LIFE SCIENCES AND POLYMERS

Problem II-1 (author Garifullin B.N.)

II-1.1 Five π-bonds can be distributed among three small molecules in three ways: $3 + 1 + 1$ (*a*), $3 + 2 + 0$ (*b*), or $2 + 2 + 1$ (*c*). However, even vinylacetylene (which contains three π-bonds) has a molecular mass far exceeding the range specified in the problem; therefore, only option (*c*) remains under consideration. Two π-bonds are contained in acetylene ($H{-}C{\equiv}C{-}H$) and hydrogen cyanide ($H{-}C{\equiv}N$) with $M_r \leq 30$ a.m.u. (N_2 and CO are formed from two atoms each, which does not satisfy the definition of a PM). Then the third compound of the set must contain one π-bond and four atoms. Under these criteria, formaldehyde (H_2CO) is appropriate.

Note which functional groups can be present in prebiotic molecules.

(0.5 points for each molecular formula; total **1.5 points**)

II-1.2 The molecular formula of cytosine is $C_4H_5N_3O$. Since the reaction equations are given in the scheme, one can easily find the sum of the atoms in molecules **X1** and **Y1** by balancing the water molecules: $C_4H_5N_3O - H_2O = C_4H_3N_3$.

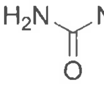
Note that both PM belong to the "simple" category, meaning they contain no more than five carbon atoms. The formula $C_4H_3N_3$ implies a total of 10 atoms ($4 + 3 + 3$); therefore, to meet the condition, the molecules **X1** and **Y1** must each be composed of exactly five atoms (combinations of $6 + 4$, $7 + 3$, or $8 + 2$ are impossible because then one of the substances would fall into the "complex" category).

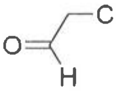
Also note that from a chemical point of view, in non-ionized molecules an even number of nitrogen atoms must be accompanied by an even number of hydrogen atoms, and an odd number by an odd number. Thus, two sets of molecular formulae are possible: $CN_2H_2 + C_3NH$ (1) and $CN_3H + C_3H_2$ (2). Here it must be understood that molecules present in interstellar gas are no different from their terrestrial counterparts and must be resistant to isomerization and decomposition (albeit at a temperature of approximately 3 K). On this basis, we exclude option (2), which would imply, for example, a cyclic structure containing an *sp*-hybridized carbon atom.

Taking the first set as the basis, it is easy to see that both molecules must contain a nitrile group and exhibit the following order of bonds between atoms:

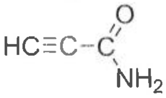
$H_2N{-}C{\equiv}N$ **X1** $\qquad$ $HC{\equiv}C{-}C{\equiv}N$ **Y1**

Considering the structure of cytosine itself, the formulae of the intermediates **X2** and **Y2** are determined uniquely (the correct association is aided by comparing the molecular masses of urea and cyanoacetaldehyde).


X2

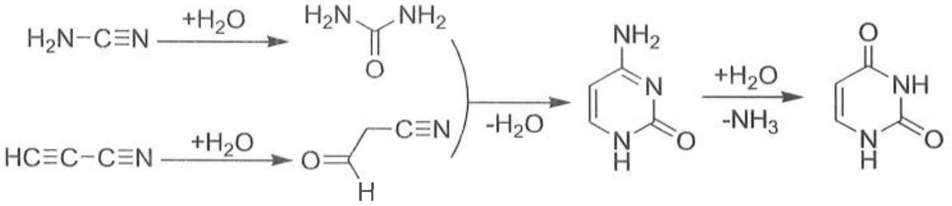

Y2

Note that the given below alternative product of the reaction of **Y1** with water (by analogy with the synthesis of urea) cannot be a direct precursor of cytosine due to its structure.



(1 point for each molecular formula; total **4 points**)

II-1.3 Based on the premise of the problem, the simplest method for synthesizing uracil from cyanamide, cyanoacetylene, and water is via the intermediate formation of cytosine, followed by its hydrolysis (using one more equivalent of water!) to yield the desired nitrogenous base:



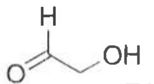
The hydrolysis reaction of cytosine yielding uracil was later "put on stream" by living matter upon the evolutionary appearance of the corresponding enzyme – cytosine deaminase.
Note that the answer to the question can be obtained without decoding the structures in the initial scheme.
(total **1 point**)

II-1.4 According to the reaction equation, the sum of the molecular masses of **Z1** and **Z2** equals the molecular mass of ribose ($M_r = 150$). Then one can write the following mathematical equation (remember that we are dealing with natural numbers):

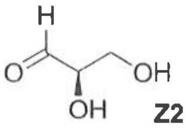
$$a_1 \cdot a_2 \cdot \ldots \cdot a_n \cdot k + a_1 \cdot a_2 \cdot \ldots \cdot a_n \cdot m = 150$$
$$a_1 \cdot a_2 \cdot \ldots \cdot a_n \cdot (k+m) = 2 \cdot 3 \cdot 5 \cdot 5$$

$k + m = 5$, since the single-digit prime factors are 2, 3, 5, and 7 – but only 5 and 7 can be represented as the sum of two others (here we applied the fundamental theorem of arithmetic). Thus, the molar masses of **Z1** and **Z2** are 60 and 90 g/mol, respectively ($k = 2$, $m = 3$).
(total **1.5 points)**

II-1.5 Based on the formula for ribose ($C_5H_{10}O_5$), one can unambiguously establish the molecular formulae of the prebiotic molecules: $C_2H_4O_2$ (**Z1**) and $C_3H_6O_3$ (**Z2**). No other formulae can be proposed for the previously obtained molar masses and elemental compositions (note that both molecules contain more than six atoms each, thus meeting the definition of complexity adopted in astrobiology).
Given the identity of the functional groups – an aldehyde and hydroxyl groups – the structures of the acyclic PM (the dioses and trioses) are determined uniquely; moreover, D-ribose, based on the mechanism for pentose synthesis (aldol condensation), should be formed specifically from D-glyceraldehyde.



Z1

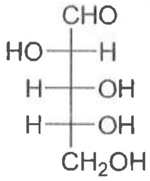


Z2

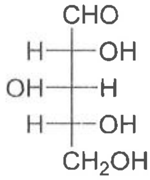
Glycoaldehyde (**Z1**) and glyceraldehyde (**Z2**) have been detected in molecular clouds from which new planetary systems form, which is indirect evidence of the existence of these compounds on early Earth.
(0.75 points for each structural formula; total **1.5 points**; −0.25 points penalty for incorrect stereoisomerism)

II-1.6 Note that the number of stereocenters in any aldopentose is three, which implies the existence of eight (2^3) possible stereoisomers. Exactly this number of compounds would be formed if a racemic mixture of the two stereoisomers of glyceraldehyde was introduced into the reaction (it should be understood that both isomers should be present in roughly equal amounts in interstellar clouds).
However, the number of obtained isomers is exactly half as many, because in the analyzed experiment one of the carbon atoms of the pentose has a predetermined configuration

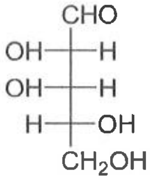
(reexamine the aldol condensation process!). The structures of the three remaining D-aldopentoses in the Fischer projection are shown below:



D-arabinose



D-xylose

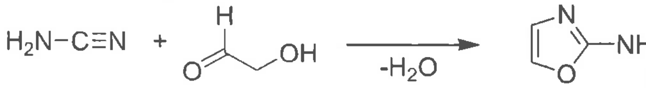


D-lyxose

At the same time, the mechanism we have analyzed for the formation of various pentoses does not imply stereoselectivity (especially under the conditions of a nascent planet), which means that there are no obstacles to the presence of all eight stereoisomers in living nature, although with varying degrees of involvement in biochemical processes due to complex and not always well-understood processes of chemical evolution.

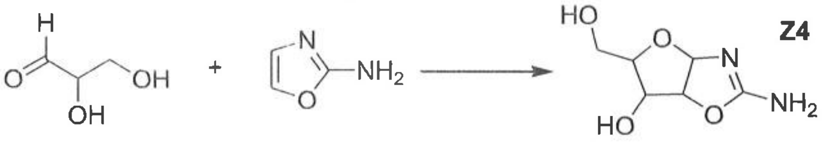
(0.5 points for each monosaccharide structure in any projection, 1 point for selecting the existence of the compounds; total **2.5 points**)

II-1.7 In the reaction of cyanamide with glycoaldehyde, by analogy with the cytosine synthesis reaction, a monocyclic product (2-aminooxazole) is formed:



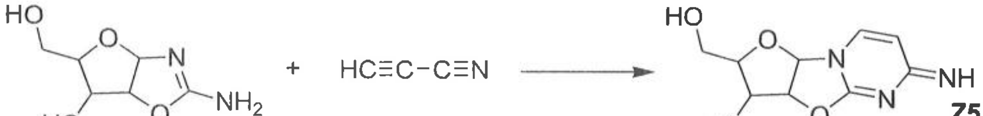
Z3

Z3 should then react with glyceraldehyde to yield a bicyclic product containing at least three heteroatoms. Moreover, since both components for the classical synthesis of ribose are already engaged, a precursor of the carbohydrate portion (containing four oxygen atoms) linked with a fragment of the future nitrogenous base should be formed:



Z4

Z5 is a tricyclic compound containing at least four heteroatoms, which must already include a pyrimidine fragment with a specified position of the exocyclic groups of cytosine, as the final stage of the synthesis is formally the attachment of a phosphate group to the carbohydrate part of the molecule.

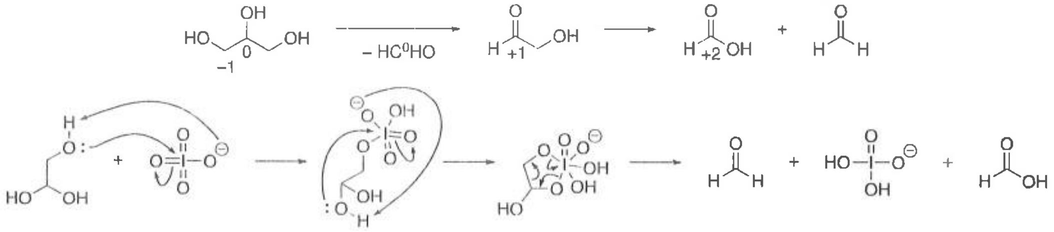


Z5

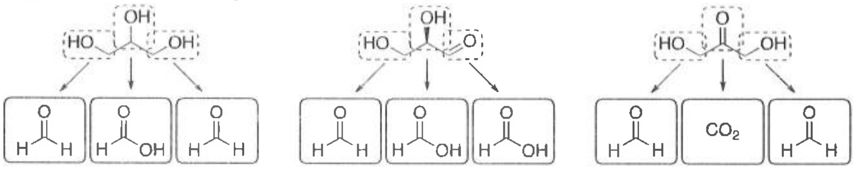
(1 point for each structure of **Z3–Z5**; total **3 points**)

Problem II-2 (authors Grishin D.A., Ozhimalov I.D.)

II-2.1 From the mechanism of ethylene glycol cleavage provided in the problem statement, it can be concluded that fragments containing primary hydroxyl groups will yield formaldehyde as a result of the Malaprade reaction. Such a C–C bond oxidation by an equimolar amount of metaperiodate is a two-electron process (each carbon of the cleaved bond increases its oxidation state by 1). If, during the cleavage of a more complex polyol, carbonyl compounds are formed, they may undergo further cleavage in an excess of metaperiodate. This reaction occurs because, in aqueous solution, aldehydes and ketones can convert into geminal diols and be cleaved via the Malaprade reaction according to the following scheme:



Thus, glycerol, D-glyceraldehyde, and dihydroxyacetone will yield the following products of oxidative cleavage via the Malaprade reaction.



(0.25 points for each product of oxidative cleavage corresponding to the enframed fragment of the starting substrate; total **1.5 points**)

II-2.2 D underwent partial oxidative cleavage of its vicinal diols, during which the hydroxyl groups are transformed into aldehyde groups and the carbonyl groups into carboxyl groups. Note that the pairwise combination of the reaction products in each case is unique in terms of yielding a single fragment (without stereoisomerism) – the cleaved C–C bond is conceptually reformed in only one way due to the nonequivalence of the terminal groups of the molecules. Combination via the keto-group is not possible, based on the condition that **D** is unbranched. The total number of combinations of the products can be calculated using the formula $C_k^n = \frac{n!}{k!(n-k)!}$, where *n* is the number of elements in the group, and *k* is the number of elements in the combination.

$$C_2^6 = \frac{6!}{2!\,4!} = 15$$

The uniqueness of the resulting chemical structure (fragment) means that the order of selection of elements in the subset is not important (i.e., it does not matter whether we conceptually attach product 1 to product 2 or vice versa). The diol cleaved into two aldehydes can have any configuration of its chiral centers, so that for each combination there are 4 fragments. In the fragment obtained by a combination where one product contains a carboxyl group there is only one chiral center, yielding 2 variants for that combination (there are 5 such combinations out of 15). Hence, the total number of variants of fragments of compound **D** is $10 \cdot 4 + 5 \cdot 2 = 50$.

(1.5 points for the number of theoretically possible unbranched fragments of **D**; total **1.5 points**)

II-2.3 As a result of the complete oxidative cleavage of **C** with an excess of sodium metaperiodate, a mixture of formic acid and formaldehyde, as well as sodium iodate, is formed. Upon addition of an excess of potassium iodide solution in aqueous sulfuric acid to the obtained mixture, the following reactions occur:

– the excess metaperiodate is reduced by iodide to molecular iodine

$IO_4^- + 11I^- + 8H^+ = 4I_3^- + 4H_2O$ (**reaction 1**);

– the iodate produced in the Malaprade reaction is reduced by iodide

$IO_3^- + 8I^- + 6H^+ = 3I_3^- + 3H_2O$ (**reaction 2**).

Oxidation of iodine by thiosulfate during titration:

$$I_3^- + 2S_2O_3^{2-} = 3I^- + S_4O_6^{2-}$$ **(reaction 3)**

Variants of writing the reactions with I_2 instead of I_3^- and with $H_2IO_4^-$ instead of IO_3^- are acceptable.

(0.5 points for each reaction equation; total **1.5 points**)

II-2.4 The amount of thiosulfate used for titration is

$$n = \frac{14.0}{1000}\,\mathrm{L} \cdot \left(0.0500\,\frac{\mathrm{mol}}{\mathrm{L}}\right) = 7 \cdot 10^{-4}\ \mathrm{mol}.$$

Thus, the amount of the molecular iodine complex formed in the solution, according to ***reaction 3***, is $3.5 \cdot 10^{-4}$ mol. The initial amount of sodium metaperiodate added to **C** is

$$n = \frac{0.2139\ \mathrm{g}}{213.89\ \mathrm{g/mol}} = 1 \cdot 10^{-3}\ \mathrm{mol}.$$

Let the amount of sodium metaperiodate involved in the complete oxidative cleavage of **C** be x mol. Then the amount of metaperiodate remaining after the reaction is $(1 \cdot 10^{-3} - x)$ mol, and that in the aliquot is $0.1 \cdot (1 \cdot 10^{-3} - x)$ mol. The amount of iodate formed is x mol, and that in the aliquot it is $0.1x$ mol.

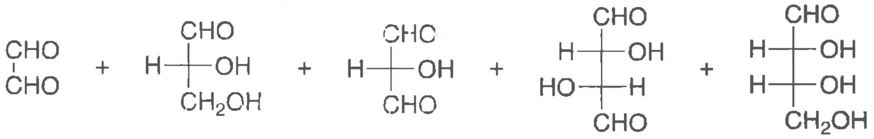
According to ***reaction 1***, the amount of I_3^- formed is $0.4 \cdot (1 \cdot 10^{-3} - x)$ mol; according to ***reaction 2***, it is $0.3x$ mol. Then the total amount of I_3^- equals $4 \cdot 10^{-4} - 0.1x$ mol. Knowing from titration that the amount of molecular iodine formed is $3.5 \cdot 10^{-4}$ mol, we calculate the amount of metaperiodate that reacted: $x = 5 \cdot 10^{-4}$ mol.

The amounts of substance **C** and metaperiodate are in the ratio $1 \cdot 10^{-4} : 5 \cdot 10^{-4} = 1 : 5$. Knowing that metaperiodate cleaves one C–C bond, it is logical to assume that there were five such bonds in substance **C**, and therefore the molecule **C** contained six carbon atoms. Since **C** and **D** are isomeric compounds, **D** also has six carbon atoms.

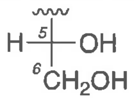
(0.25 points for each of the amount of thiosulfate used in titration, the amount of the molecular iodine complex, the initial amount of sodium metaperiodate added to **C**, and the number of carbon atoms in **C** and **D**; 1.25 points for the amount of metaperiodate that reacted; total **2.5 points**)

II-2.5 Analyzing the structures of the products of partial cleavage of **C**, one can assume that **C** is an aldohexose. Similarly, since ketones are present among the cleavage products of **D**, **D** is a ketohexose.

Upon partial oxidation of **C** by the Malaprade reaction, the following products are formed (for convenience, shown in Fisher projections):



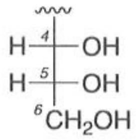
The first product, glyoxal, does not convey any information about the arrangement of substituents at the chiral centers in **C**. The second product, D-glyceraldehyde, contains a CH_2OH fragment, which represents the C6 portion of substance **C**. Thus, the structural formula of **C** in a Fisher projection can be depicted as follows (figure at right).



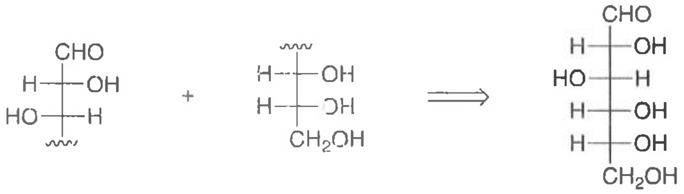
The third product may have been formed either from the C1–C3 fragment of the aldohexose or from an internal fragment; hence, it does not provide information about the spatial arrangement of substituents at the chiral carbon in **C**.

The fifth product is D-erythrose. By reasoning analogous to that for D-glyceraldehyde, it can be deduced that the erythrose fragment was formed from the terminal C2–C4 segment. The configuration of the C3 atom of erythrose coincides with that of the C2 atom in

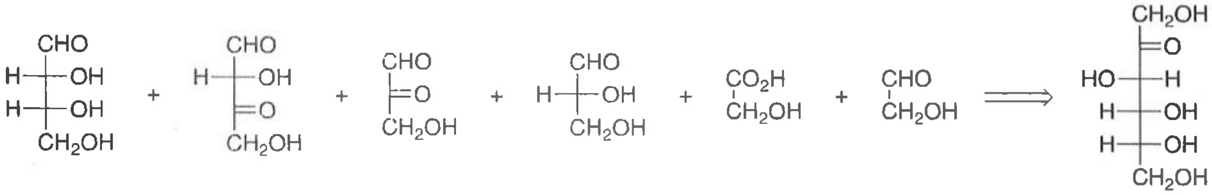
D-glyceraldehyde. Therefore, the structural formula of **C** in a Fisher projection can be depicted as follows (figure at right).



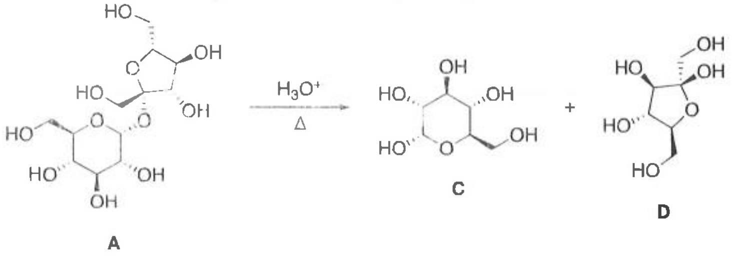
Analyzing the structural formula of the fourth product, (2R,3R)-2,3-dihydroxysuccinaldehyde, two cases can be considered: 1) the carbon skeleton of this product corresponds to the C2−C5 part of the original hexose; 2) that one of the aldehyde groups was present in the original molecule, corresponding to the C1−C4 part. The first option is invalid because the configuration of the C3 atom in dihydroxysuccinaldehyde does not match the obtained configuration of the C4 atom in the original hexose. Therefore, **C** can be obtained by combining two fragments:



Thus, we conclude that **C** is D-glucose.
By applying a similar approach, we conclude that **D** is D-fructose.

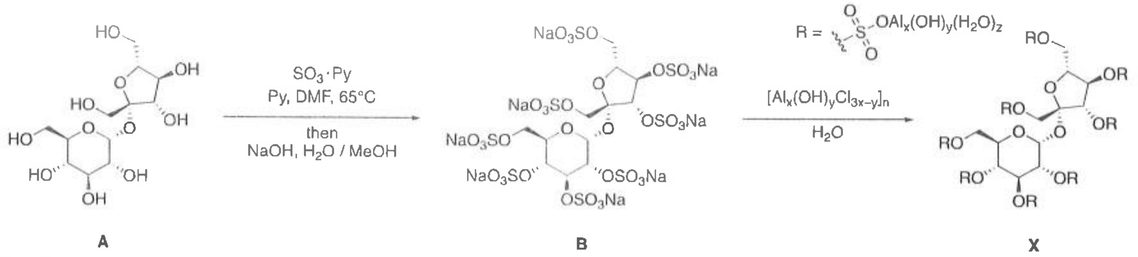


The problem states that **A** exists in solution as a single optically active isomer, the complete acidic hydrolysis of which yields isomeric compounds **C** and **D** in equimolar amounts. Therefore, compounds **C** and **D** are linked via a glycosidic bond whose formation involves two anomeric centers simultaneously, making mutarotation impossible. This supports the conclusion that **A** is sucrose. Moreover, sucrose is indeed produced industrially from plant raw materials. The scheme for complete acidic hydrolysis of sucrose is as follows:



(1 point for the correct structures of **A**, **C**, and **D**; total **3 points**)

II-2.6 The starting material in the synthesis is sucrose. In the first step, under the action of an SO_3−pyridine complex, all of sucrose's hydroxyl groups are sulfated, followed by neutralization of the acidic groups. Treatment of the resulting sucrose octasulfate with aluminum polyhydroxy chloride leads to the formation of aluminum salts of sucrose octasulfate. Given that sucralfate can raise pH by neutralizing the hydrochloric acid in gastric juice, we may suggest the presence of basic groups. According to the synthesis of sucralfate provided in the problem, the only suitable option are hydroxyl groups. It is also plausible that water molecules are present in the inner coordination sphere of aluminum, since the final stage of the synthesis of **X** is carried out in aqueous solution.



To further determine the formula of the drug, it is necessary to establish its quantitative composition, in particular the ratio of sulfate groups, aluminum, and hydroxide anions.
Let us calculate the amount of aluminum in one mole of **X**. After dissolving **X** in gastric juice, all aluminum is present as Al^{3+}. Then, after titration with a KOH solution and raising the pH to 4.00, a precipitate is observed which, upon burning, yields 1.327 g of aluminum oxide. Thus, the amount of precipitated aluminum is:

$$n(\mathrm{Al})_{\mathrm{precip}} = 2\frac{n(\mathrm{Al_2O_3})}{M(\mathrm{Al_2O_3})} = 2\cdot\frac{1.327}{101.95} = 2.603\cdot10^{-2}\ \mathrm{mol}$$

However, at pH = 4 some aluminum may remain in solution as Al^{3+}. To calculate this, we use the solubility product (K_{sp}).

$$K_{sp} = [\mathrm{Al^{3+}}][\mathrm{OH^-}]^3 \rightarrow [\mathrm{Al^{3+}}] = \frac{K_{sp}}{[\mathrm{OH^-}]^3} = \frac{2\cdot10^{-33}}{(10^{-10})^3} = 2\cdot10^{-3}\ \mathrm{M}$$

Then, the amount of aluminum is:

$$n(\mathrm{Al}) = n(\mathrm{Al})_{\mathrm{precip}} + [\mathrm{Al^{3+}}]\cdot V_{\mathrm{solution}} = 2.603\cdot10^{-2} + 2\cdot10^{-3}\cdot(0.973+0.0132) = \\ = 2.800\cdot10^{-2}\ \mathrm{mol}$$

Then, the amount of aluminum in the structure of **X** is:

$$\frac{n(\mathrm{Al^{3+}})}{\nu_{\mathrm{X}}} = \frac{2.800\cdot10^{-2}}{1.7505\cdot10^{-3}} = 16$$

(0.25 points for the amount of precipitated aluminum, the equilibrium concentration of aluminum cation in solution, the total amount of aluminum, and the amount of aluminum in the structure of **X**; total **1 point**)

II-2.7 Analyzing the gastric juice experiment results, let us calculate the number of hydroxide anions in the structure of **X**. The increase in pH from 1.12 to 2.41 occurs due to the neutralization of hydrochloric acid by OH groups. Since the pH of the solution exceeds the pK_b of aluminum hydroxide by more than 2 units, it can be assumed that all the aluminum is present as Al^{3+} and that all hydroxide anions were consumed in neutralization. Then:

$$c(\mathrm{OH^-}) = \Delta c(\mathrm{H^+}) = 10^{-\mathrm{pH}_1} - 10^{-\mathrm{pH}_2} = 10^{-1.12} - 10^{-2.41} = 0.07197\ \mathrm{M}$$

The total amount of **X** administered is calculated as follows:

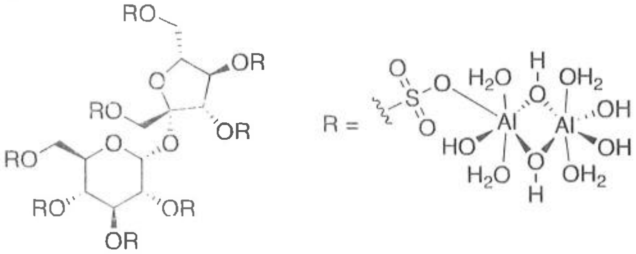
$$n_{\mathrm{X}} = \frac{m_{\mathrm{X}}}{M_{\mathrm{X}}} = \frac{4.660}{2662.04} = 1.7505\cdot10^{-3}\ \mathrm{mol}$$

Then, the number of hydroxide anions in the structure of **X** is:

$$\frac{c(\mathrm{OH^-})\cdot V_{\mathrm{solution}}}{n_{\mathrm{X}}} = \frac{0.07197\cdot0.973}{1.7505\cdot10^{-3}} = 40$$

(0.25 points for the value of c(OH^-), the amount of **X** administered, and the number of hydroxide anions in the structure of **X**; total **0.75 points**)

II-2.8 Considering that the structure of **X** contains 8 sulfate groups, which can form basic aluminum salts, we can establish the atomic ratio in the substituent R as: $SO_3Al_2(OH)_5$. Thus, the empirical formula of **X** is $C_{12}H_{54}O_{75}S_8Al_{16}$, and its molar mass is 2086 g/mol. The remaining mass is due to water molecules, the number of which is: (2662 − 2086) / 18 = 32. Therefore, R is $SO_3Al_2(OH)_5 \cdot 4H_2O$, and the structure of **X** is:



(1.25 points for the empirical formula of **X**, 1 point each for the structures of **X** and **B**; total **3.25 points**)

References:

1) Oates, J. A., Wood, A. J. J., & McCarthy, D. M. (1991). Sucralfate. New England Journal of Medicine, 325(14), 1017-1025. doi:10.1056/nejm199110033251

2) Bogatko, S., & Geerlings, P. (2012). Factors influencing Al3+-dimer speciation and stability from density functional theory calculations. Physical Chemistry Chemical Physics, 14(22), 8058. doi:10.1039/c2cp40885f

Problem II-3 (Author: Ozhimalov I.D.)

> *– "Doctor, I'm always sleepy and tired. What should I do?"*
> *– "You need to get your hormones checked!"*
> *Folk medical wisdom*

II-3.1 The steroids presented in the problem are soluble in nonpolar solvents and are readily extracted by them, since they contain a large aliphatic skeleton. However, the presence of functional groups such as hydroxyl and carbonyl ones decreases the solubility of steroids in nonpolar solvents. The presence of charged fragments almost completely prevents extraction.

a) In an alkaline medium, the acidic groups of steroids become ionized. Among the compounds presented, ionization is possible only if a phenolic fragment is present. Consequently, quantitative extraction by a nonpolar solvent of compounds **D**, **I**, and **R** under alkaline conditions is impossible.

b) One hour after treatment of the homogenate with a solution of silver oxide in aqueous ammonia, oxidation of the aldehyde groups to carboxyl groups occurs. This reaction is possible only for compound **B**. As a result, compounds **D**, **I**, **R** (as phenolates) and **B** (as a carboxylate) become ionized, indicating their minimal ability to be extracted under the given conditions.

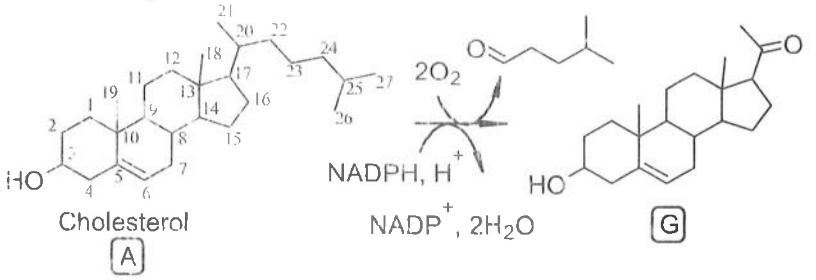
(0.25 points for each correct substance; total **1.75 points**)

II-3.2 The scheme shows 18 metabolites. The minimum number of reactions linking these metabolites into a single scheme is 18 − 1 = 17. According to the problem, the total number of reactions is 21 + 1 = 22. Then there are additional 22 − 17 = 5 reactions that link the presented metabolites. Since no metabolite can be formed in more than two reactions (as stated in the problem), all 5 "additional" reactions proceed with different metabolites. Hence, **5 metabolites** are the products of two different reactions simultaneously.

(total **1 point**)

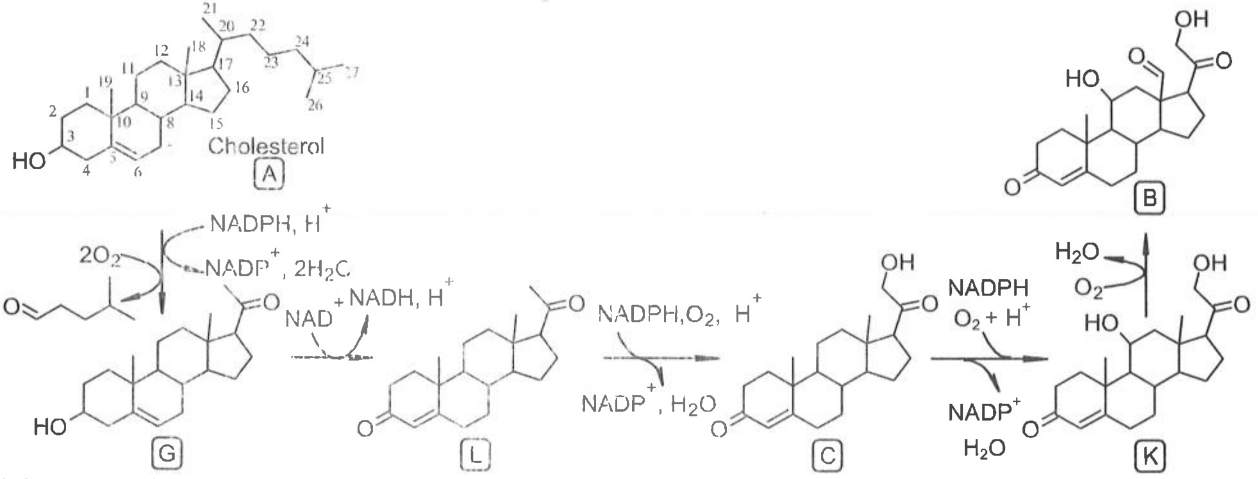
II-3.3, II-3.4 One possible approach to solving the problem is to analyze the length of the carbon skeletons of the various metabolites isolated from the adrenal gland. The cholesterol molecule **A** is the starting substance in steroidogenesis and is involved in only one reaction.

Analyzing the carbon skeletons of the other isolated steroids, one may deduce that, in the first stage, the aliphatic side chain of cholesterol is cleaved while retaining C20 and C21 (cleavage of the C–C bond between C17 and C18 would make it impossible to complete the carbon skeleton, since the steroidogenic enzymes are oxidoreductases or hydrolases). Thus, the cleavage of cholesterol leads to the formation of steroids containing 21 carbon atoms. Possible candidates are the metabolites **B, C, F, G, K, L, M, Q,** and **P**. The steroid nucleus must remain unchanged during the cleavage of cholesterol, i.e., no additional hydroxyl groups should appear (as in **F, M, P, Q**), no oxidation of the C3 hydroxyl group of cholesterol should occur (as in **B, C, K, L**), and no oxidation of the C18 methyl substituent should occur (which would lead to **B**). Then the only suitable product of the reaction is compound **G**. The conversion **A** → **G** likely occurs via a dioxygenase mechanism with the formation of 4-methylpentanal as a side product.

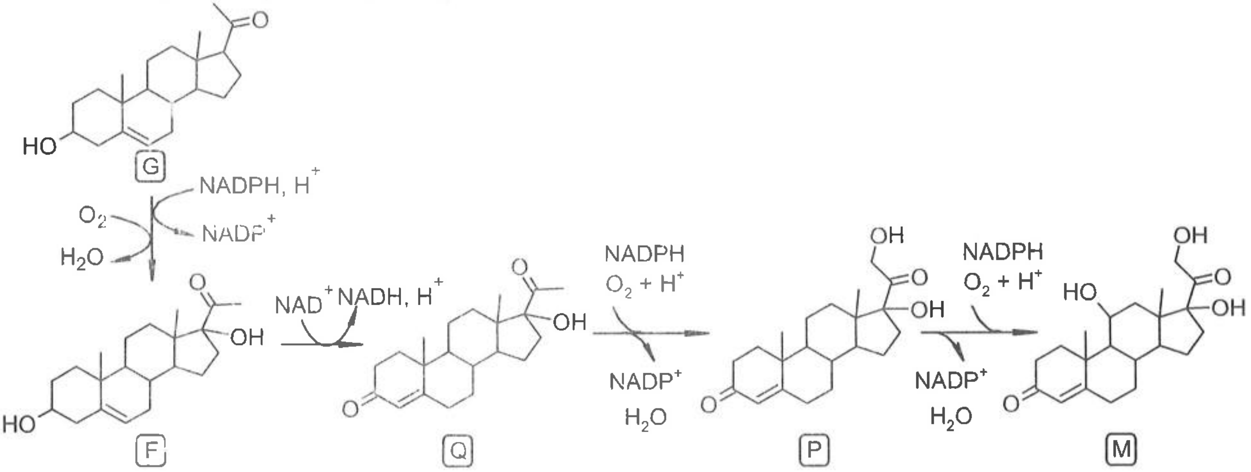


The further pathway of steroidogenesis has several directions.

The first option is the oxidation of the C3-OH group with the formation of an α,β-unsaturated ketone while retaining the remainder of the steroid structure. Compound **L** is suitable as the product of such a reaction. This reaction should be of a dehydrogenase nature. Subsequently, compound **L** may be transformed into compound **C** via C21-hydroxylation, which is of the monooxygenase type (this reaction is not the only one for compound **L**). Further transformation of compound **C** will be unique, since 21-hydroxysteroids participate in only one reaction according to the problem. Compound **C** may be hydroxylated at position 11 to form compound **K**. Further, compound **K**, is converted into compound **B** (the final product of one of the branches of aldosterone steroidogenesis) as a result of oxygenase oxidation at the C18. It is possible to suggest oxidation of **C** into compound **P**, but in that case the formation of aldosterone **B** would be impossible.



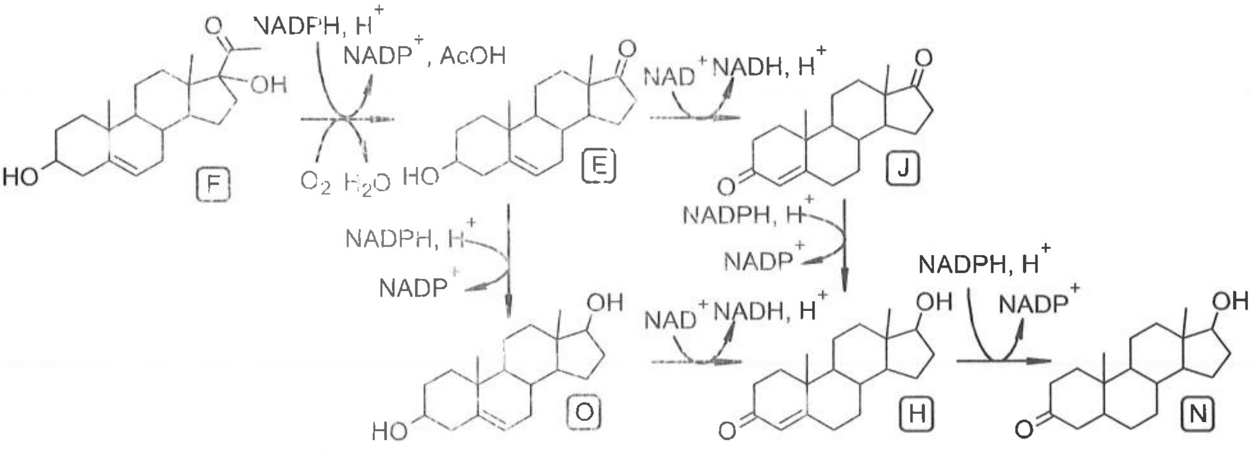
The second option for the metabolism of **G** is the C17-hydroxylation to form compound **F**. The subsequent transformation pathway is similar to the sequence described above: oxidation of the C3-OH group with the formation of an α,β-unsaturated ketone **Q** while retaining the rest of the steroid structure, followed by C21-hydroxylation yielding compound **P**, and further C17-hydroxylation yielding compound **M**.



After describing the metabolism of steroids containing 21 carbon atoms, one can proceed to steroids containing 19 carbon atoms. One of the possibilities for the formation of such steroids is the cleavage of the C17–C20 bond in **F**. Two substances, **E** and **O**, can be the products. The mechanism of this reaction is quite complex and not obvious, so we use the hint that the metabolite **E** is formed from cholesterol in three stages. Two stages are already deciphered: **A** → **G** → **F**. Since the cleavage of **F** to **O** would result in an additional stage (**A** → **G** → **F** → **O** → **E**), we can unambiguously conclude that the product of the cleavage of **F** is **E**. Then, several transformation options can be described for **E**.

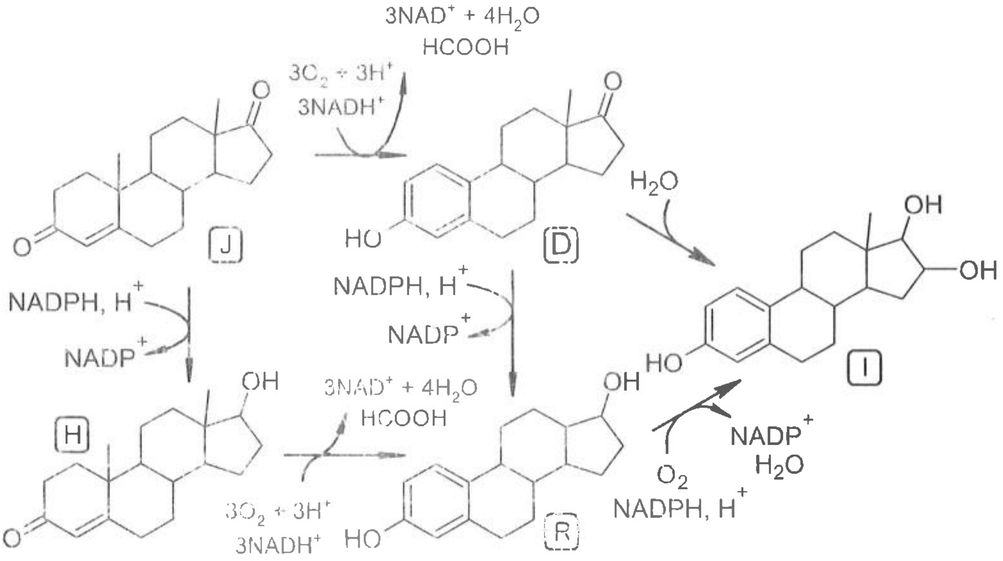
The first option is the oxidation of the C3-OH group with formation of an α,β-unsaturated ketone **J**. Next, **J** can be reduced to form the C17-hydroxy derivative **H**, which in turn can be reduced at the C4–C5 double bond to form **N**.

Another direction for the metabolism of **E** is the reduction of the C17-carbonyl group into the hydroxyl one to form **O**, which can then be oxidized at the C3-OH group to yield **H**.

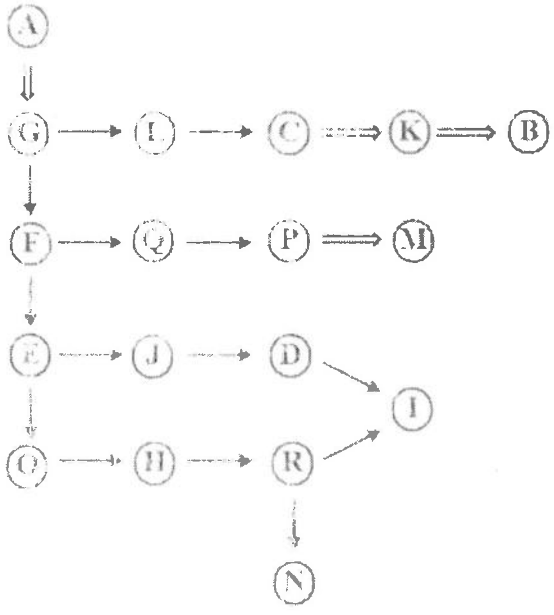


Metabolites **D**, **I**, and **R**, which contain an aromatic ring, have remained uninvolved in the steroidogenesis. It is logical to assume that they are formed via the oxidation of α,β-unsaturated ketones. However, during this oxidation, a nontrivial cleavage of the C19-methyl group occurs. Such a cleavage may occur through the sequential oxidation of the methyl substituent into the hydroxymethyl group, then to a formyl moiety, and finally, elimination of formic acid. Since this reaction is completely non-obvious and is established by the residual principle, any logical variant is accepted. Accordingly, **R** may be formed upon oxidation of **H**, and **D** upon oxidation of **J**. The last metabolite **I** is formed either upon

C16-hydroxylation of **R** or via hydration of **D** (the mechanism of this hydration reaction differs from the typical hydration reaction in organic chemistry because it involves an isoelectronic oxidation and reduction of the substrate in the enzyme's active center).

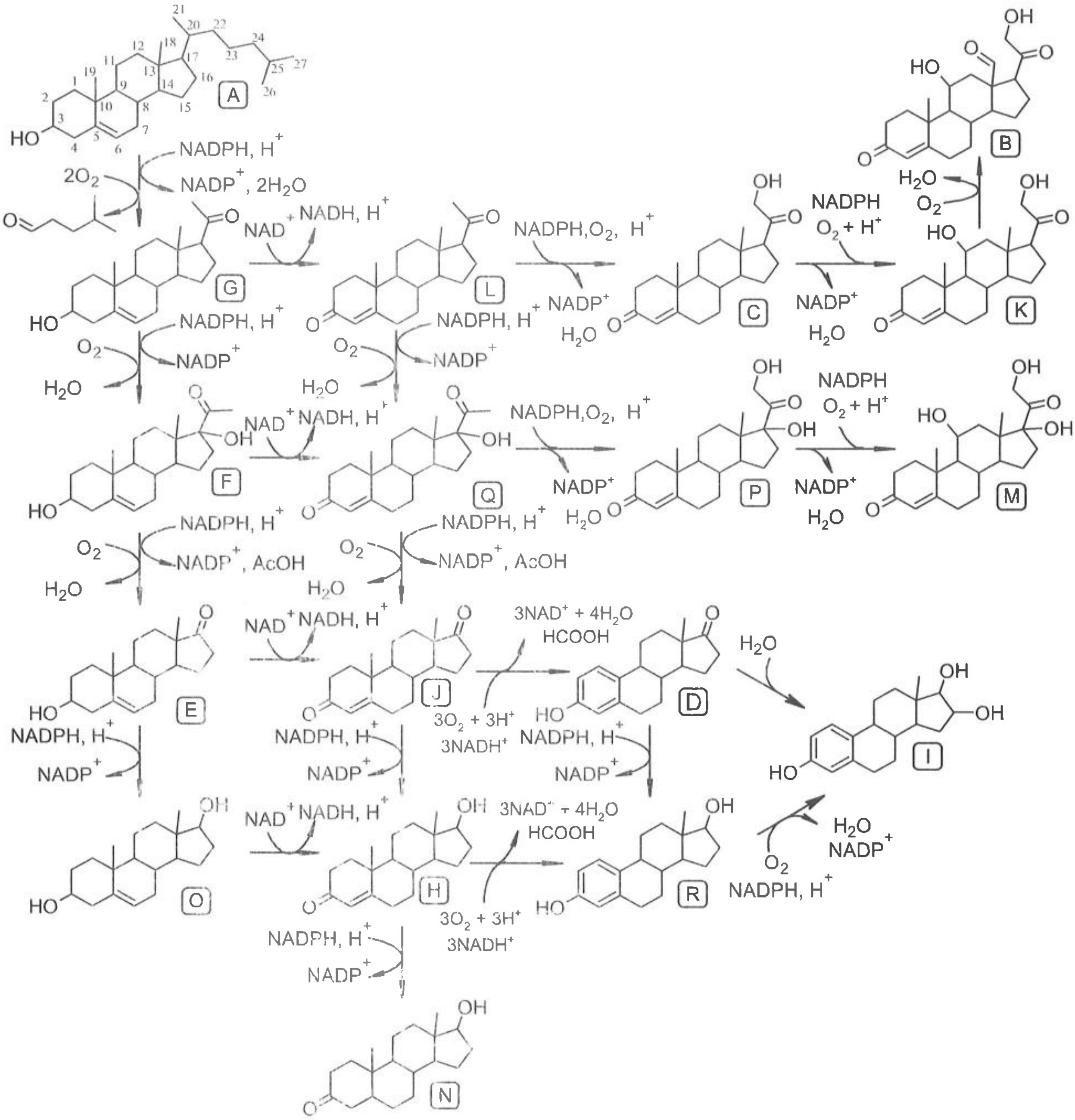


The transformations described above can be organized in the following scheme, which contains 19 reactions out of 22 (the hollow arrows indicate the uniqueness of the reaction for the given reagent).



The three missing reactions are the transformations of metabolites between the steroidogenic pathways. The transformations **C** → **P** and **K** → **M** are ruled out by the uniqueness of the reaction for 21-hydroxysteroids. The most possible remaining transitions are **L** → **Q** in the process of C17-hydroxylation, **Q** → **J** in the process of C17–C20 cleavage (analogous to the **F** → **E** reaction), and **D** → **R** in the process of oxidation of the C17-hydroxyl group.

Overall scheme of steroidogenesis with the structural formulae of the steroids:

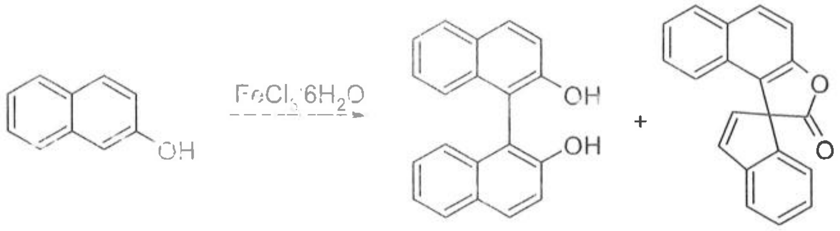


(II-3.3 0.5 points for each reaction scheme: 0.3 points for the deciphered metabolites and 0.2 points for showing other substances in the reaction; total **11 points**;
II-3.4 for the complete scheme of steroidogenesis: total **1.25 points**)

ORGANIC CHEMISTRY

Problem II-4 (author Zima A.)

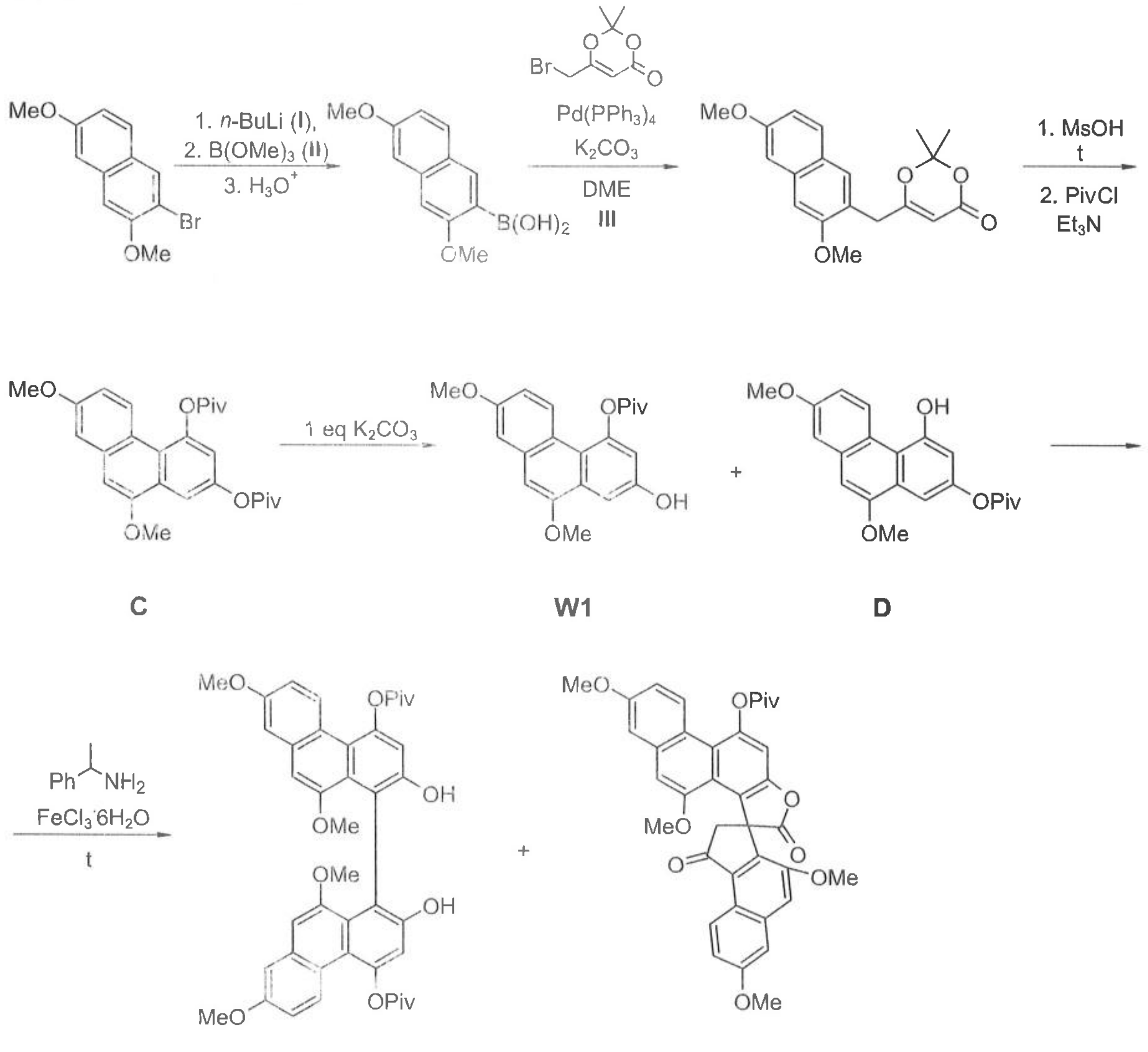
II-4.1 Based on the IR and ^{13}C NMR data, the compound **A** contains an ester group. From its molecular formula, the presence of a spiro fragment, and structural similarity to **X**, the structure of **A** can be determined.



A

(total **0.5 points**)

II-4.2. The starting compound differs from the nearest known one by a group that replaced bromine in the initial molecule.



C **W1** **D**

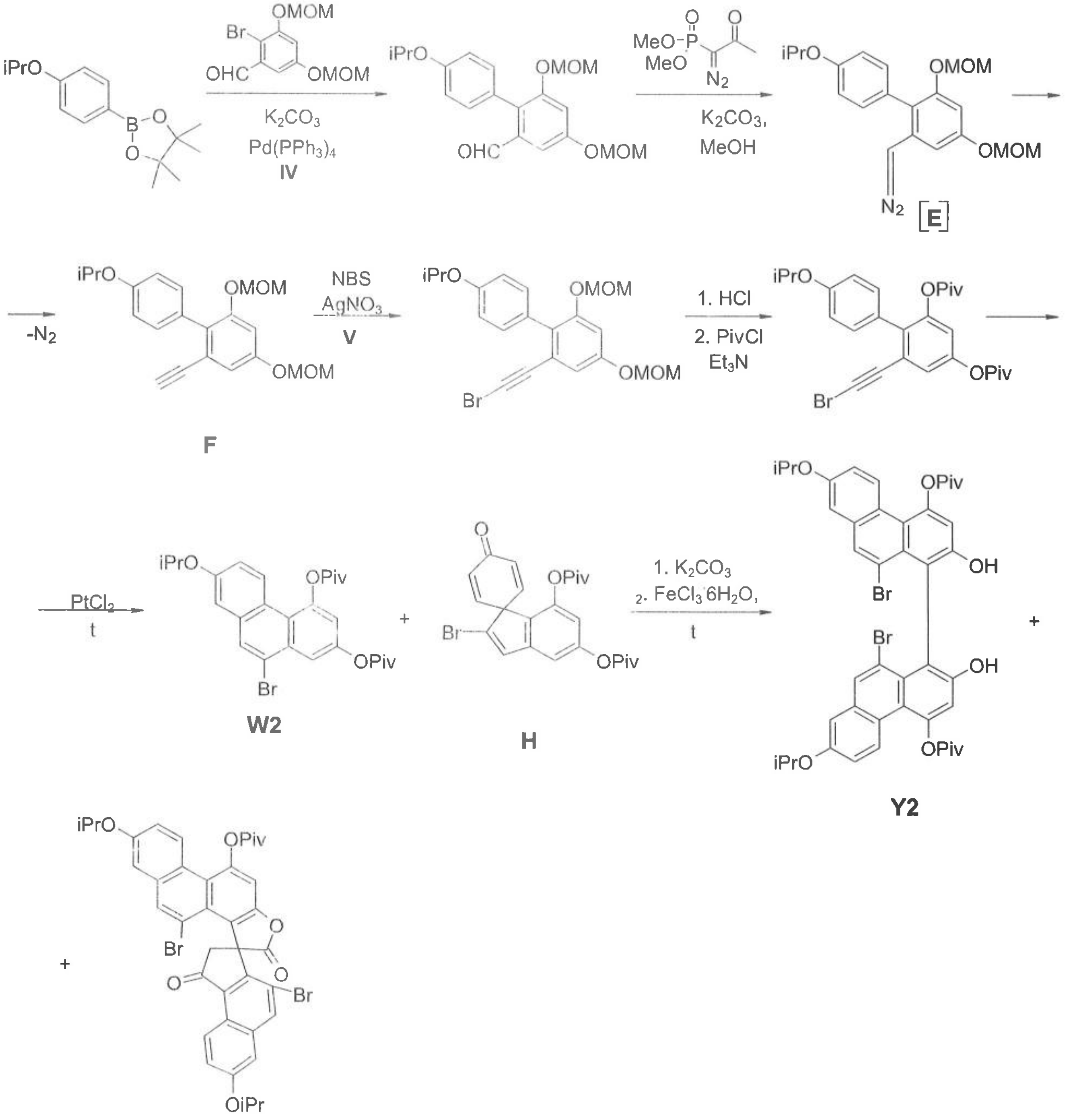
Y1 **X1**

Therefore, the following reaction conditions can be proposed: treatment with *n*-BuLi (**I**) and $B(OMe)_3$ (**II**), then hydrolysis of the methyl groups in HCl, and the Suzuki coupling between the resulting substituted boronic acid **B** and the required bromide with $Pd(PPh_3)_4$ and K_2CO_3 (**III**). The obtained compound gives the aromatic precursor of **C** with free hydroxyl groups via sequential deprotection and a Friedel–Crafts cyclization in the presence of methanesulfonic acid. In the second step, the OH groups are protected, resulting in **C**. The presence of three aromatic rings in **C** can be confirmed by the provided NMR data. Next, one protecting group is hydrolyzed, leading to the predominant product **W1** (removal of the less sterically hindered pivaloyl group) and the minor product **D**. The following synthesis step has been mentioned in the problem as a tandem reaction; hence it is logical to assume that compound **Y1** is a dimer of **W1**, and that **R1** = OPiv, **R2** = **R3** = OMe in the spiro compound **X1**.

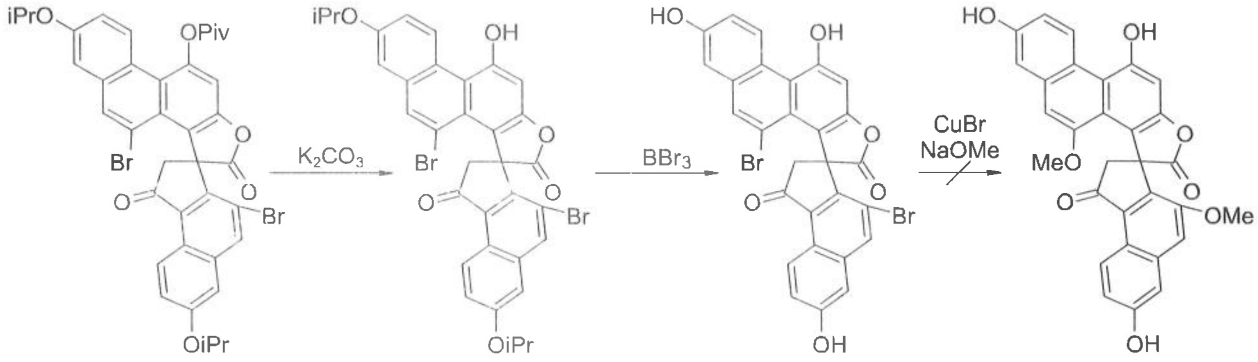
(**B–D**: 1 point each; **W1, Y1, X1**: 0.5 points each; **I–III**: 0.5 points for each condition; total **6 points**)

II-4.3 The second open compound can be synthesized from the first one via the Suzuki coupling with the desired bromide using $Pd(PPh_3)_4$ and K_2CO_3 (**IV**). Then, its formyl group can be converted into a terminal alkyne **F** using the Ohira–Bestmann reagent. As stated in the problem, the mechanism of this reaction resembles the Wittig reaction, and the intermediate **E** is a diazoalkene, which loses a nitrogen molecule upon heating to room temperature, turning first into a carbene and then into alkyne **F**. The terminal alkyne group can be converted into the bromoalkyne one using NBS/$AgNO_3$ (**V**). Subsequently, the two MOM protecting groups were replaced by pivaloyl groups to form compound **G**. Since it is known that **W2** is structurally similar to **W1**, it is likely also a phenanthrene derivative, and a cyclization occurs at this step. Under the action of a transition metal salt, the triple bond is activated, causing ipso-attack on the activated aromatic ring, forming the spiro compound **H**. An alternative pathway involves a 1,2-bromide shift, yielding compound **W2**. Final selective deprotection of the less hindered pivaloyl group, followed by dimerization of **W2** and the previously deciphered rearrangement, leads to the formation of compounds **Y2** and **X2**.

(**E–H**: 1 point each; **W2, Y2, X2**: 0.5 points each; **IV** and **V**: 0.5 points each; total **6.5 points**)

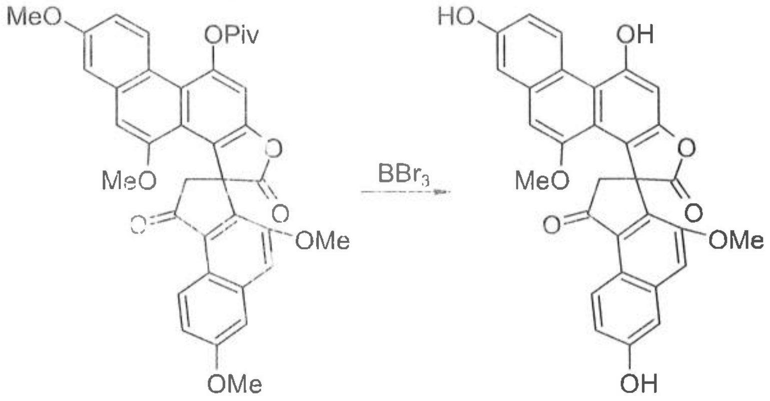


II-4.4 The pivaloyl group in **X2** can be gently removed under K_2CO_3/MeOH conditions to form compound **X3**, and the resulting two isopropyl groups are removed with BBr_3, yielding product **X4**.



X2 **X3** **X4** **X**

From the second part of the transformation sequence, it is evident that two sterically more accessible methyl groups and the pivaloyl group are removed using BBr_3, yielding **X**, while the **R3** substituents remain unchanged.



X1 **X**

(**X3**, **X4**, and **X**: 0.5 points each; total **1.5 points**)

II-4.5 The synthesis pathways "a" and "b" differ in the approach to replace substituent **R3** in **X**. In "a", **R3** does not undergo substitution reactions, whereas in "b", the replacement of **R3** is a key step. Clearly, only one of these pathways is feasible – pathway "a", since the **R3** substituent is sterically inaccessible (correct options *c* and *d*).

(0.25 points for choosing the synthesis route, 0.25 points for choosing both correct statements, −0.1 points penalty for each incorrect choice; **total 0.5 points**, minimum 0)

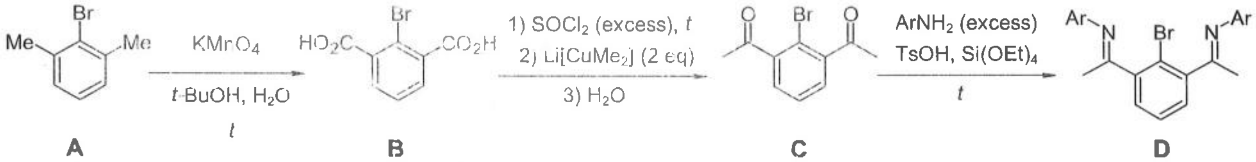
Problem II-5 (author Koronatov A.)

According to the hints provided, the numbers of protons in the nuclei of elements **X** and **Y** are different by exactly 3.4 times. This gives an idea that the number of protons in **X** should be divisible by 5, i. e., the element number in the Periodic table should end with either 5 or 0. Reviewing the possibilities (see the table below) reveals that zinc is the heaviest option for **X**. This allows for straightforward analysis of all the options. The only pair of elements **X** and **Y** from the same group is **X** = P and **Y** = Sb.

Atomic number of **X**	5	10	15	20	25	30	35	40
Atomic number of **Y**	17	34	51	68	85	102	119	136
Element **X**	B	Ne	P	Ca	Mn	Zn	Br	Zr
Element **Y**	Cl	Se	Sb	Ce	At	No	*None*	*None*

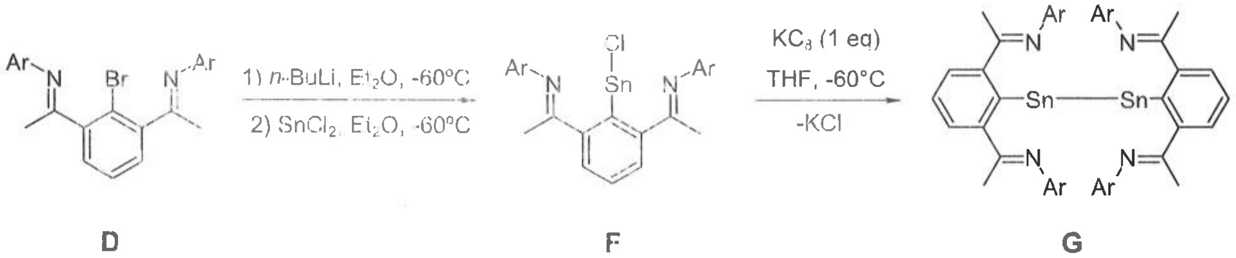
There are two options for the element **W**. Since **W** and **Y** are different by one proton in the nuclei, **W** is either Sn or Te. The fact that **W**–**W** bond may be hypothetically triple rules out Te, thus, **W** is Sn. The halides of elements P, Sb, and Sn stable at room temperature and not corresponding to the highest oxidation state of the central atom are PCl_3, $SbCl_3$, and $SnCl_2$.

II-5.1 Compound **D** is obtained via the reaction of an amine with **C**, which is evidently a carbonyl compound ($Si(OEt)_4$ acts as a dehydrating reagent, while TsOH is a typical acid used in imine synthesis). Since **D** is a double imine, **C** is a dicarbonyl compound. The reaction with thionyl chloride is used to transform oxygen-containing functional groups to chlorides; then, the intermediate is treated with organocuprate, which is used as a mild nucleophile. From this fact, along with the way of synthesis of **B**, we can infer that **B** is a dicarboxylic acid. Since **A** and **B** have the same amount of carbon atoms, **A** is 1,3-dimethyl benzene with a halogen at position 2. From the elemental composition, the only reasonable option is $n(C) : n(Br) = 8 : 1$. Thus, the structures of **A**–**C** are as follows.



(1 point for each structure, potassium salt of **B** is accepted; **3 points** in total)

II-5.2 Formula of WCl_n was deciphered above. Metal-halogen exchange is a faster process than deprotonation of any protons in **D**. Additionally, **D** contains bromine, while **G** gives a negative Beilstein test; this hint also excludes deprotonation reaction of **D** with *n*-butyllithium. ArLi reacts with tin dichloride to produce the transmetalation product **F**. When **F** is reduced with KC_8, it produces a Sn–Sn bond as stated in the hints.

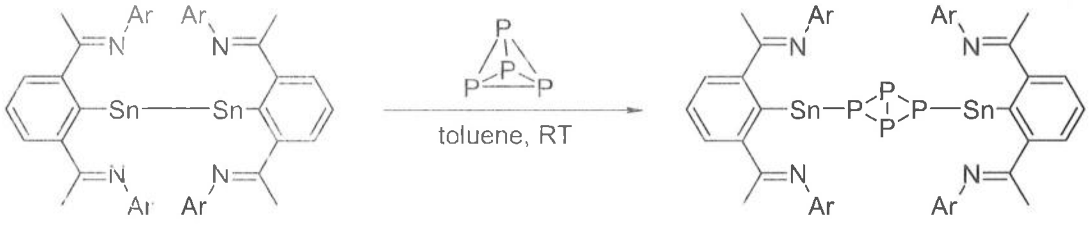


(1 point for each formula/structure, accepted if the imine nitrogen atoms are coordinated to tin in the compound **G**; **3 points** in total)

II-5.3 G contains Sn^{+1}.

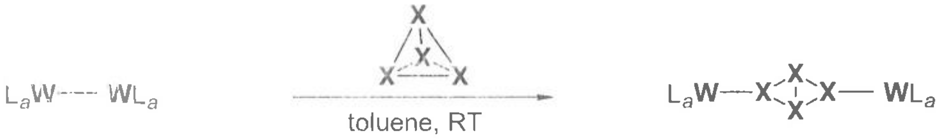
(0.5 points in total)

II-5.4 The element **X** was deciphered above. Since only one P–P bond is cleaved, the formula of **H** is as follows.



G **H**

The following answer is also accepted.



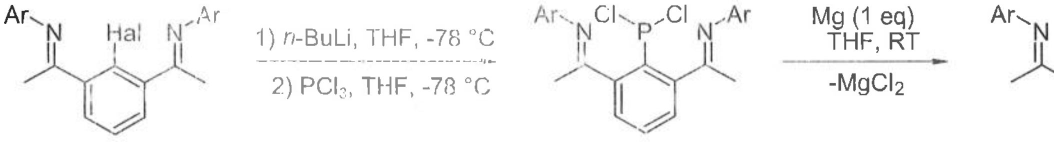
G **H**

(1 point for each formula/structure; **2 points** in total)

II-5.5 The formula to calculate the signal multiplicity is $2N{\cdot}s + 1$ (N being the number of nuclei, s is the nucleus spin). Since $s = ½$ and each chemically equivalent phosphorous atom has 2 adjacent phosphorous atoms, $2 \cdot 2 \cdot ½ + 1 = 3$. Therefore, both signals are triplets.

(0.5 points for each correct multiplicity; **1 point** in total)

II-5.6 Formula of XCl_m was deciphered above. Synthesis of **I** resembles that of **F**, however, a phosphorous atom prefers to form at least three covalent bonds (compared to Sb, for instance). Therefore, the isophosphazole is formed upon the reduction of **I**. The structure of **J** is clear from the presented reaction scheme, additional hints come from i. **II-5.7** and **II-5.8**.

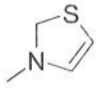


D **I** **J**

(1 point for each formula/structure; **3 points** in total)

II-5.7 Only isoxazole 4 fits the criteria, since it has the same connectivity between five elements and the same number of π-electrons in its aromatic system as the heterocycle in **J** (two double bonds and one lone-electron pair of the heteroatom).

1



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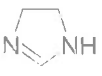

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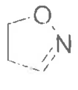

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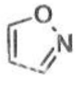

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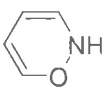

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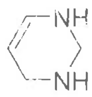

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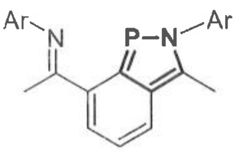
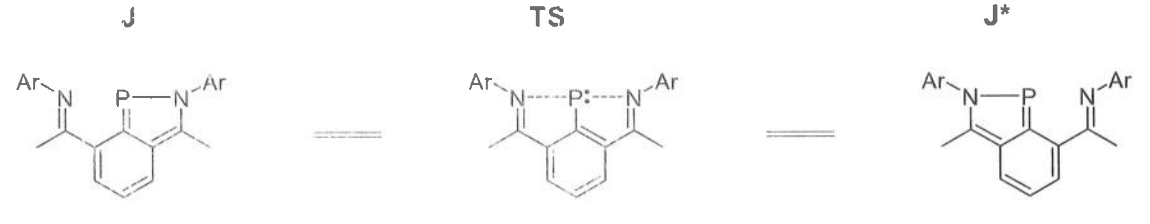
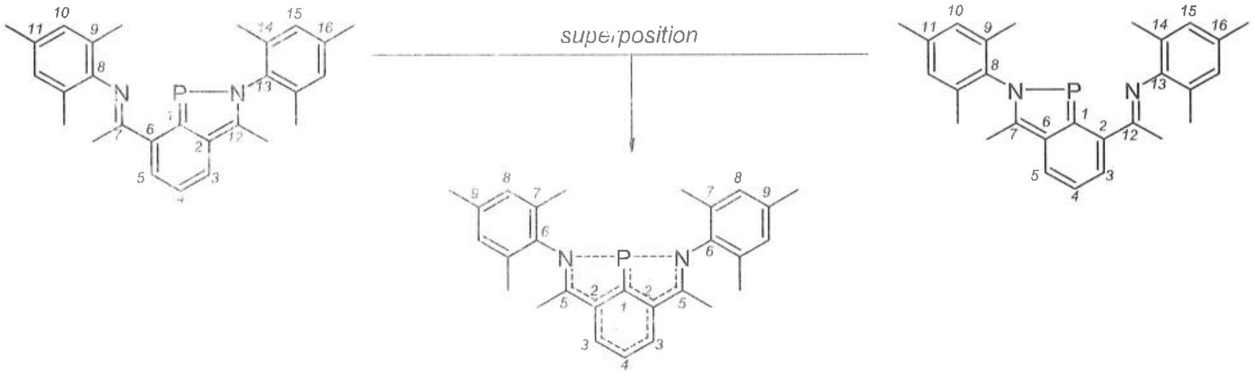


(**0.5 points** in total)

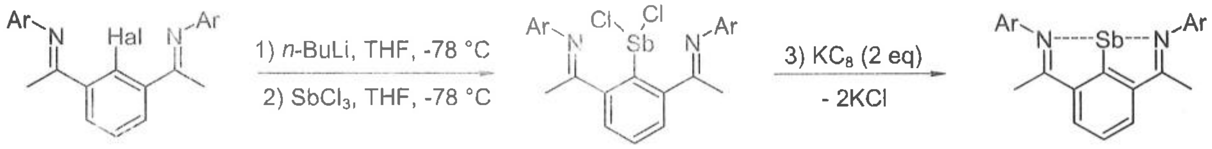
II-5.8 The compound **J** is unsymmetrical. However, a fast tautomerization via transition state **TS** can transform **J** into its tautomer **J***. Since there is no difference between **J** and **J***, the superposition of them should give the average structure similar to **TS**. In such a structure, there are only 9 distinct carbon atoms with NMR signals in the range above 100 ppm. The low-temperature ^{13}C NMR experiment may reveal 16 distinct signals. Therefore, the correct answer is e) (fast tautomerism).





(**1 point** in total)

II-5.9 Formula of **Y**Cl$_k$ was deciphered above. The synthesis of **K** resembles that of **J** and **G**. However, the reduction does not lead to antimony analog of isoxazole. Instead, low-valence compound **K** is generated, which is not isostructural to **J** (as stated in the hints).

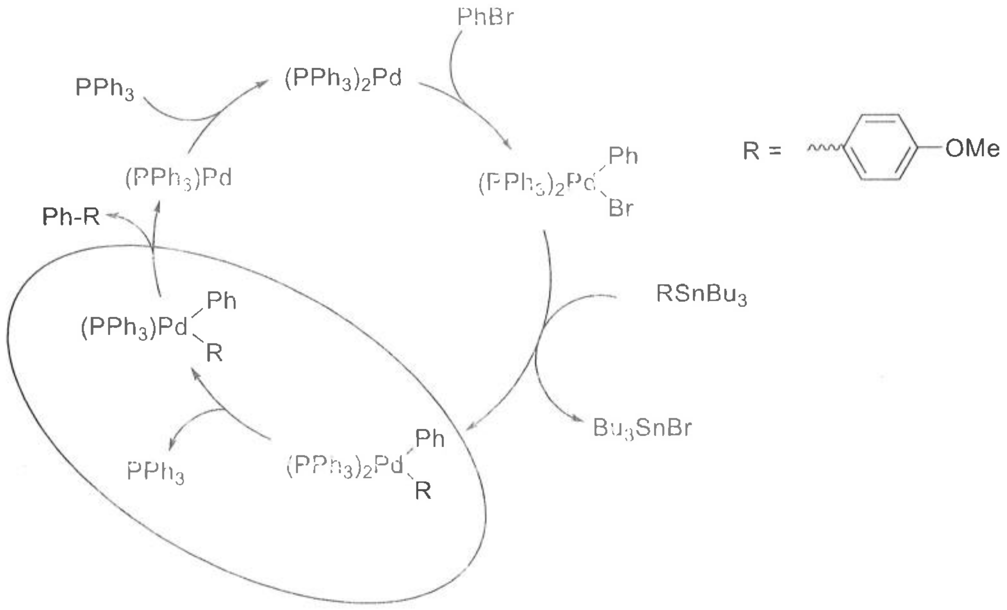


H **K**

(0.25 points for element **Y**, 0.75 points for structure of **K**; **1 point** in total)

Problem II-6 (author Romashov L.V.)

II-6.1 Reductive elimination proceeds much faster from the complexes with a coordination number (CN) of 3; therefore, the step of phosphine dissociation, which slows down at high concentrations of free phosphine in the reaction mixture, precedes the reductive elimination :



(overall mechanism of the Stille reaction, including oxidative addition, transmetallation, and reductive elimination: 1 point; the phosphine dissociation step: 1 point (variants with phosphine dissociation occurring before oxidative addition or transmetallation are accepted); total **2 points**)

II-6.2 At too low a concentration of phosphine, Pd(0) is not stabilized by complexation and precipitates as elementary substance; thus, **Z** is metallic Pd.

(total **1 point**)

II-6.3 For the complex to be coordinatively unsaturated, it is necessary that the ligands be sufficiently bulky to hinder the formation of complexes with a high CN. Ligands **A**, **C**, and **D** satisfy this condition. Bidentate ligands dppf and dppe form stable chelates that are not prone to lowering the CN. Trimethyl phosphite is a sufficiently small ligand that readily forms complexes with CN = 4.

(selection of three ligands correctly – 1 point, selection of two ligands correctly – 0.5 points, otherwise 0 points; total **1 point**)

II-6.4 The mechanism of oxidative addition via nucleophilic aromatic substitution is highly sensitive to the electronic effects of substituents on the aromatic ring; therefore, this mechanism corresponds to an inclined line. The concerted three-center mechanism, on the other hand, is only weakly affected by electronic effects, and thus corresponds to an almost horizontal line.

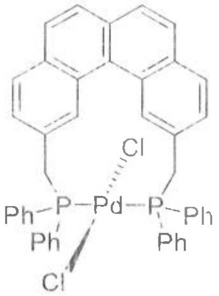
Substituent	Concerted three-center addition	Nucleophilic aromatic substitution
p-OMe	■	☐
m-CO_2Me	☐	■
p-CN	☐	■
m-Me	■	☐

(each mechanism 0.25 points; total **1 point**)

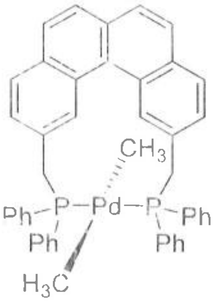
II-6.5 It is impossible to unambiguously determine the mechanism of oxidative addition for *p*-Cl because its corresponding point is at the intersection of the two lines.

(total **0.5 points**)

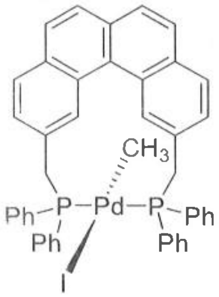
II-6.6 Due to its geometric features, the given ligand cannot provide for a *cis*-substitution of palladium; it forms a *trans*-complex that is incapable of undergoing reductive elimination.



M



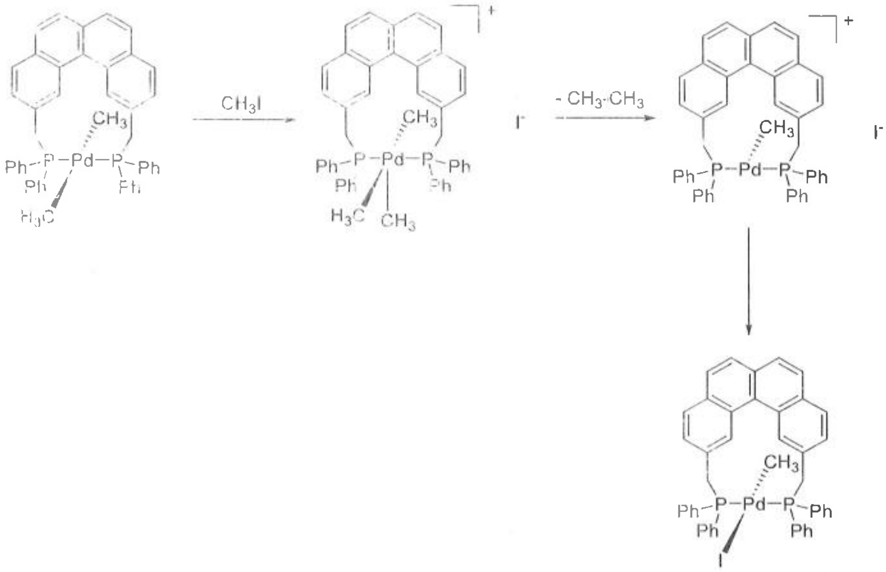
N



O

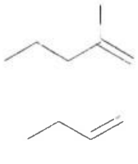
(1 point for each structure; total **3 points**)

II-6.7 When the complex **N** reacts with methyl iodide, a cationic complex with CN = 5 is formed, in which the methyl group in the apical position is *cis* to the other two groups and, accordingly, can participate in reductive elimination. Since the original complex is not regenerated after completion of the reaction. the stage cannot be catalytic

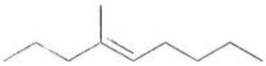


(correct mechanism – 1 point (mechanism with formation of a complex with CN = 6: 0.5 points), noncatalytic stage – 0.5 points; total **1.5 points**)

II-6.8 The main problem in conducting cross-coupling reactions with aliphatic substrates is β-hydride elimination, which competes with the reductive elimination step and leads to the formation of alkenes rather than coupling products. Chelating ligands, such as dppf, bring the substituents closer together on palladium, thereby significantly accelerating reductive elimination.



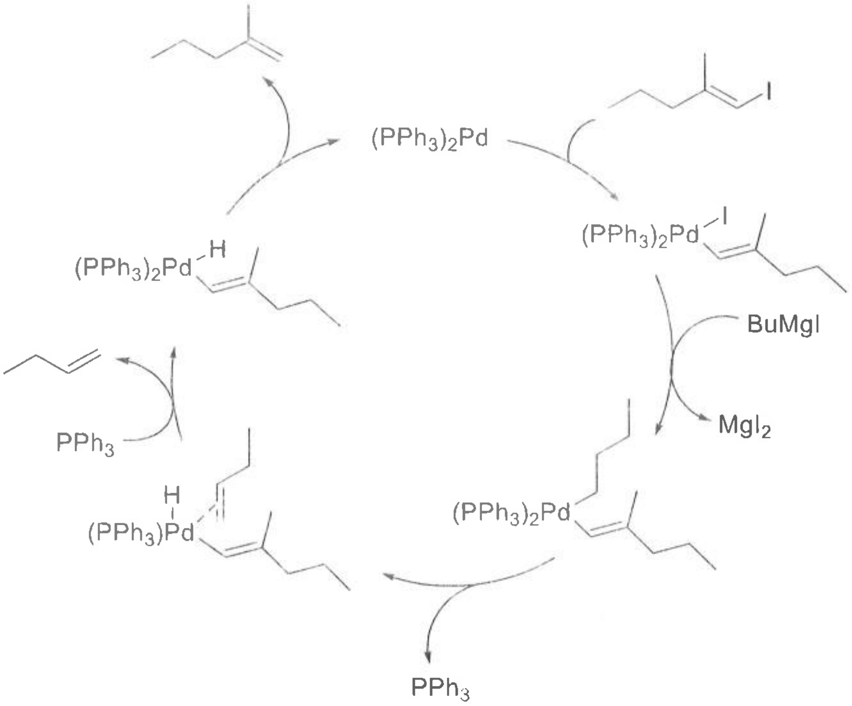
P + Q



R

(1 point for each structure; total **3 points**)

II-6.9 The formation of products **P** and **Q** is described by the following mechanism:



(total **2 points**)

PHYSICAL CHEMISTRY

Problem II-7 (author Kozlov M.I.)

II-7.1 The partition function ensures the normalization constraint:

$$1.1=\sum\rho(E_n)=\frac{1}{Q}\sum\exp\left(-\frac{E_n}{k_\mathrm{B}T}\right),\qquad Q=\sum\exp\left(-\frac{E_n}{k_\mathrm{B}T}\right)$$

Substituting the vibrational level energies $E_n = h\nu n$, we obtain

$$Q_\mathrm{vib}=\sum_{n=0}^{\infty}\left[\exp\left(-\frac{h\nu}{k_\mathrm{B}T}\right)\right]^n.$$

We have the sum of an infinite geometric progression, whose ratio q is the expression in the square brackets (with $q < 1$). Hence,

$$Q_\mathrm{vib}=\frac{1}{1-\exp\left(-\frac{h\nu}{k_\mathrm{B}T}\right)}.$$

(total **3 points**)

II-7.2 The probability that a particle is in the ground ($n = 0$) vibrational state is

$$\rho(E_0)=\frac{1}{Q_\mathrm{vib}}=1-\exp\left(-\frac{h\nu}{k_\mathrm{B}T}\right)=0.999.$$

Solving the resulting equation for the temperature, we obtain

$$T=\frac{h\nu}{3\cdot\ln10\cdot k_\mathrm{B}}=\frac{6.626\cdot10^{-34}\cdot3\cdot2.9979\cdot10^{13}}{3\cdot\ln10\cdot1.381\cdot10^{-23}}=624.68\ \mathrm{K}.$$

(total **2 points**)

II-7.3 a) With the chosen energy reference level, the expression for Q_vib is

$$Q_\mathrm{vib}=\frac{\exp\left(-\frac{h\nu}{2k_\mathrm{B}T}\right)}{1-\exp\left(-\frac{h\nu}{k_\mathrm{B}T}\right)},$$

and we obtain

$$G_\mathrm{vib}=-k_\mathrm{B}T\ln Q_\mathrm{vib}=-k_\mathrm{B}T\ln\left[\frac{\exp\left(-\frac{h\nu}{2k_\mathrm{B}T}\right)}{1-\exp\left(-\frac{h\nu}{k_\mathrm{B}T}\right)}\right].$$

b) If we neglect all vibrational levels except the ground state, the partition function includes only one term:

$$Q_\mathrm{vib}=\exp\left(-\frac{h\nu}{2k_\mathrm{B}T}\right).$$

Then the vibrational contribution to the Gibbs energy equals the energy of the ground state (i.e., one half of the vibrational quantum):

$$G_\mathrm{vib}=-k_\mathrm{B}T\ln Q_\mathrm{vib}=-k_\mathrm{B}T\ln\left[\exp\left(-\frac{h\nu}{2k_\mathrm{B}T}\right)\right]=\frac{h\nu}{2}.$$

(1 point per expression; total **2 points**)

II-7.4 The electronic contribution includes the energy of the Coulomb interaction between electrons and nuclei, which is independent of their masses. The kinetic energy depends on the mass of the molecule; therefore, it will change upon isotopic substitution. The energy of the rotational levels is inversely proportional to the moment of inertia, which depends on the masses of the nuclei in the molecule. Therefore, the rotational contribution changes upon isotopic substitution. Intermolecular interactions include Coulomb and van der Waals interactions, which do not depend on the nuclear masses. Thus, the correct answers b) and c). (+0.5 points for each correct option, −0.5 points for an incorrect one; maximum **1 point**, minimum 0 points)

II-7.5 Enthalpy and entropy are related to the equilibrium constant via the Gibbs energy:

$$\Delta G = \Delta H - T\Delta S = -RT\ln K_w = RT \cdot pK_w \cdot \ln 10.$$

Thus, the dependence of $RT \cdot pK_w \cdot \ln 10$ on temperature should be linear. Using the least squares method, one can determine its parameters, which are equal to ΔH and ΔS.

For light water, $\Delta H = 55142$ J/mol and $\Delta S = -83.163$ J/(mol·K).

For heavy water, $\Delta H = 56722$ J/mol and $\Delta S = -96.085$ J/(mol·K).

(0.5 points for each value; total **2 points**)

II-7.6 Using the calculated values of enthalpy and entropy, one can find the Gibbs energies and ionization constants at the desired temperature. In a neutral medium, pH and pK_w differ by a factor of two:

$$\mathrm{pH} = \frac{1}{2}\mathrm{p}K_w = -\frac{1}{2}\lg e^{\frac{\Delta H - T\Delta S}{RT}} = \frac{\Delta H - T\Delta S}{2RT}\lg e.$$

Substituting the numeric values, we obtain pH = 6.03 and pD = 6.47.

(0.5 points for each value; total **1 point**)

II-7.7 Comparing the entropies obtained in **II-7.5**, it is easy to see that the difference in the Gibbs energies of dissociation for light and heavy water depends on temperature:

$$\Delta_r G(D_2O) - \Delta_r G(H_2O) = \Delta_r H(D_2O) - \Delta_r H(H_2O) - T[\Delta_r S(D_2O) - \Delta_r S(H_2O)].$$

This is caused by the contribution of excited vibrational levels to the Gibbs energy, which can be taken into account using the more accurate expression obtained in **II-7.3**. However, the temperature dependence may also be explained by other modes of motion and intermolecular interactions, which cannot be considered within the framework of this problem. Thus, to eliminate all unnecessary contributions to the energy, the temperature should be taken to zero:

$$\Delta_r G(D_2O) - \Delta_r G(H_2O) = \Delta_r H(D_2O) - \Delta_r H(H_2O) = 1580\ \mathrm{J/mol} = 132.1\ cm^{-1}.$$

In this case, all particles are in the ground state, and hence their energy approaches a constant value.

For the reaction $2H_2O = H_3O^+ + OH^-$, the change in Gibbs energy is

$$\Delta_r G(H_2O) = G(OH^-) + G(H_3O^+) - 2G(H_2O) =$$
$$= G_0(OH^-) + G_0(H_3O^+) - 2G_0(H_2O) + G_{vib}(OH^-) + G_{vib}(H_3O^+) -$$
$$-2G_{vib}(H_2O) = \Delta_r G_0(H_2O) + \frac{h\nu(OH^-)}{2} + \sum_{H_3O^+}\frac{h\nu}{2} - 2\sum_{H_2O}\frac{h\nu}{2} =$$
$$= \Delta_r G_0(H_2O) + \frac{h\nu(OH^-)}{2} - 1973.1\ \mathrm{cm}^{-1}.$$

Similarly, for heavy water

$$\Delta_r G(D_2O) = \Delta_r G_0(D_2O) + \frac{h\nu(OD^-)}{2} - 1373.2\ \mathrm{cm}^{-1}.$$

The force constants for OH^- and OD^- are the same; therefore, the corresponding vibrational frequencies are related by

$$\nu(OD^-) = \nu(OH^-)\sqrt{\frac{\mu(OH)}{\mu(OD)}} = \nu(OH^-)\sqrt{\frac{m(O)m(H)[m(O)+m(D)]}{m(O)m(D)[m(O)+m(H)]}} =$$

$$= \nu(\mathrm{OH}^-)\sqrt{\frac{m(\mathrm{H})[m(\mathrm{O})+m(\mathrm{D})]}{m(\mathrm{D})[m(\mathrm{O})+m(\mathrm{H})]}}.$$

The non-vibrational contributions to the Gibbs energy at 0 K are equal

$$\Delta_\mathrm{r}G_0(\mathrm{H_2O}) = \Delta_\mathrm{r}G_0(\mathrm{D_2O})$$

since they include Coulomb energy (which does not depend on the isotope masses) and the translational and rotational kinetic energies, which are zero at 0 K. Thus:

$$\Delta_\mathrm{r}G(\mathrm{D_2O}) = \Delta_\mathrm{r}G(\mathrm{H_2O}) = 132.1\ \mathrm{cm^{-1}} =$$

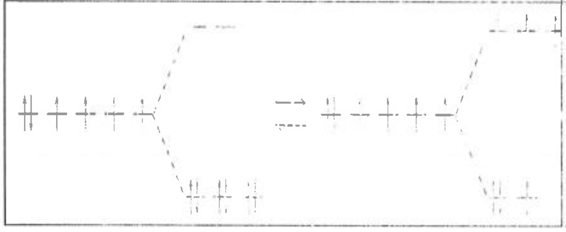
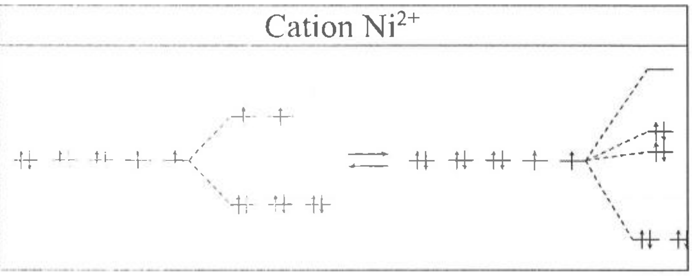
$$= \Delta_\mathrm{r}G_0(\mathrm{D_2O}) + \frac{h\nu(\mathrm{OD}^-)}{2} - 1373.2\ \mathrm{cm^{-1}} - \left[\Delta_\mathrm{r}G_0(\mathrm{H_2O}) + \frac{h\nu(\mathrm{OH}^-)}{2} - 1973.1\ \mathrm{cm^{-1}}\right] =$$

$$= \frac{h\nu(\mathrm{OH}^-)}{2}\left(\sqrt{\frac{m(\mathrm{H})[m(\mathrm{O})+m(\mathrm{D})]}{m(\mathrm{D})[m(\mathrm{O})+m(\mathrm{H})]}} - 1\right) + 599.9\ \mathrm{cm^{-1}}.$$

Solving the resulting equation, we obtain $\nu(\mathrm{OH}^-) = 3439.78\ \mathrm{cm^{-1}}$. Then the vibrational frequency of the deuterated ion is $\nu(\mathrm{OD}^-) = 2504.17\ \mathrm{cm^{-1}}$.
(2 points for the idea of taking the temperature to zero, 1 point for the values; total **4 points**)

Problem II-8 (author Schwartzman V.E.)

II-8.1 In the dissociation of octahedral complexes $\mathrm{M(A_2)_3 \rightleftarrows M(A_2)_2 + A_2}$, either tetrahedral $\mathrm{Fe(A_2)_2}$, which is characteristic of the d^6 configuration of $\mathrm{Fe^{2+}}$, or square planar $\mathrm{Ni(A_2)_2}$, which is characteristic of the d^8 configuration of $\mathrm{Ni^{2+}}$, is formed. In these complexes, the LFSE may be either higher or lower than that of the octahedral complex.

Cation $\mathrm{Fe^{2+}}$	Cation $\mathrm{Ni^{2+}}$
	

In $\mathrm{Fe(A_2)_3}$ with the electron configuration $d_{xy}^2d_{yz}^2d_{zx}^2$, the ligand field stabilization energy (LFSE = $6\cdot(-4) = -24Dq$) is greater than that in $\mathrm{Fe(A_2)_2}$ with the electron configuration $d_{x2-y2}^2d_{z2}^1d_{xy}^1d_{yz}^1d_{zx}^1$ (where LFSE = $3\cdot(-2.67) + 3\cdot(1.78) = -2.67Dq$). Therefore, $\mathrm{Fe(A_2)_2}$ is more labile than $\mathrm{Fe(A_2)_3}$, dissociates more easily, and $k_1 < k_2$. (1 point)
In $\mathrm{Ni(A_2)_3}$ with the electron configuration $d_{xy}^2d_{yz}^2d_{zx}^2d_{x2-y2}^1d_{z2}^1$, the LFSE = $6\cdot(-4) + 2\cdot(6) = -12Dq$ is lower than that in $\mathrm{Ni(A_2)_2}$ with the configuration $d_{yz}^2d_{zx}^2d_{z2}^2d_{xy}^2$ (LFSE = $4\cdot(-5.14) + 2\cdot(-4.28) + 2\cdot(2.28) = -24.56Dq$). Therefore, $\mathrm{Ni(A_2)_3}$ is more labile than $\mathrm{Ni(A_2)_2}$, dissociates more readily, and $k_1 > k_2$. (1 point)
(total **2 points**)

II-8.2 Electrophilic ("electron-loving") reagents are particles (cations or molecules) possessing an available orbital in the outer electron shell. They attach to $\mathrm{A_2^{2-}}$ (scheme 2): $\mathrm{H^+}$, $\mathrm{Zn^{2+}}$, $\mathrm{Cu^{2+}}$. (0.25 points each)

Nucleophilic reagents are particles (anions or molecules) that have a nonbonding pair of electrons in the outer electron shell. They attach to M^{2+} (scheme 1): OH^-, CN^-. (0.25 points each)
(choice of scheme 1 0.75 points; total **2 points**)

II-8.3 The mechanism of the first pathway of the reaction $PbY^{2-} + Zn^{2+}$ includes three stages:
Pb–OCO bond cleavage $PbY^{2-} \rightleftarrows (PbY-)^{2-}$ (k_1, k_{-1});
protonation $(PbY-)^{2-} + H^+ \rightarrow (PbY-H)^-$ (k_2);
attack by Zn^{2+} $(PbY-H)^- + Zn^{2+} \rightarrow ZnY^{2-} + Pb^{2+} + H^+$ (k_3).

The rate of the first pathway $\frac{dc_{ZnY^{2-}}}{d\tau} = k_3 \cdot c_{(PbY-H)^-} \cdot c_{Zn^{2+}}$. Using the steady-state approximation for $(PbY-H)^-$: $\frac{dc_{(PbY-H)^-}}{d\tau} = 0$; the rate of formation of $(PbY-H)^-$ equals the rate of its decomposition: $k_3 \cdot c_{(PbY-H)^-} \cdot c_{Zn^{2+}} = k_2 \cdot c_{(PbY-)^{2-}} \cdot c_{H^+}$, so that after substitution the rate equation takes the form $\frac{dc_{ZnY^{2-}}}{d\tau} = k_2 \cdot c_{(PbY-)^{2-}} \cdot c_{H^+}$. (1 point)
Using the steady-state approximation for $(PbY-)^-$:
$\frac{dc_{(PbY-)^-}}{d\tau} = 0$; the rate of formation of $(PbY-)^-$ equals the rate of its decomposition: $k_1 \cdot c_{PbY^{2-}} = k_2 \cdot c_{(PbY-)^{2-}} \cdot c_{H^+} + k_{-1} \cdot c_{(PbY-)^{2-}}$, concentration $c_{(PbY-)^{2-}} = \frac{k_1 \cdot c_{PbY^{2-}}}{k_2 \cdot c_{H^+} + k_{-1}}$, and after substitution of $c_{(PbY-)^{2-}}$ into the rate equation we obtain: $\frac{dc_{ZnY^{2-}}}{d\tau} = \frac{k_2 \cdot k_1 \cdot c_{H^+}}{k_2 \cdot c_{H^+} + k_{-1}} \cdot c_{PbY^{2-}}$. (1 point)
(total **2 points**)

II-8.4 If the second pathway is independent of $[H^+]$ and the kinetic equation is $\frac{dc_{ZnY^{2-}}}{d\tau} = \frac{k_4 \cdot k_1 \cdot c_{PbY^{2-}}}{k_4 \cdot c_{Zn^{2+}} + k_{-1}}$, then a two-step mechanism can be proposed for it:
Pb–OCO bond cleavage $PbY^{2-} \rightleftarrows (PbY-)^{2-}$ (k_1, k_{-1}) (1 point);
Attack by Zn^{2+} $(PbY-)^{2-} + Zn^{2+} \rightarrow ZnY^{2-} + Pb^{2+}$ (k_4) (1 point).
(total **2 points**)

II-8.5 To derive the equation for calculating the acid dissociation constant $NiHY^- \rightleftarrows NiY^{2-} + H^+$ ($\Delta G_a = -RT\ln K_a$), one should use the formation constants for the nickel complexes: $Ni^{2+} + Y^{4-} \rightleftarrows NiY^{2-}$ ($\Delta G_1 = -RT\ln\beta_1$), $Ni^{2+} + HY^{3-} \rightleftarrows NiHY^-$ ($\Delta G_2 = -RT\ln\beta_2$) and the dissociation constant of the ligand: $HY^{3-} \rightleftarrows H^+ + Y^{4-}$ ($\Delta G_4 = -RT\ln K_4$).
According to Hess's law $\Delta G_a = \Delta G_1 - \Delta G_2 + \Delta G_4$; $-RT\ln K_a = -RT\ln\beta_1 + RT\ln\beta_2 - RT\ln K_4$;
$\ln K_a = \ln(\beta_1 \cdot K_4 / \beta_2)$; $K_a = \beta_1 \cdot K_4 / \beta_2$ (1 point)
$K_a = 5.5 \cdot 10^{-11} \cdot 4.2 \cdot 10^{18} / 3.6 \cdot 10^{11} = 6.4 \cdot 10^{-4}$ (1 point).
(total **2 points**)

II-8.6 At first glance, the equation for k_{obs} does not explicitly include $[H^+]$, but the proposed rate equation $\frac{dc_{ZnY^{2-}}}{d\tau} = (k_5[NiY^{2-}] + k_6[NiHY^-])c_{Zn^{2+}}$ incorporates equilibrium concentrations that depend on pH. To derive the equation for k_{obs} that depends solely on K_a and $[H^+]$, it is sufficient to combine the equation for the dissociation constant with the material balance $NiHY^- \rightleftarrows NiY^{2-} + H^+$ ($K_a = [NiY^{2-}][H^+]/[NiHY^-]$, as the initial concentration $c_{NiY^{2-}} = [NiY^{2-}] + [NiHY^-]$).
Then, $c_{NiY^{2-}} = [NiY^{2-}] + \frac{[NiY^{2-}][H^+]}{K_a}$; $[NiY^{2-}] = \frac{K_a c_{NiY^{2-}}}{K_a + [H^+]}$;
$[NiHY^-] = c_{NiY^{2-}} - [NiY^{2-}] = c_{NiY^{2-}} - \frac{K_a c_{NiY^{2-}}}{K_a + [H^+]} = \frac{[H^+] c_{NiY^{2-}}}{K_a + [H^+]}$.

After substituting into $k_{obs} = k_5[\mathrm{NiY}^{2-}] + k_6[\mathrm{NiHY}^{-}]$, we obtain $k_{obs} = \frac{k_5K_a+k_6[\mathrm{H}^+]}{K_a+[\mathrm{H}^+]}$, that depends on pH. (1 point).

By substituting the experimental data $k_{obs} = f(\mathrm{pH})$ and $K_a = 6.4\cdot10^{-4}$ in $k_{obs} = \frac{k_5K_a+k_6[\mathrm{H}^+]}{K_a+[\mathrm{H}^+]}$, one obtains a system of two linear equations which can be solved to determine k_5 and k_6.
For $[\mathrm{H}^+] = 10^{-3}$ and $k_{obs} = 1.56\cdot10^{-6}$: $1.56\cdot10^{-6} = (6.4\cdot10^{-4}k_5 + 10^{-3}k_6) / (6.4\cdot10^{-4} + 10^{-3})$;
For $[\mathrm{H}^+] = 10^{-4}$ and $k_{obs} = 2.23\cdot10^{-6}$: $2.23\cdot10^{-6} = (6.4\cdot10^{-4}k_5 + 10^{-4} k_6) / (6.4\cdot10^{-4} + 10^{-4})$).
Solving this system yields $k_5 = 2.5\cdot10^{-6}$ and $k_6 = 10^{-6}$. (1 point)
(total **2 points**)

II-8.7 For the reaction $\mathrm{NiY}^{2-} + \mathrm{Me}^{2+}$, the two-stage mechanism includes:
Formation of the intermediate (associate): $\mathrm{NiY}^{2-} + \mathrm{Me}^{2+} \rightleftarrows \mathrm{NiYMe}$ (K);
Formation of the reaction product: $\mathrm{NiYMe} \rightarrow \mathrm{MeY}^{2-} + \mathrm{Ni}^{2+}$ (k).
The reaction rate is $\frac{dc_{\mathrm{NiY}^{2-}}}{d\tau} = k[\mathrm{NiYMe}]$, the steady-state approximation $\frac{d[\mathrm{NiYMe}]}{d\tau} = 0$, the concentration of the $[\mathrm{NiYMe}] = K[\mathrm{NiY}^{2-}][\mathrm{Me}^{2+}]$, after substitution, the rate becomes $\frac{dc_{\mathrm{NiY}^{2-}}}{d\tau} = kK[\mathrm{NiY}^{2-}][\mathrm{Me}^{2+}] = k_5[\mathrm{NiY}^{2-}][\mathrm{Me}^{2+}]$ (1 point).
According to the equation $\lg k_5 = -12.35 + 1.01 \cdot \lg K$, one can find $\lg K = (12.35 - \lg k_5) / 1.01 = (12.35 - \lg 2.5\cdot10^{-6}) / 1.01 = 6.68$ (1 point).
Then, the equilibrium constant $K = 4.79\cdot10^6$, and the rate constant $k = k_5 / K = 2.5\cdot10^{-6} / 4.79\cdot10^6 = 5.22\cdot10^{-13}$. (1 point)
(total **3 points**)

Problem II-9 (author Roslyakov S.N.)

II-9.1 a) For the cylindrical wire:

$$p = p_2 = \frac{\sigma}{r} = \frac{3\ \frac{\mathrm{mN}}{\mathrm{cm}}}{\frac{0.5}{2}\ \mathrm{mm}} = \frac{0.3\ \frac{\mathrm{N}}{\mathrm{m}}}{0.25\cdot10^{-3}\ \mathrm{m}} = 1200\ \mathrm{Pa} = 0.0118\ \mathrm{atm}.$$

b) For the spherical nanoparticles with a diameter of 15 nm:

$$p = p_1 = \frac{2\sigma}{r} = \frac{2\cdot3\ \frac{\mathrm{mN}}{\mathrm{cm}}}{\frac{15}{2}\ \mathrm{nm}} = \frac{2\cdot0.3\ \frac{\mathrm{N}}{\mathrm{m}}}{7.5\cdot10^{-9}\ \mathrm{m}} = 8\cdot10^7\ \mathrm{Pa} = 790\ \mathrm{atm}.$$

It is evident that the excess surface pressure for nanoparticles considerably exceeds the excess pressure for a wire of macroscopic dimensions.
(0.5 points per each calculation; total **1 point**)

II-9.2 At the temperature $T_{\mathrm{melt}}^{\infty}$ the macrophase melts. Since $G_{\mathrm{solid}}^{\infty}(T_{\mathrm{melt}}^{\infty}) = G_{\mathrm{liq}}(T_{\mathrm{melt}}^{\infty})$, then

$$H_{\mathrm{solid}} - T_{\mathrm{melt}}^{\infty}\cdot S_{\mathrm{solid}} = H_{\mathrm{liq}} - T_{\mathrm{melt}}^{\infty}\cdot S_{\mathrm{liq}}. \qquad (1)$$

At temperature T_{melt} the nanoparticles melt:

$$G_{\mathrm{solid}}(T_{\mathrm{melt}}) = G_{\mathrm{liq}}(T_{\mathrm{melt}}).$$

Taking into account the contribution of the surface tension to the Gibbs energy:

$$G_{\text{solid}}(T_{\text{melt}}) = G^{\infty}_{\text{solid}}(T_{\text{melt}}) + pV_{\text{m}} = G^{\infty}_{\text{solid}}(T_{\text{melt}}) + \frac{2\sigma V_{\text{m}}}{r}.$$

Thus:

$$G^{\infty}_{\text{solid}}(T_{\text{melt}}) + \frac{2\sigma V_{\text{m}}}{r} = G_{\text{liq}}(T_{\text{melt}}).$$

$$H_{\text{solid}} - T_{\text{melt}} \cdot S_{\text{solid}} + \frac{2\sigma V_{\text{m}}}{r} = H_{\text{liq}} - T_{\text{melt}} \cdot S_{\text{liq}} \qquad (2)$$

Subtracting equation (1) from (2) we obtain

$$S_{\text{solid}} \cdot (T^{\infty}_{\text{melt}} - T_{\text{melt}}) + \frac{2\sigma V_{\text{m}}}{r} = S_{\text{liq}} \cdot (T^{\infty}_{\text{melt}} - T_{\text{melt}}),$$

$$\frac{2\sigma V_{\text{m}}}{r} = (T^{\infty}_{\text{melt}} - T_{\text{melt}}) \cdot (S_{\text{liq}} - S_{\text{solid}}) = (T^{\infty}_{\text{melt}} - T_{\text{melt}}) \cdot \Delta S_{\text{melt}}.$$

Considering that $\Delta S_{\text{melt}} = \Delta H_{\text{melt}}/T^{\infty}_{\text{melt}}$, we arrive at the Gibbs–Thomson equation:

$$\frac{2\sigma V_{\text{m}}}{r} = (T^{\infty}_{\text{melt}} - T_{\text{melt}}) \cdot \frac{\Delta H_{\text{melt}}}{T^{\infty}_{\text{melt}}},$$

$$T^{\infty}_{\text{melt}} \cdot \frac{2\sigma V_{\text{m}}}{r} = T^{\infty}_{\text{melt}} \cdot \Delta H_{\text{melt}} - T_{\text{melt}} \cdot \Delta H_{\text{melt}},$$

$$T_{\text{melt}} = T^{\infty}_{\text{melt}} \cdot \left(1 - \frac{2\sigma V_{\text{m}}}{r\Delta H_{\text{melt}}}\right).$$

Thus, $a = 2\sigma V_{\text{m}}/\Delta H_{\text{melt}}$, $V_{\text{m}} = M_{\text{Au}}/\rho$, then

$$a = \frac{2\sigma M_{\text{Au}}}{\Delta H_{\text{melt}}\rho},$$

$$\rho = \frac{2\sigma M_{\text{Au}}}{a\Delta H_{\text{melt}}} = \frac{2 \cdot 0.3\ \frac{\text{N}}{\text{m}} \cdot 197 \cdot 10^{-3}\ \frac{\text{kg}}{\text{mol}}}{12.55 \cdot 10^{3}\ \frac{\text{J}}{\text{mol}} \cdot 4.88 \cdot 10^{-10}\ \text{m}} = 19300\ \frac{\text{kg}}{\text{m}^3}.$$

(expression for a: 2 points, density calculation: 1 point; total **3 points**)

II-9.3 In accordance with the Gibbs–Thomson equation, the melting temperature of nanoparticles is lower than the melting temperature of the macrophase. Thus,

$$T^{\infty}_{\text{melt}} - T_{\text{melt}} = 100,$$

$$T^{\infty}_{\text{melt}} - T^{\infty}_{\text{melt}} \cdot \left(1 - \frac{a}{r}\right) = 100,$$

$$T^{\infty}_{\text{melt}} \cdot \frac{a}{r} = 100 \rightarrow T^{\infty}_{\text{melt}} = \frac{100\,r}{a} = \frac{100 \cdot 6.5 \cdot 10^{-9}}{4.88 \cdot 10^{-10}} = 1332\ \text{K},$$

$$\Delta S_{\text{melt}} = \frac{\Delta H_{\text{melt}}}{T^{\infty}_{\text{melt}}} = \frac{12.55 \cdot 10^{3}}{1332} = 9.42\ \frac{\text{J}}{\text{mol} \cdot \text{K}}.$$

(total **1.5 points**)

II-9.4 $E^0_{[\text{AuI}_2]^-/\text{Au}} = E^0_{\text{Au}^+/\text{Au}} + 0.0592\lg[\text{Au}^+] = E^0_{\text{Au}^+/\text{Au}} + 0.0592\lg\frac{[[\text{AuI}_2]^-]}{\beta_{\text{AuI}_2^-} \cdot [\text{I}^-]^2}$,

$$E^0_{[\text{AuI}_2]^-/\text{Au}} = E^0_{\text{Au}^+/\text{Au}} + 0.0592\lg\frac{1}{\beta_{\text{AuI}_2^-}} = 1.69 + 0.0592 \cdot \lg\frac{1}{5.6 \cdot 10^{18}} = 0.580\ \text{V}.$$

(total **1.5 points**)

II-9.5 The ionic equation for the reaction can be written in two forms:

$$2Au + I_2 + 2I^- \rightarrow 2AuI_2^-$$

or

$$2Au + I_3^- + I^- \rightarrow 2AuI_2^-.$$

No preference can be given to either form because I_2 is present in the KI_3 (1 M.) + KI (1 M.) solution as I_2 and I_3^- in equal amounts and $E^0_{I_2^-/2I^-} = E^0_{I_3^-/2I^-}$ ($\beta_{I_3^-} \approx 1$):

$$E^0_{I_3^-/2I^-} = E^0_{I_2^-/2I^-} + \frac{0.0592}{2}\lg[I_2] = E^0_{I_2^-/2I^-} + \frac{0.0592}{2}\lg\frac{[I_3^-]}{\beta_{I_3^-}\cdot[I^-]} =$$

$$= E^0_{I_2^-/2I^-} + \frac{0.0592}{2}\lg\frac{1}{1\cdot 1},\ E^0_{I_3^-/2I^-} = E^0_{I_2^-/2I^-}.$$

For a gold nanowire (cylinder), the surface tension increases the Gibbs energy of the solid phase according to the equation:

$$G_{\text{solid}} = G^{\circ}_{\text{solid}} + \frac{\sigma V_m}{r}.$$

Thus, the potential $E^0_{[AuI_2]^-/Au(nano)}$ becomes lower than $E^0_{[AuI_2]^-/Au}$. Taking into account that $\Delta G = -nFE$, the equation for the dependence of the standard electrode potential on the wire radius takes the form:

$$E^0_{[AuI_2]^-/Au(nano)} = E^0_{[AuI_2]^-/Au} - \frac{\sigma V_m}{Fr} = E^0_{[AuI_2]^-/Au} - \frac{\sigma M_{Au}}{Fr\rho}$$

$$= 0.580 - \frac{0.55\ \frac{N}{m}\cdot 197\cdot 10^{-3}\ \frac{kg}{mol}}{96485\ \frac{C}{mol}\cdot\frac{10}{2}\cdot 10^{-9}\ m\cdot 19300\ \frac{kg}{m^3}} = 0.568\ V.$$

For the dissolution reaction of the gold nanowire, one can determine E^0_r:

$$E^0_r = E^0_{I_2^-/2I^-} - E^0_{[AuI_2]^-/Au(nano)} = 0.536 - 0.568 = -0.032\ V.$$

Then, for the reactions given above,

$$\Delta G^0 = -nFE^0_r = -2\cdot 96485\cdot(-0.032) = 6175\ J/mol.$$

$$\Delta G^0 = -RT\ln K_p$$

$$K_p = \exp\left(-\frac{\Delta G^0}{RT}\right) = \exp\left(-\frac{6175}{8.314\cdot 298}\right) = 0.0827.$$

If the reaction equation is written in the form

$$Au + 0.5I_2 + I^- \rightarrow AuI_2^-,$$

or

$$Au + 0.5I_3^- + 0.5I^- \rightarrow AuI_2^-,$$

then the equilibrium constant for this process is

$$K_p' = \sqrt{K_p} = \sqrt{0.0827} = 0.288.$$

(reaction equation: 1 point; potential calculation: 1 point; equilibrium constant calculation: 1 point; total **3 points**)

II-9.6 Specific electrical conductivity is the reciprocal of the specific resistivity (this can also be deduced from the units of the respective quantities in the problem, [$\Omega^{-1}\cdot m^{-1}$] and [$\Omega\cdot m$]):

$$\rho = \frac{1}{\sigma}.$$

$\sigma, \Omega^{-1}\cdot m^{-1}$	36.10	39.82	41.35	42.24	44.15	44.85
d, nm	40	60	80	100	140	180
$\rho, \Omega\cdot m$	0.0277	0.0251	0.0242	0.0237	0.0227	0.0223

It is evident that with increasing film thickness the resistivity of the film decreases.

$$\rho = \rho_0 \cdot \left(1 + \frac{3l}{8d}\right) = \frac{3l\rho_0}{8} \cdot \frac{1}{d} + \rho_0.$$

The equation describing the dependence of the film's resistivity on its thickness is linear in the coordinates (ρ, $1/d$). Let us determine the parameters of this linear dependence:

$\rho, \Omega\cdot m$	0.0277	0.0251	0.0242	0.0237	0.0227	0.0223
$1/d, 1/m$	$2.5 \cdot 10^7$	$1.67 \cdot 10^7$	$1.25 \cdot 10^7$	$1 \cdot 10^7$	$7.14 \cdot 10^6$	$5.56 \cdot 10^6$

From this, $\rho_0 = 0.0208\ \Omega \cdot m$, $3l\rho_0/8 = 2.725 \cdot 10^{-10}\ \Omega \cdot m^2$. Then,

$$l = \frac{2.725 \cdot 10^{-10} \cdot 8}{3\rho_0} = \frac{2.725 \cdot 10^{-10} \cdot 8}{3 \cdot 0.0208} = 3.50 \cdot 10^{-8}\ m = 35\ nm.$$

(derivation of the equation: 1 point, two values, 1 point each; total **3 points**)

II-9.7 $\sigma_0 = \frac{1}{\rho_0} = 48.08\ \Omega^{-1} \cdot m^{-1}$, $3.50 \cdot 10^{-8} = 1.24 \cdot 10^6 \cdot \sqrt[3]{\frac{3}{8\pi}} \cdot \frac{6.626\cdot 10^{-34}}{(1.602\cdot 10^{-19})^2\sqrt[3]{n^2}} \cdot$ 48.08, and $n = 5.92\cdot 10^{28}\ m^{-3}$. In 1 m^3, there are $N_{Au} = \frac{19300\cdot 10^3}{197} = 6.022 \cdot 10^{23} = 5.9 \cdot 10^{28}$, then $N_e = \frac{n}{N_{Au}} = \frac{5.92\cdot 10^{28}}{5.9\cdot 10^{28}} \approx 1$. Thus, there is one conduction electron per gold atom.

(total **2 points**)

INORGANIC CHEMISTRY

Problem II-10 (authors Likhanov M., Karpova E.V.)

II-10.1 Electrical conductivity is directly proportional to the number of ions in solution. The degree of dissociation of NaCl and $CaCl_2$ in water is ~100%; in alcohol the dissociation of NaCl is significantly lower; H_2SO_4 dissociates well in its first ionization step but less so in the second; $[PdCl_2(NH_3)_2]$ does not dissociate into ions. Thus, the conductivity of the solutions increases in the following order:

$[PdCl_2(NH_3)_2]$ < NaCl in ethanol < NaCl in water < H_2SO_4 in water < $CaCl_2$ in water.

(total **1 point**)

II-10.2. Each **M1** atom is adjacent to six atoms of another element, and each such atom is shared among three **M1** atoms. Thus, there are two atoms of the other element per **M1**.

(total **0.5 points**)

II-10.3 The composition of mineral **A** can be written as $\mathbf{M1}Q_2$. Based on the mass fraction of the metal, we find that $M(\mathbf{M1}) = 3M(Q)$. Suitable elements are, for example, Mo and S. This also agrees with the layered structure of the mineral MoS_2. Thus, **A** = MoS_2.

Upon calcination in oxygen the highest oxide of molybdenum is formed:

$$2MoS_2 + 7O_2 = 2MoO_3 + 4SO_2. \quad \mathbf{B} = MoO_3.$$

Since the mineral contains impurities (most often rhenium), the obtained oxide is then dissolved in a concentrated ammonia solution. Due to the moderately low pH of the medium, ammonium heptamolybdate is formed (an orthomolybdate would be formed in a strongly alkaline medium):

$$7MoO_3 + 6NH_3\cdot H_2O = (NH_4)_6Mo_7O_{24} + 3H_2O.$$

From this solution the tetrahydrate crystallizes: **C** = $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$.

Upon thermal decomposition, ammonium heptamolybdate again yields molybdenum oxide:

$$(NH_4)_6Mo_7O_{24}\cdot 4H_2O = 7MoO_3 + 6NH_3 + 7H_2O.$$

Reduction of MoO_3 with hydrogen upon heating yields pure metallic molybdenum:

$$MoO_3 + 3H_2 = Mo + 3H_2O.$$

(0.5 points for each of substances **A**, **B**, and **C** and each reaction equation, total **3.5 points**)

II-10.4 The description corresponds to beryllium (a light, rare metal that does not react with water but dissolves in an ammonium fluoride solution). Thus, **M2** = Be. As a result of the reaction, a beryllium fluoride complex is formed, in which the metal is in tetrahedral environment.

$$Be + 4NH_4F = (NH_4)_2[BeF_4] + 2NH_3 + H_2. \quad \mathbf{X1} = (NH_4)_2[BeF_4].$$

X2, $Na_2[BeF_4]$, has molar mass of 131 g/mol, which is 42 g/mol greater than the mass number of **Y**. 42 g/mol corresponds to the molar mass of sodium fluoride, NaF. Thus, the composition of **Y** corresponds to $Na[BeF_3]$. In the composition of substance **Z**, silicon must evidently be present. Then the molar mass of **Z** can be represented as: $M(Si) + 54 = 28 + 54$, where $54 = M(O) + 2M(F)$. Thus, **Z** = $SiOF_2$.

The reaction for obtaining beryllium orthosilicate, Be_2SiO_4, can be written as:

$$2Na[BeF_3] + 4SiOF_2 = Be_2SiO_4 + 2NaF + 3SiF_4.$$

(0.5 points for each of substances **M2**, **Y**, **Z** and the reaction equations; total **2.5 points**)

II-10.5 According to VSEPR (the Gillespie method), $SiOF_2$ has trigonal (triangular) structure. An analogous answer is obtained using the principles of VB theory.

(total **0.5 points**)

II-10.6 Salts **S1**–**S3** all have the same anion, which contains nitrogen. Assume this anion is nitrate. In salt **S1** the ratio of the mass fractions of the cation and nitrogen is 4.9. Assume the composition of **S1** is $Me(NO_3)_x$; then, with a metal : nitrogen ratio of 1 : 2, the molar mass of the metal is given by $M(\text{Me}) = 14.01 \cdot 2 \cdot 4.9 = 137.3$ g/mol, which corresponds to barium. Thus, **S1** = $Ba(NO_3)_2$.

The compositions of **S2** and **S3** can be written as $Me(NO_3)_x \cdot mH_2O$. Based on the given mass fractions, one obtains **S2** = $Ca(NO_3)_2 \cdot 4H_2O$, **S3** = $Cu(NO_3)_2 \cdot 3H_2O$.

Upon sintering the three salts in a 2 : 1 : 2 molar ratio, a complex oxide is obtained; since the reaction proceeds in an oxygen atmosphere, copper retains the +2 oxidation state.

$$2Ba(NO_3)_2 + Ca(NO_3)_2 \cdot 4H_2O + 2Cu(NO_3)_2 \cdot 3H_2O = Ba_2CaCu_2O_5 + 10NO_2 + 2.5O_2 + 7H_2O$$

R – $Ba_2CaCu_2O_5$

It is evident that **T** is an oxide; the metal mass fraction in **T** is 92.61%, corresponding to a heavy element. With a metal : oxygen ratio of 1 : 1, **T** is mercury(II) oxide HgO. Indeed, mercury(II) oxide cannot be obtained by the thermal decomposition of mercury(II) nitrate; however, HgO precipitates upon treatment of a mercury(II) nitrate solution with an alkali:

$$Hg(NO_3)_2 + 2NaOH = HgO\downarrow + 2NaNO_3 + H_2O.$$

The formation of **N** occurs under elevated oxygen pressure, so it is logical to assume the oxidation of copper to the +3 oxidation state (which may be only partial). The reaction is:

$$Ba_2CaCu_2O_5 + HgO + \delta/2O_2 = HgBa_2CaCu_2O_{6+\delta}$$

From the mass fraction of the heaviest cation,

$$w(\text{Ba}) = 137.33 \cdot 2 / (200.59 + 137.33 \cdot 2 + 40.08 + 63.55 \cdot 2 + 16 \cdot (6 + \delta)) = 0.3692$$

and $\delta = 0.34$. Thus, **N** is $HgBa_2CaCu_2O_{6.34}$.

(1 point for the calculations, 0.5 points for each of **S1**, **S2**, **S2**, **R**, **T**, **N**, and equation of the reaction for obtaining **R**; total **4.5 points**)

II-10.7 In the sphalerite structure, layers of metal and non-metal alternate, with the element ratio in each layer equal to 1 : 1, then the composition of one layer is Cd_1 or Te_1. Since the nanosheet has cadmium atom layers on both its top and bottom surfaces, the gross formula of the nanosheet can be written as $Cd_{n+1}Te_n$, where n is the number of tellurium layers in the nanosheet. In addition, for every surface cadmium atom there is one oleate residue; taking this into account, the complete composition of the nanosheet can be represented as: $Cd_{n+1}Te_n(OOCR)_2$, where R is $C_{17}H_{33}$. Let us represent the ligand exchange reaction as:

$$Cd_{n+1}Te_n(OOCR)_2 + 2R'SH = Cd_{n+1}Te_n(SR') + 2RCOOH,\ R' – C_{16}H_{34}.$$

The equation for the mass loss to determine n is:

$(M(Cd_{n+1}Te_n(OOCR)_2) – M(Cd_{n+1}Te_n(SR'))\ /\ M(Cd_{n+1}Te_n(OOCR)_2 = 0.04148$, from which $n = 2$.

Thus, the nanosheet has the gross formula Cd_3Te_2, corresponding to one unit cell of sphalerite. The thickness of the cadmium telluride nanosheet is equal to the lattice parameter of the unit cell, 6.48 Å.

(1 point for the ligand exchange equation, 1 point for the calculation of the nanosheet thickness; total **2 points**)

II-10.8 Compounds of beryllium, mercury, and cadmium pose a special risk (b, c, d).

(0.2 points for selection of one or two correct options, **0.5 points** for correct choice of three metals, 0 points for marking all metals)

Problem II-11 (author Khvalyuk V.N.)

II-11.1 If we assume that compound **B** contains only one sodium atom, its molar mass is 22.99 / 0.4107 = 55.98 g/mol. Subtracting the mass of sodium (22.99 g/mol) leaves 55.98 – 22.99 = 32.99 g/mol for the anion. Assuming that the anion is composed solely of nonmetals, the molar mass permits only combinations from H, B, C, N, O, F, Si, P, and S. A brief examination reveals an acceptable mass combination for the anion and gas **C** – namely, PH_2 and PH_3. Thus, compound **B** is $NaPH_2$ and compound **C** is PH_3. According to the problem, compound **A** and water are produced in the reaction of $NaPH_2$ with CO:

$$NaPH_2 + CO = \mathbf{A} + H_2O.$$

Then the composition of **A** is NaCP, and the anion **X** is CP^-, a distinct analog of the well-studied cyanide ion CN^- (the two elements, nitrogen and phosphorus, being neighbors in the periodic table).

Assuming that compound **D** contains only one sodium atom, its molar mass is calculated as 22.99 / 0.3380 = 68.02 g/mol. Subtracting the sodium mass yields an anion mass of 68.02 – 22.99 = 45.03 g/mol, which may consist of C, O, and H (the phosphorus atom is transferred to compound **C**). Therefore, the composition of **D** is HCOONa.

(1 point for each of compounds **A**, **B**, **C**, and **D**; total **4 points**)

II-11.2 The following reactions took place:

$$NaPH_2 + CO = NaCP + H_2O;$$
$$NaCP + 2H_2O = HCOONa + PH_3.$$

(0.5 points for each reaction; total **1 point**)

II-11.3 The molar masses of salts **E** and **F** equal 22.99 / 0.2805 = 81.96 g/mol and 22.99 / 0.2737 = 84.00 g/mol, respectively, which are approximately 16 g/mol and 18 g/mol greater than the molar mass of NaCP (65.97 g/mol). Considering the chemical elements involved, it is reasonable to assume that these differences correspond to an extra oxygen atom and a water molecule, respectively. Thus, the formulae are **E** – NaOCP and **F** – NaH_2OCP. The anions of salts **E** and **F** have the following structure:

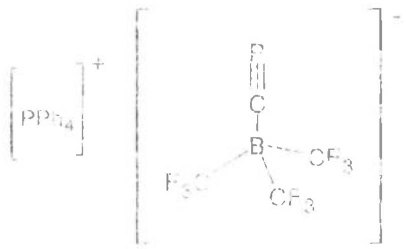
$$P{\equiv}C{-}O^- \qquad HP{=}CH{-}O^-.$$

(0.5 points for each formula and each structure; total **2 points**)

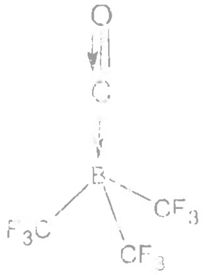
II-11.4 Compound **G** is the product of the addition of 2 moles of HCl at the triple bond in HCP:

(1 point for the reaction and the structure: total 2 points)

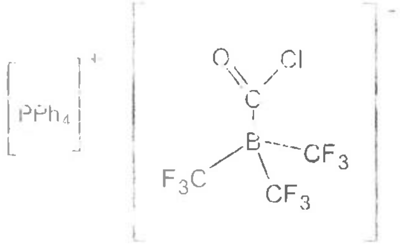
II-11.5 The composition of **H** is described in the problem – it is a salt consisting of the tetraphenylphosphonium cation (PPh_4^+) and an anion that is the adduct of $B(CF_3)_3$ and **X**, i.e., $[PPh_4]\cdot[B(CF_3)_3\cdot CP]$. Its structure is:



Comparing the composition of the reactants with that of the final product, one can note that the oxygen atom, which is eliminated as $Me_3SiOSiMe_3$, must have been present in **H1**. The same applies to the carbon atom from the CP^- anion in **H**. Therefore, **H1** is the adduct $B(CF_3)_3{\cdot}CO$. Its structure is:

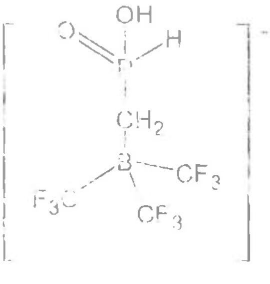


The intermediate product **H2** is assumed to be formed by the addition of $[PPh_4]Cl$ to **H1**. The structure of **H2** is:



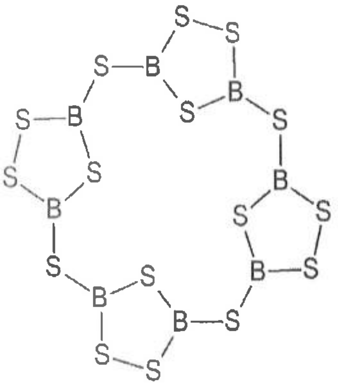
(1 point for each of compounds **H**, **H1**, and **H2**: total **3 points**)

II-11.6 With $w(K) = 11.64\%$, the molar mass of salt **J** should be $39.10 / 0.1164 = 335.91$ g/mol. This value is 36.00 g/mol higher than the molar mass of the expected salt $K[B(CF_3)_3CP]$ (299.91 g/mol). Since the synthesis was carried out "*in the presence of moisture*", it can be assumed that this difference is due to the action of water on the expected product. From the atoms of H and O, several compositions for the additional 36 g/mol can be hypothesized: H_4O_2, $H_{20}O$, H_{36}. Only the first option appears reasonable, as the other two would require the formation of a significant number of new chemical bonds. Therefore, the composition of **J** is $K[B(CF_3)_3{\cdot}CPH_4O_2]$. It is most reasonable to assume that water adds across the C≡P triple bond (analogous to the addition of HCl). Considering the traditional valences (IV for carbon and V for phosphorus) and the special affinity of phosphorus for oxygen, the following structure for the anion of salt **J** can be proposed:



(total **3 points**)

Problem II-12 (author Efendiev R.A.)

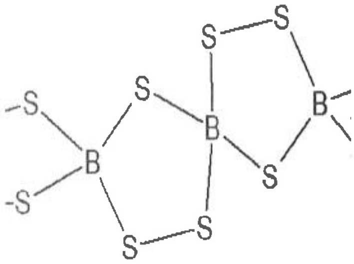


II-12.1 $V_{cell} = a \cdot b \cdot c \cdot \sin\beta = 1040.377$ Å^3, $M_r(\mathbf{A}) = N_A \cdot \rho \cdot V_{cell}/Z =$ $= 598.4$ g/mol. Accounting for the stated constraints, only one highly symmetric structure is possible, X_8S_{16}. We obtain B_8S_{16}, hence, **X** = B and **A** = B_8S_{16}. Alternatively, one can find the correct answer by trial: compound **A** contains 24 atoms, so one may write the equation: $598.4 = n \cdot A_r(\mathbf{X}) + (24 - n) \cdot 32$;

$A_r(\mathbf{X}) = \frac{598.4 - 32 \cdot (24 - n)}{n}$; for $n = 8$, **X** = B.

Reaction 1: $8B_2S_3 + S_8 = 2B_8S_{16}$

(0.25 points for each of **X** and **A**, 0.75 points for the molar mass, 0.75 points for the structure, 0.25 points for equation of reaction 1; total **2.25 points**).



II-12.2 From the problem it follows that in each cycle of compound **B** there are two atoms of **X** which belong simultaneously to two cycles; hence, the remaining three atoms are S. Thus, each five-membered cycle contains 2B, S^{2-}, and S_2^{2-}. Since each B is shared between two cycles, the formula of the anion can be written as $[BS_3]^-$. Therefore, compound **B** is $RbBS_3$. The structure of **B** (without charges) is shown in the figure.

In compound **C**, an additional S atom is incorporated in every third cycle, forming six-membered cycles $-B(S_2)_2B-$, formula of which can be written as $[BS_4]^-$. Hence, the overall formula of the anion is $[B_3S_{10}]^{3-}$ and compound **C** is $Tl_3B_3S_{10}$.

Reaction 2: $8Rb_2S + 5S_8 + 16B = 16RbBS_3$

Reaction 3: $24Tl_2S + 17S_8 + 48B = 16Tl_3B_3S_{10}$

(0.5 points for each of **B**, **C**, and the structure of the anion in **B**, 0.25 points for each reaction; total **2 points**).

II-12.3 One can easily find **Y** and **Z** by reasoning based on their mass ratio $\frac{A_r(\mathbf{Z})}{A_r(\mathbf{X})} \approx A_r(\mathbf{Y})$. The heaviest mass belongs to Og, so the upper limit for the mass of **Y** is 27 g/mol. Moreover, in the cases of Al, Mg, and Na, the mass of **Z** would correspond to very heavy elements whose chemistry is scarcely studied due to their high instability; hence **Y** must be an element from the period 2. Also, discard H (since the mass of **Z** would equal that of B), Li and B (already present in **D**), He and Ne (noble gases), and F (no conceivable anion **I** can be formed).

Reaction 4 is an addition reaction, meaning one of the binary compounds (or both) contains **Y**. A compound of Li with **Y** that hydrolyzes easily is required. A Li compound with a 2nd-period element that can hydrolyze to yield a gaseous product is Li_3N; hence **Y** = N. (One could also find N by trial among the possible options for **D**). The only variant that satisfies the task is Li_3BN_2. Thus, **Y** = N, **D** = Li_3BN_2, and **F** = Li_3N. Subtracting **F** from **D** gives **E** = BN.

Z = Eu, which exhibits oxidation states +2 (with a stable $4f^7$ configuration) and +3 in its compounds. Its mass is slightly greater than $A_r(\mathbf{Y}) \cdot A_r(\mathbf{X})$, which satisfies the task. Compound **G**, like **F**, yields NH_3 upon hydrolysis and has a NaCl-type structure; therefore, **G** = EuN. The highest chloride of europium is $EuCl_3$.

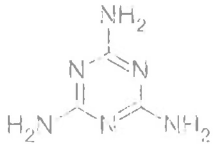
Reaction 6 is redox in nature; from the problem it is evident that it is the oxidation state of Eu that changes. **I** = $Eu_3B_3N_6$, which follows from electrical neutrality considerations. **I** is

formed during the oxidation of **H**, meaning that in **H** Eu is in the +2 oxidation state; hence, **H** = $Eu_3B_2N_4$.
The formation of **J** is most simply represented as: $Eu_3B_3N_6 + n\mathrm{Li} = \mathrm{Li}_nEu_3B_3N_6$, i.e., a fraction of Eu atoms is reduced to +2. Then the maximum charge q (in C) per 1 g of **J** is $q = 20.492 \cdot 3600 / 1000 = 73.7705 = n \cdot F$. Thus, **J** = $Li_{0.44}Eu_3B_3N_6$ (M_r(**J**) = 575.5 g/mol; $\frac{n \cdot F}{M(Eu_3B_3N_6) + M(\mathrm{Li}) n} = q$; $n = 0.44$).
(1 point for each of elements **Y** and **Z**, 0.75 point for each of **D**–**J**, 0.5 points for the molar masses of each of **D** and **J**; total **8.25 points**).
II-12.4 In ***reactions*** 5 and 7, Eu acts as an oxidizing agent, transitioning from oxidation state +3 to +2. The only reducing agent in these systems is N; therefore, these reactions are accompanied by the evolution of N_2. In order to balance ***reaction*** 7, BN must be included among the products.
Reaction 4: $Li_3N + BN = Li_3BN_2$
Reaction 5: $6EuN + 4BN = 2Eu_3B_2N_4 + N_2$
Reaction 6: $6Eu_3B_2N_4 + 9Br_2 = 4Eu_3B_3N_6 + 6EuBr_3$
Reaction 7: $472Li_3BN_2 + 450EuCl_3 = 150Li_{0.44}Eu_3B_3N_6 + 1350LiCl + 11N_2 + 22BN$
(0.25 points for each of ***reactions*** 4–6, 0.75 points for ***reaction*** 7; total **1.5 points**).
II-12.5 $n(LiC_6) = m(LiC_6) / M(LiC_6) = 1 / 79 = 0.01266$ mol.
Capacity: $C(LiC_6) = n \cdot F \cdot (1000 / 3600) = 339.5$ mA·h/g. The maximum capacity of LiC_6 is higher (option 1).
(0.9 points for the calculation of $C(LiC_6)$, 0.1 points for the choice; total **1 point**).

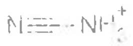
ANALYTICAL CHEMISTRY

Problem II-13 (authors Ratova D.-M.V., Shved A.M.)

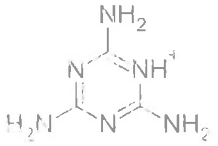
II-13.1 Since **A** is an organic compound containing amino groups, it must be composed of at least C, H, and N. Analyzing the mass spectrum, one can assume that the ion at *m/z* 127 is the protonated molecular ion $[M+H]^+$, as electrospray ionization is a soft ionization method. Therefore, the molecular mass of **A** is 126. The signal at *m/z* 43 corresponds to 1/3 of **A** with an additional proton due to ionization. This may indicate that **A** is a trimer, which is consistent with the presence of three equivalent amino groups, as stated in the problem.
A mass fraction of 66.67% of 126 is $0.6667 \cdot 126 = 84$, which corresponds to either 7 carbon atoms or 6 nitrogen atoms. Since **A** is a trimer and 7 is not a multiple of 3, **A** contains 6 nitrogen atoms. The remaining mass of $126 - 84 = 42$ corresponds to 3 carbon atoms and 6 hydrogen atoms, thus the molecular formula of **A** is $(CH_2N_2)_3$ or $C_3H_6N_6$.
Since **A** contains three equivalent amino groups, its structure is:



This is melamine. The structures of the species corresponding to the signals in the mass spectrum are:



m/z 43



m/z 127

(1 point for the formula of A, 1 point for each structure of the species; total **3 points**)

II-13.2 When proteins and melamine are heated with concentrated sulfuric acid, nitrogen is converted into an ammonium salt, which, upon heating with alkali, releases gas **B** – NH_3. Its reaction equation with boric acid forming tetraborate:

$$2NH_3 + 4H_3BO_3 \rightarrow (NH_4)_2B_4O_7 + 5H_2O$$

(1 point for the formula of **B**, 1 point for the reaction equation; total **2 points**)

II-13.3 During the titration of tetraborate, the following reaction occurs:

$$(NH_4)_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NH_4Cl + 4H_3BO_3$$

Thus, the amount of HCl corresponds to the amount of nitrogen in the sample:

$$n(N) = n(HCl) = 0.00715 \cdot 0.100 = 7.15 \cdot 10^{-4} \text{ mol}$$

Then, the mass and mass fraction of nitrogen in the sample:

$$m(N) = 14.0 \cdot 7.15 \cdot 10^{-4} = 0.0100 \text{ g}$$

$$\omega(N) = 0.0100 / 2.00 \cdot 100\% = 0.500\%$$

(1 point for the reaction equation, 1 point for calculations; total **2 points**)

II-13.4 Reaction equations:

a) $R{-}NH_3^+ + CH_2O \rightarrow R{-}NH{-}CH_2OH + H^+$ (or $R{-}N{=}CH_2 + H^+ + H_2O$)

b) $H^+ + OH^- \rightarrow H_2O$

c) $HCOOH + OH^- \rightarrow HCOO^- + H_2O$ (formaldehyde solution contains a small amount of formic acid due to oxidation)

(1 point for equation a), 0.5 points each for equations b) and c); total **2 points**)

II-13.5 The second titration required 14.15 − 9.60 = 4.55 mL of NaOH solution. Out of this, 2.35 mL was used to neutralize formic acid in the formaldehyde solution. Thus, only 4.55 − 2.35 = 2.20 mL of NaOH solution was used to titrate the protons released from the reaction of amino groups with formaldehyde, so:

$$n(\text{R–NH}_3^+) = n(\text{H}^+) = 0.00220 \cdot 0.100 = 2.20 \cdot 10^{-4}\ \text{mol}$$

The amount of nitrogen in the protein:

$$n(\text{N})_{\text{protein}} = 2.20 \cdot 10^{-4} / 0.047 = 4.68 \cdot 10^{-3}\ \text{mol}$$

The amount of **A** is determined from the results of analysis No 1 using the Kjeldahl method:

$$n(\textbf{A}) = (7.15 \cdot 10^{-4} \cdot 20.0 / 2.00 - 4.68 \cdot 10^{-3}) / 6 = 4.12 \cdot 10^{-4}\ \text{mol}$$

Then the mass and mass fraction of **A**:

$$m(\textbf{A}) = 126 \cdot 4.12 \cdot 10^{-4} = 0.0519\ \text{g}$$

$$w(\textbf{A}) = 0.0519 / 20.0 \cdot 100\% = 0.26\%$$

Protein mass in the analyzed sample:

$$m(\text{protein}) = 14.0 \cdot 4.68 \cdot 10^{-3} / 0.157 = 0.417\ \text{g}$$

Protein mass in a standard 20.0 g sample:

$$m(\text{protein})_{\text{st}} = 3.20 / 100.0 \cdot 20.0 = 0.640\ \text{g}$$

Thus, the analyzed sample contains $x = 0.640 / 0.417 = 1.53$ times less protein than the standard value.

If the alternative nitrogen mass fraction of 1.00% was used for calculations, then the total amount of nitrogen in a 20.0 g sample is:

$$n(\text{N}) = 0.0100 \cdot 20.0 / 14.0 = 1.43 \cdot 10^{-2}\ \text{mol}$$

Therefore, the amount of **A**:

$$n(\textbf{A}) = (1.43 \cdot 10^{-2} - 4.68 \cdot 10^{-3}) / 6 = 1.60 \cdot 10^{-3}\ \text{mol}$$

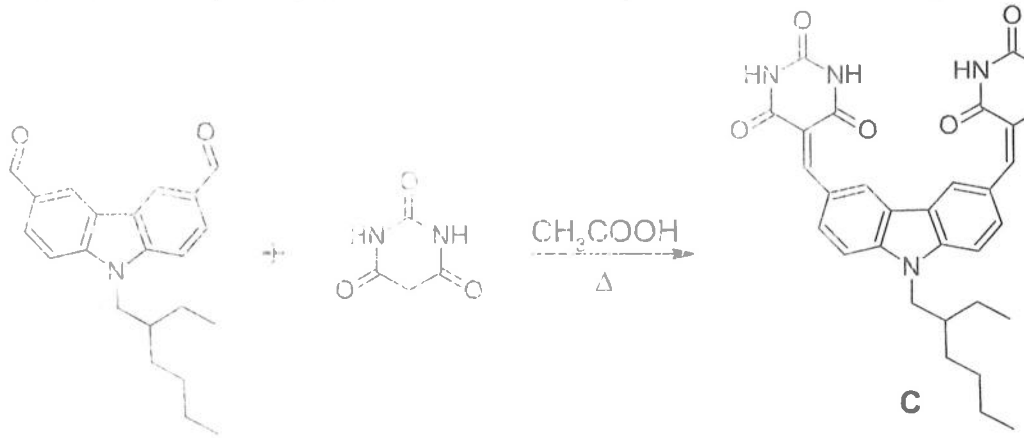
Then, the mass and mass fraction of **A**:

$$m(\textbf{A}) = 126 \cdot 1.60 \cdot 10^{-3} = 0.202\ \text{g}$$

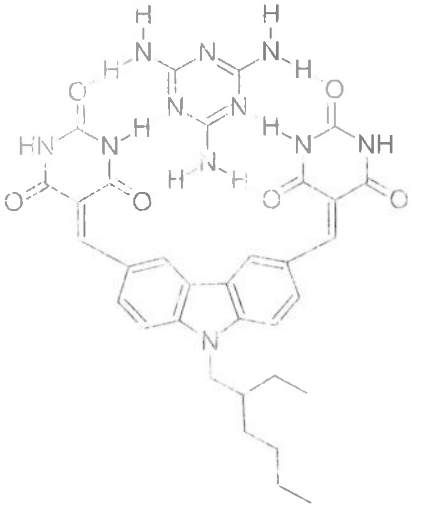
$$w(\textbf{A}) = 0.202 / 20.0 \cdot 100\% = 1.01\%$$

(1 point for determining the amount of R–NH_3^+, 1 point for determining the mass fraction of **A**, 1 point for finding x; total **3 points**)

II-13.6 **C** is formed by the condensation of an aldehyde and a 1,3-dicarbonyl compound:



The ability to form six hydrogen bonds with **A** confirms its structure:



(1 point for structure **C**; total **1 point**)

II-13.7 Let us assume 200 μL of milk sample contains m mg of **A**. During the preparation of the ***solution 2***, $500 \cdot 0.00200 = 1.00$ mg of **A** was added. Fluorescence intensity (after background subtraction) is directly proportional to the concentration of the substance. Since dilution was identical for all solutions, the following equation can be written:

$$\frac{m}{m + 1.00} = \frac{I_1 - I_0}{I_2 - I_0} = \frac{3.46 - 2.72}{4.87 - 2.72} = \frac{0.74}{2.15}$$

Solving this equation, we obtain $m = 0.525$ mg.
Thus, the concentration of **A** according to fluorescence analysis:

$$c(\mathrm{A}) = 0.525 / 0.200 = 2.63 \text{ mg/mL}$$

(1 point for the equation, 1 point for determining the concentration of **A**; total **2 points**)

Problem II-14 (author Roslyakov S.N.)

II-14.1 $\alpha_{PO_4^{3-}} = \frac{[PO_4^{3-}]}{c_0^{PO_4^{3-}}}$, consequently $[PO_4^{3-}] = \alpha_{PO_4^{3-}} \cdot c_{PO_4^{3-}}$

$$c_{CePO_4} = \frac{m_{CePO_4}}{M_{CePO_4} \cdot V} = \frac{28.82 \cdot 10^{-3}}{235 \cdot 1000} = 1.23 \cdot 10^{-7}\ \mathrm{M}$$

$$[Ce^{3+}] = c_{CePO_4}$$

$$c_{PO_4^{3-}} = c_0^{PO_4^{3-}} + c_{CePO_4} = c_0^{P} + c_{CePO_4} = \frac{2 \cdot 10^{-6}}{31} + 1.23 \cdot 10^{-7} = 1.88 \cdot 10^{-7}\ \mathrm{M}$$

$$K_{sp}^{monazite} = [Ce^{3+}] \cdot [PO_4^{3-}] = [Ce^{3+}] \cdot \alpha_{PO_4^{3-}} \cdot c_{PO_4^{3-}} =$$
$$= 1.23 \cdot 10^{-7} \cdot 1.88 \cdot 10^{-7} \cdot 2.34 \cdot 10^{-5} = 5.41 \cdot 10^{-19}$$

(total **2 points**; penalty −0.5 points for calculation errors; failure to account for protonation of PO_4^{3-} or initial inorganic phosphorus - 0 points)

II-14.2. If x mol/L of $Ca_{9.54}Na_{0.33}Mg_{0.13}(PO_4)_{4.8}(CO_3)_{1.4}F_{2.48}$ was dissolved, then:

$c_0^{Ca^{2+}} = 9.54x$, $c_0^{Na^+} = 0.33x$, $c_0^{Mg^{2+}} = 0.13x$, $c_0^{PO_4^{3-}} = 4.8x$, $c_0^{CO_3^{2-}} = 1.4x$, $c_0^{F^-} = 2.48x$

$[PO_4^{3-}] = \alpha_{PO_4^{3-}} \cdot c_0^{PO_4^{3-}}$, $[CO_3^{2-}] = \alpha_{CO_3^{2-}} \cdot c_0^{CO_3^{2-}}$, $[F^-] = \alpha_{F^-} \cdot c_0^{F^-}$

$c_0^{Ca^{2+}} = [Ca^{2+}]$, $c_0^{Na^+} = [Na^+]$, $c_0^{Mg^{2+}} = [Mg^{2+}]$

Next, we use the known equilibrium concentrations and the expression for $K_{sp}^{francolite}$:

$$K_{sp}^{\text{francolite}} = [Ca^{2+}]^{9.54}[Na^{+}]^{0.33}[Mg^{2+}]^{0.13}[PO_4^{3-}]^{4.8}[CO_3^{2-}]^{1.4}[F^{-}]^{2.48}$$

$$K_{sp}^{\text{francolite}} = (9.54x)^{9.54}(0.33x)^{0.33}(0.13x)^{0.13} \times$$
$$\times (\alpha_{PO_4^{3-}} \cdot 4.8x)^{4.8}(\alpha_{CO_3^{2-}} \cdot 1.4x)^{1.4}(\alpha_{F^-} \cdot 2.48x)^{2.48}$$

(total **2 points**)

II-14.3. a) Using the expression obtained in i. **II-14.2** and the required mole fractions of anions at pH 7.46.

$$K_{sp}^{\text{francolite}} = (9.54x)^{9.54}(0.33x)^{0.33}(0.13x)^{0.13}(2.34 \cdot 10^{-5} \cdot 4.8x)^{4.8} \times$$
$$\times (1.25 \cdot 10^{-3} \cdot 1.4x)^{1.4}(1 \cdot 2.48x)^{2.48} = 1.7 \cdot 10^{-13} \cdot x^{18.68}$$

$$x = \sqrt[18.68]{\frac{K_{sp}^{\text{francolite}}}{1.7 \cdot 10^{-13}}} = \sqrt[18.68]{\frac{10^{-94.7}}{1.7 \cdot 10^{-13}}} = 4.11 \cdot 10^{-5}\ \text{M}$$

$$s_{\text{francolite}} = x \cdot M_{\text{francolite}} = 4.11 \cdot 10^{-5} \cdot 980.23 = 0.0403\ \frac{\text{g}}{\text{L}} = 40.3\ \frac{\text{mg}}{\text{L}}$$

$$s_{\text{P}} = s_{\text{francolite}} \cdot \omega_{\text{francolite}}^{\text{P}} = 40.3 \cdot \frac{31 \cdot 4.8}{980.23} = 6.12\frac{\text{mg}}{\text{L}}$$

b) At pH 3.83:

$$K_{sp}^{\text{francolite}} = (9.54x)^{9.54}(0.33x)^{0.33}(0.13x)^{0.13}(3.56 \cdot 10^{-12} \cdot 4.8x)^{4.8} \times$$
$$\times (9.52 \cdot 10^{-10} \cdot 1.4x)^{1.4}(0.817 \cdot 2.48x)^{2.48} = 5.28 \cdot 10^{-55} \cdot x^{18.68}$$

$$x = \sqrt[18.68]{\frac{K_{sp}^{\text{francolite}}}{5.28 \cdot 10^{-55}}} = \sqrt[18.68]{\frac{10^{-94.7}}{5.28 \cdot 10^{-55}}} = 6.64 \cdot 10^{-3}\ \text{M}$$

$$s_{\text{francolite}} = x \cdot M_{\text{francolite}} = 6.64 \cdot 10^{-3} \cdot 980.23 = 6.51\ \frac{\text{g}}{\text{L}}$$

$$s_{\text{P}} = s_{\text{francolite}} \cdot \omega_{\text{francolite}}^{\text{P}} = 6.51 \cdot \frac{31 \cdot 4.8}{980.23} = 0.988\ \frac{\text{g}}{\text{L}}$$

Note that the solubility of the mineral has increased by almost 160 times compared to that in nearly neutral water.

(1.5 points each for (a) and (b), −0.5 points penalty for calculation errors, −0.5 points penalty for incorrect mole fractions: **total 3 points**)

II-14.4. For francolites $Ca_{10}(PO_4)_{5.83-0.57x}(CO_3)_xF_{2.52-0.3x}$, the following ratios are obtained based on the matter balance.

$$c_0^{PO_4^{3-}} = \frac{5.83-0.57x}{10} \cdot c_0^{Ca^{2+}},\ c_0^{CO_3^{2-}} = \frac{x}{10} \cdot c_0^{Ca^{2+}},\ c_0^{F^-} = \frac{2.52-0.3x}{10} \cdot c_0^{Ca^{2+}},\ c_0^{Ca^{2+}} = [Ca^{2+}]$$

From where $[PO_4^{3-}] = \frac{5.83-0.57x}{10} \cdot [Ca^{2+}] \cdot \alpha_{PO_4^{3-}}$, $[CO_3^{2-}] = \frac{x}{10} \cdot [Ca^{2+}] \cdot \alpha_{CO_3^{2-}}$,

$[F^-] = \frac{2.52-0.3x}{10} \cdot [Ca^{2+}] \cdot \alpha_{F^-}$.

Thus, we can calculate the equilibrium concentrations necessary to determine the $K_{sp}^{\text{francolite}}$:

x	0.25	0.5	1	1.25
$[Ca^{2+}]$, M	$4.60 \cdot 10^{-7}$	$9.05 \cdot 10^{-7}$	$1.72 \cdot 10^{-6}$	$2.75 \cdot 10^{-6}$
$[PO_4^{3-}]$, M	$1.07 \cdot 10^{-7}$	$2.06 \cdot 10^{-7}$	$3.71 \cdot 10^{-7}$	$5.80 \cdot 10^{-7}$
$[CO_3^{2-}]$, M	$1.10 \cdot 10^{-8}$	$4.35 \cdot 10^{-8}$	$1.65 \cdot 10^{-7}$	$3.30 \cdot 10^{-7}$
$[F^-]$, M	$1.12 \cdot 10^{-7}$	$2.15 \cdot 10^{-7}$	$3.82 \cdot 10^{-7}$	$5.90 \cdot 10^{-7}$
$K_{sp}^{\text{francolite}}$	$1.01 \cdot 10^{-122}$	$1.01 \cdot 10^{-117}$	$3.19 \cdot 10^{-113}$	$1.01 \cdot 10^{-109}$

Let us determine the parameters of the linear dependence of $\log_{10} K_{sp}^{\text{francolite}}$ on x:

x	0.25	0.5	1	1.25
$\log_{10} K_{sp}^{\text{francolite}}$	−122	−117	−112.5	−109

$$\log_{10} K_{sp}^{\text{francolite}} = -124.3 + 12.2x$$

Thus, $k = 12.2$, $K_{sp}^{\text{fluorapatite}} = 10^{-124.3} = 5.012 \cdot 10^{-125}$.

(0.5 points for each correct expression for calculating $[PO_4^{3-}]$, $[CO_3^{2-}]$, $[F^-]$, 0.5 points for each correct order of values of $K_{sp}^{\text{francolite}}$, 1.25 points for each of coefficients k and $K_{sp}^{\text{fluorapatite}}$; **total 6 points**)

II-14.5. Since the francolite has the composition $Ca_{10}(PO_4)_{5.4}(CO_3)_{0.75}F_{2.3}$, $x = 0.75$ (coefficient at CO_3^{2-} in the general composition $Ca_{10}(PO_4)_{5.83-0.57x}(CO_3)_xF_{2.52-0.3x}$).

For $x = 0.75$, we have $\log_{10} K_{sp}^{\text{francolite}} = 12.2 \cdot 0.75 - 124.3 = -115.15$

$$K_{sp}^{\text{francolite}} = 10^{-115.15} = 7.08 \cdot 10^{-116}$$

(0.5 points)

$$K_{sp}^{\text{francolite}} = [Ca^{2+}]^{10}[PO_4^{3-}]^{5.4}[CO_3^{2-}]^{0.75}[F^-]^{2.3} =$$

$$= (10x)^{10}\left(5.4x \cdot \alpha_{PO_4^{3-}}\right)^{5.4}\left(0.75x \cdot \alpha_{CO_3^{2-}}\right)^{0.75}(2.3x \cdot \alpha_{F^-})^{2.3} =$$

$$= (10x)^{10}(5.4x \cdot 3.56 \cdot 10^{-12})^{5.4}(0.75x \cdot 9.52 \cdot 10^{-10})^{0.75}(2.3x \cdot 0.817)^{2.3} =$$

$$= 8.000 \cdot 10^{-55}x^{18.45} = 10^{-115.15}$$

$$x = \sqrt[18.45]{\frac{10^{-115.15}}{8.000 \cdot 10^{-55}}} = \sqrt[18.45]{\frac{10^{-99}}{8.000 \cdot 10^{-55}}} \cdot 10^{-16.15} = 4.908 \cdot 10^{-4}\ \text{M}$$

$$s_{\text{francolite}} = x \cdot M_{\text{francolite}} = 4.908 \cdot 10^{-4} \cdot 1002.32 = 0.4919\ \frac{\text{g}}{\text{L}}$$

Let us calculate the volume of water in which 50 tons of mineral can dissolve:

$$V_{H_2O} = \frac{50 \cdot 10^6\ \text{g}}{0.4919\ \text{g/L}} = 1.016 \cdot 10^8\ \text{L}$$

$$t = \frac{V_{H_2O}}{V_{H_2O}^{\text{year}}} = \frac{1.016 \cdot 10^8}{15 \cdot 10^6} = 6.77 \approx 7\ \text{years}$$

(1.5 points: **2** points total; −0.5 points penalty for calculation errors)

Problem II-15 (author Shved A.M.)

II-15.1 A – $FeSO_4$, **B** – $Fe_2(SO_4)_3$, **C** – $(NH_4)_2S_2$, **D** and **E** – $CuSO_4$ and $(NH_4)_2S$ (in any order)

Reaction equations:

Experiment 1

$$6CN^- + Fe^{2+} \rightarrow [Fe(CN)_6]^{4-}$$

$$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \rightarrow Fe_4[Fe(CN)_6]_3(s)$$

Experiment 2:

$$CN^- + S_2^{2-} \rightarrow SCN^- + S^{2-}$$

$$SCN^- + Fe^{3+} \rightarrow [Fe(SCN)]^{2+}$$

(or $[Fe(SCN)(H_2O)_5]^{2+}$, $Fe(SCN)_3$, etc.)

Experiment 3:

$$Cu^{2+} + S^{2-} \rightarrow CuS(s)$$

$$2CuS(s) + 10CN^- \rightarrow 2[Cu(CN)_4]^{3-} + (CN)_2(g) + 2S^{2-}$$

(0.5 points for selecting each reagent, 0.5 points per reaction equation; total **5.5 points**)

II-15.2 One bitter almond kernel contains (44 / 1000) · 3.2 = 0.14 g of amygdalin, i.e., 0.14 / (12.01 · 20 + 1.008 · 27 + 14.01 + 16.00 · 11) = $3.1 \cdot 10^{-4}$ mol. Since the amygdalin molecule contains only one nitrogen atom, it produces one molecule of HCN per molecule of amygdalin. Therefore, the amount of HCN per one bitter almond kernel is $3.1 \cdot 10^{-4}$ mol, i.e., $3.1 \cdot 10^{-4}$ · (1.008 + 12.01 + 14.01) · 1000 = 8.4 mg. In a day, one person weighing 65 kg can safely intake 0.6 · 65 = 39 mg HCN. Then the maximum number of almond kernels is 39 / 8.4 = 4.6, i.e., $N = 4$ whole kernels.

(−0.5 points penalty for answering 4.6 or 5 instead of 4; total **2 points**)

II-15.3 During the two-electron oxidation of the cyanide ion CN^- (oxidation state of carbon +2), the cyanate ion OCN^- (ion **F**, oxidation state of carbon +4) is formed. The same oxidation product can be seen in the reaction with ninhydrin, given later in the problem.

From the described stoichiometry, it can be concluded that two out of three Cu(II) atoms are reduced to Cu(I); then, considering that **G** is a neutral complex containing an equal number of NH_3 and CN^- ligands, its formula is $(Cu^{II})(Cu^{I})_2(NH_3)_4(CN)_4$, or $Cu_3(NH_3)_4(CN)_4$.

Reaction equation (not required):

$$3[Cu(NH_3)_4]^{2+} + 5CN^- + 2OH^- \rightarrow Cu_3(NH_3)_4(CN)_4 + OCN^- + 8NH_3 + H_2O$$

or

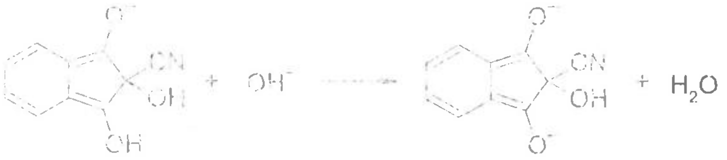
$$3[Cu(NH_3)_4]^{2+} + 5CN^- + H_2O \rightarrow Cu_3(NH_3)_4(CN)_4 + OCN^- + 2NH_4^+ + 6NH_3$$

(1 point for ion **F**, 1 point for the composition of complex **G**; total **2 points**)

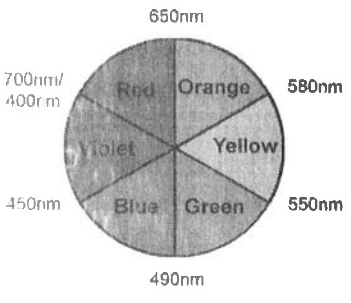
II-15.4 Average absorbance: A = (0.277 + 0.265 + 0.274) / 3 = 0.272. According to the Beer–Bouguer–Lambert law: $c(\mathbf{Y}) = A / (\varepsilon \cdot l) = 0.272 / (1.40 \cdot 10^5 \cdot 1) = 1.94 \cdot 10^{-6}$ M. The total volume of each sample after adding ninhydrin: V = 1.50 mL, then the amount of **Y**: $n(\mathbf{Y}) = c(\mathbf{Y}) \cdot V = 1.94 \cdot 10^{-6} \cdot 1.50 \cdot 10^{-3} = 2.91 \cdot 10^{-9}$ mol, and the amount of HCN according to the reaction equation: $n(HCN) = 2n(\mathbf{Y}) = 2 \cdot 2.91 \cdot 10^{-9} = 5.82 \cdot 10^{-9}$ mol. The initial volume of Na_2CO_3 solution is 40 times larger than the sampled aliquot, so the amount of HCN in the smoke from one cigarette is: $n(HCN)_{smoke} = 40n(HCN) = 40 \cdot 5.82 \cdot 10^{-9} = 2.33 \cdot 10^{-7}$ mol, i.e., $m(HCN)_{smoke} = 2.33 \cdot 10^{-7} \cdot (1.008 + 12.01 + 14.01) = 6.3 \cdot 10^{-6}$ g = 6.3 μg. Only 10% of HCN passes through the filter, therefore, the total amount of HCN produced by one cigarette is: $m(HCN)_0 = 6.3 / 0.10 = 63$ μg.

(total 3 points)

II-15.5 When NaOH is added to **Y**, deprotonation occurs:



Y **Z**



The color transition from yellow (**X**) to red (**Y**) and then to blue (**Z**) corresponds to the following complementary colors of absorbed light: violet (**X**), green (**Y**), orange (**Z**). In this series, the wavelength increases, therefore **I** – **X**, **II** – **Y**, **III** – **Z**. Another way of matching is to notice that transitioning from **X** to **Y**, leads to an increase in the length of the conjugated system, whereas deprotonation of **Y** to form **Z** results in an increase in its electron density. This leads to a decrease in the energy gap between the HOMO and LUMO, which is reflected as an increase of the absorbed light.

(0.5 points for the structure of Z, 2 points for the correct spectrum assignment; total **2.5 points**)