# Theoretical tour 2. Solutions
## Organic chemistry

Problem 1 (author Bakhtin S.G.)

1. CS$_2$ can be used to obtain dithiocarboxylic acid **II** by its interaction with a Grignard reagent (similar to the synthesis of RCOOH from RMgBr and CO$_2$). Oxidation of toluene by permanganate produces benzoic acid which is converted to the acyl chloride by the action of thionyl chloride. Subsequent reaction with sodium hydrosulfide and acidification leads to **I**. (0.25 Points for each reactant in the right place and 0.25 points for each product in six reactions, 3 points in total).
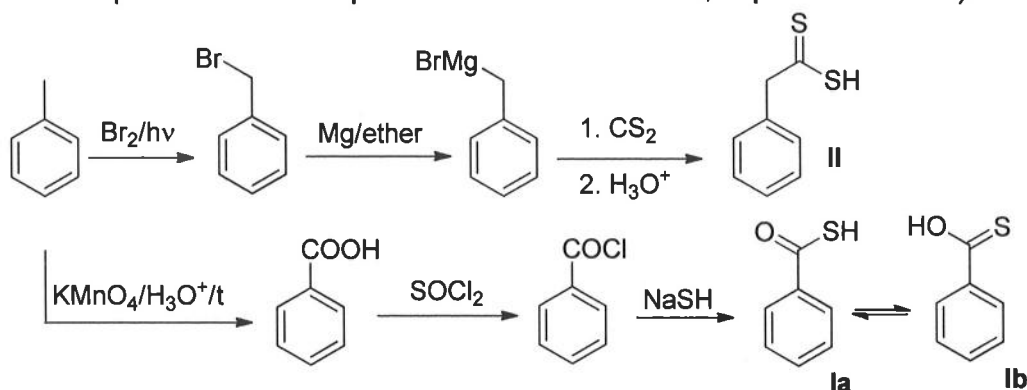

2. From the w_C, w_H, and w_N data the residual in **C** accounts for 30.48%. If it is oxygen, then for **C** ($C_cH_hN_nO_o$) c : h : n : o = 45.71/12 : 10.48/1 : 13.33/14 : 30.48/16 = 3.81 : 10.48 : 0.95 : 1.91 = 4 : 11 : 1 : 2, $C_4H_{11}NO_2$. Let us assume the simplest variant that the empirical formula coincides with the molecular one. Then the compound with such a formula is not aromatic, which means that **C** in the presence of sulfuric acid is not sulfonated, but dehydrated. This allows us to determine the molecular formula **D** - C_4H_9NO. To assemble a saturated six-membered ring (chair conformation) from this overall composition, the N and O atoms in the sp^3 hybridization must be part of the ring. Then, taking into account the molar ratio of **A** and **B**, the equivalence of all hydrogen atoms in their molecules (one signal in the 1H NMR spectrum), it is concluded that **D** is morpholine, A is ammonia, and **B** is ethylene oxide. (intramolecular dehydration of **C** under the action of H$_2$SO$_4$). (0.5 Points for each structure, 2 points in total).
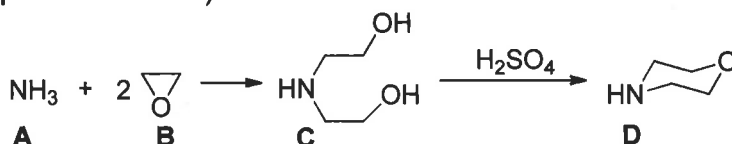

3. **F** is formed by the interaction of **E** with morpholine (**D**). Then, based on the given molecular formula of **F**, the number of carbon atoms in the ketone **E** 12 - 4 = 8 and its molecular formula is C_8H_8O (C_nH_nO), i.e. it's acetophenone. In products **F** and **H**, two multiplets (2×4H) correspond to the fragment of the starting morpholine (C_4H_8NO). The aliphatic part of **F** also contains one more singlet corresponding to an isolated CH$_2$ group. Then in the remainder we have 15 - 8 - 2 = 5 protons, which correspond to the phenyl group (C_6H_5) from acetophenone. Let us sum up the balance of the empirical formula, taking into account the fragments found in the NMR spectrum: $C_{12}H_{15}NOS – C_4H_8NO – CH_2 – C_6H_5 = CS$ – a thiocarbonyl group present in **F** and **H** by condition. **G** is a homologue of **E**, and **H** is a homologue of **F**. Since there is one carbon atom more in **H** than in **F**, the molecular formula of the ketone **G** is $C_9H_{10}O$. Taking into account the absence of singlets in its spectrum, we can

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conclude that this is 1-phenylpropanone. In the aliphatic part of the ^{1}H NMR spectrum of **H**, in addition to morpholine signals, there are two 2H triplets corresponding to the –CH$_2$–CH$_2$– fragment. Now we can write the structure of thioamide **H**. Thus, the length of the side chain is not crucial for the WK reaction to proceed. (0.5 Points for each structures **E** and **G**, 1.25 points each for **F** and **H**, 3.5 points in total).
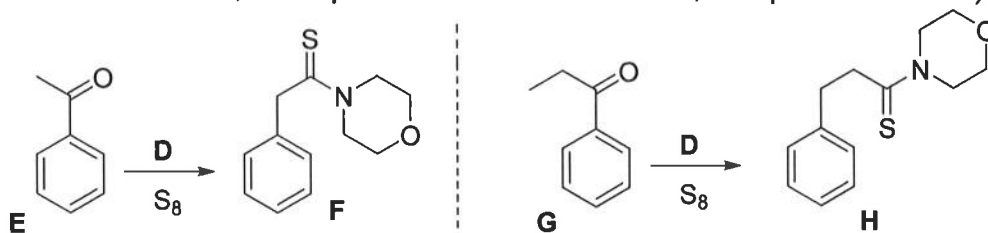

4. Under the action of the Lewis acid on cresol acetate the acetyl group is transferred to the *ortho*-position (it follows from the given structure of the precursor of **X**), that is, the Fries rearrangement proceeds. Further transformations include methylation of the phenolic group in **K** with the formation of **L**, the WK reaction, methylation of the thiocarboxylic acid morpholide followed by the hydrolysis (morpholine is released):
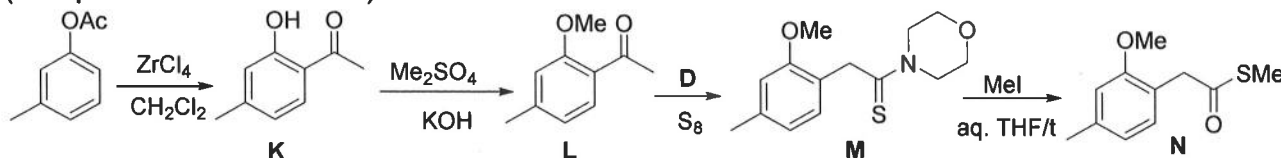

Then the deprotonation and alkylation of the methylene group in thioester **N** is carried out with the participation of C$_x$H$_y$I. Upon comparing the molecular formulas of **N** and **O**, the molecular formula C$_x$H$_y$ could be determined: C$_{15}$H$_{20}$O$_2$S – (C$_{11}$H$_{14}$O$_2$S – 1H) = C$_4$H$_7$; the degree of unsaturation of the iodide C$_4$H$_7$I is equal to 1, that is, it contains one C=C bond or one cycle. The transformation of **O** into **P** is accompanied by the loss of two carbon atoms and one sulfur atom. Demethylation of the methoxy group by the action of boron chloride and subsequent cyclization into lactone **P** occur. This is followed by deprotonation/methylation of the CH at the position adjacent to the carbonyl group forming **Q**. Methyleneation with Tebbe's reagent leads to the formation of **R**. When comparing the structures of **R** and the intermediate product shown in the scheme the structure of C$_4$H$_7$ can be determined:
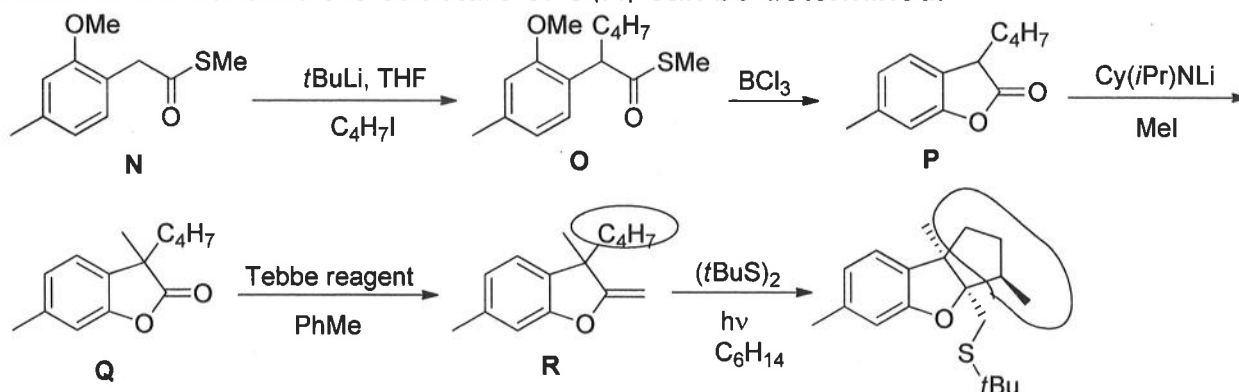
It follows from a comparison of the structures that C$_4$H$_7$ is acyclic and unbranched which means that it should contain one C=C bond. The reaction conditions and the structure of the intermediate product indicate that during the reaction the *t*BuS radical formed in the photolysis of 1,2-di-*tert*-butyl disulfide is added to the C=C bond, the radical intermediate attacks the second C=C bond from C$_4$H$_7$, and hydrogen atom is abstracted from solvent (hexane).

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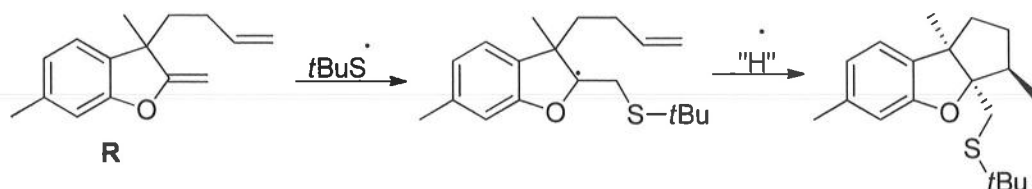
Basing on the empirical formulas of the intermediate product and **X** it follows that upon the reduction the C-S bond is broken under the action of Raney nickel:
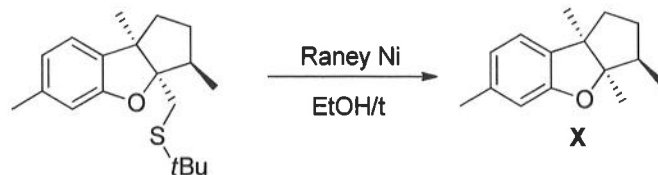

(0.5 Points for each of the structures **K – N, O – R, X**, 0.25 points each for the molecular and structural formulas of iodide, 5 points in total).

5. Configurations of chiral centers: a – *R*, b – *R*, c – *R*. (0.5 Points for each center, 1.5 points in total).
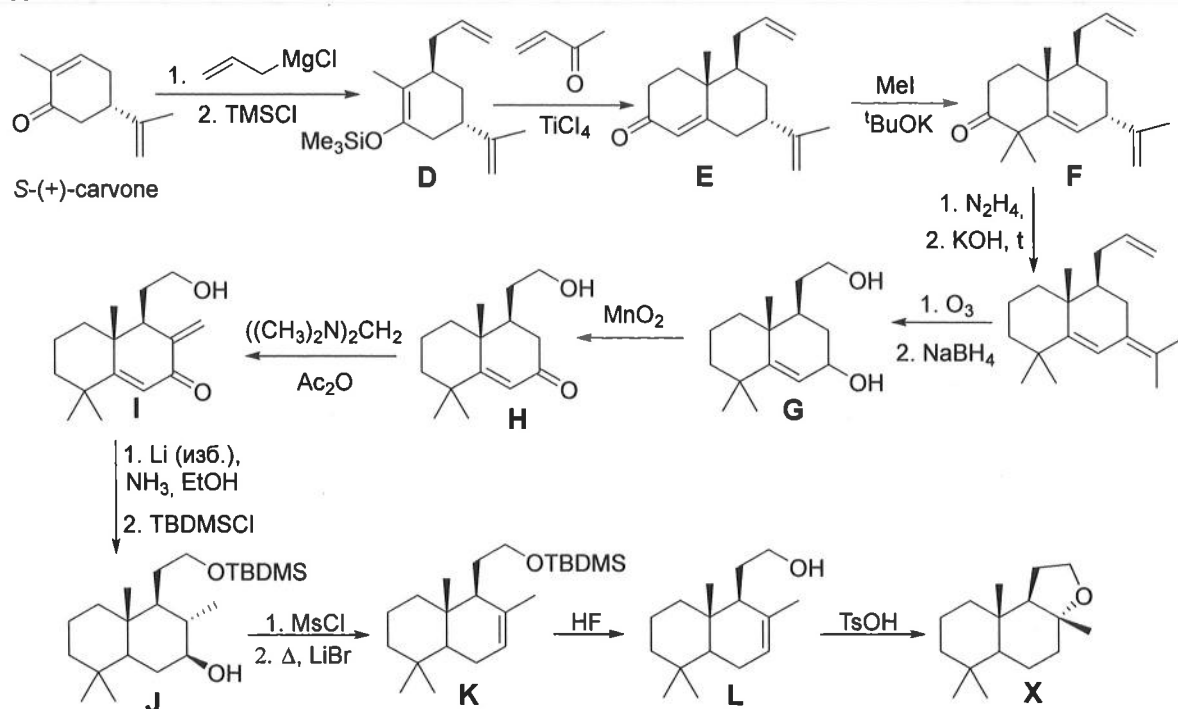

Problem 2 (author Zima A.M.)

1. Let us determine the structure of substance **Y**. The ozonolysis of sclareolide **Y** leads to the cleavage of the double bond with the formation of a carboxyl and acetate group of the compound **A**. Subsequent alkaline hydrolysis gave the compound **B**. Heating in the presence of an acid leads to the closure of the 5-membered lactone **Y**. Then the lactone is reduced to diol **C** by complex aluminum hydride reducing agent. Cyclization by tosyl chloride and a base, which is indicated by the presence of only one oxygen atom in the molecular formula of ambroxide **X**, completes the synthesis (1 point per structures of **A-C, X** and **Y**, 5 points in total).
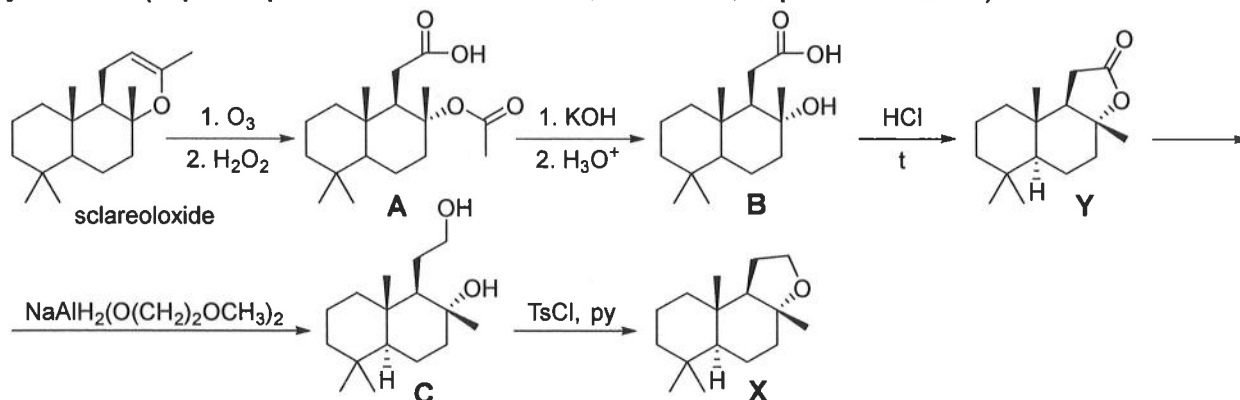
2. At the first stage of ambroxide synthesis from carvone, conjugate addition of allyl magnesium chloride to carvone and trapping of the intermediate enolate gave silyl enol ether **D**. The addition of methyl vinyl ketone to **D** by the Michael reaction (silyl ether in this case uses as a nucleophile) is called the reaction Mukaiyama-Michael. Subsequent the Robinson annulation leads to the formation of **E**. Substance **F** (3 chiral centers) contains two methyl groups, which is also seen from the ambroxide structure. Reduction of the keto group under the conditions of the Wolff-Kishner leads to the formation of a conjugated diene system. From the molecular formula of the product **G** and the conditions of reductive ozonolysis, it can be seen that **G** must contain two hydroxyl groups, and in the next stage, one or both are oxidized with manganese dioxide, which is usually used for the oxidation of allyl hydroxyl groups. Ozonolysis is accompanied by intramolecular aldol condensation, the closure of a 6-

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membered ring, and subsequent reduction of the keto group in the conjugated system.

S-(+)-carvone   1. ⟍MgCl 2. TMSCI   Me₃SiO   **D**   TiCl₄ **E**   MeI ᵗBuOK **F**

1. N₂H₄,
2. KOH, t

((CH₃)₂N)₂CH₂ Ac₂O   **I**   **H**   MnO₂   **G**   1. O₃ 2. NaBH₄

1. Li (изб.),
NH₃, EtOH
2. TBDMSCI

J   OTBDMS 1. MsCl 2. Δ, LiBr   **K**   OTBDMS HF   **L** OH TsOH   **X**

The number of carbon atoms in the molecular formula **G** also confirms our assumption and allows us to finally establish the structures of **G** and **H**. At the next stage enone **H** gave dienone **I** in the Mannich reaction. From the molecular formula **J**, we can conclude that the *tert*-butyldimethylsilyl protecting group is located only on the primary hydroxyl group of the two available, and lithium also reduced all double bonds in compound **I**. Finally, the structure of **J** can be established based on the known structure of ambroxide. Dehydration of **J** (compound **K**) followed by deprotection of the silyl group gave product **L**. Refluxing of **L** in the presence of *p*-toluenesulfonic acid gave the desired ambroxide (1 point per the structures of **D-F**, **H-L**, **G** - 2 points, 10 points in total).

Problem 3 ((author Ilievsky F.)

1. Given the reaction conditions, the first step to obtain **A** includes nitrosation of the amino group, followed by reduction to obtain p-phenylhydrazinesulphonic acid. The next steps involve hydrazone formation with 3-methyl-butanone and subsequent Fischer's indole synthesis to form 5-indolyl sulphonic acid, which is subsequently transformed to its' potassium salt. The fact that mass fraction of carbon in **B** is 47.63% further confirms the fact that **B** contains potassium. Analysis of the reagents for the synthesis of **D** and **C**, using an alkyl-carboxylic acid and a cyclic solfonate, infer that that these steps include N-alkylation, giving rise to structurally similar molecules, containing different N-alkyl moieties. Formation of **D** is N-alkylation via a classical S_N2 reaction of the potassium salt of the indole to give the corresponsive carboxylic acid. Note that the potassium is lost in the form of KBr, to preserve the overall neutrality of the molecule. Obtaining **C** follows a similar trend – the cyclic sulfonate undergoes nucleophilic attack from the indole in order to obtain the potassium sulphonate. Reaction of **C** with the iminium salt gives the conjugated product. The fact that the reaction is performed in acetic anhydride allows for subsequent N-acetylation of the imine. Note that based on mass fraction of **C** in **F**,

there is no potassium in the structure. The presence of polar groups improve the solubility of this cyanine dye, known as Sulfo-Cy5. (**6 structures, 1 point per structure, 6 points in total**)

2. Starting from the brominated diphenylether, the first step is palladium-mediated cross-coupling amination to give the N-azetidine derivative **H**, followed by NBS dibromination.

The reaction with t-BuLi results in formation of the dianion, followed by trans-metalation in the presence of Mg^{2+} which tolerates the phthalic anhydride better to

give the final product **JF549**. (**3 structures, 1 point each, 3 points in total**) The lactone form of **JF549** is also accepted. The one-step synthesis of fluorescein includes the reaction of 2 equivalents of resorcinol and 1 equivalent of phthalic anhydride in the presence of a Lewis acid such as $ZnCl_2$. (**1 point**)
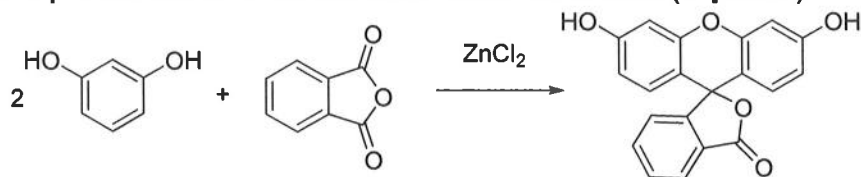
3. Let us analyze the synthesis of BODIPY consists of bridged rings with a tetrazine moiety. Knowing the nucleophilic properties of pyrrole, it is possible to prepare **L** which is the precursor of BODIPY by the reaction of 4-methyl-tetrazine-aldehyde with pyrrole. **K** is the 4-methytetrazine aldehyde in this case. Subsequent oxidation of L and the reaction of formed dipyrromethene with BF_3 ether complex resulted in target BODIPY dye. The final step is inverse electron demand Diels-Alder reaction. Tetrazine reacts as diene with strained cyclic alkyne and molecule of N_2 is eliminated. This type of reactions is known as 'click chemistry' reactions, due to their instantaneous reactivity and high specificity. In fact, the 2022 Nobel Prize in Chemistry was awarded to M. Meldal, K. B. Sharpless and C. Bertozzi for their development of click chemistry and bioorthgonal reactions.
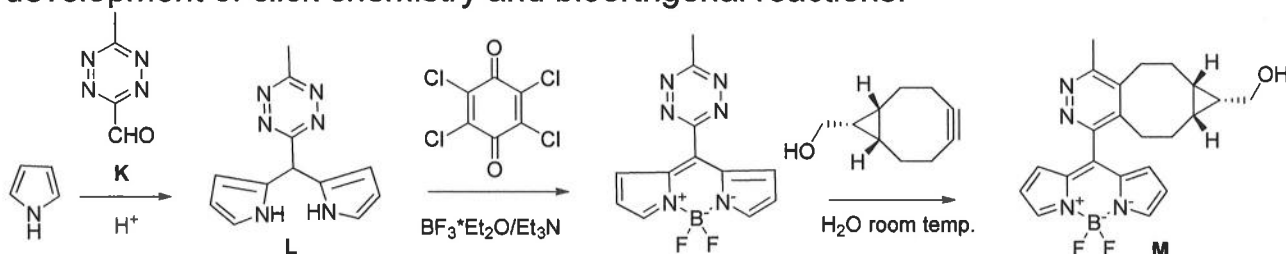
Finally, the structure of aza-BODPIY contains nitrogen in the meso-position. It is reasonable to propose that the second step is the same as for BODIPY synthesis – the cyclization with BF_3. Therefeore, the structure **N** can be decoded easily. This precursor can be prepared by the nitrosation of starting diphenylpyrrole. (**4 structures, 1 point each; 2 reagent conditions, 0.5 points each, 5 point in total**).
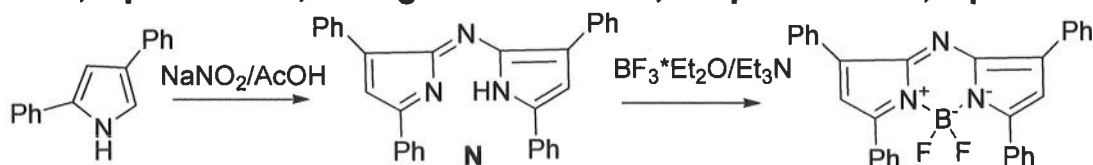
Physical chemistry

Problem 1

1. Content of en in geometric isomers *cis*(*trans*)-[**Me**(en)$_2$Cl$_2$]Cl: $120/(A_{Me} + 226.5) = 0.42$, $A_{Me} = 59.2$ g·mol^{-1} and **Me–Co** (1 point). Green **A** – *trans*-[Co(en)$_2$Cl$_2$]Cl (in the cation Co(en)$_2$Cl$_2^+$ is *i*) (0.5 points); violet **B** – *cis*-[Co(en)$_2$Cl$_2$]Cl (in the cation Co(en)$_2$Cl$_2^+$ there is no *i*) (0.5 points). **2.0 points in total**

2. Formula **D** includes **A**, HCl and H$_2$O, that is **D** – Co(en)$_2$Cl$_3$(HCl)$_a$(H$_2$O)$_b$. At $w_{HCl} = w_{H2O} = 0.1$; $36.5a/(285.7 + 36.5a + 18b) = 18b/(285.7 + 36.5a + 18b)$, then $2a = b$, $36.5a/(285.7 + 72.5a) = 0.1$ and $a = 1$ (0.5 points); $b = 2$ (0.5 points). Taking into account XRD and ^{1}H NMR formula **D** – [Co(en)$_2$Cl$_2$]Cl·H$_5$O$_2$Cl (0.5 points). **1.5 points in total**
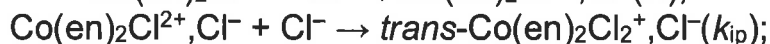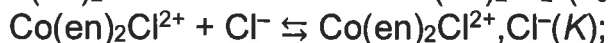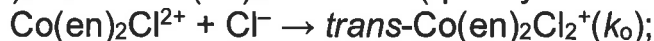
3. At [Cl$^-$] = 0 $k_{obs} = k_o = 3.2 \cdot 10^{-3}$ min^{-1} (0.5 points). Let us substitute [Cl$^-$] into the expression for k_{obs}: $5.5 \cdot 10^{-3} = (3.2 \cdot 10^{-3} + 5 \cdot 10^{-3} K \cdot k_{ip})/(1 + 5 \cdot 10^{-3} K)$ and $7.0 \cdot 10^{-3} = (3.2 \cdot 10^{-3} + 7.5 \cdot 10^{-2} K \cdot k_{ip})/(1 + 7.5 \cdot 10^{-2} K)$. Solving the system of equations $2.3 \cdot 10^{-3} + 2.75 \cdot 10^{-5} K = 5 \cdot 10^{-3} K \cdot k_{ip}$ and $3.8 \cdot 10^{-3} + 5.25 \cdot 10^{-4} K = 7.5 \cdot 10^{-2} K \cdot k_{ip}$, we obtain k_{ip} and K: $k_{ip} = 7.2 \cdot 10^{-3}$ min^{-1} (1.5 points); $K = 273$ l·mol^{-1} (1.5 points). **3.5 points in total**

4. The value k_{obs} corresponds to Brown's data, if K[Cl$^-$] >> 1 at a high concentration of chlorine anion. Then $k_{obs} = k_{ip}$ (0.5 points). At [Cl$^-$] = 0.5 mol·l^{-1} $k_{obs} = (3.2 \cdot 10^{-3} + 7.2 \cdot 10^{-3} \cdot 273.15 \cdot 0.5)/(1 + 273.15 \cdot 0.5) = 7.2 \cdot 10^{-3}$ min^{-1} (0.5 points). At [Cl$^-$] = 1.0 mol·l^{-1} $k_{obs} = (3.2 \cdot 10^{-3} + 7.2 \cdot 10^{-3} \cdot 273.15 \cdot 1.0)/(1 + 273.15 \cdot 1.0) = 7.2 \cdot 10^{-3}$ min^{-1} (0.5 points). (More accurate values $7.17 \cdot 10^{-3}$ and $7.18 \cdot 10^{-3}$ min^{-1} are identical within the Brown's experimental error). **1.5 points in total**

5. For Co(en)$_2$Cl$_2^+$,Cl$^-$ $\Delta G° = [-1 \cdot 1 \cdot (1.602 \cdot 10^{-19}) \cdot 2 \cdot 6.02 \cdot 10^{23}]/ (4 \cdot 3.14 \cdot 32 \cdot 8.854 \cdot 10^{-12} \cdot 6.2 \cdot 10^{-10}) = -7002.5$ J·mol^{-1} (0.5 points), $K = \exp[7002.5/(8.314 \cdot 303.15)] = 15.4$ (0.5 points), which is much less than $K = 273$ of Bosnich, Ingold and Tobe. For Co(en)$_2$Cl^{2+},Cl$^-$ $\Delta G° = -7002.5 \cdot 2 = 14005$ J·mol^{-1} (0.5 points), $K = \exp[14004/(8.314 \cdot 303.15)] = 237$ (0.5 points), which is slightly lower than of Bosnich, Ingold and Tobe. It is possible that, in addition to electrostatic interaction, one should take into account the covalent interaction in calculations. Therefore, it is better to use Co(en)$_2$Cl^{2+},Cl$^-$ in the isomerization mechanism (0.5 points). **2.5 points in total**

6. Taking into account the complete dissociation of Co(en)$_2$Cl$_2^+$ and the formation of the ion pair Co(en)$_2$Cl^{2+},Cl$^-$ it is possible to propose a mechanism similar to that proposed by Bosnich, Ingold and Tobe: **2.5 points in total**

$$cis\text{-}Co(en)_2Cl_2^+ \rightarrow Co(en)_2Cl^{2+} + Cl^- \text{ (quickly and completely)};$$
$$Co(en)_2Cl^{2+} + Cl^- \rightarrow trans\text{-}Co(en)_2Cl_2^+ (k_o);$$
$$Co(en)_2Cl^{2+} + Cl^- \leftrightarrows Co(en)_2Cl^{2+},Cl^- (K);$$
$$Co(en)_2Cl^{2+},Cl^- + Cl^- \rightarrow trans\text{-}Co(en)_2Cl_2^+,Cl^- (k_{ip});$$
$$trans\text{-}Co(en)_2Cl_2^+,Cl^- \rightarrow trans\text{-}Co(en)_2Cl_2^+ + Cl^- (k_1).$$
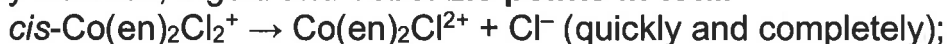
7. 1st stream speed: $r_o = k_o$[Co(en)$_2$Cl^{2+}][Cl$^-$]. Taking into account the stationary approximation k_1[*trans*-Co(en)$_2$Cl$_2^+$,Cl$^-$] = k_{ip}[Co(en)$_2$Cl^{2+},Cl$^-$][Cl$^-$] The speed of the 2nd stream is equal to $r_{ip} = k_1$[*trans*-Co(en)$_2$Cl$_2^+$,Cl$^-$] = k_{ip}[Co(en)$_2$Cl^{2+},Cl$^-$][Cl$^-$]. The total speed is equal to the sum: $r = r_o + r_{ip} = \{k_o$[Co(en)$_2$Cl^{2+}][Cl$^-$] + k_{ip}[Co(en)$_2$Cl^{2+},Cl$^-$]$\}$[Cl$^-$]. If Co(en)$_2$Cl$_2^+$ completely dissociates, then C(Co(en)$_2$Cl$_2^+$) = C(Co(en)$_2$Cl^{2+}) = $= C$ (mol·l^{-1}). C = [Co(en)$_2$Cl^{2+}] + [Co(en)$_2$Cl^{2+},Cl$^-$] = [Co(en)$_2$Cl^{2+}](1 + K[Cl$^-$]). Molar fractions: α(Co(en)$_2$Cl^{2+}) = $1/(1 + K$[Cl$^-$]); α(Co(en)$_2$Cl^{2+},Cl$^-$) = K[Cl$^-$]$/(1 + K$[Cl$^-$])
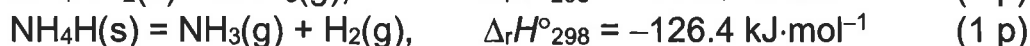
(0.5 points). The concentrations in the equation for r are $[C](i) = C \cdot \alpha(i)$. After substituting them into the velocity equation: $r = (k_o + k_{ip}K[Cl^-]) \cdot C \cdot [Cl^-]/(1 + K[Cl])$ (0.5 points), and $k_{obs} = (k_o + k_{ip} \cdot K[Cl^-])/(1 + K[Cl^-])$ (0.5 points). The same expression is proposed in the mechanism of Bosnich, Ingold and Tobe. **1.5 points in total**

Problem 2 (author Borschevsky A. Ya.)

1. The ionic radii of NH_4^+ and Rb^+ are so close, that according to (1) the lattice energies of each pair of salts are almost the same. By definition, $L_0(NH_4X) = \Delta_r H°(0\ K)$ of the reaction $NH_4X(s) = NH_4^+(g) + X^-(g)$, and $L_{298} = L_0 - 2RT$. This implies that the difference $\Delta_r H°$ for the salts should be close to the difference $\Delta_f H°(NH_4^+, g) - \Delta_f H°(Rb^+, g)$. From the data in Table 3 it is easy to verify that this constant value is equal to 128 kJ·mol^{-1} (**2 points**).

2. a) Adding to $\Delta_f H°$ of rubidium compounds from the first three columns of Table 3 128 kJ·mol^{-1} we obtain the desired values of $\Delta_f H°$ for similar ammonium compounds: -290.4 ($NH_4^+OH^-$), $+18.4$ ($NH_4^+NH_2^-$), $+80.3$ ($NH_4^+H^-$) kJ·mol^{-1} (0.5 p); **b)** Unstable with respect to the elements are compounds with a positive $\Delta_f H°$ (0.5 p) (**1 point in total**).

3. The most probable decomposition reactions: (**3 points in total**)

$NH_4OH(s) = NH_3 \cdot H_2O(l)$, $\Delta_r H°_{298} = -70.8$ kJ·mol^{-1} (1 p)
$NH_4NH_2(s) = 2NH_3(g)$, $\Delta_r H°_{298} = -110.6$ kJ·mol^{-1} (1 p)
$NH_4H(s) = NH_3(g) + H_2(g)$, $\Delta_r H°_{298} = -126.4$ kJ·mol^{-1} (1 p)

4. a) Rectangular parallelepiped with different edge lengths (1 p); **b)** Cell with nodes at the vertices of the box and the centers of all its faces (1 p); **c)** Molar volume $V_m(NH_3 \cdot H_2O) = a \cdot b \cdot c \cdot N_A/4 = 451 \cdot 558.7 \cdot 970 \cdot 10^{-36} \cdot 6.022 \cdot 10^{23}/4 = 0.368 \cdot 10^{-4}$ m^3·mol^{-1} = 36.8 cm^3·mol^{-1}. Volume change $\Delta_r V_m = 27.8 - 36.8 = -9$ cm^3·mol^{-1} (1 p) (**3 points in total**).

5. If $\Delta_r S° = 0$ and the enthalpy of product formation does not depend on temperature, then $\Delta_r G° = \Delta_r H° = -290.4 + 368.9 = 78.5$ kJ·mol^{-1} (**0.5 points**).

6. At constant temperature $d(\Delta G) = \Delta V_m dP$, $\Delta(\Delta G) = \Delta V_m \Delta P$. The phase $NH_4^+OH^-(s)$ becomes stable compared to $NH_3 \cdot H_2O(s)$, when ΔG of conversion $NH_3 \cdot H_2O(s) = NH_4^+OH^-(s)$ decreases by 78.5 kJ·mol^{-1} with increasing pressure. From here $\Delta P = (-78.5 \cdot 10^3\ J)/(-9 \cdot 10^{-6}\ m^3) = 8.72 \cdot 10^9$ Pa $= 8.72 \cdot 10^4$ bar $= 86060$ atm (**3 points**).

7. Water and ammonia are present on the distant massive planets – Jupiter, Saturn and Uranus. At greater depths, high pressure can stabilize the ionic phase $NH_4^+OH^-(s)$ (0.33 p for each planet) (**1 point in total**).

8. a) $\Delta_f H°(NH_4, s) = \Delta_f H°(NH_4^+, g) = 619 - 500 = 119$ kJ·mol^{-1} (0.5 p); **b)** $\Delta_r H° = -46.1 - 119 = -165$ kJ·mol^{-1} (0.5 p); The negative sign implies that ammonium metal is unstable with respect to decomposition into gases; **c)** Will not change, since taking into account the entropy factor when calculating the Gibbs energy of the reaction will make the value even more negative (0.5 p), (**1.5 points in total**).

Problem 3 (author Karpushkin E. A.)

1. Quantum energy of the exciting light is $\dfrac{hc}{\lambda} = \dfrac{6.63 \cdot 10^{-34} \times 3 \cdot 10^8}{365 \cdot 10^{-9}} = 5.45 \cdot 10^{-19}$ J; this energy is just what is gained by CNP during the transition into the excited state.

Quantum energy of the emitted light is $\frac{hc}{\lambda} = \frac{6.63 \cdot 10^{-34} \times 3 \cdot 10^8}{550 \cdot 10^{-9}} = 3.62 \cdot 10^{-19}$ J. Hence, the energy of emitted light is 3.62/5.45 = 66.4% of this of the absorbed light, the remaining 33.6% being lost in nonradiative processes (**2 points**).

2. Using the data in the task, the value of $F(c_{Hg} = 0)/F(c_{Hg})$ in the Stern–Volmer equation can be calculated:

c_{Hg}, nmol·L^{-1}	F, arb.un.	$F(c_{Hg} = 0)/F(c_{Hg})$
0	12000	1.000
10	11483	1.045
30	10573	1.135
60	9449	1.270
90	8541	1.405

It is to be seen that this parameter is changed linearly with mercury concentration in the solution, the increase being 0.045 per 10 nmol·L^{-1} of mercury. Then, from the Stern–Volmer equation, $K_{SV} = 4.5 \cdot 10^6$ L·mol^{-1} (**2 points**).

3. If accuracy of determination of F is of 5%, the highest intensity of fluorescence reliably different from the value in the absence of mercury (12000) is 12000·0.95 = 11400. Then from the Stern–Volmer equation, $c_{Hg} = \frac{1}{K_{SV}}\left(\frac{F(c_{Hg}=0)}{F(c_{Hg})} - 1\right) = \frac{1}{4.5 \cdot 10^6}\left(\frac{12000}{11400} - 1\right) = 1.17 \cdot 10^{-8}$ mol·L^{-1} or 11.7 nmol·L^{-1} (**2 points**).

4. Decrease in the intensity of the exciting light of 40% corresponds to the absorbance $A = -\lg\frac{0.6}{1} = 0.222$. The emitting volume of the specimen is in the center of the cell; therefore, this absorbance corresponds to the optical path length of 1 cm. The iron(III) concentration is then $c(\text{Fe}) = \frac{A}{\varepsilon l} = \frac{0.222}{2000 \cdot 1} = 1.11 \cdot 10^{-4}$ mol·L^{-1} (**3 points**).

5. The calculation as above gives the solution absorbance $A = -\lg\frac{0.97}{1} = 0.013$ and the iron(III) concentration $c(\text{Fe}) = \frac{A}{\varepsilon l} = \frac{0.013}{2000 \cdot 1} = 6.5 \cdot 10^{-6}$ mol·L^{-1}. This is the concentration of free iron(III) ions, not bound in the colorless complex. According to the definition of the stability constant and accounting for total iron concentration of $1.11 \cdot 10^{-4}$ mol·L^{-1}, $10^{-8.5} = \frac{(1.11 \cdot 10^{-4} - 6.5 \cdot 10^{-6})}{6.5 \cdot 10^{-6} \cdot 10^{14-3.8} \cdot [\text{Citr}]}$ and [Citr] = 0.32 mol·L^{-1}. In comparison with this value, the amount of citrate ions in the complex is negligible, and the amount of citric acid in 100 mL of the solution is 0.032 mol (**3 points**).

6. Since the fluorescence intensity was somewhat lowered even upon the iron binding into the complex (12000·0.97 = 11640), the highest intensity of fluorescence still reliably evidencing the presence of mercury(II) possibly in the presence of iron(III) is 11640·0.95 = 11058. From the Stern–Volmer equation, this intensity corresponds to mercury(II) concentration $c_{Hg} = \frac{1}{4.5 \cdot 10^6}\left(\frac{12000}{11058} - 1\right) = 1.89 \cdot 10^{-8}$ mol·L^{-1} or 18.9 nmol·L^{-1} (**2 points**).

7. $4\text{Hg}^{2+} + 4\text{F}^- + 2\text{H}_2\text{O} \rightarrow 2\text{Hg}_2\text{F}_2 + 4\text{H}^+ + \text{O}_2$ (**1 point**).

Inorganic chemistry

Problem 1 (author M.S. Likhanov)

1. From the above dependence for $n = 1.6305$ we obtain $d = (1.6305 - 1.2078)/0.1152 = 3.67$ g/cm^3. From the above list of minerals, minerals with a lower density will float on the surface of the Clerici solution: garnet (3.48 g/cm^3), diamond (3.55 g/cm^3) and quartz (2.62 g/cm^3). Mirabilite will dissolve in Clerici's solution. (0.5 points for calculation, 0.2 points for each correct choice, 0 points for choosing all minerals. 1.1 points in total)

2. Since the inversion center is located in the center of the cube, the composition of the entire elementary cell can be expressed as the composition of the octant. The composition of the octant is M_4O_6, hence the gross formula of the oxide is M_2O_3. The composition of the entire unit cell is $8M_4O_6$, therefore the number of formula units $Z(M_2O_3) = 16$. (0.5 points for the calculation, 0.2 points for the gross composition, 0.2 points for the number of formula units. 0.9 points in total).

3. Clerici's solution is a mixture of thallium(+1) formate and malonate. Today, this solution is no longer used due to the high toxicity of thallium. Thallium is also indicated by the properties of an unknown metal described in the problem - insoluble black sulfide, the possibility of oxidation to a higher unstable oxidation state. The higher oxide oxidizes hydrochloric acid with the release of chlorine, and when the resulting solution is diluted, a white precipitate forms – it is obvious that this is thallium(+1) chloride. Thus, **M - Tl**.

Let us write down the equations of the mentioned reactions. Precipitation of sulfide:
$2HCOOTl + (NH_4)_2S = Tl_2S + 2(NH_4)HCOO$ (0.5 points), **A – Tl_2S**.
Formation of thallium(+3) oxide:
$2TlNO_3 + 2Cl_2 + 6KOH = Tl_2O_3 + 2KNO_3 + 4KCl + 3H_2O$ (0.5 points), **B – Tl_2O_3**.
Thallium oxide Tl_2O_3 oxidizes hydrochloric acid to form a complex salt solution:
$Tl_2O_3 + 8HCl = 2H[TlCl_2] + 2Cl_2 + 3H_2O$ (1 point, 0.5 points in case of indicating TlCl as a product)
When diluted with water, the complex is also destroyed by the formation of water-insoluble thallium(+1) chloride: $H[TlCl_2] =H_2O= TlCl + HCl$, **C – TlCl**.
When TlCl is oxidized with chlorine, a higher chloride is formed: $TlCl + Cl_2 = TlCl_3$, **D – $TlCl_3$**. The two chlorides mutually form substance **E**, the composition of which is Tl_2Cl_3 ($\omega(Cl) = 20.7$ %). $3TlCl + TlCl_3 = 2Tl_2Cl_3$ (0.5 points)
(0.5 points for each unknown substance, 3 points in total, 2.5 points for reactions. 5.5 points in total)

4. In the composition of Tl_2Cl_3, thallium exists in two oxidation states +1 and +3; therefore, it is correct to write the composition of Tl_2Cl_3 as double Tl_4Cl_6 or $Tl_3[TlCl_6]$ (0.5 points). In this chloride, Tl^{+3} is in an octahedral environment, that is, it forms the $[TlCl_6]^{3-}$ anion. Tl_4Cl_6 dissociates into ions in water: $Tl_3[TlCl_6] = 3Tl^+ + [TlCl_6]^{3-}$
or $Tl_3[TlCl_6] + 18H_2O = 3[Tl(H_2O)_6]^{3+} + [TlCl_6]^{3-}$ (0.5 points).

5. The electrical conductivity of a salt solution depends on the number of particles into which the salt dissociates. Then, the salts can be placed in the next row.
$$NaCl < CaCl_2 < Tl_3[TlCl_6] \text{ (0.5 points)}$$

6. The reaction for Tl_4Cl_6 obtaining using ozone in $POCl_3$ as an oxidizing agent can be written as follows. $4TlCl + O_3 + POCl_3 = Tl_4Cl_6 + O_2 + PO_2Cl$ (1 point)
Let us find the molar mass of another oxidizing gas **F**, $M(F) = 3.88 \cdot 22.4 = 87$ g/mol (0.5 points). Most likely, the unknown gas contains chlorine, then its composition Cl_2O is chlorine(+1) oxide, indeed, a brownish-yellow poisonous gas (0.5 points).

10

G consists of molecules in which thallium is located in an octahedron. Since the molecule has only 2 optical isomers, it can be assumed that thallium is surrounded by three bidentate ligands. Such ligands can be $PO_2Cl_2^-$ anions (phosphorus does not change the oxidation state), since it is known that the solvent also reacts. The composition of **G** – $Tl(PO_2Cl_2)_3$ is confirmed by the reduced mass fraction of phosphorus (0.5 points for the composition, 0.5 points for the calculation). Synthesis of **G**: $TlCl + 3POCl_3 + 3Cl_2O = Tl(PO_2Cl_2)_3 + 5Cl_2$ (1 point)
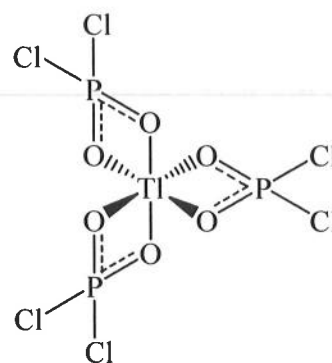
Structure of **G** (1 point)

7.   One of the ways to synthesize Cl_2O is to pass chlorine over freshly precipitated dry mercury(+2) oxide: $3HgO + 2Cl_2 = Cl_2O + Hg_3O_2Cl_2$ (1 point)

Problem 2 (Khvaljuk V.N.)

1.   Composition of **A** – $FeC_2O_4 \cdot 2H_2O$.

Molar mass $FeC_2O_4 \cdot 2H_2O$ is equal to 180 g/mol. Mass loss on 20 % for 1 mol **A** is equal to $180 \cdot 0.20 = 36$ g. It corresponds to mass of 2 mol of water.

Equation of the reaction conversion **A** to **B**: $FeC_2O_4 \cdot 2H_2O = FeC_2O_4 + 2H_2O$.

Substance **B** – FeC_2O_4.   (1 pt. for **A**, **B**, equation, total 3 pt.)

2. On the second stage the decomposition of 1 mol **B** (144 g) leads to $144 \cdot 0.535 = 77$ g of substance **C**. Obviously, all iron atoms (1 mol or 56 g) from **B** remained in the solid phase (substance **C**), but carbon and oxygen atoms could pass into gaseous substances (CO and CO_2). The share of other atoms (except iron) in 1 mol of substance **C** accounts for $(77 - 56) = 21$ g. Taking into account the high affinity of iron for oxygen, we can assume that these are oxygen atoms. The amount of [O] atoms will be approximately equal to $21/16 = 1.32$ mol. In substance **C**, 1 mole of [Fe] accounts for 1.32 moles of [O], which approximately corresponds to the stoichiometry of Fe_3O_4.

The equation of decomposition **B**: $3FeC_2O_4 = Fe_3O_4 + 4CO + 2CO_2$.

Substance **C** – Fe_3O_4.   (1 pt. for **C**, 1 pt. for equation)

There are no options for any reaction between FeC_2O_4 and CO_2. Taking into account the high reducing ability of CO at high temperature, it seems more probable that a reaction between FeC_2O_4 and CO occurs. In this case, the essence of the reaction can be reduced to the conversion of CO into CO_2: $[O] + CO = CO_2$.

From 1 mol **B** (144 g) it is formed about $144 \cdot 0.42 = 60.5$ g of substance **D**, from which 56 g related to [Fe] atoms and $(60.5 - 56) = 4.5$ g to other atoms. According to condition, that **D** is binary substance, then such atoms could be only [C] or [O] (there are no other atoms in the system).

In the case [O] we have $4.5/16 = 0.30$ and in **D** 0.30 mol [O] related to 1 mol [Fe], what pass to the composition Fe_3O. In the case [C] we have $4.5/12 = 0.375$ and in **D** 0.375 mol [C] related to 1 mol [Fe], that approximately corresponds to stoichiometry Fe_3C. The equation of reaction **B**: $3FeC_2O_4 + 2CO = Fe_3C + 7CO_2$.

Substance **D** – Fe_3C.   (1 pt. for **D**, 1 pt. for equation, total 4 pt.)

3. The reactions pass on the third stage: $Fe_3C = 3Fe + C$.

CO perfectly suit for transformation of **C** into final pyrophoric product (FeO):

$$Fe_3O_4 + CO = 3FeO + CO_2.$$
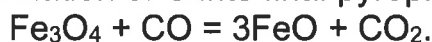
Substance **E** – FeO.   (1 pt. for **E**, 1 pt. for each equation, total 3 pt.)

4. In case of iron deficiency, the formula will be $Fe_{1-x}O$, in case of excess of oxygen

– FeO_{1+y}. $M(Fe) = 55.85$ g/mol. $M(O) = 16.00$ g/mol.

For the first case: $\dfrac{16.00}{55.85\cdot(1-x) + 16.00} = 0.2336$.

Solving this equation, we get $x = 0.060$ and the formula is $Fe_{0,940}O$.

For the second case: $\dfrac{16.00\cdot(1 + y)}{55.85 + 16.00\cdot(1 + y)} = 0.2336$.

Solving this equation, we get $y = 0,064$ and the formula is $FeO_{1.064}$. ($FeO_{1/0.940} = FeO_{1.064}$)   for each formula, total 2 pt.)

5. To establish the true formula, we calculate the density of a substance for two compositions: $Fe_{0.940}O$ and $FeO_{1.064}$. In NaCl structure, one unit cell has 4 formula units.

$$M(Fe_{0,940}O) = 55.85\cdot0.940 + 1\cdot16.00 = 68.50 \text{ g/mol};$$
$$M(FeO_{1,064}) = 1\cdot55.85 + 16.00\cdot1.064 = 72.87 \text{ g/mol}.$$

Theoretical density of $Fe_{0.940}O$ is equal to:

$$\frac{4\cdot M(Fe_{0.940}O)}{a^3\cdot N_A} = \frac{4\cdot68.50}{(4.307\cdot10^{-8})^3\cdot6.02\cdot10^{23}} = 5.70 \text{ g/cm}^3.$$

Theoretical density of $FeO_{1.064}$ is equal to:

$$\frac{4\cdot M(FeO_{1.064})}{a^3\cdot N_A} = \frac{4\cdot72.87}{(4.307\cdot10^{-8})^3\cdot6.02\cdot10^{23}} = 6.06 \text{ g/cm}^3.$$

The first value coincides with the experimental density given in the condition. This means that the true formula of the sample is $Fe_{0.940}O$ (iron deficiency).

(1 pt. for each value, 1 pt. for final formula, total 3 pt.)

Problem 3 (author Shwartzman V.E.)

1. Based on the electrical neutrality in the equation $M^{n+} + (n-2)\bar{e} = M^{(n-1)+}$ we have $n - n +2 = n - 1$ and $n = 3$ (0.5 point). Number of unpaired electrons ($\bar{e}$) $X = 2S$ we find from $\mu = [2S (2S + 2)]^{1/2}$; $4.90^2 = (X + 2) X$; $X = 4\bar{e}$ (0.5 point). The number of valence electrons in the case $t_{2g}^3 e_g^1$ configuration is equal to $n + X = 3 + 4 = 7\bar{e}$ (0.25 point) and metal of Mn subgroup, and in the case $t_{2g}^4 e_g^2$ is equal to $n + X = 3 + 6 = 9\bar{e}$ (0.25 point) and metal of Co subgroup.

A slightly pinkish precipitate is metal hydroxide $M(OH)_2$, formed by the reaction: $M^{2+} + 2OH^- = M(OH)_2$, and the amount of moles of hydroxide $v_1 = 4.45 / (A_M + 34)$. Over time, after the loss of H_2O, there should have remained $\Delta m = 4.45 - 0.45 = 4.00$ g of precipitate, what less, than $m = 4.40$ g of brown precipitate, containing a stabilizing group MO. This is possible if there is oxidation by oxygen in the air with the formation of $MO_z(OH)_{3-2z}$ with ox. st. of metal +3, the amount of moles of which $v_2 = 4.40 / (A_M + 51 - 18z)$. As during reaction $v_2 = v_1$ we have $4.45 / (A_M + 34) = 4.40 / (A_M + 51 - 18z)$ and $A_M = 1602z - 1547$ (2 points). When $z = 1$ $A_M = 55$ g/mol and metal M – Mn (0.5 point).   Total 4 points.

2. It is known Mn^{3+} oxidizes even H_2O in acidic media, what one can prove by calculating E_3^0 for reaction: $4Mn^{3+} + 2H_2O = 4Mn^{2+} + O_2 + 4H^+$. Taking into account that $Mn^{3+} + \bar{e} = Mn^{2+}$ ($E_1^0 =1.52$ V) and $O_2 + 4H^+ +4\bar{e} = 2H_2O$ ($E_2^0 =1.23$ V), we get $E_3^0 = E_1^0 - E_2^0 = 1.52 - 1.23 = 0.29$ (V) >0, oxidation in progress (1 point). The value of the Gibbs energy for the reaction of water oxidation by the complex $4MnL_x^{(3-x)+} + 2H_2O = 4MnL_x^{(2-x)+} + O_2 + 4H^+$ (ΔG^0) related to the Gibbs energies of complexation reactions $Mn^{3+} + xL^- = MnL_x^{(3-x)+}$ ($\Delta G_x^0 = -RT\ln\beta_x$); $Mn^{2+} + xL^- = MnL_x^{(2-x)+}$ ($\Delta G_y^0 = -RT\ln\beta_y$) and oxidation reaction $4Mn^{3+} + 2H_2O = 4Mn^{2+} +O_2 + 4H^+$ ($\Delta G_3^0= -4FE_3^0$) by equation

$\Delta G^0 =. 4\Delta G_y^0 + \Delta G_3^0 - 4\Delta G_x^0$. To stabilize Mn^{3+} in solution it is necessary, that $\Delta G^0 > 0$, and minimum value of $ln\beta_x - ln\beta_y$ will when $\Delta G^0 = 0$. Then $4\Delta G_x^0 - 4\Delta G_y^0 = \Delta G_3^0$ and $ln\beta_x - ln\beta_y = FE_3^0/RT = (96485 \cdot 0.29)/(8.314 \cdot 298.15) = 11.29$. (1 point). Total 2 points.

3. Black crystals **B** have composition $[Mn_aO_b(CH_3COO)_{2a}Py_a]$ and the amount of mole $v_1 = 3.01/0.60 \cdot 0.65 \cdot (252a+16b)$. Initial acetate $Mn(CH_3COO)_2 \cdot 4H_2O$ was taken in amount $v_2 = 7.35/245 = 0.03$ mole. For reaction of complex **B** formation $Mn(CH_3COO)_2 \cdot 4H_2O \rightarrow [Mn_aO_b(CH_3COO)_{2a}Py_a]$ $7.72/ (252a+16b) = 0.03$ and $3b = a$. When **b** = 1 (0.5point) **a** = 3 (0.5 point). Formula $A^+ - [Mn_3O(CH_3COO)_6Py_3]^+$ (1 point), ox. st. Mn: +3 (0.5 point); molecular formula of complex **B** – $[Mn_3O(CH_3COO)_6Py_3]$ (0.5 point), ox. st. of manganese – $2Mn^{+3}$ and $1Mn^{+2}$ (0.5 point). Ionic equation of formation reaction $[Mn_3O(CH_3COO)_6Py_3]^+$ in brown solution растворе (0.5 point):

$2Mn^{+2} + 15Py + MnO_4^- + 16CH_3COO^- + 14CH_3COOH = 5[Mn_3O(CH_3COO)_6Py_3]^+ + 7H_2O$

If angles in Mn_3O about $120°$, and bond distances $1.82Å$ and $2.15Å$, then 3 Mn atoms located at the vertices of an isosceles triangle. One of the bonds is longer because the radius $Mn^{+2} > Mn^{+3}$. Structural formula of Mn_3O:
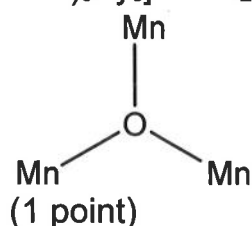
Total 5 points

(1 point)

4. In 100 g D^+: $v(Mn) : v(N) : v(O) = 19.4/55 : 7.41/14 : 22.6/16 = 0.353 : 0.529 : 1.41 = 1 : 1.5 : 4$. As the whole Py replaced by bipy, then the amount of moles N must be even, it is possible for $v(Mn) : v(N) : v(O) = 4 : 6 : 16$. Then group $Mn_dO_2 - Mn_4O_2$ (1 point), and 14 O included in $7CH_3COO^-$ and formula $D^+ - [Mn_4O_2(CH_3COO)_7bipy_3]^+$ (0.25 point), ox. st. $4Mn^{+3}$ (0.25 point). In the case of **E**: $v(Mn) : v(N) : v(O) = 20.5/55 : 7.82/14 : 20.9/16 = 0.373 : 0.559 : 1.31 = 1 : 1.5 : 3.5 = 4 : 6 : 14$. Based on this, the molecular formula $E - [Mn_4O_2(CH_3COO)_6bipy_3]$ (0.25 point), ox. st. $2Mn^{+3}$ and $2Mn^{+2}$ (0.25 point). Total 2 points

5. Taking into account that the base in both complexes Mn_2O_2 is rhomb with $l_{M-O} = 1.88$ Å and angles MnOMn $97°$ и OMnO $83°$. In $[Mn_4O_2(CH_3COO)_6bipy_3]$ there are 2 bonds else with $l_{M-O} = 2.10$ Å and angle O...OMn $180°$ in rhomb plane, therefore center of inversion is present, and in complex $[Mn_4O_2(CH_3COO)_7bipy_3]^+$ there are 2 bonds else with $l_{M-O} = 2.10$ Å and angle O...OM $130°$ not in the rhomb plane, therefor inversion center is absent (on 1 point for every structure). Total 2 points

$[Mn_4O_2(CH_3COO)_7bipy_3]^+$	$[Mn_4O_2(CH_3COO)_6bipy_3]$
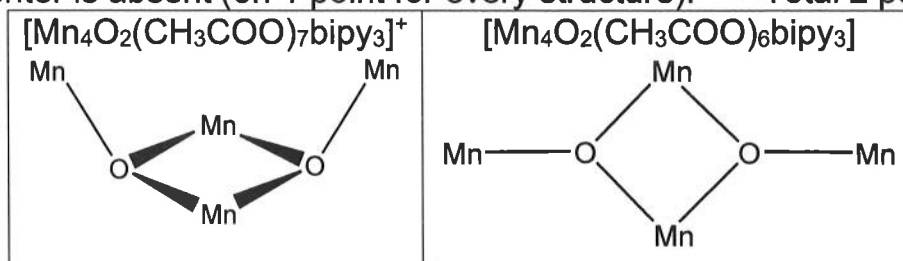
Life sciences and polymers

Problem 1 (author Garifullin B.N.)

1.   The difference between the pK values of H_3A is high, thus only two ions (H_2A^- и HA_2^-) would be found in an aqueous solution with the pH value close to that of pK_{a2}. The ratio between ions would be by one order shifted towards HA_2^- (1 point):

$$pH = pK_{a2} + \lg\left(\frac{[HA^{2-}]}{[H_2A^-]}\right), \text{ thus } \lg\left(\frac{[HA^{2-}]}{[H_2A^-]}\right) = 8 - 7 = 1$$

2.   The entire $H_3A \rightarrow B$ pathway involves eight compounds, four of which (including the starting one) have the same oxidation state (OS) of the element **X**. Since the OS of **X** changes by the same absolute value at each step, the only possible set of their positions is (underlined): $\underline{1} \rightarrow 2 \rightarrow \underline{3} \rightarrow 4 \rightarrow \underline{5} \rightarrow 6 \rightarrow \underline{7} \rightarrow 8$

The variant with two intermediates between compounds with the same OS of **X** (e.g. the fragment $\underline{1} \rightarrow 2 \rightarrow 3 \rightarrow \underline{4}$) is invalid, since it is impossible to compose a cycle using three iterations of two actions (subtraction and addition of the same number) to return to the initial state. With due account for possible OS change (+2 or -2), one can put forward two marginal variants of OS changes (n is OS of **X** in H_3A):

The equations matching the above variants are: $8 \cdot n + 8 = 32$ (1) и $8 \cdot n - 8 = 32$ (2) with the solutions of 3 and 5, respectively. Besides, there are variants with a sole intermediate integer n as the four times repeating OS; an example ($n=4$) is given hereunder:
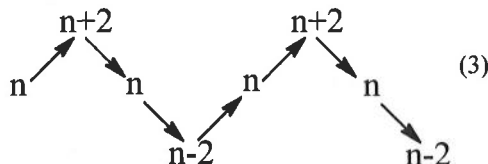
Thus, **X** in H_3A can have three variants of OS: +3, +4, or +5 (0.5 point for each OS, 1.5 in total).

3.   Since odd OS values are typical of **X**, only +3 and +5 are left under consideration. The values can also include +1 and +7, depending on the scheme. Groups 15 and 17 of the Periodic table of elements are thus left under consideration (0.75 point for each group, 1.5 point in total).

4.   The total number of atoms in **C** and **D** equals 11 and 12, respectively. Besides, if ΔM is the difference in molecular masses of **D** and **C**, then:

$$\frac{A_X}{\left(\frac{A_X}{0.6141} + \Delta M\right)} = 0.5429, \text{ and } \Delta M = \frac{A_X}{4.68}.$$

Since **C** and **D** are adjacent to each other on the scheme, the absolute difference in their OS values of **X** equals 2. One atom of an unknown element (with the OS value of either +2 or -2) typical of organic acids must be incorporated upon the **C** $\rightarrow$ **D** (or **D** $\rightarrow$ **C**) transformation to meet the requirement of electroneutrality. Close inspection of the elements present in groups 15 and 17 of the Periodic table suggest only one reasonable combination of arsenic ($A_r = 74.92$) as **X** and oxygen ($\Delta M = 16.00$ g/mol). With an account for the total number of atoms and the residual molecular mass, one can the formulae of the organoelement acids as C_2H_7AsO (**C**) и $C_2H_7AsO_2$ (**D**, cacodylic acid) with the corresponding structures (1.5 point each, 3 points in total):

$$H_3C-\underset{\underset{CH_3}{|}}{As}-OH \quad \mathbf{C}$$

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{O}{\underset{||}{As}}}-OH \quad \mathbf{D}$$

5. The residual molecular mass of **B** after subtracting the atomic mass of As equals 45.0 g/mol, thus suggesting **B** as trimethylarsine, $(CH_3)_3As$, with due account for methyl groups present in **C** и **D**,. Since the relative electronegativity of As is lower than that of carbon, the OS of As in **B** is +3. Thus, the OS values of As change along the pathway as suggested in variant (2) in i. 2. The tribasic acid **H₃A**, containing one As atom with the OS value of +5 and found in sea water, is unambiguously an inorganic compound. It is orthoarsenic acid, H_3AsO_4.

The information about the number of enzymes in the metabolic pathway suggests that there are some repeated reactions (methylation and oxidation/reduction or their combination catalyzed by a sole enzyme) upon the transformation of **H₃A** into **B**. The location of 3 compounds can decided with an account for the stepwise increase in the number of methyl groups: $H_3AsO_4 \rightarrow 2 \rightarrow \underline{3} \rightarrow 4 \rightarrow C_2H_7AsO_2$ (**D**) $\rightarrow 6 \rightarrow \underline{7} \rightarrow (CH_3)_3As$

The structures $\underline{3}$ and $\underline{7}$ are found similarly (the number of methyl groups; OS of As +5):

$$H_3C-\underset{\underset{OH}{|}}{\overset{O}{\underset{||}{As}}}-OH \quad (3) \qquad H_3C-\underset{\underset{CH_3}{|}}{\overset{O}{\underset{||}{As}}}-CH_3 \quad (7)$$
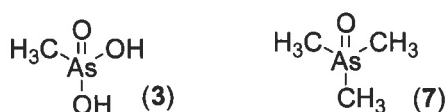
The similarity of the **H₃A**→2 and 3→4 steps with the **D**→**C** reaction finally allows deciphering the entire scheme (arcR is arsenate reductase, and arcM – is arsenite methyltransferase) (1 point for each of **H₃A** and **B**, 0.25 point for each of the rest structures, 3 points in total):
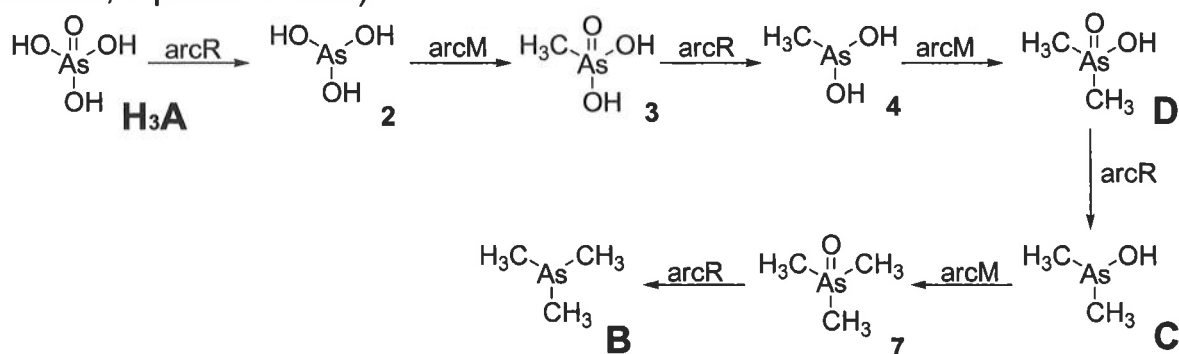

6. Orthoarsenic and orthophosphorus (H_3PO_4) acids are very similar with respect to their physical dimensions and values of acidity constants, the metabolites of the latter playing the key role in various vitally important biochemical processes. Thus, cells must be equipped with an <u>ionic</u> channel to transport H_3PO_4 (mostly in the form of hydrogen phosphate ion HPO_4^{2-}) from the environmental medium. This channel is also responsible for the penetration of orthoarsenic acid in the form of $HAsO_4^{2-}$ into cells (1 point).

7. N, O and **X** atoms can be directly bound with C atoms of the benzene ring in **Z** (6 C atoms forming the benzene ring). If **Z** were free of C-N and C-**X** bonds, it would contain only C-O bonds, and the product described in the task would be a factor of 8 (the atonic number of O), which is not true ($\frac{86}{8} \notin \mathbb{N}$) (0.25 point for giving all atoms, 0.75 for the proof, 1 point in total).

8. The As atom as a part of the higher priority substituent is directly bound to a C atom of the benzene ring. Then the sum of the products of the rest substituents is 86 − 33·1 = 53. Due to the oddity of the result, the N atom (as Z = 7) is definitely present

in the sum, since the O atom ($Z = 8$) would give rise to even numbers despite of its location. Checking both variants for N (locants of 3 and 5) allows attributing N and O atoms to the third and fourth C atoms of the benzene ring, respectively. Then the fragment of **Z** is:
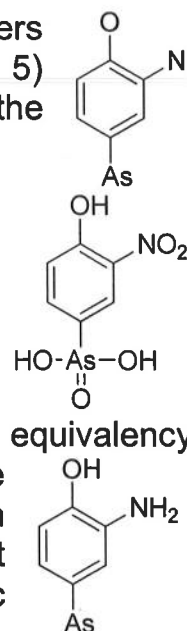
Finally, the distribution of three H and five O atoms among three substituents proceeds as follows: one H atom is attributed to the O atom, whereas two O atoms to the N atom (otherwise the As atom would have an extreme OS value). The structure of **Z** is (1.5 point):


9. With an account for high symmetry of the structures arising from equivalency of all the As atoms, it is necessary to find the common factor for the three given values (366, 549, and 915). It equals 183, which corresponds to the molecule fragment (C_6H_6ONAs), formed as a result of non-selective reduction of **Z** with dithionite (also resulting in arsenic reduction to As (III)):

Thus, the dimer, trimer, and pentamer with equivalent As atoms are possible structures of **Y**, the drug Salvarsan previously used to cure syphilis and African trypanosomiasis (Tsetse-fly disease) (0.5 point for each structure, 1.5 in total):
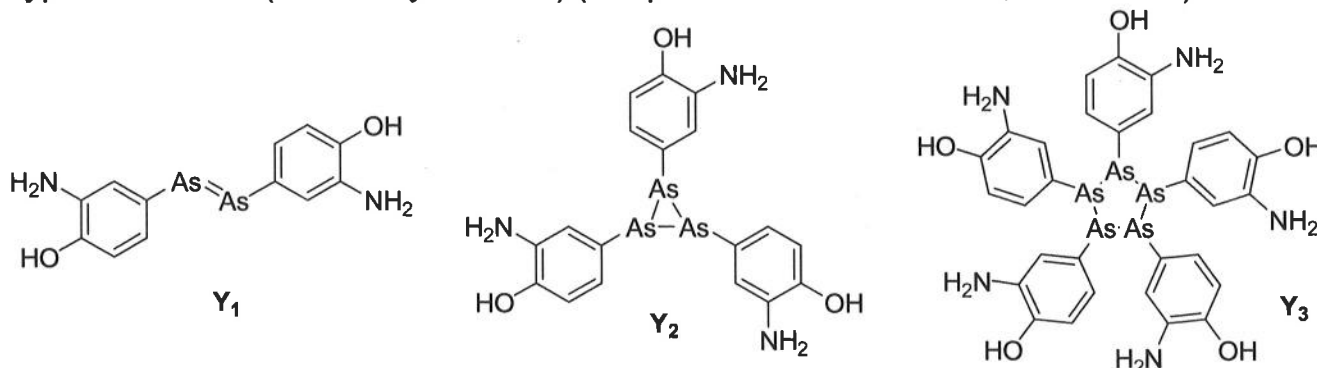
Problem 2 (author Garifullin B.N.)

1. Upon the **A→B** transformation, the difference in the molecular masses of the corresponding compounds equals 2 g/mol, which can be due to dehydrogenation. The molecular mass of the next step product is by 16 g/mol higher than that of the substrate, which formally corresponds to the addition of the oxygen atom. The two possible sequences of transformations are (0.5 point for each variant, 1 point in total):

$$R{-}CH_2OH \rightarrow R{-}CHO \rightarrow R{-}COOH \quad (1);$$
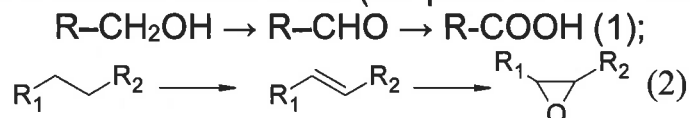
2. Since **E** is the only substrate of the enzyme catalyzing the **E→F** reaction, the evolving gas must have the molecular mass of 44 g/mol or its multiple. This is CO_2, since the formation of C_3H_8 or N_2O in biological systems is hardly possible. Based on the equal molar fractions of C in **E** and **F**, one can derive the following equation, where n is the number of C atoms in **E**, and m is the total number of atoms in **E**:

$$n/m = (n - 1)/(m - 3).$$

Then $n = m/3$, i.e. the molar fraction of C in **D-F** equals 33% (1.5 point).

3. The molar ratio of $n(C){:}n$(all the rest elements in total) equals 1:2 in **F**. Since it is possible to unambiguously determine the degree of unsaturation of **F** based on the given information, its elemental composition must include C, H, and Hal only (exotic

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variants are rejected due to their improbability in biological systems). Then, the degree of unsaturation of **F** coincides with that for alkenes and equals 1 (1 point).

4. Atoms of one element (**El$_1$**) must substitute the same number of atoms of the other element (**El$_2$**) to meet the requirement of equal molar fractions of carbon in **D** and **E**. Only if so, the total amount of all atoms and that of carbon atoms in the molecules is kept constant. If carbon turns out to be **El$_1$** (it cannot be **El$_2$** because of the M(**D**) − M(**E**) value), it is impossible to get a reasonable atomic mass of **El$_2$**: $(18 − 12)/2 =$In other words, $A_r(El_1) − A_r(El_2) = 18/n$, where n is the number of atoms of the elements that are substituted. Of four elements found in **D** and **E**, two (H and O) could be **El$_1$** and **El$_2$** (but not both as a pair); enumeration of possibilities allows determining the fourth element, fluorine (**El$_1$=F**, **El$_2$=H**, if n=1). The loss of the molecular mass of 20 g/mol as a result of the **C→D** transformation is due to elimination of hydrogen fluoride HF (1 point for each element, 2 points in total).

5. F is a fluorine-substituted alkene (atoms of other halogens in the molecule are impossible due to the limitation of the number of elements forming **D**). Then one can write the system of equations (x, y, and z are the numbers of H, F, and C atoms, respectively): $\begin{cases} x + 19 \cdot y + 12 \cdot z = 396 \\ x + y = 2 \cdot z \end{cases}$; then: $7 \cdot x + 25 \cdot y = 396$. There are three sets of integer solutions, and thus three molecular formulae ($C_{27}H_{53}F$, $C_{18}H_{28}F_8$ и $C_9H_3F_{15}$), only the latter containing no more than 15 C atoms.

E is a carboxylic acid capable of enzymatic decarboxylation, whereas the **C→D** and **D→E** transformations do not affect the carboxylic group. Thus, **C** is also a carboxylic acid. With due account for the valid variant in i. 1, one can decide on all the molecular formulae in the **A→E** pathway (0.5 point for each formula, 3 points in total):
$C_{10}H_5F_{17}O$ (**A**) → $C_{10}H_3F_{17}O$ (**B**) → $C_{10}H_3F_{17}O_2$ (**C**) → $C_{10}H_2F_{16}O_2$ (**D**) → $C_{10}H_3F_{15}O_2$ (**E**) → $C_9H_3F_{15}$ (**F**).

6. First, it is worth mentioning that the sum of the figures in the ratio (e.g. 8+2 = 10 for **A**) equals the number of carbon atoms in the compound. Next, the chemistry behind the processes (of **D→E**, in particular) suggests that the first figure reflects the number of C atoms bound with fluorine, whereas the second one that of the rest C atoms. This can be demonstrated for a structural isomer of **A** as follows (1.5 point):

$$\underbrace{CF_3(CF_2)_7}_{8C} : \underbrace{CH_2CH_2OH}_{2C}$$
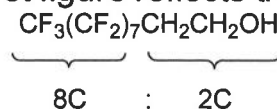
7. The compound **X** is the product of oxidation of **G**. **X** contains seven fluorinated carbon atoms. The molecular mass of the $CF_3(CF_2)_6$ fragment is 369 g/mol. The residual including the atomic mass of one C atom equals 45 g/mol, thus **X** is the perfluorooctanoic acid:
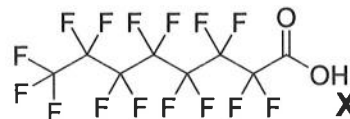
The difference between the molecular masses of **F** and **G** (+18 g/mol) can be due to substitution of a hydrogen atom by the fluorine one (fluorination) or addition of one water molecule. The former variant would lead to the change of the ratio from 7:2 to 8:1, thus the molecular formula of an alcohol $C_9H_5F_{15}O$ can be proposed for **G**.

Formation of the carboxylic acid **X** ($C_8HF_{15}O_2$) from the fluorinated alkene ($C_9H_3F_{15}$) with the alcohol ($C_9H_5F_{15}O$) as an intermediate suggests that the alkene is terminal (note that all the molecules are unbranched). Thus, there is only one structure of **F** matching **X**:

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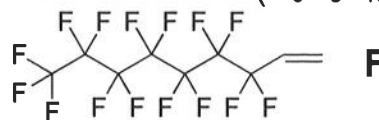
Since enzymes can catalyze formation of both major and minor (according to organic chemistry rules) products, two liner structures can be proposed for **A** and **D** using the retrograde approach:
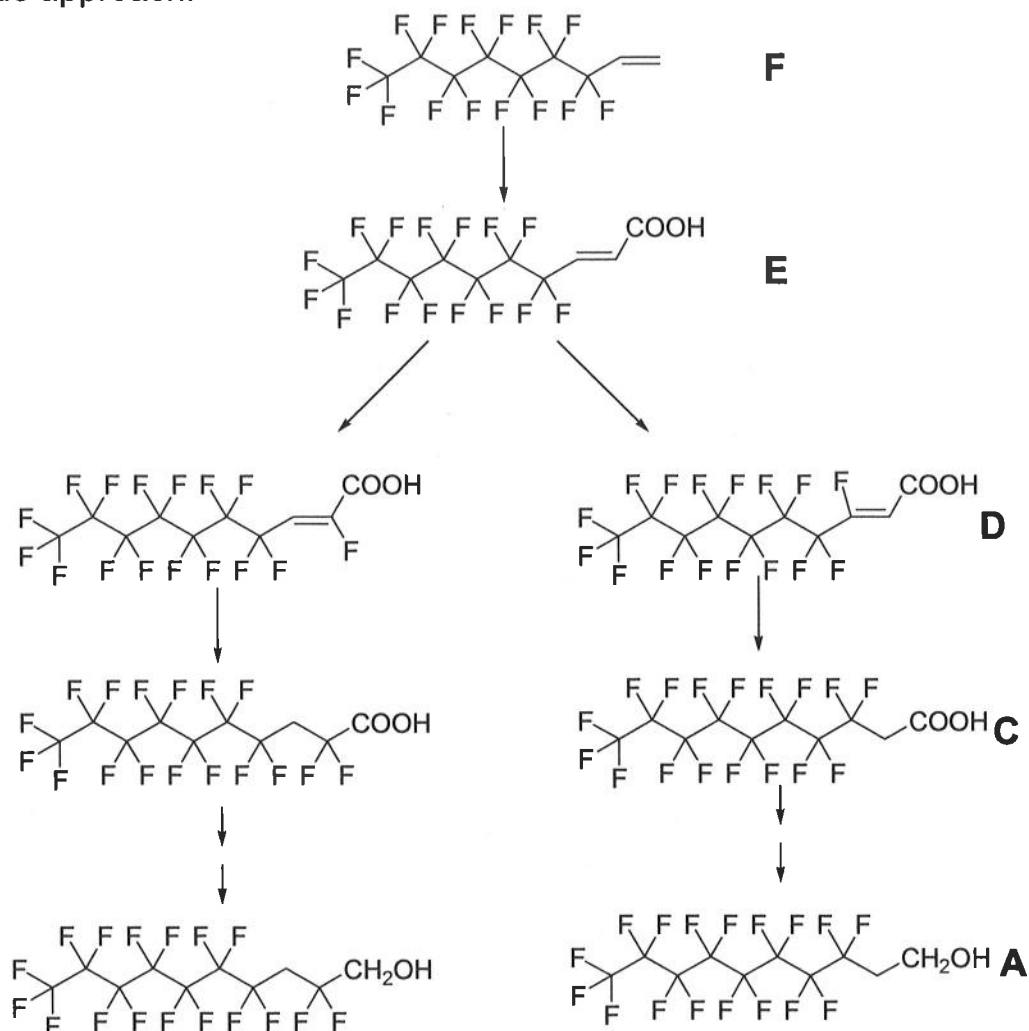
G has the structure of the secondary alcohol ($CF_3(CF_2)_6CH(OH)CH_3$).

Reference information: the actual structures of **A** and **D** are those given rightward (0.5 point for each structure, 3.5 points in total).

8. Due to high hydrophobicity, fluorinated waxes (mostly those of perfluorooctanoic acid) significantly decrease the friction factor of ski sliding on the snow (actually over the water film formed as a result of melting of ice crystals), thus contributing to higher skiing speed. Highly carcinogenic perfluorooctanoic acid is not degraded in nature because of its extremely inert perfluorinated skeleton (by contrast to **A-F**, there are no methylene groups necessary for biodegradation). This leads to its environmental accumulation with subsequent penetration into man with water or food (0.75 point for each variant, 1.5 points in total).

Problem 3 (author Ozhimalov I.D.)

1. The knockout of besD leads to disappearance of all metabolites, thus it is responsible for the **Lys** → **2** reaction. When besC is knocked out, the process is terminated with accumulation of the metabolite **2**, suggesting that besC encodes the enzyme catalyzing the **2** → **3** reaction. Similarly, besB is responsible for the **3** → **4** step. Then the situation becomes less obvious. For some reason, the knockout of the besA gene does not terminate the metabolic pathway completely, as one can see

that **5**, **6**, and **7** continue accumulating in the cells. This can be explained by the presence of low-specific analogues of the besA enzyme, which catalyze the synthesis of subsequent metabolites. The reaction catalyzed by the besA enzyme can be decided analyzing the results of the besE knockdown (accumulation of **4**, **5** and complete absence of **6**, **7**). Finally, besE encodes the enzyme catalyzing the **5 → 6** reaction, and besA that catalyzing the **4 → 5** one (0.25 point for each correct enzyme-reaction pair, 1.25 point in total)

Lys → 2	besD	4 → 5	besA
2 → 3	besC	5 → 6	besE
3 → 4	besB	6 → 7	hydrolases

2.   Let us consider the statements.

No 1 is true, since the knockout of besA does not prevent from the formation of the subsequent metabolites, including the final product **7**.

No 2 is false. If the rates are equal, the quasi-stationary state is achieved and the change of concentration (dC/dt) equals zero.

No 3 is false. If both metabolites had been the substrates of the besA enzyme, **5** would have not been formed at all (its relative quantity would have been 0).

No 4 is false. The addition of the solution **2** would initially lead to an increased relative content of the metabolite, followed by transformation of **2** into **3/4/5/6/7**, since the ΔbesD line contains all the enzymes but the besD one, the latter catalyzing the formation of **2**. No 1 is correct (1 point).

3.   The material balance of the reactants atoms should be written to determine **X** and **2**. $C_6H_{15}O_2N_2^+ + X + H^+ + O_2 + C_5H_4O_5^{2-} = 2 + C_4H_4O_4^{2-} + H_2O + CO_2$

The process involves two reactions: oxidative decarboxylation of α-ketoglutarate affording succinate and addition or substitution with **X** in lysin.

$$1)   1/2 O_2 + C_5H_4O_5^{2-} = C_4H_4O_4^{2-} + CO_2$$
$$2)   C_6H_{15}O_2N_2^+ + X + H^+ + 1/2 O_2 = 2 + H_2O$$
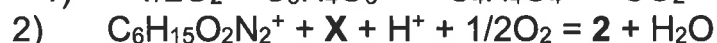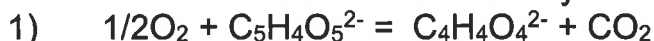
Arithmetic expression with respect to **2** gives: $2 = C_6H_{15}O_2N_2^+ + X - H^+$

So, the difference in molar masses of lysine and **2** equal to the mass of **X**-1.

$$\Delta m = 2 - C_6H_{15}O_2N_2^+ = X - H^+ = M(X)-1$$

The change in the lysine mass referred to **2** can be determined from the mass spectrum by subtracting the lysine mass from the value of each peak (take care of protonation).

$$\Delta m = 181 - 147 = 36\,g/mol   =>   M(X)= 36 - 1 = 35\,g/mol$$
$$\Delta m = 183 - 147 = 38\,g/mol   =>   M(X)= 38 - 1 = 37\,g/mol$$

The obtained values approximately correspond to the chlorine atom, hence **X** is the chloride ion and **2** is chlorolysine. The double peak appears because the chlorine atoms are represented by a mixture of the ^{35}Cl and ^{37}Cl isotopes with the masses calculated above.

The ^1H NMR spectroscopy data allows determining the position of lysine chlorination. The expected signals for all possible structures of **2** are given in the table below as the ratios of intensities. It is seen that only 4-chlorolysine fits the data (1 point for the definition of **X**, 1.5 point for the structure of **2**, 2.5 points in total).

3- chlorolysine	m:m:m:t:d=2:2:1:2:1
4- chlorolysine	m:m:t:t:dd=2:1:2:1:2
5- chlorolysine	m:m:m:t:d=2:2:1:1:2
6- chlorolysine	m:m:m:t:t=2:2:2:1:1

4.   It is possible to calculate the ratio of the peaks remembering that the atomic mass in the Periodic table of elements is the sum of products of the isotope masses and their abundances. Since chlorine is mostly represented by two isotopes, the system of equations is:

$$35.45 = \chi(Cl^{35})M(Cl^{35}) + \chi(Cl^{37})M(Cl^{37}) \qquad 1 = \chi(Cl^{35}) + \chi(Cl^{37})$$

So, $\chi(Cl^{35}) = 0.775, \chi(Cl^{37}) = 0.225$, and the ratio is $0.225 : 0.775 = 0.29$ or 29% (1 point).

5.   The synthesis of **3** involves oxidation and deamination. Since an α-amino acid is the the final product, deamination occurs at the ε-amino group of lysine and is accompanied by oxidation of the terminal carbon atom to formaldehyde. Since reaction equations are given in the diagram, one should "subtract" formaldehyde, ammonia, and water from 4-chlorolysine and add the oxygen molecule and 2 protons.

$$C_6N_2H_{13}O_2Cl + O_2 + 2H^+ - NH_3 - H_2O - CH_2O = C_5NH_8O_2Cl$$
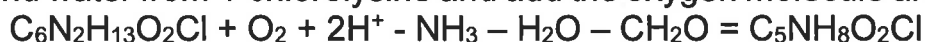
Judged from the formula, one additional unsaturated bond appears in **3**. Since the oxidation occurs at the terminal side of the amino acid, the double bond is formed terminally (other options are omitted after further analysis of the metabolic pathway). Subsequent elimination of hydrochloric acid leads to the formation of the terminal alkyne **4**, propargylglycine. The amide bond formation could involve both γ- and α-carboxyl groups of glutamate. The fact that low-specific γ-glutamyl transpeptidases can be a substitution for besA allows unambiguous determination of **5** as γ-glutamyl-propargylglycine (in case of wrong answer in i. 2, both α- and γ-glutamyl-propargylglycine are accepted). Further, besE catalyzes the monooxygenase introduction of a hydroxyl group in **5**. The position of this group is determined unambiguously because glutamate is hydrolyzed without any modification at the next step, whereas there is only one available position in propargylglycine. Then, **6** is γ-glutamyl-β-ethynylserine, and **7** is β-ethynylserine (1 point for each of **3-7**, 5 points in total).
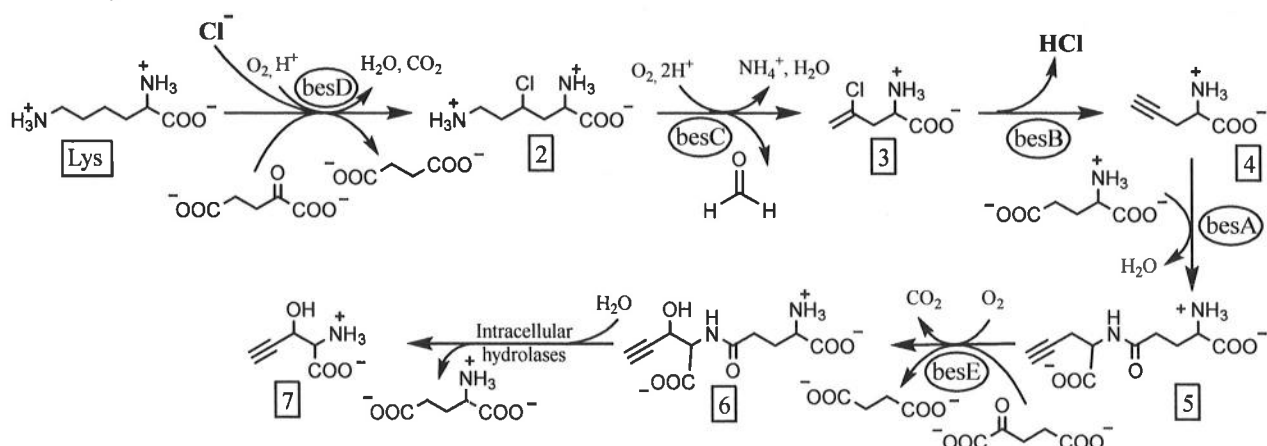

6.   Non-enzymatic cyclization results in the nucleophilic substitution of chlorine affording the cyclic molecule **8**, 4-hydroxylysine γ-lactone. It can be either hydrolyzed to 4-hydroxylysine **10** directly or *via* formation of 4-hydroxylysine ε-lactam **9** (0.75 points for each of **8-10**, 2.25 points in total).
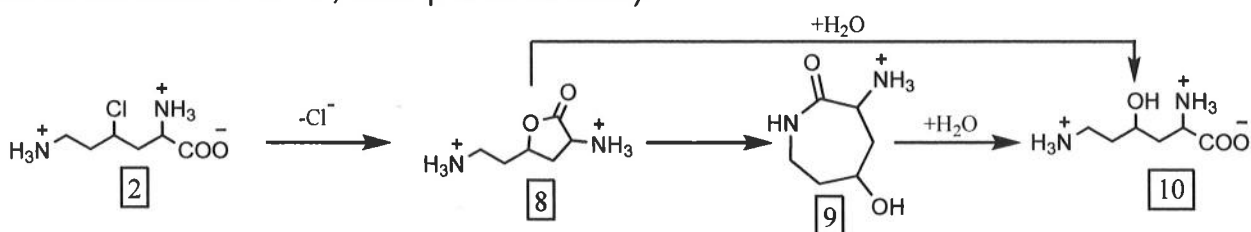
7. (0.5 point for each of **11,12**, 1 point for **Y**, 2 points total).
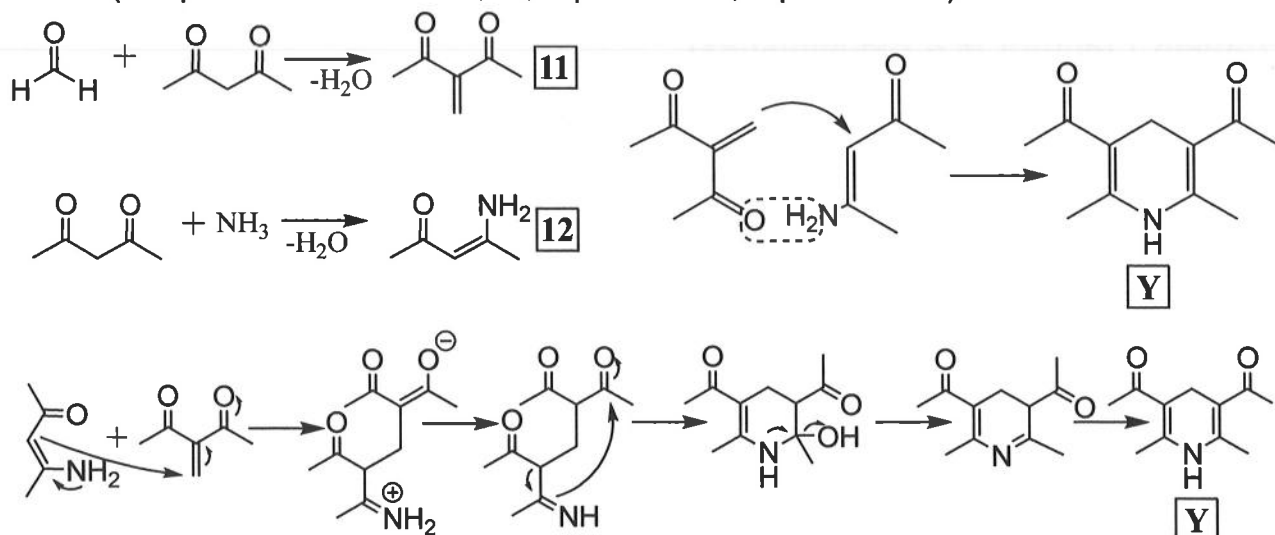
For your information: **7** can be incorporated into proteins and further used in the Cu⁺-catalyzed azide cycloaddition reaction ([3+2]-cycloaddition referred to as Huesgen reaction or copper-catalyzed azide-alkyne cycloaddition, see below). This was initially behind bioorthogonal reactions; however, the use of Cu⁺ leads to the formation of reactive oxygen species in high concentrations, thus nowadays researches carry out copper-free bioorthogonal reactions.
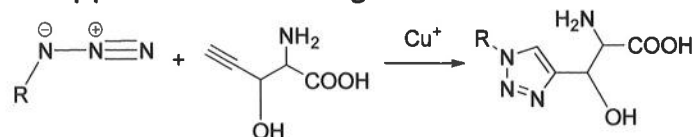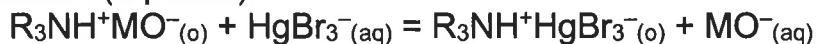

Marchand, J.A., Neugebauer, M.E., Ing, M.C. et al. Discovery of a pathway for terminal-alkyne amino acid biosynthesis. Nature 567, 420–424 (2019). doi.org/10.1038/s41586-019-1020-y.

Analytical chemistry

Problem 1 (author M.K.Beklemishev)

1. Extraction reaction (2 points):

$$R_3NH^+MO^-_{(o)} + HgBr_3^-_{(aq)} = R_3NH^+HgBr_3^-_{(o)} + MO^-_{(aq)}$$

2. Bromide prevents the dissociation of mercury complex (2 points):

$$HgBr_3^-_{(aq)} = HgBr_{2(aq)} + Br^-_{(aq)}$$

The uncharged $HgBr_2$ particle, like mercury cations, is not extracted.

3. By the yellow form (NaOH) (2 points).

4. In the presence of a free amine, mercury will be extracted not only according to the main equation, but also according to the following reaction:

$$R_3N_{(o)} + HgBr_3^-_{(aq)} + H^+_{(aq)} = R_3NH^+HgBr_3^-_{(o)}$$
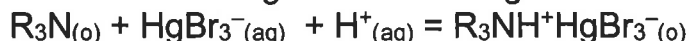
In this case, methyl orange is not released from the organic phase, so the result of mercury determination will be underestimated (1 point for the correct guess, 2 points for the equation).

5. Since the volumes of the aqueous and organic phases are the same, $1 \cdot 10^{-5}$ M of copper will displace $1 \cdot 10^{-5} \cdot 10\% = 1 \cdot 10^{-6}$ M MO^-. This is the error in the determination of mercury (1 point).

6. a) At equilibrium more copper will be present in the aqueous phase than in the organic phase (remember that it was extracted by only 10%), therefore, when organic extract **2** comes into contact with the new aqueous phase **4** (washing), the following reaction occurs: $R_3NH^+CuBr_3^-_{(o)} + Br^-_{(aq)} = R_3NH^+Br^-_{(o)} + CuBr_3^-_{(aq)}$ (2 points)

b) Both during extraction and back extraction (at equilibrium and equal volumes of phases) there will be 10% of the total amount of copper in the organic phase and 90% in the aqueous phase. In other words, if $2.0 \cdot 10^{-6}$ M of copper was found in aqueous phase **4**, then in the equilibrium organic phase **2** there was additionally $2.2 \cdot 10^{-7}$ M, which implies that there was originally $2.22 \cdot 10^{-6}$ M copper in extract **2**. This means that in the equilibrium aqueous phase **1** there was $2.22 \cdot 10^{-6} \times 9 = 2.0 \cdot 10^{-5}$ M of copper. But that refers to the situation after distribution, whereas initially there was $2.22 \cdot 10^{-5}$ M of copper in aqueous phase **1**. Answer: $2.2 \cdot 10^{-5}$ M (1 point).

7. An error in the determination of mercury occurs due to the transition of a certain amount of methyl orange to the aqueous phase according to the indicated reaction. If the extraction of mercury is quantitative and ion exchange with the release of MO^- is also quantitative, then the concentration of MO^- in the aqueous phase is equal to the concentration of mercury and will be equal to $5 \cdot 10^{-6}$ M; 5% of this value will be $2.5 \cdot 10^{-7}$ M. The limiting value of the concentration of $R_3NH^+Br^-_{(o)}$, formed in this reaction, judging by the reaction equation, is equal to the concentration of the formed MO^-, that is, $2.5 \cdot 10^{-7}$ M, and according to the condition, there are no other sources of this compound; the $MO^-_{(aq)}$ concentration is determined by the mercury concentration and is equal to $5 \cdot 10^{-6} + 2.5 \cdot 10^{-7}$ M; the concentrations of bromide and the initial salt of the amine are given by the condition (their consumption can be neglected). Then we can have for the value of the constant:

$K_1 = [R_3NH^+Br^-]_{(o)} \cdot [MO^-]_{(aq)} / [R_3NH^+MO^-]_{(o)} \cdot [Br^-_{(aq)}] = 2.5 \cdot 10^{-7} \cdot 5.25 \cdot 10^{-6} / 0.001 \cdot 0.05 = 2.6 \cdot 10^{-8}$. The equilibrium constant should not exceed this value (2 points).

Problem 2 (A.A. Kudako, M.G. Galuza, T.N. Vorobyeva, M.K. Beklemishev)

1. At the first stage of titration, iodine is released:

$$2IO_3^- + 5Sn^{2+} + 12H^+ + 30Cl^- = I_2 + 5SnCl_6^{2-} + 6H_2O \text{ (1 point)}$$
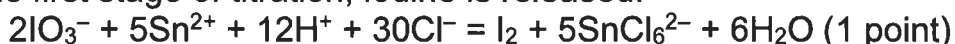
2.   a) The final equation of the titration reaction (in HCl medium $HICl_2$ can be also formed):

$$IO_3^- + 2Sn^{2+} + 6H^+ + 13Cl^- = ICl + 2SnCl_6^{2-} + 3H_2O \text{ (1 point)}$$

b) Mainly copper(II) chloride complexes, since ICl has a slightly yellow color (1 point).

3.   a) The undesirable process: $Sn^{2+} + 2Cu^{2+} = Sn(IV) + 2Cu(I)$ or

$$SnCl_4^{2-} + 2Cu^{2+} + 6Cl^- = SnCl_6^{2-} + 2CuCl_2^- \text{ (1 point)}$$

b) Complexation: $Sn^{2+} + 2C_2O_4^{2-} = Sn(C_2O_4)_2^{2-}$ (1 point)

c) Formation of the blue precipitate: $Cu^{2+} + H_2C_2O_4 = CuC_2O_4\downarrow + 2H^+$; dissolution: $CuC_2O_4 + C_2O_4^{2-} = Cu(C_2O_4)_2^{2-}$ (2 points).

4.   a) Aluminum dissolves in acid: $2Al + 6H^+ = 2Al^{3+} + 3H_2$ (1 point).

b) Aluminum reduces copper(II) to copper(I), if copper is in excess:

$$Al + 3Cu^{2+} + 6Cl^- = Al^{3+} + 3CuCl_2^- \text{ (product } \mathbf{P}) \text{ (1 point)}$$

c) Copper(I) can be detected, for example, by the formation of a red precipitate of copper(I) oxide (yellow hydroxide forms first):

$$2CuCl_2^- + 2OH^- = Cu_2O\downarrow + 4Cl^- + H_2O \text{ (1 point)}$$

d) Copper(I) will also reduce iodate, which will lead to its overuse:

$$CuCl_2^- + IO_3^- + 6H^+ = Cu^{2+} + ICl + Cl^- + 3H_2O \text{ (1 point)}$$
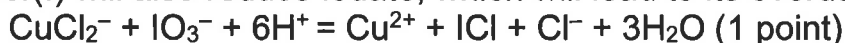
e) The interfering effect of copper can be eliminated by its precipitation with oxalate, followed by separation of the precipitate (item 3, c): $CuC_2O_4 + C_2O_4^{2-} = Cu(C_2O_4)_2^{2-}$ (1 point).

5. In accordance with the stoichiometry of the reaction given in paragraph 2, we have:
$c(Sn^{2+}) = 2c(IO_3^-)V(IO_3^-) / V(Sn^{2+}) = 2\cdot0.05\cdot7.2 / 10 = 0.072M$ without reduction (1 point), similarly we get 0.144M after reduction (1 point). The first value corresponds to the content of Sn(II), and the second to the sum of Sn(II and IV), whence $c(Sn^{2+}) = c(Sn(IV)) = 0.072M$ (1 point).

Problem (author Shved A.M.)

1.   Structural formulas of anions:

$$\mathbf{X^{2-}} \qquad \mathbf{Y^-} \qquad \mathbf{Z^{2-}}$$
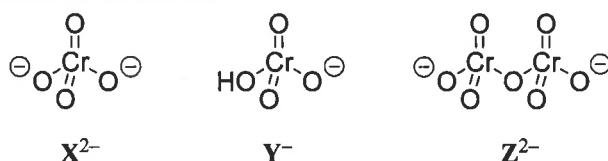
2.   Reaction equation: $2CrO_4^{2-} + 2H^+ \rightleftarrows Cr_2O_7^{2-} + H_2O$ ($2\mathbf{X^{2-}} + 2H^+ \rightleftarrows \mathbf{Z^{2-}} + H_2O$)

$$K_3 = \frac{[Z^{2-}]}{[X^{2-}]^2[H^+]^2} = \frac{[Cr_2O_7^{2-}]}{[CrO_4^{2-}]^2[H^+]^2} = K_1^2 K_2$$

3.   The mole fractions of all chromium-containing species depend on the initial concentration of Na_2CrO_4 since the provided mechanism includes a polycondensation step, where 1 $Cr_2O_7^{2-}$ species is formed from 2 $HCrO_4^-$ species. Therefore, according to Le Chatelier's principle, the higher the initial concentration of CrO_4^{2-}, the more the polycondensation equilibrium shifts towards $Cr_2O_7^{2-}$.

a) The equilibrium concentration of $HCrO_4^-$ can be expressed using the material (mass) balance for chromium:

$$c_0 = [CrO_4^{2-}] + [HCrO_4^-] + 2[Cr_2O_7^{2-}] = \frac{[HCrO_4^-]}{[H^+]K_1} + [HCrO_4^-] + 2K_2[HCrO_4^-]^2$$

$$2K_2[HCrO_4^-]^2 + \left(\frac{1}{[H^+]K_1} + 1\right)[HCrO_4^-] - c_0 = 0$$

$$[HCrO_4^-] = \frac{-\left(\frac{1}{[H^+]K_1} + 1\right) + \sqrt{\left(\frac{1}{[H^+]K_1} + 1\right)^2 + 4 \cdot 2K_2 \cdot c_0}}{2 \cdot 2K_2}$$

6) To find the mole fraction, let us express the total concentration of all chromium-containing species in terms of $[HCrO_4^-]$:

$$c_{total} = [CrO_4^{2-}] + [HCrO_4^-] + [Cr_2O_7^{2-}] = K_2[HCrO_4^-]^2 + \left(\frac{1}{[H^+]K_1} + 1\right)[HCrO_4^-]$$

The mole fraction of $HCrO_4^-$:

$$\alpha_{HCrO_4^-} = \frac{[HCrO_4^-]}{c_{total}} = \frac{[HCrO_4^-]}{K_2[HCrO_4^-]^2 + \left(\frac{1}{[H^+]K_1} + 1\right)[HCrO_4^-]} = \frac{1}{K_2[HCrO_4^-] + \left(\frac{1}{[H^+]K_1} + 1\right)}$$

When substituting the expression for $[HCrO_4^-]$ obtained above into the expression for the mole fraction, the dependence on c_0 is retained.

4. Conversion to absorbances $A = -\lg T$:

pH	A_1	A_2
1.0	0.224	0.167
6.0	0.307	0.378
11	0.491	0.799

In an acidic medium (for example, pH 1.0 in the table), $Cr_2O_7^{2-}$ is the predominant form with the concentration: $[Cr_2O_7^{2-}]_1 \approx c_0/2 = 1.50 \cdot 10^{-4}/2 = 7.5 \cdot 10^{-5}$ (M).

Therefore: $\varepsilon_{352}(Cr_2O_7^{2-}) = \frac{A_{11}}{l \cdot [Cr_2O_7^{2-}]_1} = \frac{0.224}{1 \text{ cm} \cdot 7.5 \cdot 10^{-5} \text{ mol}/L} = 2987 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$

$\varepsilon_{373}(Cr_2O_7^{2-}) = \frac{A_{12}}{l \cdot [Cr_2O_7^{2-}]_1} = \frac{0.167}{1 \text{ cm} \cdot 7.5 \cdot 10^{-5} \text{ mol}/L} = 2227 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$

In a basic medium (pH 11 in the table), CrO_4^{2-} is the predominant form with the concentration: $[CrO_4^{2-}]_3 \approx c_0 = 1.50 \cdot 10^{-4}$ M. Therefore:

$\varepsilon_{352}(CrO_4^{2-}) = \frac{A_{31}}{l \cdot [CrO_4^{2-}]_3} = \frac{0.491}{1 \text{ cm} \cdot 1.50 \cdot 10^{-4} \text{ mol}/L} = 3273 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$

$\varepsilon_{373}(CrO_4^{2-}) = \frac{A_{32}}{l \cdot [CrO_4^{2-}]_3} = \frac{0.799}{1 \text{ cm} \cdot 1.50 \cdot 10^{-4} \text{ mol}/L} = 5327 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$

5. To calculate the equilibrium constants, the experiment at pH 6 should be considered, and the equilibrium concentrations of all chromium-containing ions should be found:

$$\begin{cases} A_{21} = \varepsilon_{352}(CrO_4^{2-}) \cdot l \cdot [CrO_4^{2-}]_2 + \varepsilon_{352}(Cr_2O_7^{2-}) \cdot l \cdot [Cr_2O_7^{2-}]_2 \\ A_{22} = \varepsilon_{373}(CrO_4^{2-}) \cdot l \cdot [CrO_4^{2-}]_2 + \varepsilon_{373}(Cr_2O_7^{2-}) \cdot l \cdot [Cr_2O_7^{2-}]_2 \end{cases}$$

$$\begin{cases} [CrO_4^{2-}]_2 = \dfrac{A_{21} \cdot \varepsilon_{373}(Cr_2O_7^{2-}) - A_{22} \cdot \varepsilon_{352}(Cr_2O_7^{2-})}{\varepsilon_{352}(CrO_4^{2-}) \cdot \varepsilon_{373}(Cr_2O_7^{2-}) \cdot l - \varepsilon_{373}(CrO_4^{2-}) \cdot \varepsilon_{352}(Cr_2O_7^{2-}) \cdot l} \\[4mm] [Cr_2O_7^{2-}]_2 = \dfrac{A_{21} \cdot \varepsilon_{373}(CrO_4^{2-}) - A_{22} \cdot \varepsilon_{352}(CrO_4^{2-})}{\varepsilon_{352}(Cr_2O_7^{2-}) \cdot \varepsilon_{373}(CrO_4^{2-}) \cdot l - \varepsilon_{373}(Cr_2O_7^{2-}) \cdot \varepsilon_{352}(CrO_4^{2-}) \cdot l} \end{cases}$$

The equilibrium concentration of species:

$$[CrO_4^{2-}]_2 = \frac{0.307 \cdot 2227 - 0.378 \cdot 2987}{3273 \cdot 2227 \cdot 1 - 5327 \cdot 2987 \cdot 1} = 5.17 \cdot 10^{-5} \text{ (M)}$$

$$[Cr_2O_7^{2-}]_2 = \frac{0.307 \cdot 5327 - 0.378 \cdot 3273}{2987 \cdot 5327 \cdot 1 - 2227 \cdot 3273 \cdot 1} = 4.62 \cdot 10^{-5} \text{ (M)}$$

$$[HCrO_4^-] = c_0 - [CrO_4^{2-}] - 2[Cr_2O_7^{2-}] = 1.50 \cdot 10^{-4} - 5.17 \cdot 10^{-5} - 2 \cdot 4.62 \cdot 10^{-5} = 5.9 \cdot 10^{-6} \text{ (M)}$$

$$K_1 = \frac{[HCrO_4^-]}{[CrO_4^{2-}][H^+]} = \frac{5.9 \cdot 10^{-6}}{5.17 \cdot 10^{-5} \cdot 10^{-6.0}} = 1.14 \cdot 10^5$$

Equilibrium constants:
$$K_2 = \frac{[Cr_2O_7^{2-}]}{[HCrO_4^-]^2} = \frac{4.62 \cdot 10^{-5}}{(5.9 \cdot 10^{-6})^2} = 1.33 \cdot 10^6$$

$$K_3 = \frac{[Cr_2O_7^{2-}]}{[CrO_4^{2-}]^2[H^+]^2} = \frac{4.62 \cdot 10^{-5}}{(5.17 \cdot 10^{-5})^2 (10^{-6.0})^2} = 1.73 \cdot 10^{16}$$