SECTION I. PHYSICAL CHEMISTRY

Problem 1 (author Kandaskalov D.V.)

1. We know the approximate half-life of the nucleus, this allows us to calculate the possible values of the atomic mass of the nucleus, calculating the number of atoms decayed in $t = 2$ years ($N_0 - N$):

$$\ln\frac{N}{N_0} = -\lambda \cdot t = -\frac{\ln 2}{t_{1/2}} \cdot t \rightarrow N = N_0 \exp\left(-\frac{\ln 2}{t_{1/2}} \cdot t\right) \rightarrow N_0 - N = N_0\left(1 - \exp\left(-\frac{\ln 2}{t_{1/2}} \cdot t\right)\right).$$

Substitute the two extreme values (10 and 16 years) for the half-life:

$$N_0 - N = 2.82 \cdot 10^{21}\left(1 - \exp\left(-\frac{\ln 2}{10} \cdot 2\right)\right) = 0.365 \cdot 10^{21} \text{ nuclei},$$

$$N_0 - N = 2.82 \cdot 10^{21}\left(1 - \exp\left(-\frac{\ln 2}{16} \cdot 2\right)\right) = 0.234 \cdot 10^{21} \text{ nuclei}.$$

On the other hand, one can calculate the mass of decomposed nuclei **Y** (without knowing the meaning of the unit Ci). If the specific activity is 9650 Ci/g, then the loss of activity of 14.475 Ci should correspond to 14.475/9650 = 0.0015 g of the substance, from which the atomic mass **Y** can be estimated:

$$\frac{N_0 - N}{N_A} = \frac{\Delta m}{M} \rightarrow M = \frac{\Delta m \cdot N_A}{N_0 - N} = \frac{0.0015 \cdot 6.02 \cdot 10^{23}}{(0.234 \text{ or } 0.365) \cdot 10^{21}} = 2.47 - 3.85 \text{ g/mol}.$$

The only integer in the resulting interval is 3 g/mol (1 point), so we can find the exact half-life of the nucleus. First we write:

$$N_0 - N = \frac{\Delta m}{M} \cdot N_A = \frac{0.0015}{3} \cdot 6.02 \cdot 10^{23} = 3.01 \cdot 10^{20} \text{ nuclei}$$

$$\rightarrow N = 2.82 \cdot 10^{21} - 3.01 \cdot 10^{20} = 2.52 \cdot 10^{21} \text{ nuclei} \rightarrow N/N_0 = 0.893.$$

Now calculate the exact half-life (1 point):

$$\ln\frac{N}{N_0} = -\frac{\ln 2}{t_{1/2}} \cdot t \rightarrow t_{1/2} = -\frac{\ln 2}{\ln N/N_0} \cdot t = -\frac{\ln 2}{\ln 0.893} \cdot 2 = 12.25 \text{ years}. \text{ (2 points in total)}$$

2. Let's calculate what part of the **Y** nuclei will decay in 2 months (0.167 years):

$$\ln\frac{N}{N_0} = -\lambda \cdot t = -\frac{\ln 2}{t_{1/2}} \cdot t \rightarrow N = N_0 \exp\left(-\frac{\ln 2}{t_{1/2}} \cdot t\right) \rightarrow$$

$$\frac{N_0 - N}{N_0} = 1 - \exp\left(-\frac{\ln 2}{t_{1/2}} \cdot t\right) = 1 - \exp\left(-\frac{\ln 2}{12.25} \cdot 0{,}167\right) = 0.0041.$$

This part corresponds to 2.46 g and thus the loss of the budget will be $ 73,500. (1 point in total)

3. **a**) We know that the atomic mass of **Y** is 3, but we don't know the number of protons in the nucleus. Possible values: 1 (tritium), 2 (helium), or 3 (lithium). The last option can be excluded, since a nucleus consisting of only three protons does not exist. Let's take the reaction of artificial fusion of the **Y** nucleus: ${}^{2Z}_{Z}\mathbf{A} + {}^{1}_{0}n \rightarrow {}^{2Z'}_{Z'}\mathbf{Z} + {}^{3}_{Z''}\mathbf{Y}$. From here we get a system of equations:

$$\begin{cases} 2Z + 1 = 2Z' + 3 \\ Z + 0 = Z' + Z'' \end{cases} \Rightarrow \begin{cases} Z - Z' = 1 \\ Z - Z' = Z'' \end{cases} \Rightarrow Z'' = 1.$$

Thus, the nucleus **Y** – T (tritium) (1 point). Then the nucleus **X** must be hydrogen or deuterium. **b**) Write the reaction in the reactor: ${}^{3}_{1}\mathrm{T} + {}^{A}_{1}\mathbf{X} \rightarrow {}^{2Z'}_{Z'}\mathbf{Z} + {}^{1}_{0}n$. It turns out that $Z' = 2$, then it is helium and $A = 2$, that is, **X** is deuterium (**1 point**). Returning to the first reaction, we find that **A** is ^{6}Li. Then **X** – ^{2}D, **Y** – ^{3}T, **Z** – ^{4}He, **A** – ^{6}Li. We will get the following three reactions: (1 point for each reaction)

${}^{6}_{3}\mathrm{Li} + {}^{1}_{0}n \rightarrow {}^{4}_{2}\mathrm{He} + {}^{3}_{1}\mathrm{T}$, ${}^{3}_{1}\mathrm{T} + {}^{2}_{1}\mathrm{D} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}n$, ${}^{14}_{7}\mathrm{N} + {}^{1}_{0}n \rightarrow {}^{12}_{6}\mathrm{C} + {}^{3}_{1}\mathrm{T}$. (5 points in total)

4. Calculate the number of particles in the reactor through its volume: $V = 2\pi^2 R^2 r = 2 \cdot \pi^2 \cdot 9^2 \cdot 0.52 = 831.4\ \text{m}^3$. Number of pairs of nuclei:

$$p = \frac{C \cdot V}{2} = \frac{10^{16} \cdot 831.4 \cdot 10^3}{2} = 4.16 \cdot 10^{21}\ \text{pairs}.\ (1\ \text{point})$$

So the released energy

$$E_{\text{tot}} = p \cdot E_{p=1} = 4.15 \cdot 10^{21} \cdot 3 \cdot 10^{-12} = 1.25 \cdot 10^{10}\ \text{J}.\ (1\ \text{point})$$

Let's find the enthalpy of combustion of one mole of propane and one mole of butane to get the average value of the heat of combustion of 1 mole of a mixture (1: 1) of propane and butane: $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$, $C_4H_{10} + 6.5O_2 \rightarrow 4CO_2 + 5H_2O$.

$$\Delta H_1 = 3\Delta_f H(CO_2) + 4\Delta_f H(H_2O) - \Delta_f H(C_3H_8) =$$
$$= 3 \cdot (-393.5) + 4 \cdot (-285.8) - (-103.9) = -2220\ \text{kJ/mol},$$
$$\Delta H_2 = 4\Delta_f H(CO_2) + 5\Delta_f H(H_2O) - \Delta_f H(C_4H_{10}) =$$
$$= 4 \cdot (-393.5) + 5 \cdot (-285.8) - (-126.2) = -2877\ \text{kJ/mol},$$
$$\Delta H_{\text{mix}} = 0.5(\Delta H_1 + \Delta H_2) = 0.5(-2220 - 2877) = -2548\ \text{kJ/mol},$$
$$n_{\text{mix}} = \frac{E_{\text{tot}}}{|\Delta H_{\text{mix}}|} = \frac{1.25 \cdot 10^{10}}{|-2.55 \cdot 10^6|} = 0.49 \cdot 10^4\ \text{mol}.\ (2\ \text{points in total})$$

The total mass of deuterium and tritium in the reactor is 34 mg and the energy effect of the reaction is equivalent to the combustion of 4900 moles of the mixture. It should be taken into account that the total energy costs for maintaining the plasma were not taken into account, which can be equivalent to 75–90% of the energy received.

5. Let us write the equation for the density of metal **M** and compound **N**:

$$\rho_M = \frac{M_M \cdot N_M}{V_M \cdot N_A}, \qquad \rho_N = \frac{M_N \cdot N_N}{V_N \cdot N_A}, \qquad \frac{\rho_M}{\rho_N} = \frac{M_M \cdot N_M \cdot V_N}{V_M \cdot M_N \cdot N_N} = 1.23.\ (1\ \text{point})$$

We do not know which cubic cell the metal **M** has, then **NM** can be 1, 2 or 4 for cubic, body-centered and face-centered lattices. Let's leave it as a parameter. The formula unit of **N** is **MA**, where **M** is metal and **A** is the second element (we don't know if it's metal or non-metal), $N_N = 1$, and $M_N = M_M + x$. The unit cell volume of metal **M**, compounds **N** and their ratio will be:

$$V_M = a^3 = 3.16^3 = 31.55\ \text{A}^3,$$
$$V_N = \frac{\sqrt{3}}{2} \cdot a^2 \cdot c = \frac{\sqrt{3}}{2} \cdot 2.92^2 \cdot 2.82 = 20.82\ \text{A}^3,$$
$$\frac{V_N}{V_M} == 0.660.$$
$$\frac{\rho_M}{\rho_N} = \frac{M_M \cdot N_M \cdot V_N}{V_M \cdot M_N \cdot N_N} = 0.660 \cdot \frac{M_M}{M_M + x} \cdot \frac{N_M}{1} = 1.23,$$
$$\omega_M = \frac{M_M}{M_M + x} = \frac{1.239}{0.660 \cdot N_M} = \frac{1.877}{N_M}. \qquad (2\ \text{points for}\ \omega_M)$$

We have found that the mass fraction is in the range of 0.50–1.00. Since the value of N_M can only be equal to 2 (body-centered cell), the mass fraction of metal is 0.9386. That is, the atomic mass of **M** is 15.3 times greater than **A**. (1 point) Knowing that **M** can have an atomic mass of 140–260 (if we exclude radioactive elements, then not higher than 210), we conclude that the atomic mass of **A** lies in the range of 9.15-17 (not higher than 13.7 without radioactive elements). (1 point) So it could be B, C, (N, O, including radioactive elements). By simple selection, we get **N** – WC, **M** – W. (5 points in total)

Problem 2 (authors Rozantsev G.M., Shved E.N.)

1. As a result of hydrolysis of Me^{3+}, $Me^{3+}$and $MeOH^{2+}$ participate in the routes: $Me^{3+} + X^- \rightarrow MeX^{2+}$ (k_1) and $MeOH^{2+} + X^- \rightarrow MeOHX^+$ (k_2). (**1 point in total**)

2. Reaction rate of $[Fe(H_2O)_6]^{3+} + Cl^-$, proceeding in two routes, $r = k_1[Fe^{3+}]\ C(Cl^-) + k_2[FeOH^{2+}]\cdot C(Cl^-)$. Since $[Fe^{3+}]$ and $[FeOH^{2+}] >> [FeCl^{2+}]$ and $[FeOHCl^+]$, then the latter can be neglected and $C(Fe) = [Fe^{3+}] + [FeOH^{2+}] = [Fe^{3+}]([H^+] + K_a)/[H^+])$, $[Fe^{3+}] = [H^+]\cdot C(Fe)/([H^+] + K_a)$, $[FeOH^{2+}] = K_aC(Fe)/([H^+] + K_a)$ (1 point). After substitution into the equation for r we have the kinetic equation $r = (k_1[H^+] + k_2K_a)/([H^+] + K_a)C(Fe)\ C(Cl^-)$ and $r = k_{obs}C(Fe)\ C(Cl^-)$ (1.5 points). The observed rate constant, as it was obtained by Connick and Coppel, equals $k_{obs} = (k_1[H^+] + k_2K_a)/([H^+] + K_a)$.

For the values of k_{obs} at $[H^+] = 0.1$, 0.05 and 0.01 mol/L one can compose a system of three equations with three unknowns:

$709.2 = (0.1k_1 + k_2K_a)/(0.1 + K_a)$,

$1325.2 = (0.05k_1 + k_2K_a)/(0.05 + K_a)$,

$4458.0 = (0.01k_1 + k_2K_a)/(0.01 + K_a)$.

Solving the system of equations gives the value of $K_a = 6.8\cdot10^{-3}$ (1 point), $k_1 = 9.42$ (1 point), $k_2 = 11000$ (1 point). (5.5 point in total)

3. For the reaction $Fe^{3+} + HN_3 \rightleftarrows FeN_3^{2+} + H^+K = [FeN_3^{2+}][H^+]/([Fe^{3+}][HN_3])$. Since the reaction proceeds in two routes and is reversible, then its rate equals to the sum of the forward (r_+) and backward (r_-) reaction rates: $r = r_+ - r_-$. Considering both of these points, $r = k_3[Fe^{3+}][HN_3] + k_4[FeOH^{2+}][HN_3] - k_{-3}[H^+]C(FeN_3^{2+}) - k_{-4}C(FeN_3^{2+})$.

For the forward reaction $r_+ = (k_3[Fe^{3+}] + k_4[FeOH^{2+}])[HN_3]$. Since $[Fe^{3+}] = [H^+]\ C(Fe)/([H^+] + K_a)$ and $[FeOH^{2+}] = K_aC(Fe)/([H^+] + K_a)$, then substituting the concentrations in the expression for r_+ we obtain: $r_+ = (k_3[H^+] + k_4K_a)/([H^+] + K_a)\ C(Fe)[HN_3]$ (1 point).

In equilibrium $C(FeN_3^{2+}) = [FeN_3^{2+}]$, $r_+ = r_-$. Therefore, we get the equation $(k_{-3}[H^+] + k_{-4})[FeN_3^{2+}] = (k_3[H^+] + k_4K_a)/([H^+] + K_a)C(Fe)\ [HN_3]$ and $(k_{-3}[H^+] + k_{-4}) = C(Fe)\ [HN_3](k_3[H^+] + k_4K_a)/([H^+] + K_a)[FeN_3^{2+}]$. After substitution into the equation for the total rate, k_{-3}, k_{-4} disappear and we obtain $r = ((k_3[H^+] + k_4K_a)/([H^+] + K_a))C(Fe)[HN_3] - k_3[H^+] + k_4K_a)/([H^+] + K_a)(C(Fe)[HN_3]C(FeN_3^{2+})/[FeN_3^{2+}])$.

After conversion: $r = (k_3[H^+] + k_4K_a)/([H^+] + K_a)\ C(Fe)\ [HN_3]\ ([FeN_3^{2+}] - C(FeN_3^{2+})/[FeN_3^{2+}])$ (1 point) or $r = k'_{obs}\ ([FeN_3^{2+}] - C(FeN_3^{2+}))$. Since $C(Fe) = [Fe^{3+}]([H^+] + K_a)/[H^+]$, then $k'_{obs} = (k_3[H^+] + k_4K_a)/([H^+] + K_a)\ ([H^+] + K_a)\ [Fe^{3+}]\ [HN_3]/[H^+][FeN_3^{2+}])$ and $k'_{obs} = (k_3[H^+] + k_4K_a)/K_x$ (0.5 points).

Using the table data, we have three equations:

$79.05 = (0.1k_3 + 6.8\cdot10^{-3}k_4)/0.59$,

$78.71 = (0.05k_3 + 6.8\cdot10^{-3}k_4)/0.59$,

$78.44 = (0.01k_3 + 6.8\cdot10^{-3}k_4)/0.59$.

Solving any pair of equations gives $k_3 = 4.0$ (0.5 points), $k_4 = 6800$ (0.5 points). Based on $K = k_3/k_{-3}$, $k_{-3} = k_3/K$ and $k_{-3} = 4.0/0.59 = 6.8$ (0.5 points).

(4 points in total)

4. In the case of anions of weak acids, the anation mechanism includes two stages: reversible $[Fe(H_2O)_6]^{3+} + N_3^-\ k'_{obs} \rightleftarrows [Fe(H_2O)_5OH]^{2+} + HN_3$ (K_x), and irreversible $[Fe(H_2O)_5OH]^{2+} + HN_3 \rightarrow Fe(H_2O)_5N_3 + H_2O$ ($k_4 = 6800$) (0.5 points). Reaction equation with K_x can be obtained by the difference of two equations:

$[Fe(H_2O)_6]^{3+} \rightleftarrows [Fe(H_2O)_5OH]^{2+} + H^+$ (K_a),

$HN_3 \rightleftarrows H^+ + N_3^-$ (K_{a1}).

Then $K_x = K_a/K_{a1} = 6.8\cdot10^{-3}/1.9\cdot10^{-5} = 358$ and the reaction goes almost to completion (0.5 points).

The rate of the irreversible stage $r = k_4[Fe(H_2O)_5OH^{2+}][HN_3]$. From the equilibrium constant of the reversible stage $[Fe(H_2O)_5OH^{2+}] = K_x[Fe(H_2O)_6^{3+}][N_3^-]/[HN_3]$. Hence $r = k_4K_x[Fe(H_2O)_6^{3+}][N_3^-]$ (0.5 points) and the observed constant equals to $k''_{obs} = k_4K_x = 6800\cdot358 = 2.43\cdot10^6$ L·mol·s) (0.5 points).

(2 points in total)

5. The activation energy is found from the Van't Hoff equation:

$$\ln(k_{T2}/k_{T1}) = (E_a/R)(1/T_1 - 1/T_2)E_a = (T_1T_2\cdot R\ln(k_{T2}/k_{T1}))/(T_2 - T_1)).$$

$E_a = (298\cdot313\cdot8.314\cdot\ln(275.9/83.6))/(313 - 298) = 61728$ J/mol. (1.5 points in total)

6. For a strong acid HCl:

1st stage – reversible $[Fe(H_2O)_6]^{3+} \rightleftarrows [Fe(H_2O)_5]^{3+} + H_2O$,

2nd stage – irreversible $[Fe(H_2O)_5]^{3+} + Cl^- \rightarrow Fe(H_2O)_5Cl^{2+}$ (0.5 points).

For a weak acid HN_3:

1st stage – reversible $[Fe(H_2O)_6]^{3+} + HN_3 \rightleftarrows Fe(H_2O)_6^{3+}, N_3^-$,

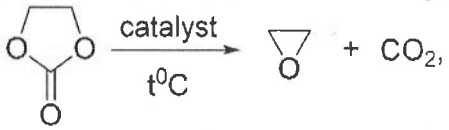
2nd stage – irreversible $[Fe(H_2O)_6]^{3+}N_3^- \rightarrow [Fe(H_2O)_5OH]^{2+} + HN_3^-$ (0.5 points).

The formation of an ion pair at the first stage, accompanied by the formation of a hydrogen bond, ensures the transfer of a proton and obtaining products at the second stage ($[Fe(H_2O)_5OH]^{2+}$ and HN_3), which further in the fast stage give the final products according to the reaction $[Fe(H_2O)_5OH]^{2+} + HN_3 \rightarrow [Fe(H_2O)_5N_3]^{2+} + H_2O$. (1 point in total)

Problem 3 (author Gulevich D.G.)

1. From the proposed structures, polymers **A** (polyamide 12) and **E** (copolymer of 4,4'-methylenediphenyldiisocyanate and THF) have less polar units than **B**, **C** and **D**, and therefore are more hydrophobic. (0.5 points per structure, 1 point in total)

2. **a**) Ethylene carbonate decomposes into carbon dioxide and ethylene oxide (**G**):



which is confirmed by data about M_{av}: $0.5M(\mathbf{G}) + 0.5M(CO_2) = 44$ g/mol, $M(\mathbf{G}) = 44$ g/mol. Therefore, **F** – polyethylene oxide $[-CH_2CH_2O-]_n$.

b) Let's write down the equations for the rates of each polymerization stage:

$$V_i = k_i[H^+A^-][\mathbf{G}],\ V_p = k_p[M^+A^-][\mathbf{G}],\ V_{tr} = k_{tr}[M^+A^-][\mathbf{G}],\ V_t = k_t[M^+A^-].$$

From the stationary approximation $V_i = V_t$ determine $[M^+A^-] = k_i[H^+A^-][\mathbf{G}]/k_t$. Then

$$V_p = \frac{k_i k_p [H^+A^-][\mathbf{G}]^2}{k_t}.$$

c) $$X_{av.} = \frac{V_p}{V_t + V_{tr}} = \frac{k_p[\mathbf{G}]}{k_t + k_{tr}[\mathbf{G}]} = \frac{0.94 \cdot 2.15}{7.5 \cdot 10^{-2} + 8.0 \cdot 10^{-3} \cdot 2.15} = 22.$$

(determination of **G** 1 point, 0.25 points for **F**, 1.75 points for obtaining the expression for the polymerization reaction rate, 0.5 points for calculating X_{av}, 3.5 points in total)

3. **a**) According to the first law of thermodynamics $\Delta U = Q + A$. Calculate the amount of work done by the runner from the data on the generated power–$A = 235 \cdot 3600 = 846$ kJ. Negative values of internal energy, heat and work related to the fact that heat is released into the environment and work is done by the thermodynamic system itself. $Q = \Delta U - A = -3380 - (-846) = -2.534$ MJ. **b**) The air temperature in the room where the person is training will increase by

$$\Delta T = \frac{Q}{c_{air} \cdot m_{air}} = \frac{Q}{c_{air} \cdot \rho_{air} \cdot V_{air}} = \frac{2.534 \cdot 10^6}{1.005 \cdot 10^3 \cdot 1.165 \cdot 2500 \cdot 5} = 0.173\text{K}.$$

(calculation of the amount of heat 1.5 points, 1 point for ΔT, 2.5 points in total)

4. **a**) $V_{micro} = 4/3\pi r^3 = 4/3 \cdot 3.14 \cdot (20 \cdot 10^{-6})^3 = 3.3 \cdot 10^{-14}$ m^3. Mass of one microsphere $m_{micro} = \rho_F \cdot V = 1200$ kg/m$^3 \cdot 3.3 \cdot 10^{-14}$ m^3 $= 3.96 \cdot 10^{-11}$ kg. The molar mass of polyethylene oxide is $22 \cdot 44$ g/mol $= 968$ g/mol, and its mass, taking into account the reaction yield, is equal to 2.15 mol·968 g/mol·0.95 = 1.98 kg. The total number of microspheres that are obtained and incorporate into the runner's clothing $N = 1.98/3.96 \cdot 10^{-11} = 5 \cdot 10^{10}$. **b**) Heat that can be absorbed by a material with a reversible phase change:

$$Q_{abs.} = \int_{T_0}^{T_{p.c.}} c_s dT + \Delta H_{p.c.} + \int_{T_{p.c.}}^{T_f} c_l dT.$$

Taking into account the number of the obtained microspheres $Q_{abs} = 8.48 \cdot 10^{-11} - 5 \cdot 10^{10} \cdot (311 - 307) + 6.11 \cdot 10^{-9} \cdot 5 \cdot 10^{10} + 6.28 \cdot 10^{-11} \cdot 5 \cdot 10^{10} \cdot (313 - 311) = 329$ kJ:

$$\frac{329 \cdot 0.8}{2534} \cdot 100\% = 10\%.$$

(calculation of the polymer mass 0.5 point, 1.5 point for the number of microspheres, 1.75 point for the amount of absorbed heat, 3.75 points in total)

5. **a)** Calculate the generated output voltage:

$$U = \frac{\gamma Ph}{\varepsilon\varepsilon_0} = \frac{\gamma mgh}{\varepsilon\varepsilon_0 S} = \frac{49.6 \cdot 10^{-12} \cdot 55 \cdot 9.8 \cdot 30 \cdot 10^{-6}}{10 \cdot 8.85 \cdot 10^{-12} \cdot 2 \cdot 0.0189} = 0.24\,\text{V}.$$

The current strength is determined by power data: $I = W/U = 10^{-3}/0.24 = 4.2$ mA.

b) For an hour of running, a person can charge the heart rate sensor for $\frac{4.2 \cdot 10^{-3}}{130 \cdot 10^{-3}} \cdot 100\% = 3.2\%$.

c) Determine **L** – $C_xH_yX_z$. Based on mass spectrometry data, it can be assumed that the molar mass **L** is equal to 64 g/mol, then $x = 0.375 \cdot 64/12 = 2$, $y = 0.031 \cdot 64 \approx 2$. Further, $zA_r(X) = 64 - 26 = 38$ g/mol, consequently, X – F, $z = 2$ and **L** – $C_2H_2F_2$. Mass spectrometry data will help to establish the isomer of difluoroethylene. Let us determine which ions correspond to the peaks in the spectrum:

m/z	ion
64	$\mathbf{C_2H_2F_2^+}$
63	$C_2H_2F_2^+ \rightarrow \mathbf{C_2HF_2^+} + H$
50	$C_2H_2F_2^+ \rightarrow \mathbf{CF_2^+} + CH_2$
14	$C_2H_2F_2^+ \rightarrow \mathbf{CH_2^+} + CF_2$

Based on the presence of CF_2^+ and CH_2^+ ions, it can be concluded that **L** is 1,1-difluoroethylene. Therefore, **K** is poly(1,1-difluoroethylene).

(calculation of the output voltage – 1.25 points, 0.75 points for the current strength, 0.25 points for the charge percentage, 1 point for determination **K** and **L**, 1 point for determination the isomer of **L**, 4.25 points in total).

SECTION II. ORGANIC CHEMISTRY

Problem 1 (author Shved A.M.)

1. Since "carbon oxide" **X1** is formed by the reaction of ozone (O_3) with a simple substance **A**, it can be concluded that **A** is one of the allotropic modifications of carbon, and the formula of **X1** is C_xO_y.

Having a mass fraction of oxygen in **X1**, we get: $w(O)_{C_xO_y} = \frac{16.00y}{12.01x+16.00y} = 0.0624 \Rightarrow \frac{x}{y} = 20$

When **X1** decomposes, an oxygen molecule (O_2) is released, and a new "carbon oxide" **X2** is formed. So, **X1** most likely contains at least 3 oxygen atoms, and if $y = 3$, then $x = 60$. This correlates with the use of ozone to oxidize fullerene C_{60}. Then **A** – C_{60}, **X1** – $C_{60}O_3$, and **X2** – $C_{60}O$ (0.5 points per formulas of **A**, **X1**, and **X2**, 0.25 points for calculations, 1.75 points in total).

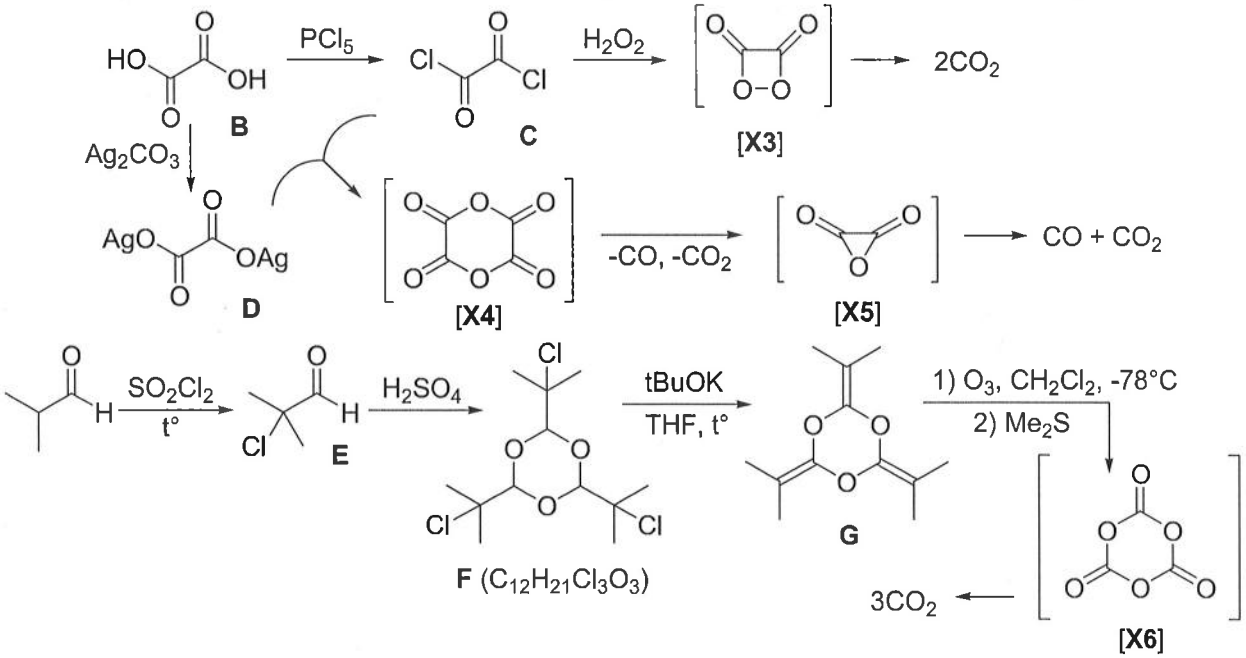
2. The simplest dicarboxylic acid **B** is ethanedioic (oxalic) acid. When phosphorus (V) chloride and silver carbonate react with it, diacyl chloride **C** and silver oxalate (**D**) are formed, respectively. When **C** and **D** react with each other, it is logical to assume a 1:1 reaction with the release of 2 equivalents of AgCl and the closure of the cycle. This gives the desired structure of the "carbon oxide" **X4** with the molecular formula C_4O_6.

This substance successively decomposes to form an equimolar mixture of two gases and substance **X5**, which then also decomposes into the same mixture of gases. Hence, **X4** is formally an **X5** dimer with the formula C_2O_3. The same formula is the sum of the formulas of the gases CO and CO_2, the actual decomposition products. Based on the structure of **X4**, the most likely structure of **X5** is cyclic oxalic acid anhydride.

The stage of **X3** formation from **C** and H_2O_2 can be considered analogous to the reaction of hydrolysis of acyl chlorides. Allowing for an equimolar ratio of reactants and subtracting 2 molecules of HCl as a product, we get **X3** – C_2O_4 with a cyclic structure having a peroxide bridge. Then the **X3** decomposition product, the gas with a density, and therefore a molar mass, higher than the air, is carbon dioxide CO_2. Thus, formally, **X3** is a CO_2 dimer. **X6** also decomposes with the formation of the same gas, and then its molecular formula is C_nO_{2n}.

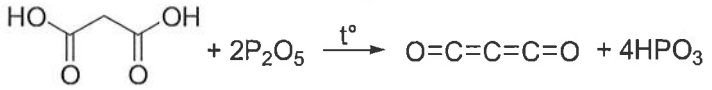
The stage of formation of **E** from isobutyraldehyde is most likely the chlorination in the alpha position to the aldehyde group, i.e., **E** – α-chloroisobutyraldehyde (C_4H_7ClO). A threefold increase in the number of all atoms during the synthesis of **F** corresponds to trimerization to form the structure of trioxane **F**. The last stage of synthesis reminds the ozonolysis of double bonds in **G**, which can be formed by elimination of **F** with potassium *tert*-butoxide. Overall, **X6** has the formula C_3O_6 and is a carbon dioxide trimer.

Schemes (0.5 points per the structure of **B**–**G**, 0.75 points per the structure of **X3**–**X6**, 6 points in total):

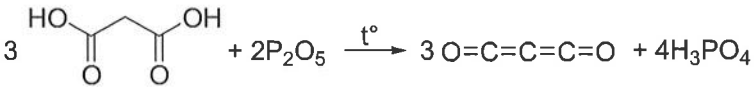


3. The adjacent homolog of oxalic (ethanedioic) acid is malonic (propanedioic) acid $C_3H_4O_4$. Phosphorus (V) oxide serves as a dehydrating agent so that when two water molecules are eliminated from $C_3H_4O_4$, a malonic anhydride C_3O_2 is formed.

Reaction equation (0.25 points per formula of $C_3H_4O_4$, C_3O_2, HPO_3, or H_3PO_4, 0.25 points per structures of $C_3H_4O_4$ and C_3O_2, 0.25 points for coefficients, 1.5 points in total):



or

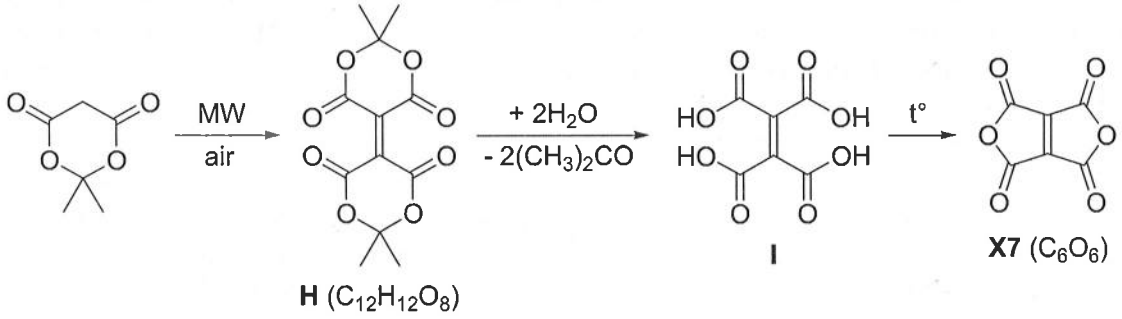


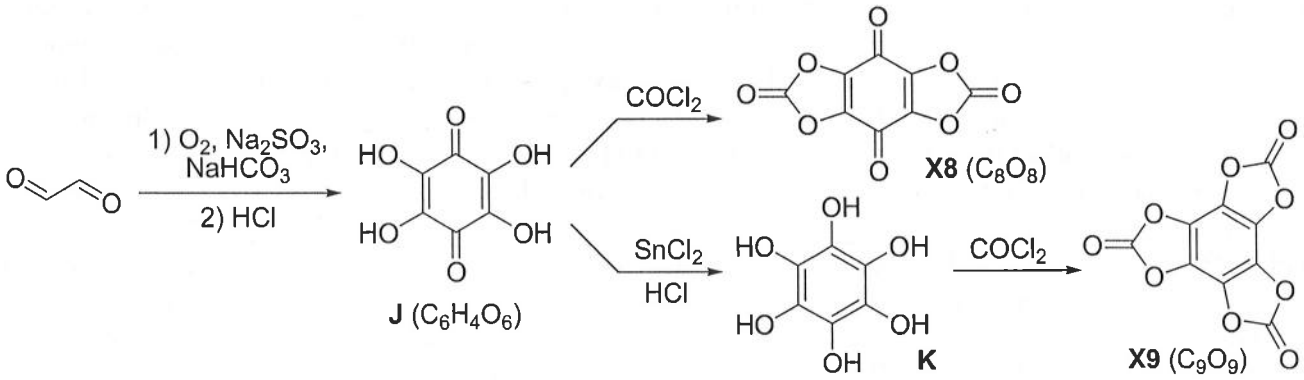
4. The lightest carbon oxide is carbon monoxide CO. Thus, **X7–X9** have molecular formulas with equal numbers of carbon and oxygen atoms.

The molecular formula of the starting material in the synthesis of **H** is $C_6H_8O_4$. Since the reaction takes place in the air, and **H** contains twice the number of carbon and oxygen atoms but a smaller number of hydrogen atoms, it can be assumed that this is an oxidative dimerization reaction. **H** has only 1 type of protons – probably methyl groups protons, and 4 types of carbon atoms – just like in the initial compound. This allows for determining the symmetric structure of compound **H**. The next step is the hydrolysis of the ester bonds, resulting in tetracarboxylic acid **I** ($C_6H_4O_8$). It contains 1 type of hydrogen atoms and only 2 types of carbon atoms, which correlates with the number of signals in NMR spectra. Dehydration of **I** with the elimination of 2 water molecules and the closure of 2 cycles gives the desired "carbon oxide" **X7**, which has the formula C_6O_6 and is an anhydride of acid **I**.

The formation step of **K** from **J** is a reduction reaction. Given the molecular formula of **J** and the fact that **K** has only 1 type of carbon and hydrogen atoms in its structure, it can be assumed that the reduction of **J** led to symmetrical hexahydroxybenzene $C_6H_6O_6$. **J** could then have the structure of a tetrahydroxy-substituted *p*-benzoquinone, which has 1 type of H atoms and 2 types of C atoms. Hence, **X8** and **X9** are carbonic acid and polyphenols esters with the formulas C_8O_8 (tricyclic compound) and C_9O_9 (tetracyclic compound), respectively.

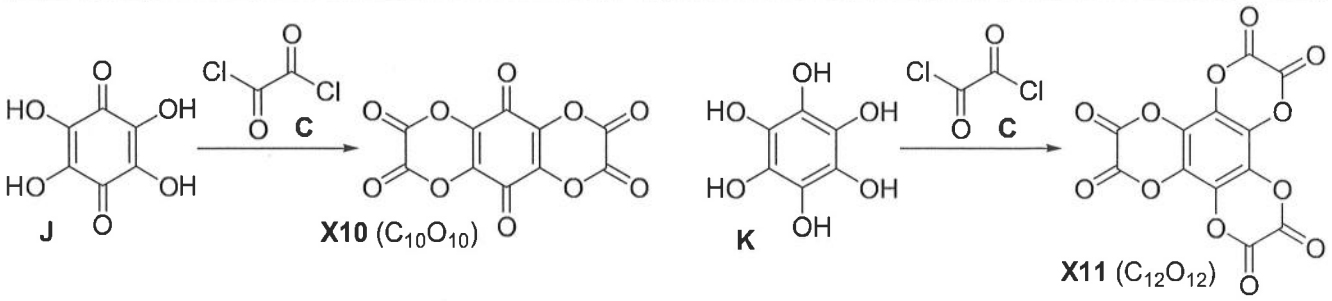
Schemes (0.5 points per structures of **H–K**, 0.75 points per structures **X7–X9**, 4.25 points in total):





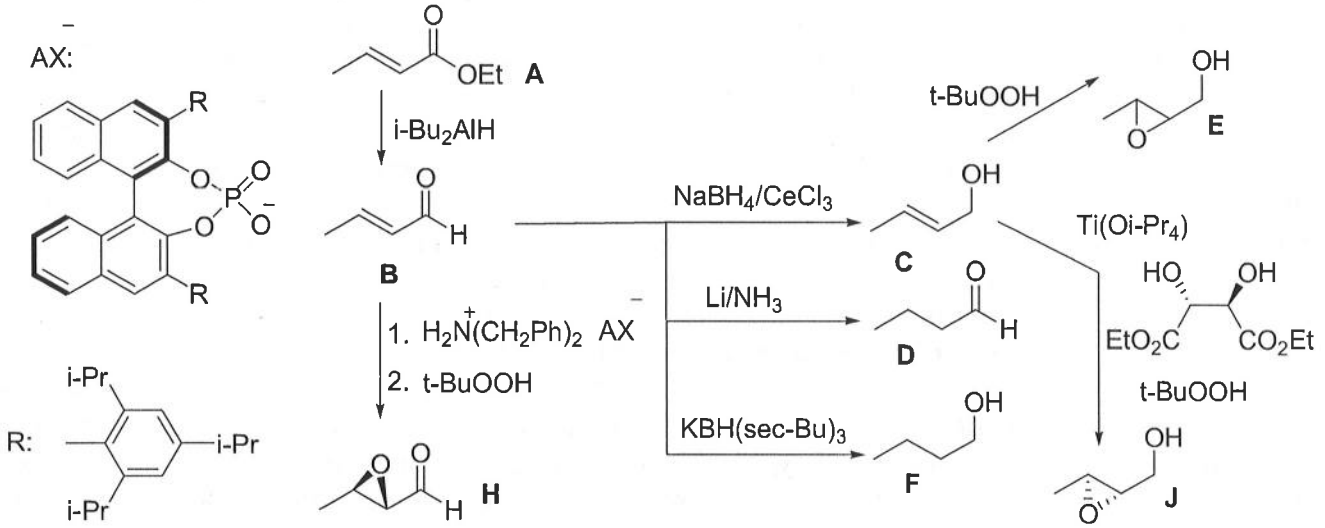
5. Knowing the number of carbon atoms in **X10** and **X11** and the fact that their empirical formula also corresponds to the CO formula, it is possible to unambiguously determine the molecular formulas: **X10** – $C_{10}O_{10}$ and **X11** – $C_{12}O_{12}$. It is not difficult to draw the structures if the formulas of **C**, **J**, and **K** have been determined. Or conversely, this question can help determine the formulas of **K** and **C** if they have not been found earlier.

Schemes (0.75 per structures **X10** and **X11**, 1.5 points in total):



Problem 2 (author Shved E.N.)

1. **A – H** (0.5 points, 3.5 points totally)

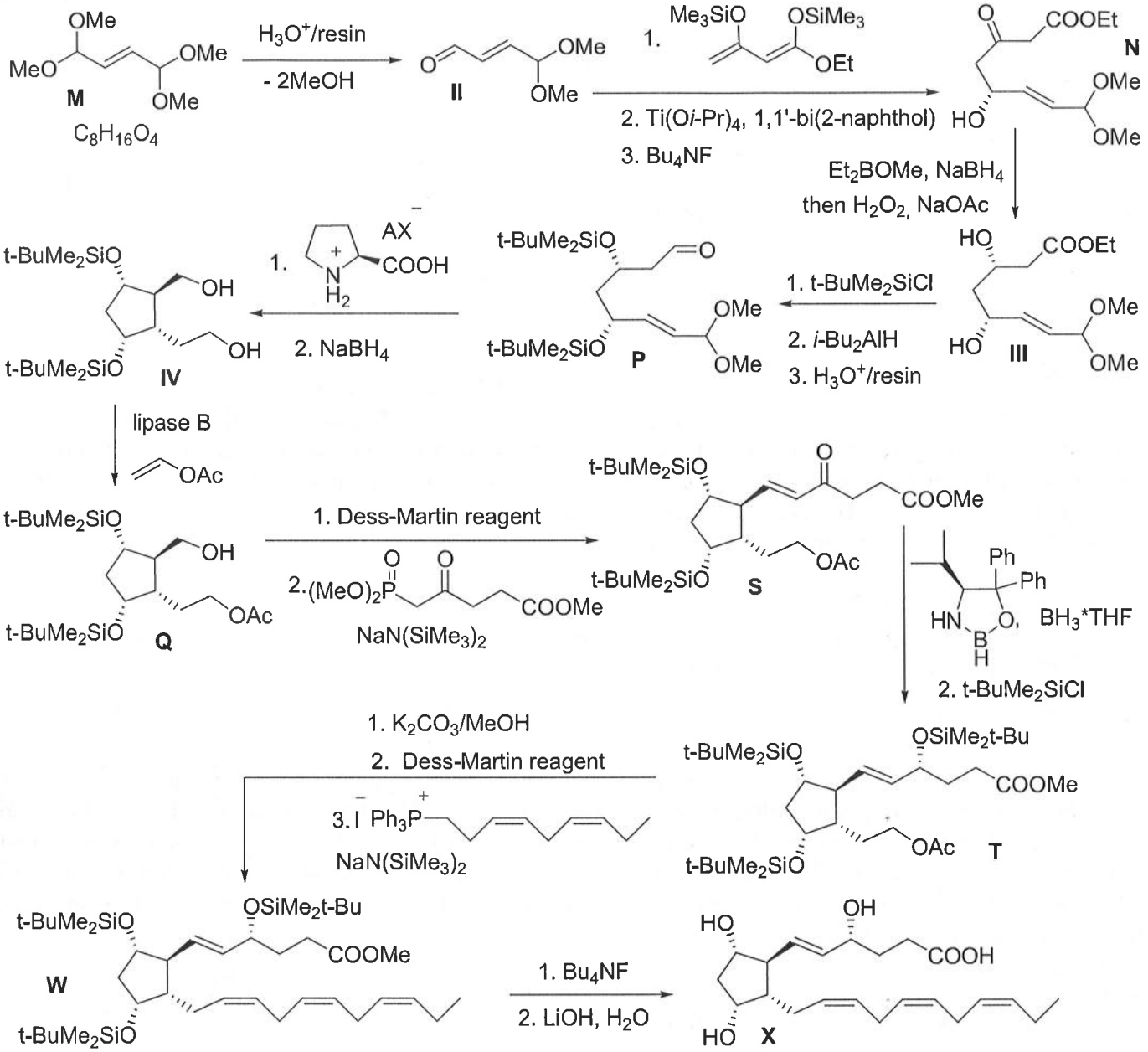


2. Structures of **H** and **G** are given above (0.5 points each, 1 point totally)

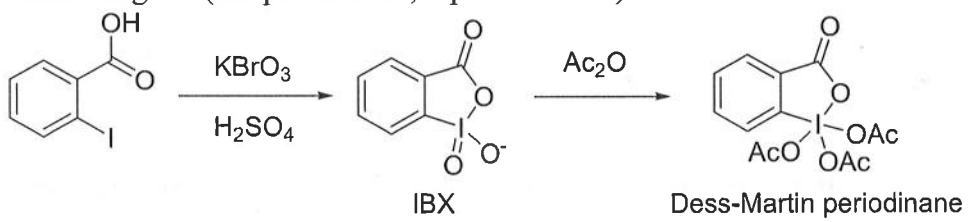
3. Chemoselective reactions: **A** to **B**, **B** to **C**, **B** to **D**, **C** to **E**, **C** to **J**, **B** to **H**. Regioselective reactions: none. Stereoselective reactions: transformation of **C** into **J**, **B** into **H**. Enantioselective reactions: transformation of **C** into **J**, **B** into **H** (0.25 points per reaction, total: 2.5 points, for wrong answers - 0.25 point penalty).

4. At the first stage, the acetal of **M** is hydrolyzed in the presence of acid catalyst. The resulting aldehyde reacts with the diene containing electron-donating ethoxy and silyloxy groups. A chiral Lewis acid is formed from chiral binaphthol and titanium isopropylate to provide enantioselective formation of the stereocenter at the hydroxyl group. The subsequent reaction with tetrabutylammonium fluoride makes it possible to remove the silyl protection. After the conversion of enol to the carbonyl form **N** was isolated. Then, the enantioselective reduction of the carbonyl group is carried out in the presence of Et_2BOMe. This Lewis acid provides the formation of a boron chelate, through the formation of which **III** is obtained. Then, the silyl protection of the alcohol groups of t-$BuMe_2SiCl$ is carried out and then the ester group is selectively reduced to aldehyde **P**. The next step is enantioselective cyclization in the presence of an organocatalyst which is phosphoric acid based on substituted binaphthol and proline. After reduction of the aldehyde fragment compound **IV** is formed. It is converted to **Q** by enzymatic acylation of the sterically more accessible alcohol group in the presence of lipase. The remaining unprotected alcohol fragment is oxidized using the Dess-Martin reagent to an aldehyde, and then the Wadsword-Horner-Emmons reaction is carried out in the presence of sodium hexamethyldisilazide as a base to give compound **S**. The ketone fragment in its structure is enantioselectively reduced using a chiral oxazaborolidine (reduction CBS). **T** is obtained after silylation of the resulting alcohol. Hydrolysis of the acetate in the presence of potash and subsequent oxidation with a Dess-Martin reagent afford the aldehyde. Under Wittig reaction conditions with a phosphorus ylide prepared from a phosphonium salt in the presence of a base, the lower chain of the target structure is constructed to form **W**. Note that the phosphonium salt used for this has the desired configuration of two double bonds. The prepared double bond has Z-configuration, which is typical for non-activated phosphorus ylides. The synthesis of X is

completed by the removal of silyl groups and hydrolysis of the ester. (1 point for each structure, total 7 points)

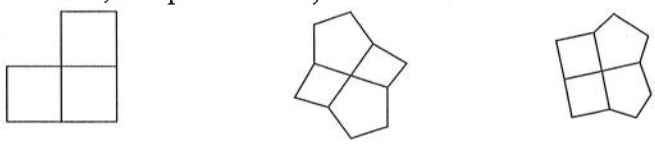


5. Oxidation of *ortho*-iodobenzoic acid with the $KBrO_3$-H_2SO_4 system leads to the formation of the IBX reagent, which is a compound of hypervalent iodine (in this case, pentavalent). Subsequent acylation gives the Dess-Martin reagent. (0.5 points each, 1 point in total)



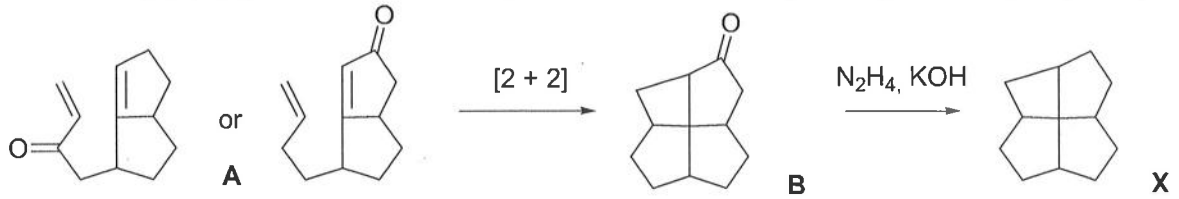
Problem 3 (author Kandaskalov D.V.)

1. (0.5 points each for structure, 1.5 points total).

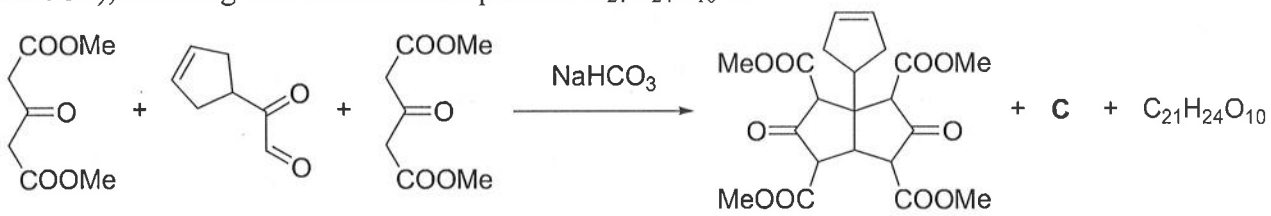


[4.4.4]fenestrane [4.5.4.5]fenestrane [4.4.5.5]fenestrane

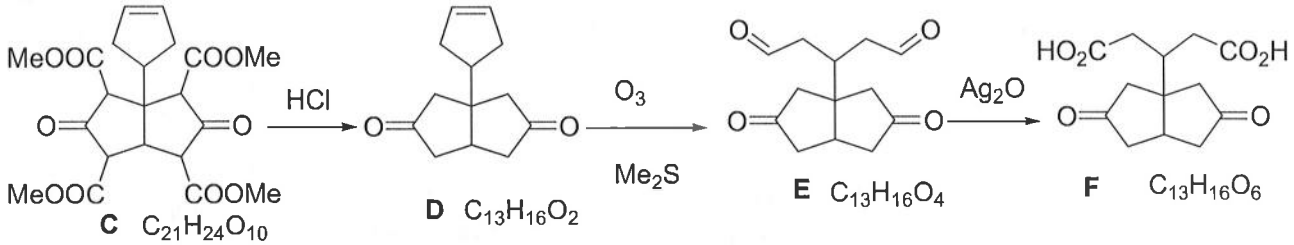
2. Based on the number of carbon atoms in **A** and the closure of the 4-membered ring, it can be assumed that **X** is [4,5,5,5]-fenestrane, and its precursor is the corresponding ketone. (1.5 points)



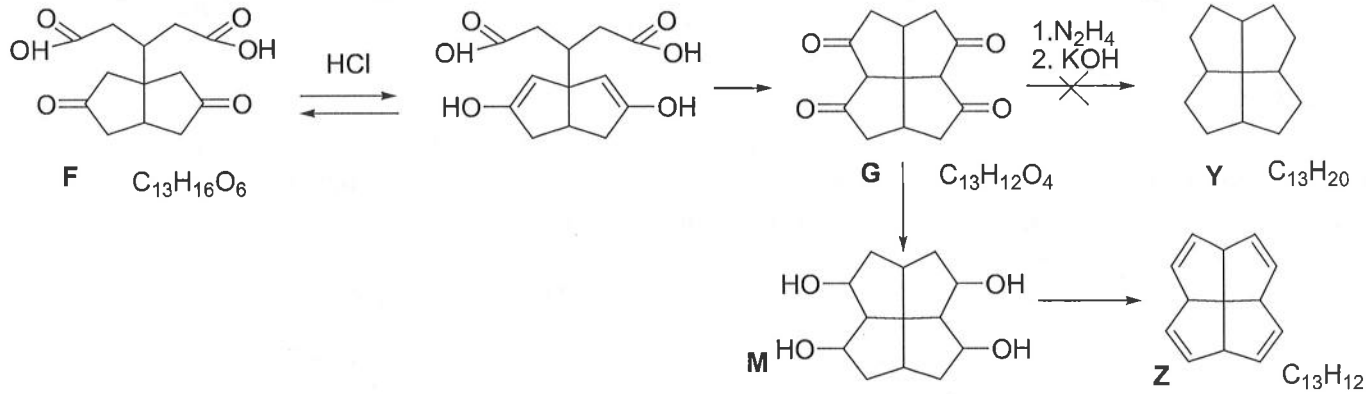
3. 1,2-Dicarbonyl compound reacts with two equivalents of an acetone dicarboxylic acid ester (C7H10O5), resulting in a condensation product $C_{21}H_{24}O_{10}$ **C**.



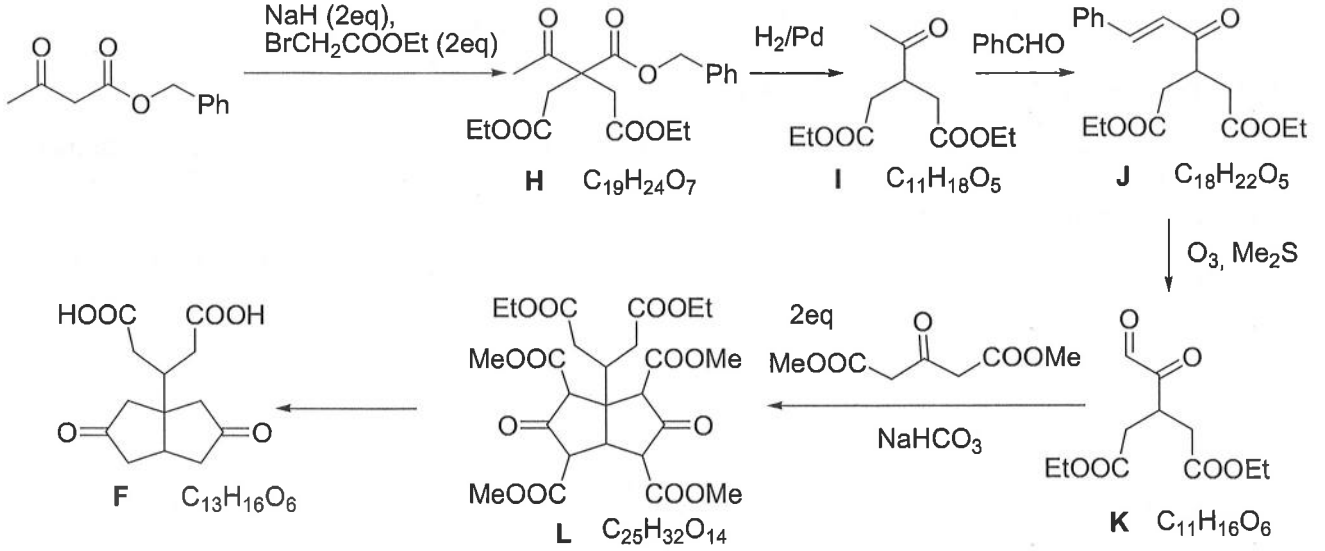
We do not know the molecular formulas of substances **D** and **E**, but by analyzing the stages **D** → **E** → **F** (double bond ozonolysis and subsequent oxidation of the aldehyde), we can assume that the number of carbon atoms is conserved at these stages. Since F contains 13 carbon atoms, it means that 8 carbon atoms are lost during the **C** → **D** transformation. It can be assumed that this is the hydrolysis of four ester groups, followed by the elimination of CO_2 molecules.



It becomes clear that a very symmetrical compound **Y** is being synthesized. Knowing the molecular formula of **Z**, we can assume that **Y** is [5,5,5,5]-fenestrane. The transformation of **F** to **G** is an intramolecular acylation (through the enol form of the ketone), with the formation of a symmetrical tetraketone. The Kizhner-Wolf reaction failed because the cycle breaks. Reduction of the tetraketone with diborane results in the reduction of the ketone to the alcohol **M**. Subsequent elimination of water gives the final product **Z** containing 4 double bonds.



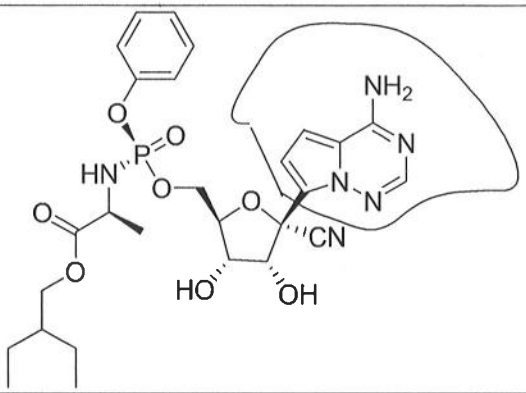
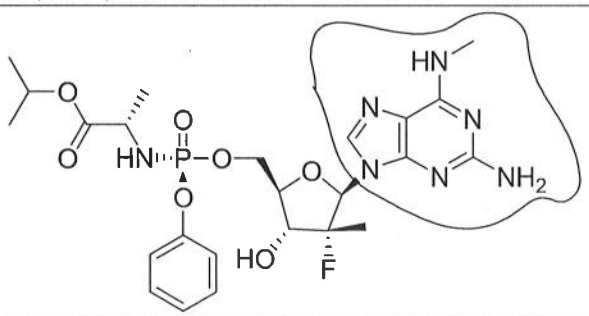
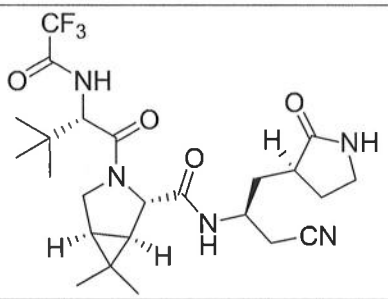
An alternative synthesis starts with double alkylation of the ketoester with ethyl bromoacetate to form **H**. Subsequent removal of the benzyl protection and decarboxylation leads to the formation of **I**. Condensation of this ketone with benzaldehyde leads to **J**, which is oxidized with ozone to form the dicarbonyl compound **K**. This is followed by a step similar to that given on the first diagram. Condensation occurs with two equivalents of the acetone dicarboxylic acid ester to form **L**, which has 2 five-membered rings in its structure. Treatment with acid results in hydrolysis of the ester moieties and removal of 4 CO_2 molecules giving **F**. (Structures **C** and **H** 0.5 points each, the rest 1 point each, total 12 points)


NaH (2eq),
BrCH2COOEt (2eq)
H2/Pd
PhCHO
O3, Me2S
2eq
NaHCO3
EtOOC
COOEt
MeOOC
COOMe
HOOC
COOH
Ph
H C19H24O7
I C11H18O5
J C18H22O5
K C11H16O6
L C25H32O14
F C13H16O6

SECTION III. LIFE SCIENCES AND POLYMERS

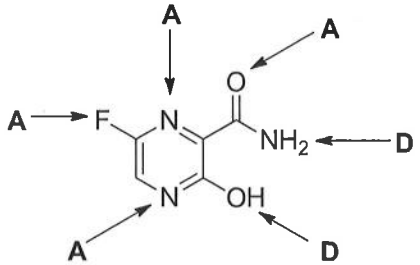
Problem 1 (author Garifullin B.N.)

1. Natural analogs of Remdesivir and AT-527 are found following the characteristic fragments of nitrogenous bases (encircled). Paxlovid does not belong to the group of nucleoside analogs (having peptide bonds, the drug is a protease inhibitor) (0.5 point for each correlation, 1.5 points in total).

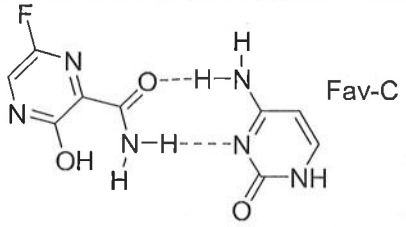
Drug	Formula	Nucleoside analog (designation)
Remdesivir		A
AT-527		G
Paxlovid		No analog

For further parts of the task, it may be helpful to notice some approaches towards the design of antiviral preparations. These are mostly based on modification of nucleosides including: *C*-glycoside bond (Remdesivir), heterocycles with alternative positions of nitrogen atoms (Remdesivir), modified exocyclic groups of the nitrogenous base (AT-527), alterations of the ribose residue (Remdesivir, AT-527).

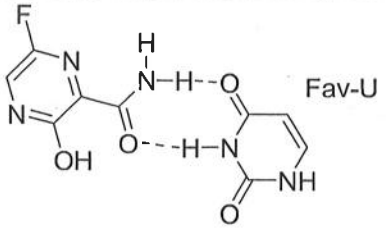
2. (0.25 point for each correct D and A indication, 1.5 points in total)



3. Favipiravir can exist in two confirmations: *cis* (N1 of the heterocycle and N of the amide group on the same side as regard to the C-C bond between the amide group and heterocycle) and *trans* (*vise versa*). The complementary pairs are (1 point each, 2 points in total):



Fav-C

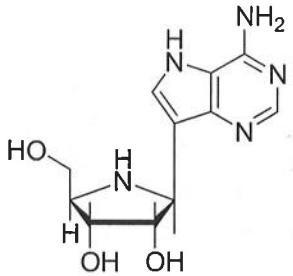


Fav-U

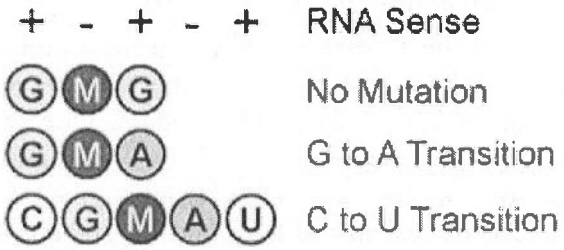
4. A reasonable sequence exists, only if the increment equals 1. Since the members are consecutive, one can make the hereunder correlation (**X** is composed of atoms of four types)

Rounded molar mass, g/mol	Atom or group of atoms
12	C
13	CH
14	N (или CH_2)
15	NH (или CH_3)
16	NH_2 (или O)
17	OH

CH_3, NH_2, and OH can be exocyclic groups of atoms ($\mathbf{R_1}$ and $\mathbf{R_6}$). However CH_3 does not match, since there are already 9 carbon atoms in the skeleton of **A**, whereas the rest two C atoms must be present in the molecule as C and CH (there are no other variants for the values of 12 and 13 g/mol). Since the visible part of the skeleton of X contains only one O atom, one of two combinations of the oxygen containing species (OH + O or 2OH) is present in the $\mathbf{R_1}$ – $\mathbf{R_6}$ group. $\mathbf{R_3}$ and $\mathbf{R_5}$ could be O (can form two bonds), still both groups are twice found in **X**, making the variant of OH + O impossible. Then, $\mathbf{R_1}$ is the hydroxyl ($\mathbf{R_6}$ is found in **X** only once), and $\mathbf{R_6}$ is the amino group. Since the number of nitrogen atoms in **X** equals 5, the members with the molar masses of 14 and15 are decided unambiguously as N and NH (2 of each). Only two paired groups ($\mathbf{R_3}$ and $\mathbf{R_5}$) are left under consideration. However, the number of bonds of the nitrogen atom in $\mathbf{R_3}$ (note that the omitted multiple bonds are found only in the heterocycle) suggests that $\mathbf{R_3}$ is NH, and $\mathbf{R_5}$ is N. Similarly, the rest atoms and groups of atoms are attributed to $\mathbf{R_4}$ (C) and $\mathbf{R_2}$ (CH). With due account for the multiple bonds, the structure of **X** (Galidecevir) is (0.5 point for each of $\mathbf{R_1}$ – $\mathbf{R_6}$, 3 points in total):



5. (+)RNA is formed from (+)RNA after two cycles of replication with (-)RNA as the intermediate. Thus, the following variants are possible with respect to two bases (G and C, M is Molnupiravir):



Thus, four variants of the daughter (+)RNA are possible (note that the normal nucleosides are also present in the infected cell) (0.75 each, 3 points):

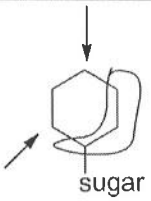
…AGAACUU… (1), …AAAACUU… (2), …AGAAUUU… (3), …AAAAUUU… (4).

6. 68 g/mol are left for the fragment of the nitrogenous base in **Y1** and **Y2**. **Y** being an isomer of a major nitrogenous base, its element composition is found unambiguously. Thus, the valid set of equations (variables designate the number of atoms: x of C, y of N, z of O, and a of H) is:

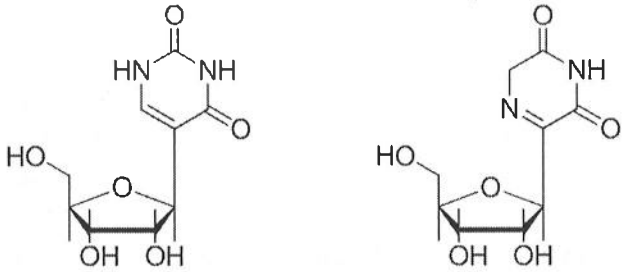
$$12x + 14y + 16z + a = 68 \ (1);$$

$$x + y + z + a = 7 \ (2)$$

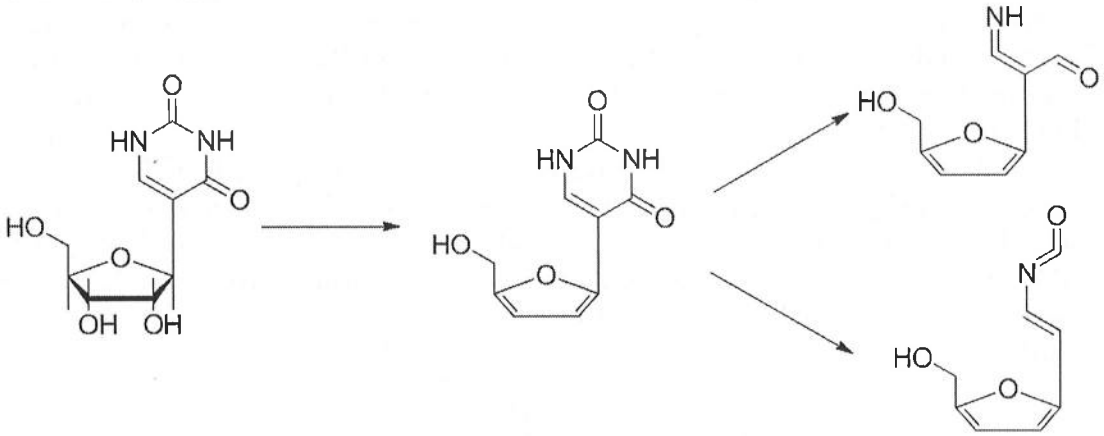
a equals 2. Then $2x + y = 7$, which (with respect to chemical reasons) leads to the solely possible molecular formula of C_3H_2NO. With due account for isomerism and overlapping of the fragments of the nitrogenous bases in Y1 and Y2, it is possible to find equivalent groups of atoms in the positions indicated with arrows:



Since O is not found in the heterocycles of the nitrogenous bases, -C=O is the group present in duplicate. Then **Y** contains two O atoms and is an isomer of U. Moreover, there is an imino group between two -C=O groups in the heterocycle. Three pyrimidine bases can be formulated from the remaining two C and one N atom, U being one of those. Thus the two isomers are (1.5 points each, 3 points in total):



Reference data: pseudouridine (to the left on the above fig.) is widely used in mRMA vaccines. Upon LC-MS, it evolves as following:



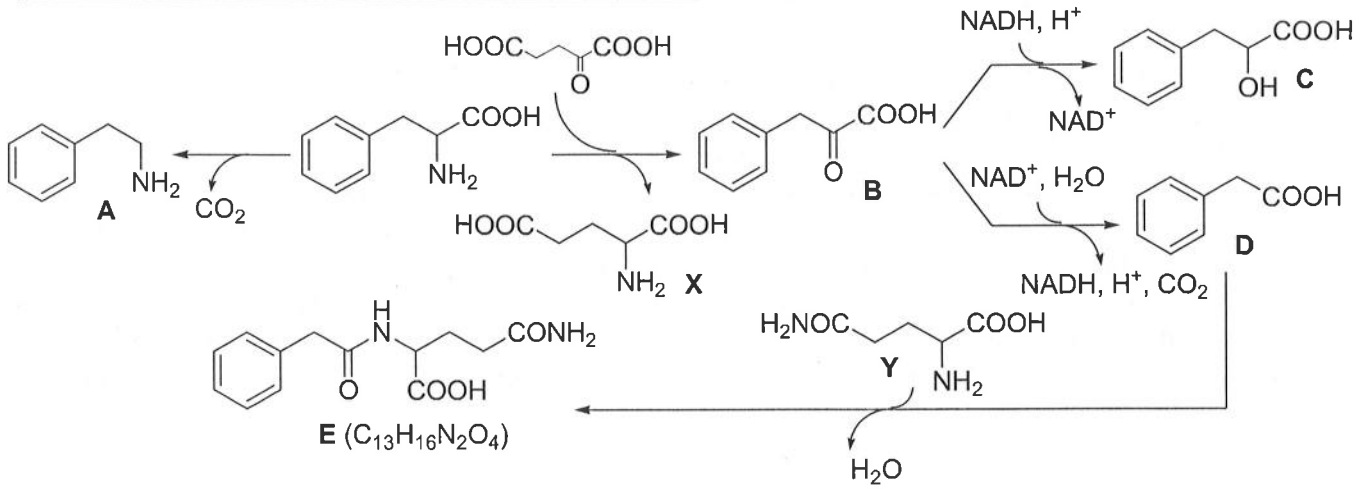
7. The number of hydrogen bonds that pseudouridine and uridine form with anticodon G during translation is the same and equals three. Isomerization of pseudouridine into uridine is an enzymatic process possible with nucleosides rather than larger molecules (mRNA). Presence of the *C*-glycoside bond which is much more resistant towards hydrolysis than the *N*-glycoside one is the main advantage of pseudouridine as compared to its major analog (1 point).

Problem 2 (authors Kutsenok E.O., Shved A.M.)

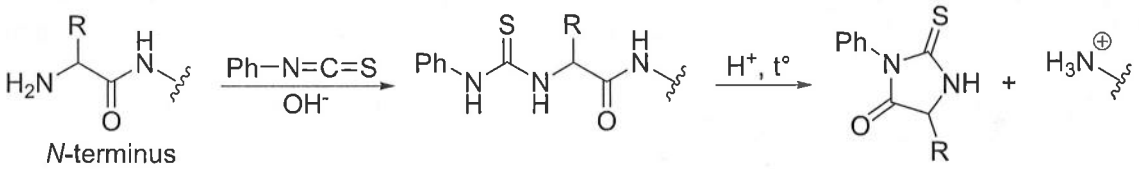
1. The release of CO_2 suggests that the formation of **A** is a decarboxylation reaction. Thus, **A** is 2-phenylethylamine. **B** is formed in the reaction of phenylalanine with the keto acid (α-ketoglutaric acid), giving the amino acid **X** with 5 carbon atoms as a side-product. One can assume the transamination reaction, i.e., the exchange of the keto- and amino groups. Then **X** is glutamic acid (canonical), and **B** is phenylpyruvic acid. When reduced, **B** gives hydroxy acid **C** (3-phenyllactic acid).

The formation of **D** from **B** is due to both release of CO_2 and the reduction of NAD^+. Therefore, this is oxidative decarboxylation of phenylpyruvic acid. Since **Y** and **E** have 5 and 8 carbon atoms, respectively, **D** contains 13 – 5 = 8 C atoms. **D** is phenylacetic acid.

The hydrolysis of **Y** gives glutamic acid **X** ($C_5H_9NO_4$). On the other hand, the reaction of **D** ($C_8H_8O_2$) and **Y** affords H_2O and **E** ($C_{13}H_{16}N_2O_4$). The molecular formula of **Y** is $C_{13}H_{16}N_2O_4 + H_2O - C_8H_8O_2 = C_5H_{10}N_2O_3$. **Y** is the canonical amino acid glutamine, whereas the formation of **E** requires the amide bond between the acid group of **D** and the α-amino group of glutamine (0.5 points for the structure, 3.5 points in total):

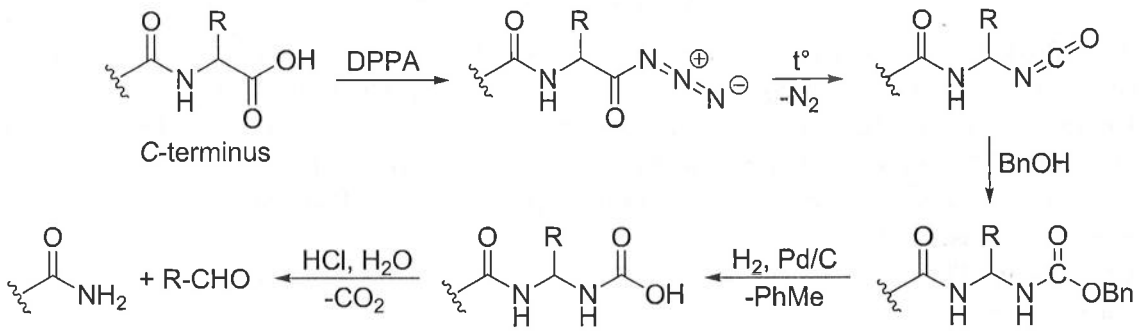


2. In Edman's degradation, a reaction with phenylisothiocyanate occurs. This reagent acts as an electrophile when a free amino group on the *N*-terminus of a peptide attacks it. The second step is a transamidation reaction in an acidic medium leading to a cyclic product phenylthiohydantoin (0.25 points for selecting the *N*-terminus, 0.5 points for each of the intermediate and products, 1.75 points in total for the Edman degradation):



N-terminus

The Bergmann degradation is used to cleave *C*-terminal amino acids. The first step is the formation of an acyl azide, which produces an isocyanate at heating (the Curtius rearrangement). It reacts with benzyl alcohol to form a carbamate. Hydrogenolysis removes the benzyl protecting group, resulting in the formation of an unstable carbamic acid. After its decarboxylation, the generated semi-aminal is hydrolyzed in an acidic medium, which leads to the cleavage of an aldehyde with a side chain of the *C*-terminal amino acid of the initial peptide (0.25 point for selecting the *C*-terminus, 0.5 point for each of the intermediates and products, 3.25 points in total for the Bergmann degradation method, 5 points in total for the question):



3. Based on the answer in i. **2** and the structures of the final products, it is possible to determine the side chains of the amino acids at the termini of the peptides **I** and **II**. Thus, according to the results of the Edman degradation, Ile (with *sec*-butyl as the side chain) is located at the *N*-terminus of the peptide **I**, while Ala (with methyl as the side chain) at that of the peptide **II**. According to the results of the Bergmann degradation, the *C*-terminus of the peptide **I** contains Phe (with benzyl as the side chain) and that of the peptide **II** – Trp (with 3-indolylmethyl ab side chain) (0.25 point per amino acid, 1 point in total).

4. Partial hydrolysis of the tripeptides produces a mixture of amino acids, dipeptides, and the initial tripeptide. Let us consider all the possible variants of the initial tripeptide structure (from *N*- to *C*-terminus) and the composition of the mixtures after partial hydrolysis:

1) Tripeptide *N*-AAA-*C* gives a mixture of A + *N*-AA-*C* + *N*-AAA-*C*;

2) Tripeptides *N*-AAB-*C* or *N*-BAA-*C* give a mixture of A + B + *N*-AA-*C* + + *N*-(AB/BA)-*C* + *N*-(AAB/BAA)-*C*;

3) Tripeptide *N*-ABA-*C*, after hydrolysis gives a mixture of A + B + *N*-(AB/BA)-*C* + + *N*-ABA-*C*;

4) Tripeptides *N*-ABC-*C* or *N*-CBA-*C*, after hydrolysis give a mixture of A + B + C + + *N*-(AB/BA)-*C* + *N*-(BC/CB)-*C* + *N*-ABC-*C*.

None of the *m/z* values obtained from the analysis corresponds to a mono- or diprotonated ion of individual amino acid. Hence, the values presented refer to the di- and tripeptides.

For the peptide **I'**, there are only two *m/z* values of the di- and tripeptides. Thus, tripeptide consists of amino acids of either one type or two types (*N*-AAA-*C* or *N*-ABA-*C*, respectively). Also, one of the *m/z* values is half-integer. This may mean that the charge of the protonated molecular ion is 2 (MH_2^{2+}), and one of the amino acids is basic: Lys, Arg, or His. *N*-ABA-*C*, where B is Lys, Arg, or His, is the only option. Then $M_r(ABH_2^{2+}$ or $BAH_2^{2+}) = 136.5 \cdot 2 = 273$, and $M_r(ABAH_2^+) = 185 \cdot 2 = 370$. Taking into account that one water molecule ($M_r = 18$) is eliminated during the formation of each peptide bond, one gets the hereunder system of equations:

$$\begin{cases} M_r(\text{A}) + M_r(\text{B}) + 2 - 18 = 273 \\ 2M_r(\text{A}) + M_r(\text{B}) + 2 - 2 \cdot 18 = 370 \end{cases}$$

M_r(A) = 115 (Pro), and M_r(B) = 174 (Arg). Then **I'** is *N*-Pro-Arg-Pro-*C* (1 point, the indication of the *N*- and *C*-termini is not obligatory).

For the peptide **II'**, there are three *m/z* values of di- and tripeptides. Thus the tripeptide is either *N*-AAB-*C* (or *N*-BAA-*C*) or *N*-ABC-*C* (or *N*-CBA-*C*). The *m/z* values suggest that the molecular ions are monoprotonated (MH^+). For *N*-AAB-*C* (or *N*-BAA-*C*), two systems of equations are possible (the signal of 229 corresponds to a dipeptide consisting of two identical or two different amino acids):

$$\begin{cases} 2M_r(\text{A}) + 1 - 18 = 229 \\ M_r(\text{A}) + M_r(\text{B}) + 1 - 18 = 233 \\ 2M_r(\text{A}) + M_r(\text{B}) + 1 - 2 \cdot 18 = 330 \end{cases} \qquad \begin{cases} 2M_r(\text{A}) + 1 - 18 = 233 \\ M_r(\text{A}) + M_r(\text{B}) + 1 - 18 = 229 \\ 2M_r(\text{A}) + M_r(\text{B}) + 1 - 2 \cdot 18 = 330 \end{cases}$$

Both systems do not have a set of solutions that satisfies all three equations. So, **II'** cannot be the tripeptide of this type. For the option with three different amino acids (N-ABC-C or N-CBA-C), the system is:

$$\begin{cases} M_r(\text{A}) + M_r(\text{B}) + 1 - 18 = 229 \\ M_r(\text{B}) + M_r(\text{C}) + 1 - 18 = 233 \\ M_r(\text{A}) + M_r(\text{B}) + M_r(\text{C}) + 1 - 2 \cdot 18 = 330 \end{cases}$$

M_r(A) = 115 (Pro), M_r(B) = 131 (Leu or Ile), M_r(C) = 119 (Thr). Thus, the variants for **II'** are as follows: *N*-Pro-Leu-Thr-*C*, or *N*-Pro-Ile-Thr-*C*, or *N*-Thr-Leu-Pro-*C*, or *N*-Thr-Ile--Pro-*C* (1 point for each of the sequences Pro-Leu-Thr and Pro-Ile-Thr with any order of the amino acids, the indication of the *N*- and *C*-termini is not obligatory, 3 points in total).

5. The structure of **I** is deciphered unambiguously: *N*-Ile-Pro-Arg-Pro-Phe-*C*.

There are more options for the structure of **II**:

II-1) *N*-Ala-Pro-Leu-Thr-Trp-*C*,

II-2) *N*-Ala-Pro-Ile-Thr-Trp-*C*,

II-3) *N*-Ala-Thr-Leu-Pro-Trp-*C*,

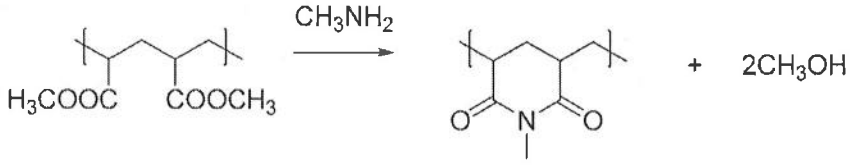
II-4) *N*-Ala-Thr-Ile-Pro-Trp-*C*.

The question has a definite solution if the peptides **I** and **II** have a coincidental fragment with the length of at least one amino acid located near the mutation site. If Ile coincides, then either Thr or Trp must also coincide in the case of **II**-2, which is not observed. In the case of **II**-4, the Ile-Pro fragment coincides, which means that there is a mutation in the subsequent amino acid, i.e. the replacement of Arg by Trp.

If Pro is considered the coincidental amino acid, it should be either to the right of Ile or Arg or to the left of Arg or Phe in **II**, making **II-4** the only option. Arg and Phe cannot be coincidental since none of the options for **II** has such amino acids. Thus, the structure of **II** is *N*-Ala-Thr-Ile-Pro-Trp-*C*. During the mutation, Arg was replaced by Trp. Actually, this question can be answered based on the one-letter designations of the amino acids: R408W is the replacement of arginine (R) with tryptophan (W) in the position 408 of the peptide chain of PAH (0.5 points for each of the peptide sequences, 0.75 points for each of the replacement details (Arg with Trp), 2.5 points in total).

Problem 3 (authors Karpushkin E.A., Berkovich A.K.)

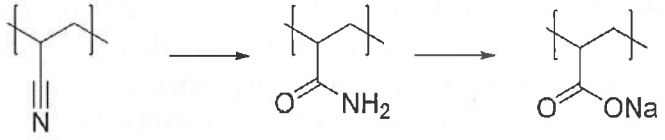
1. The molar mass of **X** per a nitrogen atom: 14.01 / 0.1007 = 139.1 g/mol. The molar mass of the repeat unit in poly(methyl acrylate) is as low as 86.1 g/mol, and the reaction is known to be accompanied by the loss of mass. Thus, one nitrogen atom in **X** should correspond to at least two repeat units of the starting polymer. Formation of a cyclic imide involving two adjacent units of poly(methyl acrylate) is in agreement with the above data:



X

The degree of polymerization of the starting poly(methyl acrylate) is 25000 / 86.1 ≈ 290. At the conversion of 40%, 290·0.4 = 116 starting units form 58 units of **X**, and 290 – 116 = 174 of the starting units are left unchanged. Thus, the degree of polymerization of the product is 174 + 58 = 232. The formation of **X** leads to the mass loss of $2 \cdot 86.1 - 139.1 = 33.1$ g/mol. For the polymer under consideration, the mass loss is $58 \cdot 33.1 / 25000 = 7.68\%$. (1 point for the reaction scheme including the structure of **X**, 1 point for the calculation of the polymerization degree, 1 point for the calculation of the mass loss; 3 points in total).

2. The molar mass of the units **A** per one nitrogen atom is 14.01 / 0.264 = 53.07 g/mol. This corresponds to C_3H_3N (there are no reasonable oxygen-containing alternatives). The degree of unsaturation of a compound with this net formula points suggests multiple bond(s) in the monomer unit, which is true for acrylonitrile. Alkaline hydrolysis of nitriles affords salts of carboxylic acids (note that there is no nitrogen in **C**). Since the polymer **P** contains sodium, the hydrolysis was performed in the presence of NaOH, hence **C** is sodium acrylate. The structure of **B** (acrylamide) can be determined from the hydrolysis mechanism or from the molar mass 14.01 / 0.1971 = 71.08 g/mol corresponding to C_3H_5NO (1 point for each structure, 3 points in total):



A **B** **C**

3. Denoting the molar fractions of the units **A**, **B**, **C** as a, b, c and their molar masses as M_A, M_B, M_C, respectively, one can express the mass fractions of the elements (with an account for the number of atoms per the repeat unit) as:

$$\begin{cases} \omega_N = \dfrac{M(N) \cdot (a+b)}{a \cdot M_A + b \cdot M_B + c \cdot M_C} \\ \omega_O = \dfrac{M(O) \cdot (b+2c)}{a \cdot M_A + b \cdot M_B + c \cdot M_C} \\ \omega_{Na} = \dfrac{M(Na) \cdot c}{a \cdot M_A + b \cdot M_B + c \cdot M_C} \end{cases}$$

Substitution with the numerical values gives a set of three equations with three unknowns

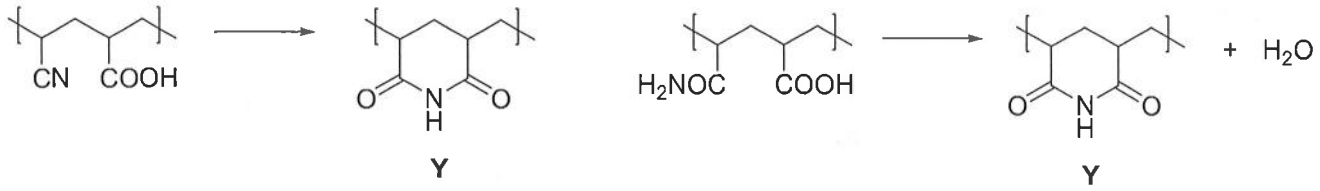
$$\begin{cases} 0.0735 = \dfrac{14.01 \cdot (a+b)}{a \cdot 53.07 + b \cdot 71.08 + c \cdot 94.05} \\ 0.2829 = \dfrac{16.00 \cdot (b+2c)}{a \cdot 53.07 + b \cdot 71.08 + c \cdot 94.05} \\ 0.1598 = \dfrac{22.99 \cdot c}{a \cdot 53.07 + b \cdot 71.08 + c \cdot 94.05} \end{cases}$$

which can be reduced to the system of linear equations and solved by standard procedures, giving a = 0.12, b = 0.31, c= 0.57.

Note that the solution can be simplified by expressing the denominator of each equation and equaling them: $\dfrac{14.01 \cdot (a+b)}{0.0735} = \dfrac{16.00 \cdot (b+2c)}{0.2829} = \dfrac{22.99 \cdot c}{0.1598}$. This double equality is equivalent to a set of two

equations which three unknowns, which can be solved, if $a + b + c = 1$ (1 point for each correct molar fraction; 3 points in total; 1 point for a correct set of equations without solution).

4. The formation of a cyclic imide without a mass loss is possible due to the interaction of a nitrile and a carboxylic acid (i.e. **A** and the acidic form of **C**). The interaction between **B** and the acidic form of **C** is the only way to obtain **Y** with a mass loss (elimination of a low-molecular product) without additional reactants:



Y **Y**

To calculate the mass loss, let us consider the copolymer fragment of 100 units. It contains 12 **A**, 31 **B**, and 57 **C** (in the acidic form). The molar mass of this fragment is $12 \cdot 53.07 + 31 \cdot 71.08 + 57 \cdot 72.06 = 6947.7$ g/mol. The maximum possible conversion at the first step (the interaction of **A** and **C** in the ratio of 1:1) leaves 31 **B** and $57 - 12 = 45$ **C** unreacted. The maximum possible conversion of the latter with the formation of **Y** leads to elimination of 31 water molecules, which corresponds to $31 \cdot 18.02 = 558.6$ g/mol. This mass loss is equal to $558.6 / 6947.7 = 8.04\%$ of the initial mass of the sample (1 point for each reaction with the structures or 1 point for structure of **Y** and 0.5 point for each reaction scheme; 1 point for the calculation of the mass loss; 3 points in total).

5. The second reaction to occur requires the presence of **B** and **C** in **P**. Since **B** is not involved in the first reaction, $b > 0$ is enough for these units. The unit of **C** participate in the first reaction (1:1 interaction with **A**), and are partially retained after the first step, if $c > a$. (0.25 point for the first condition, 0.75 for the second condition; 1 point in total).

6. Let us consider the limiting cases first. Units of **Y** are formed in the reactions **A** + **C** and **B** + **C**, and thus cannot be present in the product of thermolysis of **P1** (the latter contains no **C**). The optimal ratio between the units allowing complete transformation of **A**, **B**, and **C** into **Y** (at least hypothetically, at certain distribution of the units) is $a + b = c$, which is true for **P3**. Next, let us again consider the copolymer fragments containing 100 units of **A**, **B**, and **C** in total. **P2** contains about 33–34 units of each of **A**, **B**, and **C**, thus **A** and **B** are completely converted at the first step, affording 33 units of **Y** in the product, and making the **B** + **C** reaction at the second step impossible. In the cases of **P4** and **P5**, the **A** + **C** interaction is only possible, the highest number of units of **Y** not exceeding 20, which is significantly lower than in the case of **P2**. Since the reaction **A** + **C** occurs between the adjacent units in the chain, it is possible only at the boundaries between the blocks in the case of the block copolymer (**P5**). Thus, the number of **Y** is much less **in P5** as compared to **P4** containing more adjacent **A–C** pairs. Finally, **P1** < **P5** < **P4** < **P2** <**P3** (up to 2 points for entirely correct sequence).

SECTION IV. INORGANIC CHEMISTRY

Problem 1 (author Likhanov M.S.)

1. An unknown white pigment is basic lead carbonate – the so-called white lead. Let us determine the composition **A** by the thermal decomposition reaction:

$$Pb(OH)_2 \cdot xPbCO_3 = (1+x)PbO + H_2O + xCO_2$$

The mass loss: $(18 + x \cdot 44)/(241 + x \cdot 267) = 0.137$, whence $x = 2$.

Thus, **A** – $Pb(OH)_2 \cdot 2PbCO_3$

(1 point for calculation, 0.5 points for **A** composition, 1.5 points in total)

2. Lead white does indeed turn black over time due to the formation of lead sulfide:

$$Pb(OH)_2 \cdot 2PbCO_3 + 3H_2S = 3PbS + 2CO_2 + 4H_2O$$

Old paintings restoration experts know a simple way – to treat lead sulfide with hydrogen peroxide:

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O$$

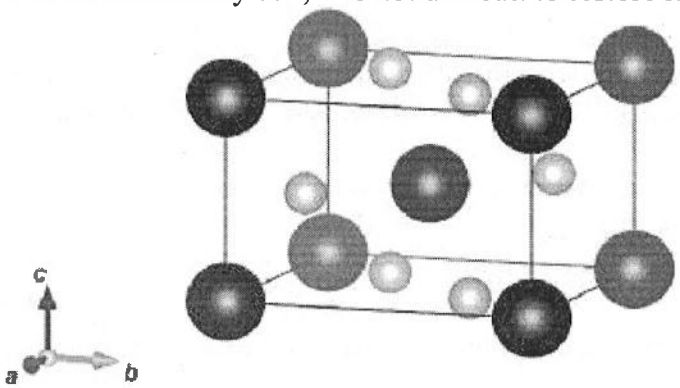
(0.75 points for each reaction equation, 1.5 points in total)

3. Determine the molar mass of an unknown hydrogen compound: $M = \rho \cdot V_m = 0.714 \cdot 22.4 = 16$ g/mol. By selection we get that the unknown substance is methane. During its incomplete combustion soot is formed, which is used as a black pigment. **C** – C.

$$CH_4 + 2O_2 = C + 2H_2O$$

(0.5 points for calculation, 0.5 points for **C** composition, 0.5 points for reaction equation, 1.5 points in total)

4. By the projection of an elementary cell, it is not difficult to restore its volumetric appearance:



Obviously, the unknown metal is in octahedral environment of oxygen atoms.

Let us calculate the number of atoms of each kind in one elementary cell:

$$N(\text{of unknown metal}) = 1 + 8 \cdot 1/8 = 2$$

$$N(O) = 2 + 4 \cdot 1/2 = 4$$

Thus, the gross composition of **D** can be written as MO_2, where M is an unknown metal. In this case, the number of formula units in one unit cell $Z = 2$. Let us calculate the molar mass of the oxide:

$$M(MO_2) = V_{\text{unit cell}} \cdot d \cdot N_A/Z = a^2 \cdot c \cdot d \cdot N_A/Z = 86.9 \text{ g/mol},$$

then $M(M) = 54.9$ g/mol, hence the unknown metal is Mn.

(1 point for gross composition determination, 0.5 points for molar mass calculation, 0.5 points for **D** composition, 1 point for coordination environment, 3 points in total)

5. According to the condition, Thénard's blue has a spinel structure with the composition AB_2O_4, where A is a metal in the oxidation state +2, B is a metal in the oxidation state +3. The aluminum that should be part of the blue is definitely in the +3 oxidation state, so the unknown transition metal has a +2 oxidation state. Based on the magnetic data, it is not difficult to calculate the number of unpaired electrons:

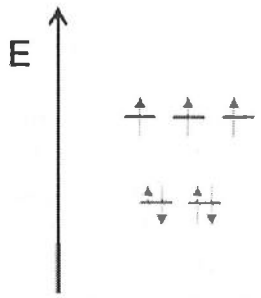
$$\mu_{eff} = (n(n+2))^{1/2} = 3.87, \; n = 3.$$

Therefore, the electronic configuration of the unknown metal may be d^3 or d^7. Of the 3d metals in the oxidation state +2, V^{+2} or Co^{+2} can have such an electronic configuration. Vanadium in the +2 oxidation state is extremely unstable and cannot be obtained under the specified synthesis conditions. Thus, the unknown transition metal is cobalt, and the Thénard's blue formula is $CoAl_2O_4$. The preparation reaction can be written as follows:

$$CoCl_2 + 2NaAlO_2 = CoAl_2O_4 + 2NaCl$$

(2 points for calculation, 0.5 points for Thénard's blue composition, 0.5 points for reaction equation, 3 points in total)

6. There are two positions for the distribution of metals in spinel – in an octahedral environment of oxygen atoms and a tetrahedral one. Aluminum is in the +3 oxidation state in an octahedral environment, and cobalt is located in a tetrahedral one. The splitting of cobalt d-orbitals in a tetrahedral field of oxygen atoms looks like this:



(0.5 points for the correct choice of diagram, 0.25 points for the distribution of electrons, 0.75 points in total)

7. Calcining of iron chromite with potassium carbonate in the presence of atmospheric oxygen results in chromium oxidation to the highest oxidation state, while iron turns into oxide, which is insoluble in water and can be separated by filtration:

$$FeCr_2O_4 + K_2CO_3 + O_2 = Fe_2O_3 + K_2CrO_4 + CO_2$$

Then, by chromate solution acidification, potassium dichromate is obtained, which has low solubility and precipitates upon cooling:

$$K_2CrO_4 + H_2SO_4 = K_2Cr_2O_7\downarrow + K_2SO_4$$

By sintering potassium dichromate with sulfur, the target product – chromium oxide (+3), a green pigment, – is obtained. Potassium sulfate is further dissolved in water, and chromium oxide is separated by filtration:

$$K_2Cr_2O_7 + S = Cr_2O_3 + K_2SO_4$$

The final scheme looks like this:

$FeCr_2O_4$ —(1. K_2CO_3, O_2, t° 2. H_2O, filtration)→ K_2CrO_4 —(1. H_2SO_4 solution 2. Cooling)→ $K_2Cr_2O_7$ —(1. S, t° 2. H_2O, filtration)→ Cr_2O_3

(0.75 points for each reaction equation, 0.5 points for each substance in the scheme, 3.75 points in total)

Problem 2 (author Karpova E.V.)

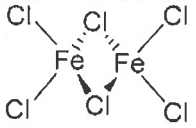
1. Based on the description, it is clear that the simple substance **X1** is a metal that has been known to mankind for a long time, for example, iron, copper, gold. Substance **A1**, gaseous, slightly colored, can be both simple and complex substances. Let's start by considering the case if **A1** is a simple substance formed by atoms of element **A**. According to the description of A_2, we can conclude that this is a hydrogen compound of element **A**, then **Y1** and **Y2** are binary substances differing in the content of element **X** and **A**. Let's designate the compound **A2** as H_aA, **Y2** as X_aA_b. The ratio of the mole fractions of the element **A** $\frac{1\cdot(a+b)}{(1+a)\cdot b} = 1.334$. Substituting the possible values, with a=1, b=2, i.e. HA and XA_2.

The ratio of the mass fractions of the element **A**: $\frac{M(A)\cdot(M(X)+2M(A))}{(M(A)+1)\cdot 2M(A)} = 1.7377$.

$M(X) = 1.4754M(A) + 3.4754$. Simple gaseous and slightly colored substances **A1** are fluorine, chlorine, ozone. Only fluorine and chlorine are suitable for the HA formula. If $M(A) = M(Cl) = 35.45$ g/mol, then $M(X) = 55.78$ g/mol, which corresponds to the molar mass of iron.

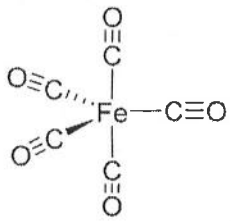
X = Fe, **Y1** = $FeCl_3$, **Y2** = $FeCl_2$, **A1** = Cl_2, **A2** = HCl.

$$2Fe + 3Cl_2 = 2FeCl_3;$$
$$FeCl_3 =t= FeCl_2 + Cl_2;$$
$$2FeCl_3 + Fe = 3FeCl_2;$$
$$Fe + 2HCl = FeCl_2 + H_2$$

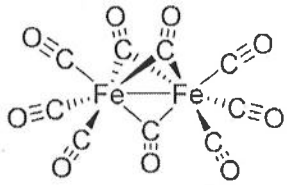


(for calculation 2 points, each substance 0.3 point, for each reaction equation 0.2 point, structure $FeCl_3$ 1 point, total 5.3 points)

2. The molecule isoelectronic to nitrogen is carbon monoxide. Metal carbonyls are obtained in various ways, for example, the interaction of a metal and carbon monoxide at elevated pressure and temperature, the interaction of anhydrous halides with active metals and carbon monoxide also at elevated temperature and pressure. The simplest iron carbonyl (you can use Sidgwick's rule) is $Fe(CO)_5$. This substance has a molecular structure in the condensed and gas phases, which explains the low temperatures of phase transitions. The structure of the molecule is a trigonal bipyramid, which corresponds to the set of symmetry elements listed in the condition. The simplest carbonyls under various physical influences often undergo chemical transformations with the formation of new molecules containing a different number of metal and CO atoms. **Y5** is formed from **Y3** under the action of radiation. The formula of **Y5** can be described as $Fe_t(CO)_d$, t:d = $\frac{1.077 \cdot \left(\frac{55.85}{55.85 + 5 \cdot 28}\right)}{55.85} : \frac{1 - 1.077 \cdot \left(\frac{55.85}{55.85 + 5 \cdot 28}\right)}{28}$ = 2:9. Based on the symmetry elements, as well as information on the diamagnetism of the resulting compound, we can conclude that the structure of this molecule is two $Fe(CO)_6$ octahedra united by a common face and with a Fe-Fe bond.



$Y_3 = Fe(CO)_5$,



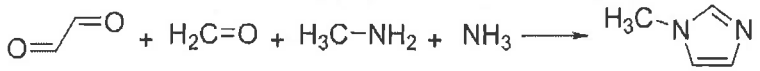
$Y_5 = Fe_2(CO)_9$.

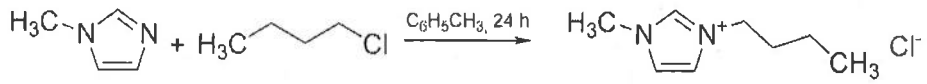
$$2Fe(CO)_5 \xrightarrow{h\nu} Fe_2(CO)_9 + CO;$$

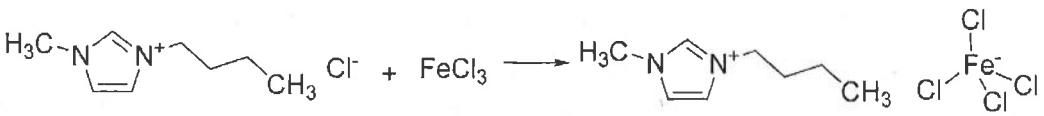
$$2Fe(CO)_5 + 3Cl_2 = 2FeCl_3 + 10CO$$

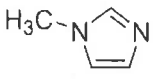
(for calculation 1 point, for each substance 0.3 point and for each reaction equation 0.2 point, for the structure of $Fe(CO)_5$ 1 point, for the structure of $Fe_2(CO)_9$ 2 point, total 5.2 points)

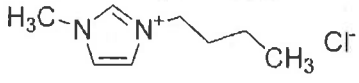
3. Compound **Y4**, as seen from the proposed synthesis scheme, contains an organic fragment.

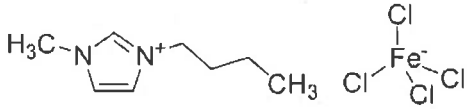






I =  1-methyimidazole,

II =  1-butyl-3-methylimidazolium chloride,

Y4 =  1-butyl-3-methylimidazolium tetrachloroferrate(III)

The example of inorganic compound: $Cs[FeCl_4]$, $K[FeCl_4]$.

(for each structure of compounds 0.8 point, for formula of inorganic compound 0.3 point, for each reaction equation 0.2 point, total 3.3 point)

4. The $Fe(CO)_5$ substance is a liquid under normal conditions due to weak intermolecular interactions. Compound **Y4** is ionic, but with a large, asymmetric organic cation and a small, symmetrical, uniformly charged inorganic anion, resulting in a low solid-liquid transition temperature. Ionic compounds with melting points below 100°C are referred to as ionic liquids. Ionic liquids have almost zero vapor pressure. $Fe(CO)_5$ passes into the gas phase. (for each correct answer 0.4 point, total 1.2 points)

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

1. $w_A = M_A / (M_A + 71)$ and $w'_A = M_A / (M_A + 87)$ in the salts $KAO_2 + KAO_3$, correspondingly, and $w_A - w'_A = M_A(M_A + 71) - M_A(M_A + 87) = 0.0261$. Solving the equation $M_A^2 - 455M_A + 6176 = 0$, we obtain $M_A = 14$ (g/mol). Then A – N (1 point); A_2O_n – NO (0.5 points) (NO – colorless, paramagnetic, short strong bond, dimer at low temperature); B – N_2O_2 (0.5 points). The reduction reaction of the mixture with chromium oxide (III):

$$3KNO_2 + KNO_3 + Cr_2O_3 = K_2CrO_4 + 4NO \qquad (0.5 \text{ points}).$$

Only another oxide can have a blue color, and this oxide is N_2O_3:

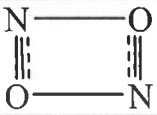
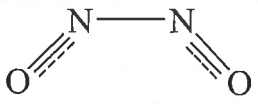
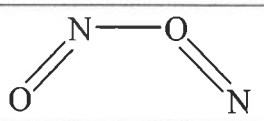
$$4NO = N_2O_3 + N_2O \qquad (0.5 \text{ points}). \qquad (\text{Total 3 points})$$

2. $2NO \rightleftarrows N_2O_2$ $\Delta_rG° = 39.00 - 2 \cdot 12.3\ 5 = 14.3$ (kJ/mol) (0.5 points)

	1	0
ν_i	α	$\alpha/2$
	$1-\alpha$	$\alpha/2$
χ_i	$2(1-\alpha)/(2-\alpha)$	$\alpha/(2-\alpha)$
P_i	$2P(1-\alpha)/(2-\alpha)$	$P\alpha/(2-\alpha)$

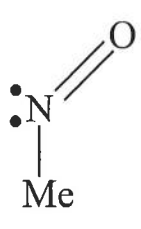
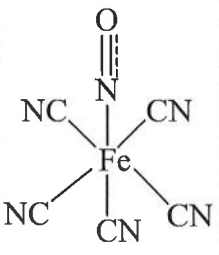
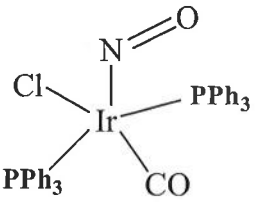
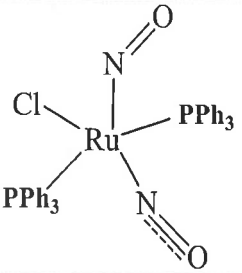
$\Delta_rG° = -RT\ln K$; $14300 = -8.314 \cdot 298 \ln K$;
$K = P_{N2O2}/P^2_{NO} = 3.11 \cdot 10^{-3}$ (0.5 points)
$K_P = \alpha(2-\alpha)^2P/(2-\alpha)4P^2(1-\alpha)^2$. At p = 1 atm
$\alpha^2 - 2\alpha + 1{,}23 \cdot 10^{-2} = 0$ and $\alpha = 6{,}17 \cdot 10^{-3}$.
$\chi = \alpha/(2-\alpha)$. $\chi = 0{,}0031 (0{,}31\%)$ (1 point)

The 11 electron NO formula in the MO method: $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2 2\pi^1 4\sigma^0$ or $((\sigma_s)^2(\sigma_s^*)^2\ (\pi_{y,z})^4\ (\sigma_x)^2\ (\pi_{y,z}^*)^1\ (\sigma_x^*)^0)$, bond multiplicity 2.5 and N≡≡≡O (0.5 points).

B1	B2	B3
		
(0.5 points)	(0.5 points)	(0.5 points)

(Total 4 points)

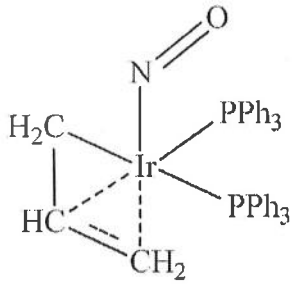
3. Considering the bond lengths, angles and positions of absorption bands in the IR spectrum, the structural formulas are:

1 σ-donor	2 σ-donor π-acceptor	3 one-electron	$[Fe(CN)_5NO]^{2-}$	$[IrCl(CO)(PPh_3)_2NO]^+$	$[RuCl(PPh_3)_2(NO)_2]^+$
					
(0.5 points)	(0.5 points)	(0.5 points)	(0.5 points)	(0.5 points)	(0.5 points)

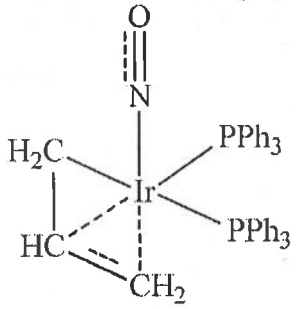
The analysis of the bond lengths and frequencies in the IR spectrum indicates a linear fragment for the Fe and Ru complexes and a bent fragment for Ir and Ru. (Total 3 points)

4. If E^+ cation is $[MeCl_a(PPh_3)_b(NO)_c]^+$, $w_{Cl} = 35.5a/(A_{Me} + 35.5a + 262b + 30c) = 0.0454$ and the first equation $A_{Me} + 35.5a + 262b + 30c = 35.5a / 0.0454$, and it is formed by the reaction $MeCl_3 \rightarrow E^+$, then, considering the yield, we have the second equation $3.73/(A + 106.5) = 7.82/0.8(A + 35.5a + 262b + 30c)$. By solving these two equations, we get $A_{Me} = 298.8a - 106.5$ (1 point). With the only possible a = 1 we obtain $A_{Me} = 298.8 - 106.5 = 192.3$ (g/mol). Me – Ir (0.5 points). Then $\nu_{Ir} = 3.73 / 298.7 = 0.0125$ (mol), $\nu_{Me}:\nu_{PPh3} = 00125:0.025 = 1:2$ and b = 2 (0.5 points). By substituting A_{Mc}, a and b in $0.0454 = 35.5 /$

(192.2 + 35.5 + 524 + 30c), we find c = 1 (0.5 points), thus E^+ is $[IrCl(PPh_3)_2NO]^+$ (0,25 points) and D^+ is $[Ir(C_3H_5)(PPh_3)_2NO]^+$(0,25 points). Structural formulas of D^+ in salts (Total 4 points):



$[Ir(C_3H_5)(PPh_3)_2NO]BF_4$
(0.5 points)



$[Ir(C_3H_5)(PPh_3)_2NO]PF_6$
(0.5 points)

5. To estimate $\Delta_rH°$ of the transition, we use the data in the table:

Intensity	Y ⇄ X		$K_t = I_x / I_y$
I (25°C)	1	1	$K_{25} = 1 / 1$
I (0°C)	0,69	1.31	$K_0 = 1,31 / 0,69 = 1,90$

The values of K_{25} and K_0 are obtained considering changes in the IR spectrum of intensities at temperatures of 25 and 0°C.

From the Van't Hoff equation, the enthalpy of transition Y ⇄ X is: $\Delta_rH° = RT_1T_2\ln(K_2/K_1)/(T_2–T_1) = 8.314·273·298·\ln(1,90/1)/(273–298) = –17365$ (J/mol). (Total 1 point)

SECTION V. ANALYTICAL CHEMISTRY

Problem 1 (author Kandaskalov D.V.)

1. Sequence: $ZnO > Pb_2(OH)_2CO_3 > BaSO_4$ (0.5 points).

For the zinc white paint: $ZnO + HOH = Zn^{2+} + 2OH^-$

$K_S(ZnO) = [Zn^{2+}][OH^-]^2 \rightarrow S(ZnO) = [Zn^{2+}] = K_S(ZnO) / [OH^-]^2 = 1.2 \cdot 10^{-17} / (1 \cdot 10^{-13})^2 \approx 10^9$

For barium sulfate: $BaSO_4 = Ba^{2+} + SO_4^{2-}$

$$K_S(BaSO_4) = [Ba^{2+}][SO_4^{2-}] \cdot \alpha_{SO_4^{2-}} = \alpha_{SO_4^{2-}} \cdot S^2_{BaSO_4} \longrightarrow$$

$$\alpha_{SO_4^{2-}} = \frac{[SO_4^{2-}]}{[SO_4^{2-}] + [HSO_4^-] + [H_2SO_4]} = \frac{1}{1 + \frac{[H^+]}{K_{a2}} + \frac{[H^+]^2}{K_{a1} \cdot K_{a2}}} = \frac{1}{1 + \frac{0.1}{10^{-1.9}} + \frac{(10^{-1})^2}{10^0 \cdot 10^{-1.9}}}$$

$$= 0.102$$

$$S_{BaSO_4} = \left(\frac{K_S(BaSO_4)}{\alpha_{SO_4^{2-}}}\right)^{1/2} = \left(\frac{1.1 \cdot 10^{-10}}{0.102}\right)^{1/2} = 3.3 \cdot 10^{-5}\ M$$

For basic lead carbonate: $Pb_2(OH)_2CO_3 = 2Pb^{2+} + CO_3^{2-} + 2OH^-$

$$K_S(Pb_2(OH)_2CO_3) = [Pb^{2+}]^2[OH^-]^2[CO_3^{2-}] \cdot \alpha_{CO_3^{2-}} = \alpha_{CO_3^{2-}} \cdot S^3 \cdot [OH^-]^2$$

$$\alpha_{CO_3^{2-}} = \frac{[CO_3^{2-}]}{[CO_3^{2-}] + [HCO_3^-] + [H_2CO_3]} = \frac{1}{1 + \frac{[H^+]}{K_{a2}} + \frac{[H^+]^2}{K_{a1} \cdot K_{a2}}}$$

$$= \frac{1}{1 + \frac{0.1}{10^{-10.35}} + \frac{(10^{-1})^2}{10^{-6.35} \cdot 10^{-10.35}}} = 2 \cdot 10^{-15}$$

$$S_{Pb_2(OH)_2CO_3} = \left(\frac{K_S(Pb_2(OH)_2CO_3)}{\alpha_{CO_3^{2-}} \cdot [OH^-]^2}\right)^{1/3} = \left(\frac{3.5 \cdot 10^{-46}}{2 \cdot 10^{-15} \cdot (10^{-13})^2}\right)^{1/3} = 0.026\ M$$

$S(BaSO_4)=3.3 \cdot 10^{-5}$ M, $S(Pb_2(OH_2)CO_3)=0.026$ M, $S(ZnO)>>1$M, that is, barium sulfate is the least soluble (0.5 points for the calculation of each solubility, 1.5 points in all, 2 points totally for item 1)

2. $2Ba^{2+} + Cr_2O_7^{2-} + H_2O \rightarrow 2BaCrO_4\downarrow + 2H^+$

$Pb^{2+} + 2I^- \rightarrow PbI_2\downarrow$

$Zn^{2+} + Cu^{2+} + 2(NH_4)_2[Hg(SCN)_4] \rightarrow Zn[Hg(SCN)_4] \cdot Cu[Hg(SCN)_4]\downarrow + 4NH_4^+$ (0.5 point for each equation, 1.5 points in all)

3. Increasing pH of the solution reduces the solubility of barium chromate:

$H^+ + Ac^- \rightarrow HAc$ (1 point)

4. $Pb_2(OH)_2CO_3 + 2H_2S \rightarrow 2PbS + 3H_2O + CO_2$ (1 point)

$PbS + H_2O_2 \rightarrow PbSO_4$ (1 point)

5. a) $(x + 2)CuAc_2 + yAs_2O_3 + H_2O \rightarrow xCuAc_2 \cdot yCu(AsO_2)_2 + 2HAc$ (1.5 points)

b) $2Cu(OH)_2 + AsO_2^- + 2OH^- \rightarrow Cu_2O + AsO_4^{3-} + 3H_2O$ (1.5 points)

c) Arsenite is unreacted arsenic, i.e. for each arsenate, according to the recorded reaction, we have two more arsenites: Cu_2As(arsenate)As_2(arsenite), totally we have Cu : As = 2 : 3. Then the composition of Paris Green: $Cu(CH_3COO)_2 \cdot 3Cu(AsO_2)_2$ (1 point)

6. Oxidation of the sample with strong nitric acid leads to the dissolution of the sample, but arsenic is not oxidized to the maximum oxidation state (+5), since then sodium bromate acts as an oxidizing agent. Thus, bromate should convert arsenic +3 to arsenic +5:

$$3AsO_3^{3-} + BrO_3^- + 9H^+ \rightarrow Br^- + 3H_3AsO_4 \text{ (1 point)}$$

The amount of arsenic in the initial solution (500 mL), i.e. in a sample with a total area of 100 cm^2:

$$n(As) = \frac{500}{100} \cdot \frac{3}{1} \cdot c(BrO_3) \cdot V = 1500 \cdot 0.002 \cdot 0.00165 = 4.95 \cdot 10^{-5}\ mol$$

Then the amout of arsenic in the wallpaper with an area of 50 m^2 will be:

$$n(As_{all}) = \frac{50}{0.01} \cdot 4.95 \cdot 10^{-5} = 0.2475\ mol$$

This amount corresponds to 18.56 g of arsenic. Considering that 1/1000 of arsenic passes into the air in the form of arsine (AsH_3), it turns out that 0.01856 g of arsenic is in the air, in this case the mass of arsine is 0.01931 g = 19.31 mg and its concentration in a room of 60 m_3 is 0.32 mg / m_3, which is 32 times higher than the maximum permissible concentration (1 point).

7. For simplicity, let us write the reaction equations for the double bonds of ethylene:

$C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$

$Br_2 + 2I^- \rightarrow I_2 + 2Br^-$

$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$ (1.5 points for three reactions)

8. The difference between the two titrations is as follows. In the control experiment all bromine is titrated (in the form of iodine), and in the first experiment only the remainder of bromine is titrated (in the form of iodine), that is, the difference will correspond to the bromine that has reacted with oil (in the form of iodine). The concentration of thiosulfate solution:

$$c(Na_2S_2O_3) = \frac{49.62}{248.11 \cdot 0.5} = 0.400\ M$$

Then the diffrerence in the amounts of iodine:

$$n(I_2) = 0.5n(Na_2S_2O_3) = 0.5c(Na_2S_2O_3) \cdot \Delta V(Na_2S_2O_3) = 0.5 \cdot 0.400 \cdot \left(\frac{56.25 - 6.75}{1000}\right)$$
$$= 0.0099\ mol$$

This corresponds to 2.51 g of iodine. This amount reacts with 1.8·0.92 = 1.66 g of oil; then 151.6 g of iodine will react with 100 g of oil, which will correspond to the iodine number (1 point).

Problem 2 (author Beklemishev M.K.)

1. It makes sense to work in the spectral region in which the difference between the signals of the dye and the complex is maximum, i.e. at 480 nm (1 point).

2. a) For the process $Z + n\text{SDS} = Z(SDS)_n$ we can have:

$$K = \frac{[Z(SDS)_n]}{[Z][SDS]^n} = \frac{[Z(SDS)_n]}{[Z]c_{SDS}{}^n}$$ (1 point),

$c(Z) = [Z] + [Z(SDS)_n]$ (1 point),

б) $A \approx \varepsilon[Z(SDS)_n]$ (1 point).

3. a) Substituting the written expressions into the expression for the equilibrium constant, we have:

$$K = \frac{A/\varepsilon}{(c(Z) - A/\varepsilon) \cdot c(SDS)^n}$$ (1 point)

б) After the transformations, we can obtain the Benesi-Hildebrand equation:

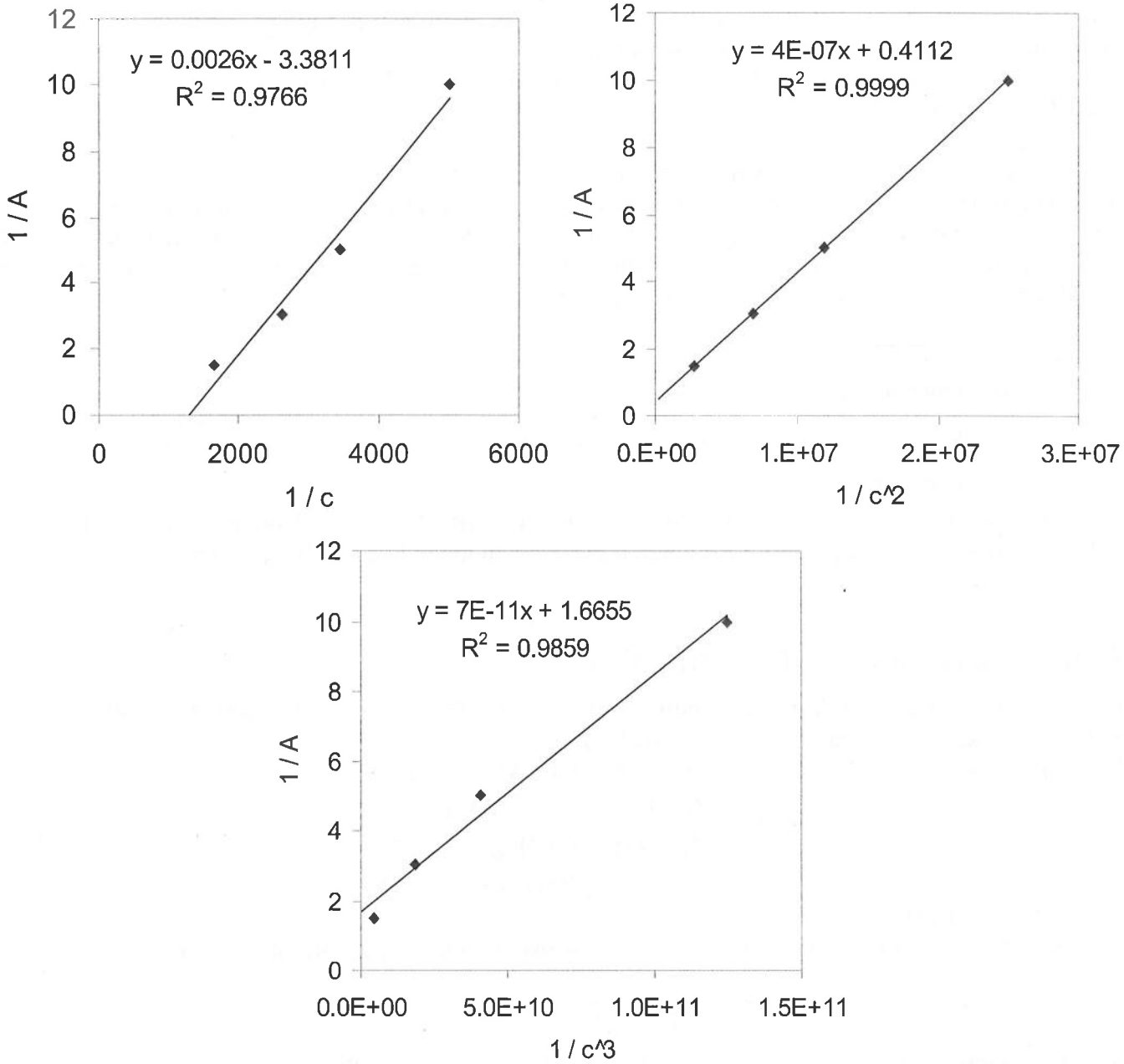
$\frac{1}{A} = \frac{1}{\varepsilon \cdot c(Z)} + \frac{1}{\varepsilon \cdot c(Z) \cdot K \cdot c(SDS)^n}$, which is an equation of the form: $y = y_0 + Bx$, where

$\frac{1}{A} = y$, $\frac{1}{c(SDS)^n} = x$, $\frac{1}{\varepsilon \cdot c(Z)} = y_0$, $\frac{1}{\varepsilon \cdot c(Z) \cdot K} = B$ (y_0 is the cutoff segment, B is the tangent of the slope of the straight line) (2 points).

4. a) As indicated in item 2 of the condition, the equilibrium concentration of surfactant is equal to the initial one (c_{SDS} = [SDS]). When calculating $1/A$ and $1/[SDS]^n$, the following values will be obtained, which are given with two significant digits, necessary for plotting:

[SDS], M	$2.0 \cdot 10^{-4}$	$2.9 \cdot 10^{-4}$	$3.8 \cdot 10^{-4}$	$6.0 \cdot 10^{-4}$
A	0.10	0.20	0.33	0.67
$1/A$	10.0	5.0	3.0	1.5
1/[SDS]	5.0E+03	3.4E+03	2.6E+03	1.7E+03
$1/[SDS]^2$	2.5E+07	1.2E+07	6.9E+06	2.8E+06
$1/[SDS]^3$	1.3E+11	4.1E+10	1.8E+10	4.6E+09

The graphs constructed according to this table in the coordinates $1/A$ – $1/[SDS]^n$ look like this (1 point for three graphs):



b) From the graphs for n = 1, 2 and 3, the best linearity is achieved for n = 2, so the complex has the composition $Z(SDS)_2$ (1 point).

c) The constant K from the graph for n = 2 can be found as y_0 / B (see point 3) (1 point)

Problem 3 (author Shved A.M.)

1. Iodine, as a non-polar substance, dissolves better in organic solvents. If the solvent is non-polar, then the solution acquires a purple color, and if it is polar, then the color is, as in water, brown. Then the assignment (0.5 points per each substance, 3 points in total):

a) non-polar solvent, lighter than water and not reacting with iodine – benzene;

b) non-polar solvent, heavier than water – carbon tetrachloride;

c) water-soluble substance, gives a blue color with iodine – starch;

d) water-soluble polar solvent – ethyl alcohol;

e) polar solvent that is poorly soluble in water – isoamyl alcohol;

f) non-polar solvent, lighter than water, slowly reacting with iodine – cyclohexene (during the reaction, 1,2-diiodocyclohexane, which is heavier than water, is formed).

2. Obtaining an expression that explains the linear correlation: $\frac{1}{D_X} = a + b[X^-]_{aq}$ (1 point):

$$D_X = \frac{c(I_2)_{org}}{c(I_2)_{aq}} = \frac{[I_2]_{org}}{[I_2]_{aq} + [I_2X^-]_{aq}} = \frac{K_D[I_2]_{aq}}{[I_2]_{aq} + K_X[I_2]_{aq}[X^-]_{aq}} = \frac{K_D}{1 + K_X[X^-]_{aq}}$$

$$\frac{1}{D_X} = \frac{1 + K_X[X^-]_{aq}}{K_D} = \frac{1}{K_D} + \frac{K_X}{K_D}[X^-]_{aq} \Rightarrow a = \frac{1}{K_D}; b = \frac{K_X}{K_D}$$

Expressions for the constants: $K_D = \frac{1}{a}$; $K_X = \frac{b}{a}$ (0.5 points per constant, 2 points in total).

3. I_2 and I_2X^- react with thiosulfate in a 1:2 ratio according to the reactions:

$$I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-}$$
$$I_2X^- + 2S_2O_3^{2-} = 2I^- + X^- + S_4O_6^{2-}$$

Obtaining an expression for the relation of D_X to the volumes of thiosulfate and phases (2 points):

$$D_X = \frac{c(I_2)_{org}}{c(I_2)_{aq}} = \frac{n(I_2)_{org}}{V_{org}} \cdot \frac{V_{aq}}{n(I_2)_{aq} + n(I_2X^-)_{aq}} = \frac{1/2\, n(S_2O_3^{2-})_{org} V_{aq}}{1/2\, n(S_2O_3^{2-})_{aq} V_{org}} = \frac{V(S_2O_3^{2-})_{org} V_{aq}}{V(S_2O_3^{2-})_{aq} V_{org}}$$

4. In order for the expression from question **2** to explain the linear dependence of $1/D_X$ also on $[X^-]_0$, it is necessary to assume that $[X^-]_{aq} \approx [X^-]_0$, i.e. (2 points, the answer without providing calculations is not graded):

$$[X^-]_0 = [X^-]_{aq} + [I_2X^-]_{aq} = [X^-]_{aq} + K_X[I_2]_{aq}[X^-]_{aq} \approx [X^-]_{aq}$$
$$K_X[I_2]_{aq}[X^-]_{aq} << [X^-]_{aq} \Rightarrow K_X[I_2]_{aq} << 1$$

5. This inequality is only valid for less stable complexes with small K_X values, then the case **D** with a nonlinear dependence corresponds to the formation of the most stable complex I_3^-. From question **2**, it can be concluded that K_X directly correlates with the coefficient b of the linear equation, i.e., with the tangent of the angle of inclination of the line on the graph. Then from the case **A** to **C**, the stability of the complexes decreases and, accordingly, **A** – Br^-, **B** – Cl^- and **C** – F^-. The same conclusion can be reached without analyzing the exact expression. It is clear that in the case of a more stable complex, more and more iodine will bind to the complex at the same initial halide concentration in the aqueous phase. Consequently, less and less iodine will be extracted into the organic phase, corresponding to higher values of $1/D_X$ (0.5 points per assignment, 2 points in total).

6. Based on the solution to question **2**: $K_D = \frac{1}{a} \approx \frac{1}{0.011} = 91$. The same conclusion can be reached without knowing the answer to question **2**: at the initial zero concentration of halide ions, the iodine complex is not formed, which means that D_X will be numerically equal to K_D.

To find the K_X constants, it is necessary to estimate the tangents of the slope angles of the graphs, for example, graphically, and use the expression from the solution to question **2** (1 point per constant, 4 points in total):

$$b_{Br} \approx \frac{0.038 - 0.011}{0.25} = 0.108 \Rightarrow K_{Br} = \frac{0.108}{0.011} = 9.82$$
$$b_{Cl} \approx \frac{0.0275 - 0.011}{1.65} = 0.010 \Rightarrow K_{Cl} = \frac{0.010}{0.011} = 0.91$$
$$b_F \approx \frac{0.016 - 0.011}{3.2} = 1.56 \cdot 10^{-3} \Rightarrow K_F = \frac{1.56 \cdot 10^{-3}}{0.011} = 0.14$$