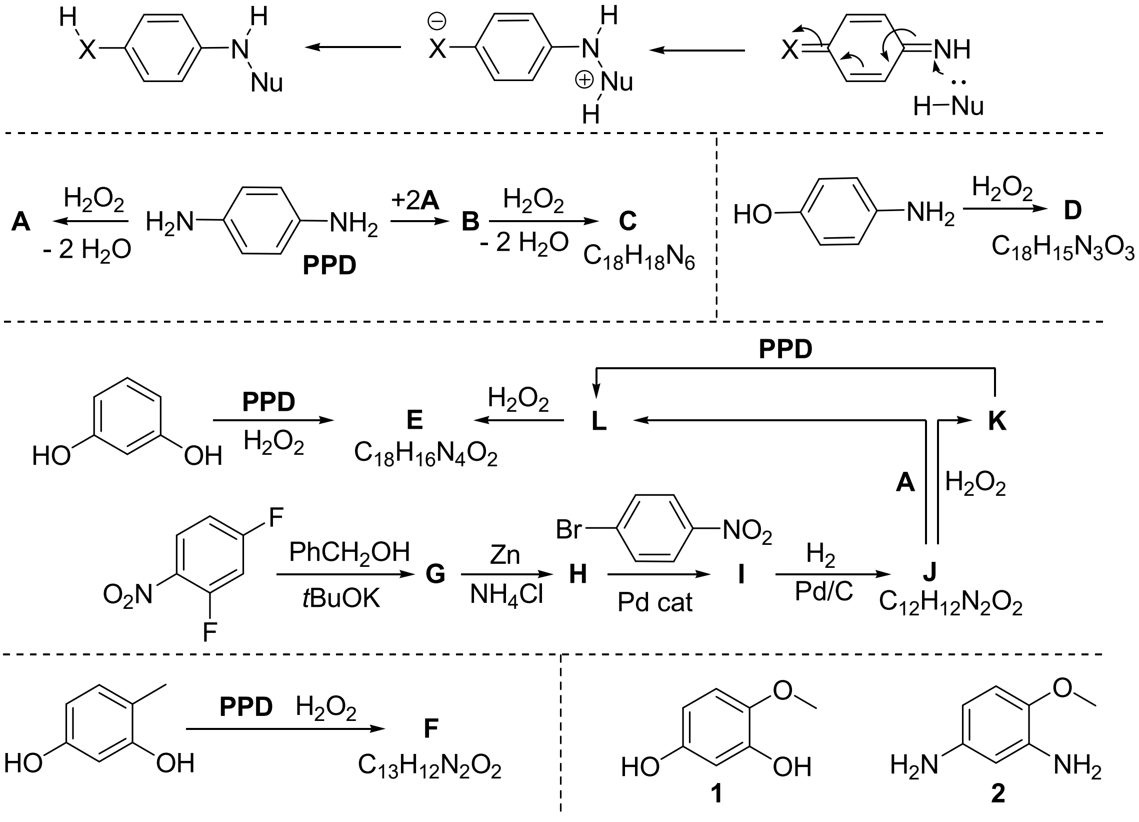
SECTION I. ORGANIC CHEMISTRY

Problem 1

The main components of hair dye are the primary intermediate, coupling agent, the oxidant, and the base for creating the necessary pH. The primary intermediate is typically para-aminoaniline (PPD) or para-aminophenol. The most commonly used oxidizer is H_2O_2 and the base is NH_3. The essential point in dye formation is that during reaction intermediate with iminoquinone structure is formed, which plays the role of N-electrophile. In the absence of a coupling agent, the primary intermediate undergoes homo-coupling. So, PPD reacts with H_2O_2 with the formation of intermediate **A**, the two molecules of which interact with PPD to form **B**, the oxidation of which results in the formation of the Bandrowski's base **C** (has inversion center, the plane of symmetry, and symmetry axis of second-order, and in ^{1}H NMR spectrum exactly two types of exchange protons). If resorcinol is a coupling agent, then **E** is formed. If 4-methylresorcinol is used as the coupling agent, then **F** is formed. In the case of **E**, its formation has been studied from **J**, the synthesis of which is illustrated in the scheme.



1. Draw the structure of compounds **A** – **C**. Draw the structure of **D** – the product of analogous transformations in which para-aminophenol is used instead of **PPD**.

2. Draw the structure of **E** – **L**.

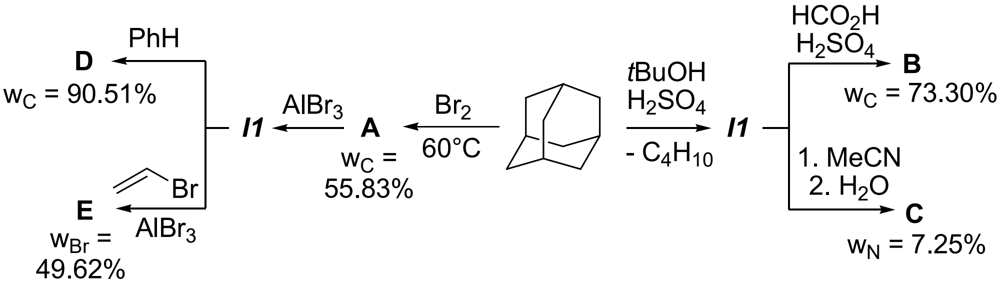
3. Fill the table with the corresponding structures – products of oxidative coupling of compounds **1** and **2** with (para-aminoaniline) **PPD** and para-aminophenol.

4. It is known that in the case of the first primary intermediate (PPD or para-aminophenol), the color of the resultant substances from task 3 was red and yellow, and in the case of the second - yellow and blue. Define the color of each compound.

Problem 2

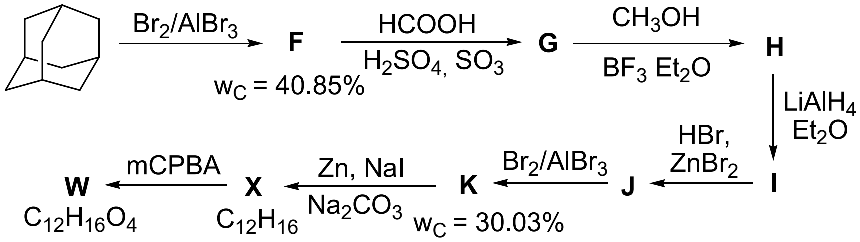
> *"In the first place, symmetry is fascinating to the human mind"*
> *Richard Feynman*

Despite its high stability, adamantane and its derivatives are quite reactive. Thus, adamantane reacts with bromine to form compound **A**. This reaction can proceed *via* formation of intermediate ***I1***. Such intermediate can also be generated from adamantane in the *t*-BuOH – H_2SO_4 system or from **A** by treatment with Lewis acid. It is used to synthesize adamantane derivatives **B** – **E**.



1. Decode compounds **A** – **E** and intermediate ***I1***. It is known that compound **A** has *3*-fold rotational symmetry, and **B** does not undergo alkaline hydrolysis. The mass contents of some elements are shown on the scheme.

In 2014, very interesting monocyclic hydrocarbon **X** was synthesized from adamantane. Its treatment with peracids leads to the formation of a number of stereoisomers of **W**.



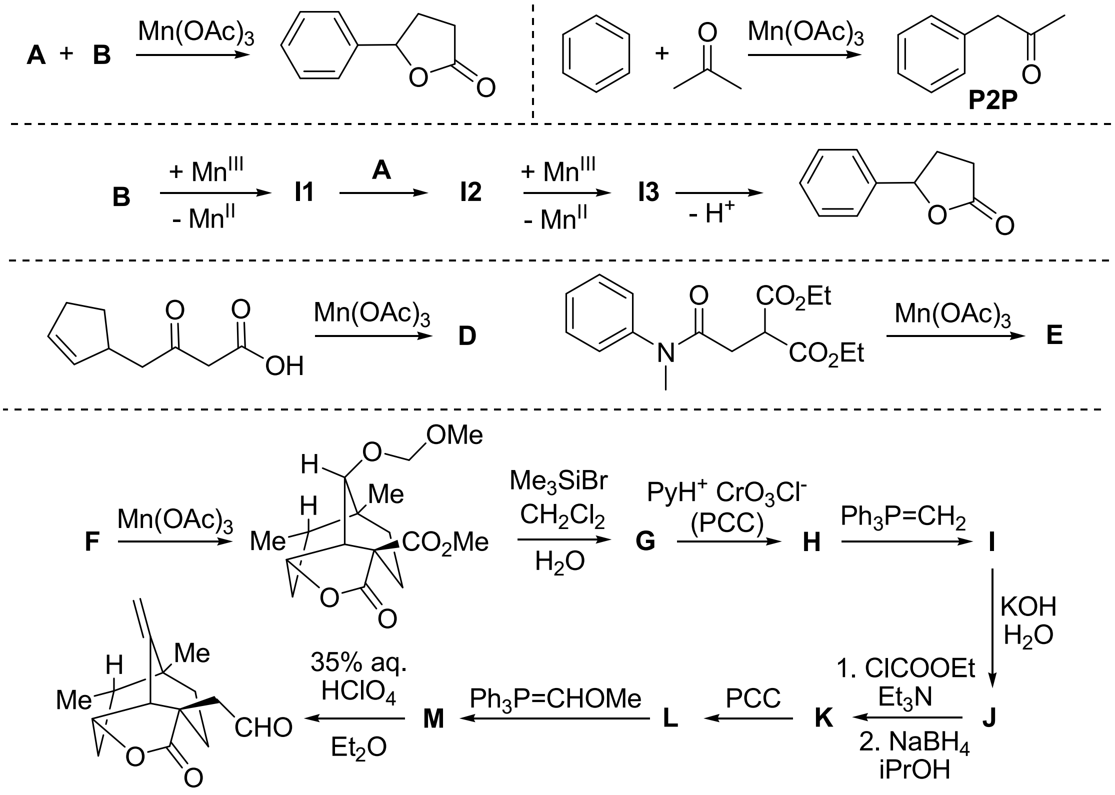
2. Decode compounds **F** – **K**, **X** and **W** if: (i) the symmetry of the molecules **F** and **K** is the same; (ii) the ^{1}H NMR spectrum of compound **X** shows two singlets with an integrated intensity ratio of 1:1; (iii) the ^{13}C NMR spectrum of compound **X** has 3 signals.

3. How many diastereomers are possible for **W** and how many of them are optically active.

Problem 3

> *"Every time, the greatest success is achieved when*
> *it is possible to introduce a new mineral reagent into organic chemistry"*
> *Claude Darzan*

$Mn(OAc)_3$ was introduced into synthetic practice by Bush and Heiba independently in 1968. Its synthetic potential can be demonstrated by the transformations encrypted below. The first transformation has been discovered by Bush and second one discovered by Vinogradov in 1972, which leads to **P2P**. Lactone formation occurs as a double one-electron oxidation through intermediates **I1** – **I3**. Reactions involving $Mn(OAc)_3$ can also occur intramolecularly, it was demonstrated by Corey in 1984 and used in 1989 by Puckett in the synthesis of epimer of the natural product upial.



14-epiupial

1. Decipher **A**, **B** and **C** if known: **A** is a hydrocarbon (w_C = 92.29%, w_H = 7.71%), which, under the action of $KMnO_4/H^+$, forms **C** (w_C = 68.85%, w_H = 4.92%), of the same class as **B**.

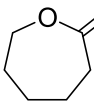
2. Give the structures of intermediates **I1** – **I3** and structures **D** – **M**, taking into account the stereochemistry. **I** contains 68.16% carbon.

SECTION II. LIFE SCIENCES AND POLYMERS

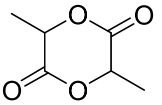
Problem 1

Copolymerization of an equimolar mixture of monomers **M1** and **M2** in the presence of tin(II) octanoate (2-ethylhexanoate) gives either polymer **P1** or polymer **P2** depending on the co-initiator (**I1** or **I2**) used. Certain information about **I1** and **I2** in comparison with **M1** and **M2** is given in the table. All of **M1**, **M2**, **I1**, and **I2** are composed of C, H, and O; all oxygen-containing functional groups in **I1** and **I2** are of the same chemical nature. **I1** and **I2** contain four and two structurally different types of carbon atoms, respectively; difference in their molecular masses is of about 4 g/mol.

number of C atoms	**I1 > M1 = M2 > I2**
number of H atoms	**I1 > I2 > M1 > M2**
molecular mass	**M2 > I2 > I1 > M1**

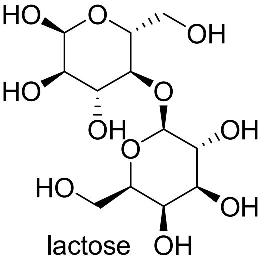


M1



M2

1. How many isomers (including optical) of **M2** do exist? Draw their structures.



lactose

One of the routes to **M2** is via lactic acid fermentation of lactose and dimerization of the lactic acid formed.

2. Write the equation of glucose fermentation to lactic acid (adenosine diphosphate is consumed and adenosine triphosphate is formed in this process). Calculate the mass (g) of **M2**, which can be produced from 1 kg of disaccharide lactose via the above fermentation pathway.

3. Determine the gross formulae and draw the structures of **I1** and **I2**.

Polymerization of **M2** starts with the interaction between **I1** (or **I2**) with tin(II) octanoate. The Sn atom in the product of this interaction is then coordinated to the carbonyl oxygen atom of **M2** and then inserted at its C−O bond, leading to the ring opening. The polymerization mechanism of **M1** is similar.

4. a) How many repeat units are produced via ring-opening of a molecule of each of **M1** and **M2**?

b) Draw the structures of repeat units corresponding to the monomer units of **M1** and **M2** in the structure of the copolymers.

c) Represent the structures of polymers **P1** and **P2** with overall degree of polymerization *n* (degree of polymerization is the number of monomer units in a macromolecule) using $\mathbf{M^1}$ and $\mathbf{M^2}$ to denote the repeat units of the corresponding monomers. Take into account that isolation of the polymers involved after quenching with HCl. Consider reactivities of **M1** and **M2** under the polymerization conditions as equal. *Use one or more of the following symbols in the structure representation: block (block copolymer), ran (random copolymer), alt (alternating copolymer), grad (gradient copolymer), graft (grafted copolymer). For example,* $(M^1_{65}\text{-}graft\text{-}M^3_{100})\text{-}ran\text{-}M^2_{34}$ *means that 100 units of* M^3 *are grafted on units* M^1 *in the random copolymer of* M^1 *and* M^2 *with the units ratio 65:34.*

d) At degree of polymerization $n = 160$, calculate the ratio of integral intensities of ^{1}H NMR signals assignable to the $\mathbf{M^1}$ units, $\mathbf{M^2}$ units, and the initiator residue in the spectrum of **P2**.

e) Draw structurally different dimers (sequences of two repeat units) which can be produced via hydrolytic cleavage of the backbone of **P2**, neglecting the optical isomers.

f) How many dimers are possible if optical isomerism is taken into account?

Problem 2

Polyenes currently obtained from fossil fuel are widely used in the production of pharmaceuticals and polymer synthesis. Metabolic engineering is one of renewable alternatives affording these substances. British researchers used genetically modified bacterium *E. Coli* to produce an acyclic unbranched polyene **A** (M < 115 g/mol). Ozonolysis of **A** in the presence of dimethyl sulfide gives a mixture of three organic products **B** – **D** with the molar masses obeying the following equations: M(**C**) – M(**B**) = *x*; M(**D**) – M(**C**) = *x*, where *x* is a natural number (with atomic masses rounded to integers).

1. Write the equation of isobutene ozonolysis in the presence of dimethyl sulfide.

2. Draw all variants of the structure of **A** in agreement with the above conditions.

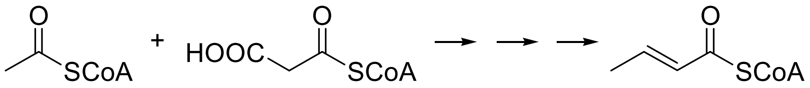
The amount of substance of **B** and **D** formed as a result of ozonolysis are not equal.

3. Deduce the exact structure of **A** clearly showing its spatial details. Note that it does not contain *Z* double bonds.

A is formed in *E. Coli* as a result of a one-step enzymatic transformation from the compound **E**, containing 3 extra atoms of 2 elements as compared to **A**.

4. Propose two variants of the structure of **E** corresponding to two different types of enzymatic reactions leading to **A**. If you failed to deduce the structure of **A** in i. 2, give the structure of **E** leading to any acyclic polyene (be sure to draw this polyene).

E is synthesized via a number of reactions according to the following scheme (only the principal molecules shown, SCoA denotes the residue of co-enzyme A):



(1)

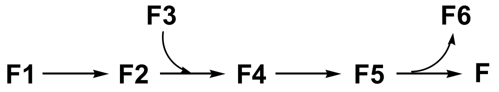
Note that malonyl-CoA can enter the reaction several times.

5. Deduce the exact structure of **E**, if no other molecules but those given in the scheme are needed to synthesize its carbon skeleton. Prove the answer by writing the scheme of biosynthesis of **E**.

Methyl ketone **G** can be produced in *E. Coli* from an acyclic intermediate **G1** ($C_4H_8O_2$, R-isomer; free of C–C π-bonds) in two enzymatic steps with intermediate formation of the compound **G2** (R,R-isomer).

6. Draw **G**, **G1**, and **G2** with stereochemical details

The compound **F** (a homolog of **G**, M < 100 g/mol) is used as a solvent. It belongs to the class of methyl ketones. The *E. Coli* BW25113 strain was used to produce **F**. Note that two of three substances present in the scheme of the synthesis of **E** are intermediates (**F1** and **F3**) of the hereunder metabolic pathway.



Compound	**F1**	**F2**	**F4**	**F5**	**F**
The number of C atoms	*n*	*n*	*n* + 2	*n* – 19	*n* – 20

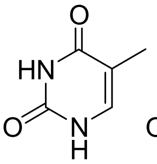
7. Calculate the number of carbon atoms in co-enzyme A, if all the molecules containing C atoms initially present in **F1** and **F3** are given in the scheme (without those forming the co-enzyme A). Calculation obligatory.

8. Decipher **F**, **F1** – **F6**.

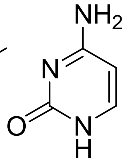
Problem 3

Methylation is kind of DNA modification, having no effect on the duplex formation and the system of hydrogen bonds. It alters gene expression and thus cellular phenotype. This particular process is behind the fact that children born by continuously starving mothers (e.g. those who survived during the Siege of Leningrad) were slim and short statured throughout entire life. Starvation caused abnormal methylation of the gene of insulin like growth factor-2, the key protein in fetation.

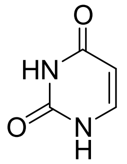
1. On the structures of the major nitrogenous bases show those positions, methylation of which would not alter the DNA duplex.



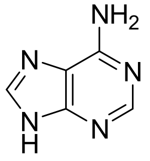
thymine



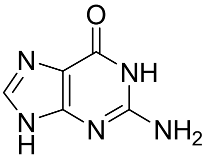
cytosine



uracil



adenine



guanine

Enzymatic methylation of only one major nitrogenous base **X** affording a minor base **Y** plays a key role in gene expression. The numbers of the atoms forming the molecule of **Y** are members of a 4-membered arithmetic progression.

2. Determine the structures of **X** and **Y**. Prove your answer.

In somatic cells, methylation of DNA is typically observed in palindromic dinucleotides 5`-**X-**dRib-p-**Z-**dRib-3` (p is a phosphate group; dRib is a deoxyribose residue, palindrome is a fragment of a double-stranded DNA molecule with both chains having the same sequence from 5'- to 3'-terminus).

3. Calculate the **Y**/**X** ratio inside the fragment of a double-stranded DNA, which had several sequential dinucleotides 5`-**X-**dRib-p-**Z-**dRib-3` prior to methylation, if the molar mass of all the residues of nitrogenous bases in the modified fragment is higher than that in the initial non-modified fragment by factor 1.0203.

4. Give the number of possible variants of this methylated DNA fragment with the lowest molar mass, if the difference of the number of **Y** residues between the chains equals 3. Take that the DNA chains are identical excluding the fragment under consideration.

The reverse biological process of demethylation of **Y** is also of importance. A nucleoside containing nitrogenous base **A** is a key metabolite of the process. Other nitrogenous bases **B**, **C** as well as thymine are also metabolites of demethylation of. Mass fractions of oxygen and nitrogen in **A** – **C** are given in the table.

Nitrogenous base	ω (O), %	ω (N), %
A	22.67	29.78
B	30.94	27.10
C	33.77	19.72

5. Determine the structures of **A** – **C**, if **Y** → **A** is a one-step transition.

6. Based on the structures of **A** – **C**, which major nitrogenous bases can be formed in the process of demethylation of **Y**, if the types of reactions occurring in **Y** → **X** и **Y** → **C** transitions can be combined independently?

Comparison of the data on the genotype of individuals prone to oncological deceases with the profile of their DNA methylation suggests definite correlation. An anti-cancer drug **D**, widely used in the therapy of several types of leucosis, is a close analog (the structures differ in one position only) of a deoxyribonucleoside **E** containing **X**. Administration of **D** leads to suppression of methylation of definite DNA fragments.

7. Determine the structure of **D**, taking into account the mechanism of its action and the fact that the molar masses of **E** and **D** differ by 1.0 g/mol.

Commercial medicines based of **D** cannot be used in clinical practice by ingestion.

8. In the Answer Sheet, tick one correct statement explaining this fact.

SECTION III. ANALYTICAL CHEMISTRY

Problem 1

Hydrazine (N_2H_4) is a weak base which can add one or two protons, forming hydrazinium ($N_2H_5^+$) and hydrazonium ($N_2H_6^{2+}$) ions. The basicity constants (pK_b) of hydrazine are 5.90 and 15.10 for the first and second step, respectively.

1. Give the formulas for the other two simplest bases with the oxidation states of nitrogen –3 and –1 with a difference in molecular weights of 16. Arrange the compounds you proposed and hydrazine by increasing basicity.

2. Calculate the stepwise acidity constants (pK_a) for the $N_2H_6^{2+}$ ion.

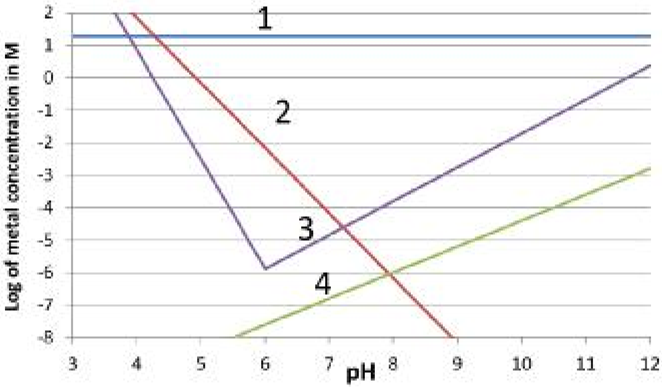
3. Calculate the pH of 0.30M hydrazine solution.

4. Calculate the pH of solutions obtained by adding to the solution from item 3: a) half the volume, b) the same volume, c) twice the volume of 0.30M HCl.

An interesting fact is that the compound $N_2H_6SO_4$ exists in crystal in the form of hydrazonium sulfate ($N_2H_6^{2+}SO_4^{2-}$), while in solution it is almost entirely in the form of hydrazinium hydrosulfate ($N_2H_5^+HSO_4^-$). This compound was obtained by adding 20 mL of 2M H_2SO_4 to a solution of 3.0 g of hydrazinium azide ($N_2H_5^+N_3^-$) in 25 mL of water. During this, $N_2H_6SO_4$ precipitates as a white solid weighing 3.7 g. The acidity constants (pK_a) for H_2SO_4 are: –2.8, 1.99, for HN_3: 4.6.

5. Determine the solubility product (K_{sp}) of $N_2H_6^{2+}SO_4^{2-}{}_{(s)}$, i.e., the equilibrium constant of the process $N_2H_6SO_{4\,(s)} \rightleftarrows N_2H_6^{2+} + SO_4^{2-}$.

Problem 2



The hydroxide ions, present even in pure water, can react with different cations in solution, forming complex ions or precipitations, thus it is very important to control the pH of the solution to avoid undesirable processes (for example, when binding harmful metals in wastewater).

The graph shows 4 dependencies (**1** – **4**) of the maximum possible concentrations of metal ions from the pH of the solution, avoiding the precipitation. One of these curves cannot exist, the other three correspond to the ions Na^+, Cu^{2+} and Al^{3+}.

1. Find the correspondence between the graphs and given ions.

2. In which pH diapason the aluminum hydroxide is not forming while $c(Al_{aq}) = 0.010$M?

3. Find the solubility constant $Cu(OH)_2$ using the graph.

4. Find the solubility of $Fe(OH)_3$ in water, knowing that $K_S(Fe(OH)_3) = 3.8 \cdot 10^{-38}$.

Specie	logK_n	logβ_n
$Pb(OH)^+$		
$Pb(OH)_2$	3.0	10.5
$Pb(OH)_3^-$		

Pb^{2+} ions from next complexes with hydroxide ions: $Pb(OH)_n^{2-n}$, where n = 1 – 3. Stepwise constants (K_n) and cumulative stability constants (β_n) of these complexes are partially given in Table; also it is known that pH of maximal precipitation of $M(OH)_n$ compound corresponds to pH, where the ion concentrations $M(OH)_{n-1}$ and $M(OH)_{n+1}$ in solution are equal, and for $Pb(OH)_2$ this value is pH = 10.75.

5. Complete the table with missing values of constants.

If we take the second cumulative constant β_2, which describe the equilibrium $Pb^{2+} + 2OH^- \rightleftarrows Pb(OH)_2$, it seems that this constant correspond to the reverse value of solubility constant of $Pb(OH)_2$. But, it is not true, as $Pb(OH)_2$ in the first case is aqueous form while in the second case it is the solid. Indeed, these two constants are relating through the own solubility constant K_0 which describes the next process: $Pb(OH)_{2(s)} \rightleftarrows Pb(OH)_{2(aq)}$

6. Find own solubility constant for $Pb(OH)_2$, if $K_S = 5.5\cdot10^{-16}$.

7. Taking into account that lead may exist in the form of metal cation, hydroxide complexes and be in precipitation, calculate the concentration of Pb^{2+} in the solution at pH 11.25 and find whether the lead is completely precipitated (i.e. total concentration of lead in solution $\le 1\cdot10^{-6}$M).

Problem 3

Suppose that in an alternative universe the equilibrium constant for the reaction

$$aA + bB = dD + pP \qquad (1)$$

is written as a function of the sum of concentrations:

$$K = \frac{d[D] + p[P]}{a[A] + b[B]}.$$

1. Compound A at a concentration of $[A]_0$ and compound B at a concentration of $[B]_0$ were mixed. Let equilibrium (1) correspond to the situation when 0.1 mol/L of each of these compounds has reacted (x = 0.1M). All stoichiometric coefficients in equation (1) are equal to unity. Find the relation between the variable concentrations $[A]_0 = m$ and $[B]_0 = n$, if the constant K is always equal to 0.1000 (let x always remain constant).

2. What is the maximum attainable degree of conversion α of compounds A and B by reaction (1) ($\alpha = \frac{x}{m+n}$), if the constant K can take any values?

3. a) Write down the expression for the dissociation constant of HA, an acid of average strength, in the alternative universe (do not show the concentration of water).

b) Write down the expression for calculating the pH of the pure HA solution.

c) Calculate the pH of a 1M acid HA solution if its dissociation constant equals 1.

d) Write down the expression for calculating the pH of a not completely titrated equilibrium mixture formed upon titration of V_1 = 20 mL of 1M acid with 0.5M alkali of volume V_2.

e) Calculate the pH values of the solutions for the volumes of added alkali of 2, 6 and 12 mL.

4. a) Find the first dissociation constant of a weak dibasic acid H_2A if the slope of the linear dependence of the concentration of hydrogen ions $[H^+]$ on the total concentration of the acid $c(H_2A)$ in its solution is $5\cdot10^{-6}$.

b) Find the pH of 1M H_2A solution. Find the pH of 20 mL of the same solution after adding 5 mL of $1\cdot10^{-5}$M NaOH solution.

SECTION IV. PHYSICAL CHEMISTRY

Problem 1

For the nucleophilic substitution reaction $MA_3X + Y \rightarrow MA_3Y + X$, Basolo and Pearson proposed a two-route $[H^+]$-independent S_N2 (lim) mechanism with an observed rate constant $k_{obs} = k_s + k_y[Y]$, where k_s depends only on the nature of the solvent S, and k_y depends on nucleophilic nature. In 1965 Belluco obtained the dependence $k_{obs} = f([NO_2^-])$ for the reaction $[Pt(pip)_2Cl_2] + NO_2^- \rightarrow [Pt(pip)_2Cl(NO_2)] + Cl^-$ (pip – piperidine) at 30°C:

$[NO_2^-]\cdot10^3$, mol/L	1.0	1.5	2.0	3.0
$k_{obs}\cdot10^5$, s^{-1}	1.404	1.506	1.608	1.812

1. Calculate k_s and k_y ($Y{-}NO_2^-$).

2. Calculate the activation energies of the routes, if at 45°C $k_s = 5.00\cdot10^{-5}$ s^{-1}, and $k_y = 6.25\cdot10^{-3}$ $L\cdot mol^{-1}s^{-1}$.

The obtained linear dependence and the k_s value confirmed the proposed two-route mechanism, but it turned out that the increase of $[HNO_2]$, which is present in the solution due to hydrolysis, leads to the appearance of a third route, which corresponds to an electrophilic catalysis by S_N2 (lim) mechanism:

$$[Pt(pip)_2Cl_2S_2] + HNO_2 \rightleftarrows [Pt(pip)_2Cl_2(HNO_2)S] + S \qquad (K)$$

$$[Pt(pip)_2Cl_2(HNO_2)S] + NO_2^- \rightarrow [Pt(pip)_2Cl_2(NO_2^-)]^- + HNO_2 + S \qquad (k_1)$$

$$[Pt(pip)_2Cl_2(NO_2^-)]^- + 2S \rightarrow [Pt(pip)_2Cl(NO_2^-)S_2] + Cl^- \qquad (k_2)$$

The catalysis adds a third term into the $k_{obs} = k_s + k_y[NO_2^-] + k_{cat}[NO_2^-][HNO_2]$. If $[NO_2^-]$ is constant and the same as in $2\cdot10^{-3}$M solution and $[HNO_2]$ is variable, then $k_{obs} = 1.608\cdot10^{-5} + 0.027[HNO_2]$.

3. Calculate $[NO_2^-]$ and pH in the $NaNO_2$ solution ($C^0 = 2\cdot10^{-3}$ mol/L), if the dissociation constant for HNO_2 is $K_a = 5.1\cdot10^{-4}$.

4. Derive a kinetic equation of the catalysis, write down the complete three-term expression for k_{obs}, and calculate k_{cat}.

A more detailed analysis of the kinetics of this reaction in buffer solutions with $C_N = [NO_2^-] + [HNO_2] = 2\cdot10^{-3}$ mol/L shows that linear dependences of Basolo, Pearson and Beluco are satisfied only in alkaline and weakly acidic solutions. If we consider the reaction rate in a wider range of pH, then the dependence $k_{obs} = f([pH])$ is more complex, which you have to establish.

5. Derive the equation for the mole fraction $\alpha(NO^{2-})$ in the buffer solution and get from it a three-term expression for k_{obs}.

6. Calculate k_{obs} at $[H^+]$, mol/L: $1\cdot10^{-6}$; $1\cdot10^{-5}$; $1\cdot10^{-4}$; $4\cdot10^{-4}$; $7\cdot10^{-4}$; $1\cdot10^{-3}$; $3\cdot10^{-3}$ (at pH > 6, $k_{obs} = 1.608\cdot10^{-5}$ s^{-1}).

7. Draw the plot $k_{obs} = f([pH])$ and estimate pH, which corresponds to the maximum rate.

Problem 2

Nickel-based catalysts are widely used in modern chemical industry, for example, in steam reforming of hydrocarbons to produce hydrogen. The reaction mechanism can be roughly assumed to be independent of the catalyst particles shape, and its rate is then determined by the number of surface metal atoms.

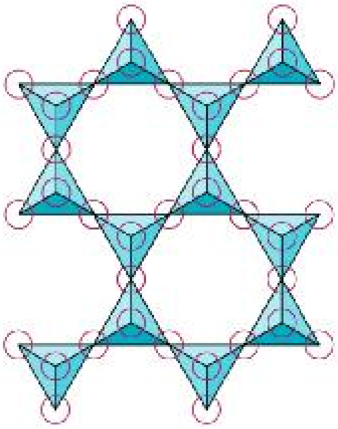
1. Write down the reaction equations reflecting a simplified two-stage mechanism of ethane reforming into hydrogen under the action of water vapor (steam).

2. Determine the ratio of the specific (per 1 g of the catalyst) catalytic activity of the nickel disc (thickness 1 mm), chips (length 1 mm, width 0.1 mm, thickness 0.05 mm), and spherical nanoparticles (diameter 10 nm) in the reaction of hydrocarbons reforming. Nickel density 8.9 g/cm^3.

A drawback of the nanosized catalysts is their particles instability which can be aggregated and fused under conditions of the high-temperature reaction.

3. How much is the Ni nanoparticles catalytic activity decreased due to fusion? Consider that larger spherical particles are formed via fusion of three initial nanoparticles with diameter of 10 nm.

To prevent aggregation of metal nanoparticles, they can be immobilized on a suitable support, which prevents their aggregation even at elevated temperature. One of the possible synthesis consists in mixing of a solution of 2.375 g of $NiCl_2 \cdot 6H_2O$ in 150 mL of water with 40 mL of 0.5 mol/L solution of Na_2SiO_3, hydrothermal treatment of the obtained mixture in excess of NaOH, and annealing of the obtained solid product under reductive atmosphere.



The product formed via hydrothermal treatment is a layered phyllosilicate. The structure of these compounds consists of regular SiO_4 tetrahedrons linked so that silicon atoms form a regular hexagonal planar lattice, and the unshared oxygen atoms are to the same side of this plane.

4. In the phyllosilicate structure in the Answers Sheets select the unit cell (the smallest repeat unit) and determine its composition (gross formula). Calculate specific surface area of the phyllosilicate single-walled nanotube (m^2/g) if the O–O distance in the SiO_4 tetrahedrons is 0.26 nm. Consider sodium ions as the phyllosilicate cations (only in this question!).

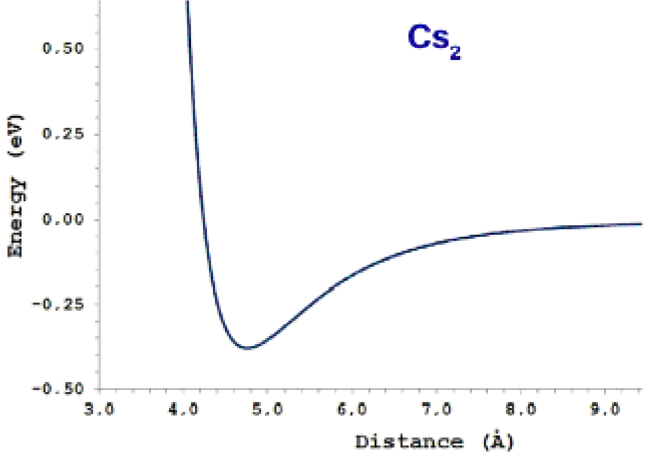
5. Determine the gross formula of the product obtained via the hydrothermal treatment if it consists of four elements, mass fraction of nickel being 46.3%. Write down the overall equation of its formation reaction.

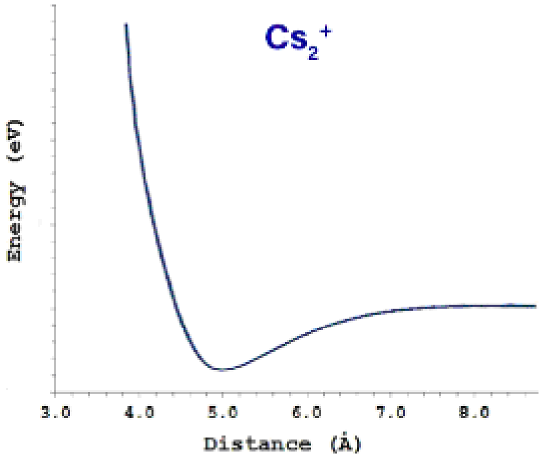
6. The product formed via annealing consists of the phyllosilicate nanotubes (diameter 25 nm, length 300 nm), the surface of which contains semispherical Ni particles (diameter 10 nm). Considering that nickel reduction occurs with conversion 20%, calculate how much the specific catalytic activity of the obtained catalyst differs from that of the spherical Ni nanoparticles of the same size. Take the phyllosilicate density equal to that of nickel and consider that the catalytic activity is owing exclusively to Ni(0).

Problem 3

This year, the Mendeleev Olympiad begins its sixth cycle, as it is associated with cesium (55th element) – the first representative of the 6th period of Mendeleev's periodic system. In the proposed problem you have to solve some questions related to the atomic and molecular forms of cesium.

The potential energy curves for Cs_2 molecule and Cs_2^+ ion are shown on figures below. The energy of infinitely distant cesium atoms is taken as zero.





1. Estimate a) the bond length in Cs_2 and Cs_2^+; b) the binding energy of Cs–Cs in Cs_2.

2. Which average bond length could be expected for the Cs_2 molecule in the vibration excited level with the energy $E = -0.25$ eV?

3. Which radius for Cs^+ ion (Å) is expected: a) 4.2; b) 2.5; c) 2.0; d) 1.7?

График кривой для иона Cs_2^+ не имеет вертикальной шкалы из-за отсутствия The curve plot for Cs_2^+ ion has no vertical scale due to the lack of data, but it is known that the energies corresponding to the minima on the curves for Cs_2 and Cs_2^+ differ by 4.09 eV. In addition, there is data (0 K, kJ/mol) from the Born – Haber cycle (1 eV = 96485 J/mol):

(1)	$Cs(s) + ½F_2(g) = CsF(s)$	$\Delta H_1 = -553.5$
(2)	$Cs(s) = Cs(g)$	$\Delta H_2 = 76.5$
(3)	$Cs(g) = Cs^+(g) + e^-(g)$	$\Delta H_3 = x$
(4)	$F_2(g) = 2F(g)$	$\Delta H_4 = 159.2$
(5)	$F(g) + e^-(g) = F^-(g)$	$\Delta H_5 = -328.2$
(6)	$CsF(s) = Cs^+(g) + F^-(g)$	$\Delta H_6 = 756.9$

4. Make the correspondence between the reactions (1) – (6) and next processes:

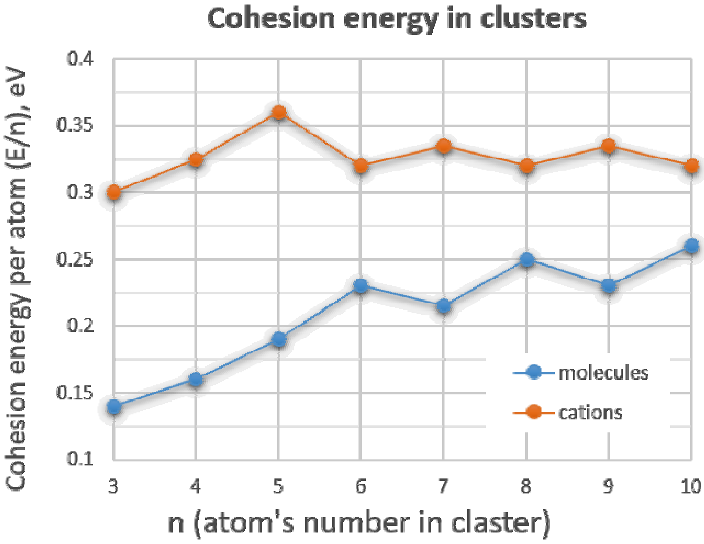
(a) Electron affinity
(b) Sublimation enthalpy
(c) Crystalline lattice energy
(d) Ionization energy
(e) Dissociation energy
(f) Formation enthalpy of compound

5. Calculate a) the ionization energy of Cs and b) the binding energy of Cs–Cs^+ in Cs_2^+.

Cesium forms neutral and charged clusters Cs_n and Cs_n^+, some of which have been investigated (n = 3 – 10). Figure at the right shows the binding energy of atoms in a cluster per particle (*cohesion* energy).

6. Indicate the most stable neutral and charged clusters.

7. Calculate the ionization energy of Cs_{10} cluster.

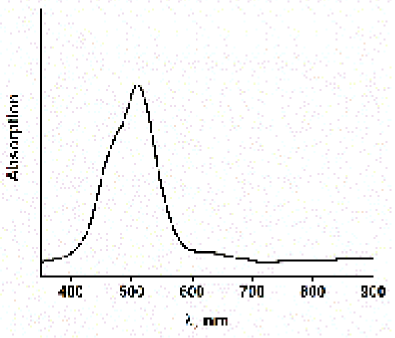


SECTION V. INORGANIC CHEMISTRY

Problem 1

A – transition metal oxide crystallizes in a cubic unit cell with a parameter $a = 8.08$ Å, the number of formula units is Z = 8, and the density is 6.07 g/cm^3. In the crystal structure of this oxide transition metal cations are located at the vertices, on the faces (18 pieces) and inside (14 pieces) of the unit cell, and oxygen anions on the edges (24 pieces), faces (24 pieces) and inside (14 pieces) of the unit cell. Due to high oxidative activity **A** does not occur in nature; however, it can be obtained by burning the sulfide of unknown metal.

When **A** is exposed to an excess of concentrated hydrochloric acid, a yellow-green gas evolves, and the solution turns into a bright blue colour, caused by the formation of a coordination complex ion **B**. A colour of solution containing **B** is changed and a coordination complex ion **C** is formed upon the dilution with water. This process is associated with the replacement of ligands and a change in the coordination of an unknown metal ion. The absorption spectrum of **C** is shown on the figure.



1. Calculate the empirical formula of **A**. What is the structure type of **A**?

2. Determine the colour of the solution containing the coordination complex ion **C**.

When an excess of ammonia solution is added to a solution containing **C**, a coordination complex cation **D** is formed, the molar mass of which is 6 g/mol less than the molar mass of the coordination complex ion **C**. Coordination complex **D** is best obtained in the presence of ammonium salts due to the possibility of a side reaction.

3. Calculate the mass of ammonium chloride which to be added to 100 mL of 0.5M ammonia solution to achieve a pH = 9.5. Neglect the change in solution volume. $K_b(NH_3 \cdot H_2O) = 1.8 \cdot 10^{-5}$.

When air is passed into a solution of **D** chloride and ammonium chloride, a red-pink color appears due to the formation of a coordination compound **E**. If the same reaction is carried out in the presence of activated carbon, then a yellow-orange coordination compound **F** is formed in the solution. The molar masses of **E** and **F** differ by 17 g/mol, and **D** chloride and **F** by 35.5 g/mol.

4. Determine the substances **A** – **F** and write the equations of the described reactions.

It is known that coordination complex **F** is a diamagnetic, and **D** chloride is a paramagnetic with the effective magnetic moment on the transition metal ion being $\mu_{eff} = 3.87$ mB. The magnetic moment is calculated by the formula $\mu_{eff} = 2\sqrt{S(S + 1)}$, where *S* is the total spin of the ion.

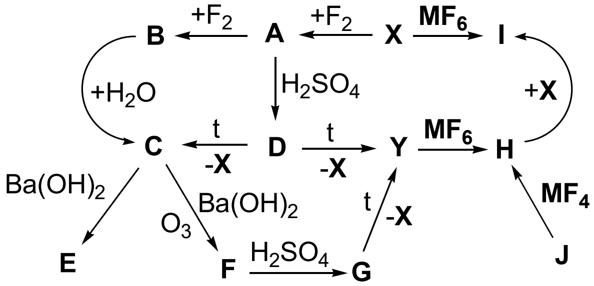
5. The answer sheets contain the splitting of the unknown transition metal's *d*-orbitals in the **D** and **F** coordination complex particles. Draw the distribution of the transition metal's *d*-electrons in these orbitals for each compound.

With the gradual addition of an excess of potassium oxalate and hydrogen peroxide to the solution containing the coordination complex anion **C**, the colour of the solution changes to dark green; the dark green crystals of **G** substance containing 7.56 mass.% of crystallization water can be obtained upon cooling of this solution.

6. Indicate the composition of **G**, and draw all stereoisomers of the coordination complex ion that is part of **G**.

Problem 2

Simple substances **X** and **Y** differ greatly in their chemical properties. The diagram shows the chemical transformations of these substances.



Unstable yellow substance **D** was synthesized in 2011 by the action of concentrated sulfuric acid on binary substance **A**. On heating **D** can decompose: 1) with the formation of simple substances **X** and **Y** or 2) with the formation of **X** and solid colorless substance **C** in an amount one third less than the initial amount **D**. **C** can also be obtained by controlled hydrolysis of substance **B**. The action of barium hydroxide on substance **C** results in the formation of two white precipitates **E** and **F** (the latter is formed in the presence of ozone). Salts **E** and **F** are not hydrates. Based on the same amount of substance **C**, the ratio of the masses of the resulting precipitates m(**E**):m(**F**) is 1.273. Precipitates contain one **X** atom per formula unit and the same spatial structure of the anion. The action of a sulfuric acid solution on precipitate **F** leads to the formation of a white solid **G** of the same qualitative composition as **C** and **D**. Substance **G** is unstable and easily decomposes into simple substances **X** and **Y** and cannot be obtained directly from **C**. In 1962, it was studied the reaction of a simple substance **Y** with a metal fluoride **MF_6**, which leads to the formation of a red salt **H**. The similar reaction of substance **X** with **MF_6** is even more surprising, it leads to the production of several substances, one of which is an orange substance **I** formed by reaction with a stoichiometry of 1:2, but not 1:1 as in the reaction **Y** + **MF_6**. Salt **H** turns into salt **I** under the action of substance **X**. Salt **H** has one signal in the ^{19}F NMR spectrum and can be obtained by the reaction of fluoride **MF_4** and binary gas **J**, taken in equimolar amounts. The mass fraction of one of the elements in **J** is 45.7%. It is also known that the mass fraction of metal in **MF_4** is 1.14 times greater than in **MF_6**.

1. Determine all unknown substances **A** – **G**, **J**, **X**, **Y** and **M**.
2. For salts **H** and **I**, indicate their cations and anions, if the oxidation state of **M** is the same, and the cations have a charge of +1 and contain the same number of atoms.
3. Write down the equations for all the reactions mentioned.
4. Indicate the geometric structure and hybridization of the central atom for substances **A**, **C**, **G** and **J**.

Problem 3

In 1961 there was synthesized mononuclear yellow complex Vaska (**CV**) from green **MeCl*n*** (5.97 g) and excess of PPh_3 (Ph – C_6H_5) (**CV**: 13.1 g; yield 84.0%; $W_{\mathbf{Me}}$ = 24.63%; W_{Cl} = 4.56%; W_P = 7.95%; $\mu = 0\mu_B$; PPh_3 – in trans-positions; IR-spectrum has a band $\nu = 1944\ cm^{-1}$ as for carbonyls). In 1963 Vaska showed that 10^{-2} mol/L solution of **CV** in C_6H_6 reversibly binds O_2 to form **I** at 25ºC ($\mu = 0\mu_B$; in equilibrium yield 70.0%, P_{O2} = 0.171 atm).

1. Calculate $A_{\mathbf{Me}}$(g/mol), decipher **MeCl*n***, **CV** and the reaction for obtaining of **CV**.

2. Write down formula **I** (molar mass **I** more on 4.10% than for **CV**).

3. Calculate the equilibrium constant (atm^{-1}) for O_2 transfer reaction.

O_2 transfer is important for understanding biochemical processes; therefore, a large number of complexes were synthesized, which can be divided into 4 types according to the coordination of the dioxygen with the central atom and according to the form of the dioxygen.

Characteris-tics	Dioxygen form			Type of coordination of O_2 ($\nu_{Me} : \nu_{O2}$)			
	O_2	O_2^-	O_2^{2-}	**1a** (1:1)	**1b** (2:1)	**2a** (1:1)	**2b** (2:1)
$l_{O–O}$, Å	1.21	1.28	1.49	1.25–1.35	1.26–1.36	1.34–1.55	1.44–1.49
ν, cm^{-1} in IR	1555	1145	842	1130–1195	1075–1122	800–932	790–884

4. Using table data draw structures **1a**, **1b**, **2a**, **2b** and indicate the form of dioxygen in them (like dioxygen, peroxide or superoxide).

These complexes can be synthesized by the action of O_2 either on the initial complex or on a mixture of salt and ligand in an organic solvent. Thus, complex **II** ($l_{O–O}$ = 1.52 Å; ν = 825 cm^{-1}) was obtained from the iodide analogue **CV** by the action of O_2. Complex **III** ($l_{Co–Py}$ = 2.02 Å; $l_{O–O}$ = 1.35 Å; $l_{Co–O2}$ = 1.87 Å (1 bond); ν = 1127 cm^{-1}) was produced from an equimolar mixture of N,N′-ethylene-bis(3-t-Bu′-salicylideniminato)cobalt with pyridine (Py) at –18°C by the action of dry O_2. Brown solution of cation **IV** ($l_{O–O}$ = 1.49 Å; $l_{Co–O}$ = 1.88 Å; $\varphi_{Co–O–O}$ = 122°; $\mu = 0\mu_B$; W_{Co} = 36.9%; W_O = 10.0%) was obtained under oxidation of Co^{2+} in ammonia solution by air. On oxidation of this solution by $S_2O_8^{2-}$ green solution of cation **V** ($l_{O–O}$= 1.31 Å; $l_{Co–O}$ = 1.88 Å; $\mu = 1.7\mu_B$; W_i,% as in **IV**) is formed.

5. Decipher structures **II** – **V**, indicate oxidation state of **Me** (central atom charge) and assignment to types **1a**, **1b**, **2a**, **2b**. According to EPR data, cobalt is the same in **V**; the central Co–O groups in **V** are located in trans-, and in **IV** in gosh-positions.