Section I. Inorganic chemistry

Problem 1 (author Likhanov M.S.)

1. In a modern chemical laboratory, the question of the economical use of reagents is especially acute, particularly if they contain expensive components. In some cases, for example, when we work with noble metals, it is necessary to separate (regenerate) them after the end of work and reuse them. From the data presented in the first part, the molar mass of $\mathbf{A_3B}$ compound can be calculated (taking into account that the number of formula units is 1!). Using the formula:

$$M(\mathbf{A_3B}) = V_{u.c.} \cdot d \cdot N_A/Z = (3.887 \cdot 10^{-8})^3 \cdot 14.674 \cdot 6.02 \cdot 10^{23} / 1 = 518.8 \text{ g/cm}^3.$$

From the precipitation reaction with ammonium nitrate after dissolution of the starting compound in aqua regia the noble metal **B** is platinum. Then the mass of **A** is 107.9 – therefore this element is a silver, and the initial compound is Ag_3Pt. **A** – Ag, **B** – Pt.

The reaction of dissolution in aqua regia:

$$3Ag_3Pt + 7HNO_3 + 36HCl = 3H_2PtCl_6 + 9HAgCl_2 + 7NO + 14H_2O$$

Reactions with the formation of other soluble silver salts are also correct:

$$3Ag_3Pt + 16HNO_3 + 18HCl = 3H_2PtCl_6 + 9AgNO_3 + 7NO + 14H_2O$$

The addition of ammonium nitrate causes the formation of a yellow precipitate:

$$H_2PtCl_6 + 2NH_4NO_3 = (NH_4)_2PtCl_6\downarrow + 2NH_4NO_3, \mathbf{C} – (NH_4)_2PtCl_6$$

Thermal decomposition of ammonium hexachloroplatinate leads to the production of finely dispersed platinum – "platinum black":

$$(NH_4)_2PtCl_6 = Pt + 2NH_4Cl\uparrow + 2Cl_2\uparrow$$

(0.6 points for each compound and reaction, 1 point for calculation, 4.6 points in total)

2. To calculate the amount of regenerated platinum, it is necessary to determine the mass of precipitated ammonium hexachloroplatinate. For this, it is necessary to calculate the equilibrium concentrations of $PtCl_6^{2-}$ and NH_4^+ ions after precipitation and substitute them in the solubility constant.

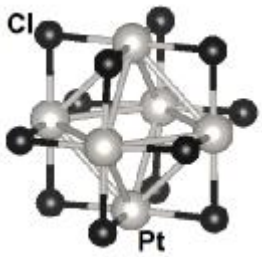
In 50 mL of solution after the dissolving in aqua regia $n(H_2PtCl_6) = n(Ag_3Pt) = 1.9275 \cdot 10^{-3}$ mol, then after adding of 50 mL NH_4NO_3 solution the concertation of $[PtCl_6]^{2-}$ ions until precipitation was $[PtCl_6^{2-}] = 1.9275 \cdot 10^{-3} / 0.1 = 1.9275 \cdot 10^{-2}$ mol/L. Similarly, the concentration of NH_4^+ ions before precipitation was $[NH_4^+] = 0.05$ mol/L (1 point).

The ions concentrations after precipitation: $[PtCl_6^{2-}] = 1.9275 \cdot 10^{-2} - x$ mol/L,
$[NH_4^+] = 0.05 - 2x$ mol/L, when x is the number of moles of the precipitate in 1 liter of solution, then: $(1.9275 \cdot 10^{-2} - x) \cdot (0.05 - 2x)^2 = 9 \cdot 10^{-6}$ (1 point).

Solving this equation, we get one answer that makes sense: $x = 9.68 \cdot 10^{-3}$. Then, $9.68 \cdot 10^{-4}$ mol $(NH_4)_2PtCl_6$ precipitated from 100 mL of solution (1 point).

After decomposition of ammonium hexachloroplatinate in air, $9.68 \cdot 10^{-4}$ mol of platinum is formed. Thus, from the initial $1.9275 \cdot 10^{-3}$ mol of Ag_3Pt, $9.68 \cdot 10^{-4}$ mol of Pt was obtained; i.e., $9.68 \cdot 10^{-4} / 1.9275 \cdot 10^{-3} \approx 50.2\%$ of platinum was regenerated (0.1 points, 3.1 points in total).

3. The formula of **D** substance can be obtained from the given crystal structure of the compound in which the Pt_6Cl_{12} cluster is the structural unit (see Fig.). **D** – $PtCl_2$.



Dissolution of $PtCl_2$ in hydrochloric acid at the cold:

$$PtCl_2 + 2HCl = H_2[PtCl_4], \qquad \mathbf{E} - H_2[PtCl_4].$$

Rapid uncontrolled addition of ammonia to a $H_2[PtCl_4]$ solution leads to the obtaining of the so-called "Peyrone's salt" is formed – *cis*-$Pt(NH_3)_2Cl_2$, which isomerized to "chloride of the second Reise's base" under heating – *trans*-$Pt(NH_3)_2Cl_2$:

$$H_2[PtCl_4] + 4NH_3 = Pt(NH_3)_2Cl_2 + 2NH_4Cl, \ \mathbf{F} - Pt(NH_3)_2Cl_2.$$

Slow addition of ammonia to the $H_2[PtCl_4]$ solution leads to the formation of another compound that has a brutto formula the same as **F**, but a different structure:

$$2H_2[PtCl_4] + 8NH_3 = [Pt(NH_3)_4][PtCl_4] + 4NH_4Cl, \ \mathbf{G} - [Pt(NH_3)_4][PtCl_4].$$

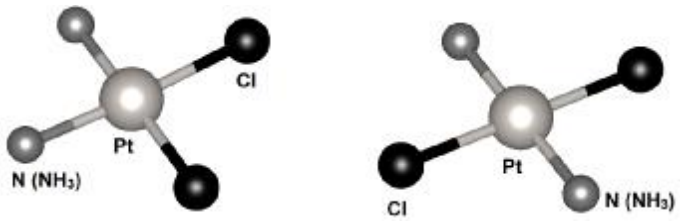
Formally, this reaction can be represented as the sequential formation of $[Pt(NH_3)_4]^{2+}$ complex particles in a solution, which form **G** with the initial chloride complex (0.7 points for each compound and reaction, 4.9 points in total):

$$H_2[PtCl_4] + 6NH_3 = [Pt(NH_3)_4]Cl_2 + 2NH_4Cl$$

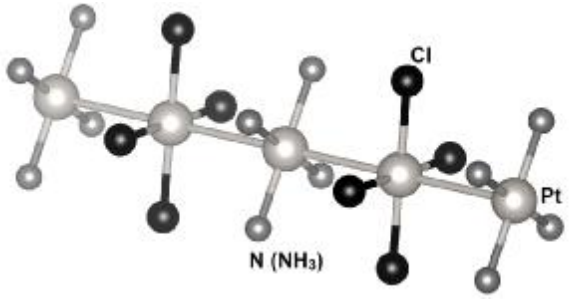
$$H_2[PtCl_4] + [Pt(NH_3)_4]Cl_2 = [Pt(NH_3)_4][PtCl_4] + 2HCl$$

or $$(NH_4)_2[PtCl_4] + [Pt(NH_3)_4]Cl_2 = [Pt(NH_3)_4][PtCl_4] + 2NH_4Cl$$

4. $Pt(NH_3)_2Cl_2$ has a square structure and 2 geometric isomers (*cis*- and *trans*-) (0.7 pints for each structure, 1.4 points in total):



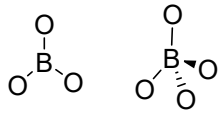
5. The squares of the $[Pt(NH_3)_4]^{2+}$ complex cation and the $[PtCl_4]^{2-}$ complex anion alternate sequentially in the $[Pt(NH_3)_4][PtCl_4]$ crystal structure. The separation of ligands – ammonia and chloride ion – is also consistent with a formal 2-fold increase in a molecular weight in comparison with cis-trans isomers. Sometimes, compounds such as $[Pt(NH_3)_4][PtCl_4]$ are called an *inorganic polymer* due to the fact that platinum atoms form an endless chain (0.5 points):



6. The trivial name of $[Pt(NH_3)_4][PtCl_4]$ is a "Magnus salt" by the name of its discoverer (0.5 points).

Problem 2 (author Khvalyuk V.N.)

1. Boron atom in BO_3 group exists in sp^2-hybrid state and therefore this fragment is planar triangle (all atoms are in one plane). In group BO_4 boron atom exists in sp^3-hybrid state and therefore this fragment is tetrahedral (oxygen atoms lie in tetrahedron vertices, boron atom lies in a center of tetrahedron) (0.5 points for each fragment, 1 point in total).



2. The synthetic reaction is not redox, therefore taking into account reagents the composition of product (substance **X**) can be written as formula $(aLi_2O \cdot bB_2O_3 \cdot cH_2O)_n$.

In synthetic procedure it is said the mother liquor was stayed therefore water was in excess. The final product **X** represents the salt of weak acid (polyborate anion **A**). In such conditions for synthesis the excess of alkali should be taken to suppress hydrolysis processes. Only boric acid was taken in stoichiometric quantity (1 point).

3. Under calculation we should base that boric acid is in stoichiometric quantity.

Including losses it was formed $\frac{2.103}{0.820} = 2.565$ g of salt **X**.

$M(H_3BO_3) = 61.83$ g/mol. $M(B_2O_3) = 69.62$ g/mol. $M(Li_2O) = 29.88$ g/mol.
$M(H_2O) = 18.02$ g/mol. $M(Li) = 6.94$ g/mol.

For synthesis it was taken $\frac{3.092}{61.83} = 0.0500$ mol H_3BO_3, which corresponds to 0.0250 mol or $0.0250 \cdot 69.62 = 1.741$ g B_2O_3.

The mass of lithium in obtained salt is equal to $0.0677 \cdot 2.565 = 0.1737$ g, which corresponds to $\frac{0.1737}{2 \cdot 6.94} = 0.0125$ mol or $0.0125 \cdot 29.88 = 0.3735$ g Li_2O.

The mass of water in obtained salt is equal to $(2.565 - 1.741 - 0.3735) = 0.4505$ g, which corresponds to $\frac{0.4505}{18.02} = 0.0250$ mol H_2O.

The simplest formula of **X** is $(Li_2O)_{0.0125}\cdot(B_2O_3)_{0.0250}\cdot(H_2O)_{0.0250}$ or $Li_2O\cdot2B_2O_3\cdot2H_2O$.

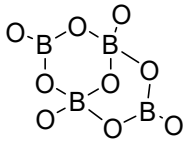
From condition the fragment **C** contains 2 groups BO_3 and 2 groups BO_4, i.e. 4 boron atoms, respectively the cluster **B** contains 8 boron atoms, therefore, the anion **A** includes 16 boron atoms. Since the simplest formula **X** contains only 4 boron atoms, the proper formula is $(Li_2O\cdot2B_2O_3\cdot2H_2O)_4$ or $4Li_2O\cdot8B_2O_3\cdot8H_2O$.

One OH-group is in each fragment **C**, two such groups are in the cluster **B**, therefore, four such groups are in anion **A**. So four hydrogen atoms (it is two water molecules) includes in anion **A**. The number of water molecules is equal to (8 – 2) = 6. Then the formula **X** is $Li_8[B_{16}O_{30}H_4]\cdot6H_2O$ or $Li_8[B_{16}O_{26}(OH)_4]\cdot6H_2O$, and formula of anion **A** is $[B_{16}O_{26}(OH)_4]^{8-}$ (2 points for **X** and 1 point for **A**, 3 points in total)

4. The synthetic reaction equation for **X** (1 балл):

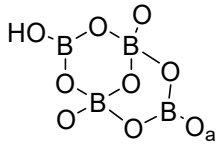
$$8LiOH\cdot H_2O + 16H_3BO_3 = Li_8[B_{16}O_{26}(OH)_4]\cdot6H_2O + 28H_2O$$

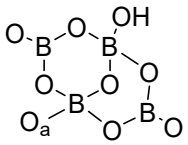
5. The formation of strong bonds B–O–B is very characteristic of boron, so each of six-membered cycles in fragment **C** should contain on three boron atoms. Given that, by condition two boron atoms must be common, the number of boron atoms in two cycles of fragment **C** must be equal to 4. By condition each fragment **C** must contain two groups BO_3 and two groups BO_4. We conclude to the following common structure for two fragments **C**:



The difference between the two fragments **C** including in cluster **B** lies in the position of protonated oxygen. In one group it places near boron atom in sp^3-hybrid state (BO_4 group), in second one it places near boron atom in sp^2-hybrid state (BO_3 group).

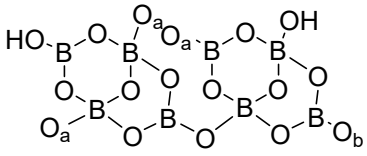
Two fragments **C** have the following structures:





The common oxygen atom (for groups BO_3 and BO_4 from different fragments **C**) is noted as O_a. Both fragments connected through atom O_a (1.5 points for each fragment **C**, 3 points in total).

6. In cluster **B** the fragments **C** linked through the common oxygen atom. The cluster **B** has the following structure:



The common for fragments **B** oxygen atom is noted as O_b. Both fragments **B** are bonded through this atom O_b. Each fragment **B** contains three oxygen atom (six such atoms are in anion **A**), through which anions **A** connected each other (such atoms are noted as O_a).

The molecular formula **B** is $B_8O_{13}(OH)_2^{4-}$. When drawing up the formula, it should be noted that three oxygen atoms (O_a) in each cluster **B** are common for neighboring anions (i.e. only 3 · 05 = 1.5 oxygen atoms belongs to each cluster **B**), linked to 2D-network and one oxygen atom (O_b) is common for two clusters **B** as part of anion **A** (only 0.5 oxygen atoms belongs to each cluster **B**). Totally (13+ 1.5 + 0.5) = 15 oxygen atoms belongs to drawn fragment **B** (2 point for the structure **B** and 2 pointsfor the molecular formula **B**, 4 points in total).

7. The first peak (at 160°C) corresponds to the temperature range from 35 to 245°C. $M(Li_8[B_{16}O_{26}(OH)_4]\cdot 6H_2O)$ = 820.6 g/mol.

In this range a weight loss 8.77% from mass is equal to 820.6 · 0.0877 = 71.97 g/mol, what corresponds to loss of 4 water molecule (18.02 · 4 = 72.08) theoretically.

It is reasonable to assume that in the second temperature range from 245 to 326°C (peak at 291°C) the remaining two water molecules are cleaved to form $Li_8[B_{16}O_{26}(OH)_4]$.

On the further heating in the range from 326 to 736°C (peak at 368°C) the complete dehydration takes place due to polycondensation of hydroxyl-groups to form water. The weight loss is equal to 820.6 · 0.0439 = 36.02 g/mol, which corresponds to loss of two water molecules. Then the composition of **Y** is $Li_8[B_{16}O_{28}]$ (1 point).

8. The reaction is carried out (1 point):

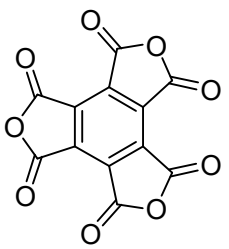
$$Li_8[B_{16}O_{26}(OH)_4]\cdot 2H_2O = Li_8[B_{16}O_{26}(OH)_4] + 2H_2O$$

Problem 3 (authors Rozantsev G.M., Shvartsman V.E.)

1. If **X3** is designated as $\mathbf{X}_aO_2$, and **X2** as $\mathbf{X}_bO_2$, then $A_X(a - b) = 24$. The atomic mass of the element **X**: $\mathbf{A_X} = 24 / (a - b)$. For b = 1 and a = 2, it is equal to $\mathbf{A_X}$ = 24 g/mol (Mg is not suitable, since element **X** has too many oxides). For b = 1 and a = 3, AX = 12 g/mol. (0.5 point). So, element **X** is carbon; then oxides: **X2** – CO_2; **X3** – C_3O_2; **X5** – C_5O_2 ($M_{C5O2} - M_{C3O2}$ = 24 g/mol); **X1** – CO (short bond). **X4** compound includes: $6C + 6CO_{1.5}$ and its formula $C_{12}O_9$ (2.5 points, 3 points in total).

2. Considering the bond lengths given in the task – double C–C (0.128 nm) and triple and double C–O (0.113 and 0.117 nm), structural formulas can be represented as: C≡O; O=C=O; O=C=C=C=O; O=C=C=C=C=C=O (1.5 points).

In the case of $C_{12}O_9$, there are one-and-a-half (0.139 nm) C–C bonds in the cycle and single (0.149 nm) between the cycle and $CO_{1.5}$ with double C-O bonds (0.119 nm) and single (0.140 nm) (1.5 oxygens in $CO_{1.5}$ group) (0.5 points, 2 points in total)



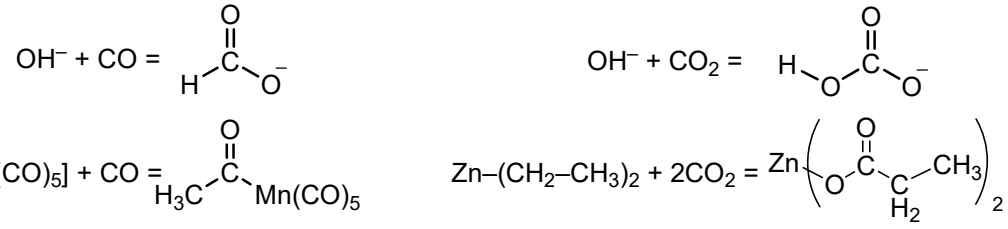
$C_{12}O_9$

3. In solution of CO_2 in water, there are several equilibria, two of which are:

$CO_2 + H_2O = H_2CO_3$ with constant $K = [H_2CO_3] / [CO_2] = 1.67\cdot10^{-3}$ and $H_2CO_3 = H^+ + HCO_3^-$ with $K_1 = [H^+][HCO_3^-] / ([H_2CO_3] + [CO_2]) = 4.45\cdot10^{-7}$ ($K_a = [H^+]\,[HCO_3^-] / [H_2CO_3]$) (0.5 points).

From the first equilibrium, the concentration $[CO_2] = [H_2CO_3] / K$ is substituted into the expression for K_1: $K_1 = [H^+]\,[HCO_3^-] / ([H_2CO_3] + [H_2CO_3]/ K)$. Then $K_1 = K\,[H^+]\,[HCO_3^-] / \{[H_2CO_3](1 + K)\}$ and, finally, $K_1 = K_aK / (1 + K)$ (1 point). Hence $K_a = K_1(1 + K) / K$, which allows to calculate $K_a = 4.45\cdot10^{-7}(1 + 1.67\cdot10^{-3}) / 1.67\cdot10^{-3} = 2.67\cdot10^{-4}$ (obtained value corresponds to Pauling's prediction for $(OH)_2ЭO$) (0.5 points, 2 points in total).

4. (0.5 point for each reaction, 2 points in total)

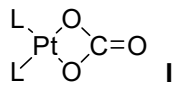


5. One phosphine was substituted by CO_n, which is accompanied by the release of 1/3 of phosphine. Then **I** is $[Pt\{P(C_6H_5)_3\}_2CO_n]$, and 16n / (731 + 16n) = 0.0612; n = 3. That is, the ligand in **I** is CO_3^{2-}, not CO_2 (1.5 points in total).

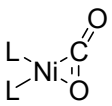
6. Let's represent solvated complex **II** in the form of the following formula: $[Ni\{P(C_6H_{11})_3\}_n(CO_2)_m]\cdot aC_6H_5CH_3$. Using mass fractions from the condition, we obtain two equations: 92a / (280n + 44m + 92a + 59) = 0.0943 and 32m / (280n + 44m + 92a + 59) = 0.0437. With the same denominator: 92a / 0.0943 = 32m / 0.0437, and the ratio m : a = 1 : 0.75. We substitute m = 1 and a = 0.75 into one of the equations and we obtain that n = 2. In this case, complex **II** has the simplest formula $[Ni\{P(C_6H_{11})_3\}_2(CO_2)]\cdot0.75C_6H_5CH_3$ (1.5 points).

For the complex **III** M = m / ν= 6.143 / $4.445\cdot10^{-3}$ = 1382 g/mol, what indicates its binuclear structure. Then taking into account the release of carbon monoxide and formic acid we can write the equation: $2ReC_{31}H_{27}P_2O_5 = CO + HCOOH + Re_2C_{60}P_4O_7H_{52}$ and formula **III** is $[\{(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2\}(CO)_2ReCO_2Re(CO)_3\{(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2\}]$ (1.5 points)

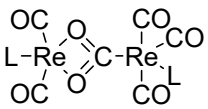
7. Using the X-ray diffraction data shown in the table one can depict the structural formulas of the synthesized complexes (L – alkylphosphine) (0.5 points for each structure, 1.5 points in total):



I



II



III

Section II. Analytical chemistry

Problem 1 (author Beklemishev M.K.)

1. 5.00 mL of a 0.0375 M solution of BzHgCl corresponds to 0.1875 mmol, while 1.80 mL of 0.104 M of hydrocarbonate is 0.1872 mmol, that is, one proton is titrated (2 points):

$$4\text{-HOOC–}C_6H_4\text{–HgCl} + NaHCO_3 = NaOOC\text{–}C_6H_4\text{–HgCl} + H_2O + CO_2$$

б) The reaction with cysteine: 0.375 mmol is twice the amount of BzHgCl. However, cysteine $^-OOC\text{–}CH(NH_3^+)\text{–}CH_2\text{–SH}$ itself has two protons, both with pKa ≈ 10, and therefore they are not titrated with hydrocarbonate at pH 7–8. However, the titration with hydrocarbonate yielded $3.6 \cdot 0.104 = 0.374$ mmol of protons, or twice as much as BzHgCl. So, there were two protons in the reaction products of BzHgCl with cysteine: one of the carboxyl group of the starting reagent and one of the released hydrochloric acid:

$$^-OOC\text{–}CH(NH_3^+)\text{–}CH_2\text{–SH} + Cl\text{–Hg–}C_6H_4\text{–COOH} =$$
$$^-OOC\text{–}CH(NH_3^+)\text{–}CH_2\text{–S–Hg–}C_6H_4\text{–COO}\mathbf{H} + \mathbf{H}Cl \text{ (2 points)}$$

2. a) The amount of iodine was $5 \cdot 0.05 = 0.25$ mmol, the amount of thiosulfate spent was 0.1 mmol, the reaction equation is $I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-}$, that is, the amount of iodine titrated was 0.05 mmol, or the amount of iodine reacted was 0.25 – 0.05 = 0.2 mmol. The aliquot contained 1/10 of the sample weight, or 74 mg of BzHgCl, or 0.207 mmol (the molar weight is 357 g/mol). Probably, the interaction of BzHgCl with iodine occurs in a 1:1 ratio, and this should be a redox reaction (and not, for example, chloride substitution) (3 points):

$$^-OOC\text{–}C_6H_4\text{–HgCl} + I_2 + OH^- =$$
$$^-OOC\text{–}C_6H_4\text{–OH} + Cl^- + HgI_2 \text{ (in the presence of } I^-, HgI_4^{2-} \text{ is formed)}$$

б) The theoretical mass of BzHgCl (in an amount of 0.200 mmol) is 71 mg, that is, the preparation could contain 3 mg = 4% of impurities (2 points).

3. We assume that after the reaction of the products with sodium sulfite, the SH-groups arose again. This could happen by reducing the –S–S– disulfide groups:

$$SO_3^{2-} + RSSR + H_2O = SO_4^{2-} + 2RSH \text{ (2 points)}$$

Oxygen-containing sulfur compounds cannot be reduced by this method. So, one of the reaction products with bromate is disulfide (2 points):

$$6RSH + BrO_3^- = 3RSSR + Br^- + 3H_2O$$

In this case, 0.167 mol of bromate will be required per 1 mol of mercapto groups, but we have consumed more of it, that is, there are higher oxidation products. However, we know the number of mercapto groups formed after reduction with sulfite (the amount of BzHgCl spent is 0.9 mmol, and it interacts with mercapto groups in a 1:1 stoichiometry, as it can be seen from the previous paragraphs); according to the foregoing, it is equal to the amount of the initial mercapto groups converted to disulfide. Then 1.00 – 0.90 = 0.10 mmol have passed into the form of another, more oxidized product. Suppose it is sulfinate RSO_2H, then the reaction equation with bromate is:

$$3RSH + 2BrO_3^- = 3RSO_2H + 2Br^-$$

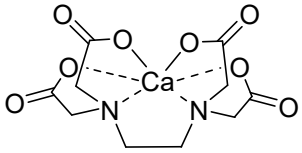
In this case, 0.1 mmol of RSH will require 0.067 mmol of bromate, which does not meet the condition (an oxidation of 0.9 mmol of RSH to ½RSSR required 0.9 / 6 = 0.15 mmol of bromate, and totally 0.25 mmol of it was consumed, so, 0.1 mmol of bromate remains to be allocated). Suppose that the product is sulfonic acid RSO_3H, then we have the following process (2 points):

$$RSH + BrO_3^- = RSO_3H + Br^-$$

In this case, 0.1 mmol of RSH requires 0.1 mmol of bromate, which meets the condition. On the whole, we have 0.1 mmol of sulfonic acid RSO_3H and 0.45 mmol of disulfide RSSR.

Problem 2 (author Kuzin S.V.)

1. а) EDTA anion serves as a hexadentate ligand (1 point):



б) Averaged EDTA volume required for the titration: $V_{av} = \frac{V_1 + V_2 + V_3}{3} = \frac{23.10}{3} = 7.70$ mL. Calcium concentration is then as follows (2 points): $c(\text{Ca}) = \frac{m(\text{Ca})}{V_a} = \frac{V_{av} \cdot C(\text{EDTA}) \cdot M(\text{Ca})}{V_a} =$ 63.2 mg/L

в) The electroneutrality principle requires that all positive charges of cations would balance the negative ones of anions. Thus,

$$2[Ca^{2+}] + [\mathbf{X}^+] = [Cl^-] + [HCO_3^-]$$

$$2 \cdot \frac{63.2}{40} + \frac{14.2}{M(\mathbf{X})} = \frac{84.1}{35.5} + \frac{68.8}{61}$$

Therefore, M(**X**) = 23 g/mol, **X** = Na (2 points, answer without calculations is not considered).

2. а) $Ca^{2+} + 2F^- = CaF_2$, $Ag^+ + Cl^- = AgCl$, $2Ag^+ + CO_3^{2-} = Ag_2CO_3$

$m(CaF_2) = 0.1 \cdot \frac{63.2}{40} \cdot 78 = 12.3$ mg

$m(AgCl) = 0.1 \cdot \frac{94.1}{35.5} \cdot 143.3 = 38.0$ mg

$m(Ag_2CO_3) = 0.1 \cdot \frac{68.8}{61} \cdot 275.6 = 31.1$ mg

Total weight of the precipitate is 81.4 mg (0.5 points for each reaction, 2 points for the weight of the precipitate. 3.5 points totally)

б) Silver carbonate and chloride will dissolve ($AgCl_2^-$ complex will be formed). The only residue is CaF_2 (dissolves in concentrated sulfuric acid). The answer is "–69.1 mg" (1 point, 0.5 point if without the sign)

3. At pH 8.0:

$[HCO_3^-] = 1.13\cdot10^{-3}$ M

$[CO_3^{2-}] = \frac{K_a(HCO_3^-)\,HCO_3^-]}{[H^+]} = 5.31\cdot10^{-6}$ M, $[H_2CO_3] = \frac{[H^+][HCO_3^-]}{K_a(H_2CO_3)} = 2.83\cdot10^{-5}$ M

$[Ca^{2+}] = 1.58\cdot10^{-3}$ M

Assume that after precipitation calcium concentration decreased by x M. Then the *overall* carbonate concentration decreased by the same value.

$$c(CO_3^{2-}) = 1.13\cdot10^{-3} + 5.29\cdot10^{-6} + 2.83\cdot10^{-5} - x = 1.16\cdot10^{-3} - x$$

Herewith carbonate concentration $[CO_3^{2-}]' = \alpha(CO_3^{2-})c(CO_3^{2-})$

$[Ca^{2+}]'[CO_3^{2-}]' = K_S$ (3 points for the weight of the precipitate)

$$\left(1.58\cdot10^{-3} - x\right)\left[\frac{K_{a1}K_{a2}}{K_{a1}K_{a2} + K_{a1}[H^+] + [H^+]^2}\left(1.16\cdot10^{-3} - x\right)\right] = 4.76\cdot10^{-9}$$

$$\left(1.58\cdot10^{-3} - x\right)\left(1.16\cdot10^{-3} - x\right) = 1.32\cdot10^{-6}$$

$$x = 2.02\cdot10^{-4} \text{ M}$$

4. The electroneutrality equation for the precipitate $Ca_{10-x}(HPO_4)_y(PO_4)_{6-x}(OH)_{2-y}$

$$2(10 - x) = 2y + 3(6 - x) + (2 - y)$$

After simplifying, one receives: $x = y$. Then, the ratio is $Ca{:}P = \frac{10-x}{6} = 1.6 \Rightarrow x = 0.4$

$$9.6Ca^{2+} + 6PO_4^{3-} + H_2O = Ca_{9.6}(HPO_4)_{0.4}(PO_4)_{5.6}(OH)_{1.6}\downarrow + 1.2H^+$$

As stated in the problem, the amount of Ca in 1 m^3 will decrease by 1.58 – 0.158 = 1.422 mol

m(precipitate) = $\frac{1.422}{9.6} \cdot 310 = 145.40$ g (1 point for the equation, 1.5 points for the weight of the precipitate, totally 2.5 points)

Problem 3 (author Shved A.M.)

1. The solubility of aspirin in dichloromethane is much higher than in water, that is confirmed by a high distribution constant. However, when using the alkaline solution aspirin is deprotonated to form a salt – ionic compound, which is soluble in water. This results in the quantitative extraction of aspirin from the organic phase (1 point in total).

2. Let us denote aspirin, which has acidic properties, as ***HA***. During the extraction the equilibrium transfer of aspirin from the organic phase to the aqueous phase occurs, that can be described by the following equilibrium:

$$\boldsymbol{HA}_{(aq)} \rightleftarrows \boldsymbol{HA}_{(org)} \qquad K_D = \frac{[\boldsymbol{HA}]_{org}}{[\boldsymbol{HA}]_{aq}}$$

In its turn, the carboxylic group of aspirin dissociates in aqueous phase forming a salt, that is described by acidity constant:

$$\boldsymbol{HA}_{(aq)} \rightleftarrows \mathrm{H}^+ + \boldsymbol{A}^- \qquad K_a = \frac{[H^+][\boldsymbol{A}^-]}{[\boldsymbol{HA}]_{aq}}$$

The recovery of aspirin is determined as the ratio between the quantity of acid extracted from organic to aqueous phase and initial total quantity of the acid:

$$R = \frac{n(\boldsymbol{HA})_{aq}}{n(\boldsymbol{HA})_0} = \frac{([\boldsymbol{HA}]_{aq} + [\boldsymbol{A}^-])V_{aq}}{c(\boldsymbol{HA})_0 V_{org}} = \frac{([\boldsymbol{HA}]_{aq} + [\boldsymbol{A}^-])V_{aq}}{[\boldsymbol{HA}]_{org} V_{org} + ([\boldsymbol{HA}]_{aq} + [\boldsymbol{A}^-])V_{aq}}$$

Using the expressions for distribution and acidity constants we get:

$$R = \frac{[\boldsymbol{HA}]_{aq}\left(1 + \frac{K_a}{[H^+]}\right)V_{aq}}{[\boldsymbol{HA}]_{aq} K_D V_{org} + [\boldsymbol{HA}]_{aq}\left(1 + \frac{K_a}{[H^+]}\right)V_{aq}} = \frac{\left(1 + \frac{K_a}{[H^+]}\right)V_{aq}}{K_D V_{org} + \left(1 + \frac{K_a}{[H^+]}\right)V_{aq}}$$

By the extraction of aspirin from 100 mL solution in dichloromethane with a buffer solution at pH 7 the recovery is (3 points in total):

$$R = \frac{\left(1 + \frac{10^{-3.5}}{10^{-7}}\right)\cdot 40}{10^5 \cdot 100 + \left(1 + \frac{10^{-3.5}}{10^{-7}}\right)\cdot 40} = 0.0125\ (1.25\%)$$

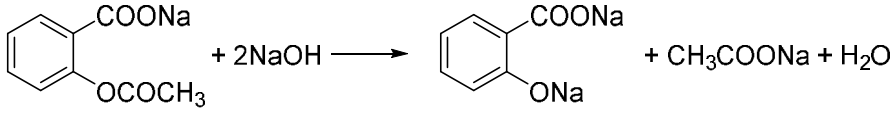
3. From the expression for the recovery R we can find the concentration of H^+ ions:

$$[H^+] = \frac{K_a}{K_D \frac{R}{1-R}\frac{V_{org}}{V_{aq}} - 1}$$

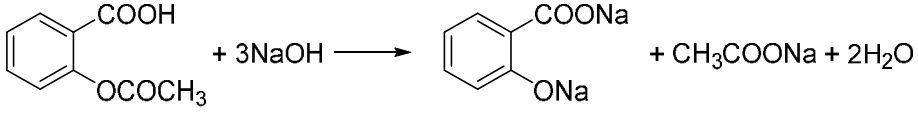
Then the pH of aqueous phase for $R = 0.99$ have to be at least (2 points in total):

$$\mathrm{pH} = -\lg[H^+] = -\lg\left(\frac{K_a}{K_D \frac{R}{1-R}\frac{V_{org}}{V_{aq}} - 1}\right) = -\lg\left(\frac{10^{-3.5}}{10^5 \cdot \frac{0.99}{1-0.99}\cdot\frac{100}{40} - 1}\right) = 10.89$$

4. During the boiling of aspirin solution in the excess of alkali, or more correctly, its salt, the hydrolysis of the ester group occurs:

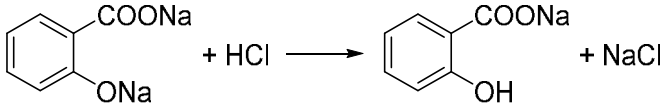


Therefore, the summarised reaction of aspirin with alkali considering the hydrolysis (1 point for hydrolysis equation or summarised reaction):



During the titration with hydrochloric acid in the presence of phenolphthalein the neutralisation reaction of alkali left in the solution and protonation on phenolate ion occur (1 point for each reaction, total 3 points for the question):

$$\mathrm{NaOH + HCl = NaCl + H_2O}$$



5. The initial quantity of sodium hydroxide:

$$c(NaOH)\cdot V(NaOH) = 3n(\mathbf{A}) + n(NaOH)_{left}$$

For titration of the total volume (100 mL) $100/10.00 = 10$ times more HCl solution would be used compared to the aliquot (10.00 mL), then

$$10\cdot c(HCl)\cdot V(HCl) = n(\mathbf{A}) + n(NaOH)_{left}$$

$$c(NaOH)\cdot V(NaOH) = 2n(\mathbf{A}) + 10\cdot c(HCl)\cdot V(HCl)$$

$$n(\mathbf{A}) = \frac{1}{2}c(NaOH)\cdot V(NaOH) - 5\cdot c(HCl)\cdot V(HCl) = \frac{1}{2}\cdot 0.100\cdot 40 - 5\cdot 0.020\cdot 7.80 = 1.22 \text{ (mmol)}$$

The mass fraction of aspirin in the sample of **APC** tablet (2 points):

$$w(\mathbf{A}) = \frac{n(\mathbf{A})\cdot M(\mathbf{A})}{m(\mathbf{APC})} = \frac{1.22\cdot 180}{500} = 0.439\ (43.9\%)$$

6. Spectrophotometric method of determination of mixtures composition is based on the additivity of components absorbance, i.e.:

$$\begin{cases} A_{250} = \varepsilon_{250}(\mathbf{P})c(\mathbf{P})l + \varepsilon_{250}(\mathbf{C})c(\mathbf{C})l \\ A_{275} = \varepsilon_{275}(\mathbf{P})c(\mathbf{P})l + \varepsilon_{275}(\mathbf{C})c(\mathbf{C})l \end{cases}$$

Solving the system of equations, we get the expressions for concentrations of phenacetin (**P**) and caffeine (**C**) in analysed solution:

$$c(\mathbf{P}) = \frac{A_{250}\varepsilon_{275}(\mathbf{C}) - A_{275}\varepsilon_{250}(\mathbf{C})}{\varepsilon_{250}(\mathbf{P})\varepsilon_{275}(\mathbf{C})l - \varepsilon_{275}(\mathbf{P})\varepsilon_{250}(\mathbf{C})l} = \frac{0.465\cdot 9409 - 0.160\cdot 2541}{12566\cdot 9409\cdot 1 - 2846\cdot 2541\cdot 1} = 3.58\cdot 10^{-5}\,(\text{M})$$

$$c(\mathbf{C}) = \frac{A_{250}\varepsilon_{275}(\mathbf{P}) - A_{275}\varepsilon_{250}(\mathbf{P})}{\varepsilon_{250}(\mathbf{C})\varepsilon_{275}(\mathbf{P})l - \varepsilon_{275}(\mathbf{C})\varepsilon_{250}(\mathbf{P})l} = \frac{0.465\cdot 2846 - 0.160\cdot 12566}{2541\cdot 2846\cdot 1 - 9409\cdot 12566\cdot 1} = 6.19\cdot 10^{-6}\,(\text{M})$$

As from the initial solution 1.00 mL aliquot was taken and diluted to 100 mL, the quantities of phenacetin and caffeine in the solution after extraction (250 mL) were:

$$n(\mathbf{P}) = 100\cdot c(\mathbf{P})\cdot 250 = 0.895 \text{ (ммоль)}$$

$$n(\mathbf{C}) = 100\cdot c(\mathbf{C})\cdot 250 = 0.155 \text{ (ммоль)}$$

Then the mass fractions of compounds in the sample of a tablet are (2 points each, total 4 points for the question):

$$w(\mathbf{P}) = \frac{n(\mathbf{P})\cdot M(\mathbf{P})}{m(\mathbf{APC})} = \frac{0.895\cdot 179}{500} = 0.320\ (32.0\%)$$

$$w(\mathbf{C}) = \frac{n(\mathbf{C})\cdot M(\mathbf{C})}{m(\mathbf{APC})} = \frac{0.155\cdot 194}{500} = 0.060\ (6.0\%)$$

Section III. Life sciences and polymers

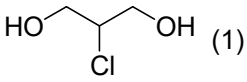
Problem 1 (author Garifullin B.N.)

1. The molar ratio of C to H for **A** – **C** is:

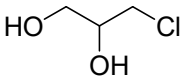
$$n(\mathrm{C}):n(\mathrm{H}) = \frac{\omega(\mathrm{C})}{A_r(\mathrm{C})} : \frac{\omega(\mathrm{H})}{A_r(\mathrm{H})} = 3:7$$

Triacylglycerols are the major components of plant oils. Taking also into account the number of C and H atoms, one can suppose that **A** – **C** are glycerol derivatives. The molar mass left over for the other elements equals 67.45 g/mol. Varying the number of oxygen atoms, one finds that the combination of two O and one Cl atoms is the only possible variant. Thus, the molecular formula of **A** – **C** is $C_3H_7ClO_2$ (0.5 points for the calculation, 0.5 points for the formula, 1 point in total).

2. Two structural isomers correspond to the above molecular formula:

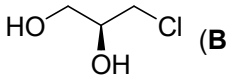


(1)

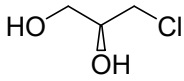


(2)

There are no optical isomers possible for the compound (1), thus A is 2-monochloropropane-1,3-diol. Any ester of 3-monochloropropane-1,2-diol is present as a racemate in plant oil (the molar ratio of the components of 1:1), thus the hereunder structures are ascribed to **B** and **C** (exact attribution impossible) (1 point for each structure, 3 points in total, –0.5 points penalty for the exact attribution of **B** and **C**):



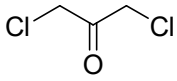
(**B** or **C**)



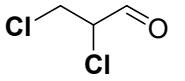
(**B** or **C**)

3. **X** undoubtedly contains chlorine, since its content in native plant oils is approaching zero. Actually, substitution of a hydroxyl group by the chlorine atom occurs upon the formation of esters of **A** – **C**. With due account for the process conditions, **X** is deciphered as hydrogen chloride (0.5 points).

4. **D** and **E** have a common formula of $C_3H_xCl_yO_z$ (note that these are volatile substances). Taking into account that the number of C atoms equals 3, whereas $x + y \leq 8$ ($x + y$ is an even number), one finds that there are two progressions possible: 1, 3, 5, 7 and 1, 2, 3, 4. The former variant is not reasonable from the point of view of chemistry, and the latter one can be rewritten as $C_3H_4Cl_2O$ with two possible structures (1 point for each structure, 2 points in total, –0.5 points penalty in case of no calculations shown):

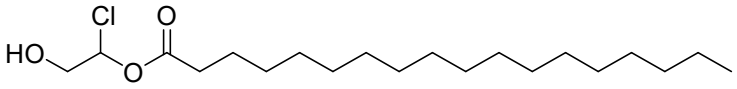


(**D**)



(**E**)

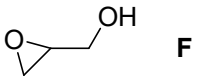
5. **Y** can be either mono- or diester with two corresponding O to C ratios of 3:21 and 4:28. 18 C atoms are left over for the fatty acid residue in the former case, which suggests stearic acid with the molecular formula of $C_{21}H_{41}ClO_3$ with due account for its saturation. 25 C atoms would be totally available for two residues of fatty acids in the latter case. If so, one of these would contain an odd number of C atoms, which does not meet the problem conditions. Thus, **Y** is the monoester of stearic acid with one corresponding structural isomer (1.5 points):



6. The empirical formula of **F** with oxygen as the third element is:

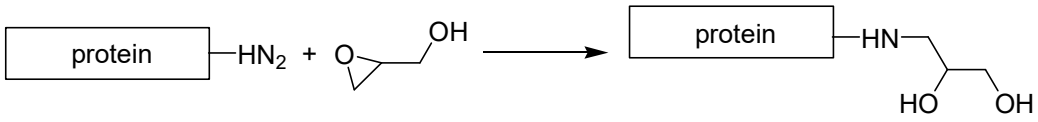
$$n(\mathrm{C}):n(\mathrm{H}):n(\mathrm{O}) = \frac{\omega(\mathrm{C})}{A_r(\mathrm{C})} : \frac{\omega(\mathrm{H})}{A_r(\mathrm{H})} : \frac{\omega(\mathrm{O})}{A_r(\mathrm{O})} = 3{:}6{:}2$$

Only one optically active compound, glycidol, corresponds to the formula (1 point):

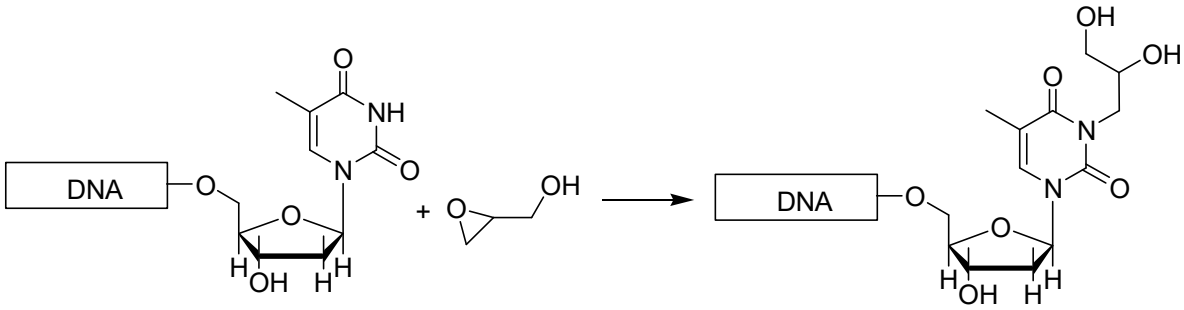


F

7. In the case of proteins, glycidol can interact with both free amino (in particular, *N*-terminal) and imine (e.g., those of proline) groups:



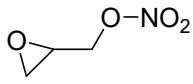
In nucleic acids, glycidol interacts with nitrogenous bases (1 point for each reaction scheme, 2 points in total):



8. The ratio of C to H molar fractions in **G** equals 3:5. Then (with the mass fraction of C higher than that of H):

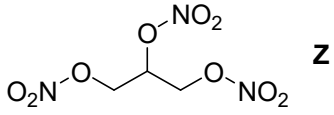
$$\cdot\, 5 = \frac{\omega(\mathrm{C}) - 26.03}{1.008} \cdot 3$$

ω(C) = 30.26%. 78 g/mol is left over for the rest elements in the empirical formula of **G**, which corresponds to four O and one N atoms (explaining the odd number of H atoms). Based on the structure of **F**, one can suppose that the empirical and molecular formulae of **G** coincide. Thus, the molecular formula of the ester of **G**:



G

G is formed as a metabolite of nitroglycerin **Z**, used as a drug to cure coronary heart disease (1 point for each structure, 2 points in total):

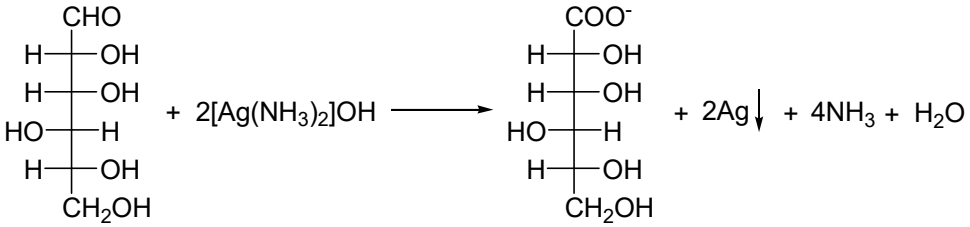


Z

9. Explosive decomposition of poly glycidyl nitrate (**H**) can lead to two obvious products with the molar mass of 44 – CO_2 and N_2O. The other two particles are less obvious. These are CH_2NO and C_2H_4O (0.5 point for each particle, 2 points in total).

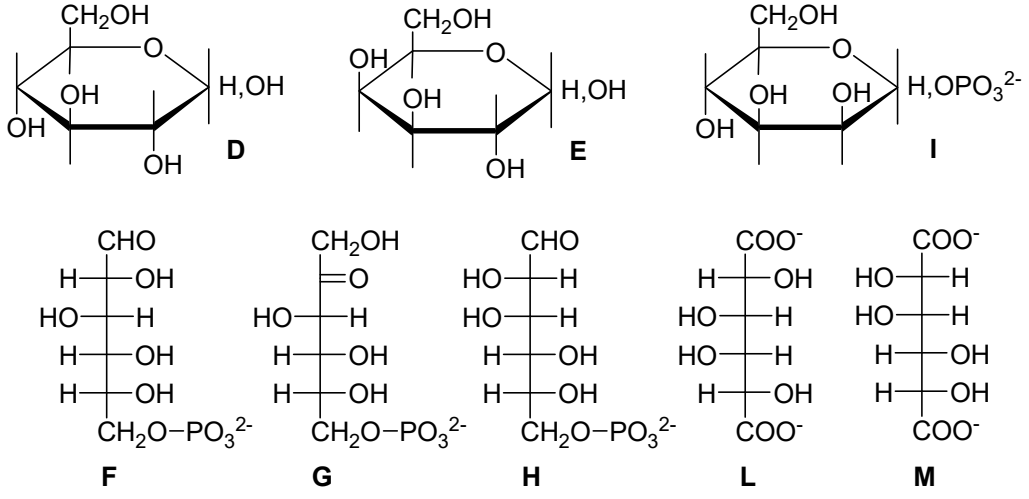
Problem 2 (author Gladilin A.K.)

1. (0.5 points)

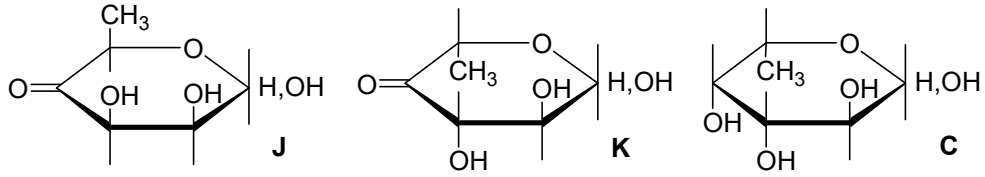


2. Large body of data given in the task allows following different strategies. One of possible variants is given below. **C** is a hexose. The transformation of **D** into GDP-**C** does not alter the number of carbon atoms in the carbohydrate moiety, thus **D** is also a hexose. **M** is a D-dicarboxylic acid with self-coinciding Fischer projection when rotated through 180°. D-Mannaric acid is the only possible variant. Then, **H** is *D*-mannose phosphate. There is no transfer of phosphorylated fragments of phosphate group on the way from **I** to GDP-**C**, whereas the carbohydrate residue is linked with the phosphate group via the first carbon atom in в GDP-**C.** Then, the phosphate group is also connected with the first carbon atom in **I**. The phosphate group is transferred only once within the pathway from **F** to **I**, thus it is definitely **H** to **I** step (the interconversion of aldoses and ketoses would have been impossible, if this reaction had happened earlier). Thus, **I** is *D*-mannose 1-phosphate. Since two other isomerization reactions involve the interconversion of aldoses and ketoses, **D** is glucose, **F** is *D*-glucose 6-phosphate, and **G** is *D*-fructose 6-phosphate. Such attribution is confirmed by the results of the Tollens' test.

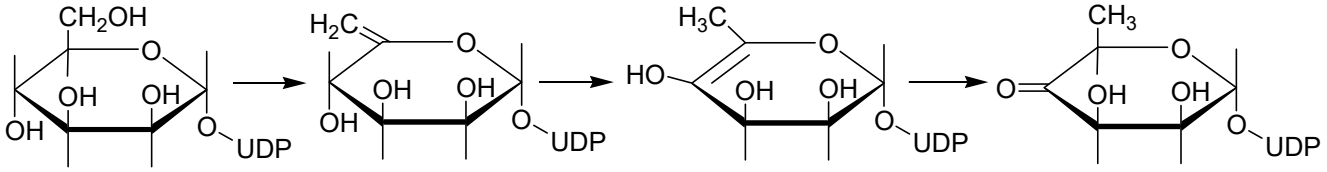
E is also classified as hexose based on the value of M(**B**) with an account taken of M(H_2O). Oxidation of **E**, which is a *D*-compound, with concentrated nitric acid leads to an optically inactive compound **L** with hydroxyl groups oriented both sides in its Fischer projection. Then, **L** is *D*-galactaric acid, and **E** is *D*-galactose (0.5 points for each compound, any correct representation of carbohydrates, carbohydrate moieties and derivatives accepted, identification of an exact anomer not graded, 4 points in total).



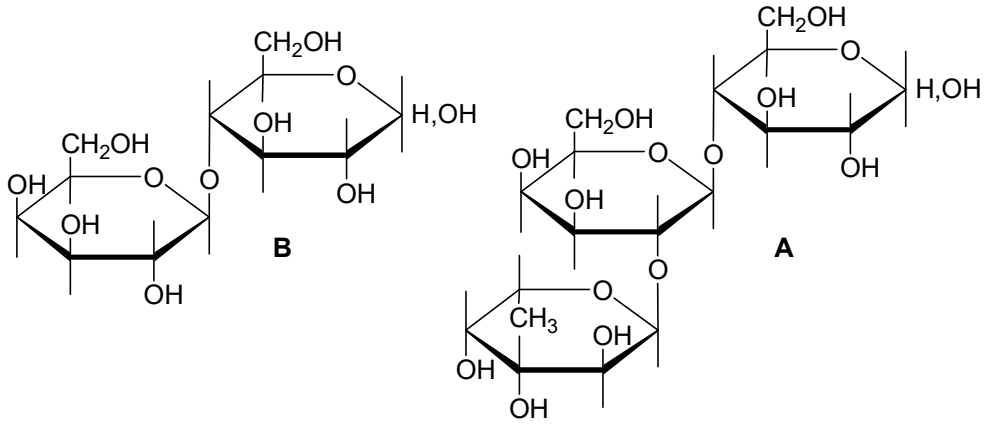
3. Formation of acetaldehyde as a result of oxidation of **C** with an excess of periodate strongly suggests the terminal CH_3-group, which can be found only in the 6th position, since the 1st one is modified with the GDP residue. If so, dehydration of **I** leads to GDP-4-keto-6-deoxy-*D*-mannose (**J**), which is further subjected to isomerization, which is neither interconversion of aldoses and ketoses, not transfer of phosphorylated fragments. This isomerization has a simultaneous effect on the 3rd and 5th carbon atoms. Alteration of absolute configuration of the mentioned above carbon atoms is the only reasonable variant from the biochemical point of view. Then, **K** is GDP-4-keto-6-deoxy-*L*-galactose. Reduction of the keto-group in the latter compound leads to GDP-*L*-fucose (**C**). Note that orientation of the OH-group at the 4th carbon atom is determined due to propinquity of **C, E**, and **L** (2 points for **C**, 1 point for each of **E** and **L**, 4 points in total).



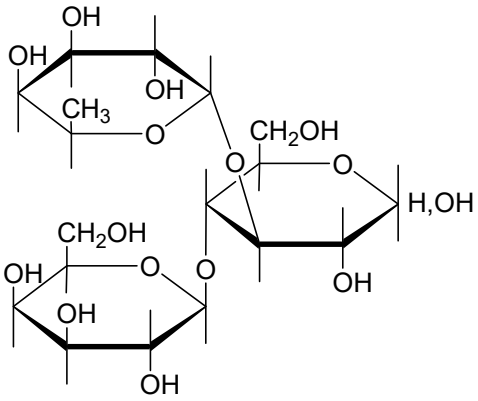
4. The reaction sequence is best deciphered starting from the end. Only the enol intermediate formed from mannose-en can give rise to the keto-compound (0.5 points for each step, 1.5 points in total).



5. Analysis of the results of methylation and subsequent hydrolysis suggests that the residue of **E** is located in the center of the trisaccharide, the residues of **D** and **E** are linked via 1,4-glycoside bond, whereas the first carbon atom of the residue of **C** is involved in the linkage with that of **E**. Then, **B** is *D*-lactose (or milk sugar, and **A** is 2-L-fucosyllactose (1 point for **B**, 2 points for **A**, 3 points in total).

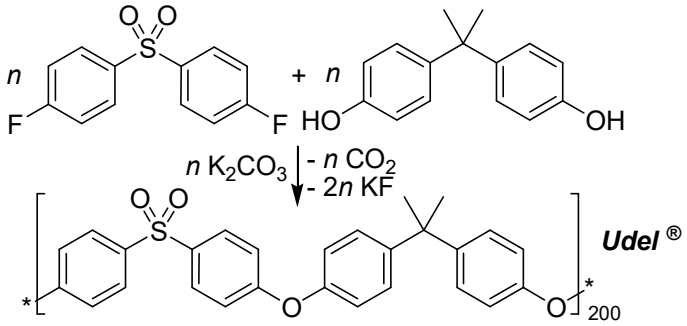


6. Comparison of hydrolysis products of **A** and **N** shows that the residue of **D** is the central unit in **N**. **D** is linked to **C** via the 3rd carbon atom. **N** is 3-L-fucosyllactose (2 points).



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

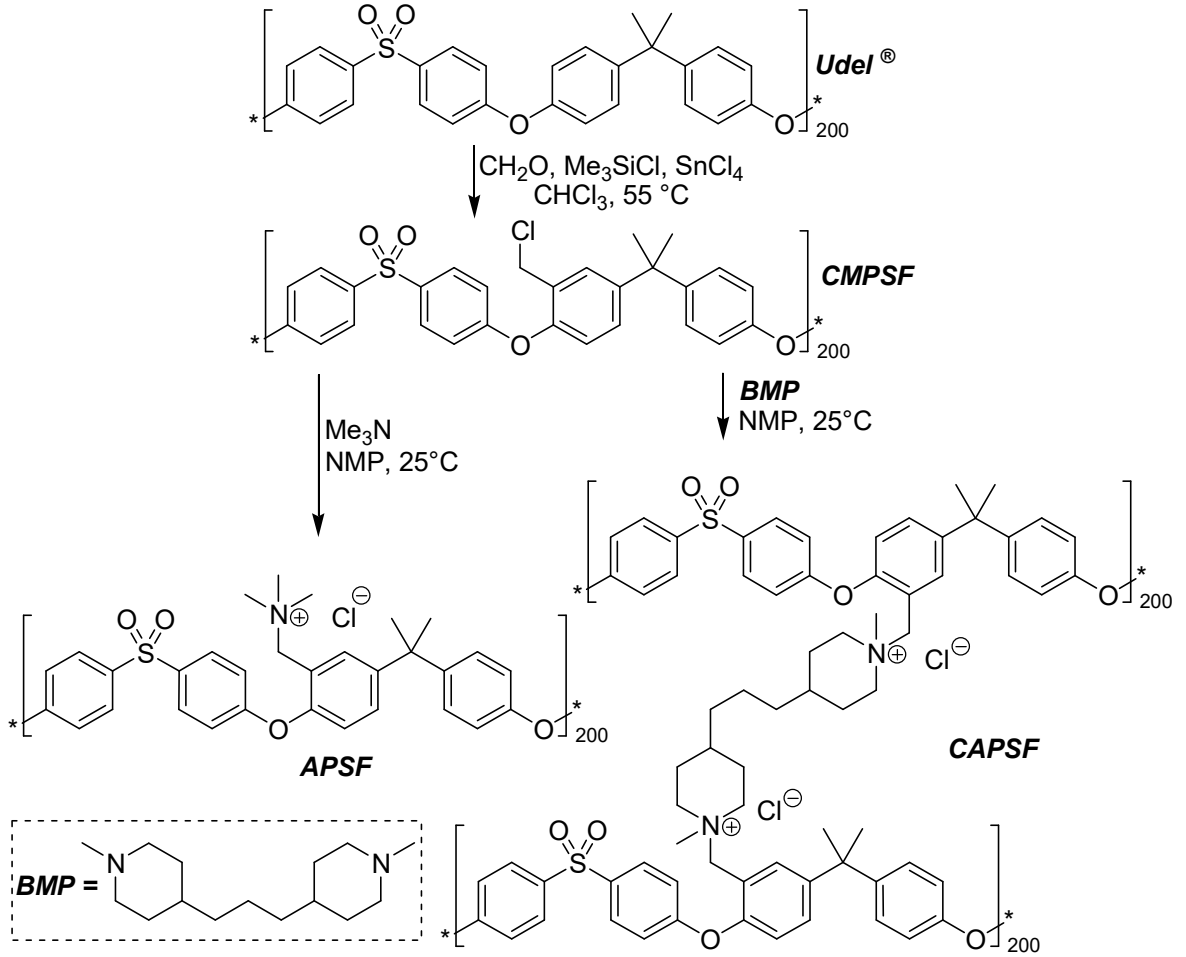
1. Synthesis of ***Udel***® (cf. Scheme 1) is based on the condensation between reactive fluorine and phenol groups. The degree of polymerization of ***Udel***® can be determined accounting for the potassium fluoride formed. The amounts of the starting monomers are of 50.85/254.25 = 0.200 and 45.66/228.29 = 0.202 mol, and that of potassium fluoride is of 23.18/58.1 = 0.3990 mol, or 99.75% of the theoretical amount. Hence, there is a pair of unreacted functional groups (which turn out to be terminal in the macromolecule) per 399 reacted pairs. In other words, each macromolecule contains 399 bonds formed due to condensation. Since a repeat unit of ***Udel***® contains two of such bonds, its degree of polymerization is 200 (199 is acceptable) (1 point for the structure, 1 point for the degree of polymerization, 2 points in total).



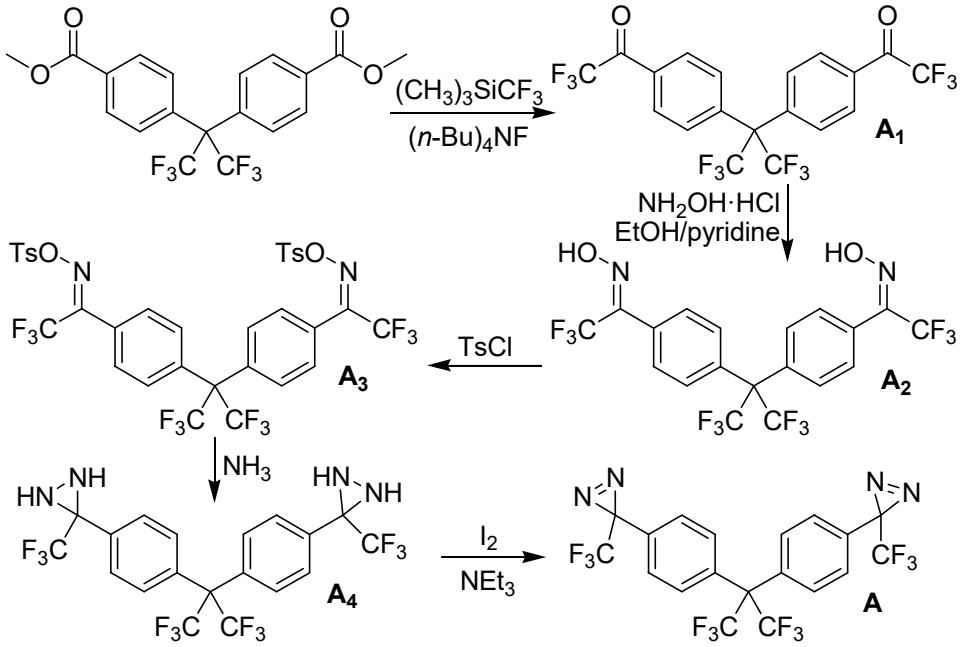
Scheme 1. Synthesis of ***Udel***®.

2. Since ***CMPSF*** interacts with tertiary amines, it contains alkylating groups. From the reaction conditions, it is clear that they have appeared due to chloromethylation. The repeat unit of ***Udel***® contains two equivalent aromatic rings prone to chloromethylation. The number of chloromethylated rings can be determined from the amount of paraform consumed in the reaction. The ***Udel***® sample contains 0.2 · 2 = 0.4 mol of the rings (cf. i. 1), whereas the amount of paraform is 6.0/30.03 = 0.2 mol, thus only one ring is involved in the reaction. Structures of ***CMPSF***, ***APSF***, and ***CAPSF*** are given in Scheme 2 (1 point for each structure, 3 points in total).

3. ***APSF*** and ***CAPSF*** are anionites (substances capable of exchanging their anions with those from the external medium). ***APSF*** is a linear polymer, whereas ***CAPSF*** is a crosslinked one (is characterized by an enhanced mechanical strength) (1 point for the completely correct assignment per each polymer, 2 points in total).



Scheme 2. Synthesis of ***APSF*** and ***CAPSF***.

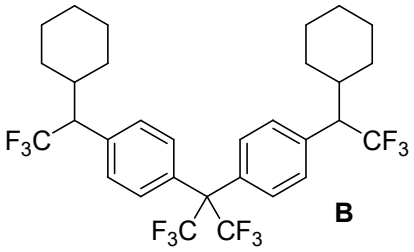


Scheme 3. Synthesis of crosslinker **A**.

4. The scheme of the chemical transformations suggests that $\mathbf{A_1}$ is a diketone, and the $\mathbf{A_1} \rightarrow \mathbf{A_2}$ stage corresponds to the formation of oxime. Then, the gross formula of $\mathbf{A_1}$ is $C_{19}H_8F_{12}O_2$, and the first stage in the scheme corresponds to formal substitution of OMe groups with CF_3 ones. Thus, $\mathbf{A_1}$ is a di(trifluoromethyl ketone), $\mathbf{A_2}$ is a dioxime, and $\mathbf{A_3}$ is a di-tosyloxime (Scheme 3). The remaining part of the scheme can be deciphered from comparison of the gross formulae of $\mathbf{A_1}$

(see above) and **A** ($C_{19}H_8F_{12}N_4$). The transformation is formally a substitution of 2 O atoms by 4 N atoms, corresponding to the conversion of a ketone into the diazo compound $R_2C{=}O \rightarrow R_2C{=}N^+{=}N^-$. However, the latter are thermally unstable, whereas the compound **A** is "activated" at 110°C. Then, **A** should be an isomer of the corresponding diazo compound – diazirine. It is formed via the oxidation of diaziridine $\mathbf{A_4}$, which is formed, in its turn, as a result of NH_3 (1,1-binucleophile) reaction with the tosylated oxime $\mathbf{A_3}$ **(**1,2-bielectrophile) (1 point for each structure, 5 points in total).

5. The structure of **B** can be elucidated from the comparison of the gross formulae of **A** ($C_{19}H_8F_{12}N_4$) and **B** ($C_{31}H_{32}F_{12}$), suggesting elimination of N atoms and addition of 2 cyclohexyl fragments. Indeed, elimination of molecular nitrogen from a diazirine yields the corresponding highly reactive carbene, which can be introduced at the C–H bonds. The structure is further confirmed by its existence as two diastereomers (due to two chiral sites) and the number of signals in the NMR spectra.



B

Although the diazirine fragments are completely consumed, the low yield of **B** shows that they were only partially involved in the corresponding process. Evidently, other reactions are possible under the process conditions. Therefore, the efficiency of the reaction yielding **B** can be estimated from the product yield. If a reacting diazirine group is substituted by the cyclohexyl moiety with the probability of x, **B** is obtained from the molecules with both diazirine groups having reacted via this path. Since the diazirine groups are separated by a fairly long spacer, their reactivity can be considered as independent. Thus $x^2 = 0.095$ and $x = 31\%$ (1 point for **B**, 1 point for the probability, 2 points in total).

6. At least one molecule of **A** must be attached to each macromolecule for complete crosslinking of polyethylene (with complete loss of its solubility). Let us consider that the reaction of the diazirine fragment with the C–H bonds of polyethylene yields the structure similar to the adduct **B** with the probability of 31%, whereas all the other reactions involving diazirine do not lead to the addition of **A** to the macromolecule. If so, the probability of the crosslink formation equals the yield of **B** in the reaction of **A** with cyclohexane (9.5%), and the mass fraction of **A** is 520.3/0.095/50000 = 0.11 (520.3 is the molar mass of **A**, 50000 is that of polyethylene, the intramolecular crosslinking is neglected, since the lowest concentration of **A** sufficient for complete curing is being determined. Finally, ω(A) ~ 11% (1 point).

References:

1. McHattie, J. S., Koros, W. J., & Paul, D. R. (1991). *Gas transport properties of polysulphones: 1. Role of symmetry of methyl group placement on bisphenol rings. Polymer, 32(5), 840–850.* doi:10.1016/0032-3861(91)90508-g.

2. Wang, C., Pan, N., Jiang, Y., Liao, J., Sotto, A., Ruan, H., … Shen, J. (2019). *A facile approach to prepare crosslinked polysulfone-based anion exchange membranes with enhanced*

alkali resistance and dimensional stability. RSC Advances, 9(62), 36374–36385. doi:10.1039/c9ra07433c

3. Lepage, M. L., Simhadri, C., Liu, C., Takaffoli, M., Bi, L., Crawford, B., Milani, A. S., Wulff, J. E. (2019) *A broadly applicable cross-linker for aliphatic polymers containing C–H bonds. Science, 366, 875–878.* doi: 10.1126/science.aay6230.

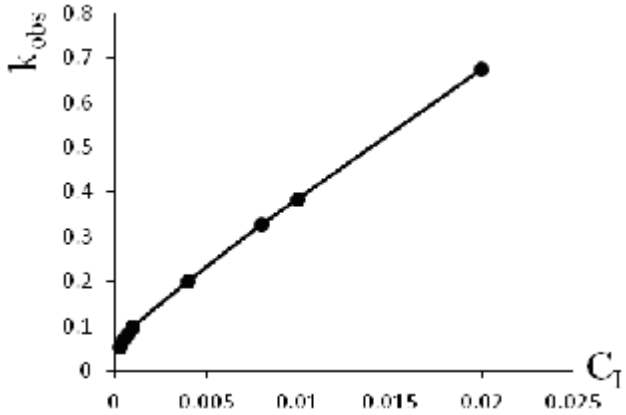
Section IV. Physical chemistry

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

1. $PtRBr^+ + I^- \rightleftarrows PtRBr^+,I^-$ $K = [PtRBr^+,I^-] / [PtRBr^+][I^-]$. In the material balance $C_0 = [PtRBr^+,I^-] + [PtRBr^+]$ there is a substitution $[PtRBr^+,I^-] = K[PtRBr^+]C_I$ from the equilibrium constant. Then $C_0 = [PtRBr^+](1 + KC_I)$ and $\alpha(PtRBr^+) = [PtRBr^+] / C_0 = 1 / (1 + KC_I)$ (1.5 points), $\alpha(PtRBr^+,I^-) = 1 – 1 / (1 + K \cdot C_I) = KC_I / (1 + KC_I)$ (1.5 points, 3 points in total)

2. The reaction proceeds through the two routes: without ion pairing $r_1 = k_0[PtRBr^+]C_I$ and with forming of the ion pair $r_{ip} = k_{ip}[PtRBr^+,I^-]$. Using stationary approximations $d[PtRBr^+,I^-]/dt = 0$, we have $k_1[PtRI^+,I^-] = k_{ip}[PtRBr^+,I^-]C_I$ and $r_{ip} = k_{ip}[PtRBr^+,I^-]C_I$. Total rate $r = r_0 + r_{ip} = k_0[PtRBr^+]C_I + k_{ip}[PtRBr^+,I^-]C_I$. Considering the mole fractions, $r = k_0C_0C_I / (1 + KC_I) + Kk_{ip}C_0C_I^2 / (1 + KC_I)$ (1.5 points) и $k_{obs} = (k_0 + Kk_{ip}C_I) / (1 + KC_I)$ (1 point, 2.5 points in total)

3. At high C_I, $K \cdot C_I >> 1$, $r = (k_0/K + k_{ip}C_I)C_0$ and $k_{obs} = k_0/K + k_{ip}C_I$ – linear equations (1 point)



(0.5 points)

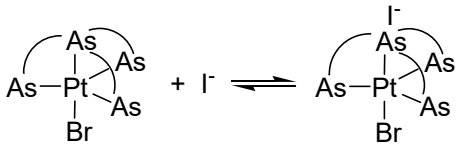
4. On the plot, a linear section with the equation $k_{obs} = k + k_{ip}C_I$ is observed at $C_I > 4 \cdot 10^{-3}$ mol/L (0.5 points). Considering that k_{ip} is equal to the tangent of inclination angle with positive direction of the abscissa axis, we have $k_{ip} = (0.674 – 0.326) / (20 – 8) \cdot 10^{-3} = 29$ s^{-1} (0.5 points) and $k = 0.674 – 29 \cdot 0.02 = 0.094$ s^{-1} (0.5 points) (the same are the values of the constants for the other combinations with $C_I > 4 \cdot 10^{-3}$ mol/L). In case $C_I = 4 \cdot 10^{-3}$ mol/L $k_{ip} = (0.674 – 0.199)/(20 – 4) \cdot 10^{-3} = 29.7$ s^{-1}, i.e. the point with $C_I = 4 \cdot 10^{-3}$ mol/L no longer lies on a straight line. The constant $k = k_0/K$ depends on the nature of nucleophile, since the equilibrium constant of formation K depends on it (0.5 points, 2.5 points in total)

5. Molar conductivity is connected with specific one through C_M: $\Lambda_{av} = 1000L / C$: $\Lambda(PtRBr^+) = 1000 \cdot 1.54 \cdot 10^{-5} / 1.33 \cdot 10^{-4} = 115.8$ (0.5 points), a $\Lambda(I^-) = 1000 \cdot 1.53 \cdot 10^{-5} / 1.33 \cdot 10^{-4} = 115$ ($Ohm^{-1}cm^2mol^{-1}$) (0.5 points). An average molar conductivity of ions $\Lambda_{av} = (115.8 + 115) / 2 = 115.4$ $Ohm^{-1}cm^2mol^{-1}$. Considering that $C_0 = [PtRBr^+,I^-] + [PtRBr^+]$ and $[PtRBr^+] = [I^-]$ for the equal initial concentrations, we have $K = [PtRBr^+,I^-]/[PtRBr^+]^2$. The equilibrium concentration $[PtRBr^+] = 1000L / 2\Lambda_{av} = 1000 \cdot 2.35 \cdot 10^{-5}/(2 \cdot 115.4) = 1.02 \cdot 10^{-4}$ mol/L, $[PtRBr^+,I^-] = C_0 – [PtRBr^+] = (1.33 – 1.02) \cdot 10^{-4} = 3.10 \cdot 10^{-5}$ mol/L. The constant $K = 3.10 \cdot 10^{-5}/(1.02 \cdot 10^{-4})^2 = 2980$ $L \cdot mol^{-1}$ (1 point), $k_0 = K \cdot k = 2980 \cdot 0.094 = 280.1$ c^{-1} (0.5 points, 2.5 points in total)

6. Reaction rates for the two routes: $r_{ip} = Kk_{ip}C_0C_I^2 / (1 + KC_I)$ and $r_0 = k_0C_0C_I / (1 + KC_I)$, and their ratio $r_0/r_{ip} = k_0/(Kk_{ip}C_I)$. In case $C_I = 10^{-3}$ $r0/r_{ip} = 280.1/(2980 \cdot 29 \cdot 10^{-3}) = 3.24$ (p the reaction mostly proceeds through the route without ion pair formation) (1 point). When $C_I = 10^{-2}$ $r_{ip}/r_0 = (2980 \cdot 29 \cdot 10^{-2})/280.1 = 3.09$ (0.5 point, 1.5 points in total) (the reaction mostly proceeds through the route with ion pair formation)

7. Since iodine does not attack Pt^{2+} and complex is polar, then the most probable attack is on the As atom, which is intrans-position to Br^- and carries small positive charge. In this case, the

formation of an ion pair can be carried out due to the van der Waals forces. The formation of the second ion pair and the square of the I^- concentration in the kinetic equation also indicate the same orientation of iodine (1 point, 2 points in total).



Problem 2 (author Karpushkin E.A.)

1. $$5HAuCl_4 + 3P + 12H_2O \rightarrow 5Au + 3H_3PO_4 + 20HCl,$$

$$4HAuCl_4 + 3H_2CO + 3H_2O \rightarrow 4Au + 3CO_2 + 16HCl.$$

Formic acid is not an acceptable product of formaldehyde oxidation, since from question 5 it follows that it reacts with $HAuCl_4$ (1 point for each equation, 2 points in total).

2. The considered samples contain 400·0.788 = 315.2 mg and 754.9·0.626 = 472.6 mg of element Z, respectively (the ratio is 315.2:472.6 = 2:3). The ratio of the gold amounts in the samples is the same (348.7:[901.9/339.8·196.97] = 1:1.502). Hence, the described reaction is the oxidation of compound **B** with chloroauric acid to yield compound **A**. The most probable product is the oxide of Z. If an oxide of Z contains 78.8% of Z, the equivalent mass of Z is 29.7 g/mol, and the only reasonable solution is **A** = SnO_2 (Y_2O_3 is suitable as far as the mass fraction is considered, but complex compounds which can be oxidized into the oxide via the interaction with $HAuCl_4$ are not typical of yttrium). The next step is to find a tin(II) compound containing 62.6% of the metal. Under the simplest assumption that the compound is binary, the equivalent mass of the second element is 35.5 g/mol, and it is chlorine (**B** = $SnCl_2$). Finally

$$3SnCl_2 + 2HAuCl_4 + 6H_2O \rightarrow 3SnO_2 + 2Au + 14HCl$$

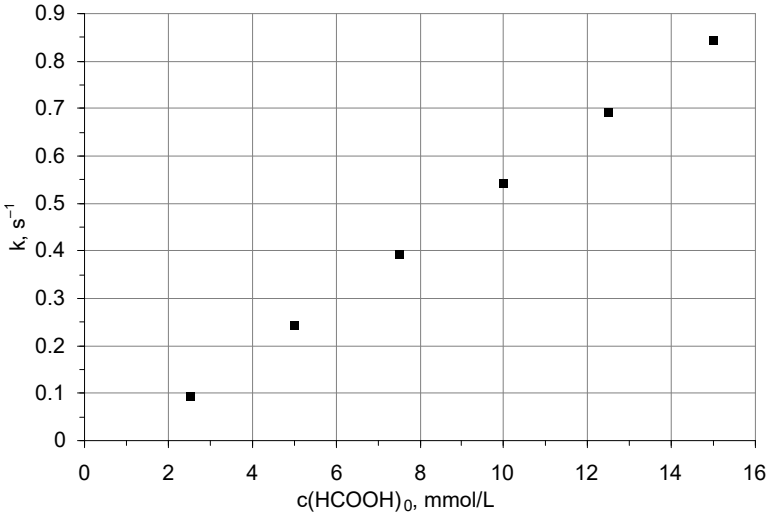
The dye is the Purple of Cassius. The described reaction is used for qualitative determination of gold compounds (0.5 points for Z, **A**, **B**, and the reaction equation, 2 points in total).

3. A salt containing tin and gold can be either tin aurate or gold stannate. Typical oxidation state for gold is (+3), hence $Sn(AuO_2)_2$ and $Sn(AuO_2)_4$ are the possible formulas for tin(II) and tin(IV) aurate, respectively. The Au/Sn ratio in these hypothetic compounds is 2:1 or 4:1, which contradicts the given data. The gold(III) stannate formula is $Au_2(SnO_3)_3$ with the Au/Sn ratio being 2:3, coinciding with the composition of the Au–SnO_2 mixture according to the data in the task (1.5 points).

4. Let us determine the gold nanoparticle density. The unit cell volume is $(4.07\ Å)^3 = 6.74 \cdot 10^{-29}\ m^3$. Each unit cell of the face-centered unit cell contains 4 atoms of gold (8 atoms in the cube corner, each belonging to 8 cells, plus 6 atoms in the face centers, each belonging to 2 cells; 8/8 + 6/2 = 4). Total mass of these atoms is $4 \cdot 0.19697\ kg/mol / 6.023 \cdot 10^{23}\ mol^{-1} = 1.31 \cdot 10^{-24}$ kg. Hence, gold density is $1.31 \cdot 10^{-24}\ kg / 6.74 \cdot 10^{-29}\ m^3 = 19430\ kg/m^3$.

Volume of a spherical particle with diameter of 5 nm is $4\pi/3\cdot(2.50\cdot10^{-9})^3 = 6.54\cdot10^{-26}$ m^3, its mass is $6.54\cdot10^{-26}$ m^3 · 19430 kg/m^3 = $1.27\cdot10^{-21}$ kg, and hence it contains $1.27\cdot10^{-21}$ kg / 0.19697 kg/mol · $6.023\cdot10^{23}$ mol^{-1} = 3883 atoms.

To estimate the number of gold atoms at the nanoparticle surface let us determine the atomic radius of gold in its lattice. The shortest distance between the atoms centers in the face-centered cubic cell equals half of the unit cell face diagonal (2.88 Å = 0.288 nm). Hence, the volume of the surface shell with thickness equal to the atomic diameter of gold is $4\pi/3\cdot(2.50\cdot10^{-9})^3 - 4\pi/3\cdot(2.21\cdot10^{-9})^3 = 2.0\cdot10^{-26}$ m^3, which is $2.0\cdot10^{-26}$ m^3 / $6.54\cdot10^{-26}$ m^3 = 0.306 (30.6%) of the total nanoparticle volume. Therefore, this surface layer contains 0.306·3883 = 1188 atoms. (4 points)



5. а) It is to be easily seen that the apparent reaction rate constant is linear with the formic acid concentration, the chloroauric acid concentration being constant. The equation coefficients can be obtained, for example, from the rate constant values at the lowest and the highest concentration of formic acid: $k = 0.06c(\mathrm{HCOOH})_0 - 0.057$.

б) Let us start with the formal kinetic equation for the considered reaction:

$$\frac{dc_{\mathrm{Au(III)}}}{dt} = -k_0 c_{\mathrm{Au(III)}}{}^{a} c_{\mathrm{HCOOH}}{}^{b},$$

with a and b being the reaction rate orders with respect to chloroaurate and formic acid, respectively. At high excess of the reducing agent, the change in its concentration at the initial stage is negligible, and the equation is as follows

$$\frac{dc_{\mathrm{Au(III)}}}{dt} = -kc_{\mathrm{Au(III)}}{}^{a}, \text{ где } k = k_0 c_{\mathrm{HCOOH}}{}^{b},$$

the apparent reaction rate constant k being determined in the experiment and is given in the table. Hence, $k = k_0 c_{\mathrm{HCOOH}}{}^{b} = 0.06c_{\mathrm{HCOOH}} - 0.057$. These equation show that the reduction of $HAuCl_4$ with formic acid is accompanied by another process leading to consumption of Au(III), its rate being independent of the formic acid concentration. At the same time, this process is related to the presence of formic acid, since Au(III) is not consumed in its absence. The apparent rate constant cannot include the concentration of tetrachloroaurate, as seen from the equality of the rate constants at $HAuCl_4$ concentrations of 0.075 and 0.15 mmol/L and equal concentrations of formic acid. The mentioned facts can be explained suggesting that a fraction of the formic acid is not involved in the reaction with the rate constant of k_0. Indeed, since the experiments are performed at pH 3.0, a fraction of formic acid exists as formate anion (this fraction is

approximately the same: 1 mmol/L, neglecting the amount of protons provided by $HAuCl_4$ dissociation; the account for complete or partial dissociation of $HAuCl_4$ does not affect the discussion). At the same time, when the starting formic acid concentration is 1 mmol/L (meaning that it is completely converted to formate), the apparent reaction rate constant is not zero, hence, formate ion can be involved in the reaction with $HAuCl_4$. In other words,

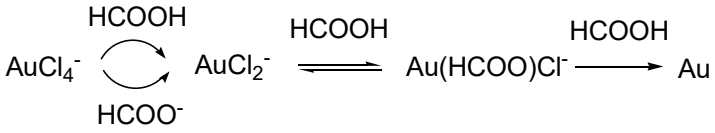
$$k = 0.06c_{HCOOH} - 0.057 = k_0[HCOOH]^b + k'_0[HCOO^-]^{b'} = k_0(c_{HCOOH} - [HCOO^-])^b + k'_0[HCOO^-]^{b'},$$

and the second term is constant independently of the rate order of the reaction of formate with tetrachloroaurate, since the formate concentration is the same. Hence, the following equation

$$0.06c_{HCOOH} - 0.057 = k_0[HCOOH]^b + k'_0[HCOO^-]^{b'}$$

is held only of the reaction rate order with respect to formic acid $b = 1$ (1 point for the equation, 2 points for the rate order with respect to HCOOH, 3 points in total).

6. Considering the discussion above, the first stage is the interaction of $HAuCl_4$ (or, more strictly, $AuCl_4^-$) with HCOOH and $HCOO^-$ simultaneously. Since Au(0) is formed later than Au(III) is consumed, it can be suggested that gold is reduced in at least two stages, the first one yielding Au(I) (as $AuCl_2^-$). The influence of chloride ions on the rate of the nanoparticles appearance shows that the rate-limiting stage is the conversion of the mixed-ligand complex formed in its turn via the reversible substitution of a chloride in $AuCl_2^-$ with formate. The substitution of chloride into formate cannot precede the reduction of Au(III), since the latter process rate is independent of NaCl concentration. The data given in the task are compatible with the ligand exchange under the action of formate ions or neutral formic acid (both possibilities are accepted):



(0.5 point for the reduction of Au(III) in two stages, for simultaneous reduction of Au(III) by formic acid and formate, for the presence of the ligand exchange stage, for reversibility of the ligand exchange, and for the position of the ligand exchange stage between the reduction stages, 2.5 points in total)

Problem 3 (автор Кузин С.В.)

1. At pH 3.0 hydroxyl amine is completely non-ionized. The reacted amount of TEMPONE

$$10^{-3} - \frac{10^{-3}}{22.5} = 10^{-3}\cdot\frac{21.5}{22.5} = 9.56\cdot10^{-4}\ \text{M}$$

The changes of the rest concentrations are calculated from the chemical equation. As acidic medium results from the presence of strong acid, the change of its concentration should be also considered (2 points for the calculation of the constant; 1 point if the change of $[H^+]$ was not considered).

$$\text{K} = \frac{[R_2NO^+][R_2NOH]}{[RN_2O^{\cdot}]^2[H^+]} = \frac{(10^{-3}\cdot\frac{10.75}{22}\cdot 5)^2}{(10^{-3}\cdot\frac{1}{22}\cdot 5)^2(10^{-3}-\frac{9.56}{2}\cdot 10^{-4})} = 221\cdot10^3$$

2. а) (1.5 points for calculation)

$$K_2 = \frac{[R_2NO^+][R_2NO^-]}{[RN_2O^{\cdot}]^2} = \frac{[R_2NO^+][R_2NOH][R_2NO^-][H^+]}{[RN_2O^{\cdot}]^2[H^+]\quad[R_2NOH]} = K\cdot K_a = 0.00221$$

б) Let us denote the fraction to find by x, that is $[R_2NO^{\cdot}] = x\cdot C(R_2NO^{\cdot})$. Then $1 - x$ represents the fraction of non-radical species that are formed in equal amounts. Thus

$$\frac{\left(\frac{1-x}{2}\right)^2}{x^2} = K_2.$$

From here we get $x = 0.914$ (1.5 points).

3. а) Let us calculate the standard EMF of the reaction from the data provided $\Delta_r G^0 = -RT\ln K = -nFE^0$

$$E^0 = \frac{RT\ln K}{F} = 0.316\ \text{V} = E_{\text{Ox}}{}^0 - 0.946 \Rightarrow E_{\text{Ox}}{}^0 = 1.262\ \text{V (1 point)}$$

б) After the equilibrium is reached $E_{\text{Ox}}{}^0 = E_{\text{Red}}{}^0$, thus the potential may be calculated either via oxidized or reduced forms:

$$E_{\text{Ox}} = E_{\text{Red}} = E_{\text{Red}}{}^0 + \frac{RT}{nF}\ln\frac{[R_2NO^+]}{[RN_2O^{\cdot}]} = 0.946 + 0.0257\ln10.75 = 1.01\ \text{V}$$

Calculation via the oxidized form leads obviously to the same result (2 points).

4. To begin with let us clarify how nitroxyl radical was formed. From the data provided it results that after acidic treatment of hydroxylamine the following reaction took place

$$R_2NOH + [O] \rightarrow R_2NO^+.$$

If the oxidation is not complete the comproportionation takes place after alkalizing:

$$R_2NOH + R_2NO^+ \rightarrow 2R_2NO^{\cdot} + H^+.$$

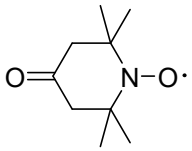
The analyte contains $1.69 \cdot \frac{10^{16}}{N_A} = 2.8 \cdot 10^{-8}$ mole of nitroxyl radical. The concentration of the substance in the analyte is equal to its concentration in the initial solution. Then, the amount of the hydroxylamine left exceeds far that of the radical. Thus, one can consider the equilibrium totally shifted to the nitoxyl formation. This amount of the radical resulted from 2 mM of oxidized and reduced forms. Then, during 2 days 2 mM of TEMPOL-H were oxidized that leads to the average reaction rate (3 points):

$$r_{av} = -\frac{\Delta C}{\Delta t} = 1 \text{ mM/day}$$

5. From the given scheme it follows that NaClO oxidizes the alcohol in 1:1 ratio, TEMPO being catalyst. From the given data, there are 0.05 mole of NaClO and 0.01 mole TEMPO. Thus 0.05 mole of the alcohol is oxidized (1 point).

6. $OCl^- + Br^- \rightarrow OBr^- + Cl^-$; $OBr^- + \text{alcohol} \rightarrow Br^- + \text{carbonyl}$ (2 points)

7. TEMPOL has a hydroxyl group that is oxidized as it is stated in the task. A new radical is TEMPONE (1 point).



TEMPONE

Section V. Organic chemistry

Problem 1 (authors Avramenko N.N., Gorlova A.A.)

1. As we can see, many steps were carried without isolation of intermediates. But increasing the number of chemical reactions shouldn't influence on the difficulty of solving a problem, as most of them are well-known transformations of functional groups. (Scheme 1).

Step 1. Initially, the nucleophilic substitution of bromine to the nitrile group occurs. It is followed by the protection of the alcohol group by tert-butyldimethylsilyl chloride (TBDMSCl) and the formation of substance **A**.

Step 2. At this stage, DIBAL-H reduces nitrile to aldehyde, and then the aldehyde is oxidized to the acid. The acid is converted to methyl ester **B** by using trimethylsilyldiazomethane - a safer diazomethane analogue.

Step 3. Preparation of the reagent for the HWE reaction (Horner – Wadsworth – Emmons) **C** by acylation of a phosphorus-containing carbanion.

Step 4. The HWE reaction occurres with the formation of olefin **D**. Lithium salt is added to the exceptional formation of the E-isomer - which is more thermodynamically stable.

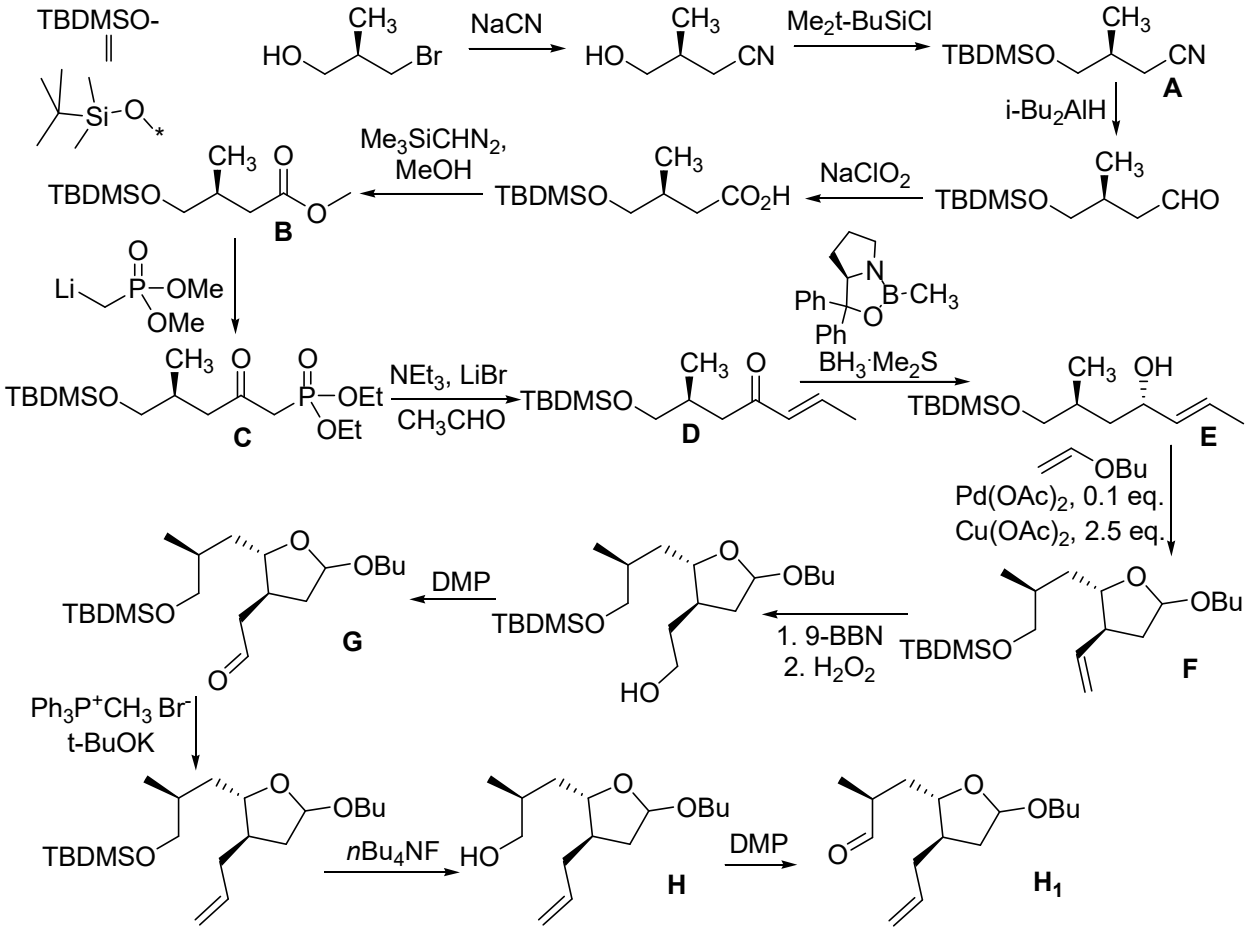
Step 5. Enantioselective reduction of the ketone was carried out with the formation of compound **D** by using a CBS catalyst (Corey-Bakshi-Shibata). The stereochemistry of the product can be determined based on the stereochemistry of the final product.

Step 6. Oshima-Utimoto reaction with the formation of compound **F** (the product can be determined basis on Scheme 2 in task). At this step, the configurations of the newly formed stereocenters can be determined from the final compound (as in the further compounds).

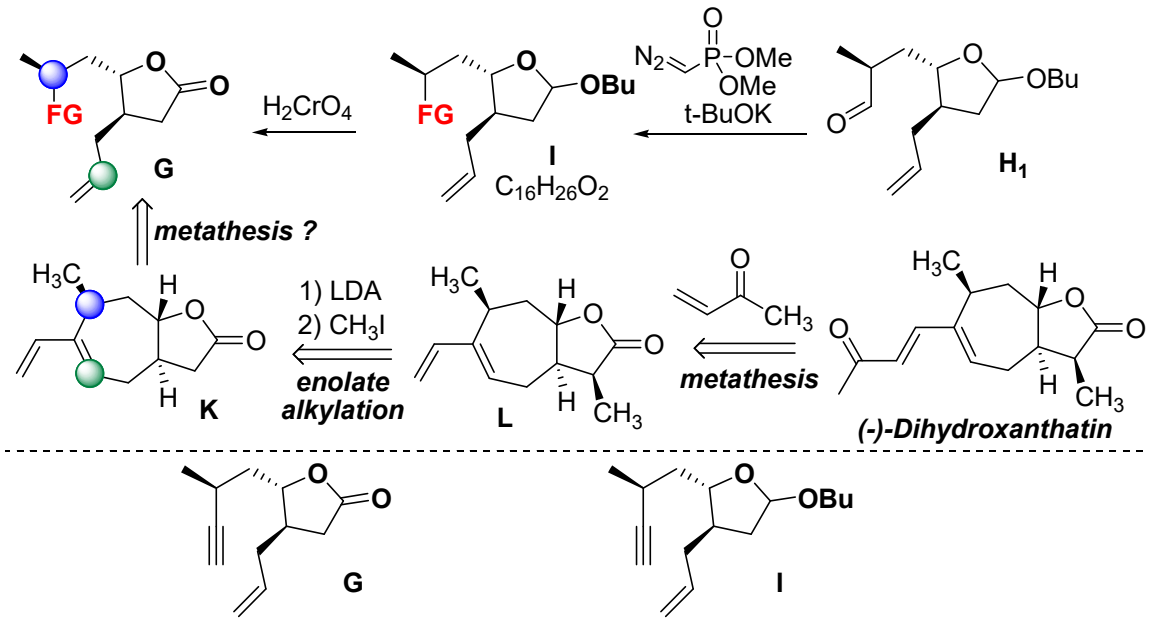
Step 7. Compound **F** adds the borane against the Markovnikov rule, which is oxidized to alcohol by hydrogen peroxide, and then to aldehyde **G** (Dess-Martin reagent).

Step 8. First step – Wittig reaction, which is followed by the deprotection of the hydroxyl group by TBAF with the formation of alcohol **H**.

In the **step 9**, only the oxidation of alcohol **H** to the corresponding aldehyde is obvious, denote it as $\mathbf{H_1}$. It is advisable to use further integrated approach: retrosynthesis and knowledge of the properties of the reagents. Analyzing the reagents and catalysts on **steps 12** and **13**, it is easy to understand that they are the steps of alkylation of the corresponding enolate and cross-metathesis, respectively. Based on this, the substances **L** and **K** can be easily determined (Scheme 2). On the other hand, it is clear that upon conversion to **I**, a transformation occurs with the participation of the aldehyde group and its transformation into another (FG highlighted in red in Scheme 2). Then, in substance **I**, cyclic acetal is oxidized to lactone (Jones reagent is the only reagent in the chain that can oxidize acetal to lactone) with the formation of **G**. To decipher this transformation, we can analyze formula of **I** and understand that FG is terminal acetylene. It is also easy to come to this conclusion if notice, that Seyfert-Hilbert reaction takes place on this step. Actually, when dimethyl (diazomethyl) phosphonate $(MeO)_2POCH_2N_2$ interact with an aldehyde, the formation of terminal acetylenes occurs.



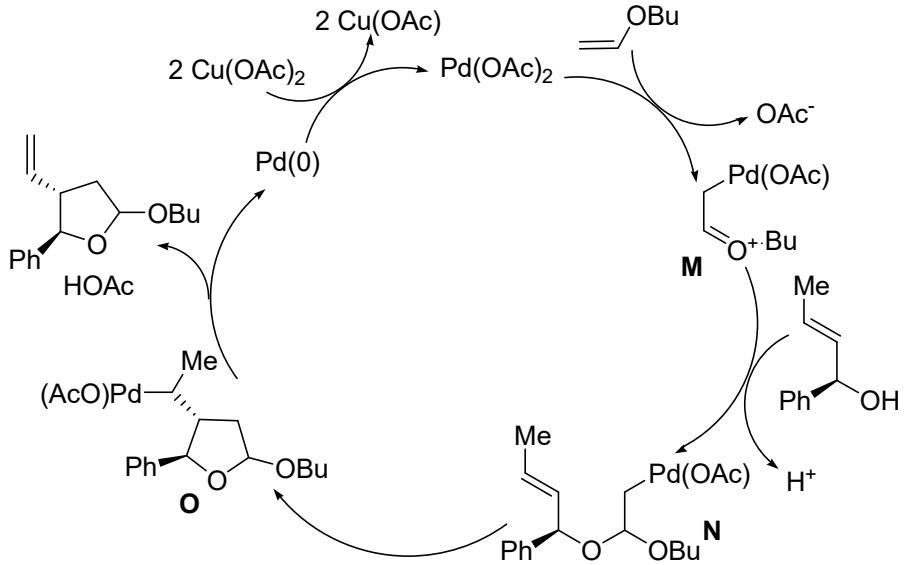
Scheme 1. Total synthesis of ***(-)-Dihydroxanthatin***, determination of structures of compounds **A** – **H**.



Scheme 2. Total synthesis of ***(-)-Dihydroxanthatin***, determination of structures of compounds **I** – **L**.

From an educational point of view, the catalytic cycle of the Oshima-Utimoto reaction is also given below. The mechanisms of the other reactions can be easily found using various sources. The first stage of the cycle is the electrophilic palladination of vinyl ester with the formation of intermediate **M** with increased electrophilicity of the carbonyl group, which contributes to the addition of alcohol at this double bond to form **N**. Next, the stages are similar to the Heck

reaction - double bond addition and beta elimination. To restore the oxidized form of palladium, some kind of oxidizing agent is required, in this case $Cu(OAc)_2$ (Scheme 3).



Scheme 3. Catalytic cycle of Oshima-Utimoto reaction.

(all compounds except **K**, **E**, **I** – 1 point; compounds **K**, **E**, **I** – 2 points, 15 points in total. For incorrectly determined stereochemistry of one stereocenter, penalty is 0.25 points, for one compound no less than 0 points, if the penalty has already been applied to one stereocenter in one compound, it is not reused in followed compounds. If stereochemistry is not indicated, a penalty for each stereocenter in each compound)

Literature:

1. Evans, M. A., & Morken, J. P., Stereoselective Synthesis of Furans by the Pd-Catalyzed Oshima−Utimoto Reaction. *Organic Letters,* **2005**, *7(15)*, 3367–3370. DOI: 10.1021/ol051275s.

2. Evans, M. A., & Morken, J. P., Asymmetric Synthesis of (−)-Dihydroxanthatin by the Stereoselective Oshima−Utimoto Reaction. *Organic Letters*, **2005**, *7(15)*, 3371–3373. DOI: 10.1021/ol051276k.

3. Corey, E. J., & Helal, C. J., Reduction of Carbonyl Compounds with Chiral Oxazaborolidine Catalysts: A New Paradigm for Enantioselective Catalysis and a Powerful New Synthetic Method. *Angewandte Chemie International Edition,* **1998**, *37(15)*, 1986–2012. DOI: 10.1002/(SICI)1521-3773(19980817)37:15<1986::AID-ANIE1986>3.0.CO;2-Z.

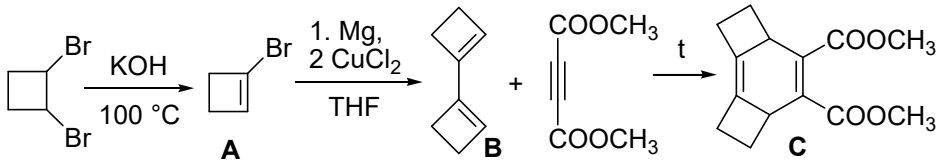
4. J. C. Gilbert, U. Weerasooriya, Diazoethenes: their attempted synthesis from aldehydes and aromatic ketones by way of the Horner-Emmons modification of the Wittig reaction. A facile synthesis of alkynes. *J. Org. Chem.*, **1982**, *47*, 1837-1845. DOI: 10.1021/jo00349a007.

5. S. Müller, B. Liepold, G. J. Roth, H. J. Bestmann, An Improved One-pot Procedure for the Synthesis of Alkynes from Aldehydes, *Synlett*, **1996**, 521-522. DOI: 10.1055/s-1996-5474.

Problem 2 (author Kandaskalov D.V.)

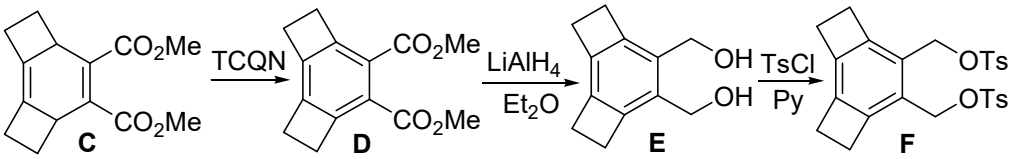
1. Let's start by the substance **B**. This is a hydrocarbon, which, according to the conditions of the problem, must enter into similar reactions with DMAD and cyclobutene dicarboxylic acid. It is logical to assume that this is a Diels-Alder reaction, since the reagents mentioned above are good dienophiles. Thus, hydrocarbon **B** must be a 1,3-diene. Then substance **A** must contain one bromine atom, and the second is eliminated with the formation of a double bond. This substance **A** gives a Grignard reagent, which under the action of Cu (II), as an oxidizing agent, dimerizes with the formation of diene **B**, which can enter into the Diels-Alder DMAD reaction (Scheme 1). In addition, gross formula **B** corresponds to that given in the condition (C_8H_{10}).

Scheme 1



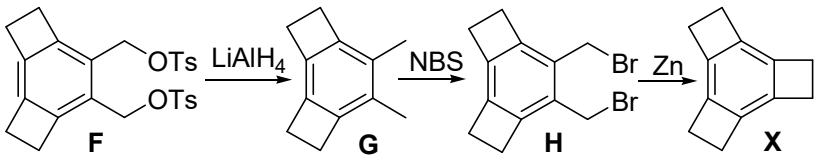
The next step in the synthesis is the quinone oxidation of substance **C**, which leads to the formation of aromatic compound **D**, the molecular formula of which corresponds to the $C_{14}H_{14}O_4$. The following stages are classical reactions of the reduction of ether groups to alcohol and the activation of alcohol groups with tosyl chloride to form compound **F** (Scheme 2).

Scheme 2



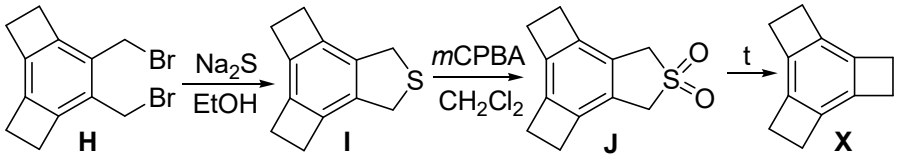
Based on the structural formula of substance **D** and the fact that substance **X** has a third-order axis of symmetry, we conclude that **X** is tricyclobutabenzene. An analysis of the molecular formula **G** ($C_{12}H_{14}$) and the structure **F** found by us indicates that the reaction **F** → **G** is the transformation of the corresponding $-CH_2OTs$ groups to methyl groups. Further, radical bromination of NBS over these methyl groups leads to the formation of dibromide **N**. The last stage of the synthesis is the intramolecular Wurtz reaction, which leads to the formation of a third cyclobutane cycle (Scheme 3).

Scheme 3



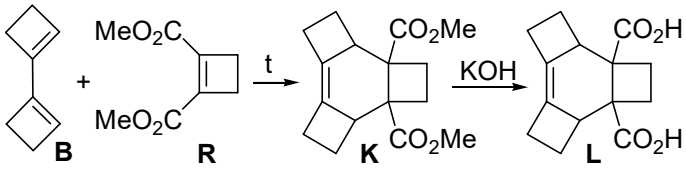
Based on the molecular formula of substance **I** ($C_{12}H_{12}S$) it is easy to guess that the transformation **H** → **I** is the intramolecular cyclization with the participation of the sulfide ion and the formation of condensed dihydrothiophene **I**. The oxidation gives the corresponding sulfone **J**, which, as a result of thermal elimination of SO_2, gives the target compound **X** (Scheme 4).

Scheme 4



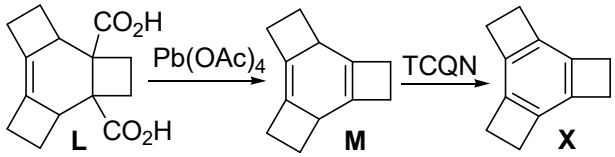
We found the first part of the synthesis, now the left part remains. The **B** → **K** conversion is also a Diels-Alder reaction, which leads to a polycyclic compound **K**. The next stage is the saponification of ether in an acidic medium with the formation of diacid **L** (Scheme 5).

Scheme 5



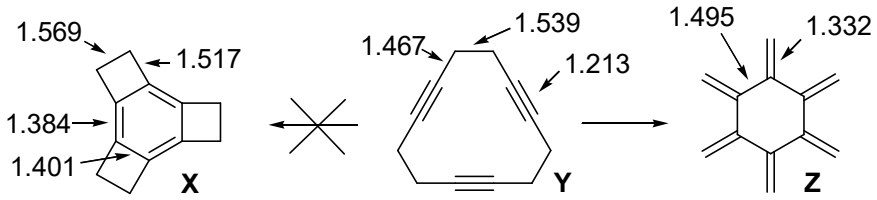
The last stages of the synthesis are easily deciphered. Substance **M** must be a diene, which is oxidized by quinone to an aromatic system, which indicates that stage **L** → **M**, this is oxidative decarboxylation (Scheme 6).

Scheme 6



(structure formula of all compound: 0.75 points per each, 10.5 points in total)

2. Based on the condition, that **Y** can only be a cyclic triyne [2 + 2 + 2] whose cyclization can lead to **X**. However, this reaction leads to a thermodynamically more favorable [6] -radialene **Z** (0.75 points per structure, 1.5 points in total).



3. The correspondence of C–C bonding is given on the figure above (1 point per structure, 3 points in total).

Literature:

1. Nutakul, W.; Thummel, R. P.; Taggart, A. D. *J. Am. Chem. Soc.* **1979**, *101*, 770-771.

2. Doecke, C. W.; Garratt, P. J.; Shahriari-Zavareh, H.; Zahler, R. *J. Org. Chem*. **1984**, *49*, 1412-1417.

3. Boese, R.; Blaser, D.; Billups, W. E.; Haley, M. M.; Maulitz, A. H.; Mohler, D. L.; Vollhardt,

K. P. C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 313-317.

4. Marsh, W. and Dunitz, J.D. *Helvetica Chimica Acta* **1975**, *58*, 707-712.

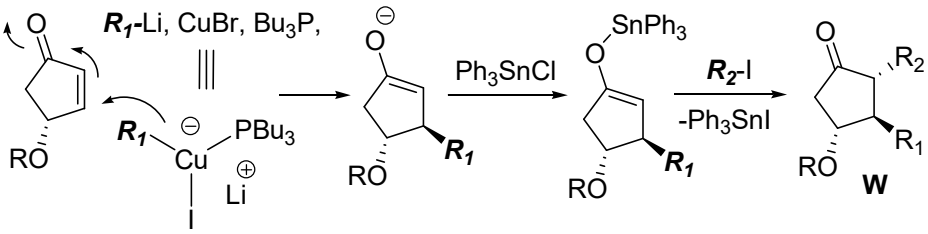
5. Schiess, P. and Heitzmann, M. *Helvetica Chimica Acta*, **1978**, *61*, 844–847.

6. Barkovich, A. J., Vollhardt, K. P. C. *J. Am. Chem. Soc.*, **1976**, *98*, 2667–2668.

7. Houk, K. N., Strozier, R. W., Santiago, C., Gandour, R. W., & Vollhardt, K. P. C. *J. Am. Chem. Soc.*, **1979**, *101*, 5183–5185.

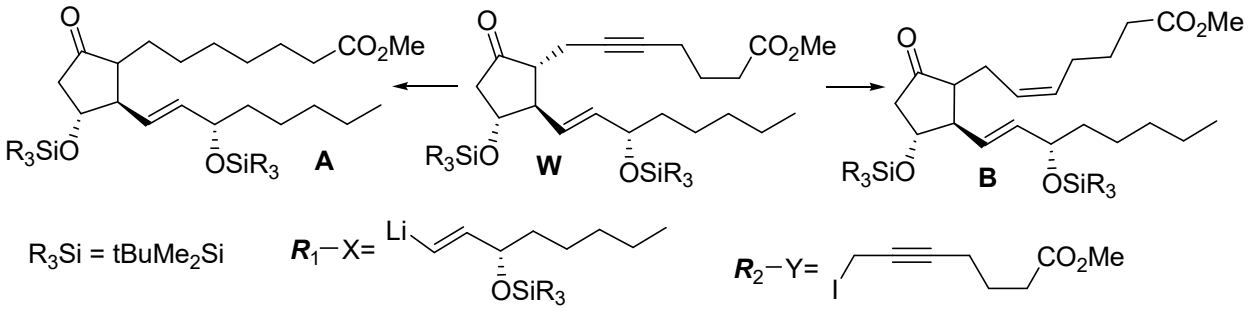
Problem 3 (authors Shved E.N., Volochnyuk D.M.)

1. Analyzing the structure of the initial cyclopentenone for the "three-component" approach, it is easy to conclude that it is an electrophile, which can undergo 1,4- additions by Michael. Then the first stage of the reaction should be the stereoselective addition of the nucleophilic particle $\boldsymbol{R}_1^-$ to cyclopentenone. The subsequent stages include the "stabilization" of the formed enolate by its reaction with Ph_3SnCl and subsequent alkylation with the electrophilic $\boldsymbol{R_2}^+$ particle (Scheme 1). Therefor the correct variant of the conditions and sequence of addition of reagents in this approach will be option No 4 from the above scheme (the correct conditions 0.5 points, the structure of the intermediates 1 point, 2.5 points in total).



Scheme 1. Three-component synthesis of prostaglandins

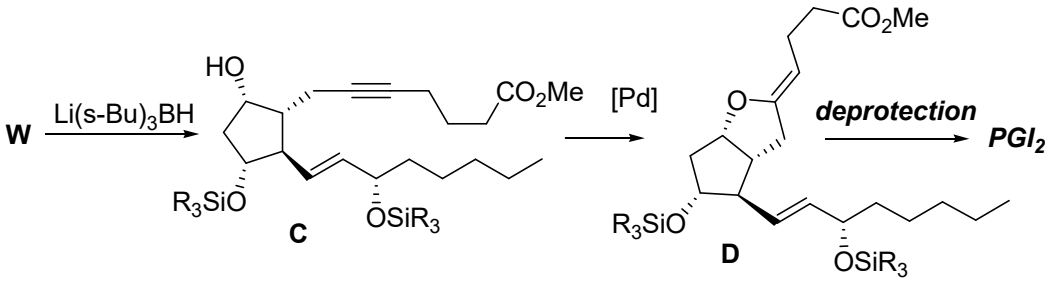
2. By analyzing the structure of the prostaglandins $\boldsymbol{PGE_1}$ and $\boldsymbol{PGE_2}$, which can be obtained from compound **W**, obviously that $\boldsymbol{PGE_1}$ is a hydrogenated analogue of $\boldsymbol{PGE_2}$. Moreover, the configuration of the double bond in $\boldsymbol{PGE_2}$ is *cis*. It is easy to assume that **W** is an protected analogue of these two prostaglandins by alcohol and carboxy group that contains a triple bond. This is confirmed by the fact that hydrogenating alkynes on ordinary palladium on coal impossible to stop at the alkene stage. At the same time, the using the Lindlar catalyst (with reduced catalytic activity compared to conventional palladium-on-charcoal), make possible to selectively reduce alkynes to cis alkenes (Conditions 5 in the scheme from the condition). In this case, 5% Pd/BaSO4 was used. Using data from the conditions of the task that **W** is a methyl ester and has the equal protective groups at alcohol oxygens, it is easy to solve its structure, as well as the structure of compounds **A** and **B**. Knowing the structure and conclusions from section 1 of the task, it is also easy to solve the structures $\boldsymbol{R_1}$-X and $\boldsymbol{R_2}$-Y (Scheme 2) (correct condition is 0.5 points, structure 1 point, 5.5 points in total)



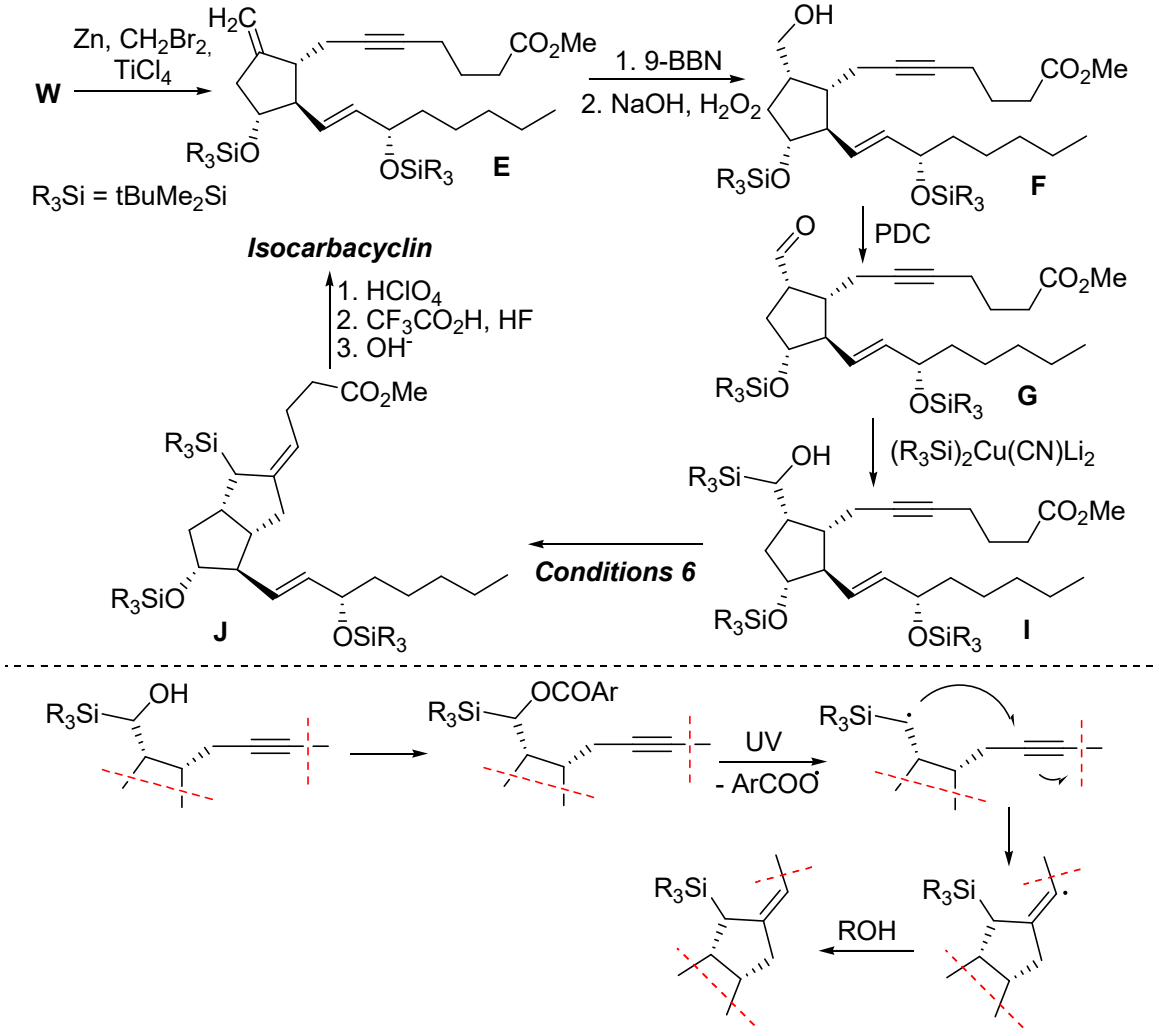
Scheme 2.

3. We could start the solution of this part of the problem by deciphering the $\boldsymbol{PGI_2}$ synthesis scheme. Based on the fact that the last stage of **D** → $\boldsymbol{PGI_2}$ is the removal of protective groups, it is obvious that **D** is a double-silylated methyl ester of $\boldsymbol{PGI_2}$. On the other hand, the **W** → **C** stage is a reduction with a sterically hindered borohydride type reducing agent. In the structure of **W**, the only group capable of such a reduction is the keto-group of the cyclopentane ring. In addition, the approach of the reducing agent to such substrate should be carried out from the less sterically

hindered side with the formation of a formally *cis*-product. Analyzing all these facts, we conclude that the **C** → **D** stage is the Pd-mediated intramolecular addition of the hydroxyl group to the triple bond (Scheme 3).



Scheme 3.



Scheme 4.

Deciphering the Isocarbacyclin synthesis is much more complicated and requires a lot of logical effort. First, we should analyze the difference in the structures of ***PGI₂*** and Isocarbacyclin. When we compare them, it is easy to notice that Isocarbacyclin is a substance in which the oxygen atom is replaced by a methylene group, followed by isomerization of the double bond compared to ***PGI₂***. Since both molecules were obtained from one compound, the source of this additional carbon atom should be found in the Scheme. Of all the reagents, only the $Zn–CH_2Br_2–TiCl_4$ (Lombardo reagent) can play this role. Based on the fact that the next stage **E** → **F** is hydroboration by Brown, it follows that the Lombardo reagent is an olefinating reagent. Further stages **F** → **G** are the oxidation of alcohol to an aldehyde; **G** → **I** is the formal addition of R_3Si^-

particles to the aldehyde. The interpretation of compound **J** requires a careful reading of the condition. Firstly, it is important not to miss the information that deoxygenation occurs under these conditions. Secondly, carefully read the condition that **J** is a bicyclic compound bearing an allylsilane fragment. Compiling all these facts, we unambiguously obtain the structure **J**, which is depicted on Scheme 4. Really, at this stage the photochemical reduction of the corresponding benzoates was used, which was developed earlier for deoxygenation of ribonucleosides. Under these conditions, a radical stabilized by the R_3Si-group was generated, which than entered into the intramolecular addition to the triple bond by analogy with compound **C** (1 point for each structure, 7 points in total).

Literature:

Synthesis of prostaglandins:

1. Suzuki, M., Yanagisawa, A., & Noyori, R. (1988). Prostaglandin synthesis. 16. The three-component coupling synthesis of prostaglandins. Journal of the American Chemical Society, 110(14), 4718–4726. doi:10.1021/ja00222a033.

2. Suzuki, M., Koyano, H., & Noyori, R. (1987). Prostaglandin synthesis. 14. A controlled synthesis of isocarbacyclin. The Journal of Organic Chemistry, 52(25), 5583–5588. doi:10.1021/jo00234a014

3. Noyori, R., & Suzuki, M. (1993). Organic synthesis of prostaglandins: advancing biology. Science, 259(5091), 44–45. doi:10.1126/science.8418493

4. Suzuki, M., Koyama, H., Ishii, H., Kato, K., Ögren, M., & Doi, H. (2018). Green Process of Three-Component Prostaglandin Synthesis and Rapid 11C Labelings for Short-Lived PET Tracers. Green Process of Three-Component Prostaglandin Synthesis and Rapid 11C Labelings for Short-Lived PET Tracers. doi:10.5772/intechopen.72868

Lombardo reagents:

5. Chand, H. (2009). Lombardo's Reagent. Synlett, 2009(15), 2545–2546. doi:10.1055/s-0029-1217801

Photochemical deoxygenation of secondary alcohols:

6. Saito, I., Ikehira, H., Kasatani, R., Watanabe, M., & Matsuura, T. (1986). Photoinduced reactions. 167. Selective deoxygenation of secondary alcohols by photosensitized electron-transfer reaction. A general procedure for deoxygenation of ribonucleosides. Journal of the American Chemical Society, 108(11), 3115–3117. doi:10.1021/ja00271a057