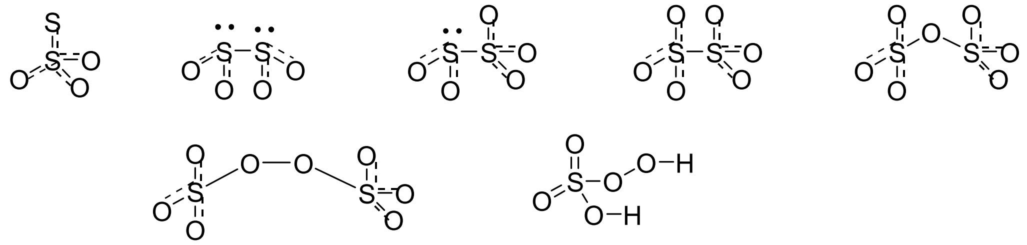
SECTION I. INORGANIC CHEMISTRY

Problem 1 (authors Rozantsev G.M., Shvartsman V.E.)

1. $\mathbf{E}_m\mathbf{O}_{n+o}{}^{2-}$ $\dfrac{m\mathrm{A_E}}{m\mathrm{A_E}+16n}=0.572$; $\mathbf{E}_m\mathbf{O}_{n+5}{}^{2-}$ $\dfrac{m\mathrm{A_E}}{m\mathrm{A_E}+(n+5)16}=0.334$. By solving set of equations one obtains $\mathrm{A_E} = 64.2/m$ (1 point).

When $m = 2$ $\mathrm{A_E} = 32.1$ g/mol and E – S (0.5 points). $n = 3$ (0.25 points). $\mathbf{EO}_{\boldsymbol{n}}{}^{2-}$ – $SO_3{}^{2-}$; $\mathbf{HEO}_{\boldsymbol{n}}{}^{-}$ – $HSO_3{}^{-}$; $\mathbf{HEO}_{\boldsymbol{n+1}}{}^{-}$ – $HSO_4{}^{-}$; $\mathbf{EO}_{\boldsymbol{n+1}}{}^{2-}$ – $SO_4{}^{2-}$; $\mathbf{EO}_{\boldsymbol{n+2}}{}^{-}$ – $HSO_5{}^{-}$; **I** – $S_2O_3{}^{2-}$; **II** – $S_2O_4{}^{2-}$; **III** – $S_2O_5{}^{2-}$; **IV** – $S_2O_6{}^{2-}$; **V** – $S_2O_7{}^{2-}$; **VI** – $S_2O_8{}^{2-}$ (0.25 points for each of I – VI and $HSO_5{}^{-}$, 3.5 points in total).

2. (0.25 points for each structure, 1.75 points in total)



3. (0.25 points for each reaction, 2.5 points in total)

$SO_3{}^{2-} + S = S_2O_3{}^{2-}$

$4HSO_3{}^{-} + 2HS^{-} = 3S_2O_3{}^{2-} + 3H_2O$

$2HSO_3{}^{-} + Zn + SO_2 = ZnSO_3 + S_2O_4{}^{2-} + H_2O$

$2HSO_3{}^{-} = S_2O_5{}^{2-} + H_2O$

$3HSO_3{}^{-} + 2MnO_2 + 3H^{+} = SO_4{}^{2-} + S_2O_6{}^{2-} + 2Mn^{2+} + 3H_2O$

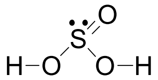
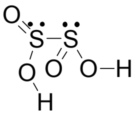
$2HSO_4{}^{-} = S_2O_7{}^{2-} + H_2O$

$HSO_3{}^{-} + 2Fe^{3+} + H_2O = HSO_4{}^{-} + 2Fe^{2+} + 2H^{+}$

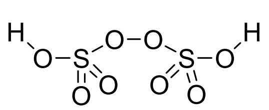
$2HSO_4{}^{-} \xrightarrow{\text{electrolysis}} S_2O_8{}^{2-} + H_2$

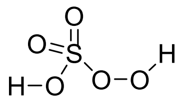
$HSO_5{}^{-} + OH^{-} = SO_4{}^{2-} + H_2O_2$

$S_2O_8{}^{2-} + H_2O = HSO_5{}^{-} + HSO_4{}^{-}$

4. OH-groups of mononuclear acids bind with single Sulfur atom and the difference of constants is 5 – 6 orders . In case of $H_2S_2O_4$ OH-groups are by different Sulfur atoms:  and constants have little difference (0.25 points in total).

5. Second H binds with peroxide group (0.25 points in total).





6. $H_2SO_3 = H^{+} + HSO_3{}^{-}$ $K_1 = \dfrac{[H^{+}][HSO_3{}^{-}]}{[H_2SO_3]}$ $HSO_3{}^{-} = H^{+} + SO_3{}^{2-}$ $K_2 = \dfrac{[H^{+}][SO_3{}^{2-}]}{[HSO_3{}^{-}]}$

$2HSO_3{}^{-} = S_2O_5{}^{2-} + H_2O$ $K = \dfrac{[S_2O_5{}^{2-}]}{[HSO_3{}^{-}]^2}$ $C = [H_2SO_3] + [HSO_3{}^{-}] + [SO_3{}^{2-}] + 2[S_2O_5{}^{2-}] =$

$$\frac{[H^+][HSO_3^-]}{K_1}+[HSO_3^-]+\frac{K_2[HSO_3^-]}{[H^+]}+2K[HSO_3^-]^2=[HSO_3^-]\left(\frac{[H^+]^2+K_1[H^+]+K_1K_2}{K_1[H^+]}\right)+2K[HSO_3^-]^2$$

$[HSO_3^-]^2 + 7.563[HSO_3^-] – 0.7143 = 0$ (0.75 points) $[HSO_3^-] = 9.33\cdot10^{-2}$ (mol/L).

$[S_2O_5^{2-}] = 6.1\cdot10^{-4}$; $[SO_3^{2-}] = 5.9\cdot10^{-6}$; $[H_2SO_3] = 5.5\cdot10^{-3}$ (mol/L) (0.25 points for each concentration, 1.75 points in total).

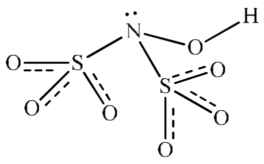
7. There is no Hydrogen in **D** and **B** but Oxygen is present with $w_O = 100 – 23.92 – 5.22 – 29.14 = 41.78\%$. Then $\nu_S : \nu_N : \nu_K : \nu_O = 23.92/32.1 : 5.22/14.0 : 29.14/39.1 : 41.78/16.0 = 2 : 1 : 2 : 7$ and **B** – $[ON(SO_3)_2]^{2-}$(1 point). Considering element content, magnetic properties, bond quantity and length N–O, one can suppose that anion in **D** is dimer of anion **B**, and salt **D** is $K_4[ON(SO_3)_2]_2$ (0.5 points). **A** contains Hydrogen with very low quantity as well as Oxygen. Proxumity of element weights allows to suggest that there is $ON(SO_3)_2$ group in **A** – the same as in **D** and **B**. Then $w_O=(23.83\cdot16.0\cdot7)/(32.1\cdot2)=41.57\%$, $w_H=100–23.83–5.20–29.03–41.57=0.37\ \%$, $\nu_S : \nu_N : \nu_K : \nu_O = 23.83/32.1 : 5.20/14.0 : 29.03/39.1 : 41.57/16.0 : 0.37/1.0 = 2 : 1 : 2 : 7 : 1$, **A** – $K_2[HON(SO_3)_2]$ (1 point).

$2KHSO_3 + KNO_2 = K_2[HON(SO_3)_2] + KOH$ (0.25 points)

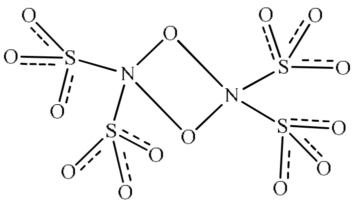
$2\ K_2[HON(SO_3)_2] + PbO_2 = Pb(OH)_2 + K_4[ON(SO_3)_2]_2$ (0.25 points, 3 points in total).

8. Structural formulae **A**, **D** and 2 variants of **B** (0.25 points for each structure)

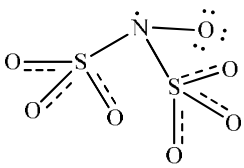
A



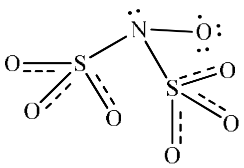
D



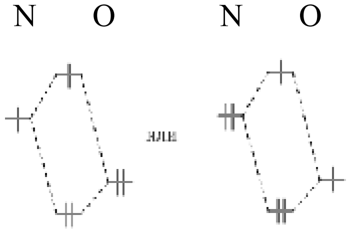
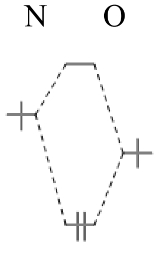
B



B



Bond length N–O depends on bond multiplicity which can be obtained by LMO method.

	
For long bond N–O one can suppose two variants of LMO diagram, from which bond multiplicity (2–1)/2 = 0.5 (0.75 points)	For short bond LMO diagram indicates of N–O bond multiplicity (2–0)/2 = 1 (0.25 points, 2 points in total)

Problem 2 (author Khvaluk V.N.)

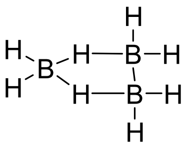
1. For example, white phosphorus P_4 is a regular tetrahedron of phosphorus atoms, sodium hexahydrohexaborate (2–) $Na_2[B_6H_6]$ is a regular octahedron from boron atoms, cuban C_8H_8 is a regular cube of carbon atoms. Other examples are also acceptable. (3 · 0.5 points**,** 1.5 points in total)

2. In the dodecahydododecaborate (2–) anion there are only two types of bonds: B–H and B–B. The number of the former in the anion is 12, as there are 12 hydrogen atoms. As is shown in the problem condition there are 20 faces in the icosahedron, which are the equilateral triangles. Each side of this triangle is the B–B connection. Since each side of the triangle simultaneously belongs to two adjacent triangles, the number of edges in the entire icosahedron (it is equal to the number of B–B bonds) is $\frac{20\cdot3}{2} = 30$. In the anion there are 12 electrons from 12 hydrogen atoms, 36 electrons from 12 boron atoms and 2 electron from the total charge of the anion, totally 12 + 36 + 2 = 50 electrons, or 25 electron pairs. The B–H bond is a conventional two-center two-electron covalent bond (2c–2e), which is realized by one common electron pair. Therefore, the multiplicity of this connection is 1. (1.5 points)

12 pairs of electrons are necessary for the formation of 12 B–H bonds. The bond between the boron atoms can not be ordinary (2c–2e), since there is not enough electrons for all the bonds. This bond is multicenter (it is characteristic for boron and its hydrides). The formation of 30 such bonds remains 25 – 12 = 13 electron pairs. Therefore, the multiplicity of each B-B bond is $\frac{13}{30} = 0.433$ (2 point, 3.5 points in total)

It can not be the acid $H_2[B_{12}H_{12}]$, since it is nothing more than $B_{12}H_{14}$, which, as said in the condition, does not exist. $(H_3O)_2[B_{12}H_{12}]\cdot nH_2O$ was isolated from the aqueous solution. In fact, the acids with n = 4 and 5 are isolated. The calculation is estimated with any n, or n = 0, i.e. $(H_3O)_2[B_{12}H_{12}]$. The mass fraction of boron in such an acid is 72.12% (formula 2.0 points, mass fraction 1 point, 3 pointsin total).

3. Structural formula of octahydrotriborate(2–) anion (1 point):



4. Equations of reactions for the preparation of sodium dodecahydododecaborate (2–):

$$Na[BH_4] + B_2H_6 = Na[B_3H_8] + H_2;$$

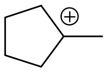
$$4Na[B_3H_8] = Na_2[B_{12}H_{12}] + 2NaH + 9H_2$$ (1 point each, 2 points in total)

5. The carbon atom has 4 electrons, and the boron atom has 3. Replacement of the boron atom by the carbon atom leads to the appearance of an additional electron, therefore, to preserve the isoelectronicity and aromaticity of the anion, its charge should be equal to 1–. Its formula is $[CHB_{11}H_{11}]^{1-}$. After the cesium salt is chlorinated, the $[CHB_{11}Cl_{11}]^{1-}$ anion is formed. The formula of the carborane superacid is $H[CHB_{11}Cl_{11}]$ (2 points).

6. When the $CH_3[CHB_{11}Cl_{11}]$ salt is washed with hexane, a new salt forms:

$$C_6H_{12} + CH_3[CHB_{11}Cl_{11}] = C_6H_{11}[CHB_{11}Cl_{11}] + CH_4;$$

However, during the production process, the secondary carbocation $C_6H_{11}^+$ is isomerized to a more stable tertiary and a salt is formed in which the cation is a tertiary methylcyclopentyl carbocation (for the equation 0.5 points, the structure 0.5 points, 1 point in total):



The sharp increase in acidity when replacing B–H bonds on B–Cl bonds can be attributed to the greater electronegativity of chlorine. Then the replacement of chlorine atoms by fluorine atoms should lead to an even stronger effect. Indeed, in 2013, the superacid H $[CHB_{11}F_{11}]$ was synthesized, which at the moment is the strongest superacid. The mass fraction of boron in it is equal to 34.78% (the formula is 0.5 points, the mass fraction is 0.5 points, 1 point in total)

Problem 3 (author Kandaskalov D.V.)

1. The main unknown compounds are the binary ones **A-I**. The analysis of the scheme shows us that one of the elements is the Hydrogen (**X** or **Y**) as the compound **L** which forms from **F** and oxygen is the acid.

We can calculate the molecular weight of **H**, using the fact that **H**·HCl contains only one chlorine atom:

$$M(H+HCl)=\frac{A_r(Cl)}{w_{Cl}}\cdot 100\%=\frac{35.5}{42.5}\cdot 100\%=83.5 g/mol$$

The molar weight of **H** is 47 g/mol. We could say for sure that this compound does not contain the non-metals of third period: Si, P, S, as **H** could have no more than one of these atoms, but the number of hydrogen atoms would be more than 10 which is unrealistic. The atoms of Cl and Ar are excluded automatically. Thus remains only second period of elements. **H** could not be a hydrocarbon as it molar mass is uneven. We have only two variants, **B** or **N**: N_3H_5 or B_4H_4.

Then, we can proceed with triangle: **K–A–B**.

The molar weight of **W:** $M=\rho\cdot V_M=1.964\cdot 22.4 = 44$ g/mol permits us to conclude that this gas is CO_2 or N_2O. Knowing, that there no many ways for N_2O synthesis we exclude this variant, thus the gas is CO_2.

Let's write the reaction **K**→**B** with known compounds:

$$\mathbf{K} + NaOCl \rightarrow \mathbf{B} + CO_2 + NaCl$$

From conservation mass law, we conclude that molecules **K** and **B** differs by CO fragment i.e. by 28 g/mol. Now, we can calculate the molar masses of both compounds (*x* - the molar weight of **B**):

$$\frac{0.72}{x+28}=\frac{0.384}{x}\Rightarrow x=32$$

Thus, the molar weight of **B** is 32 g/mol or its multiple. Supposing that the molar weight is 32 g/mol, we find only one correct compound: N_2H_4 (hydrazine), no one option with bore. Then **K** – N_2H_4CO (urea) and **A** – NH_3 (ammonia):

$$(NH_2)_2CO + HOH \rightarrow CO_2 + 2NH_3$$

Then **H** – N_3H_5 and taking into account that $N_3H_5 \cdot HCl$ is obtained as a unique product from hydrazine and **J,** the last compound is NH_2Cl. The structure of **H** we can write unequivocally as $H_2N–NH–NH_2$ (triazan) and we see it's structurally similar to urea: $H_2N–CO–NH_2$, which confirm our solution.

From the next reaction we deduce **G** as diazen: N_2H_2 (HN=NH):

$$N_3H_5 \cdot HCl \rightarrow N_2H_2 + NH_3 + HCl$$

Thus, we finished left side of the scheme.

Continue with the right side of the scheme. Let's analyze the sequence of reactions **B→C→E,** where the liquid **C** is formed from the hydrazine (80% yield) and then the hydrazine takes a part also in the second reaction: the formation of **E** with 95% yield. Let's suppose that we have 1 mol of **B**. In this case we obtain 0.8 mol of **C**, and we need 0.8 mol of hyfrazine for the second reaction. As a result we obtain 0.76 mol of the salt **E (**95% yield**)**. Thus, we obtain 0.76 mol of **E** from 1.8 mol of hydrazine. Now we can calculate the molar mass of **E.** The quantity of hydrazine is n=0.864/32=0.027 mol, which gives us 0.0114 mol of the salt **E**, thus M_E=0.855/0.0114=75 g/mol. This molecular weight is corresponding to N_5H_5, which we can write as $N_2H_4 \cdot HN_3$ ($N_2H_5N_3$). Thus **C** – is hydronitric acid HN_3 and the salt **D** is its ammonium salt: NH_4N_3

The salt **D** is obtained by isomerization of covalent compound **I**, thereby **I** is also N_4H_4. As it is similar to N_2H_2 and form N_2H_4 and N_2 it structure is $H_2N-N=N-NH_2$ (tetrazan).

Finally, the salt **M** – $[H_2N_3^+][SbF_6^-]$ which could be seen from the reaction:

$$HN_3 + SbF_5 + HF \rightarrow [H_2N_3^+][SbF_6^-]$$

Instable compound **F** – NH (monohydryde of nitrogen). Its formula is confirmed by the dimerization to N_2H_2 and the synthesis from HN_3. NH reacts with oxygen and the product is HNO_2 (**L**), which is confirming also by the reaction: $N_2H_4 + HNO_2 \rightarrow HN_3 + 2HOH$

And this reactions: $HN_3 + HNO_2 \rightarrow N_2O + N_2 + HOH$, permits us to find **Z** – N_2O.

Thus 17 unknown compounds are (0.5 points for each compound, 8.5 points in total):

A – NH_3, **B** – N_2H_4, **C** – HN_3, **D** – NH_4N_3, **E** – $N_2H_5N_3$, **F** – NH, **G** – N_2H_2, **H** – N_3H_5, **I** – N_4H_4, **J** – NH_2Cl, **K** – $CO(NH_2)_2$, **L** – HNO_2, **M** – $[H_2N_3^+][SbF_6^-]$, **W** – CO_2, **X** – H_2, **Y** – N_2, **Z** – N_2O

2. We have 16 equation of chemical reactions (0.25 points for each, 4 points in total):

$CO(NH_2)_2 + HOH \rightarrow CO_2 + 2NH_3$ $N_2H_4 + NH_2Cl \rightarrow N_3H_5 \cdot HCl$

$CO(NH_2)_2 + NaOCl \rightarrow N_2H_4 + NaCl + CO_2$ $N_3H_5 \cdot HCl \rightarrow N_2H_2 + NH_3 + HCl$

$2NH_3 + NaOCl \rightarrow N_2H_4 + NaCl + HOH$

$N_2H_4 + HNO_2 \rightarrow HN_3 + 2HOH$

$HN_3 \rightarrow HN + N_2$

$2NH \rightarrow N_2H_2$

$NH + O_2 \rightarrow HNO_2$

$2N_2H_2 \rightarrow N_2H_4 + N_2$

$HN_3 + SbF_5 + HF \rightarrow [H_2N_3^+][SbF_6^-]$

$HN_3 + HNO_2 \rightarrow N_2O + N_2 + HOH$

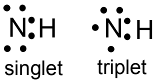
$HN_3 + NH_3 \rightarrow NH_4N_3$

$HN_3 + N_2H_4 \rightarrow N_2H_5N_3$

$H_2N\text{-}N{=}N\text{-}NH_2 \rightarrow NH_4N_3$

$H_2N\text{-}N{=}N\text{-}NH_2 \rightarrow N_2H_4 + N_2$

3.



The particle NH is isoelectronic to CH_2 or to atomic oxygen O, which could also exist in singlet of triplet states (0.5 points for each Lewis structure and 0.5 points for particle, 1.5 points in total)

4. The compound NH_2Cl is intermediate product during the synthesis of hydrazine:

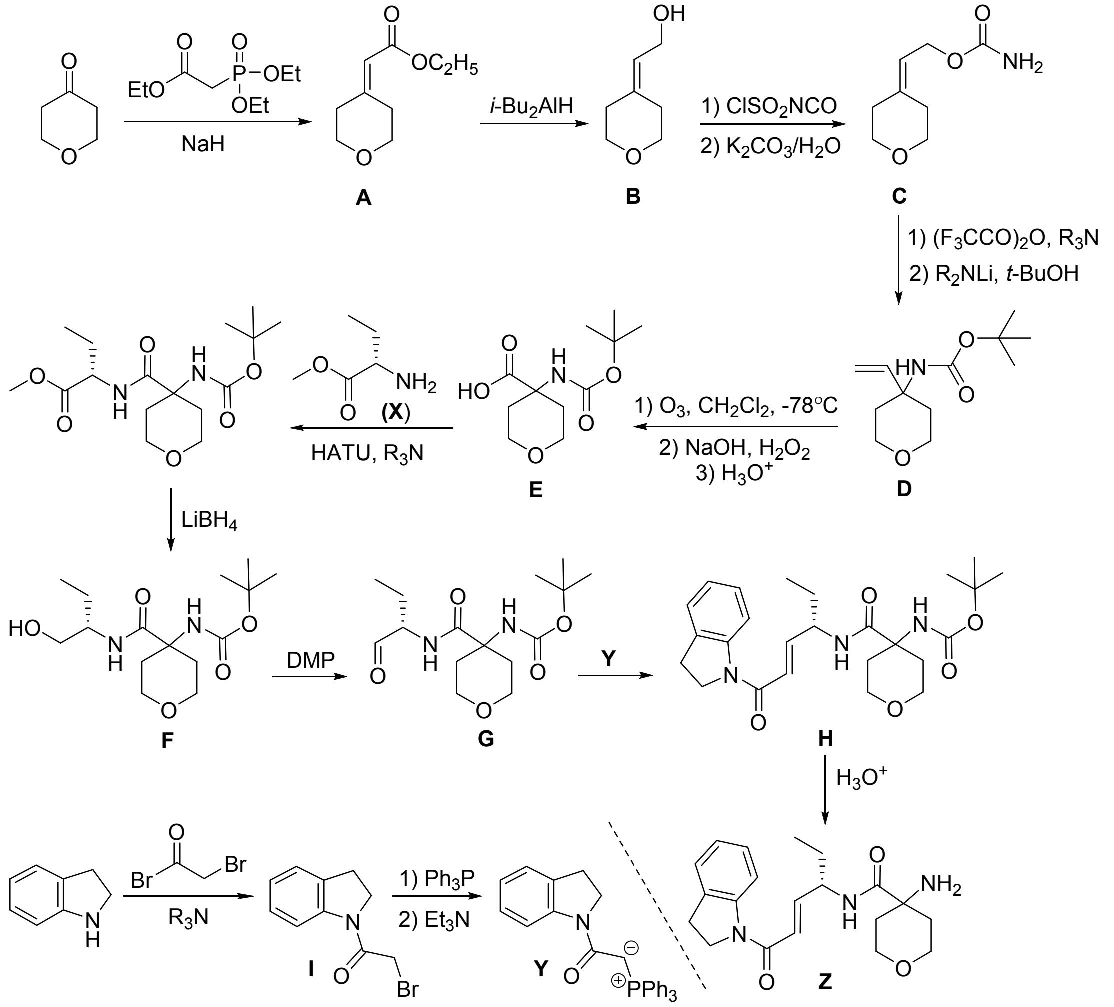
$$NH_3 + NaOCl \rightarrow NH_2Cl + NaOH$$

During its reaction with hydrazine the triazan is formed: $N_2H_4 + NH_2Cl \rightarrow N_3H_5 \cdot HCl$ (1 point)

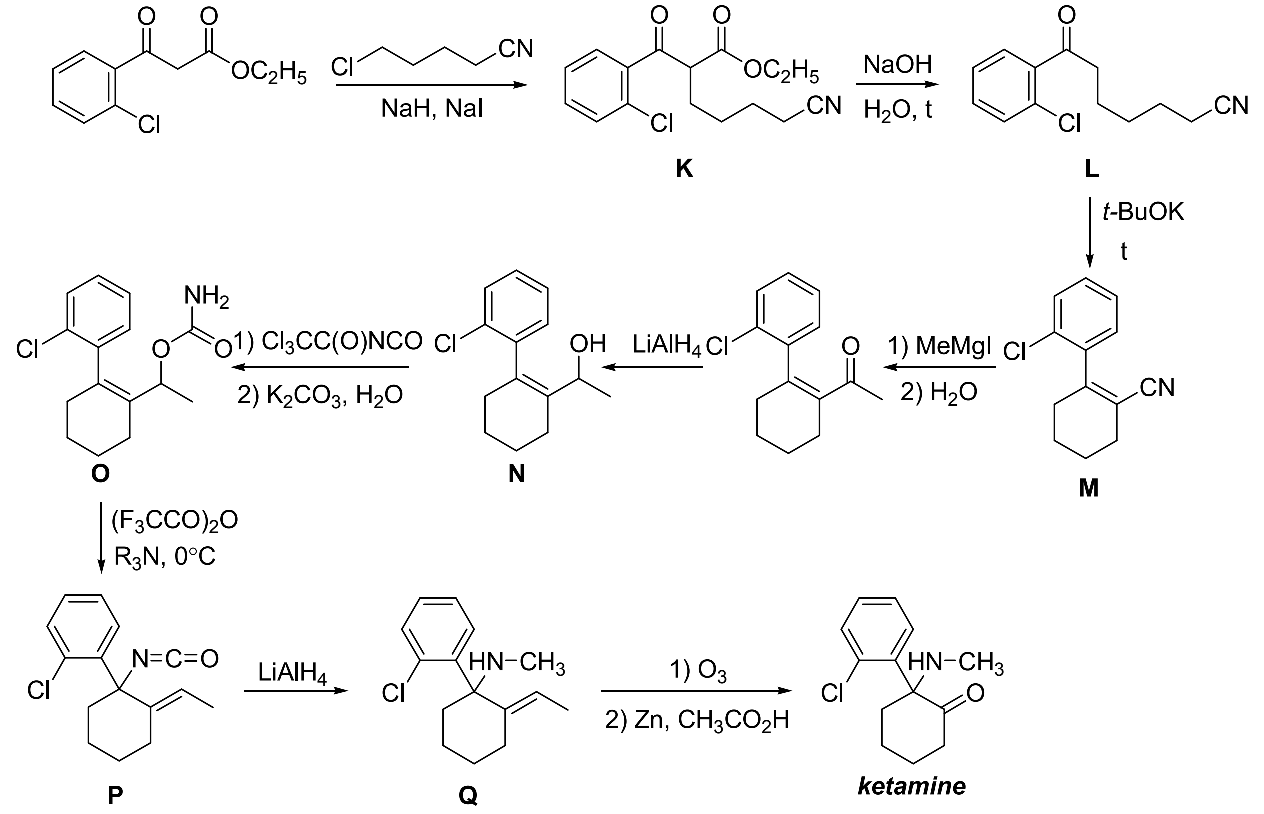
SECTION II. ORGANIC CHEMISTRY

Problem 1 (author Plodukhin A.Yu., Trushkov I.V.)

1. From brutto-formula of **A** we can see that formation of this compound is accompanied by the introduction of 4 carbon atoms, 6 hydrogen atoms and 1 oxygen atom. Accounting for reagent type, it is possible to say that this reaction is the Horner-Wadsworth-Emmons olefination during which carbonyl oxygen atom is substituted by $=CHCO_2C_2H_5$ fragment. Diisobutylaluminium hydride is the reducing agent using for the transformation of esters into either alcohols or aldehydes depending on the reaction conditions. As compound **B** reacts with isocyanate, we can conclude that this is alcohol but not aldehyde. The formed allyl carbamate **C** was treated with trifluoroacetic anhydride in the presence of trialkylamine and then with a strong base and *tert*-butanol. These steps corresponds to those in the scheme describing the allyl cyanate-to-isocyanate rearrangement (Ishikawa rearrangement). So, we can write down structural formula of compound **D** following the mechanism of this rearrangement given in the problem. Ozonation of **D** and oxidative decomposition of ozonide produce the corresponding acid which was then introduced into the reaction of amide bond formation. The open structure of the product allows for writing structural formulae of both **E** and **X**. Lithium borohydride reduces selectively ester function modifying no amide and carbamate functions. Alcohol **F**, formed during this reduction, was oxidized by Dess-Martin periodinane to aldehyde **G** which reacts with phosphonium ylide **Y** producing alkene **H**. The acid hydrolysis leads to *tert*-butoxycarbonyl group removal keeping amide groups intact. It is definitely clear from the molecular formula of compound **Z**. Structure of compound **Y** is quite clear. Indoline is acylated by bromoacetyl bromide (acyl bromide are more reactive than alkyl bromides$ moreover, alkylation product cannot form zwitter-ionic species). The formed amide reacts with triphenylphosphine affording phosphonium salt deprotonation of which leads to the phosphonium ylide (zwitter-ionic species). Therefore, we can write down all structures enciphered in the first scheme (12 structural formulae, 0.75 points for each; 9 points in total).



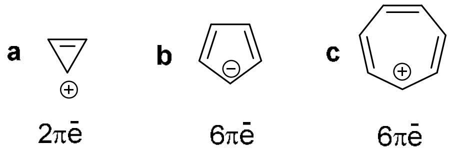
2. In the second scheme the first step is sodium iodide-catalyzed alkylation of enolate ion formed by ketoester deprotonation (highly nucleophilic iodide ion substitutes chlorine in the alkylating agent producing alkyl iodide which is very reactive electrophile; iodide ion serves now as leaving group). The alkaline hydrolysis of product **K** is accompanied by decarboxylation furnishing keton **L**. The next step is intramolecular aldol condensation herein methylene component is CH_2-moiety in α-position to the nitrile group. Product of this condensation is 2-aryl-1-cyanocyclohexene **M** which is attacked by Grignard reagent yielding intermediated hydrolysis of which affords ketone structure of which is given in the problem. The reduction of this ketone leads to allyl alcohol **N**. Its reaction with trichloroacetyl isocyanate produces carbamate **O** which then was introduced into the Ishikawa rearrangement. The reduction of formed allyl isocyanate **P** with $LiAlH_4$ yields 1-aryl-1-methylamino-2-ethylidenecyclohexane **Q**. Ozonation of product leads to C=C bond cleavage and C=O bond formation.



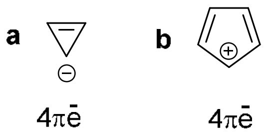
(8 structural formulae, 0.75 points for each; 6 points in total)

Problem 2 (author Shved E.N.)

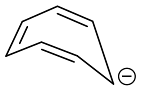
1. Accounting for number of delocalized π-electrons the following ions are aromatic (**A**):



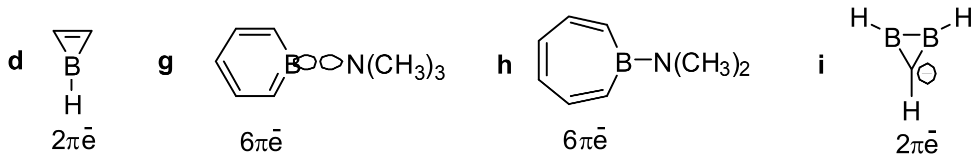
Two ions, which should exist in planar conformation only, are antiaromatic (**AA**):



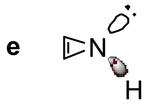
Oppositely, cycloheptatrienyl anion, similarly to cyclooctatetraene, can accept non-planar conformation in which destabilized effect of antiaromaticity is absent. Therefore, this anion is non-aromatic (**NA**). It was proved by fact that cycloheptatriene acidity is approximately equal to that of 1,3-pentadiene (**0.25 points for every right answer, 1.5 points in total**).

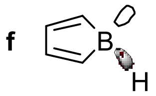


2. Heterocycles **d**, **g**, **h**, **i** are aromatic; they have (4n+2)-π-electrons.



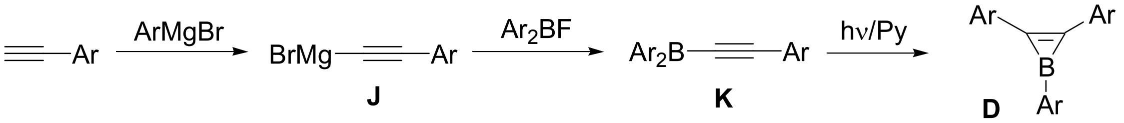
Heterocycles **e** and **f** are non-aromatic (**NA**).





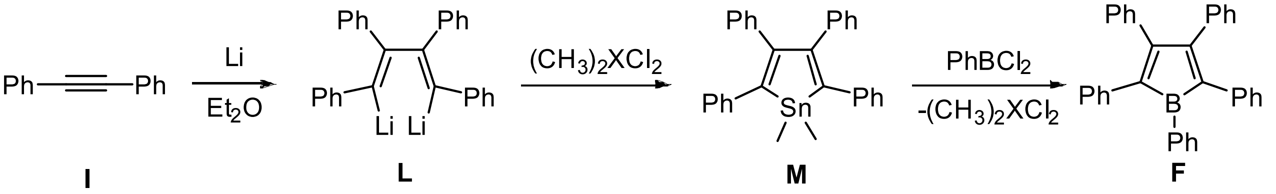
In compounds **d**, **h** and **i** free orbital of boron atoms participate in the formation of the fully conjugated π-electron system of aromatic system. In compound **g** free orbital of the boron atom is perpendicular to π-orbitals forming the aromatic electron system. In compounds **e** and **f** heteroatoms have tetrahedral configuration, free orbital of boron atom and occupied orbital of nitrogen atom do not interact with π-orbitals of double bonds (0.25 points for every right answer, 3 points in total).

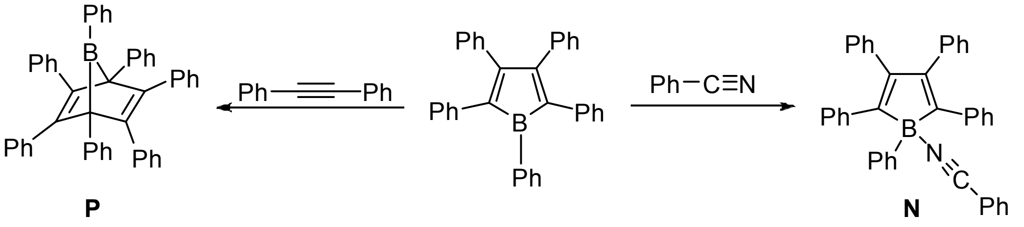
3. Accounting for fact that compound **D** containing ring **d** is isomer of **K**, we can decipher scheme of the **D** preparation:

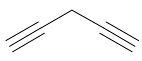


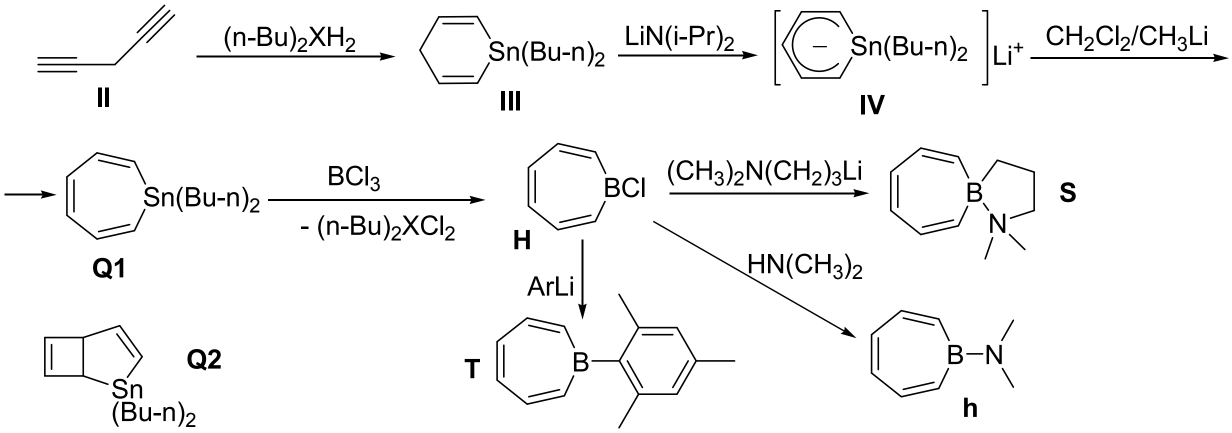
Carbon content in compound **D** supports this conclusion (0.5 points for every structure, 1.5 points in total).

4. As **F** is pentaphenyl derivative of ring **f**, M(**F**) = 444.384 g/mol. Therefore, M(**M**) = 444.384×1.137 ≈ 505.26 (g/mol). M(**X**) = 505.26×0.235 ≈ 118.7 (g/mmol). So, **X** is **Sn**. Therefore, $(CH_3)_2XCl_2$ is $(CH_3)_2SnCl_2$. Diphenylacetylene, on the contrary to PhCN, can not work as Lewis base. We can conclude that in reaction with diphenylacetylene **F** works as diene and in the reaction with benzonitrile as Lewis acid (0.75 points for every structure, 3 points in total).



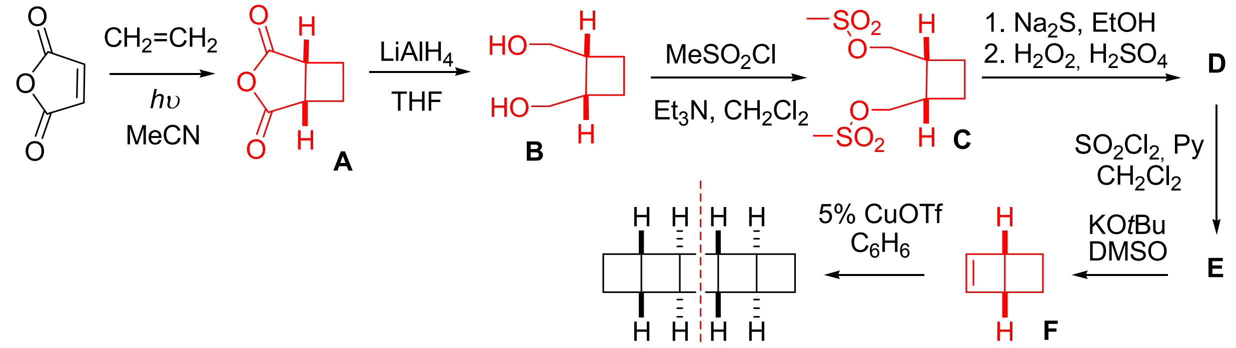


5. Knowning the NMR data of compound **II** and fragment which is present in this molecule, we can determine it as 1,4-pentadiyne,  (C_5H_4). All other compounds in the Scheme are cyclic, only heteroatoms have substituents. Therefore, **III** is product of [5+1]-annulation. Compound **H** contain seven-membered ring which is present in **h**. Therefore, **IV** → **Q1** step is the ring expansion. Compound **Q2** is bicyclic isomer of **Q1**. So (0.75 points for every structure, 6 points in total),

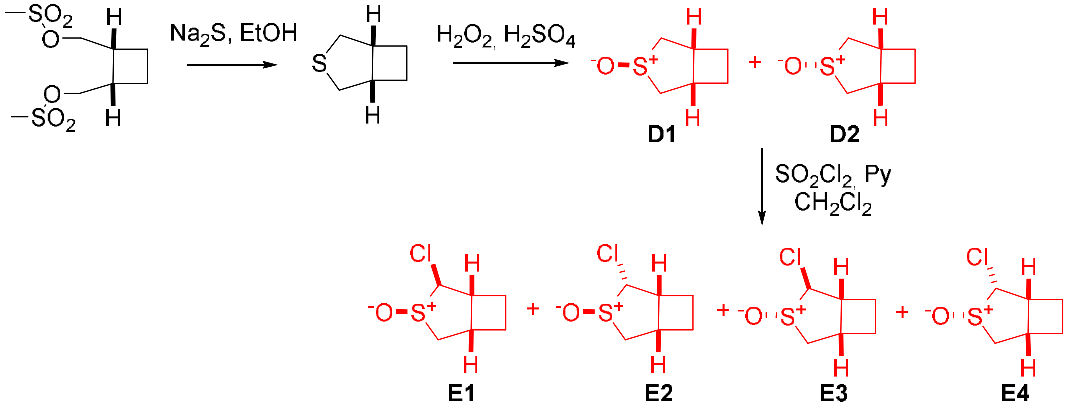


Problem 3 (author Volochnyuk D.M.)

1. Transformation of maleic anhydride to **C** can be easily deciphered on the basis of supposition that the first step is photochemical [2+2]-cycloaddition. This is supported by brutto-formula and symmetry of compound **A**. Moreover, statement that [5]-ladderane was obtained by dimerization of hydrocarbon **F** demonstrates that brutto-formula of **F** is C_6H_8. From symmetry of **F** and simple chemical logic it is possible to deduce that this is bicycle[2.2.0]hex-2-ene. This photochemical [2+2]-cycloaddition is usually referred to as Salomon-Kochi reaction.

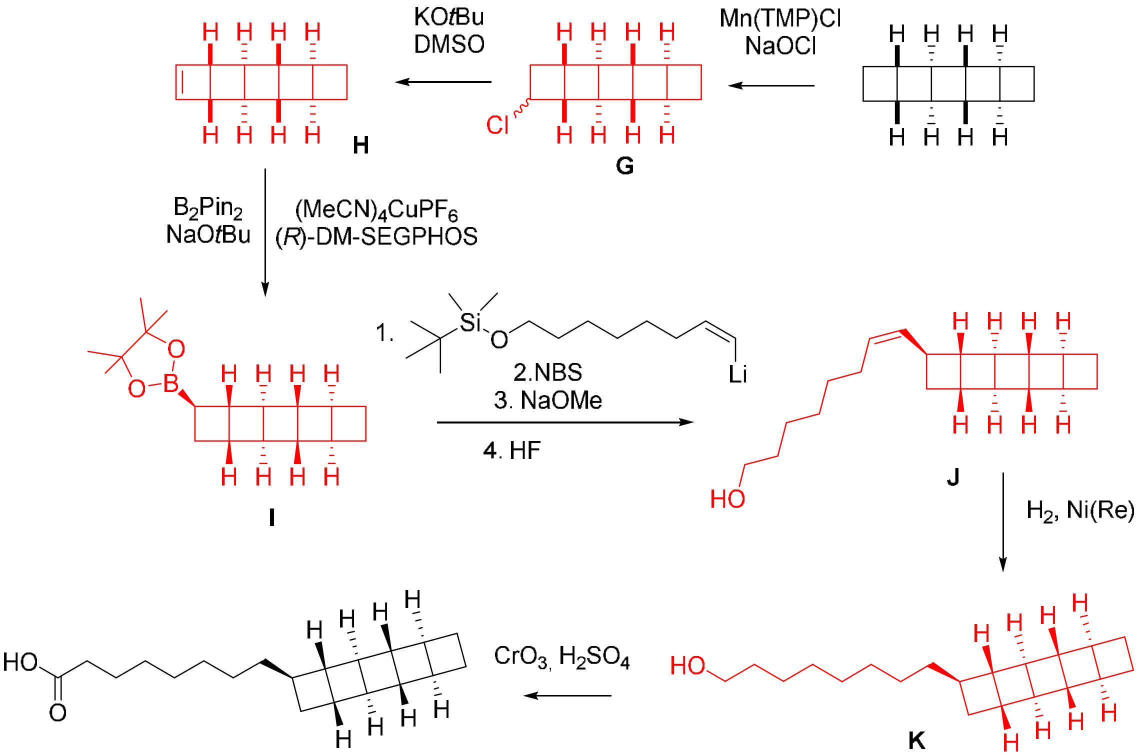


The reaction of biselectrophilic compound **C** with sodium sulfide can be interpreted as double nucleophilic substitution affording tetrahdydrothiophene ring closure. The further oxidation produces sulfoxide that is confirmed be brutto-formula of **D**. The chlorination of **D** yields α-chlorosulfoxide that can exist in four diastereomeric forms. The treatment of this compound with base leads to elimination giving rise to alkene **F** (Ramber-Backlund reaction).

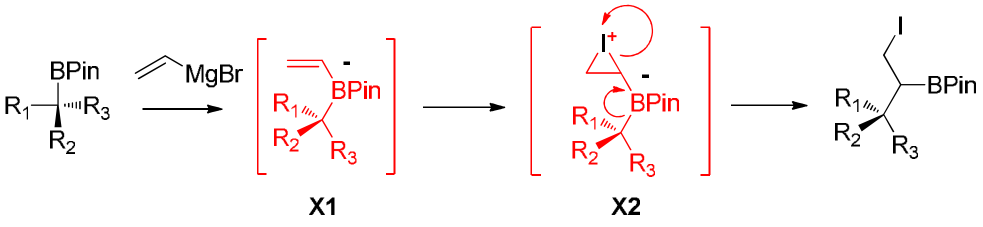


Further solution requires determination of structure of hydrocarbon **H**. From its brutto-formula we can say that its unsaturation degree is larger than that of [5]-ladderane by 1. Accounting for keeping the ladderane structure intact and next step (hydroboration), we can suppose that **H** is cycloalkene. From the data on the synthesis of **H** it is possible to conclude that **G** is some chloride obtained by selective chlorination of ladderane. Indeed, formation of **G** is the mild chlorination developed by John T. Groves from Princeton University in 2010.

To continue, we need to use prompt in the Scheme 1 of Problem (Zweifel coupling). From this scheme, we can conclude that compound **I** is ladderaneboronic acid pinacolate with the absolute configuration that corresponds to that in the final product. Compound **J** is desilylated product (treatment of the reaction mixture with HF) of its olefination (coupling). Structure of the last compound **K** can be determined on the basis of both retrosynthetic analysis (Jones reaction) and analysis of hydrogenation product **J**. (11 structural formulae, 1 point for each. 11 points in total)



2. To answer this question we need remember that: a) boron compounds are prone to form four-coordinated anionic complexes; b) the intermediates in the reaction of alkenes with iodine are three-membered cyclic iodonium cations. This helps us to write structures of **X1** and **X2** (2 points, 1 point for every intermediate):

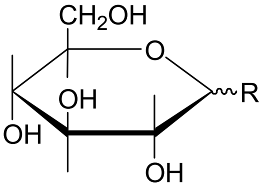


3. It is known that the introduction of double bonds into the lipid structures increases their fluidity (compare, for example, sunflower and product of its hydrogenation, margarine) and decreases density. Therefore, ladderane frameworks, which can be closely packed, should produce ultradense membranes (answer **b**). Moreover, high steric strains in ladderanes allow them to react with highly reactive intermediates of anammox (answer **d**). (two right answer, 1 point for each; for wrong answer – 0.5 points penalty; pointing out all four answers – 0 points; from 0 to 2 points in total).

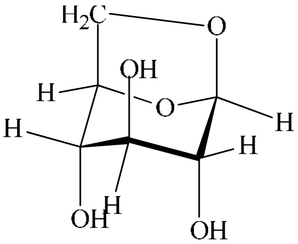
SECTION III. LIFE SCIENCES AND POLYMERS

Problem 1 (author Golovko Yu.S., Garifullin B.N.)

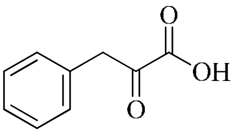
1. Taking into account that the anomeric configuration is not specified, one gets (1 point):

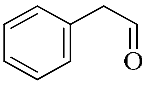


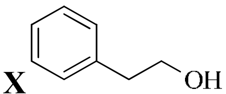
2. The molecular formula of **X** is $C_6H_{10}O_5$, which formally corresponds to a glucose "anhydride". The release of the aglycone is possible only as a result of an intramolecular nucleophilic attack on the anomeric center. High stability of the compound implies only five- or six-membered rings, while the chair form allows excluding 1,4-anhydride. Due to sterical reasons, the condensing groups should adopt axial positions. Thus, the structure of levoglucosan **X0** is (3 points):



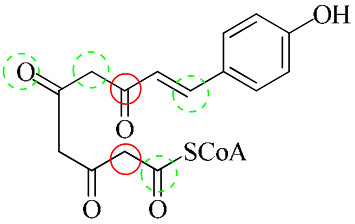
3. Assuming one oxygen atom in alcohol **X**, one gets its molecular mass of $\frac{16.00}{0.1310} = 122.1$. This corresponds to the molecular formula of $C_8H_{10}O$, which is in a good correlation with nine carbon atoms in phenylalanine and one decarboxylation step. Transamination should be the first step (decarboxylation would result in an oxygen free product, whereas reduction would give a chiral one). Similarly, decarboxylation is followed by reduction. Finally (1 point for each structure, 3 points in total):


X1

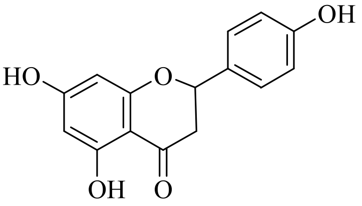

X2


X

4-5. Three repeating steps of malonyl-CoA addition to the starting molecule lead to **Y**. Existence of the common motif in 4-coumaroyl-CoA (**Y**) and resveratrol together with the fact that a carbonyl and methylene groups are needed for aldol condensation (encircled red) are good hints for the folding pattern. The thioester group should be involved in Claisen condensation during naringenin (**Z**) synthesis. Be careful deciding on the sets of six carbon atoms involved in each of Claisen condensation and Michael addition (encircled green) (2 points for each structure, 4 points in total).



Y



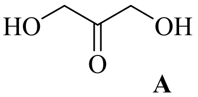
Z

6. Since the anomeric configuration is not specified, both α- and β-pyranosides are possible. With an account for two types of phenolic hydroxyl groups in resveratrol, 2·2= 4 different structures are possible (0.5 points).

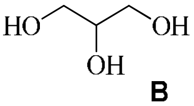
7. **A** is a monosaccharide with the general formula of $(CH_2O)_n$, containing 6.71% H by mass. **A** is a ketose. According to the *Acetobacteraceae* metabolism, the carbonyl group is formed by oxidation of the hydroxyl one (note the ethanol→acetaldehyde transformation). **B** can be represented as $C_nH_{2n+2}O_n$. Then:

$$\frac{1.008\cdot(2\cdot n+2)}{30.03\cdot n+2.016}=\frac{6.71+2.05}{100}$$

and n = 3. Thus, **A** is dihydroxyacetone (the only ketose with 3 C atoms), and **B** is glycerol (0.5 points for the calculations, 1 point for each of **A** and **B**, 2.5. points in total).

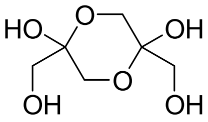


A



B

8. Formation of hemiketal is behind dimerization of **A** (1 point):



Problem 2 (author Garifullin B.N.)

1. Since the HCV RNA fragment is given in the 5'→3' direction, the miR-122 must follow the reverse 3'→5' direction due to anti-parallel orientation of complementary chains (0.5 point).

2. Let us rewrite the miR-122 sequence according to the answer in i. 1:

3'-UGUUUGUGGUAACAGUGUGAGGU-5'.

Next, one can exclude from consideration the stem-loop fragment of the viral RNA containing six consecutive G-C pairs, since their disruption is thermodynamically unfavorable. Rewriting the rest parts as the totally complementary RNA chain, one gets:

3'-UGGA-…-AUUAU-…-CUGUGAGGUGGUACUUAGUGAGGGG-5'

The matching is unambiguous for the first molecule:

miR-122 3'-UGUUUG**UGG**UAACAG**UGUGAGG**U-5'
compl. RNA 3'-**UGG**A-…-AUUAU-…-C**UGUGAGG**UGGUACUUAGUGAGGGG-5'

With due account for the fragment left, there is only one option for the second molecule:

miR-122 3'-UGUUUGU**GGU**AACAGU**GUGAGG**U-5'

compl. RNA 3'-UGGA-…-AUUAU-…-CUGUGAGGU**GGU**ACUUA**GUGAGG**GG-5'

(1.5 point for each miR-122 molecule, 3 points in total).

3. Since thymidine is opposite to adenosine in a DNA-RNA duplex, one needs to find vicinal adenosines (AA) in the miR-122 molecule. This is found only once:

3'-UGUUUGUGGU**AA**CAGUGUGAGGU-5'

The 9th adenosine located next by one nucleotide residue to the AA pair allows choosing the further direction:

3'-UGUUUGUGGU**AA**C**A**GUGUG**A**GGU-5'

The DNA analog of miravirsen being anti-parallel to miR-122, its structure is (2 points):

5'-CCATTGTCACACTCC-3'

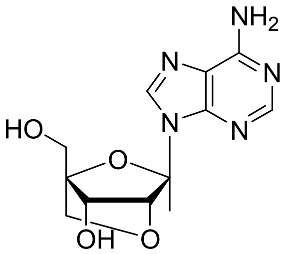
4. The completely protonated form of adenosine-5'-monophosphate has the molecular formula of $C_{10}H_{14}N_5O_7P$. Comparison of the latter with that of **Z** reveals that AMP formally loses one O atom and gains C and S atoms as a result of the AMP→**Z** transformation. Since:

- Hydroxyl groups at the 3'- and 5'- C atoms are involved in phosphodiester bonds formation;

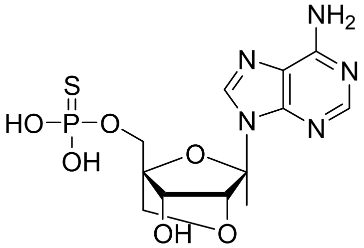
With due account for:

- The structure of intermediates in the synthesis of **Z**;
- High resistance of **Z**-based polymers towards hydrolysis (lacking 2'-OH);
- Presence of an additional cycle together with the "extra" carbon atom

one can conclude that the hydrocarbon moiety should contain the additional methylene bridge between 2'- and 4'- C atoms. The corresponding nucleoside is:



The unchanged nitrogenous base residue together with calculation of the molecular formula of the phosphoric acid residue reveal that O atom is substituted by S atom in it:



Z

The tautomeric form with –SH group is also accepted. Phosphorothioate (PS) modification of the RNA chain skeleton protects miravirsen from fast nuclease-assisted degradation (3.5 points).

5. Since the nucleic acids are quite easily hydrolyzed in gastrointestinal tract in man (consecutive action of the acidic medium in stomach and pancreatic nucleases in small intestine lumen), the peroral administration is least favorable if drug bioavailability is considered (1 point).

6. Nitrogenous bases in **X** and **Y** do not contain atoms/groups of atoms, which can be involved in hydrogen bond formation. Thus, only hydrophobic interactions are behind formation of the complementary pair. Such insertion does not alter the natural Watson-Crick DNA structure and does not interfere with DNA polymerase activity (1.5 points).

7. Presence of phosphorus in **W** as well as direct hints in the task text allow concluding that the metabolite is a nucleotide. The phosphorus to oxygen molar ratio in **W** is:

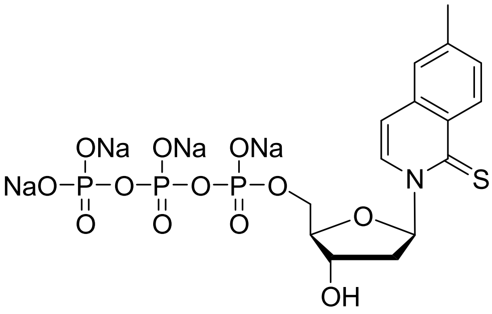
$$n(P):n(O) = \frac{15.00}{30.97}:\frac{31.01}{16.00} = 1:4$$

The general formula of any nucleotide derived from d5SICS is written as $C_{15}H_{n+17}NSO_{3n+3}P_n$. Thus, $\frac{3n+3}{n} = 4$, and $n = 3$ (triphosphate).

The molar mass of **W** is 619.2 g/mole, which exceeds that for $C_{15}H_{20}NSO_{12}P_3$ (531.3 g/mole). The solution comes if **W** is supposed to be a salt of an unknown cation with the atomic mass of:

$$A_r(\text{cat.}) = \frac{619.2 + 4\cdot 1.008 - 531.3}{4} = 22.98\ \text{AMU}$$

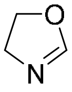
Thus, **W** is the tetrasodium salt of d5SICS-triphosphate (3.5 points).



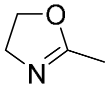
W

Problem 3 (authors Karpushkin E.A., Volochnyuk D.M., Zaborova O.V.)

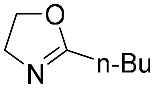
1. The parent heterocylic compouns **A** is an unsaturated representative. The empirical formula of the polymer unit coincides with that of the monomer (C_3H_5ON) upon the cycle opening polymerization. Among unsaturated heterocycles, only oxazoline meets the above mentioned empirical formula. The alternative solution (acylated aziridines) is partially granted, since being in contradiction to the given monomer synthesis (1.25 points for the structures of **A**, 0.25 point for each of the structures of **A1** – **A3**, 2 points in total; 1 + 0.75 points for aziridines).



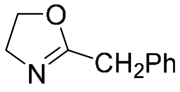
A



A1



A2



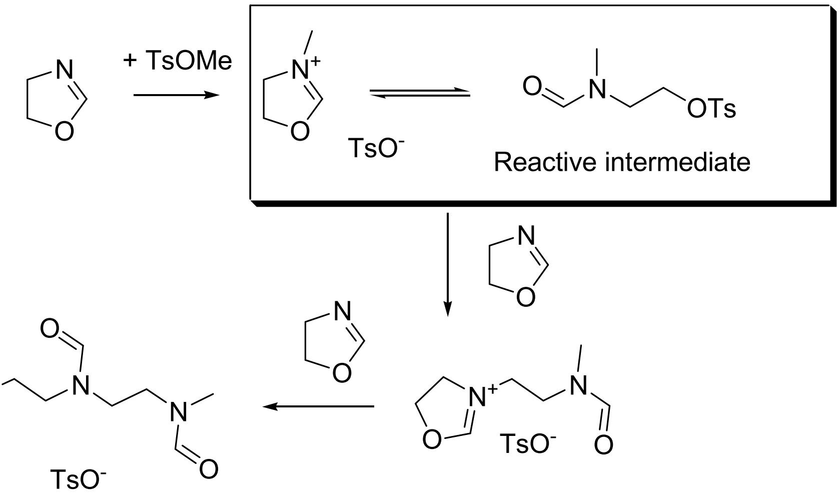
A3

2. The co-polymer containing **A1**, **A2**, and **A3** units in molar ratio of 68:13:5 is formed in both cases. The difference originates from the monomer loading. In the first case, the monomers are added sequentially leading to a block co-polymer. In the second case, all the monomers are loaded in a single batch resulting in a statistical co-polymer. The polymerization degree is calculated from the monomer-initiator ratio (0.93 g, 0.005 mol) taking into account that each initiator molecule gives rise to one macromolecule. In the case of **Q** each macromolecule additionally bears two terminal **A1** units in the head incorporated at the primary initiation step. Finally (3+2 points for complexly correct **P** and **Q** structures, 5 points in total; penalty: 0.25 point for each of an incorrect terminal group structure, wrong ratio, number or distribution of units (separate penalties for the mistakes in **P** blocks and statistical fragment):

$\mathbf{P} = \text{Me–}[\mathbf{A1}_{34}\text{–}(\mathbf{A2}_{13}\text{–}\mathbf{A3}_{5})_{\text{stat}}\text{–}\mathbf{A1}_{34}]_{\text{block}}\text{–pip}$

$\mathbf{Q} = \text{Me–}\mathbf{A1}_{2}\text{–}(\mathbf{A1}_{66}\text{–}\mathbf{A2}_{13}\text{–}\mathbf{A3}_{5})_{\text{stat}}\text{–OH}$

3. The polymerization mechanism with the intermediate (2 points):



4. The molar mass of the drug is 854 g/mol. The molar mass of **P** is 68×85.05 + 13×127.1 + 5×161.08 + 99.10 ≈ 8340 g/mol. $LC = m_{\text{drug}}/(m_{\text{drug}} + m_{\text{polymer}})\times 100\% = 0.45 \leftrightarrow m_{\text{drug}}/m_{\text{polymer}} = 0.818 \leftrightarrow n_{\text{polymer}}/n_{\text{polymer}} = 8$ (2 points)

5. 0.37 nmol/L × $17.7\cdot 10^{6}$ = 6.55 μmol/L = 5.6 g/L. (1 point)

6. 5.6 g/L: 6.7 mg/L = 836 times. (1 point)

7. $n\mathbf{P} \rightarrow \mathbf{P}_{n}$.; $K = [\mathbf{P}_n]/[\mathbf{P}]^{n}$; $\Delta G = -(1/n)RT\ln K = -(1/n)RT(\ln[\mathbf{P}_{\text{n}}] - n\ln[\mathbf{P}]) = -\text{RT}\{(1/n)\ln[\mathbf{P}_{\text{n}}] - \ln[\mathbf{P}]\} \approx \text{RT}\ln[\mathbf{P}] = RT\ln\text{KKM} = 8.314\cdot 298\cdot\ln(4.4\times 10^{-6}\ \text{mol/L}) = -30.6$ kJ/mol (2 points)

SECTION IV. ANALYTICAL CHEMISTRY

Problem 1 (author Dubenskiy A.S.)

1. In reaction **A,** a precipitate of bismuth oxalate is formed:

$$2Bi^{3+} + 3C_2O_4^{2-} = Bi_2(C_2O_4)_3\downarrow \text{ (0.75 points)}$$

2. Since 1 mL of oxalate solution corresponds to 13.93 mg of Bi, the amount of oxalate is $n(C_2O_4^{2-})$ = 1/1000 · 0.1000 = $1\cdot10^{-4}$ mol (0.75 points), the amount of bismuth n(Bi) = 13.93 / 1000 / 208.98 = $6.67\cdot10^{-5}$ mol (0.75 points), and the ratio n(Bi) : $n(C_2O_4^{2-})$ = $6.67\cdot10^{-5}$: $1\cdot10^{-4}$ = 2 : 3 (0.75 points). Thus, the composition of the obtained precipitate corresponds to formula $Bi_2(C_2O_4)_3$ (2.25 points in total).

3. According to the results of titration,

$n(C_2O_4^{2-})$ = 14.36 / 1000 · 0.1000 = $1.436\cdot10^{-3}$ mol (0.75 points),

n(Bi) = 2/3 · $n(C_2O_4^{2-})$ = 2/3 ·$1.436\cdot10^{-3}$ = $9.57\cdot10^{-4}$ mol (0.75 points),

c(Bi) = $9.57\cdot10^{-4}$ ·1000 / 25 = 0.03829 mol/L, or 0.03829·208.98 = 8.00 g/L (0.75 points, 2.25 points in total).

4. At the endpoint of titration, the BiInd complex is destroyed, releasing the free yellow indicator (reaction **C**):

$2BiInd + 3C_2O_4^{2-} = Bi_2(C_2O_4)_3\downarrow + 2\underline{Ind^{3-}}$ (0.75 points)

5. Reactions **D** – **L**:

$Bi^{3+} + Br^- + H_2O = \underline{BiOBr\downarrow} + 2H^+$ (reaction **D**) (0.75 points)

$BiOBr\downarrow + 5Br^- + 2H^+ = \underline{[BiBr_6]^{3-}} + H_2O$ (reaction **E**) (0.75 points)

$[BiBr_6]^{3-} + 3OH^- = BiOOH\downarrow + 6Br^- + H_2O$ (reaction **F**) (0.75 points)

$[Cr(NH_3)_6]^{3+} + [BiBr_6]^{3-} = [Cr(NH_3)_6][BiBr_6]\downarrow$ (reaction **G**) (0.75 points)

$[Cr(NH_3)_6][BiBr_6] + H_2O = [Cr(NH_3)_6]^{3+} + \underline{BiOBr\downarrow} + 2H^+ + 5Br^-$ (reaction **H**) (0.75 points)

$[Cr(NH_3)_6]^{3+} + 3OH^- = Cr(OH)_3\downarrow + 6NH_3\uparrow$ (reaction **J**) (0.75 points)

$4H_3BO_3 + 2NH_3 = B_4O_7^{2-} + 2NH_4^+ + 5H_2O$ или $H_3BO_3 + NH_3 = NH_4^+ + BO_2^- + H_2O$ (reaction **K**) (0.75 points)

$B_4O_7^{2-} + 2H^+ + 5H_2O = 4H_3BO_3$ or $BO_2^- + H^+ + H_2O = H_3BO_3$ (reaction **L**) (0.75 points, 6 points in total)

6. According to the results of titration:

$n(H^+)$ = 17.20 / 1000 ·0.1000 = $1.72\cdot10^{-3}$ mol (0.75 points),

$n(NH_3) = n(H^+)$ = $1.72\cdot10^{-3}$ mol (0.75 points),

n(Bi) = $n(NH_3)$ / 6 = $1.72\cdot10^{-3}$ / 6 = $0.29\cdot10^{-3}$ mol (0.75 points),

c(Bi) = $0.29\cdot10^{-3}$·1000 / 100 = 0.0029 mol/L (0.75 points).

Problem 2 (author Malinina L.I.)

1. a) $\alpha(Fe^{3+}) = [Fe^{3+}]/([Fe^{3+}] + [Fe(OH)^{2+}] + [Fe(OH)_2^{+}] + [Fe(OH)_3]) =$
$= (1 + \beta_1[OH^-] + \beta_2[OH^-]^2 + \beta_3[OH^-]^3)^{-1} = 2\cdot10^{-10}$ (1 point)

b) $Fe^{3+} + 3OH^- = Fe(OH)_3\downarrow$ or $Fe^{3+} + 3H_2O = Fe(OH)_3\downarrow + 3H^+$ (1 point)

c) Since the concentration of iron in the solution is limited by the condition of precipitate formation, we can estimate the maximal concentration of iron in the solution from the solubility product. Taking into account the fact that some iron is bound into hydroxocomplexes, $K_s = [Fe^{3+}][OH^-]^3 = \alpha(Fe^{3+})c(Fe)[OH^-]^3$, i.e. $c(Fe) = K_s/\alpha(Fe^{3+})[OH^-]^3 = 4\cdot10^{-8} - 8\cdot10^{-7}$ (depending on the calculation accuracy), i.e. the concentration is about 2 orders lower than the recommended concentration of 2 μM. Therefore, adding salts of iron(III) as fertilizers is useless because the recommended concentration cannot be achieved under these conditions (2 points).

2. a) Oxidation of iron(2+) and hydrolysis of the product: $4Fe^{2+} + O_2 + 2H_2O + 8OH^- = 4Fe(OH)_3$ and similar reactions (1 point).

b) The equilibrium constant of the reaction from the task is $K = [Fe^{3+}][OH^-]/[Fe^{2+}][O_2]^{0.25}$, and since $[Fe^{3+}] = K_s/[OH^-]^3$, $[Fe^{2+}] = K_s/(K[OH^-]^2[O_2]^{0.25}) \approx 10^{-28}$ M, i.e. extremely low, about 10^{-19} % of $c(Fe)$ (2 points).

3. a) In the presence of two ligands (EDTA and hydroxide ions) the total concentration of dissolved iron is $c(Fe) = [Fe^{3+}] + [FeY^-] + [Fe(OH)^{2+}] + [Fe(OH)_2^{+}] + [Fe(OH)_3]$. Using the equations for complex stability constants and the given values and taking into account that $[Y^{4-}] = \alpha(Y^{4-})c(EDTA) = 8\cdot10^{-4}\cdot3\cdot10^{-6} = 2.4\cdot10^{-9}$, we can obtain $\alpha(Fe^{3+}) = (1+\beta^{III}[Y^{4-}]+\beta_1[OH^-]+\beta_2[OH^-]^2 + \beta_3[OH^-]^3)^{-1} = 4\cdot10^{-17}$ (2 points). The dominating form of iron is its complex with EDTA: $\alpha(FeY^-) = [FeY^-]/(1+\beta^{III}[Y^{4-}]+\beta_1[OH^-]+\beta_2[OH^-]^2+\beta_3[OH^-]^3)=0.99$ (1 point).

b) Using the earlier calculated molar fraction, we can estimate the value of $[Fe^{3+}][OH^-]^3 = c(Fe)\alpha(Fe^{3+})[OH^-]^3 \sim 10^{-43}$ (2 points), which is lower than $K_s(Fe(OH)_3) = 10^{-38}$. Therefore, iron(III) does not precipitate in the presence of 1.5-fold excess of EDTA (2 points).

c) Both iron(II and III) form stable complexes with EDTA, so oxygen oxidizes iron according to the following scheme: $Fe^{2+}Y + ¼O_2 +½H_2O = Fe^{3+}Y + OH^-$. In this case the fraction of iron(II) can be estimated from the ratio $[Fe^{2+}Y]/[Fe^{3+}Y]$. Using the expressions for free iron ions obtained from the corresponding stability constants we can find that $[Fe^{3+}]/[Fe^{2+}]=[Fe^{3+}Y]/[Fe^{2+}Y]\cdot\beta^{II}/\beta^{III}$. The equilibrium constant of the redox reaction K is given in the task, so $[Fe^{2+}Y]/[Fe^{3+}Y] = \beta^{II}/\beta^{III}[OH^-]/[O_2]^{0.25}/K = 10^{-22}$, i.e. despite the presence of EDTA only about 10^{-20} % iron is iron(II) (3 points).

Problem 3 (author Kandaskalov D.V.)

1. Correct answers are: could be larger than 100 (b) and always positive (c) (0.25 points for each right answer, 1 point in all).

2. $A = \log\frac{I_0}{I} = -\log\frac{I}{I_0} = -\log\frac{T}{100} = 2 - \log T$ (1 point).

3. For the oxidation of oxalic acid we use the oxidized form of the coenzyme, NAD$^+$. Oxidation of oxalate is possible only to CO_2:

$$\begin{array}{l}
H_2C_2O_4 \longrightarrow 2CO_2 + 2H^+ + 2e^- \\
NAD^+ + H^+ + 2e^- \longrightarrow NADH \\
\hline
H_2C_2O_4 + NAD^+ + H^+ + 2e^- \longrightarrow 2CO_2 + 2H^+ + 2e^- + NADH
\end{array}$$

Reaction equation: $H_2C_2O_4 + NAD^+ \rightarrow NADH + 2CO_2 + H^+$ (1 point; 0.5 points for reaction and coefficients).

We should specify that there is no more oxalic acid in the solution, as it was in deficiency and thus it was completely oxidized. Carbon dioxide (CO_2) is a gas. Thus, we have the final solution with only NADH and NAD$^+$.

4. The visible region of spectrum begins at 400 nm, but neither form of NAD absorbs in this region; thus, the solution is colorless (answer: b) (1 point).

5. We have a mixture of two compounds. Taking into account that absorbance is an additive quantity, the spectrum is the superposition of the two spectra represented in the figure. The maximum value of T corresponds to minimal value of A (see question 2). Thus, the maximal value of T is at 390 nm (1 point).

6. Let us write the equation of light absorbance at two wavelengths for solution **2** (1 point):

$$A_{260}(2) = \left(\varepsilon_{260}(NADH)\cdot c(NADH) + \varepsilon_{260}(NAD^+)\cdot c(NAD^+)\right)\cdot l$$
$$A_{340}(2) = \left(\varepsilon_{340}(NADH)\cdot c(NADH) + \varepsilon_{340}(NAD^+)\cdot c(NAD^+)\right)\cdot l$$

Similar equations can be written for solution **3** (pure NADH) (1 point):

$$A_{260}(3) = \varepsilon_{260}(NADH)\cdot c(NADH)\cdot l$$
$$A_{340}(3) = \varepsilon_{340}(NADH)\cdot c(NADH)\cdot l$$

Also, we need the equation of material balance in coenzyme:

$$c(all) = c(NAD^+) + c(NADH)$$

(1 point, 3 points in all for writing *n* equations with *n* + *1* unknowns).

Let us analyze the UV-spectra: NAD$^+$ does not absorb at 340 nm, thus, $\varepsilon_{340}(NAD^+) = 0$ (0.5 points). The second important observation is practical equivalence of extinction coefficients of NAD$^+$ and NADH at 260 nm (1 point). Thereby, we obtain a system of *n* equations with *n* unknowns:

$$A_{260}(2) = \left(c(NADH) + c(NAD^+)\right)\cdot \varepsilon_{260}(NADH)\cdot l$$

$$A_{340}(2) = \varepsilon_{340}(NADH)\cdot c(NADH)\cdot l$$

We can also notice that the quantity of NAD$^+$ reacted is equal to the NADH quantity formed. It implies that the sum of these two concentrations is always equal to the initial concentration of NAD$^+$. As solution **1** was diluted 200-fold to obtain solution **2**, the total concentration of these two compounds is 0.125 mM. From the first equation we can calculate ε_{260}:

$$A_{260}(2) = \left(c(NADH) + c(NAD^+)\right)\cdot \varepsilon_{260}(NADH)\cdot l \Rightarrow$$

$$\varepsilon_{260}(NADH) = \varepsilon_{260}(NAD^+) = \frac{A_{260}(2)}{\left(c(NADH)+c(NAD^+)\right)\cdot l} = \frac{0{,}981}{0.125\cdot 10^{-3}\cdot 0.5} = 15700$$

Though we do not know the exact concentration of diluted NADH in solution **3**, we can use the fact that the ratio of absorbances at two different wavelengths is equal to the ratio of the corresponding extinction coefficients:

$$\frac{A_{340}(3)}{A_{260}(3)} = \frac{\varepsilon_{340}(NADH)\cdot c\cdot l}{\varepsilon_{260}(NADH)\cdot c\cdot l} = \frac{\varepsilon_{340}(NADH)}{\varepsilon_{260}(NADH)} \Rightarrow$$

$$\Rightarrow \varepsilon_{260}(NADH) = \frac{A_{260}(3)}{A_{340}(3)}\cdot \varepsilon_{340}(NADH) = \frac{0.433}{1.047}\cdot 15700 = 6500$$

Now we can calculate the NADH concentration:

$$c(NADH) = \frac{A_{340}(2)}{\varepsilon_{340}(NADH)\cdot l} = \frac{0.325}{6500\cdot 0.5} = 10^{-4}\,M = 0.1\,mM$$

Hence, NAD$^+$ concentration is 0.025 mM, as the sum of the two concentrations is 0.125 mM. Knowing that the concentrations in solution **1** are 200 times larger, we can obtain the initial concentrations for NADH and NAD$^+$: 20 and 5 mM.

Results (0.5 points for each of 6 values in the table, 3 points in all; 0.25 points in case of an arithmetic error):

Form of NAD	*c*, mM	ε_{260}, M^{-1}cm^{-1}	ε_{340}, M^{-1}cm^{-1}
NAD$^+$	20.0	15700	0
NADH	5.0	15700	6500

An alternative way of calculation involves taking into account the ratio of absorbances for solution **2**:

$$\frac{c(NADH)}{c(NADH)+c(NAD^+)} = \frac{A_{340}(2)}{A_{260}(2)}\cdot\frac{\varepsilon_{260}(NADH)}{\varepsilon_{340}(NADH)}$$

Using the relation for solution 3:

$$\frac{A_{340}(3)}{A_{260}(3)} = \frac{\varepsilon_{340}(NADH)}{\varepsilon_{260}(NADH)}$$

we obtain:

$$\frac{c(NADH)}{c(NADH)+c(NAD^+)} = \frac{A_{340}(2)}{A_{260}(2)}\cdot\frac{\varepsilon_{260}(NADH)}{\varepsilon_{340}(NADH)} = \frac{A_{340}(2)}{A_{260}(2)}\cdot\frac{A_{260}(3)}{A_{340}(3)} = \frac{0.325}{0.981}\cdot\frac{1.047}{0.433} = 0.80$$

Thereby, this formula shows us that the concentration of NADH is equal to $0.8\cdot c_0(NADH) = 0.8 \cdot 25 = 20$ mM. Then the concentration of NAD^+ is 5 mM. The extinction coefficients can be easily found (do not forget the 200-fold dilution).

7. Let us calculate NADH concentration in solution **1** at a given wavelength, for example, 260 nm:

$$c(NADH) = \frac{A_{260}(3)}{\varepsilon_{260}\cdot l} = \frac{1.047}{15700\cdot 0.5} = 1.333\cdot 10^{-4} M = 0.1333\ mM$$

Then, the coefficient of dilution will be:

$$k = \frac{c_0(NADH)}{c(NADH)} = \frac{4}{0.1333} = 30 \text{ (1 point).}$$

8. To obtain the minimal value of concentration in Beer-Lambert equation $c = \frac{A}{\varepsilon \cdot l}$, the numerator have to be minimal and the denominator maximal:

$$c_{\min} = \frac{A_{\min}}{\varepsilon_{\max}\cdot l} = \frac{2-\log T_{\max}}{\varepsilon_{\max}\cdot l} = \frac{2-\log 99}{15700\cdot 0.5} = 5.6\cdot 10^{-7} M \qquad \text{(1 point)}$$

The detection limit for both compounds is the same, since $\varepsilon_{\max}$ at 260 nm is the same for both compounds (0.5 points: 1.5 points in all).

SECTION V. PHYSICAL CHEMISTRY

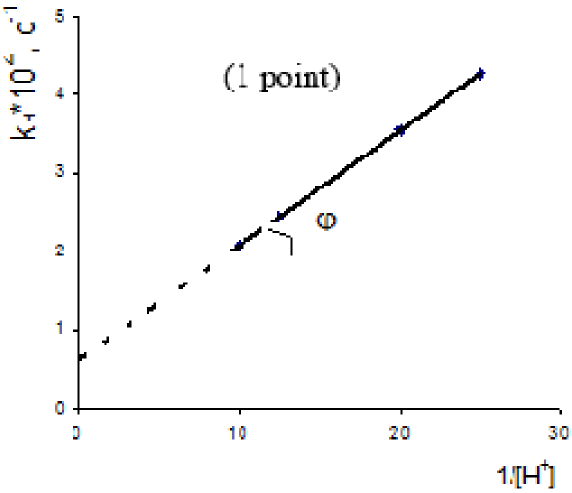
Problem 1 (authors Shved E.N., Rozantsev G.M.)

1. Isomerism of bond – ligand is bonded with central atom by different donor atoms (0.5 points): Cr–thiocyanate Cr–S–C≡N (0.5 points), Cr–N=C=S (0.5 points, 1.5 points in total).

2. According to Pearson, more stable combination is strong acid – strong base. Therefore isothiocyanate is stable and isomerization Cr–SCN → Cr–NCS goes spontaneously (1.5 points).

3. $[Co(en)_2(H_2O)\text{–}NCS]^{2+} + [Cr(H_2O)_6]^{2+} \rightarrow [Co(en)_2(H_2O)_2]^{2+} + [Cr(H_2O)_5\text{–}SCN]^{2+}$ (1 point). Structure fragment of intermediate: $[Co \cdots N{=}C\text{–}S \cdots Cr]^{4+}$ (1 point, 2 points in total)

4. Isothiocyanate has the largest splitting parameter $\Delta = hc/\lambda$ (ligand of strong field) and thiocyanate has the smallest (ligand of weak field) (0.5 points). λ_1 – $[Cr(H_2O)_5NCS]^{2+}$, λ_2 – $[Cr(H_2O)_5SCN]^{2+}$, λ_3 – $[Cr(H_2O)_6]^{3+}$ (1.5 points, total 2 points)



(1 point)

5. Since there is a straight-line equation $k_{obs} = a + b/[H^+]$, then $a = (k_i + k_a)$ – intercept on «y» axis (0.5 points).

$b = (k'_i + k'_a)\cdot K_a = \mathrm{tg}\,\varphi$ (0.5 points).

$$\begin{cases} 3.54\cdot10^{-4} = a + 20b \\ 2.08\cdot10^{-4} = a + 10b \end{cases}$$

$a = (k_i + k_a) = 6.20\cdot10^{-5}$ (s^{-1}) (0.5 points)

$b = (k'_i + k'_a)\cdot K_a = 1.46\cdot10^{-5}$ ($mol\cdot L^{-1}\cdot s^{-1}$) (0.5 points, total 2 points)

6. From the initial mixture there is only $[Cr(H_2O)_5SCN]^{2+}$ that reacts. Obtained in the result of reaction $[Cr(H_2O)_5NCS]^{2+}$ to $[Cr(H_2O)_6]^{3+}$ ratio is equal to ratio $k_i : k_a$. Similarly, $[Cr(H_2O)_4(OH)NCS]^{+} : [Cr(H_2O)_5(OH)]^{2+} = k'_iK_a : k'_aK_a$.

	$[(H_2O)_5Cr\text{-}SCN]^{2+}\rightarrow$	$[(H_2O)_5Cr\text{-}NCS]^{2+}$	$[(H_2O)_5Cr\text{-}SCN]^{2+}\rightarrow$	$[Cr(H_2O)_6]^{3+}$
init	0.45	0.55	0.45	0
react	x	x	y	y
fin	$0.45 - x$	$0.55 + x$	$0.45 - y$	y

There is no $[Cr(H_2O)_6]^{3+}$ in the initial state (λ_3 is absent in the spectrum) and $[Cr(H_2O)_5SCN]^{2+}$ in the final state (λ_2 is absent).

$\dfrac{0.55 + x}{y} = 2.46$ $x + y = 0.45$ $x = 0.161$ $y = 0.289$. Then $k_i : k_{H2O} = k'_iK_a/k'_aK_a$

$\dfrac{x}{y} = \dfrac{0.161}{0.289} = 0.557$ (1 point)

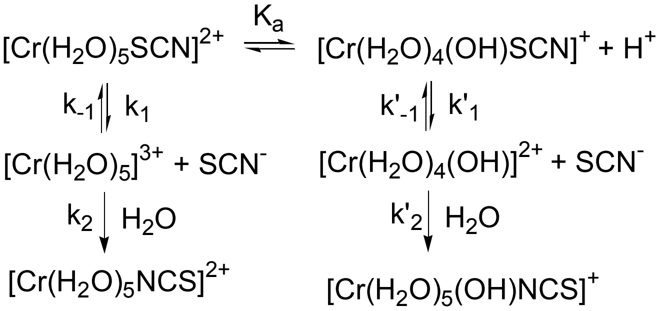
$$\begin{cases} k_\text{i} + k_\text{a} = 6.2\cdot10^{-5} \\ k_\text{i}{:}k_\text{a} = 0.557 \end{cases} \qquad \begin{cases} k'_\text{i}K_a + k'_\text{a}K_\text{a} = 1.46\cdot10^{-5} \\ k'_\text{i}K_a{:}k'_\text{a}K_\text{a} = 0.557 \end{cases}$$

$k_\text{i} = 2.22\cdot10^{-5}$ (s^{-1}); $k_\text{a} = 3.98\cdot10^{-5}$ (s^{-1}), $k'_\text{a}K_\text{a} = 9.38\cdot10^{-6}$ (M·s^{-1}); $k_\text{i}K_\text{a} = 5.22\cdot10^{-6}$ (M·s^{-1})

(0.5 points) (0.5 points)

(2 points in total)

7. (1 point)



8.

$$\frac{d[\mathrm{Cr(H_2O)_5}^{3+}]}{dt} = 0, \qquad k_1[\mathrm{Cr(H_2O)_5SCN^{2+}}] = k_{-1}[\mathrm{Cr(H_2O)_5}^{3+}][\mathrm{SCN^-}] + k_2[\mathrm{Cr(H_2O)_5}^{3+}][\mathrm{SCN^-}]$$

$$\frac{d[\mathrm{Cr(H_2O)_4(OH)^{2+}}]}{dt} = 0, \qquad k'_1[\mathrm{Cr(H_2O)_4(OH)SCN^+}] = k'_{-1}[\mathrm{Cr(H_2O)_4(OH)^{2+}}][\mathrm{SCN^-}] +$$

$$k'_2[\mathrm{Cr(H_2O)_4(OH)^{2+}}][\mathrm{SCN^-}]$$

$$[\mathrm{Cr(H_2O)_5}^{3+}] = \frac{k_1}{(k_{-1}+k_2)[\mathrm{SCN^-}]}[\mathrm{Cr(H_2O)_5SCN^{2+}}]$$

$$[\mathrm{Cr(H_2O)_4(OH)^{2+}}] = \frac{k'_1}{(k'_{-1}+k'_2)[\mathrm{SCN^-}]}[\mathrm{Cr(H_2O)_4(OH)SCN^+}]$$

$$w = \frac{k_2k_1}{k_{-1}+k_2}[\mathrm{Cr(H_2O)_5SCN^{2+}}] + \frac{k'_2k'_1}{k'_{-1}+k'_2}[\mathrm{Cr(H_2O)_4(OH)SCN^+}]$$

$$w = k_\text{i}[\mathrm{Cr(H_2O)_5SCN^{2+}}] + k'_\text{i}[\mathrm{Cr(H_2O)_4(OH)SCN^+}] \text{ (1 point)}$$

$$C^0 = [\mathrm{Cr(H_2O)_5SCN^{2+}}] + [\mathrm{Cr(H_2O)_4(OH)SCN^+}] = [\mathrm{Cr(H_2O)_5SCN^{2+}}] + \frac{K_\text{a}[\mathrm{Cr(H_2O)_5SCN^{2+}}]}{[\mathrm{H^+}]}$$

$$[\mathrm{Cr(H_2O)_5SCN^{2+}}] = \frac{[\mathrm{H^+}]C^0}{[\mathrm{H^+}]+K_\text{a}};\ [\mathrm{Cr(H_2O)_4(OH)SCN^+}] = C^0 - \frac{[\mathrm{H^+}]C^0}{[\mathrm{H^+}]+K_\text{a}} = \frac{K_\text{a}C^0}{[\mathrm{H^+}]+K_\text{a}}$$

$$w = \frac{k_\text{i}[\mathrm{H^+}]}{[\mathrm{H^+}]+K_\text{a}}\mathrm{C}^0 + \frac{k'_\text{i}K_\text{a}}{[\mathrm{H^+}]+K_\text{a}}C^0.\ \text{ If } [\mathrm{H^+}] >> K_\text{a} \quad w = (k_\text{i} + k'_\text{i}K_\text{a}/[\mathrm{H^+}])C^0$$

$$k_{obs} = k_\text{i} + k'_\text{i}K_\text{a}/[\mathrm{H^+}] \text{ (1 point, 2 points in total)}$$

Problem 2 (author Karpushkin E.A.)

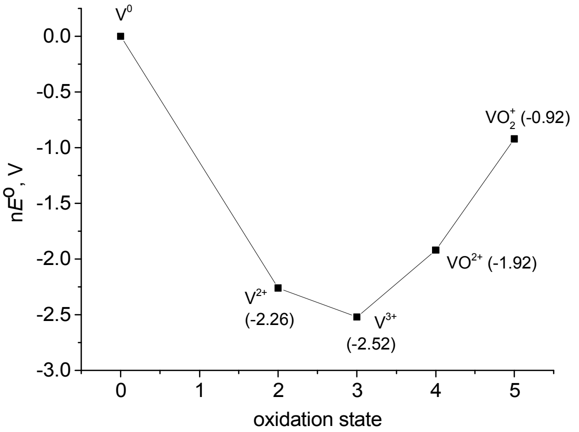
1. $E°(\mathrm{Fe^{3+}/Fe^{2+}}) > E°(\mathrm{Cr^{3+}/Cr^{2+}})$, hence the spontaneous ($\Delta G° < 0$) reaction during the battery discharge involves oxidation of chromium and reduction of iron. Then the following reactions accompany the battery charging: $\mathrm{Cr^{3+} + e^- \rightarrow Cr^{2+}}$, $\mathrm{Fe^{2+} \rightarrow Fe^{3+} + e^-}$ (0.5 point for the half reaction, 1 point in total).

2. $E = \Delta E^\circ = 0.77 + 0.41 = 1.18$ V (1 point)

3. Since $E^\circ(Cr^{3+}/Cr^{2+}) < E^\circ(H^+/H_2)$, reaction $Cr^{2+} + H^+ \rightarrow Cr^{3+} + ½H_2$ can occur spontaneously. In other words, hydrogen evolution ($2H^+ + 2e^- \rightarrow H_2$) will accompany reduction of Cr^{3+} during the battery charging. If this side reaction is not prevented, it reduces the real capacity of the battery and leads to disbalance of the anolyte and catholyte compositions (1 point).

4. M is a transition metal forming the compounds in oxidation states +2, +3, +4, and +5 (cf. the referenced potentials). Since the contents of O and S in compound **A** are high, it is likely sulfate of the metal (oxidation state of S other than +6 is unlikely, since the redox reaction involves the metal, and the anion should not be redox active). The S:O ratio in the compound (13.64/32.06 : 61.26/15.99 = 1:9) is less than that in sulfate anion (1:4). The sum of mass fractions of M, S, and O = 96.57%. The rest may be hydrogen, and part of oxygen constitutes the crystal hydrate water. Then S:H = 13.64/32.06 : 3.43/1.008 = 1:8, and the following part of the structure is decoded: $(?)OSO_4 \times 4H_2O$. Molar mass of M (at M:S = 1:1) is 21.64×32.08/13.64 = 50.9 g/mol, corresponding to vanadium. Other simple M:S ratios do not give reasonable solutions. Vanadium is known for the ability to form a series of oxygen-containing cations (i. e. vanadyl VO^{2+}) and exhibits the oxidation states listed in the task for M. Hence, M is vanadium and **A** is $VOSO_4 \times 4H_2O$, vanadyl sulfate tetrahydrate (1.5 point for the metal, 1.5 point for the salt, 1 point for hydrate = 4 points in total).

5. Evident restrictions for the anolyte and catholyte composition are as follows. First, V(0) cannot be a redox pair component, since it is unstable at pH = 0. Second, a redox pair components should not comproportionate in the solution. Stability of the redox pairs against comproportionation can be conveniently estimated from the Frost diagram (see the figure; the diagram is plotted using the standard oxidation potentials, the plotting is evident from the given coordinates): is the point corresponding to an intermediate oxidation state is below the line connecting the points for a higher and a lower oxidation state, the comproportionation is thermodynamically favorable. For example, compounds of V^{II} and V^{IV} comproportionate in aqueous solution to form a V^{III} compound.



From the diagram, it is evident that possible redox pairs are $V^{II} + V^{III}$, $V^{III} + V^{IV}$ and $V^{IV} + V^{V}$. (The same can be concluded from calculation of ΔG° of the possible comproportionation reaction, $\Delta G^\circ < 0$ will mean the instability of the redox pair) (1 point for each pair, 3 points in total).

6. Let us calculate $\Delta E°$ for the possible electrolytes:

$V^{II} + V^{III}$ and $V^{III} + V^{IV}$; $\Delta E° = 0.34 + 0.25 = 0.59$ V

$V^{II} + V^{III}$ and $V^{IV} + V^{V}$; $\Delta E° = 1.00 + 0.25 = 1.25$ V – the highest voltage

$V^{III} + V^{IV}$ and $V^{IV} + V^{V}$; $\Delta E° = 1.00 – 0.34 = 0.66$ V

(0.25 point for the calculation + 0.25 point for the correct selection – 1 point in total. Correct calculation for no more than 3 pairs is graded).

7. $V^{3+} + e^- \rightarrow V^{2+}$ and $VO_2^+ + e^- + 2H^+ \rightarrow VO^{2+} + H_2O$

It is incorrect to give vanadate (VO_3^-) as the V^V compound due to instability in acidic medium. From the second equation it follows that the electrons transfer (current in the external circuit) during the battery charge/discharge should be compensated by the protons transport through the membrane, i. e. it should exhibit proton conductivity. At the same time the membrane should not pass through the vanadium containing ions. Development of such selective membranes is a complex issue currently run at Chemistry department of MSU (0.5 point for each equation, 0.5 point for proton conductivity, 0.25 point for each vanadium-containing cation, 2 points in total).

Note: the half reactions can be alternatively written as

$V_2(SO_4)_3 + 2e^- \rightarrow 2VSO_4 + SO_4^{2-}$ and $(VO_2)_2SO_4 + 2e^- \rightarrow 2VOSO_4 + SO_4^{2-}$.

From this scheme, the membrane should be permeable to sulfate (or hydrosulfate at pH = 0) ions. In reality, proton transfer is much easier, but statement of (hydro)sulfate conductivity of the membrane is not incorrect.

8. For the redox flow battery, $\Delta E° = 1.25$ V (i. 6), $\Delta G° = 120.6$ kJ/mol. In view of the solutions concentration and the stated losses, useful energy capacity of 1 L of the anolyte (catholyte) solution is 120.6×2×0.9×0.93 = 201.9 kJ. On the other hand, for the commercial UPS, 10 kW×2 h = 10 kJ/s×7200 s = 72000 kJ. Hence, the UPS can be substituted by a redox flow battery with the 356 L tanks for anolyte and catholyte. The calculated mass of the electrolytes (without the tanks!) is just slightly higher than that of the commercial UPS of the stated capacity (about 200 kg) (2 points for correct calculation).

Problem 3 (author Borshchevsky A.Ya.)

1. Insertion of $q = CU$ in (**1**), gives

$$E = \frac{CU}{4\pi\varepsilon_0 r^2} = \frac{U}{4\pi\varepsilon_0 r^2}\cdot 4\pi\varepsilon_0 r = \frac{U}{r} = \frac{2000}{500\times10^{-10}} = \underline{4\cdot10^{10}\ \text{V/m}}. \qquad \text{(1.5 points)}$$

2. For lack of the intrinsic dipole moments for hydrogen and oxygen the matter is reduced to calculation of P for 1 mol of gaseous water: $P = N_A d_0 = 6.02\cdot10^{23}\times6.17\cdot10^{-30} = 3.714\cdot10^{-6}$ C·m. With the help of (**3**) one finds

$$K/K_0-1=\exp\left(\frac{3\cdot10^6\times3.714\cdot10^{-6}}{2\times8.314\times300}\right)-1=\underline{0.0022359}\,. \qquad \text{(2 points)}$$

3. The dipole moment of 1 mol of gas in standard state $P_\mathrm{m} = V_\mathrm{m}\chi E$. As $V_\mathrm{m} = RT/p°$, $p° = nk_\text{Б}T$ and $R = N_\mathrm{A}k_\text{Б}$, according to (**2**) we obtain

$$G° = G_0° - \frac{1}{2}P_\mathrm{m}E = -\frac{1}{6}\frac{nd_0^2}{k_\text{Б}T}\frac{RT}{p°}E^2 = \underline{-\frac{1}{6}\frac{(N_\mathrm{A}d_0E)^2}{RT}}\,. \qquad \text{(3 points)}$$

4. With the help of (**3**) one finds:

$$K/K_0-1=\exp\left[\frac{1}{6}\left(\frac{N_\mathrm{A}d_0E}{RT}\right)^2\right]-1=\exp\left[\frac{1}{6}\left(\frac{6.02\cdot10^{23}\times6.17\cdot10^{-30}\times3\cdot10^{6}}{8.314\times300}\right)^2\right]-1=\underline{0.0000033}$$

As is seen, the effect of electric field is about three orders of magnitude weaker, than in previous case (2 points).

5. For a triplet state $2S + 1 = 3$, whence $S = 1$ (1 point). $\mu_0(\mathrm{O}_2) = 2\mu_\mathrm{B}\sqrt{1(1+1)} = \sqrt{8}\cdot\mu_\mathrm{B}$ (0.5 points, totally 1.5 points).

6. The molecular volume concentration is $n = p/k_\text{Б}T$. For the standard pressure $p° = 1.01325\cdot10^6$ dyne/sm^2 from the formula (**9**) we find: (2 points)

$$\text{æ}(\mathrm{O}_2,\text{г})=\frac{p°\mu_0^2}{3(k_\text{Б}T)^2}=\frac{8p°\mu_\mathrm{B}^2}{3(k_\text{Б}T)^2}=\frac{8\times1.01325\cdot10^6\times(0.927\cdot10^{-20})^2}{3\times(1.38\cdot10^{-16}\times300)^2}=\underline{1.337\cdot10^{-7}}$$

7. Intrinsic magnetic moment for the molecules H_2 and H_2O is absent, therefore the change of magnetic moment in reaction (**4**) equals $-M(\mathrm{O}_2)/2 = -\text{æ}V_\mathrm{m}B/2$, where V_m – molar volume of gaseous oxygen at a pressure $p°$. In view of $V_\mathrm{m} = RT/p°$ from the formula (**7**) we find (3 points)

$$K/K_0-1=\exp\left[-\frac{M(\mathrm{O}_2)\cdot B}{4RT}\right]-1=\exp\left(-\frac{\text{æ}B^2}{4p°}\right)-1=\exp\left[-\frac{2}{3}\left(\frac{\mu_\mathrm{B}B}{k_\text{Б}T}\right)^2\right]-1=$$

$$=\exp\left[-\frac{2}{3}\times\left(\frac{0.927\cdot10^{-20}\times10^4}{1.38\cdot10^{-16}\times300}\right)^2\right]-1=\underline{-0.0000033}$$

By this means the shift of equilibrium is quite negligible.