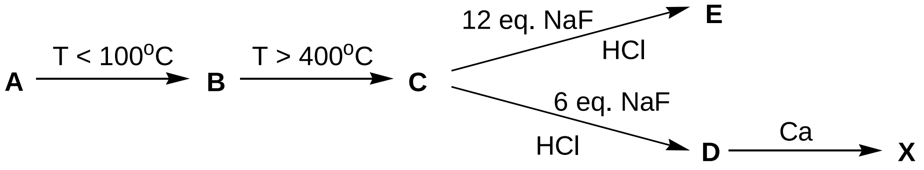
# Problem 1

2019 is the year of the 150th anniversary of the discovery the Periodic Law by the great Russian scientist D.I. Mendeleev. Dmitri Menedeleev's genius consists not only in the systematization of all the elements known by that time, but also in the prediction of new elements and their properties. Thus, in 1879, the Swedish chemist Lars Nilson discover a new element **X**, which is a light silver metal with a characteristic yellowish tinge and related to rare and trace elements. The discovery of **X** along with other new elements described by Mendeleev became the triumph of the Periodic Law, showed its predictive power and led to the worldwide recognition of this fundamental law of the universe.

Obtaining of **X** is a very difficult task, as it requires enrichment and purification through multiple procedures of extraction and precipitation. In the end, sodium oxalate is added to the enriched solution of **X** chloride, resulting in the formation of an insoluble substance **A**. During the thermal decomposition of **A** under the temperature less than 100ºC on air with formation of **B** the mass loss is ~ 20%. Upon further heating above 400ºC, a white water-insoluble substance **C** is formed. The reaction of product **C** with sodium fluoride in concentrated hydrochloric acid solution resulting in precipitation of **D**, that produces chemically pure metal **X** under the calcium thermic reaction. Worth noting that complex compound **E** is formed due to an excess of sodium fluoride that used for precipitation of **D** in industry. Molecular weight of **E** 2.235 times higher than that of **D**.

**1.** Determine all unknown compound and write the equations of the reactions according to the scheme:



Metal **X** can form clusters in subhalogenide phases, especially with chlorine, which have become known due to work under supervision of the eminent American scientist J. Corbett. In the **F**, **G**, **H**, **I** range of subchlorides, the mass fraction of **X** increases. **F** was synthesized by fusing higher **X** metal chloride with powdered **X** in a molar ratio of 4:3, respectively, in tantalum crucibles placed in evacuated and sealed quartz ampoules. Prolonged heating of **F** leads to its decomposition and the formation of **I**, the mass loss in this process is 23.95%. The fusion of **F** and **H** is a reaction of coproportionation with the formation of **G**, during this reaction the oxidation state of **X** changes from **F** to **G** by $\frac{20}{3}$% and changes from **H** to **G** by 12%. The number of metal atoms in the formula unit of **F** and **H** is the same.

**2.** Calculate the composition of all subchlorides **F – I** and write the mentioned chemical reaction equations.

## Problem 2

The mole fraction of element **X** in binary compounds **A1**, **A2** and **A3** is 25%, and in compound **A2** it is nearly equal to mass fraction. At 0°C they are solids with ionic crystal structure which decompose at moderate heating. Moreover, at least one simple substance is necessarily present among the decomposition products of each compound. The substance **A3** with **X** substituted by its lightest analog in the group has a peculiar “mirror twin” **B3** (molar fraction of analog of **X** equals 75%). The substance **A1** can be obtained by the acting of simple substance **Y** (gaseous at 0°C) on hydroxide formed by **X** at 20°C. In this way 1.207 g **A1** can be obtained from 1.000 g of hydroxide.

The substances **D1** and **D2** being in crystalline state contain the same anion as **A1**, but they possess rather less stability than **A1**. The substance **D1** decompose totally for 48 hours at ambient temperature, and **D2** can exist only at temperatures below –100°C. Mass fractions of carbon, hydrogen and nitrogen in **D1** are equal to 39.33%, 9.90% and 11.47%, respectively, and **D2** does not contain carbon. A portion of **D2** decompose totally at temperatures above –100°C, furthermore one of the decomposition products is ionic solid, which can be melt at careful heating (at temperatures above 100°C) without decomposition, its mass is 1.65 times less than the mass of initial portion.

**1.** Determine formulas **A1**, **A2**, **A3** and **B3**.

**2.** Write down formulas of three substances which have the same qualitative content as **A1**, but the different quantitative one.

**3.** Determine formulas **D1** and **D2**.

**4.** Write down the molecular equations of the all reactions with **A1 – A3**, **B3**, **D2** mentioned in the problem.

**5.** Specify in Answer Sheets the spatial structure of anions in the crystal structures of **A1**, **A2** and **A3**.

**6.** Which of binary substances **A1 – A3** can be obtained by the direct synthesis starting from simple substances? Write down the equations of respective reactions for their syntheses by such way.

## Problem 3

A cathode of modern lithium-ion batteries contains redox-active lithium salt (for example, lithium iron phosphate) as the active component. This compound can be prepared via heating of an aqueous solution of stoichiometric mixture of LiOH, $H_3PO_4$, and $FeSO_4$ at pH 7–8 ($LiFePO_4$ is the least soluble and is therefore the only reaction product under the said conditions).

**1.** Write the equation of $LiFePO_4$ synthesis from the above-listed starting compounds. Determine the stoichiometric ratio between LiOH and $FeSO_4$.

**2.** Which admixture insoluble phases can be formed along with $LiFePO_4$ at a) pH < 7 and b) pH > 8?

The following reaction occurs at the cathode during charging of the battery: $LiFePO_4 \rightarrow x Li^+ + x e^- + Li_{1-x}FePO_4$. Specific charge capacity of such cathode is $q_m$ = 168 mA·h/g, which corresponds to specific energy capacity $E_m$ = 580 W·h/kg (in the battery with metal Li as the anode). The Faraday constant is $F$ = 96500 Q/mol.

**3.** Write the equation relating the charge capacity of the cathode $q_m$, molar mass of the formula unit of the active material $M$, and degree of conversion in the cathodic reaction $x$. Determine the degree of conversion of the cathodic reaction involving lithium iron phosphate?

To improve the operational characteristics of the battery, modified cathode materials, for example, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ are used. For this material, the experimentally determined specific charge capacity equals 160 mA·h/g at average potential of 3.8 V relative to metal lithium.

**4.** For the described modified cathode: write the equation of the reaction occurring during charging of the battery and calculate the degree of conversion of the cathodic reaction and specific energy capacity. Basing on the obtained data, select the advantage(s) of this cathode material in comparison with $LiFePO_4$ (fill in the table in the Answer Sheet).

Graphite or carbon black is usually used as anode of lithium-ion battery. Specific charge capacity of such anode equals 372 mA·h/g.

**5.** Determine the formula of the compound formed during charging of the lithium-ion battery. Write the equation of the occurring reaction.

**6.** Calculate the total mass of lithium-ion battery (cathode – $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, anode – graphite, mass of other components is 20% of the battery mass) which has the capacity sufficient for charging three times a typical smartphone (its battery capacity is 3500 mA·h). Take into account that the highest capacity of the battery is achieved when the ratio of the masses of the cathode and anode equals the ratio between their reciprocal specific capacities.

## Problem 4

In chemical kinetics a notion "rate-determining step" is often used in study of reaction mechanisms. This notion relates to the approximation in experimental kinetic curves analysis. It is assumed that specific part of the curve or maybe the whole curve corresponds to the particular kinetic step which determines the rate of the complex process under consideration in given moment of time. It was found that in consecutive reactions the slowest step is rate-determining while in parallel reactions the fastest one.

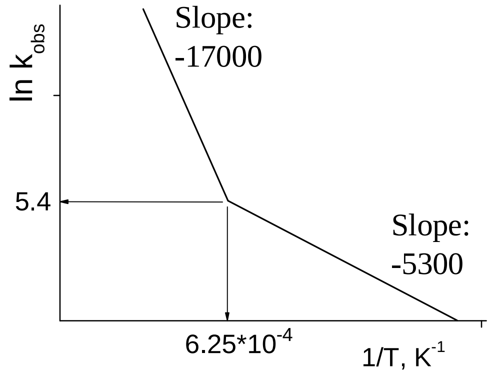
**1.** For the following scheme of obtaining of the substance **Z** (all steps are elementary and take place in solution) find the rate-determining step and prove it *via* calculation of instantaneous rates, where possible. Consider two cases: (a) [**X**] = 2.0 M, (b) [**X**] = 0.01 M.

1) $2\mathbf{X} \rightarrow \mathbf{Z}$ ($k_1 = 6.1\cdot10^{-1}$ $M^{-1}min^{-1}$)

2) $\mathbf{X} \rightarrow \mathbf{Y}$ ($k_2 = 8.2\cdot10^{-2}$ $min^{-1}$)

3) $\mathbf{Y} + \mathbf{X} \rightarrow \mathbf{Z}$ ($k_3 = 1.0\cdot10^{-4}$ $M^{-1}min^{-1}$)

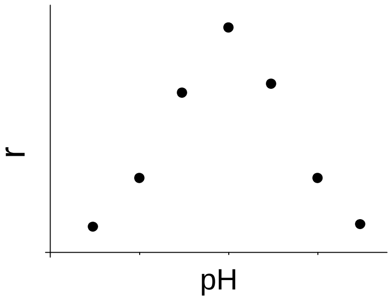
If the rate of a complex reaction is determined by single step, the temperature dependence of the rate is governed by the same step. The plot below shows $\ln k_{obs}$ *vs* $1/T$ where $k_{obs}$ (measured in hours$^{-1}$) is the observed rate constant of competitive first-order decomposition of acetic acid vapors to methane (reaction 1) and to methanol (reaction 2). The visible fracture implies the switch of rate-determining step with the temperature changing.

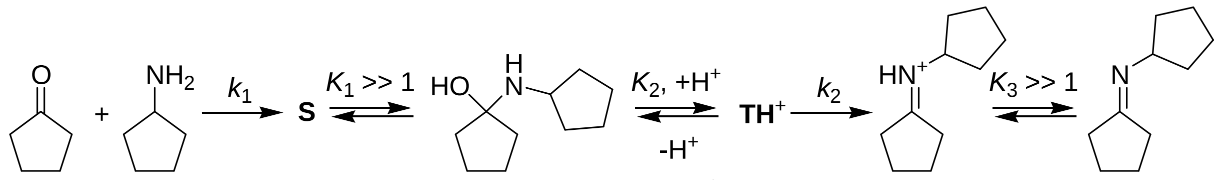


**2.** Write the equations of reactions 1 and 2.

**3.** Calculate from the plot data activation energies ($E_a$) and pre-exponent factors ($A$) for both reactions. Additionally, it is known that $A_1 > A_2$.

The figure at the right demonstrate show the rate of cyclopentanone and cyclopentylamine condensation depends on solution pH. The plot is followed by the mechanism of condensation.

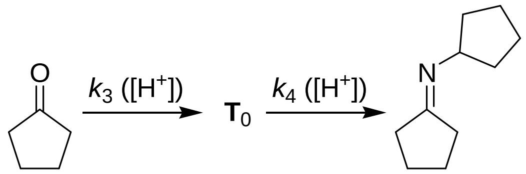




**4.** Depict the structures of the intermediates **S** and **TH**$^+$.

**5.** Which step is rate determining at low pH, high pH? Write the equation of corresponding steps.

For convenience of kinetic analysis we replace the scheme above with a formal equivalent one:



Herein $\mathbf{T_0}$ stands for the mixture of **T** and $\mathbf{TH^+}$ and $[\mathbf{T_0}] = [\mathbf{T}] + [\mathbf{TH^+}]$; $k_3 = k_1[RNH_2]$, and the constant $k_4$ satisfies the condition $k_4[\mathbf{T_0}] = k_2[\mathbf{TH^+}]$.The rates of both steps are pH dependent, so the existing maximum indicated the switch of rate-limiting process. Therefore, at maximum $k_3([H^+]_{max}) = k_4([H^+]_{max})$.

**6.** Calculate pH corresponding to the rate maximum if $K_a(RNH_3^+) = 5{\cdot}10^{-4}$, $K_2 = 10^{-1}$, $k_2 / k_1 = 10^5$ and total concentration of amine $C(RNH_2) = 1$ M.

## Problem 5

Linear unbranched substances **A**, **B**, **C**, **D**, and **E** form an extremely important family of biologically active compounds involved in regulation of various bioprocesses, mostly in cell nucleus.

The 1.00 g weighed amounts of **B – E** were burned in an excess of oxygen. The masses (m) of carbon dioxide formed and the volumes (V) of the gas **X** left unabsorbed after bubbling the combustion products through an alkali solution are given in the hereunder table. Besides, the numbers of atom types of an element found in **X** and hydrogen for each of **B – E** are given there.

| Compound | $m(CO_2)$, g | V(**X**), ml | The number of atom types of an element found in **X** | The number of atom types of H |
|---|---|---|---|---|
| **B** | 2.175 | 221 | 2 | 7 |
| **C** | 2.21 | 211 | 2 | 6 |
| **D** | 2.00 | 254 | 1 | 3 |
| **E** | 1.78 | 302 | 1 | 3 |

**1.** Determine **X**, if it is an elementary substance. For any two substances found in living nature, write down combustion reactions affording **X**.

**2.** Deduce the molecular formulae of **B – E**, showing the calculations.

**3.** Give the general formula valid for the class of organic compounds comprising **B – E**.

**4.** Is it possible to unambiguously determine the net formulae of **A – E** based on the data of their complete combustion? Support your answer by calculations.

**5.** Draw all possible structural formulae of **D** and **E**.

**6.** Draw the finally decided structural formulae of **C – E**, knowing that none of these contains methyl groups.

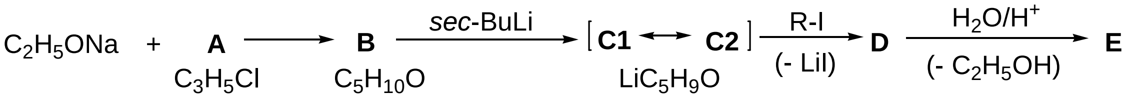
**E** is a valuable monomer used in manufacture of plastics. A new industrial method of **E** production from biomass with an aid of gene modified bacteria *E. coli.* was proposed in 2015. The final stage of the bioprocess involves an enzyme catalyzing the reaction described by the hereunder equation:

$$\mathbf{A} + \mathbf{D} \rightarrow \mathbf{C} + \mathbf{E}$$

**7.** Deduce the structural formulae of **A** and **B**, if **B** is formed from **D** via two identical steps, **A** being the intermediate.

## Problem 6

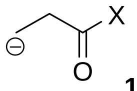
In the 1970s, a carbon chain building method was developed, consisting of the interaction of various electrophilic reagents (halogen derivatives, carbonyl compounds) with the nucleophile **C** (which corresponds to a particular case of the synthon **S**); the structure of its carbanion can be represented as two resonant structures **C1** and **C2**, and its synthesis is conducted according to the scheme:



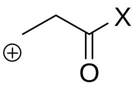
$$C_2H_5ONa + \underset{C_3H_5Cl}{\mathbf{A}} \longrightarrow \underset{C_5H_{10}O}{\mathbf{B}} \xrightarrow{sec\text{-}BuLi} \underset{LiC_5H_9O}{[\mathbf{C1} \longleftrightarrow \mathbf{C2}]} \xrightarrow[(-\ LiI)]{R\text{-}I} \mathbf{D} \xrightarrow[(-\ C_2H_5OH)]{H_2O/H^+} \mathbf{E}$$

**1.** Determine the structural formulas of **A**, **B**, **C1**, **C2**, RI, **D** and **E** if **D** is the main product (79%) of **C** alkylation with unbranched alkyl iodide R-I, and according to $^1$H NMR, in **D** the ratio of $n_H$ at C(sp$^3$) to $n_H$ at C(sp$^2$) is 10.0.

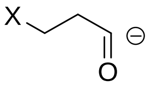
**2.** Select from the range of synthons **1** – **4** the one that corresponds to synthon **S** and determine X in the case of using reagent **B**.



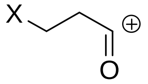
**1**



**2**

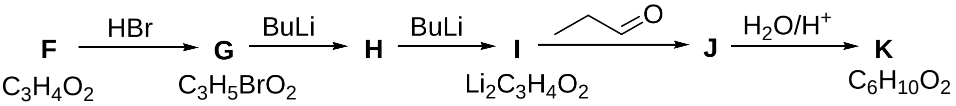


**3**



**4**

An alternative method of carbon chain building by **S** is possible when using nucleophile **I** (which corresponds to another special case of synthon **S**):

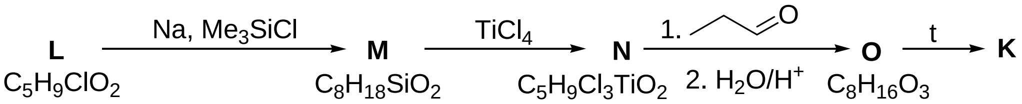


**3.** Determine the structures of **F** – **K** if the IR spectrum of **F** contains a wide band in the region 3300–2500 см$^{-1}$ and a strong absorption band at 1710 cm$^{-1}$, **G** is optically inactive, and **K** does not discolor bromine water.

It was found that **I** predominantly exists in the form of a tautomer **Ia**, although for the system **I** $\rightleftharpoons$ **Ia** a reactive species is **I**.

**4.** Propose the structure of **Ia** if there is only one singlet in its $^1$H NMR spectrum.

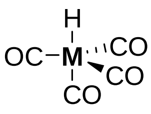
Counter synthesis of **K** using nucleophile **N** (which also corresponds to synthon **S**) was carried out according to the scheme:



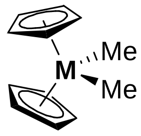
**5.** Determine the structural formulas of **L** – **O**, taking into account that the stage **O** → **K** is a transesterification reaction, **M** is the analog of form **Ia**, and **N** is that of form **I**, and the coordination number of Ti in **N** is 5.

## Problem 7

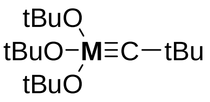
Organometallic compounds containing a metal–carbon bond are widely used in catalysis. At the moment the catalysts based on transition metals of all the groups of *d*-block elements are known. Organometallic compounds **I** – **X** are the examples of these complexes (all of them contain the metals of different groups, the total number of valence electrons per atom and the period of corresponding metal are provided). These compounds catalyze the reactions **1 – 10**. The total number of valence electrons could be counted as a sum of valence electrons of metal and ligand's electrons participating in complex formation. For example bis(benzene)chromium $(C_6H_6)_2Cr$ have 18 total electrons and Wilkinson's catalyst $(PPh_3)_3RhCl$ have 16 total electrons.



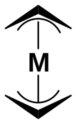
**I**
18$e^-$, 3*d*



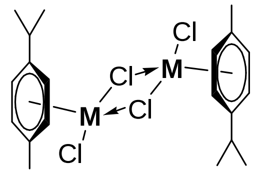
**II**
16$e^-$, 3*d*



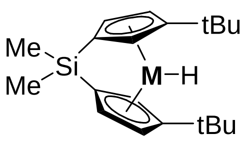
**III**
12$e^-$, 5*d*



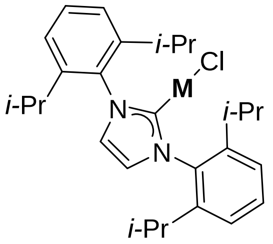
**IV**
16$e^-$, 3*d*



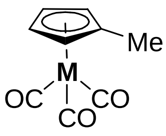
**V**
18$e^-$, 4*d*



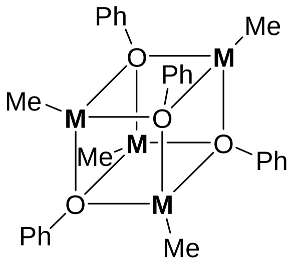
**VI**
14$e^-$, 3*d*



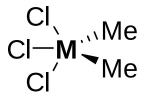
**VII**
14$e^-$, 5*d*



**VIII**
18$e^-$, 3*d*



**IX**
18$e^-$, 3*d*

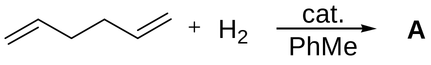
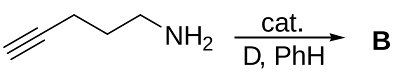
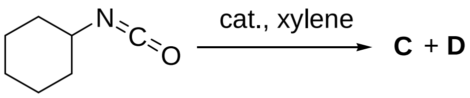
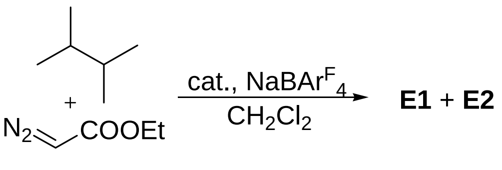


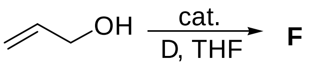
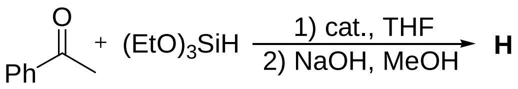
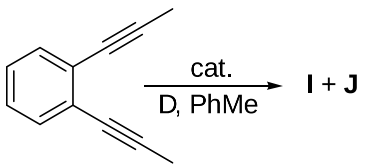
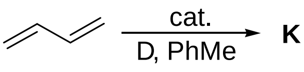
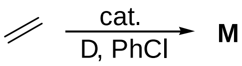
**X**
10$e^-$, 5*d*

**1.** Determine the unknown metals in compounds **I – X**.

**2.** Match the compounds **I – X** with the reactions **1 – 10**, where they act as catalysts, if it is known that the reactions are numbered in accordance with the increase of metal mass fraction in corresponding catalyst.

**3.** Determine the products of each reaction and draw their structural formulas.

| # | **Reaction** | **Comments about reaction products** |
|---|---|---|
| 1 |  | The product **A** ($M^+ = 84$) has 4 signals in $^{13}C$ NMR spectrum. It is stable towards hydrogenation under elevated pressure in the presence of Pd on carbon. |
| 2 |  | The product **B** ($M^+ = 83$) has an intense peak in IR spectrum at 1650 cm$^{-1}$. Under catalytic hydrogenation it turns to 2-methylpyrrolidine. In $^1H$ NMR spectrum of the compound **B** there are no signals with $\delta > 4$ ppm. |
| 3 |  | The reaction proceeds with the evolution of gas **C** and the formation of compound **D** with $M^+ = 206$, which has a peak in IR spectrum at 2115 cm$^{-1}$ and is widely used in peptide synthesis. |
| 4 |  | The reaction proceeds with the evolution of nitrogen as a statistical insertion of a carbene forming two isomeric products **E1** and **E2** in the ratio 83:17, having $M^+ = 172$. |

| # | Reaction | Comments about reaction products |
|---|---|---|
| 5 |  | The product **F** ($M^+ = 58$). $^1$H NMR: 9.80 (d, 1H), 2.39–2.56 (m, 2H), 1.11 (t, 3H). |
| 6 | $\mathbf{M} + CO + H_2 \xrightarrow[t,\ p]{cat.} \mathbf{G}$ | The main product **G** ($M^+ = 114$) gives positive reaction with 2,4-dinitrophenylhydrazine and takes part in silver mirror reaction, it has unbranched structure. |
| 7 |  | The product **H** ($M^+ = 122$) gives a positive Lucas test with $ZnCl_2$ in HCl. |
| 8 |  | By the reaction the low-boiling-point (b.p. 27°C) liquid **I**, having 1 signal in $^1$H NMR spectrum, and the compound **J** with $M^+ = 300$, having 3-fold symmetry axis, are formed. |
| 9 |  | The reaction product **K** (all the double bonds have *E*-configuration) is a low-melting compound (m.p. 35°C), it gives only succinic dialdehyde upon reductive ozonolysis. The reaction of **K** with $BH_3{\cdot}NEt_3$ gives a compound **L**, which has 3-fold symmetry axis. |
| 10 |  | The reaction product **M** (liquid with a b.p. 63°C) is used as a starting compound in the reaction **6**. |

## Problem 8

Reverse titration is a technique often used in titrimetry. It involves introducing an excess of titrant and titrating the unreacted titrant upon the completion of the reaction. This technique was used to determine the concentration of $CO_2$ absorbed from the air by an excess of ammonia solution. With that purpose, 5.00 mL of the resulting solution were mixed with 20 mL of $BaCl_2$ solution (5 wt.%), 10.00 mL of 0.5000 M NaOH solution, an indicator and an excess of formaldehyde forming hexamethylene tetramine $(CH_2)_6N_4$ with ammonia. The obtained solution was titrated with 0.5000 M solution HCl, which required $V_1$ mL of the acid.

**1.** Write down the equations: a) of the reaction occurring during $CO_2$ binding with the $NH_3$ solution; formaldehyde reactions: b) with ammonia; c) with the resulting ammonium salt.

**2.** What form of $CO_2$ prevails in an aqueous solution at pH 8.0? Justify the answer. The acidity constants of carbonic acid: $K_1 = 4.3{\cdot}10^{-7}$, $K_2 = 4.7{\cdot}10^{-11}$.

**3.** a) What is the added alkali spent for? Write down the reaction equation. What is the role of the added barium salt? Write in ionic form the equation of the barium ion reaction. What is HCl spent for when titrating in the presence of $BaCl_2$ and using phenolphthalein as indicator (color transition occurs at pH ~ 8)? Write down the reaction (note that HCl does not dissolve the precipitate during the titration).

b) What would HCl be consumed for during the described determination of $CO_2$ if the barium salt would *not* have been added to the mixture? Write down the equations of these reactions.

**4.** a) Calculate the $CO_2$ content (mol/L) in the ammonia solution being analyzed, if the hydrochloric acid volume $V_1$ spent for titration equals 9.80 mL.

b) What volume of HCl would be spent for the titration without the barium salt?

**5.** An ammonia solution titrated according to this protocol, containing some excess of HCl and having a pH of 4.0, was decanted and left in the laboratory in a stoppered vessel. After 1 month, the pH of the mixture became equal to 4.4.

a) What reaction could have led to such a change?

b) How would the pH of the mixture change if its initial pH value was 3.0 and it would be stored for the same time? Choose the correct option in the answer sheet.