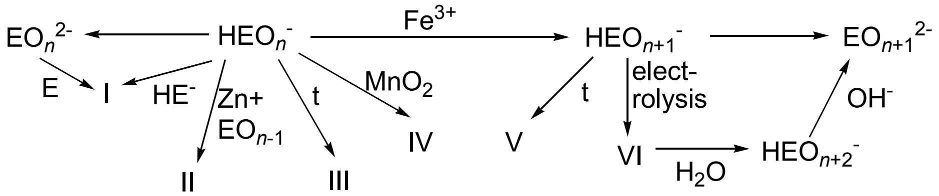
SECTION I. INORGANIC CHEMISTRY

Problem 1

Anion $\mathbf{HEO}_{n}^{-}$ is commonly used in synthesis of different compounds. Thus, one can obtain monomeric and polymeric anions of element **E** from $\mathbf{HEO}_{n}^{-}$ by the scheme:



Polynuclear anions (**I** – **VI**) with general formula $E_mO_{n+i}^{2-}$ ($0 \le i \le 5$) contain element **E** from 33.4 to 57.2% mass., whereby in the row **I** – **IV** ***i*** increases monotonically. There are oxygen containing bridges in the structures of anions **V** and **VI**.

1. Decode **E** and formulae in the scheme.
2. Figure structural formulae **I** – **VI** and $\mathbf{H_2EO_{n+2}}$.
3. Write down ionic reaction equations.

Dissociation constants of polybasic acids usually differ by 5–6 orders. $\mathbf{H_2EO_n}$ has $K_1 = 1.7\cdot10^{-2}$; $K_2 = 6.3\cdot10^{-8}$ and there is an equilibrium $m\mathbf{HEO}_n^- \rightleftharpoons \mathbf{III} + \ldots$ $K = 7.0\cdot10^{-2}$.

4. Denote the reason of small difference $K_1 = 5.0\cdot10^{-1}$ and $K_2 = 3.6\cdot10^{-2}$ between acid and anion **II**.
5. Draw fragment in structure of acids which explains the difference of acid strength: one with anion **VI** is strong by two stages and $\mathbf{H_2EO_{n+2}}$ is strong by the first one ($K_2 = 4.0\cdot10^{-10}$).
6. Calculate particle concentration in 0.1 mol/L solution $\mathbf{H_2EO_n}$ with pH = 3.00.

Fremy used anion $\mathbf{HEO}_n^-$ to obtain salt **D** with unusual N–O bond length. For this purpose, he added KNO_2 to $\mathbf{KHEO_n}$ solution and isolated salt **A.** He oxidized slightly heated solution of **A** by PbO_2 up to formation of hydroxide precipitate and of violet containing paramagnetic anion **B**. By cooling of this solution yellow diamagnetic salt **D** was crystalized. Chemical and XRD analysis of salts is given in the table.

Salt	Containing, % mass.			Bond length, nm (number of bonds)			
	E	N	K	**E–O**	**E–N**	N–O	O–H
A	23.83	5.20	29.03	0.148	0.169	0.132	0.097
D	23.92	5.22	29.14	0.144	0.166	0.128 (2); 0.284 (2)	–
K_2**B**	23.92	5.22	29.14	0.145	0.166	0.129 (1)	–

7. Decode **A, B, D** and write reaction equations of obtaining **A** and **D**.
8. Draw structural formulae **B** and anions in **A** and **D**. Explain different length of σ-bonds N–O in **D** by the localized molecular orbitales method (LMO), considering them two-centered.

Problem 2

The most compounds containing the chemical bond B–H have a high reactivity. However, there are exceptions to this rule. In 1955 on the basis of theoretical calculations it was shown that dodecahydrododecaborate(2–) anion and isoelectronic structures should be high stable. Formally, this anion can be considered a derivative of a non-existent dodecaboran (14). In 1960, the corresponding salt of sodium dodecahydrododecaborate(2–) was first obtained, which really had enviable stability. The matter turned out to be in the spatial structure of an anion having a regular highly symmetric structure. All the boron atoms in it are located at the vertices of the regular polyhedron with 12 vertices (icosahedron), and each of the 20 faces is an equilateral triangle with boron atoms at its vertices. It is believed that the icosahedron of boron atoms and isoelectronic structures have spatial aromaticity and this explains their high stability.

1. Give the formulas and names of three really existing substances, the molecules of which have a spatial framework, which is a polyhedron, in the vertices of which atoms of one chemical element connected by chemical bonds are located.

2. Calculate the multiplicity of each chemical bond in the dodecahydrododecaborate (2–) anion.

The dodecahydododecaborate (2–) anion is not destroyed at 95°C in concentrated aqueous solutions of alkali (NaOH) and acids (HCl). The corresponding acid (A) isolated from the aqueous solution is slightly stronger than sulfuric acid.

3. Calculate the mass fraction of boron in acid A, give your calculations.

To obtain the sodium dodecahydrododecaborate(2–) can be as follows. In the first step, sodium octahydrotriborate(1–) is obtained from sodium tetrahydroborate(1–) and diborane (6). In the second step the pyrolysis of the product at 180 ° C is carried out and the final product is obtained.

4. Draw the structural formula of the anion product of the first step synthesis.

5. Give the reaction equations for the preparation of sodium dodecahydrododecaborate(2–).

If in the dodecahydrododecaborate(2–) anion one boron atom is replaced by a carbon atom without disturbing the three-dimensional aromaticity of the system, a very stable anion (B) is obtained, which made it possible to synthesize one of the most powerful superacids (C) at the present time. To produce it, the anion B (as a cesium salt) is first chlorinated with an excess of SO_2Cl_2 (in argon atmosphere) in a suitable solvent, whereby all hydrogen atoms in the B-H bonds are replaced by chlorine atoms. The obtaining salt can be converted to a superacid (C), called carborane acid, as a result of several additional steps.

6. Give the formula of carborane acid C.

Carborane acid is capable of protonating methane at room temperature. In this case, its solid stable salt is formed with methyl carbocation. When this salt is washed on the filter with cyclohexane at room temperature, the product is contaminated with another solid salt.

7. Give a scheme of the reaction proceeding at hexane washing and explain the structure of the salt, which is formed.

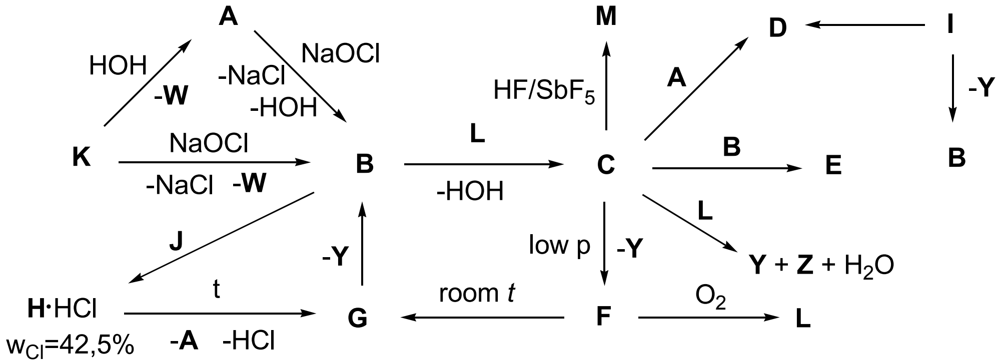
In 2013, the super acid D was obtained even more strongly than carborane.

8. What is the mass fraction of boron in D? Show your calculations.

(The nomenclature of boron compounds with hydrogen includes the designation of the number of boron atoms in the Latin numerals with the addition of *borane* and the addition at the end in parentheses of the Arabic number of hydrogen atoms, for example, B_4H_{10} – tetraborane(10). For anions the number of hydrogen atoms and the number of boron atoms indicate with the addition of *borate* , and the charge of the anion indicates in parentheses at the end.For example, $Ca[B_3H_8]_2$ – octahydrotriborate (1–) of calcium).

Problem 3

Two chemical elements (**X** and **Y**) combine to form different binary compounds, which could be gases, liquids or even solids. Nine of these binary compounds (**A** – **I**) are descripted on this scheme:



The treatment of compound **A** by the solution of sodium hypochlorite (Raschig processes) is used to obtain colorless liquid **B**, which it is not possible to obtain by the direct interaction of simple compounds of **X** and **Y**. This liquid **B** is mostly used as a racket fuel. **B** could be obtained from the white compound **К**: the reaction of 0.72 g of **К** with the excess of sodium hypochlorite solution, gives 0.384 g of liquid **B**. The hydrolysis of the compound **K** produces two gases **A** and **W** (ρ_W=1,964 g/L at the normal conditions). The volatile and caustic liquid **C** was obtained for the first time by the reaction of **B** with the acid **L.** The using of excess of the acid **L** leads to the further oxidation of compound **C** with the formation of equimolar quantities of gases **Y, Z** and water. The compound **C** is a basic when reacts with strong acids (for example the formation of salt **M**) or it is an acid when reacts with the compounds **A** and **B** giving salts **D** and **E** respectively. For synthesis of 0.855 g of the salt **E** by the sequences **B** → **C** → **E**, 0.864 g of compound **B** have to be used taking into account that the yield on two stages is respectively 80% and 95%. By gradual heating at low pressure the unstable compound **F** could be obtained from the liquid **C**. The compound **F** transforms to the yellow gas **G** and reacting with oxygen forms the acid **L** **e**ven at the room temperature. The compound **F** could exist in the singlet and triplet states. The compound **H** was never obtained in a pure state, but it exists as salt **H**·HCl and it is a side product of Raschig processes. The compound **H**·HCl is the only product of the reaction **B+J**. The covalent compound **I** is the derivative of the compound **G**, which exists in different isomeric forms. The heating of **I** leads to the isomerization reaction giving the salt **D**, or to the formation of **B** with emission of one equivalent of gas **Y**. The compounds **К** and **H** are similar structurally.

1. Decipher binary compounds **A** – **I** and also compounds **J** – **M**, **W**, **X** – **Z**.

2. Write the equations of all described reactions.

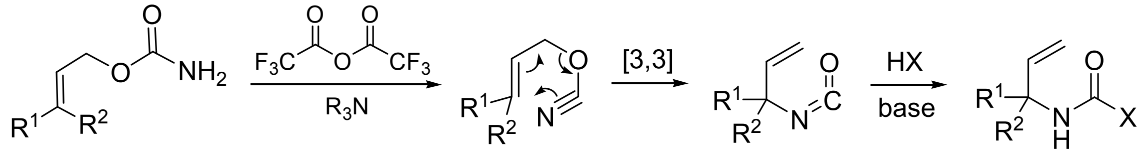
3. Write Lewis structures for singlet and triplet states of compound **F**. Give a particle (molecule or atom) which is isoelectronic to **F**.

4. Why **H**·HCl could be a side product during the Raschig processes? Write down the equation of this chemical reaction.

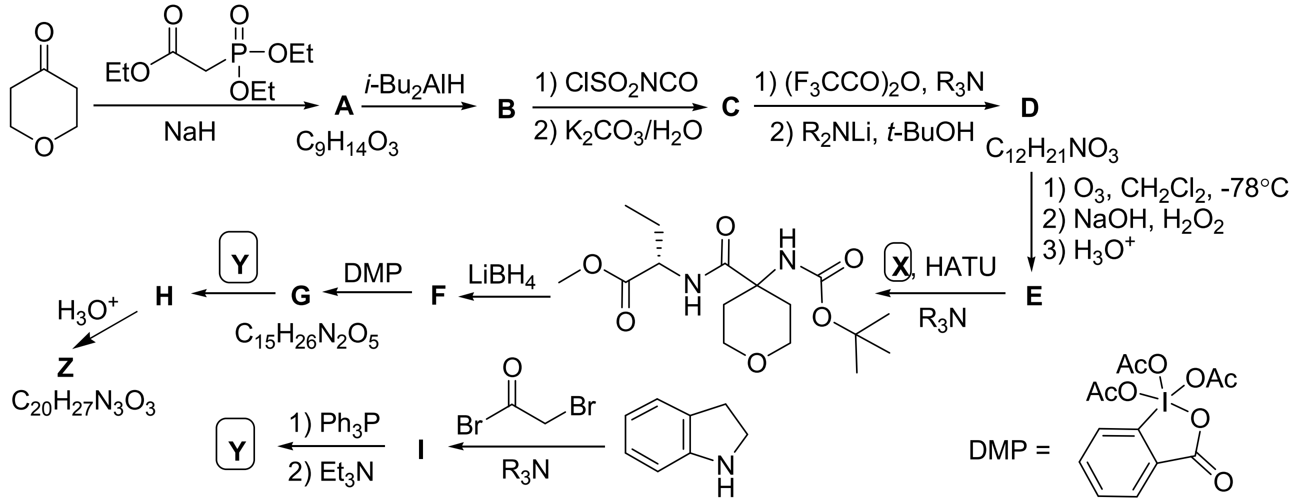
SECTION II. ORGANIC CHEMISTRY

Problem 1

Cyclic α,α-disubstituted-α-amino acids having the increased conformational rigidity and stability to proteases form the important class of unnatural amino acids. One of the most efficient methods for the synthesis of such amino acids based on the use of allyl cyanate to isocyanate rearrangement scheme of which is given below.

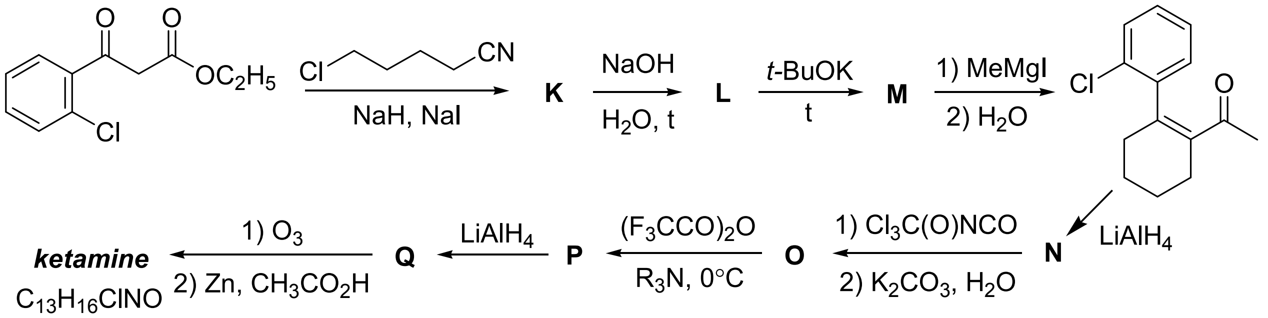


This approach was used, in particularly, for the synthesis of compound **Z** which is efficient inhibitor of the synthesis of *cathepsin C* and, as a result, demonstrates high efficiency in the treatment of bronchiectasis and vasculite (inflammation of blood vessels).



1. Write down structural formulae of compounds **A** – **I**, **X**, **Y** and **Z**, accounting for: a) reagent HATU is widely used for the formation of the peptide bond –CO–NH–, b) Dess-Martin periodinane (DMP) is mild oxidant, c) **Y** could be considered as zwitter-ion.

Allyl cyanate-to-isocyanate rearrangement was also applied in the synthesis of ketamine (Ketalar), medication used for anesthesia in human and animal medicine.

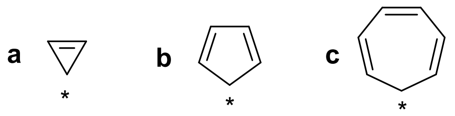


2. Write down structural formulae of ketamine and compounds **K** – **Q**.

Problem 2

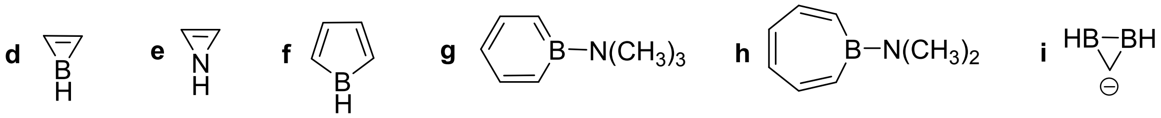
It is known that completely conjugated monocyclic hydrocarbons with the general formula $(CH)_{2m}$ (annulenes) can be divided onto three groups: aromatic (**A**), antiaromatic (**AA**) and non-aromatic (**NA**). Analogous classification can be applied to the cyclic ions with a system of conjugated double bonds.

1. Below some cyclic structures are given. Point out group to which group (**A**, **AA**, **NA**) cations and anions corresponding to these structures belong (change * by the corresponding sign of charge).

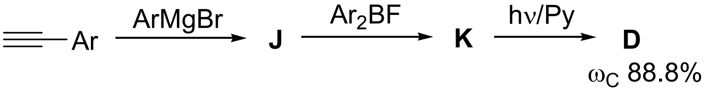


Heteroatoms can also participate in the delocalization of π electrons in the related cyclic structures.

2. Six heterocycles **d** – **i** are given below. Point out aromatic heterocycles, non-aromatic heterocycles, antiaromatic heterocycles. For all heterocycles point out the character of the participation of heteroatom *p* orbital (free orbital or occupied orbital) in the formation of the conjugated electron system (participate or not participate).

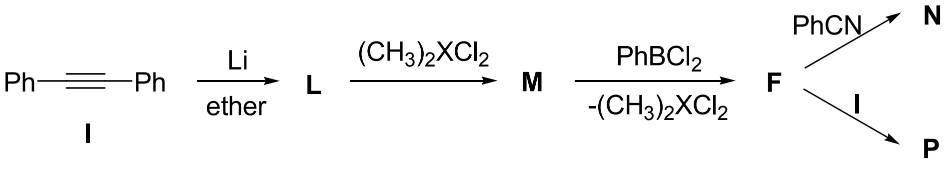


Alkynes are convenient starting compounds for the synthesis of boron-containing ring systems. For example, compound **D** (containing ring **d**) was obtained by the reaction sequence presented in the Scheme below (Ar – 2,4,6-$(CH_3)_3C_6H_2$):



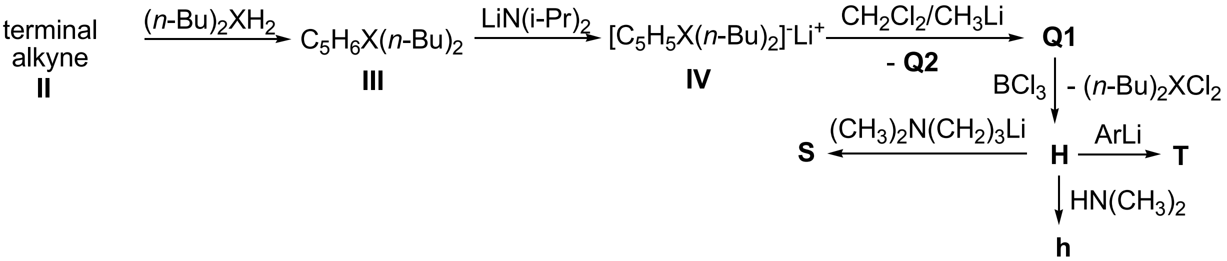
3. Write down structural formulae of compounds **J**, **K**, **D**, if **D** is isomer of **K**.

Compounds containing ring **f** are usually strongly activated Lewis acids. One of them, namely pentaphenyl-substituted compound **F**, was synthesized according to the scheme below.



4. Write down structural formulae of compounds **L** – **N**, **P**, if **L** contains 3.75 weight % of lithium, for compound **M** $\omega_X = 23.50\%$, M(**M**)/M(**F**) = 1.137. Use the exact atomic weights in your calculations. Take into account that compound **F** reacts in one of two reactions as diene, but in another one as Lewis acid.

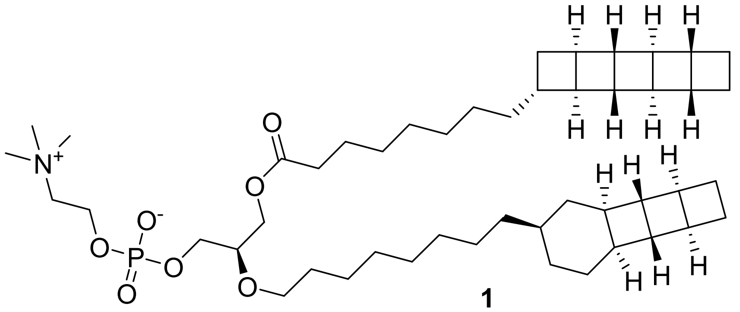
The quite stable compound **H** (containing ring which is present in **h**) was synthesized by reactions given in the scheme below.



5. Write down structural formulae of compounds **II** – **IV**, **Q**, **H**, **T**, **S**, if ^{1}H NMR spectrum of compound **II** consists of two singlets with the relative intensities of 1:1; except **II**, all other compounds are cyclic and have substituents at an heteroatom only; **S** has spiro-conjugated rings; **Q2** is bicyclic isomer of **Q1**, two rings in **Q2** being isoelectronic.

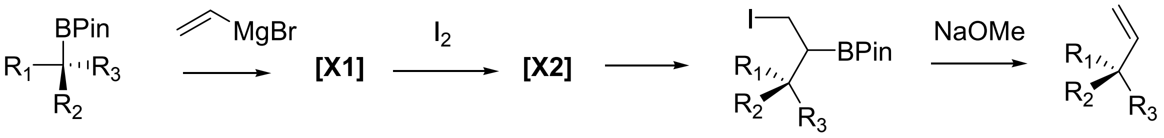
Problem 3

Pentacycloanammoxic acid is component of phospholipid **1** forming membrane of anammoxosome (organelle wherein anammox proceeds). Anammox (ANaerobic AMMonium OXidation) is globally important microbial process of the nitrogen cycle. This process ($NH_4^+ + NO_2^-$ → $N_2 + 2H_2O$) is very slow and includes toxic N_2H_4 and NH_2OH, as well as reactive radicals as intermediates. This is why anammoxosome membrane is formed by so unusual phospholipids that prevent diffusion of these toxic intermediates into the cell. In 2004–2006 Corey and co-workers synthesized pentacycloanammoxic acid in both racemic and optically active forms. However, these syntheses do not provide to prepare this interesting compound in gram quantities. Only in 2016, group from Stanford University developed the preparative method for the synthesis of such compounds including lipid **1**.

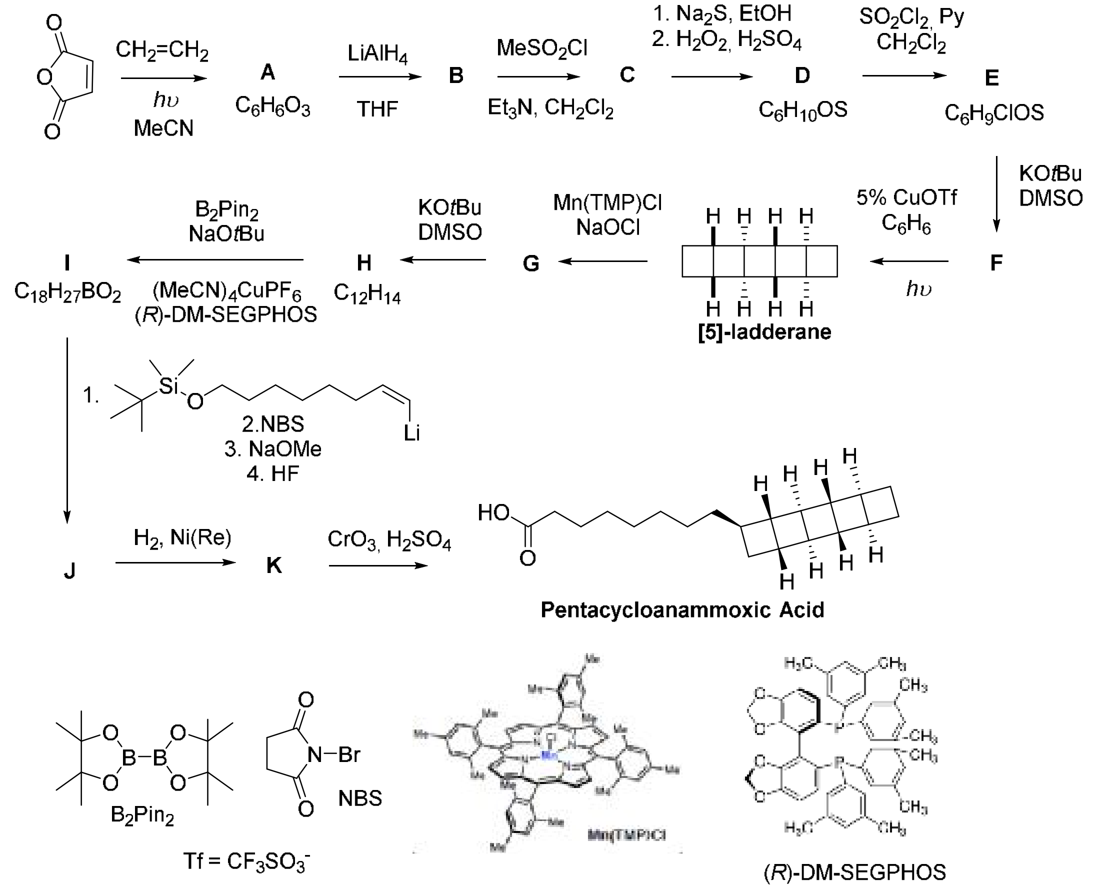


1

The key to the success of this synthesis was the development of multi-gram approach to [5]-ladderane based on dimerization of hydrocarbon **F** (scheme 2). Among further steps it is needed to point out enantioselective hydroboration of hydrocarbon **H** followed by Zweifel coupling (**I**-to-**J** step). The sequence of transformation during this coupling is given in Scheme 1 using a general example of reaction between chiral organoboron compound, vinylmagnesium bromide and iodine.



Scheme 1. Zweifel coupling.



Scheme 2. Synthesis of pentacycloanammoxic acid.

1. Write down structural formulae of compounds **A-K** if it is known that:

– **A, B, C, F** and **H** have plane of symmetry

– compound **D** can exist in two diastereomeric forms; both diastereomers have plane of symmetry

– compound **E** can exist in four diastereomeric forms; all diastereomers are chiral.

2. Propose structures of intermediates **X1** and **X2** as well as mechanism for further transformation of **X2**.

3. Propose evolutionary factor(s) influenced the emerging of this unusual type of ladderane membranes of anammoxosomes in the Nature (point out right answer in the list given).

a) highly reactive intermediates of anammox catalyze biosynthesis of ladderanes;

b) ladderane skeleton allows for formation of ultradense membranes;

c) highly reactive anammox intermediates are starting compounds in ladderanes biosynthesis;

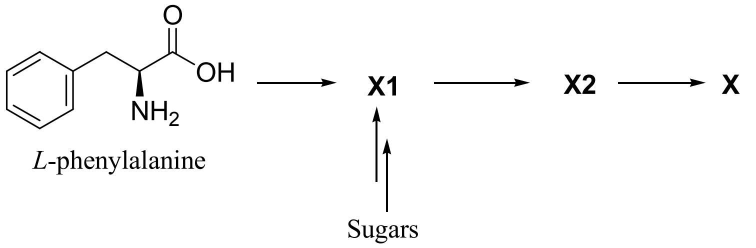
d) ladderane can react with highly reactive intermediates of anammox.

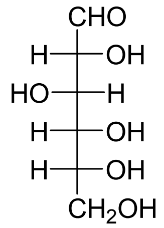
SECTION III. LIFE SCIENCES AND POLYMERS

Problem 1

Wine flavor and properties are mostly predetermined during the yeast fermentation of wine materials. Carbohydrates known to be the major source for ethanol production and thus recognized as the key substances in fermentation are also involved in the formation of glycosides. The latter are molecules in which a sugar residue is bound to another molecule residue (known as aglycone) via a glycosidic bond.

An alcohol **X** (13.10% O by mass) is behind the flavor of vintage wines and cognacs. It can be formed from the amino acid L-phenylalanine via three enzymatic steps (decarboxylation, reduction, and transamination given in an arbitrary order) and from sugars.





D-glucose

In wines **X** exists in the form of its glycoside with *D*-glucose.

1. Draw the Haworth projection of *D*-glucopyranoside of **X**. Use R- for the aglycone.

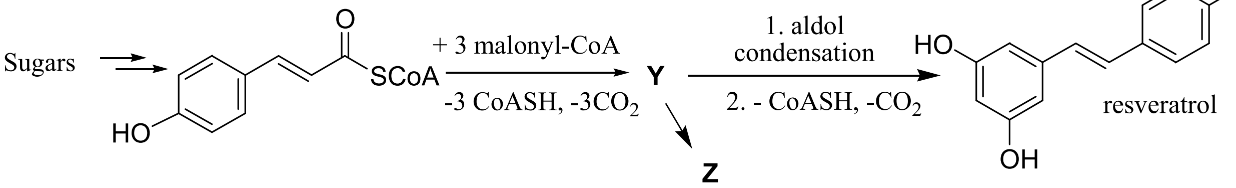
Usually glycosides are easily hydrolyzed by acids, but not by alkalis. However, under aqueous alkali treatment *D*-glucoside of **X** affords the aglycone and an extremely stable substance **X0** with the molecular formula coinciding with the empirical one of starch.

2. Draw the most stable chair conformer of **X0**.

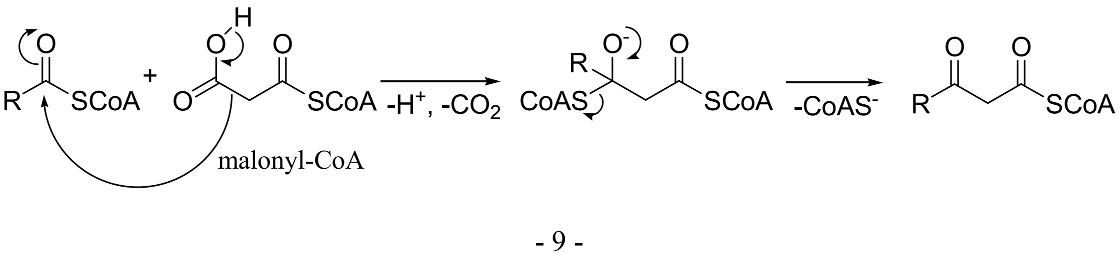
3. Deduce the composition and draw the structures of **X**, **X1**, and **X2**, if all of these contain oxygen, whereas phenylalanine is the only chiral compound in the reaction sequence.

Flavonoid aglycones such as resveratrol are assumed to possess antioxidant and cancer preventative properties. Such aglycones are also formed from sugars:

CoASH - coenzyme A



Malonyl-CoA is a typical two-carbon source in biosynthesis:



4. Draw the structure of **Y**.

5. Propose the structure of **Z** if it contains three six-membered rings formed as a result of Claisen condensation of **Y** followed by intramolecular Michael addition.

6. How many *D*-glucopyranosides of resveratrol are possible?

Excessive content of ketose **A** in the wine material may adversely affect the flavor of the beverage. **A** formation during the fermentation of grape juice occurs in a single enzymatic step from metabolite **B**. The reaction is carried out by *Acetobacteraceae* bacteria, which gets energy from a two-step oxidation of ethanol to acetic acid with acetaldehyde as an intermediate.

7. Deduce and draw the structures of **A** and **B**, if their hydrogen mass content differs by 2.05%.

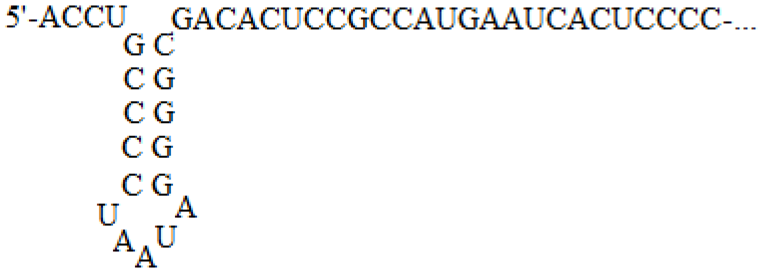
8. **A** exists as a cyclic dimer in the crystalline state. Draw the structure of this dimer.

Problem 2

MicroRNA are small non-coding RNA molecules composed of 18-25 nucleotide residues and found in plants, animals and some viruses. miR-122 is the prevailing microRNA in liver cells. There it regulates energy production and lipid metabolism as well as facilitates replication of hepatitis C (HCV) virus, which negatively influences the disease prognosis. The nucleotide sequence of miR-122 is:

5'-UGGAGUGUGACAAUGGUGUUUGU-3'

Two miR-122 molecules must interact with the hereunder fragment of the viral genome to potentiate the HCV amplification. It was discovered that one of these miR-122 molecules forms 10 nucleotide pairs (3 sequential pairs at the first site and 7 sequential pairs at the second site, that is 3+7), whereas the second one forms 9 pairs (3+6).



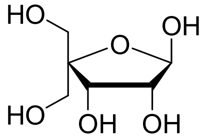
1. Determine the direction of the miR-122 chains attached to the HCV RNA fragment.

2. In the Answer Sheet, underline the nucleotides in the miR-122 molecules involved in coupling with the HCV RNA fragment. Note that RNA molecules can form loops bringing together nucleotides that are far apart in the primary structure (for instance, see the above fragment of the HCV genome).

Miravirsen is an experimental drug for the treatment of viral hepatitis C. The substance blocks the HCV replication by binding with miR-122. Miravirsen is composed of 15 nucleotide residues linked to each other by phosphodiester bonds between 3' and 5' C atoms. If counted from one of the molecule ends, 2'-deoxythymidines are found at the 3rd, 9th, 11th and 12th positions. All the 15 nucleotide residues of miravirsen consecutively (without loops and omissions) bind to a fragment of miR-122.

3. Draw a single strain DNA, which, being a miravirsen analog, binds with exactly the same RNA fragment of miR-122 as the drug does.

Beside 2'-deoxynucleotide residues, miravirsen contains locked nucleotides (LNA). The ribose moiety and phosphate residues of the latter are modified as compared to their natural analogs. Thus, the compound **Z** with the molecular formula of $C_{11}H_{14}N_5O_6SP$ contains 4 cycles. Being an adenosine-5'-monophosphate analog, **Z** belongs to the LNA class. Derivatives of the hereunder substance play the key role in the laboratory synthesis of **Z**:

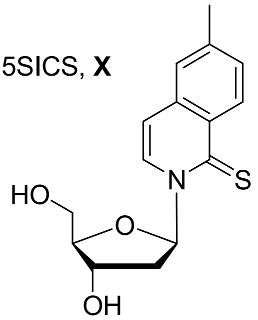


4. Deduce the structure of **Z**. Note that **Z**-based RNA is much more resistant towards hydrolysis than a natural one.

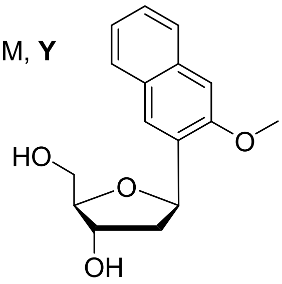
5. Indicate which method of miravirsen administration is <u>least</u> favorable.

A DNA duplex can also be modified. In 2014, researchers from University of California, San Diego have designed the first living thing (originating from *E.coli*) with 6 nitrogenous bases. A synthetic **X-Y** pair supplemented two conventional A–T and G–C ones.

d5SICS, **X**



dNaM, **Y**



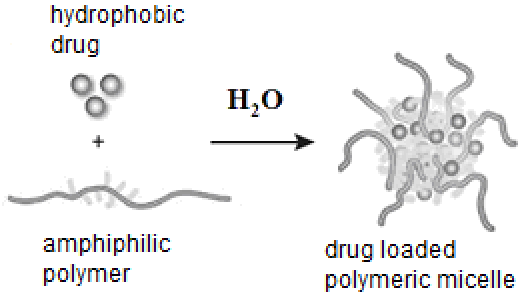
6. How many hydrogen bonds do exist in the complementary **X-Y** pair within the duplex of the semi-synthetic DNA?

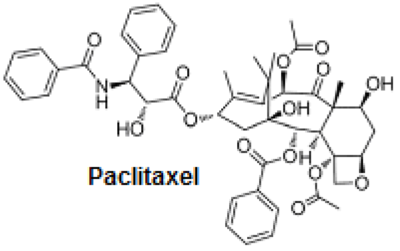
In 2016, the researchers introduced changes in the nucleotides transporter and obtained a colony of semi-synthetic bacteria containing **X–Y** pair, which underwent replication with high accuracy, was presumed and inherited. The improvements became possible due to introduction of a diatom *Phaeodactylum tricornutum* gene into *E.coli* genome. The gene encodes the NTT protein, which is very efficient in transporting **X** and **Y** containing nucleotides from nutrient medium into the cell.

7. Deduce the structure of the substance **W** (15.00% P and 31.01% O by mass), which, being an **X** metabolite, was added to the nutrient medium and then efficiently transported by the NTT protein inside *E.coli*.

Problem 3

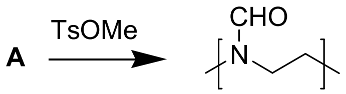
State-of-art chemistry allows designing drugs highly efficient at both molecular and cellular level. However, lack of target delivery of biologically active molecules often hinders the resulting effect. Thus, many promising drugs are poorly soluble in water, which makes attaining therapeutical concentrations (i.e., IC_{50}) in body impossible. For instance, the solubility of an anti-cancer remedy *Paclitaxel* (M = 854 g/mole) in water is as low as 6.7 mg/L. Use of amphiphilic polymers capable of small (up to 50 nm) micelles formation is one of the options. Polymers with high drug-loading capacity LC = 45%. ($LC = m_{drug}/(m_{drug} + m_{polymer})\cdot 100\%$, where m_{drug} and $m_{polymer}$ are the drug and polymer masses in the solution, respectively) have been recently developed (see the hereunder scheme):

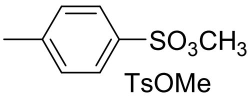




Paclitaxel

The polymer shown in the scheme was obtained by co-polymerization of heterocyclic compounds **A1** – **A3** belonging to one and the same class. These compounds can be prepared by the interaction of corresponding nitriles (R–CN, R^1 = Me, R^2 = *n*-Bu, R^3 = CH_2Ph) with $H_2N–CH_2CH_2–OH$ mediated by $Cd(CH_3COO)_2·2H_2O$. The structure of the parent polymer obtained from the simplest heterocyclic monomer (**A**) of the class (end groups omitted) is shown hereunder:

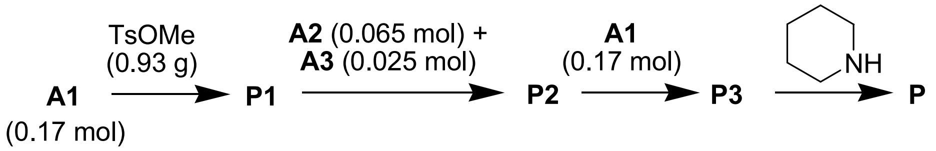


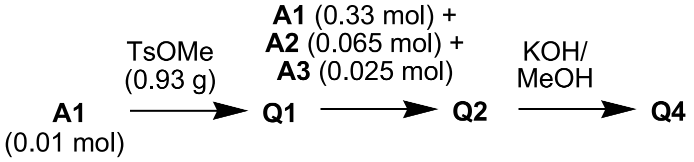


TsOMe

1. Draw the structures of **A**, **A1** – **A3**.

Cationic polymerization of monomers of **A** class proceeds via «living chains» mechanism, i.e. active centers are infinitely long retained in the system when the entire monomer is consumed, whereas addition of new portions of monomer(s) re-initializes the polymerization process. Co-polymers **P** and **Q** were obtained according to the hereunder scheme (all polymerization steps were conducted till complete consumption of corresponding monomer(s)).





2. Draw the structures of co-polymers **P** and **Q**, clearly showing the degree of polymerization and terminal groups.

3. Draw the reactive intermediate formed upon **A** interaction with TsOMe. Use the intermediate structure to demonstrate the mechanism of the cationic polymerization. Note that the reactive intermediate exists in solution in two equilibrium forms (cyclic and acyclic).

4. Calculate the molar ratio of **P** and *Paclitaxel* in the micelle.

5. Calculate the *Paclitaxel* solubility in water in the presence of **P** if it is known that the saturated micellar solution achieves IC_{50} = 0.37 nmol/L (for cancer cell lines PC3) at $17.7 \cdot 10^6$ dilution.

6. Calculate the increase factor of *Paclitaxel* solubility in water when **P** is present in the system.

7. Critical micelle concentration (concentration of a polymer above which micelles form) of **P** is of 4.4 μmol/L. Estimate the standard free Gibbs energy of micelle formation for 1 mole of **P**.

SECTION IV. ANALYTICAL CHEMISTRY

Problem 1

To determine the concentration of bismuth, 25.0 mL of an acidified Bi^{3+} solution were mixed with 20 mL of chloroform, methyltimol blue as indicator was added and the mixture was titrated with a standard ammonium oxalate solution (reaction **A**) with shaking the flask after addition of each portion of the titrant. Upon addition of 14.36 mL 0.1000 M oxalate solution, the blue color of the suspension changed into green, which could be observed after phase separation. It is given that 1.000 mL of the oxalate solution corresponds to 13.93 mg of Bi.

1. Write down reaction **A**, indicating the insoluble product formed in it.

2. Confirm the composition of the product by calculation.

3. Calculate the concentration of Bi^{3+} in the analyzed solution in mol/L and g/L.

4. When methyltimol blue indicator is added to the solution containing the bismuth salt, a blue complex is formed (reaction **B**): $Bi^{3+} + Ind^{3-} = BiInd$. Explain the principle of this metalchromic indicator by writing down the reaction of this complex with an excess of titrant (reaction **C**). Which of the substances formed in the reaction is yellow? Underline it.

Lower concentrations of bismuth were determined by adding KBr to 100.0 mL of the test solution so that the precipitate forming at the beginning (reaction **D**) could completely dissolve (reaction **E**) forming a slightly yellow solution. The resulting solution was neutralized with sodium hydroxide until faint turbidity, not disappearing on stirring (reaction **F**); then hexaammine chromium(III) nitrate solution was added for the quantitative precipitation of a bismuth compound (reaction **G**). The precipitate was filtered off, washed with KBr solution and quantitatively washed off with hot water. While doing that, the precipitate was hydrolyzed to form an insoluble bismuth compound (reaction **H**). To the resulting suspension, an excess of NaOH was added and heated (reaction **J** with the chromium compound); the releasing ammonia was absorbed by a boric acid solution (reaction **K**). The solution in the receiver was titrated 0.1000 M HCl in the presence of methyl orange (reaction **L**); 17.2 mL of acid was required.

5. Write down the reactions **D** – **L**. Underline which substance precipitates in reactions **D** and **H**. Circle the yellow substance in reaction **E**.

6. Calculate the concentration of Bi^{3+} in the initial solution in mol/L.

Problem 2

Vasya's hobby is keeping an aquarium (pH 7.2, dissolved oxygen concentration $3.12\cdot10^{-4}$ M). He read in a book that his aquatic plants demand some soluble form of iron and its optimal concentration is c(Fe) = 2 μM.

For reference: solubility product of $Fe(OH)_3$ $K_s = [Fe^{3+}][OH^-]^3 = 4\cdot10^{-38}$; at pH 7.2 the molar fraction of complex-forming ion of EDTA (Y^{4-}) equals $8\cdot10^{-4}$; equilibrium constant of the reaction $Fe^{2+} + \frac{1}{4}O_2 + \frac{1}{2}H_2O = Fe^{3+} + OH^-$ in aqueous solution is $K = 10^5$; the parameters of the complexes formed by iron ions are as follows:

Complex	$Fe^{2+}Y$	$Fe^{3+}Y$	$Fe(OH)^{2+}$	$Fe(OH)_2^+$	$Fe(OH)_3$
Stability constant	$\beta^{II}=\frac{[FeY^{2-}]}{[Fe^{2+}][Y^{4-}]}$	$\beta^{III}=\frac{[FeY^-]}{[Fe^{3+}][Y^{4-}]}$	$\beta_1=\frac{[FeOH^{2+}]}{[Fe^{3+}][OH^-]}$	$\beta_2=\frac{[Fe(OH)_2^+]}{[Fe^{3+}][OH^-]^2}$	$\beta_3=\frac{[Fe(OH)_3]}{[Fe^{3+}][OH^-]^3}$
Constant value	10^{14}	10^{25}	10^{12}	10^{22}	10^{30}

1. a) Calculate the fraction α of free Fe^{3+} cation in the solution at this pH.

b) Which process limits iron concentration in the solution at this pH?

c) Can one provide the required concentration of dissolved iron by adding, for example, iron(III) sulfate as fertilizer? Calculate the maximal total concertation of dissolved iron c(Fe) in the aquarium.

2. Vasya was told that the plants consume iron more efficiently if its oxidation state is +2.

a) Which processes will start after the addition of iron(II) sulfate into this aquarium? Write the total reaction equation.

b) What percentage of dissolved iron will be present in the 2+ form, if 2 μM of iron(II) sulfate have been added at pH 7.2 and the equilibrium is reached?

3. There is a popular advice to increase the solubility of iron and its stability as iron(II) by adding iron as a chelate that can be prepared by mixing iron sulfate and EDTA.

a) Calculate the molar fraction of free Fe^{3+} $\alpha(Fe^{3+})$ in the solution at this pH, if Vasya added simultaneously the iron salt (2 μM) and a 1.5-fold molar excess of EDTA. What is the dominating form of iron(III) under these conditions? Calculate its molar fraction.

b) Will iron(III) precipitate, if Vasya has added 2 μM of Fe^{3+} along with a 1.5-fold molar excess of EDTA? Confirm your answer by calculation.

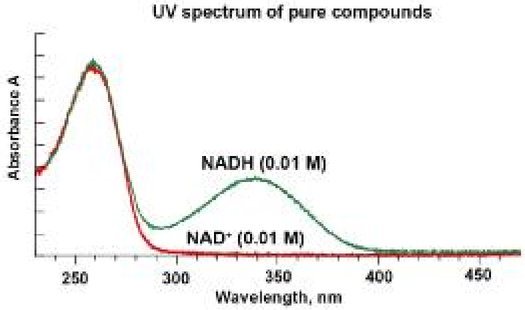
c) Estimate which percent of dissolved iron is present as iron(II), if iron(II) is added simultaneously with a 1.5-molar excess of EDTA. Is it possible to preserve some noticeable amount of iron(II)?

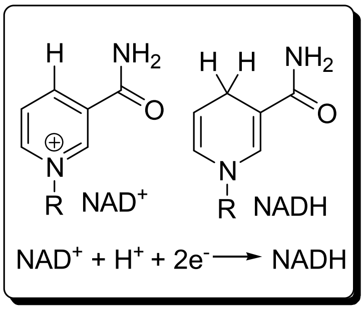
Problem 3

Spectrophotometry is sensitive method of analysis which allows determining small concentrations of compounds. This method is based on absorption of light of certain wavelength by molecules, which is related to specific electron transitions. The Beer-Lambert law describes the relation between light absorption and compound concentration: $A = \log\frac{I_0}{I} = \varepsilon c l = \sum_i \varepsilon_i c_i l$, where A is absorbance, I and I_0 are intensities of passed and initial light, ε – extinction coefficient, l – path length and c – concentration. Absorption A is additive quantity.

1. Choose all correct answers: absorbance: a) could be negative value, b) could be larger than 100, c) is always positive, d) does not depend on ε.

2. Express absorbance as function of light transmittance $T = (I / I_0)\cdot 100\%$.





λ, nm	A(2)	A(3)
260	0.981	1.047
340	0.325	0.433

Nicotinamide adenine dinucleotide (NAD) is a coenzyme existing in oxidized (NAD^+) and reduced (NADH) forms (see the scheme) which take part in redox reactions of all live cells.

3. Write the reaction of oxalic acid $H_2C_2O_4$ oxidation by this coenzyme.

From initial solution **1** containing 25 mM of NAD^+ and a deficient quantity of $H_2C_2O_4$, a 5.0-mL aliquot was taken and diluted to 1000 mL, to obtain solution **2**. The absorbance of solution **2** was measured at two wavelengths: 260 and 340 nm (A(2)). Simultaneously, 5.0 mL of 4.0 mM of NADH solution was diluted (to give solution **3**) and absorbance A(3) was measured at the same both wavelengths. However, the laboratory assistant forgot what fold he diluted the solution. All the results are presented in the table. In all absorbance experiments $l = 5$ mm.

4. Using the absorption spectrum (see Fig.) point out which color has solution **1**:

a) bluish, b) colorless, c) pale green, d) rich red.

5. At which wavelength in the range of 240 – 390 nm the light transmittance T of solution **1** is maximal?

6. From the table data, estimate the NAD^+ and NADH concentrations in solution **1** and find the extinction coefficients ε for NAD^+ and NADH at 260 and 340 nm.

7. What fold did the poor laboratory assistant dilute the solution of NADH to obtain solution **3**?

8. Estimate the minimal concentration of NAD detectable by this method (limit of detection), if the maximal detectable transmittance (T) is 99%.

SECTION V. PHYSICAL CHEMISTRY

Problem 1

For a great while isomerization of chromium thiocyanates has not been explored because of synthesis of one isomer failure.

1. Define isomerism type and write down structural formulae of fragments Cr–thiocyanate and Cr–isothiocyanate.

2. Point more stable isomer, if Cr^{3+} is a strong acid and thiocyanate (SCN^{-}) is weaker base than isothiocyanate (NCS^{-}).

In the mid-1960s Haim и Sutin succeeded to synthesize mixture of isothiocyanate (55 mol.%) and thiocyanate (45 mol.%) and to study kinetics of parallel running isomerization and aquatation. For the synthesis they used transfer of non-symmetrical bridge ligand and electron transfer in the reaction $[Co(en)_2(H_2O)NCS]^{2+} + [Cr(H_2O)_6]^{2+}$.

3. Write down the reaction equation of synthesis $[Cr(H_2O)_5SCN]^{2+}$ and draw the intermediate structure with non-symmetrical bridge –S–C–N–.

While studying kinetics they used bands in electronic spectrum λ_1 and λ_2 nm (initial solution, λ_3 is absent) and λ_1 and λ_3 nm (final solution, λ_2 is absent), whereby $\lambda_2 > \lambda_3 > \lambda_1$.

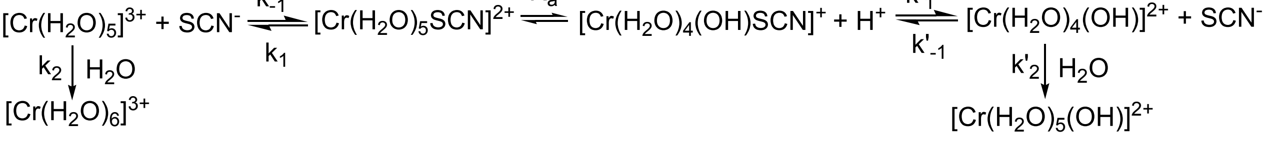
4. Define complexes associated with these wave lengths if NCS^{-} is ligand of strong, H_2O – of middle and SCN^{-} – weak field.

As a result of kinetic studies the relation for observed rate constant $k_{obs} = f([H^+])$ was obtained and equation $k_{obs} = (k_i + k_a) + [(k'_i + k'_a)\cdot K_a]/[H^+]$, where k_i, k'_i – isomerization constants, k_a and k'_a – aquatation constants, was suggested.

$[H^+]$	$4\cdot10^{-2}$	$5\cdot10^{-2}$	$8\cdot10^{-2}$	$10\cdot10^{-2}$
k_{obs}, s^{-1}	$4.27\cdot10^{-4}$	$3.54\cdot10^{-4}$	$2.44\cdot10^{-4}$	$2.08\cdot10^{-4}$

5. Figure the plot $k_{obs} = f(1/[H^+])$ and define how to obtain $(k_i + k_a)$ and $(k'_i\cdot K_a + k'_a\cdot K_a)$ from it. Calculate these values using $[H^+] = 5\cdot10^{-2}$ and $10\cdot10^{-2}$.

6. Calculate k_i, $k_i\cdot K_a$, k_a and $k_a\cdot K_a$ if concentration ratio $[Cr(H_2O)_5NCS]^{2+}$ to $[Cr(H_2O)_6]^{3+}$ and $[Cr(H_2O)_4(OH)NCS]^{+}$ to $[Cr(H_2O)_4(OH)]^{2+}$ in final system is 2.46 independently from $[H^+]$.



In opposition to isomerization, aquatation mechanism of this type of complexes has already been known ($k_{obs} = k_u + k_u\cdot K_a/[H^+]$).

7. Suggest similar to aquatation scheme of isomerization of $[Cr(H_2O)_5SCN]^{2+}$ if the first reaction in both schemes is equal.

8. Derive the expression for isomerization k_{obs} ($[H^+] >> K_a$) by the stationary approximation method.

Problem 2

Redox flow battery is a promising type of chemical accumulators of electric energy. They are special in that the reactants yielding electricity in the redox reaction are stored in separate tanks in solutions and are pumped through an electrochemical cell where the redox reaction occurs. This provides virtually unlimited battery capacity as well as safety (since at any moment the reaction volume contains a small volume of solutions of the reacting species).

1. Draw the equations of half reactions occurring during charging of the flow battery containing solutions of iron(II) and iron(III) sulfates (electrolyte A) and chromium(II) and chromium(III) sulfates (electrolyte B) in aqueous sulfuric acid (pH = 0). **Note: hereafter consider the standard conditions if not stated otherwise.**

2. Calculate the voltage that can be achieved using the described battery.

3. State the side reaction that will compete with one of the reactions written in i. 1.

To avoid cross contamination of the anolyte and catholyte, it is preferable to use redox pairs containing the same metal in redox flow batteries. For example, compound **A** used in redox flow batteries contains 21.67 wt% M, 13.64 wt% S, and 61.26 wt% O.

4. Determine formula of **A** and metal M.

5. List the possible pairs of electrolytes (anolyte + catholyte) based on compounds of M suitable for redox flow batteries application. Confirm the answer by the necessary calculation, or draw the corresponding Frost diagram. (**the solutions are considered different if different redox reactions occur during the battery operation when using the corresponding pairs**)

6. Select the anolyte + catholyte pair providing the highest battery voltage.

Solutions of anolyte and catholyte are separated by semi-permeable membrane that is permeable to the ions providing for the solutions electroneutrality but prevents direct contact of the ions involved in the redox reaction (i. e. prevents anolyte and catholyte mixing).

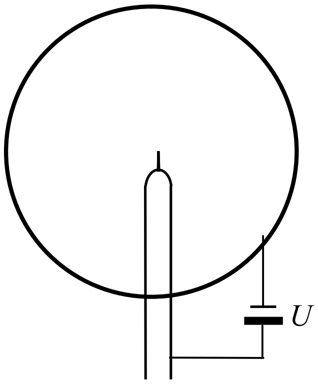
7. Draw half reactions of oxidation and reduction of compounds corresponding to the compositions of anolyte and catholyte selected in i. 6. State the ions that should permeate through the membrane and these that should not pass through.

8. Calculate the volumes of the selected anolyte and catholyte required for substitution of the industrial UPS with net power 10 kW operating during 2 h from the internal battery. Assume that solubility of the anolyte and catholyte components equals 2 mol/L, 7% of the redox flow battery power is consumed to pump the solutions through the electrochemical cell, and redox reactions occur with 90% efficiency (*if you have failed to select the electrolytes pair or calculate the electromotive force of the cell, use E for the EMF and express the answer using this value*).

Reference data: $E°(Fe^{3+}/Fe^{2+})$ = 0.77 V, $E°(Cr^{3+}/Cr^{2+})$ = –0.41 V, $E°(H^+/H_2)$ = 0.00 V, $E°(O_2/H_2O)$ = 1.23 V, $E°(M^V/M^{IV})$ = 1.00 V, $E°(M^{IV}/M^{III})$ = 0.34 V, $E°(M^{III}/M^{II})$ = –0.25 V, $E°(M^{II}/M^0)$ = –1.13 V; $\Delta G° = -nF(E°_{\text{oxidant}} - E°_{\text{reductant}})$

Problem 3

Strong electric and magnetic fields have influence on the equilibrium constant of a chemical reaction. Electrostatic field of high intensity exists near sharp ledges (tips) on the surface of charged conductors. A tip is characterized be the radius of rounding r at its end, which can be brought to several hundreds of angstrom. If a tip is placed in the centre of a conducting sphere the construction shown in figure comes out. The volume of the sphere is filled with gaseous reaction mixture.



Getting into the tip region, molecules are subjected to a strong electric field. On a small ball surface $E = q / 4\pi\varepsilon\varepsilon_0 r^2$ (**1**).

1. Find the field intensity E (V/m) on the surface of a tip, considering it to be a small ball with r = 500 Å. Between the tip and the outer sphere electric tension U = 2000 V is applied. Instructions: 1) Electric capacity of a ball $C = 4\pi\varepsilon\varepsilon_0 r$; 2) The relation between the ball charge and the tension $q = CU$.

In electric field there appears an additive member to the Gibbs energy of a compound, depending on intensity of the field: $G = G_0 - ½PE$ (**2**), where G_0 – Gibbs energy without field, P – *complete* dipole moment of matter. Due to this, in the expression of the reaction equilibrium constant $K = \exp(-\Delta_r G°/RT)$ additional factor appears:

$$K = K_0 \exp\left\{\frac{E\left[\left(\sum \nu_i P_i\right)_{\text{product}} - \left(\sum \nu_i P_i\right)_{\text{reagent}}\right]}{2RT}\right\} = K_0 \exp\left(\frac{E \cdot \Delta_r P}{2RT}\right) \qquad (\mathbf{3})$$

ν_i – stoichiometrical coefficients in the reaction equation, $\Delta_r P$ – dipole moment change in the reaction, K_0 – equilibrium constant without field.

2. In how many times will change the equilibrium constant of ideal-gas reaction

$$H_2(g) + ½O_2(g) = H_2O(g) \qquad (\mathbf{4})$$

at 300 K in the field 30 kV/cm, if to consider that the dipole moments of all molecules are directed along the field? *Intrinsic* dipole moment of H_2O molecule $d_0 = 6.17 \cdot 10^{-30}$ C·m. Instruction: Calculate $K/K_0 - 1$.

It is necessary to improve the calculation, because due to a thermal motion the dipole moments of gas molecules in the electric field are oriented according to Boltzmann distribution. Then the dipole moment of gas $P = V\chi E$ (**5**) depends on E and temperature. Here $\chi(T)$ – dielectric receptivity of matter (dimensionless value in SGS system), V – substance volume. Theory gives the following formula (in SGS system):

$$\chi = \frac{nd_0^2}{3k_\mathrm{B}T} \qquad (\mathbf{6})$$

where n – number of molecules in a volume unit.

3. With the help of formula (**2**) deduce an expression (including only d_0, E and T as variables) for the Gibbs energy of 1 mol of gas in electric field at standard pressure $p° = 101325$ Pa.

Influence of magnetic field on equilibrium constant of a reaction is described by an expression, analogous to (**3**). It is enough to do replacement $P \to M$, $E \to B$, where B – magnetic induction, M – *complete* magnetic moment of matter:

$$K = K_0 \exp\left(\frac{B \cdot \Delta_\mathrm{r} M}{2RT}\right) \qquad (\mathbf{7})$$

Correlations, analogous to (**5**) и (**6**) also take place: $M = V æB$ (**8**), $æ = n\mu_0^2 / 3k_\mathrm{Б}T$ (**9**), where $æ(T)$ – magnetic receptivity of matter (dimensionless value in SGS system), μ_0 – *intrinsic* dipole moment of molecule.

4. Calculate, in how many times will change the equilibrium constant of reaction (**4**) in the field 30 kV/cm at 300 K. Instruction: Calculate $K/K_0 - 1$.

Molecule O_2 is one of the few diatomic molecules, having a different from zero spin in the ground state (triplet state), therefore oxygen is paramagnetic.

5. Specify the value of quantum number (S) for total spin of oxygen molecule and find the value of intrinsic magnetic moment of O_2 molecule in Bohr magnetons (μ_B) according to formula $\mu_0 = 2\mu_\mathrm{B}\sqrt{S(S+1)}$.

6. Calculate magnetic receptivity of gaseous oxygen at pressure $p°$ and 300 K.

Magnetic resonance tomography (MRT), in which an organism is exposed to a strong magnetic field, is widely used in modern medicine. In high resolution devices magnetic induction may be as much as $B = 10000$ gausse (Gs). It is generally possible that the magnetic field influences on the chemical processes in a living being.

7. Verify this statement by calculating the change in equilibrium constant of reaction (**4**) at 300 K in a magnetic field with $B = 10000$ Gs? Instructions: 1) Use SGS units (cm, g, s, dyne, Gs); 1 N = 10^5 dyne, 1 J = 10^7 erg; 2) Calculate $K/K_0 - 1$.

Constants: $R = 8.314$ J/mol·K, $k_\mathrm{B} = 1.38\cdot10^{-16}$ erg/K, $N_\mathrm{A} = 6.02\cdot10^{23}$ mol^{-1}, $\mu_\mathrm{B} = 0.927\cdot10^{-20}$ erg/Gs.