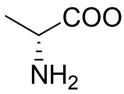
SECTION I. LIFE SCIENCES AND POLYMERS

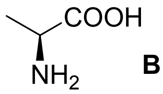
Problem 1 (author Garifullin B.N.)

1. The net formula of **A** is:

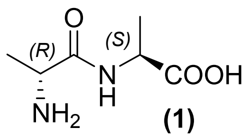
$$n(C):n(H):n(N):n(O) = \frac{w(C)}{A_r(C)}:\frac{w(H)}{A_r(H)}:\frac{w(N)}{A_r(N)}:\frac{w(O)}{A_r(O)} = 3:7:1:2$$

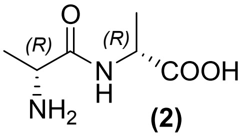
Only α-amino acid alanine is possible if the net and molecular formulas coincide. However, *L*-alanine is a canonical amino acid, which is in contradiction to the data given. Still, it is impossible to suggest any canonical acid **B** affording **A** in one step without any other reagents, if the molecular formula is given as $(C_3H_7NO_2)_n$ with $n \geq 2$. Thus, deciphering **A** as *D*-alanine is the only reasonable option. Then, **B** is *L*-alanine, which undergoes racemization affording *D*-alanine in alkaline medium (1.25 point for each structure, 2.5 points in total).


A


B

2. Based on the molar fractions of the elements, the net (as well as molecular) formula of **C** is found as $C_6H_{14}N_2O_3$ (two atoms not mentioned in the text are nitrogens, since a dipeptide is considered). For an acyclic dipeptide, the sum of molecular formulas of amino acids forming it equals $C_6H_{14}N_2O_3 + H_2O = C_6H_{16}N_2O_4$. Subtracting the formula of ***D***-alanine, one gets that of the second amino acid as $C_3H_7NO_2$, that is alanine again. The data given in the text do not allow distinguishing between ***L***-alanine and ***D***-alanine, since both are found in bacterial cells. Thus, the possible structures of **C** are:


(1)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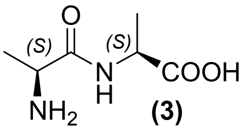

(3)

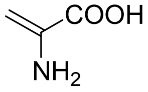
Hydrolysis of any of these dipeptides under extreme conditions leads to the racemic mixture, containing equivalent amounts of both alanine stereoisomers (the compound **D**).

For your information: **C** is the *D*-Ala-*D*-Ala dipeptide formed in an ATP-dependent process catalyzed by *D*-Ala-*D*-Ala ligase (0.75 point for each variant, 3 points in total).

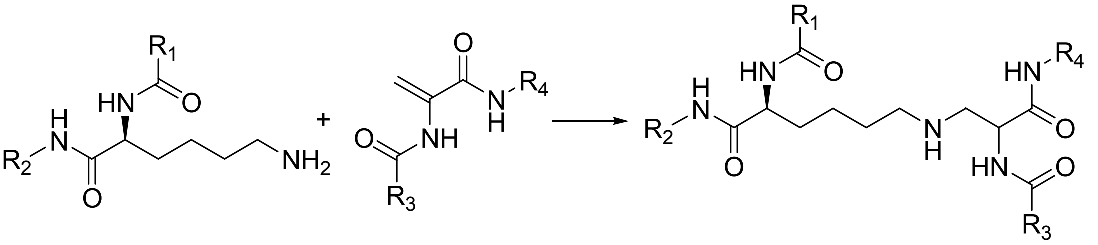
3. The net formula of **Y** is:

$$n(C):n(H):n(N):n(O) = \frac{w(C)}{A_r(C)}:\frac{w(H)}{A_r(H)}:\frac{w(N)}{A_r(N)}:\frac{w(O)}{A_r(O)} = 3:5:1:2$$

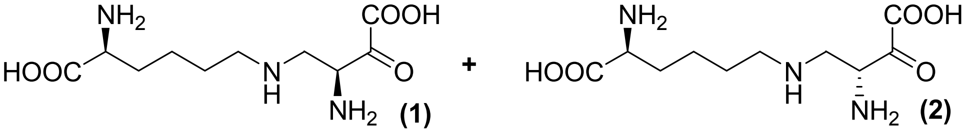
Since **Y** is an <u>**α-amino acid**</u> (neither imino nor β-amino acids are considered), the only hereunder structure is valid for **Y**:


Y, dehydroalanine

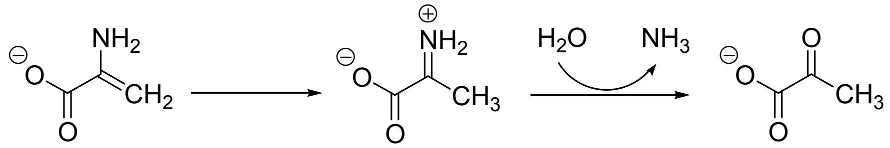
Amino group is the only reactive moiety in the side chain of *L*-lysine. Its interaction with the CH2=C fragment of the dehydroalanine residue leads to protein cross-linking via *L*-lysinoalanine (X) residue:



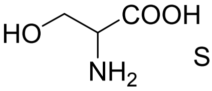
Since dehydroalanine is optically inactive, two stereoisomers of X are formed (1 point for each structure of X and Y, 3 points in total):



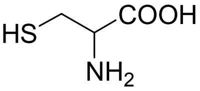
4. **(**1.5 points**)**



5. The dehydroalanine residue can be formed because of elimination of H_2O and H_2S molecules in the presence of hydroxide ions from the residues of canonical amino acids serine (Ser) and cysteine (Cys), respectively. Note that these amino acids are similar to Y with respect to the hydrocarbon skeleton (0.75 point for each amino acid, 1.5 points in total):



Ser



Cys

6. The net formulas of **Z1** and **Z2** are:

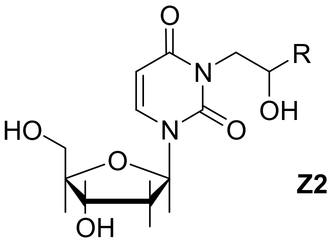
Z1

$$n(C):n(H):n(N):n(O) = \frac{41.71}{12.01}:\frac{5.43}{1.008}:\frac{35.53}{16.00}:\frac{13.33}{14.01} = 12:17:7:3$$

Z2

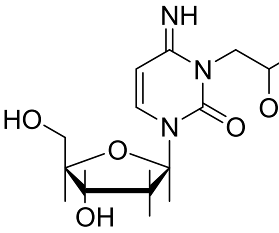
$$n(C):n(H):n(N):n(O) = \frac{45.57}{12.01}:\frac{5.10}{1.008}:\frac{40.47}{16.00}:\frac{8.86}{14.01} = 6:8:4:1$$

Taking into account similarity of **Z1** and **Z2** structures, their molecular formulae are $C_{12}H_{17}N_3O_7$ and $C_{12}H_{16}N_2O_8$, respectively. The 2'-deoxyribose residue is intact towards glycidamide action. Since epoxides readily react with nucleophiles with the ring opening, whereas **Z2** is a 2'-deoxyuridine residue, the general formula of **Z2** is given as:

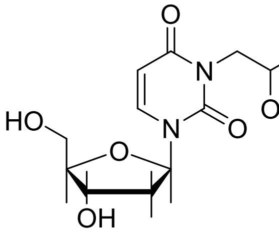


Z2

R corresponds to the carboxylic group. By contrast to **Z2**, **Z1** contains NH fragment instead of the oxygen atom, and there is only one variant of the fragment allocation (**Z1** is still the 2'-deoxycitidine residue) (1.75 point for each structure, 3.5 points in total):



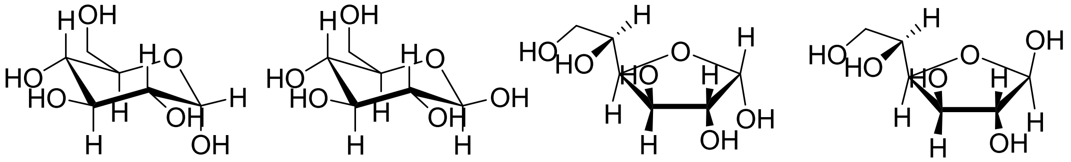
Z1



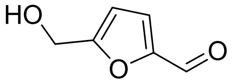
Z2

Problem 2 (authors Lukianova M.A., Karpushkin E.A.)

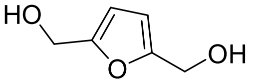
1. Two furanose and two pyranose forms coexist in the solution (1 point):



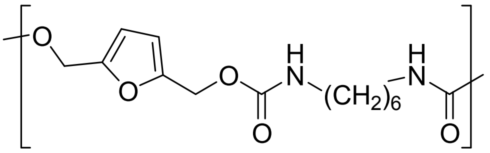
2. (3.5 points in total)



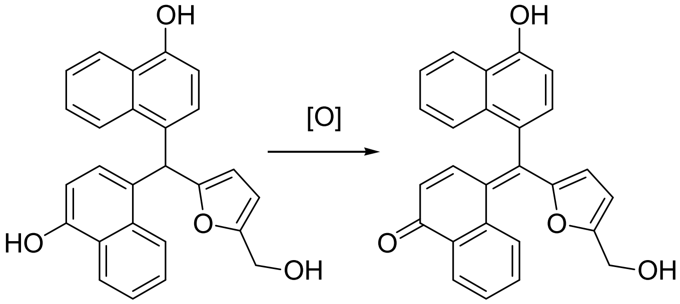
A (1.25 point)



B (0.5 points)

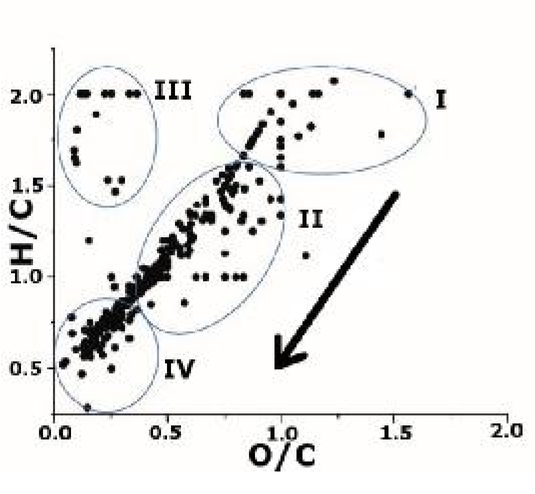


Copolymer of **B** with hexamethylene-1,6-diisocyanate (0.5 points)



The product of **A** interaction with two molecules of α-naphthol (1.25 points for any of the structures)

3. a) Dehydration of glucose does not change the number of carbon atoms in the molecule, that of oxygen atoms is reduced by x, and that of hydrogen atoms by $2x$ (x being the number of eliminated water molecules). Hence, the arrow slope is −2.

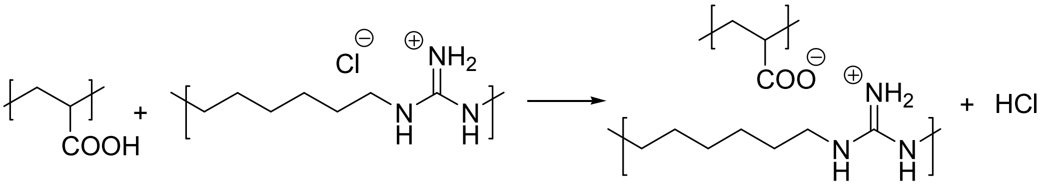


б) The group III compounds are formed from the starting glucose accompanied by the decrease in the O/C ratio with the H/C ratio being constant, or from aromatic products IV accompanied by the increase in the H/C ratio with the O/C ratio being constant. Both processes are redox reactions, the answer is disproportionation (1 point for each of ii. A and b, 2 points in total).

4. Since the particle core consists of graphite (pure carbon), whereas hydrogens and oxygens are found only at the surface, the obtained products are characterized by low O/C and H/C ratios, thus belonging to group IV (0.5 points).

5. Incubation of the particles in a solution of sodium hydrocarbonate leads to neutralization of the carboxylic groups (–COOH + $NaHCO_3$ → –COONa + H_2O + CO_2; *reaction 1*), whereas sodium hydroxide neutralizes both carboxylic and phenolic groups (–OH + NaOH → –ONa + H_2O, –COOH + NaOH → –COONa + H_2O; *reactions 2 and 3*). Further addition of an excess of hydrochloric acid neutralizes the excessive bases (HCl + NaOH → NaCl + H_2O, $NaHCO_3$ + HCl → NaCl + H_2O + CO_2) accompanied by consumption of the equivalent amount of hydrochloric acid. The unreacted hydrochloric acid is then titrated with alkali. 50.00 mL of the solutions added to the samples contained 5.0 mmol of sodium hydrocarbonate or hydroxide. In the case of the sample treated with sodium hydrocarbonate, the excessive acid was titrated with 7.1·1.00 = 7.1 mmol of NaOH. Since 1.00·10 = 10.0 mmol of hydrochloric acid was introduced into the sample, 2.9 mmol of it was consumed in the reaction with excess of sodium hydrocarbonate. Hence, 5.0 – 2.9 = 2.1 mmol of sodium hydrocarbonate reacted with the carboxylic groups at the particles surface according to the reaction *1*. Similarly, 3.5 mmol of NaOH reacted with the initial particles according to the reactions *2* and *3*. The difference in the reacted amounts of the hydroxide and the hydrocarbonate (1.25 mmol) corresponds to the content of the phenolic groups in 0.5000 g of the particles. Finally, the nanoparticles contain 2.5 mmol/g of phenolic and 4.2 mmol/g of carboxylic groups (1 point for NaOH consumption, $NaHCO_3$ consumption, and calculation of their difference, 0.5 points for the account for the mass; 3.5 points in total).

6. pH of the starting solutions was 4, i.e. the carboxylic groups of polyacrylic acid were protonated, and the amount of protons released into the solution as a result of interaction with Biopag is equivalent to that of the reacting groups:



Concentrations of the mixed solutions of Biopag and polyacrylic acid were equal (0.25 mol/L with respect to a monomer unit). The absence of chloride ions in the precipitate means that all guanidinium groups of the polycation in the precipitate are involved in the interaction with the carboxylic groups. Since 0.22 mol of protons is released into the solution, whereas polyacrylic acid is completely precipitated, the precipitate contains 0.22 mol of Biopag units. Hence, 0.03/0.25 = 12% of Biopag (with respect to the total amount) was left over in the solution.

The precipitate contains 0.22 mol of the Biopag units (142.2 g/mol with regard to release of chloride), 0.22 mol of the acrylate units interacting with Biopag (71.01 g/mol with regard to release of protons), and 0.03 mol of the polyacrylic acid units not involved in the interaction (72.02 g/mol). Mass fraction of the Biopag units in the precipitate is (0.22·142.2)/(0.22·142.2 + 0.22·71.01 + 0.03·72.02) = 63.8% (1.5 point for the fraction in the solution, 1 point for that in the precipitate, 2.5 points in total).

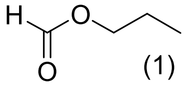
7. Since the fraction of the interacting acidic groups at the carbonaceous particles is 88%, 1.000 g of the these contains (2.5+4.2)·0.88 = 5.9 mmol of the groups capable of interaction with the polycation. With due account for the molar mass of the Biopag unit (177.7 g/mol), this corresponds to binding of 1.0 g of the polycation per 1 g of the particles (2 points)

Problem 3 (author Garifullin B.N.)

1. The net formula of X is found as:

$$\mathrm{n(C):n(H):n(N)} = \frac{\mathrm{w(C)}}{\mathrm{A_r(C)}}:\frac{\mathrm{w(H)}}{\mathrm{A_r(H)}}:\frac{\mathrm{w(N)}}{\mathrm{A_r(N)}} = 2:4:1$$

Taking into account the information about **A** oxidation into **B** (loss of two H atoms and incorporation of one O atom), one can decide in favor of a hydroxyl group transformation into the carboxylic one. This is supported by the fact that both groups are elaborated as a result of an ester bond hydrolysis (some enzymes in the digestive tract lumen are esterases). Then **X** is an ester containing at least two O atoms with the molecular formal of $C_4H_8O_2$. Four variants are in agreement with the formula: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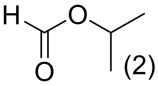
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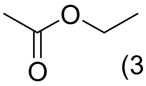
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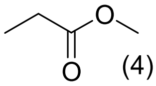

(4)

Still, only ethyl acetate coincides with **A** transformation into **B** (0.75 point for the molecular formula, 0.75 point for ethyl acetate, 1.5 points in total; 0.25 point penalty for each extra structure).

2. Let us re-write the formula of **X** as $C_{2n}H_{4n}O_n$. Then the hydrolysis reaction is:

$$C_{2n}H_{4n}O_n + H_2O \rightarrow C_nH_{2n}O_{0.5n+1} + C_nH_{2n+2}O_{0.5n}$$

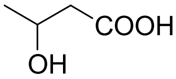
The difference between molar fractions of C and O in **B** is:

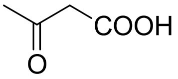
$$\frac{n}{n + 2n + 0.5n + 1} - \frac{0.5n + 1}{n + 2n + 0.5n + 1} = 0.067, \text{ откуда } n = 4$$

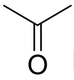
Finally, true molecular formula of **X** is $C_8H_{16}O_4$ (2.5 points).

3. **B** has the molecular formula of $C_4H_8O_3$, thus being a saturated carboxylic acid. The possibility of biological oxidation of **B** leading to the loss of two hydrogen atoms excludes from consideration compounds containing fragments of saturated ethers. Thus, either primary or secondary hydroxyl group must be present in **B**.

Decarboxylation of **D** affords an aldehyde or ketone (the compound **E**). Monoaldehydes always contain at least two types of hydrogen atoms. Thus, it is dimethylketone (acetone) formed as a result of acetoacetic acid (**D**) decomposition, the latter being the product of β-hydtroxybutyric acid (**B**) oxidation:

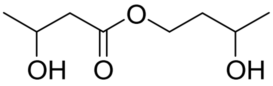

B

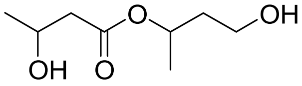

D


E

The compounds **B** – **D** form the so-called group of ketone bodies.

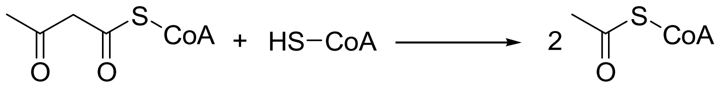
Since it is not clear from the text which of alcohol groups in butanediol-1,3 (**A**) is involved in the ester bond formation, there are two valid structures of **X**:


(1)


(2)

For your information: the isomer (1) was used to prepare Ketone (1 point for each of **A** and two **X** structures, 3 points in total).

4. The equation of acetyl-CoA formation is:



Thus, two molecules of acetyl-CoA are formed from one molecule of **B**, and four molecules of acetyl-CoA from one molecule of **X**. 25 g or 0.14 moles of **X** (M=176 g/mol) are found in one Ketone bottle. Disregarding all other processes but complete aerobic oxidation of acetyl-CoA, one gets the energy value of one bottle as:

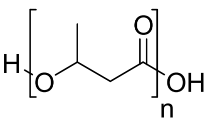
$$E\text{ (bot.)} = 4 \cdot 0.14\text{ mol} \cdot 360\text{ kJ/mol} = 135\text{ kJ}$$

Maintaining a constant speed is the most rational strategy leading to the best possible result. The average speed that allows being within the desired time at the marathon distance is 42.2 km / 2.3 h ≈ 18 km/h, which corresponds to the energy consumption of 95 kJ/min. Then, the number of bottles needed is:

$$n\text{(bot.)} = \frac{95\text{ kJ/min} \cdot 140\text{ min}}{135\text{ kJ}} \approx 100$$

Of course, this is an overdone estimation, since organism of a running man switches on various mechanisms of energy generation, oxidation of exogenic ketone bodies hardly being the major one. However it was found that using Ketone allowed top cyclers covering by 400 meters (2%) longer distance in 30 minutes as compared to that after conventional energetic drink based on carbohydrates and fats (3 points).

5. (0.5 points)

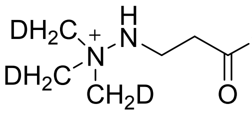
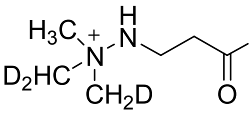


6. Some microorganisms use poly-(3)-hydroxybutyrate granules as a reserve energy source (0.5 point).

7. Based on the molar fractions of the elements, the net formula of **Y** in the switter-ionic form is C_3H_7NO. With an account for the molecular mass range, its molecular formula is $C_6H_{14}N_2O_2$, which coincides with that for Meldonium itself. The threemethylamino group is the most vulnerable one in the Meldonium structure when subjected to ionization, which is supported by the peaks with *m/z* 58 (C_3H_8N) и 59 (C_3H_9N). Still, Meldonium cannot be responsible for the other three mentioned peaks. Then, they must originate from the compound **Y** having the molar composition identical to that of Meldonium.

This can be true if some protium atoms in the Meldonium structure are substituted by heavier hydrogen isotopes in **Y**. In the case of a deuterated compound, there must be three **D** atoms, the peak with с *m/z* 60 corresponding to $C_3H_6D_2N$. Compounds with tritium do not match the mass-spectrum.

Thus, there are three valid structures of **Y**:


(1)

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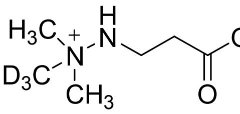

(3)

For your information: isomer (3) is used in laboratory practice (2 points for any one of the above structures, 0.5 point for the additional structures from those above, 3 points in total).

8. Since there are neither key parameters of the Meldonium pharmacokinetics (e.g. the process order), nor the preparation dose and schedule of its administration given, it is impossible to draw any conclusions. Moreover, Meldonium is characterized by pronounced non-linear metabolic parameters with dynamically changing biological half-life (from few hours to days), which seriously complicates any calculations. Thus, the time and place of Meldoinum administration by the curler are still unknown, which embarrasses the case investigation (1 point)

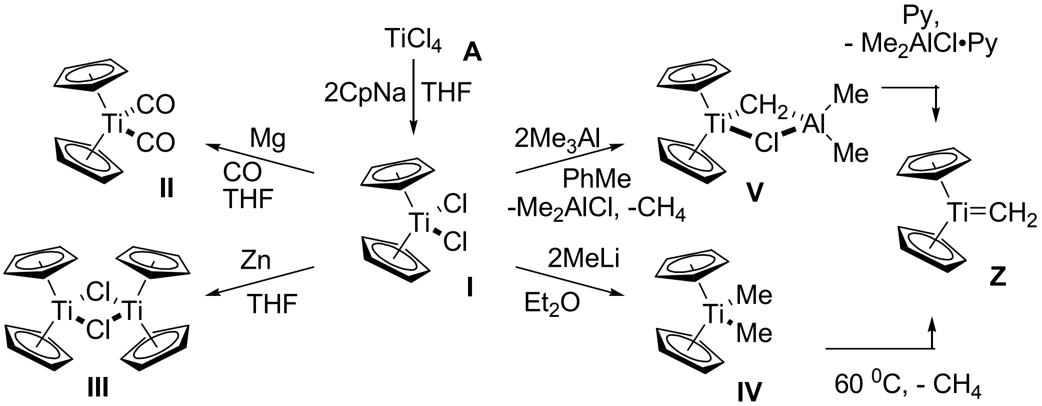
SECTION II. ORGANIC CHEMISTRY

Problem 1 (author Shved A.M.)

1. For determination of the unknown metal the equation based on reaction $MCl_n + mCpNa = MCp_mCl_{n-m}$ can be composed: w(M) = 0.1923 = A(M) / [A(M) + 35.5(n – m) + 65m].

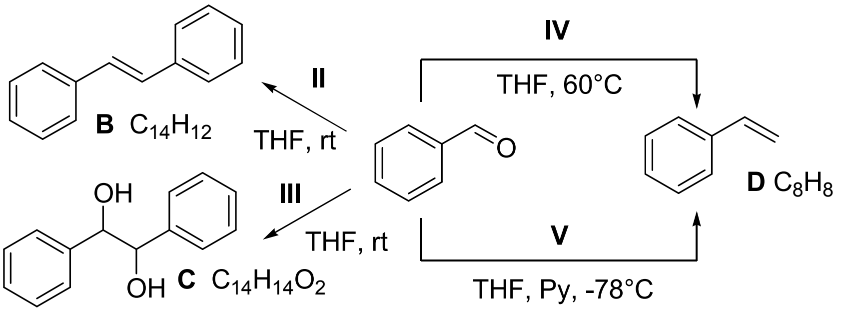
$$0.1923\ A(M) + 6.827\ (n - m) + 12.45\ m = A(M)$$

A(M) = 8.452 (n – m) + 15.41 m = 47.72 when n = 4 and m = 2, what exactly corresponds to **titanium** (Ti, 1 point). Then the scheme of transformations can be presented as (the correctness of reasoning can be additionally confirmed by the verification of mass fractions of titanium in unknow compounds, 1 point for each compound, 8 points in total):



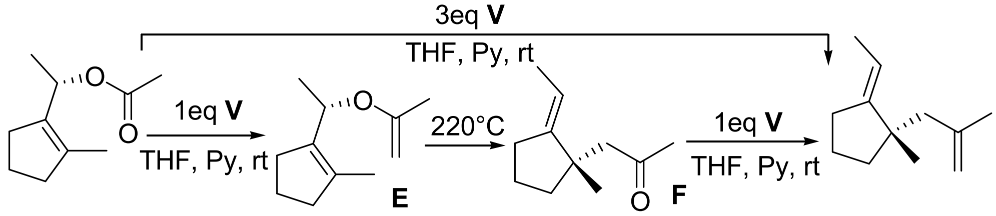
The formal oxidation states in titanium derivatives are the following: **I** – +4; **II** – +2; **III** – +3; **IV** – +4; **V** – +4; **A** – +4; **Z** – +4 (0.25 points for each, 1.75 points in total).

2. The unknown compounds can be easily determined based on their chemical formulae. While choosing between *cis*/*trans* isomers of **B**, with the help of information about the thermodynamic stability, the *trans*-isomer is determined. Analogously, in accordance with chirality of **C**, it can be concluded, that it is *dl*-diastereomer, as the *meso*-isomer is achiral (0.5 point for each, 1.5 points in total).



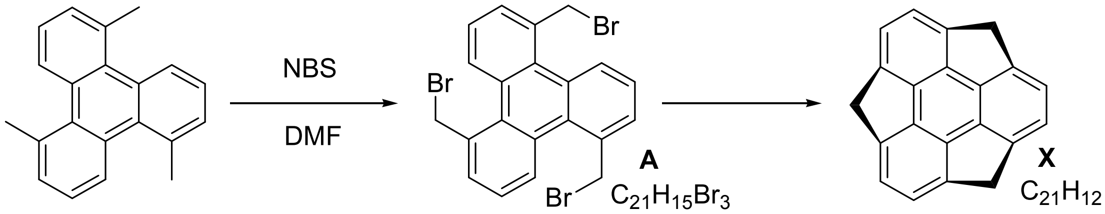
Based on the solved scheme, it is not complicated to answer the question about the role of reagents in organic synthesis: olefinating reagent – **IV, V**; deoxygenative reagent – **II**; one-electron reductant – **III** (0.25 each = 0.75). In reality, all these reagents are extensively used in organic synthesis, and olefinating are even named: **IV** is a Petasis reagent and **V** is Tebbe's reagent. This information is also extremely useful for compound **Z** determination from the first part of the problem. The olefinating ability of these two reagents with the same reactive intermediate had to give an idea that **Z** contains the double metal-carbon bond.

Finally, knowing that the compound **V** is an olefinating reagent, the last scheme can be solved. From all has been said it is clear, that **F** is corresponding ketone, which was subjected to olefination. At the same time, the compound **E** is a product of initial ether olefination, i.e. corresponding vinyl ether, which gives **F** as the result of thermal [3+3] Claisen rearrangement. Then the scheme can be presented as (1 point for structure, 2 points in total):

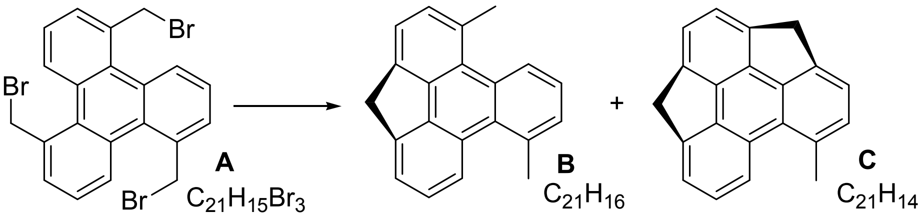


Problem 2 (author Kandaskalov D.V.)

1. Let's begin with the fact that sumanene can be considered as a fragment of fullerene, we will try to determine its symmetry at first. We know that **X** contains 21 carbon atoms and 12 hydrogen atoms, we come to the conclusion that there is a third-order symmetry axis, since the common divisor of the numbers **21** and **12** is the number **3**. This is indirectly confirmed by the structure of the initial compound for synthesis of substance **A**. Interpretation of the mass spectrum of substance **A** (gives a quartet in the region of the molecular ion) gives us information that **A** contains three bromine atoms. Then it is logical to assume that the first reaction occurs with three equivalents of N-bromosuccinimide, and in the second stage, the elimination of three HBr molecules is expected:

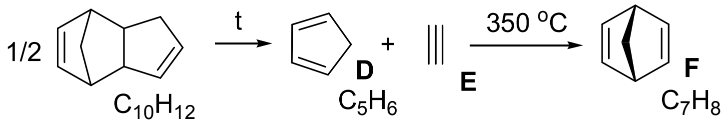


It is important to note that the CH_2 groups (as well as the 3 aromatic rings they connect) come out of the plane and are directed only to one side due to steric stresses. The molecule really looks like a flower with six petals. Then the substances **B** and **C** are "unfinished" sumanenes:

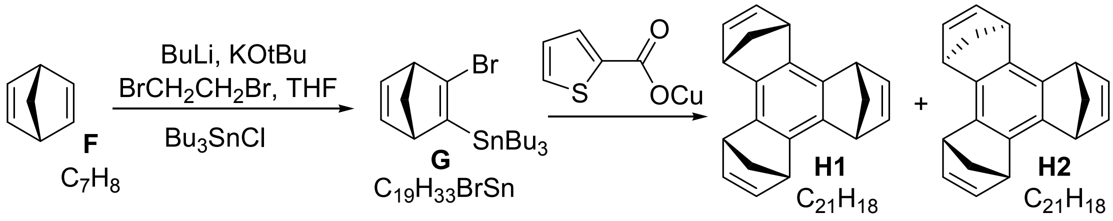


In this reaction scheme, it is not entirely clear why the bromine atoms have been replaced by hydrogen, but given the pyrolysis conditions (850°C), as well as the fact that there is a resource of hydrogen atoms in the molecules formed (HBr) or in possible by-products (1 poin for each structure, 4 points in total).

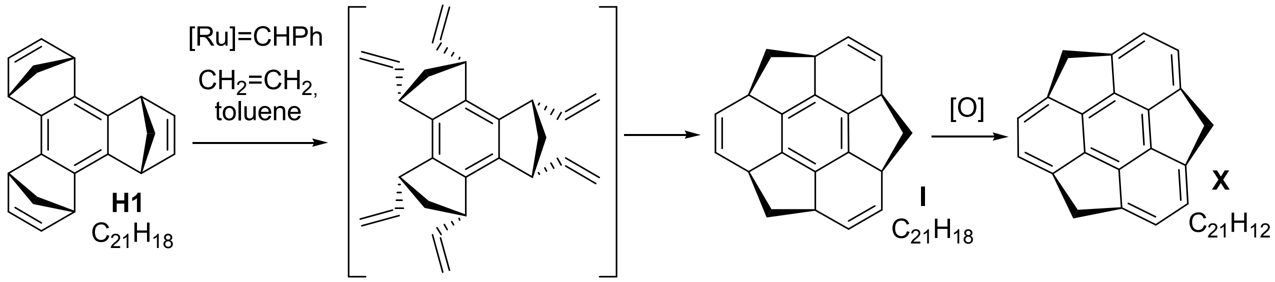
2. To find the structure of compound **F**, we will start with gas **E**, which has the empirical formula CH. This is obviously acetylene C_2H_2. Surprisingly, substance **F** can be very symmetrical, but is obtained from a low-symmetry $C_{10}H_{12}$ hydrocarbon. Further, it is necessary to know that the starting material is a dimer of C_5H_6 – cyclopentadiene. Then everything becomes obvious **F** – norbornadiene:



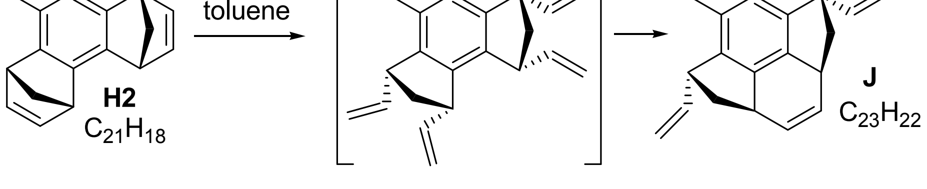
Taking into account that the stereoisomers of **H** contain 21 carbon atoms and 18 hydrogen atoms, suggests that there is trimerization of the C_7H_6 fragment. Compound **G** is bifunctional, respectively, both functions are more likely to be with one double bond (in addition, it corresponds to the brute formula). Then this part of the synthesis looks like this, taking into account the fact that the minor isomer **H1** should have a symmetry similar to that of sumanene.



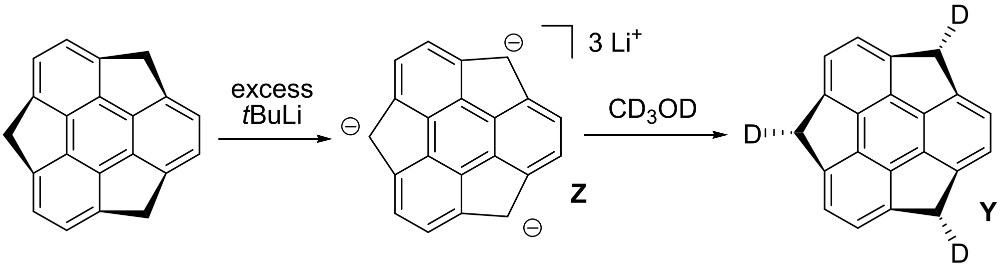
To reach the Sumanene molecule **X**, only a symmetric stereoisomer can give us positive result, with a metathesis reaction with three equivalents of ethylene first followed by a metathesis reaction with the cleavage of three ethylene molecules. Subsequent oxidation of **K** leads to **X**:



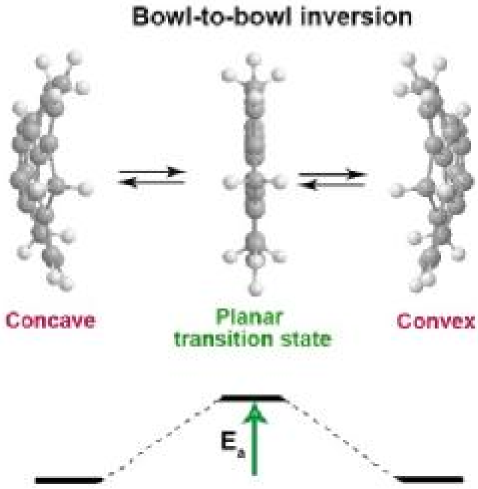
In his turn the similar transformation of **H2** cannot lead to a triple “exchange” of double bonds because of steric conditions and the reaction is finished of **J** compound (1 point for each structure, 8 points in total).



3. Sumanene molecule has three methylene groups, capable to deprotonation, which occurs when it interacts with an excess of such strong base as tBuLi. Subsequent deuterium leads to compound **Z** (0.5 points for each structure, 1 point in total).



4. As the molecule is sterically strained, it is not flat and it has a conformation of the bowl (cup); accordingly, methylene protons are nonequivalent. However, this bowl (in the far approximation as an ammonia molecule) can be reconciled, changing the position of the methylene protons. This phenomenon is easier to observe with the example of a deuterated analog compound. When choosing two conformers for chemical shift of the methylene proton, we take into account the anisotropic effect of the central benzene nucleus, which will lead to a signal at 4.71 ppm corresponds to the conformer where the proton looks "out of the bowl" (0.5 points for each conformer, 1 point in total).



5. We have the frequency transformation between two forms "Concave-Convex" at two different temperatures. It is all we need to calculate activation energy E_a using Arrhenius equation (1 point):

$$k_1 = A\cdot\exp(-\frac{E_a}{RT_1}) \text{ и } k_2 = A\cdot\exp(-\frac{E_a}{RT_2})$$

$$\ln\frac{k_1}{k_2} = -\frac{E_a}{R}(\frac{1}{T_1}-\frac{1}{T_2}) \Rightarrow$$

$$E_a = -R\cdot\ln\left(\frac{k_1}{k_2}\right)\cdot\left(\frac{1}{T_1}-\frac{1}{T_2}\right)^{-1} = -8{,}314\cdot\ln\left(\frac{0.066}{0.007}\right)\cdot\left(\frac{1}{318}-\frac{1}{298}\right)^{-1} = 88389 \text{ J/mol}$$

Problem 3 (authors Volochnyuk D.M., Gorlova A.A.)

To successfully solve this problem, the brute force approach is not effective. Despite the problem could be solved " brute force" it contains a large number of hints in different parts and a more efficient method for its solution is the analysis of the data and its assembly according to the "puzzle principle”.

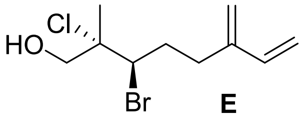
To decipher and calculate the empirical formula of halomon, it is necessary to pay attention to the fact that in both syntheses the starting compound has 10 carbon atoms, and there are no reagents able to lengthening or shortening of the carbon skeleton. Therefore, it is rational to assume that halomon also contains 10 carbon atoms. In addition, the picture of the molecular peak, as well as the regents of the functionalization of β-myrcene, indicate that the halomon molecule contains both bromine and chlorine atoms. Based on the analysis data ($n(CO_2):n(H_2O) = 24.9:12.5 = 2:1$), the general equation of halomon and its combustion could be written as:

$$C_{10}H_{10}\cdot x(HCl)\cdot y(HBr) + 12.5O_2 = 10CO_2 + 5H_2O + xHCl + yHBr$$

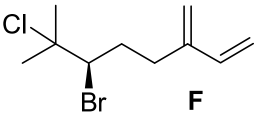
Then the molecular mass of halomon is $1.00 \cdot 10 / n(CO_2) = 401.6$. Accordingly, the "contribution" x (HCl) + y (HBr) in the formula unit will be 271.6. This value is realized by two HBr molecules and three HCl molecules, which is confirmed by the mass of the silver bromide and chloride mixture formed ($1.00 \cdot 2 \cdot 187.77 / 401.6 + 1.00 \cdot 3 \cdot 143.32 / 401.6 = 2.01$ г).

So the empirical formula of Halomon is $C_{10}H_{15}Br_2Cl_3$, indicating the degree of unsaturation is 1, possible in a case of cycle in the structure or a double bond. The first assumption about the cycle is discarded by the indication of the stereochemical indexes of halomon (when the terpene skeleton is cyclized the maximum cycle is 5, and accordingly there would be no stereochemical index *6-R*) (3 points for the formula proved by calculations).

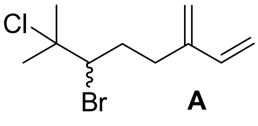
The further solution of the problem should be continued by the analysis of the second scheme. Based on the general scheme of chiral (inter)halogenation and the formula of **F**, it is easy to decipher the compounds **E** and **F**, and it is easy to see that compound **A** is a racemate of **F**:



E

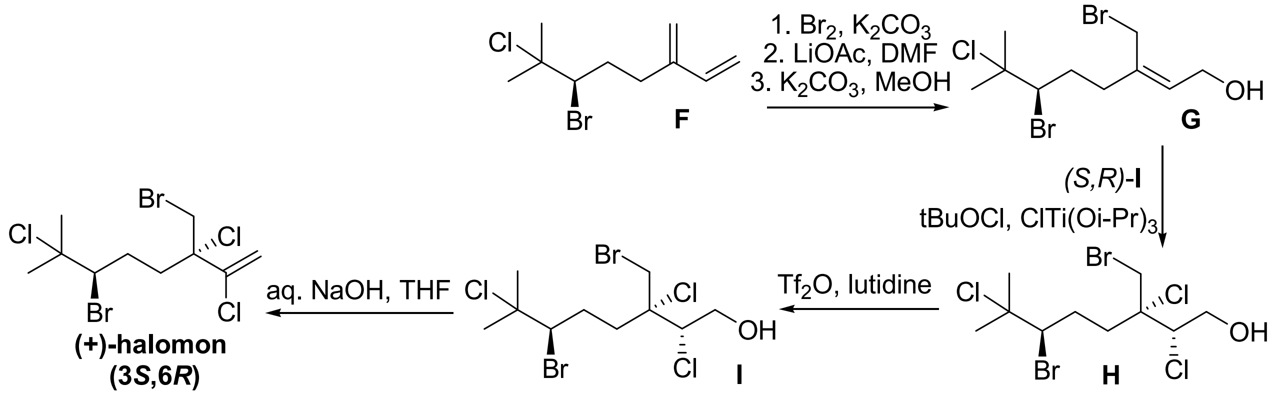


F



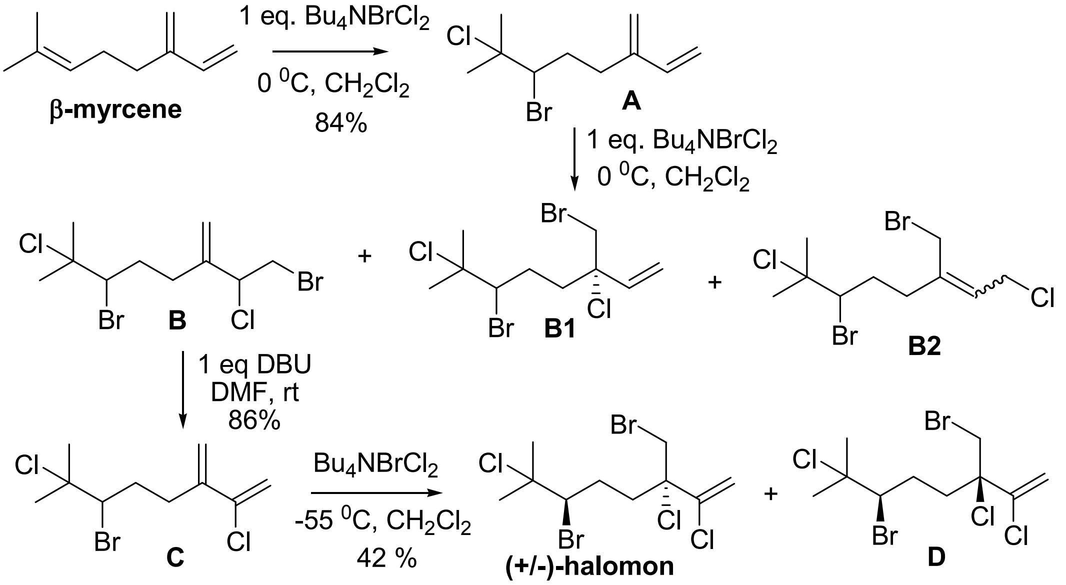
A

Further, analysis of the second scheme shows that compound **G** must be allyl alcohol could be subjected into chiral halogenation but giving opposite configuration compared to the first stage (different enantiomers of the catalyst were used). Then the second scheme takes a complete view and the structure of the natural halomon is revealed:



The self-test shows that the conclusions, based on which we came to the structure of natural halomon, are correct, since we obtained a compound with the correct stereochemical indexes.

The last stage, based on the deciphered structure of natural halomon deciphers the synthesis of its racemate (1 point for each structure, 12 points in total):



SECTION III. ANALYTICAL CHEMISTRY

Problem 1 (author Beklemishev M.K.)

1. a. It is necessary to introduce (2.9 + 2.0) – 1.5 = 3.4 mM EDTA, or 3.4 L of 1 M solution (1 point)

b. Note that 6.3 = pH = pK_1 of the carbonic acid, i.e. at this acidity, a half of the carbonic acid is in the form of H_2CO_3, and the other half is in the form of HCO_3^- (which is evident from the expression $K_1 = [H^+][HCO_3^-] / [H_2CO_3]$). Hence, $[HCO_3^-] = 1.8 / 2 = 0.9$ mM (1.5 points), $[CO_2] = [HCO_3^-] = 0.9$ mM (1.5 points).

c. The condition for non-precipitation of the least soluble carbonate ($CaCO_3$) will be the following:

$[CO_3^{2-}][Ca^{2+}] < K_S$, or $[CO_3^{2-}]\cdot 2.9\cdot 10^{-3} < 3.8\cdot 10^{-9}$, or $[CO_3^{2-}] < 1.31\cdot 10^{-6}$ M (1 point). From the expression for the dissociation constant of H_2CO_3 by the second stage $K_2 = [H^+][CO_3^{2-}] / [HCO_3^-]$ we can obtain: $[H^+] = K_2\cdot[HCO_3^-] / [CO_3^{2-}]$ (1 point for the solution in general form).

Assuming that the concentration of hydrocarbonate is equal to the total concentration of carbonate, and substituting the equilibrium concentration of carbonate from the inequality (see above), we will have:

$[H^+] = 4.8\cdot 10^{-11}\cdot 1.8\cdot 10^{-3} / 1.31\cdot 10^{-6} = 6.6\cdot 10^{-8}$, pH 7.2 (1 point for the numerical answer).

To verify the assumptions made above, we can estimate the molar fractions of the forms of carbonic acid at pH 7.2. In the expression for the molar fraction of the carbonate ion

$$\alpha(CO_3^{2-}) = 1 / (1 + [H^+]/K_2 + [H^+]^2/K_1K_2)$$

the terms corresponding to carbonate, hydrocarbonate and carbonic acid are equal to unity, 1375 and $2\cdot 10^{-20}$, respectively, i.e. hydrocarbonate is really the predominant form.

2. a. As stated in the problem situation, metals form stable complexes with EDTA having the composition of $MetY^{(4-x)-}$; therefore, the reactions should be written as follows:

$$Ca^{2+} + H_2Y^{2-} \rightarrow CaY^{2-} + 2H^+ \text{ (1 point) and}$$

$$Mg^{2+} + H_2Y^{2-} \rightarrow MgY^{2-} + 2H^+ \text{ (1 point),}$$

or, taking into account the binding of protons by the excess of EDTA:

$$(Ca, Mg)^{2+} + 3H_2Y^{2-} \rightarrow (Ca, Mg)Y^{2-} + 2H_3Y^-$$

Since complexation, as we can see, is accompanied by a decrease in pH, the following reaction also occurs:

$$HCO_3^- + H^+ \rightarrow H_2CO_3 \text{ (1 point).}$$

b. First of all, we may note that the added solution of Na_2H_2Y is acidic (its pH is 4.4; this value is an intermediate between pK_2 и pK_3 of EDTA and can be obtained from the formula for pH of an ampholyte: $[H^+] = \sqrt{K_2K_3} = 10^{-4.4}$. This is not required for the solution). As can be seen from paragraph 2a, the complexation reaction $(Ca, Mg)^{2+} + H_2Y^{2-} \rightarrow (Ca, Mg)Y^{2-} + 2H^+$ acidifies the medium even further; therefore. $H_2Y_2^-$ and its monoprotonated form H_3Y^- will be present in the solution. We can calculate their concentrations: the amount of EDTA added: 30 L · 1.00 M / 10^3 L = 30 mM, then the excess of EDTA after the complexation was: 30.0 – (2.9 + 2.0) = 25.1 mM. When interacting with the metal ions, the above reaction produces a double amount of hydrogen ions: 2 · (2.9 + 2.0) = 9.8 mM, some of which will react with hydrocarbonate (0.9 mM), which will form CO_2, while 9.8 – 0.9 = 8.9 mM of H^+ will react with an excess of H_2Y^{2-} to form 8.9 mM of H_3Y^-, leaving 25.1 – 8.9 = 16.2 mM H_2Y^{2-} (where 25.1 mM is the total concentration of EDTA not bound to metals). So, the pH will be determined by H_3Y^- (8.9 mM) and H_2Y^{2-} (16.2 mM). It is possible to estimate the pH of such a mixture from the expression for the second acidity constant of EDTA (Henderson-Hasselbach formula): $K_2 = [H^+][H_2Y^{2-}] / [H_3Y^-]$, whence $[H^+] = K_2 \cdot [H_3Y^-] / [H_2Y^{2-}] = 2.1 \cdot 10^{-3} \cdot 8.9 / 16.2 = 1.2 \cdot 10^{-3}$, **pH 2.9** (2 points). At this acidity the dissolved CO_2 will not affect the pH. In this calculation, we neglected some amount of H_4Y, which will be present at pH 2.9. However, the result obtained is purely theoretical: in fact, such a low pH value will not be achieved upon adding EDTA. The reason for this is that the acidity increases significantly upon complexation, which is therefore incomplete (calcium and magnesium complexes with EDTA in an acidic medium are unstable).

c. Upon the addition of alkali, practically all of the CO_2 will transfer into the hydrocarbonate (it can be shown that this form of carbonic acid predominates at pH 8.0). By problem situation, CO_2 did not evaporate; then its concentration is **1.8 mM**. Besides, the following formula should be fulfilled: $K_3 = [H^+][HY^{3-}] / [H_2Y^{2-}]$, or $6.9 \cdot 10^{-7} = 1 \cdot 10^{-8} \cdot [HY^{3-}] / [H_2Y^{2-}]$, or $[HY^{3-}] / [H_2Y^{2-}] = 69$ (i.e., almost all EDTA at pH 8.0 exists as HY^{3-}). Then, with a total concentration of *free* EDTA equal to 25.1 mM (see the previous paragraph), we should have 0.36 mM H_2Y^{2-} and 24.74 mM HY^{3-}. Before the addition of alkali, there were 8.9 mM H_3Y^- and 16.2 mM H_2Y^{2-} (1 point), then 8.9 mmol of alkali would be required for the conversion of all HY^{3-} into H_2Y^{2-} and 24.74 mM for the conversion of H_2Y^{2-} to HY^{3-} (the required 0.36 mM H_2Y^{2-} will remain), totally **33.7 mM** (1 point), and together with the alkali spent for CO_2, it will amount to **35.5 mM**, or 35.5 L of 1 M alkali per cubic meter of the mixture (1 point, 3 points in total).

Problem 2 (author Kandaskalov D.V.)

1. Using equation (1), we can write potential E as a function of pH:

$$\Delta E = S \cdot \log \frac{[H^+]_{test}}{[H^+]_{inner}} = S \cdot \left(pH_{inner} - pH_{test}\right)$$

Having two test solutions, we obtain a system of two equations:

$$\begin{cases} 0.2094 = S\cdot\left(pH_{inner} - 4.00\right) \\ 0.0352 = S\cdot\left(pH_{inner} - 7.00\right) \end{cases} \Rightarrow \begin{cases} pH_{inner} = \dfrac{0.2094}{S} + 4.00 \\ pH_{inner} = \dfrac{0.0352}{S} + 7.00 \end{cases}$$

As a result, we can find parameter S and pH of electrode inner solution:

$$\frac{0.0352}{S} + 7.00 = \frac{0.2094}{S} + 4.00 \Rightarrow S = 0.0581 \Rightarrow pH_{inner} = 7.604$$

(1 point for each correct answer, 2 points in total).

2. A 2018% error in the concentration measurement is due to presence of Na^+ ions, which increases the total ion concentration. For the measurement error we have the next equation:

$$\chi = \frac{[H^+]_{test} + k_{H/Na}\cdot[Na^+]}{[H^+]_{test}}\cdot 100\% = 2018\%$$

We obtain: (2.5 points)

$$\frac{2018-100}{100}\cdot[H^+]_{test} = k_{H/Na}\cdot[Na^+] \Rightarrow 19.18\cdot\frac{K_W}{[OH^-]} = k_{H/Na}\cdot[Na^+] \Rightarrow$$

$$k_{H/Na} = 19.18\cdot\frac{K_W}{[OH^-]^2} = 19.18\cdot\frac{10^{-14}}{0.2018^2} = 4.71\cdot10^{-12}$$

3. In the diagram, we see 4 curves, each corresponds to one of the A-containing particles. Considering that one form is completely deprotonated, H_nA acid should be tribasic ($n = 3$) and has the following forms: H_3A, H_2A^-, HA^{2-}, and A^{3-} (1 point).

4. Taking into account the fact that at low pH the concentration of protons is high, the more to the left of the diagram the form is located, the more protons it should contain. Thus, from left to right, we have graphs, respectively, for particles: H_3A, H_2A^-, HA^{2-}, A^{3-}(0,25 points for each correct answer, 1 point in total).

5. Knowing the calculated parameters, we can calculate the pH of these two solutions. For a solution of Na_nA salt, taking into account the selectivity to sodium ions (1 point):

$$\Delta E = 0.0581\cdot\log\frac{[H^+]_{test} + k_{H/M}\cdot[M^+]}{[H^+]_{inner}} \Rightarrow$$

$$-0.2376 = 0.0581\cdot\log\frac{[H^+]_{test} + 4.71\cdot10^{-12}\cdot0.1\cdot3}{10^{-7.604}} \Rightarrow$$

$$[H^+]_{test} = 6.17\cdot10^{-13} \Rightarrow pH = 12.21$$

For a solution of the acidic salt, the selectivity to sodium ions can be neglected, since the second term in the numerator will be 7–8 orders of magnitude smaller than the first term (1 балл):

$$0.1803 = 0.0581\cdot\left(7.604 - pH_{test}\right) \Rightarrow pH_{test} = 4.50 \qquad A^{3-} + HOH \Leftrightarrow HA^{2-} + OH^-$$

$$K_{.} = \frac{[HA^{2-}]\cdot[OH^-]}{[\mathrm{A}^{3-}]} = \frac{[HA^{2-}]\cdot[OH^-]\cdot[H^+]}{[\mathrm{A}^{3-}]\cdot[H^+]} = \frac{K_w}{K_3} \Rightarrow$$

$$\frac{K_w}{K_3} = \frac{[OH^-]^2}{[\mathrm{A}^{3-}]_0 - [OH^-]} \Rightarrow K_3 = K_w \cdot \frac{[\mathrm{A}^{3-}]_0 - [OH^-]}{[OH^-]^2}$$

$$K_3 = 10^{-14}\cdot\frac{0.1-10^{-1.79}}{(10^{-1.79})^2} = 3.18\cdot10^{-12} = pK_3 = 11.50$$

Thus, we have found the third dissociation constant:

$$K_{3.} = \frac{[\mathrm{A}^{3-}]\cdot[H^+]}{[HA^{2-}]}$$

When two given concentrations are the same, we obtain:

$$[\mathrm{A}^{3-}] = [HA^{2-}] \Rightarrow K_3 = [H^+] \Rightarrow pK_3 = pH$$

Graphically, the equality of these concentrations corresponds to the intersection of the third and fourth curves. Hence, this intersection point on the graph corresponds to pH 11.50.

Regarding the acidic salt, it can be either Na_2HA or NaH_2A. Graphically pH of acidic salts corresponds to the maximum content of a given anion in the solution: HA^{2-} or H_2A^-. It can be seen from the graph that the disubstituted Na_2HA salt cannot have a pH of 4.50, since in that case the left part of the distribution diagram would go behind pH –20 or even –30. Thus, the acidic salt is NaH_2A, and the maximum concentration of H_2A^- corresponds to a pH of 4.50. The same value is the arithmetic average of pK_1 and pK_2, which will allow us to find the maximum of the second curve more accurately.

Having these two points on the graph (pH 4.50 and 11.50), we can restore the pH scale, knowing that each intersection of the two curves gives the corresponding pK (similarly to the example above). As a result, we get graphically pK_1=2.0, pK_2=7.0 and pK_3=11.5, thus $K_1=10^{-2.0}$, $K_2=10^{-7.0}$, $K_3=10^{-11.5}$ (1 point for each correct answer, 5 points in total).

6. The sodium chromate serves as indicator, since a characteristic yellow precipitate of silver chromate is formed on the complete precipitation of Ag_3A:

$$2Ag^+ + CrO_4^{2-} \rightarrow Ag_2CrO_4$$

Sodium acetate is necessary to neutralize the solution, since a strong acid forms during titration (0.75 points for each correct answer, 1.5 points in total):

$$AgNO_3 + H_3A \rightarrow Ag_3A + 3HNO_3$$

$$H^+ + CH_3COO^- \rightarrow CH_3COOH$$

7. Let us calculate the amount of acid $H_3A\cdot0.5H_2O$ containing in an aliquot, starting from the above reaction equation. The average volume of the solution of silver nitrate is 12.175 mL (the third titration is not taken into account as outlier). The amount of silver nitrate is:

$$\nu(AgNO_3) = C_M(AgNO_3)\cdot V = 0.500\cdot0.012175 = 6.0875\cdot10^{-3}\,\mathrm{mol}$$

By the equation, the amount of acid H_3A is three times smaller: $2.0292\cdot 10^{-3}$ mol, then in the initial solution the amount of acid will be $1.0145\cdot 10^{-2}$ mol. We can calculate its molecular weight:

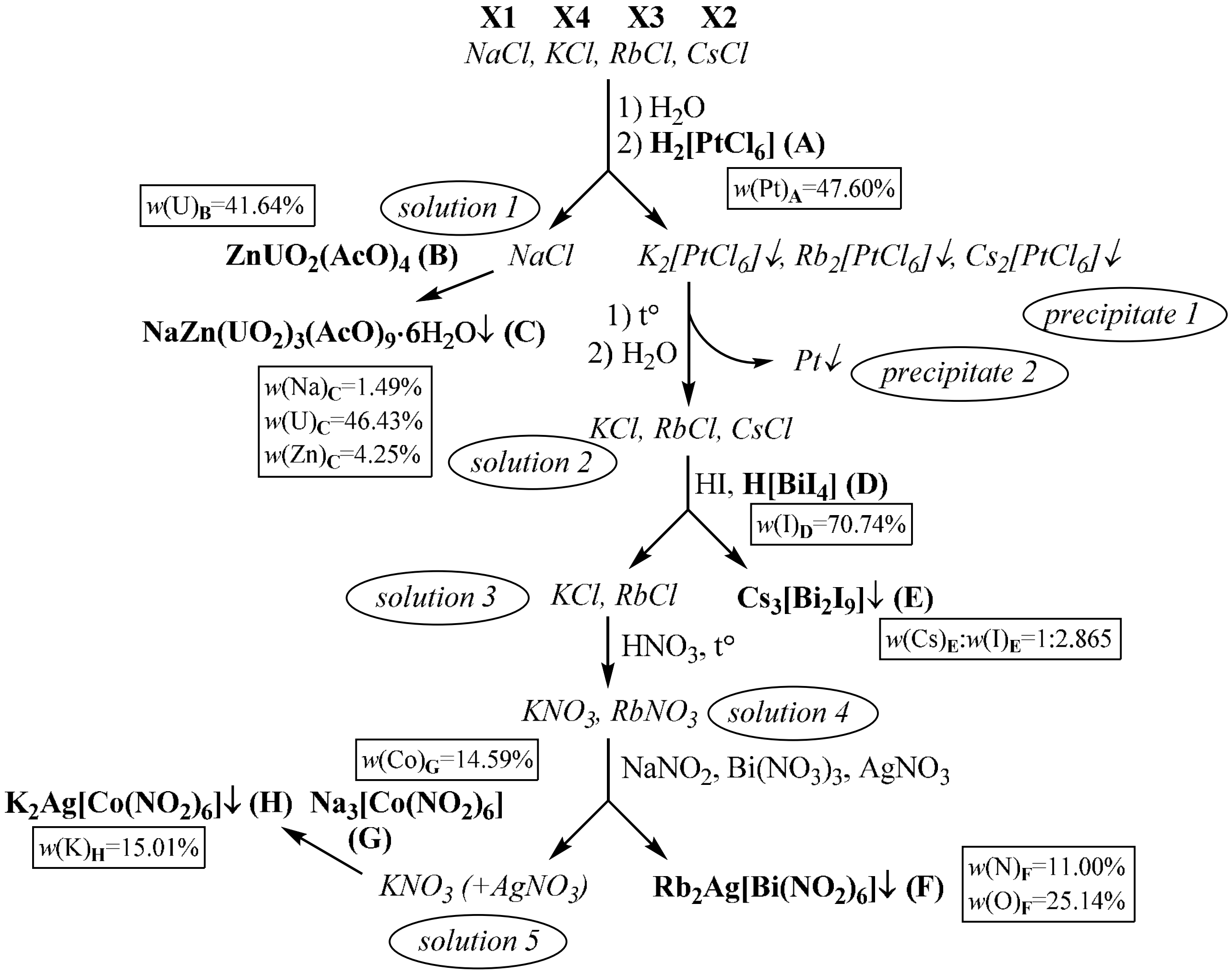
$$M(H_3A\cdot 0{,}5H_2O)=\frac{m(H_3A\cdot 0.5H_2O)}{\nu(H_3A\cdot 0.5H_2O)}=\frac{1.53}{1.0145\cdot 10^{-2}}=150.8\text{ g/mol}$$

Thus, the molecular weight of the anhydrous acid is 141.8 g/mol. Given that the acid is inorganic, we can write down its formula as $(HO)_3XO_m$.

Supposing that $m = 1$ we obtain $M_X = 74.8$, i.e. the fomula of the acid is H_3AsO_4; if $m > 1$ we cannot obtain satisfying results (1 point for a molecular mass of the acid, 1 point for it formula, 2 points in total).

Problem 3 (author Shved A.M.)

1. The answer presented as a scheme:



Detection of elements **X1** – **X4** is independent, so the problem could be solved starting from any part. Here in turn the stepwise determination of composition of unknown compounds is given in the order in which they are mentioned in the task.

Platinum group metals include 6 elements: Ru, Rh, Pd, Os, Ir and Pt. It is well known that quite stable chloride complexes of these elements tend to have acidic properties. A prominent representative of such complexes is hexachloroplatinic acid **$H_2[PtCl_6]$,** the unknown reagent **A**, which can be proved by the given mass fraction of platinum:

$$w(Pt)_{H_2[PtCl_6]} = \frac{195.08}{1.01\cdot 2 + 195.08 + 35.45\cdot 6} = 0.4760\ (47.60\%).$$

If there were some difficulties with determination of compound **A** composition, its formula can be presented as $H_n[MeCl_m]$, where Me is a metal of the platinum group. Hence the m can be expressed as:

$$w(Me)_{\mathbf{A}} = \frac{M}{1.01n + M + 35.45m} = 0.4760 \Rightarrow m = \frac{1.101M - 1.01n}{35.45}\ ,$$

where M is relative atomic mass of Me. It is clear that m and n are small integer numbers, and $m > n$. Then, inserting known M and n, for example, from 1 to 4, possible values of m are obtained:

Me / *n*	Ru (*M*=101.07)	Rh (*M*=102.91)	Pd (*M*=106.42)	Os (*M*=190.23)	Ir (*M*=192.22)	Pt (*M*=195.08)
1	3.11	3.17	3.28	5.88	5.94	6.03
2	3.08	3.14	3.25	5.85	5.91	**6.00**
3	3.05	3.11	3.22	5.82	5.88	5.97
4	3.03	3.08	3.19	5.79	5.86	5.94

The only acceptable answer is **$H_2[PtCl_6]$**. Then *precipitate 1* is, probably, a mixture of insoluble hexachloroplatinates of metals **X2** – **X4**, because only **X1** is left in the *solution 1.*

Reagent **B** contains acetate ions, together with zinc and uranium. Moreover, for the last one such ions stable in aqueous solutions as uranyl ions UO_2^{2+} are known. Besides, the reagent for qualitative analysis such as uranyl zinc acetate can be remembered. In any case, admitting that **B** has 1 atom of U, the excess on other elements can be calculated: $\frac{238.03}{0.4164} - 238.03 = 333.61$. Taking the atomic mass of zinc (Zn^{2+}) from this excess, we obtain: $333.61 - 65.39 = 268.22$, that corresponds to 4 acetate ions (CH_3COO^-). The excess now is $268.22 - 59.05\cdot 4 = 32.02$, i.e. exactly 2 oxygen atoms, which together with uranium atom correspond to double charged ion UO_2^{2+}, required in this case for charge balance. As a result, **B** is **$ZnUO_2(CH_3COO)_4$**.

Next it could be called to memory that uranyl zinc acetate is often mentioned as reagent for sodium ions precipitation. This can be proved also by calculations. As uranium is a heavy element, it is most probably that the biggest mass fraction of metal in **C** (46.43%) accounts exactly for uranium. Then one of two remained values corresponds to zinc, i.e. the ratio of U to Zn in triple salt **C** can be estimated:

$$U : Zn = \frac{46.43}{238.03} : \frac{1.49}{65.39} = 8.56 : 1 \quad \text{or} \quad U : Zn = \frac{46.43}{238.03} : \frac{4.25}{65.39} = 3.00 : 1.$$

The second variant suits best of all, so the molecular mass of **C** can be calculated either by uranium or by zinc (the difference arises only because of initial rounding of elements mass fractions):

$$M_r(\mathbf{C}) = \frac{3 \cdot 238.03}{0.4643} = 1537.99 \quad \text{or} \quad M_r(\mathbf{C}) = \frac{65.39}{0.0425} = 1538.59.$$

In this case, 1.49% is a mass percentage of metal **X1**, which allows to evaluate its relative atomic mass:

$$A_r(\mathbf{X1}) = 0.0149 \cdot 1537.99 / k = 22.92 / k \quad \text{or} \quad A_r(\mathbf{X1}) = 0.0149 \cdot 1538.59 = 22.92 / k,$$

where k is the number of atoms **X1** in **C**. The only one acceptable variant can be obtained if $k = 1$, then **X1** is **Na**, and **C** contains 3 ions of UO_2^{2+}, 6 molecules of H_2O, and, as reflected by charges balance, 9 ions of CH_3COO^-. Then **C** has a composition **$NaZn(UO_2)_3(CH_3COO)_9 \cdot 6H_2O$**, and its molecular weight is:

$$M_r = 22.99 + 65.39 + 3 \cdot (238.03 + 32) + 9 \cdot 59.05 + 6 \cdot 18.02 = 1538.04,$$

that corresponds to the previously obtained results.

In such a manner, the right answers in the first part of the problem are: **X1** = Na, corresponding initial chloride – NaCl (1 point), A = $H_2[PtCl_6]$ (0.75 points), B = $ZnUO_2(CH_3COO)_4$ (0.75 points), C = $NaZn(UO_2)_3(CH_3COO)_9 \cdot 6H_2O$ (0.75 points).

As it was previously mentioned, *precipitate 1* is, probably, a mixture of insoluble hexachloroplatinates of metals **X2** – **X4**. Then the metallic *precipitate 2* is platinum (Pt), and the residual chlorides of corresponding metals passed into *solution 2*.

The complex acid **D** consists of hydrogen, bismuth and iodine. The right answer could be given instantaneously, confirming it with mass fraction verification, but here the detailed solution will be given. The formula of **D** can be presented as $H_a[Bi_bI_c]$, where a, b and c are small integer numbers, hence a can be expressed as:

$$w(I)_{\mathbf{D}} = \frac{126.90c}{1.01a + 208.98b + 126.90c} = 0.7074 \Rightarrow a = \frac{52.49c - 208.98b}{1.01}.$$

The numerator of this expression, evidently, must be positive, thus if $b = 1$ then the value of c must be equal to at least 4, but this way we will obtain:

$$a = \frac{52.49 \cdot 4 - 208.98}{1.01} = 0.97 \approx 1,$$

i.e. **D** is **$H[BiI_4]$**, or hydrogen tetraiodobismuthate (III).

Compound **E** has more complex composition and structure. It is also a complex iodide of bismuth, but containing cations of metal **X2**. The composition of **E** can be determined by the description of its anion structure: the octahedron, which is mentioned in the task, is, obviously, $[BiI_6]^{3-}$. Then by combining two such octahedra with vertices (through iodine atom), the anion will be $[Bi_2I_{11}]^{5-}$; if there is a common edge – $[Bi_2I_{10}]^{4-}$; through the face – $[Bi_2I_9]^{3-}$ (see the structure below). Then **E** can be presented by the formula $(\mathbf{X2})_3[Bi_2I_9]_d$, where d – valency of **X2**. In this way:

$$\frac{w(\mathbf{X2})_{\mathbf{E}}}{w(I)_{\mathbf{E}}}=\frac{A_r(\mathbf{X2})\cdot 3}{126.90\cdot 9d}=\frac{1}{2.865}\Rightarrow A_r(\mathbf{X2})=132.88d\,.$$

If $d=1$, we obtain that **X2** is **Cs**, then **E** – $\mathbf{Cs_3[Bi_2I_9]}$.

In such a manner, the right answers in the second part of the problem are: **X2** = Cs, the corresponding initial chloride – CsCl (1 point), D = $H[BiI_4]$ (0.75 points), E = $Cs_3[Bi_2I_9]$ (0.75 points).

The evaporation of *solution 3* with nitric acid, which contains, probably, the chlorides of only metals **X3** and **X4**, converts these chlorides into nitrates, i.e. *solution 4* is a solution of nitrates of **X3** and **X4**. The addition of $NaNO_2$, $Bi(NO_3)_3$ and $AgNO_3$ to it results in precipitation of complex salt of bismuth **F**. As there are only nitrate and nitrite anions in the system, one of them serves as a ligand. Most likely is the formation of nitrite complex, i.e. the anion of **F** will have the composition $[Bi(NO_2)_6]^{3-}$. This can be confirmed by the ratio of mass fractions of nitrogen and oxygen in **F**:

$$\mathrm{N:O}=\frac{11.00}{14.01}:\frac{25.14}{16.00}=1:2.00=6:12,$$

so, the suggestion is correct. This ratio of elements excludes the variant of composition of **F** with crystallization water. Now the molecular mass of **F** can be found, by using the mass fraction of nitrogen or oxygen and on the assumption that **F** contains just one anion $[Bi(NO_2)_6]^{3-}$:

$$M_r(\mathbf{F})=\frac{6\cdot 14.01}{0.1100}=764.18 \quad \text{or} \quad M_r(\mathbf{F})=\frac{12\cdot 16.00}{0.2514}=763.72\,.$$

Now we can consider the reagents added to *solution 4* at the following step: $Bi(NO_3)_3$ is the source of bismuth ions containing in anion **F**, $NaNO_2$ is the source of nitrite ions, forming the complex with bismuth, then $AgNO_3$ should also contribute to the composition of **F**. This can be explained only by the presence of Ag^+ ions in **F**, beside the metal **X3** cations. Then the possible variants are: $(\mathbf{X3})Ag[Bi(NO_2)_6]$ (**X3** is double charged), $(\mathbf{X3})_2Ag[Bi(NO_2)_6]$ and $(\mathbf{X3})Ag_2[Bi(NO_2)_6]$ (**X3** is single charged).

Subtracting the mass corresponding to $[Bi(NO_2)_6]^{3-}$ from the molecular mass of **F**, we can obtain the molecular mass corresponding to cations:

$$764.18-208.98-46.01\cdot 6=279.14 \quad \text{or} \quad 763.72-208.98-46.01\cdot 6=278.68\,.$$

The relative atomic mass of Ag can be subtracted:

$$279.14-107.87=171.27 \quad \text{or} \quad 278.68-107.87=170.81\,.$$

There are no metals with such an atomic mass, so the variant $(\mathbf{X3})Ag[Bi(NO_2)_6]$ does not match the task. Checking the second variant, $(\mathbf{X3})_2Ag[Bi(NO_2)_6]$:

$$A_r(\mathbf{X3})=171.27/2=85.64 \quad \text{or} \quad A_r(\mathbf{X3})=170.81/2=85.41,$$

shows that rubidium is a matching element. The third variant – (**X3**)$Ag_2[Bi(NO_2)_6]$ – also does not fit because in this case:

$$A_r(\mathbf{X3}) = 171.27 - 107.87 = 63.40 \quad \text{or} \quad A_r(\mathbf{X3}) = 170.81 - 107.87 = 62.94$$

so, there are not adequate variants for metal **X3**. That means that the only acceptable variant for **X3** is **Rb**, then **F** = $\mathbf{Rb_2Ag[Bi(NO_2)_6]}$.

Thus, the right answers in the third part of the problem are: **X3** – Rb, the corresponding initial chloride is RbCl (1 point), **F** = $Rb_2Ag[Bi(NO_2)_6]$ (0.75 point). Since that moment, the idea of the problem – qualitative analysis of the mixture of alkaline metals salts – can be noticed

Finally, the last metal **X4** can be determined. Reagent **F** is a complex sodium salt of cobalt. It can be clear enough already, that it is sodium hexanitritocobaltate(III), a reagent for potassium anions precipitation, which corresponds to the above mentioned idea of the problem. The same answer can be obtained using calculations. So, **F** can be presented as $Na_x[CoL_y]$, where $x+2=y$ (complex of Co^{2+}) or $x+3=y$ (complex of Co^{3+}), and $y=4$ or $y=6$ (characteristic coordination numbers of cobalt, L is a monodentate anionic ligand). Then the molecular mass of L is:

$$M_r(\mathrm{L}) = \left(\frac{58.93}{0.1459} - 58.93 - 22.99x\right)\frac{1}{y} = \frac{344.98 - 22.99x}{y}$$

F	$Na_2[CoL_4]$	$Na_4[CoL_6]$	$Na[CoL_4]$	$Na_3[CoL_6]$
M_r(L)	74.75	42.17	80.50	46.00

The most probable variant is the last one, because it exactly matches the nitrite ion, i.e. complex **G** is $\mathbf{Na_3[Co(NO_2)_6]}$.

For determination of **H** and **X4** the attention should be paid on the phrase "in the presence of remaining silver nitrate in the solution", which again points to the presence of Ag^+ in **H**. Then its formula can be presented as (**X4**)$Ag[Co(NO_2)_6]$, (**X4**)$_2Ag[Co(NO_2)_6]$ or (**X4**)$Ag_2[Co(NO_2)_6]$ by analogy with variants for **F**. For the first variant:

$$A_r(\mathbf{X4}) = (107.87 + 58.93 + 6\cdot 46.01)\left(\frac{1}{1-0.1501} - 1\right) = 78.21.$$

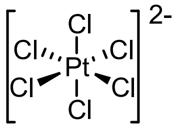
There are no double charged metals with such a relative atomic mass, that is why this variant does not fit. For the second variant A_r(**X4**) will be 2 times less than for the first one, i.e. $A_r(\mathbf{X4}) = 78.21/2 = 39.11$, that corresponds to potassium and correlates with the idea of the task. The third variant also does not match, because in this case:

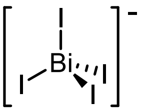
$$A_r(\mathbf{X4}) = (2\cdot 107.87 + 58.93 + 6\cdot 46.01)\left(\frac{1}{1-0.1501} - 1\right) = 97.26,$$

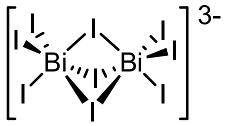
and there are no single charged metals with such a relative atomic mass. Then **X4** is **K**, and **H** is $\mathbf{K_2Ag[Co(NO_2)_6]}$.

So, the right answers in the fourth part of the problem are: **X4** = K, the corresponding initial chloride is KCl (1 point), **G** = $Na_3[Co(NO_2)_6]$ (0.75 point), **H** = $K_2Ag[Co(NO_2)_6]$ (0.75 points, 10 points in total for part 1).

2. Structural formulae of complex anions of compounds: **A** – $[PtCl_6]^{2-}$ (octahedron, 0.75 points), D – $[BiI_4]^-$ (tetrahedron, 0.75 points) and E – $[Bi_2I_9]^{3-}$ (two octahedra sharing a common face, 1.5 points, 3 points in total for part 2).







3. The equations of reactions (2 points in total for part 3):

1. $2KCl + H_2[PtCl_6] = K_2[PtCl_6]\downarrow + 2HCl$ (0.1 points)
2. $2RbCl + H_2[PtCl_6] = Rb_2[PtCl_6]\downarrow + 2HCl$ (0.1 points)
3. $2CsCl + H_2[PtCl_6] = Cs_2[PtCl_6]\downarrow + 2HCl$ (0.1 points)
4. $2NaCl + 6ZnUO_2(CH_3COO)_4 + 12H_2O = 2NaZn(UO_2)_3(CH_3COO)_9\cdot 6H_2O\downarrow + ZnCl_2 + 3Zn(CH_3COO)_2$ (0.3 points)
5. $K_2[PtCl_6] = 2KCl + Pt + 2Cl_2\uparrow$ (0.1 points)
6. $Rb_2[PtCl_6] = 2RbCl + Pt + 2Cl_2\uparrow$ (0.1 points)
7. $Cs_2[PtCl_6] = 2CsCl + Pt + 2Cl_2\uparrow$ (0.1 points)
8. $3CsCl + 2H[BiI_4] + HI = Cs_3[Bi_2I_9]\downarrow + 3HCl$ (0.3 points)
9. $KCl + HNO_3 = KNO_3 + HCl\uparrow$ (0.1 points)
10. $RbCl + HNO_3 = RbNO_3 + HCl\uparrow$ (0.1 points)
11. $2RbNO_3 + 6NaNO_2 + Bi(NO_3)_3 + AgNO_3 = Rb_2Ag[Bi(NO_2)_6]\downarrow + 6NaNO_3$ (0.3 points)
12. $2KNO_3 + Na_3[Co(NO_2)_6] + AgNO_3 = K_2Ag[Co(NO_2)_6]\downarrow + 3NaNO_3$ (0.3 points)

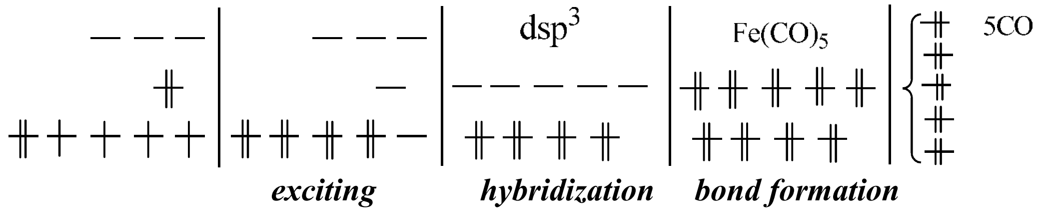
SECTION IV. PHYSICAL CHEMISTRY

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

1. From NH_3(g) + H^+(g) = NH_4^+(g) (A_p.); 0.5N_2(g) + 2H_2(g) – e^- = NH_4^+(g) (ΔH°_{NH4+}); 0.5H_2(g) = H(g) (ΔH°_H); H(g) – e^- = H^+(g) (ΔH°_{H+}); 0.5N_2(g) + 1.5H_2(g) = NH_3(g) (ΔH°_{NH3}) and Hess law, we can find the affinity for the proton: $A_p = \Delta H^\circ_{NH4+} - \Delta H^\circ_{NH3} - \Delta H^\circ_{H+} - \Delta H^\circ_H = 664 + 46.0 - 13.6\cdot 96.485 - 218 = -820$ kJ/mol (2 points).

Based on N(g) + 3H(g) + H^+(g) = NH_4^+(g) (ΔH°); 0.5N_2(g) = N(g) (ΔH°_N), and using ΔH°_H and ΔH°_{H+}, we can find the average N–H bond energy in NH_4^+ $E_{av} = \Delta H^\circ/4 = -(\Delta H^\circ_{NH4+} - \Delta H^\circ_N - 4\Delta H^\circ_H - \Delta H^\circ_{H+})/4 = -(664 - 473 - 4\cdot 218 - 13.6\cdot 96.458)/4 = 498$ kJ/mol (2 points, 4 points in total).

2. In carbonyl **Me**(CO)$_a$: $W_C = 12a\cdot 100/(A_{Me} + 28a) = 30.6$; $A_{Me} = 39.2a - 28a = 11.2\,a$; when $a = 5$ $A_{Me} = 56$ g/mol. Therefore **Me–Fe**; carbonyl – **Fe(CO)$_5$** (2 points)



3. From C(s) + 0.5O_2(g) = CO(g) (ΔH°_{CO}); Fe(s) = Fe(g) (ΔH°_{Fe})

Fe(s) + 5C(s) + 2.5O_2(g) = Fe(CO)$_5$(g) ($\Delta H^\circ_{Fe(CO)5}$), we can calculate the enthalpy Fe(g) + 5CO(g) = Fe(CO)$_5$(g), $\Delta H^\circ_x = \Delta H^\circ_{Fe(CO)5} - 5\Delta H^\circ_{CO} - \Delta H^\circ_{CO} = -732 + 5\cdot 110 - 424 = -606$ kJ/mol (1 point) and the average bond energy $E_{av} = -\Delta H^\circ_x/5 = 606/5 = 121$ kJ/mol (1 point). The calculation did not take into account the excitation of the iron atom ($3d^6 4s^2 p^0$) into ($3d^8 4s^0 p^0$) $(\Delta H^\circ)^* = 251\cdot 5 - 606 = 900$ kJ/mol (1 point, 3 points in total)

4. The potential energy $U = U_{kd} + U_{kid} + U_{dd} + U_{va} = -1395 - 897 + 513 + 407 = -1372$ kJ/mol (0.5 points). The average bond energy $E_{av} = -U/6 = 1372/6 = 229$ kJ/mol (0.5 points, 1 point in total)

5. The distance between the cations $r = 2(r_{Fe+2} + D_{H2O}) = 2(0.83 + 2.76) = 7.18$ Å or $7.18\cdot 10^{-10}$ m. $k = N_A e^2/(4\pi\varepsilon_0) = 6.02\cdot 10^{23}(1.602\cdot 10^{-19})^2/(4\cdot 3.14\cdot 8.854\cdot 10^{-12}) = 1.389\cdot 10^{-4}$ (0.5 points). Knowing r and k, it is possible to calculate the thermodynamic functions: $\Delta H^\circ_B = -1.389\cdot 10^4\cdot 2^2\cdot(1 - 1/78 + 0.356\cdot 298/78^2)/7.18\cdot 10^{-10} = -777389$ J/mol or -777.4 kJ/mol (0.5 points). $\Delta S^\circ_B = -1.389\cdot 10^{-4}\cdot 2^2\cdot 0.356/(78^2\ 7.18\cdot 10^{-10}) = -45.3$ J/mol·K (0.5 points). $\Delta G^\circ_B = \Delta H^\circ_B - T\Delta S^\circ_B = -777.4 + 45.3\ 298\cdot 10^{-3} = -763.9$ kJ/mol (0.5 points, 2 points in total)

6. Starting from H_2O(l) = H_2O(g) (ΔH°_i), Fe$(H_2O)_6^{2+}$(g) = Fe$(H_2O)_6^{2+}$(aq) (ΔH°_B) и Fe^{+2}(g) + 6H_2O(l) = Fe$(H_2O)_6^{2+}$(aq) (ΔH°_g), we can find the enthalpy for Fe^{2+}(g) + 6H_2O(g) = Fe$(H_2O)_6^{2+}$(g), $\Delta H^\circ_x = \Delta H^\circ_g - 6\Delta H^\circ_I - \Delta H^\circ_B$. $\Delta H^\circ_x = -1958.1 - 6\ 44 + 777.4 = -1444.7$ kJ/mol (1 point) and the average bond energy $E_{av} = -\Delta H^\circ_x/6 = 1444.7/6 = 241$ kJ/mol (0.5 points, 1.5 points in total)

7. The energy of stabilization by the crystal field is not taken into account. In the case of configurations d^0, d^{10}, d^5 (weak field), the energy of stabilization by the crystal field is E = 0, and for Fe2+ it is equal to $E = 5(241 – 229) = 60$ кДж/моль (1.5 points)

Problem 2 (authors Lukianova M.A., Karpushkin E.A.)

1. OH, H, $TiCl_3$, $VOSO_4$ (0.5 points for each correct choice, –0.5 for each incorrect choice, maximum 2 points)

2. Kinetic scheme:

$$\mathrm{M} \rightarrow \mathrm{R}\cdot \qquad v_1 = GI\rho$$

$$2\mathrm{R}\cdot \rightarrow \mathrm{R–R} \qquad v_2 = 2k[\mathrm{R}\cdot]^2$$

Since the radicals are in the steady state, the rates of their generation and disappearance are equal: $GI\rho = 2k[\mathrm{R}\cdot]^2$

$$[\mathrm{R}\cdot] = \sqrt{\frac{Gl\rho}{2k}} = \sqrt{\frac{2\,\frac{\text{radicals}}{100\text{eV}}/1.6\cdot10^{-19}\,\frac{\text{J}}{\text{eV}}/100/6.02\cdot10^{23}\,\frac{\text{radicals}}{\text{mol}}\cdot10\,\frac{\text{J}}{\text{kg}\cdot\text{s}}\cdot1\,\frac{\text{kg}}{\text{L}}}{2\cdot10^{10}\,\frac{\text{L}}{\text{mol}\cdot\text{s}}}} = 1.02\cdot10^{-8}\ \text{mol/L}$$

$$n(\mathrm{R}\cdot) = 10\cdot10^{-6}\text{L}\cdot1.02\cdot10^{-8}\ \text{mol/L} = 1.02\cdot10^{-13}\ \text{mol}$$

$$N(\mathrm{R}\cdot) = 1.02\cdot10^{-13}\ \text{mol}\cdot6.02\cdot10^{23}\text{mol}^{-1} = 6.13\cdot10^{10}$$

The determined number of radicals falls outside the sensitivity 2 range of the ESR spectrometer (2 points for calculation, 0.5 points for comparison, 5 points in total)

3. Radiation-chemical yield is $G = N_{\text{рад}}/E$. During the irradiation, the sample absorbs (taking into account the sample geometry) $E = Itm = It\rho V = It\rho\pi\frac{d^2}{4}l$ = 10 J/kg·s · 20 · 60 s · 0.98 kg/L · 3.14 · $\frac{(0.04\ \text{dm})^2}{4}$ · 0.15 dm = 2.2 J of energy. The reference sample contains 0.150 g / 171 g/mol · $6.02\cdot10^{23}$ spins/mol = $5.3\cdot10^{20}$ spins. The number of radicals in the sample: $N_{\text{rad}} = \frac{\text{I}_{\text{sample}}}{\text{I}_{\text{ref}}}N_{\text{ref}}$ = 0.0366 / 52.4 · $5.3\cdot10^{20} = 3.7\cdot10^{17}$.

Hence the radiation-chemical yield is G = $\frac{3.7\cdot10^{17}}{2.2\ \text{J}}$ = 2.7 radicals/100 eV (2.5 points)

4. We will use the Beer's law, $A = \varepsilon cd$. Then $\varepsilon = A/cd$. To determine ε, the radicals concentration in the sample is required. The sample volume is $V = \pi d^2/4l$ = 3.14·(0.04 dm)^2/4·0.15 dm = $1.9\cdot10^{-4}$ L. The number of radicals (i. 3) is $N_{\text{rad}} = 3.7\cdot10^{17}$. The concentration of radicals is hence $c = N_{\text{rad}}/N_{\text{A}}/V$ = $3.7\cdot10^{17}/6.02\cdot10^{23}$ mol^{-1}/$1.9\cdot10^{-4}$ L =$3.2\cdot10^{-3}$ mol/L. Then ε = 1.33/$3.2\cdot10^{-3}$ mol/L/0.4 cm = 1028 L/mol/cm. (2.5 points)

а) $c_{\text{min}} = A_{\text{min}}/\varepsilon/d$ = 0.01/1028 L/mol/cm/0.4 cm = $2.4\cdot10^{-5}$ mol/L (1.5 points); б) c_{min} = $10^{11}/6.02\cdot10^{23}$ mol^{-1}/$1.9\cdot10^{-4}$ L = $8.7\cdot10^{-10}$ mol/L (1.5 points)

5. Let us consider m = 1 kg of the polymer. It contains n = 1000 g/100000 g/mol = 0.01 mol of macromolecules. After absorption of the gel dose, each macromolecule should be linked with two other macromolecules. Hence the number of radicals forming the linkages should be twice the number of macromolecules, $n_{\text{rad}} = 0.02$ mol. $G = 3$ radicals/100 eV = (3 radicals/100 eV)/$1.6\cdot10^{-19}$J/eV/100/$6.02\cdot10^{23}$ radicals/mol = $3.11\cdot10^{-7}$ mol/J. Hence, the energy required for generation of the radicals is $E = n_{\text{rad}}/G = 0.02$ mol/$3.11\cdot10^{-7}$ mol/J = 64.3 kJ. Gel dose $D = E/m = 64.3$ kJ/1 kg = 64.3 kJ/kg (2.5 points)

Problem 3 (author Gulevich D.G.)

1. Wavelength of de Broglie $\lambda = h/\sqrt{2mE_\text{K}}$, therefore for the same kinetic energy, the tunneling probability for light particles is larger: $e^- > H > D > C > Cl$ (0.75 points)

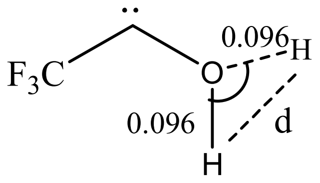
2. By replacing λ in the Gol'danskii equation by the expression $\lambda = h/\sqrt{2mE}$, and solving the inequality with respect to temperature, we obtain (2 points):

$$T_\text{K} = \frac{h}{k_\text{Б} d}\sqrt{\frac{E}{2m}}$$

3. The width of the energy barrier is $d = d_0 - d_\text{f} = 0.320 - 0.0155 = 0.305$ nm. After substituting the numerical values, we get (1 point for each d and T_K, 2 points in total):

$$T_\text{K} = \frac{6.63\cdot10^{-34}}{2\cdot3.14\cdot1.38\cdot10^{-23}\cdot0.320\cdot10^{-9}}\sqrt{\frac{0.1\cdot1.6\cdot10^{-19}}{2\cdot30\cdot10^{-3}/6.02\cdot10^{23}}} = 13.6 \approx 14\,\text{K}$$

4. $\ln\frac{\tau_{02}}{\tau_{01}} = \frac{E_a(T_1 - T_2)}{RT_1T_2} = \frac{8.4\cdot10^3\cdot70}{8.314\cdot80\cdot10} = 88.4,\ \tau_{02} = \tau_{01}\cdot e^{88.4} = 2.5\cdot10^{33}\,\text{c} \approx 8\cdot10^{25}$ years (2 points)

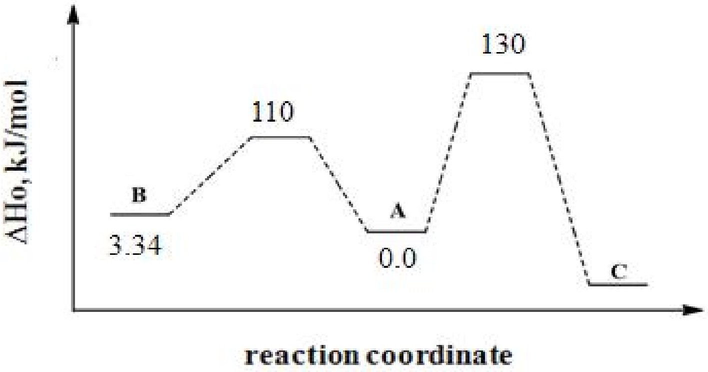


5. Isomerization reaction **A** ↔ **B** was carried out by irradiating the reaction medium with light of the wavelength 465 nm, therefore the transferred energy $E = hc/\lambda = 4.28\cdot10^{-19}\,J = 2.68$ eV, which is 2.4 times larger than the energy barrier for reaction **1**. The width of the barrier is determined from the data on the length of the O–H bond. By the cosine theorem $d^2 = 0.096^2 + 0.096^2 - 2\cdot0.096\cdot0.096\cdot\cos111° = 0.024$, $d = 0.15$ nm. To determine the height of the reaction barrier **A** → **C**, at first we will calculate the value $k = \ln2/\tau_{1/2} = 0.693/(72\cdot24\cdot3600) = 1.11\cdot10^{-7}\ \text{s}^{-1}$. Substituting this value in the formula for calculating k by the classical theory of the transition state, we determine $\Delta G^{\neq} = 44.4$ kJ/mol $= \Delta H^{\neq} + T\Delta S^{\neq}$, hence $\Delta H^{\neq} = 130$ kJ/mol or 1.35 eV. The completed table:

№	reaction	d, nm	$\Delta H^{\neq}$, eV
1	**A↔B**	0.15	1.15
2	**A→C**	0.13	1.35
3	**B→C**	0.20	1.18

From the obtained data it can be concluded that tunneling is possible for reaction **2**, since in this case the width of the barrier is the smallest and the height is the largest and considerably exceeds k_BT (determination of 1st reaction barrier width 1.5 points, calculating of k 1 point, $\Delta G^{\neq}$ 1 point, barrier height 1.5 points, determination of the reaction for which tunneling is possible 2 points, total 7 points)

6. a)



б) Pyrolysis produces *cis*-trifluoromethylhydroxycarbene, which means that it is more stable than the *trans*- isomer (correct arrangement of each substance on the energy diagram 0.25 points, determination of the most stable isomer 0.5 points, total 1.25 points)

SECTION V. INORGANIC CHEMISTRY

Problem 1 (author Likhanov M.S.)

1. **A** metal is Re. This is not difficult to show from the calculation of the composition of **I** compound:

m(K) = 0.1065·1101.33 = 117.29, n(K) = 3

m(Cl) = 0.3863·1101.33 = 425.44, n(Cl) = 12

m(**A**) = 0.5072·1101.33 = 558.59 и при n(**A**) = 3 M(**A**) = 186.2 therefore **A** metal is Re. And **I** compound is $K_3Re_3Cl_{12}$.

Rhenium reacts with concentrated hydrogen peroxide forming perrhenic acid (the oxidation state of rhenium in it is maximal):

$$2Re + 7H_2O_2 = 2HReO_4 + 6H_2O,\ \mathbf{B} – HReO_4.$$

In reaction with ammonia, ammonium perrhenate is formed, from which metallic rhenium is produced in industry:

$$HReO_4 + NH_3 = NH_4ReO_4,\ \mathbf{C} – NH_4ReO_4$$

$$2NH_4ReO_4 + 7H_2 = 2Re + 2NH_3 + 8H_2O \text{ or } 2NH_4ReO_4 + 4H_2 = 2Re + 2N_2 + 8H_2O$$

In acidic medium, perrhenates oxidize under the action of strong reducing agents, for example, iodides:

$$2NH_4ReO_4 + 6NH_4I + 16HCl = 2(NH_4)_2[ReCl_6] + 3J_2 + 4NH_4Cl + 8H_2O \text{ или}$$

$$2NH_4ReO_4 + 9NH_4I + 16HCl = 2(NH_4)_2[ReCl_6] + 3NH_4J_3 + 4NH_4Cl + 8H_2O,\ \mathbf{D} – (NH_4)_2[ReCl_6]$$

The fusing of $(NH_4)_2[ReCl_6]$ with potassium hydroxide leads to the formation of potassium renite and ammonia:

$$(NH_4)_2[ReCl_6] + 8KOH = K_2ReO_3 + 6KCl + 2NH_3 + 5H_2O,\ \mathbf{E} – K_2ReO_3$$

In reaction of liquid $SOCl_2$ and renites, $[ReCl_6]^{2-}$ complexes are obtained, which solutions are green: $K_2ReO_3 + 3SOCl_2 = K_2ReCl_6 + 3SO_2$, **F** – K_2ReCl_6

The oxidation of tetravalent rhenium complexes with hydrogen peroxide leads again to perrhenates formation: $2K_2ReCl_6 + 10NH_3 + 3H_2O_2 + 2H_2O = 2NH_4ReO_4 + 4KCl + 8NH_4Cl$.

Rhenium forms many halides. Chlorination at a temperature of 400°C produces rhenium(V)chloride. The composition can also be easily determined from the given crystal structure: two octahedra $[ReCl_6]$ bound along the edge have the general formula Re_2Cl_{10}, from which the formula of rhenium (V) chloride follows:

$$2Re + 5Cl_2 = 2ReCl_5,\ \mathbf{G} – ReCl_5.$$

Melting of $ReCl_5$ with potassium chloride leads to the K_2ReCl_6 formation, while the rhenium oxidation state decreases from an unstable +5 to a more stable +4, which also corresponds to the statement of the problem (in the **G**, **F** range the rhenium oxidation state decreases):

$$2ReCl_5 + 4KCl = 2K_2ReCl_6 + Cl_2$$

In water rhenium (V) chloride disproportionates to compounds with more stable oxidation states, namely, $HReO_4$ and hydrated rhenium (IV) oxide:

$$3ReCl_5 + 12H_2O = HReO_4 + 2ReO_2{\cdot}2H_2O\downarrow + 15HCl$$

When heated, $ReCl_5$ decomposes to trivalent chloride. The composition of **H** substance is also easy to obtain by "reverse" synthesis from $K_3[Re_3Cl_{12}]$, by calculating the rhenium oxidation state in it.

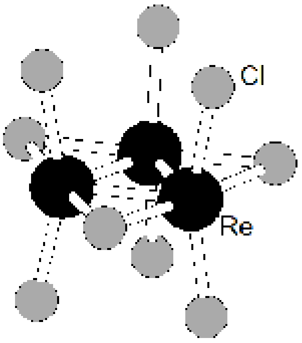
$3ReCl_5 = Re_3Cl_9 + 3Cl_2$ ($ReCl_3$ formula is also considered correct), **H** – Re_3Cl_9

Interaction with potassium chloride in concentrated hydrochloric acid leads to the formation of red crystals of the complex compound:

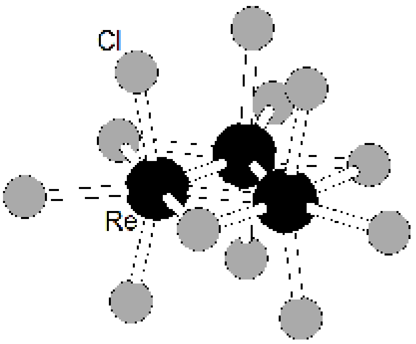
$$Re_3Cl_9 + 3KCl = K_3[Re_3Cl_{12}]$$

(0.5 points for each substance and reaction, 10.5 points in total)

2. Taking into account the symmetry elements in Re_3Cl_9 and in the $Re_3Cl_{12}^{3-}$ anion, as well as the information about the presence of rhenium-rhenium bonds, it follows that the rhenium atoms form a triangle. Chlorine atoms can be either bridged between rhenium atoms, or be terminal, and their ratio is 2:1 in Re_3Cl_9. Considering the presence of the mirror plane, the quantity of bridge atoms should be 3 and the quantity of terminal should be 6, in $Re_3Cl_{12}^{3-}$ to each rhenium atom the terminal atom lying in the triangle plane will be added (1.4 points for each structure, 2.8 points in total).

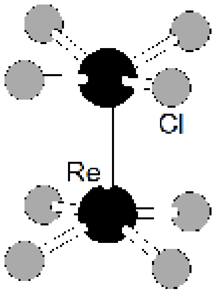


Re_3Cl_9



$Re_3Cl_{12}^{3-}$

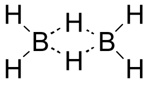
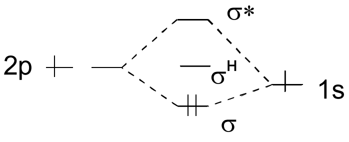
3. С учетом молярной массы состав изомера: $K_2Re_2Cl_8$ (0.3 балла). Диамагнетизм свидетельствует о наличии связей рений-рений в соединении. Таким образом рений образует гантель рений-рений, а атомы хлора поровну распределены между атомами металла, и анион соединения имеет следующее кристаллическое строение (1.4 балла за структуру, всего 1.7 балла):



$Re_2Cl_8^{2-}$

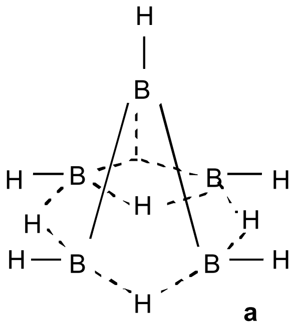
Problem 2 (authors Rozantsev G.M., Shvartsman V.E.)

1. For $\mathbf{X_mH_{m+4}}$ $w_X = \frac{mA_X}{mA_X + m + 4} = 0.783$ $A_X = 3.61 + 14.4/m$ (1 point). At m = 2 $A_X = 10.8$ (g/mol) **X** – B, hydride B_2H_6 (0.5 points). The second hydride was obtained by pyrolysis $\mathbf{n}B_2H_6 \rightarrow 2\mathbf{B_nH_{n+4}}$ and $\frac{2\cdot 0.138}{27.6} = \frac{0.0315\cdot n}{0.25(11.8n+4)}$ **n** = 5 (1 point). Hydride B_5H_9 (0.5 points), anion $B_5H_8^-$ (0.5 points, 3.5 points in total).

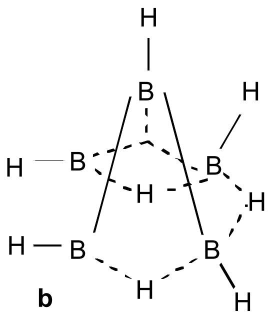
2.  (1 point) 

(1 point).

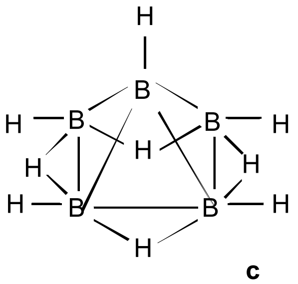
3. If **n** = 5, then skeleton is a square pyramid, where 5 + 2 = 7 = 4 + **t** + **y** bonds, 4 B are in the base, hence are four bonds BHB and s = 4 (0.5 points). Then **t** + **y** = 3 and **t** = 1 (0.5 points), **y** = 2 (0.5 points) since **y** > **t**. There are 2·7 = 14 electrons involved in the skeleton formation from 3·5 + 9 = 24, i.e. 10 electrons form 5 non-skeleton bonds BH (**a**). With $B_5H_8^-$ formation, the more mobile H leaves the bridge bond BHB (**b**) (0.5 points). (This structures are represented in the monographs in the form of polyhedrons or without regard to valence possibilities of boron, or with considering the occurrence of one five-center bond BBBBB, and structure formulae will be **c**,**d**).



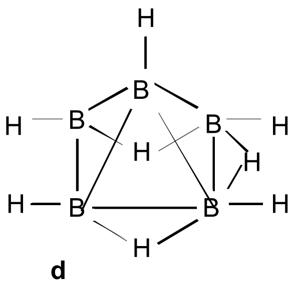
a



b



c



d

For nido-borane B_5H_9 there is five-center bond, all the bonds B – B with vertex have to be longer than bonds in the base, where are also three-center BHB. However, in the structure B_5H_9 bond lengths of B – B (vertex – base) = 0.168 nm, and B – B (base – base) = 0.178 nm, which counts in favor of one three-center (BBB) and two two-center (BB) bonds in skeleton. (For **a** and **b** structures – 1 point; **c** and **d** only – 0.5 points, 3 points in total).

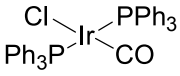
4. $5B_2H_6 \xrightarrow{225\ ^\circ C,\, 0.2\ atm} 2B_5H_9 + 6H_2$ (0.5 points) $B_5H_9 + KH \xrightarrow{-60\ ^\circ C/THF} K[B_5H_8] + H_2$ (0.5 points). $\Delta H^0 = 5(2\cdot 441 + 4\cdot 381) - 6\cdot 436 - 2(380 + 2\cdot 332 + 4\cdot 441 + 5\cdot 381) = -12$ (kJ/mol) (0.5 points, 1.5 points in total).

5. In the Vaska's complex, ligands are CO, PPh_3 and Cl^-, and central atom is $\mathbf{Me}^+$. On the basis of $\mathbf{Me}Cl_3$ $w_{Me} = \frac{A_{Me}}{A_{Me} + 106.5} = 0.643$ $A_{\mathbf{Me}} = 191.8$ g/mol, **Me** – Ir (**A** = 192.2 g/mol) (1 point).

The Vaska's complex is $[Ir_{\mathbf{a}}(CO)_{\mathbf{b}}(PPh_3)_{\mathbf{c}}Cl_{\mathbf{d}}]$. According to the electroneutrality:

$$\frac{67.2}{262}(0) + \frac{3.57}{28}(0) + \frac{w_{Ir}}{192.2}(1) + \frac{100 - 67.2 - 3.57 - w_{Ir}}{35.5}(-1) = 0$$

$\frac{w_{Ir}}{192.2} = \frac{29.23 - w_{Ir}}{35.5}$ $w_{Ir} = 24.7\%$ $w_{Cl-} = 29.23 - 24.7 = 4.53\%$. Then **a:b:c:d** = 24.7/192.2 : 3.57/28 : 67.2/262 : 4.53/35.5 = 0.129 : 0.128 : 0.256 : 0.128 = 1:1:2:1. The Vaska's complex is $[Ir(CO)(PPh_3)_2Cl]$ (1 point). For Ir+ ($6s^15d^7 \rightleftarrows 5d^86s^0$) dsp^2-hybridization is typical (0.5 point). Structural formula is

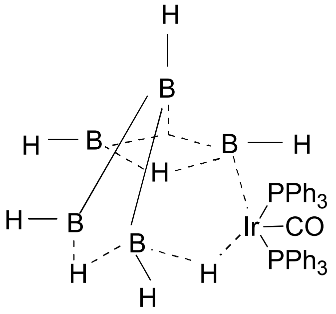


(0.5 points, 3 points in total).

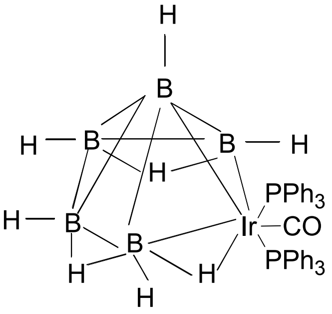
6. In the reaction, Cl^- exchanges with $B_5H_8^-$, and the formula of the complex **A** is $[Ir(CO)(PPh_3)_2(B_5H_8)]$ (0.5 points) $[Ir(CO)(PPh_3)_2Cl] + K[B_5H_8] = [Ir(CO)(PPh_3)_2(B_5H_8)] + KCl$ (0.5 points). $\nu_{\mathbf{B}} = 0.390/779.7 = 5\cdot10^{-4}$ mol; $\nu_{K[B5H8]} = \nu_{B5H9} = 0.315/63 = 5\cdot10^{-4}$ (mol) (stoichiometry);

$\nu_{\mathbf{A}} = 0.0720/806.2 = 8.93\cdot10^{-5}$ mol, yield $= \frac{8.93\cdot10^{-5}\cdot100\%}{5\cdot10^{-4}} = 17.9\%$ (0.5 points, 1.5 points in total)

7. (0.25 points for **a**, 0.25 points for **b**, 0.5 points in total)



a



b

Problem 3 (author Likhanov M.S.)

1. **A** oxide is V_2O_5, the yellow vanadium(V)oxide, what can be easily confirmed by calculating the mass fraction of oxygen scanning various oxide variants. It is widely known that at the result of the interaction of freshly precipitated vanadium oxide or acidified solutions of VO_2^+ vanadates with hydrogen peroxide peroxycomplexes are formed, what is accompanied by intense red coloration of the solution:

$$V_2O_5 + 2H_2O_2 + H_2SO_4 = [VO(O_2)]_2SO_4 + 3H_2O, \mathbf{B} - [VO(O_2)]_2SO_4$$

The interaction of vanadium oxide with oxalic acid and hydrogen peroxide in an alkaline medium leads to the formation of a complex with seven-coordinated vanadium, and the crystals of this complex salt can be isolated from the solution by adding alcohol:

$$V_2O_5 + 6KOH + 4H_2O_2 + 2H_2C_2O_4 = 2K_3[VO(O_2)_2(C_2O_4)] + 9H_2O, \mathbf{E} - K_3[VO(O_2)_2(C_2O_4)]$$

The reaction of the peroxyvanadine cation reduction to the vanadyl with the formation of oxygen molecule occurs under the action of strong oxidizing agents, but in the presence of silver this reaction occurs with persulfate, where Ag^+ plays the role of a catalyst:

$[VO(O_2)]_2SO_4 + K_2S_2O_8 = 2(VO)SO_4 + K_2SO_4 + 2O_2$, **D** - $K_2S_2O_8$, **C** – $(VO)SO_4$

Potassium persulphate is synthesized by electrolysis of potassium hydrogen sulfate solution, and because of the poor solubility, the product precipitates:

$2KHSO_4 = K_2S_2O_8 + H_2$, **G** – $KHSO_4$

The careful interaction of persulfates with concentrated sulfuric acid upon cooling leads to the formation of peroxodisulfuric acid solution:

$K_2S_2O_8 + H_2SO_{4\,conc} = H_2S_2O_8 + K_2SO_4$, **F** – $H_2S_2O_8$

This acid is decomposed with water by itself to form of hydrogen peroxide, however, upon cooling, the formation of peroxymonosulfuric acid, Caro's acid, occurs:

$2H_2S_2O_8 + H_2O = 2H_2SO_5 + H_2SO_4$, **H** – H_2SO_5

In industry, the Caro's acid is obtained from sulfuric anhydride SO_3 ($\omega(O) = 59.95\%$) by reaction with hydrogen chloride with the formation of chlorosulfonic acid:

$SO_3 + HCl = HOSO_2Cl$, **I** – SO_3, **K** – $HOSO_2Cl$

Further, the interaction of anhydrous hydrogen peroxide with chlorosulfonic acid: $HOSO_2Cl + H_2O_2 = H_2SO_5 + HCl$ (0.5 points for each compound and reaction, 9 points in total)

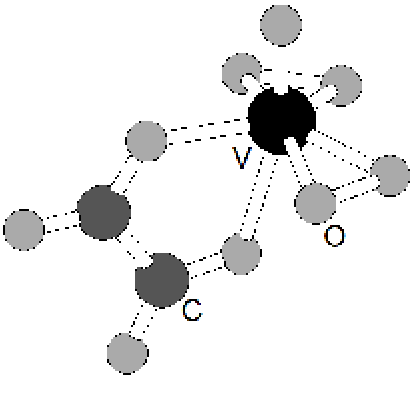
2. The mechanism of potassium persulfate with a peroxyvanadium complex interaction involves the formation of divalent silver ions, which oxidize VO_3^+ to VO_3^{2+}, with following decomposition into oxygen and the vanadyl cation:

$S_2O_8^{2-} + 2Ag^+ = 2SO_4^{2-} + 2Ag^{2+}$ (0.5 points)

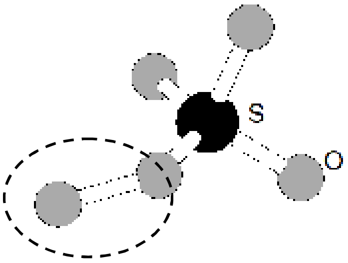
$VO_3^+ + Ag^{2+} = Ag^+ + VO_3^{2+}$ (0.5 points)

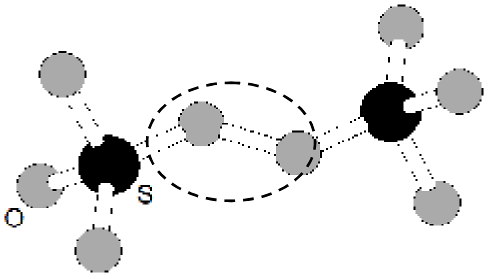
$VO_3^{2+} = VO^{2+} + O_2$ (0.5 points, 1.5 points in total)

3. In $K_3[VO(O_2)_2(C_2O_4)]$ compound, the vanadium atom coordinates four oxygen atoms from two peroxide ions, one oxygen atom with a short vanadyl bond and two oxygen atoms from the oxalate ion. Thus, the coordination number of vanadium is 7 (0.5 points for coordination number, 1 point for structure, 1.5 points in total)



4. H_2SO_5 and $H_2S_2O_8$ belong to the class of peroxy acids, and the presence of peroxide group (0.5 points) determines their features. The anion of peroxomonosulfuric acid is a tetrahedron with a sulfur atom in the center of it, and the anion of peroxydisulfuric acid is two tetrahedra connected through a peroxide bridge. (0.5 points for each structure, 1.5 points in total)





5. Since α-type vanadium bronze is a solid solution of lithium introduced in V_2O_5, it is not difficult to write the formula of such bronze as $Li_xV_2O_5$. In it some fraction of vanadium has +4 oxidation state. When heated in the air, the oxidation to the lithium vanadate and the initial vanadium (V) oxide occurs (0.5 points for the equation):

$$Li_xV_2O_5 + \frac{x}{4}O_2 = \frac{x}{3}Li_3VO_4 + \frac{2-x}{2}V_2O_5$$

Hence, it is not difficult to write down the equation for increasing the mass of the sample after calcination in the air (0.5 points for the calculations):

$$\frac{m(O_2)}{m(Li_xV_2O_5)} = 0.01733$$

$$\frac{\frac{x}{4}\cdot 32}{x\cdot 6.94 + 181.88} = 0.01733$$

$$x = 0.4$$

Consequently, $Li_{0.4}V_2O_5$ is the composition of the bronze (0.5 points for the composition, 1.5 points in total)