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|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

## SECTION I. PHYSICAL CHEMISTRY

### Problem 1 (author Kozlov M.I.)

In case the participant provides a correct answer but uses units of measurements different from those requested in the task, the participant gets the penalty equal to the quarter of the points awarded for the answer.

1. The energy of the rotational-vibrational level in the “Harmonic oscillator – rigid rotor” approximation is:

$$E_{\text{vib}} = \omega_e \left( n + \frac{1}{2} \right) + B_e J(J + 1).$$

Thus, the transition energies are:

$$\Delta E(0, 0 \rightarrow 1, 1) = E_{11} - E_{00} = 1.5\omega_e + 2B_e - 0.5\omega_e - 0B_e = \omega_e + 2B_e = 4180.23,$$

$$\Delta E(0, 1 \rightarrow 1, 0) = E_{10} - E_{01} = 1.5\omega_e + 0B_e - 0.5\omega_e - 2B_e = \omega_e - 2B_e = 4096.41.$$

Solving the system of the equations we obtain  $\omega_e = 4138.32 \text{ cm}^{-1}$ ,  $B_e = 20.955 \text{ cm}^{-1}$ .

(0.25 points for each equation, 0.5 points for each value, **1.5 points** in total).

2.  $\omega_e = h\nu$  and  $\omega_e(J) = 100hc\omega_e(\text{cm}^{-1})$ , thus  $\nu = 100c\omega_e(\text{cm}^{-1}) = 100 \cdot 299792458 \cdot 4138.32 = 1.241 \cdot 10^{14} \text{ Hz}$ . Rearranging the formula for the rotational constant, we obtain:  $r_e = h^2/(8\pi^2\mu B_e)^{1/2}$ . Substituting  $B_e(J) = 100hcB_e(\text{cm}^{-1})$  and  $\mu(\text{HF}) = m_{\text{H}}m_{\text{F}}/(m_{\text{H}} + m_{\text{F}}) \cdot (0.001/N_{\text{A}})$  in this equation, we obtain:

$$r_e = \sqrt{\frac{6.626 \cdot 10^{-34} \cdot (1.0078 + 18.9984) \cdot 6.022 \cdot 10^{23}}{8\pi^2 \cdot 0.1 \cdot 1.0078 \cdot 18.9984 \cdot 2.998 \cdot 10^5 \cdot 20.955}} = 9.168 \cdot 10^{-11} \text{ m} = 0.9168 \text{ \AA}.$$

(0.75 points for the frequency, 1.5 points for the bond length, **2.25 points** in total).

3. Equating the energies of  $n^{\text{th}}$  and  $(n + 1)^{\text{th}}$  levels, we derive:

$$\omega_e(n + \frac{1}{2}) - \omega_e x_e(n + \frac{1}{2})^2 = \omega_e(n + 1 + \frac{1}{2}) - \omega_e x_e(n + 1 + \frac{1}{2})^2,$$

which leads to:  $n_{\text{max}} = \omega_e/2\omega_e x_e - 1$ .

(**2 points** in total).

4. The energy of dissociation equals the energy of the  $n_{\text{max}}$  vibrational level:

$$E = \omega_e(n_{\text{max}} + \frac{1}{2}) - \omega_e x_e(n_{\text{max}} + \frac{1}{2})^2 = (\omega_e^2 - \omega_e x_e^2)/4\omega_e x_e.$$

(penalty of 1 point if the expression is not simplified or errors made, **2 points** in total).

5. a) As  $n$  increases, the kinetic energy of rotation of the molecule increases.

True

False

The vibrational and rotational energies of the molecule are independent.

b) As  $n$  increases, the average bond length in the molecule changes.

True

False

The potential energy of the anharmonic oscillator is asymmetric, thus the corresponding wave function asymmetric. This leads to the difference of the average coordinate for the wave function and equilibrium bond length. The rotational constant depends on the average bond length; hence, the constant also changes.

c) Due to the repulsion of the atoms, the molecule is rather stretched than compressed during oscillations.

True

False

Repulsion of the atoms is the reason of the asymmetry of the anharmonic potential mentioned above. As the internuclear distance tends to zero, the energy of the molecule tends to infinity, while the distance approaches to infinity energy equals to the dissociation energy. Thus, molecule stretching is energetically preferable than compression.

|                                                    |           |
|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

d) Due to the Heisenberg uncertainty principle, the bond length permanently changes.

True

False

The Heisenberg uncertainty principle indeed states that coordinates of the atoms always vary and, consequently, the bond length changes. But this principle does not say anything about the average value, so it does not predict the average bond length and the value of the rotational constant.

(0.25 points for each correct answer, penalty of 0.25 points for each incorrect answer, no negative total results, **1 point** in total).

6. The energy of the rotational-vibrational level with an account for anharmonicity is:

$$E_{nJ} = \omega_e(n + 1/2) - \omega_e x_e(n + 1/2)^2 + [B_e - \alpha_e(n + 1/2)]J(J + 1).$$

The energies of the states of interest are:

$$\begin{aligned} E_{00} &= \omega_e/2 - \omega_e x_e/4, \\ E_{01} &= \omega_e/2 - \omega_e x_e/4 + 2B_e - \alpha_e, \\ E_{02} &= \omega_e/2 - \omega_e x_e/4 + 6B_e - 3\alpha_e, \\ E_{10} &= 3\omega_e/2 - 9\omega_e x_e/4, \\ E_{11} &= 3\omega_e/2 - 9\omega_e x_e/4 + 2B_e - 3\alpha_e, \\ E_{12} &= 3\omega_e/2 - 9\omega_e x_e/4 + 6B_e - 9\alpha_e, \\ E_{20} &= 5\omega_e/2 - 25\omega_e x_e/4, \\ E_{21} &= 5\omega_e/2 - 25\omega_e x_e/4 + 2B_e - 5\alpha_e, \\ E_{22} &= 5\omega_e/2 - 25\omega_e x_e/4 + 6B_e - 15\alpha_e. \end{aligned}$$

Thus, the transition energies (cm<sup>-1</sup>) equal:

$$\begin{aligned} \Delta E(0, 0 \rightarrow 1, 1) &= \omega_e - 2\omega_e x_e + 2B_e - 3\alpha_e = 2759.77, \\ \Delta E(0, 1 \rightarrow 1, 2) &= \omega_e - 2\omega_e x_e + 4B_e - 8\alpha_e = 2785.97, \\ \Delta E(1, 0 \rightarrow 2, 1) &= \omega_e - 4\omega_e x_e + 2B_e - 5\alpha_e = 2632.66, \\ \Delta E(1, 1 \rightarrow 2, 2) &= \omega_e - 4\omega_e x_e + 4B_e - 12\alpha_e = 2657.79. \end{aligned}$$

Solving the system of the equations, we obtain:

$$\begin{aligned} \omega_e &= 2858.54 \text{ cm}^{-1}, \\ \omega_e x_e &= 63.02 \text{ cm}^{-1}, \\ B_e &= 14.4375 \text{ cm}^{-1}, \\ \alpha_e &= 0.535 \text{ cm}^{-1}. \end{aligned}$$

(0.5 points for each equation and each value, **4 points** in total).

7. The dissociation energy  $E = (\omega_e^2 - \omega_e x_e^2)/4\omega_e x_e = 32399.55 \text{ cm}^{-1}$ , the approximate value of the dissociation energy  $E = \omega_e^2/4\omega_e x_e = 32415.31 \text{ cm}^{-1}$ .

(**0.75 points** in total)

8. Similarly to i. 2, the bond length can be calculated using the rotational constant:

$$r_e = \sqrt{\frac{6.626 \cdot 10^{-34} \cdot (1.0078 + 12.0000) \cdot 6.022 \cdot 10^{23}}{8\pi^2 \cdot 0.1 \cdot 1.0078 \cdot 12.0000 \cdot 2.998 \cdot 10^5 \cdot 14.4375}} = 1.1207 \cdot 10^{-10} \text{ m} = 1.1207 \text{ \AA}.$$

(**1.5 points** in total)

## Problem 2 (authors Gulevich D.G, Borschevsky A.Ya.)

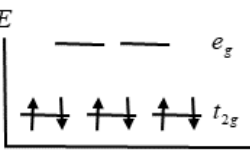
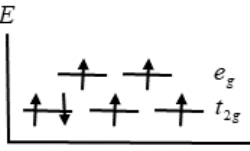
1. The orbital quantum number  $l$  for  $d$ -states equals 2. The quantum number of the projection of angular momentum runs thorough the values of 2, 1, 0, -1, -2. In the field of spherical symmetry specific to an isolated atom or ion, the energy does not depend on the magnitude of the projection, therefore the level is five-fold ( $g = 5$ ) degenerate. (**2 points** in total)

|                                                    |           |
|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

2. Branches of equivalent orbitals  $d_{z^2}$  and  $d_{x^2-y^2}$  (and the density of negative charge on them) are elongated towards the negative charges of the ligands. In the case of  $H_2O$  ligands, the charge is partially localized on oxygen atoms. On the contrary, the  $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$  orbitals are directed at the angle of  $45^\circ$  to the previous ones and are thus located further from the charges of the ligands. As a result, the repulsive energy in the former case is higher than in the latter one, and the doubly degenerate levels have a higher energy than the triply degenerate levels. Thus, a five-fold degenerate level of an isolated atom is split into two levels with a degeneracy factor of 3 (designation  $t_{2g}$ ) for the lower one and 2 (designation  $e_g$ ) for the upper one (see the table).

(2 points for the scheme, 1.5 points for term symbols, **3.5 points** in total).

3. See the correct answers in the table:

| Configuration        | LS                                                                                | HS                                                                                  |
|----------------------|-----------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
| $Fe^{2+}: d^6$       |  |  |
| Total spin (S):      | 0                                                                                 | 2                                                                                   |
| Magnetic properties: | diamagnetic                                                                       | paramagnetic                                                                        |

(1 point for the scheme, 0.25 points for spin, 0.25 points for the type of magnetism, **1.5 points** in total)

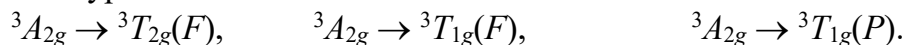
4. The value of  $P$  is positive, that is, the electron pairing requires energy.  $E_{LS} = -12/5\Delta_o + 3P$ ,  $E_{HS} = -2/5\Delta_o + P$ . Equating the expressions, we obtain the condition  $\Delta_o = P$ .

(**1 point** in total)

5. For  $[Fe(H_2O)_6]^{2+}$   $\Delta_o < P$ , and for  $[Fe(CN)_6]^{4-}$   $\Delta_o > P$ , therefore the former complex is high-spin, and the latter one is low-spin.

(**0.5 points** in total)

6. Optical transitions are allowed only between states of the same multiplicity. There are three transitions of such type:



Let's set the scale on the axes and measure the intervals between energy levels corresponding to  $\Delta_o = 10800 \text{ cm}^{-1}$ . The approximate frequencies ( $\text{cm}^{-1}$ ) are: 10750, 17600, 30400.

(1.5 points for the number of bands, 0.5 points for each frequency, **3 points** in total).

7. The number of unit cells in  $1 \text{ cm}^3$  of the crystal is  $(1/a)^3$ . Using the pre-calculated molecular mass of the salt ( $M = 392 \text{ a.m.u.}$ ), we find:

$$\rho = \frac{ZM}{a^3} = \frac{4 \cdot 392 \cdot 1.66 \cdot 10^{-24}}{(1.2318 \cdot 10^{-7})^3} = 1.393 \text{ g/cm}^3.$$

The specific susceptibility is calculated using formula (2):

$$\chi_s = \frac{9.5 \cdot 10^{-3}}{298.15 + 1} = 3.18 \cdot 10^{-5} \text{ cm}^3/\text{g}.$$

The magnetic force acting on the sample is equivalent to an increase in its weight by  $\Delta m \cdot g$ .

Writing the equation according to formula (1) and solving it with respect to  $\chi_v$ , we obtain:

$$\chi_v = \frac{2\Delta m \cdot g}{\sigma H^2} = \frac{2 \cdot 0.868 \cdot 981}{1.54 \cdot 10^{-7} \cdot 5000^2} = 4.423 \cdot 10^{-5}.$$

|                                                    |           |
|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

The increase in the weight is because the sample is paramagnetic and therefore drawn into the region of a stronger field.

(1 point for density, 0.25 points for  $\chi_S$ , 0.5 points for  $\chi_V$ , **1.75 points** in total)

8. The molar susceptibility  $\chi_M = M \cdot \chi_S = 392 \cdot 3.176 \cdot 10^{-5} = 0.01245 \text{ cm}^3/\text{mol}$ . Substituting the numerical values of the fundamental constants into formula (3), we obtain

$$\mu_{\text{eff}} = 2.84 \cdot \sqrt{\chi_M \cdot T} = 2.84 \cdot \sqrt{0.01245 \cdot 298.15} = 5.47 \mu_B.$$

(0.25 points for  $\chi_M$ , 0.5 points for  $\mu_{\text{eff}}$ , **0.75 points** in total)

9. Relationship (4) is the quadratic equation with respect to the number  $n$ :  $n^2 + 2n - \mu_{\text{eff}}^2 = 0$ . Solving it, we find:

$$n = \sqrt{\mu_{\text{eff}}^2 + 1} - 1 = \sqrt{5.47^2 + 1} - 1 = 4.56.$$

The obtained  $\mu_{\text{eff}}$  value may be slightly overestimated, but in a low-spin complex, unpaired electrons should be completely absent. Therefore, Mohr's salt is a high-spin complex.

(0.25 points for  $n$ , 0.75 points for the answer, **1 point** in total).

### Problem 3 (author Shwartzman V.E.)

1. Homolytic cleavage of the H–H bond:  $\text{H:H} \rightarrow 2\text{H}\cdot$  (0.5 points)

Heterolytic cleavage of the H–H bond:  $\text{H:H} \rightarrow \text{H}\cdot + \text{H}^+$  (0.5 points)

(**1 point** in total)

2. To derive the formulas for calculation of  $\Delta_{\text{hom}}H^\circ$  and  $\Delta_{\text{het}}H^\circ$ , we use the enthalpy of hydration ( $\Delta_{\text{hyd}}H^\circ$ ) and the standard enthalpy of formation ( $\Delta_fH^\circ$ ):

| Hydration, $\Delta_{\text{hyd}}H^\circ$ , kJ/mol          |       | Formation, $\Delta_fH^\circ$ , kJ/mol         |      |
|-----------------------------------------------------------|-------|-----------------------------------------------|------|
| (1) $\text{H}^+ + \text{aq} = \text{H}^+(\text{aq})$      | –1088 | (5) $1/2\text{H}_2 = \text{H}$                | 218  |
| (2) $\text{H}\cdot + \text{aq} = \text{H}^-(\text{aq})$   | –452  | (6) $1/2\text{H}_2 + \text{e}^- = \text{H}^-$ | 140  |
| (3) $\text{H}_2\cdot + \text{aq} = \text{H}_2(\text{aq})$ | –9    | (7) $1/2\text{H}_2 - \text{e}^- = \text{H}^+$ | 1536 |
| (4) $\text{H}\cdot + \text{aq} = \text{H}(\text{aq})$     | –13   |                                               |      |

Calculation of the enthalpy of homolytic cleavage of the H–H bond, which occurs according to the scheme  $\text{H}_2(\text{aq}) = 2\text{H}(\text{aq})$ :  $\Delta_{\text{hom}}H^\circ = 2\Delta H^\circ_4 - \Delta H^\circ_3 + 2\Delta H^\circ_5 = 2(-13 + 218) + 9 = 419 \text{ kJ/mol}$  (1 point).

Calculation of the enthalpy of heterolytic cleavage of the H–H bond, which occurs according to the scheme  $\text{H}_2(\text{aq}) = \text{H}^+(\text{aq}) + \text{H}^-(\text{aq})$ :  $\Delta_{\text{het}}H^\circ = \Delta H^\circ_1 + \Delta H^\circ_2 - \Delta H^\circ_3 + \Delta H^\circ_6 + \Delta H^\circ_7 = -1088 - 452 + 9 + 140 + 1536 = 145 \text{ kJ/mol}$  (1 point) (**2 points** in total).

3. Reaction rate  $r = k_2[(\text{Cu}^+\text{H})_2][\text{Cu}^{2+}]^2$ . Based on the stationary approximation,  $d[(\text{Cu}^+\text{H})_2]/d\tau = 0$ , the rate of  $(\text{Cu}^+\text{H})_2$  dimer formation is equal to the rate of its decomposition  $k_1[\text{Cu}^+]^2[\text{H}_2] = k_{-1}[(\text{Cu}^+\text{H})_2] + k_2[(\text{Cu}^+\text{H})_2][\text{Cu}^{2+}]^2$ , the concentration of the dimer is  $[(\text{Cu}^+\text{H})_2] = k_1[\text{Cu}^+]^2[\text{H}_2]/(k_{-1} + k_2[\text{Cu}^{2+}]^2)$  and the reaction rate equation  $r = k_1k_2[\text{Cu}^+]^2[\text{H}_2][\text{Cu}^{2+}]^2/(k_{-1} + k_2[\text{Cu}^{2+}]^2)$  (1.5 points). With an account for the rate-limiting step,  $k_2[\text{Cu}^{2+}]^2 > k_{-1}$ , we obtain  $r = k[\text{Cu}^+]^2[\text{H}_2]$  (0.5 points) (**2 points** in total).

4. The reaction rate  $r = k_{\text{ox}}[(\text{Cr(VI)})][\text{Cu}^+]^2$ . Stationary approximation for  $d[\text{Cu}^+]/d\tau = 0$ ; the rate of  $\text{Cu}^+$  formation is equal to the rate of its decomposition  $k_4[\text{CuH}^+][\text{Cu}^{2+}] = k_{\text{ox}}[(\text{Cr(VI)})][\text{Cu}^+]^2$  and  $r = k_4[\text{CuH}^+][\text{Cu}^{2+}]$ . Stationary approximation for  $\text{CuH}^+$ :  $d[\text{CuH}^+]/d\tau = 0$ ; the rate of  $\text{CuH}^+$  formation is equal to the rate of its decomposition:  $k_3[\text{Cu}^{2+}][\text{H}_2] = k_{-3}[\text{CuH}^+][\text{H}^+] + k_4[\text{CuH}^+][\text{Cu}^{2+}]$ ; the concentration of the  $\text{CuH}^+$  cation is

|                                                    |           |
|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

equal to  $[\text{CuH}^+] = k_3[\text{Cu}^{2+}][\text{H}_2]/(k_{-3}[\text{H}^+] + k_4[\text{Cu}^{2+}])$ ; after substituting the concentration of the  $[\text{CuH}^+]$  cation into the rate equation, it becomes equal to  $r = k_3k_4[\text{Cu}^{2+}]^2[\text{H}_2]/(k_{-3}[\text{H}^+] + k_4[\text{Cu}^{2+}])$  (1.5 points). If  $k_4[\text{Cu}^{2+}] > k_{-3}[\text{H}^+]$ , then  $r = k_3[\text{Cu}^{2+}][\text{H}_2]$  with the second reaction order (0.5 points). If  $k_{-3}[\text{H}^+] > k_4[\text{Cu}^{2+}]$ , then  $r = k_3k_4[\text{Cu}^{2+}]^2[\text{H}_2]/k_{-3}[\text{H}^+]$  with the third reaction order (0.5 points) (total **2.5 points**)

5. The first term of the kinetic equation  $r = k[\text{Ag}^+]^2[\text{H}_2]$  is the same as the Calvin's rate equation at homolytic cleavage of the H–H bond and the second term as the Halpern's and Peters's rate equation for heterolytic cleavage of the H–H bond. Therefore, the mechanism is two-flow. The flows are:

with homolytic cleavage of the H–H bond:

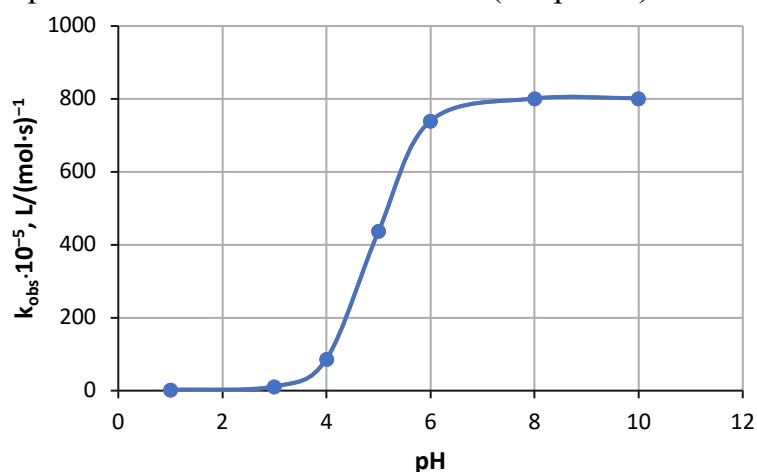
$2\text{Ag}^+ + \text{H}_2 \rightleftharpoons (\text{Ag}^+\cdot\text{H})_2$  ( $k_7$ ;  $k_{-7}$ ) (0.5 points);  $(\text{Ag}^+\cdot\text{H})_2 \rightarrow 2\text{Ag} + 2\text{H}^+$  ( $k_8$ ) (derivation as in i. 3 gives  $r_1 = k[\text{Ag}^+]^2[\text{H}_2]$ ) (0.5 points);

with heterolytic cleavage of the H–H bond:

$\text{Ag}^+ + \text{H}_2 \rightleftharpoons \text{AgH} + \text{H}^+$  ( $k_5$ ;  $k_{-5}$ ) (0.5 points);  $\text{AgH} + \text{Ag}^+ \rightarrow \text{Ag}_2\text{H}^+$  ( $k_6$ );

$\text{Ag}_2\text{H}^+ + \text{Cr(VI) substrate} \rightarrow \text{Cr(III) products} + 2\text{Ag}^+$  ( $k_{\text{ox}}$ , fast) (derivation as in i. 4 gives  $r_2 = k_5[\text{Ag}^+]^2[\text{H}_2]/([\text{Ag}^+] + k_{-5}/k_6[\text{H}^+])$ ). The total reaction rate  $r = r_1 + r_2$ . Then  $r = k[\text{Ag}^+]^2[\text{H}_2] + k_5[\text{Ag}^+]^2[\text{H}_2]/([\text{Ag}^+] + k_{-5}/k_6[\text{H}^+])$  (0.5 points). The observed rate constant  $k_{\text{obs}} = k + k_5/([\text{Ag}^+] + k_{-5}/k_6[\text{H}^+])$  (0.5 points) (**2.5 points** in total).

6. The S-shape of the plot is associated with two flows (0.5 points).



At high  $[\text{H}^+]$ ,  $r_1 > r_2$  ( $\text{pH} < 4$ ); at low  $[\text{H}^+]$ ,  $r_2 > r_1$  ( $\text{pH} > 6$ ) – the areas where the rate is almost independent of pH (1 point). In the interval of  $\text{pH} = 4$  to 6,  $r_1 \approx r_2$ , so the rate increases greatly (**1.5 points** in total).

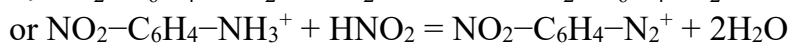
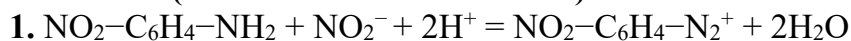
7. In the equation for the rate constant  $k_{\text{obs}} = k + k_5/([\text{Ag}^+] + k_{-5}/k_6[\text{H}^+])$ , denoting  $k_{-5}/k_6 = a$ , we get  $k_{\text{obs}} - k = k_5/([\text{Ag}^+] + a[\text{H}^+])$ . The linear dependence in  $1/(k_{\text{obs}} - k) = f(\text{pH})$  coordinates follows from the equation:  $1/(k_{\text{obs}} - k) = [\text{Ag}^+]/k_5 + a[\text{H}^+]/k_5$  (0.5 points). The intercept is equal to  $[\text{Ag}^+]/k_5$  (0.5 points) and the slope is equal to  $a/k_5$  (0.5 points) (**1.5 points** in total).

8. At  $273 + 27 = 300$  K, the value of constant  $k = 6.8 \cdot 10^7 e^{-14666/8.314 \cdot 300} = 1.90 \cdot 10^5$ . To find  $k_5$  and  $a = k_{-5}/k_6$ , we solve the system of equations  $87.01 \cdot 10^5 = 1.90 \cdot 10^5 + k_5/(1 + 10^{-4}a)$  and  $436.7 \cdot 10^5 = 1.90 \cdot 10^5 + k_5/(1 + 10^{-5}a)$ . As a result,  $a = k_{-5}/k_6 = 8.40 \cdot 10^4$  (1 point) and  $k_5 = 8.00 \cdot 10^7$  (1 point) (**2 points** in total).

|                                                    |           |
|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

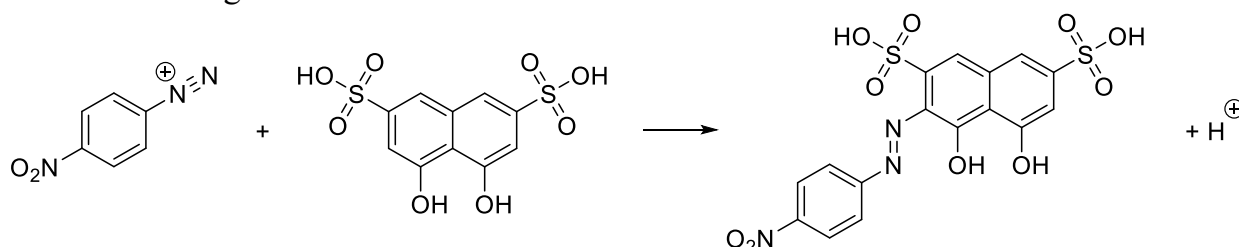
## SECTION II. ANALYTICAL CHEMISTRY

### Problem 1 (author: Beklemishev M.K.)



(1 point in total)

2. Azo coupling reactions often occurs in an alkaline environment, but to create a chemical dosimeter the reagents that interact in an acidic environment were selected:



(1 point in total)

3. a)  $v_1 = k_1[\text{NO}_2]^2_{\text{r}}$

b)  $v_2 = k_2[\text{NO}_2^-]_{\text{(aq)}}[4\text{-NA}]_{\text{(aq)}}$

c)  $v_3 = k_3[\text{R-N}_2^+][\text{Chr}]$

(1 point each, 3 points in total)

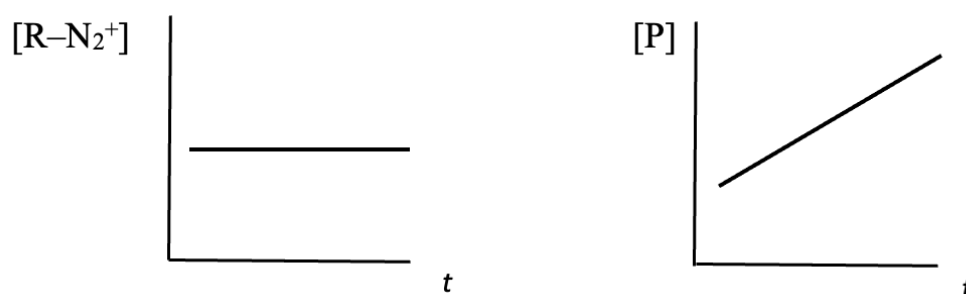
4. a) For the reaction of nitrite formation (1):  $v_1 = k_1[\text{NO}_2]^2_{\text{(g)}} = \frac{10^5 \text{ L} \cdot (0.005 \text{ g})^2 \text{ m}^6 \text{ mol}^2}{\text{mol} \cdot \text{s} \cdot \text{m}^6 (1000 \text{ L})^2 (46 \text{ g})^2} = 1.2 \cdot 10^{-9} \text{ mol}/(\text{L} \cdot \text{s})$  (46 g/mol is the molar weight of  $\text{NO}_2$ ). Since the volume of air in the production facilities is large, the initial concentration of nitrogen dioxide does not change over time due to reactions with the assay system, and the obtained reaction rate (1) will remain unchanged for a long time (1.5 points).

b) It is seen from i. a, that when  $v_1 = v_2$  the following equality must valid:  $k_1[\text{NO}_2]^2_{\text{(g)}} = k_2 \cdot k_1[\text{NO}_2]^2_{\text{(g)}} \cdot t \cdot [4\text{-NA}]$ ; so,  $t = 1 / (k_2 \cdot [4\text{-NA}]) = 1 / 1.0 \cdot 0.1 = 10 \text{ s}$  (1 point).

c) As follows from i. b,  $v_1 = v_2$  at high reaction times (much longer than 10 s, the stationary mode), while  $v_2 = v_3$ , i.e. the rates of the three reactions are the same and equal to that of nitrite formation. That is, the rate of formation of Acid Red  $v_3$  is equal to  $1.2 \cdot 10^{-9} \text{ mol}/(\text{L} \cdot \text{s})$  (1.5 points).

d) In the stationary mode, the diazonium salt  $\text{R-N}_2^+$  is formed relatively slowly and is quickly consumed, therefore its concentration is low and almost constant:  $v_1 = v_2 = v_3 = k_3[\text{R-N}_2^+][\text{Chr}] = \text{const}$ , and  $[\text{R-N}_2^+] = \text{const}$ .

Since the rate of formation of P  $v_3$  is constant,  $[\text{P}]$  increases linearly with time (2 points):



e) As found in i. (d), the rate of formation of Acid Red  $v_3$  equals  $1.2 \cdot 10^{-9} \text{ mol}/(\text{L} \cdot \text{s})$ , and its concentration at time  $t$  is  $1.2 \cdot 10^{-9} t \text{ mol/L}$ . If  $5 \cdot 10^{-11} \text{ mol}$  of Acid Red are contained

|                                                    |           |
|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

in a volume of 50  $\mu\text{L}$ , then its concentration is  $1 \cdot 10^{-6}$  M. Equating it to  $1.2 \cdot 10^{-9} \cdot t$ , we obtain:  
 $t = 1 \cdot 10^{-6} / 1.2 \cdot 10^{-9} = 833$  s (14 min) (2 points).

**(8 points in total)**

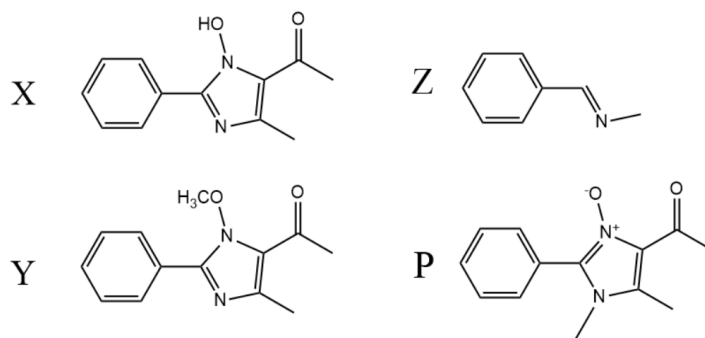
5. a) If one experiment is carried out, the probability of the positive answer is 90%. In the second experiment, the probability of the positive answer is also 90%, and the probability that both answers are positive (i.e., in this case, correct) is 81%. Thus, two experiments give a less reliable result than a single experiment, since the uncertainty increases (1 point).

b) Let three parallel experiments be carried out. The probability of getting all three positive results (1, 1, 1) is  $0.9 \cdot 0.9 \cdot 0.9 = 72.9\%$ . In the case of one negative result, two positive ones “outweigh”, and the overall result of the determination is decided as positive. These cases are: (1, 1, 0), (1, 0, 1), (0, 1, 1). The probability of getting one of these is  $0.9 \cdot 0.9 \cdot 0.1 = 0.081$ . Then the probability of any of these three variants is:  $3 \cdot 8.1\% = 24.3\%$ , which together with the probability of (1, 1, 1) gives 97.2%. So, three experiments are sufficient to ensure more than 95% accuracy of determination (1 point).

**(2 points in total)**

### Problem 2 (author Roslyakov S.N.)

1. According to the transition from **X** to **Y**, this is a methylation reaction, which means that the 1-hydroxyimidazole skeleton is built up at the step of the formation of **X**. So, the 1-hydroxy group is methylated at the next step. The reaction of the formation of **Z** is a simple condensation of methylamine with aldehyde. The skeleton similar to **X** (but isomeric to it) is formed at the next step. In the pathway towards **Y**, oxygen is methylated, and in that towards **P**, nitrogen is methylated, leaving oxygen of the 1-hydroxy group unmodified. Considering that **P** is a zwitter ion, **Y** is different from **P** in the location of the double bond in the cycle and in the heteroatom methylated. Structures of the unknown compounds:



(0.75 points for each of **X–P**, **3 points in total**)

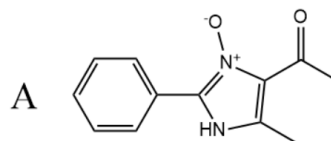
$$2. K_{AX} = \frac{[X]_{\text{aq}}}{[A]_{\text{aq}}} = 0.09 = \frac{\alpha_X}{1 - \alpha_X}$$

$$\alpha_X = 0.083 = 8.3\%$$

**(1 point in total)**

|                                                    |           |
|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

3.



(0.75 points in total)

4. Let us express  $[A]_0^{\text{aq}}$  via  $[A]$ , using the material balance on the amount of substance:

$$n_A^0 = n_A^{\text{aq}} + n_X^{\text{aq}} + n_A^{\text{org}} + n_X^{\text{org}} \quad (1 \text{ point})$$

$$[A]_0^{\text{aq}} V_0^{\text{aq}} = [A] V^{\text{aq}} + [X] V^{\text{aq}} + [A_1] V^{\text{org}} + [X_1] V^{\text{org}}$$

Since  $V_0^{\text{aq}} = V^{\text{aq}} = 0.5 V^{\text{org}}$ , so

$$[A]_0^{\text{aq}} = [A] + [X] + 2[A_1] + 2[X_1]$$

With an account for  $K_{AX} = \frac{[X]}{[A]} = 0.09$ ;  $K_{A_1X_1} = \frac{[X_1]}{[A_1]} = 0.09 \cdot 25 = 2.25$ ;

$K_{AA_1} = \frac{[A_1]}{[A]} = 1$  the following is obtained:

$$[A]_0^{\text{aq}} = [A] + [X] + 2[A_1] + 2[X_1] = [A] + K_{AX}[A] + 2K_{AA_1}[A] + 2K_{A_1X_1}K_{AA_1}[A] = 7.59[A] \quad (1 \text{ point})$$

By expressing  $[X_1]$  via  $[A]$ , we get the yield:

$$\eta_X^{\text{org}} = \frac{2[X_1]}{[A]_0^{\text{aq}}} = \frac{2K_{A_1X_1}K_{AA_1}[A]}{[A]_0^{\text{aq}}} = \frac{2 \cdot 2.25[A]}{7.59[A]} = 0.593 = 59.3\% \quad (1 \text{ point})$$

(3 points in total)

5. According to Hess's Law:

$$K_{XX_1} = \frac{[X_1]}{[X]} = \frac{K_{A_1X_1}K_{AA_1}[A]}{K_{AX}[A]} = 25 \quad (1 \text{ point})$$

$$\Delta_r G_{AX} = \Delta_r G_{AA_1} + \Delta_r G_{A_1A_2} + \Delta_r G_{A_2X_2} - \Delta_r G_{X_1X_2} - \Delta_r G_{XX_1}$$

$$-RT \ln K_{AX} = -RT \ln K_{AA_1} - RT \ln K_{A_1A_2} - RT \ln K_{A_2X_2} + RT \ln K_{X_1X_2} + RT \ln K_{XX_1}$$

$$\ln K_{AX} = \ln K_{AA_1} + \ln K_{A_1A_2} + \ln K_{A_2X_2} - \ln K_{X_1X_2} - \ln K_{XX_1}$$

$$K_{AX} = \frac{K_{AA_1}K_{A_1A_2}K_{A_2X_2}}{K_{XX_1}K_{X_1X_2}}$$

Note that the constants that “go clockwise” are found in the numerator, and those that “go counterclockwise” in the denominator. This is a remarkable feature of such circular equilibria.

$$K_{A_2X_2} = \frac{K_{AX}K_{X_1X_2}K_{XX_1}}{K_{AA_1}K_{A_1A_2}} = \frac{0.09 \cdot 16 \cdot 25}{1 \cdot 4} = 9 \quad (1 \text{ point})$$

$K_{A_1X_1} = 0.09 \cdot 25 = 2.25$  (by convention) (1 point) (3 points in total)

6.  $[A]_0^{\text{aq}} V_0^{\text{aq}} = [A] V^{\text{aq}} + [X] V^{\text{aq}} + [A_1] V_1^{\text{org}} + [X_1] V_1^{\text{org}} + [A_2] V_2^{\text{org}} + [X_2] V_2^{\text{org}}$

Since  $V_0^{\text{aq}} = V^{\text{aq}} = V_1^{\text{org}} = V_2^{\text{org}}$ , so

$$[A]_0^{\text{aq}} = [A] + [X] + [A_1] + [X_1] + [A_2] + [X_2] \quad (1 \text{ point})$$

$$[A]_0^{\text{aq}} = [A] + K_{AX}[A] + K_{AA_1}[A] + K_{A_1X_1}K_{AA_1}[A] + K_{A_1A_2}K_{AA_1}[A] + K_{X_1X_2}K_{A_1X_1}K_{AA_1}[A] = 44.34[A]$$

$$\eta_X^{\text{org}} = \frac{[X_1] + [X_2]}{[A]_0^{\text{aq}}} = \frac{K_{A_1X_1}K_{AA_1}[A] + K_{X_1X_2}K_{A_1X_1}K_{AA_1}[A]}{44.34[A]} = \frac{2.25[A] + 36[A]}{44.34[A]} = 0.863 = 86.3\% \quad (1 \text{ point})$$

(2 points in total)

7. When extracted with an equal volume of aniline, the yield will be lower than in the case of extraction with twice the volume of anything on the list. Extraction with twice the volume of aniline will lead to the yield lower than that with aniline and hexane, because, according to the values of the constants, the products are much more efficiently transferred to hexane.

|                                                    |           |
|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

Moreover, the equilibrium of the transition of **A** to **X** is shifted to the right in hexane as compared to that in aniline. Following the same logics, we can conclude that the highest yield will be reached in the case of extraction with twice the volume of hexane: b)-d)-a)-c). (0.75 points for the lowest yield in b), 0.75 points for the highest yield in c), 0.75 points if the yield in d) is less than in a), **2.25 points** in total)

### Problem 3 (author Shved A.M.)

1. Lethal outcome occurs at a certain alcohol concentration in the blood, so the corresponding BAC value is the same for male (m) and female (f):

$$\frac{a_m}{m_m \cdot k_{d,m}} - \beta t = \frac{a_f}{m_f \cdot k_{d,f}} - \beta t$$

From this, we obtain the lethal dose ratio:

$$\frac{a_m}{a_f} = \frac{k_{d,m} \cdot m_m}{k_{d,f} \cdot m_f} = \frac{0.71 \frac{\text{L}}{\text{kg}} \cdot 80 \text{ kg}}{0.58 \frac{\text{L}}{\text{kg}} \cdot 60 \text{ kg}} = 1.63$$

(1 point in total)

2. BAC of 0.02% corresponds to 0.2 g/L. Let us find the ultimate mass of ethanol using the Widmark formula:

$$a = (\text{BAC} + \beta t) \cdot m_m \cdot k_{d,m} = \left( 0.2 \frac{\text{g}}{\text{L}} + 0.15 \frac{\text{g}}{\text{L} \cdot \text{h}} \cdot 0.5 \text{ h} \right) \cdot 80 \text{ kg} \cdot 0.71 \frac{\text{L}}{\text{kg}} = 15.62 \text{ g}$$

The volume of pure ethanol:

$$V(\text{EtOH}) = \frac{a}{\rho} = \frac{15.62 \text{ g}}{0.789 \text{ g/mL}} = 19.8 \text{ mL}$$

The volume of alcoholic beverage Huangjiu:

$$V_{\max} = \frac{V(\text{EtOH})}{\varphi(\text{EtOH})} = \frac{19.8 \text{ mL}}{0.10} = 198 \text{ mL}$$

(2 points in total)

3. The reaction equation:



(1 point in total)

4. Considering that the measurements were carried out at such a wavelength that the reaction products do not absorb, the value of the absorbance is most likely related to the amount of initial  $\text{K}_2\text{Cr}_2\text{O}_7$ , which has an intense orange coloration. This is confirmed by analysing the table, where the absorbance decreases and then no longer changes with increasing BAC due to the use up of  $\text{K}_2\text{Cr}_2\text{O}_7$ .

According to the Beer–Lambert law, the absorbance depends linearly on the concentration of the absorbing agent, i.e.,  $\text{K}_2\text{Cr}_2\text{O}_7$  in this case. In turn, the concentration of  $\text{K}_2\text{Cr}_2\text{O}_7$  is linearly related to BAC, which causes a linear dependence of  $A$  on BAC:

$$A = k \cdot \text{BAC} + A_0$$

The same relationship can be obtained by directly analysing the numerical data in the table. Using any two points from the first three, we can find the line equation. For example:

$$\begin{cases} 0.898 = k \cdot 0.000\% + A_0 \\ 0.640 = k \cdot 0.030\% + A_0 \end{cases} \Rightarrow A = -8.60 \cdot \text{BAC}(\%) + 0.898$$

|                                                    |           |
|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

The absorbance value of 0.150 corresponds to the BAC at which all  $\text{K}_2\text{Cr}_2\text{O}_7$  has been consumed, i.e., the maximum BAC value that can be determined with this breathalyzer. Therefore:

$$0.150 = -8.60 \cdot \text{BAC}_{\max}(\%) + 0.898$$

$$\text{BAC}_{\max} = 0.087\%$$

**(3 points in total)**

5. There are several ways to find the concentration of  $\text{K}_2\text{Cr}_2\text{O}_7$ : from the calculated  $\text{BAC}_{\max}$  value (option 1) or from initial data (option 2).

Option 1:

BAC of 0.087% corresponds to 0.87 g/L.

$$n(\text{EtOH})_{\max} = \frac{m(\text{EtOH})_{\text{breath}}}{M(\text{EtOH})} = \frac{\frac{\text{BAC}}{2100} V_{\text{breath}}}{M(\text{EtOH})} = \frac{0.87 \frac{\text{g}}{\text{L}} \cdot 1 \text{ L}}{2100 \cdot 46 \frac{\text{g}}{\text{mol}}} = 9.00 \cdot 10^{-6} \text{ mol}$$

$$n(\text{K}_2\text{Cr}_2\text{O}_7)_0 = n(\text{EtOH}) \cdot \frac{2}{3} = 9.00 \cdot 10^{-6} \text{ mol} \cdot \frac{2}{3} = 6.00 \cdot 10^{-6} \text{ mol}$$

$$c(\text{K}_2\text{Cr}_2\text{O}_7)_0 = \frac{n(\text{K}_2\text{Cr}_2\text{O}_7)}{V_{\text{solution}}} = \frac{6.00 \cdot 10^{-6} \text{ mol}}{0.0030 \text{ L}} = 2.00 \cdot 10^{-3} \text{ M} = 2.00 \text{ mM}$$

Option 2:

According to the Beer–Lambert law:

$$A = \varepsilon l c(\text{K}_2\text{Cr}_2\text{O}_7) + A_{\text{background}} = \varepsilon l \left( c(\text{K}_2\text{Cr}_2\text{O}_7)_0 - c(\text{EtOH}) \cdot \frac{2}{3} \right) + A_{\text{background}}$$

$$\begin{cases} 0.898 = \varepsilon l c(\text{K}_2\text{Cr}_2\text{O}_7)_0 + A_{\text{background}} \\ 0.150 = \varepsilon l \cdot 0 + A_{\text{background}} \end{cases} \Rightarrow \varepsilon l c(\text{K}_2\text{Cr}_2\text{O}_7)_0 = 0.748$$

Next, either in general form or using one of the points, we can find  $\varepsilon l$ . For example, when  $\text{BAC} = 0.030\% = 0.30 \text{ g/L}$ :

$$n(\text{EtOH}) = \frac{m(\text{EtOH})_{\text{breath}}}{M(\text{EtOH})} = \frac{\frac{\text{BAC}}{2100} V_{\text{breath}}}{M(\text{EtOH})} = \frac{0.30 \frac{\text{g}}{\text{L}} \cdot 1 \text{ L}}{2100 \cdot 46 \frac{\text{g}}{\text{mol}}} = 3.11 \cdot 10^{-6} \text{ mol}$$

$$c(\text{EtOH}) = \frac{n(\text{EtOH})}{V_{\text{solution}}} = \frac{3.11 \cdot 10^{-6} \text{ mol}}{0.0030 \text{ L}} = 1.04 \cdot 10^{-3} \text{ M}$$

Using the absorbance value:

$$A = 0.748 - \varepsilon l \cdot c(\text{EtOH}) \cdot \frac{2}{3} + 0.150 = 0.640$$

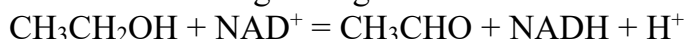
$$\varepsilon l = 372 \frac{1}{\text{M}}$$

Then the initial concentration of  $\text{K}_2\text{Cr}_2\text{O}_7$ :

$$c(\text{K}_2\text{Cr}_2\text{O}_7)_0 = \frac{0.748}{372 \frac{1}{\text{M}}} = 2.00 \cdot 10^{-3} \text{ M} = 2.00 \text{ mM}$$

**(4 points in total)**

6. The equation of the reaction occurring during the EA of ethanol:



**(1 point in total)**

7. It is optimal to perform measurements at the wavelength at which the absorbance is due to only one form with as large value of the molar extinction coefficient as possible. Then

|                                                    |           |
|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

the absorbance will be linearly related to the concentration of one of the components and the analysis will be most sensitive. In this case, it is the wavelength of 340 nm, at which only NADH absorbs.

(1 point in total)

8. According to the Beer–Lambert law for absorbance:

$$A = \varepsilon l c(\text{NADH}) = \varepsilon l (c(\text{EtOH}) + c_{\text{add}}) = \varepsilon l c_{\text{add}} + \varepsilon l c(\text{EtOH}) = \\ = 6.20 \cdot 10^{-3} \cdot c_{\text{add}} + 0.155$$

Concentration in the calibrating solutions:

$$c(\text{EtOH}) = \frac{0.155}{6.20 \cdot 10^{-3} \frac{1}{\mu\text{M}}} = 25.0 \mu\text{M}$$

Concentration in the initial blood serum:

$$c(\text{EtOH})_0 = \frac{25.0 \mu\text{M} \cdot 1000 \mu\text{L}}{100 \mu\text{L}} = 250 \mu\text{M}$$

(2 points in total)

### SECTION III. LIFE SCIENCES AND POLYMERS

**Problem 1 (author Garifullin B.N.)**

1. Three of the four elements are explicitly disclosed (<sup>12</sup>C, <sup>14</sup>N, and <sup>16</sup>O). For the most abundant in nature isotopes of these three elements the ratio of the atomic mass and number of protons (identical to the atomic number) is the same and equal to two, i.e., the nuclei of these isotopes consist of equal numbers of protons and neutrons. Therefore, the following transformations can be carried out for the elements, leading to equality given in the task text ( $m(\text{El})$  is the mass of all atoms of a particular element in the molecule):

$$\frac{\omega(\text{El}_1)}{\omega(\text{El}_2)} = \frac{m(\text{El}_1)}{m(\text{El}_2)} = \frac{2 \cdot N_p(\text{El}_1)}{2 \cdot N_p(\text{El}_2)} = \frac{N_p(\text{El}_1)}{N_p(\text{El}_2)}$$

(0.5 points for one pair of elements; 1 point in total)

2. When calculating the ratio of the number of atoms, it is necessary to make additional transformations, which are presented below using the example of the carbon-hydrogen pair ( $N_a$  is the number of atoms of a given element in the molecule of **Y**):

$$\frac{N_p(\text{C})}{N_p(\text{H})} = \frac{6 \cdot N_a(\text{C})}{N_a(\text{H})} = \frac{15.93}{8.85} \Rightarrow \frac{N_a(\text{H})}{N_a(\text{C})} = \frac{8.85 \cdot 6}{15.93} = \frac{3.33}{1} = \frac{10}{3}$$

A similar calculation for the nitrogen-hydrogen pair leads to the molar ratio H : N = 10 : 1. Summing up the information, we find that C<sub>3</sub>H<sub>10</sub>N (14 atoms, 35 protons) is a fragment of the net formula of **Y**.

If we assume that the empirical formula coincides with the molecular one, then the total number of protons in the molecule of **Y** is:  $3 \cdot 6 \cdot 100 / 15.93 = 113$ , of which 78 (113 – 35) protons account for the remaining two elements with the number of atoms 30 (44 – 14). It can be seen that the average number of protons per atomic nucleus for two elements (oxygen is definitely one of which) is 2.6. Hence, hydrogen must be the fifth element in **Y**, which is impossible, since it has been already involved in previous calculations and reasoning.

On the other hand, if C<sub>9</sub>H<sub>30</sub>N<sub>3</sub> (42 atoms, 105 protons) is a fragment of the molecular formula of **Y**, then the remaining two elements in its molecule are represented by only one atom each.

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|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

Moreover, the number of types of oxygen atoms in **Y** is two, which contradicts the conclusion just made. Hence,  $C_6H_{20}N_2$  is the fragment of the molecular formula of **Y** (without two elements), and the total number of protons in the molecule of the acid is  $113 \cdot 2 = 226$ .

(1 point for calculation of the fragment of the molecular formula; **1.5 points** in total)

3. We now know both the number of atoms (16) and the total number of protons (156) accounted for by the remaining two elements in **Y** (one of which is oxygen). Let us write a system of equations, taking  $x$  to be the number of oxygen atoms,  $y$  to be the number of atoms of the unknown fifth element, the atomic number of which will be denoted as  $Z$ :

$$\begin{cases} x + y = 16 \\ 8 \cdot x + Z \cdot y = 156 \end{cases} \Rightarrow Z - 8 = \frac{28}{y}$$

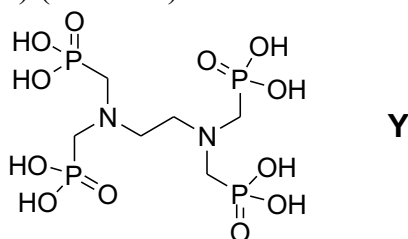
Let's go through the options for integer values of  $y$  (in other words, let us check all the natural divisors of the number 28, see the first column on the left)

| $y$ | Value ( $Z - 8$ ) | $Z$ | Element |
|-----|-------------------|-----|---------|
| 28  | 1                 | 9   | $x < 0$ |
| 14  | 2                 | 10  | Ne      |
| 7   | 4                 | 12  | Mg      |
| 4   | 7                 | 15  | P       |
| 2   | 14                | 22  | Ti      |
| 1   | 28                | 36  | Kr      |

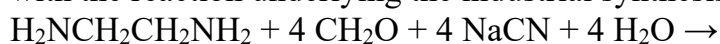
From the resulting list, the organic acid can only contain phosphorus in the amount of 4 atoms, hence the molecular formula of **Y** is  $C_6H_{20}N_2O_{12}P_4$ .

(2 points for derivation of the formula for checking the variants; **3 points** in total)

4. The molecular formula of **Y** can be represented as  $(C_3H_{10}NO_6P_2)_2$  due to its symmetry (see the number of types of atoms of elements in the task text). When building the structure of **Y** from individual blocks, it is necessary to place the ethylenediamine residue in the center (one type of N atoms), and the residues of inorganic acid **A** (most likely orthophosphoric acid) shifted to the periphery. Then the structure of **Y** corresponding to ethylenediamine tetra(methylene phosphonic acid) (EDTMP):



Due to the structural similarity of the EDTA and EDTMP molecules, an analogy can be drawn with the reaction underlying the industrial synthesis of ethylenediaminetetraacetic acid:



(**2 points** in total)

5. Since **X** is a medium salt, all eight protons (meaning  $H^+$  cations) in the structure of **Y** must be replaced by cations of two metals (double salt), one of which belongs to in Group I of the Periodic Table. Based on the total number of atoms, the salt **X** contains only one anion

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|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

of the acid **Y** in its formula unit. Then,  $335 - 226 + 8 = 117$  protons account for 6 ( $42 - 36$ ) atoms of two metals.

Taking into account the principle of electrical neutrality, two combinations are possible:

| Option | The number of cations of an alkali metal (charge of +1) | The number of cations of an unknown metal /its charge |
|--------|---------------------------------------------------------|-------------------------------------------------------|
| 1      | 5                                                       | 1/+3                                                  |
| 2      | 4                                                       | 2/+2                                                  |

Proceeding with option 1 in search of an unknown element, let us run through the alkali metals using the formula:

$$Z(\text{the second Me}) = 117 - 5 \cdot Z(\text{alkali Me}).$$

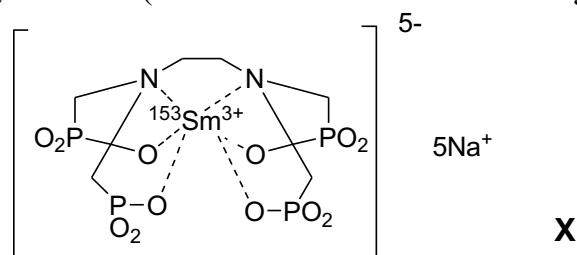
| Alkali metal | The second element |
|--------------|--------------------|
| Li           | No                 |
| <b>Na</b>    | <b>Sm</b>          |
| <b>K</b>     | <b>Ti</b>          |
| Rb           | $M < 0$            |

The formula is as follows for the option 2:

$$Z(\text{the second Me}) = \frac{117 - 4 \cdot Z(\text{alkali Me})}{2},$$

There are no integer solutions, whereas the atomic number of an alkali metal is a natural number by definition.

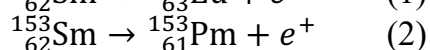
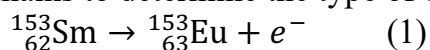
One can choose between samarium and titanium based on the molecular weight of **X**: in the case of samarium, it is Sm-153, for titanium it is Ti-73. The isotope of titanium with such a high neutron content (see the atomic mass of titanium in the Periodic Table as a reflection of the stability range for its isotopes) cannot exist, so **X** contains the samarium ion and has the following structure (the active substance of the drug Quadramet):



(0.75 points for determination of each metal, 1.5 points for the ion structure; **3 points** in total)

**6.** It is quite problematic to propose the isomerization reaction of **X** to **Z** if we follow the simplest logical path, based on the equality of the molecular masses of the two compounds. It is also difficult to predict how the isomerization reaction might affect cancer cells forming bone metastases.

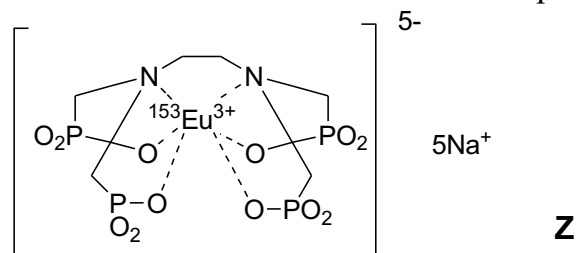
The only reasonable explanation is that the samarium-153 isotope is radioactive and undergoes beta decay, in which the atomic mass of the daughter isotope coincides with the mass of the parent one. It remains to determine the type of decay ( $\beta^-$  or  $\beta^+$ ) in this case:



In the case of positron emission (option 2), a promethium atom is formed, which, in accordance with the Periodic Table, does not have a single stable isotope (the atomic mass

|                                                    |           |
|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

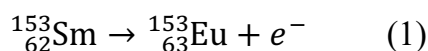
is in parentheses). However, it is written in the task text that **Z** is a stable substance, so the radioactive decay product contains the non-radioactive isotope Eu-153:



The oxidation state of +3 is characteristic of europium (a typical lanthanide).

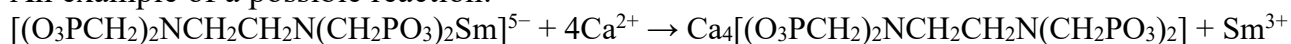
(1.5 points for determination of europium; **2 points** in total)

7. The Sm-153 isotope acts as a source of soft beta radiation aimed at tumour cells, close to which the drug accumulates (the path length of beta particles in biological tissues does not exceed 1 cm). The equation for the nuclear reaction behind the therapeutic effect of a radiopharmaceutical is:



(**1 point** in total)

8. Due to the larger number of phosphorous acid residues and low solubility of the corresponding salts, X binds to calcium ions present in the area of high tumour metabolism in bone tissue, forming poorly soluble deposits and releasing the samarium-153 ion. An example of a possible reaction:



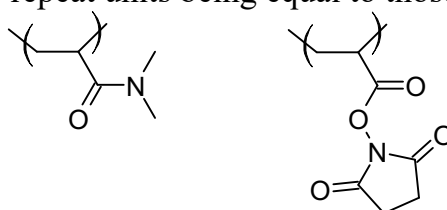
(**1 point** in total)

9. Intravenous administration is the only rational way (of the proposed ones) of introducing **X** into the body. It ensures rapid delivery of the drug through the bloodstream to the site of action (the half-life of the radiopharmaceutical isotope cannot be too long), avoiding problems of intake of the ionized compound in the intestines/lungs and its interaction with calcium ions in the lumen of the gastrointestinal tract.

(**0.5 points** in total)

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

1. Radical polymerization in the presence of AIBN leads to the opening of the C=C double bond, the molar masses of the repeat units being equal to those of the monomers.

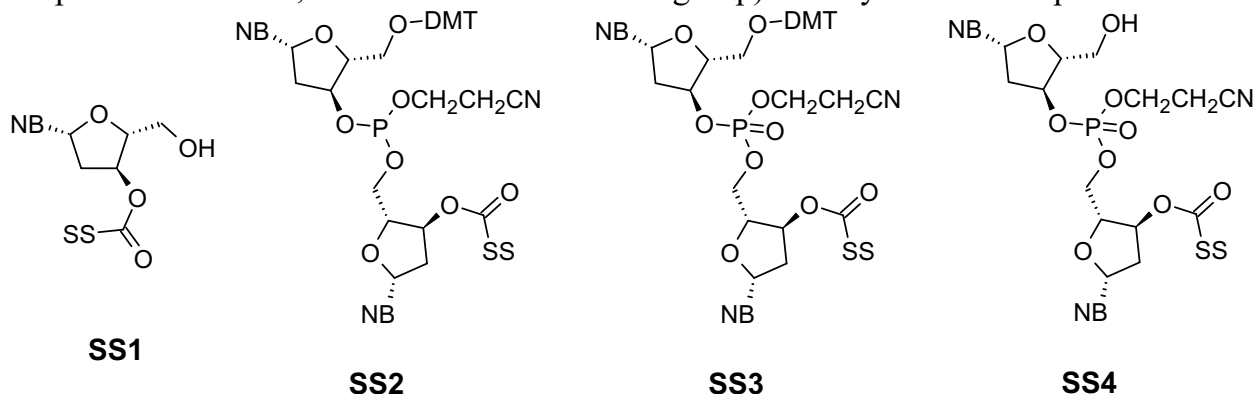


If the desired molar fraction of the succinimide units is  $x$ , then 2 g of **P** contain  $x \cdot \{2 / [99.15 \cdot (1 - x) + 169.15 \cdot x]\}$  mol of the succinimide units (99.15 and 169.15 are the molar masses of the monomers). The succinimide units in **P** were titrated with  $1.6 \cdot 0.4 - 10 \cdot 0.1 = 0.36$  mmol of NaOH. Then  $2x / [99.15 \cdot (1 - x) + 169.15 \cdot x] = 3.6 \cdot 10^{-4}$  and  $x = 0.018$  (1.8%).

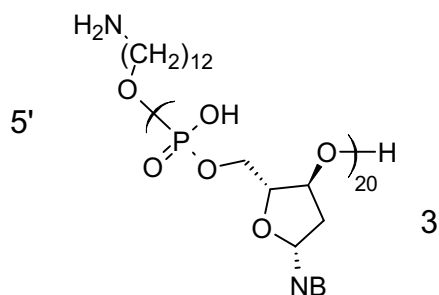
(0.5 points for each unit, 1 point for calculation; **2 points** in total)

|                                                    |           |
|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

2. Acylation of **X** during the formation of **SS1** occurs at the free 3'-OH groups, and then the **DMT** protecting groups is removed from the 5'-OH group at step 2. Steps 3–5 result in the chain growth (addition at the deprotected 5'-OH group, oxidation of phosphite into phosphate with iodine, and removal of the **DMT** group). The cycle is then repeated.



Hence, the growth of the oligonucleotide sequence occurs from the 3'-end (fixed at the surface of **SS**) to the 5'-end; the following **ODN** molecule is formed after addition of **Z**, deprotection, and rupture of the bond with the solid substrate:



(0.5 points for each of **SS1–SS4**, 1 point for **ODN**; **3 points** in total)

3. The antiparallel orientation of the chains affords the most efficient pairing of the oligonucleotide fragments yielding the double helix fragment. Consideration of a pair of the **ODN** molecules in such mutual orientation allows determination of the missing complementary units in the sequence:



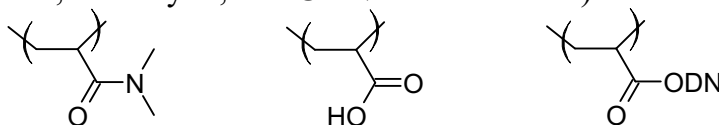
Note that in the case of parallel orientation of the chains neither the double helix forms, nor complementary binding of all 20 nucleotides occurs (at least pairing between the first units at the 5'-end of the sequences, A–A, is impossible).

To calculate the molar mass of **ODN**, let us take the nucleotide composition as A<sub>5</sub>C<sub>5</sub>G<sub>5</sub>T<sub>5</sub> and the gross composition of the terminal groups as C<sub>12</sub>H<sub>27</sub>NO. Next, 20 water molecules are eliminated during the formation of the phosphodiester bonds.  $M = M(\text{C}_{12}\text{H}_{27}\text{NO}) + 5M(\text{AMP}) + 5M(\text{CMP}) + 5M(\text{GMP}) + 5M(\text{TMP}) - 20M(\text{H}_2\text{O}) = 6620.25 \text{ g/mol}$ .

$M(\text{ODN}) = 6395.1 \text{ g/mol}$  for the alternative nucleotide composition A<sub>4</sub>C<sub>10</sub>T<sub>6</sub>.

(1 point for the correct sequence and for the molar mass; **2 points** in total)

4. Hydrolysis of succinimide units yields these of acrylic acid. Hence, **P1** contains three types of units (dimethylamide, carboxylic, and **ODN**-modified ones):



|                                                    |           |
|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

The molar masses of the first two types of the units are 99.15 and 72.07 g/mol, respectively. The molar mass of the **ODN**-modified unit equals the sum of the molar masses of the carboxylic unit and **ODN** minus the water molecule eliminated during formation of the amide bond:  $M = 72.07 + 6620.25 - 18.02 = 6674.3$  g/mol.

If the molar fraction of the **ODN**-modified units in **P1** equals  $a$ , then average molar mass of a repeat unit in **P1** is  $99.15 \cdot 0.982 + 72.07 \cdot (0.018 - a) + 6674.3a = 98.66 + 6602.2a$  (provided the sum of the molar fractions of the **ODN**-modified and the hydrolysed units in **P1** equals that of the succinimide units in **P**, i.e. 1.8%). The mass of the phosphorus atoms per an “average” unit in **P1** equals  $30.97 \cdot 20 \cdot a = 619.4a$ . Accounting for the mass fraction of phosphorus given in the task,  $619.4a / (98.66 + 6602.2a) = 0.0219$  and  $a = 4.55 \cdot 10^{-3}$ ; the ratio between the amounts of the **ODN**-modified and hydrolysed units in **P1** equals  $4.55 \cdot 10^{-3} : (0.018 - 4.55 \cdot 10^{-3})$  or 1 : 2.96.

$a = 4.50 \cdot 10^{-3}$  and the unit ratio is 1:3.00 for the alternative nucleotide composition  $A_4C_{10}T_6$ . (0.5 points for each of the units, 2 points for the calculation; **3.5 points** in total)

**5.** To unite all macromolecules of **P1** into a joint structure, each macromolecule should form at least two nucleotide crosslinks, i.e. it should contain at least two **ODN**-modified units. In view of the molar fraction of such units in the polymer ( $4.55 \cdot 10^{-3}$ ), the degree of polymerization of **P1** should be at least  $2 / 4.55 \cdot 10^{-3} = 440$ . Hence its average molar mass should exceed  $440 \cdot 128.7 = 56600$  ( $128.7 = 98.66 + 6602.2 \cdot 4.55 \cdot 10^{-3}$  is the average molar mass of the repeat unit).

(**1 point** in total)

**6.** Complementary pairing of a nucleotide affording a double helix is poorly efficient at  $\text{pH} < 4$  and  $\text{pH} > 9$  due to protonation of the exocyclic amino groups and deprotonation of the cyclic nitrogen atoms, respectively (which disrupts the optimal structure of the hydrogen bonds between the nucleobases). Disruption of the complementary crosslinks formed by the **ODN** fragments leads to the conversion of the gel into the polymer solution. Since the particular values of  $\text{pK}_a$  are not given, any reasonable range between moderately acidic ( $\text{pH}$  3–4) and moderately alkaline ( $\text{pH}$  9–10) solutions is accepted.

Since the hydrogel is nonporous, the amount of water absorbed by it in an equilibrium with an aqueous phase depends on the hydration of its functional groups. Within the  $\text{pH}$  range, where the hydrogel is stable, a decrease in the acidity leads to ionization of the carboxylic groups of acrylic acid and the phosphate groups in the **ODN** fragment. Since the pair of the phosphate/sodium (and carboxylate/sodium) ions is hydrated stronger than the corresponding non-dissociated acidic group, an increase in  $\text{pH}$  of the aqueous phase should lead to an enhanced hydrogel swelling. The rightmost “alkaline” point of the chosen range where the gel is stable should be pointed.

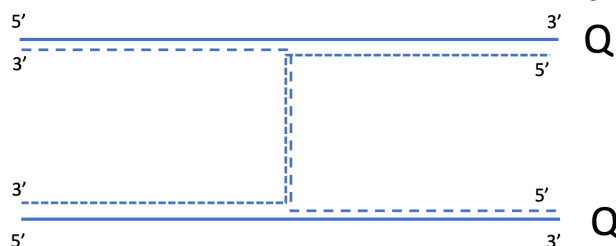
(0.5 points for each boundary at reasonable  $\text{pH}$  values, 0.5 points for  $\text{pH}$  of the maximum swelling; **1.5 points** in total)

**7.** One of the approaches to obtain the target sequence is as follows. Let us divide the sequence of **Q** into two equal parts: 5'–CACAGTCGCGTT–AGGTAAACGAAT–3'. The target sequence, starting from the 3'-end, should be complementary to the 5'-end of **Q**: 3'–GTGTCAGCGCAA. The target sequence, starting from the 5'-end, should be complementary to the second part of **Q**: TCCATTTGCTTA–5'. The proposed above parts of the target sequence will completely bind **Q** into a double helix. Since the length of the linker between the macromolecules **Q** is 12 base pairs, the target sequence should contain a fragment of 12 nucleotides, self-complementary at the antiparallel orientation,

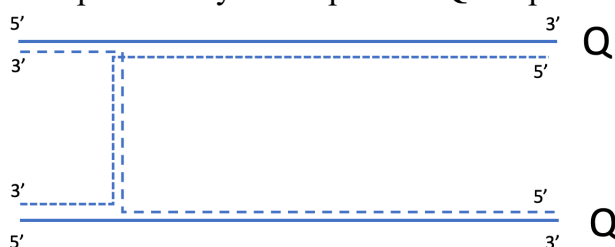
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|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

for example, CCCCCCGGGG. Then the following sequence meeting all the requirements can form a network upon interaction with **Q**:

3'-GTGTCAGCGCAA-CCCCCGGGG-TCCATTTGCTTA-5'.



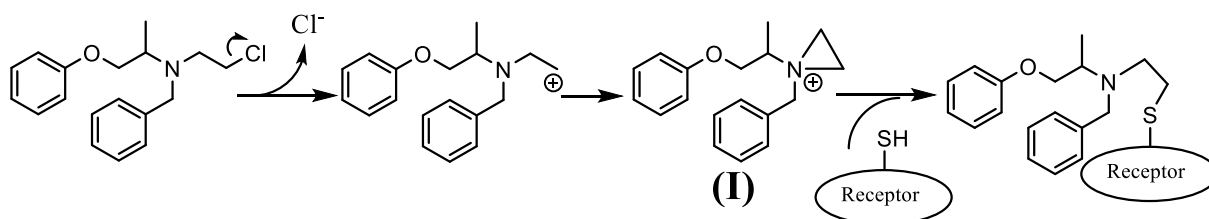
Other variants, differing in the composition of the self-complementary insert as well as in the lengths of the fragments complementary to the parts of **Q** are possible, for example:



(1 point for the sequence, 1 point for the structure of the fragment; **2 points** in total)

### Problem 3 (author Ozhimalov I.D.)

**1.** Phenoxybenzamine reacts with the receptor according to S<sub>N</sub>1 mechanism, therefore the best leaving group (Cl<sup>-</sup>) is cleaved off as the first step. The resulting carbocation is not the most stable form of the intermediate, thus it undergoes isomerization with cyclization of the aziridine fragment. Further, the nucleophilic sulfhydryl group of cysteine attacks the aziridine cycle, resulting in the covalent bond formation between phenoxybenzamine and the receptor, which leads to conformational changes of the latter and its inactivation.



(0.5 points for each of **I** and the product, **1 point** in total)

**2.** The interaction of a receptor with a hormone is described by the dissociation constant:

$$K_d = \frac{[L][R]}{[LR]}$$

Fraction of the receptors associated with the hormone:

$$\theta = \frac{[LR]}{[R]_0}$$

From the material balance equation and the expression of the dissociation constant one gets:

$$\theta = \frac{[LR]}{[R] + [LR]} = \frac{[LR]}{\frac{[LR]K_d}{[L]} + [LR]}; \quad \theta = \frac{[L]}{K_d + [L]}$$

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|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

(0.25 points for each of expressions for  $K_d$  and  $\theta$ , 0.5 points for the dependence of  $\theta$  on ligand concentration; **1 point** in total)

3. The possibility of interaction with several ligands will affect the expression of  $K_d$ , still leaving the calculations and the expression for the fraction of receptors associated with the hormone similar to those in i. 2:

$$K_d = \frac{[L]^n[R]}{[LR]}; \quad \theta = \frac{[L]^n}{K_d + [L]^n}$$

(0.75 points for each of the expression for  $K_d$  and the dependence of  $\theta$  on ligand concentration; **1.5 points** in total)

4. The following transformations result in linearization of the Hill equation:

$$[L]^n = \theta K_d + \theta [L]^n \Rightarrow [L]^n(1 - \theta) = \theta K_d$$

$$\frac{\theta}{(1 - \theta)} = \frac{[L]^n}{K_d} \quad \Rightarrow \quad \lg\left(\frac{\theta}{(1 - \theta)}\right) = n \lg([L]) - \lg(K_d)$$

(**2 points** in total)

5. Since phenoxybenzamine is an irreversible receptor blocker, its effect on all the receptor molecules results in a decrease in the maximum stimulation effect. Graphically, this manifests as a downward shift of the asymptote, the effective dose of the hormone causing half-effect remaining constant (no. 3).

(**1 point** in total)

6. Based on the Hill equation, the half-maximal effect occurs when half of all the receptors are bound ( $\theta = 0.5$ ). In this case:

$$\frac{1}{2} = \frac{[L]^n}{K_d + [L]^n} \quad \Rightarrow \quad K_d = [L]^n \quad \Rightarrow \quad [L] = \sqrt[n]{K_d}$$

(**1 point** in total)

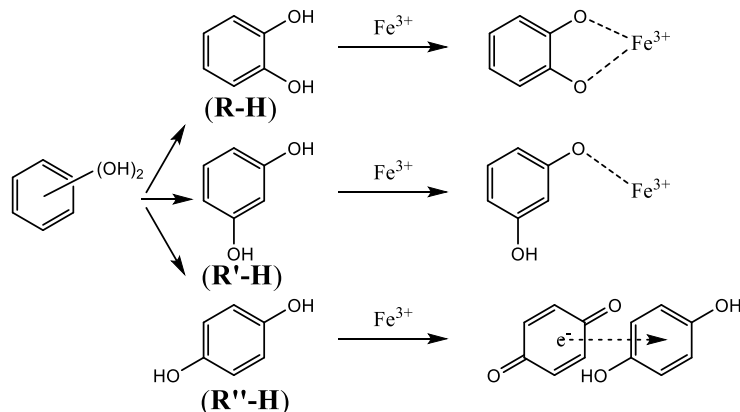
7. Beside the scheme of metabolism of pheochromocytoma hormone, that of organic synthesis of **B** is to be taken into account. It is seen that a methylated **R-H** derivative condensed with glyoxal is the final metabolite of pheochromocytoma hormone. The attached two-carbon skeleton of glyoxal is similar to the ethanolamine fragment in the structure of the initial compound affording **M1** and **M2**. Then the metabolic process involving **X** is similar to the step of organic synthesis involving dimethyl carbonate. These turn out to be methylations. If the mass of the initial R-substituted ethanolamine is  $R + 60.09$ , then the mass of **M1** is  $R + 74.12$  (increased by the  $\text{CH}_2$  fragment), and that of **M2** is  $R + 88.15$ . Since **M1** is a mono- and **M2** a dimethylated derivative, they have the same number of oxygen atoms, and the ratio of oxygen mass fractions is equal to that of molecular masses:

$$\frac{\omega(\text{O})_{\text{M1}}}{\omega(\text{O})_{\text{M2}}} = \frac{16x \cdot (R + 88.15)}{(R + 74.12) \cdot 16x} = 1.0767$$

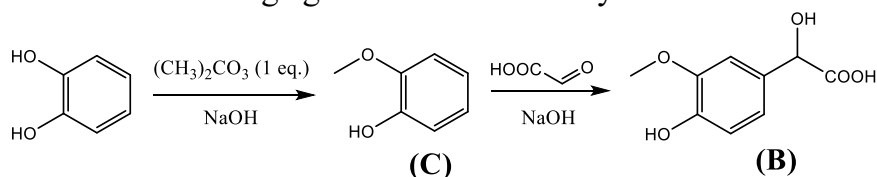
The mass of the substituent  $R = 109$  g/mol. **A** forms emerald-green complexes with Fe(III), which indicates the presence of an aromatic fragment in R. The violet coloration of **R'-H** complexes with Fe(III) indicates that **R'-H** is a phenol or its analogue. For the simplest variant of the skeleton (benzene molecule), the mass of all atoms besides carbon is  $109 - 72 = 37$  g/mol. Taking into account the high probability of a hydroxyl group in R (based on the color of the complex with iron III), the mass residue corresponds to two hydroxyl groups and three hydrogen atoms. Thus, R is dihydroxyphenyl. The position of hydroxyl groups can be determined based on the coloration of the complexes with Fe(III): emerald

|                                                    |           |
|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

green for pyrocatechol, dark purple for resorcinol **R'-H** (similar to phenol, since only one OH-group is involved in the complex formation), and brown for hydroquinone **R''-H** due to oxidation by iron to benzoquinone followed by the formation of the complexes with charge transfer.

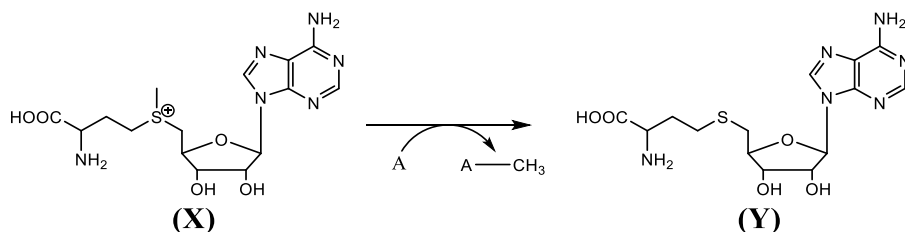


Pyrocatechol is the starting compound for organic synthesis. First, a monomethylated derivative of pyrocatechol, guaiacol (**C**), is formed as a result of the reaction with dimethyl carbonate. This is followed by electrophilic substitution in the aromatic ring, its direction being determined by the positive mesomeric effect of the  $\text{RO}^-$  guaiacol group formed in an alkaline medium (the effect is stronger than that of the methoxy group). Finally, the glyoxal molecule is attached in the para-position (relative to OH) to form vanillylmandelic acid (**B**), from which the flavoring agent vanillin can be synthesized.



(0.75 points for each of **B** and **C** structures, 0.5 points for each of **R-H**, **R'-H**, **R''-H** structure, **3 points** in total)

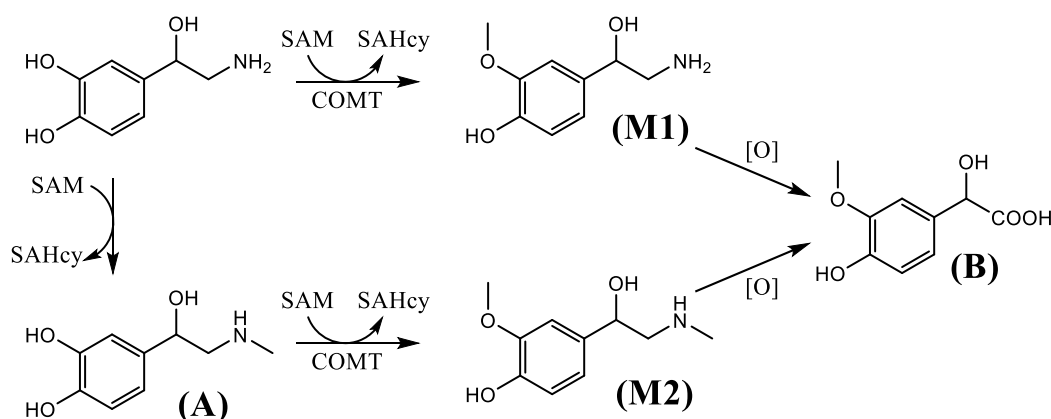
**8.** **X** is a common methylating agent, which should contain an easily detachable methyl moiety. *S*-adenosylmethionine (SAM) with the demethylation product *S*-adenosylhomocysteine **Y** (SAHcy) is the best option.



(1 point for **X**, 0.5 points for **Y**; **1.5 points** in total)

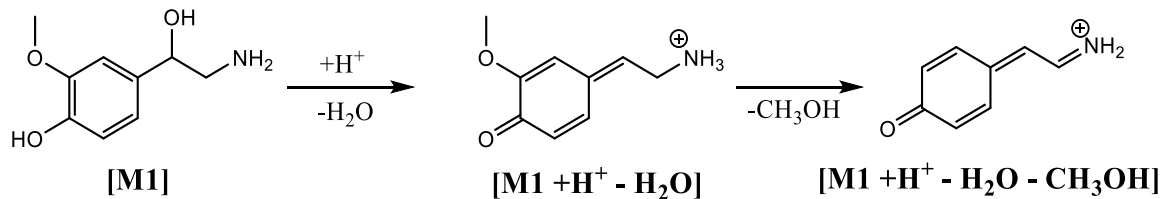
**9.** The starting compound, norepinephrine, can be methylated in two ways. The reaction catalyzed by the enzyme catecholamine-*O*-methyltransferase (COMT) leads to its inactive derivative **M1** (normetanephrine) with methylation occurring in the pyrocatechol ring. Alternatively, methylation results in adrenaline (**A**). The direction of methylation is disclosed based on the fact that the hydroxyl group in the aliphatic fragment of adrenaline remains free up to the compound **B**, whereas the pyrocatechol ring is methylated only by the enzyme COMT. Then adrenaline is an *N*-methyl derivative of noradrenaline.

|                                                    |           |
|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |



(0.5 points for each of **A**, **M1**, and **M2**; 1.5 points in total)

**10.** During LC–MS in the first quadrupole, normetanephrine **M1** is ionized to form the  $[\text{M1} + \text{H}^+ - \text{H}_2\text{O}]$  ion. Addition of proton suggests protonation of the basic center in the molecule, whereas elimination of water turns out to be dehydration of the aliphatic alcohol. In **M1**, the amino group is the most suitable basic center. The dehydration is accompanied by the transition of the molecule into the quinoid form due to the instability of the enamine. The cleavage of the formed ion takes place in the second quadrupole, and the  $[\text{M1} + \text{H}^+ - \text{H}_2\text{O} - \text{CH}_3\text{OH}]$  ion is released in the third quadrupole. The changes in its structure include the loss of the hydroxymethyl substituent in the aromatic ring with the formation of imine.



(0.75 points for each ion; 1.5 points in total)

For reference: Pheochromocytoma (PCC) is a tumor of the adrenal medulla that produces excessive amounts of adrenaline and noradrenaline. Most often PCC is a histologically benign tumor, but it can pose a threat in terms of hormonal activity. The hormones released into the blood lead to an acute increase in blood pressure including possible development of hypertensive crises. The latter are dangerous because they drastically increase the risks of hemorrhagic strokes, infarcts of various organs, acute kidney damage and other life-threatening conditions. Diagnosis of PCC is complicated by pulse mode of secretion of hormones and their short half-lives (several minutes) Thus, the hormone metabolites (metanephrine and normetanephrine) are analyzed. Diagnosis and treatment of PCC are important challenges that endocrinologists face.

#### Literature:

Whiting MJ. Simultaneous measurement of urinary metanephrines and catecholamines by liquid chromatography with tandem mass spectrometric detection. *Annals of Clinical Biochemistry*. 2009;46(2):129–136. doi:10.1258/acb.2008.008180

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|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

## SECTION IV. INORGANIC CHEMISTRY

### Problem 1 (authors Gulevich D.G., Karpova E.V.)

1. The electrical resistance of metals increases at elevated temperatures due to an increase in thermal vibrations of atoms, which impede the movement of charge carriers. The superconducting transition is characterized by a drop in resistance to zero, while above the critical temperature such substances are characterized by the metallic behavior. In semiconductors, the number of charge carriers increases with increasing the temperature, which leads to a simultaneous decrease in resistance. Thus, 1 refers to substances with a metallic conductivity, 2 to substances that have a transition to the superconducting state, 3 to substances with the semiconductor conductivity.

(0.25 points for each correct answer, total **0.75 points**)

2. To calculate the critical value of the field strength  $H_c$  at the temperature  $T = 3$  K, we use the formula:  $H_c = H_{c0} \left(1 - \frac{T^2}{T_c^2}\right) = 3.2627 \cdot \left(1 - \frac{3.00^2}{4.156^2}\right) = 1.5626$  kA/m. The critical field strength decreases with increasing the temperature above 0 K.

(0.75 points for calculation of  $H_c$ , **0.75 points** in total)

3. From the relation:  $\frac{T_c(\text{Hg})}{T_c(^{198}\text{Hg})} = \frac{M(^{198}\text{Hg})^\zeta}{M(\text{Hg})^\zeta}$ , therefore  $\zeta = \frac{\lg \frac{4.156}{4.177}}{\lg \frac{197.97}{200.59}} = 0.383$ .

(1 point for calculation of  $\zeta$ , **1 point** in total)

4. Isotopes with the maximum difference in the molar masses have the maximum difference in the  $T_c$  values.

$$T_c(^{196}\text{Hg}) = 4.156 \cdot \frac{200.59^{0.383}}{195.97^{0.383}} = 4.193 \text{ K}, T_c(^{204}\text{Hg}) = 4.156 \cdot \frac{200.59^{0.383}}{203.97^{0.383}} = 4.129 \text{ K}.$$

(0.5 points for the choice of the isotope pair, 1 point for calculation of the range for  $T_c$ , **1.5 point** in total)

5. Phase transitions of the 2<sup>nd</sup> order, as indicated in the condition, are characterized by the absence of a jump in entropy, i.e.  $\Delta S = 0$ . This is possible only in the case when  $H_c = 0$ . It follows from the formula  $H_c = H_{c0}(1 - T^2/T_c^2)$  that the critical value of the field strength becomes zero at  $T = T_c$ , which is also true for  $\Delta S$ . Thus, the type 2 transition for the type I superconductors occurs at  $T = T_c$ .

(0.25 points for the  $\Delta S$  value, 0.25 points for  $H_c$  value, 0.5 points for  $T$ , **1 point** in total)

6. The equality of heat capacities in two states means that their difference  $\Delta C = 0$ . Using the expression for  $\Delta C$ , we obtain the equation:  $\Delta C = \frac{H_{c0}^2 T}{\pi T_c^2} \left(3 \frac{T^2}{T_c^2} - 1\right) = 0$ .

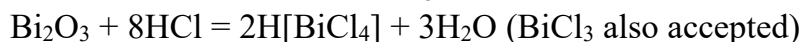
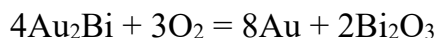
The equality of  $\Delta C$  to 0 is possible, if at least one of the factors equals 0. This is only possible when  $(1 - 3T^2/T_c^2) = 0$ , thus  $T = T_c/\sqrt{3} = 4.156/\sqrt{3} \approx 2.4$  K.

(0.25 points for the  $\Delta C$  value, 0.5 points for the  $T$  value, **0.75 points** in total)

7. Heating in air most often leads to the formation of an oxide, whereas the least active metals (gold, platinum, etc.) do not enter the oxidation reaction. The presence of a precipitate of the colored metal **B** after roasting in air and interaction with an acid solution allows assuming that **B** is gold, a yellow metal. The metal **A**, when heated in air, produces an oxide, which reacts with a solution of hydrochloric acid to form a chloride or chloride complex. Addition of cesium iodide results in the formation of a complex salt  $\text{Cs}_x[\text{A}_a\text{I}_y]$ . If  $a = 1$ , then  $x(\text{A}) = \frac{1}{x+1+y} = 0.1667$ ;  $x + y = 5$ . For  $x = 1$  and  $y = 4$  the molar mass of **A**:

|                                                    |           |
|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

$\omega(\mathbf{A}) = \frac{M(\mathbf{A})}{M(\mathbf{A}) + 132.91 + 4 \cdot 126.90} = 0.246$ ;  $M(\mathbf{A}) = 208.97$  g/mol,  $\mathbf{A} = \text{Bi}$ . A bismuth and gold compound  $\text{Au}_b\text{Bi}$  is the intermetallic compound  $\mathbf{X}$ ;  $b = \frac{208.98 \cdot 0.6534}{196.97 \cdot (1 - 0.6534)} = 2$ ;  $\mathbf{X} = \text{Au}_2\text{Bi}$ .



(2 points for the metal  $\mathbf{A}$ , 1 point for each of  $\mathbf{B}$  and the formula of  $\mathbf{X}$ , 0.5 points for each reaction equation, **5.5 points** in total)

8. The picture of the  $\mathbf{T3}$  unit cell shows a binary compound. The ratio of  $\mathbf{L}$  and  $\mathbf{Q}$  included in  $\mathbf{T3}$ :  $N(\mathbf{L})$  in the unit cell  $= 8 \cdot \frac{1}{8} + 1 = 2$ ,  $N(\mathbf{Q})$

in the unit cell  $= 12 \cdot \frac{1}{4} + 6 \cdot \frac{1}{2} = 6$ ;  $\mathbf{T3} = \mathbf{LQ}_3$ , the number of the formula units in the cell  $Z = 2$ . Then  $M(\mathbf{T3}) = d \cdot V_M = d \cdot V(\text{unit cell}) \cdot N_A / Z = 4.388 \cdot 2.984^3 \cdot 10^{-24} \cdot 6.02 \cdot 10^{23} / 2 = 35.09$  g/mol.

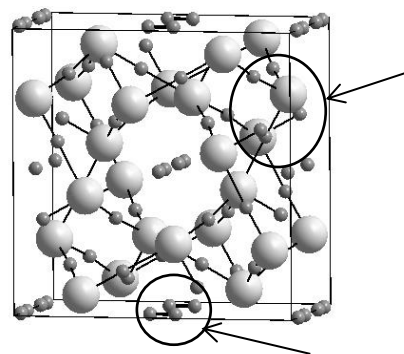
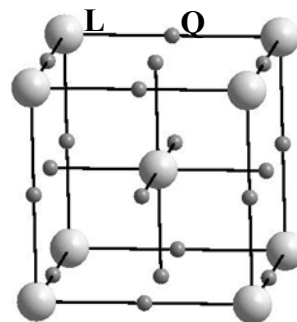
Since the molar mass is small for a tetraatomic formula unit  $\mathbf{LQ}_3$ , it is reasonable to assume that  $\mathbf{Q} = \text{H}$ , then  $M(\mathbf{L}) = 35.09 - 3 \cdot 1.01 = 32.06$  g/mol, which corresponds to sulfur.  $\mathbf{T3} = \text{H}_3\text{S}$ . The compound  $\mathbf{T1}$  undergoes decomposition at elevated pressures, but is stable under normal conditions;  $\mathbf{T1} = \text{H}_2\text{S}$ .

(0.25 points for the atomic ratio in  $\mathbf{T3}$ , 0.5 points for calculation of the molar mass, 0.5 points for determination of the qualitative content of  $\mathbf{T3}$ , 0.5 points for  $\mathbf{T1}$ , **1.75 points** in total)

9.  $\mathbf{T2}$  has the same quantitative composition as  $\mathbf{T3}$  with the ratio of hydrogen to sulfur atoms of 3:1. In the starting compound  $\mathbf{T1}$ , this ratio is of 2:1.  $\mathbf{T2}$  is enriched with hydrogen compared to  $\mathbf{T1}$ . One can see molecular diatomic fragments of  $\text{H}_2$  and molecular fragments of  $\text{H}_2\text{S}$ , interconnected by a hydrogen bonding system in the structure of  $\mathbf{T2}$ . The ratio of  $\text{H}_2$  and  $\text{H}_2\text{S}$  fragments should lead to that of hydrogen and sulfur atoms of 3:1. This is possible if there is one  $\text{H}_2$  fragment per two  $\text{H}_2\text{S}$  ones. With an account for structural fragments, the formula of  $\mathbf{T2}$  is  $(\text{H}_2\text{S})_2\text{H}_2$ .

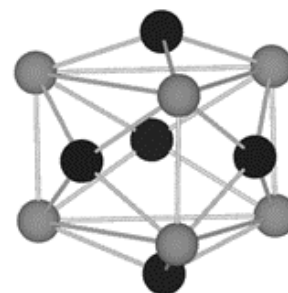
The reaction of  $\mathbf{T1}$  decomposition at high pressures:  $3\text{H}_2\text{S} = (\text{H}_2\text{S})_2\text{H}_2 + \text{S}$ .

(0.5 points for each molecular fragment, 0.5 points for each of the  $\mathbf{T2}$  formula and reaction, **2 points** in total)



## Problem 2 (author Likhanov M.)

1. The simplest composition of  $\mathbf{M}$  is  $\text{Cs}_8\text{Y}_{11}$  can be put forward based on the mole fraction of cesium. Suppose that the cluster consists of 11  $\mathbf{Y}$  atoms, then 5 more  $\mathbf{Y}$  atoms are to be added to the trigonal prism  $\mathbf{Y}_6$ . This can be done by placing the atoms over the five faces of the trigonal prism. Moreover, if all the atoms are located strictly above the centers of the faces, there will be three  $\mathbf{Y}$  atoms at 4 identical distances to the  $\mathbf{Y}$  atoms that form the vertices of the rectangular faces of the prism, as well as two atoms at three identical distances to the three atoms that form the triangular faces.

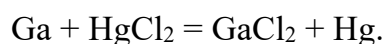


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|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

Thus, an  $Y_{11}$  cluster is formed in structure of **M**. The cluster has the shape of a five-capped trigonal prism, and its symmetry will not differ in any way from the initial symmetry of the trigonal prism. The gray circles in the figure show the **Y** atoms forming the trigonal prism, and the black ones the atoms located above the faces of the prism.

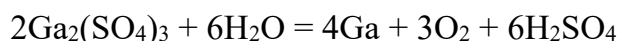
(0.5 points for the composition of **M**; 1 point for the structure; **1.5 points** in total)

2. Let us determine the composition of the binary halide **I**. From the known mass fraction of chlorine, we obtain the best result for the formula of  $YCl_2$ , then  $M(Y) = 69.77$  g/mol, which corresponds to the metal gallium. Thus, **I** is gallium chloride  $GaCl_2$ , **Y** is Ga. The reaction affording **I** is accompanied by the release of mercury, which can be easily removed by decantation:

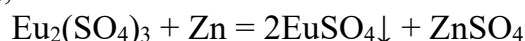


When the intermetallic compound  $XY_{a-\delta}Z_\delta$  is dissolved in nitric acid, the metal nitrates are formed. Next, when adding an excess of a concentrated alkali solution, a mixture of precipitates of hydroxides of **X** and **Z** is formed, and gallium proceeds to the solution as a hydroxo complex.  $Na_3[Ga(OH)_6] + NaNO_3$  (or  $Na[Ga(OH)_4] + NaNO_3$ ) is the **C1** solution.

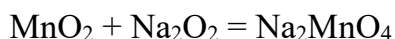
When sulfuric acid is added to the **C1** solution, a white precipitate of gallium hydroxide  $Ga(OH)_3$  is formed first, which then easily dissolves affording gallium sulfate. Thus, the **C2** solution contains the following salts:  $Ga_2(SO_4)_3$ ,  $Na_2SO_4$ , and  $NaNO_3$ . Gallium metal can be obtained by electrolysis of this solution:



A mixture of precipitates of hydroxides **A** and **B** was isolated and kept in air, which may indicate their oxidation, while only one of the precipitates further dissolves in dilute sulfuric acid. Thus, the solution of **D** is that of metal **X** sulfate. A white precipitate forms when zinc is added to the solution of **D**. Reduction of **X** to a lower oxidation state or to the metallic state is possible in such a process. Actually, the former process occurs, since **F** is a complex substance containing **X**. Of the insoluble white sulfates, it is europium sulfate that suits. Then, **D** is  $Eu_2(SO_4)_3$ , **F** is  $EuSO_4$ , **X** is Eu.



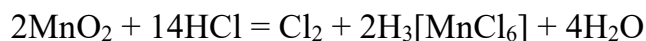
**E** is described similarly to the manganese oxide  $MnO_2$ , which can exhibit oxidizing and reducing properties. Indeed, when manganese oxide(+4) is fused with sodium peroxide, green sodium manganate(+6) is formed:



Sodium manganate is unstable and decomposes in water:



Sodium manganate oxidizes concentrated hydrochloric acid, releasing chlorine. It is known that the manganese complex is formed with  $\mu_{eff} = 4.9 \mu_B$ , which corresponds to 4 unpaired electrons and the oxidation state of manganese of +3. Thus, **H** is the manganese chloride complex  $H_3[MnCl_6]$ .



**E**,  $MnO_2$ , initially precipitates in the hydrated form  $MnO_2 \cdot xH_2O$ , which is completely dehydrated after heating to  $120^\circ C$ . Thus, Mn is the metal **Z**.  $Eu(OH)_3$  and  $Mn(OH)_2$  is the mixture of the precipitates **A** and **B**, and the latter is oxidized in air to brown  $MnO_2 \cdot xH_2O$ . (0.5 points for each of **A–I** and each reaction; **8 points** in total)

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|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

3. In gallium chloride  $\text{GaCl}_2$ , gallium is present in two oxidation states of +1 and +3, chlorine has the oxidation state of -1, thus, the halide is  $\text{Ga}_2\text{Cl}_4$ .

(1 point in total)

4. In the octahedral complex  $\text{H}_3[\text{MnCl}_6]$ , manganese has the oxidation state of +3 and contains 4 unpaired electrons. Since the complex is high-spin, one of the electrons should be located at the  $e_g$  level, which leads to the octahedron stretching due to the Jahn–Teller effect. The energy diagram is shown in the figure.

(0.5 points for each of the diagram, electron arrangement, and labels; 1.5 points in total)

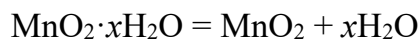
5. Analysis of the projections of the unit cell of N gives the following number of atoms.

Eu: 2 atoms inside the unit cell and 4 atoms on the  $bc$  faces, 4 atoms per cell in total.

Ga/Mn: 4 atoms inside and 8 atoms on the  $bc$  faces, 8 atoms per cell in total.

Thus, the gross formula of the intermetallic compound is  $\text{EuGa}_{2-\delta}\text{Mn}_\delta$ . Let us find the exact value of  $\delta$ .

The mass of the  $\text{MnO}_2 \cdot x\text{H}_2\text{O}$  precipitate equals 8.545 g, while 23.67 wt.% of the mass is lost after dehydration.



Thus,  $v(\text{MnO}_2) = 8.545(1 - 0.2367) / 86.94 = 0.075$  mol.

The  $\text{EuGa}_{2-\delta}\text{Mn}_\delta$  intermetallic compound with the mass 42.60 g contains 0.075 mol of manganese. Then  $42.60 / (151.96 + 69.72 \cdot (2 - \delta) + 54.94 \cdot \delta) = 0.075 / \delta$ , and  $\delta = 0.5$ .

The exact composition of the intermetallic compound is  $\text{EuGa}_{1.5}\text{Mn}_{0.5}$ .

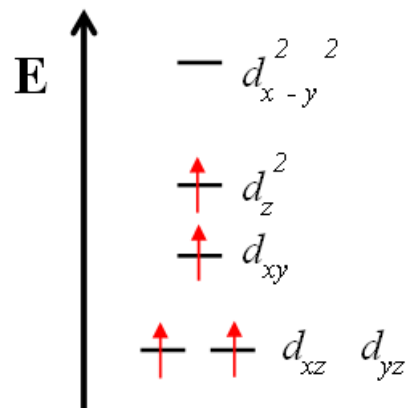
(1 point for the calculation, 0.5 points for the composition; 1.5 points in total)

6. It is known that the density of the  $\text{EuGa}_{2-\delta}\text{Mn}_\delta$  intermetallic solid solution varies in the range of 6.847–7.118 g/cm<sup>3</sup>. The density of  $\text{EuGa}_{1.5}\text{Mn}_{0.5}$  is  $d = 6.864$  g/cm<sup>3</sup>. Since density is the ratio of mass to volume, the molar masses of the boundary compositions of the solid solution can be calculated.

The density of 6.847 g/cm<sup>3</sup> corresponds to  $M = 280.315$  g/mol, and that of 7.118 g/cm<sup>3</sup> to  $M = 291.4$  g/mol. The former corresponds to the value  $\delta = 0.75$ , and the latter to  $\delta = 0$ .

Thus, the boundaries are  $\text{EuGa}_{1.25}\text{Mn}_{0.75}$  and  $\text{EuGa}_2$ .

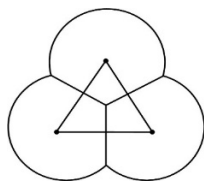
(0.5 points for calculation, 0.5 points for each of  $\delta_{\min}$  and  $\delta_{\max}$ ; 1.5 points in total)



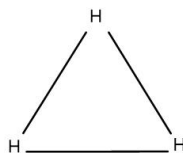
### Problem 3 (author Shwartzman V.E.)

1. If the hydrogen atoms are equidistant from each other in the  $\text{H}_3^+$  cation, they are located at the vertices of an equilateral triangle. The three  $s$ -orbitals of H overlap at the center of an equilateral triangle. In this case, two electrons are delocalized and simultaneously bind three hydrogen atoms. This bond is referred to as a three-center two-electron (0.25 points). Therefore, the structure of  $\text{H}_3^+$  can be depicted either as a triangle or as a three-armed figure (0.25 points).

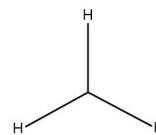
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|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |



Molecular orbital  $a_1$   
in  $H_3^+$  (0.25 points)

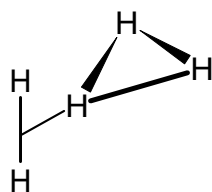


Triangle ion  $H_3^+$

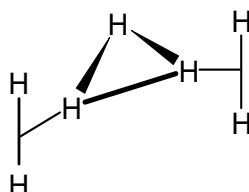


Three-armed figure for three-center two-electron bond  $H_3^+$

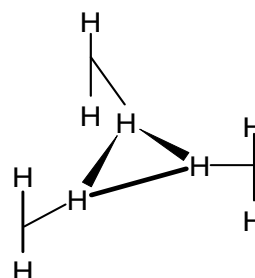
In the structures of  $H_n^+$  cations,  $H_2$  molecules are bound to H and are located perpendicularly to the plane, in which the atoms of the  $H_3^+$  cation are located.



$H_5^+$  (0.5 points)



$H_7^+$  (0.5 points)



$H_9^+$  (0.5 points)

(2.25 points in total)

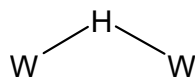
2. Unbound  $H^+$  and  $H^-$  in an aqueous solution react with  $H_2O$  molecules in different ways.  $H^+$  forms a hydronium ion with  $H_2O$ :  $H_2O + H^+ \rightarrow H_3O^+$  (0.5 points) (in addition to hydronium,  $H_5O_2^+$ ,  $H_7O_3^+$ ,  $H_9O_4^+$  can be formed due to hydrogen bonds). The  $H^-$  anion acts as a reducing agent:  $H_2O + H^- \rightarrow H_2 + OH^-$  (0.5 points).

To confirm that the existence of the unbound  $H^-$  in a solution is impossible, we first calculate the  $E^\circ$  of the reaction  $H_2O + H^- \rightarrow H_2 + OH^-$ :

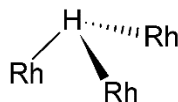
$E^\circ = E^\circ_{\text{Ox}} - E^\circ_{\text{Red}} = E^\circ_{H_2O/H_2} - E^\circ_{H_2/H^-} = -0.83 + 2.23 = 1.40 \text{ V}$  (0.75 points). Then we calculate the Gibbs energy:  $\Delta_r G^\circ = -nFE^\circ = -1 \cdot 96485 \cdot 1.40 = -135079 \text{ J/mol}$  (0.5 points). A negative value of  $\Delta_r G^\circ$  indicates a spontaneous reaction.

(2.25 points in total)

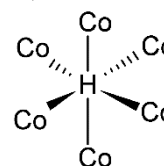
3. Structures of the  $HM_n$  fragments in complexes (0.5 points per formula):



$[(CO)_5WHW(CO)_5]^+$



$[HRh_3(C_5H_5)_4]$



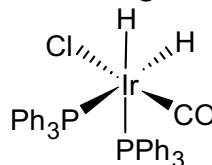
$[HCo_6(CO)_{15}]^-$

(1.5 points in total)

4. The formula of the resulting complex **A** is  $[MClH_{2n}CO(PPh_3)_2]$ , the content of  $Cl^-$  in it is  $\omega_{Cl} = M_{Cl} \cdot 100 / M_{\text{complex}}$ ;  $4.53 = 35.45 \cdot 100 / (M_M + 2n \cdot 1.01 + 588.06)$ ;  $M_M = 194.5 - 2n$ . The ratio between  $n_{Cl}$  and  $n_H$  is:  $4.53/35.45 : 4.13/1.01 = 1 : 32$ . The H atoms are also found in Ph groups. This means that  $n = (32 - 3 \cdot 2 \cdot 5) : 2 = 1$  and  $M_M = 194.5 - 2.02 = 192.48 \text{ g/mol}$  (1 point). Then M is Ir, and **A** has the formula of  $[MCl(H)_2CO(PPh_3)_2]$ , whereas the reaction equation is  $[IrClCO(PPh_3)_2] + H_2 = [IrCl(H)_2CO(PPh_3)_2]$  (0.5 points). Ir has 9 valence electrons, Cl and H are one-electron ligands, and CO and  $PPh_3$  are two-

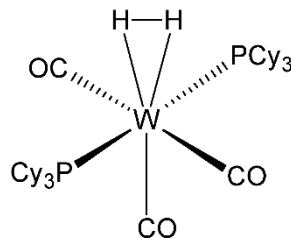
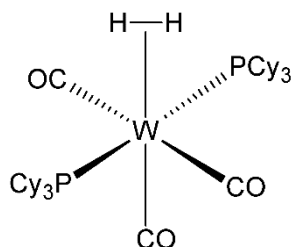
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|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

electron ones. Therefore,  $[\text{IrClCO}(\text{PPh}_3)_2]$  is a 16-electron complex, and  $[\text{IrCl}(\text{H})_2\text{CO}(\text{PPh}_3)_2]$  is an 18-electron one (0.25 points for each compound). The oxidation state of Ir changes from +1 in  $[\text{IrClCO}(\text{PPh}_3)_2]$  to +3 in  $[\text{IrCl}(\text{H})_2\text{CO}(\text{PPh}_3)_2]$  (0.25 points for each compound). The structure of  $[\text{IrCl}(\text{H})_2\text{CO}(\text{PPh}_3)_2]$  with the ligands  $\text{H}^-$  in *cis*-position (0.5 points):



(3 points in total)

5. Based on the band in the IR spectrum ( $\nu = 2690 \text{ cm}^{-1}$ ) and the bond length  $r_{\text{H-H}} = 0.084 \text{ nm}$ ,  $\text{H}_2$  molecule is the ligand in the complex **B** (0.5 point). The formula of **B** can be written as  $[\text{M}'(\text{H}_2)_x(\text{CO})_3(\text{PCy}_3)_2]$ . The mass fraction of the metal  $\text{M}'$  in **B** is  $\omega_{\text{M}'} = M/(M + 2x \cdot 1.01 + 644.99) = 0.2213$ . At  $x = 1$   $M = 183.87 \text{ g/mol}$ ,  $\text{M}' = \text{W}$  (1 point). Taking into account that the ligand ( $\eta^2\text{-H}_2$ ) is bidentate in the complex, two variants of the spatial structure can be given (0.5 points for any formula).



(2 points in total)

6. The distance  $r_{\text{H-H}} = 0.087 \text{ nm}$  in  $\text{E}^+$  corresponds to the  $\text{H}_2$  ligand, whereas  $r_{\text{H-H}} = 0.180 \text{ nm}$  indicates the presence of two  $\text{H}^-$  ligands. If so, the formula of  $\text{E}^+$  can be written as  $[\text{ReH}_2(\eta^2\text{-H}_2)(\text{CO})(\text{PMe}_2\text{Ph})_3]^+$  (0.5 point). The only bonds with  $r_{\text{H-H}} = 0.176 \text{ nm}$  present in  $\text{D}^+$  are found in hydrides, so the formula  $\text{D}^+$  is  $[\text{ReH}_4(\text{CO})(\text{PMe}_2\text{Ph})_3]^+$  (0.5 points).

(1 point in total)

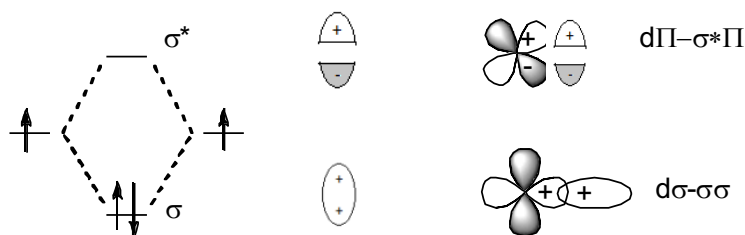
7. The equilibrium constant  $\text{D}^+ \rightleftharpoons \text{E}^+$  was calculated by Luo and Harbtree from the linear dependence  $\ln K = f(1/T)$ , arising from the equation  $\ln K = \Delta_r S^\circ/R - \Delta_r H^\circ/RT$ , derived from the equations  $\Delta_r G^\circ = -RT \ln K$  and  $\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$  (provided  $\Delta_r S^\circ$  and  $\Delta_r H^\circ$  are independent of temperature in a narrow temperature range).

Thus,  $\ln K = -10 / 8.314 + 4600 / (8.314 \cdot 193.2)$ , at  $T = 193.2 \text{ K}$ ;  $K = 5.265$  (1 point).

The equilibrium constant  $\text{D}^+ \rightleftharpoons \text{E}^+$ ;  $K = [\text{E}^+]/[\text{D}^+] = \chi_{\text{E}^+}/\chi_{\text{D}^+}$  can be expressed in terms of the molar fractions. Denoting the molar fraction of  $\text{E}^+$  as  $\chi_{\text{E}^+}$ , we get that of  $\text{D}^+$ :  $\chi_{\text{D}^+} = (1 - \chi_{\text{E}^+})$ . Then  $5.265 = \chi_{\text{E}^+}/(1 - \chi_{\text{E}^+})$  and  $\chi_{\text{E}^+} = 0.16$  (16%), and  $\chi_{\text{D}^+} = 100 - 16 = 84\%$  (1 point).

(2 points in total)

8. In the MO diagram (0.5 points), the bond multiplicity for the  $\text{H}_2$  ligand is:  $(2 - 0)/2 = 1$  (0.2 points).



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|----------------------------------------------------|-----------|
| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

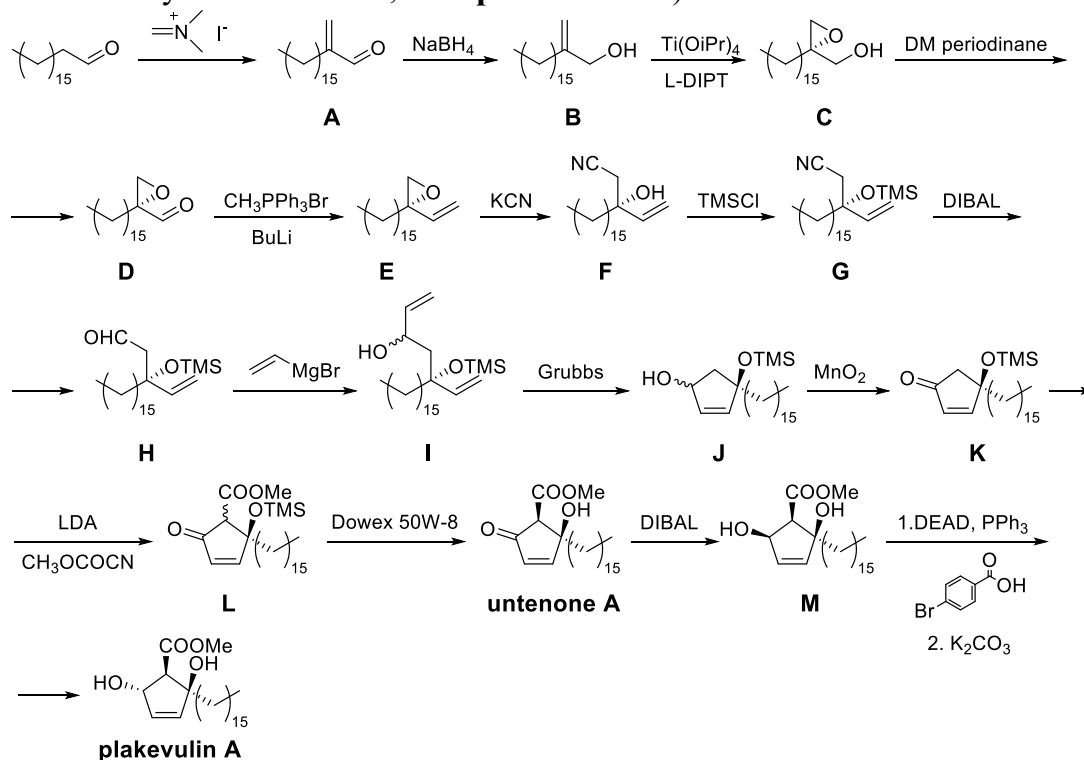
The transfer of electrons between the  $\pi_d$ -orbitals of M and the molecular orbitals of H<sub>2</sub> can proceed in two ways:  $\sigma \rightarrow \pi_d$  and  $\pi_d \rightarrow \sigma^*$  (0.15 points for each scheme):  
(1 point in total)

## SECTION V. ORGANIC CHEMISTRY

### Problem 1 (author Zima A.M.)

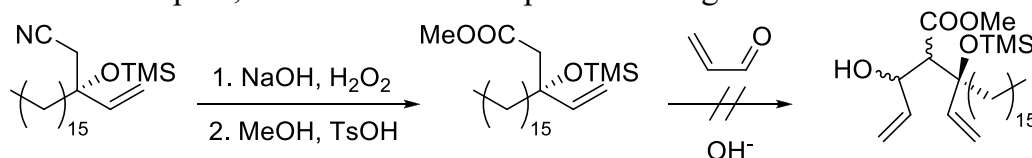
1. At the first step of the synthesis, the starting octadecanal reacts with an Eschenmoser salt to form the unsaturated aldehyde **A**, which, on reduction with sodium borohydride, affords the alcohol **B**. An asymmetric Sharpless epoxidation is the next step. Treatment of the resulting epoxide **C** with Dess–Martin periodinane followed by Wittig methylenation of the product **D** furnishes the corresponding vinyl epoxide **E**. Regioselective cyanation reaction of epoxide **E** is accomplished by treatment with potassium cyanide to give the cyanide **F** which, on protection of the *tert*-alcohol with TMSCl, provides the silyl ether **G**. The cyanide **G** is treated with DIBAL to give the aldehyde **H**, which on further treatment with vinylmagnesium bromide in THF provides an inseparable diastereomeric mixture of the allyl alcohol (product **I**). The next stage is the ring-closing metathesis reaction. Oxidation of an allylic alcohol in **J** with manganese oxide gives the cyclopentenone **K**, which is further subjected to nucleophilic methoxycarbonylation with LDA and methyl cyanocarbonate to give  $\beta$ -ketoester **L** as a 5:1 diastereomeric mixture. Deprotection of the TMS group and epimerization at the C-5 position of **L** with Dowex 50W-8 furnishes **untenone A**, further treated with DIBAL to give the allyl alcohol **M**. The Mitsunobu reaction of **M**, followed by hydrolysis of the corresponding benzoate under alkaline conditions affords **plakevulin A**.

(0.75 points for the structure of each of **A–M** and **untenone A**, –0.25 points for each error in the stereochemistry of the reaction; 10.5 points in total)

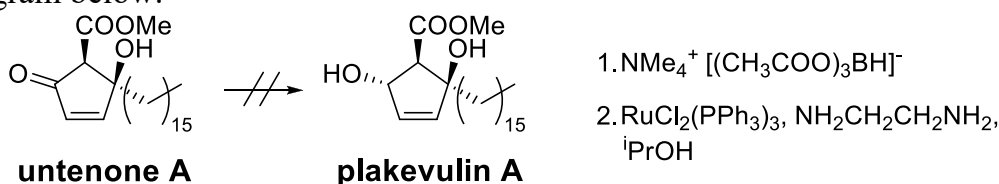


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| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

2. The authors of the article actually tried to obtain **untene A** from **G** according to the given part of the transformation scheme. At the first step, hydrolysis of the cyanide **G** under alkaline reaction conditions followed by methylation of the resulting carboxylic acid was carried out to give the methyl ester. Although aldol reaction with acrolein under various reaction conditions was attempted, none of the desired product was generated.



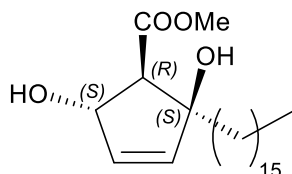
It was also impossible to obtain **plakevulin A** in one step from **untene A**. The authors tested the conditions for the 1,2-reduction of the **untene A** conjugated system shown in the diagram below.



Thus, the following options are taken into account: **I** – alkaline hydrolysis, **II** – formation of the methyl ester, **III** – condensation with acrolein under basic conditions, **IV** – reduction with the hydride reducing agents.

(0.75 points for each correct reagent/condition **I–IV**; **3 points** in total)

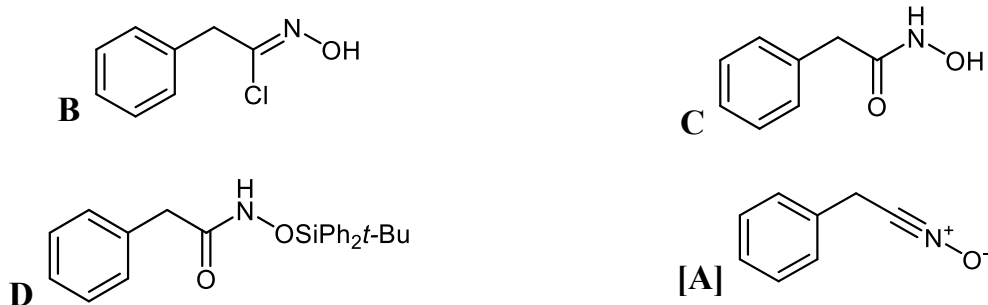
3.



(1.5 points for identifying all configurations, –1 point for 1 error, 0 points for 2 or 3 errors; **1.5 points** in total)

### Problem 2 (author Romashov L.V.)

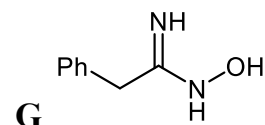
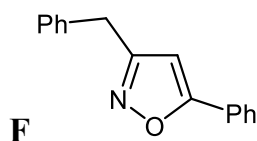
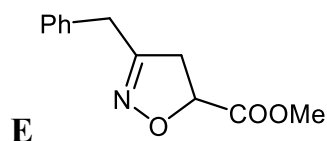
1. The problem is devoted to the chemistry of nitrile oxides. The first scheme shows three approaches to the generation of nitrile oxides: Huisgen protocol (through the chlorination of aldoximes), Mukayama protocol (through the dehydration of nitroalkanes) and Carreira protocol (through the activation of *O*-silylhydroxamic acids).



(0.25 points for each structure; **1 point** in total)

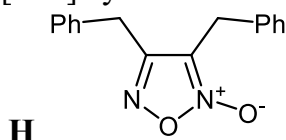
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| 2 <sup>nd</sup> theoretical exam                   | Solutions |

2. Nitrile oxides can act as 1,3-dipoles and electrophiles.



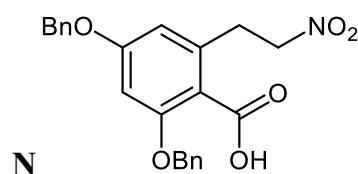
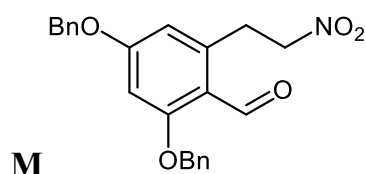
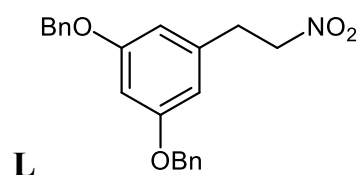
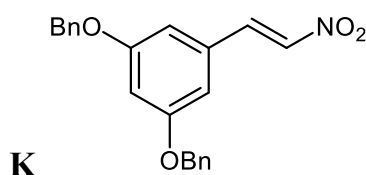
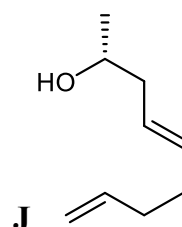
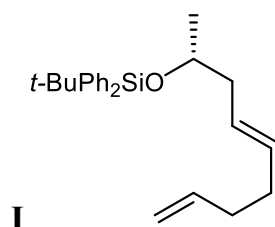
(0.5 points for each structure, 0.25 points if regioselectivity of cycloaddition is incorrect;  
**1.5 points** in total)

3. Nitrile oxides can dimerize via [3+2] cycloaddition to form furoxans.

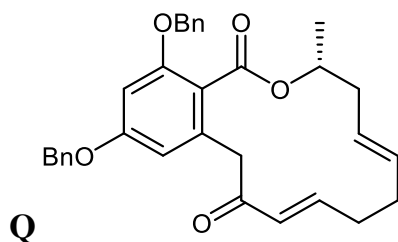
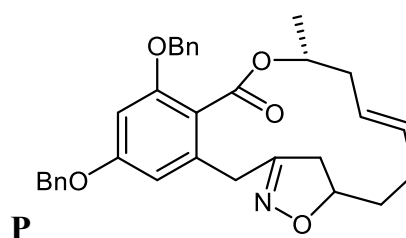
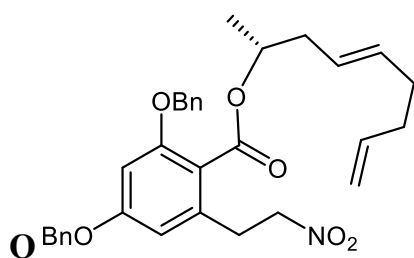


(**1 point** in total, 0.5 points if regioselectivity of cycloaddition is incorrect)

4. In the first part of the synthesis of **monocillin II**, the aldehyde is olefinated according to Julia–Kocienski, followed by silyl deprotection. In the second part of the synthesis, the aromatic aldehyde undergoes a Henri reaction, followed by dehydration to form nitroalkene **K**. Next, the nitroalkene is reduced with sodium borohydride to a nitroalkane. The resulting compound **L** undergoes Vilsmeier–Haack formylation, followed by Pinnick oxidation to the carboxylic acid **N**. Next, the ester **O** is obtained from the acid **N** and alcohol **J**. Under the action of phenyl isocyanate, nitrile oxide is generated (Mukayama protocol), which immediately undergoes intramolecular cycloaddition to the double bond to form **S**. Molybdenum carbonyl opens isoxazoline to form  $\beta$ -hydroxyketone, which is further dehydrated by the  $\text{MsCl}/\text{NEt}_3$  system. At the last step, the benzyl groups are removed from the resorcinol fragment.

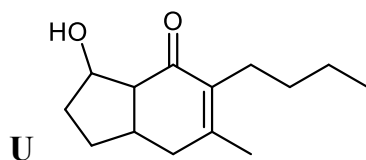
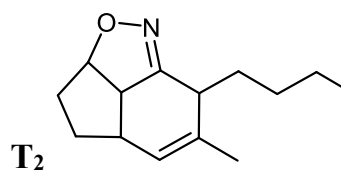
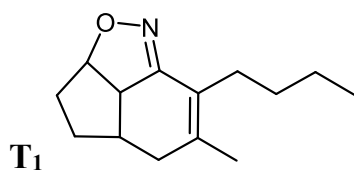
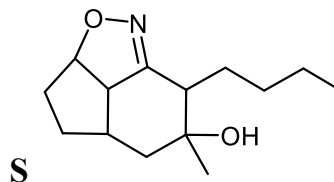
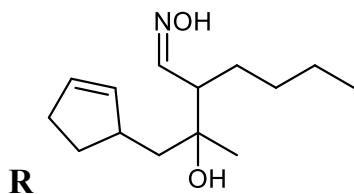


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| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |



(1 point for each structure; **9 points** in total)

**5.** At the first step, double deprotonation of the aldoxime occurs, followed by attack of the resulting C-nucleophile at the carbonyl group of the ketone. Under the action of sodium hypochlorite, the aldoxime **R** is chlorinated and HCl immediately eliminates (NaClO solution is very alkaline), giving nitrile oxide, which undergoes intramolecular [3+2] cycloaddition. Dehydration using SOCl<sub>2</sub>/Py occurs non-regioselectively and gives two regioisomers **T<sub>1</sub>** and **T<sub>2</sub>**. During hydrogenation on Raney nickel, the isoxazoline ring opens and the double bond migrates, giving the compound **U**.



(0.5 points for each structure; **2.5 points** in total)

|                                                    |           |
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| 58 <sup>th</sup> International Mendeleev Olympiad, |           |
| 2 <sup>nd</sup> theoretical exam                   | Solutions |

### Problem 3 (author Romashov L.V.)

1. The rate of solvolysis increases as the polarity of a solvent increases. Ethanol is the least polar and water is the most polar solvent in this series:  $\text{H}_2\text{O}$  (335000) >  $\text{HCOOH}$  (12200) >  $\text{CH}_3\text{OH}$  (9) >  $\text{C}_2\text{H}_5\text{OH}$  (1).

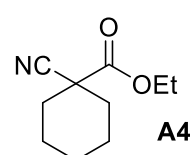
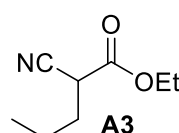
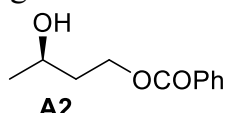
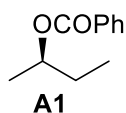
(0.25 points for each correct match; **1 point in total**)

2. Primary derivatives are characterized by bimolecular substitution reactions, while tertiary derivatives by monomolecular ones. Hydroxyl groups in an acidic environment are protonated and the corresponding alkyloxonium ions enter into a substitution reaction. The halide and azide ions are anionic nucleophiles, while water and ammonia are neutral. We obtain the following picture of the charge distribution in the transition state and the effect of increasing the solvent polarity:

| Reaction | Mechanism              | Change in charge distribution in the transition state | Reaction rate change with increasing the solvent polarity |
|----------|------------------------|-------------------------------------------------------|-----------------------------------------------------------|
| 1        | $\text{S}_{\text{N}}2$ | Separation of charges                                 | Increase                                                  |
| 2        | $\text{S}_{\text{N}}2$ | Neutralization of charges                             | Decrease                                                  |
| 3        | $\text{S}_{\text{N}}1$ | Separation of charges                                 | Increase                                                  |
| 4        | $\text{S}_{\text{N}}1$ | Charge distribution                                   | Decrease                                                  |
| 5        | $\text{S}_{\text{N}}2$ | Charge distribution                                   | Decrease                                                  |
| 6        | $\text{S}_{\text{N}}2$ | Charge distribution                                   | Decrease                                                  |

(0.5 points for each completely correct line, 0 points for any error in a line; **3 points in total**)

3. Based on the stereochemistry of the Mitsunobu reaction and the  $^1\text{H}$  NMR spectral data, **A1–A4** have the following structures:



Reaction 8) is regioselective, reaction 7) is stereoselective.

(0.25 points for each structure, regioselectivity of 8) and stereoselectivity of 7), 0.25 points penalty for indicating additional reactions; **1.5 points in total**)

4. Taking into account the structures of the reagents, additional information and IR spectral data, the synthesis of (–)-Spongidepsin is described by the scheme:

