

Problem 1 (author Kandaskalov D.V.)

1. a) The zinc electrode will dissolve in nitric acid; b) Due to the lack of inert metals on the island, you can try to look for graphite. (0.25 points for each correct answer, 0.5 point in total)

2. (1) "jar", (2) "tube", (3) "positive", (4) "negative" (0.25 points for each correct answer, 1 point in total)

3. a) The Gibbs energy of the final transition $\text{NO}_3^- \rightarrow \text{NO}$ is the sum of these quantities for intermediate transitions: $\Delta G = \Delta G_1 + \Delta G_2 + \dots + \Delta G_k$ or $-nEF = -n_1E_1F - n_2E_2F - \dots - n_kE_kF$, where n_i – the number of electrons involved in the corresponding transition. Hence $E_x = (n_1E_1 + n_2E_2 + \dots + n_kE_k)/n$. Applying the obtained formula, we find the desired potentials (1 point):

$$E_x^\circ = (1 \cdot E_1^\circ + 1 \cdot E_2^\circ) / 2 = (0.8 + 1.07) / 2 = 0.935 \approx 0.94 \text{ V},$$

$$E_y^\circ = (1 \cdot E_1^\circ + 1 \cdot E_2^\circ + 1 \cdot E_3^\circ) / 3 = (0.8 + 1.07 + 1.00) / 3 = 0.957 \approx 0.96 \text{ V}.$$

b) Let's write the Nernst equation $E = E^\circ + \frac{RT}{nF} \ln \frac{[\text{Ox}]}{[\text{Red}]}$, where n – the number of electrons

involved in the reaction. Considering that at 25°C $RT/F = 0.02569$, and $\ln x = \ln 10 \cdot \lg x$, we write:

$$\text{NO}_3^- + 2\text{H}^+ + e = \text{NO}_2 + \text{H}_2\text{O}, \quad E_1 = E_1^\circ + \frac{0.06}{1} \lg \frac{[\text{NO}_3^-][\text{H}^+]^2}{p(\text{NO}_2)} = 0.80 - 0.12 \cdot \text{pH} + 0.06 \cdot \lg \frac{[\text{NO}_3^-]}{p(\text{NO}_2)};$$

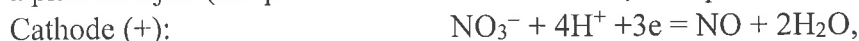
$$\text{NO}_3^- + 3\text{H}^+ + 2e = \text{HNO}_2 + \text{H}_2\text{O}, \quad E_x = E_x^\circ + \frac{0.06}{2} \lg \frac{[\text{NO}_3^-][\text{H}^+]^3}{[\text{HNO}_2]} = 0.94 - 0.09 \cdot \text{pH} + 0.03 \cdot \lg \frac{[\text{NO}_3^-]}{[\text{HNO}_2]};$$

$$\text{NO}_3^- + 4\text{H}^+ + 3e = \text{NO} + 2\text{H}_2\text{O}, \quad E_y = E_y^\circ + \frac{0.06}{3} \lg \frac{[\text{NO}_3^-][\text{H}^+]^4}{p(\text{NO})} = 0.96 - 0.08 \cdot \text{pH} + 0.02 \cdot \lg \frac{[\text{NO}_3^-]}{p(\text{NO})}.$$

(0.25 points for each potential)

c) At $[\text{NO}_3^-] = [\text{HNO}_2] = 1 \text{ mol/L}$, $p(\text{NO}_2) = p(\text{NO}) = 1 \text{ bar}$, we get three linear functions of pH. In the range of positive pH values, the lines do not intersect, and the last line lies entirely under the others. That is, under these conditions, the latter process is thermodynamically favorable. (1 point, 3.5 points in total)

4. The jar contains ions H^+ and NO_3^- , which can be restored, and water, which can oxidize. The tube contains potash (K_2CO_3). Potassium and carbonate ions are inactive, as they have a low oxidizing potential. Thus, an electrochemical reaction occurs with water (oxidation or reduction). Considering that the process in the battery is spontaneous, the only process that can take place is the reduction of nitrate ions to nitrogen oxide, and in the tube, the oxidation of water. The role of the potash is to raise the pH of the solution in order to increase the EMF of the battery. Thus, the anode is a plate in a tube, the cathode is a plate in a jar. (0.5 point for cathode and anode, 0.25 points for full reaction, 0.75 points in total)



5. Again we compose the Nernst equations for the reactions written above, assuming in them $[\text{NO}_3^-] = [\text{H}^+] = 10^{-2} \text{ mol/L}$, $p(\text{NO}) = p(\text{O}_2) = 1 \text{ bar}$ (2 points in total):

$$E_c = E_y = E_y^\circ + \frac{0.06}{3} \lg \frac{[\text{NO}_3^-][\text{H}^+]^4}{p(\text{NO})} = 0.96 - 0.08 \cdot \text{pH} + 0.02 \cdot \lg 10^{-2} = 0.96 - 0.08 \cdot 2 - 0.02 \cdot 2 = 0.76 \text{ V},$$

$$E_a = E(\text{O}_2/\text{H}_2\text{O}) = E^\circ(\text{O}_2/\text{H}_2\text{O}) + \frac{0.06}{4} \lg [\text{H}^+]^4 = 1.23 - 0.06 \cdot \text{pH} = 1.23 - 0.06 \cdot 11 = 0.57 \text{ V},$$

$$E = \text{EMF} = E_c - E_a = 0.76 - 0.57 = 0.19 \text{ V}.$$

6. When current sources are connected in series, electromotive forces add up, therefore $N = 4.5/0.19 = 23.68 = 24$ batteries (0.25 points in total)

7. Standard potential of the battery $E^\circ = 0.96 - 1.23 = -0.27 \text{ V}$, then (1 point for each correct answer, 2 points in total)

$$\Delta G^\circ = -nE^\circ F = 12 \cdot 0.27 \cdot 96485 = 312611.4 = 312.6 \text{ kJ/mol},$$

$$K = \exp\left(\frac{-\Delta G^\circ}{RT}\right) = \exp\left(-\frac{312611.4}{8.314 \cdot 298.15}\right) = 1.7 \cdot 10^{-55}.$$

Problem 2 (author Karpushkin E.A.)

- Concentration of the alcohol in pure water $c = 0$, hence $\sigma = K - L\ln(1) = K$, i.e. 72.8 mN/m (1 point)
- If the surface tension is measured with accuracy $\pm 2\%$, minimal deviation of the value for pure water to be reliably detected is $72.8 \cdot 0.02 = 1.46$ mN/m. The alcohol concentration in such solution can be calculated using the Szyszkowski equation: $72.8 - 1.46 = 72.8 - 16.7\ln(1 + 66c)$, $c = 1.38$ mmol/L (2 points)
- Comparison of the equations shows that $\Gamma_{\max} = \frac{L}{RT}$. Substituting with the numerical values and accounting for $J = Nm$, one gets $\Gamma_{\max} = 6.74 \mu\text{mol}/\text{m}^2$. This amount corresponds to $6.74 \cdot 10^{-6} \cdot 6.02 \cdot 10^{23} = 4.06 \cdot 10^{18}$ of the molecules, hence the area per a molecule is $1/4.06 \cdot 10^{18} = 2.46 \cdot 10^{-19} \text{ m}^2$ (1 point)
- Plugging the numerical values the Szyszkowski equation affords the equilibrium concentrations of the alcohol upon its adsorption:

$$\sigma = 72.8 - 16.7\ln(1 + 66c) \Rightarrow c = \frac{\exp\left(\frac{72.8 - \sigma}{16.7}\right) - 1}{66}$$

Since the obtained values are in mol/L, the solution volume is 0.025 L, and the carbon specimen mass is 1 g, the adsorption in each experiment is numerically equal to $(c_0 - c)/40$ (2 points)

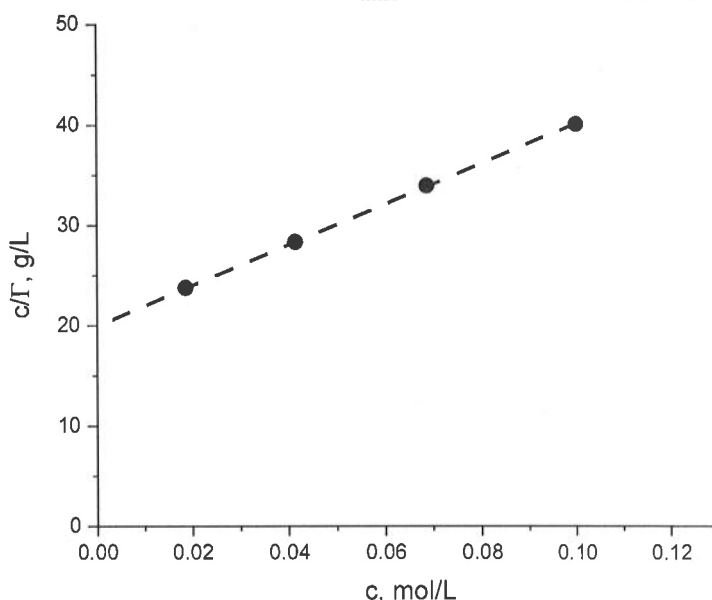
c_0 , mol/L	σ , mN/m	c , mol/L	Γ , mol/g
0.05	59.4	0.0186	$7.85 \cdot 10^{-4}$
0.10	50.8	0.0414	$1.465 \cdot 10^{-3}$
0.15	44.2	0.0688	$2.03 \cdot 10^{-3}$
0.2	38.9	0.1000	$2.5 \cdot 10^{-3}$

- The points in the plot given below show a linear dependence. To derive its parameters, let us

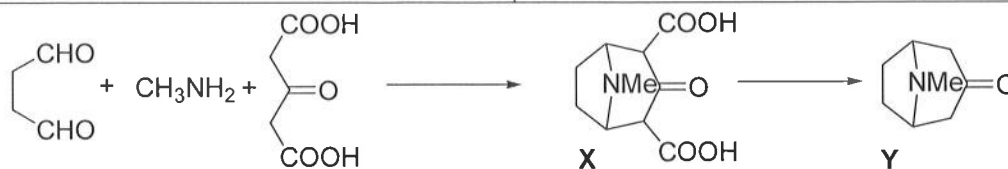
transform the Gibbs equation: $\Gamma = \frac{\Gamma_{\max} \cdot Mc}{1 + Mc} \Rightarrow \Gamma(1 + Mc) = \Gamma_{\max} \cdot Mc \Rightarrow \frac{1 + Mc}{\Gamma_{\max} \cdot M} = \frac{c}{\Gamma} \Rightarrow \frac{c}{\Gamma} = \frac{\Gamma_{\max} + 1}{\Gamma_{\max} \cdot M}$

From the latter equation it is to be seen that the line slope equals $1/\Gamma_{\max}$. From the plot (or coordinates of any pair of the points), $1/\Gamma_{\max} \approx 200$ and therefore $\Gamma_{\max} = 0.005$ mol/g (3 points)

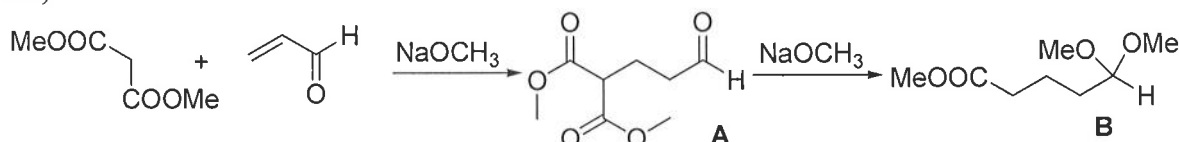
- The maximum adsorption Γ_{\max} value shows that 1 g of the carbon can accommodate 5 mmol ($3.01 \cdot 10^{21}$ molecules) of the alcohol. Since each molecule occupies $2.46 \cdot 10^{-19} \text{ m}^2$, the surface area of 1 g of the carbon equals $2.46 \cdot 10^{-19} \cdot 3.01 \cdot 10^{21} = 740 \text{ m}^2/\text{g}$ (1 point)

**Problem 3 (author Kandaskalov D.V.)**

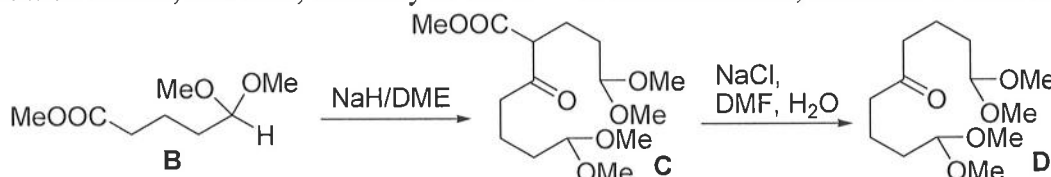
- Based on the molecular formulas of substances **X** and **Y**, one can conclude that elimination of two CO_2 molecules takes place in the second stage. The first step is the double Mannich reaction. The formation of a bicyclic structure proceeds using methylamine which "crosslinks" the cycle. This way we get structures **X** and **Y** (1 point)



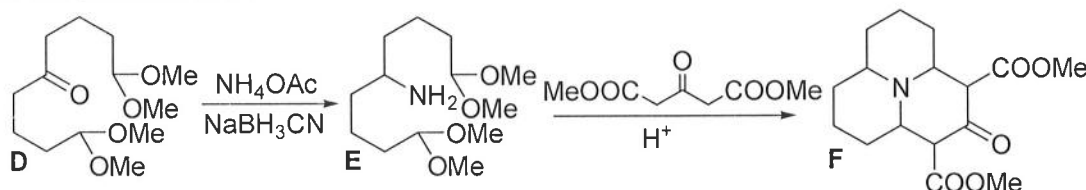
2. Let's start deciphering the scheme from substance **A**. No by-products are released during its formation ($C_5H_8O_4 + C_3H_4O = C_8H_{12}O_5$) to indicate an addition reaction. The presence of a band in the IR spectrum at 1720 cm^{-1} indicates the presence of a carbonyl group. Therefore, 1,4-addition to acrolein occurs. Then the aldol is formed from aldehyde and methanol, while the number of carbon atoms is preserved, 4 new hydrogen atoms appear and one oxygen atom disappears in compound **B**. Oxygen cannot leave in the form of water, then it must probably leave in the form of carbon dioxide, which leads followed by the removal of the COOMe group. This assumption is confirmed by the molecular formula of **B** (1 point)



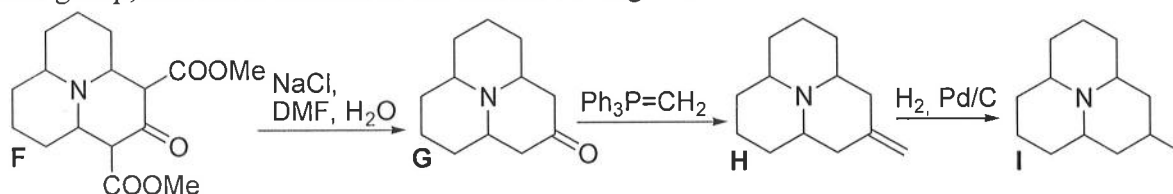
An almost doubling of carbon atoms in the third stage indicates the condensation of two **B** molecules. An ester condensation occurs, and then, similarly to the $A \rightarrow B$ transformation, ketoester **C** turns into ketone **D**.



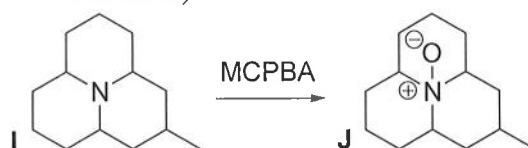
Based on the ^1H NMR spectrum and the ratio of integral intensities of **D**, it could be concluded that **D** is a symmetrical substance. Based on the gross formula, **E** should be an amine. An oxygen atom is lost and NH_3 is added. We also see that the next step in the reaction is a Robinson-Scheppf reaction, with **E** playing a dual role providing the carbonyl and amine components. Given the latter fact, the reaction product must be tricyclic. The formula of **F**:



The molecule of **F** ($C_{16}H_{23}NO_5$) undergoes a double decarboxylation reaction, turning into ketoamine **G** ($C_{12}H_{19}NO$). The subsequent Wittig reaction results in the replacement of the carbonyl oxygen with a methylene group, and the reduction of the double bond gives **I**.

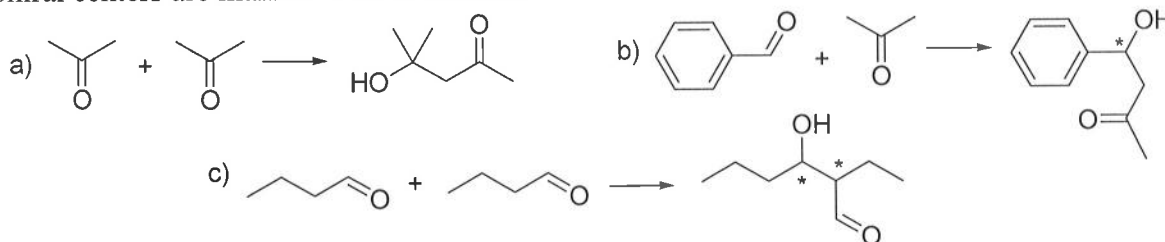


The last step is oxidation. The only atom (group) that can be oxidized is nitrogen. Thus, we get the structure of **J**. (1 point for the **C – J** structures)



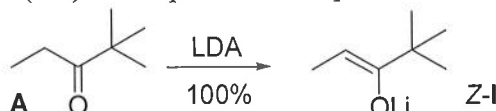
Problem 4 (author Bakhtin S.G.)

1. Chiral centers are marked with an asterisk:



Other answers satisfying the conditions are also accepted (1.5 points)

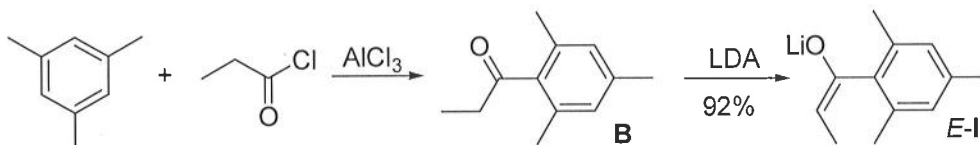
2. Both **A** and **B** contain ethyl group which appears in the ¹H NMR spectrum as quadruplet (2H) and triplet (3H). The remaining singlet (9H) corresponds to the protons of the *tert*-butyl group.



Following exactly the same logic, R₂ of ketone **B** contains in the spectrum three singlets of 2H, 3H, and 6H. According to the condition, **B** can be obtained by the Friedel-Crafts reaction. Therefore, some of signals correspond to aromatic protons, while others correspond to side chain protons. At the same time, the singlet with intensity 6H hardly corresponds to the aromatic, most likely it is 2CH₃. A singlet (3H) also cannot correspond to benzene protons, since it is difficult to have 3 equivalent aromatic hydrogen atoms in the compound C₂H₅C(O)-Ar by symmetry. Hence, this signal is another CH₃. Only the last singlet of 2 equivalent H atoms remains for aromatics, i.e. the ring in the ketone contains 4 substituents. There are two ways to put it all together:



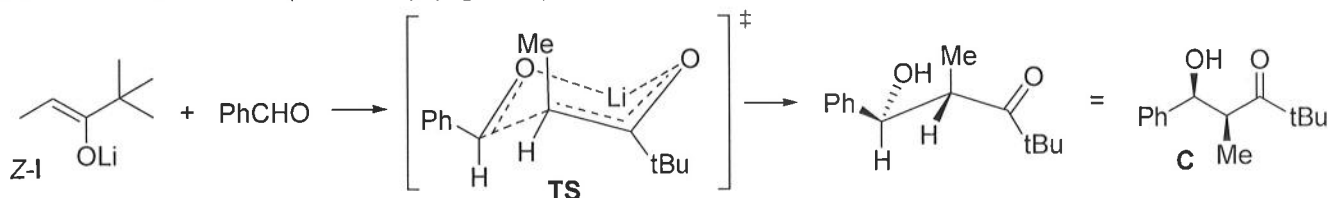
However, only the second ketone can be obtained regioselectively by the Friedel-Crafts reaction. (2 points)

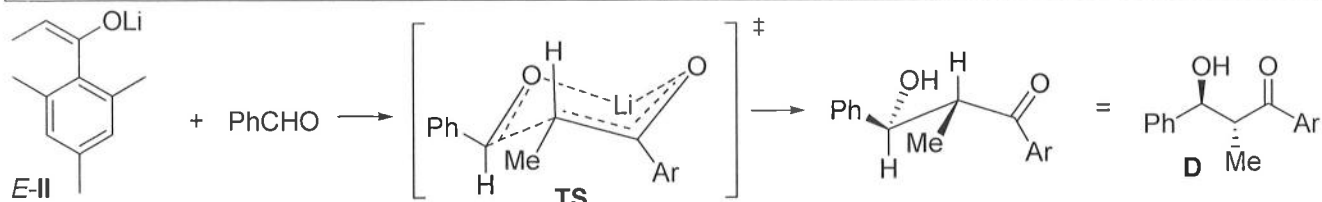


3. Fragments of the initial carbonyl component (benzaldehyde) and lithium enolate are easily detected in the **TS** structure:



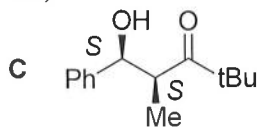
To add substituents, it is necessary to take into account the fact that, according to the condition, the phenyl substituent will take the equatorial position, and the hydrogen atom will take the axial position. Substituents in the enolate are determined based on the geometry of the enolate – *Z/E*. Based on this, the structures of the condensation products can be established. In both cases, the products are formed along with their enantiomers (racemate) (2 points)



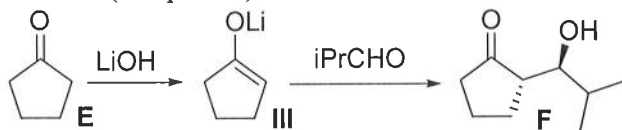


4. The results of p. 3 allow us to conclude that the *syn*-diastereomer is formed from the *Z*-enolates, and the *anti*-diastereomer is formed from the *E*-enolates (1 point)

5. The configuration of the chiral centers of **C**. If its enantiomer has been depicted, then the configuration indices will be opposite (1 point)

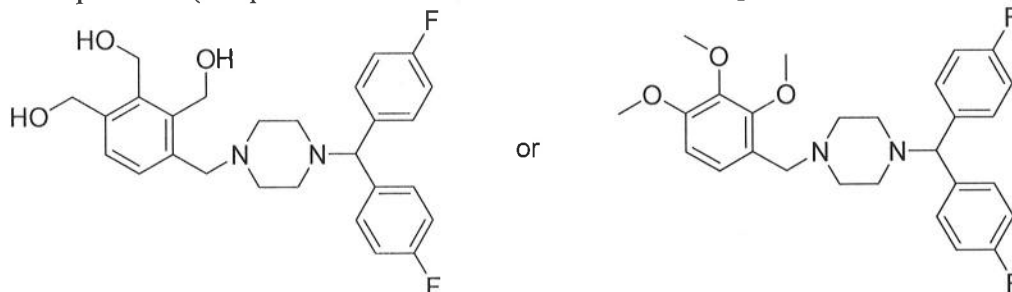


6. Aldol condensation of **E** (C_nH_mO) with isobutyric aldehyde occurs according to the equation: $C_nH_mO + C_4H_8O = C_{n+4}H_{m+8}O_2$ (**F**). Since **F** contains 2 oxygen atoms, then $M_F = 32/0.2051 = 156$. Hence $M_E = 156 - M_{C_4H_8O} = 84$. This condition is satisfied only by the only option when $n = 5$, $m = 8$, C_5H_8O . Then 8H atoms and two signals of the same intensity in the 1H NMR spectrum indicate the presence of $2CH_2$ and $2CH_2$ groups, which unambiguously allows us to conclude that this is cyclopentanone. *E*-enolate is formed from the cyclic ketone, which means that, taking into account step 4, the condensation product will be an *anti*-diastereomer (2.5 points)

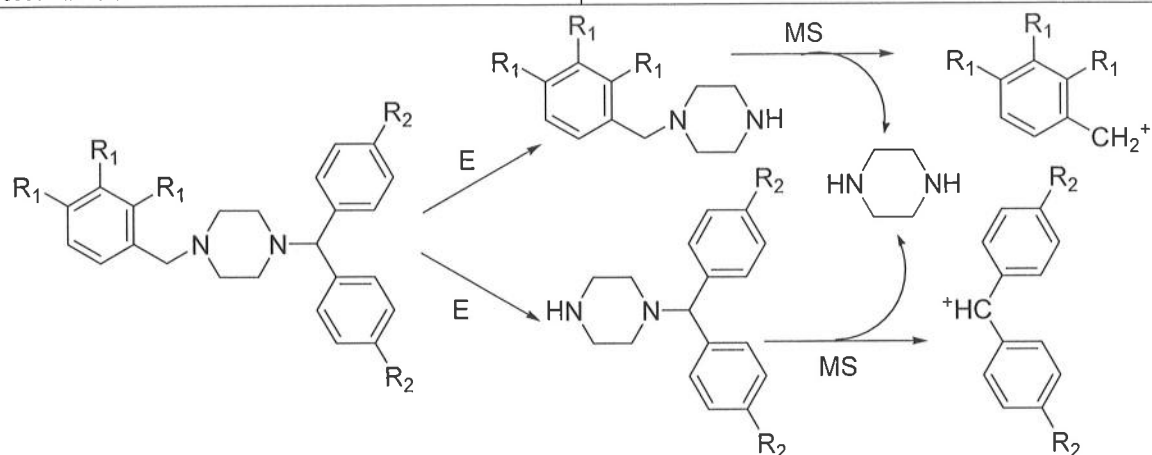


Problem 5 (author Garifullin B.N.)

1. The total molar mass of three R_1 and two R_2 groups equals 131 g/mol (it is needed to subtract the molar mass of the known fragment from that of **Y**). There is no reason to consider the molar ratios of the elements $e_1:e_2:e_3:e_4$ multiple of 2:3:3:9 (e.g. 4:6:6:18), since the average value for $e_1 - e_3$ (if $e_4 = H$) in the latter case would be less than 7 g/mol. The set of substituents can be arranged in two variants: $R_1=(e_2)(e_3)(e_4)$ and $R_2=(e_1)(e_4)_3$ or $R_1=(e_2)(e_3)(e_4)_3$ and $R_2=e_1$. There are no reasonable combinations of four elements for the former variant, whereas the latter one can be deciphered, if $R_2=e_1=Hal$. The molar mass left for R_1 is 31 g/mol in the case of fluorine, and 20 g/mol in the case of chlorine. Thus, it is fluorine with the total atomic mass of e_2 and e_3 of 28 g/mol, which corresponds to C and O. Thus, two structures of **Y** are possible (0.5 point for each correct substituent, 1.5 point in total):

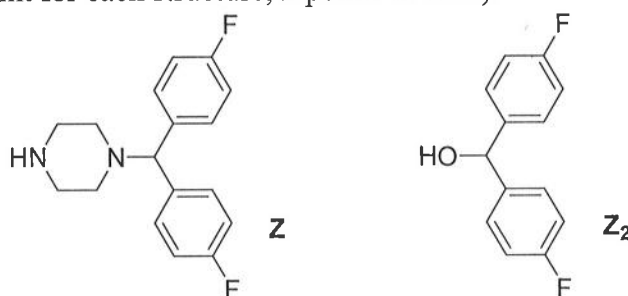


2. Comparison of the spectral data of **X** and **Z** reveals that one and the same fragment of Lomerizine is being lost as result of their destruction. With due respect to protonation and ionization of the initial/resulting molecules, the fragment has the molar mass of $86-2=84$ g/mol (according to the task conditions, the charge of any ionized particle equal +1, thus m/z transforms into m). Such a fragment must be located in the center of the molecule and should contain two similar moieties serving as targets for one and the same enzyme. Piperazine residue ($C_4H_8N_2$) turns out to be the only possible variant. Then the enzyme (E) and the ionization source of the mass-spectrometer (MS) sequentially act upon both C-N bonds in the Lomerizine molecule leading to the X_1^+ и Z_1^+ ions according to the scheme (1.5 point):

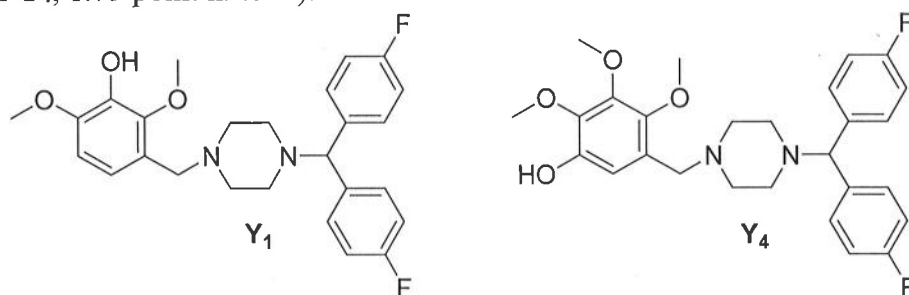


Thus, the total molecular mass of **X** and **Z** equals $468 + 86 = 554$ g/mol. It is not yet possible to exactly attribute the structures on the scheme (**X** or **Z**).

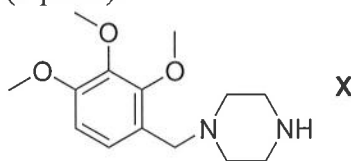
3. The fluorine containing fragment of the Lomerizine molecule is highly symmetric. Taking into account the presence of O atom in **Z**₂ and high abundance of hydrolases, the following structures can be proposed for **Z** and **Z**₂ (1 point for each structure, 2 points in total):



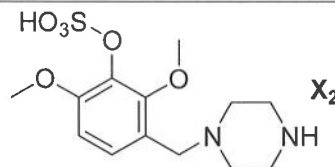
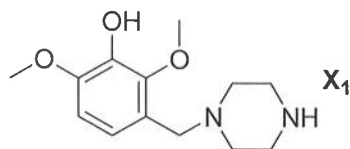
4. The variant of the structure of **Y** with three hydroxyl groups (see above) is already quite hydrophilic, and no modifications described for **Y**₁ – **Y**₄ can be proposed for it. Such variant can be put forward for the other variant of the structure of **Y**, including hydrolysis of any of the methoxy groups affording the hydroxyl one (formation of **Y**₁ – **Y**₃) as well as oxidation (e.g. of a C atom of the benzene ring) leading to an additional hydroxyl group (**Y**₄). Note that the retained methoxy group and the additional O atom totally increase the molecular mass (compared to **Y**₁) by $14+16=30$ g/mol (0.75 point for **Y**₁, 1 point for **Y**₄, 1.75 point in total).



5. The structure of Trimetazidine is (1 point):



6. The difference of the m/z values of the protonated **X**₁ molecule and the common ionic product formed as a result of fragmentation equals $253-167=86$ g/mol, which suggests that the piperazine fragment is metabolically unchanged. Then, the transition from Trimetazidine ($M=266$ g/mol) to **X**₁ leads to the loss of $266-252=14$ g/mol, which is due to (see above) hydrolysis of a methoxy group on the way from **X** to **X**₁. The difference of the m/z values of **X**₁ and **X**₂ equals $333-253=80$ g/mol. With due account for further increase of hydrophilicity and readiness of a sulfo group elimination as a result ionization in the mass-spectrometer, formation of Desmethyl trimetazidine-O-sulfate can be proposed (one of three variants of each compound in given below) (0.75 point **X**₁, 1.5 point **X**₂, 2.25 point in total):



Problem 6 (author Shved A.M.)

1. The molar concentration of iodine in saturated solution (1 point):

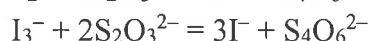
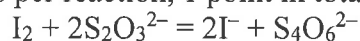
$$c(I_2) = \frac{n(I_2)}{V(sol)} = \frac{m(I_2)}{M(I_2) \cdot V(sol)} = \frac{1.00 \text{ g}}{254 \text{ g/mol} \cdot 3.450 \text{ L}} = 1.14 \cdot 10^{-3} \text{ M}$$

2. The expression for K_D is directly related to the ratio of mass fractions of iodine (1 point):

$$K_D = \frac{[I_2]_{org}}{[I_2]_{aq}} = \frac{n(I_2)_{org} V_{aq}}{n(I_2)_{aq} V_{org}} = \frac{m(I_2)_{org} V_{aq}}{m(I_2)_{aq} V_{org}} = \frac{w(I_2)_{org} m_{org} V_{aq}}{w(I_2)_{aq} m_{aq} V_{org}} = \frac{w(I_2)_{org} \rho_{org}}{w(I_2)_{aq} \rho_{aq}} = \frac{57.2 \cdot 1.59}{1} = 91$$

3. According to VSEPR theory: AX_2E_3 has a linear structure, I–I–I angle is 180° (0.5 points per index in AX_nE_m and 0.5 points for the angle, 1.5 points in total).

4. Reaction equations (0.5 points per reaction, 1 point in total):



5. From the readings of titrations, it is possible to determine the total concentrations of iodine in the organic (0.5 points) and aqueous phases (0.5 points):

$$[I_2]_{org} = \frac{c(Na_2S_2O_3) \cdot V(Na_2S_2O_3)_{org}}{2V_{aliq}} = \frac{0.2500 \text{ M} \cdot 3.70 \text{ mL}}{2 \cdot 10.00 \text{ mL}} = 0.04625 \text{ M}$$

$$[I_2]_{aq} + [I_3^-]_{aq} = \frac{c(Na_2S_2O_3) \cdot V(Na_2S_2O_3)_{aq}}{2V_{aliq}} = \frac{0.2500 \text{ M} \cdot 13.90 \text{ mL}}{2 \cdot 10.00 \text{ mL}} = 0.17375 \text{ M}$$

Then the initial chemical amount of iodine in the Lugol's solution (0.5 points):

$$n(I_2)_0 = [I_2]_{org} V_{org} + ([I_2]_{aq} + [I_3^-]_{aq}) V_{aq} = 0.0463 \text{ M} \cdot 0.050 \text{ L} + 0.1738 \text{ M} \cdot 0.100 \text{ L} = 0.0197 \text{ mol}$$

And its mass fraction (1 point):

$$w(I_2) = \frac{m(I_2)}{m_{aq}} = \frac{M(I_2)n(I_2)_0}{\rho_{aq} V_{aq}} = \frac{254 \text{ g/mol} \cdot 0.0197 \text{ mol}}{1 \text{ g/mL} \cdot 100 \text{ mL}} = 0.050 \text{ (5.0\%)}$$

Knowing the iodine distribution constant and its concentration in the organic phase, it is possible to find the equilibrium concentration of I_2 in the aqueous phase (0.5 points):

$$[I_2]_{aq} = \frac{[I_2]_{org}}{K_D} = \frac{0.0463 \text{ M}}{91} = 5.09 \cdot 10^{-4} \text{ M}$$

Then the concentration of the complex (0.5 points):

$$[I_3^-]_{aq} = 0.1738 \text{ M} - 5.09 \cdot 10^{-4} \text{ M} = 0.1733 \text{ M}$$

It remains to find the concentration of free iodide ions in the solution via the initial molar concentration of potassium iodide (0.5 points) and the concentration of the resulting complex (0.5 points):

$$c(I^-)_0 = \frac{n(KI)}{V_{aq}} = \frac{w(KI) \cdot m_{aq}}{M(KI)V_{aq}} = \frac{w(KI) \cdot \rho_{aq}}{M(KI)} = \frac{0.10 \cdot 1000 \text{ g/L}}{166 \text{ g/mol}} = 0.6024 \text{ M}$$

$$[I^-]_{aq} = c(I^-)_0 - [I_3^-]_{aq} = 0.6024 \text{ M} - 0.1733 \text{ M} = 0.4291 \text{ M}$$

Finally, the constant of formation of the complex I_3^- (1 point):

$$K_I = \frac{[I_3^-]_{aq}}{[I_2]_{aq}[I^-]_{aq}} = \frac{0.1733}{5.09 \cdot 10^{-4} \cdot 0.4291} = 793.$$

In the case of using $K_D = 150$:

$$[I_2]_{aq} = \frac{[I_2]_{org}}{K_D} = \frac{0.0463 \text{ M}}{150} = 3.09 \cdot 10^{-4} \text{ M}$$

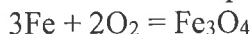
$$[I_3^-]_{aq} = 0.1738M - 3.09 \cdot 10^{-4}M = 0.1735M$$

$$[I^-]_{aq} = c(I^-)_0 - [I_3^-]_{aq} = 0.6024M - 0.1735M = 0.4289M$$

$$K_1 = \frac{[I_3^-]_{aq}}{[I_2]_{aq}[I^-]_{aq}} = \frac{0.1735}{3.09 \cdot 10^{-4} \cdot 0.4289} = 1309$$

Problem 7 (author Khvalyuk V.N.)

1. Black iron(II,III) oxide is formed due to the reaction equation (0.5 points):



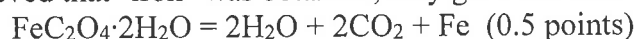
2. The mass fraction of oxygen in iron (II) and (III) oxalates is less than the value given in the task condition. It can be assumed that is the crystalline hydrate of the composition $FeC_2O_4 \cdot xH_2O$.

$$M_r(O) = 16.00; M_r(FeC_2O_4) = 143.9; M_r(H_2O) = 18.01;$$

$$0.5336 = \frac{16.00 \cdot (4 + x)}{143.9 + x \cdot 18.01}$$

Solving this equation, we get $x = 2$. **A** – $FeC_2O_4 \cdot 2H_2O$ (1.0 point)

3. Since the authors believed that "iron" was obtained, they gave the following reaction equation:



4. If the composition of the gas mixture corresponded to the above equation (2 mol CO_2 + 2 mol H_2O , molar mass 31.0 g/mol), then the density of the gas mixture at 280°C and 110.8 kPa would be equal to:

$$M(H_2O) = 18.01 \text{ g/mol}; M(CO_2) = 44.01 \text{ g/mol};$$

$$\frac{110.8 \cdot (2 \cdot 18.01 + 2 \cdot 44.01)}{(2 + 2) \cdot 8.314 \cdot (273 + 280)} = 0.747 \text{ g/dm}^3.$$

This value is more than indicated in the problem condition. It means that the composition of the mixture does not correspond to the stoichiometrical ratio of the given reaction. Therefore, it should be concluded that there is one more component (or several) with a molar mass less than 31.0 g/mol. Based on the elemental composition, such substances could be H_2 and CO , and the additional oxygen atoms could be associated with iron atoms. The presence of CO seems more likely, since the ability to remove oxygen from iron is higher for hydrogen. We will assume that the mixture consists of 2 mol H_2O , $(2 - y)$ mol CO_2 , and y mol CO . $M(CO) = 28.01$ g/mol. The molar mass of a real gas mixture is:

$$\frac{\rho RT}{p} = \frac{0.6507 \cdot 8.314 \cdot (273 + 280)}{110.8} = 27.00 \text{ g/mol.}$$

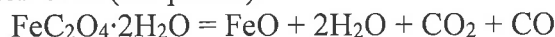
Knowing the molar composition of the mixture, we can make an equation:

$$M = \frac{m}{n} = \frac{2 \cdot 18.01 + (2 - y) \cdot 44.01 + y \cdot 28.01}{2 + (2 - y) + y} = 27.00 \text{ g/mol.}$$

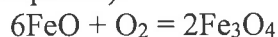
Solving this equation, we get $y = 1.00$. In the gas mixture there is 1 mole of CO_2 and 1 mol of CO per 2 moles of H_2O .

Molar fractions of components are: H_2O – 50.0 %, CO_2 – 25.0 % and CO – 25.0 % (4.0 points)

5. The decomposition reaction of **A** (2.0 points):



6. The burning of "pyrophoric iron" (1.0 points):



7. The reason for the high activity of the obtained product is the very small particle size (FeO nanoparticles are formed) (1.0 point)

Problem 8 (author Likhanov M.S.)

1. The unknown element **X** – phosphorus, which can be determined from the knowledge of its chemical properties, as well as by confirming the calculations. For example, from the mass fraction of water in **A2**, it is not difficult to calculate its molar mass:

$$M(A2 \cdot 2H_2O) = 2 \cdot 18 / 0.1818 = 198 \text{ g/mol, and } M(A2) = 162 \text{ g/mol.}$$

Since **A2** and **A3** are isomers, and there are two nonequivalent **X** atoms in the NMR spectrum of **A3**, we can assume the following composition of acids **A2** and **A3** as $H_nX_2O_z$. Since the **X** atom is in a tetrahedral

environment, the acid can contain a maximum of 6 oxygen atoms, then the H_aX_2 fragment accounts for $162 - 6 \cdot 16 = 66$ g/mole. Phosphorus is closest in mass, so the composition of acids **A2** and **A3** can be written as $H_4P_2O_6$.

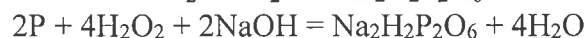
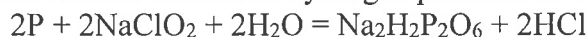
Thus, **X** is P, the composition of **A2** and **A3** is $H_4P_2O_6$.

White phosphorus dissolves in alkali to form phosphine and hypophosphite:



G – PH_3 , **B1** – NaH_2PO_2 . Then **A1** – H_3PO_2 .

Red phosphorus is oxidized with sodium chlorite or hydrogen peroxide to form hypophosphoric acid:



(any of the reactions is counted as correct; it is possible to record salt in the form of $Na_4P_2O_6$).

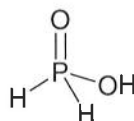
B2 – $Na_2H_2P_2O_6$ or $Na_4P_2O_6$.

When hypophosphoric acid **A2** is heated, it isomerizes into iso-hypophosphoric acid **A3**, and also disproportionates:

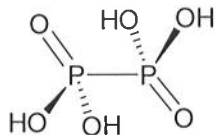


Acid containing a smaller number of oxygen atoms **A4** – $H_4P_2O_5$ – pyrophosphorous acid, and **A5** – $H_4P_2O_7$ – pyrophosphoric acid (0.4 points for each compound and equation of the reaction, 4.4 points in total)

2. H_3PO_2 – has a distorted tetrahedral structure – in the center with a phosphorus atom, and two hydrogen atoms are attached directly to phosphorus, as a result of which this acid is monobasic.

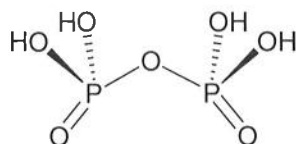


In **A2**, the two phosphorus atoms are also in a tetrahedral environment, with the phosphorus atoms directly bonded to each other. Then with each phosphorus atom there should be a double bond with oxygen and two more single bonds with $-OH$ groups. Taking into account the presence of an inversion center, a 2-fold rotation axis, and a mirror plane perpendicular to it, two $-PO(OH)_2$ groups should be located relative to each other in a staggered conformation:

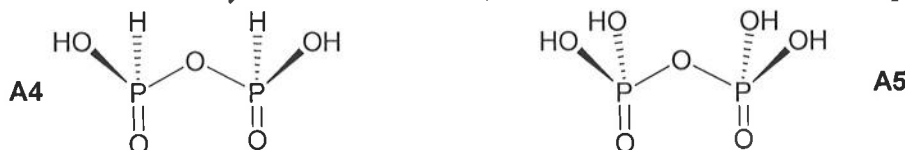


In this molecule, the inversion center lies in the middle of the P–P bond, the 2-fold rotation axis passes through the inversion center perpendicular to the figure plane, and the mirror plane lies in the pattern plane and contains the P–P bond and oxygen atoms (from P=O).

In acid **A3**, which has a composition similar to **A2**, there are no symmetry elements; therefore, it can be assumed that one of the oxygen atoms has become a bridge between phosphorus atoms. Due to the presence of one P–H bond, symmetry is lost::



A4 and **A5** also contain a bridging oxygen atom, however, due to the fact that **A4** has two P–H and two P–OH bonds, the molecule is less symmetrical than **A5**, in which the P–H bonds are replaced by P–OH:



In **A4**, the mirror plane runs perpendicular to the pattern plane through the bridging oxygen atom. In **A5**, an additional mirror plane appears, which lies in the plane of the figure and contains phosphorus atoms. (0.5 points for each structure, 2.5 points in total)

3. To calculate the composition of salts, we denote their composition by the following formulas: **B6** – $Na_xP_yO_z$, **B7** – $Na_xP_yO_{z+1}$, **B8** – $Na_xP_yO_{z+2}$.

Then it is possible to compose a system of two equations for the mass fractions of oxygen. M is the molar mass of **B6**:

$$16z/M = 0.3810 \quad \text{and} \quad (16z + 16)/(M + 16) = 0.4091.$$

$z = 8$, $M = 336$ g/mol.

Thus, the composition of **B6** is $\text{Na}_x\text{P}_y\text{O}_8$, $M(\text{Na}_x\text{P}_y^{16+}) = 208$ g/mol. The only reasonable solution by iterating is $x = 5$, $y = 3$.

Thus, **B6** – $\text{Na}_5\text{P}_3\text{O}_8$, **B7** – $\text{Na}_5\text{P}_3\text{O}_9$, **B8** – $\text{Na}_5\text{P}_3\text{O}_{10}$.

(0.2 points for each compound, 1 point for calculations, 1.6 points in total)

4. It is easy to assume the structure of the anionic residue **B6** – all phosphorus atoms are connected in a chain, the terminal phosphorus atoms contain one $\text{P}=\text{O}$ bond and two $\text{P}-\text{O}^-$ bonds each, and the middle phosphorus atom has one double bond $\text{P}=\text{O}$ and one $\text{P}-\text{O}^-$ bond. Only in this way is the condition of the tetrahedral environment of phosphorus and the presence of at least one $\text{P}=\text{O}$ bond fulfilled. Further, when moving to **B7** and **B8**, the basicity of the acid does not change, but one oxygen atom is added. It is logical to assume that an additional oxygen atom is successively inserted between phosphorus atoms, becoming a bridge (0.5 points for each structure, 1.5 point in total)

