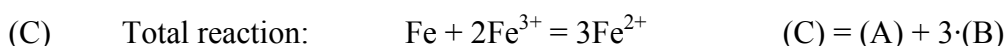
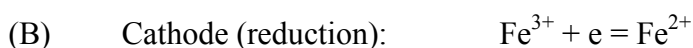
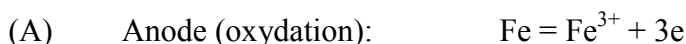


Problem 1 (author Kandaskalov D.V.)

1. The iron electrode is oxidized, so the left half-cell is the anode, then the right is the cathode. The first half-cell consists of a metal (Fe) and a solution containing ions of the same metal (Fe^{3+}), an electrode of the first kind. The second electrode is graphite, which is not involved in the reaction, the solution has a redox $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple thus it is an electrode of the third kind (0.25 points for each right question, 1 point in total).

2. $(-)\text{Fe}|\text{Fe}^{3+}||\text{Fe}^{2+}, \text{Fe}^{3+}|\text{C}(+)$ (0.5 points)

3. The two half-reactions and total reaction (0.25 points for each reaction, 0.75 points in total):



4. For the salt bridges, the most advantageous is to use salts in which the cation and the anion have the same mobility which assure the absence of so-called diffusion potential in the half-cell boundary. Thus, the most suitable salts are KNO_3 and NH_4NO_3 (0.75 points)

5. a) This ion is $\text{H}^+(\text{aq})$ (0.5 points); b) The higher the charge of the ion, the stronger its electrostatic field, and therefore the better the ordering of the dipole molecules of the solvent located near the ion (0.5 points); c) The entropy change of the reaction $\text{Fe} + 2\text{Fe}^{3+} = 3\text{Fe}^{2+}$:

$$\Delta_r S^0 = 3S^0(\text{Fe}^{2+}) - S^0(\text{Fe}) - 2S^0(\text{Fe}^{3+}) = -3 \cdot 137.7 - 27.3 + 2 \cdot 316 = \underline{191.6} \text{ Дж/(моль} \cdot \text{К)}.$$

Let's calculate the reaction enthalpy $\Delta_r H^0$:

$$\Delta_r G^0 = -RT \ln K \rightarrow \ln K = \frac{1}{R} \left(-\frac{\Delta_r H^0}{T} + \Delta_r S^0 \right) \rightarrow \ln \frac{K_1}{K_2} = \frac{\Delta_r H^0}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right).$$

We find

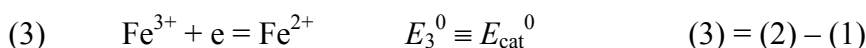
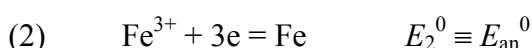
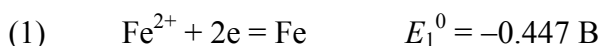
$$\Delta_r H^0 = R \frac{T_1 T_2}{T_1 - T_2} \ln \frac{K_1}{K_2} = 8.314 \cdot \frac{298.15 \cdot 318.15}{20} \cdot \ln 85 = \underline{-175182} \text{ J/mol}.$$

Gibbs energy at 25°C is:

$$\Delta_r G^0(298.15) = \Delta_r H^0 - T \Delta_r S^0 = -175182 - 298.15 \cdot 191.6 = \underline{-232308} \text{ J/mol}.$$

($\Delta_r S^0$ – 1 point, $\Delta_r H^0$ – 1 point, $\Delta_r G^0$ – 0.5 points, 3.5 points in total)

6. We have the half-reactions:



The initial EMF of the EC cell is the difference between the potentials of the cathode and the anode at initial concentrations (C is the potential-forming reaction, see subsection 3). We write:

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$$E_{\text{cat}} = E_3^0 + \frac{RT}{F} \ln \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} = E_3^0 + \frac{0.059}{1} \cdot \lg \frac{0.3}{0.05} = E_3^0 + 0.046 \text{ V},$$

$$E_{\text{an}} = E_2^0 + \frac{RT}{3F} \ln [\text{Fe}^{3+}] = E_2^0 + \frac{0.059}{3} \cdot \lg 0.01 = E_2^0 - 0.039 \text{ V},$$

$$E_C = E_{\text{cat}} - E_{\text{an}} = E_3^0 - E_2^0 + 0.085 \text{ V}.$$

As (C) = 3·(3) – (2), using general formula $\Delta_r G = -nFE$, where n – the number of electrons in the reaction, we can write

$$-3FE_3^0 + 3FE_2^0 = \Delta_r G_C^0 \rightarrow E_3^0 - E_2^0 = -\frac{\Delta_r G_C^0}{3F} = -\frac{-232308}{3 \cdot 96485} = 0.803 \text{ V}.$$

Then, we obtain $\Delta C = E_C = 0.803 + 0.085 = \underline{0.888} \text{ V}$ (1 point)

To find the cathode and anode potentials separately, one must know their standard electrode potentials. For this purpose, in addition to the previously calculated difference $E_3^0 - E_2^0 = 0.803 \text{ V}$ let's use next equation $\Delta_r G_3^0 = \Delta_r G_2^0 - \Delta_r G_1^0$ or $-FE_3^0 = -3FE_2^0 + 2FE_1^0$. Then we obtain a system of equations:

$$\begin{cases} E_3^0 - 3E_2^0 = -2E_1^0, \\ E_3^0 - E_2^0 = 0.803. \end{cases}$$

Using given value $E_1^0 = -0.447 \text{ V}$ we finally find (1 point):

$$E_2^0 = -0.046 \text{ V}, \quad E_3^0 = 0.758 \text{ V}.$$

Now, we can calculate the initial electrode potentials (0.5 points, 2.5 points in total):

$$E_{\text{cat}} = E_3^0 + 0.046 = 0.758 + 0.046 = \underline{0.804} \text{ V},$$

$$E_{\text{an}} = E_2^0 - 0.039 = -0.046 - 0.039 = \underline{-0.085} \text{ V}.$$

7. The cell stops working when all Fe^{3+} (0.30 mol) in the cathode space is reduced to Fe^{2+} . To reduce $N = 0.30$ mole of Fe^{3+} , 0.30 moles of electrons are necessary. The amount of electricity flowing in the circuit $q = NF = 0.30 \cdot 96465 = 28940 \text{ C}$, then the average current in the cell is (1 point)

$$I = \frac{q}{t} = \frac{28940}{200 \cdot 60} = 2.41 \text{ A}$$

Задача 2 (author Khvalyuk V.N.)

1. Since compound **D** decomposes without a solid residue, we can assume that **A** is a nonmetal. Let us test the hypothesis that the sequence **A**→**B**→**C**→**D**→*nothing* represents the formation of an oxoacid **B**, followed by a two-step dehydration and complete decomposition of the oxide of **A** (compound **D**). There are nine nonmetals that are solid at STP: B, C, Si, P, S, As, Se, Te and I. Water-soluble acids that exist as solids at STP are known for P(+1), P(+5), S(+6), Se(+4), Se(+6), Te(+6), I(+5) and I(+7). The acids of P(+5), S(+6), Se(+6) cannot be isolated as solids by evaporation from an aqueous solution. The acids of Se(+4), Te(+6) and I(+7) are weak, whereas acid **B** is moderately strong ($pK_a = 0.77$). The acid of P(+1), H_3PO_2 , is also unlikely, partly because

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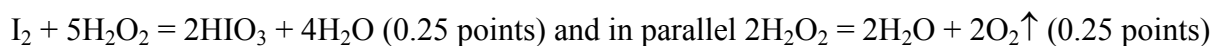
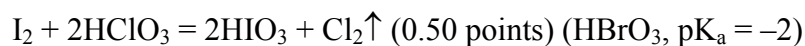
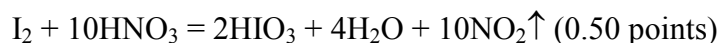
there is no known oxide of P(+1). Thus, **A** = I₂ (0.25 points), **B** = HIO₃ (0.25 points), and **D** = I₂O₅ (0.25 points).

Assuming that **C**, which is 74.69% iodine by mass, has the composition $x\text{I}_2\text{O}_5 \cdot y\text{H}_2\text{O}$ and solving equation

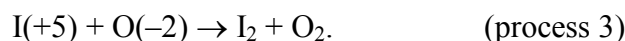
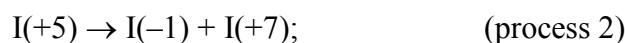
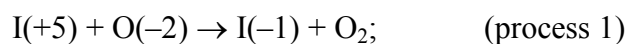
$$w(\text{I}) = 0.7469 = \frac{x \cdot M(\text{I}_2)}{x \cdot M(\text{I}_2\text{O}_5) + y \cdot M(\text{H}_2\text{O})} = \frac{x \cdot 253.8}{x \cdot 333.8 + y \cdot 18.0}$$

or $\frac{x}{y}$, we obtain $x = 3 \cdot y$. Thus, **C** = 3I₂O₅·H₂O or I₂O₅·HIO₃ (0.50 points). The strong acids **X** and **Y** must be strong oxidizing agents that leave no reduction products in the final solution. This suggests that **X** and **Y** are HNO₃ (0.25 points) and HClO₃ (0.25 points), respectively, although other possibilities cannot be ruled out. Acid **Z** must be H₂O₂ (0.25 points) because it is binary and very weak (всего 2.0 балла).

2. The reactions in question are as follows (2 points in total):



3. Since the +1 and +3 oxidation states of iodine are unstable at high temperatures, only the following processes need to be considered:



Note that process 2 may be accompanied by $\text{I}(-1) + \text{I}(+5) \rightarrow \text{I}_2$ (process 4).

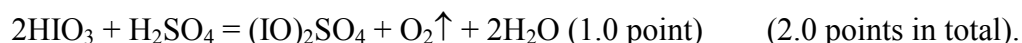
Process 1 is ruled out because salt **E** cannot be BaI₂, which is a stable and readily soluble compound. Process 3 does not lead to the formation of a salt and therefore is possible only as another side reaction. Thus, the principal reaction is process 2, possibly accompanied by 3 and 4. Salt **E** must contain I(+7) but it cannot be Ba(IO₄)₂ because the reaction $\text{Ba}(\text{IO}_3)_2 \rightarrow \text{Ba}(\text{IO}_4)_2$ is accompanied by an increase in mass, which contradicts the experimental data. Thus, salt **E** must be Ba₅(IO₆)₂ (1.0 points). This salt cannot be obtained in aqueous solution. The reaction of formation of **E** is:

$$5\text{Ba}(\text{IO}_3)_2 = \text{Ba}_5(\text{IO}_6)_2 + 4\text{I}_2 \uparrow + 9\text{O}_2 \uparrow \quad (1 \text{ point}) \quad (2.0 \text{ points in total})$$

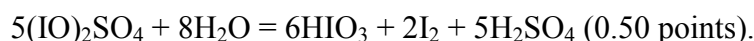
4. The gas produced by the reaction of **B** with excess concentrated sulfuric acid is slightly heavier than air. Considering that the elements involved are H, I, S, and O, the only possibility is O₂ gas. The reactants contain oxygen in the form of O(-2) atoms. Since the oxygen is oxidized, some other element must be reduced. S(+6) atoms cannot oxidize O(-2) to O₂ but I(+5) can. The reaction produced $\frac{0.382}{22.4} = 17.05 \text{ mmol}$ of O₂ which means that $17.05 \cdot 4 = 68.2 \text{ mmol}$ of electrons was

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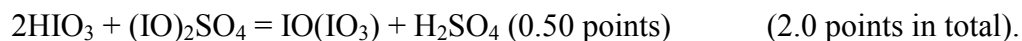
transferred from O(-2) atoms. The amount of reacted HIO₃ is equals to $\frac{6.00}{M(\text{HIO}_3)} = \frac{6.00}{176} = 34.1$ mmol and is precisely half that number. Therefore, the final oxidation state of iodine is +3. Sulfuric acid is not involved in the redox reaction and serves only as a source of SO₄²⁻ anions (and also to bind the water molecules formed). Taking into account the propensity of I(+3) to form cationic forms such as IO⁺, we deduce that substance **F** is (IO)₂SO₄ (1.0 points). The corresponding reaction is:



The mass fraction of oxygen in **D** is 23.97%, so the mass fraction of oxygen in **G** is 23.97 · 1.190 = 20.14%. Thus, the empirical formula of **G** is IO₂. Such an oxide does not exist. However, if we consider the molecular formula I₂O₄ and take into account the presence of IO⁺ in **F**, then compound **G** can be identified as IO(IO₃) (1.0 points). The appearance of I(+5) can be explained by the disproportionation of I(+3), which I(+3) compounds undergo readily in the presence of water:



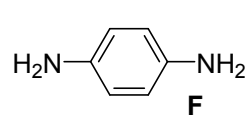
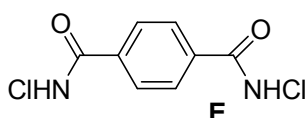
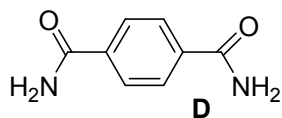
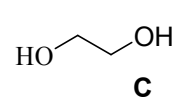
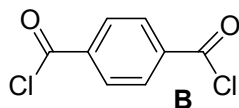
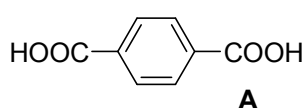
The resulting HIO₃ reacts with (IO)₂SO₄ to form the final product IO(IO₃)₂:



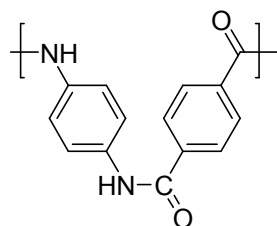
5. Compound **H** could be H₂SO₃ (0.25 points). Reaction of **B** and **H** under ambient conditions produces two acids: HIO₃ + 3H₂SO₃ = HI + 3H₂SO₄ (0.25 points) (0.50 points in total).

Problem 3 (authors Gulevich D.G., Karpushkin E.A.)

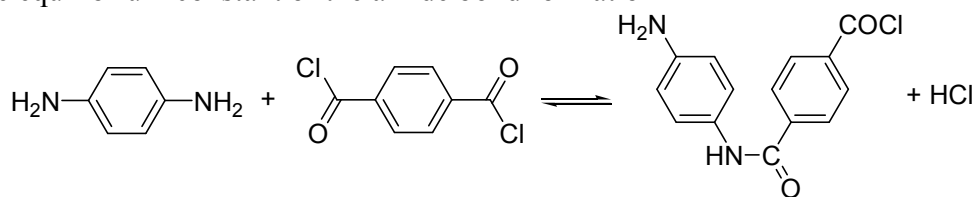
1. (0.5 point for each of the A – F structures, 3 points in total)



2. a) Polycondensation of *p*-phenylenediamine (**F**) and terephthaloyl chloride (**B**) affords poly(*p*-phenylene terephthalamide) (1 point). This fiber is called Kevlar.



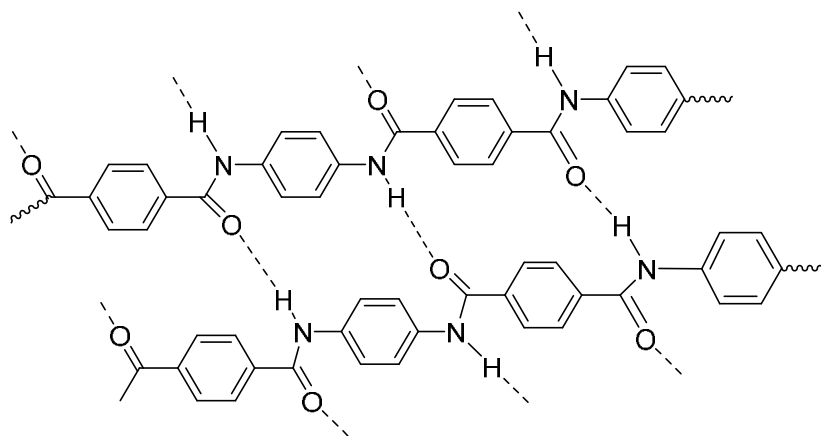
b) The equilibrium constant of the amide bond formation



$K = \frac{[-\text{NHCO-}][\text{HCl}]}{[-\text{NH}_2][-\text{COCl}]} = 10^6$. Denoting the starting quantities of the amine and acyl chloride groups as x mol (remember that the mixture of **B** and **F** is equimolar) and the conversion degree into amide bonds as α , one gets $\frac{\alpha x \cdot \alpha x}{(1-\alpha)x \cdot (1-\alpha)x} = 10^6 \leftrightarrow \alpha = 0.999$. The conversion degree of 99.9% means that 999 of the formed amide bonds are in equilibrium with a pair of unreacted $-\text{NH}_2$ and $-\text{COCl}$ groups. These groups are found at the termini of the formed macromolecule. Finally, since each repeating unit contains two amide bonds, the average polymerization degree of Kevlar (n) is 500 (1.5 points, 2.5 points in total).

3. Mass of the repeating unit of **X** is 238.25 g/mol. Hence, 2 kg of **X** are produced from $2000/238.25 = 8.39$ mol of each of **B** and **F**. Both **B** and **F** are obtained from terephthalate moiety of PET, thus must be prepared from different PET batches. **B** is produced from PET in two steps, thus preparation of 8.39 mol of **B** requires $8.39/0.9^2 = 10.36$ mol of the repeating units of PET. Similarly, 8.39 mol of **F** is prepared in three steps from $8.39/0.9^3 = 11.51$ mol of the repeating units of PET. In total, 21.87 mol of PET is needed. Taking into account the mass of the repeating unit of PET (192.17 g/mol), one finally gets that 4202 g (about 210 bottles) of PET is required (1 point for each of the PET portions, 0.5 point for the recalculation into bottles, 2.5 points in total).

4.



Each repeating unit forms 4 hydrogen bonds (1 point for drawing the bonds, 0.5 point for the number of bonds, 1.5 points in total).

5. The required thickness of the protective elements is equal to the depth of the bullet penetration. For Kevlar it is calculated as $L = \frac{1.35 \cdot 10^{-9} \cdot 4.7 \cdot 10^{-3} \cdot (247)^2}{(5 \cdot 10^{-3})^2} = 0.0155 \text{ m} = 1.55 \text{ cm}$;

whereas for steel as $L = \frac{5.84 \cdot 10^{-10} \cdot 4.7 \cdot 10^{-3} \cdot (247)^2}{(5 \cdot 10^{-3})^2} = 0.67 \text{ cm}$. The corresponding masses of the

body armor elements are $m_{\text{steel}} = 60 \cdot 60 \cdot 0.67 \cdot 7.7 = 18.6 \text{ kg}$. $m_{\text{Kevlar}} = 60 \cdot 60 \cdot 1.55 \cdot 1.44 = 8.04 \text{ kg}$ (0.25 points for each calculation, 0.5 point in total).

Problem 4 (author Gulevich D.G.)

1. From the data from the condition of the problem it follows that **B** is a simple substance that

forms part of **C**, **D**, **H** and **L**. In the reaction $\mathbf{G} + \mathbf{B} \nu = \frac{pV}{RT} = \frac{101325 \cdot 690 \cdot 10^{-6}}{8.314 \cdot 673} = 0.0125 \text{ mol}$ is

formed, in the oxidation reaction $\nu = \frac{101325 \cdot 1.51 \cdot 10^{-3}}{8.314 \cdot 1473} = 0.0125 \text{ mol}$ of gas **E**. Consequently, the

products of the reaction $\mathbf{G} + \mathbf{B}$ formed in a molar ratio of 1:1 (0.5 points). Then $M(\mathbf{B}) = 0.80 / 0.025 = 32 \text{ g/mol}$, **B** – is sulphur, **E** – SO_2 . Hence, **G** – is metal oxide, and one of the reaction products is sulphide of this metal. The molar mass of black substance $2.99 \text{ g} / 0.0125 \text{ mol} = 239 \text{ g/mol}$. $239 - 32 = 207 \text{ g/mol}$, hence **L** is PbS (0.5 points) and $\mathbf{G} - \text{PbO}_2$. $\text{PbO}_2 + 2\text{S} \xrightarrow{t^\circ\text{C}} \text{PbS} + \text{SO}_2$; $2\text{PbS} + 3\text{O}_2 \xrightarrow{t^\circ\text{C}} 2\text{PbO} + 2\text{SO}_2$.

By the condition of the problem, white phosphorus is suitable as the substance **A**. Under heating, it passes into **J** – red phosphorus. **H** is P_4S_3 .

Let us determine the molecular mass of **D** (0.5 points):

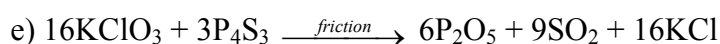
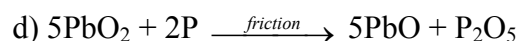
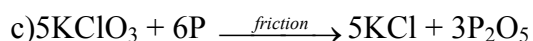
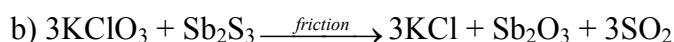
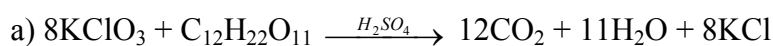
$$M = \frac{m}{\nu} = \frac{\rho V}{\nu} = \frac{\rho V N_A}{z} = \frac{4.63 \cdot 10^6 \cdot 1.131 \cdot 0.3837 \cdot 1.123 \cdot 10^{-27} \cdot 6.02 \cdot 10^{23}}{4} = 339.6 \text{ g/mol}$$

Denoting **D** as Me_2S_n , we determine the metal sulphide:

In total: **A** – KClO_3 ; **B** – S ; **C** – HgS ; **D** – Sb_2S_3 ; **E** – SO_2 ; **F** – P_4 ; **G** – PbO_2 ; **H** – P_4S_3 ; **J** – P . (0.5 points for determination of each **B**, **G**, **D**, **J**, **F**, 0.25 points for **C**, **H**, **E** and **A**, 5 points in total)

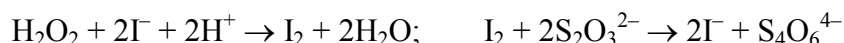
<i>n</i>	$A_r, \text{ g/mol}$	Me
1	153.8	–
2	307.6	–
3	121.8	Sb
4	275.6	–

2. (1 point for each reaction equation, 5 points in total)



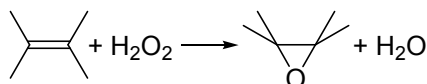
Problem 5 (author Beklemishev M.K.)

1. The amount of thiosulfate spent was equal to: $8.8 \text{ mL} \cdot 0.5 \text{ M} = 4.4 \text{ mmol}$, that is equivalent to 2.2 mmol of hydrogen peroxide (0.5 points):



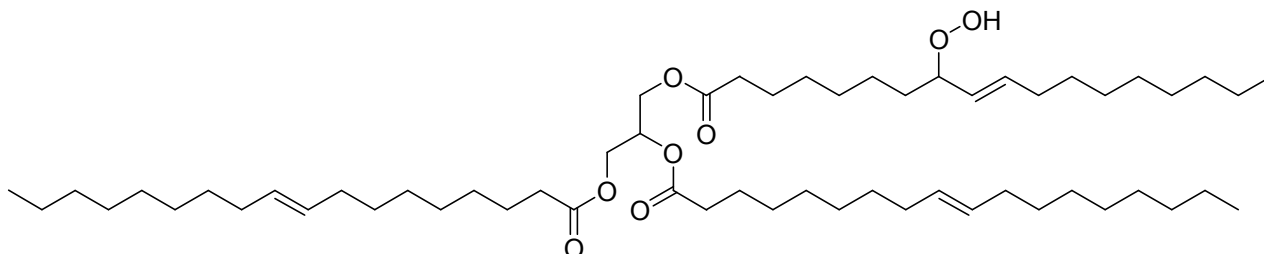
Initially there was $0.5 \text{ mL} \cdot 5.0 \text{ M} = 2.5 \text{ mmol H}_2\text{O}_2$, i.e. 0.3 mmol of peroxide reacted.

Epoxidation reaction (1 point):

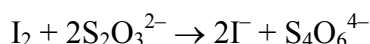
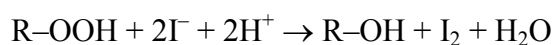
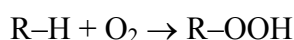


(stoichiometry 1:1, Prilezhaev reaction). Thus, 88 mg of fat contained 0.3 mmol of double bonds (0.5 points). The general formula for fat is $\text{C}_3\text{H}_5(\text{OCOR})_3$, its molar weight is $173 + 3R$. If each fatty acid residue contains one double bond (and by the problem situation, all the residues are the same), we will get that there was 0.1 mmol of fat, and its molar weight is $88 : 0.1 = 880 \text{ g/mol}$, and $R = \text{C}_{17}\text{H}_{33}$ (oleic acid residue, then $M_{\text{fat}} = 884$). If there were two double bonds in each fatty acid, there would be 0.05 mmol of fat, and its molar weight would be $88 : 0.05 = 1760 \text{ g/mol}$, then $R = \text{C}_{38}\text{H}_{73}$ ($M_{\text{fat}} = 1760$), which is impossible (0.5 points for the gross formula and molar weight, and 1 point for the structure, 3.5 points in total for paragraph 1).

2. Fat is oxidized by a radical mechanism, and the most stable radical should be formed next to the double bond. A probable structure of R–OOH hydroperoxide is as follows (1 point):



Reactions (1 point):

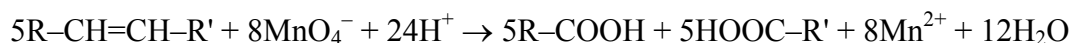


Thus, 2 moles of thiosulfate are equivalent to 1 mole of hydroperoxide, or 1 mole of O_2 absorbed. Then the amount of O_2 equals $2.2 \text{ mL} \cdot 0.10 \text{ M} / 2 = 0.11 \text{ mmol}$, and $\text{PN} = 0.11 / 0.01 \text{ kg} = 11 \text{ mmol O}_2 / \text{kg fat}$ (1 point, 3 points in total for paragraph 2).

3. a) 0.48 mmol of KMnO_4 was consumed for the oxidation of fat, which corresponds to 2.4 mmol-equivalents (taking into account the production of 5 electrons upon reduction of KMnO_4 in an acidic medium). The amount of fat was 0.1 mmol, i.e. each molecule of fat lost 24 electrons (1 point), or each fatty acid residue lost 8 electrons, or each atom near the double bond – 4 electrons. Since the initial formal oxidation state of carbon in the $-\text{CH}=\text{}$ group is -1 , it became $+3$, which

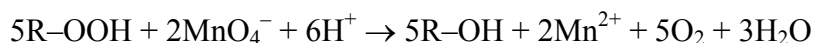
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corresponds to the carboxylic group. Thus, the oxidation of unsaturated fats with permanganate under severe conditions causes the break of double bonds with the formation of two carboxylic groups:

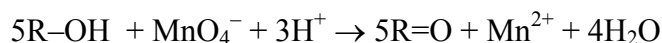


(1 point for the formulas of carboxylic acids. The products of the ester hydrolysis are also possible).

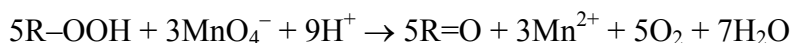
b) In this experiment, permanganate oxidizes double bonds, as in (a), for which 0.48 mmol of permanganate will be spent also. Secondly, oxidation of hydroperoxides formed during thermal destruction at 50°C will occur. Oxidation of hydroperoxide proceeds similarly to the oxidation of hydrogen peroxide (with the loss of two electrons):



Thirdly, it is necessary to take into account the oxidation of the group C–O, belonging to the hydroperoxide, to the keto group:



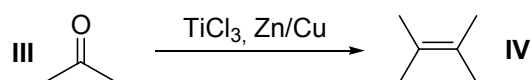
Overall (1 point):



This reaction required $0.54 - 0.48 = 0.06$ mmol of permanganate, hence the amount of the oxidized hydroperoxide groups is $5/3 \cdot 0.06$ mmol = 0.1 mmol, i.e., on average, each molecule of fat acquired one hydroperoxide group (0.5 points for the calculations, 3.5 points in total for paragraph 4).

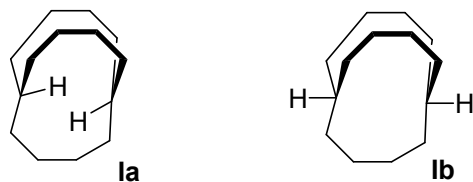
Problem 6 (author Bakhtin S.G.)

1. The band in the IR spectrum of **III** at $\nu = 1715 \text{ cm}^{-1}$ indicates the presence of the carbonyl group C=O ($\text{CH}_3\text{CH}_2\text{CHO}$ or CH_3COCH_3). On the basis of formulas of **III** and **IV**, the McMurry reaction consists in doubling the carbonyl compound molecules, probably with the participation of C=O carbon atoms, to form an alkene. Then the singlet in the ^1H NMR spectrum corresponds to 2,3-dimethyl-but-2-ene, which means that the substance **III** is acetone (0.75 points each substance, 1.5 points in total):

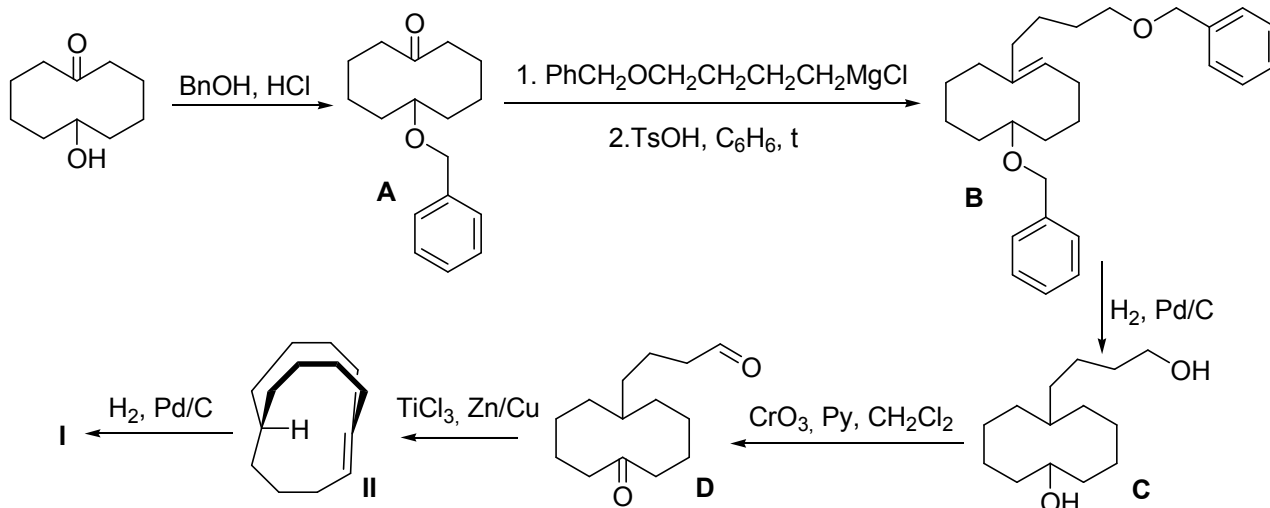


2. In/out-stereoisomerism is characteristic of bicyclic systems having sufficiently long bridged carbon chains, which allows the bond (unshared pair of electrons) in the head of the bridge to occupy a position inside (in) or out the structure. This can be guessed from an analysis of the

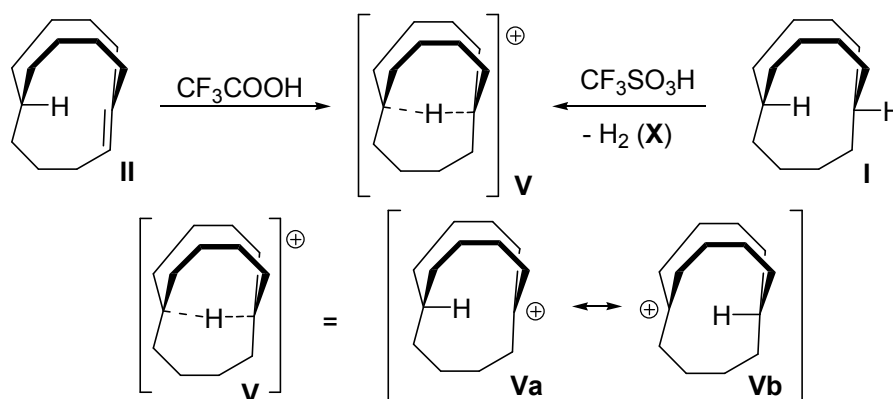
structure of **I** in the task and from the type of stereoisomerism. In the chain of transformation in, out-isomer of bicyclo[4.4.4]tetradecane is represented. Then the structures of **Ia** and **Ib** are following (0.75 points each structure, 1.5 points in total):



3. The reaction of the initial hydroxy ketone with benzyl alcohol is accompanied by the elimination of water – benzyl protection of the OH group. $M(\text{RMgCl}) = 24.30/0.1079 = 223.0$; $n(\text{C}) = 223.0 \cdot 0.5924/12.01 = 11$; according to $^1\text{H NMR}$, RMgCl contains the number of H atoms, which is a multiple of $2+2+2+2+2+5 = 15$; if $n(\text{H}) = 15$, $\Delta M = 223.0 - 24.30 - 11 \cdot 12.01 - 35.45 - 15 \cdot 1.008 = 16$, that corresponds to the presence of one oxygen atom in RMgCl ; if $n(\text{H}) = 30$, $\Delta M = 223.0 - 24.30 - 11 \cdot 12.01 - 35.45 - 30 \cdot 1.008 \approx 1$, that is impossible on the basis of $^1\text{H NMR}$. Hence, the molecular formula of RMgCl is $\text{C}_{11}\text{H}_{15}\text{OMgCl}$. According to the spectrum, its structure corresponds to $\text{C}_6\text{H}_5\text{-CH}_2\text{-O-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{-MgCl}$. After the addition of the Grignard reagent to the C=O group of **A** followed by acid treatment, not only did the decomposition of the magnesium alcoholate occur, but also further dehydration of alcohol took place, that can be detected from the molecular formula of **B**, as well as from the possibility of Z/E -stereoisomerism for it (**B** is an E -isomer, otherwise the Z -diastereomer will have a significant steric strain). Stage **B** \rightarrow **C** is accompanied by the loss of 14 C atoms, which can be due to only the double removal of benzyl protection. Analysis of the molecular formula of **C** also indicates that in addition to removal of Bn, hydrogenation of the C=C bond has occurred. The reaction **C** \rightarrow **D** is the oxidation of the OH group to the carbonyl one. Further, the McMurry reaction proceeds. Since the number of C atoms did not change under the transformation **C** \rightarrow **D** \rightarrow **II** \rightarrow **I**, the McMurry reaction was intramolecular. Then **D** must contain two carbonyl groups (the oxidation of both OH in **C**). Consequently, the step **II** \rightarrow **I** is the hydrogenation of the bicyclic alkene **II** (H_2 , Pd/C). Since upon the catalytic hydrogenation of **II** it is unlikely that the internal hydrogen atom in the head of the bridge is formed during this reaction (due to steric hindrances), this H atom must be formed at the stage of synthesis of **II** (in-isomer) (0.5 points for each **A** – **D**, **II**, 1 point for RMgCl , 4.5 points in total).



4. Treatment of **II** with CF_3COOH leads to protonation of the $=\text{CH}$ atom of the double bond. As a result, the tertiary C atom in the head of the bridge will become a carbocation center, that will be further stabilized by partial transfer of the H in-atom; a similar carbocation can be generated from bicycloalkane **I** by protonation with a strong acid (0.5 points for each **V**, **Va**, **Vb** and **X**):



The ability to undergo the described transformations is due to the presence of H in-atom, which participates in the formation of a bridged two-electron three-center bond. Consequently, a similar reactivity should be expected for **Ia**, but not for **Ib** (0.5 points, 2.5 points in total).

Problem 7 (author Kuzin S.V.)

1. Non-monotonic dependence of absorbance on time with the only maximum is only possible when at least 2 successive steps are present. The increase of absorbance indicates appearance of intermediate substance that absorbs light stronger. Following decrease of absorbance (up to $t = \infty$) corresponds to conversion to the final product (1 point).

2. Under the statement of the problem there was only pure substance **X** in solution at $t = 0$. Using Beer – Lambert – Bouguer law (0.5 points):

$$\varepsilon_{\text{X}} = \frac{A}{lc} = \frac{0.982}{0.5 \cdot 0.00131} = 1500 \text{ M}^{-1} \text{ cm}^{-1}$$

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3. Data analysis reveals that absorbance is not directly proportional to the concentration despite BLB law implies it. Perhaps there is a systematic error (bias). It is the case! This is linear dependence but shifted to 0.04. Thus, $\varepsilon_W = (1.08 - 0.56)/(0.002 - 0.001)/1 = 520 \text{ M}^{-1}\text{cm}^{-1}$. Positive bias in UV-vis spectroscopy could be due to additional absorbance or scattering of light. For instance, between calibration to pure water and direct measurement of solution absorbance surface of a cuvette is fingered (1 point).

4. Above all, we calculate concentration of **W** at the end point. Using data from the table $c(\mathbf{W}, t = \infty) = 0.681/0.5/520 = 0.00262 \text{ M}$ which is *two times* bigger than the initial concentration of **X**. This means that 2 two equivalent molecules are obtained at the first or the second step (only this assumption is in agreement with the statement of the problem). Both variants $\mathbf{X} \rightarrow \mathbf{Y} \rightarrow 2\mathbf{W}$ and $\mathbf{X} \rightarrow 2\mathbf{Y} \rightarrow 2\mathbf{W}$ are acceptable (2 points).

5. One can notice that the maximum of absorbance comes very rapidly in comparison with total time. So, as a good approximation we could assume that at the point of maximum only substance **Y** is in solution. Then $\varepsilon_Y = 2.883/0.00131/0.5 = 4400 \text{ M}^{-1}\text{cm}^{-1}$ if the scheme with production of 1 molecule of **Y** is taken and $\varepsilon_Y = 2200 \text{ M}^{-1}\text{cm}^{-1}$ otherwise (1.5 points).

6. There is only 1 intermediate substance, so 2 rate constants (k_1 and k_2) are to be estimated. When final product is not produced in significant amount, absorbance is as follows: $A = c_0(\mathbf{X})\exp(-k_1t)\varepsilon_X l + c_0(\mathbf{X})[1 - \exp(-k_1t)]\varepsilon_Y l$. In case the scheme $\mathbf{X} \rightarrow 2\mathbf{Y}$ is taken, the second sum and gains multiplier 2. For the moment $t = 2 \text{ min}$ and $\varepsilon_Y = 4400 \text{ M}^{-1}\text{cm}^{-1}$ $k_1 = 0.43 \text{ min}^{-1}$. This value doesn't depend on the scheme considered (1 point).

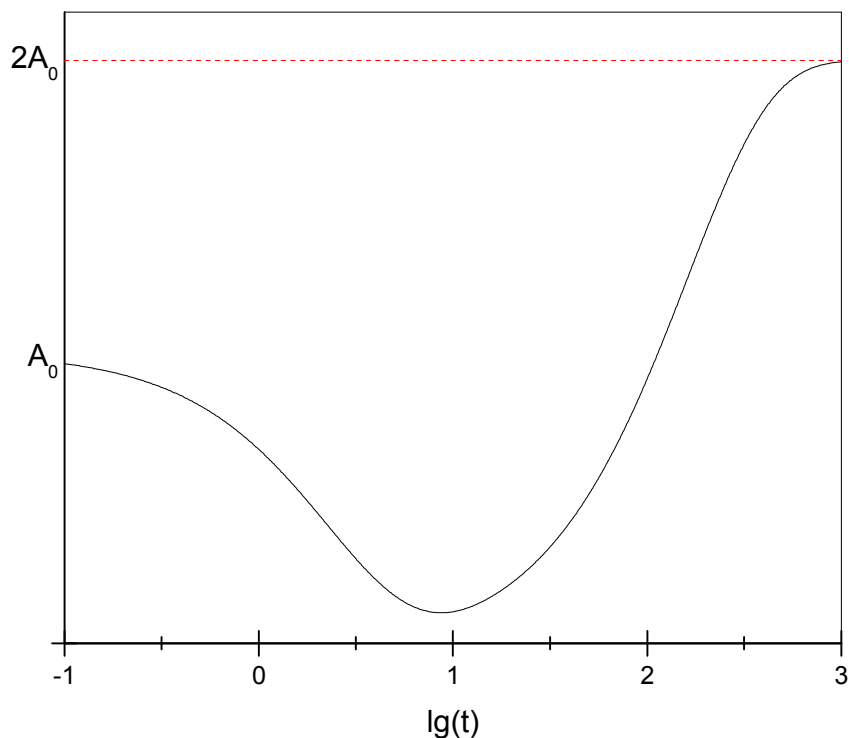
Estimation of the second constant cannot be performed in the same way. Correct way is to calculate the composition of the solution at large times (assuming **X** is run out) followed by usage of expression $c(\mathbf{Y}, t_1)/c(\mathbf{Y}, t_2) = \exp[k_2(t_2 - t_1)]$. Calculation using last two suggested moments (50 min and 100 min) gives rise to $k_2 = 0.0062 \text{ min}^{-1}$ that also doesn't depend on the kinetic scheme (1.5 points, 2.5 points in total).

Calculation in approach that at $t = 10 \text{ min}$ only substance **Y** is in the solution followed by its 1 order decay is also acceptable. This approximation leads to $k_2 = 0.0064 \text{ min}^{-1}$ (by $t = 100 \text{ min}$).

7. As the intermediate substance does not absorb light at wavelength λ_2 , the plot has 2 branches. Fast decrease (almost to zero) of absorbance due to fast decay of **X** and slow increase as **W** is being produced. It is obligatory to demonstrate on the plot that absorbance at the end is two times bigger than one at the beginning, because isosbestic wavelength is considered (0.5 points for 2 branches with correct monotony, 1 point for indicating two times increase of absorbance, 1.5 points in total):

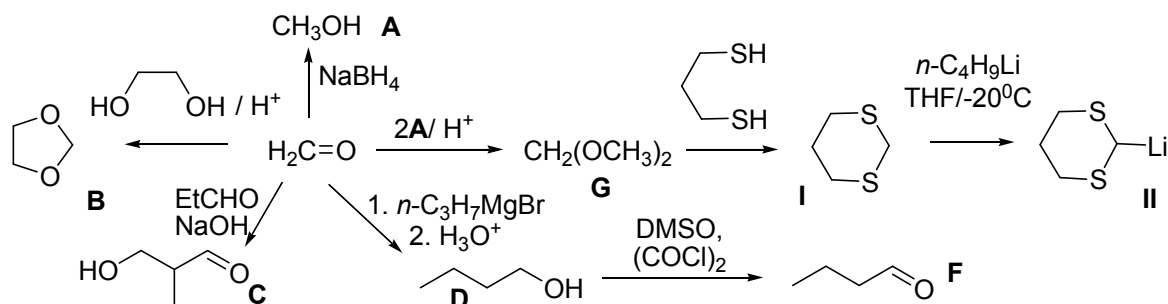
$$\frac{A(t = \infty)}{A(t = 0)} = \frac{\varepsilon_W l c(\mathbf{W})}{\varepsilon_X l c(\mathbf{X})} = 2$$

As an illustration, $A(t)$ calculated with parameters of this problem is plotted below (pay attention: the time scale is logarithmic).

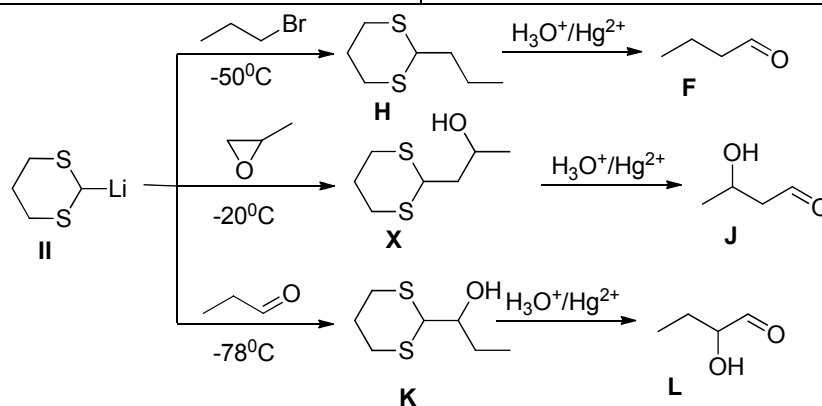


Problem 8 (author Shved E.N.)

1. Taking into account the properties of $\text{H}_2\text{C}=\text{O}$, dithiane **I** and reagent's role the structures of **A**, **B**, **C**, **D**, **F**, **G**, **II** depicted below (each structure 0.5 points, 3.5 points in total):



2. According to ^1H NMR spectra and the reagent's role, compounds **J**, **L** and **C** bearing an aldehyde function. Doublet in ^1H NMR of **L** and **C** indicate one α -proton towards aldehyde group moreover triplet in ^1H NMR of **J** showed two ones. The structures of compounds **H**, **X**, **J**, **K**, **L** depicted below (each structure 0.5 points, 2.5 points in total):



3. The formula of **IV** is $\text{C}_{13}\text{H}_{24}\text{S}_4\text{O}$, $M(\text{IV}) = 324 \text{ Da}$, then $M(\text{Q}) = 324 \cdot 1.0864 = 352 \text{ Da}$. The molar mass increased by 28 Da, which, taking into account the reagent – DMF corresponds to the formylation, i.e. **Q** has formula $\text{C}_{14}\text{H}_{24}\text{S}_4\text{O}_2$. Since the structures of **T** and **VI** are isocyclic, **T** has a hexadecane ring with two O atoms in positions 1 and 9. Taking into account the formula of **VI** is $\text{C}_{20}\text{H}_{24}\text{O}_8$ and $M(\text{VI}) = 392 \text{ Da}$, as well as information on the number of hydrogen atoms, oxygen and carbon in **T** in comparison with **IV**, we can conclude that the compound **T** contains 32 C atoms, 48 H atoms and 4 O atoms. Given the known structure **IV** containing two dithiane cycles, it should be assumed that **T** contains four dithianes. Therefore the formula of **T** is $\text{C}_{32}\text{H}_{48}\text{S}_8\text{O}_4$. Structures for the compounds **M**, **N**, **O**, **P**, **Q**, **T** are given in the scheme (0.5 point for each structure **M**, **N**, **O**, **P**, **Q**, **R**, **S**, **T**, 4 points in total):

