

SECTION I. ANALYTICAL CHEMISTRY

Problem 1 (author D.V. Kandaskalov)

1. From the equation $\lambda = |z| \cdot \mu \cdot F$ we can calculate the molar conductivity:

$$\lambda(\text{H}^+) = z \cdot \mu \cdot F = 1 \cdot 3.63 \cdot 10^{-7} \cdot 96500 = 35.03 \text{ mS} \cdot \text{m}^2 / \text{mol}$$

$$\lambda(\text{OH}^-) = z \cdot \mu \cdot F = 1 \cdot 2.07 \cdot 10^{-7} \cdot 96500 = 19.98 \text{ mS} \cdot \text{m}^2 / \text{mol}$$

(0.5 points for each value, total 1 point).

The autoprotolysis of water gives the next concentration of ions: $[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ M}$, so:

$$\begin{aligned} \sigma &= \sum \lambda_i \cdot c_i = \lambda_{\text{H}^+} \cdot c_{\text{H}^+} + \lambda_{\text{OH}^-} \cdot c_{\text{OH}^-} = (\lambda_{\text{H}^+} + \lambda_{\text{OH}^-}) \cdot 10^{-7} \cdot 10^3 = \\ &= (35.03 \cdot 10^{-3} + 19.98 \cdot 10^{-3}) \cdot 10^{-7} \cdot 10^3 = 5.50 \cdot 10^{-6} \text{ S/m} \end{aligned}$$

The concentration was taken in mol/m^3 , and the molar conductivity in $\text{S} \cdot \text{m}^2 / \text{mol}$ (1 point).

2. During the titration we add the ions Me^+ and OH^- to H^+ and A^- . The ions OH^- and H^+ form H_2O . Thus, before the equivalent point we have: Me^+ , A^- , H^+ ; in the equivalent point: Me^+ , A^- ; after the equivalent point: Me^+ , A^- , OH^- (0.5 points for each answer, total 1.5 points).

3. The nature of ions is changing after the equivalence point, thus the conductivity changes also. The intersection of the two lines corresponds to the equivalence point ($V_{\text{eq}} = 2.75 \text{ mL}$). From the graph we can determine that conductivity at the equivalence point is equal to 0.30 S/m. This conductivity is related to Me^+ and A^- ions. Thus:

$$\begin{aligned} \sigma &= \sum \lambda_i \cdot c_i = \lambda_{\text{M}^+} \cdot c_{\text{M}^+} + \lambda_{\text{A}^-} \cdot c_{\text{A}^-} = (\lambda_{\text{M}^+} + \lambda_{\text{A}^-}) \cdot \frac{c_{\text{MOH}} \cdot V_{\text{eq}}}{V_{\text{HA}} + V_{\text{eq}}} \Rightarrow \\ \lambda_{\text{M}^+} + \lambda_{\text{A}^-} &= \frac{\sigma}{c_{\text{MOH}} \cdot V_{\text{eq}}} \cdot (V_{\text{HA}} + V_{\text{eq}}) = \frac{0.300}{0.500 \cdot 10^3 \cdot 2.75 \cdot 10^{-6}} \cdot 52.75 \cdot 10^{-6} = \\ &= 11.51 \cdot 10^{-3} \text{ S} \cdot \text{m}^2 / \text{mol} \end{aligned}$$

Comparing the sum of molar conductivities with possible combinations of “cation–anion” we can see that there are only two combinations: (Na^+ , ClO_4^-) with $\Sigma\lambda = 11.53$ or (Li^+ , Cl^-), with $\Sigma\lambda = 11.49$.

Let analyze the initial point ($V = 0 \text{ mL}$). There are only two ions: H^+ and A^- . We can calculate the sum of molar conductivities:

$$\begin{aligned} \sigma &= \sum \lambda_i \cdot c_i = \lambda_{\text{H}^+} \cdot c_{\text{H}^+} + \lambda_{\text{A}^-} \cdot c_{\text{A}^-} = (\lambda_{\text{H}^+} + \lambda_{\text{A}^-}) \cdot c_{\text{HA}} \Rightarrow \\ \lambda_{\text{H}^+} + \lambda_{\text{A}^-} &= \frac{\sigma}{c_{\text{HA}}} = \frac{\sigma}{c_{\text{MOH}} \cdot V} \cdot V_{\text{HA}} = \frac{1.175}{0.500 \cdot 10^3 \cdot 2.75 \cdot 10^{-6}} \cdot (50 \cdot 10^{-6}) = 42.73 \text{ S} \cdot \text{m}^2 / \text{mol} \\ \Rightarrow \lambda_{\text{A}^-} &= 42.73 - 35.03 = 7.70 \text{ S} \cdot \text{m}^2 / \text{mol} \end{aligned}$$

The obtained value could correspond to Cl^- ($\lambda = 7.63$) or to Br^- ($\lambda = 7.80$). As we have already shown that Br^- is not possible, then the acid is HCl . In this case, the alkali is LiOH (2 points for each of both compounds, total 4 points).

4. After the equivalence point the solution conductivity depends on three ions: Li^+ , Cl^- and OH^- :

$$\begin{aligned}
 \sigma &= \sum \lambda_i \cdot c_i = \lambda_{\text{Li}^+} \cdot c_{\text{Li}^+} + \lambda_{\text{Cl}^-} \cdot c_{\text{Cl}^-} + \lambda_{\text{OH}^-} \cdot c_{\text{OH}^-} = \\
 &= \lambda_{\text{Li}^+} \cdot \frac{c_{\text{LiOH}} \cdot V}{V_{\text{HA}} + V} + \lambda_{\text{Cl}^-} \cdot \frac{c_{\text{HA}} \cdot V_{\text{HA}}}{V_{\text{HA}} + V} + \lambda_{\text{OH}^-} \cdot \frac{c_{\text{LiOH}} \cdot (V - V_{\text{eq}})}{V_{\text{HA}} + V} = \\
 &= 3.86 \cdot 10^{-3} \cdot \frac{0.500 \cdot 10^3 \cdot 6 \cdot 10^{-6}}{(50 + 6) \cdot 10^{-6}} + 7.63 \cdot 10^{-3} \cdot \frac{0.0275 \cdot 10^3 \cdot 50 \cdot 10^{-6}}{(50 + 6) \cdot 10^{-6}} + \\
 &\quad + 19.98 \cdot 10^{-3} \cdot \frac{0.500 \cdot 10^3 \cdot (6 - 2.75) \cdot 10^{-6}}{(50 + 6) \cdot 10^{-6}} = 0.974 \text{ S/m}
 \end{aligned}$$

The concentration is given in mol/m³, volume in m³ and molar conductivity in S·m²/mol (2.5 points).

5. Instead of drawing the graph $\sigma = f(V)$ we can calculate $\Delta\sigma/\Delta V$:

σ	0.600	0.489	0.377	0.267	0.233	0.278	0.324	0.489	0.655	0.985
$\Delta\sigma/\Delta V$	0.111	0.112	0.110	0.034	-0.045	-0.046	-0.165	-0.166	-0.165	-0.164
V, mL	0	1	2	3	4	5	6	7	8	10

We observe that the curve consists of 3 linear segments. First segment finishes between 3 and 4 mL (if the equivalence point would be exactly at 3 or 4 mL, we would not have the intermediate value $\Delta\sigma/\Delta V = -0.034$). The second segment finishes and the third one starts at 6.0 mL.

The first segment corresponds to the titration of strong acid (HCl), and at that time the dissociation of weak acid can be neglected. The second segment corresponds to the titration of the weak acid. The equivalence point $V_{\text{eq}} = 6.0$ mL is related to the titration end-point. As the curve has only two inflection points and the first one corresponds to HCl, thus, only one proton of the weak acid is titrated (1 point).

It is interesting to notice that one of the advantages of the conductometry titration, compared to other titration methods, is the possibility to calculate the concentration of a strong and a weak acid from one titration. This method also permits titrating very weak acids.

6. Let us calculate the concentrations of both acids. The first equivalence point is between 3 and 4 mL. To find the precise value for this point, we have to find the equation of two lines, and their intersection will give us this equivalence volume. For the first line: $y = kx + b$, $k = \Delta\sigma/\Delta V = -0.111$, and $y = b = 0.600$ when $x = 0$. Thus, the equation of line is $y = -0.111x + 0.600$. We can find the equation of the second line using values for $V = 4$ mL and 5 mL: $k = 0.0455$, thus, $0.233 = 0.0455 \cdot 4 + b \Rightarrow b = 0.051$. The equation of the second line is: $y = 0.0455x + 0.051$. If we set equal the equations of both lines, we will obtain x which corresponds to the first equivalence point: $-0.111x + 0.600 = 0.0455x + 0.051$, thus $x = 3.50$ mL (1 point).

So the volume of the alkali solution used for the titration of the strong acid is $V_1 = 3.5$ mL, then the volume used for the titration of the weak acid is $V_2 = 6.0 - 3.5 = 2.5$ mL (1 point). The concentrations of acids are:

50 th International Mendeleev Olympiad, 2016	Moscow
2 nd theoretical tour	Solutions

$$c_{\text{HCl}} \cdot V_{\text{solution}} = c_{\text{KOH}} \cdot V_1 \Rightarrow$$

$$c_{\text{HCl}} = \frac{c_{\text{KOH}} \cdot V_1}{V_{\text{solution}}} = \frac{0.600 \cdot 3.5}{100} = 0.014 \text{ M}$$

$$c_{\text{H}_n\text{B}} \cdot V_{\text{solution}} = c_{\text{KOH}} \cdot V_2 \Rightarrow$$

$$c_{\text{H}_n\text{B}} = \frac{c_{\text{KOH}} \cdot V_2}{V_{\text{solution}}} = \frac{0.600 \cdot 2.5}{100} = 0.010 \text{ M}$$

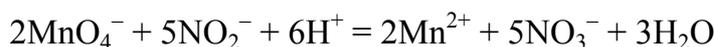
As the initial solution was diluted 5-fold, the initial concentrations of HCl and H_nB are five times larger: 0.070 and 0.050 M, respectively (1 point for each concentration, 4 points total).

Problem 2 (authors A.S. Dubenskiy, M.K. Beklemishev)

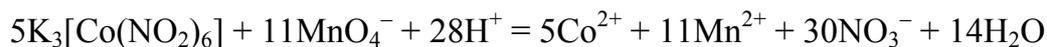
1. a) Formation of potassium hexanitritocobaltate(III) (1 point):



б) Reaction between permanganate and nitrite ions in acidic medium (1 point):



в) Reaction between permanganate and hexanitritocobaltate(III) (2 points):



2. Calculation of the amount of cobalt salt in analyte solution using titration results:

$n_{\text{Co}} = 5/11 \times c(\text{MnO}_4^-) \times V(\text{MnO}_4^-) = 5/11 \times 0.0500 \times 13.75 / 1000 = 3.125 \cdot 10^{-4} \text{ mol}$
in the 10.00-mL aliquote. In a 100-mL flask this amount is 10 times higher. Thus, the concentration of cobalt salt in initial solution:

$$c(\text{Co(II)}) = 3.125 \cdot 10^{-4} \text{ mol} \times 10 / 0.1 \text{ L} = 0.03125 \text{ M (2 points)}.$$

3. All mentioned factors are right (a, b, c, d, e) (0.4 points for each right answer, total 2 points).

4. Calculation of salt solubility in the stock solution:

a) concentration of added potassium salt:

$$c(\text{K}^+) = 5.0 \text{ mL} \times 0.20 \text{ M} / (100 + 2 + 5) \text{ mL} = 9.35 \cdot 10^{-3} \text{ M (0.5 points)};$$

б) concentration of the complex ion calculated using the solubility product value given:

$$[\text{Co}(\text{NO}_2)_6]^{3-} = K_s / [\text{K}^+]^3 = 4.3 \cdot 10^{-10} / (9.35 \cdot 10^{-3})^3 = 5.3 \cdot 10^{-4} \text{ M (1 point)};$$

в) solubility, g/L:

$$S = [\text{Co}(\text{NO}_2)_6]^{3-} \times M(\text{K}_3[\text{Co}(\text{NO}_2)_6]) = 5.3 \cdot 10^{-4} \text{ M} \times 374 \text{ g/mol} = 0.20 \text{ g/L (0.5 point, total 2 points)}.$$

50 th International Mendeleev Olympiad, 2016	Moscow
2 nd theoretical tour	Solutions

5. The complex cobalt salt precipitate partially dissolves in the stock solution, for which reason cobalt(III) passes to the titrated solution incompletely. This fact determines the titration error. According to the titration results, the concentration of cobalt(III) was found to be $3.125 \cdot 10^{-2}$ M. Using the calculated solubility of $[\text{Co}(\text{NO}_2)_6]^{3-}$ of $5.3 \cdot 10^{-4}$ M, we can calculate the ratio of the amount of cobalt in the stock solution to that one in the initial solution:

$$\Delta = (S \times V_{\text{final}}) / (c_{\text{Co}} \times V_{\text{initial}}) = (5.3 \cdot 10^{-4} \text{ M} \times 107 \text{ mL} / (3.125 \cdot 10^{-2} \text{ M} \times 100 \text{ mL})) \times 100\% = 1.8\% \text{ (1 point)}.$$

Thus, the error is 1.8% of the concentration determined.

6. Solubility of the precipitate in the washing solution (0.01M KNO_3) is:

$$S = [\text{Co}(\text{NO}_2)_6]^{3-} = K_S / [\text{K}^+]^3 = 4.3 \cdot 10^{-10} / (0.01)^3 = 4.3 \cdot 10^{-4} \text{ M}.$$

The amount of precipitate dissolved in volume V_y (L) of the washing solution is determined as $V_y \cdot S$ (mol). The titration error is proportional to this value. The result of titration is underestimated and the titration error is negative (1 point).

The volume of the stock solution captured by the precipitate is $\frac{1}{2}m$ (mL, if the density is equal to 1 g/mL and mass is taken in grams), or $0.0005m$ (liters). The stock solution contained 0.2M nitrate (see p. 1), but $6 \times 0.03125 = 0.1875\text{M}$ of that amount was used to precipitate potassium hexanitritocobaltate. Therefore, the concentration of nitrite remained is 0.0125M. Thus, the mass m of precipitate captures $0.0005m \times 0.0125 = 6.25 \cdot 10^{-6} \cdot m$ mol of nitrite.

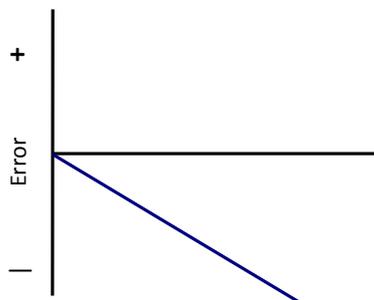
If each milliliter of the washing solution removes 1% of the captured stock solution volume, then the amount of nitrite remained is $6.25 \cdot 10^{-6} \cdot m \cdot (1 - 0.01 \cdot V_y \cdot 1000)$ mol. So the obtained titration result is overestimated and the error is positive (1 point). Moreover, this error is decreasing with volume V_y increase, reaching zero at a certain moment (when all nitrite is removed from the precipitate). Mass of the precipitate is determined in terms of the concentration of cobalt: $m = c_{\text{Co}} \times V \times M(\text{K}_3[\text{Co}(\text{NO}_2)_6]) \times 1.017 = 0.03125 \text{ M} \times 0.1 \text{ L} \times 374 \text{ g/mol} \times 1.017 = 1.19 \text{ g}$.

The minimal error equal to zero is achieved if positive and negative components of the error mentioned above are counterbalanced: $V_y \cdot 4.3 \cdot 10^{-4} = 6.25 \cdot 10^{-6} \cdot 1.19 \cdot (1 - 0.01 \cdot V_y \cdot 1000)$.

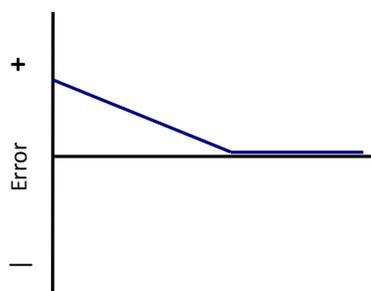
Solving the equation one obtains $V_y = 0.0147 \text{ L}$ (15 mL) (0.5 point, total 2.5 points).

The graphic dependences of titration error on the volume of washing solution used are shown below (0.5 point for each, total 1.5 points):

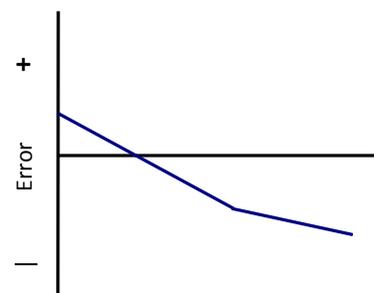
Error caused by the dissolution of precipitate



Error caused by the capture of nitrite ions from the stock solution



Total error



Problem 3 (author V.N. Nikitina)

1. As the wave height is directly proportional to the concentration, one can calculate the lead concentration:

$$c_x = \frac{c_2 \times V_2 \times h_1}{h_2 \times (V_2 + V_1) - h_1 \times V_1} = \frac{3 \text{ mg/L} \times 4.5 \text{ mL} \times 5 \text{ mm}}{8.1 \text{ mm} \times 14.5 \text{ mL} - 5 \text{ mm} \times 10 \text{ mL}} = 0.001 \text{ g/L (1 point).}$$

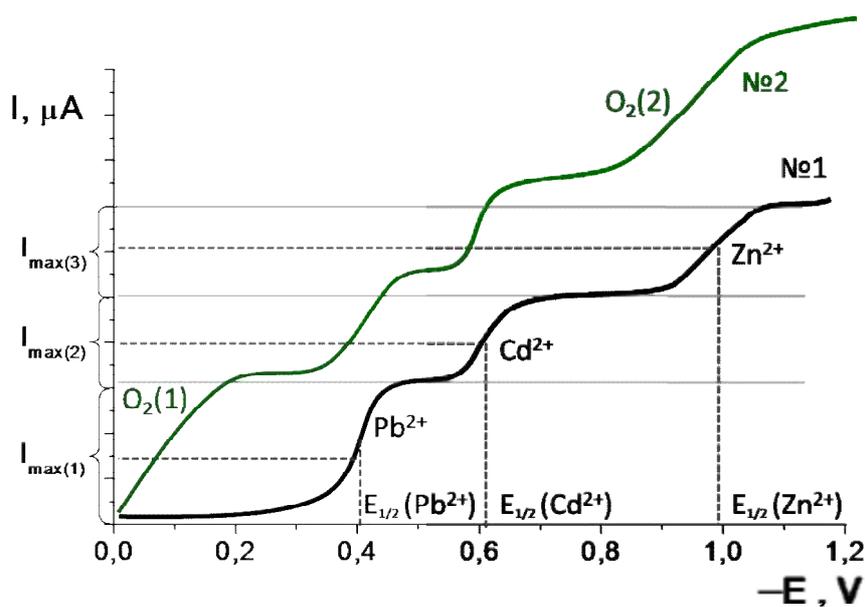
The corresponding unknown mass is $m_x = 0.001 \times 100 = 0.10 \text{ mg}$ (1 point).

2. a) The concentration of Pb^{2+} in its saturated solution is:

$$c = 5.0 \times 43.2 / 13.6 = 15.9 \text{ mM (1 point).}$$

$$K_S(\text{PbCl}_2) = [\text{Pb}^{2+}] \cdot [\text{Cl}^-]^2 = 15.9 / 1000 \times (2 \times 15.9 / 1000)^2 = 1.6 \cdot 10^{-5} \text{ (1 point).}$$

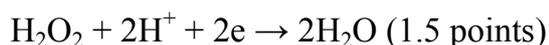
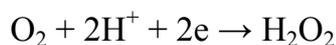
3. a) The required curves № 1 and № 2 are shown in the graph:



(1 point for each curve)

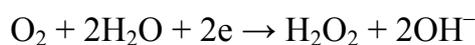
50 th International Mendeleev Olympiad, 2016	Moscow
2 nd theoretical tour	Solutions

b) Oxygen dissolved in the solution reduces at the dropping mercury electrode under potentials shown in the table (−0.1 and −0.9 V) resulting in two corresponding waves on the polarogram. This allows proposing that reduction of oxygen proceeds in two stages: the first is the reduction of oxygen to hydrogen peroxide that further reduces to water on the second stage. In the acidic solution (a):



(1 point is given for the full half-reaction written in one stage: $\text{O}_2 + 4\text{H}^+ + 4\text{e} \rightarrow 2\text{H}_2\text{O}$)

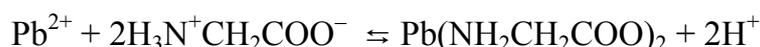
In the basic medium (b):



(1 point is given for the full half-reaction written in one stage: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e} \rightarrow 4\text{OH}^-$).



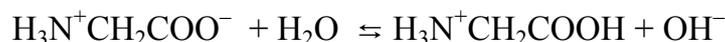
or



(reactions of the zwitterionic or anionic form of glycine are accepted).

$$\beta_2 = \frac{[\text{Pb}(\text{NH}_2\text{CH}_2\text{COO})_2]}{[\text{Pb}^{2+}][\text{NH}_2\text{CH}_2\text{COO}^-]^2} \text{ (0.5 points);}$$

Competitive reactions: in a neutral medium glycine exists in its zwitterionic form $\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-$. The protonation of this ion makes it less reactive with respect to the complexation with metal ions:



Moreover, the zwitterion dissociates as a weak acid:



Lead(II) cation may be hydrolyzed:



б) Expressing $[\text{Pb}^{2+}]$ from the equation for the stability constant gives:

$$E_{1/2}(\text{Pb}^{2+}) + 0.059/2 \cdot \lg[\text{Pb}^{2+}] = E_{1/2}(\text{Pb}^{2+}) + 0.059/2 \cdot \lg\left(\frac{[\text{Pb}(\text{gly})_2]}{\beta_2 \times [\text{gly}]^2}\right).$$

On the other hand, according to the equation given in the text of the task (p. 4) we have:

50 th International Mendeleev Olympiad, 2016	Moscow
2 nd theoretical tour	Solutions

$$E_{1/2}(\text{Pb}^{2+}) + 0.059/2 \cdot \lg[\text{Pb}^{2+}] = E_{1/2}(\text{Pb}(\text{gly})_2) + 0.059/2 \cdot \lg[\text{Pb}(\text{gly})_2].$$

Equating the right parts of both equations one obtains:

$$E_{1/2}(\text{Pb}(\text{gly})_2) = E_{1/2}(\text{Pb}^{2+}) - 0.059/2 \cdot \lg\beta_2 - 0.059 \lg[\text{gly}] \text{ (2 points), and}$$

$$E_{1/2}(\text{Pb}(\text{gly})_2) = -0.41 - 0.0295 \cdot \lg(3.2 \cdot 10^7) - 0.059 \cdot \lg 0.5 = -0.61 \text{ V (0.5 points).}$$

Thus, the complex is reduced under more negative potential, which is more difficult than reducing the aqua-ion ($E_{1/2}(\text{Pb}^{2+}) = -0.41 \text{ V}$, p. 3) (0.5 points).

SECTION II. INORGANIC CHEMISTRY

Problem 1 (authors G.M. Rozantsev, V.E. Shvartsman)

1. Addition reaction $\text{MeO}_n + \text{NaO}_n = \text{NaMeO}_{2n}$ (0.5 points), then

$$\frac{4.098}{23 + A_{\text{Me}} + 32n} = \frac{3.273}{A_{\text{Me}} + 16n}; \quad A_{\text{Me}} = \frac{23 + 11.96n}{0.2521} \quad (0.5 \text{ points}) \text{ when } n = 2; \quad \text{Me} - \text{Re} \quad (0.5 \text{ points}),$$

B – NaReO_4 (0.5 points, in total 2 points).

2. There are two types of ligands in **C**: first – Me_2PhP , second Cl^- since the complex is

electroneutral. The ratio $\nu(\text{Re}):\nu(\text{Me}_2\text{PhP}) = \frac{4.098}{218.2} : \frac{6.210}{138} = 1:3$, if $\text{Re}(3+)$, so $\nu(\text{Cl}^-) = 3$.

C – $[\text{ReCl}_3(\text{Me}_2\text{PhP})_3]$ (1 point), its mass $m = \frac{4.098 \cdot 0.8 \cdot 706.6}{218.2} = 8.479$ (g) (0.5 points).

For **D**: $\nu(\text{D}) = \frac{8.479 \cdot 0.5}{706.6} = 0.006$ (mole); $M_{\text{D}} = \frac{4.408}{0.006} = 734.7$ (g/mole); $M_{\text{D}} - M_{\text{E}} = 734.7 - 706.6 =$

28.1 (g/mole), that corresponds 1 mole CO. **D** – $[\text{ReCl}_3\text{CO}(\text{Me}_2\text{PhP})_3]$ (1 point).

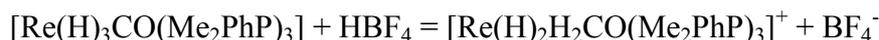
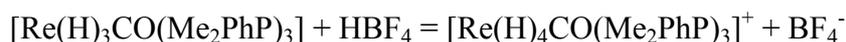
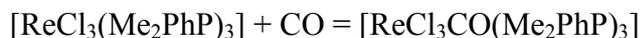
For **E** $\nu(\text{Re}):\nu(\text{P}):\nu(\text{O}) = \frac{29.5}{186.2} : \frac{14.73}{31} : \frac{2.53}{16} = 1:3:1$. So $\text{ReCO}(\text{Me}_2\text{PhP})_3$ remained in **E**, and 3Cl^-

were substituted by 3L^- . $w_{3\text{L}} = 100 - 29.5 - \frac{14.73 \cdot 138}{31} - \frac{2.53 \cdot 28}{16} = 0.50\%$. At such low value, the

L^- could be only H^- . **E** – $[\text{Re}(\text{H})_3\text{CO}(\text{Me}_2\text{PhP})_3]$ (1 point, in total 3.5 points).

3. G^+ , J^+ and BF_4^- are formed in solution (the conductivity like in the solution of Li^+ , AlH_4^-). In the composition of **J** there are four ligands H^- (one band at 1832 cm^{-1} in the IR-spectrum), and in the composition of **G** there are 2H^- (band 1838 cm^{-1}) and H_2 (band 2692 cm^{-1} , which is shifted by the reason of coordination to $\text{Re}(+3)$ in comparison with 4159 cm^{-1} of the gaseous H_2). **G** – $[\text{Re}(\text{H})_2\text{H}_2\text{CO}(\text{Me}_2\text{PhP})_3]^+$ (1 point), **J** – $[\text{Re}(\text{H})_4\text{CO}(\text{Me}_2\text{PhP})_3]^+$ (1 point, in total 2 points).

4. $\text{NaReO}_4 + 3\text{Me}_2\text{PhP} + 8\text{HCl} = [\text{ReCl}_3(\text{Me}_2\text{PhP})_3] + 2\text{Cl}_2 + \text{NaCl} + 4\text{H}_2\text{O}$



(0.5 points for each reaction, in total 2.5 points).

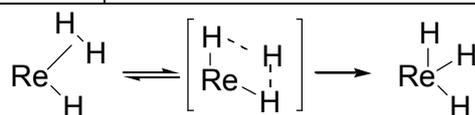
5. $\Delta G^0 = \Delta H^0 - T\Delta S^0 = -4600 + 208 \cdot 10 = -2520$ (J/mole) (1 point)

$$\Delta G^0 = -RT \ln K; \quad -2520 = -8.314 \cdot 208 \ln K \quad K = 4.294 \quad (1 \text{ point})$$

$$K = \chi_{\text{J}}/\chi_{\text{G}} = (1 - \chi_{\text{G}})/\chi_{\text{G}} = 4.294 \quad \chi_{\text{G}} = 0.8111 \quad (81.11\%) \quad (0.5 \text{ балла}) \quad \chi_{\text{J}} = 18.89\%$$

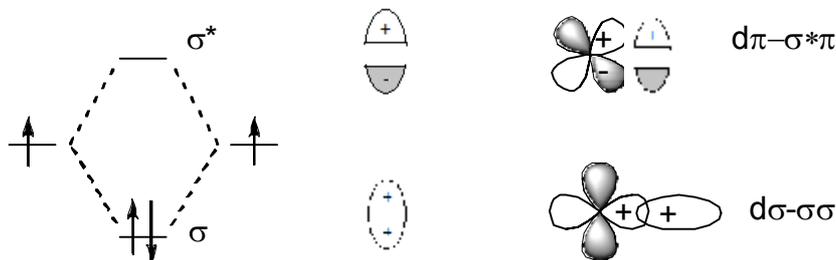
(2.5 points in total)

6. (1 point)



Tree-centered bond H---H---H, with bond distance $l = 0.138$ nm, that lies between the distance of two H in hydride (0.160 nm) and bond H–H in H₂ (0.084 nm).

7.



(0.5 points for each, in total 1.5 points).

Problem 2 (author D.V. Kandaskalov)

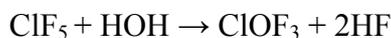
1. Let's start to resolve the problem from compound **A**. Based on the mass composition we could determine the relative molecular mass of **A**:

$$M(A) = \frac{n \cdot A_r(F) \cdot 100\%}{\omega_F} = \frac{n \cdot 19 \cdot 100\%}{34.86} = 54.5n$$

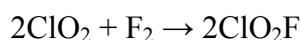
Knowing that the fluor in **A** has molecular weight $19n$ g/mol, the other element has molecular mass $35.5n$ g/mol, which corresponds to chlorine (when $n=1$). So **A** – ClF (0.55 point). Thus, the compound **B** could be ClF₃ or ClF₅ (the formation of ClF₇ is sterically difficult). We should determine at first the molecular formula of **Y**₁ to know the molecular formula of **B**:

$$M(Y_1) = \frac{n \cdot A_r(F) \cdot 100\%}{\omega_F} = \frac{n \cdot 19 \cdot 100\%}{52.53} = 36.17n$$

As molecular mass of **Y**₁ should be integer or half-integer number thus n should be multiple of 3. If $n=3$ then $M(Y_1)=108.5$ g/mol. Thus, this compound contains 3 atoms of fluor, odd number of Cl atoms (in this case maximum 1 atom) and remaining 16 g/mol corresponds well to one oxygen atom. So **Y**₁ – ClOF₃ (1 point). The central atom is Cl with oxidation number +5, so **B** - ClF₅:



The hydrolysis of **Y**₁ gives **Y**₂ which contains fluorine (taking into account the reaction **D**→**Y**₂). As this compound is the product of ClOF₃ hydrolysis, only one variant is possible for **Y**₂ – ClO₂F. In this case **D** – ClO₂ (oxidation number +4):



Thus **C**, **E** are also chlorine oxides.

Now, we could determine the molecular formula of **X**, as we know that it disproportionates on equimolar quantities of ClO₂F and ClF. Thus **X** – ClOF according to the reaction:



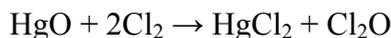
50 th International Mendeleev Olympiad, 2016	Moscow
2 nd theoretical tour	Solutions

The oxidation number of Cl in **X** is +3.

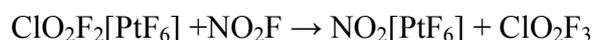
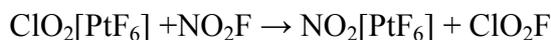
The compound **E** – is the chlorine oxide where Cl has the oxidation number bigger than +4. Knowing that the oxidation number cannot be +5, it remains two possibilities +6 and +7.

Also we know that **F** – is the simple compound, thus it is Cl₂. The compound **C** has the chlorine atom in the same oxidation level then **A** i.e. +1. so **C** - Cl₂O.

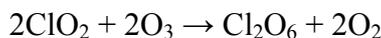
The reaction of **C** synthesis **C**:



Now, we are going to the right part of the scheme: oxidation of **Y**₂ by PtF₆. The molecular formula of **G** according to the reaction of interchange of cations is: ClO₂[PtF₆]. Taking into account that **G** and **H** are formed in the equimolar quantities - **H** should contain 2 atoms of F: ClO₂F₂[PtF₆]. Finally **Z** – ClO₂F₃:

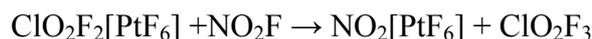
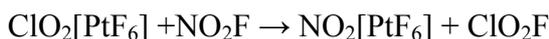
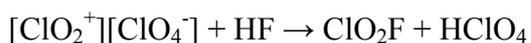
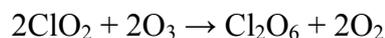
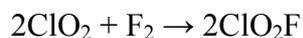
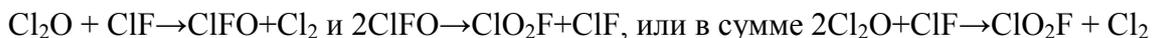
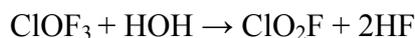
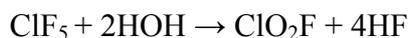
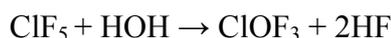


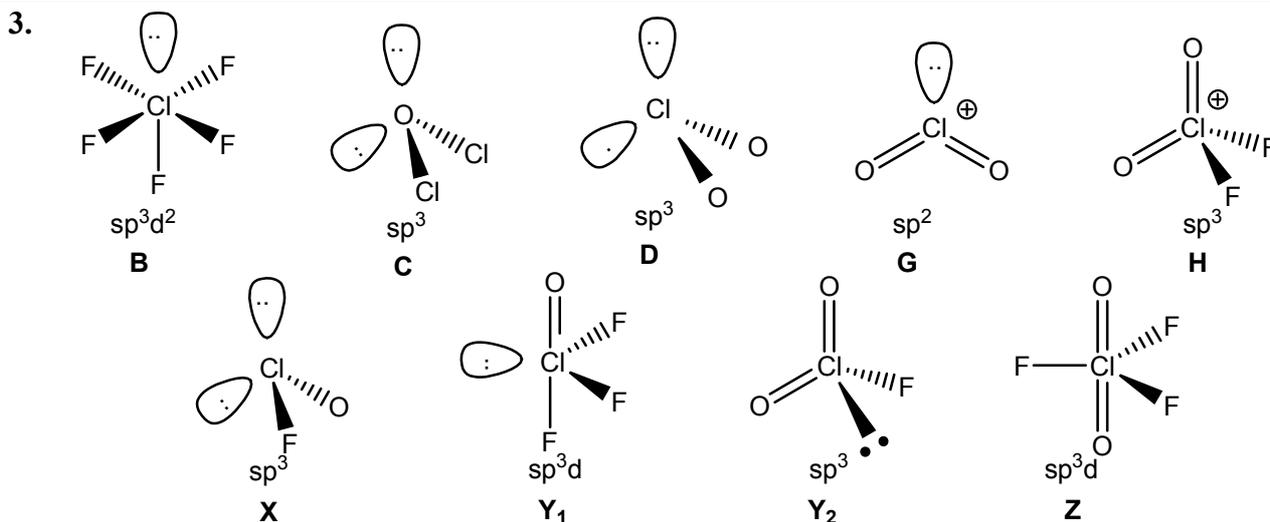
Now we know that **Z** contains chlorine atom with oxidation number +7, we could conclude unequivocally that **E** has oxidation number +6 so it is ClO₃ or more precisely Cl₂O₆ = [ClO₂⁺][ClO₄⁻]:



Thus: **A** – ClF, **B** – ClF₅, **C** - Cl₂O, **D** – ClO₂, **E** - Cl₂O₆, **F** - Cl₂, **G** -ClO₂[PtF₆], **H** - ClO₂F₂[PtF₆], **X** – Cl₂O₂F₂, **Y**₁ – ClOF₃, **Y**₂ – ClO₂F, **Z** - ClO₂F₃ (0.35 points for each substance **A** – **Z**, 5.75 points in total)

2. (0.5 points for each reaction, 6 points in total)

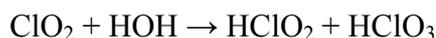




(0.25 points for each structure, 2.25 points in total)

4. The current conduction of **E** is related to the ionic structure of this compound $[\text{ClO}_2^+][\text{ClO}_4^-]$ (0.25 points)

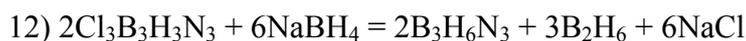
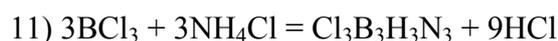
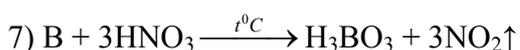
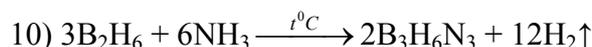
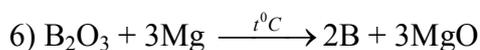
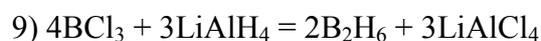
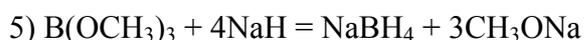
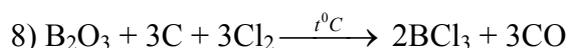
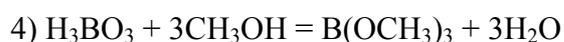
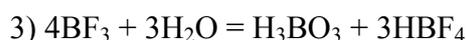
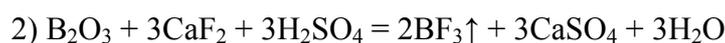
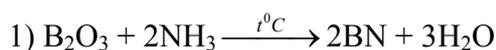
5. (0.25 points for each reaction, 0.75 in total)



Problem 3 (author D.G. Gulevich)

1. As the condition it is known that **E** is two-element substance, formed by the reaction with A_2O_3 and ammonia, so rewrite it in the form of AN. Element **A** we will define from the data on isoelectronic $(\text{AN})_3$ and C_6 . $n_e(\text{A}) = [6 \cdot 6e(\text{C}) - 3 \cdot 7e(\text{N})] / 3 = 5e$. So, **A** – boron, **E** – BN. (1 point).

Chemical reaction equations:



M – borazine $\text{B}_3\text{H}_6\text{N}_3$. (0.25 points for **M**, chemical reactions by 0.5 points, 7.25 points in total).

2. At the place of contact of the diamond polish wheel to steel (alloy of iron with carbon and dopants) the temperature can reach values sufficient to reaction $\text{C} + 3\text{Fe} \xrightarrow{t^\circ\text{C}} \text{Fe}_3\text{C}$. This causes a reduce service of diamond polish wheels (0.25 points)

50 th International Mendeleev Olympiad, 2016	Moscow
2 nd theoretical tour	Solutions

3. Forming oxide and water vapor during the decomposition of the salt indicates the presence of oxygen in its composition. Let **B** through $(\text{NH}_4)_n\text{R}_m\text{O}_k$ and write down the decomposition reaction in general form: $a(\text{NH}_4)_n\text{R}_m\text{O}_k \xrightarrow{t^\circ\text{C}} b\text{NH}_3\uparrow + c\text{H}_2\text{O}\uparrow + d\text{CO}_3$. Calculate the amount of released

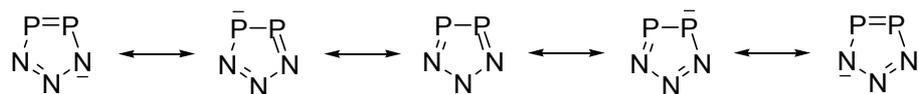
$$\text{ammonia } (v_1) \text{ and water vapor } (v_2): v_1 = \frac{p \cdot V_1}{R \cdot T} = \frac{101325 \cdot 178.1 \cdot 10^{-6}}{8.314 \cdot 363} = 5.98 \cdot 10^{-3} \approx 6 \cdot 10^{-3} \text{ mol},$$

$v_2 = v_1 / 2 = 3 \cdot 10^{-3} \text{ mol}$. From the ratio of the quantity of the formed substances and initial salt we find the stoichiometric coefficients of the reaction: $a = 1, b = 6, c = 3$. Knowing the oxygen content by weight in **O** oxide, determine its molar mass, a metal **C**, a coefficient d and molecular formula of salt **B**. $M = (3 \cdot 16) / \omega(\text{O}) = 144 \text{ g/mol}$. $M(\text{C}) = 0.667 \cdot 144 = 96 \text{ g/mol}$. **C** – Mo. $v(\text{MoO}_3) = 1.008 / 144 = 7 \cdot 10^{-3} \text{ mol}$. $d = 7$. Then from the known stoichiometry of the reaction we defined the molecular formula of salt. $k = c + 3d = 3 + 7 \cdot 3 = 24$. $n = b = 6$. $m = d = 7$, so **B** – $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$.

$\text{MoO}_3 + 3\text{H}_2\text{S} \xrightarrow{t^\circ\text{C}} \text{MoS}_2 + \text{S} + 3\text{H}_2\text{O}$. Inorganic graphene **N** – MoS_2 . Side product is sulfur which formed on conducting the reaction without current of hydrogen. In the presence of hydrogen the reaction is $\text{H}_2 + \text{S} \xrightarrow{t^\circ\text{C}} \text{H}_2\text{S}$ and additional quantities of hydrogen sulfide is formed. (Determination **B** 1.9 points, **C** 1 point, 0.5 points for **N**, a byproduct of the reaction and its formation by 0.25 points, 2.9 points in total).

4. a) on the number of signals in the ^{15}N NMR spectrum, define $y = 3$. x is determined from the value of the molecular weight: $\text{Ar}(\text{P}) \cdot x + \text{Ar}(\text{N}) \cdot 3 = 104$. By solving the equation, we get $x = 2$. The molecular formula of inorganic analogue of cyclopentadienyl anion is P_2N_3^- (1 point)

b) resonance structures of P_2N_3^- (0.75 points in total)



c) cyclopentadienyl anion contains 6π electrons, respectively, it is isoelectronic to the following ions and molecules: SN_2P_2 , S_2NP_2^+ , N_2P_3^- . (0.5 points for each formula, 3.25 points in total)

5. a) according to the Hückel rule, in order to be aromatic, a monocyclic planar hydrocarbons must have a conjugated system of double bonds containing $(4n+2)$ number of π -electrons, where n – integer number. (0.15 points);

b) $\text{B}_3\text{H}_6\text{N}_3$ (**M**) contains 6π -electrons, as benzene. Cyclopentadienyl anion and P_2N_3^- are isoelectronic and contain 6π -electrons (determination of the number of π -electrons by 0.10 points, 0.35 points in total).

SECTION III. PHYSICAL CHEMISTRY

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

1. Atom H has one proton, that's why for *o*-H₂ $I = \frac{1}{2} + \frac{1}{2} = 1$ ($\uparrow\uparrow$), for *p*-H₂ $I = \frac{1}{2} - \frac{1}{2} = 0$ ($\uparrow\downarrow$) (1 point).

2. $\Delta G^\circ = -RT \ln K$ and $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, then $\ln K = \Delta S^\circ/R - \Delta H^\circ/RT$. If $\Delta S^\circ/R = A$ and $\Delta H^\circ/R = B$, we obtain $\ln K = A - B/T$ (1.5 points). For reaction *o*-H₂ = *p*-H₂ $\ln K = \ln(\chi_o/\chi_p) = \ln[\chi_o/(1 - \chi_o)] = A - B/T$ the equations can be solved in pairs.

$$\text{a) } \ln(0.03/0.97) = A + B/30, \quad \text{б) } \ln(0.342/0.658) = A + B/60, \quad \text{в) } \ln(0.614/0.386) = A + B/100$$

From a) and б) $A = 2.17$, $B = -169.3$. From б) and в) $A = 2.14$, $B = -167.5$. From a) and в) $A = 2.15$, $B = -168.5$.

$$A_{\text{av}} = 2.15 \text{ (0.5 points)}, \quad B_{\text{av}} = -168.5 \text{ (0.5 points)}.$$

$$\chi_p = 1 - K/(1 + K) = 1/(1 + K): \chi_p = 99.8 \text{ (20 K)} \text{ и } 88.7 \text{ (40 K)} \text{ (1 point)}.$$

$$K = 1 - (1 - \chi_p)/\chi_p: K = 3.09 \cdot 10^{-2} \text{ (30 K)}, 0.520 \text{ (60 K)} \text{ и } 1.59 \text{ (100 K)} \text{ (1.5 points, 5 points in total)}.$$

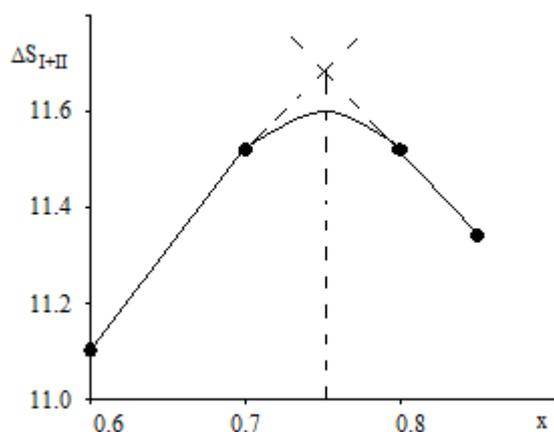
$$3. \quad \Delta H^\circ = B \cdot R = -168.4 \cdot 8.314 = -1400 \text{ J/mol}, \quad \Delta S^\circ = A \cdot R = 2.15 \cdot 8.314 = 17.9 \text{ J/mol}\cdot\text{K} \text{ (1 point)}.$$

$$4. \quad d \ln K / dT = \Delta H^\circ / RT^2, \quad K \neq f(T) \text{ only if } \Delta H^\circ = 0 \text{ (1 point)}.$$

$$5. \quad \Delta S_{\text{I+II}} = \Delta S_{\text{I}} + \Delta S_{\text{II}} = 9.2 \cdot x - 8.314 \cdot [x \ln x + (1 - x) \ln(1 - x)] \text{ (0.5 points)}$$

x	0.6	0.7	0.8	0.85
$\Delta S_{\text{I+II}}$	11.10	11.52	11.52	11.34

(0.5 points for the graph)



From the graph $\Delta S_{\text{I+II}} = \max$ at $x \approx 0.75$. More precise can be found if $d(\Delta S_{\text{I+II}})/dx = 0$. Then $9.2 - R \ln[x/(1-x)] = 0$; $x/(1-x) = 3.02$ and $x = 0.75$ (0.5 points). Since $K = x/(1-x) = 0.75/(1-0.75) = 3$ (0.5 points), that coincides with that provided in the condition (0.5 points, in total 2.5 points).

6. If the change of entropy in the reaction and at the change of T are equal, then the total entropy doesn't change, and $\Delta S_{\text{I+II}} = -\Delta S_{\text{III}}$, $x = 0.75$. In this

case $9.2 \cdot 0.75 - 8.314 \cdot (0.75 \cdot \ln 0.75 + 0.25 \cdot \ln 0.25) = -20.9 \cdot \ln(T/600)$ and $T = 345$ K. At $T \geq 345$ K the scheme works (1 point).

7. D has one proton and 1 neutron, so D₂ $I = 4 \cdot \frac{1}{2} = 2$ (0.5 points). Possible spin states I : 0, 1, 2 (0.5 points). For *o*-D₂ they are 0 and 2, for *p*-D₂ it is 1. (in total 1 point).

50 th International Mendeleev Olympiad, 2016	Moscow
2 nd theoretical tour	Solutions

8. For H₂ $2I + 1 = 2 \cdot 1 + 1 = 3$, for *o*-H₂ and $2 \cdot 0 + 1 = 1$ for *p*-H₂. The content of isomers $\chi_o = 3/(1 + 3) = 0.75$ (75%), $\chi_p = 0.25$ (25%). For D₂: $2I + 1 = 2 \cdot 2 + 1 = 5$ and $2I + 1 = 2 \cdot 0 + 1 = 1$, for *o*-D₂, $2 \cdot 1 + 1 = 3$ for *p*-D₂. Then $\chi_o = (5+1)/(5+1+3) = 0.67$ (67%), $\chi_p = 0.33$ (33%). The stable ones will be *p*-H₂ and *o*-D₂. (0.5 points for each mole part and giving isomers, in total 2.5 points).

Problem 2 (author D.G. Gulevich)

1. The thermochemical equation for dehydration: $\text{ACl}_2 \cdot 6\text{H}_2\text{O} = \text{ACl}_2 + 6\text{H}_2\text{O}(\text{g}) - 344.3 \text{ kJ}$ (for 1 mole of hexahydrate). From the standard enthalpies of formation we determine the enthalpy of formation of ACl_2 for further calculating the lattice energy. $\Delta_f H(\text{ACl}_2) = E_1 = \Delta_r H - 6\Delta_f H(\text{H}_2\text{O}) + \Delta_f H(\text{ACl}_2 \cdot 6\text{H}_2\text{O}) = 344.3 - 6x(-241.8) + (-2624) = -828.9 \text{ kJ/mol}$ (0.5 points). a) From the Hess law the lattice energy: $E_{\text{lat}}(E_{\text{VII}}) = -2E_{\text{VI}} - E_{\text{V}} - E_{\text{IV}} - E_{\text{III}} - E_{\text{II}} + E_1 = -2x(-349) - 243 - 1064 - 549 - 164 - 828.9 = -2151 \text{ kJ/mol}$ (2.75 points). b) The particles corresponding to the state **B**: $\text{A}^{2+} + 2\text{Cl}^-$ (0.25 points, total 3.5 points).

2. a) In the face-centered cubic lattice of metal **A** one unit cell contains 4 atoms, their mass $m = 4 \times A_r(\text{A})/N_A$. The density of the metal $\rho_A = m/V = 4 \times A_r(\text{A})/(N_A \times a^3)$. Express the known atomic radius through the parameter a of the unit cell: $a^2 + a^2 = 16r^2$, $r = a\sqrt{2}/4$ (2 points)

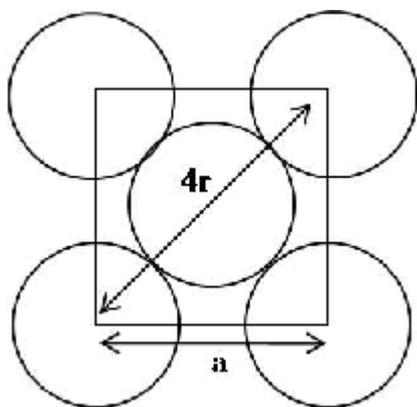
b) $V = r^3 \times 8^{3/2}$.

$$A_r(\text{A}) = (\rho \times r^3 \times 8^{3/2} \times N_A) / 4 = (2.54 \times 10^6 \times (0.217 \times 10^{-9})^3 \times 8^{3/2} \times 6.02 \times 10^{23}) / 4 = 88.1 \text{ g/mol}$$

Metal **A** – strontium (2 points, total 4 points).

3. $\mathbf{b} = \Delta_f H_{348}^{\circ}(\text{Sr}^{2+}) + 2\Delta_f H_{348}^{\circ}(\text{Cl}^-)$; $\mathbf{d} = [2C_p(\text{HCl}, \text{g}) + C_p(\text{Sr}, \text{s})]\Delta T$; $\mathbf{e} = [C_p(\text{H}_2, \text{g}) + C_p(\text{Cl}_2, \text{g}) + C_p(\text{A}, \text{s})]\Delta T$ (1 point for each expression for **b**, **d** and **e**, total 3 points).

4. The easiest way to express $\Delta_r H_{348}^{\circ}$: $-2\mathbf{a} + \mathbf{b} - \mathbf{c}$.



Face-centered cubic lattice of metal **A**

$$\Delta_f H_{348}^{\circ}(\text{HCl}, \text{g}) = \Delta_f H_{298}^{\circ}(\text{HCl}, \text{g}) + \int_{T_1}^{T_2} \Delta_r C_p dT.$$

For the reaction $\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{g}) = \text{HCl}(\text{g})$ $\Delta_r C_p = -2.175 \text{ J/mol} \cdot \text{K}$. From this $\Delta_f H_{348}^{\circ}(\text{HCl}, \text{g}) = -92300 + (-2.175 \times 50) = -92.41 \text{ kJ/mol}$ (0.5 points). $\Delta_r H_{348}^{\circ} = -2 \times (-92.41) - 2976 - (-2151 + 3 \times 8.314 \times 348 \times 10^{-3}) = -648.86 \text{ kJ/mol}$ (1 point). $\Delta_r H_{298}^{\circ}$ can be expressed as $\Delta_r H_{298}^{\circ} = \Delta_r H_{348}^{\circ} + \mathbf{d} - \mathbf{g}$. Then $\mathbf{g} = [C_p(\text{SrCl}_2, \text{s}) + C_p(\text{H}_2, \text{g})]\Delta T = [54.42 + 28.83] \times 50 = 4.163 \text{ kJ/mol}$. $\Delta_r H_{298}^{\circ} = -648.9 + 4.171 - 4.163 = -648.89 \text{ kJ/mol} \approx \Delta_r H_{348}^{\circ}$ (1 point).

50 th International Mendeleev Olympiad, 2016	Moscow
2 nd theoretical tour	Solutions

$\Delta_r H^\circ_{170}$ is defined in several ways: 1) $\Delta_r H^\circ_{170} = \Delta_r H^\circ_{348} + 2\mathbf{a} + \mathbf{e} + \mathbf{l} - \mathbf{o} - \mathbf{n} - \mathbf{g}$; 2) $\Delta_r H^\circ_{170} = \Delta_r H^\circ_{348} + \mathbf{d} + \mathbf{k} - \mathbf{n} - \mathbf{g}$. To calculate $\Delta_r H^\circ_{170}$ by the first method we need to determine

$$\Delta_f H^\circ_{170}(\text{HCl}, \text{l}) = \Delta_f H^\circ_{298}(\text{HCl}, \text{l}) + \int_{T_1}^{T_2} \Delta_r C_p dT. \text{ The standard enthalpy of formation of hydrogen}$$

chloride in liquid state we can determine from the data of paragraph 1 of the problem:

$\text{SrCO}_3(\text{s}) + 2\text{HCl}(\text{l}) = \text{SrCl}_2(\text{l}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) - 69.7 \text{ kJ/mol}$. $\Delta_r H^\circ_{298}(\text{HCl}, \text{l}) = \frac{1}{2}[\Delta_f H^\circ_{298}(\text{H}_2\text{O}, \text{l}) + \Delta_f H^\circ_{298}(\text{CO}_2, \text{g}) + \Delta_f H^\circ_{298}(\text{SrCl}_2, \text{l}) - \Delta_f H^\circ_{298}(\text{SrCO}_3, \text{s}) - \Delta_r H_{298}] = \frac{1}{2}[-285.8 - 393.5 - 805.4 + 1220 - 69.7] = -167.2 \text{ kJ/mol}$ (0.25 points). For the reaction $\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{l}) = \text{HCl}(\text{l})$ $\Delta_r C_p = 104.7 \text{ J/mol}\cdot\text{K}$. $\Delta_f H^\circ_{170}(\text{HCl}, \text{l}) = -167200 + 104.7 \times (-128) = -180.6 \text{ kJ/mol}$ (0.5 points). $\Delta_r H^\circ_{170} = -648.9 + 2 \times (-92.41) + 4.39 - 92.09 - (-180.6) - (-76.97) - 4.163 = -663.9 \text{ kJ/mol}$. Checking the second method: $\Delta_r H^\circ_{170} = \Delta_r H^\circ_{348} + \mathbf{d} + \mathbf{k} - \mathbf{n} - \mathbf{g} = -648.9 + 4.171 - 92.0 - (-76.97) - 4.163 = -663.9 \text{ kJ/mol}$ (1 point for one of calculation methods, total 4.5 points).

Problem 3 (author A.V. Yakimov)

1. (1 point) *A priory* yield of product X is the ratio of the amount of X obtained to the theoretical amount of X. Taking into account stoichiometry of the reaction, one can equate theoretical amount of X to the amount of raw fed. Therefore:

$$Y(X) = \frac{n(X)}{n(A)} = \frac{n(X)}{n_{\text{prod}}} * \frac{n_{\text{prod}}}{n(A)},$$

where $Y(X)$ is yield of X, $n(X)$ – amount of X obtained, $n(A)$ – amount of raw fed and n_{prod} – total amount of products obtained. Using the definitions of conversion and selectivity, we get:

$$Y(X) = S(X) * C,$$

where $S(X)$ – selectivity on X and C – conversion of the raw.

2. (1.5 points) Using raw feed rate V , we define linear raw feeding velocity:

$$v = V / S,$$

where S – cross-sectional area of the reactor. Using weight m and bulk density ρ of catalyst, we define height of catalyst layer h :

$$h = \frac{V_{\text{cat}}}{S} = \frac{m}{\rho S},$$

where V_{cat} – catalyst volume. Then considering evenly raw flow, we define time of passing of catalyst layer for raw meaning contact time τ :

$$\tau = \frac{h}{v} = \frac{m}{\rho V}$$

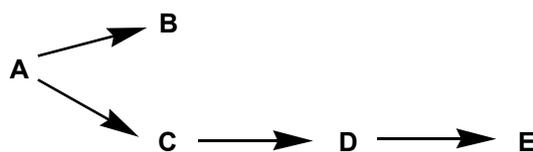
3. a. (0.5 points) Using the equation obtained in (2), we calculate contact times for each feed rate value giving a Table:

τ, s	Yield, %			
	B	C	D	E
1	0	2	0	9
6	2	18	4	26
12	6	22	9	38
20	17	15	12	46
30	40	5	2	50

b. (5 points) In revealing the kinetic scheme of reaction investigation of yield of each product on contact time plays a key role. The most demonstrative results can be obtained in graphical representation of $Y(X_i)$ – contact time dependence for each product X_i . However, for such simple reaction one can reveal kinetic scheme even analytically.

Notice, that increase of contact time leads to increase in yield (or selectivity) for secondary stable products. That means if some product is secondary, its yield should be close to 0 at low contact times because it have no time to form; for some primary product one has to observe a sharp increase of its yield at low contact times. Furthermore, if the product is stable, its yield should grow with contact time even at high values of that; if it is unstable, its yield has to pass through a maximum and be close to 0 at high values.

Analyzing the dependences of yields on contact times and investigating of each product for it is primary/secondary (P/S) and stable/unstable (s/u), one reveal the kinetic scheme. In our case: **B** – Ps, **C** – Pu, **D** – Su, **E** – Ss. Therefore, the kinetic scheme should be the following:



4. a. (2 points) Notice, that sum of selectivities of all products at fixed contact time is equal to 100% (or 1). Suppose C_i – conversion of **A** at contact time τ_i . Then, using the fact that selectivity $S(X)_i$ is the ratio of yield $Y(X)_i$ to conversion C_i (see (1)):

$$S(X)_i = \frac{Y(X)_i}{C_i}$$

we get the following equation for the sum of selectivities of all products at contact time τ_i :

$$\sum_{\text{prod}} S(X)_i = \sum_{\text{prod}} \frac{Y(X)_i}{C_i} = 1,$$

where “prod” means sum of all products. Since conversion is fixed at the same contact time:

$$C_i = \sum_{\text{prod}} Y(X)_i$$

Using the equation obtained, we calculate conversion of **A** at each contact time:

τ , s	Yield, %				C_i , %
	B	C	D	E	
1	0	2	0	9	11
6	2	18	4	26	50
12	6	22	9	38	75
20	17	15	12	46	90
30	40	5	2	50	97

b. (4 points) To describe dependence of conversion of **A** on contact time, consider the kinetics of reaction in the catalyst layer. Since **A** to **B** is irreversible first-order reaction, we can integrate the mass action law:

$$v = -\frac{dA}{dt} = kA,$$

where v is the reaction rate, A – concentration of **A** and k – rate constant, getting:

$$A = A_0 e^{-k\tau},$$

where A_0 – concentration of **A** at the initial time. Thus, concentration of **A** decrease exponentially with the time of passing through catalyst layer, *i. e.* contact time. Then, conversion of **A** is equal to

$$C = \frac{A_0 - A}{A_0} = \frac{A_0 - A_0 e^{-k\tau}}{A_0} = 1 - e^{-k\tau}$$

5. (1 point) To define how conversion of **A** depends on temperature we only need to calculate rate constants at each temperature (4). Rate constants depend on temperature via Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}},$$

where E_a is activation energy, T – absolute temperature, R – universal gas constant and A – pre-exponential factor.

To calculate rate constant at 210°C we divide Arrhenius equation written for $T_1 = 200^\circ\text{C}$ to that for $T_2 = 210^\circ\text{C}$:

$$\frac{k_1}{k_2} = e^{\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

Using the value of $k_1 = 7 \text{ min}^{-1}$ calculated from the equation

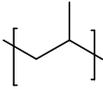
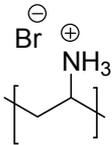
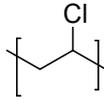
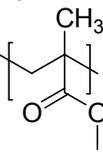
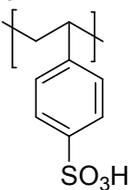
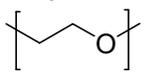
$$C = 1 - e^{-k\tau}$$

we obtain $k_2 = 9 \text{ min}^{-1}$. Therefore, conversion of **A** at this temperature will be 60%.

SECTION IV. LIFE SCIENCES AND POLYMERS

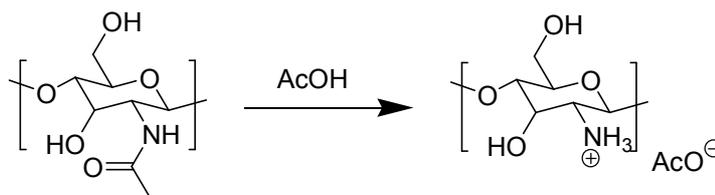
Problem 1 (author E.A. Karpushkin)

1. (0.5 point for each structure)

Polypropylene 	Polyvinylammonium bromide 	Polyvinyl chloride 
Poly(methyl methacrylate) 	Poly-4-styrenesulfonic acid 	Polyethylene oxide 

Polyvinylammonium bromide and poly-4-styrenesulfonic acid are the only polyelectrolytes in the list. Being a polyacid and polybase, these polymers are capable of the interpolyelectrolyte complex formation (0.5 point for each PE choice, 4 points in total).

2.



Average molar mass of the repeating unit (164.10 g/mol) is intermediate between those of chitin (203.20 g/mol) and chitosan (161.16 g/mol), which points out at incomplete hydrolysis. If α is the hydrolysis conversion; the average molar mass of the repeating unit is $164.10 = \alpha \cdot 161.16 + (1 - \alpha) \cdot 203.20$, and $\alpha = 0.93$. Then the polymerization degree of the chitosan macromolecule is $492310/164.10 = 3000$, and the number of the ionic groups in the macromolecule is $3000 \cdot 0.93 = 2790$ (1 point for the reaction scheme, 2 points for the calculations, 3 points in total).

3. Molar ratio of the elements in A: C:H:O=50.00/12.011:5.60/1.008:44.40/16.00=4.16:5.55:2.775, thus, the gross formula of A is $C_3H_4O_2$. Since this compound forms the sodium salt, it should contain either phenolic or carboxylic oxygen. The unsaturation degree corresponding to the gross formula does not allow finding a reasonable aromatic structure. If A is a carboxylic acid, then the simplest variant is $CH_2=CHCOOH$ (acrylic acid). Since A forms a polyelectrolyte complex with chitosan, it should be a polyacid. Let us denote its polymerization degree as x . Then, $1000 \cdot 0.01 / (94.05x)$ of the macromolecules giving $(x+1) \cdot 1000 \cdot 0.01 / (94.05x)$ of dissolved particles upon complete dissociation are found in 1 kg of 1 wt.% solution of the polyacid sodium salt. According to the Raoult's law for the freezing point, $-0.208 = 1.86 \times (x+1) \cdot 1000 \cdot 0.01 / (94.05x)$, and $x = 19.3$. Then, the average

50 th International Mendeleev Olympiad, 2016	Moscow
2 nd theoretical tour	Solutions

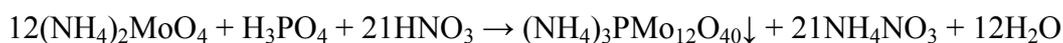
molecular mass of A equals $19.3 \cdot 72.04 = 1390$ g/mol ($19 \cdot 72.04 = 1369$ g/mol is acceptable)
(1 point for the gross formula, 2 points for the molecular mass, 3 points in total).

4. Synthesis of a salt of phosphoric-molybdanic acid is described. Since this is a non-redox reaction, the ammonium salt is produced. Its general formula is $(\text{NH}_4)_{2z-6y-5}\text{PMo}_y\text{O}_z$ (the index for ammonium is written accounting for the electric neutrality condition). Then, a set of the equations can be written:

$$0.0165 = 30.97/[18.04(2z-6y-5) + 30.97 + 95.96y + 16z]$$

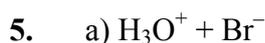
$$0.6136 = 95.96y/[18.04(2z-6y-5) + 30.97 + 95.96y + 16z]$$

Solution of the set gives $30.97/0.0165 = 96.96y/0.6136$, and $y = 12$, $z = 40$. Finally:



The stoichiometric complex with chitosan contains $2790/3 = 930$ anions of **B** per the polycation macromolecule.

Note. The salt **B** is in fact water-insoluble and thus does not react with chitosan. However, the anion of the corresponding acid is bound to chitosan in the above-calculated ratio (1 point for reaction scheme, 1 point for the formula, 1 point for the complex composition, 3 points in total).

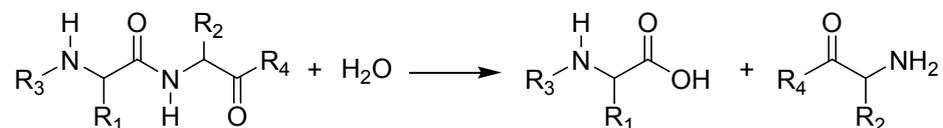


Any other pairs coinciding with the answers to i) 1, 2, and 4 are acceptable (0.25 point for each ion, 1 point in total).

6. The entropy decrease due to localization of the components of a polyelectrolyte reaction is lower when the polymerization degree of the components is higher. The reason is that the entropy of a polymer chain is initially lower than that of the corresponding number of free monomer molecules, whereas the entropy of the polyelectrolyte complex in the precipitate is independent of the polymerization degree of the components. Then the sequence is $\mathbf{C} < \mathbf{B} < \mathbf{A}$. When all the three mentioned acids are present in chitosan solution, polyacrylic acid is predominantly involved in the complex formation. The mass fraction of carbon is the highest of all the elements in both chitosan and polyacrylic acid; hence, its fraction will be the highest in the complex as well. (0.75 point for the correct order (0.25 point in the case of $\text{A} \leftrightarrow \text{B}$ displacement, 0.25 point for the choice of the element, 1 point in total).

Problem 2 (authors Yu.S. Golovko, B.N. Garifullin)

1. Water is always present in fresh meat (e.g. the intercellular liquid in myocytes). The peptide bonds are hydrolyzed when collagen is being heated in the presence of water, which results in shorter fragments forming gelatin (1 point):



2. Fresh-killed meat being practically free of MMb⁺, its two colors (reach-read outside and deep-red inside) are due to the other myoglobin forms: Mb и MbO₂. The external part of a meat slab being in contact with oxygen, MbO₂ is found there, whereas Mb is the dominating form in the inner parts lacking oxygen and containing intercellular water. The grey color of MMb⁺ can be determined based on the *Well done* steak appearance or on general considerations (browning of apple slices, the coloration of a number of iron(III) compounds).

Then the *Extra-rare* or *Blue* steak mostly contains MbO₂, and the *Well done* is rich in MMb⁺, though having also a significant fraction of denatured myoglobin. Nothing definite can be decided in the case of the *Medium* steak. Overcooking leads to complete myoglobin denaturation (T>100°C!) accompanied by partial coaling of organic compounds (0.75 point for each variant, 3 points in total).

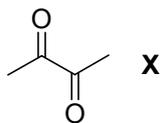
The degree of steak doneness	Myoglobin form(s)
Extra-rare or Blue (<i>bleu</i>)	MbO ₂
Medium (<i>demi-anglais</i>)	Mb, MbO ₂ or MMb ⁺
Well done (<i>bien cuit</i>)	MMb ⁺
Overcooked (<i>trop cuit</i>)	Pending. Indication of any form is considered as a wrong answer

3. Fats have relatively high melting points and start melting when heated above 45°C. This process mostly determine the steak succulence. Complete non-enzymatic hydrolysis of disaccharides affording monosaccharides is impossible under *sous-vide* conditions; starch is a vegetational polysaccharide; testosterone can be obtained non-enzymatically only by means of fine organic synthesis. Moderate heating of a meat slab does not allow occurring this reaction (1 point).

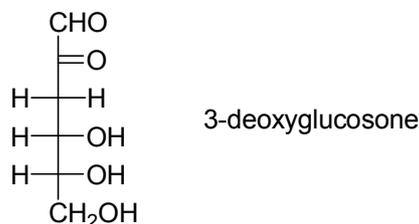
4. Values of p , q , and r can be found exactly, which is better than enumeration of possibilities. Number 48 can be represented as a product of prime numbers: $1^3 \cdot 2^4 \cdot 3$. Since the sum of p , q , and r is even, variants with two odd numbers (1 and 1, 1 and 3) in the triple can be neglected. Thus, 2, 4, and 6 are unambiguously found for p , q , and r .

Range limits of hydrogen mass content in all possible compounds need to be found in order to attribute the above values to p , q and r . C₄H₆O₂ is characterized by the highest hydrogen mass content (7.03%). The nearest $\omega_m(\text{H})$ value of 6.43% is found for C₂H₆O₄. Thus, the molecular formula of X is C₄H₆O₂ (2 points).

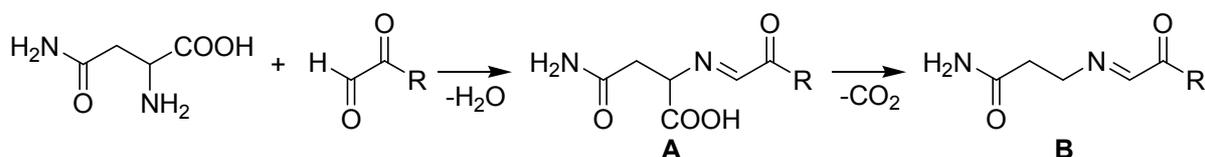
5. The data on the number of atom types of the elements forming X strongly suggests high symmetry of the compound. Diacetyl (2,3-butanedione) is the only suitable variant (1.5 points):



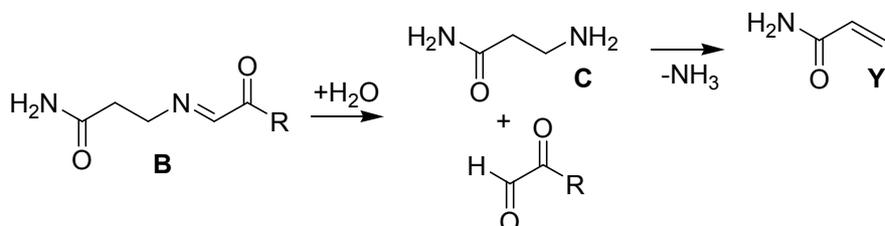
6. The formula of 3-deoxyglucosone in the Fischer projection (1 point):



7. Two initial stages are deciphered easily:



The other two stages require determination of the molecular formula of the intermediate C: $RC_5N_2H_7O_2 + G = RC_2HO_2 + C$, thus $C = C_3N_2H_6 + G$. The next stage is accompanied by the loss of L: $C_3N_2H_6G = L + C_3H_5NO$. Then G contains oxygen, whereas L nitrogen and hydrogen (and nothing else). Then G contains either N or H as the second element. The former variant is impossible, since stable substances with the formula of $N_{2+n}O_2$ (where n is a natural number) are not known. Finally, G is H_2O , L is NH_3 , and X is acryl amide:



The recommended cooking methods providing for the decreased probability of acryl amide formation are always given in oven manuals (0.5 point for each compound, 3 points in total).

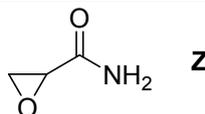
8. The calculation of carbon and oxygen atoms ratio in Z:

$$n(C):n(O) = \frac{41.38}{12.01} : \frac{36.75}{16.00} = 3:2$$

The molecular mass accounting for the residue:

$$M(\text{res.}) = \frac{(100 - 41.38 - 36.75) \cdot 36.03}{41.38} = 19.04 \frac{g}{mol}$$

The value corresponds to one nitrogen and five hydrogen atoms. Thus, the molecular formula of Z is $C_3H_5NO_2$. Z contains an extra oxygen atom as compared to Y. Taking also into account the presence of asymmetric carbon atom, one finally gets the only possible formula of glycidoyl amide (oxyran-2-carboxyl amide) formed as result of Cytochrome P450-dependent monooxygenase interaction with acryl amide:



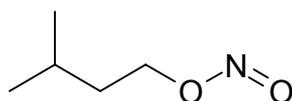
Interaction of **Z** with DNA nucleic bases (with an attack on the nitrogen atom in the cycle) is behind its mutagenic properties (2.5 points).

Problem 3 (author Yu.S. Holovko)

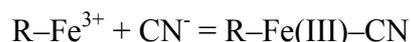
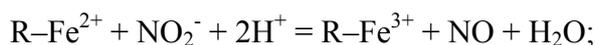
1. CO is the only gas in the Table. It has neither color, nor odor, thus being very insidious. It is known to bind to hemoglobin hindering gas exchange. Thus, exhalation of oxygen is recommended as a measure upon intoxication with CO. HF is a weak acid. It is characterized by high solubility both in water and lipids. Accordingly, calcium gluconate binding the poison to form CaF₂ is used as the antidote, which allows avoiding hypocalcaemia and similar cases. Chelate therapy, e.g. tetacium-calcium (a derivative of a well-known complexon EDTA) is used for diminishing the effect of lead(II) compounds (as well as of other transition metals). Ethanol is used as an antidote in the case of intoxication with methanol, the former competing with the latter for enzymatic systems in organisms. Arsenic compounds suppress metalloenzymes (e.g. pyruvate dehydrogenase). Their toxic effect is eased by the substances with high affinity towards arsenic, dimercaprol also known as British anti-Lewisite (remember the form of arsenic existence in nature!) being one of such antidotes.

Thus, 1 – **E**, 2 – **B**, 3 – **D**, 4 – **C**, 5 – **A** (0.5 point for each choice, 2.5 points in total).

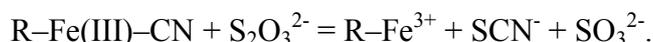
2. Isoamyl nitrite is an ester of nitrous acid and isoamyl alcohol:



Hemoglobin is the major iron-containing protein in blood with the normal oxidation state of the metal of +2. Nitrite oxidizes hemoglobin to methemoglobin (Fe(III)). Cyanide have higher affinity towards methemoglobin, which prevents blocking of cytochrome c oxidase system (0.5 point for the structure and each equation, 2 point in total):



3. The hereunder reaction is used to remove cyanmethemoglobin from bloodstream:

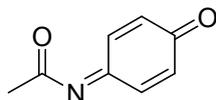


(Other reasonable variants including also simultaneous reduction of Fe(III) to Fe(II)) (1 point).

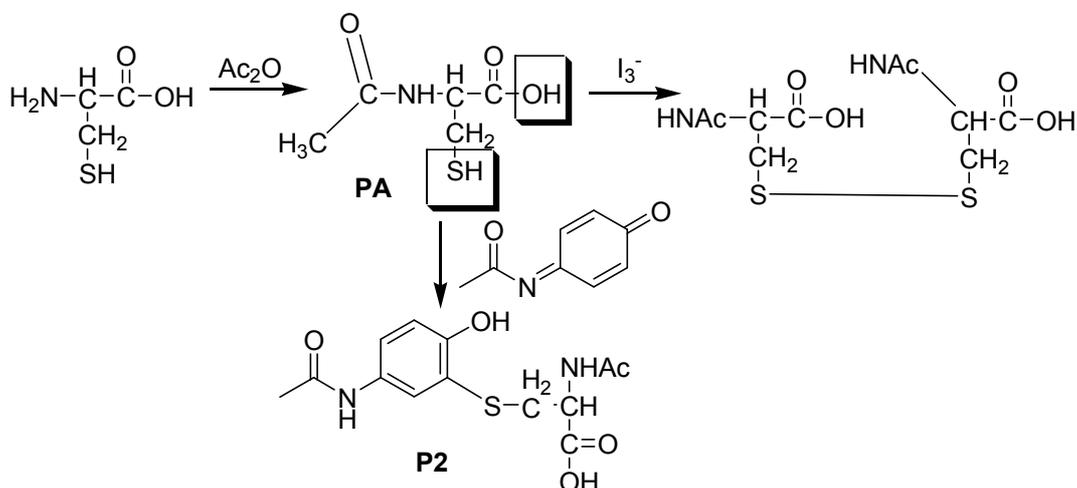
4. The number of carbon atoms does not change upon **P** transformation into **P1**. Supposed the only nitrogen atom is retained, the molar mass of the product equals 149 g/mol, which is by 2 g/mol

50 th International Mendeleev Olympiad, 2016	Moscow
2 nd theoretical tour	Solutions

less compared to the reagent (paracetamol). All these suggest dehydrogenase reaction involving oxygen. With an account of the substitution character in the reagent, one gets the product with quinoid structure (1.5 point):

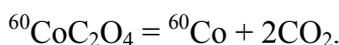
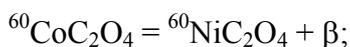


5. Cystein ($C_3H_7NO_2S$) and methionine ($C_5H_{11}NO_2S$) are the only sulfur-containing canonical amino acids. $C_5H_9NO_3S$ can formally correspond to the product of methionine oxidation, still this substance with blocked sulfur atom would not decolorize KI_3 solution. Then, it is an addition (to cystein) of C_2H_2O fragment typical of acetylation reactions. The acidity constants data suggest that the amino group is subjected to acetylation. Finally, sulfur acts as the nucleophile, and the addition is of the Michaelis type allowing rearomatization (1 point for each of **PA** and **P2**, 2 points for the scheme, 4 points in total):



6. Benzoquinone formation leads to glutathione depletion in liver (1 point)

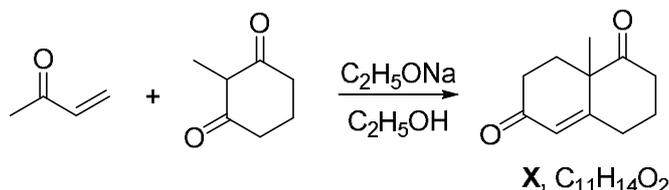
7. **X1** is a carbon-containing metal salt composed of three elements. Note that only two geometrical progressions of the atom numbers in the formula unit (1, 2, 4 and 1, 3, 9) meet the requirement of the total number of atoms not exceeding 15. Oxygen being the most probable third element, one can represent the substance as MC_2O_4 . With an account of the carbon mass content, one finds the molar mass of 148 g/mol, which corresponds to a metal with relative atomic mass of 60. One will not find such an element in the Periodic Table. On the other hand, traits of radiation sickness are described in the text, which points out at a salt of a radioactive nuclide (short-living isotopes are among the most potent poisons if swallowed):



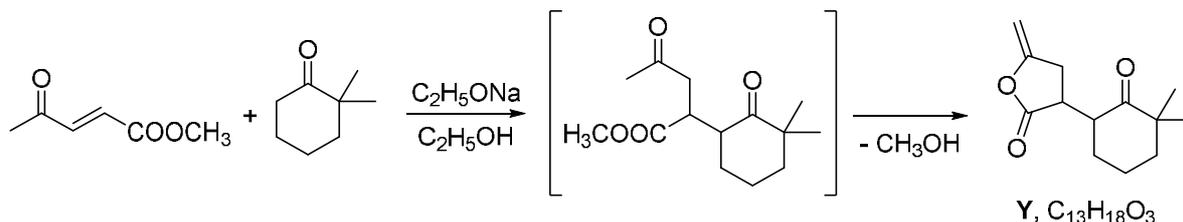
Other radioactive nuclides meeting all the criteria accepted (1 point for calculation, 1 point for the composition, 0.5 point for each reaction, 3 points in total).

SECTION V. ORGANIC CHEMISTRY**Problem 1 (author D.V. Kandaskalov)**

1. **X** is the product of the Robinson annulation. In 2-methylcyclohexane-1,3-dione atom C2 is the most acidic as the formed anion is stabilized in this case by two carbonyl groups. So, we can write down structural formula of the Robinson annulation product.

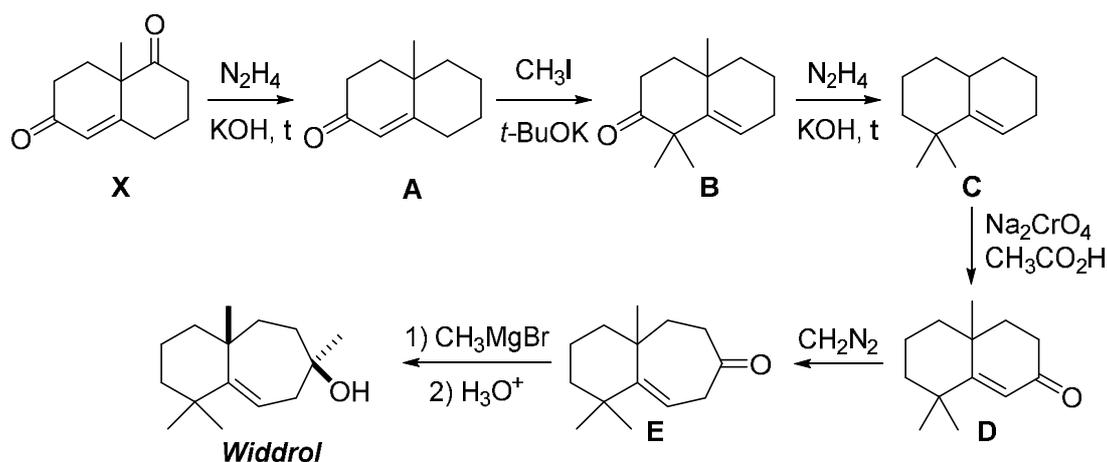


According to the problem condition, the second reaction consists of Michael addition but annulation product is not formed. From the molecular formula of **Y**, which has no annulated rings, we can conclude that **Y** formation is accompanied by methanol elimination. This is possible if the enolate ion attacks ester moiety producing new five-membered ring. There are two possibilities: ester function is attacked by either carbon or oxygen atom. In the first case product should have three carbonyl groups. This is not consistent with the problem condition. Therefore, **Y** is formed by the oxygen atom attack (structural formulae of **X** and **Y** – 1 point for each, 2 points in total)

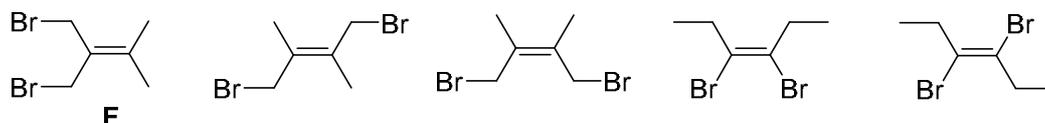


2. Molecular formula of **B** demonstrates that two carbon atoms were introduced into the molecule of **A** during the methylation step. Therefore, molecular formula of **A** is C₁₁H₁₆O. This formula differs from formula of **X** by the absence of one oxygen atom and presence of two hydrogen atoms. Indeed, the first step is the Wolff-Kishner reduction. **X** has two carbonyl groups; unconjugated one is the more active. As a result, this group is selectively reduced. Unsaturated ketones under Wolff-Kishner conditions are usually transformed into cyclopropanes but this reaction is impossible for **X** due to restrictions by the molecular geometry. Regiochemistry of **A** methylation can be easily determined by comparison with the structure of widdrol. Firstly, two methyl groups in this terpenoid are connected to the same carbon atom. Secondly, their position as well as position of C=C bond show that deprotonation leads to methylation at the α -position to the carbonyl group with the simultaneous C=C bond shift. Then, the second carbonyl group is reduced. However, molecular formula of **D** is the same as that of **B**. It means that CH₂ group in **C** is oxidized to C=O. In this compound allylic carbon atom is oxidized easier than other atoms. Two next steps are the

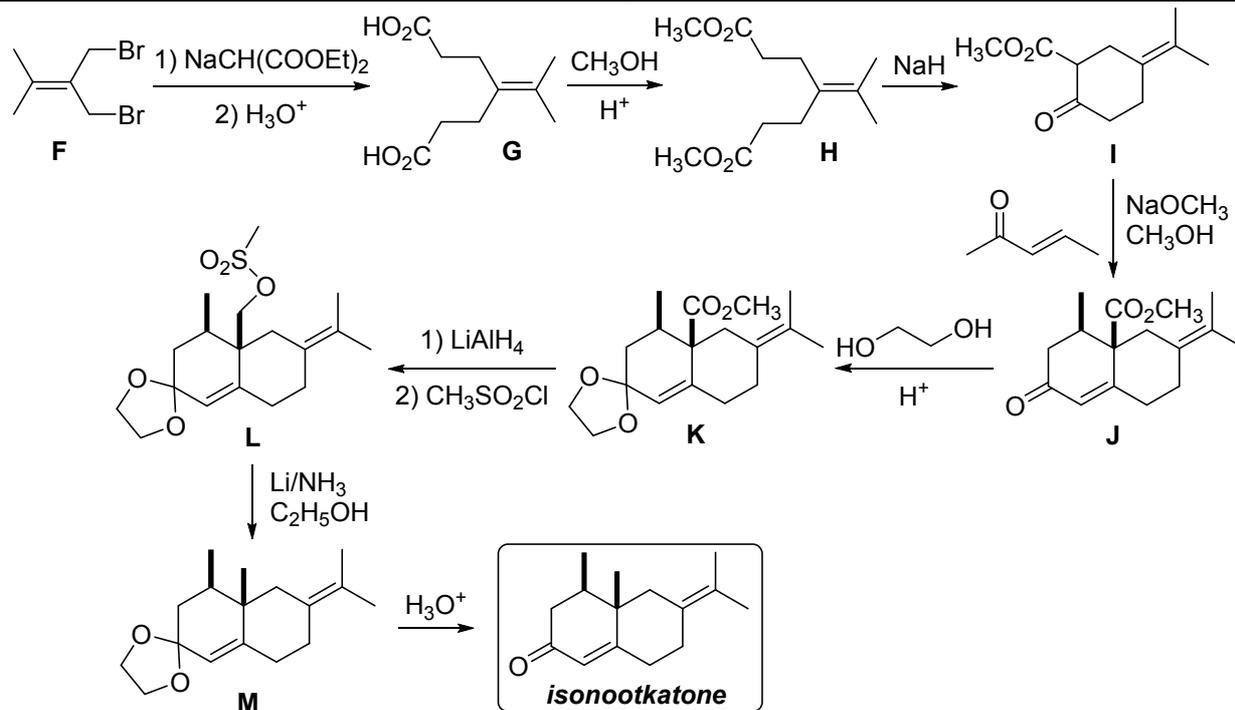
six-membered ring enlargement and the transformation of the carbonyl group into tertiary alcohol as a result of Grignard reaction (structural formulae of **A** – **E** – 1 point for each, 5 points in total)



3. ¹H NMR spectrum of compound **F** has 2 signals with the relative intensities of 2:3. Therefore, the number of hydrogen atoms is 5n. So, formula of **F** is (C₃H₅Br)_n. From the molecular formula of **G** we can conclude that $n \leq 2$. On the another hand, compound producing acetone during ozonolysis should have at least 4 carbon atoms. Therefore, formula of **F** is C₆H₁₀Br₂. There are five isomers which satisfy to the above description of NMR spectrum. Only first of them produces acetone during ozonolysis.

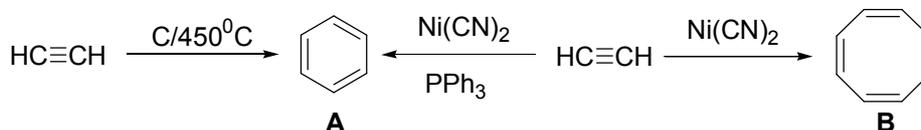


The synthesis is started by the nucleophilic substitution of bromine atoms with the malonate group followed by hydrolysis and decarboxylation affording diacid **G** which then was transformed into ester **H**. Its treatment with strong base (NaH) produces compound **I** which was introduced into the Robinson annulation. From the molecular formula of **J** it is possible to determine formula of **I** (C₁₆H₂₂O₃ - C₅H₈O + H₂O = C₁₁H₁₆O₃). Therefore, during the **H**→**I** step methanol was eliminated. This reaction is referred to as Dieckmann condensation. Then the protection of the carbonyl group with ethylene glycol furnishes the corresponding ketal. Reduction of the ester moiety in **K** with LiAlH₄ yields alcohol which was transformed into sulfonate **L** by treatment with CH₃SO₂Cl. The last step is, evidently, the protecting group removal by the acid-induced ketal decomposition. So, the transformation of **L** into **M** is the substitution of OSO₂CH₃ group by hydrogen atom (structural formulae of **F** – **M** – 1 point for each, 8 points in total).



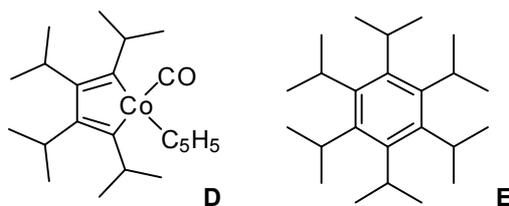
Problem 2 (author E.N. Shved)

1. Structure of **A** is evident from trimerization of acetylene in the presence of activated charcoal (450°C): **A** is benzene. From $M(\mathbf{A})/M(\mathbf{B}) = 0.75$ we determined $M(\mathbf{B}) = 104$ a.e. So, **B** is cyclooctatetraene, C_8H_8 . (Structural formulae of **A** and **B** – 0.5 points for each, 1 point in total).

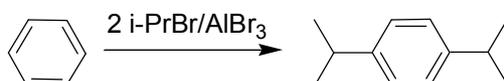


2. Following to IUPAC recommendations, the process of **A** formation is (2+2+2)-cycloaddition, **B** formation is (2+2+2+2)-cycloaddition (every type of cycloaddition – 0.5 points, 1 point in total).

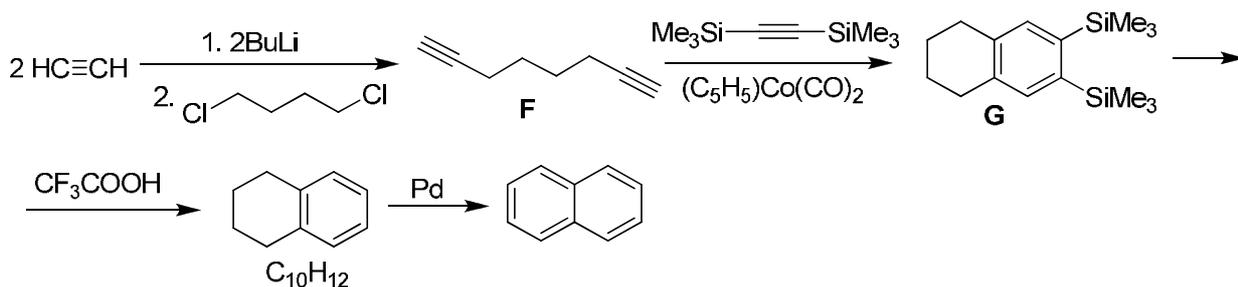
3. **D** is a product of (2+2+1)-cycloaddition. This is five-membered ring containing cobalt atom. **E** is benzene homologue, i.e. consists of benzene ring. From NMR data, fragment R contains 7 hydrogen atoms, 6 of them are identical and differ from the seventh one. This is isopropyl group, $(CH_3)_2CH$ (*i*-Pr). Accounting for cobalt content in **D** as well as scheme in the question 1, we can determine structural formulae of **D** and **E** (1 point for structural formula, 2 points in total).



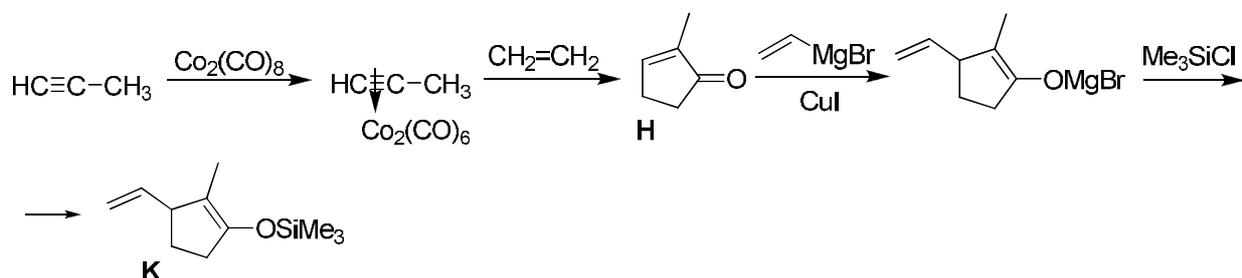
4. Under kinetic control the major product of benzene dialkylation is *para*-dialkylbenzene (1 point):



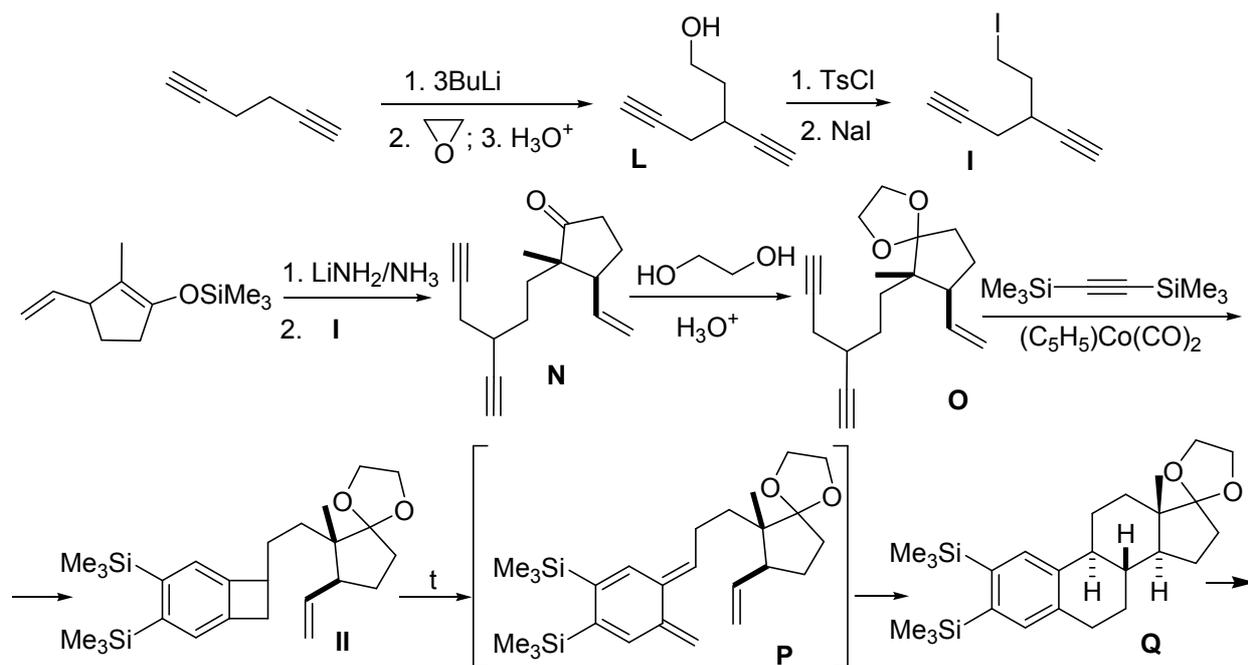
5. a) Structure of **F** is the product of acetylene alkylation. Structures of $C_{10}H_{12}$ and **G** can be determined from the structure of the final product (naphthalene).

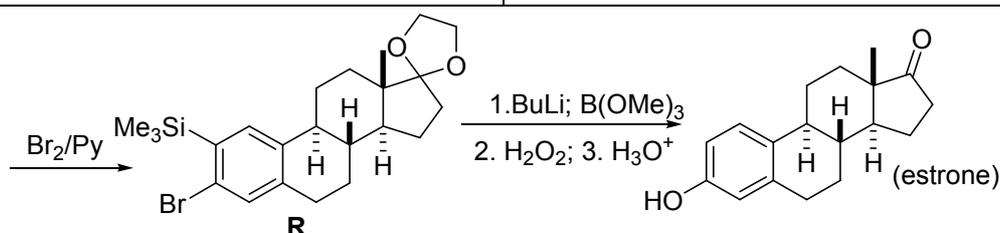


b) **H** is product of (2+2+1)-cycloaddition with the introduction of some functional group. Accounting for further transformations, this functionality is carbonyl group (structural formulae of **F – H**, $C_{10}H_{12}$, **K** – 1 point for each, 5 points in total)



6. Accounting for carbon content and reagents used, **I** is alkyl iodide containing two $C\equiv C$ groups (C_8H_9X). Indeed, $M(\text{I}) = (8 \cdot 12)100/41.38 = 232$ a.e. and $M(\text{X}) = 127$ a.e. **X** is iodine. **N** was obtained by the transformation of silyl ether **K** into lithium enolate followed by its alkylation with iodide. Step **N**→**O** is a protection of the carbonyl group. Step **O**→**II** is cycloaddition similar to the **F**→**G** reaction. The last two steps do not change carbon skeleton, **II**, **P** and **Q** are isomers; **Q** has two rings more than **P**. Therefore, **Q** has a polycyclic structure similar to that of estrone:

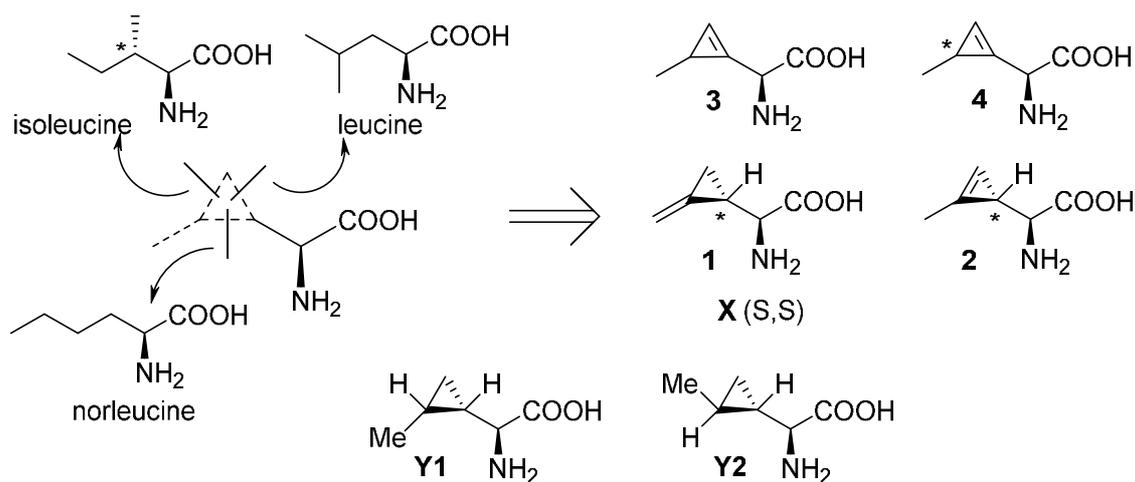




(structural formulae of **L**, **O**, **P**, **R** – 0.5 points for each; structural formulae of **I**, **N** and **Q** – 1 point for each, 5 points in total)

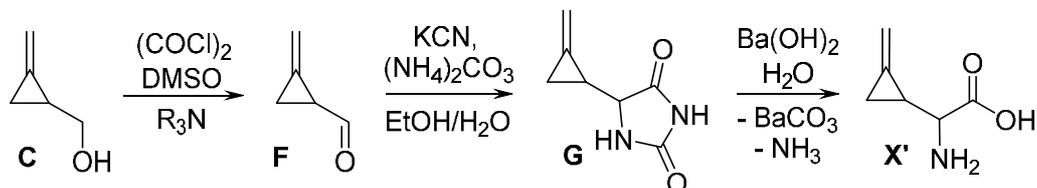
Problem 3 (author D.M. Volochnyuk)

1-2. From brutto-formula of α -amino acid **X** it is possible to determine that the degree of unsaturation of substituent **R** (which contains 4 carbon atoms) is 2. Analysis of hydrogenation products shows that carbon skeleton consists of one double bond and three-membered ring. There are four possibilities (see below). Amino acid **3** should be rejected as its hydrogenation leads to the formation of mixture of 4 but not 2 saturated amino acids. Among compounds **1**, **2** and **4** amino acid **1** only has two vinylic protons. Other two acids do not correspond to NMR data. Therefore, **X** is (2*S*,1'*S*)-2-amino-2-(2-methylenecyclopropan-1-yl)acetic acid, or α -((1*S*)-2-methylenecyclopropan-1-yl)glycine. Knowledge of its structure allows for determining structural formulae of the optically active amino acids **Y1** and **Y2** (stereochemistry of the chiral center in three-membered ring is deduced from the stereochemistry of isoleucine given in the text). (Any amino acid with the correct carbon skeleton is estimated by 2 points. The correct choice of **X** – 1 point more; correct absolute configuration – 1 point more, name of **X** according to IUPAC nomenclature – 1 point more. Structural formulae of **Y1** and **Y2** – 1 point for each, 7 points in total)

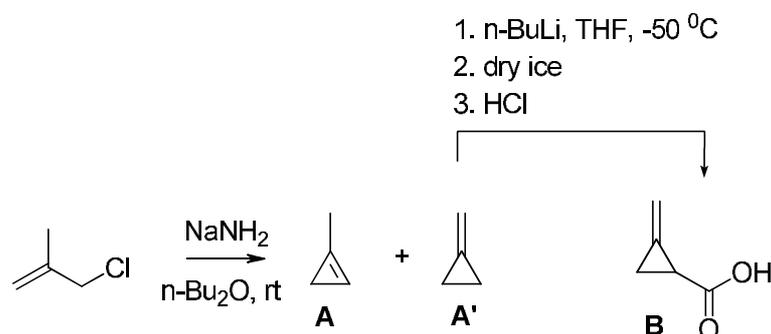


3. Decoding of scheme 2 can be started by analysis of transformation of **C** into **X'**. The first step is the Swern oxidation of alcohol into aldehyde. Then an imidazole derivative is formed; under treatment with $\text{Ba}(\text{OH})_2$ and H_2O this eliminates NH_3 producing BaCO_3 and amino acid. Independently on the knowledge of the synthesis of amino acid via hydantoins, it is possible to conclude that the carbonyl group of amino acid should be connected in five-membered ring to

nitrogen atom which eliminates as ammonia. The nitrogen atom of amino acid moiety should be connected with the second nitrogen atom by carbonyl tether. This carbonyl eliminates as CO_2 which is fixed by $\text{Ba}(\text{OH})_2$. As a result, this part of scheme takes such form:



Next, let us decode transformation of methallyl chloride into **B**. Accounting for reagents given in the scheme, **B** is carboxylic acid. Then **A'** is the corresponding hydrocarbon structure of which can be determined from NMR data:



At last, we should determine structural formulae of **D** and **E**. Compound **E** is equivalent of Wittig reagent **E'**. To realize the goal transformation and accounting for bicyclic structure and presence of pentacoordinated phosphorus atom, we should write structural formula of **E** as given below. Now **D** is the phosphonium salt which is obtained by alkylation of ylide $\text{Ph}_3\text{P}=\text{CH}_2$ with epichlorohydrin (structural formulae of **A** – **G**, **A'** – 1 point for each, 8 points in total).

