

Devoted to 175<sup>th</sup> anniversary of the birth of  
*Dmitriy Mendeleev*

# **46<sup>th</sup> Ukrainian Chemistry Olympiad**

## **Final National Competition**

*THEORETICAL EXAM FOR STUDENTS  
OF THE 11<sup>th</sup> FORM*

Odessa

22-26 March

2009

<b>Head of Jury</b>	Prof. Yuriy Kholin
<b>Deputy heads of Jury</b>	Dr. Kostiantyn Gavrylenko Prof. Sergiy Nedilko
<b>Supervisors of forms and rounds</b>	Mr. Olexander Usenko Dr. Maxim Kolosov Dr. Oleg Zhikol Dr. Dmytro Volochnyuk Dr. Olexander Lyapunov
<b>Expert</b>	Prof. Igor Komarov
<b>Chief executive organizer</b>	Mrs. Galyna Malchenko

The set of theoretical tasks was composed on the base of author's problems and ideas of

Prof. Viktor Vargalyuk	Dr. Olexander Lyapunov
Mr. Mykhaylo Vybornyy	Mr. Kostiantyn Melnikov
Dr. Dmytro Volochnyuk	Mr. Yeugen Ostapchuk
Dr. Kostiantyn Gavrylenko	Mr. Sergiy Pavlenko
Dr. Olexander Grygorenko	Dr. Pavlo Popel'
Mr. Dmytro Kandaskalov	Mr. Ruslan Polunin
Dr. Olena Kovalenko	Mr. Sergiy Punin
Dr. Maxim Kolosov	Dr. Vladimir Stetsik
Dr. Sergiy Kolotilov	Mr. Olexander Usenko
Mr. Vladimir Kubishkin	Prof. Yuriy Kholin

Translated by Sergiy Kolotilov

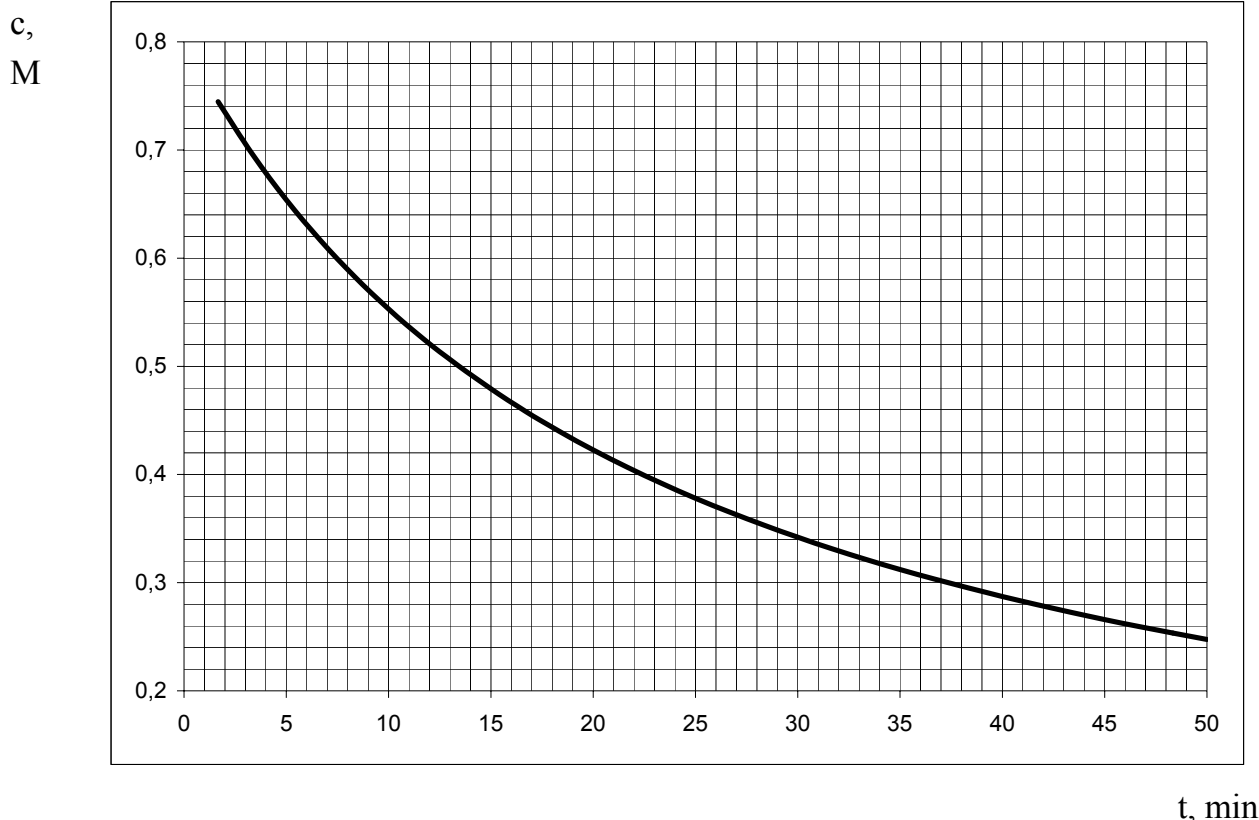
Web-site of Ukrainian Chemistry Olympiads

<http://www-chemo.univer.kharkov.ua/olympiad.htm>

## I round

## Task 1. Hypobromite

The study of disproportionation rate of hypobromite ion ( $\text{BrO}^-$ ), which results in bromate ( $\text{BrO}_3^-$ ) formation, in aqueous solution at 80 °C gave the following dependency of hypobromite concentration on time:



1. Write down the equation for the disproportionation of hypobromite ion.
2. Determine reaction order and confirm the answer by calculation.
3. Estimate rate constant for this reaction.
4. Propose a mechanism of this reaction, which corresponds to experimental data.
5. Which method can be used to obtain the curve, shown on the figure, in chemical laboratory, if all reagents and glassware are available, but there are no instruments for physical measurements (except the balances and thermometer with one mark at 80 °C)?

## Solution



2, 3. The most convenient in this case is to determine reaction order by the dependence of half-reaction time on concentration. For the reactions of the first order half-reaction time does not depend on concentration, and for the reactions of other orders it does depend. Choose two any pairs of points on the graph, for which  $c_2 = c_1/2$ , for example, such:

The first pair:

$$c_1 = 0.68 \text{ M}, t_1 = 4,0 \text{ min.}$$

$$c_2 = 0.68/2 = 0.34 \text{ M},$$

from the graph  $t_2 = 30.0 \text{ min.}$

Verification shows that this reaction has the second order.

$$k = 1/(c_0 t_{1/2});$$

$k = 0.057 \text{ l}/(\text{mol}\cdot\text{min})$  according to the first pair of points, and

$k = 0.056 \text{ l}/(\text{mol}\cdot\text{min})$  according to the second pair of points.

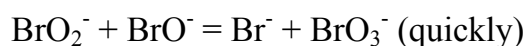
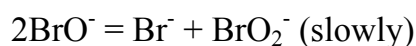
The second pair:

$$c_1 = 0.52 \text{ M}, t_1 = 12.0 \text{ min.}$$

$$c_2 = 0.52/2 = 0.26 \text{ M},$$

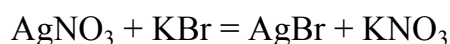
from the graph  $t_2 = 46,5 \text{ min.}$

4. Since the order is 2, elementary act has to involve collision of two hypobromite particles. Probably, in this case electron and oxygen ion are transferred. But the particle, which is formed, is more reactive, and this intermediate further quickly reacts with other hypobromite ion:



Note that this mechanism agrees with experimental data, but this experiment is not sufficient for exact determination of reaction mechanism, because other mechanisms can be proposed, which will also correspond to the reaction of the second order.

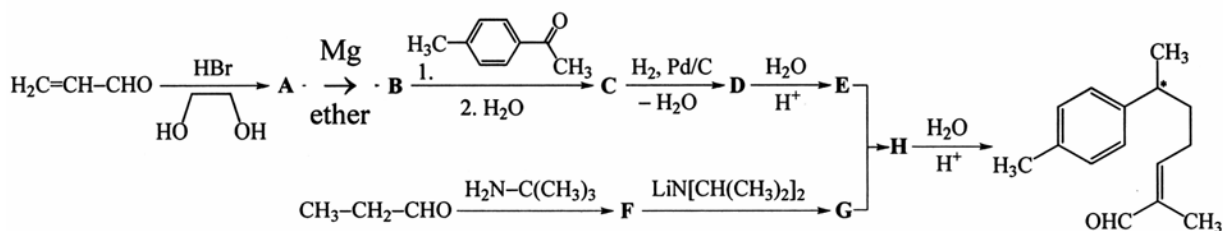
5. To obtain presented curve the one should find the method, which will allow to determine the dependency of concentration of any reagent on time. The most simple is to determine the concentration of bromide ion on time according to reaction



Samples should be taken from reaction mixture, they should be quickly cooled (since reaction rate decreases in average in 2-4 times with temperature decrease on 10°C, cooling from 80°C to room temperature will result in reaction rate decrease in 2<sup>6</sup> times as minimum), and then the mixture should be titrated by the solution of AgNO<sub>3</sub> or AgBr should be precipitated.

## Task 2. Nuciferal

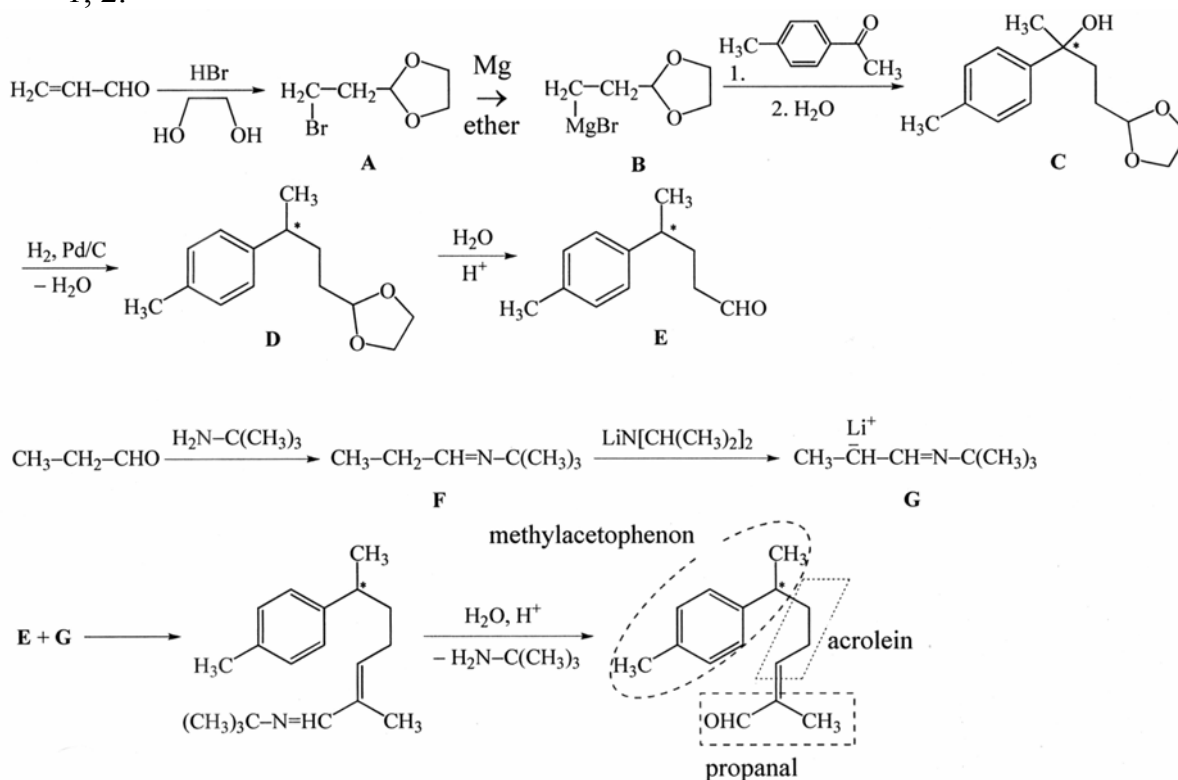
Pine oil of *Torreya nucifera* is used in perfumery and confectionery industry due to its unusual odor. Its main component is terpenoid nuciferal, containing reactive  $\alpha,\beta$ -unsaturated aldehyde group. In the laboratory ( $\pm$ )-nuciferal can be synthesized starting from acrolein, methylacetophenone and propanal.



1. Mark in structural formula of nucleiferal fragments of molecules, which constitute its hydrocarbon core.
2. Draw structural formulas of compounds A – H.
3. For what purpose is ethyleneglycol required at hydrogen bromide addition to acrolein?
4. Why direct reaction between propanal and E can not be carried out?

### Solution

1, 2.



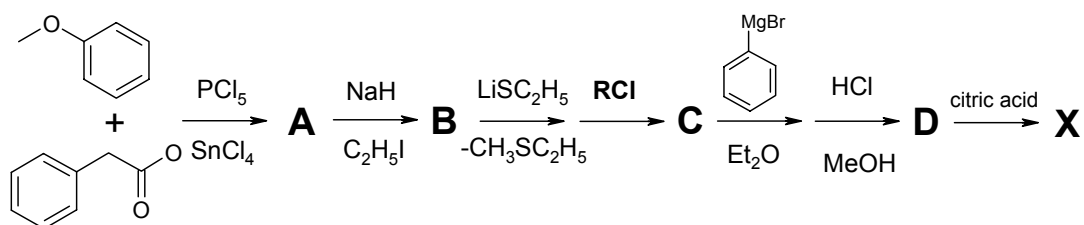
3. In acidic medium ethyleneglycol reacts with the propanal hydrogen bromide addition, forming cyclic acetal. "Dioxolane protection" blocks free aldehyde group, prevents self-condensation of active aldehyde and protects aldehyde group from further transformations (interaction with Grignard reagent and reduction by hydrogen).

4. Direct interaction of propanal with **E** leads to complex mixture of products, since each of them may act both as methylene and carbonyl component. Aldimine formation excludes reaction of propanal by carbonyl group, and carboanion generation at action of base makes reaction course unambiguous.

### Task 3. Tomoxifen

Treatment and prevention of mammal cancer is believed to be one of the main problems of medicine. The preparations from the group of *antiestrogens* are widely used for fight with this disease. The first and the most well-known representative of this group – "TOMOXIFEN" – was synthesized in 1963 as contraceptive agent, but later its use in the treatment and prevention of this disease has been started.

Below non-stereospecific synthesis of main component of "TOMOXIFEN" – compound **X**, is presented. **X** is crystalline compound, well soluble in water:



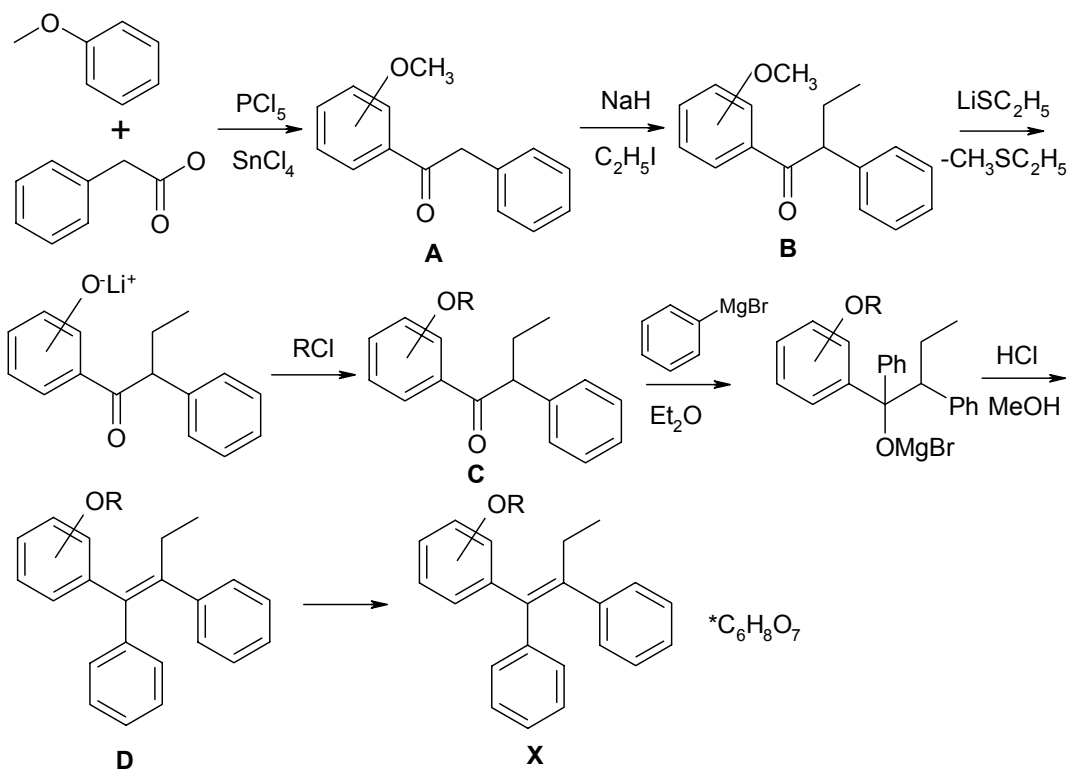
This method provides the mixture of *E,Z*-isomers of compound **D**, but only the derivative of *Z*-isomer is active, which is separated by chromatographic methods.

It is known that mass-spectrum of compound **D** contains intensive peak  $M+1$  of ion with mass 372, and PMR spectrum of this compound contains the following signals (ppm): 0.90 (3H, triplet), 2.3-2.8 (4H, multiplet), 2.25 (6H, singlet), 3.90 (2H, triplet), 6.50 (2H, doublet), 6.75 (2H, doublet), 7.15 (5H, singlet), 7.30 (5H, singlet).

1. Determine compounds **A** – **D** and **X**.
2. Which chloro-derivative (**RCl**) was used in the synthesis of compound **X**?
3. Draw the structure of *R,S*-isomers of compound **B**.
4. Draw the structure of *E,Z*-isomers of compound **D**. Why the activity of "TOMOXIFEN" is significantly reduced at long storage of preparation (especially in the place which is illuminated by sun light)?

## Solution

1.



Compound **A** is formed due to reaction of electrophilic substitution, that is why  $\text{OCH}_3$ -group should be in *o*- or *p*-position. Compound **D** must be alkene, because it exists in the form of a pair of *E,Z*-isomers. Since compound **X** is crystalline compound, well soluble in water, we can conclude that **X** is citrate of compound **D**.

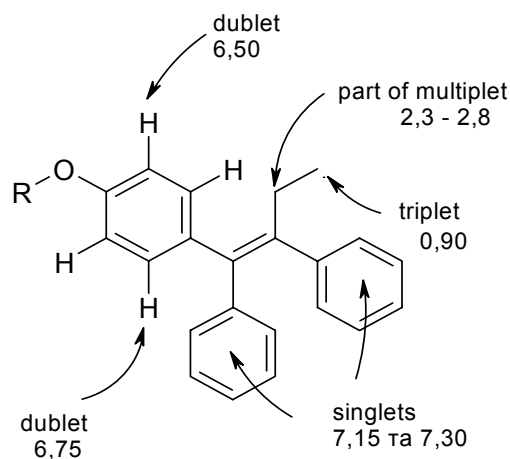
Let us determine **RCl**:

- according to the data of mass-spectrometry  $\mathbf{M(R)} = 372 - 299 - 1 = 72$  (g/mol);
- according to the data of PMR spectroscopy

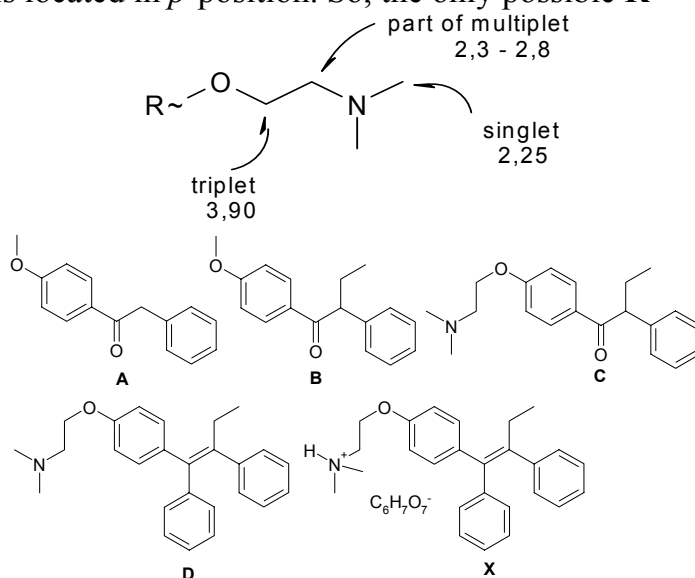
$$\mathbf{n(H\ in\ RX)} = (5 + 5 + 4 + 2 + 4 + 6 + 3) - 19 = 10.$$

Since compound **X** is citrate, **R** should include basic nitrogen atom (in this case one, because  $M+1$  value is even). Then,  $\mathbf{R} = \text{C}_4\text{H}_{10}\text{N}$ .

Determine compound **D** by spectral data,

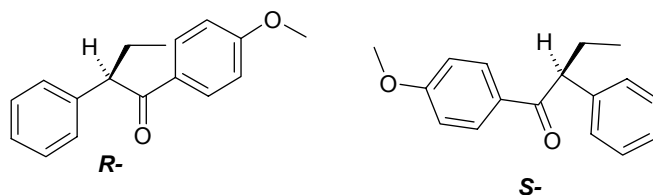


Signals assignment: 6H singlet at 2.25 ppm – most probably, from protons of  $N(CH_3)_2$  group, 2H triplet at 3.90 ppm and a part of multiplet at 2.3-2.8 ppm – signals of protons from **R**, which is located in *p*-position. So, the only possible **R** –

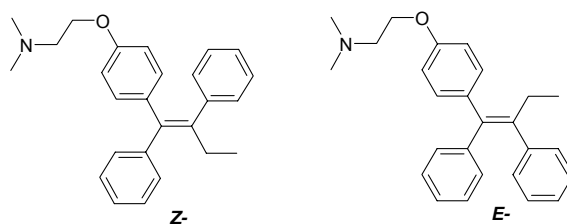


2. **RCl** =  $ClCH_2CH_2N(CH_3)_2$ .

3.



4.



5. Isomerization of active *Z*-isomer into inactive *E*-isomer takes place.



**Task 4. Titration**

A sample of crystallohydrate **Z** of unknown salt **A**, which is used in analytical chemistry, of mass 0.392 g was dissolved in water. Obtained solution was treated by the excess of BaCl<sub>2</sub> solution, after which 0.466 g of white precipitate **B** formed, which was not soluble in acids. The precipitate was filtered, excess of alkaline was added to filtrate and it was boiled. In the result of reaction 46.7 ml of gas **C** (collected at temperature 20 °C and pressure 104.3 kPa) and pale-green precipitate of hydroxide of metal **X**, which became brown at storage on air, were obtained. Gas **C** has specific strong odor and is completely absorbed by the solution of sulfuric acid.

Laboratory assistant prepared a sample of crystallohydrate **Z** and for unknown reason decided to dry it in vacuum before use. This resulted in partial water loss. In order to determine the composition of crystallohydrate after drying its sample (weight 0.3796 g) was dissolved in the solution of sulfuric acid with molar concentration 0.5 mol/l, and potentiometric titration by the solution of cerium (IV) sulfate with molar concentration 0.0500 mol/l was performed. The following results were obtained (*V* is the volume of added solution of titrant, *E* is electric force of galvanic cell):

<i>V</i> , ml	10.00	18.00	19.80	20.00	20.20	22.00	30.00
<i>E</i> , mV	771	830	889	1110	1332	1391	1453

At titration the only reaction of oxidation of ion of metal **X** takes place.

1. Determine salt **A**, precipitate **B**, gas **C**, metal **X** and crystallohydrate **Z**. Write equation of mentioned reactions.
2. How end point of titration can be determined in cerimetry?
3. Draw integral (*E*, mV – *V*, ml) and differential ( $\Delta E/\Delta V$  – *V*, ml) curves of potentiometric titration. Show on the graphs end point of titration (EPT). Find the volume of added titrant in EPT.
4. Determine mass fraction of metal **X** in crystallohydrate after storage and new composition of crystallohydrate.

**Solution**

1. Precipitate **B**, not soluble in acids – BaSO<sub>4</sub>. Gas **C** – NH<sub>3</sub>, metal **X** – Fe.

$$n(\text{BaSO}_4) = M/m = 0.466/233 = 0.002 \text{ (mol)},$$

$$n(\text{NH}_3) = PV/RT = 104.3 \cdot 0.0467 / (8.314 \cdot 293.15) = 0.002 \text{ (mol)}.$$

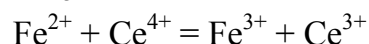
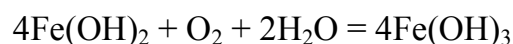
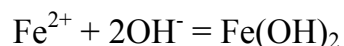
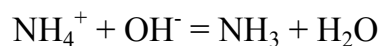
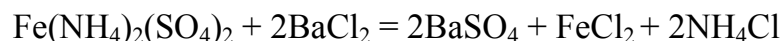
**A** – Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>, crystallohydrate **Z** – Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>·*x*H<sub>2</sub>O,

$$M(\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2) = 284 \text{ g/mol},$$

$$M(\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot x\text{H}_2\text{O}) = 0.392/0.001 = 392 \text{ (g/mol)}.$$

From this we can find the quantity of water molecules:  $x = (392 - 284)/18 = 6$ .

So, crystallohydrate **Z** has composition  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .

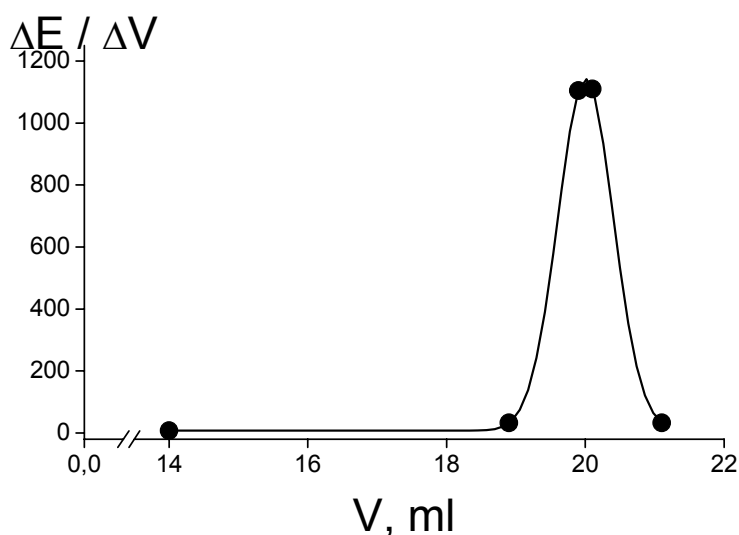


2. End point of titration in cerimetry is determined by potentiometric methods or using redox-indicators (ferroine, diphenylamine, 2,2'-bipyridile).

3.

V, ml	10.00	18.00	19.80	20.00	20.20	22.00	30.00
E, mV	771	830	889	1110	1332	1391	1453

$\Delta V$ , ml	8.00	1.80	0.20	0.20	1.80	8.00
$V+0.5\Delta V$ , ml	14.00	18.9	19.9	20.1	21.1	26.0
$\Delta E$ , mV	59	59	221	222	59	62
$\Delta E/\Delta V$ , mV/ml	7.4	32.8	1105.0	1110.0	32.8	7.7



The volume in the end point of titration  $V(\text{EPT}) = 20 \text{ ml}$ .

4. Mass fraction of Fe in the sample of crystallohydrate after storage can be found using formula:

$$w(\text{Fe}) = (M(\text{Fe}^{2+}) \cdot V(\text{EPT}) \cdot c(\text{titrant})) / m(\text{crystallohydrate}) = \\ = (56 \cdot 0.02 \cdot 0.05) / 0.3796 = 0.1475 = 14.75\%$$

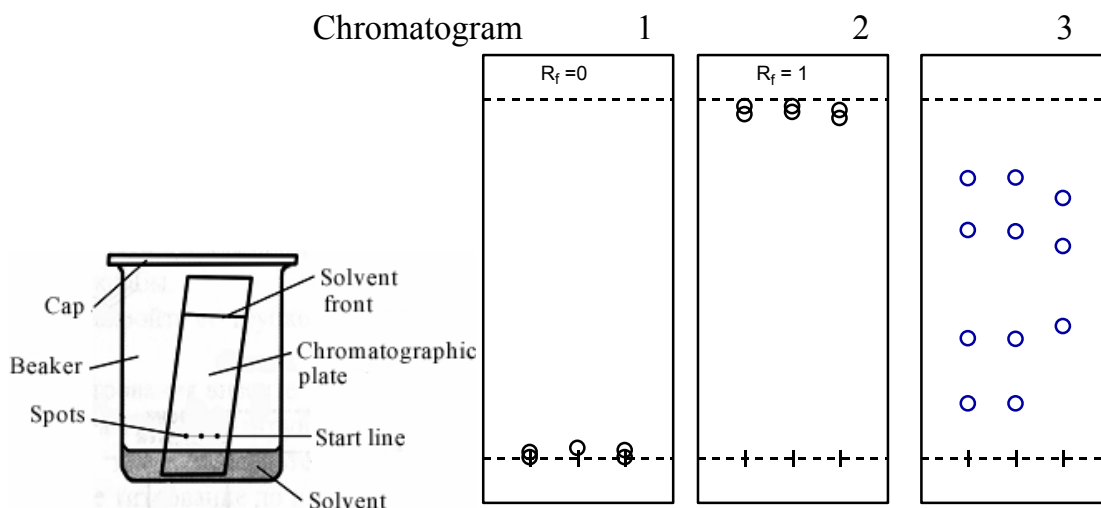
$$w(\text{Fe}) = 56 / (284 + 18 \cdot x), \text{ from this } x = (56 - 284 \cdot w(\text{Fe})) / 2.655 = 5.3.$$

So, new composition of crystallohydrate is  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 5.3\text{H}_2\text{O}$ .

### Task 5. Chromatography

Once a lady who had temporary financial problems because she was not able to vanquish temptation caused by fashion novelty, decided to borrow 500 UAH from her colleague. However in the note of hand the lady indicated the sum not by words, but by figures. In the day of salary the hero of a story pushed forward to return her debt to the creditor, but she was very surprised that he demanded to return the debt in the sum as high as 5 000 UAH, which was written in the note of hand.

This case was submitted to the court. The note of hand was delivered for expertise, which was carried out by thin layer chromatography. An expert cut paper samples from the note of hand in such way that each contained a part of each of figures "0", and placed them on the start line of the plate. He put the edge of the plate in the solvent - benzene, and after this obtained chromatogram 1. Similar experiment with ethanol as the solvent led to chromatogram 2. After this he obtained chromatogram 3 with unknown solvent.



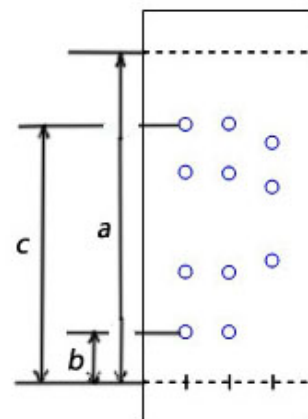
Answer the following questions:

1. Write not less than three types of chromatography, known to you.
2. Due to which forces does a solvent rise up, counteracting to gravity force?

- Indicate, which one of the solvents – methanol, acetone, tetrahydrofurane, cyclopentane – was used by the expert in order to obtain the third chromatogram, if polarity of the solvents decreases in the row: methanol > ethanol > acetone > tetrahydrofurane > benzene > cyclopentane.
- Which one of the chromatograms was used by the expert for interpretation and why did he refuse from two other chromatograms?
- Determine the largest and the lowest values of  $R_f$  on this chromatogram.
- What conclusion did the expert make?

### Solution

- Thin layer, ion exchange, gas, gas-liquid chromatography.
  - Due to capillary forces.
  - Taking into account chromatograms 1 and 2, the solvent should be less polar than ethanol, and more polar than benzene. Acetone and tetrahydrofurane correspond to this.
  - The third chromatogram, because the spots are separated on it.
- $$R_f(\text{min}) = \frac{b}{a} = \frac{2}{12.5} = 0.16$$
- $$R_f(\text{max}) = \frac{c}{a} = \frac{10}{12.5} = 0.8$$
- Conclusion: the inks, by which the first two zeros were written, are different from the ink by which the last zero is written.



### Task 6. Selenocysteine

The importance of selenium compounds for normal activity of the human organism is being actively discussed during recent time in popular medical literature. Human body contains selenium predominantly in the form of *selenocysteine*  $C_3H_7NO_2Se$  – close analogue of  $\alpha$ -aminoacid cysteine, in which sulfur atom is replaced by selenium atom.

1. Draw structural formulas of cysteine and selenocysteine. Take into account that their molecules have *R*-configuration.

The residues of cysteine in peptides has  $pK_a = 8.3$ , whereas for the residue of selenocysteine  $pK_a$  is 5.3.

2. Which fraction of the residues of these aminoacids is in anionic form at physiological pH value 7.4?

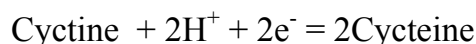
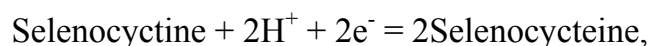
Biological role of selenocysteine is determined by its ability to be easily oxidized with formation of selenocystine as follows:



Similarly, cystine is formed at oxidation of cysteine.

3. Draw structural formulas of cystine and selenocystine.

Standard electrode potentials of half-reactions

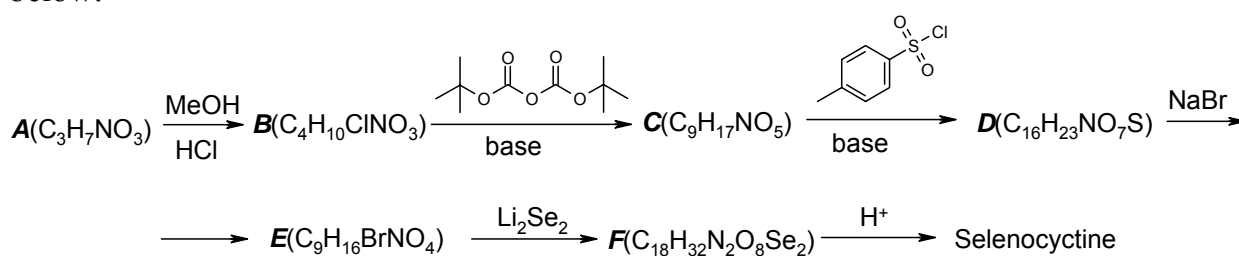


are equal to  $-0.381$  V and  $-0.145$  V, respectively.

1 ml of 0.02 M solution of selenocysteine and ml of 0.01 M solution of cystine were mixed in the test tube.

4. Determine concentrations of selenocysteine and cysteine in obtained solution when equilibrium is set at 298 K. Consider that formation of mixed oxidation product, containing the fragments of both mentioned aminoacids, makes no influence on the equilibrium state.

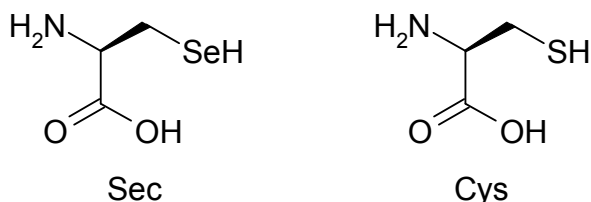
The scheme of selenocysteine synthesis starting from natural compound **A** is presented below.



5. Draw the structures of compounds **A** – **F**. For convenience you may use abbreviations  $(\text{CH}_3)_3\text{COC}(\text{O}) = \text{Boc}$ ,  $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2 = \text{Ts}$ .

### Solution

1.



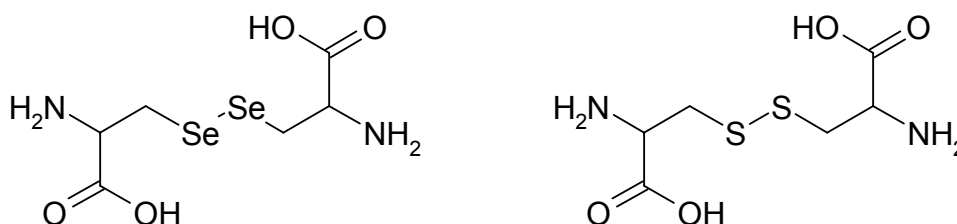
2.

$$\begin{aligned} K_a &= [\text{H}^+][\text{A}^-]/[\text{HA}], \\ [\text{A}^-]/[\text{HA}] &= K_a/[\text{H}^+] = 10^{\text{pH}-\text{p}K_a}, \\ \alpha &= [\text{A}^-]/([\text{HA}] + [\text{A}^-]) = 1/(1 + 10^{\text{p}K_a-\text{pH}}), \end{aligned}$$

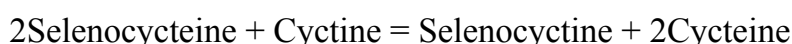
$$\alpha(\text{Sec}) = 1/(1 + 10^{5.3-7.4}) = 0.99, \text{ or } 99\%,$$

$$\alpha(\text{Cys}) = 1/(1 + 10^{8.3-7.4}) = 0.11, \text{ or } 11\%.$$

3.



4. The reaction takes place:



For this reaction

$$\begin{aligned} \text{EMF} &= E_{\text{Selenocystine/Selenocysteine}} - E_{\text{Cysteine/Cysteine}}, \\ E_{\text{Selenocystine/Selenocysteine}} &= E^0_{\text{Selenocystine/Selenocysteine}} + \frac{RT}{2F} \ln \frac{[\text{Selenocystine}]}{[\text{Selenocysteine}]^2}, \\ E_{\text{Cysteine/Cysteine}} &= E^0_{\text{Cysteine/Cysteine}} + \frac{RT}{2F} \ln \frac{[\text{Cysteine}]}{[\text{Cysteine}]^2}. \end{aligned}$$

In equilibrium state  $\text{EMF} = 0$ , that is

$$\begin{aligned} E^0_{\text{Selenocystine/Selenocysteine}} + \frac{RT}{2F} \ln \frac{[\text{Selenocystine}]}{[\text{Selenocysteine}]^2} &= E^0_{\text{Cysteine/Cysteine}} + \frac{RT}{2F} \ln \frac{[\text{Cysteine}]}{[\text{Cysteine}]^2}, \\ \frac{RT}{2F} \ln \frac{[\text{Selenocystine}][\text{Cysteine}]^2}{[\text{Selenocysteine}]^2[\text{Cysteine}]} &= E^0_{\text{Cysteine/Cysteine}} - E^0_{\text{Selenocystine/Selenocysteine}} = \\ &= -0.145 - (-0.381) = 0.236 \text{ (V)}, \\ \frac{[\text{Selenocystine}][\text{Cysteine}]^2}{[\text{Selenocysteine}]^2[\text{Cysteine}]} &= 9.6 \cdot 10^7. \end{aligned}$$

This means that the equilibrium of the above reaction is almost completely shifted to right side. So, in equilibrium state (taking into account two-fold dilution of the solution!)

$$[\text{Cysteine}] \approx 0.01 \text{ M.}$$

Since in initial mixture selenocysteine and cysteine were absent, their concentrations are related by the equation

$$2[\text{Selenocystine}] = [\text{Cysteine}].$$

And since initial ratio of the quantities of the compounds selenocysteine and cysteine was 2 : 1, then

$$2[\text{Cysteine}] = [\text{Selenocysteine}].$$

So,

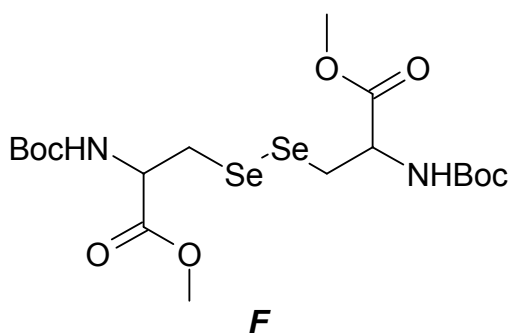
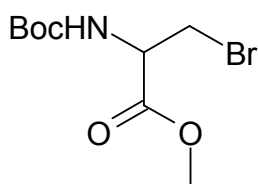
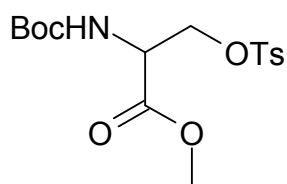
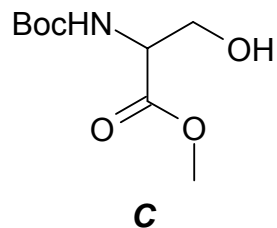
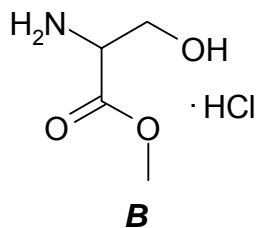
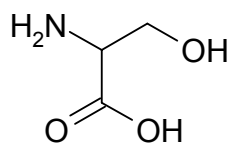
$$\frac{[\text{Selenocystine}][\text{Cysteine}]^2}{[\text{Selenocysteine}]^2[\text{Cysteine}]} = 9.6 \cdot 10^7,$$

$$[\text{Cysteine}]^3/[\text{Selenocysteine}]^3 = 9.6 \cdot 10^7,$$

$$[\text{Cysteine}]/[\text{Selenocysteine}] = 460,$$

$$[\text{Selenocysteine}] = [\text{Cysteine}]/460 = 2.2 \cdot 10^{-5} \text{ M}.$$

5.



## II round

## Task 1. Gases

It is known that there are no absolutely irreversible processes in the nature. For example, FeO, which is "stable" at usual conditions, is heated to 1000 K, then equilibrium oxygen pressure over this compound will be  $4.13 \cdot 10^{-16}$  Pa.

1. Calculate the value of equilibrium constant ( $K_p$ ) for this reaction and  $\Delta G^\circ$  of the process at mentioned temperature.

Equilibrium mixture of CO and CO<sub>2</sub> over FeO at 1000 K and normal atmospheric pressure contains 43 mol. % of CO<sub>2</sub>.

2. Calculate the value of corresponding equilibrium constant of the process ( $K_p$ ).

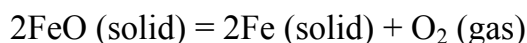
3. Using the data from sub-tasks 1 and 2, estimate the degree of dissociation of CO<sub>2</sub> under these conditions.

4. Does the task contain sufficient data to estimate the degree of dissociation of CO<sub>2</sub> at pressure 10 atm? Or at temperature 700 K? If "yes", calculate corresponding values, and if "no", explain, which data are lacking.

5. How the degree of dissociation of CO<sub>2</sub> is changed when the pressure grows? Rationalize your answer.

## Solution

1. In these conditions:



$$K_{P1} = P_{\text{O}_2} = 4,13 \cdot 10^{-16} \text{ Pa,}$$

$$K_{a1} = K_{P1} / P_{\text{stand}} = \frac{4,13 \cdot 10^{-16} \text{ Pa}}{1,013 \cdot 10^5 \text{ Pa}} = 4,08 \cdot 10^{-21},$$

$$\Delta G^\circ_1 = -RT \ln K_{a1} = -8.314 \cdot 10^3 \cdot \ln 4,08 \cdot 10^{-21} = 390,3 \text{ kJ}$$

2.  $\text{FeO (solid)} + \text{CO (gas)} = \text{Fe (solid)} + \text{CO}_2 \text{ (gas)}$

$$K_{P2} = \frac{P_{\text{CO}_2}}{P_{\text{CO}}} = \frac{\chi_{\text{CO}_2}}{\chi_{\text{CO}}} = \frac{0.43}{0.57} = 0.754$$

3. The equation of CO<sub>2</sub> dissociation



Gibbs free energy is the function of system's state. So, its change in the course of the reaction is determined only by initial and final states of the system and does not depend on the way how final state was achieved. The value of  $\Delta G^\circ$  of any reaction may be obtained



similarly to the values of  $\Delta H^\circ$ , namely: when required chemical equation is obtained from other ones by formally-algebraic way, the same procedure is performed with corresponding function of state. Then, for reaction (3):

$$\Delta G^\circ_3 = \Delta G^\circ_1 - 2\Delta G^\circ_2;$$

respectively, for equilibrium constant we get  $K_{P3} = \frac{K_{P1}}{K_{P2}^2}$ ;  $K_{P3} = 7,26 \cdot 10^{-16}$  Pa.

Equilibrium constant can be related to the degree of dissociation  $\alpha$ :

$$K_{P3} = \frac{\alpha^3}{2 \cdot (1 - \alpha)^2 (1 + \alpha/2)} P_{total} = 7.26 \cdot 10^{-16} \text{ Pa.}$$

Taking in mind that dissociation constant is small, we can neglect the value of  $\alpha$  in denominator compared to 1. Then

$$\alpha = \sqrt[3]{\frac{2K_{P3}}{P_{total}}} = 2.43 \cdot 10^{-7}.$$

4. At pressure 10 atm  $\alpha = \sqrt[3]{\frac{2K_{P3}}{P_{total}}} = 1.13 \cdot 10^{-7}$ , that is it will decrease completely

according to the Le Chatelier principle.

In order to estimate the degree of dissociation of  $\text{CO}_2$  at other temperature  $\Delta H^\circ$  of reaction in this temperature range should be known.

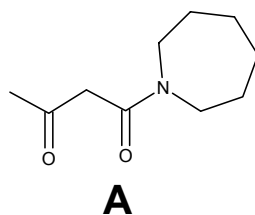
5. When pressure increases dissociation level decreases, since, according to the Le Chatelier principle, in these conditions reaction goes towards reduction of system's volume.

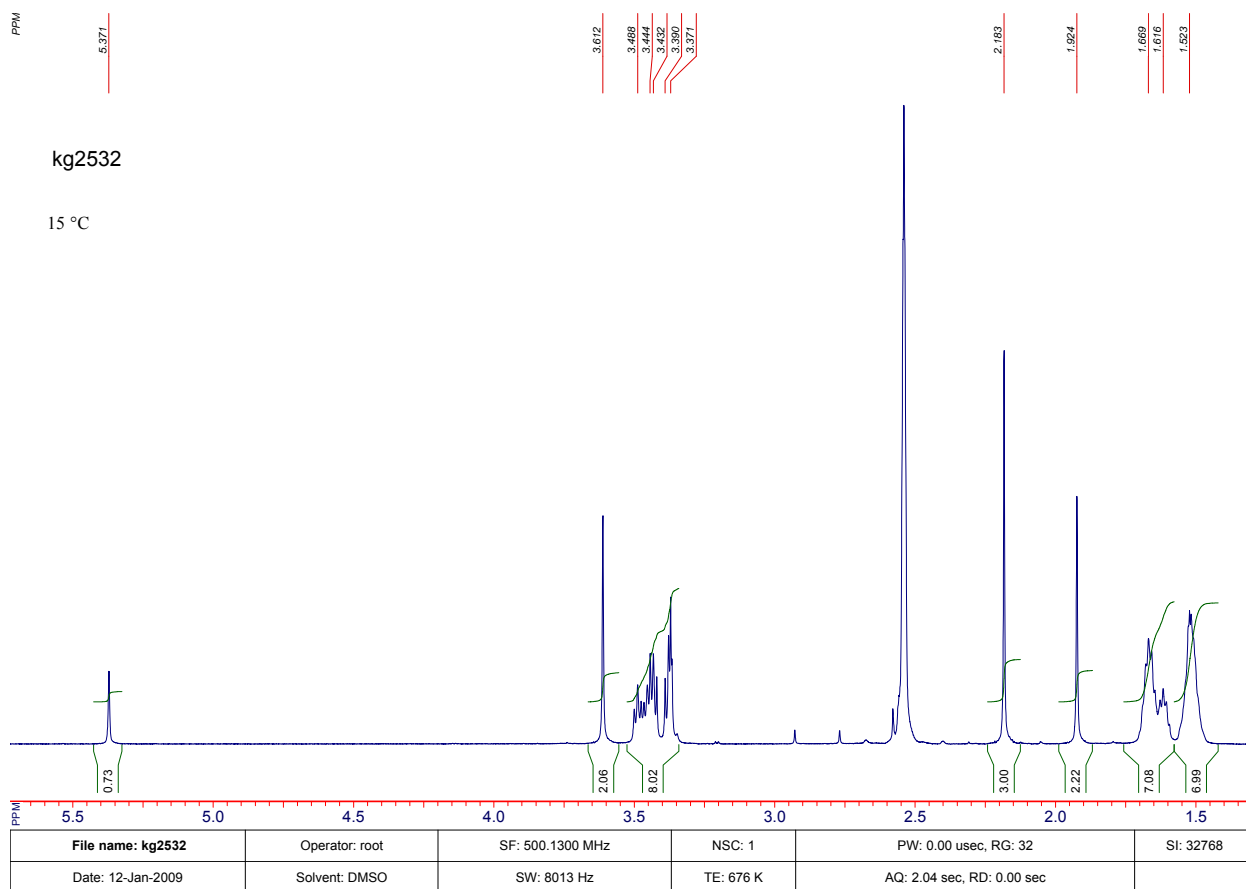
## Task 2. A keto-enolic equilibrium

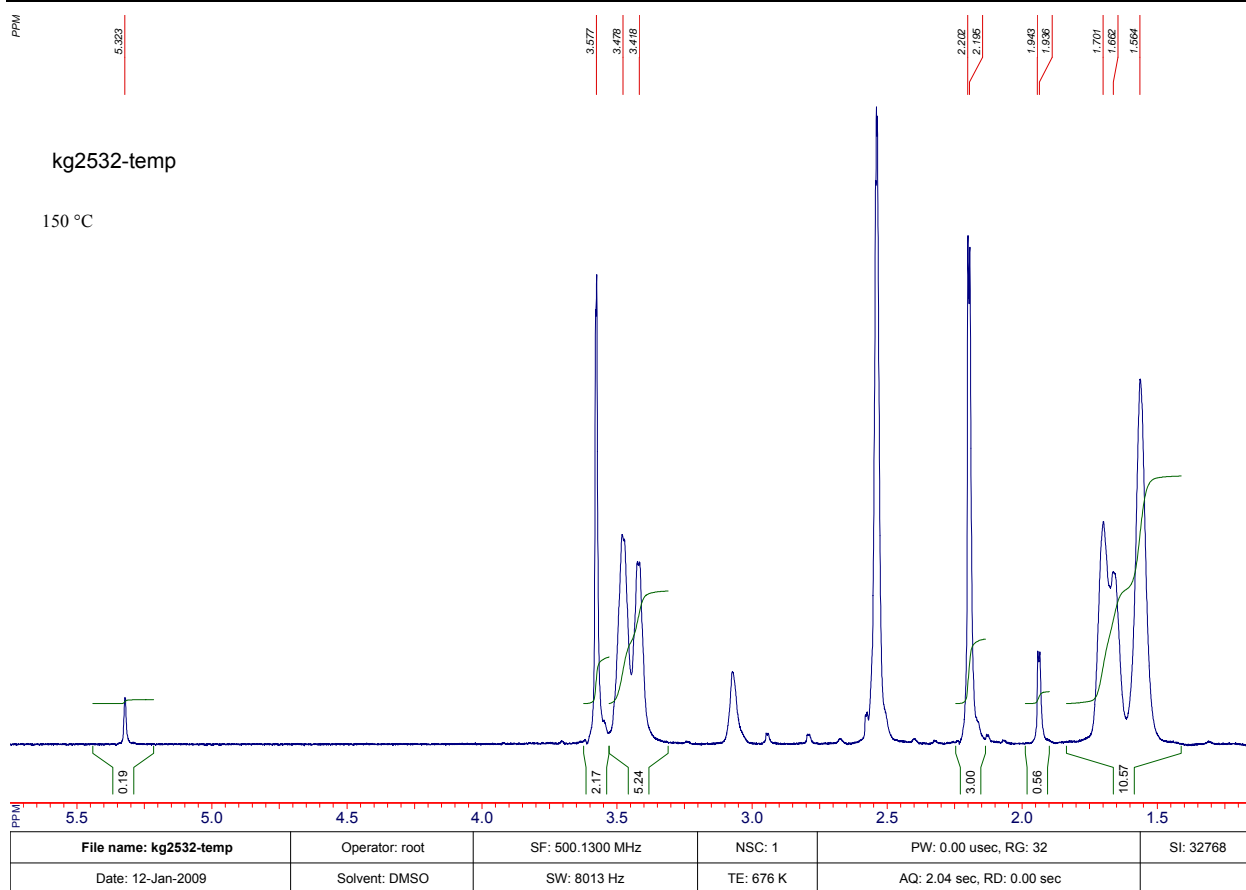
Carbonyl compounds are known to adopt two forms in the solution: ketonic ( $-\text{CH}_2-\text{C}=\text{O}$ ) and enolic ( $-\text{CH}=\text{C}-\text{OH}$ ).

The equilibrium between these two forms of carbonyl compounds plays very important role in biochemical processes and in chemical reactions. The method of NMR is widely used to study this equilibrium.

Below the spectra of solution of compound **A** in deuterated dimethylsulphoxide ( $\text{DMSO-d}_6$ ), measured at 15 °C and 150 °C, are presented:

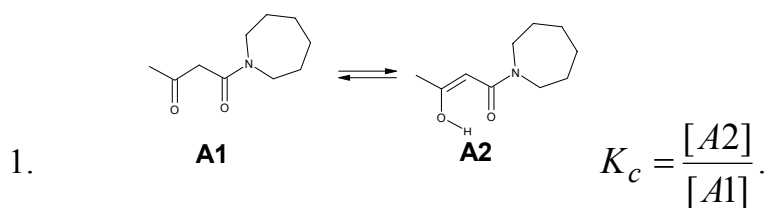




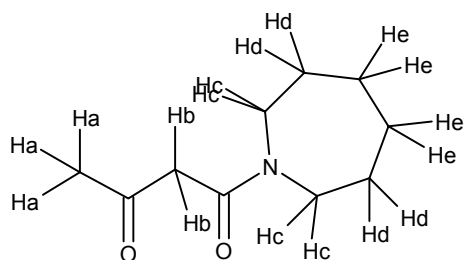
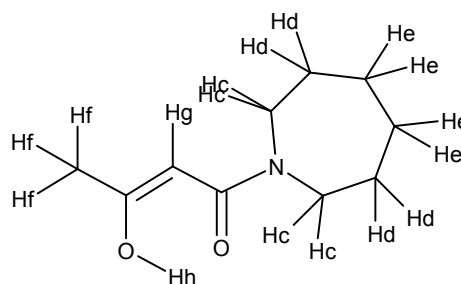


- Write down the equation of keto-enolic equilibrium for this compound and the expression for equilibrium constant  $K$ .
- Assign main signals in PMR spectra of the solution of compound **A**.
- Calculate the ratio of ketonic and enolic forms of this compound at both temperatures and the values of equilibrium constants (if you are not able to calculate this ratio from the spectra, take that  $\frac{[-\text{CH}=\text{C}-\text{OH}]}{[-\text{CH}_2-\text{C}=\text{O}]} = 0.3$  and  $0.8$  at  $150^\circ\text{C}$  and  $15^\circ\text{C}$ , respectively).
- Calculate  $\Delta H^0$  of this reaction.

### Solution



2.

**A1****A2**

	H <sub>a</sub>	H <sub>b</sub>	H <sub>c</sub>	H <sub>d</sub>	H <sub>e</sub>	H <sub>f</sub>	H <sub>g</sub>	H <sub>h</sub>
15°C	2.183	3.612	3.488- 3.371	1.659 – 1.523		1.924	5.371	>14
150°C	2.198	3.577	3.478. 3.418	1.701 – 1.564		1.940	5.323	>14

3. **A1/A2** ratio may be calculated as the ratio of integral intensities of signals H<sub>a</sub> and H<sub>g</sub>, normalized to the number of protons:

$$\frac{[A2]}{[A1]} = \frac{I(H_g)/N(H_g)}{I(H_a)/N(H_a)} = \frac{3I(H_g)}{I(H_a)}$$

	[A1]/[A2]
15°C	0.73
150°C	0.19

4.

	K (from spectra)	K (from the values given in the task)
15°C	0.73	0.8
150°C	0.19	0.3

5.  $\Delta H^0$  of reaction may be calculated using Vant Hoff's equation:

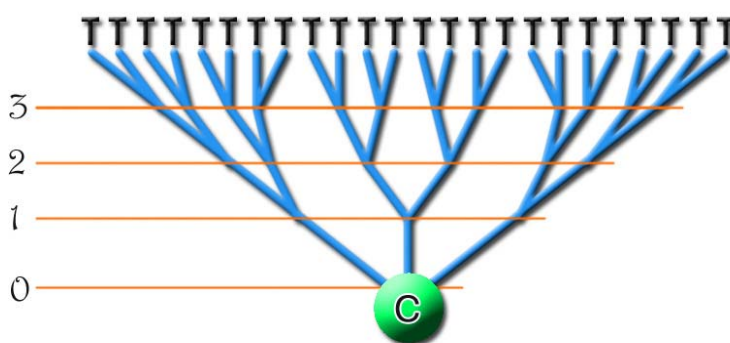
$$\ln \frac{K_{T_2}}{K_{T_1}} = \frac{\Delta H}{R} \left( \frac{T_2 - T_1}{T_1 \cdot T_2} \right) \Rightarrow \Delta H = R \cdot \ln \frac{K_{T_2}}{K_{T_1}} \cdot \left( \frac{T_1 \cdot T_2}{T_2 - T_1} \right)$$

From this  $\Delta H^0 = 8.314 \cdot \left(\frac{288.15 \cdot 423.15}{150 - 15}\right) \ln \frac{0.19}{0.73} = -10.11 \text{ kJ/mol}$  (from experimental data),  $\Delta H = 8.314 \cdot \left(\frac{288.15 \cdot 423.15}{150 - 15}\right) \ln \frac{0.3}{0.8} = -7.37 \text{ kJ/mol}$  (from the data given in the task).

### Task 3. Dendrimers

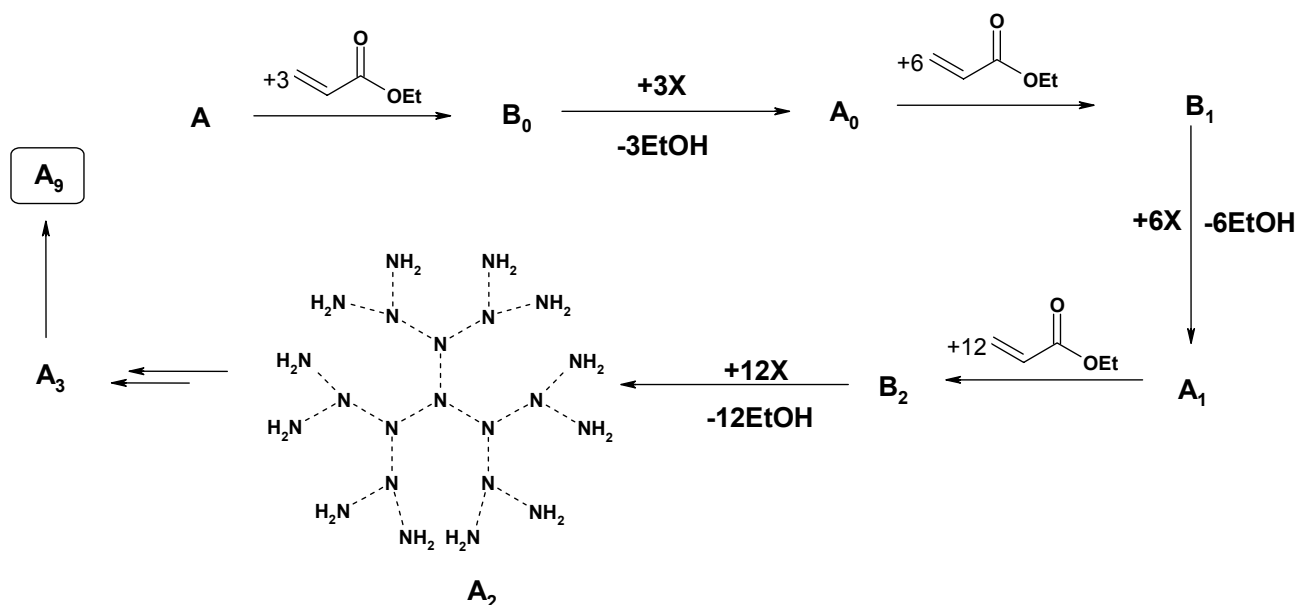
The possibility of existence of special type of polymers – dendrimers – was shown as far as in 1952 by Paul Flory, Noble prize winner 1974, which was awarded "for fundamental achievements in the field of theory and practice of physical chemistry of macromolecules". The chemistry of dendrimers has been rapidly developing in recent years. These polymers have a number of interesting properties, for example, they can be used as efficient catalysts or can act as transport agents for biologically-active compounds in the organism, etc.

Dendrimers (dendro (lat.) – a tree) are super-branched polymers, looking like the tree. They begin to grow from the center (C) and then are branched as the offshoots of the tree, giving more and more offshoots on each stage. The quantity of the offshoots grows in geometric progression.



C is the center, 0,1,2,3 – branching generations, T – terminal (end) group.

Dendrimers are usually obtained by the methods of controlled multi-step synthesis. Synthesis of some dendrimer  $A_9$  is started from gas A (lighter than the air) and is performed using a sequence of reactions of one type:



Compound A<sub>1</sub> has molecular peak in mass-spectrum ( $M^+$ ) = 1043 m/z, and compound X has 2 signals in PMR spectrum.

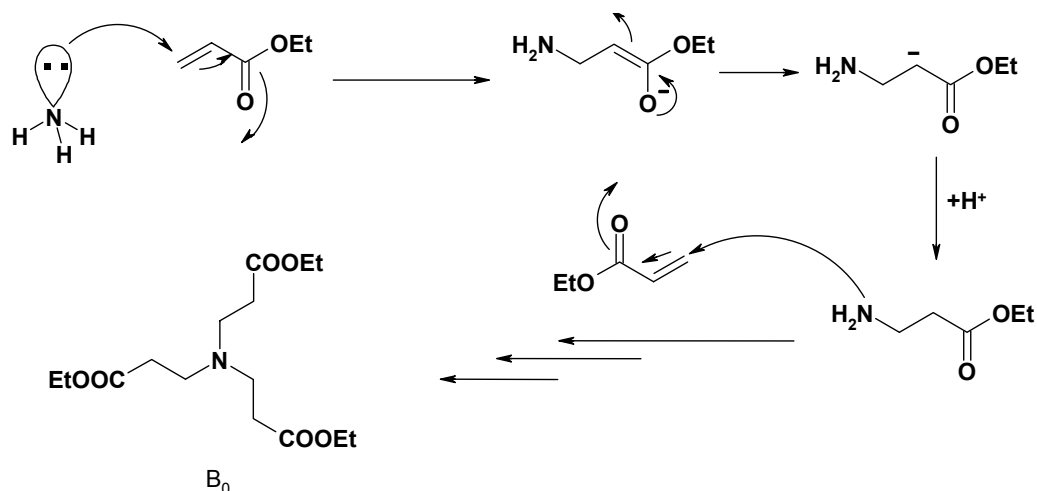
1. Find compounds X, A, A<sub>0</sub>, B<sub>0</sub>.
2. Propose a mechanism of interaction of A with ethylacrylate with formation of compound B<sub>0</sub>.
3. What is the degree of polymerization (the quantity of repeated units) of dendrimer A<sub>7</sub>?
4. Calculate the volume of 0.600 M solution of HCl, required for complete neutralization of 0.0002 moles of dendrimer A<sub>9</sub>, taking into account that 4.17 % of terminal groups A<sub>8</sub> did not react with ethylacrylate because of sterical obstacles. Consider, that H<sup>+</sup> ion protonates only -NH<sub>2</sub> groups.

### Solution

1-2. Let us start from the compound A<sub>1</sub>: it is one generation "younger" than A<sub>3</sub>, so it has 6 amino-groups, 4 nitrogen atoms and 9 links. So, we can find molar mass of the link using the data of mass-spectrum:

$$6 \cdot 16 + 4 \cdot 14 + 9 \cdot x = 1043 \Rightarrow x = 99 \text{ g/mol.}$$

Gas A acts as a core of dendrimer, then it is NX<sub>3</sub>. Since it is lighter than air, it is ammonia NH<sub>3</sub>. Ammonia reacts with three equivalents of ethylacrylate (Michael condensation):



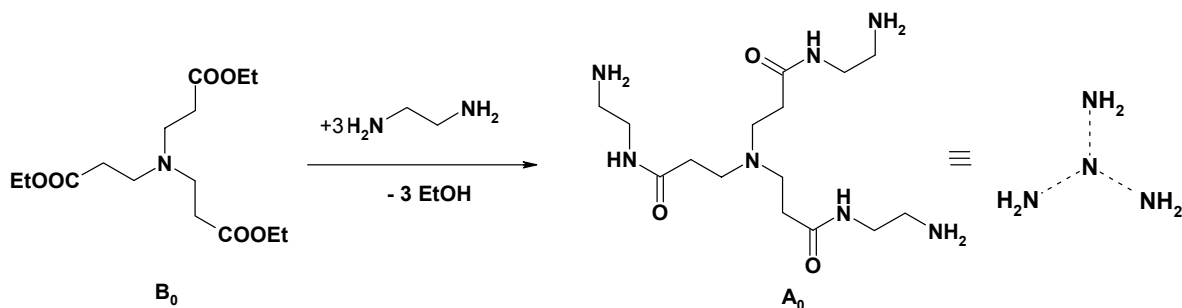
Since ethyl alcohol is by-product of other reaction, formula of compound X may be written as:  $\text{H-???-NH}_2$ , then the link has a formula  $-\text{CH}_2\text{CH}_2\text{CO-???}$ . Let us determine molar mass of «???»:

$$M(\text{???}) = 99 - 14 - 14 - 28 = 43 \text{ (g/mol)}.$$

Since X has 2 signals in PMR spectrum, the most probable that it is diamine, and the residue 28 g/mol corresponds to  $-\text{CH}_2\text{CH}_2-$ .

So, X is  $\text{H}_2\text{N-CH}_2\text{-CH}_2\text{-NH}_2$ .

Then  $\text{A}_0$ :



All subsequent reactions go in similar way.

3. The degree of polymerization is the quantity of repeated links. In  $\text{A}_0$  the degree of polymerization is 3, on the second stage 6 terminal links appear ( $\text{A}_1$ ), on the third – 12 ( $\text{A}_2$ ).

Thus, for  $\text{A}_7$  the degree of polymerization is

$$\begin{aligned} n &= 3 + 3 \cdot 2 + 3 \cdot 2^2 + 3 \cdot 2^3 + 3 \cdot 2^4 + 3 \cdot 2^5 + 3 \cdot 2^6 + 3 \cdot 2^7 = \\ &= 3 \cdot (1 + 2 + 2^2 + 2^3 + 2^4 + 2^5 + 2^6 + 2^7) = \\ &= 3 \cdot (2^8 - 1) = 765 \end{aligned}$$

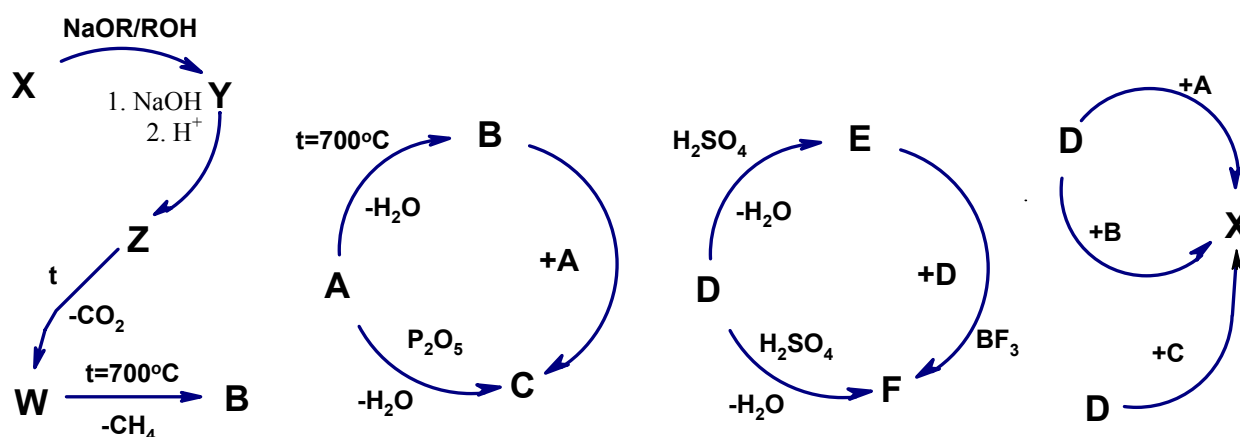
4.  $A_0$  has 3 terminal groups,  $A_1 - 6 (=3 \cdot 2)$ ,  $A_2 - 12 (=3 \cdot 2^2)$ ,  $A_3 - 24 (=3 \cdot 2^3)$ . Then  $A_8$  has  $3 \cdot 2^8 = 768$  groups, from them  $N(-NH_2) = 768 \cdot (1 - 0.0417) = 736$  group reacted in further reactions, and 32 amino-groups, which did not react, remained. In the next generation the quantity of amino-groups (736) doubled and reached 1472, and total quantity of amino-groups is  $1472 + 32 = 1504$ .

So, 1504 equivalents of HCl will react with one equivalent of  $A_8$ , that is the quantity of required HCl is  $1504 \cdot 0.0002 = 0.3008$  (mol),

$$V(HCl) = \frac{\nu(HCl)}{C_M(HCl)} = \frac{0.3008}{0.6} = 0.5013l = 501.3ml$$

#### Task 4. Transformation-2009

Compounds B and E are gaseous and have equal density in the same conditions. Liquid W has one signal in PMR spectrum. Reduction of W produces D.



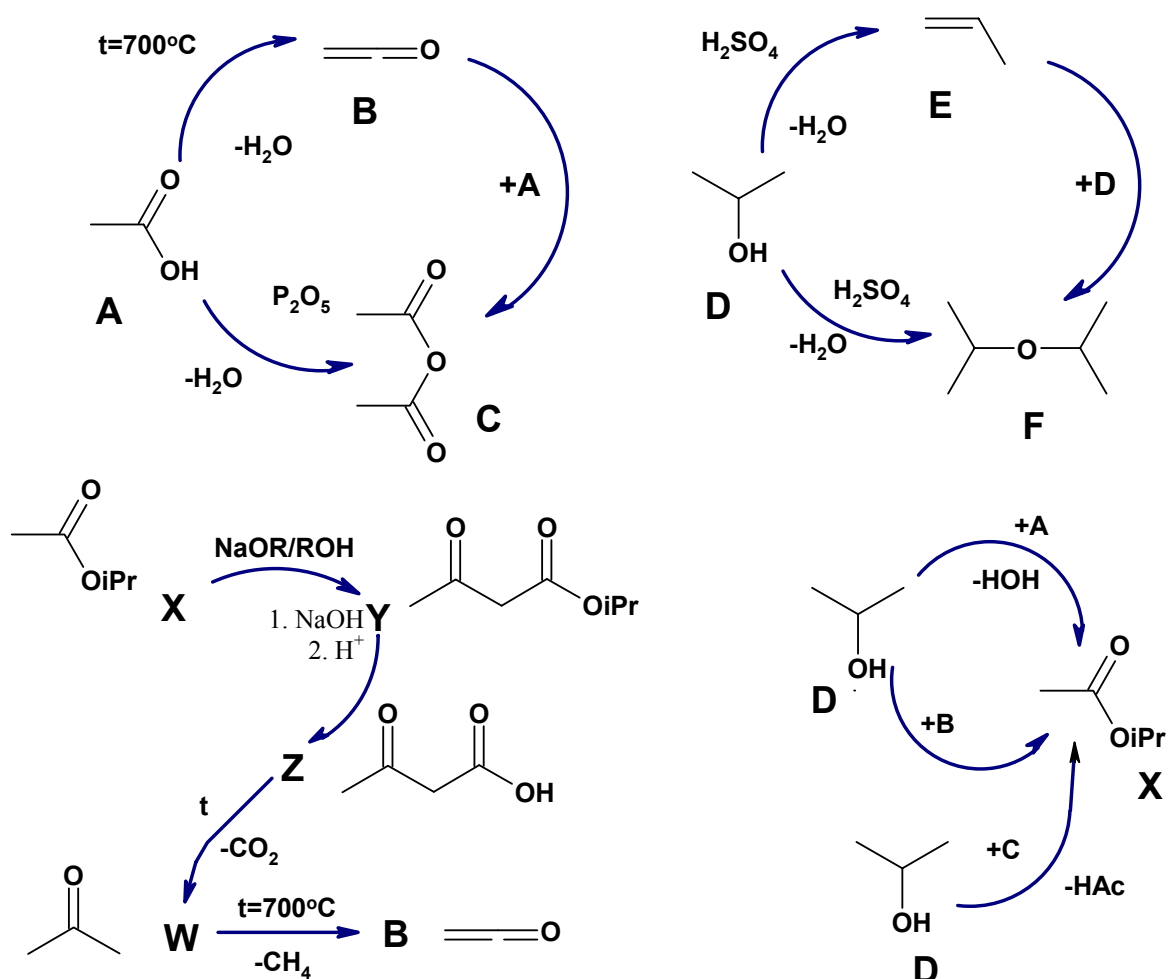
1. Find out unknown compounds A–F, W, X, Y, Z.
2. Which sodium alcoholate and alcohol should be used at transformation  $X \rightarrow Y$  in order to avoid formation of undesired products?
3. Which of compounds A–C reacts with compound D more quickly?
4. Are the densities of vapors of compounds A and D equal?
5. Propose 2 principally different reactions of reduction of W into D.
6. Propose the mechanism of decarboxylation  $Z \rightarrow W$ .
7. Which compounds may form at heating of the mixture of B and E?
8. Which of two transformations,  $D \rightarrow E$  or  $D \rightarrow F$ , will require more strong heating?



## Solution

1. Compound W has one signal in PMR spectrum, at heating it loses methane molecule (quite surprising) and is transformed into gas, that is why this compound is light and its formula mass is not high (and signal originates from methyl group).

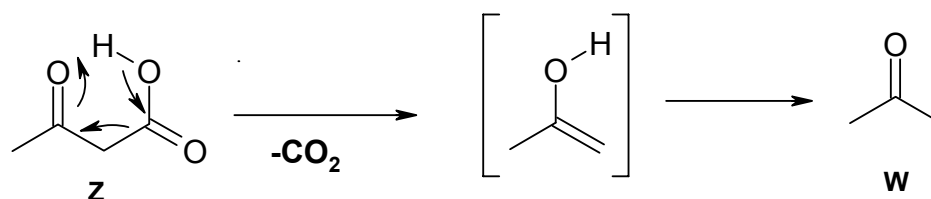
Compound A (as well as D) in different conditions loses water, and it may be concluded that 1 equivalent of A loses 1 equivalent of water forming B, and 2 equivalents of A lose 1 equivalent of water forming C. For D it is similar. It is very probable, that compound D is alcohol, E – alkene, and F is ether. Alcohol D reacts with A, B, C. It may be assumed that A is carboxylic acid, C – anhydride, in this case B is ketene, namely the first representative of a row of ketenes  $\text{CH}_2=\text{C}=\text{O}$ , since it is formed at pyrolysis of acetone (W). Then E is propene, D – propyl or isopropyl alcohol, and E is corresponding ether. Then X is isopropylacetate:



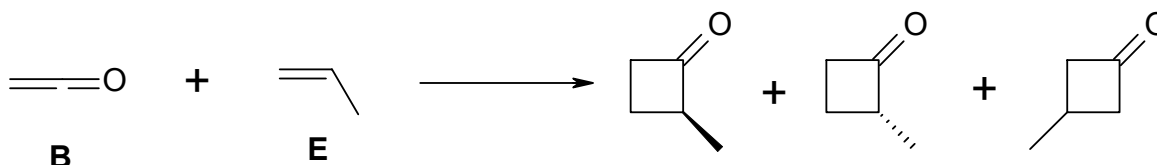
2. Sodium isopropylate, isopropyl alcohol.
3. Ketene reacts most quickly with compound D.
4. No, because in vapor acetic acid is dimerized, and isopropyl alcohol is not.

5. For example,  $\text{LiAlH}_4$  or  $\text{NaBH}_4$ ;  $\text{H}_2/\text{Pd}$ .

6.



7.



8. Stronger heating is required for formation of alkene ( $\text{D} \rightarrow \text{E}$ ).

### Task 5. Inorganic compounds

Heating to  $1500^\circ\text{C}$  of the mixture of 0.70 g of simple substance, formed by element X, with the excess of higher oxide (Y) of the same element results in distillation of 2.20 g of solid compound A. Treatment of obtained quantity of A by the solution of HF results in formation of solution of acid B and 0.58 g of solid residue C. Addition of the excess of  $\text{BaCl}_2$  to the solution of B causes precipitation of 8.38 g of salt D, which at heating decomposes forming 672 ml (n.c.) of gas Z and 5.26 g of solid compound E.

Dissolving of 0.29 g of C in aqueous solution of KOH leads to formation of 560 ml (n.c.) of hydrogen. Heating of 0.29 g of C causes formation of simple substance X and 89.60 ml of two-component gas mixture ( $D_{\text{H}_2} = 4.75$ ), which burns in oxygen forming 0.09 g of water and 0.06 g of Y. Depending on heating conditions, the volume and density of gas mixture may vary, but the mass of water, which forms at its burning, remains to be the same.

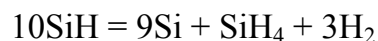
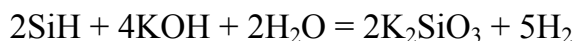
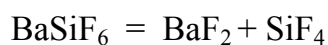
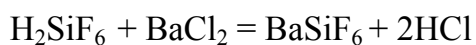
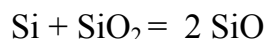
1. Find compounds A-E, X, Y, Z. Draw the equations of chemical reactions.
2. Explain why Y is solid compound with high melting point, whereas the highest oxide of the element, located over X in periodic system, is gas.
3. Draw the fragments of structure of compounds C and Y.

### Solution

1. Mass of 672 ml of gas Z is 3.12 g, so molar weight is equal to 104 g/mol, this is  $\text{SiF}_4$ .

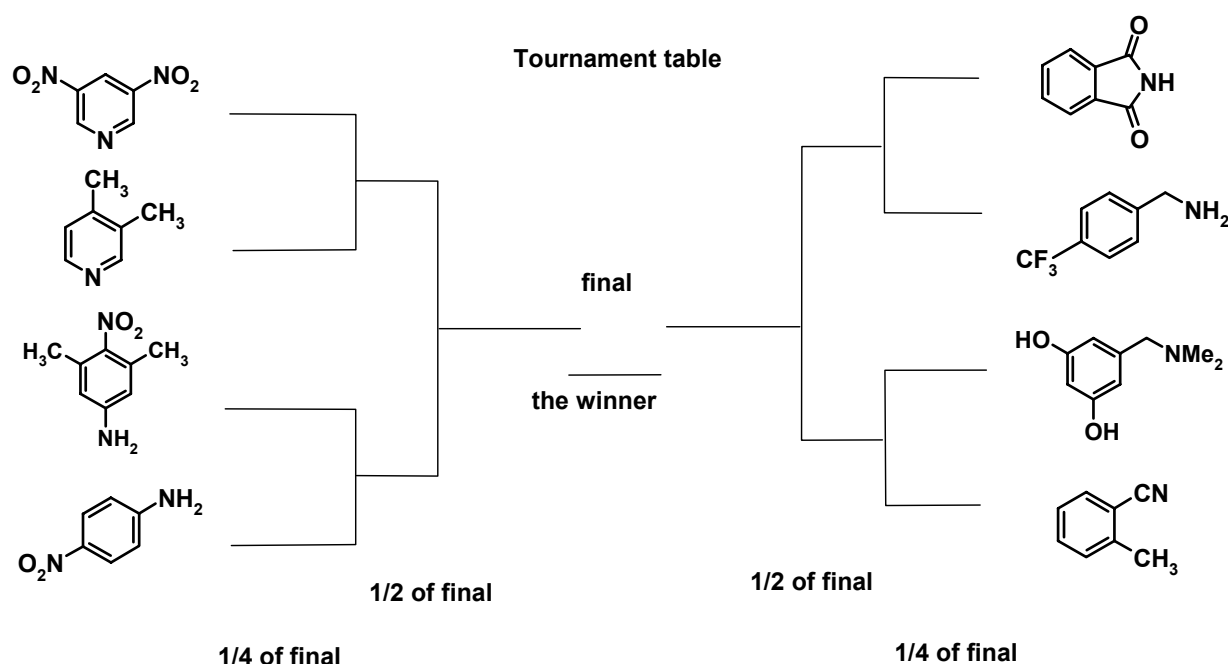
Barium salt D, decomposition of which produces SiF<sub>4</sub>, is BaSiF<sub>6</sub>.

From these data, X = Si, Y = SiO<sub>2</sub>, A = SiO, B = H<sub>2</sub>SiF<sub>6</sub>, C = SiH, E = BaF<sub>2</sub>.



### Task 6. Tournament among the molecules

Eight the strongest molecules remained in chemical tournament after group selection, which continue competition for the title of "The Best Molecule – 2009".



There are 4 pairs of compounds in 1/4 of final, and the molecule, possessing more basic properties, goes to the next round of competition. In the result 4 compounds go to 1/2 of final, that is 2 pairs. In order to determine the winners, IR spectra are measured in each pair. The compound, IR spectrum of which contains absorption band with the highest wavenumber (cm<sup>-1</sup>), becomes the winner.

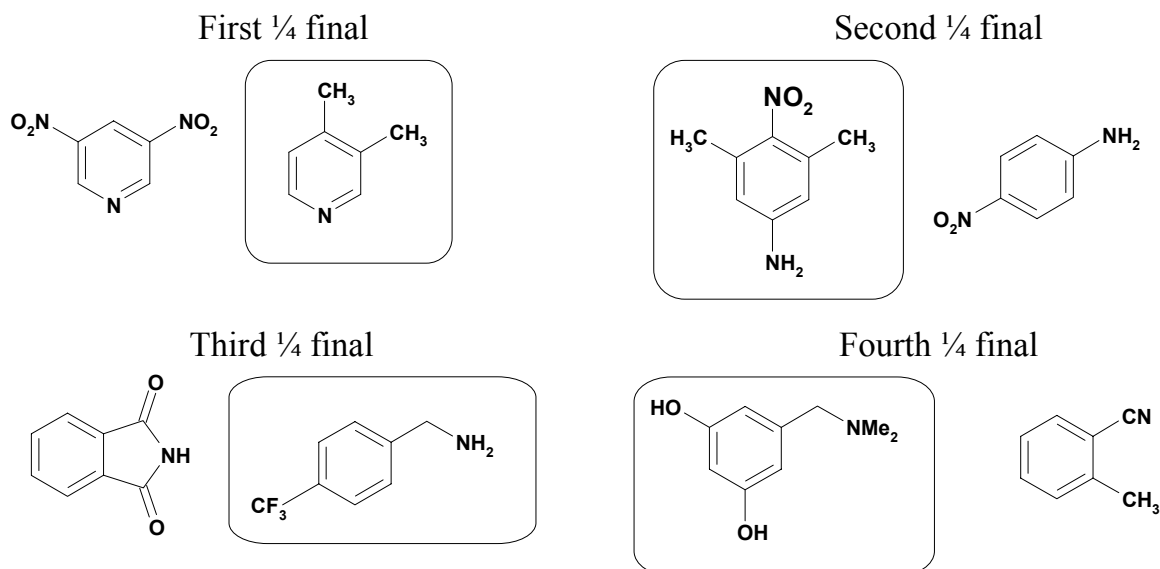
Thus, 2 compounds go to the final, and the winner is determined by the value of dipole moment. And those 2 compounds, which did no enter the final, compete for the third place on nitration simplicity.

1. Determine the compounds, which entered 1/4 of final. Substantiate your choice.
2. Determine the compounds, which entered 1/2 of final. Substantiate your choice.
3. Determine the winner of the tournament. Substantiate your choice
4. Determine the molecule which got the third place. Substantiate your choice

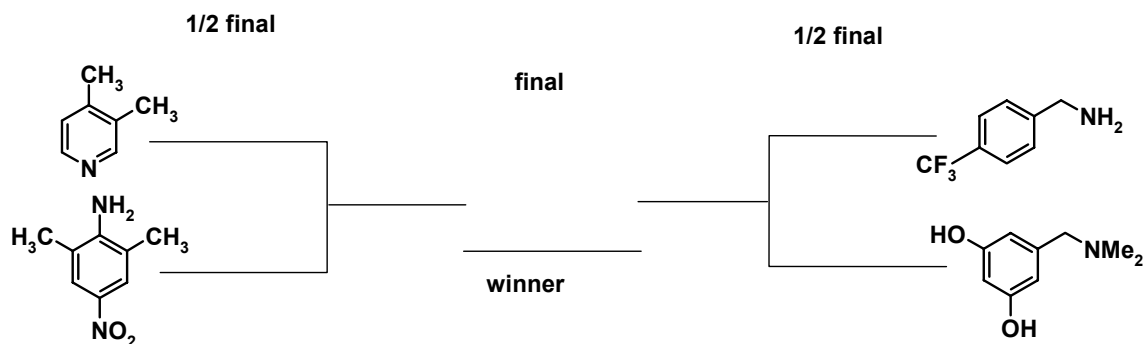
5. In the previous tournament the molecule of guanidine participated, and it had no equal opponent in 1/4 of final. Explain, why?

### Solution

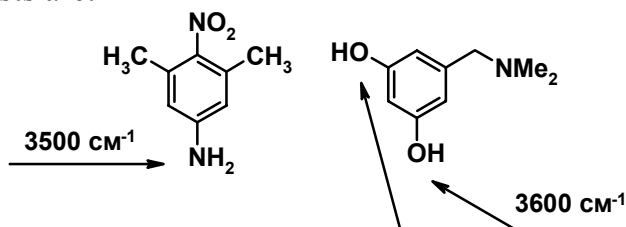
1. Basicity is determined by the ability to add hydrogen cation.



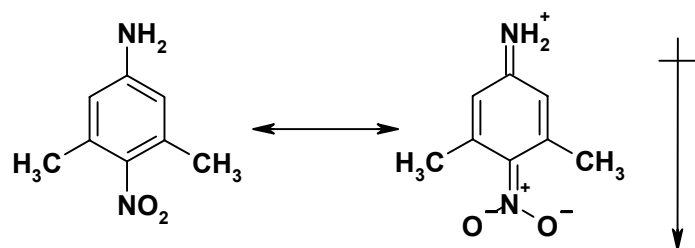
2.



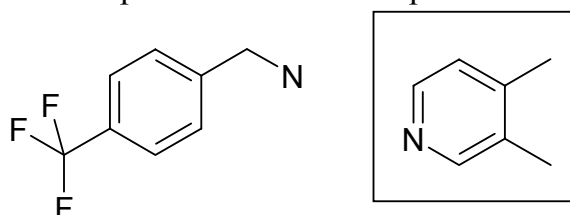
The most "high" adsorption bands in IR spectrum are related with valent (along the bond) vibrations X–H, their frequency is the highest, and in this case  $\nu(\text{O-H}) > \nu(\text{N-H}) > \nu(\text{C-H})$ . So, the finalists are:



3. Final. The aniline derivative has higher dipole moment due to higher delocalization of electronic density (+M effect of amino-group, though slightly weakened by the presence of methyl groups, –M effect of nitro-group).



4. Molecules take part in competition for the third place



Dimethylpyridine is easier subjected to nitration: two donor substituents significantly simplify electrophilic substitution in pyridine ring.

5. The molecule of guanidine is one of the strongest bases since it has three resonance structures, which have equal energies, that is, even charge distribution takes place:

