

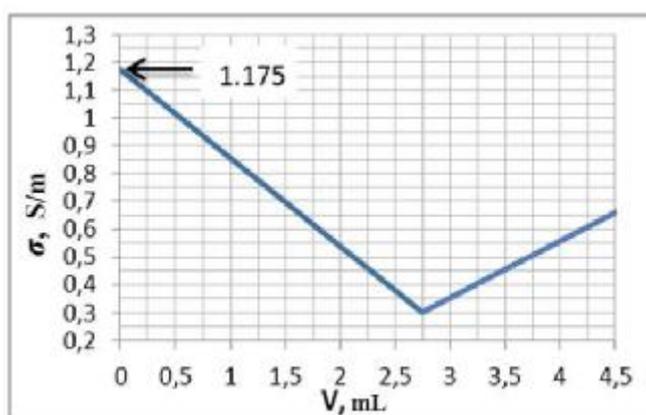
## SECTION I. ANALYTICAL CHEMISTRY

### Problem 1

Conductometry is the one of the oldest electrochemical methods of analysis. It is based on the measurement of conductivity  $\sigma$  [S/m]. Conductivity is related to the existence of ions in solution. Each ion is characterized by the molar conductivity  $\lambda$  [ $\text{S}\cdot\text{m}^2/\text{mol}$ ], which depends on its charge  $z$  and mobility  $\mu$  [ $\text{S}\cdot\text{m}^2/\text{C}$ ]:  $\lambda = |z|\cdot\mu\cdot F$ , where  $F$  is Faraday constant. The total conductivity is the sum of the conductivities of each ion:  $\sigma = \sum \sigma_i = \sum \lambda_i \cdot c_i$  where  $c_i$  is the concentration of the ion [ $\text{mol}/\text{m}^3$ ].

1. The mobilities of  $\text{OH}^-$  and  $\text{H}^+$  are  $2.07\cdot 10^{-7}$  and  $3.63\cdot 10^{-7}$   $\text{S}\cdot\text{m}^2/\text{C}$ , respectively. Calculate the molar conductivities  $\lambda(\text{OH}^-)$ ,  $\lambda(\text{H}^+)$  and the conductivity ( $\sigma$ ) of pure water.

In the first experiment, 50.0 mL of strong acid **HA** was titrated by a 0.500M solution of alkali. The graph represents the conductivity as function of the volume of the alkali solution (see Figure).



2. Which ions contribute to the conductivity before equivalence point, in the equivalence point and after the equivalence point? Consider the water dissociation as negligible.

3. Determine the acid **HA** ( $\text{HCl}$ ,  $\text{HClO}_4$  or  $\text{HBr}$ ) and alkali ( $\text{LiOH}$ ,  $\text{KOH}$  or  $\text{NaOH}$ ), taking into account that the molar conductivities of ions [ $\text{mS}\cdot\text{m}^2/\text{mol}$ ] are as follows:

$$\lambda(\text{K}^+) = 7.35, \lambda(\text{Na}^+) = 5.01, \lambda(\text{Li}^+) = 3.86, \lambda(\text{Cl}^-) = 7.63, \lambda(\text{Br}^-) = 7.80, \lambda(\text{ClO}_4^-) = 6.52.$$

4. Calculate the solution conductivity after addition of 6.0 mL of the alkali solution.

In the second experiment, 20 mL of a mixture of  $\text{HCl}$  with a weak organic acid  $\text{H}_n\text{B}$  ( $K_a \sim 10^{-5}$ ) was diluted to 100 mL and titrated by a 0.600M  $\text{KOH}$  solution. The results of titration are given in the table:

$V, \text{mL}$	0	1	2	3	4	5	6	7	8	10	12
$\sigma, \text{S/m}$	0.600	0.489	0.377	0.267	0.233	0.278	0.324	0.489	0.655	0.985	1.312

5. How many protons of the weak acid  $\text{H}_n\text{B}$  have been titrated?

6. Calculate the concentration of both acids in the non-diluted (initial) solution.

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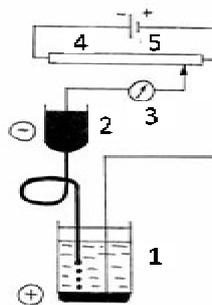
## Problem 2

For the determination of the concentration of  $\text{CoCl}_2$ , a young man added 5.0 mL of 0.2M solution of potassium nitrite to 100 mL of the analyte aqueous solution, then he added 2 mL of acetate buffer, heated the solution to boiling and left it for 4 h. The obtained yellow precipitate of potassium hexanitritocobaltate(III)  $\text{K}_3[\text{Co}(\text{NO}_2)_6]$  was filtered through a glass filter, washed on the filter with 0.01M solution of  $\text{KNO}_3$ , dissolved in sulfuric acid and transferred into a 100-mL volumetric flask. A 10.0-mL aliquot of that solution was titrated with a 0.0500M solution of potassium permanganate (until the purple color appeared). The titrant volume spent for that titration was 13.75 mL.

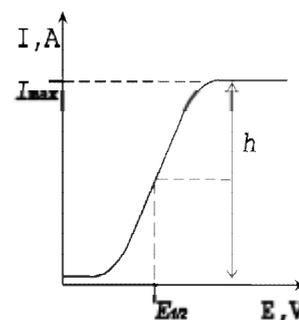
1. Give equations for the following reactions: a) formation of  $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ ; b) interaction of potassium permanganate with nitrite ion in acidic medium; c) interaction of potassium permanganate with  $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ , if cobalt is completely converted into oxidation state +2.
2. Calculate the concentration of cobalt salt in the analyte solution according to titration results.
3. What factors affect the solubility of  $\text{K}_3[\text{Co}(\text{NO}_2)_6]$  in the mother solution after precipitate formation? Choose the right answers: a) stability constant of complex ion  $[\text{Co}(\text{NO}_2)_6]^{3-}$ ; b) solubility product of the precipitate; c) concentration of  $\text{K}^+$ ; d) concentration of  $\text{Co}(\text{II})$ ; e) concentration of  $\text{NO}_2^-$ .
4. Calculate the solubility of potassium hexanitritocobaltate(III) in the mother solution (g/L) if its solubility product is equal to  $K_S = [\text{K}^+]^3[\text{Co}(\text{NO}_2)_6^{3-}] = 4.3 \times 10^{-10}$  and the stability constant of the complex ion is high enough.
5. Estimate the titration error (%) due to the solubility of precipitate in the mother solution (disregard the losses as a consequence of precipitate washing).
6. Determine the optimal volume of washing solution (0.01M  $\text{KNO}_3$ ) corresponding to the minimal titration error if the latter is caused (1) by appearance of nitrite ions in the titration flask as a result of insufficient washing of the precipitate, and (2) by losses through precipitate washing due to its solubility in the washing solution. Draw the graphs for the both components of error as functions of washing solution volume  $V_y$ . Assume that unwashed precipitate captures the mother solution in the amount equal to a half of its mass  $m$ . Take into account that each milliliter of the washing solution removes 1% of the captured mother solution volume.

**Problem 3**

Polarography is a technique applied for the determination of metal ions. The potential between a dropping mercury cathode and a mercury pool anode is varied (for example, from 0.0 to  $-1.5$  V), and the corresponding changes in current  $I$  are measured. When reducible substances are present in the solution, a sharp rise in current occurs at the certain potential. The recorded plot of current against applied voltage  $I = f(E)$  (polarogram) is characterized by wave height  $h$  (cm), or diffusion current  $I_{\max}$  (A), that are proportional to the concentration of the unknown ion, and by the potential at the midpoint of the wave  $E_{1/2}$  (half-wave potential) depending on the nature of the analyte.



Scheme of an apparatus for polarographic analysis: 1 – electrochemical cell (with pool mercury electrode); 2 – dropping mercury electrode; 3 – galvanometer; 4 – potentiometer; 5 – current source.



1. A weighed amount of  $\text{PbCl}_2$  was dissolved in 100 mL ( $V_0$ ) of 1M  $\text{KNO}_3$  solution (the salt is used to ensure conductivity). A 10.00-mL aliquote ( $V_1$ ) of the prepared solution was transferred into the electrochemical cell and subjected to polarographic analysis. The polarographic wave obtained displays a height of 5.0 mm ( $h_1$ ). After addition of 4.50 mL ( $V_2$ ) of  $\text{PbCl}_2$  solution ( $c_2 = 3$  mg/L) into the cell the wave height became 8.1 mm ( $h_2$ ). Derive the formulae and calculate the mass of  $\text{PbCl}_2$  taken for the analysis.

2. Calculate the solubility product ( $K_S$ ) of  $\text{PbCl}_2$ , if the polarographic wave recorded during analysis of its saturated solution in 1M  $\text{KNO}_3$  exhibits  $I_{\max} = 43.2$   $\mu\text{A}$ . If a standard  $\text{PbCl}_2$  solution (5.0 mM) is analyzed under the same conditions,  $I_{\max} = 13.6$   $\mu\text{A}$ .

3. A weighed sample of alloy containing zinc, lead and cadmium was dissolved and the polarogram of this solution was recorded (the potential was varied from 0 to  $-1.2$  V). Before the measurement an inert gas was passed through the solution in the cell.

Ion	$E_{1/2}$ , V
Zn(II)	-0.99
Cd(II)	-0.62
Pb(II)	-0.41
$\text{O}_2$	-0.1, -0.9

a) Draw the current–potential plot on the graph (curve No 1), using the data from the table and the marked values of  $I_{\max}$ . Point out the proper  $E_{1/2}$  values on each wave.

b) Draw the polarogram of this solution recorded without preliminary oxygen removal (curve No 2). Give the chemical equations for the half-reactions with oxygen that take place on the dropping mercury cathode in basic and acidic media.

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4. The potential corresponding to the reduction of complex  $\text{MetL}_x$  is described with equations:  $E = E_{1/2}(\text{Met}^{n+}) + 0.059/n \cdot \lg[\text{Met}^{n+}] = E_{1/2}(\text{MetL}_x) + 0.059/n \cdot \lg[\text{MetL}_x]$ , where  $E_{1/2}(\text{Met}^{n+})$  and  $E_{1/2}(\text{MetL}_x)$  are the half-wave potentials for the free and complexed metal-ions, respectively;  $[\text{MetL}_x]$  and  $[\text{Met}^{n+}]$  are the concentrations in the equilibrium, and  $n$  is the metal ion charge.

a) Give the reaction for the complex formation between lead(II) and glycine and the expression of the cumulative stability constant  $\beta_2$  for the complex  $\text{Pb}(\text{gly})_2$ . What reactions involving glycine or lead(II) may compete with the complex formation in the neutral water solution? Give at least one reaction for the metal ion and one for the ligand.

b) Derive an equation for the calculation of half-wave potential for complex  $\text{Pb}(\text{gly})_2$  reduction (use stability constant  $\beta_2$ ). Calculate  $E_{1/2}$  for  $(\text{Pb}(\text{gly})_2)$  in 0.5M glycine solution under  $\text{pH} \approx 7-8$ , if  $\beta_2 = 3.2 \cdot 10^7$ . Compare the obtained value  $E_{1/2}$  with that given in the table for  $\text{Pb}^{2+}$  ion. What is easier to reduce: complex  $\text{Pb}(\text{gly})_2$  or aqueous ion  $\text{Pb}^{2+}$ ?

## SECTION II. INORGANIC CHEMISTRY

### Problem 1

For the investigation of equilibrium between classical (**J**) and nonclassical (**G**) tautomers Luo and Crabtree in 1990 synthesized a set of mononuclear complexes (**C – J**) of d-metal (**Me**). **B** was used as an initial compound, 4.098 g of which can be obtained by the addition reaction from 3.273 g **MeO<sub>n</sub>** and the equimolar mass of **NaO<sub>n</sub>** at 250°C. The synthesis of complexes was as follows: **B** was dissolved in alcohol, then 6.210 g of (CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>P (**Me<sub>2</sub>PhP**) were added, and after addition of concentrated HCl the reaction mixture was boiled during 18 hours with reflux condenser and the orange **C** was formed (m g, yield 80%). CO was bubbled at boiling through the alcohol solution of **C** until 4.408 g of yellow **D** was formed (50% yield). To the etheric solution of **D** LiAlH<sub>4</sub> was added and boiled with reflux condenser during 40 hours till yellow **E** ( $w_{\text{Me}} = 29.50$ ;  $w_{\text{P}} = 14.73$ ;  $w_{\text{O}} = 2.53\%$ ) was formed, which contained ligand **L**, but no Cl<sup>-</sup>. **E** was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, then it was protonated using HBF<sub>4</sub> at 208 K and a daffodil solution of equilibrium mixture of **G** and **J** was obtained, which has conductivity close to LiAlH<sub>4</sub>. The complexes **D**, **E**, **G** have c.n. = 7, and in **J** c.n. = 8. For **G** ⇌ **J** Luo and Crabtree obtained  $\Delta H^0 = -4.6$  kJ/mole,  $\Delta S^0 = -10$  J/mol·K.

1. Determine **Me** and define the formula of **B**.
2. Determine the formulae of nonelectrolytes **C**, **D** and **E**, if they are complexes **Me(3+)**, and calculate m.
3. Determine **G** and **J**, if the IR-spectrum of **J** contains 1832 cm<sup>-1</sup> band, and **G** – two bands 1838 and 2692 cm<sup>-1</sup> (the IR-spectra of **KMeL<sub>4</sub>** contain band 1828 cm<sup>-1</sup>, and **L<sub>2</sub>** – 4159 cm<sup>-1</sup>).
4. Write the reaction equations of complex formation.
5. Calculate  $\Delta G^0$  and the composition of the equilibrium mixture **G** and **J** in mol.% at 208 K, considering that  $\Delta H^0$  and  $\Delta S^0$  do not depend on temperature.
6. Propose the structure of intermediate fragment at the transition of **G** to **J**, if the bond distances: L–L in **G** – 0.084; in **J** – 0.160; in the intermediate 0.138 nm.
7. Draw MO diagram for **L<sub>2</sub>** and the overlapping of orbitales in **G** in bond formation of **Me** with ligands containing **L**.

### Problem 2

*Learning without reflection is a waste,  
Reflection without learning is dangerous  
Confucius (551 – 479 BC)*

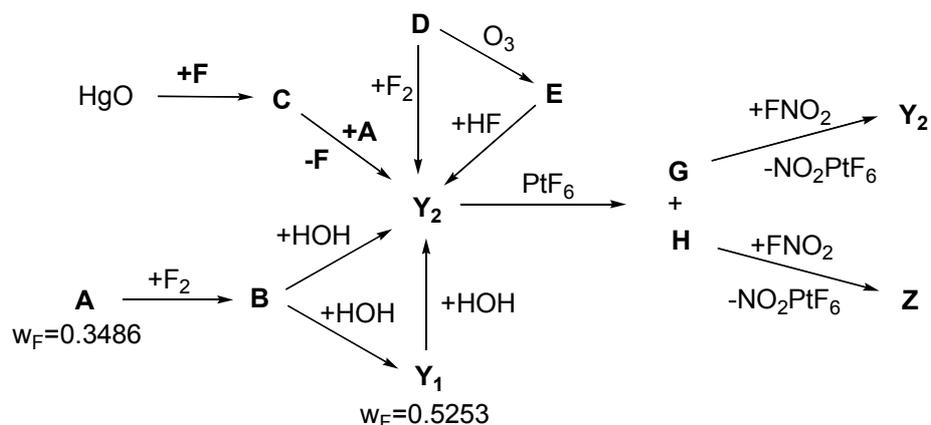
The halogens atoms have a large gamma of possible oxidation numbers which leads to a great diversity of compounds and interesting structures. However, it is important to remember that some halogens compounds could be very toxic and explosive and it is very important to pay attention working and exploring the halogen compounds.

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Compounds **X**, **Y**<sub>1,2</sub>, **Z** have the same qualitative composition. The oxidation number of central atom is growing in the row **X**, **Y**, **Z**. The compound **B**, which was obtained by fluorination of the binary compound **A** ( $\omega_F = 34.86\%$ ), could produce compounds **Y**<sub>1</sub> ( $\omega_F = 52.53\%$ ) or **Y**<sub>2</sub> by partial hydrolysis. Pure compound **Y**<sub>2</sub> could be obtained by three methods: a) by the reaction of compound **A** with the brownish- yellow gas **C**, б) by the fluorination of yellow-orange gas **D** or c) by the hydrofluorination of dark red liquid **E**. Binary compounds **C** – **E** have the same qualitative composition. One of the elements of compounds **C** – **E** is the same that the central atom of **X-Z** molecules. The oxidation number of this element is growing in a row **C**, **D**, **E**; moreover the oxidation number of this element is the same in **A** and **C** compounds. The synthesis of **C** from simple compound **F** and mercury (II) oxide is one of the few methods to obtain compound **C** in a pure state.

The compound **Y**<sub>2</sub> was oxidized by strong oxidizing agent as  $\text{PtF}_6$  to obtain equimolar quantity of salts **G** and **H**. During the action of nitryl fluoride on **G** and **H** it was obtained respectively **Y**<sub>2</sub> and new product **Z**.

All discussed reactions are represented on the scheme. Take into account that it is not always given all by-products.



- Determine all unknown compounds. Take into account that the synthesis of **Y**<sub>2</sub> from **C** is going through the formation of unstable compound **X** which disproportionates quickly on equimolar quantities of **Y**<sub>2</sub> and **A**.
- Write all equations of reactions given on the scheme.
- Give the structural formulae and the hybridization of central atom for compounds **B**, **C**, **D**, cations **G**, **H**, and also for **X**, **Y**<sub>1,2</sub>, **Z**.
- Explain why the liquid **E** conducts the current.
- Write the hydrolysis reactions of **C**, **D**, **E** compounds.

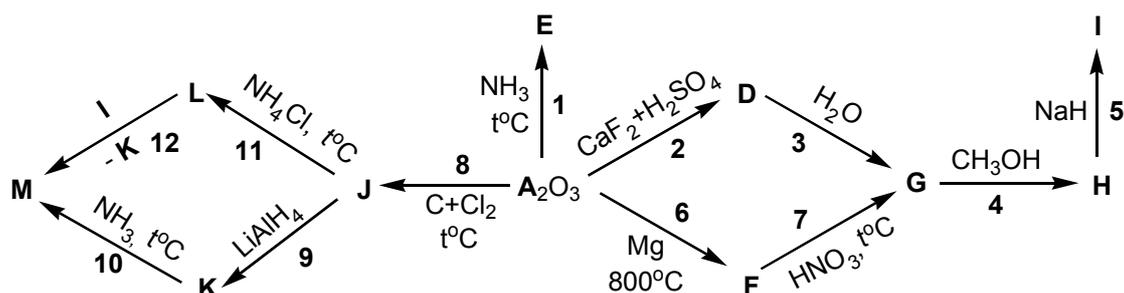
**Problem 3**

*Carbon is like gold: it is shiny and precious.  
(Russian national proverb)*

In inorganic chemistry there are substances with physical and chemical properties similar to organic. In this problem, you are invited to meet with three groups of compounds are examples of such similarities.

Carbon has a large number of allotropic modifications – graphite, diamond, fullerenes, graphene, carbon nanotubes. Inorganic binary compound **E** can form a structure similar to all of the above. (**E**)<sub>3</sub> is isoelectronic to C<sub>6</sub> cell in the graphite structure. The ratio of elements of the **E** is 1: 1. At a pressure of 7 GPa and a temperature of 1500°C **E** becomes crystal structure of diamond. The hardness of **E** is less than diamond, but more durable, heat-resistant and chemically resistant, so it is widely used for polishing steel.

The elements included in the **E**, also form **M** – a colorless liquid, which is also called "inorganic benzene" for a similar smell, and a ring structure with a system of delocalized  $\pi$ -electrons. Due to the difference in the electronegativities of the atoms included in the **M**, it is more reactive in addition reactions compared to benzene.



- Determine the **M** and **E**, write the reaction equations represented in the scheme.
- Write a reaction that may occur in the processing of steel diamond polish wheels and reduce their service.

In addition to the **E** some transition metals compounds have structures similar to allotropic carbon modifications too. The most active work is carried out to obtain "inorganic graphene" based on them for the creation of optoelectronic semiconductors. Binary substance **N** was one of the first, which managed to obtain monolayers with a similar layer structure of graphene. Obtaining a given structure of **N** occurs in several stages. At first, thermal decomposition of  $10^{-3}$  mol of ammonium salt **B** produces 178 mL of gas with a sharp odor at 90°C and a pressure of 1 atm, 1.008 g of the oxide **O** of hexavalent metal **C** (the oxygen content of the oxide **O** is 33.3% mass) and 89 mL water vapor. Further, monolayers **N** are formed after the interaction between **O** and hydrogen sulfide in a stream of hydrogen at 400°C.

- Determine the **N**, **B**, **C**. What side product will be formed if the reaction is carried out without hydrogen? Write the equation of this reaction.

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After 20 days after the closing ceremony of the 49th International Mendeleev Olympiad an article was published in Science Journal by scientist from MIT about how to obtain inorganic ion  $P_xN_y^-$  – analogue of cyclopentadienyl anion (Cp). According to the mass spectrum of  $P_xN_y^-$ , his mass number  $m/z = 104$  was defined.

4. a) determine the molecular formula of the anion, if it is known that two signals are observed in the spectrum of  $^{15}N$  NMR,  $x$  and  $y$  are integers number;

b) draw resonance structures of  $P_xN_y^-$ .

In addition to  $P_xN_y^-$  there are other inorganic compounds containing phosphorus, nitrogen and sulfur and being isoelectronic to Cp;

c) write three molecular formula of the respective cation, anion and molecule.

5. a) write a Hückel rule for aromaticity for organic substances;

b) determine the number of  $\pi$ -electrons in **M** and  $P_xN_y^-$ .

## SECTION III. PHYSICAL CHEMISTRY

### Problem 1

The molecules  $A_2$ , formed by nuclides with  $i \neq 0$ , have nucleus isomers. The nuclei of atoms  $A$  with odd number of nucleons are described by Fermi – Dirac statistics and *ortho*-isomer ( $o\text{-}A_2$ ) has odd total spin  $I$  ( $I = \sum i$ ), *para*-isomer ( $p\text{-}A_2$ ) – even.

1. Give  $I$  for  $o\text{-}H_2$  and  $p\text{-}H_2$ . Indicate the orientation of spins by arrows.

For the reaction  $p\text{-}H_2 \rightleftharpoons o\text{-}H_2$  the equilibrium constant  $K = \chi_o/\chi_p = f(T)$  at low  $T$  (see table), and at high –  $K \neq f(T)$ .  $K = 2.98$  (400 K);  $3.00$  (500 K);  $3.00$  (600 K).

2. Derivate the equation  $\ln K = A + B/T$  if  $\Delta G^0 = -RT \ln K$  and  $\Delta G^0 = \Delta H^0 - T \Delta S^0$ . Using  $\chi_i$ , calculate  $A_{av}$  and  $B_{av}$  and fill the gaps in the table.

$T, K$	20	30	40	60	100
$\chi_p, \text{mol.}\%$		97.0		65.8	38.6
$K$	$1.89 \cdot 10^{-3}$		0.127		

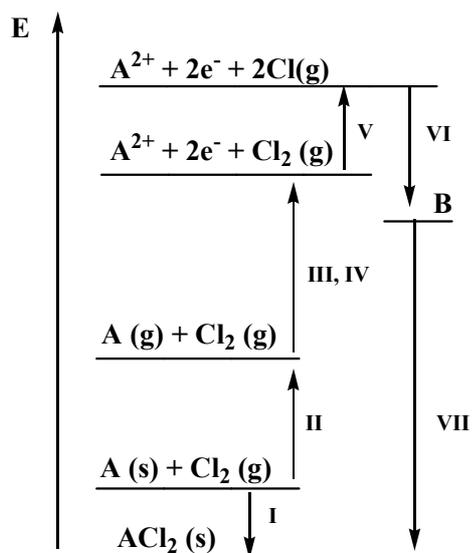
3. Calculate  $\Delta H^0$  and  $\Delta S^0$ , considering, that they are independent of  $T$ .

In 2010 J. Ingues proposed three step scheme for the reaction at high  $T$ . At the first step  $p\text{-}H_2$  (1 atm, 600 K,  $V$ ,  $\chi_p = 1$ ) transforms to  $o\text{-}H_2$  (1 atm, 600 K,  $V$ ,  $\chi_o = x$ ) and  $p\text{-}H_2$  (1 atm, 600 K,  $V$ ,  $\chi_p = 1 - x$ ) with entropy  $\Delta S_I = 9.2x$  J/K. At the second step  $o\text{-}H_2$  and  $p\text{-}H_2$  mix together and entropy equals  $\Delta S_{II} = -R[x \ln x + (1-x) \ln(1-x)]$ . At the third step –  $T$  changes and  $\Delta S_{III} = C_V \cdot \ln(T/600)$ .

4. Give the condition, at which  $K \neq f(T)$  if  $d \ln K / dT = \Delta H^0 / RT^2$ .
5. Calculate  $\Delta S_{I+II} = \Delta S_I + \Delta S_{II}$  for  $x = 0.6, 0.7, 0.8$  and  $0.85$ . Build the graph  $\Delta S_{I+II} = f(x)$ , determine  $x$  for  $\Delta S_{I+II} = \max$ , calculate for it  $K_0$  and compare with given in the condition  $K$  for high  $T$ .
6. Determine the minimal  $T$ , at which the scheme works, if entropy change in the reaction and at change of  $T$  are equal and  $C_V = 20.9$  J/mol·K.

The nuclei of atoms  $A$  with even number of nucleons are described by Bose – Einstein statistics and  $o\text{-}A_2$  has even spin, and  $p\text{-}A_2$  – odd. The value  $\chi_i$  is proportional to the possible conditions  $2I + 1$ .

7. Give  $I$  for *ortho*- and *para*-isomers of deuterium ( $o\text{-}D_2$  and  $p\text{-}D_2$ ).
8. Calculate the maximal possible content of isomers for  $H_2$  and  $D_2$  and show the stable ones.

**Problem 2**

Stage	II	III	IV	V	VI
Energy, kJ/mol	164	549	1064	243	-349

The Born – Haber cycle based on Hess law, is a convenient graphical method for studying the thermodynamics of chemical reactions. Such a cycle for the formation reaction of the chloride of metal **A**, which comparing two ways of this process – from simple substances (I) and an ideal gas of ions of the substance (VII), is shown in left figure. The latter passes through the stages: sublimation of **A** (II), ionization of **A** (III, IV), dissociation of chlorine (V), ionization of chlorine atoms (VI).

Upon dissolution of the carbonate of metal **A** in the hydrochloric acid 69.7 kJ of heat is absorbed  $\text{ACO}_3(\text{s}) + 2\text{HCl}(\text{l}) = \text{ACl}_2(\text{sol}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$ .  $\text{ACl}_2$  crystallizes from the solution as hexahydrate. For it's decomposition with the aim of obtaining anhydrous salt it is necessary to spend 344.3 kJ of heat.

1. a) Calculate the lattice energy ( $E_{\text{lat}}$ )  $\text{ACl}_2$ . б) Write the composition of the particles corresponding to state **B**.

Compound	$\text{ACO}_3(\text{s})$	$\text{ACl}_2(\text{sol})$	$\text{H}_2\text{O}(\text{l})$	$\text{H}_2\text{O}(\text{g})$	$\text{ACl}_2 \cdot 6\text{H}_2\text{O}(\text{s})$	$\text{CO}_2(\text{g})$
$\Delta_f H^\circ_{298}$ , kJ/mol	-1220	-805.4	-285.8	-241.8	-2624	-393.5

Metal **A** with a density of 2.54 g/cm<sup>3</sup> has a cubic face-centered crystal lattice. The radius of atom **A** is equal to  $r = 0.217$  nm.

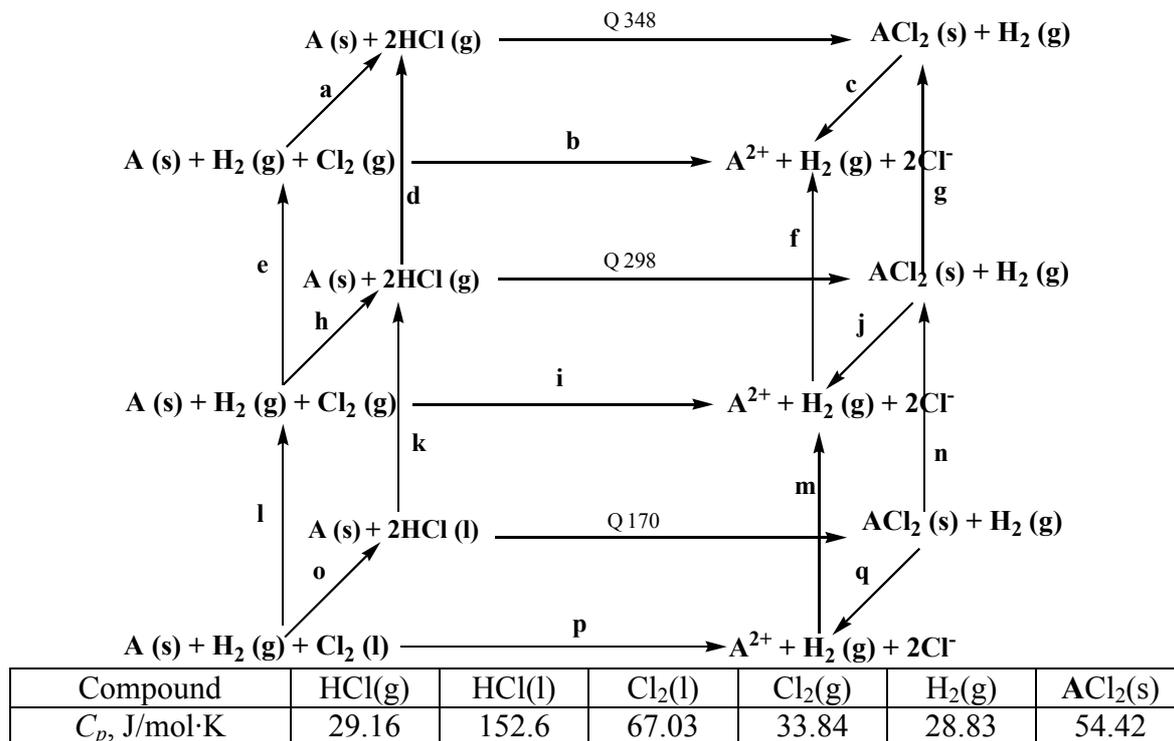
2. a) Express  $r$  through the parameter  $a$  of the unit cell. б) Determine **A**.

The above cycle describes the processes that occur at a fixed temperature, pressure and other parameters. Building of three-dimensional Born – Haber cycle with changeable external parameters allows to predict the most thermodynamically favored route of complex chemical reactions. In the following figure, as an example, a diagram of a simple reaction between metal **A** and hydrochloric acid at three different temperatures of 348, 298 and 170 K (the scale of energy is not respected) is shown. At 170 K chlorine and hydrochloric acid are the liquids.

*Description:*  $Q_T \equiv \Delta_r H^\circ_T$ ; **a** =  $\Delta_f H^\circ_{348}(\text{HCl}, \text{g})$ ; **c** =  $[\Delta H_{\text{lat}} + 3RT]$ ; **f** =  $[C_p(\text{A}^{2+}, \text{g}) + 2C_p(\text{Cl}^-, \text{g}) + 2C_p(\text{H}_2, \text{g})]\Delta T$ ; **g** =  $[C_p(\text{ACl}_2, \text{s}) + C_p(\text{H}_2, \text{g})]\Delta T$ ; **h** =  $\Delta_f H^\circ_{298}(\text{HCl}, \text{g}) = -92.3$  kJ/mol; **j** =  $[\Delta H_{\text{lat}} + 3RT]$ ; **o** =  $\Delta_f H^\circ_{170}(\text{HCl}, \text{l})$ ; **b** = -2976 kJ/mol, **e** = 4.39 kJ/mol; **d** = 4.171 kJ/mol; **k** = -92.0 kJ/mol; **l** = -92.09 kJ/mol; **n** = -76.97 kJ/mol.

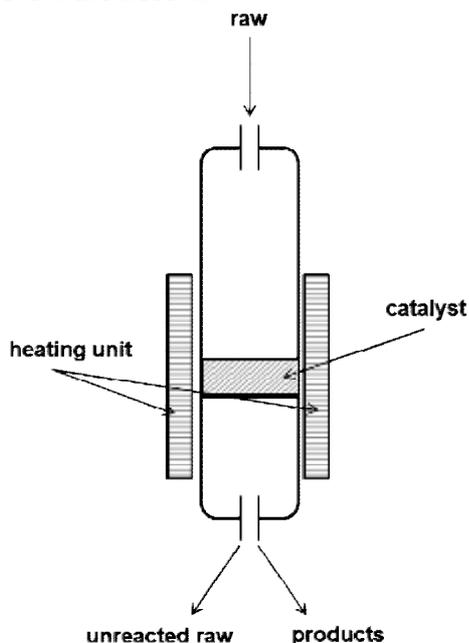
3. Write the expression of the energies of processes **b**, **d**, **e**.

4. Determine  $\Delta_r H^0_{348}$ ,  $\Delta_r H^0_{298}$ ,  $\Delta_r H^0_{170}$  (kJ/mol), using three-dimensional Born – Haber cycle and the data from paragraph 1



Physical constants: gas constant  $R = 8.314 \text{ J/mol}\cdot\text{K}$ , Avogadro's number  $N_A = 6.02 \cdot 10^{23} \text{ mol}^{-1}$ .

### Problem 3



In the physical chemistry no way exist for prediction of activity of catalyst in certain reaction based on its physico-chemical properties meaning that there is no “general theory of catalysis”. For the prediction understanding of mechanism of catalytic reaction is required. To determine the mechanism one often carry out kinetic investigation of the reaction and establish the kinetic scheme approximately. The scheme consist of sequence of intermediate compounds and by-products obtaining in the course of reaction.

A schematic diagram of reactor used in heterogeneous catalytic reactions, widespread in the industry, is illustrated in the Figure. For quantitative determination of activity of catalyst conversion  $C$  of the raw (mole fraction of reacted raw with respect to raw fed), selectivity  $S(X)$  on target product  $X$  (mole fraction of  $X$  with respect to all products) and yield  $Y(X)$  of product  $X$  are in common use.

1. Derive the equation for yield on product **X** using conversion of raw and selectivity on product **X**.

For the investigation of kinetic scheme one vary contact time of catalyst with raw. Since it is easier to change WHSV (weight hourly space velocity, or feed rate) without changes in catalyst weight, one does it by this way. After that one analyze distribution of products depending on feed rate and suppose kinetic scheme of reaction.

2. Derive the equation for contact time ( $\tau$ , s) of catalyst with raw using catalyst weight ( $m$ , kg), its bulk density ( $\rho$ , kg/m<sup>3</sup>) and raw feed rate ( $V$ , L/min).

Investigation of catalytic conversion of **A** into **B** was carried out in continous flow reactor at 200°C. The catalyst weight was 0.5 kg in all experiments and its bulk density was 1000 kg/m<sup>3</sup>. Feed rate was changed in the range of 1 – 30 L/min. It was discovered that by-products **C**, **D** and **E** are obtained beside **B** and unreacted **A**. For each feed rate yield of **A** – **E** products was calculated and given in the Table.

3. a) Calculate contact time of catalyst with raw for each feed rate value based on the data given in the Table; b) Reveal kinetic scheme of reaction using the dependence of yields on contact time. Consider all the transformations as irreversible first-order reactions.

V, L/min	Y, %			
	<b>B</b>	<b>C</b>	<b>D</b>	<b>E</b>
30.0	0	2	0	9
5.0	2	18	4	26
2.5	6	22	9	38
1.5	17	15	12	46
1.0	40	5	2	50

4. a) Calculate conversion of **A** for all feed rate values (fill the Table in the answer sheet); b) Which function describes the dependence of conversion of **A** on contact time if only irreversible **A** to **B** transformation occurs over the catalyst?
5. Calculate conversion of **A** at 210°C and feed rate 5 L/min under the same other conditions. Consider activation energy of **A** to **B** conversion as 50 kJ/mol.

## SECTION IV. LIFE SCIENCES AND POLYMERS

### Problem 1

Macromolecules of polyelectrolytes (PE) contain groups capable of dissociation in aqueous solutions. PEs can interact with other charged species via the ion exchange mechanism.

1. Draw structures of the repeating units of the polymers listed in the Answer Sheet. Of these, select a pair of PEs that react with one another in their aqueous solution to form an interpolyelectrolyte complex.

A water-soluble polymer chitosan is prepared via hydrolysis of natural polymer chitin (see the structure in the Answer Sheet) in the presence of acetic acid.

2. Draw a scheme of chitin hydrolysis yielding chitosan and determine the amount of charged groups per one chitosan macromolecule if its molecular mass is 492310 g/mol and the average molecular mass of the repeating unit is 164.10 g/mol.

Chitosan exists in the form of polycation in acidic aqueous solutions, thus being capable of interacting with negatively charged species. For example, the interaction of aqueous solutions of chitosan and compound **A** (50.00 wt.% C, 5.60 wt.% H, 44.40 wt.% O) gives a loose precipitate of the interpolyelectrolyte complex. The freezing point of 1 wt% aqueous solution of sodium salt of **A** (the cryoscopic constant of water is of 1.86 kg·deg/mol) equals  $-0.208^{\circ}\text{C}$ .

3. Determine the gross formula and molecular mass of **A**. Take that dissociation of **A** is complete.

Yellow substance **B** prepared by interaction of ammonium molybdate(VI) with phosphoric acid in an excess of nitric acid (not a redox reaction) belongs to a special class of compounds containing a polyvalent anion of complex structure. The corresponding acids behave similar to polyacids and are capable of the interacting with polybases to form interpolyelectrolyte complexes.

4. a) Write down the equation of formation of **B**. Note that drying of **B** to constant mass at  $150^{\circ}\text{C}$  leads to the residue with the metal content of 61.36% and phosphorus content of 1.65%.

b) How many anions of **B** per the chitosan molecule (see i. 2) are found in the stoichiometric polycomplex? *If you have failed to give the answer in i. 2, take  $N$  as the number of ionogenic groups in the chitosan molecule.*

Enthalpy of the reactions of polyelectrolyte complex formation being close to zero, these reactions occur owing to high positive entropy change, which is due to the release of small ions initially located in the vicinity of the polyion into the bulk solution.

5. Indicate the low-molecular weight ions released in the course of interaction of:

a) the polyelectrolytes chosen in i. 1

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b) chitosan and the acid corresponding to **B**. If you have failed to give the answer in i. 1, 2, or 4, give your own examples of the interacting polyelectrolytes (no more than two pairs), drawing their structures in the Answers Sheet.

The entropy increase owing to the small ions release into the bulk solution is partially compensated by an unfavorable change of entropy due to binding of the polyions (these polymers initially distributed in the entire volume of the reaction mixture are later found in the precipitate of the insoluble complex). Note that entropy is related to the number of microscopic states of the system which provide for its macroscopic state.

6. Arrange the following compounds in the increasing order of their tendency towards complex formation with chitosan: tribromoacetic acid **C**, acid **A**, and the acid corresponding to **B**. Determine the element with the highest content (by mass) in the dried precipitate of the chitosan complex with a mixture of these acids (each of three acids taken in an excess with respect to the stoichiometric ratio).

## Problem 2

To the authors of task 6 at IChO-2015,  
big connoisseurs of freshly baked bread

Cooking in vacuum (fr. *sous-vide*) is a method when meat or vegetables are placed into a sealed airtight plastic bag and simmered long at relatively low and controlled temperature, usually in a water-bath. The method is characterized by a number of advantages. In the case of meat slabs (usually boiled or braised) the correct choice of temperature (~60°C) provides for complete transformation of muscular collagen (fibrillar protein, the major component of connective tissue) into gelatin with maximum retention of the meat succulence.

1. Write down (in general form) the reaction equation of collagen transformation into gelatin.

The color of beef is by 90-95% due to the protein of myoglobin, specifically to the ratio of its three forms differing in the corresponding ion and/or the ligand bound:

Myoglobin (Mb), containing  $\text{Fe}^{2+}$  and water molecule;

Oxymyoglobin ( $\text{MbO}_2$ ), containing  $\text{Fe}^{2+}$  and oxygen molecule;

Metmyoglobin ( $\text{MMb}^+$ ), containing  $\text{Fe}^{3+}$  and water molecule.

Fresh-killed meat is of deeper color inside the slab as compared to its external parts, and is practically free of  $\text{MMb}^+$ . Due to precise temperature control and uniform heating of the slab, *Sous-vide* allows cooking ideal steaks with different degree of doneness accordingly differing in the meat color.

The degree of steak doneness	Color	Temperature of cooking, °C
Extra-rare or Blue ( <i>bleu</i> )	Rich red	46–49
Medium ( <i>demi-anglais</i> )	Pink in the center, more red towards the outer parts	60–65
Well done ( <i>bien cuit</i> )	Grey-brown	71
Overcooked ( <i>trop cuit</i> )	Black	>100

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2. Determine the prevailing myoglobin form (Mb, MbO<sub>2</sub> or MMb<sup>+</sup>) at each of the mentioned above degrees of steak doneness.

3. What other process developing in the course of *sous-vide* cooking of meat can be behind the taste difference depending on the degree of steak doneness.

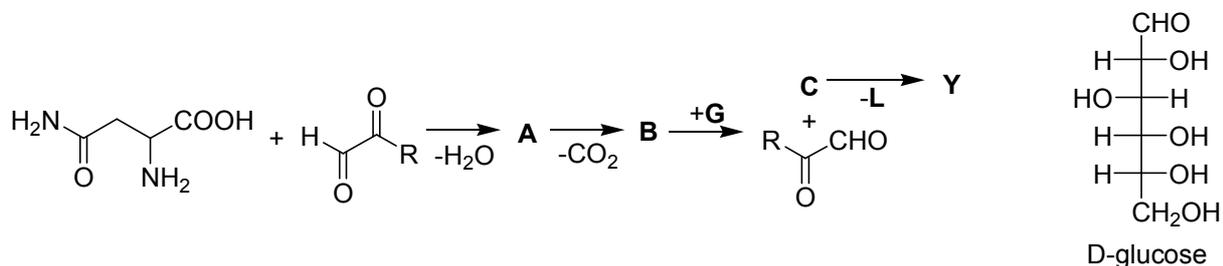
Conventional meat panbroiling leads to typical dish smell, color and taste. This is mostly due to the formation of Maillard reaction products (occurs at  $t > 150^{\circ}\text{C}$ ). Impossibility of Maillard reaction is one of *sous-vide* drawbacks disappointing gourmands.

Compound **X** providing a dish with the smell of butter is formed via Maillard reaction. The formula of **X** can be represented as C<sub>p</sub>H<sub>q</sub>O<sub>r</sub>. It obeys two following equations:  $p + q + r = 12$  (1) and  $p \cdot q \cdot r = 48$  (2).

4. Derive the molecular formula of **X** if the mass content of hydrogen in **X** exceeds 7%.

5. Draw the structural formula of **X** if it is known that **X** contains 2 types of C atoms and one type of H and O atoms each.

On the other hand, *sous-vide* allows avoiding a number of toxic products, such as **Y** (C<sub>3</sub>H<sub>5</sub>NO). **Y** is formed by Maillard reaction from amino acid asparagine and a 1,2-dicarbonyl compound (e.g., 3-deoxyglucosone, a *D*-glucose derivative) according to the hereunder scheme (reaction equations at all stages):



It is known that **G** and **L** are binary substances.

6. Draw the 3-deoxyglucosone structure in Fischer projection.

7. Draw the structural formulae of **A** – **C**, **G**, **L** and **Y**.

Compound **Z** is an **Y** metabolite. Being a mutagen **Z** is a hazardous substance for man. **X** transformation into **Z** is a single-stage enzymatically catalyzed process. **Z** contains 36.75% O and 41.38% C by mass and has an asymmetric C atom.

8. Write down the structural formula of **Z**.

### Problem 3

*All things are poison and nothing is without poison; only the dose makes a thing not a poison.*  
Paracelsus

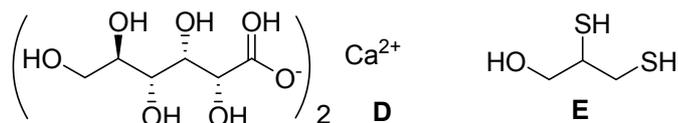
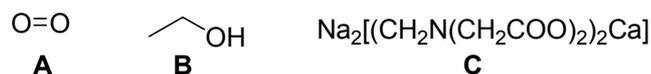
Toxicology deals with poisons and mechanisms of their action. Poisons are substances causing disruption of vital activity of an organism when present in it in relatively small doses (thus, as little as 100 ng of particular protein toxins and as much as 200 g of sodium chloride lead to fatal

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case in man). Since, a human being is in every day contact with various chemicals, knowledge of their toxicological properties as well as the first aid measures in the case of intoxication is vitally important. Substances easing the influence of poisons on organisms are referred to as antidotes.

1. Names of some substances (1 – 5) often met in chemical labs are given in the hereunder table. Penetration of these substances into organisms leads to intoxication. Based on their chemical properties, correlate in the Answer Sheet each substance with the structure of its antidote (A – E).

1	white arsenic
2	methanol
3	hydrofluoric acid
4	lead sugar
5	carbon monoxide

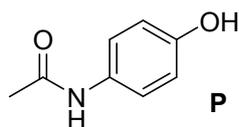


Cyanide is the favorite poison in detective novels, cytochrome c oxidase (an iron-containing enzyme of the respiratory chain) being its target in organisms. In the case of intoxication with potassium cyanide or vapors of hydrocyanic acid, it is needed to open an ampoule with isoamyl nitrite and let the sufferer inhale its vapors.

2. Draw the structure of isoamyl nitrite and write down the sequence of equations of three reactions occurring in blood, which explain the antidote action. Remember that hemoglobin is one of the blood components! Denote the unessential part of organic molecules as R.

After applying the first aid measures described above, sodium thioisulfate is administered to the patient intravenously.

3. Write down the equation of this final detoxication stage if two sulfur-containing particles are its low molecular weight products.



Overdosing of drugs often leads to intoxication. Even well known preparations like **P** can be dangerous if overdosed. The toxicity of **P** is due to the product of its single stage enzymatic transformation **P1** (9.40% N by mass)

with one of antidotes (A – E) being a reagent in this transformation.

4. Deduce the structure of **P1** if the number of the carbon atoms is not changed in the transformation from **P**.

**PA** ( $\text{C}_5\text{H}_9\text{NO}_3\text{S}$ ) obtained by a single stage synthesis from a canonical amino acid acts as an antidote in the case of such intoxication. **PA** is a diprotic acid with  $\text{p}K_a$  values of 3.2 and 11.2; its solutions decolorize  $\text{KI}_3$  solution. **PA** enters into the reaction of nucleophilic addition to **P1**, aromatic substance **P2** being the sole reaction product.

5. Deduce the structures of **PA** and **P2**, write down the reaction schemes.

Overdosing of **P** leads to liver injury induced by **P1**.

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6. Exhaustion of what biologically important molecules is behind the liver injury? Choose the correct variant in the Answer Sheet.

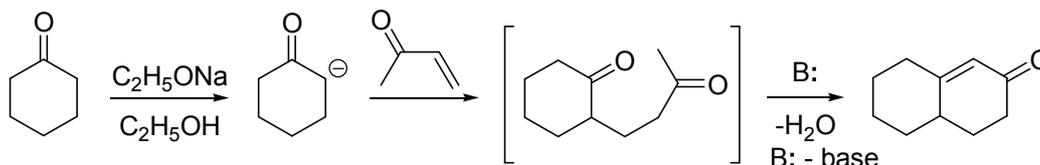
**X1** is one of the most potent (still slow-response) poisons. This is a three-element metal salt. Penetration of as low as 1 ng of this substance into the organism can turn out to be lethal. The intoxication manifests in gradual development of sickness, head-ache, hyperthermia, blood effusion, gastrointestinal upset and mental breakdown. The numbers of atoms in the formula unit of **X1** are a geometrical progression, the total sum of the numbers does not exceed 15, and the mass content of carbon equals 16.2%.

7. Do calculations to determine **X1** and write down the reaction equation explaining its toxicity. Write down the reaction of thermal decomposition of **X1**.

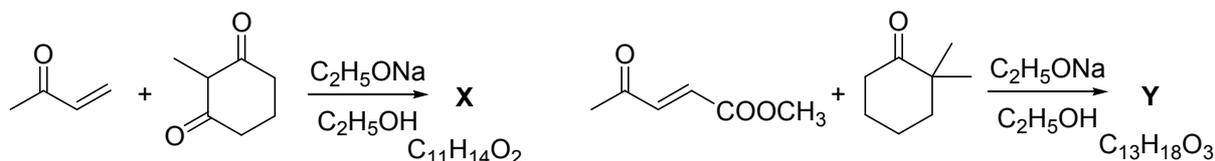
## SECTION V. ORGANIC CHEMISTRY

## Problem 1

The Robinson annulation is very important reaction in the synthesis of various natural compounds, antibiotics, steroids, etc. This reaction consists of the following steps: ketone deprotonation, Michael addition of the formed enolate ion to methyl vinyl ketone (or its derivative), aldol condensation producing the corresponding cyclohexanone derivative.

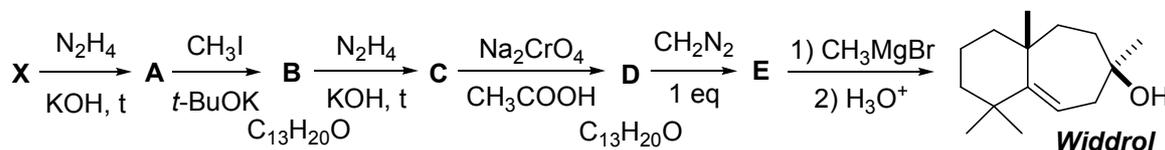


Two reactions are given below. Compound **X** is the product of the Robinson annulation. Oppositely, **Y** has no two annulated rings but has two different C=O groups despite its formation includes the Michael addition step.



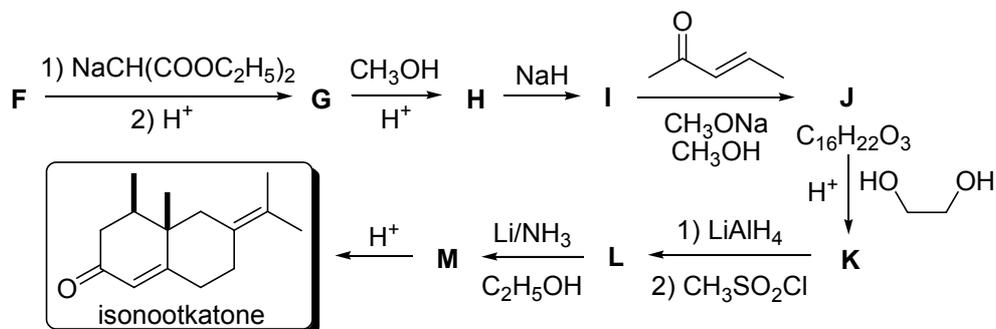
1. Write down structural formulae of **X** and **Y**.

Compound **X** was used in the total synthesis of anticancer terpenoid ( $\pm$ )-widdrol:



2. Write down structural formulae of **A** – **E**.

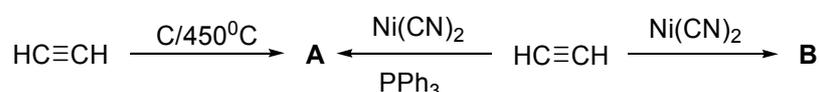
The Robinson annulation was also used in the total synthesis of another terpenoid, isonootkatone. The started compound in this synthesis is dibromoalkene **F**, <sup>1</sup>H NMR spectrum of which contains 2 signals with the relative intensities of 2:3; one of the products of its ozonolysis is acetone.



3. Write down structural formulae of **F** – **M**.

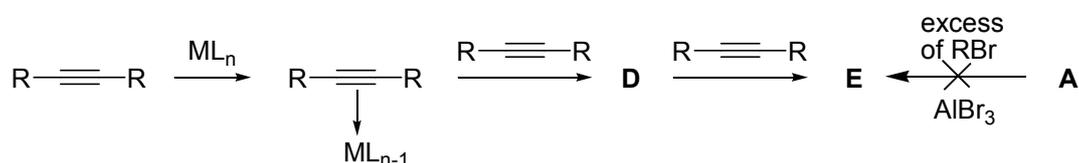
**Problem 2**

The efficient method for the synthesis of cyclic compounds is the cycloaddition reaction wherein two or more bonds are formed during a single reaction act. According to IUPAC recommendations, cycloaddition reactions can be classified by the number of participating atoms as (m+n+...)-cycloadditions.



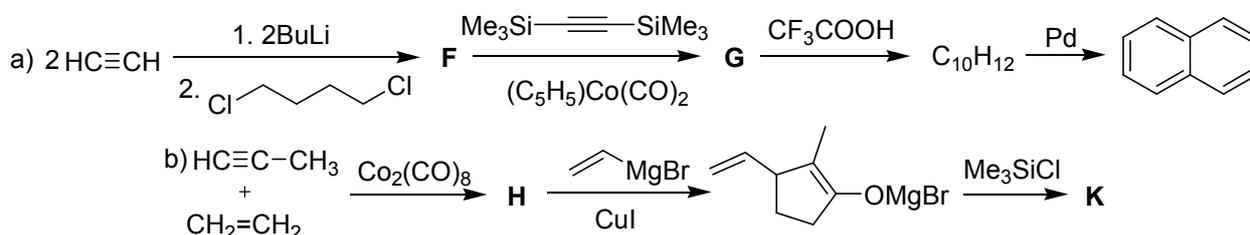
- Determine structures of **A** and **B**, if  $M(\mathbf{A}) / M(\mathbf{B}) = 0.75$ .
- Write down types of the cycloaddition reaction for the formation of **A** and **B**.

Use of transition metal complexes for catalysis of cycloadditions provides high efficiency of these processes. Mechanism for the formation of the compound **A** and its homologues in the presence of complex  $\text{ML}_n$  can be represented as:



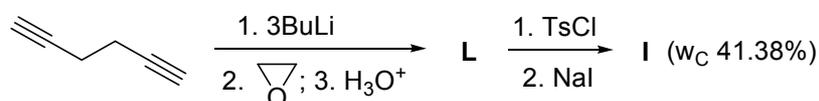
- Write down structural formulae of **D** and **E** for the reaction catalyzed by  $(\text{C}_5\text{H}_5)\text{Co}(\text{CO})_2$ , if:
  - E** ( $^1\text{H}$  NMR spectrum of which has doublet and multiplet with the relative intensity of 6:1) is homologue of **A**;
  - intermediate **D**, which can be considered as the product of formal (2+2+1)-cycloaddition, contains 15.86% of cobalt.
- Write down the major product of the reaction between **A** and 2 equivalents of  $\text{RBr}$  in the presence of  $\text{AlBr}_3$  under kinetic control.

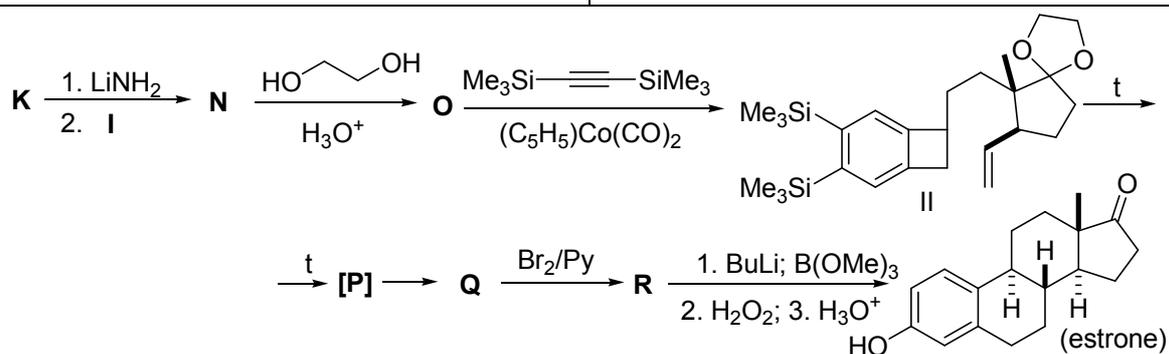
Cycloadditions in the presence of transition metal complexes allow: a) to synthesize polycyclic structures from acyclic starting compounds; b) to prepare a ring simultaneously with the introduction of a functional group:



- Write down structural formulae of **F**, **G**,  $\text{C}_{10}\text{H}_{12}$ , **H**, **K**.

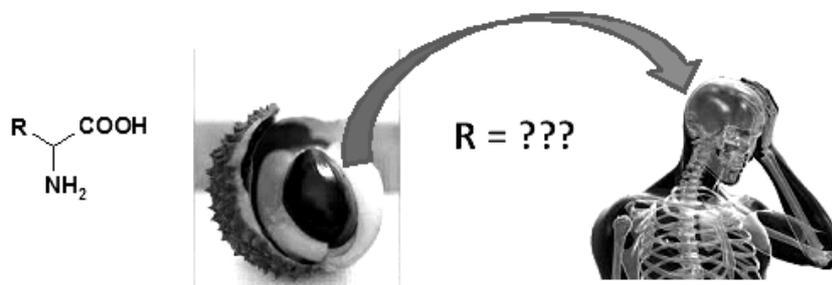
The unique set of cycloaddition reactions provides a possibility to synthesize diverse polycyclic structures with the formation of several rings in one synthetic step. Thus, in the synthesis of estrone three rings were formed in a one step:



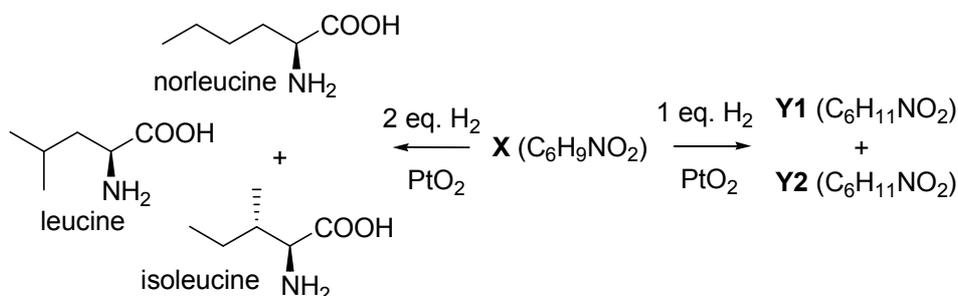


6. Write down structural formulae of **L**, **I**, **N**, **O**, **P**, **Q**, **R**, if **II**, **P**, **Q** are isomers, **Q** has two rings more than **P**.

### Problem 3

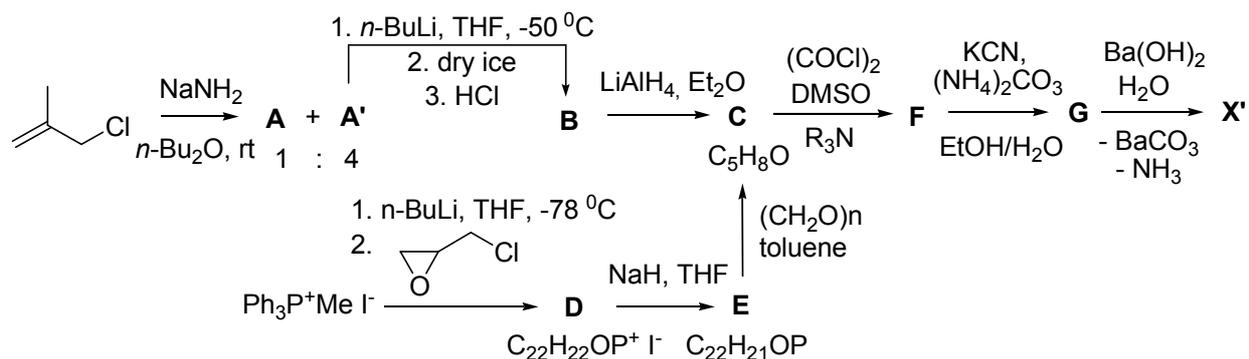


In December 2015, during the investigation of the epidemiological outbreak of hypoglycemic encephalopathy in children in Muzaffarpur (India) experts found unexpectedly that this outbreak was result of not some infection but poisoning by  $\alpha$ -amino acid **X** ( $\text{C}_6\text{H}_9\text{NO}_2$ ) which is present in seeds of lychee fruits. This amino acid significantly decreases the level of sugar in blood up to fatal case. This amino acid was isolated for the first time by British chemists in 1962. Its structure was deduced from the data of its catalytic hydrogenation in the presence of Adams catalyst. Namely, hydrogenation of **X** using 1 equivalent of dihydrogen, mixture of two diastereomeric optically active acids **Y1** and **Y2** is formed. Hydrogenation of **X** with two equiv. of  $\text{H}_2$  produces the mixture of leucine, norleucine and isoleucine. The structure of **X** was assigned unambiguously from  $^1\text{H}$  NMR spectrum, wherein multiplet with the intensity corresponding to two protons is present at 5.7 ppm.



The synthetic approaches to acid **X** were developed much later. Thus, in 2006 in Moscow State University synthesis of racemic diastereomers of **X** (**X'** in Scheme below) was proposed. The

key intermediate **C** can be obtained by two different methods. In the first one, the starting compound is methallyl chloride. In the second one, this is methyltriphenylphosphonium iodide.



- Decipher structure of amino acid **X**, point out the absolute configuration of chiral center(s) in terms of *R,S*-nomenclature, propose its name according to IUPAC nomenclature.
- Write down structural formulae of **Y1** and **Y2**.
- Decode scheme of synthesis of the mixture of racemic diastereomers **X'**, if it is known that:
  - under normal conditions compound **A'** is gaseous; its <sup>1</sup>H NMR spectrum consists of 2 signals, its <sup>13</sup>C NMR spectrum has 3 signals;
  - bicyclic compound **E** contains pentacoordinated phosphorus atom;
  - compound **G** is the derivative of imidazole (five-membered ring containing two nitrogen atoms).