

SECTION I. PHYSICAL CHEMISTRY

Problem 1

Baxendale and George showed, that the dissociation rate of $\text{Fe}(\text{NH}_4\text{C}_5\text{H}_4\text{N})_3^{2+}$ (tris-bipyridylferrum (II)) (after $\text{Fe}(\text{bipy})_3^{2+}$) depends on the H^+ concentration:

$\text{C}(\text{H}^+)$, mol/L	0	0.02	0.05	0.1	0.2	0.4	0.5	1.0	2.0
$k_{\text{H}} \cdot 10^2$	3.52	8.57	12.48	15.60	18.12	19.83	20.22	21.50	21.50

The resulting dependence they explained by protonation process, that preceded dissociation $\text{Fe}(\text{bipy})_3^{2+} + \text{H}^+ \rightleftharpoons \text{Fe}(\text{bipy})_3\text{H}^{3+}$, and considered, that $\text{Fe}(\text{bipy})_3^{2+}$ dissociates slower than $\text{Fe}(\text{bipy})_3\text{H}^{3+}$, and the speed limit is reached when only $\text{Fe}(\text{bipy})_3\text{H}^{3+}$ is present in the solution. However this mechanism was disproved by the results of electron spectroscopy and another one was proposed. It included the break of one bond Fe–N (k_1, k_{-1}) followed by two streams: the first with break of the second bond Fe–N (k_2); the second – protonation of atom N (k_3) with subsequent break of the second bond Fe–N (k_4).

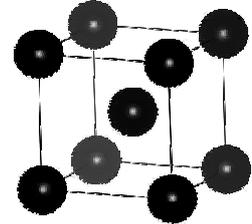
1. Draw the plot of dependence $k_{\text{H}} = f(\text{C}(\text{H}^+))$ and estimate the value of $\text{C}(\text{H}^+)$ corresponding to the start of achieving the speed limit.
2. Give the reason, why the spectra at $\text{C}(\text{H}^+) = 0$ and $\text{C}(\text{H}^+) = 2$ disproved the mechanism.
3. Write down the second mechanism with the help of structural formulae. Derivate kinetic equation and the equation for k_{H} .
4. Give the value of the rate constant k_1 , considering that at high $\text{C}(\text{H}^+)$ the limit rate is observed.
5. Find the ratio between the period of the first bond formation Fe–N and the period of breaking of the second bond Fe–N at $\text{C}(\text{H}^+) = 0$.
6. Determine the structure of low-spin $\text{Fe}(\text{bipy})_3^{2+}$ and high-spin $\text{Fe}(\text{bipy})_2^{2+}$ by the CFT method and point the dissociation rate of what complex is higher.

Problem 2

As there is no fish without bones, there are no materials without defects

The structures of real materials generally are not regular crystals as there are always different defects inside. These defects are formed in equilibrium, during material fabrication or use. The simplest defect is vacancy – absence of atoms in crystalline lattice.

Metal **A** is largely used in industry, it has body-centered cubic (bcc) lattice (see figure). If each 32^{th} elementary cell has one vacancy, this metal have the following parameters: $a_0 = 2.87 \text{ \AA}$, $\rho = 7.73 \text{ g}\cdot\text{sm}^{-3}$.

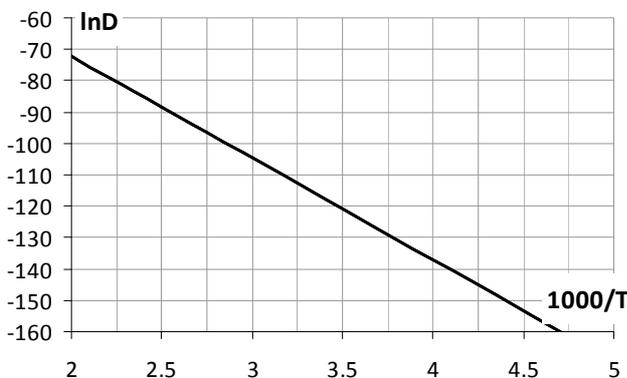


1. a) How many atoms has one elementary bcc cell?
- b) Determine the metal **A** by calculation of its molecular mass to one place decimals.

There are several characteristics of vacancies (v): concentration c_v , formation Gibbs energy $\Delta_f G_v^0$, diffusion coefficient D ($\text{sm}^2\cdot\text{sec}^{-1}$) and diffusion energy E_D . Diffusion energy E_D is the sum of vacancy formation energy $\Delta_f U_v^0$ and migration activation energy E_A :

$$c_v = \exp\left(-\frac{\Delta_f G_v^0}{RT}\right), \quad D = D_0 \exp\left(-\frac{E_D}{RT}\right) = D_0 \exp\left(-\frac{\Delta_f U_v^0 + E_A}{RT}\right).$$

Assume that vacancy formation enthalpy equals to formation energy.



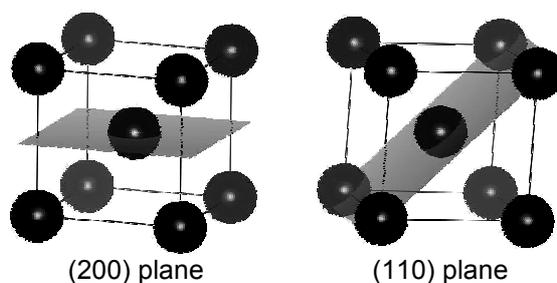
2. The change in which values should be neglected to be certain that $\Delta H \approx \Delta U$:
 - a) temperature,
 - b) pressure,
 - c) volume,
 - d) entropy?

3. Using the plot, determine D_0 and vacancy diffusion energy E_D .

4. Neglecting vacancy formation entropy and taking into account that $\Delta_f U_v^0 = 3E_A$, determine the vacancy concentration at 800K.
5. Is it possible that material with the defects concentration, pointed in question 1, is formed in equilibrium at 800K?

Diffusion coefficient is related to the vacancy jump frequency ν and jump distance d by the equation: $D_0 = \nu k d^2 / 6$, where k – the number of equivalent jumps (i.e. the number of nearest neighboring atoms).

6. Calculate jump frequency ν for a metal with bcc cell if $D_0 = 0.01 \text{ sm}^2\cdot\text{sec}^{-1}$.
7. Vacancy formation energy is directly proportional to the number of neighbors (k). Calculate $\Delta_f U_v^0$ on two surfaces, which are formed by cutting the metal by planes (200) and (110).



Problem 3

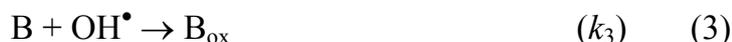
High-energy radiation can cause chemical reactions in substances. Radiolysis of water is one of the most important radiation-chemical processes. In particular, hydrogen gas is evolved. Release of $\text{H}_2(\text{g})$ from aqueous solution of radium bromide was first observed by German scientist F. Giesel in 1902. Marie Curie compared this phenomenon with "electrolysis without electrodes".

In the first experiment water was subjected to γ -radiation from ^{60}Co source, weighting 2 g. The half-life period of ^{60}Co equals $\tau_{1/2} = 5.3$ years. Contribution of γ -decay to overall radiation constitutes 0.1% (there is also β -decay). The energy of one γ -quantum equals 1.332 MeV. The radiation-chemical yield of hydrogen $G = 0.047 \mu\text{mol}\cdot\text{J}^{-1}$. Assume that radiolysis occurs under the action of γ -rays only, and they are completely absorbed by the water. $1 \text{ eV} = 1.6\cdot 10^{-19} \text{ J}$.

In the second experiment hydrogen was produced by electrolysis with the current 8 A. Faraday constant $F = 96485 \text{ C}\cdot\text{mol}^{-1}$. The duration of both processes was 1 hour.

1. a) Write down the equations of the processes at anode and cathode; b) Compare the volumes of hydrogen (at normal conditions), evolving in radiolysis and electrolysis of water.

If a diluted solution of $\text{Fe}(\text{HSO}_4)_2$ is exposed to ionizing radiation one can get Fenton's reagent – a mixture of hydrogen peroxide and a salt of Fe(II), which is used for water purification from organic pollutants of phenol series. Below are the reactions of oxidation of *p*-hydroxybenzoic acid (B):



2. Using the stationary concentrations method, deduce the kinetic equation for oxidation of B.

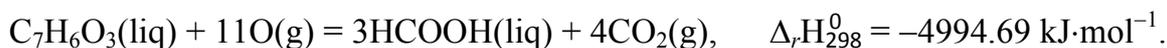
Chloride ions can serve as inhibitors for Fenton's reaction. In presence of Cl^- the following reactions occur in the solution:



Ion Cl_2^\bullet practically does not react with organic molecules, disappearing mostly in the reaction with Fe^{2+} , Electromotive force (e.m.f.) of this reaction is 1.528 V.

3. a) Write down the reaction of Cl_2^\bullet with Fe^{2+} ; b) Determine the equilibrium constant for this reaction at 298K. $E^0(\text{Cl}_2^\bullet/\text{Cl}^-) = 2.3 \text{ V}$, $E^0(\text{Fe}^{3+}/\text{Fe}) = -0.058 \text{ V}$, $E^0(\text{Fe}^{2+}/\text{Fe}) = -0.473 \text{ V}$.

p-Hydroxybenzoic acid can be oxidized catalytically to formic acid HCOOH:



Standard combustion enthalpy of formic acid: $\Delta_c H_{298}^0(\text{HCOOH}, \text{liq}) = -254.58 \text{ kJ}\cdot\text{mol}^{-1}$.

Standard formation enthalpies of the compounds: $\Delta_f H_{298}^0(\text{H}_2\text{O}, \text{liq}) = -285.83 \text{ kJ}\cdot\text{mol}^{-1}$,

$\Delta_f H_{298}^0(\text{CO}_2, \text{g}) = -393.51 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_f H_{298}^0(\text{C}_7\text{H}_6\text{O}_3, \text{liq}) = -594.5 \text{ kJ}\cdot\text{mol}^{-1}$.

4. a) Write down the combustion reaction of $\text{HCOOH}(\text{liq})$; b) Calculate the enthalpy of the bond $\Delta H_{298}^0(\text{O}-\text{O})$ in O_2 molecule; c) Calculate the energy of this bond $\Delta U_{298}^0(\text{O}-\text{O})$; d) Calculate the bond energy at zero absolute temperature $\Delta U_0^0 = D_0^0(\text{O}-\text{O})$.

SECTION II. LIFE SCIENCES AND POLYMERS

Problem 1

Minamata disease is caused by poisoning with a number of toxic compounds, in particular with substances **X** (colorless crystals, $t_{\text{melt}} = 167^{\circ}\text{C}$) and **Y** (colorless liquid). 14 people died the disease in 1956 in Japanese city of Minamata.

Production wastes of the plant manufacturing acetaldehyde (1), acetic acid (2), and vinyl chloride (3) turned out to be the mediated reasoning for people's deaths.

1. Determine the structure of the substance **S** used for the synthesis of products 1 – 3, and write down the reaction equations behind the industrial process indicating the reaction conditions.

Anaerobic bacteria utilizing **Z** (contains 26.12% by mass of halogen) are the immediate source of **X** and **Y** in nature. **Y** is formed from **Z** via two stages, both catalyzed by enzymes-transferases:



In laboratory, **X** can be obtained from **Y** using the colorless crystalline carbon-free substance **Z** according to the following equation:



2. Determine the formulae of **X** and **Y** if they contain 4.78% and 10.41% of carbon (by mass), respectively. Determine the formula of **Z**.

X and **Y** predominantly influence the human central nervous system. The degree of neurotoxicity is directly proportional to a substance hydrophobicity, which is related to its ability to cross the lipid barriers between blood and cerebrum.

3. Draw the structures of **X** and **Y**. Which of these is more toxic?

4. What was the predominant way of the environment contamination by the plant situated inside the Minamata city boundary? Choose only one variant in the Answer Sheet.

A preparation based on an optically active oxygen-containing compound **B** (29.0% C and 6.50% H by mass) can be used to cure the Minamata disease. The structure of **B** is very similar to that of **C**, a compound widely found in living nature. **C** was first obtained in a pure state as a result of olive oil treatment with lead (II) oxide as far as in the XVIII century.

5. Draw the structure of **B**.

6. Write down equation of the reaction of the first synthesis of **C**.

Problem 2

Heterochain polymers contain atoms of different elements in their main chain.

1. Draw structures of polypropylene, poly(vinylamine), polyglycine, polyethylene oxide, poly(methyl methacrylate). Show which of these polymers are heterochain.

Heterochain polymers can be obtained via condensation of functional groups of appropriate compounds.

2. Which of the above heterochain polymers can be obtained by the monomer polycondensation? Write down the reaction equation and choose the conditions from the listed in the Answer Sheet.

Silicon-containing polymers are often used in practical applications. Since the corresponding monomers are usually unstable, the polymer synthesis includes a precursor hydrolysis with immediate condensation of the hydrolysis product.

3. Write down equations of the following reactions: *a*) of tetraoxy-silane with one equivalent of water; *b*) of tetraoxy-silane with two equivalents of water; *c*) of complete tetraoxy-silane hydrolysis; *d*) of condensation between the products of reactions *a*) and *b*).

4. Draw a fragment of the product of complete condensation of entirely hydrolyzed tetraoxy-silane.

5. Draw silanes with the following substituents: chloro(diethoxy)methyl-, (diethoxy)dimethyl-, tetramethyl-, (ethoxy)trimethyl-, dichloro(diethoxy)-. From these compounds choose: *a*) the only one leading to a linear polymer; *b*) the only one leading to a non-polymeric product. Draw the structures of the polymer repeated unit (*a*) and low molecular product (*b*).

Materials with excellent mechanical characteristics can be obtained based on silsesquioxanes, silicon containing compounds of regular composition. Silsesquioxane **A** (41.8% Si, 17.9% C, 35.8% O) possesses a 3D structure, contains 8 equivalent silicon atoms and sole types of carbon and oxygen atoms.

6. Draw the structure of **A** and propose a precursor from which it can be derived.

Silsesquioxanes with only one active substituent are of particular interest. Silsesquioxane **B** (19.7% C), a structural analog of **A**, contains one group which can be involved in radical polymerization.

7. Draw the structure of **B**.

Co-polymers of **B** are non-combustible if the mass fraction of silicon is not less than 5%. On the other hand, inhomogeneous product with a limited possibility of further

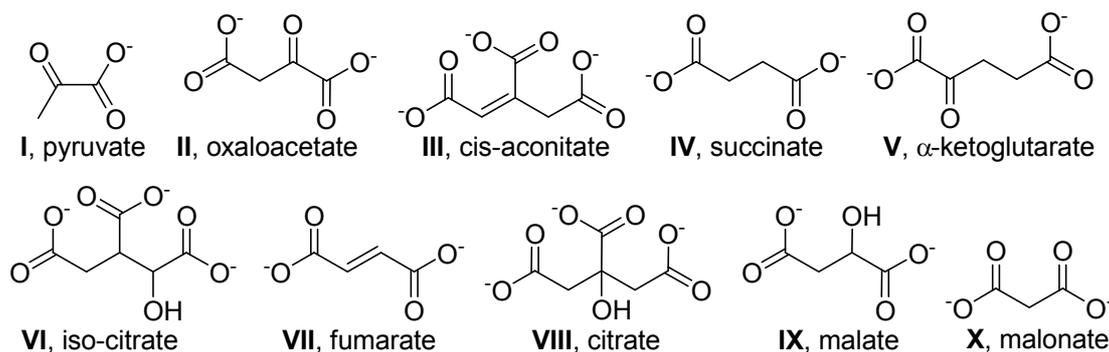
utilization is obtained if the molar fraction of **B** in the monomer mixture exceeds 2%.

8. Is it possible to obtain a homogeneous non-combustible co-polymer of **B** with butadiene-1,3? Prove your answer by calculating the minimal molar fraction of **B** in the non-combustible product.

Problem 3

One of the most important metabolic pathways of pyruvate (**I**) transformation was first described in a simplified form and did not include one of the stages known today. When disclosing the pathway, the researchers were aware of experimental facts (a – f) given below. In this task you will have to ascertain the sequence of stages of pyruvate metabolism.

A number of anions of di- and tricarboxylic acids are involved in the pathway. Formulae and names of the anions are given hereunder in a random order.



Experimental studies showed that:

- all stages are catalyzed by corresponding enzymes;
- transformation of succinate (**IV**) is catalyzed by succinate dehydrogenase. The enzyme is inhibited by malonate (**X**), which results in accumulation of metabolites **IV**, **V**, and **VIII**;
- only reactions of two-electron oxidation (in some cases accompanied by decarboxylation), hydration and dehydration are met along the metabolic pathway;
- oxidation reactions require either co-enzyme NAD^+/NADH or co-factor FAD/FADH_2 (oxidized/reduced forms, respectively);
- incubation of **I** and **II** in the presence of the enzyme leads to **VIII**;
- addition of even small amounts of any of the metabolites **II** – **IX** results in an abrupt acceleration of pyruvate consumption.

1. Write down the sequence of all stages of pyruvate metabolism.

2. Indicate the stages involving oxidation of an organic substrate.
3. In what form do the co-enzyme and co-factor enter the reactions mentioned in i. 2?
4. Which of the compounds **I – X** is(are) optically active? Draw the *R*-isomer(s) of this(ese) compound(s).

Another metabolic pathway (in addition to the described above) occurs in some organisms at the stage of their rapid growth. Formation of one equivalent of succinate from two equivalents of pyruvate turns out to be the overall result of the latter pathway.

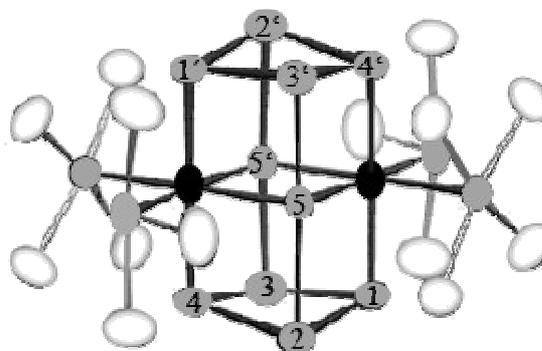
5. Write down the sequence of all stages of the additional metabolic pathway if:
 - g) it involves compounds **I, II, III, IV, VI, VIII, IX**, as well as the compound **A**, which is not utilized in the main metabolic pathway;
 - h) two pyruvate molecules enter the pathway at different points;
 - i) succinate is produced from iso-citrate;
 - j) four stages in both pathways coincide.

SECTION III. INORGANIC CHEMISTRY

Problem 1

*New and original things are born of itself,
without, their creator was thinking about it.*

Ludwig van Beethoven (1770 – 1827)



The coordination polymer chemistry has been developing and considerably growing since a couple of years. The possible structures of these compounds amaze and gladden connoisseurs of this chemical art. In 2011, it has been synthesized a complex **X** (right figure), which contains a ten atom's fragment (fragment **x**) formed by atoms 1 – 5 and 1' – 5'. This fragment **x** being formally neutral participates at the complex's stabilisation as an electron donor to the transitional metal **A**.

5.346 g of complex **X** has been formed at 250°C, by reaction between 0.768 g of the transitional metal **A**, 2.688 g of non metallic element **B** and its chloride **C**.

In the argon atmosphere at 280°C the complex **X** decomposes into 3 solids compounds: non metallic element **B** (unknown mass), **D** (2.133 g) and **E** (0.597 g). And also there is a formation of 0.4032 L ($t = 341.1^\circ\text{C}$, $p = 1 \text{ atm}$) of a gas **F**. **D** is metal's **A** complex compound, where a neutral **B** atoms' fragment is a ligand.

The compound **B** was separated and the solid residue was treated by heating. It leads to a formation of a binary compound **G** (1.792 g) and two gaseous products **F** and **C** with total volume 0.224 L ($t = 409.7^\circ\text{C}$, $p = 1 \text{ atm}$) in the equimolar quantities. It is known that gases **F** and **C** have the same elemental composition. Compound **E** is also binary and it differs from the elemental composition of **G**.

1. Determine unknown compounds **X** and **A – G** note that $M(\text{E}) / M(\text{D}) = 0.28$.
2. Write the reaction equations to be mentioned.
3. Determine oxidation state of metal **A** in the complex **X**. Take into account the 18 electrons rule.

To calculate the formal charge of 10 atoms of fragment **x**, the following consideration can be used: equivalent atoms 5 and 5' are the central atoms in the three-centres four electrons bonding (like as for I_3^- , O_3 , or HF_2^-). Remember that the fragment **x** is formally neutral.

4. Calculate the formal charge of each of 10 atoms in fragment **x**.

Problem 2

0.235 g of a fine-grained black powder of metal **A** was solved in ~2.96 mL of 10% HCl ($\rho = 1.048 \text{ g/cm}^3$) at slight heating. The formed bluish solution of a salt **B** was mixed with a solution of 3.676 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 15 mL H_2O . After the addition of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution taken in small excess, the deposition of 3.068 g yellow-orange precipitate **C** was observed. All the experiments were made under inert atmosphere, the solutions of HCl and $(\text{NH}_4)_2\text{C}_2\text{O}_4$ were preliminary degassed.

Thermal analysis revealed the obtained precipitate to decompose in 3 stages in oxygen (25...900°C) with the formation of ternary mixture **G** with 57.3% mass loss. One of the stages is accompanied by an increase of the mass.

By adding an excess of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ to the solution of the salt **B** with cobalt nitrate, a red solution **D** could be prepared. PbO_2 and CH_3COOH induces the change of the solution color from red to emerald green. Ethanol can be used to extract emerald green crystals of **E** and apple green crystals of **F**. The latter becomes colorless under the light.

It was shown by the thermal analysis that the mixture of **E** и **F** crystals decomposes in oxygen (25...900°C) with the formation of mixture **G**.

1. Decipher the compounds **A**, **B**, **C**.
2. Determine the qualitative and quantitative composition (mol. %) of the mixture **G**.
3. Define the complex ions exist in the solution **D**.
4. Write down the formation reactions of **B**, **C** and complexes in the **D** and emerald green solutions.
5. How does the oxidation state change on decomposing of **F** in light, if it is known that the magnetic moment changes from 0 to $1.73 \mu_B$.
6. Explain why **F** decomposes under light but **E** does not, using crystal field theory.

Problem 3

A complex compound, that consists the group Me_4O_2 , plays a great role in the oxidation process $2\text{H}_2\text{O} - 4e^- = \text{O}_2 + 4\text{H}^+$ in the photosynthesis of green plants. The group Me_4O_2 participates in the photo-oxidation ($\overset{+2}{\text{Me}}_x \overset{+3}{\text{Me}}_{4-x} \text{O}_2 - xe^- + h\nu = \overset{+3}{\text{Me}}_4 \text{O}_2$). Complex compounds of **Me** were synthesized to use in modelling of the similar process with participation of the

group $\text{Me}_3\text{O}^{+2,+3}$ ($\text{Me}_x\text{Me}_{3-x}\text{O} - xe^- + hv = \text{Me}_3\text{O}^{+3}$). At the first step K_aMeO_b was added to 12.88 g (0.04 mol) of tetraalkylammonium bromide $[\text{R}_4\text{N}]\text{Br}$. The purple precipitate **A** with mass 14.44 g was obtained after filtration. At the second step 0.01 mol of $\text{C}_5\text{H}_5\text{N}$ (Py) and $\text{Me}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ were dissolved in alcohol, then glacial acetic acid and a part of **A** were added until a reddish brown solution **I** was produced. At the third step 0.00333 mol of NaClO_4 were mixed with the solution **I** and brown precipitate **D** was separated. Blackish brown crystals of **B** can be isolated by a careful evaporation of the solution **I** at 65°C . The elemental composition of nonelectrolyte **B** and the cation in the salt **D** is the same (21.4% Me, 42.0% C, 4.26% H, 5.44% N и 26.9% O).

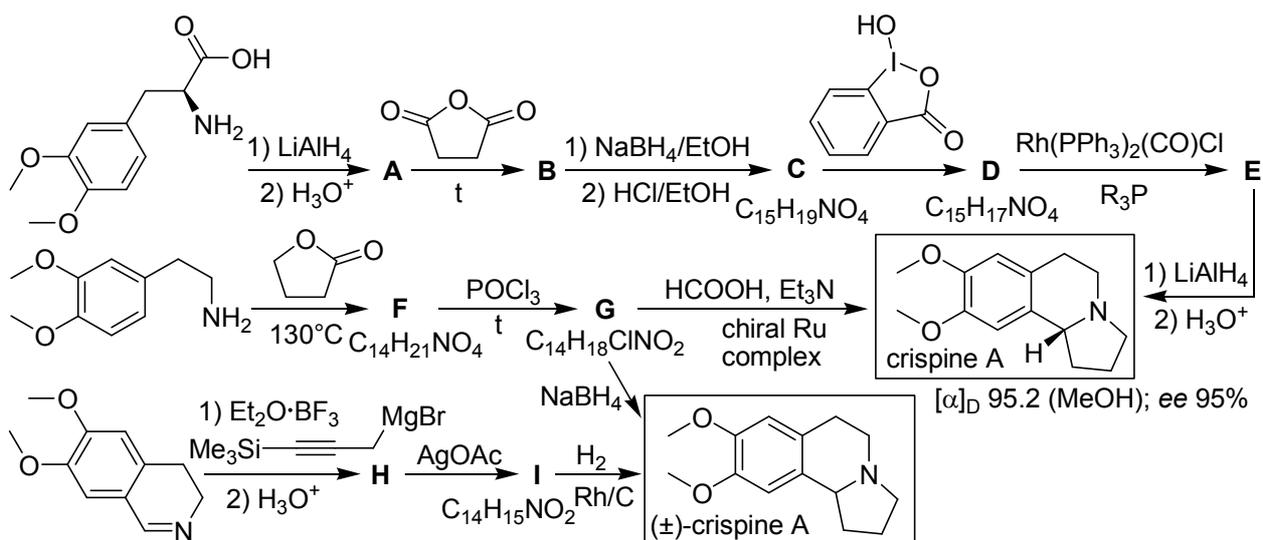
Bond length, Å (number of bonds)				Average valence angle, °			
Me-O _a	Me-O _b	Me-N	C-O _b	Me-O _a -Me	O _a -Me-O _b	O _a -Me-N	O _b -C-O _b
1.94 (3)	2.10 (12)	2.17 (3)	1.28 (12)	120	94.6	179	118.3

- Determine $[\text{R}_4\text{N}]\text{Br}$, **Me** and **A**, if $M(\text{A}) - M([\text{R}_4\text{N}]\text{Br}) = 39 \text{ g/mol}$, and **A** is formed in the exchange reaction.
- Determine **B**, draw the structural formula **B** and calculate x in $\text{Me}_x\text{Me}_{3-x}\text{O}^{+2,+3}$.
- Determine **D**. Write the formation reaction equations **B** and **D** from **A**.
- Calculate E for $\text{O}_2 + 4\text{H}^+ + 4e^- = 2\text{H}_2\text{O}$ in water ($p(\text{O}_2) = 1 \text{ atm}$, $C(\text{H}^+) = 10^{-7} \text{ mol/L}$), note that $E^0(\text{O}_2/\text{H}_2\text{O}) = 1.23 \text{ V}$.
- Calculate E^0 for Me_3O^{+3} (the group in the cation of **D**) $+ xe^- = \text{Me}_x\text{Me}_{3-x}\text{O}^{+2,+3}$ (the group in **B**), note if the reaction proceeds 66.70% $E = 0.44 \text{ V}$, concentrations of other reactants equal $C = 1 \text{ mol/L}$.
- Calculate e.m.f. at standard concentrations except $C(\text{H}^+) = 10^{-7} \text{ mol/L}$ and determine the possibility of complex **D** with group Me_3O to participate in the photosynthesis.

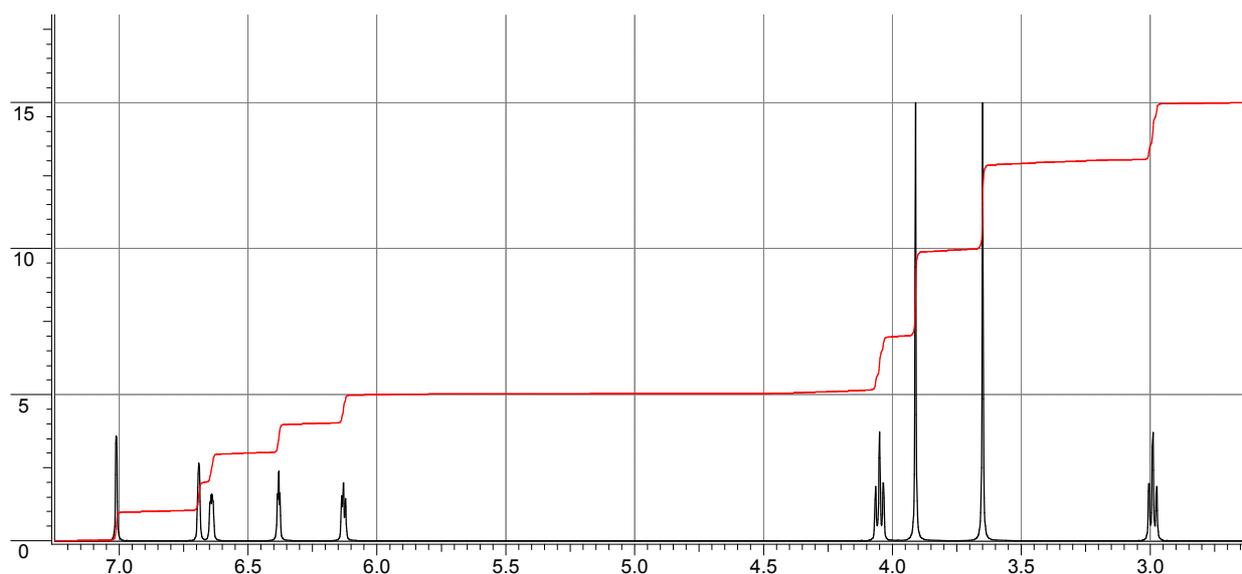
SECTION IV. ORGANIC CHEMISTRY

Problem 1

Alkaloid crispine A demonstrates high cytotoxicity and is considered as a potent agent for the cancer treatment. It stimulated the development of methods for synthesis of crispine A including the optically active one (*ee* is enantiomeric excess, *i.e.* the difference in content of two enantiomers).



1. Write down structural formulae of **A – I** accounting for fact that **C** is tricyclic compound. ^1H NMR spectrum of **I** is given below as a prompting to you. In the answer sheet attribute signals in spectrum to the corresponding fragments of molecule **I**.



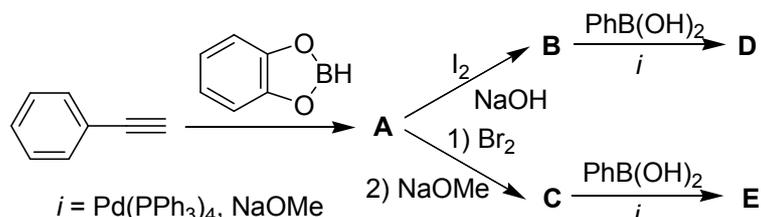
A sample of crispine A, synthesized by one of the proposed methods, has a rotation angle $[\alpha]_D 43.9^\circ$ (CH_3OH).

2. Calculate ratio of two enantiomers of crispine A in this sample.

Problem 2

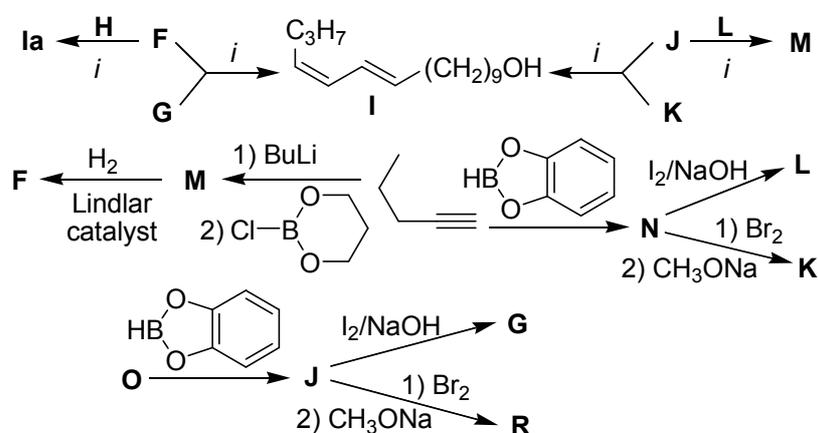
Vinylboronic acids and their derivatives are valuable reagents in organic synthesis. These compounds undergo a Pd⁰-catalyzed cross-coupling with aryl- and vinyl halides (Suzuki reaction) which proceeds with retention of configuration at C=C bond. Nevertheless, vinylboronic acid derivatives can be utilized for synthesis of vinyl halides, notably that process can proceed with either retention and inversion of configuration depending on reaction conditions.

1. Decipher scheme below accounting for isomers **D** and **E** contain 93.3% carbon, compound **E** having one plane of symmetry more than **D**.



Suzuki reaction is intensively utilized for synthesis of natural polyenes. Thus, preparations of bombykol (**I**) and its stereoisomers **Ia** and **Ib** are given in scheme below.

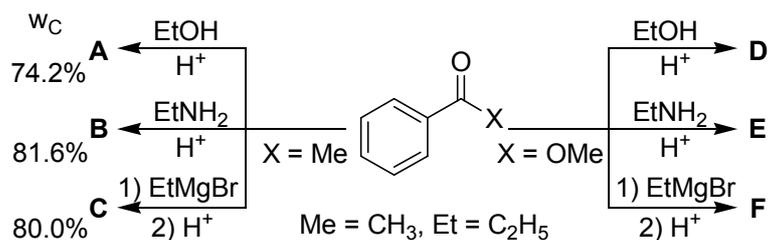
2. Decipher scheme, write down structural formulae of **F – O**, **Ia**, **Ib**.



Problem 3

The large difference in electronegativity of oxygen and carbon leads to significant polarization of C=O bond. It provides electrophilic properties of carbonyl carbon atom *versus* various nucleophilic agents.

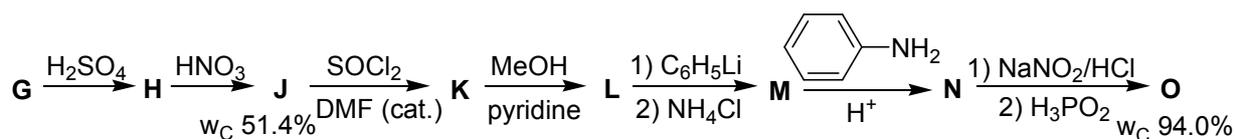
1. Write down structural formulae of compounds **A** – **F** which are formed in the reactions given below:



Among three nucleophiles, demonstrating high reactivity against alkyl halides, – NaI, NaHSO₃, NaCN (+ H⁺) – one reacts with two substrates from the list below; another one reacts with one of these substrates; the third one does not react at all.

2. Point out in Answer sheet substrate(s) with which these nucleophiles react: a) benzaldehyde; b) 1-phenylethanone; c) methyl benzoate.

Porous materials fabrication utilizes compound **O**. Its synthesis is based on the nucleophilic addition to C=O group. At the first step of its preparation compound **G** is treated with conc. H₂SO₄ affording **H**, oxidation of which furnishes **J**.



3. Write down structural formulae of **G** – **O** accounting for that carbon content in **G** and **H** is 62.1% and 90.0%, hydrogen content is 10.3% and 10.0%, respectively; ¹H NMR spectra of **H** and **L** contain 2 signals with relative intensities of 3:1; ¹H NMR spectrum of **G** contains a single signal.

Treatment of **G** with diluted acid leads to compound **P** instead of **H**.

4. Write down structural formulae of **P**.

SECTION V. ANALYTICAL CHEMISTRY

Problem 1

Ice-melting chemicals reduce the freezing point of water by increasing the number of particles (both neutral particles and ions) present in a solution. This effect is quantitatively described as $\Delta T_m = imK$, where K is cryoscopic constant of the solvent (1.86 K·kg/mol for water), m is molality (amount of the solute (in mol) divided by the mass of the solvent (in kg)), i is isotonic coefficient (number of particles produced upon the dissolution of the solute molecule). The acidity constant of formic acid is $10^{-3.75}$.

Ice-melting product **A** consists of NaCl, CaCl₂, calcium and ammonium formate and sand. This product may optionally be used with non-dissociating anticaking agent **X**.

1. What is substance **X**, if it contains only C, H, N and O atoms, and the solution obtained by adding 16.15 g of this substance to a 1 L portion of water freezes at -0.50°C ?
2. Aqueous solution of **A** (30.0 g/L) was filtered to remove sand, and four 10 mL aliquots were taken. An excess of formaldehyde was added to aliquot no. 1 which was then titrated with a 0.1000 M solution of KOH with phenolphthalein indicator; the endpoint titrant volume was 7.2 mL (this reaction yields hexamethylenetetramine (CH₂)₆N₄). 30 mL of 0.1000 M standard solution of alkaline Br₂ and then an excess of acidic solution of KI were added to aliquot no. 2; iodine in the resultant solution was titrated with 0.1000 M solution of Na₂S₂O₃ (the endpoint titrant volume was 27.2 mL). Ammonia and metal indicator were added to aliquot no. 3 and the solution was titrated with 0.1000 M solution of EDTA until the color changed (the endpoint volume of EDTA was 12.7 mL). After addition of a K₂Cr₂O₇ indicator to aliquot no. 4 it was titrated with 0.1000 M solution of AgNO₃ until the precipitate became pale orange (the endpoint titrant volume was 23.9 mL). Write down the reactions corresponding to the titrations and calculate the weight fractions of NaCl, CaCl₂ and the both formates in the dry sample.
3. Choose the most efficient component of the ice-melting chemical **A** by finding the weight of ice (g) which can be melted by 1 g of each of the following individual substances at -10°C : (a) NaCl, (b) CaCl₂, (c) ammonium formate.
4. Determine the isotonic coefficient of calcium formate in a 1 M solution. Write the equations corresponding to dissociation and hydrolysis of this salt. Calculate the contribution (in %) of hydrolysis into the value of isotonic coefficient.

Problem 2

Winkler titration is one of the methods of quantitative determination of oxygen in water. According to this method, manganese sulphate is added to an alkalized aliquot of water sample and allowed to react for a period of time. Then the sample is acidified with diluted sulphuric acid, followed by addition of potassium iodide. Next, iodine is titrated with standardized sodium thiosulphate solution.

1. Please write (and balance) all reactions this method relies on.
2. The method described above was applied to an aliquot of 0.500 L of water sample, and the volume of sodium thiosulphate (0.0423 M) spent was 8.43 mL. Please determine the concentration of oxygen in this sample in mg/L.

Winkler titration results may be affected by redox-active compounds. In particular, nitrite ions present in water samples may oxidize iodide ions, which may lead to a positive bias in the determination (overestimated results). This interference may be reduced by addition of sodium azide, urea or sulphamic acid NH_2SO_3^- .

3. Write down the reactions occurring between nitrite ions and these compounds in weak acid medium (assume that all these reactions do not yield any nitrogen oxides).
4. During a Winkler test, a sample was pre-treated with an excess of sodium azide, which lead to incorrect final results. Write the reaction which caused this error (take into consideration that one of its products is molecular nitrogen) and indicate whether the bias in determination was positive or negative.
5. Both Fe(II) and Fe(III) salts are also among the known interferences to the Winkler method.

a) A sample containing 30 mg/L of Fe(III) was taken for analysis. The concentration of oxygen determined by Winkler titration in this sample was higher by 1.3 mg/L than the actual concentration of oxygen. This can be explained by a *slow* reaction which occurs between Fe(III) and iodide ions in acidic medium. Please write the equation of this reaction.

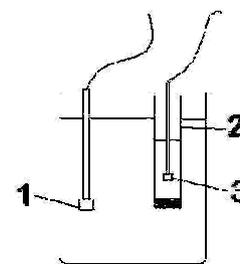
b) Fe(II) also interferes with this method. Please write the reactions explaining the causes of this interference. Would the bias be positive or negative?

c) A sample of water contains 15 mg/L of Fe(II) and 15 mg/L of Fe(III). What would be the result of determination of O_2 by Winkler titration if the actual concentration of O_2 is 9.0 mg/L? The analysis is carried under identical conditions in both parts 5a and 5c of this problem.

d) An amount of NaF was added to an aliquot of the same sample (5c), so that the concentration of NaF was 0.005 M. Determine the sign of the bias of determination of oxygen. Take into account that $\text{Fe}(\text{OH})_3$ reacts with F^- significantly faster than with I^- . Please write the reactions explaining this bias.

Problem 3

Coulometric analysis is based on measuring the amount of electricity consumed for electrolysis of the substance to be determined or equivalent amount of a reactant. To determine H_2SO_4 , 1.00 mL of the sample solution, 25 mL 0.1 M K_2SO_4 and a drop of phenolphthalein solution were placed into a cell with a platinum electrode (1) and glass



tube (2) with a diaphragm were submerged in the solution. The tube was filled with 0.1 M K_2SO_4 and another platinum electrode (3) was placed into it. The electrolysis was carried out at 25°C with 100% current efficiency (i.e., without any side electrochemical reactions) until pink coloring of the indicator appeared. It took 8 min 48.6 sec at a current of 4.50 mA. The charge of 1 mol of electrons is equal to $9.6485 \cdot 10^4$ C.

1. Is the working electrode cathode or anode? Write down the equations of electrochemical reactions at the cathode and at the anode.
2. Calculate H_2SO_4 concentration (in g/L) in the sample solution.
3. The coloring of phenolphthaleine appears at pH 8.5, i.e. in non-neutral medium. It causes some error in the endpoint detection. What is the relative error (%) of the H_2SO_4 concentration determined as described above?
4. a) At what potentials will metallic nickel deposit at the electrode from $1 \cdot 10^{-3}$ M NiSO_4 solution? Standard potential: $E^\circ(\text{Ni}^{2+}/\text{Ni}) = -0.228$ V.

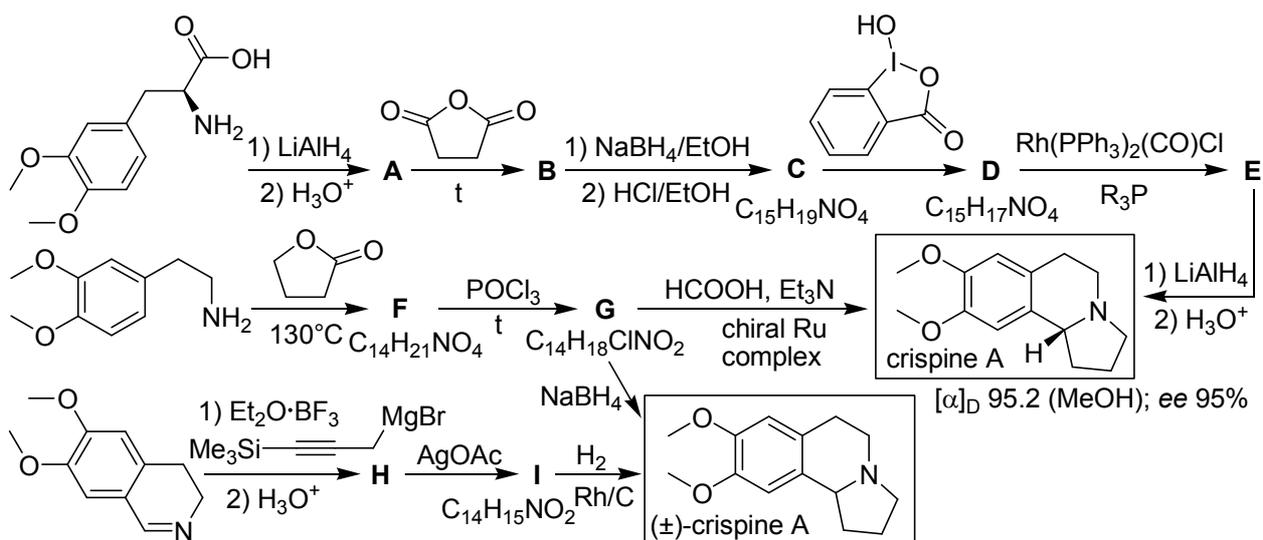
b) What side electrochemical reaction can take place during the electrodeposition of nickel?

5. Electrolysis of $1.00 \cdot 10^{-3}$ M NiSO_4 solution at pH 6.0 was stopped when current efficiency became less than 100%. What is the residual nickel concentration in the solution? Assume no Ni(II) hydroxide complexes are formed.
6. At what pH the electrodeposition of nickel will be quantitative (i.e., its residual concentration will be not greater than $1 \cdot 10^{-6}$ M) from $1.00 \cdot 10^{-3}$ M solution of Ni(II) in 2 M NH_3 , if the current efficiency is 100%? Assume that under these conditions only complex $\text{Ni}(\text{NH}_3)_6^{2+}$ exists (overall stability constant $\beta_6 = 2 \cdot 10^8$).

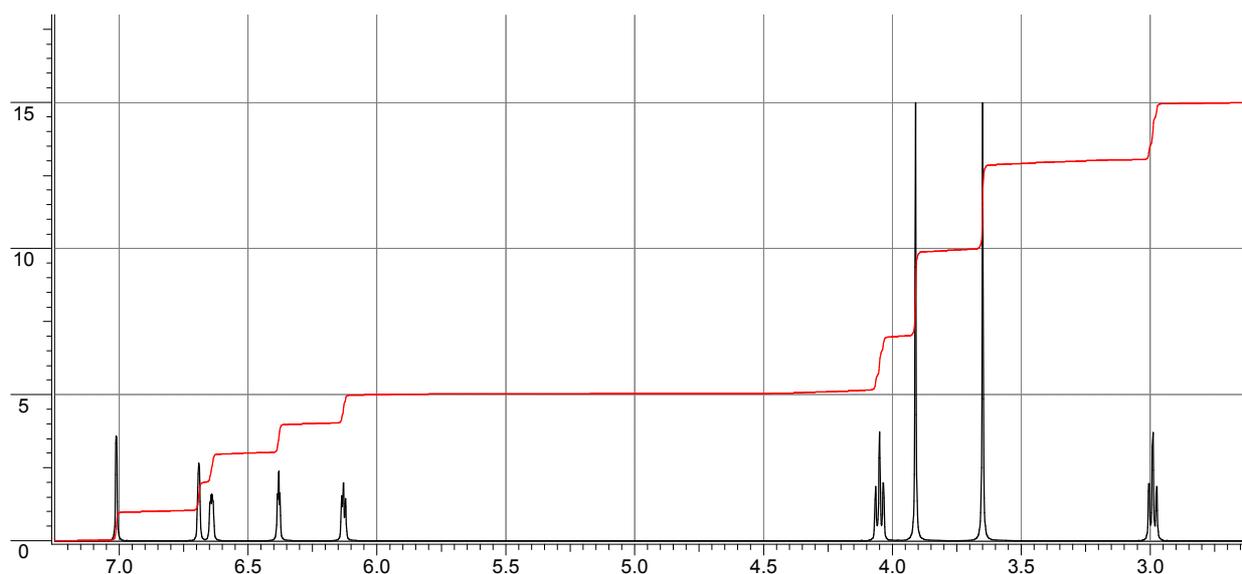
SECTION IV. ORGANIC CHEMISTRY

Problem 1

Alkaloid crispine A demonstrates high cytotoxicity and is considered as a potent agent for the cancer treatment. It stimulated the development of methods for synthesis of crispine A including the optically active one (*ee* is enantiomeric excess, *i.e.* the difference in content of two enantiomers).



1. Write down structural formulae of A – I accounting for fact that C is tricyclic compound. ^1H NMR spectrum of I is given below as a prompting to you. In the answer sheet attribute signals in spectrum to the corresponding fragments of molecule I.



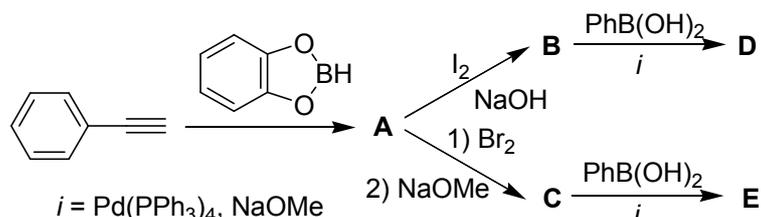
A sample of crispine A, synthesized by one of the proposed methods, has a rotation angle $[\alpha]_D 43.9^\circ$ (CH_3OH).

2. Calculate ratio of two enantiomers of crispine A in this sample.

Problem 2

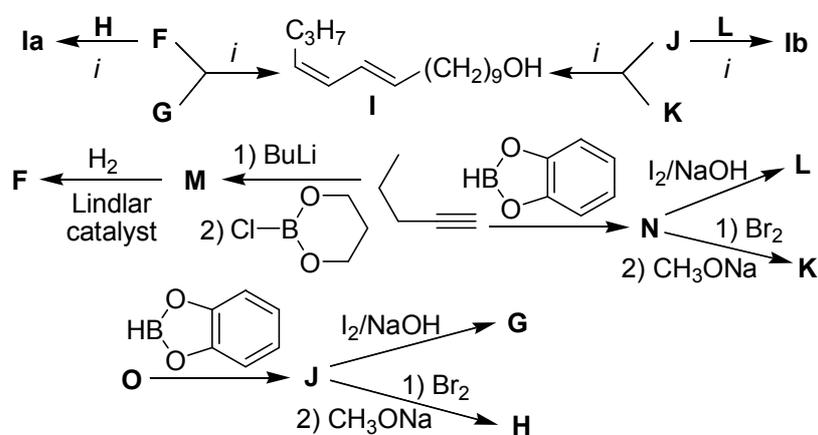
Vinylboronic acids and their derivatives are valuable reagents in organic synthesis. These compounds undergo a Pd⁰-catalyzed cross-coupling with aryl- and vinyl halides (Suzuki reaction) which proceeds with retention of configuration at C=C bond. Nevertheless, vinylboronic acid derivatives can be utilized for synthesis of vinyl halides, notably that process can proceed with either retention and inversion of configuration depending on reaction conditions.

1. Decipher scheme below accounting for isomers **D** and **E** contain 93.3% carbon, compound **E** having one plane of symmetry more than **D**.



Suzuki reaction is intensively utilized for synthesis of natural polyenes. Thus, preparations of bombykol (**I**) and its stereoisomers **Ia** and **Ib** are given in scheme below.

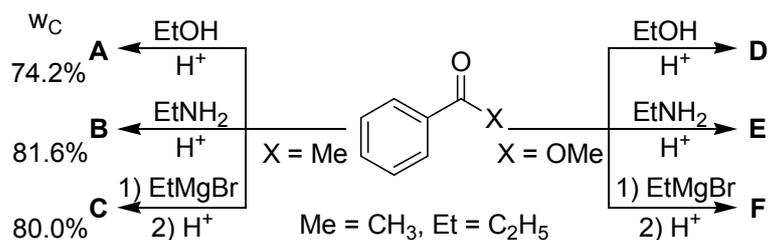
2. Decipher scheme, write down structural formulae of **F – O**, **Ia**, **Ib**.



Problem 3

The large difference in electronegativity of oxygen and carbon leads to significant polarization of C=O bond. It provides electrophilic properties of carbonyl carbon atom *versus* various nucleophilic agents.

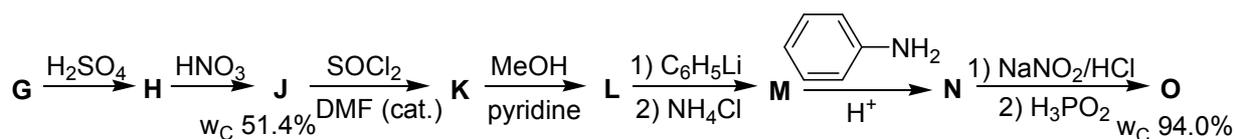
1. Write down structural formulae of compounds **A** – **F** which are formed in the reactions given below:



Among three nucleophiles, demonstrating high reactivity against alkyl halides, – NaI, NaHSO₃, NaCN (+ H⁺) – one reacts with two substrates from the list below; another one reacts with one of these substrates; the third one does not react at all.

2. Point out in Answer sheet substrate(s) with which these nucleophiles react: a) benzaldehyde; b) 1-phenylethanone; c) methyl benzoate.

Porous materials fabrication utilizes compound **O**. Its synthesis is based on the nucleophilic addition to C=O group. At the first step of its preparation compound **G** is treated with conc. H₂SO₄ affording **H**, oxidation of which furnishes **J**.



3. Write down structural formulae of **G** – **O** accounting for that carbon content in **G** and **H** is 62.1% and 90.0%, hydrogen content is 10.3% and 10.0%, respectively; ¹H NMR spectra of **H** and **L** contain 2 signals with relative intensities of 3:1; ¹H NMR spectrum of **G** contains a single signal.

Treatment of **G** with diluted acid leads to compound **P** instead of **H**.

4. Write down structural formulae of **P**.

SECTION V. ANALYTICAL CHEMISTRY

Problem 1

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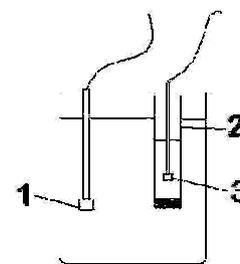
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