SECTION I. PHYSICAL CHEMISTRY

Problem 1

> *«Periodic law is not threatened with destruction*
> *but only superstructures and development are promises …»*
> D.I. Mendeleev

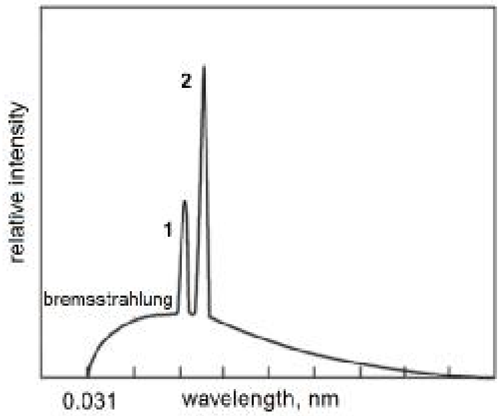


Figure 1. X-ray spectra

2019 was announced as The International Year of the Periodic Table of Chemical Elements and is dedicated to its 150th anniversary. The periodicity of properties is determined by the charge (Z) of the atomic nuclei, which was experimentally determined by Henry Moseley in the study of the X-ray spectra of chemical elements. He found that an atom of each chemical element emits X-rays of strictly defined energies. When an electron gets sufficient energy an electron is removed from the inner shell and the atom transitions to an excited state. To return to the ground state, the electron from a further shell must go to the released one. In this case, the excess energy is released in the form of X-rays. The transition from the L-shell to K causes K_α-radiation, the transition M → K gives K_β-radiation.

The wavelength of X-rays emitted during a transition from the energy level *m* to *n* is defined as

$$\frac{1}{\lambda} = R(Z - \sigma)^2\left(\frac{1}{n^2} - \frac{1}{m^2}\right),$$

where R – Rydberg constant, σ – screening constant, $(Z – \sigma)$ – effective nuclear charge. In general case, the Moseley law can be written as $1/\lambda = C(Z - \sigma)^2$.

1. Determine the constant C (in R units) for K_α - and K_β-radiation.

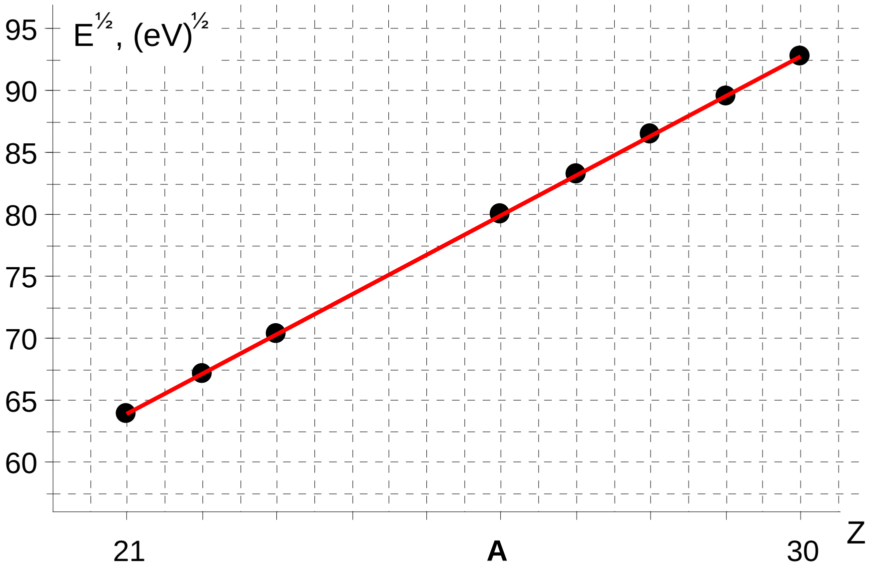
2. *Figure 1* shows a typical view of the X-ray spectrum. Match peaks 1 and 2 with K_α- and K_β-radiation.

Figure 2 shows the dependence of $E^{1/2}$ of X-ray K_α-radiation on the atomic number of chemical elements. By the dependence linearization, the equation is obtained $y = a + bx$, where $a = -3.74$; $b = 3.22$.

3. Based on these data and expressions for the Moseley law calculate: a) the screening constant σ; b) Rydberg constant (m^{-1}).

4. Determine the element **A**. *If you didn't manage to determine σ and R from previous question, accept* $R = 3.29 \cdot 10^{15}$ Hz, $\sigma = 1$.

Figure 2. Dependence of X-ray energy on the nuclear charge of elements



The main sources of X-ray radiation are X-ray tubes and radioisotopes. The voltage (U) between the electrodes of the tube determines the minimum wavelength of bremsstrahlung radiation.

5. Determine the voltage (kV) between the electrodes of the X-ray tube that was applied when recording the X-ray spectrum shown in *Figure 1*. Assume that all the energy eU (e - electron charge) imparted to the electron flux is spent on the generation of X-ray radiation with the energy $h\nu_{max}$.

6. a) Calculate the energy that must be given to an atom of the last element (Z = 30) from the series shown in *Figure 2* for removing an electron from the inner shell.

b) Which of the radioisotopes listed in the table can be used to record the spectra of a number of elements from *Figure 2*?

Radioisotope	Energy emitted in a nuclear reaction, keV
^{26}Al	1809 and 511
^{56}Co	122 and 14
^{241}Am	59.2

c) For ^{26}Al and ^{56}Co two values of energy are given, since their nuclei can undergo both β^+ decay and electron capture. Write the equations for the corresponding reactions for ^{26}Al.

7. Give an example of the sequence of arrangement of elements in the periodic table, which didn't agree with the choice of atomic mass as a criterion of the periodicity of chemical properties.

Physical constants: $h = 6.63\times10^{-34}$ J×s, $c = 2.998\times10^{8}$ m×s^{-1}, 1 eV = $1.6\cdot10^{-19}$ J, $e = 1.6\times10^{-19}$ C.

Problem 2

Mellor et al. explained the big difference in the period of the half-life of racemization in the acidic medium of *d*-Co(EDTA)$^-$ (**A**) $\leftrightarrows$ *l*-Co(EDTA)$^-$ (**B**) ($t_{½}$ = 2 weeks (30ºC) and 170 minutes (100ºC)) by the formation of the intermediate $Co[N_2(CH_2COO)_3CH_2COO]^-$(**A′**) with the cleavage of the Co–O bond.

1. Calculate k_{obs} (s^{-1}) at 100ºC and show that in $r = k_{obs}\cdot[\mathbf{A}]$, [**A**] and k_{obs} depend on pH, considering equilibria **A** $\leftrightarrows$ **A′** (k_1; k_{-1}); **A′**H $\leftrightarrows$ **A′** + H^+ (K_a) and material balance.

In 1962, Busch et al. denied this mechanism, showing that at pH ≤ 2 k_{obs} does not depend on [H^+] and equals to $4.018\cdot10^{-6}$ s^{-1} (100ºC); $3.110\cdot10^{-10}$ s^{-1} (45ºC). They explained this by trigonal twisting in the intramolecular mechanism (Bailar) **A** $\leftrightarrows$ **A′** (k_1; k_{-1}); **A′** → **B** (k_2) with the formation of the trigonal prismatic intermediate **A′**.

2. Calculate E_a and $\Delta H^{\#}$, $\Delta S^{\#}$, $K^{\#} = k_1/k_{-1}$ at 100ºC for **A** $\leftrightarrows$ **A′** (k_1; k_{-1}).

3. Describe the mechanism of **A** $\leftrightarrows$ **A′** → **B** with structural formulas, derive the kinetic equation using the method of stationary approximations.

In alkaline medium, the racemization rate is much higher and depends on the pH. Thus, at 45°C and $C_\mathbf{A}$ = 0.01 mol/L, the rate is described by a second-order reaction equation, which is possible in the case of the mechanism: **A** + OH^- $\leftrightarrows$ **A′**OH^- (k_3; k_{-3}), **A′**OH^- → **B** (k_4) with the formation of monocapped trigonal prism **A′**OH^-.

pH	10.30	11.50	12.26	13.02
r, mol/L·s	$1.08\cdot10^{-6}$	$1.71\cdot10^{-5}$	$9.83\cdot10^{-5}$	$5.65\cdot10^{-4}$

4. Derive the kinetic equation of racemization using the method of stationary approximations, and calculate k_{obs} (L/mol·s).

5. According to the derived equation, calculate the racemization rate at pH = 5 (mol/L·s) and compare it with the experimental $8.50\cdot10^{-10}$ mol/L·s.

As a result, Busch et al came to the conclusion that, at any pH, racemization is described by a two-step mechanism, in which each stage includes two elementary stages, the intermediate is a monocapped trigonal prism, and $k_{obs} = k + k'\,C_{OH^-}$

6. Suggest a mechanism common to any pH, derive the kinetic equation.

7. By calculation using this equation, show that the calculated rate for 45ºC and the experimental one at pH = 5 coincide.

<u>For reference</u>: $\ln\frac{C^0}{C} = kt$; $k = Ae^{-E_a/RT}$; $\ln\frac{k_2}{k_1} = \frac{E_a}{R}(\frac{1}{T_1} - \frac{1}{T_2})$; $E_a - \Delta H^{\#} = nRT$; $\Delta S^{\#} = R(\ln A - \ln T - \ln\frac{k_B}{h} - n)$, where *n* – molecularity of the reaction; *t* – time; $k_B = 1.381\cdot10^{-23}$ J/K; $h = 6.626\cdot10^{-34}$ J·s.

Problem 3

A common fuel for winter heating of country houses in Russia is liquefied bottled gas, usually a mixture of propane and butane.

The owner came home in winter and found that the temperature in the room and outside was - 10°C and lit the burner. The liquid *propane* balloon is outside. The barometer on the wall showed that the atmospheric pressure was 760 mm Hg. The size of the heated room is $20\ \text{m}^2 \times 2.5$ m.

1. Write the thermochemical reaction equation of propane combustion.

2. Estimate the molar heat capacity C_V (J/mol·K) of the air in the room considering that it consists only of nitrogen and oxygen.

3. Determine calorific value q_c of propane (J/g), using appropriate data from the table.

	C_3H_8(l)	C_3H_8(g)	O_2(g)	CO_2(g)	H_2O(l)	H_2O(g)
$\Delta_f H°$(298 K), kJ/mol	- 120.9	- 103.9	—	- 393.5	- 285.8	- 241.8
$S°$(298 K), J/mol·K	195.2	269.9	205.0	213.7	70.0	188.7

4. What amount of propane (g) is required to heat the air in the room to a temperature 20°C? Neglect the change in heat capacity of air with temperature. Do not take into account the thermal conductivity of the walls of the house, heating the walls and other objects. All gases are considered ideal.

5. Calculate the pressure (atm) of the saturated vapor of propane from the table data.

The number of impacts of gas molecules on the unit surface of the vessel wall is expressed by the formula (P – gas pressure, m – mass of molecules)

$$\nu = \frac{P}{\sqrt{2\pi m k_B T}} \qquad (1)$$

Usually the gas from the balloon to the burner is fed through a reducer to reduce the gas flow.

6. What is the *maximum* (theoretically possible, without reducer) intensity I of the supply (g/s) of propane when the gas enters the combustion site through a *wide* pipe, and the molecules that have left the balloon do not return to it. Inner diameter of a vertically standing liquid gas cylinder d = 20 cm.

After reaching the desired temperature in the room, the barometer still showed a pressure of 760 mm Hg.

7. How has the internal energy U of air changed in the volume of the room (J) after reaching the temperature 20°C?

Some data: 1 atm = 101325 Pa, R = 8.314 J/mol·K, $k_B = 1.38 \cdot 10^{-23}$ J/K, a.m.u. = $1.66 \cdot 10^{-27}$ kg.

SECTION II. LIFE SCIENCES AND POLYMERS

Problem 1

Isomeric α-amino or imino acids **A**, **B**, **C**, **D**, and **E** are found in a number of natural peptides revealing antimicrobial activity. Being mostly unstable in a free state, **A** – **E** determine to a large extent the properties of biomolecules, if present as residues in their structure. Thus, **A** and **B** residues are found in aciculitins, antifungal cyclic peptides synthesized by sea sponge *Aciculites orientalis*. The hereunder signals in the ^{1}H-NMR spectrum of aciculitins are attributed to those from H atoms in the **A** and **B** residues (consider that all atoms of the peptide chain are involved in multiplet splitting):

Amino acid residue **A**		Amino acid residue **B**	
Chemical shift, ppm	Multiplicity	Chemical shift, ppm	Multiplicity
1.83	d	1.81	d
6.26	q	5.90	q
9.24	s	9.74	s

1. Analyze the above data and draw a peptide chain fragment showing the amino acid **A** (or **B**) residue in a general form. Indicate, which of the signals in the ^{1}H-NMR spectrum supports the proposed structure.

The compound **C** unstable in a free state contains 47.51 % C and 6.98 % H by mass. It is found as a residue in microcystins, cyclic hepatotoxic heptapeptides produced by cyanobacteria.

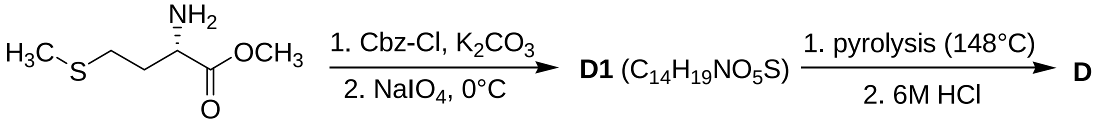
2. Deduce the molecular formula of **C**. Show your calculations.

3. Draw structures of **A** and **B** with stereochemical details. Give all isomers, if any of the structures can exist in a number of isomeric forms.

The integral intensities of the signals in the ^{1}H-NMR spectrum of **C** either coincide or obey the 3:1 ratio.

4. Draw the structure of **C** with stereochemical details.

D is found in many living things can be obtained in to steps starting from methyl ester of *L*-methionine (Cbz-Cl is BnOC(O)Cl):



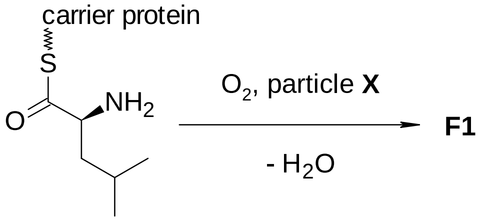
5. Draw the structures of **D1** and **D** with stereochemical details.

E produced by fungi *Rhodophyllus nidorosus.*

6. Draw the structure of **E**.

7. What compound (**A**, **B**, **C**, or **D**) is used in *Rhodophyllus nidorosus* to form **E**, if the process is catalyzed by one enzyme, whereas the substrate does not leave the active site until the transformation into the product is complete? Write down the reaction equation.

Combustion of a sample of **F** in an excess of oxygen followed by condensation of water leads to a mixture of three gaseous (25°C, 1 atm) products with molar masses exceeding 25 g/mol formed in the molar ratio of 12:6:1. The amino acid residue of **F** is synthesized by sea sponge *Dysidea herbacea* via three identical steps (one and the same carbon atom is modified) catalyzed by the same enzyme starting from leucine residue. The first step can presented as:



8. Draw all possible structures of **F** with stereochemical details, if **X** is an unknown particle.

Problem 2

Enzymatic reactions involving reversible transfer of an amino group from a donor to an acceptor play the key role in integration of nitrogen and energy metabolism in organisms. Thus, as a result of a transamination reaction, a canonical α-amino acid **A** transforms into α-keto acid **B** (54.54% O by mass), whereas α-keto acid **C** (41.09% C by mass) into canonical α-amino acid **D** bearing total negative charge at pH 7. The amino group transfer does not lead to a change of the number of carbon atoms in the donor molecule.

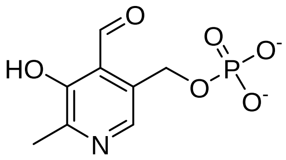
1. Draw structures of **A** – **D**.

Transamination reactions catalyzed by enzymes referred to as transaminases usually follow the so-called "ping-pong" mechanism, which can be described by the hereunder kinetic scheme:

$$\begin{aligned} E + S_1 &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES_1 \xrightarrow{k_2} E' + P_1 \\ E' + S_2 &\xrightarrow{k_3} ES_2 \xrightarrow{k_4} E + P_2 \end{aligned} \qquad (1)$$

E and E' represent the enzyme in its initial and intermediate states, respectively; S_1 and S_2 are substrates; and P_1 and P_2 are the reaction products.

Pyridoxal phosphate (PLP) is the co-factor of transaminases in their initial state. PLP is firmly bound to the protein active site via phosphate group and nitrogen atom making involvement of the latter in the catalysis impossible. It is the amino group of the substrate that interacts with PLP.


PLP

2. Choose the roles (enzyme, amino group acceptor, amino group donor, enzyme-substrate complex) specific to particles ES_1, ES_2, S_1, and S_2 (scheme (1)).

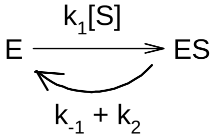
3. Based on the PLP structure, draw the cofactor forms found in particles ES_1, E', and $E'S_2$ (scheme (1)).

Kinetics of complicated enzymatic reactions can be described using the King-Altman method based on the graph theory. Let us consider the approach using the two-step Michaelis-Menten scheme as an example:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2} E + P \qquad (2)$$

a) First one has to draw a directed graph with the vertices corresponding to all the enzyme forms and the directed edges (arrows) reflecting all possible enzyme transformations. An expression of the reaction rate is attributed to each edge; all such expressions do not include the enzyme in any of its forms (E and ES are not written in the example under consideration).

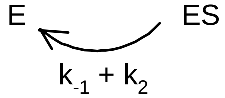
b) ES transformation into E occurs via two parallel routs: as a result of dissociation (k_{-1}) and the product formation (k_2). Parallel transformations are summed up ($k_{-1}+k_2$).



(3)

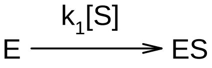
c) Next, one needs to find spanning trees for each vertex of the constructed graph. A tree is defined as a fragment of the initial graph containing all its vertices and a subset of loop-free edges, which allows reaching the target vertex starting from any other one. There is only one spanning tree for each vertex in scheme (2):

Spanning tree of E:



(4)

Spanning tree of ES:



(5)

d) For each spanning tree, expressions attributed to its edges are multiplied giving the product. If a vertex has several spanning trees, the obtained products are summed up. The finally obtained expression referred to as determinant is denoted as w(En), where En is the vertex under consideration. Thus, for scheme (2) $w(E) = k_{-1}+k_2$, $w(ES) = k_1[S]$.

e) The expression of the reaction rate is given as the determinant of the enzyme form leading to the reaction product multiplied by the rate constant of the step leading to the reaction product and the initial enzyme concentration, divided by the sum of determinants of all the enzyme forms:

$$\nu = \frac{k_2 k_1[S][E_0]}{k_{-1} + k_2 + k_1[S]} = \frac{k_2[S][E_0]}{K_M + [S]} \qquad \text{where } K_M = \frac{k_{-1} + k_2}{k_1} \qquad (6)$$

4. Draw the directed graph for the “ping-pong” mechanism.

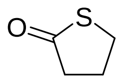
5. Draw all spanning trees for E, ES_1, E', and $E'S_2$.

6. Write down the determinants w(E), w(ES_1), w(E'), and w($E'S_2$).

7. Write down the expression for the rate of P_2 formation.

Problem 3

It is often convenient to use reactive species in the form of their cyclic derivatives which can be regarded as a protective form of the reagent. For example, nucleophilic opening of the thiolactone cycle liberates the SH group for further transformations.



g-thiobutyrolactone

Polypeptide **P** consisting of lysine, cysteine, and valine units (see the structures of canonical α-amino acids at the end of the Section) was converted into polypeptide **P1** via treatment with an excess of γ-thiobutyrolactone. The amount of thiol groups in **P1** was determined by photometry: absorbance of the solution containing 0.0146 mg/mL of **P1** after the treatment with the Ellman’s reagent (see the structure in the Answers Sheet) equals 0.815 (the optical pathway of 1 cm). Molar absorptivity of the reaction product is of 14150 L/mol·cm.

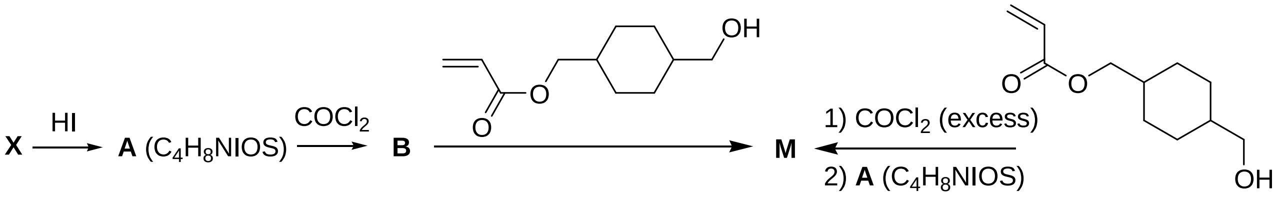
1. Write down equation of the reaction between a thiol RSH and the Ellman’s reagent, encircle the colored product, and calculate the content of the thiol groups in the peptide **P1**.

The amount of thiol groups in the peptide **P** was determined by titration with CH_3HgOD in D_2O. Titration of 10.00 mL of the solution of **P** with the concentration of 0.223 mg/mL requires 16.00 <u>μL</u> of the CH_3HgOD solution with the concentration of 0.150 mol/L.

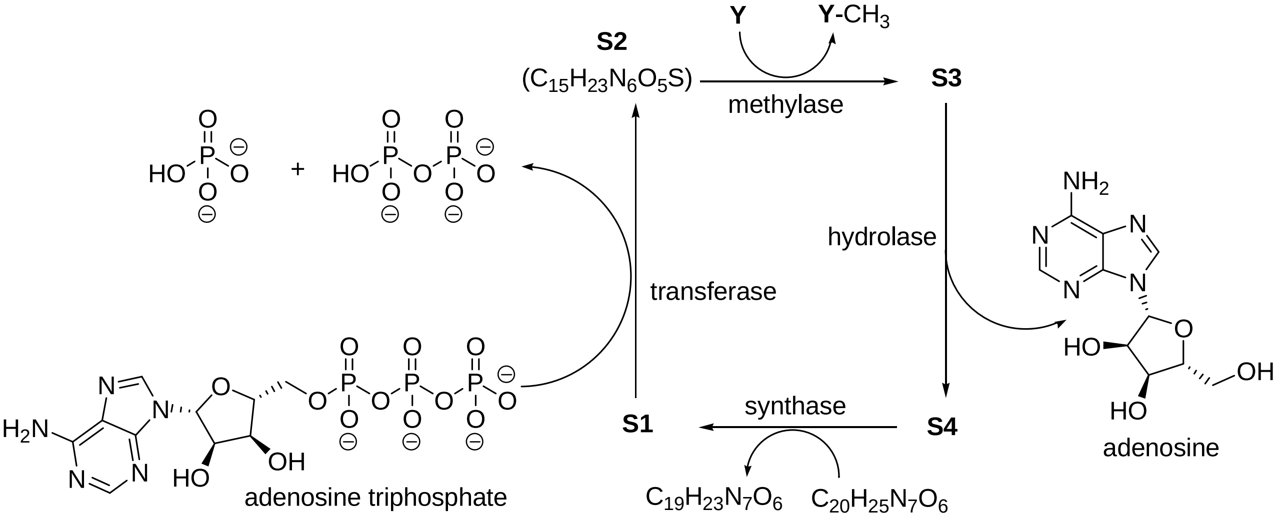
2. Write down equation of the reaction between a thiol RSH and CH_3HgOD; calculate the content of the thiol groups in the peptide **P**.

3. Representing **P** as the tripeptide Lys–Cys–Val, write down (use structural formulae) equation of the **P** to **P1** transformation. Calculate the molar ratio between lysine and cysteine residues in the peptide **P**.

The reaction of ring opening of a thiolactone derivative can be utilized in the synthesis of polymeric products. For example, bifunctional monomer **M** was obtained from a natural compound **X** in two ways:



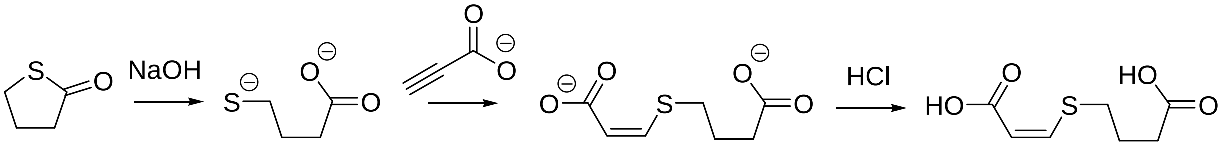
Compound **X** is involved in one of the most important biochemical cycles, resulting in methylation of many substrates denoted as **Y** in the hereunder scheme:



4. Determine the charge of **S2** (note that substrates **S1**, **S3**, and **S4** are neutral species). Determine the structures of **S1** – **S4** (note that **S1** is a zwitter ion in an aqueous solution at pH 7). Select two substrates of **S1** – **S4** that can be encoded by the compound **X**.

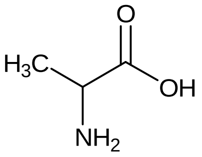
5. Determine the structures of **A**, **B**, and **M**.

Treatment of 0.001 mol of **M** with equivalent amount of propylamine led to the formation of a polymer with the molar mass of 36050, the monomer conversion being 90%. Note that the mechanism of polymerization of **M** is similar to that of the product formation in the hereunder scheme.

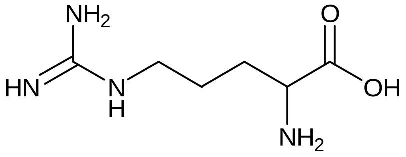


6. Write down the two-step mechanism of the chain growth (propagation) observed upon polymerization of **M** and determine the yield at each of the steps (following the direction corresponding to the chain growth).

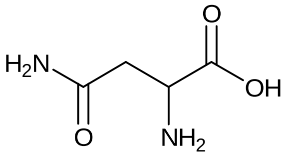
Canonical α-amino acids



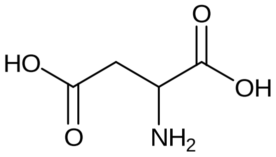
Alanine (Ala)



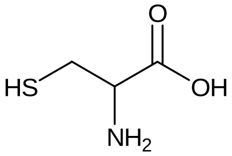
Arginine (Arg)



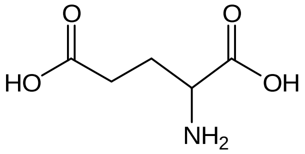
Asparagine (Asn)



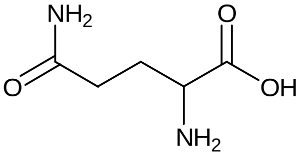
Aspartic acid (Asp)



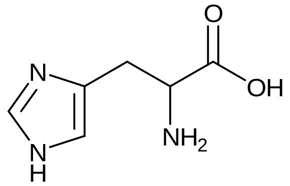
Cysteine (Cys)



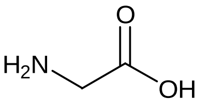
Glutamic acid (Glu)



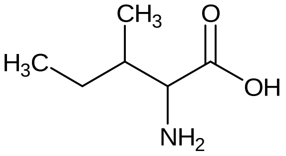
Glutamine (Gln)



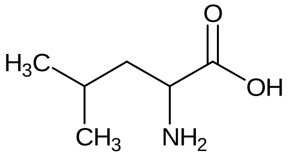
Histidine (His)



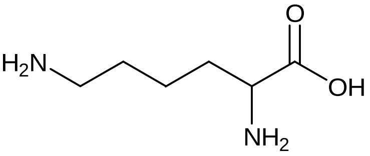
Glycine (Gly)



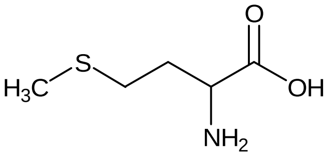
Isoleucine (Ile)



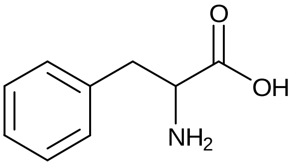
Leucine (Leu)



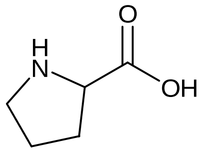
Lysine (Lys)



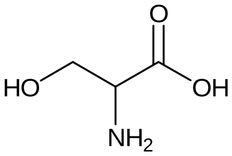
Methionine (Met)



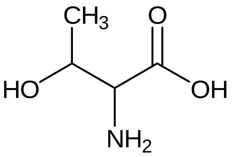
Phenylalanine (Phe)



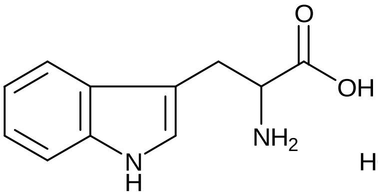
Proline (Pro)



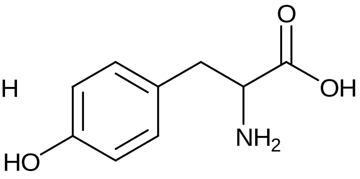
Serine (Ser)



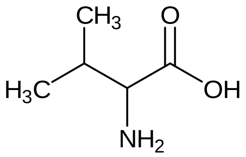
Threonine (Thr)



Tryptophan (Trp)



Tyrosine (Tyr)



Valine (Val)

SECTION III. INORGANIC CHEMISTRY

Problem 1

The generally accepted laboratory method of obtaining the **YNX₃** solution (w_N = 42.42%) is the multistage reduction of HNO_2 with the HSO_3^- solution.

1. Decode **Y**N**X**$_3$ and write the total equation of its synthesis.

YN**X**$_3$ is characterized by the formation of cations (**Z**$^+$) in acidified solutions, although a number of sulfonate derivatives with formation of anions are known.

2. Calculate the content (α, mol.%) of cations in 0.01 mol/L aqueous solution of **Y**N**X**$_3$ (pH=3, $K_B=6.6\cdot10^{-9}$).

Two of the sulfonate derivatives are formed during the synthesis of **Y**N**X**$_3$ in very fast stages, which does not allow them to be isolated from solution. Therefore, sulfonate derivatives are obtained in the form of salts from alkaline solutions. At 0ºC and 1 atm, 22.40 mL of SO_2 and 0.08500 g of KNO_2 are dissolved in 100 mL of 0.01 mol/L KOH solution, and then another 22.40 mL of SO_2 are passed through to form 0.1292 g of salt **A** (48% yield). Careful hydrolysis of **A** gives salt **B**, which has one N–S bond less than in **A**.

3. Establish two possible anions **1** and **2** that could be formed in the solution, if their M differ by 1 g/mol, and **2** has no **Y** – **X** bond. Decode **A** and **B**.

4. Give a complete scheme for the synthesis of **Y**N**X**$_3$, if after the formation of **A** and **B** the solution is treated with HCl (100ºC) until the salt with cation **Z**$^+$ is formed, further treatment of its suspension with NaOBu in butanol gives a precipitate of NaCl and a solution of **Y**N**X**$_3$..

Rubidium salt **E**, which anion does not contain **X** and the bond distances are nearly the same as in **A**, was isolated from the strong alkali solution of **A**. The salt **I** was obtained from the solution of **A**, bearing the anions **1** and **2** at pH~12. The anion of salt **I** has twice as many N–S bonds in comparison with **E**.

Salt	w, wt.%				Bond length, nm			
	N	S	**X**	Rb	N–**Y**	S–**Y**	**Y**–**X**–**Y**	N–S
E	2.80	12.79	1.20		0.143	0.145	—	0.175
I	3.25		0.81	49.57	0.142	0.144	0.241	0.172

5. Decode **E** and **I**.

6. Draw the structural formulas of anions of salts **A**, **B**, **E**, **I**.

Problem 2

Compounds in the groups **A1 – A3** and **C1 – C3** have the same qualitative composition but differ in the quantitative composition; the mass fraction of oxygen is decreased over the **A1 – A3** and **C1 – C3** series. Pale-yellow liquid **A1** is the only product of interaction between oxides **B** (43.98 wt.% O) and **C1** (74.06 wt.% O) taken in the 1:3 molar ratio (reaction 1). The treatment of oxide **B** with a mixture of oxalic and dilute nitric acids at heating yields blue-green crystals of **A2** (reaction 2), but the latter product can be prepared more conveniently via an exchange reaction in a solution (reaction 3). The interaction between elementary compound **D** and **C2** at 0°C in the presence of acetonitrile gives compounds **A3** (dark-red crystals) and **C3** (reaction 4). Heating of **A3** under inert atmosphere gives a mixture of **B** and the products of decomposition of **C1** (reaction 5). A molecule of **A1** has a mirror plane, and the atoms of the elements forming oxides **B** and **C1** are not connected in the structure of **A1**.

1. Determine compounds **A2 – A3**, **B**, **C1 – C3**, **D**. Write the equations of reactions 1 – 5.

2. For compound **A1**, draw a structure of its molecular form and of its two ionic forms differing in the nature of the central atom of the cation and anion.

3. Determine the coordination polyhedron of the central atom in **A1** and its coordination number.

Heating of oxide **B** with $SOCl_2$ gives pale-yellow liquid **E** (reaction 6), the treatment of which with HF affords white powder **F** (45.98 wt.% F) (reaction 7). The interaction of the latter with **G** (a derivative of silane, the only signal in the ^{1}H NMR spectrum is a singlet at 0.22 ppm relative to tetramethylsilane, 24.38 wt.% Si) leads to the formation of compound **A4**, qualitative composition of which is the same as that of **A1 – A3** (reaction 8). **A4** is dark-red powder, decomposing with explosion upon heating to 120°C.

4. Write the equations of reactions 6 – 8, determine compounds **E – G** and **A4**.

Another compound the qualitative composition of which is the same as for compound **A1 – A4**, can hypothetically be obtained via the scheme drawn below (this synthesis has not been succeeded yet because of extreme instability of **A5**):

Compounds **H** and **I** contain fluorine (47.0 and 37.3 wt.%, respectively).

5. Determine compounds **H – J** and **A5**.

Note: qualitative composition of the compounds forming crystal solvates is given without the solvent molecules.

Problem 3

The natural mineral tetrahedrite with composition $Cu_{12}\mathbf{X}_4S_{13}$ is currently a highly efficient thermoelectric material. The brown gas and white precipitate **A** was formed under the decomposition of tetrahedrite by concentrated nitric acid. The filtered precipitate reacts with zinc in hydrochloric acid solution to form gas **B**, which, when passed through a heated glass tube, decomposes to form a metal mirror on the inner surface of the tube. This mirror does not dissolve in alkaline sodium hypochlorite solution.

1. Identify unknown compounds and write the mentioned chemical reactions if it is known that the oxidation state of **X** element in a tetrahedrite is less than in **A**.

The mineral crystallizes in a cubic system with a unit cell parameter of 10.33Å. In single unit cell of a tetrahedrite: twenty-four copper atoms are located on the edges of the unit cell, the same number of copper atoms – on the faces, and the remaining six copper atoms are located inside the unit cell.

2. Calculate the number of formula units in single unit cell of tetrahedrite and indicate the number of sulfur atoms located inside the unit cell, if it is known that all remaining sulfur atoms occupy only the vertices of the unit cell.

3. Calculate the theoretical density of tetrahedrite.

The efficiency of a thermoelectric material is estimated using the dimensionless thermoelectric figure of merit ZT, which is calculated as $ZT = S^2 \cdot T/(\rho \cdot \kappa)$, where S is the Seebeck coefficient of the material, T is the absolute temperature, ρ is the specific electrical resistance of the material, κ is the thermal conductivity of the material. The following values were experimentally obtained for tetrahedrite (see the Table).

T, K	S, V/K	κ, W/m·K	ZT
300	$2.2 \cdot 10^{-4}$	0.5	0.9075
600	$2.5 \cdot 10^{-4}$	1.5	1.25

4. Calculate the tetrahedrite band gap E_g, if it is known that it is related to the specific electrical conductivity (σ) by the Arrhenius equation $\sigma(T) = \sigma_0 \cdot \exp(-E_g/(2k_B \cdot T))$. The Boltzmann constant is taken equal to $8.617 \cdot 10^{-5}$ eV/K.

The thermoelectric efficiency of tetrahedrite is increased by chemical modification. For example, the substitution of copper atoms by iron leads to a fast increase of the thermoelectric figure of merit.

5. Calculate the composition of iron-substituted tetrahedrite, if it is known that copper in tetrahedrite exists in two oxidation states: +1 and +2. The number of copper atoms in +2 oxidation state has decreased by 2 times, and all iron atoms possess +3 oxidation state after substitution.

SECTION IV. ORGANIC CHEMISTRY

Problem 1

For most chemists the definition of aromaticity is in the following phrase:

"In order for a molecule to be aromatic, it must contain at least one planar cycle, each of whose atoms has a p-orbital suitable for the formation of an aromatic system. In this cycle there should be 4n+2 (i.e. 2, 6, 10, 14, 18, 22, etc.) electrons"

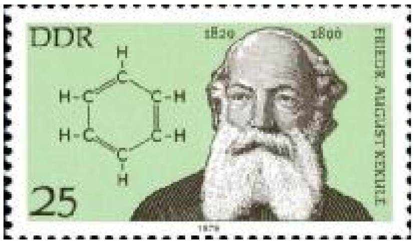


Figure 1 German mark dedicated to the discovery of the benzene molecule

Recently, however, the concept of aromaticity has significantly expanded. It was shown that planar systems formed not only by π- but also by σ-bonds can be aromatic, subject to the Hückel's rule. So, using the expanded definition of aromaticity the following facts can be easily explain:

A. Cation **A** with m/z = 3 is found in significant quantities in interstellar space

B. Laser evaporation of a mixture of Al with Na_2CO_3 leads to formation of a negatively charged **B** ion with m/z = 131, which has fourth-order symmetry axis.

C. Crystal structure of compound $Li_{12}Si_7$ is $(Li_6^{6+}[\mathbf{C}])_2\,(Li_{12}^{10+}[Si_4]^{10-})_2$

D. Crystalline sodium amalgam Na_3Hg_2 contains square planar anion **D**.

E. An anion **E** was detected during the study of the bimetallic Pt–Zn system in catalytic hydrogenation, the mass spectrum of **E** is presented in Fig. 2. It is also known that **E** has 5th order symmetry axis and all hydrogen atoms in it are in the same plane with the platinum atom.

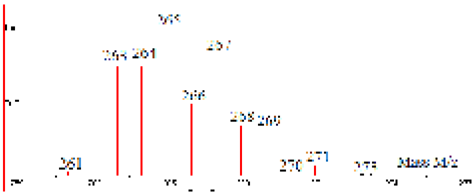
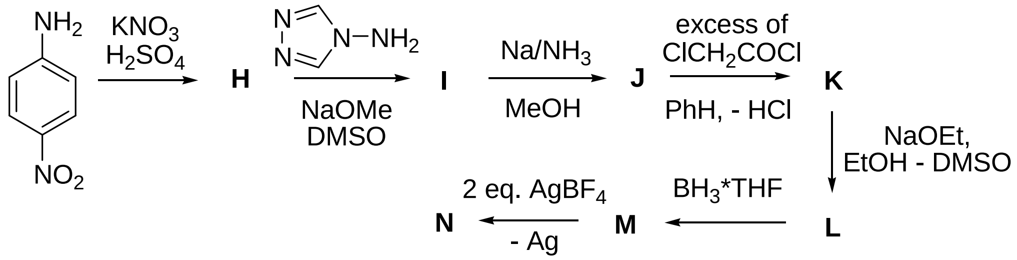


Figure 2 Mass-spectra of **D** anion

1. Give the structure of the particles **A** – **E** and indicate the number of electrons that are involved in the formation of the aromatic system.

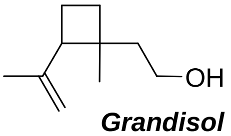
In addition to σ-aromatic compounds, chemists managed to obtain molecules, which structures are stabilized with both π-and σ-aromaticity. The history of this type of compounds began in 1988, when it was discovered that oxidation of an orange crystalline binary compound **F** (containing 8.65% of element **X**) in the H_2O_2 – $(CF_3SO_2)_2O$ – CF_3SO_3H system lead to a blue ionic compound **G** (containing 8.49% of element **X**). The spectral properties of compound **G** confirmed its double aromaticity, but it was not possible to investigate its structure in the crystalline state challenged such hypothesis. In the same year, the structure of the purple crystalline ionic compound **N** was investigated; however, in this case, it turned out that dication **N** was less symmetric than expected. It was possible to unequivocally obtain the compound and prove double aromaticity only in 2018. The synthesis was performed in two stages. In the first stage, the colorless crystalline binary compound **O** (containing 13.07% of element **X**) was treated with an excess of PhSeNa yielding yellow crystals **P**. Treatment of P with two equivalents of $NOSbF_6$ led to the formation of green-blue crystals **Q** (contains 34.07% of element **X**). Their study showed that all Se–Se distances in **P** and **Q** are equal, but their values are 3.38 Å and 3.26 Å, respectively.



Scheme 1. Synthesis of ionic cimpound N.

2. Decode element **X** and compounds **F** – **Q**. It is known that compound **I** has a third-order symmetry axis, compounds **J** and **L** have a sixth-order symmetry axis, and cation **N** – a second-order symmetry axis.

Problem 2



Grandisol

The molecule of grandisol was first isolated in 1967 and it is one of the pheromones of the cotton weevil (*Anthonomus grandis*), a large pest of cotton plants. The cotton industry was seriously affected by the weevil invasion in the 1970s. To combat these insects was used a 4-component mixture, in which Grandisol is the main component. The establishment of the constitution of the grandisol molecule was made by counter synthesis in 1969 and is shown in the figure.

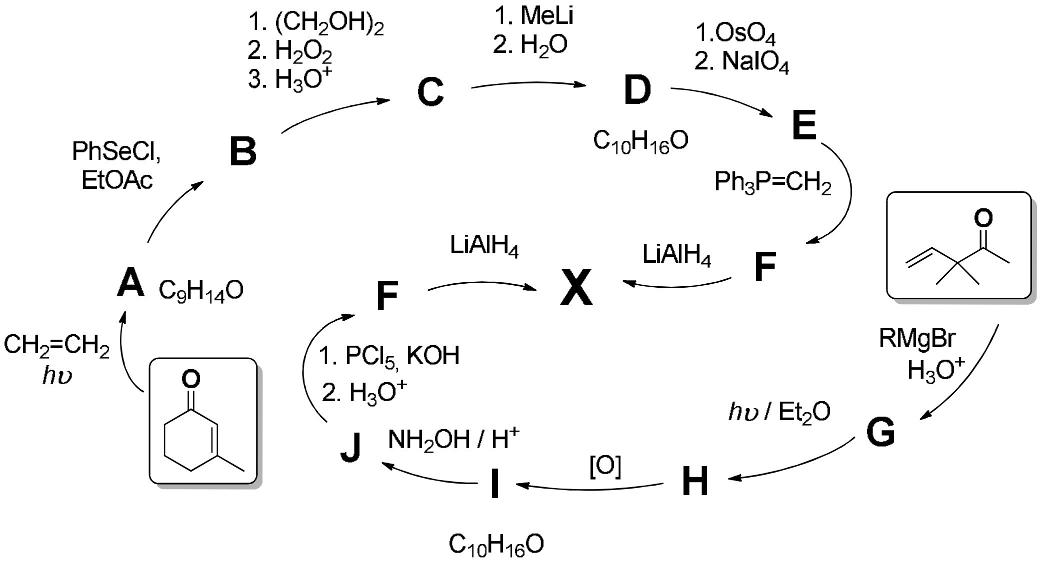
1. ***Give all possible stereoisomers*** of grandisol and define the configurations of stereocenters.

2. ***Give the structures of products*** where grandisol reacts with: 1) Na, 2) mCPBA, 3) NBS, $(PhCO_2)_2$, 4) $CrO_3{\cdot}2Py$. Neglect the stereochemistry of products.

The extraction of Grandisol from insects is a very long and laborious process, which made its synthesis a very attractive alternative. In addition, it was shown that enantioselective synthesis in this case is not at all mandatory, since the racemic diastereomerically pure mixture is sufficiently effective. This fact is explained by the fact that natural pheromone contains *1R, 2S*-gradisol and *1S, 2R*-grandisal (the corresponding aldehyde).

3. ***Give the structures*** of natural grandisol, grandisal and diasteriometrically pure synthetic grandisol **X**.

Currently, 35 different approaches to the synthesis of Grandisol are described. Taking into account the importance of the diastereomeric purity of the product, most strategies are based on the use of condensed cyclobutane derivatives, in which the relative configuration of the two stereocenters was specified. Below are two such examples:

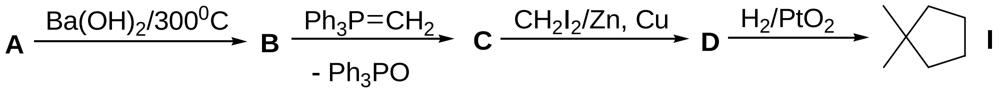


The substances **D** and **I** are isomers of $C_{10}H_{16}O$. NMR spectrum of substance **I**: δ = 0.95 (3H, s), 0.97 (3H, s), 1.00–1.30 (2H, m), 1.31 (3H, s), 1.4–2.0 (3H, m), 2.30 (1H, d, J = 19 Hz), 2.49 (1H, d, J = 19 Hz). In the IR spectrum of **I** there is an intense band at 1760 cm^{-1}. In the NMR spectrum of substance **D**, ***among others***, there are two singlets with an integrated intensity of 3 protons, 2 one-proton signals in the region of 5.8 – 6.0 ppm and one of the signals with an intensity of 1 proton disappears when adding D_2O. In the IR spectrum of compound **D**, an intense band is observed at 3480 cm^{-1}.

4. ***Find*** all unknown compounds **A** – **J** and RMgBr taking into account that RMgBr – has a branched carbon chain

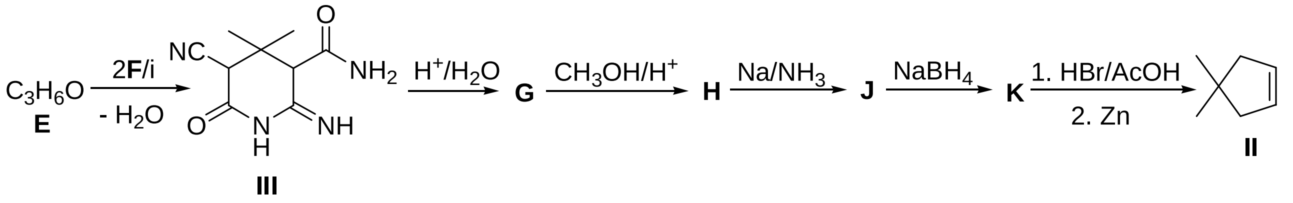
Problem 3

In synthesis of a number of natural polycyclic compounds used in perfumery, medicine, in prediction of oil reserves, an important role belongs to medium-sized cycles containing ***heme***-dimethyl fragment. Synthesis of heme-dimethylcyclopentane **I** is presented in the scheme:

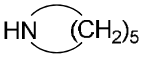


1. What is the structures of compounds **A**, **B**, **C**, **D**, if **A** has the simplest formula $C_xH_{x+y}O_y$, w(H) = 6.85%, **A** is titrated with two equivalents of alkali; **B** and **C** are monocycles; **D** is a spirocycle, its ^1H NMR spectrum has three signals of the same intensity.

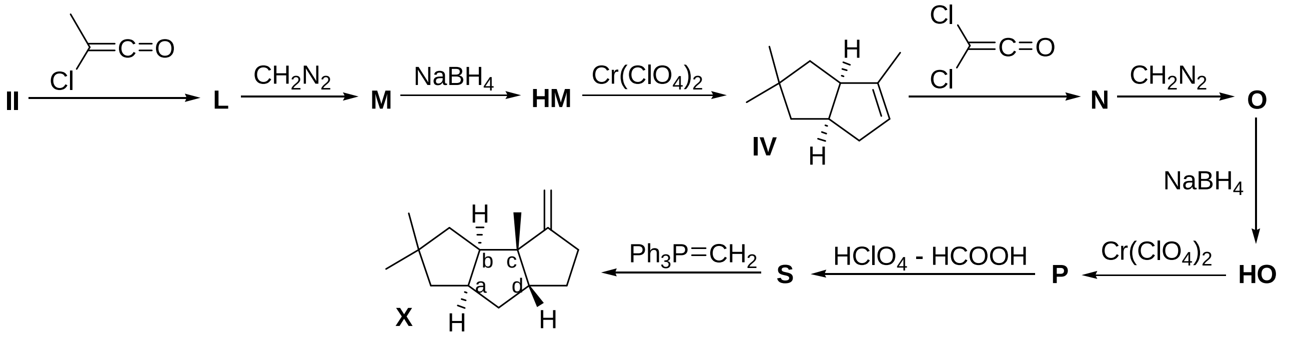
Heme dimethylcycloalkenes are used for cascade polycyclization. The synthesis of 3,3-dimethylcyclopentene (**II**) was carried out in several stages:



2. What is the structures of compounds **E**, **F**, **G**, **H**, **J**, **K**, if **G** is a homologue of **A**, ^{1}H NMR spectrum of **G** has three singlets (3 : 2 : 1); **J** and **K** are cyclic structures.

3. Select a reaction condition **E** + 2**F**: a) t; b) ; c) LiN(*i*-Pr)$_2$.

Synthesis of the natural hirsutene polycycle (**X**), including tandem cyclization, was carried out starting from *heme*-dimethylcyclopentene **II**:



4. What is the structures of compounds **L**, **M**, **HM**, **N**, **O**, **HO**, **P** and **S**, if the stages **L**→**M** and **N**→**O** pass with the extension of the cycle through the formation of unstable zwitterions **L'** and **N'**; there is a band ~ 1750 см$^{-1}$ in the IR spectra of **M**, **N**, **O**, **S**.

5. Propose the structure of intermediate **L'** obtained as a product of the nucleophilic addition of CH_2N_2 to **L**.

6. Determine the reagents from which ketenes were obtained for the reactions: **II**→**L** and **IV**→**N**: 1) $CH_3CHClCOCl$; 2)Cl_3CCOCl; 3) Zn/Cu; 4) $(C_2H_5)_3N$.

7. Specify the configuration of atoms a, b, c, d in hirsutene **X**.

SECTION V. ANALYTICAL CHEMISTRY

Problem 1

The anion of a complex salt **P**, containing trivalent chromium, is used to detect and identify certain amines and drugs based on them. A number of experiments was carried out to confirm the composition of the salt. Nitrogen in salt **P** was determined by two methods.

Method 1. A weighed amount of salt **P** (0.10 g) was placed in a round bottom flask, 40 mL of 5% NaOH added, and the flask was stoppered with a gas outlet tube leading to a receiver containing 50 mL of 2% boric acid. The mixture was distilled for 10 min and the receiver contents was titrated with hydrochloric acid solution using bromocresol green as indicator (pH of the color transition is 3.8–5.4); 14.13 mL of 0.0600 M HCl solution was used for that titration.

Method 2. The ability of ammonium cations to form hexamethylene tetramine with formaldehyde with the release of acid was used. An excess of formaldehyde was added to a weighed amount of salt **P** (0.10 g) and the solution was titrated, during which 5.65 mL of 0.0500 M alkali solution was spent.

1. Write down the equation of reaction occurring when ammonia is absorbed by the solution of boric acid (reaction **1**) and the reaction of titration of the receiver contents with hydrochloric acid (reaction **2**).

2. Write down the ionic form of reaction occurring upon addition of formaldehyde to a solution of salt **P** (reaction **3**).

3. Calculate the amount of nitrogen in the original salt, determined by methods ***1*** and ***2***. What kind of particles contain nitrogen determined by these methods?

4. What is the pH value of the solution (pH < 7, pH > 7, pH = 7) in the equivalence point of titration by method ***2***? Is it possible to apply the indicator used in method ***1*** for visual end point indication?

A weighed amount of salt **P** (0.10 g) was transferred into a conical flask, 10 mL of 0.1 M NaOH solution was added and the solution was heated. On boiling, the complex was destroyed with the release of a gas with a strong odor and formation of a green precipitate. The suspension was cooled and 10 mL of 2 M nitric acid added along with a few drops of a Fe^{3+} solution as indicator. A bright red solution was formed, which was then titrated by Volhard technique with a solution of silver salt until the color turned from red to pale gray-green; 22.6 mL of 0.0500 M $AgNO_3$ solution was used for that titration.

5. What ion was determined by Volhard titration?

6. Based on the above data, calculate the amount of this ion in salt **P**.

To determine the mass loss during heating, a portion of salt **P** (1.000 g) was kept for three hours at 105°C. The losses amounted to 5.085% by weight.

7. Calculate the amount of the component that evaporates while heating salt **P**.

8. Based on the data obtained, derive the formula for salt **P**, if its molecular weight does not exceed 600 g/mol.

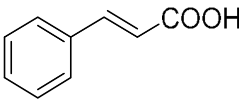
9. Propose the reaction equation of the salt **P** decomposition by alkali with a release of gas and precipitate formation (reaction **4**).

For the synthesis of salt **P**, ammonium thiocyanate is fused under constant stirring and a mixture of ammonium dichromate and thiocyanate is added. After a while, a violent reaction **5** begins, accompanied by the release of ammonia. The reaction mixture is cooled, the product is triturated and treated with cold water. The undissolved precipitate is separated from the mother liquor under vacuum and introduced into water heated to 70°C. The solution is filtered and placed overnight in a refrigerator, where crystals of salt **P** are precipitated from it.

10. Propose the reaction equation of salt **P** synthesis in the melt in molecular form (reaction **5b**). Consider that the main products of thiocyanate oxidation are sulfate and cyanate ions. To simplify the arrangement of the coefficients, write down the reaction in the melt in ionic form (reaction **5a**) with the reduction of dichromate to Cr^{3+} ion.

Problem 2

High-performance liquid chromatography (HPLC) is a powerful technique for separation, quantitative and qualitative analysis of complex mixtures of compounds. By means of this tool some other analytical tasks can be solved, for example, it can be used to determine the dissociation constants of acids in aqueous–organic solvent systems. In this problem you are offered to estimate the pK_a value of ferulic acid (*trans*-4-hydroxy-3-methoxycinnamic acid, HA) in the mixture of 30% CH_3CN – 70% formate buffer (p$K_{a,\ HCOOH}$ = 3.75).



Cinnamic acid

1. Draw the structural formula of ferulic acid and encircle the functional group which is ionizable in formate buffer solutions.

The method is based on the dependence of retention factor *k*, which is calculated using retention times of the retained (t_r) and unretained (t_m) components, on the pH ($\mathrm{pH} = -\lg a_{H^+}$). The retention factor *k* for a weak acid is, in its turn, connected with mole fractions of protonated (χ_{HA}) and deprotonated (χ_{A^-}) forms and corresponding retention factors (k_{HA} and k_{A^-}):

$$k = \frac{t_r - t_m}{t_m} = \chi_{HA} k_{HA} + \chi_{A^-} k_{A^-} .$$

For diluted aqueous solutions the impact of ionic strength and activity coefficients are usually not considered, but for the investigated buffer–acetonitrile system it can be significant. Therefore, the expression for acid dissociation constant should be written as:

$$K_\mathrm{a} = \frac{a_{H^+} a_{A^-}}{a_{HA}} = \frac{a_{H^+} \gamma_{A^-} [A^-]}{[HA]}.$$

2. Get the expression for the dependence of retention factor k from K_a and a_{H^+}.

The activity coefficient γ_{A^-} can be estimated from the Debye–Hückel equation and the expression for ionic strength of a solution I, which takes into account the impact of all ions X_i presented in the solution and their charge z_i: $-\lg\gamma = \dfrac{A\sqrt{I}}{1 + a_0 B\sqrt{I}}$, $I = 0.5\sum z_\mathrm{i}^2 [X_\mathrm{i}]$.

For the investigated mixture of solvents: $A = 0.6476$ M$^{-1/2}$, $a_0B = 1.5918$ M$^{-1/2}$.

In the performed chromatographic experiment three buffer–acetonitrile systems with pH values 3.15, 3.93 and 4.35 were used. The total concentration of HCOONa and HCOOH in these solutions was 0.010 M.

3. Fill in the following table, which describes the composition of analyzed solutions:

№	pH	c_{HCOONa}, M	c_{HCOOH}, M	I, M	γ_{A^-}
1	3.15				
2	3.93				
3	4.35				

The retention time of unretained component t_m (0.01% solution of KBr) was 100.0 s, while the retention times of ferulic acid were 233.3, 229.7 and 223.3 s for solutions **1, 2** and **3**, respectively.

4. Calculate the retention factors k for three investigated solutions.

5. Using the expression obtained in question 2, determine the pK_a of ferulic acid and the retention factors for its protonated and deprotonated forms k_{HA} and k_{A^-}. If you did not get the answer on questions 3 and 4, use the following values for γ_{A^-}: 0.90, 0.85, 0.80 and k: 1.482, 1.350, 1.151 for solutions **1**, **2** and **3**, respectively.

6. What will be the value for pK_a of ferulic acid in aqueous solution in comparison with buffer–acetonitrile system (higher, lower or the same)?

Problem 3

Enology is the study of wine, which includes the investigation of processes taking place under the fermentation of grape juice. One of these processes is the formation of “wine diamonds” – the crystals, consisting mainly of potassium hydrotartrate ($KHC_4H_4O_6$) and formed by storage of wine at low temperatures. The acid dissociation constants of tartaric acid are $9.12 \cdot 10^{-4}$ and $4.26 \cdot 10^{-5}$.

1. Calculate the values of $pK_{a,1}$ and $pK_{a,2}$ for tartaric acid.

2. At what value of pH_{max} the fraction of hydrotartrate ion is the maximum?

3. Sketch a distribution diagram for all the forms of tartaric acid (H_2A, HA^-, A^{2-}) as a function of pH. Show $pK_{a,1}$, $pK_{a,2}$ and pH_{max} on it.

Solubility product of potassium hydrotartrate at 25ºC is $5.00 \cdot 10^{-5}$, but in most cases its solubility is increased due to equilibria between tartaric acid and other ions or organic compounds. The average concentration of potassium ions in wine is 1.0 g/L, total concentration of tartaric acid is 1.4 g/L and the pH of wine is about 3.5.

4. How in theory should the pH of wine be changed when the crystals of wine diamonds are formed due to the cooling of solution, if the pH is lower than pH_{max}? If it is higher than pH_{max}? Specify the equilibria responsible for these effects.

5. What percentage of tartaric acid relative to the total amount is presented in wine in the form of free hydrotartrate anion (HA^-)?

6. What percentage of tartaric acid relative to the total amount does not take part in acid-base equilibria, i.e. is involved in complexes with other ions (not H^+) and organic compounds?

7. What is the pH range for precipitation of potassium hydrotartrate from aqueous solution, containing potassium ions and tartaric acid in the same total concentrations as in wine?