more alive and more richly colored than the day.»

Vincent Van Gogh

A lot of inorganic compounds, especially of transition metals, have various colors, what can be used to create dyes and pigments. Important properties of inorganic dyes are their high resistance to light, high temperatures, corrosion, and also good coloring ability. Some popular inorganic dyes encrypted below are used by modern industry, others have remained only in historical references and in paintings of the great artists.

Nowadays, titanium or zinc white is often used as a white pigment, however, that was not always the case. Pigment **A** is a basic carbonate. The oldest method of producing **A** was as follows: thin sheets of metal were placed in special pots, on the bottom of which a small amount of acetic acid was poured. The pots were buried in horse manure, which released a large amount of carbon dioxide during rotting. As a result, a white layer of basic carbonate formed on the metal surface. Then it was cleaned off and used in the manufacture of paint.

1. Determine **A**, if the thermal decomposition results in the mass loss of 13.7%. **A** does not contain crystallization water.

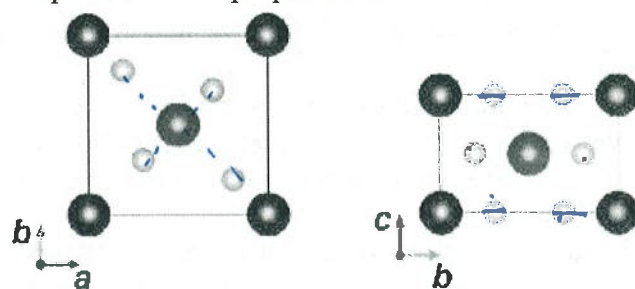
**A** stands out for its pure white color and excellent hiding power, yet **A** is hardly used today due to its high toxicity. In addition, it slowly darkens in air due to interaction with hydrogen sulfide. One way to restore such a "spoiled" white color is to treat it with hydrogen peroxide.

2. Write down the chemical reactions equations of the last two processes.

A mixed iron oxide is usually used as a black pigment, as well as substance **C**, which is formed during the incomplete combustion of a hydrogen compound with a density of 0.714 g/L (under normal conditions).

3. Determine **C** and write down the chemical reaction equation for its preparation.

The crystal structure of **D**, a metal oxide, is shown in the figure as projections of a tetragonal unit cell onto different planes (unit cell parameters are  $a = b = 4.395 \text{ \AA}$ ,  $c = 2.875 \text{ \AA}$ ,  $d = 5.20 \text{ g/cm}^3$ ). Oxide **D** itself is included in the composition of such pigments as ocher, sienna, umber, the simplified composition of which can be written as  $a\text{Fe}_2\text{O}_3 \cdot b\text{D} \cdot c\text{SiO}_2 \cdot d\text{Al}_2\text{O}_3 \cdot e\text{H}_2\text{O}$ . Furthermore, an increase in the mass fraction of **D** leads to a color change from yellow to yellow-orange and brown. In nature, **D** is also found as a distinct mineral.



○ - Oxygen atoms

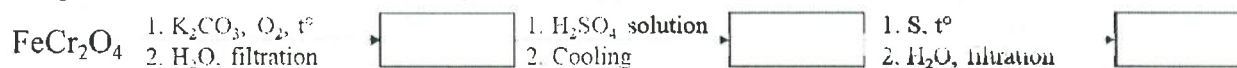
4. Determine the composition of **D** and the metal coordination environment in its crystal structure.

Thénard's blue is an extremely stable blue pigment used in paints, ceramics, and jewelry. It is obtained by sintering of aluminum oxide or sodium aluminate with salts of an unknown transition metal (nitrates, chlorides, hydrocarbonates, etc.). Thénard's blue belongs to the spinel group, and the effective magnetic moment of the transition metal atom is 3.87 mB.

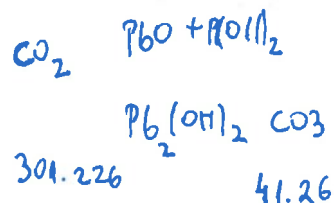
→ 5. Determine the composition of Thénard's blue and write down the chemical reaction equation of its preparation from an unknown metal chloride and sodium aluminate.

→ 6. From the d-orbitals splitting diagrams of an unknown metal, given in the answer sheets, choose the correct one and depict the distribution of electrons in the orbitals.

The most popular green dye is produced from the chromium compounds. The scheme presents the way of processing of iron chromite and obtaining the final product.



→ 7. Decipher the scheme and write down all chemical reactions equations.



## Problem 2

The element **X** is part of a large number of compounds and substances that have been used by humanity since ancient times. Most of these compounds under normal conditions are solid, crystalline, non-volatile substances, but there are examples of compounds whose melting points are below room temperature.

An elementary substance **X1** with slight heating can actively react with a gaseous, slightly colored substance **A1**, forming compound **Y1**. When heated, this substance is able to sublime, which is often used to separate compounds which are similar in their composition. In parallel with the transition into the gas phase, **Y1** undergoes partial decomposition with the formation of compound **Y2** and an elementary substance. Substance **Y2**, being crystalline, does not pass into the gas phase, but it is hygroscopic like **Y1**. **Y2** can be obtained in other ways, for example, by the reaction of **X1** with **Y1**, or by the reaction of **X1** with the binary compound **A2**, the latter includes the lightest element. The molar fractions of element **A** in **Y2** and **A2** differ by 1.334 times, and its mass fraction differ by 1.7377 times.

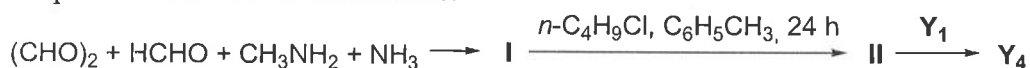
1. Determine the element **X** and the composition of the compounds **Y1**, **Y2**, **A1** and **A2**. Confirm your conclusion with calculations. Write down the equations of mentioned reactions. Draw the structure of the **Y1** molecule in the gas phase.

In addition to crystalline **Y1** and **Y2**, the element **X** may be contained in the substances **Y3** and **Y4** liquid under ambient conditions.

The compound **Y3** can be obtained by the reaction of **Y2** with aluminum and a gaseous substance, the latter is isoelectronic to nitrogen molecule. The molecular fragment of the **Y3** has one 3-fold axis of symmetry, three 2-fold axes, four mirror planes, but the inversion center is absent. This compound is diamagnetic. Under the hard UV radiation it can form a diamagnetic compound **Y5**, in which the mass fraction of the element **X** is 1.077 times more than the mass fraction in **Y3**. The molecular fragment of the **Y5** compound has two mirror planes of symmetry, one 2-fold axis. The compound **Y3** is soluble in many organic solvents. When action of **A1** excess on a solution **Y3** in tetrachloromethane **Y1** is formed.

2. Determine the compounds **Y3** and **Y5**. Confirm your conclusion with calculations. Write down the equations of these reactions. Draw structural formulas of molecular fragments, indicating all bonds.

**Y4** is used as polar solvent, catalyst, electrolyte in electrochemical devices. The scheme of obtaining the compound **Y4** is presented below in the scheme.



3. Write down the equations of the corresponding reactions, draw the structural formulas of compounds **I**, **II**, **Y4**. Give an example of an inorganic compound containing the same anion as in **Y4**.

4. For what reason are the compounds **Y3** and **Y4** fluids at ambient temperature and pressure? Select the answer from the proposed options. Which of these compounds can pass into the gas phase?

## Problem 3

The compound  $\text{A}_2\text{O}_n$  which plays an important role in the transmission of nerve signals, is obtained in the form of a bluish gas by the action of  $\text{Cr}_2\text{O}_3$  on a mixture of potassium salts ( $3\text{KAO}_2 + \text{KAO}_3$ ). Pure  $\text{A}_2\text{O}_n$  is colorless paramagnetic gas with  $l_{\text{A-O}} = 0.115 \text{ nm}$ , which condenses below  $-164^\circ\text{C}$  into a colorless diamagnetic solid mixture of isomers **B**: **B1** ( $l_{\text{A-O}} = 0.112$  и  $0.240 \text{ nm}$ ) and **B2** ( $l_{\text{A-O}} = 0.112 \text{ nm}$ ;  $l_{\text{A-A}} = 0.218 \text{ nm}$ ; cis-isomer). In 1978 Laane obtained red modification **B3** ( $l_{\text{A-O}} = 0.119 \text{ nm}$  and  $0.174 \text{ nm}$ ,  $\angle\text{AOA} = 107^\circ$ ) by  $\text{A}_2\text{O}_n$  condensation in the presence of Lewis acids.

1. Decode **A**,  $\text{A}_2\text{O}_n$  and **B**, if the mass fraction  $w_{\text{A}}$  in  $\text{KAO}_2$  and  $\text{KAO}_3$  differs by 2.61%. Write down the equation for the  $\text{A}_2\text{O}_n$  synthesis reaction and the reaction explaining the bluish color of the gas.

2. Calculate the content of **B** (mol. %) in the gas at  $25^\circ\text{C}$  and 1 atm, if  $\Delta_f G^\circ$ , kJ/mol: 12.35 ( $\text{A}_2\text{O}_n$ ) and 39.00 (**B**). Draw the structural formulas of  $\text{A}_2\text{O}_n$  (MO method) and modifications of **B**.

Being in complexes monodentate  $\text{A}_2\text{O}_n$  can donate an electron to the central Me atom and act as either  $\sigma$ -donor (1), or both  $\sigma$ -donor and  $\pi$ -acceptor (2), forming linear (**X**) fragment MeAO ( $170\text{--}180^\circ$ ), and can be one-electron (3), forming bent (**Y**) fragment MeAO ( $120\text{--}140^\circ$ ).

Complex	$\angle \text{MeAO}$	$l_{\text{Me-A}}, \text{nm}$	$l_{\text{A-O}}, \text{nm}$	$\nu \text{ cm}^{-1}$ in IR-spectrum
$[\text{Fe}(\text{CN})_5\text{A}_2\text{O}_n]^{2-}$	178	0.166	0.112	1935
$[\text{IrCl}(\text{CO})(\text{PPh}_3)_2\text{A}_2\text{O}_n]^+$	124	0.197	0.119	1680
$[\text{RuCl}(\text{PPh}_3)_2(\text{A}_2\text{O}_n)_2]^+$	178; 138	0.186; 0.172	0.118; 0.114	1845; 1687

3. Draw fragments 1-3 and the structural formulas of the complexes given in the table, assuming that Me in  $d^2sp^3$  and  $d_{x^2-y^2}sp^3$  hybridization,  $\angle \text{Me}(\text{PPh}_3)_2 \sim 180^\circ$ , and one ligand  $\text{A}_2\text{O}_n$  is in the axial position.

In 1979, Schoonover and Eisenberg showed that there is equilibrium  $\text{X} \rightleftharpoons \text{Y}$  in solution. If  $\text{A}_2\text{O}_n$  is passed through a solution of green  $\text{MeCl}_3$  (3.73 g) in  $\text{CH}_3\text{OH} + \text{N}(\text{C}_2\text{H}_5)_3$  until complete sedimentation of  $\text{CH}_3\text{OAO}$ ,  $\text{PPh}_3$  (0.025 mol) is added until a brown-red solution of the  $\text{E}^+$  cation (7.82 g, yield 80%,  $w_{\text{Cl}} = 4.54\%$ ), then salts of EAn would be obtained by the action of  $\text{BF}_4^-$  and  $\text{PF}_6^-$ . In their solution in THF at  $0^\circ\text{C}$ ,  $\text{Cl}^-$  can be replaced with  $\text{C}_3\text{H}_5^-$  by action of  $\text{Sn}(\text{C}_3\text{H}_5)_4$  with formation of light brown salt  $\text{DPF}_6$  ( $\nu = 1763 \text{ cm}^{-1}$ ) and red-brown one  $\text{DBF}_4$  ( $\nu = 1631 \text{ cm}^{-1}$ ).

4. Decode mononuclear cations  $\text{E}^+$  and  $\text{D}^+$  in the salts and depict the structural formulas of  $\text{D}^+$  ( $\text{PPh}_3$  – triphenylphosphine,  $\text{C}_3\text{H}_5$  – trihapto ligand  $\eta^3$ ).

In a solution of any of the salts with  $\text{D}^+$  at  $25^\circ\text{C}$ , bands  $1760$  and  $1630 \text{ cm}^{-1}$  of the same intensity are fixed (I), at  $0^\circ\text{C}$  the intensity of the  $1760 \text{ cm}^{-1}$  band increases by 31%, and the sum of the intensities of the two bands does not depend on temperature.

5. Estimate  $\Delta_r H^\circ$  of the transition  $\text{Y} \rightleftharpoons \text{X}$ , using the intensities in the IR spectrum and the Van't Hoff equation.



## SECTION V. ANALYTICAL CHEMISTRY

## Problem 1

*Art is the highest manifestation of power in man.**L.N. Tolstoy (1828-1890)*

An important and interesting application of chemical analysis is painting. Paints contain a pigment (most often it is an inorganic mineral) and a binder (oil in the case of oil paints). Analysis of paints is necessary for the purpose of restoration or verification of authenticity of a painting.

The main white pigments in paints are white lead paint  $\text{Pb}_2(\text{OH})_2\text{CO}_3$ , zinc white paint  $\text{ZnO}$  and barium white  $\text{BaSO}_4$ . To determine the type of white paint, it is sufficient to dissolve it in a strong acid: two out of the three paints dissolve, and the insoluble one can be dissolved by fusion with sodium carbonate.

1. Arrange the white paints in the descending order of solubility in 0.1 M strong acid. Confirm this sequence by calculating the solubility  $S$  of each of the three paints in acid, assuming that  $\text{pH} = 1$  and it is not changing during dissolution:  $K_S(\text{BaSO}_4) = 1.1 \cdot 10^{-10}$ ,  $\text{p}K_{a1}(\text{H}_2\text{SO}_4) = -6.3$ ,  $\text{p}K_{a2}(\text{H}_2\text{SO}_4) = 1.9$ ,  $K_S(\text{Pb}_2(\text{OH})_2\text{CO}_3) = 3.5 \cdot 10^{-46}$ ,  $\text{p}K_{a1}(\text{H}_2\text{CO}_3) = 6.35$ ,  $\text{p}K_{a2}(\text{H}_2\text{CO}_3) = 10.35$ ,  $K_S(\text{Zn}(\text{OH})_2) = 1.2 \cdot 10^{-17}$ .

After the dissolution of white paints, the following reagents can be used to recognize them:  $\text{K}_2\text{Cr}_2\text{O}_7$  (a yellow precipitate forms, and its amount increases when sodium acetate is added),  $\text{KI}$  (a yellow precipitate forms that dissolves easily in hot water; if the solution is cooled, the precipitate forms again, sometimes it is called "golden rain"),  $(\text{NH}_4)_2[\text{Hg}(\text{SCN})_4] + \text{CuSO}_4$  (violet precipitate).

2. Match the identified cations and reagents, write down the corresponding reaction equations.

3. Why does the amount of the first yellow precipitate increase with the addition of sodium acetate?

Knowing the nature of the white paint is important for restoring paintings or verifying their authenticity. For example, despite the beautiful color of white lead, it will eventually turn gray and even black in air (the presence of traces of a gas with a close molecular weight to oxygen). To restore the white color, restorers use a solution of hydrogen peroxide.

4. Write the appropriate reaction equations.

In the 16th-17th centuries, paints often contained such harmful elements as lead (in white paints and pigments) and arsenic, which was a component of such infamous wallpaper paints as "Scheele green" or "Paris Green" with an amazing green tint but very toxic due to arsine release in a humid atmosphere.

5. Paris Green is a mixed salt, it is obtained by the interaction of pigment "Verdigris" ( $\text{CuAc}_2$ ) with arsenic(III) oxide.

a) Write down the reaction of Paris Green formation, if both components of the mixed salt contain copper(II) as cation.

b) When alkali are added, the Paris Green suspension changes color to red-orange. Write down the redox reaction equation, circle the compound(s) responsible for the color of the mixture.

c) Determine the formula of Paris Green if the amount of copper in the product obtained after treatment with alkali is equal to the amount of arsenite. The redox reaction is quantitative.

The amount of arsenic can be determined by the following method: a wallpaper sample ( $100 \text{ cm}^2$ ) is dissolved in fuming nitric acid, the volume of the solution is adjusted to 500 mL, and an aliquot of the solution (100 mL) is titrated with sodium bromate of a concentration of 0.002 M to the equivalence point (1.65 mL).

6. Determine what fold the amount of arsine exceeds the maximum permissible concentration ( $0.1 \text{ mg/m}^3$ ) in a room with the wall area of  $50 \text{ m}^2$ , if the volume of the room is  $60 \text{ m}^3$ , assuming that 1/1000 of all arsenic has turned into arsine.

Other component of paints are oils, esters of glycerol, characterized by the ability to dry, which in turn is related to the number of  $\text{C}=\text{C}$  bonds in the oil: the more of them, the faster the paint dries due to polymerization. The number of  $\text{C}=\text{C}$  bonds is characterized by the iodine number (the mass of iodine reacting with 100 g of oil). With the iodine number less than 115, the oil does not dry out, 115–130 it is semi-drying and more than 130 – well drying.

The iodine number can be determined by iodometric titration: a sample of oil (1.500 mL,  $\rho = 0.92 \text{ g/mL}$ ) is diluted with chloroform, and a known amount of bromine is added in excess. After the reaction is completed, potassium iodide is added to the mixture, the resulting iodine is titrated with a solution of sodium thiosulfate prepared using 24.81 g of salt pentahydrate in 500 mL of solution. A similar blank



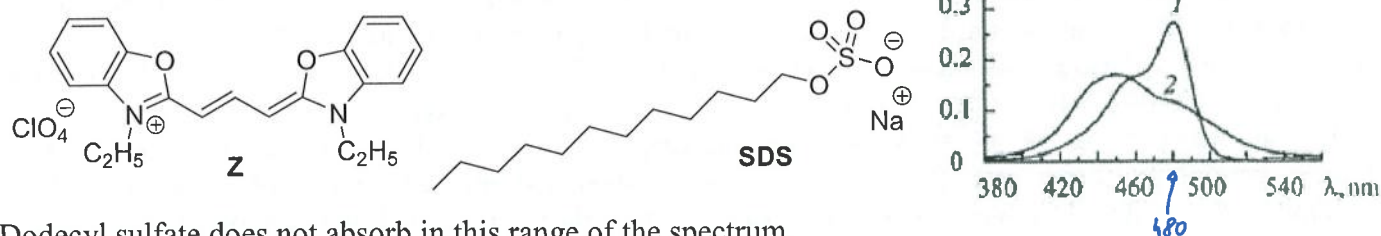
experiment is carried out without oil. For the titration of the first solution, 6.75 mL of thiosulfate solution was used, and for the titration of the blank sample, 56.25 mL of the same solution was spent.

7. Write down all the equations of the reactions that take place; instead of oil, write  $R-CH=CH-R$  for simplicity.

8. Calculate the iodine number and judge the suitability of the oil for use in a paint formulation.

## Problem 2

The spectroscopic properties of dyes (absorption of light, fluorescence, etc.) can change markedly when interacting with surfactants. For example, carbocyanine Z in the presence of sodium *n*-dodecyl sulfate (SDS) changes its absorption spectrum as follows (1 - in the presence of SDS, 2 - without SDS):



Dodecyl sulfate does not absorb in this range of the spectrum.

1. Choose the wavelength at which it is most convenient to observe the complexation of the dye with the surfactant.

To describe the equilibrium in solution, it is sufficient to apply the mass action law (the expression for the constant  $K$  of the corresponding equilibrium), the law of conservation of matter (material balance) and the Bouguer-Lambert-Beer law  $A = \varepsilon[X]l$ , where  $A$  is absorbance,  $\varepsilon$  is the molar absorption coefficient of  $X$ ;  $[X]$  is the equilibrium concentration of  $X$  (mol/L),  $l$  is the optical path of the cell (cm).

2. a) For the complexation reaction presented in the form:  $Z + n\text{SDS} = Z(\text{SDS})_n$ , write down the expression for the equilibrium constant. Designate the total concentration  $Z$  as  $c(Z)$  and the equilibrium concentration as  $[Z]$ . Write down the expression for the material balance of the dye (Ignore the material balance for SDS, because the surfactant concentration is significantly higher than the dye concentration.)

6) Write the experimental value of absorbance  $A$  as the absorbance of the  $Z(\text{SDS})_n$  complex according to the Bouguer-Lambert-Beer law for a cell with  $l = 1$  cm (neglect the absorbance of the free dye).

3. a) From the written equations, obtain an expression relating the optical density  $A$ , the molar absorption coefficient of the complex  $\varepsilon$ , the total concentrations of the dye  $c(Z)$  and dodecyl sulfate  $c(\text{SDS})$  and the complex formation constant  $K$ .

6) Bring the resulting expression to the form  $y = y_0 + Bx$ , where  $y = 1/A$ , and  $x = 1/c(\text{SDS})^n$ .

4. The following values of absorbances were obtained experimentally in the presence of various concentrations of SDS ( $l = 1$  cm; the total dye concentration  $c(Z)$  is constant and equal to  $1 \cdot 10^{-5}$  M):

$c_{\text{SDS}}, \text{M}$	$2.0 \cdot 10^{-4}$	$2.9 \cdot 10^{-4}$	$3.8 \cdot 10^{-4}$	$6.0 \cdot 10^{-4}$
$A$	0.10	0.20	0.33	0.67

a) Plot the graphs  $1/A - 1/(c_{\text{SDS}})^n$  for  $n = 1, 2$ , and  $3$  on the checkered blanks in the answer sheets.

b) Determine the composition of the complex.

c) How to calculate the value of the complex formation constant? Give the formula (do not give a numerical value).

## Problem 3

Extraction is a method of separating substances based on their different distribution between two immiscible solvents (phases). For example, when iodine is extracted from the aqueous phase with an organic solvent, an equilibrium described by the distribution constant is established:



The following organic substances were added to the saturated aqueous iodine solution: tetrachloromethane, cyclohexene, benzene, ethyl alcohol, starch, isoamyl alcohol.

1. Assign the added organic substance with the observed effect: a) separation into two phases, the upper one is colored purple; b) separation into two phases, the lower one is colored purple; c) dark blue solution; d) brown solution; e) separation into two phases, the upper one is colored brown; f) separation into two phases, the upper one turns purple, which fades over time, and the third phase forms on the bottom.

The iodine solubility in water is increased in the presence of halide ions due to the formation of complexes of type  $I_2X^-$ , where  $X = F, Cl, Br, I$ , according to the equation:



The  $D_X$  distribution coefficient is the ratio of the sums of all forms concentrations of the extracted substance in the organic phase to the aqueous. When extracting an iodine solution in the presence of halide ions, only neutrally charged iodine molecules are transferred into the organic phase.

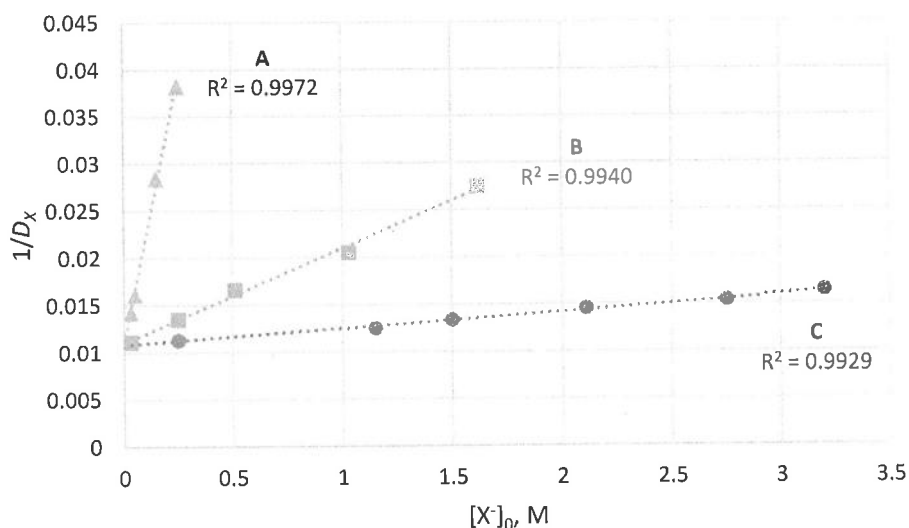
2. Get an expression that explains the linear correlation  $\frac{1}{D_X} = a + b[X^-]_{aq}$ . How are the constants  $K_D$

and  $K_X$  related to coefficients  $a$  and  $b$ ?

To determine the equilibrium constants  $K_D$  and  $K_X$ , a series of experiments was conducted to extract iodine from some organic solvent into aqueous solutions of potassium halides with a known salt concentration. After separating the phases, the iodine concentrations were determined by titration with a standard sodium thiosulfate solution.

3. Derive the expression for the relation of  $D_X$  to the volumes of thiosulfate  $V(Na_2S_2O_3)_{aq}$  and  $V(Na_2S_2O_3)_{org}$ , which went to titration of aliquots of the aqueous and organic phases with volumes  $V_{aq}$  and  $V_{org}$ , respectively.

The graph shows the dependencies of  $1/D_X$  on the initial concentration of three halide ions in the aqueous phase (cases A – C). It is known that the stability of  $I_2X^-$  complexes increases in the series of  $I_2F^- < I_2Cl^- < I_2Br^- < I_3^-$ , and in the case of one of the halides (case D), dependence  $1/D_X$  from  $[X^-]_0$  stops to be linear.



4. What approximation should be allowed for the expression in question 2 to explain the linear dependence of  $1/D_X$  also on  $[X^-]$ ? Please provide your calculations.

$$K_X[I_2]_{aq} \ll 1$$

$$K_X[I_2]_{aq} \approx 1$$

$$K_X[I_2]_{aq} \gg 1$$

5. Assign the cases A – D to the corresponding halides  $F^-$ ,  $Cl^-$ ,  $Br^-$  and  $I^-$ .

6. Estimate the values of  $K_D$  and  $K_X$  for the three halides A – C.

