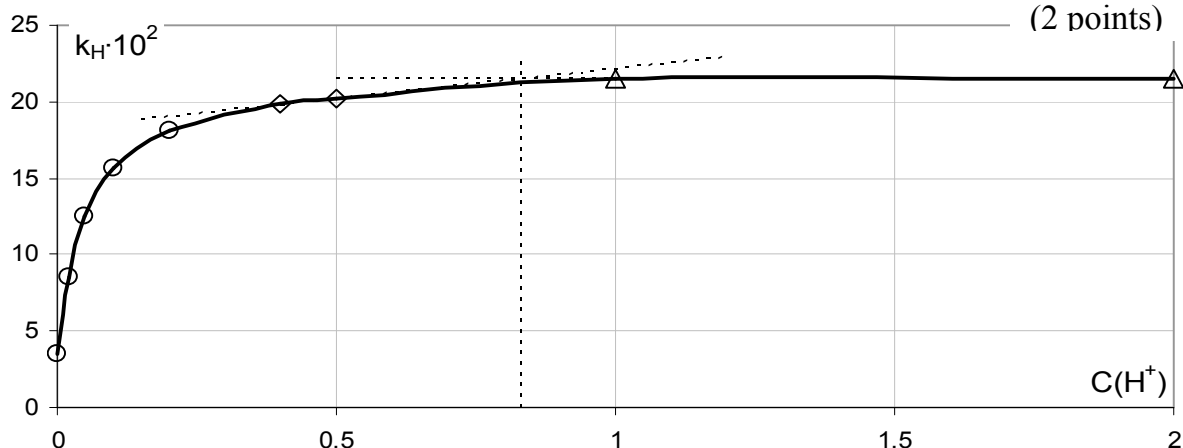


## SECTION I. PHYSICAL CHEMISTRY

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

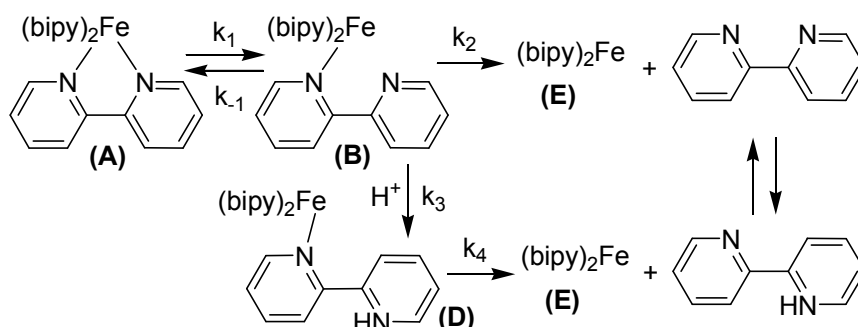
1. (2 points)



$C(H^+)$  of the start of achieving the speed limit can be assessed as the abscissa of the point of intersection of tangents on the graph.  $C(H^+) \approx 0.83$  corresponds to the start (1 point, 3 points in total)

2. Electronic spectra at  $C(H^+) = 0$  and  $C(H^+) = 2$  occurred to be the same, that indicates the absence of detectable amounts of  $Fe(bipy)_3H^{3+}$  in solution at  $C = 2$  mol/L (2 points).

3.



$W = k_2C_B + k_4C_D$  accounts for dual-stream mechanism. Use stationary approximation for B and D:  $\frac{dC_D}{dt} = 0$ , then  $k_3C_B C_{H^+} = k_4C_D$ ;  $\frac{dC_B}{dt} = 0$ , then  $k_1C_A = k_{-1}C_B + k_3C_B C_{H^+} + k_2C_B$  and

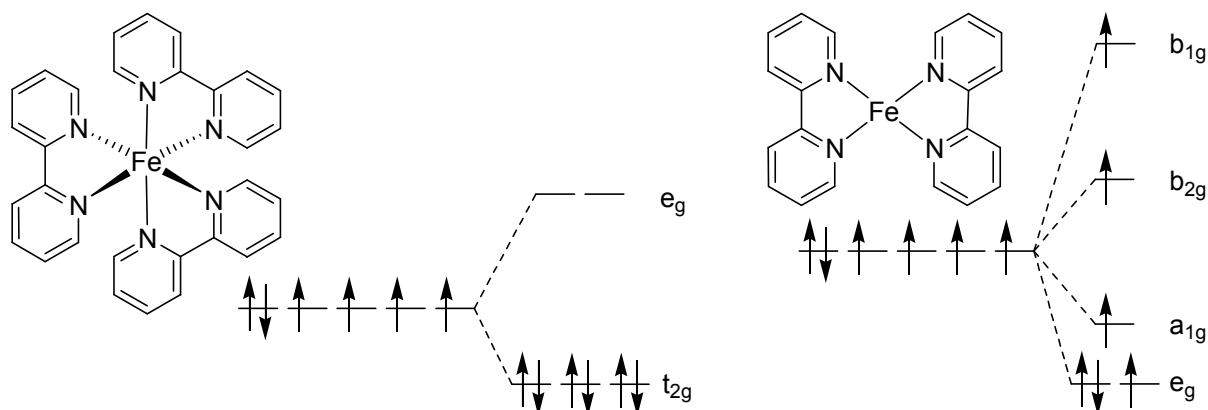
$$C_B = \frac{k_1}{k_{-1} + k_3C_{H^+} + k_2} C_A. \quad W = k_2C_B + k_3C_B C_{H^+} = C_B(k_2 + k_3C_{H^+}) = \frac{k_1(k_3C_{H^+} + k_2)}{k_{-1} + k_3C_{H^+} + k_2} C_A \quad (3 \text{ points})$$

$$k_H = \frac{k_1(k_3C_{H^+} + k_2)}{k_{-1} + k_3C_{H^+} + k_2} \quad (2 \text{ points, 5 points in total})$$

4.  $k_3C_{H^+} \gg k_2$  and  $k_3C_{H^+} \gg k_{-1}$  at high  $C_{H^+}$ , then  $k_H = k_1$  and  $W$  does not depend on  $C_{H^+}$  (the limit rate),  $k_1 = 21.50$  (1 point).

5.  $k_H = \frac{k_1k_2}{k_{-1} + k_2}$ ,  $3,52 = \frac{21.50k_2}{k_{-1} + k_2}$  at  $C_{H^+} = 0$ ;  $k_{-1}$  is proportional to the time of the first bond Fe–N formation,  $k_2$  is proportional to the time of the break of the second bond Fe–N. Then  $k_{-1} : k_2 = 5.11:1$  (84%:16%) (1 point).

6. The low-spin has smaller spin than the central atom does  $0 < 2$  (1 point). The high-spin has the same spin as the central atom does  $2 = 2$  (1 point):



$\text{Fe}(\text{bipy})_2^{2+}$  has bigger dissociation rate, because it has smaller energy of stabilization by crystal field (1 point, 3 points in total).

## Problem 2 (author D.V. Kandaskalov)

1. a) The central atom belongs to the cell completely, while each of 8 atoms in the corners – only by  $\frac{1}{8}$  part. Thereby, elementary cell contains 2 atoms (1 point).

b) Let us put down the equation for calculation of the metal molecular mass:

$$\rho = \frac{m}{V} = \frac{A_r \cdot N}{N_A \cdot a_0^3} \Rightarrow A_r = \frac{\rho \cdot N_A \cdot a_0^3}{N}$$

As each cell contains 2 atoms, each  $64^{\text{th}}$  atom of the metal is absent. This correction one can make by coefficient  $k = 63 / 64$ , which affects the average number of atoms in the cell:

$$A_r = \frac{\rho \cdot N_A \cdot a_0^3}{k \cdot N} = \frac{7.73 \cdot 6.02 \cdot 10^{23} \cdot (2.87 \cdot 10^{-8})^3}{(63/64) \cdot 2} = 55.9 \text{ g} \cdot \text{mol}^{-1},$$

Thus, the metal is iron (Fe) (4 points, 5 points in total).

2. The relationship between the enthalpy and internal energy:  $\Delta H = \Delta U + \Delta(PV)$

To neglect the second term, we must neglect the pressure and volume change (1 point).

3. Let's write the diffusion equation in logarithmic form:

$$D = D_0 \exp\left(-\frac{E_D}{RT}\right) \Rightarrow \ln D = \ln D_0 - \frac{E_D}{RT}$$

Using the plot, we should take at least 2 points to derive the equation, which describes the line. Let's take two terminal points  $(-71; 0.002)$  and  $(-160; 0.0047)$  (2 points):

$$\begin{cases} y_1 = kx_1 + b \\ y_2 = kx_2 + b \end{cases} \Rightarrow \begin{cases} -71 = k \cdot 0.002 + b \\ -160 = k \cdot 0.0047 + b \end{cases} \Rightarrow \begin{cases} k = -32963 = -E_D/R \\ b = -5.07 = \ln D_0 \end{cases} \Rightarrow \begin{cases} E_D = 241000 \text{ J} \cdot \text{mol}^{-1} \\ D_0 = 0.0062 \text{ sm}^2\text{s}^{-1} \end{cases}$$

4. Considering that migration activation energy is three times smaller than vacancy activation energy, we obtain  $\Delta_f U_v^0 = 180.75 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $E_A = 60.25 \text{ kJ}\cdot\text{mol}^{-1}$ . As vacancy formation energy is supposed to be equal to vacancy formation enthalpy and the entropy is neglected,  $\Delta_f G_v^0 = \Delta_f U_v^0 = 180.75 \text{ kJ}\cdot\text{mol}^{-1}$ . Vacancy concentration at 800K (2 points):

$$c_v = \exp\left(-\frac{180750}{8.31 \cdot 800}\right) = 3.77 \cdot 10^{-14}$$

5. The equilibrium concentration is too small (about  $10^{-14}$ ) even at high temperatures, thus the material with vacancy concentration  $1/64 = 1.5 \cdot 10^{-2}$  does not exist in equilibrium conditions (1 point).

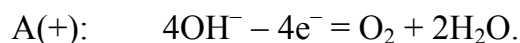
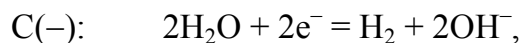
6. The vacancy (like any atom in the cell) is surrounded by 8 nearest neighbors, thus  $k = 8$ . The distance to the neighbor:  $d = \frac{\sqrt{3}}{2} \cdot a_0$ . The jump frequency:

$$D_0 = \frac{v \cdot 8 \cdot \left(\frac{\sqrt{3}}{2} \cdot a_0\right)^2}{6} = v \cdot a_0^2 \Rightarrow v = \frac{D_0}{a_0^2} = \frac{0.01}{(2.87 \cdot 10^{-8})^2} = 1.2 \cdot 10^{13} \text{ c}^{-1} = 1.2 \cdot 10^{13} \text{ Hz} \quad (2 \text{ points})$$

7. At formation of (200) surface each surface atom loses 4 of 8 nearest neighbors (it can be seen looking at the central atom in figure). Thereby, the vacancy formation energy on (200) surface is twice smaller than inside the metal:  $\Delta_f U_v^0(200) = 90.4 \text{ kJ}\cdot\text{mol}^{-1}$ . For the surface (110) the central surface atom loses 2 of 8 nearest neighbors. Thereby, the vacancy formation energy on (110) surface is 25% smaller than inside the metal:  $\Delta_f U_v^0(110) = 135.6 \text{ kJ}\cdot\text{mol}^{-1}$  (2 points).

### Problem 3 (author D.G. Syrlybaeva)

1. a) Hydrogen – at the cathode, oxygen – at the anode. Equations of processes (0.5 points for each equation, 1 point in total):



b) Let us find the number of  $\gamma$ -decays  $^{60}\text{Co}$  per time unit (source activity). According to the law of radioactive decay  $N(t) = N_0 \exp(-kt)$ , where  $N$  – current number of cobalt nuclei,  $N_0$  – their initial number,  $k = \ln 2 / \tau_{1/2}$  – decay constant. For the rate of interest we have  $-dN/dt = (\ln 2 / \tau_{1/2})N_0$ , as the cobalt quantity will change negligibly in 1 hour. The number of radioactive nuclei in 2 grams of  $^{60}\text{Co}$  is  $N_A / 30$ .  $\tau_{1/2} = 5.3 \cdot 3600 \cdot 24 \cdot 365 = 1.67 \cdot 10^8 \text{ sec}$ . Thus, having regard to the contribution of  $\gamma$ -radioactivity, equal  $10^{-3}$ , for the activity of the source one obtains (0.5 points):

$$\frac{dN}{dt} = 0.001 \cdot \frac{1}{30} \cdot \frac{\ln 2}{1.67 \cdot 10^8} = 8.33 \cdot 10^{10} \text{ decays/sec}$$

The energy of one  $\gamma$ -quantum is  $1.332 \cdot 10^6 \cdot 1.6 \cdot 10^{-19} = 2.13 \cdot 10^{-13}$  J. Release of radiant energy (and its absorption by water) per time unit comprises

$$\frac{dE}{dt} = 2.13 \cdot 10^{-13} \cdot 8.33 \cdot 10^{10} = 1.77 \cdot 10^{-2} \text{ J} \cdot \text{sec}^{-1}$$

As radiation-chemical yield is the number of particles, produced by a unit of the absorbed radiation energy (this is obvious from dimensions of the quantity), for the quantity of generated hydrogen one obtains

$$\frac{dN(\text{H}_2)}{dt} = 4.7 \cdot 10^{-8} \text{ mol} \cdot \text{J}^{-1} \cdot 1.77 \cdot 10^{-2} \text{ J} \cdot \text{sec}^{-1} = 8.32 \cdot 10^{-10} \text{ mol} \cdot \text{sec}^{-1}$$

In 1 hour  $3600 \cdot 8.32 \cdot 10^{-10} = 3.0 \cdot 10^{-6}$  mol of hydrogen is released. At normal conditions this corresponds to the volume  $V_{\text{rad}} = 3.0 \cdot 10^{-6} \cdot 22.4 = 6.72 \cdot 10^{-5} \text{ L}$  (1.5 points)

The quantity of hydrogen, produced by electrolysis, can be found from Faraday's law. Ion  $\text{H}^+$  is singly charged, and the number of  $\text{H}_2$  molecules is half as many as  $\text{H}^+$ , then

$$N(\text{H}_2) = \frac{1}{2} \frac{I \cdot t}{F} = 0.5 \cdot \frac{8 \text{ C} \cdot \text{sec}^{-1} \cdot 3600 \text{ sec}}{96485 \text{ C} \cdot \text{mol}^{-1}} = 0.15 \text{ mol}$$

Hence,  $V_{\text{el}} = 22.4 \cdot 0.15 = 3.36 \text{ L}$  (1 point, 4 points in total for q.1).

2. Let us put down the rate of change of the acid concentration, which is consumed in reactions (2) and (3):  $-d[\text{B}]/dt = k_2[\text{B}][\text{H}_2\text{O}_2] + k_3[\text{B}][\text{OH}^\bullet]$ . Concentration of intermediate (hydroxyl) can be found from the equation

$$d[\text{OH}^\bullet]/dt = k_1[\text{H}_2\text{O}_2][\text{Fe}^{2+}] - k_3[\text{OH}^\bullet][\text{B}] - k_4[\text{H}_2\text{O}_2][\text{OH}^-] - k_5[\text{OH}^\bullet][\text{Fe}^{2+}] = 0.$$

Herefrom 
$$[\text{OH}^\bullet] = \frac{k_1[\text{H}_2\text{O}_2][\text{Fe}^{2+}]}{k_3[\text{B}] + k_4[\text{H}_2\text{O}_2] + k_5[\text{Fe}^{2+}]}$$

Substituting  $[\text{OH}^\bullet]$  in the expression for the rate of consumption of **B**, we obtain (3 points):

$$-\frac{d[\text{B}]}{dt} = k_2[\text{B}][\text{H}_2\text{O}_2] + \frac{k_3[\text{B}] \cdot k_1[\text{H}_2\text{O}_2][\text{Fe}^{2+}]}{k_3[\text{B}] + k_4[\text{H}_2\text{O}_2] + k_5[\text{Fe}^{2+}]}$$

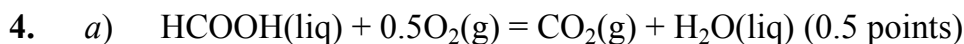
3. a)  $\text{Fe}^{2+} + \text{Cl}_2^\bullet = \text{Fe}^{3+} + 2\text{Cl}^-$ . b) From e.m.f. values of the reaction and the standard potential of  $\text{Cl}_2^\bullet/\text{Cl}^-$  couple one can find the potential of  $\text{Fe}^x/\text{Fe}^y$  couple (1 point):

$$E - E^0(\text{Cl}_2^\bullet/\text{Cl}^-) = 2.3 \text{ V} - 1.528 \text{ V} = 0.771 \text{ V}$$

The potential  $E^0(\text{Fe}^{3+}/\text{Fe}) = -0.058 \text{ V}$  does not satisfy this value. Let us find the potential of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple:  $E^0(\text{Fe}^{3+}/\text{Fe}^{2+}) = 3E^0(\text{Fe}^{3+}/\text{Fe}) - 2E^0(\text{Fe}^{2+}/\text{Fe}) = 3 \cdot (-0.058) - 2 \cdot (-0.473) = 0.771 \text{ V}$

Hence,  $\text{Cl}_2^\bullet$  consumes in the reaction  $\text{Fe}^{2+} + \text{Cl}_2^\bullet = \text{Fe}^{3+} + 2\text{Cl}^-$  (0.5 points). The equilibrium constant can be found from the Gibbs energy  $\Delta_r G^0 = -RT \ln K$ . The standard Gibbs energy is

associated with the standard e.m.f. according to the equation  $\Delta_r G^0 = -nFE^0$ , where  $F$  – Faraday constant, hence  $K = \exp(nFE^0 / RT) = 6.96 \cdot 10^{25}$  (1 point, 2.5 points in total).



b) For calculation of the energy of O–O bond from catalytic reaction one must find the enthalpy of formation of atomic oxygen O(g). Let us denote it by  $x$ . Given the standard enthalpy of formation of O<sub>2</sub>(g) is zero, from the combustion reaction of HCOOH(liq) we first obtain the heat of formation of formic acid ( $y$ ):

$$\Delta_f H_{298}^0(\text{CO}_2, \text{g}) + \Delta_f H_{298}^0(\text{H}_2\text{O}, \text{liq}) - y = \Delta_c H_{298}^0(\text{HCOOH}, \text{liq}),$$

$$y = \Delta_f H_{298}^0(\text{HCOOH}, \text{liq}) = 254.58 - 393.51 - 285.83 = -424.76 \text{ kJ}\cdot\text{mol}^{-1} \text{ (1 point).}$$

After that we have:

$$3\Delta_f H_{298}^0(\text{CH}_2\text{O}_2, \text{liq}) + 4\Delta_f H_{298}^0(\text{CO}_2, \text{g}) - \Delta_f H_{298}^0(\text{C}_7\text{H}_6\text{O}_3, \text{liq}) - 11x = -4994.69,$$

$$11x = -3 \cdot 424.76 - 4 \cdot 393.51 + 594.5 + 4994.69 = 2740.87 \text{ kJ}\cdot\text{mol}^{-1},$$

from where  $x = \Delta_f H_{298}^0(\text{O}, \text{g}) = 249.17$ ,  $\Delta H_{298}^0(\text{O–O}) = 2x = 498.34 \text{ kJ}\cdot\text{mol}^{-1}$  (1 point).

c) As for the gas reaction  $\text{O}_2(\text{g}) = 2\text{O}(\text{g})$ , expressing the breaking of the bond O–O,  $\Delta U = \Delta H - \Delta(PV) = \Delta H - RT$ , we obtain:  $\Delta U_{298}^0(\text{O–O}) = \Delta H_{298}^0(\text{O–O}) - RT = 498.34 - 8.314 \cdot 0.298 = 495.86 \text{ kJ}\cdot\text{mol}^{-1}$  (1 point).

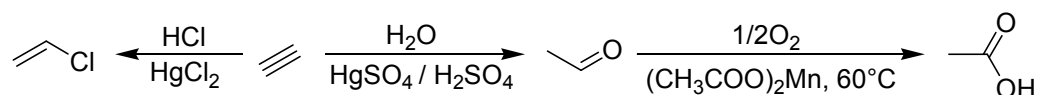
d) Since by the definition bond energy corresponds to the enthalpy of formation at absolute zero, it is necessary to use the Kirchhoff's formula. As  $C_{p,m}(\text{O}_2, \text{g}) = 7R / 2$ ,  $C_{p,m}(\text{O}, \text{g}) = 5R / 2$ , for the reaction  $\text{O}_2(\text{g}) = 2\text{O}(\text{g})$  we have (2 points, 5.5 points in total):

$$\begin{aligned} \Delta_r C_{p,m} &= 2 \cdot 5R / 2 - 7R / 2, \text{ and thus } \Delta_f H_0^0(\text{O}, \text{g}) = \Delta_f H_{298}^0(\text{O}, \text{g}) - 3R / 2 \cdot 298 = \\ &= 498.34 - 1.5 \cdot 8.314 \cdot 0.298 = 494.62 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

## SECTION II. LIFE SCIENCES AND POLYMERS

### Problem 1 (author B.N. Garifullin, Yu.S. Golovko)

1. Taking into account that we consider industrial processes of mid 20<sup>th</sup> century, **S** is acetylene:



Mercury containing catalysts were used at the plant in the production of at least two substances (1 point for **S**, 0.5 point for each reaction, 0.25 point for each of the reaction conditions, 3.25 points in total).

2. Let us consider the laboratory synthesis of **X**. Since **Z** does not contain carbon, its molecular mass can be calculated as follows ( $n$  is the number of carbon atoms in **X**):

$$M(\mathbf{A}) = 2 \cdot \frac{12.01 \cdot 100 \cdot n}{4.78} - \frac{24.02 \cdot 100 \cdot n}{10.41} = 271.8n \text{ g/mol}$$

71.0 $n$  g/mol in **Z** refers to the halogen, which corresponds to  $2n$  chlorine atoms. The residual mass of 200.8 $n$  g/mol can be ascribed to one mercury atom (if  $n = 1$ ). The description of **Z** gives additional proofs for the above conclusion (mercury (II) chloride).

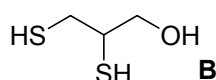
The molar mass of **X** is 251.3 g/mol. Subtracting atomic masses of Hg and C one gets 38.7 g/mol, which unambiguously corresponds to one Cl and three H atoms (presence of chlorine in **X** is obligatory based on the reaction equation of the laboratory synthesis). Then **X** is CH<sub>3</sub>HgCl, and **Y** is dimethylmercury (CH<sub>3</sub>)<sub>2</sub>Hg (based on the balance of atoms in the reaction). Besides, both stages of **Y** biosynthesis occur as methylation, a kind of transferase reaction (0.5 for each calculation, 1 point for each of **X** – **Y**, 4 points in total).

3. The description of **X** in the task (including its melting point) manifests in favor of its covalent polar composition. At the same time colorless liquid **Y** has a linear structure (CH<sub>3</sub>–Hg–CH<sub>3</sub>) with zero dipole moment. Thus, dimethylmercury is much more toxic for man (1 point for each structure, 1 point for the conclusion about toxicity, 3 points in total).

4. Mercury containing catalysts used in the technological processes penetrated into the Sea of Japan near the city of Minamata due to imperfection of the clean-up system. The catalysts were transformed into **X** and **Y** by anaerobic bacteria in the sea. Proceeding along the nutrition chains, these products further accumulated in fish used by local population as an essential food (1 point).

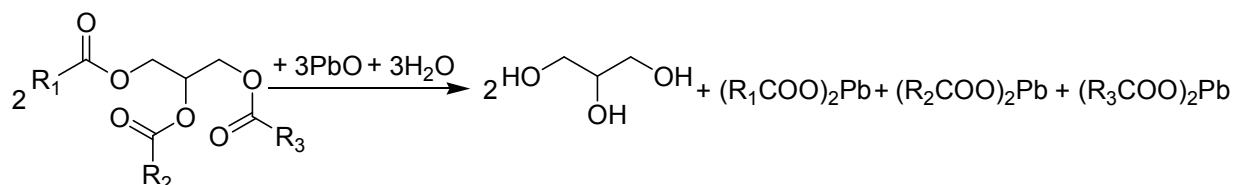
5. Calculation of the element composition of **B** shows that the molecule contains C and H atoms in the ratio of 3:8. Multiple C:H ratios (6:16, 9:24, etc.) are hardly possible because of high amount of hydrogen.

The residual mass after subtraction of C and H from M(**B**) equals 80.1 g/mol, which can correspond to five oxygen atoms (**B** is an oxygen containing compound!). However, there are no stable compounds C<sub>3</sub>H<sub>8</sub>O<sub>5</sub>. Besides, analogies with the substance **C** are unclear in the latter case. The only reasonable way consists in “substituting” four oxygen atoms by two sulfur ones. Then the formula of **B** is C<sub>3</sub>H<sub>8</sub>S<sub>2</sub>O, which, together with the data about the chiral centers, finally leads to 2,3-dimercapto-1-propanol (British anti-Lewisite), which is structurally similar to glycerol.



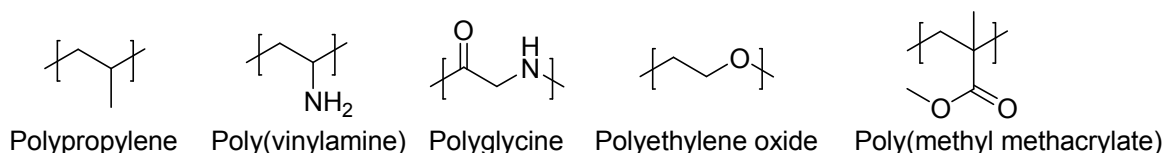
This compound competes with free thiol groups in proteins for the mercury compounds strongly chelating the latter. These complexes are further egested with urine (1.5 point for the calculation, 1 point for the structure, 2.5 points in total).

6. Compound **C** is glycerol first obtained in 1779 by C. Scheele who carried out hydrolysis (saponification) of plant oil triacylglycerols (R<sub>1-3</sub> are hydrocarbon substituents) (1.25 point):

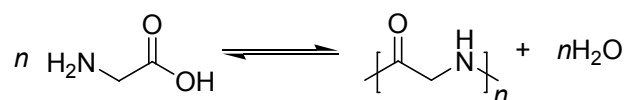


## Problem 2 (authors A.K. Berkovich, E.A. Karpushkin)

1. Polyglycine and polyethylene oxide are heterochain polymers (0.5 point for each structure, 0.25 point for the choice of heterochain polymers, 3 points in total).

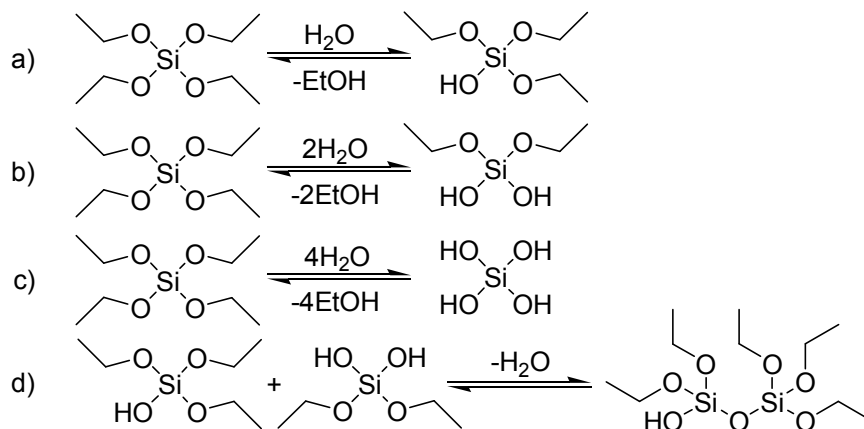


2. Ethylene oxide does not contain groups capable of condensation. Thus, only polyglycine can be prepared by the monomer condensation.



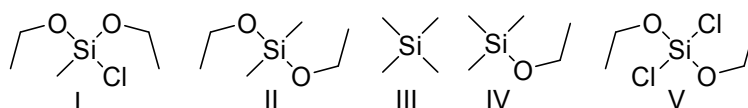
Since the amide formation is reversible, the low molecular product (water) should be constantly removed from the system. Thus, heating is the obligatory condition (0.5 point for the choice, 0.5 for the reaction, 0.25 point for heating, 1.25 points in total).

3. (0.5 point for each reaction, 2 points in total)



4. The completely condensed structure  $\text{SiO}_2$  (0.5 point)

5. (0.25 point for each of structures I – V)

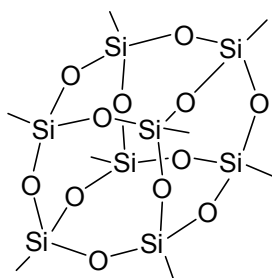


A linear polymer can be derived from the precursor with exactly two reactive groups. A low molecular product is formed in the case of a sole reactive group, whereas substances with three or four reactive groups will lead to a branched or cross-linked polymer. III is free of reactive groups. It is known from the text that ethoxy-group can be hydrolyzed. The Si-Cl bond is also hydrolyzed, otherwise I, II and IV would have led to linear polymers, which is in contradiction with the clause. Thus, IV contains one, II – two, I – three, and V – four reactive groups (0.5 point for the choice of each precursor, 0.5 point for each of the polymer and low molecular product, 3.25 points in total)



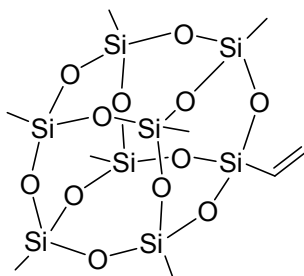
6. The sum of the given mass fractions equals 95.5%, thus **A** also contains some other element(s). Hydrogen can be a logical choice due to low residual value of mass fraction. Then,  $n(\text{Si}) : n(\text{C}) : n(\text{O}) : n(\text{H}) = 41.8/28.086 : 17.9/12.011 : 35.8/15.999 : 4.5/1.008 = 1.49:1.49:2.24:4.464 = 8:8:12:24$  ( $\text{Si}_8\text{C}_8\text{O}_{12}\text{H}_{24}$ ). Sole types of Si, C, and O atoms suggest the overall structure of high symmetry, whilst the C:H ratio of 1:3 determines C atoms present in methyl groups:





A silane with three hydrolysable groups and methyl substituent (e.g. methyltrichlorosilane) can be the **A** precursor (0.5 point for the gross formula, 1.5 points for the structure of **A**, 0.5 point for the precursor, 2.5 points in total)

7. Based on the structural similarity of **A** and **B** as well as the presence of only one polymerizable group in **B**, the formula of the latter can be written as  $(\text{SiCH}_3)_7\text{O}_{12}\text{SiR}$ , where R is the polymerizable group. The mass fraction of carbon in the  $(\text{SiCH}_3)_7\text{O}_{12}\text{Si}$  fragment equals 18.3% showing that R is not free of carbon. Let R contains  $a$  C atoms, whereas the molar mass of R equals  $X$ . Then  $0.197 = \frac{(7+a) \cdot 12.011}{521.93 + X}$ , and  $X = 61.0a - 95.1$ . If  $a = 1$ ,  $X < 0$ ; if  $a = 3$  there are no rational solutions. The case of  $a = 2$  corresponds to  $X \approx 27$  and vinyl –  $\text{CH}=\text{CH}_2$ , which is known to be active in radical polymerization (1.5 points).

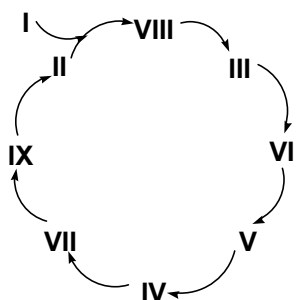


8. The gross formulae of a monomeric unit and the corresponding monomer coincide at radical polymerization with multiple bond opening. The molar masses of **B** and butadiene-1,3 are of 548.96 and 54.09 g/mol, respectively; the mass fraction of Si in **B** is 40.93%. If Si content equals 5 mas.%, the mass fraction of **B** equals  $5\% / 0.4093 = 12.21\%$ , and its molar fraction in the monomer mixture equals  $\frac{0.1221 / 548.96}{0.1221 / 548.96 + (1 - 0.1221) / 54.09} = 1.35\%$ . Thus, it is possible to obtain a non-combustible rubber based on butadiene-1,3 and **B** (0.75 point for the calculation, 0.25 point for the decision, 1 point in total).

### Problem 3 (author A.K. Gladilin)

1. The information given in the text of the task is abundant, which makes possible a variety of solution strategies. An example is considered hereunder.

Succinate dehydrogenase inhibition leads to accumulation of **IV**, **V**, and **VIII** in the medium. Since **IV** is the immediate substrate of this enzyme, **V** and **VIII** precede **IV**. Thus, 6- and 5-carbon anions precede the 4-carbon one. Since decarboxylation is the only way of changing the number of carbon atoms, the metabolic pathway starts with 6-carbon, and ends up with 4-carbon anions. 6-carbon compound **VIII** is formed in the reaction of **I** and 4-carbon compound **II** (with elimination of  $\text{CO}_2$ ), which is possible only if the process is cyclic. This is also supported by an abrupt acceleration of pyruvate consumption upon addition of any metabolite to the medium.

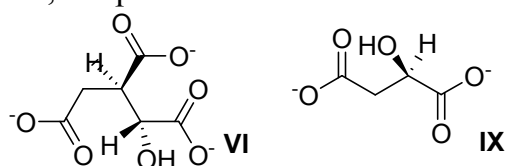


No two-electron oxidation of **VIII** (with or without  $\text{CO}_2$  elimination) leads to any other metabolite of the pathway. Thus, **VIII** is dehydrated forming **III**, which, in turn, is hydrated to produce **VI**, which is followed by **V** и **IV**. One only has to position **VII** and **IX** between **VI** and **II**. **VI** can be neither hydrated nor dehydrated, thus it is oxidized to **VII**, which is further hydrated to form

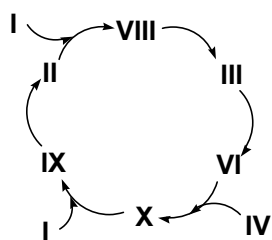
**IX**. The cycle is closed by the oxidation of **IX** to **II**.

We have considered the Tricarboxylic acid cycle (often referred to as the Citric acid cycle) in the form initially proposed by A. Krebs (0.5 point for each correct positioning of the metabolites, 1 point for the cyclicity, 5 points in total).

2.  $\text{I} + \text{II} \rightarrow \text{VIII}$ ;  $\text{VI} \rightarrow \text{V}$ ;  $\text{V} \rightarrow \text{IV}$ ;  $\text{IV} \rightarrow \text{VII}$ ;  $\text{IX} \rightarrow \text{II}$  (0.3 point each, 1.5 points in total).
3. In the oxidized forms,  $\text{NAD}^+$  and  $\text{FAD}$  (0.5 point each, 1 point in total)
4. (0.5 point for each choice, 0.5 point for each correct stereocenter, 2.5 points in total)



5. This process is also cyclic (see the logics above). Pyruvate enters the cycle, whereas succinate leaves it as the product. Both cycles have five compounds and four stages in common.



This is the fragment of the Citric acid cycle from **IX** to **VI**. Iso-citrate is further cleaved giving succinate and glyoxylate, which turns out to be **A** (this compound gave the name to the whole metabolic pathway, Glyoxylate cycle). Glyoxylate then reacts with the second pyruvate molecule giving malate (0.5 point for each correct positioning of the metabolites, 1 point for the cyclicity, 1 point for **A**, 5 points in total).

## SECTION III. INORGANIC CHEMISTRY

### Problem 1 (author D.V. Kandaskalov)

1. At first we can determine, from the given figure, the stoichiometry of the complex compound **X** which is  $A_2B_{14}Cl_{14}$ , with **A** – transitional metal, **B** – nonmetallic element. Now

let write schematically the reaction of **X** formation:  $2A + (14 - \frac{14}{x})B + \frac{14}{x}BCl_x \rightarrow A_2B_{14}Cl_{14}$

If a molecular mass of **B** is  $b$ , and  $x$  is the number of Cl atoms we can write:

$$\frac{2.688}{b} \cdot \frac{14}{x} = \frac{1.890}{b + 35.5x} \cdot (14 - \frac{14}{x}); b = \frac{35.5x}{0.703 \cdot (x - 1) - 1}$$

We could observe that  $x > 2$ . and now we can proceed to checking of  $x$ . The checkup shows us that only one possible combination is at  $x = 4$  and **B** is Te. Thus we determined two compounds: **B** – Te, **C** –  $TeCl_4$ .

To find out metal **A** we should use the stoichiometry of the **X**, let  $y$  is molar mass of **A**, then:  $\frac{0.768}{2y} = \frac{5.346}{y + 2.289}$ ;  $y = 192$ . Thus, the metal **A** is Iridium (Ir).

Then there are two consecutive thermal treatment of **X** ( $Ir_2Te_{14}Cl_{14}$ ).

We could begin from the end. Second reaction is the heat treatment of the solid residue which consists of **D** and **E** (overall mass is 2.73 g). There is formation of the solid compound **G** (1.792 g) and 0.224 L ( $t = 409.35^\circ C$ ,  $p = 1$  atm) of gaseous mixture **F** and **C**. Following the mass conservation law, the gaseous' mixture mass is  $m(F) + m(C) = 2.73 - 1.792 = 0.938$  g. Using the ideal gas law we can find the average molar mass of this mixture:

$$M = \frac{mRT}{pV} = \frac{0.938 \cdot 8.31 \cdot (273.15 + 409.7)}{101.325 \cdot 0.224} = 234.5 \text{ g/mol}$$

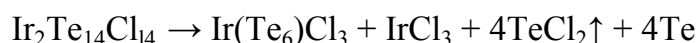
We have known yet that **C** –  $TeCl_4$ , thus we could find the molecular mass of **F** ( $TeCl_a$ ) taking into account the equimolarity of the gas mixture:  $0.5 \cdot (128 + 35.5a) + 0.5 \cdot 270 = 234.5$ ;  $a = 2$ . **F** –  $TeCl_2$ .  $v(TeCl_2) = \frac{0.4032 \cdot 1}{0.082 \cdot (273.15 + 341.1)} = 0.008$  mol

Now, we could determine the **X** compound decomposition. At first, we could find the the mass and quantity of formed compound **B**:

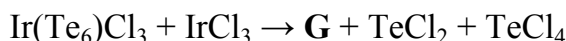
$$m(B) = 5.346 - 2.133 - 0.597 - 0.008 \cdot 199 = 1.024 \text{ g}; v(B) = \frac{1.024}{128} = 0.008 \text{ mol}$$

Thus **X** compound decomposition is:  $Ir_2Te_{14}Cl_{14} \rightarrow 4TeCl_2 + 4Te + D + E$ . Totally for **D** and **E** we have the set of atoms  $Ir_2Te_6Cl_6$ , its molar mass is 1365 g/mol. Therefore  $M(E) = \frac{1365 \cdot 0.28}{1.28} = 298.6$  g/mol, **E** –  $IrCl_3$ .

We know that **D** a complex compound and it has to contain Ir, Te as ligand and chlorine. Thus **D** is  $\text{Ir}(\text{Te})_6\text{Cl}_3$ .



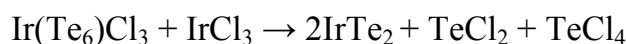
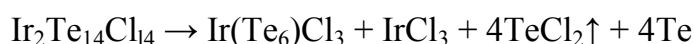
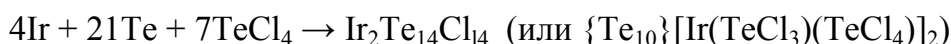
We could write the second reaction as:



Compound **G** is  $\text{IrTe}_2$ .

Finally: **A** – Ir, **B** – Te, **C** –  $\text{TeCl}_4$ , **D** –  $\text{Ir}(\text{Te})_6\text{Cl}_3$ , **E** –  $\text{IrCl}_3$ , **F** –  $\text{TeCl}_2$ , **G** –  $\text{IrTe}_2$ , **X** –  $\text{Ir}_2\text{Te}_{14}\text{Cl}_{14}$  (1.5 points for each **D** and **E**, 1 point for others, 9 points in total).

2. (1 point for each reaction equation, 3 points in total)

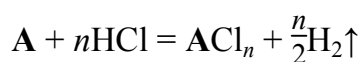


3. Each of Te atoms gives 2 electrons to Ir, thus the cation Ir has 6 own electrons to complete 18 electrons level. The neutral atom of Ir has 9 valence electrons, thus Ir oxidation number is +3 in the complex compound (1 point).

4. If atoms 5 and 5' have three centres four electrons bonding, both of them have the charge –1. The neighbors of these two atoms (2, 2', 3, 3') – have a charge +½ and 4 remaining atoms (1, 1', 4, 4') are neutral (0.2 points for each atom charge, 2 points in total).

## Problem 2 (author S.S. Fedotov)

1. The solution of a metal in hydrochloric acid can be described with the general formula:



Thus,  $n \cdot \nu(\mathbf{A}) = \nu(\text{HCl})$ , i.e.  $n \cdot \frac{0.235}{M(\mathbf{A})} = \frac{0.1 \cdot 2.96 \cdot 1.048}{36.5} = 0.0085 \text{ mol}$ . At  $n = 2$ ,  $M(\mathbf{A}) = 55.3 \text{ g/mol}$ ,

that might be corresponded to Mn or Fe (taking into account the error in volume measuring).

As a color of  $\text{Mn}^{2+}$  solutions is pale pink, we conclude that **A** – Fe, **B** –  $\text{FeCl}_2$ .

Now let us calculate the composition of the precipitate **C**:  $\nu(\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}) = \frac{3.676}{291.05} =$

$= 0.0126 \text{ mol}$ ;  $\nu(\text{Fe}) = \frac{m(\text{Fe})}{M(\text{Fe})} = \frac{0.235}{55.85} = 0.0042 \text{ mol}$ . Molar ratio  $\nu(\text{Co}) : \nu(\text{Fe}) = 0.0126 : 0.0042 =$

$= 3 : 1$ .

Then the precipitate **C** is  $\text{Co}_{0.75}\text{Fe}_{0.25}\text{C}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ . Regarding the loss in mass we obtain

the following equation  $x: \frac{146.16}{146.16 + 18x} = \frac{146.16 \cdot 0.0168}{3.068}$ ;  $x = 2$ , **C** –  $\text{Co}_{0.75}\text{Fe}_{0.25}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  (0.75 point for each compound **A** – **C**, 0.5 point for each calculation, 3.75 points in total).

2. On the basis of the thermal analysis conditions **C** has to decompose with the release of water and  $\text{CO}_2$  and to be oxidized to oxides. At the beginning  $\text{Fe}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$  form, the latter transforms in a thermodynamically more stable  $\text{CoO}$  at high temperature.

at high temperature  $\text{Co}_3\text{O}_4$  the loss in mass is:

$$\Delta m = \left(1 - \frac{\frac{1}{4}M(\text{Co}_3\text{O}_4) + \frac{1}{8}M(\text{Fe}_2\text{O}_3)}{M(\text{Co}_{0.75}\text{Fe}_{0.25}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O})}\right) \cdot 100\% = \left(1 - \frac{\frac{1}{4} \cdot 240.79 + \frac{1}{8} \cdot 159.7}{182.20}\right) \cdot 100\% = 56\%$$

For  $\text{CoO}$ :

$$\Delta m = \left(1 - \frac{\frac{3}{4}M(\text{CoO}) + \frac{1}{8}M(\text{Fe}_2\text{O}_3)}{M(\text{Co}_{0.75}\text{Fe}_{0.25}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O})}\right) \cdot 100\% = \left(1 - \frac{\frac{3}{4} \cdot 74.93 + \frac{1}{8} \cdot 159.7}{182.20}\right) \cdot 100\% = 58.2\%$$

We know that  $\Delta m = 57.3\%$ , therefore,  $\text{Co}_3\text{O}_4$  has not decomposed totally to  $\text{CoO}$ . Then **G**: presents a mixture of three oxides  $\text{Fe}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$  and  $\text{CoO}$  (1 point for the composition of **G**, 0.5 points for each calculation, 2 points in total)

In the next step we will establish the quantitative composition of **G**. We have that the amount of Fe atoms is three times less than the amount of Co atoms. The mass loss (in %) does not depend on the amount of the initial compound. If we take that initial amount of **C** was  $a$  mol, then:

$$\begin{aligned} m(\text{Fe}_2\text{O}_3) + m(\text{Co}_3\text{O}_4) + m(\text{CoO}) &= 0.125aM(\text{Fe}_2\text{O}_3) + xaM(\text{Co}_3\text{O}_4) + (0.75a - 3xa)M(\text{CoO}) = \\ &= aM(\text{Co}_{0.75}\text{Fe}_{0.25}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}) \cdot (1 - 0.573) \end{aligned}$$

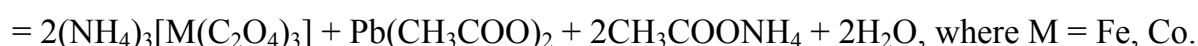
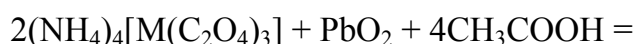
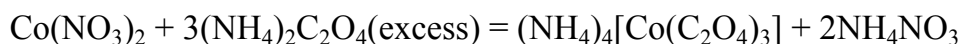
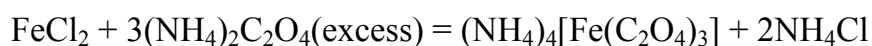
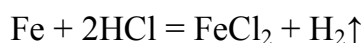
We obtain that  $x = 0.1$ . The amount of the constituents of **G**:

$$\nu(\text{Fe}_2\text{O}_3) = 0.125a \text{ mol}, \nu(\text{Co}_3\text{O}_4) = 0.1a \text{ mol}, \nu(\text{CoO}) = 0.45a \text{ mol}.$$

Molar fractions:  $\chi(\text{Fe}_2\text{O}_3) = 18.5\%$ ,  $\chi(\text{Co}_3\text{O}_4) = 14.8\%$ ,  $\chi(\text{CoO}) = 66.7\%$  (0.75 points for calculations of each molar fraction, 2.25 points in total)

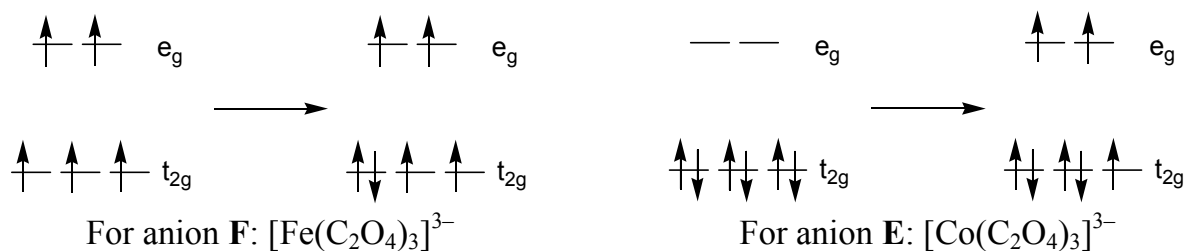
3. With the excess of oxalate-anions the following complex ions form:  $[\text{M}(\text{C}_2\text{O}_4)_x(\text{H}_2\text{O})_{6-2x}]^{(2x-2)-}$ , for example  $[\text{M}(\text{C}_2\text{O}_4)_3]^{4-}$  (1 point).

4. The equations of the given reactions (0.8 points for each reaction, 4 points in total):



5. Using the values of magnetic moments we can calculate the number of unpaired electrons in **F** and in the complex, obtained under light.  $\mu = \sqrt{n(n+2)}$ , where  $n$  – number of unpaired electrons.  $n = 0$  at  $\mu = 0 \mu_B$ ,  $n = 1$  at  $\mu = 1.73 \mu_B$ . Hence, the complex **F** undergoes one-electron transfer, what is possible for iron, as its oxidation state alter from +3 to +2 (1 point).

6. The transformation of Fe-complex under  $h\nu$  owing to the increase of crystal field stabilization energy (0.5 point for each scheme, 1 point in total):



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

1. Molar mass of  $(\text{C}_n\text{H}_{2n+1})_4\text{NBr}$  ( $[\text{R}_4\text{N}]\text{Br}$ ) equals  $M = \frac{m}{v} = \frac{12.88}{0.04} = 322 \text{ g/mol}$ , and on the basis of the formula  $322 = 4(12n + 2n + 1) + 14 + 80$ ;  $14n = 56$ ;  $n = 4$ .  $[\text{R}_4\text{N}]\text{Br} - (\text{C}_4\text{H}_9)_4\text{NBr}$  (2 points)

In the case of exchange reaction  $a(\text{C}_4\text{H}_9)_4\text{NBr} \rightarrow [(\text{C}_4\text{H}_9)_4\text{N}]_a\text{MeO}_b$  and  $\frac{0.04}{a} = \frac{14.44}{242a + M(\text{Me}) + 16b}$ . On the other hand,  $242 + M(\text{Me}) + 16b - 322 = 39$ .

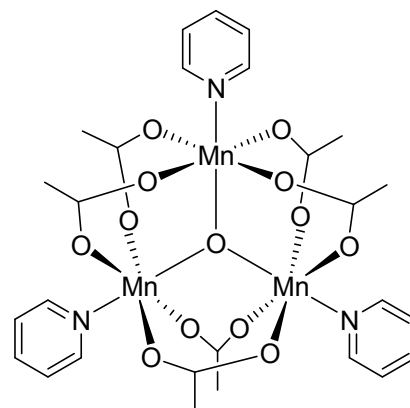
Express the molar mass of **Me** by  $a$  и  $b$ :

$$M(\text{Me}) = 119a - 16b \text{ and } M(\text{Me}) = 361 - 242a - 16b.$$

By solving these equations we have  $119a - 16b = 361 - 242a - 16b$ ,  $a = 1$  (1 point),  $M(\text{Me}) = 119 - 16b$ : if  $b = 1$ ,  $M(\text{Me}) = 103 \text{ g/mol}$ , but Rh doesn't form the salts like  $\text{KRhO}$ , therefore it is not suitable; if  $b = 4$  (1 point),  $M(\text{Me}) = 55 \text{ g/mol}$  and Mn has the salt  $\text{KMnO}_4$ . So **Me** – Mn (1 point), **A** –  $[(\text{C}_4\text{H}_9)_4\text{N}]\text{MnO}_4$  (1 point, 6 points in total).

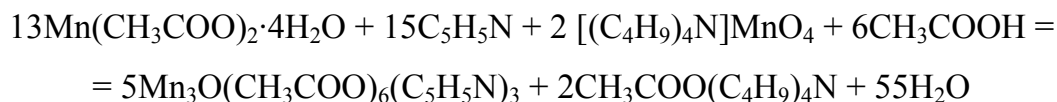
2. On the basis of elemental composition  $\nu_{\text{Mn}} : \nu_{\text{C}} : \nu_{\text{H}} : \nu_{\text{N}} : \nu_{\text{O}} = \frac{21.4}{55} : \frac{42.0}{12} : \frac{4.26}{1} : \frac{5.44}{14} : \frac{26.9}{16} = 0.389 : 3.50 : 4.26 : 0.389 : 1.68 = 1 : 9 : 11 : 1 : 4.33 = 3 : 27 : 33 : 3 : 13$  (1 point).

Taking into account the structural data and the ability of  $\text{CH}_3\text{COO}^-$  and Py to play role of ligands, formula **B** can be written like  $\text{Mn}_3\text{O}(\text{CH}_3\text{COO})_6(\text{C}_5\text{H}_5\text{N})_3$ , where in the group



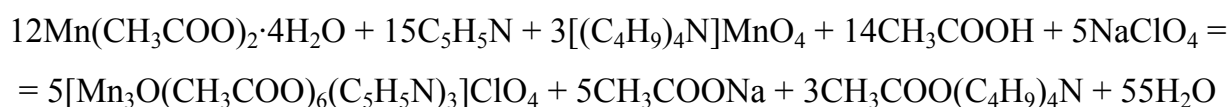
$\text{Mn}_3\text{O}$  – oxygen  $\text{O}_a$ , and in  $\text{CH}_3\text{COO}^- - \text{O}_b$  (since **B** is nonelectrolyte, it doesn't contain  $(\text{C}_4\text{H}_9)_4\text{N}^+$ ) (1 point). The group  $\text{Mn}_3\text{O}$  in **B** has the charged equaled to +6, because **B** is nonelectrolyte. Then for  $\overset{+2}{\text{Me}}_x\overset{+3}{\text{Me}}_{3-x}\text{O}$ ,  $2x - 3x + 9 - 2 = 6$ ,  $x = 1$  (1 point, 3 points in total).

3. Taking into account all the reagents the reaction equation of **B** formation (1 point):



To determine **D** find  $\nu(\text{ClO}_4^-) : \nu[\text{B}(\text{cation in D})]$ ;  $\nu(\text{B}) = \frac{\nu_{\text{PV}} \cdot 5}{15} = \frac{0.01 \cdot 5}{15} = 0.00333$ , then  $\nu(\text{ClO}_4^-) : \nu[\text{B}(\text{cation in D})] = 1:1$ . So, the charge of cation in **D** +1 and **D** –  $[\text{Mn}_3\text{O}(\text{CH}_3\text{COO})_6(\text{C}_5\text{H}_5\text{N})_3]\text{ClO}_4$  (1 point).

Taking into account all the reagents the reaction equation of **D** formation:



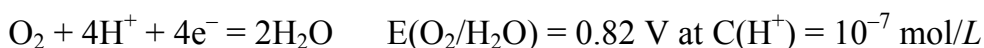
(1 point, 3 points in total)

4. From the Nernst equation  $E = E^0 + \frac{RT}{nF} \ln P$   $E = 1.23 + \frac{0.059}{5} \lg(\text{C}(\text{H}^+)^4)$

( $p(\text{O}_2) = 1 \text{ atm}$ ,  $\text{C}(\text{H}^+) = 10^{-7} \text{ M}$ )  $E = 1.23 + 0.059 \cdot \lg 10^{-7} = 0.82 \text{ V}$  (1 point)

5. For  $\text{D} + e^- = \text{B}$ ,  $E = E^0 + 0.059 \cdot \lg \frac{\text{C}_{\text{D}}}{\text{C}_{\text{B}}}$ ;  $E^0 = 0.44 - 0.059 \cdot \lg \frac{0.333}{0.667} = 0.46 \text{ V}$  (1 point).

6. E.m.f. of the reaction of oxidation of water can be calculated from:

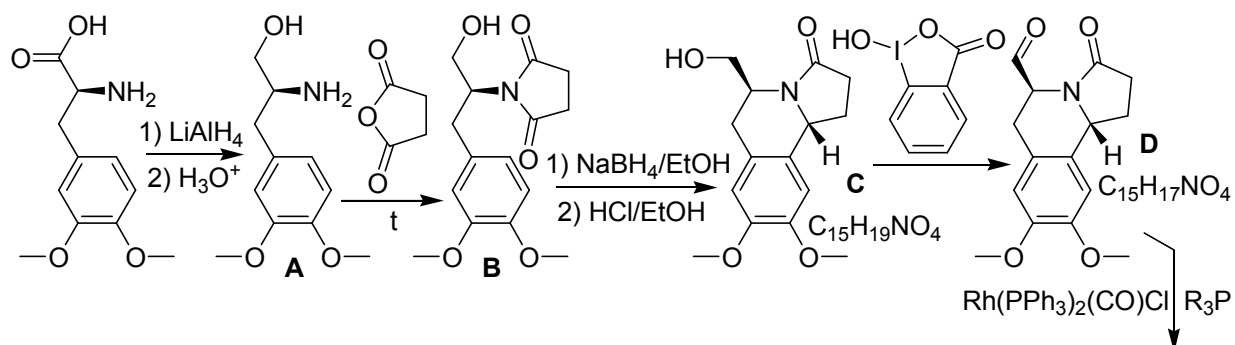


For the reaction  $E = E^0(\text{D}/\text{B}) - E^0(\text{O}_2/\text{H}_2\text{O}) = 0.46 - 0.82 = -0.36 \text{ V}$ . Oxidation of  $\text{H}_2\text{O}$  is impossible,  $\text{Mn}_3\text{O}$  doesn't take part in the photosynthesis (1 point).

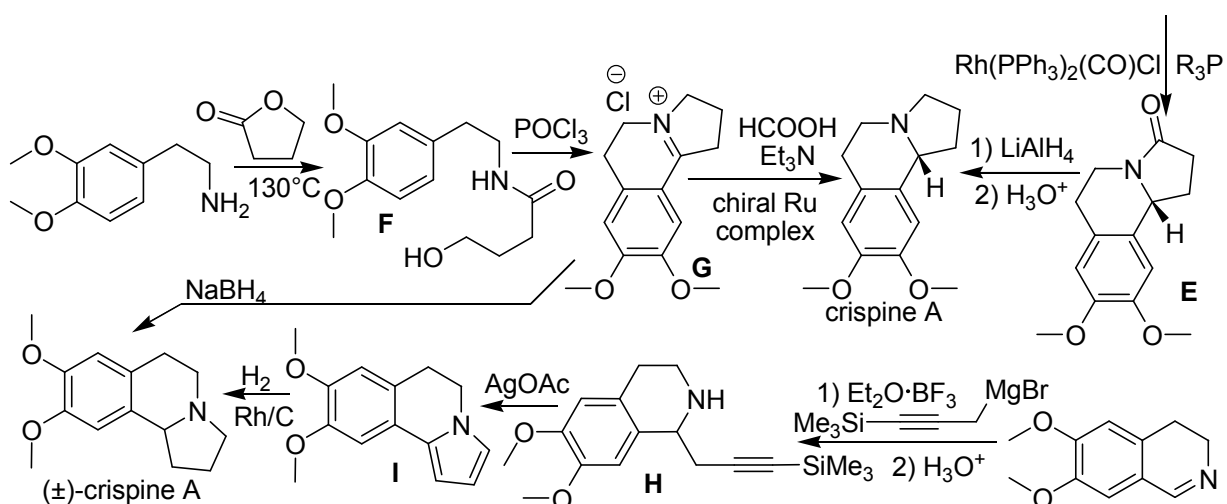
## SECTION IV. ORGANIC CHEMISTRY

### Problem 1 (author I.V. Trushkov)

1. The first step is reduction of aminoacid into aminoalcohol **A** which then reacts with succinic anhydride affording imide **B**. Reduction of imide produces tricyclic compound **C** which has 1 oxygen atom less than **B** but the same quantity of other atoms. It is possible to suppose that **C** is formed via reduction of one of carbonyl groups furnishing semiaminal. In the presence of acid this semiaminal eliminates hydroxide producing aminoalkyl cation which then attacks the proximal phenyl group. Structure of **C** can be also determined by analysis of its transformation into crispine A having also three rings. Transformation of **C** into **D** under treatment with  $I^{III}$  derivative is accompanied by loss of two hydrogen atoms. It is logical to conclude that it is oxidation of primary alcohol into aldehyde. Transformation of **E** into crispine A is the reduction of amide into amine. Therefore, formation of **E** from **D** is decarbonylation reaction. The second approach consists of reaction between 2-(3,4-dimethoxyphenyl)ethylamine and  $\gamma$ -butyrolactone producing **F**. Its molecular formula ( $C_{14}H_{21}NO_4$ ) corresponds to product of formal addition. It is possible for nucleophilic substitution at carbonyl group leading to amide of 4-hydroxybutyric acid. When this amide is treated with  $POCl_3$ , compound **G** is formed. Reduction of **G** in the presence of chiral ruthenium complexes yields crispine A. **G** has one chlorine atom more and one hydrogen atom less than crispine A. Accounting for transformations in scheme, we can conclude that **G** is iminium salt corresponding to crispine A. Reduction of **G** with  $NaBH_4$  in the absence of chiral catalyst furnishes racemic crispine A. The last route includes Lewis acid catalyzed attack of Grignard reagent onto iminium carbon atom of dihydroisoquinoline followed by  $AgOAc$ -initiated oxidative cyclization. Transformation of **I** into ( $\pm$ )-crispine A is hydrogenation. Therefore, **I** has tricyclic framework of crispine A but has 4 hydrogen atom less. It means that **I** contains aromatic pyrrole ring. So,





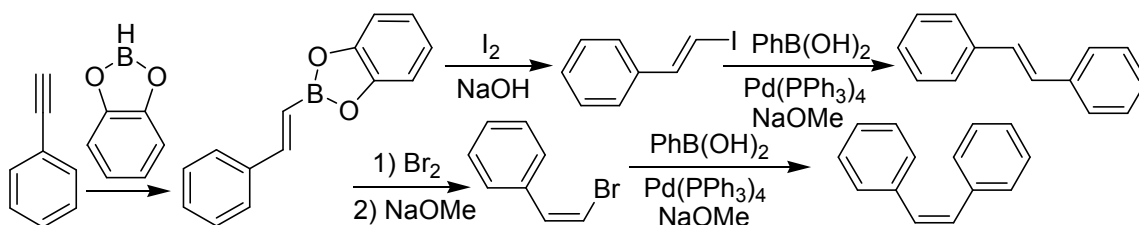


Singlets at 3.6 and 3.9 ppm in  $^1\text{H}$  NMR spectrum of **I** have the relative intensities 3 and correspond to two methoxy groups. Multiplets at 3.0 and 4.0 ppm correspond to  $\text{CH}_2$ -groups. Two singlets at 7.0 and 6.7 ppm correspond to hydrogen atoms of dimethoxyphenyl fragment. Other signals belong to protons of pyrrole ring (structural formulae of **D**, **G**, **I** – 2 points for each; structural formulae of **A** – **C**, **E**, **F**, **H** – 1 point for each; assignment of signals in  $^1\text{H}$  NMR spectrum – 2 points; 14 points in total).

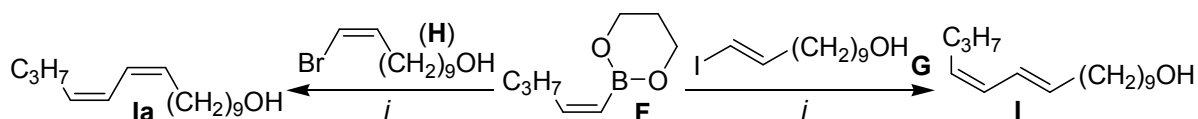
2. According to scheme, rotation angle of crispine A with *ee* 95% is  $95.2^\circ$ . Therefore, the optically pure crispine A (*ee* 100%) should have rotation angle  $95.2 / 0.95 = 100.2^\circ$ . So, rotation angle of  $43.9^\circ$  corresponds to  $ee = 100 \cdot 43.9 / 100.2 = 43.8\%$ . It means that enantiomers ratio is 71.9 : 28.1 (1 point).

## Problem 2 (author E.N. Shved)

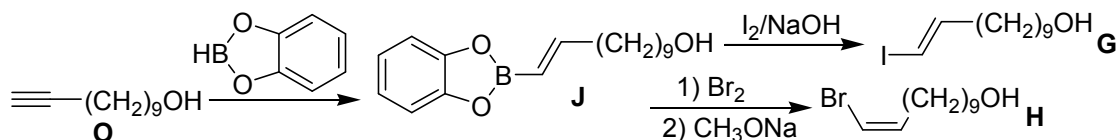
1. From carbon content we can determine molecular formulae of **D** and **E** as  $\text{C}_{14}\text{H}_{12}$ . From statement of problem **E** has one plane of symmetry more than **D**. Therefore, **D** is *trans*-stilbene, **E** is *cis*-stilbene. The first step is hydroboration of phenylacetylene which proceeds with *syn*-stereoselectivity in a such way that more electropositive boron atom adds in according to Markovnikov rule to more hydrogenated carbon atom of  $\text{C}\equiv\text{C}$  bond yielding **A**. Then, treatment of vinylborane simultaneously with iodine and base affords (*E*)-2-iodostyrene with retention of configuration at  $\text{C}=\text{C}$  bond. Oppositely, the treatment of vinylborane with bromine followed by addition of base furnishes (*Z*)-2-bromostyrene with inversion of configuration. The subsequent cross-coupling (Suzuki reaction) produces (*E*)- and (*Z*)-stilbenes **D** and **E**, respectively (structural formula of **A** – 1 point; structural formulae of **B** – **E** – 0.75 points for each; 4 points in total).



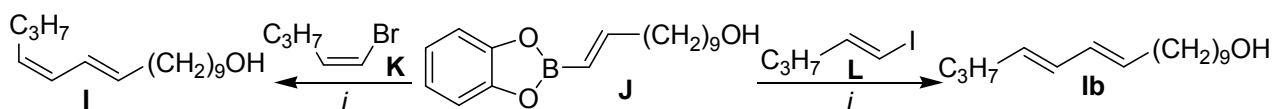
2. Analysis of scheme shows definitely that **F** is vinylboronic acid containing fragment  $(Z)\text{-C}_3\text{H}_7\text{CH}=\text{CH}-$ . Then, **G** is  $(E)\text{-11-iodoundec-10-en-1-ol}$ . As **Ia** is formed from **F**, we can conclude that **Ia** is  $(Z,Z)$ -isomer of **I**, and **H** is  $(Z)\text{-11-bromodec-10-en-1-ol}$ .



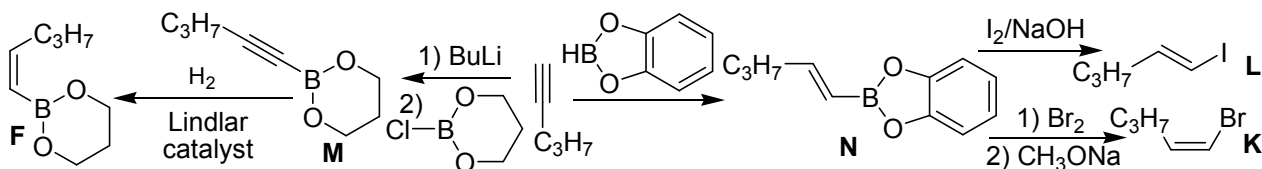
Compound **G** is formed from **J** by iodination with retention of  $(E)$ -configuration (see formation of **B** from **A**). Therefore, **J** is 11-hydroxyundec-1-en-1-ylboronate which is formed by hydroboration of 11-hydroxyundec-1-yne (**O**). **H** is formed from **J** by bromination with inversion of configuration (see formation of **C** from **A**).



**J** is vinylboronate using for synthesis **I**. Therefore, **K** is  $(Z)\text{-1-bromo-1-pentene}$ . So, **Ib** is isomer of bombykol with  $(E,E)$ -configuration, **L** is  $(E)\text{-1-iodo-1-pentene}$ .



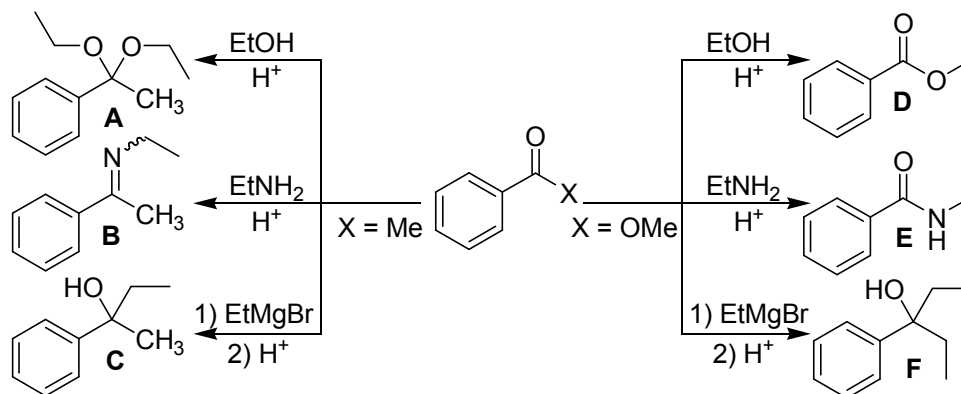
So, **N** –  $(E)\text{-pent-1-enylboronate}$ . **M** is transformed into **F** by hydrogenation in the presence of Lindlar catalyst. Therefore, **M** is the corresponding alkyne which is formed from acetylenide ion by reaction with  $\text{ClB(OR)}_2$  (11 structural formulae, 1 point for each; 11 points in total).



### Problem 3 (author E.M. Budynina)

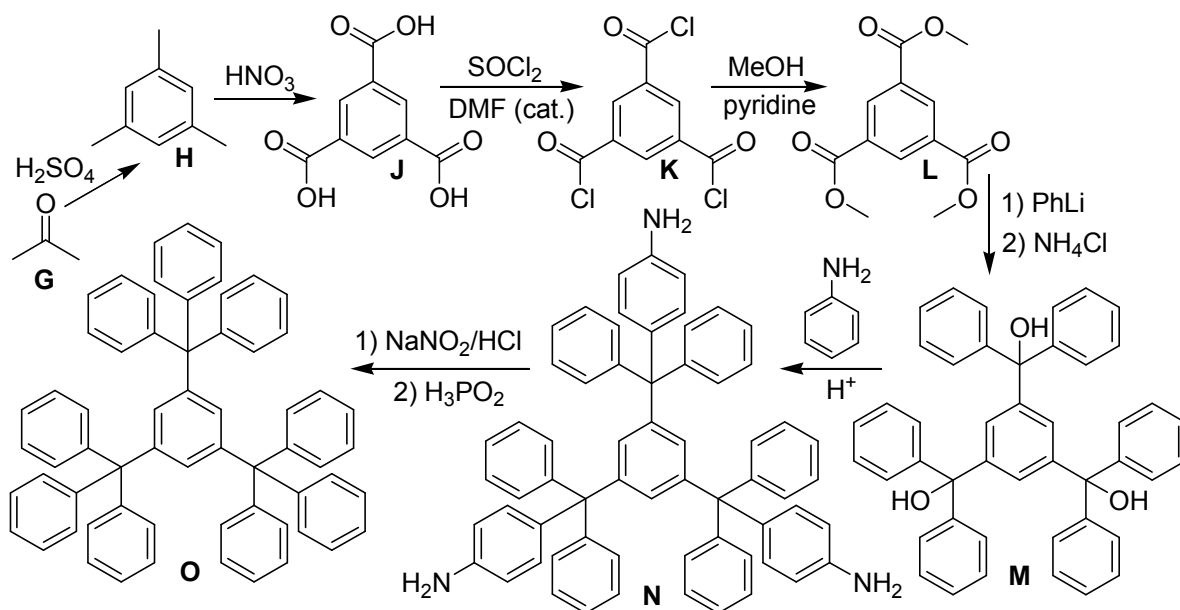
1. Acid-catalyzed reaction of ketones with alcohols produced ketals. Formation of acetal is confirmed by content of carbon in **A**. Reaction of acetophenone with amine yields imine; its interaction with Grignard reagent produces tertiary alcohol. Acid-catalyzed reaction of

methyl benzoate with ethanol is reesterification reaction giving rise to ethyl benzoate. Reaction of ester with amine affords amide; reaction with Grignard reagent furnishes tertiary alcohol because the initially formed ketone is more reactive against Grignard reagents than started ester (6 structural formulae, 0.5 point for each; 3 points in total).

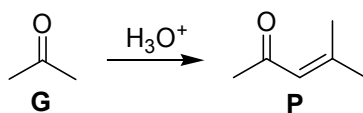


2. Iodide ion fails to form stable product with any listed substrates. In the presence of acids cyanide ion gives addition products – cyanohydrins ( $RR'C(OH)CN$ ) – when reacts with aldehydes and ketones however it fails substitute alkoxide fragment in ester.  $NaHSO_3$  reacts with  $PhCHO$  only (3 nucleophiles; 1 point for each right answer; 0.5 point if two answers for nucleophile are right, one answer is wrong; 0 point in other cases; maximum – 3 points).

3. From content of elements we can determine that simplest formula of **G** is  $(C_3H_6O)_n$ . Accounting for equivalence of all hydrogen atoms in **G**, we can conclude that it is acetone. Formula of **H** is  $(C_3H_4)_n$ . Accounting for  $^1H$  NMR data for **H** and its formation from **G** under treatment with conc.  $H_2SO_4$ , we can conclude that **H** is 1,3,5-trimethylbenzene (mesitylene). According to problem condition, reaction of **H** with nitric acid is oxidation. For methylbenzenes, oxidation products are alcohols, aldehydes, or acids. From carbon content in **J** we can determine that  $M_J = 210$ . It corresponds to tricarboxylic acid. Reaction of acid with  $SOCl_2$  produces acyl chloride reaction of which with methanol yields methyl ester **L**. Analysis of  $^1H$  NMR data allows for concluding that **L** is symmetrical trimethyl ester. It reacts with phenyllithium affording tribasic tertiary alcohol. Under acidic conditions this alcohol is converted into cation which alkylates aniline. From very high carbon content in **O** it is understandable that it is hydrocarbon. Therefore, alkylation proceeds at carbon atom of aniline (in *para*-position to aminogroup) followed by removal of aminogroup by diazotization and diazonium salt reduction (8 structural formulae, 1 point for each; 8 points in total).



4. When acetone is treated with diluted acid, aldol condensation produces 4-methylpent-3-en-2-one (P).



## SECTION V. ANALYTICAL CHEMISTRY

### Problem 1 (author L.I. Malinina)

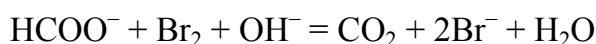
1. Let us determine the molar weight of X: its molality is  $m = 16.15 / x$  (mol/kg) and  $\Delta T_m = imK = 0.50^\circ\text{C}$ ;  $i = 1$  because the substance does not dissociate. Consequently,  $x = 16.15 \cdot 1.86 / 0.50 = 60.1$  g/mol (1 point). If the substance consists of C, N, H and O only, it is urea  $(\text{NH}_2)_2\text{CO}$  (1 point, 2 points in total).

2. Titration 1 quantifies ammonium ion (from  $\text{NH}_4\text{HCOO}$ ):

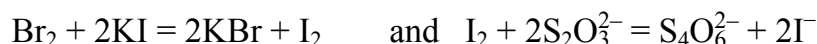


$c(\text{NH}_4^+) = c(\text{OH}^-)V(\text{OH}^-) / V_{\text{aliquot}} = 7.2 \cdot 0.1000 / 10 = 0.0720$  M, therefore, the concentration of ammonium formate in the sample is  $w = 0.0720 \cdot 1 \cdot 63 / 30 = 0.15 = 15\%$  (1.5 points)

Titration 2 quantifies formate ion (from  $\text{Ca}(\text{HCOO})_2$  and  $\text{NH}_4\text{HCOO}$ ):



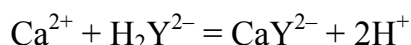
The excess of bromine reacts further as follows:



Consequently,  $c(\text{HCOO}^-) = (c(\text{Br}_2)V(\text{Br}_2) - c(\text{S}_2\text{O}_3^{2-})V(\text{S}_2\text{O}_3^{2-}) / 2) / V_{\text{aliquot}} = (30 \cdot 0.1000 - 27.2 \cdot 0.1000 / 2) / 10 = 0.1640$  M.

Since the concentration of formate from ammonium formate (see titration 1) is 0.0720 M, the concentration of calcium formate ion is  $(0.1640 - 0.0720) / 2 = 0.0460$  M, i.e. its weight fraction in the sample is 20% (1.5 points).

Titration 3 quantifies calcium (from  $\text{CaCl}_2$  and  $\text{Ca}(\text{HCOO})_2$ ).



$c(\text{Ca}^{2+}) = c(\text{EDTA})V(\text{EDTA}) / V_{\text{aliquot}} = 0.1000 \cdot 12.7 / 10 = 0.1270$  M. Calcium formate concentration is 0.0460 M, therefore, calcium chloride concentration is  $0.1270 - 0.0460 = 0.0810$  M, i.e. its weight fraction in the sample is 30% (1.5 points).

Titration 4 quantifies chloride ion (from  $\text{CaCl}_2$  and  $\text{NaCl}$ ):



Reaction with indicator is  $2\text{Ag}^+ + \text{Cr}_2\text{O}_7^{2-} = \text{Ag}_2\text{Cr}_2\text{O}_7\downarrow$  (orange precipitate)

$c(\text{Cl}^-) = c(\text{Ag}^+)V(\text{Ag}^+) / V_{\text{aliquot}} = 23.9 \cdot 0.1000 / 10 = 0.2390$  M. Calcium chloride concentration is 0.0810 M, sodium chloride concentration is  $0.2390 - 2 \cdot 0.0810 = 0.0770$  M and corresponds to its weight fraction of 15% in dry sample (1.5 points). The sample also contains 20% sand (0 points, 6 points in total).

3.  $\Delta T_m = iK_m = iK / M_{\text{salt}} / m_{\text{ice}}$ , consequently,  $m_{\text{ice}} = iK / M_{\text{salt}} / \Delta T$ . This equation yields  $m_{\text{ice}} = 6.4$  g for NaCl,  $m_{\text{ice}} = 5.0$  g for CaCl<sub>2</sub>, and  $m_{\text{ice}} = 5.9$  g for NH<sub>4</sub>HCOO. Therefore, sodium chloride has the greatest effect per weight unit (2 points).

4.  $\text{Ca}(\text{HCOO})_2 = \text{Ca}^{2+} + 2\text{HCOO}^-$ ;  $\text{HCOO}^- + \text{H}_2\text{O} = \text{HCOOH} + \text{OH}^-$  (1 point)

The isotonic coefficient is  $i = ([\text{Ca}^{2+}] + 2[\text{HCOO}^-]) / c(\text{Ca}(\text{HCOO})_2) = 3$ , or, if hydrolysis is taken into account,  $i_{\text{hydr}} = ([\text{Ca}^{2+}] + 2([\text{HCOO}^-] + [\text{HCOOH}] + [\text{OH}^-])) / c(\text{Ca}(\text{HCOO})_2) = 3 + [\text{OH}^-] / c(\text{Ca}(\text{HCOO})_2)$ , i.e.  $3 + [\text{OH}^-]$  for a 1 M salt solution (2 points).

Concentration of  $[\text{OH}^-]$  in a 2 M solution of  $\text{HCOO}^-$  can be found as follows:

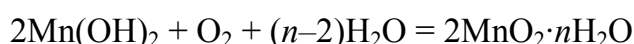
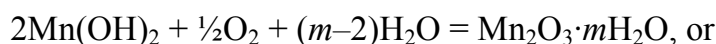
$$K_a = [\text{H}^+][\text{HCOO}^-] / [\text{HCOOH}] = \frac{K_w[\text{HCOO}^-]}{[\text{OH}^-][\text{HCOOH}]},$$

or  $K_w / K_a = [\text{HCOOH}][\text{OH}^-] / [\text{HCOO}^-]$ . According to the hydrolysis equation,  $[\text{HCOOH}] = [\text{OH}^-]$ , and the equilibrium concentration of formate is close to the total concentration, i.e. 2 M (1 point for the equation). Then:  $K_w / K_a = [\text{OH}^-]^2 / 2$  and  $[\text{OH}^-] = 1.06 \cdot 10^{-5}$ .

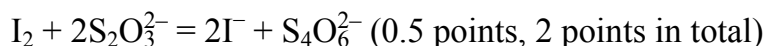
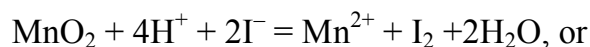
Consequently, hydrolysis contributes only  $1.06 \cdot 10^{-5} / 3 = 3.5 \cdot 10^{-4}\%$  (1 point for the equation and the result, 5 points in total), and it may be neglected in the calculation of the cryoscopic effect.

## Problem 2 (authors A.V. Bibin, M.K. Beklemishev)

1. A mixture of manganese(III and IV) hydroxides is formed during the stage of fixation of oxygen in alkaline medium (both Mn oxidation states are accepted) (0.5 points):



Iodometric titration in acidic medium:



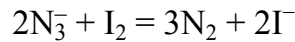
2. The normal concentration of oxygen is equal to  $8.43 \cdot 0.0423 / 500 = 7.13 \cdot 10^{-4}$  M (1 point). Given that the molar mass of an equivalent of oxygen is 8 g/mol, the concentration of O<sub>2</sub> in this sample is 5.71 mg/L (1 point, 2 points in total).

3. All three reagents reduce nitrite ions to molecular nitrogen (nitrogen oxides may also be formed, however you were not required to include those in your answer) (0.5 points for each reaction, 1.5 points in total):

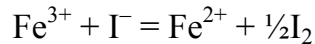




4. When added in excess, sodium aside reacts with iodide and this leads to a negative bias (0.5 point for correct bias sign, 2 points for reaction, a total of 2.5 points):

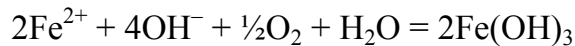


5. a) Fe(III) ions in alkaline medium form  $\text{Fe}(\text{OH})_3$  (it should be noted that  $\text{Mn}(\text{OH})_2$  is not oxidized by Fe(III) because the solution is alkalized before the addition of manganese sulphate). Fe(III) in acidic medium oxidize iodide ions, which yields iodine (0.5 points):



According to the conditions of this problem, this reaction is slow; therefore the amount of the yielded iodine may be lower than the equivalent amount. Because this reaction is slow (i.e. incomplete), the result was overestimated only by 1.3 mg/L, whilst the amount of oxygen equivalent to 30 mg/L of Fe(III) is 4.3 mg/L.

b) Fe(II) compounds will react with oxygen at the first stage of Winkler test (fixation of oxygen) and act as “competitors” for manganese(II) (1 point):



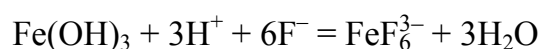
Fe(III) will further react with iodide and “regenerate” iodine ( $\text{Fe}^{3+} + \text{I}^- = \text{Fe}^{2+} + \frac{1}{2}\text{I}_2$ ). According to the condition of the problem, this reaction is slow, thus incomplete, so the result will be underestimated (0.5 points).

c) The sample contained 9 mg/L of  $\text{O}_2$ , or  $5.63 \cdot 10^{-4}$  M, which means that it could have reacted with  $2.25 \cdot 10^{-3}$  M, or 125 mg/L, of Fe(II), i.e. all Fe(II) was transformed into Fe(III) at the first stage (oxygen fixation). This means that  $6.71 \cdot 10^{-5}$  M (2.15 mg/L) of  $\text{O}_2$  was consumed for oxidizing Fe(II) (1.5 points). This, in turn, means that the concentration of Fe(III) became 30 mg/L. According to the conditions of 5a, the results in this case would be positively biased by 1.3 mg/L (1.5 points), i.e. the final result was  $9.0 - 2.2 + 1.3 = 8.1$  mg/L (0.5 points, 3.5 points in total).

d) Fluoride ions (they are in excess) will bind Fe(III), but will not affect Fe(II):



Fe(II) in this problem is completely transformed into  $\text{Fe}(\text{OH})_3$  (negative bias, see previous calculation):  $\text{Fe}^{2+} + \text{OH}^- + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} = \text{Fe}(\text{OH})_3 \downarrow$ , which also forms  $\text{FeF}_6^{3-}$  when acidified. To sum up, during the reaction with iodide only  $\text{FeF}_6^{3-}$  will be present in the solution (equivalent of 30 mg/L Fe(III)):



Part of iron hydroxide could have reacted with iodide before forming a complex with fluoride ions; however, the problem states that this reaction is slower. Answer: the result will be underestimated (1 point for at least two of the three reactions listed above, 0.5 points for a correct answer – only applies if reactions are also written).

### Problem 3 (author A.V. Garmash)

1. Cathode (0.5 points);  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$  or  $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$  (at the cathode, 0.5 points);



2.  $c(\text{H}_2\text{SO}_4) = m(\text{H}_2\text{SO}_4) / V(\text{H}_2\text{SO}_4) = n(\text{H}_2\text{SO}_4)M(\text{H}_2\text{SO}_4) / V(\text{H}_2\text{SO}_4)$

$$n(\text{H}_2\text{SO}_4) = \frac{1}{2} n(\text{e}^-) = \frac{1}{2} Q / F \quad Q = 4.50 \cdot 10^{-3} \cdot (8 \cdot 60 + 48.6) = 2.379 \text{ C}$$

$$n(\text{H}_2\text{SO}_4) = \frac{1}{2} \cdot 2.379 / 96485 = 1.232 \cdot 10^{-5} \text{ mol}$$

$$c(\text{H}_2\text{SO}_4) = 1.232 \cdot 10^{-5} \cdot 98.079 / 0.00100 = 1.21 \text{ g/L (2 points).}$$

3. At pH 8.5 the excessive  $\text{OH}^-$  concentration is equal to  $10^{8.5-14} = 3.2 \cdot 10^{-6} \text{ M}$  (0.5 points). The initial  $\text{H}^+$  concentration in the analyzed solution is  $1.232 \cdot 10^{-5} \cdot 2 / 0.026$  (solution total volume in L) =  $9.5 \cdot 10^{-4} \text{ M}$ . The relative error:  $3.2 \cdot 10^{-6} / 9.5 \cdot 10^{-4} = 0.0034$  (+0.34%) (1 point, 1.5 points in total).

4. a) Lower (0.5 points);  $E < E^0 + (0.059/2)\lg[\text{Ni}^{2+}] = -0.228 - 0.059 \cdot 3 / 2 = -0.317 \text{ V}$  (1 point for the numerical value, 1.5 points in total).

b) Side reaction:  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$  (or  $2\text{H}_2\text{O} + 2\text{e}^- = \text{H}_2 + 2\text{OH}^-$ ) (1 point).

5. For the reaction  $\text{Ni}^{2+} + 2\text{e}^- = \text{Ni}$ , 100% current efficiency will be observed until the reaction  $2\text{H}^+ + 2\text{e}^- = \text{H}_2$  begins, i.e. until the equilibrium potentials become equal:

$$E^0(\text{Ni}^{2+}/\text{Ni}) + (0.059/2)\lg[\text{Ni}^{2+}] = E^0(\text{H}^+/\text{H}_2) + (0.059/2)\lg[\text{H}^+]^2 \text{ (2 points), or}$$

$$-0.228 + (0.059/2)\lg[\text{Ni}^{2+}] = 0 - 0.059 \cdot 2 \cdot 6.0/2.$$

Therefore, at pH 6.0 we have:

$$\lg[\text{Ni}^{2+}] = (-0.059 \cdot 6 + 0.228) \cdot 2/0.059 = -4.27; [\text{Ni}^{2+}] = 5.4 \cdot 10^{-5} \text{ M (1 point, 3 points in total).}$$

$5.4 \cdot 10^{-5} \text{ M}$  of nickel remains in the solution.

6. The prerequisite of 100% current efficiency is the same:

$$E^0(\text{Ni}^{2+}/\text{Ni}) + (0.059/2)\lg[\text{Ni}^{2+}] = E^0(\text{H}^+/\text{H}_2) + (0.059/2)\lg[\text{H}^+]^2 \text{ (1 point)}$$

$$[\text{Ni}^{2+}] = c(\text{Ni}) / (\beta_6[\text{NH}_3]^6) = 1 \cdot 10^{-6} / (2 \cdot 10^8 \cdot 2^6) = 7.8 \cdot 10^{-17} \text{ M}$$

$$-0.228 + (0.059/2)\lg 7.8 \cdot 10^{-17} = 0 - 0.059\text{pH}$$

Therefore pH > 11.9 (0.5 points for "higher", 1.5 points for the numerical value; 3 points in total).