

The XXXIX
All-Ukrainian
Chemistry Olympiad
Tasks and Solutions

Dnepropetrovsk March 2002

THE FIRST THEORETICAL ROUND

Task 1. The collision theory deals with the kinetics of homogeneous reactions. According to this theory, two moving particles collide if they appear to be simultaneously located inside the cylinder with the sectional area $\sigma = \pi(r_A + r_B)^2$, where r_A and r_B are the radii of particles. The relative speed of the particles, \bar{v}_{rel} , is determined by equation:

$$\bar{v}_{\text{rel}} = \left(\frac{8KT}{\pi\mu} \right)^{1/2},$$

where

$\mu = \frac{m_A m_B}{m_A + m_B}$ is the reduced mass,

m_A and m_B are the masses of particles,

K is the Boltzman constant ($1,38 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1}$).

Hence, the volume of the cylinder is equal to

$$z = \sigma \cdot \bar{v}_{\text{OTH}}.$$

This quantity, known as the "collision factor", characterizes the theoretical frequency of collisions per second. It was found to be proportionate to k , the rate constant of the 2nd order reaction:

$$z \propto k,$$

If two particles are identical,

$$m_A = m_B = m,$$

$$r_A = r_B = r.$$

- 1) **Calculate** the average relative speed of N_2 molecules at 298 K.
- 2) Assume $r_{\text{N}_2} = 2,5 \cdot 10^{-10} \text{ m}$ and **determine** σ and z .
- 3) **Express** the collision factor z into the dimension of the rate constant k if time is measured in seconds and concentrations are expressed in $\text{mol} \cdot \text{L}^{-1}$.

For the bimolecular reactions between atoms and small molecules the calculated values $z_{\text{theoretical}}$ are in a fairly good agreement with the experimentally measured values $z_{\text{experimental}}$. The dimerization of 1,3-butadien is the bimolecular reaction. But in this case $z_{\text{theoretical}}$ and $z_{\text{experimental}}$ differ significantly.

4) **Choose** the correct statement:

a) $z_{\text{experimental}} \ll z_{\text{theoretical}}$ OR

b) $z_{\text{experimental}} \gg z_{\text{theoretical}}$

and **explain** your decision.

5) For some bimolecular reactions $z = k$. **What examples** of these reactions do you know?

Task 2. Hydrogen and nitrogen were brought into contact in the presence of a suitable catalyst at a temperature $T = 720$ K. The molar ratio $n(\text{H}_2) / n(\text{N}_2)$ was equal to 3 : 1.

1) **Calculate** the volume fractions of species at the equilibrium state when the total pressure $P = 1$ atm.

2) **Calculate** the volume fractions of species at the equilibrium state when the total pressure $P = 100$ atm.

Note: At 720 K the standard equilibrium constant $K_a = 4,21 \cdot 10^{-3}$.

The standard pressure $P_0 = 1,01325 \cdot 10^5$ Pa = 1 atm = 1,01325 Bar;

$K_p = K_a \times (P_0)^{\Delta v}$.

Task 3. A weak acid (**HA**) exists as a mixture of two tautomers S_1 and S_2 . There exists the dynamical equilibrium between these tautomers in solutions. For both tautomeric forms, the organic derivatives are well known.

Under the ordinary conditions, the molar fraction of tautomer S_1 $\chi(S_1) = 99,5$ %. With increasing the temperature the fraction of the second tautomer, $\chi(S_2)$, is increased too.

The aqueous solution of **HA** (Solution 1, $m(\text{HA}) = 1,730$ g; $V_1 = 900$ ml) was partly neutralized with KOH. In this solution, the ratio of molar concentrations $c(\text{acid}) / c(\text{salt})$ was equal to 0.1, while the pH value was 10.20. After adding the corresponding amount of KOH, the equivalence point was attained. The pH value in this solution (Solution 3, $V_3 = 1000$ ml) was found to be equal to 11.00.

1) **Calculate** the dissociation constant of **HA**.

2) **Find** the molecular formula of HA and **draw** the structural formulas of tautomers S_1 and S_2 .

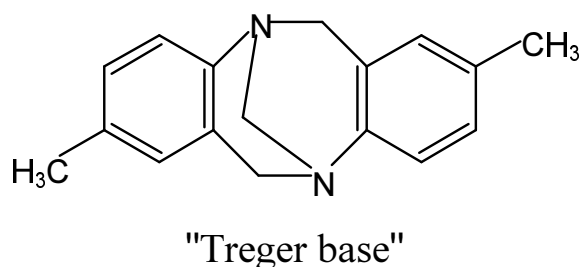
3) **Calculate** the pH value for Solution 1.

4) **Calculate** the constant of the tautomeric equilibrium K_i .

5) What is observed when NaClO is added to Solution 3? **Give** the equation of the chemical reaction.

6) **Give** the electronic configuration for the ground state of anion A^- (the filling of the molecular orbitals by electrons). Characterize the magnetic properties of this anion.

Task 4. At the close of the XIX century the interesting compound, known as the Treger base, was synthesized. Later Prelog and Wieland supposed that such compounds could show the optical activity.



Many different optically active acids were used to separate the Treger base into the enantiomers. In spite of the tenacious efforts, all attempts were failed. Only the employment of the liquid chromatography has allowed to achieve a success.

- 1) **Propose** a way to synthesize the Treger base starting from toluene.
- 2) **Draw** the formulas of *R*- and *S*-isomers of this compound.
- 3) **Explain**, why "ordinary" amines, such as N(Me)(Et)(Pr) do not demonstrate the optical activity.
- 4) What examples of triply coordinated optically active compounds do you know? **Give** at least one example.
- 5) **Why** attempts to separate the Treger base into the optical antipodes failed?
- 6) **Design** a procedure for separating the Treger base into the antipodes with the aid of the liquid chromatography.

Task 5. The molecule of compound **X** ($C_{14}H_{18}N_2$) contains two dimethylamino groups. Being dissolved in non-aqueous solvents, this substance displays surprising properties. It deprotonizes C_6H_5OH completely but does not interact with $(NO_2)_2CH_2$, though the latter is of the more acidic nature.

In the 1H -NMR spectrum of **X** there are only three signals of aromatic protons.

- 1) **Propose** the structure of compound **X**.
- 2) **Explain**, why this compound is selective in respect to hydrogen atoms of different nature.

In aqueous solution, the dissociation constant of XH^+ is equal to $3 \cdot 10^{-11} \text{ mol} \cdot L^{-1}$.

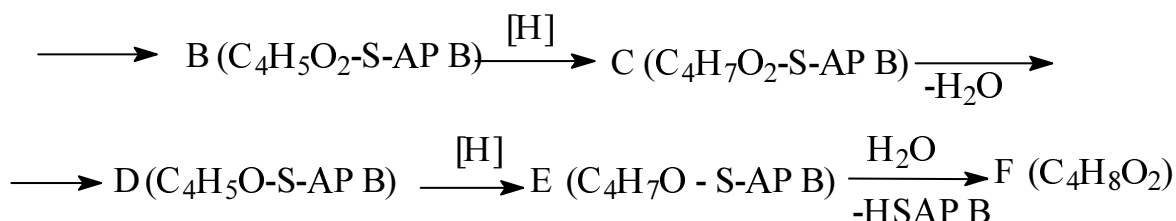
- 3) **Determine** the pH value at which the concentrations of neutral and protonated forms of **X** are equal.

Task 6. One chemist has decided to investigate the formation of macrocycles. For this, he used di-*tert*-butyl ester of octadecan-1,18-dicarboxylic acid. At first, he obtained its thorium salt. After that he synthesized the macrocycle by the pyrolysis of the salt.

One day the initial ester occasionally appeared in the flask where the formation of a macrocycle took place. To the chemist's great surprise, from the reaction mixture he has isolated (with the ~10 % yield) an interesting compound **X**. This compound was of the macrocyclic nature too, but had much higher molecular mass. In the presence of dimethyl ester of octadecan-1,18-dicarboxylic acid the formation of compound did not take place.

- 1) **What** substance was obtained?
- 2) **Why** the presence of dimethyl ester hinders compound **X** to be formed?
- 3) **Draw** the structure of **X** and **give** the schemes of all mentioned reactions.

Task 7. A biosynthesis of fats in a cell includes the following stages:
 $\text{acetyl-S-AP B} + \text{malonyl-S-AP B} \xrightarrow{-\text{AP B}} \text{A (C}_5\text{H}_5\text{O}_4\text{-S-AP B)} \longrightarrow$



where APB is a protein transporting the acyl group. All stages, except $\text{A} \rightarrow \text{B}$, are catalyzed by enzymes.

- 1) **Draw** the structures of all organic molecules present in the scheme.
- 2) **What** is the mechanism of the formation of **A**?
- 3) **Why** *malonyl* is used in this process rather than another *acyl*?
- 4) **Explain**, why the presence of enzymes is not necessary to perform the transformation $\text{A} \rightarrow \text{B}$.
- 5) **Is it possible** to synthesize in a cell an analog of **F** that contains 16 carbon atoms?

Compound $^{14}\text{CH}_3\text{CO-S-APB}$ was introduced into the reaction.

- 6) **Indicate** the position of the label in the **F** molecule.

THE SECOND THEORETICAL ROUND

Task 1. Anion NO_2^- is often included into coordination compounds as a ligand.

№	Formula	Mass fractions of elements, w , %			Bond length, l , Å		Angle, °	
		Metal	N	C	N-O _a	N-O _b	O-N-O	O-Me-O
1	$[\text{M1A}_2(\text{NO}_2)_2]$	21,68	31,04	17,74	1,21	1,29	122	180
2	$[\text{M2Q}_2\text{NO}_2]^+$	15,07	16,62	56,93	1,24	1,24	114,5	53
3	$[\text{M3R}_2(\text{NO}_2)_4]^-$	21,27	30,33	–	1,24	1,24	115,2	–

The distance l in the free anion NO_2^- is equal to 1,24 Å, and the interbond angle is 115,4°. Ligands **A**, **Q** and **R** contain nitrogen and hydrogen and do not contain oxygen. The coordination number of metal ions in all complexes is equal to 6.

- 1) **Show** the spatial configuration of NO_2^- and **write down** the state of hybridization for the nitrogen atom.
- 2) **Show** four different ways for NO_2^- ion to be connected with the central metal ion.
- 3) **Determine** the ligands and the metals in the complexes 1, 2 and 3.
- 4) **Show** the structures of all complexes. **Explain** the differences in the spatial characteristics of NO_2^- .

Task 2. Two electrodes have the same qualitative composition. At the ordinary conditions they are liquid. After immersion of these electrodes into the metal sulfate aqueous solution the galvanic cell was obtained. The complete discharge of the cell generated 144 C of electricity. The qualitative compositions of both the solution and the electrodes remained without changes, while the change of electrode masses was equal to 48,8 mg.

1) **Explain** the principle of operation of the galvanic cell. Did the quantitative composition of the solution remain without changes?

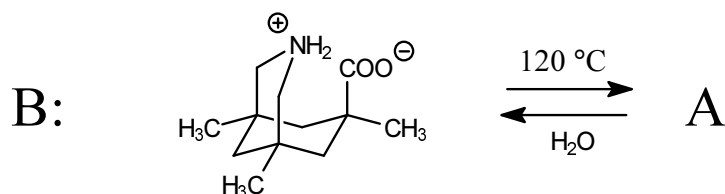
2) **What** metal sulfate was used?

3) **Which factors** affect the electromotive force of the cell?

4) **Will the galvanic cell operate** when the Na_2SO_4 aqueous solution is used as the electrolyte? Explain your answer.

The Faraday constant $F = 96500 \text{ C}\cdot\text{mol}^{-1}$.

Task 3. Compound **A** contains an amide bond. It's rapidly formed when amino acid **B** is sublimated in vacuum at a temperature 100-120 °C:



Just after the formation, the hydrolysis of **A** is passed at pH 7 during some microseconds. Under the same circumstances, the half-transformation of ordinary amides (for example, acetamide) is passed during 700-800 years.

1) **Draw** the structure of **A**. Why this compound is formed simply?

2) **Explain** for which reasons the hydrolysis of compound **A** is very fast. Do you know other compounds for which the interaction with **A** is fast too? If so, give the corresponding examples.

3) Keeping in mind facts described in the task, **give** your explanation for the enzymatically catalyzed formation and hydrolysis of peptides.

Task 4. Compound **A** interacts with 2,4-dinitrophenylhydrazine but does not give the silver mirror reaction. Compound **A** reacts easily with bromine yielding mono bromine derivative **B** (the mass fraction of Br 45,20 %). Substance **B** reacts in ethanol with NaOC_2H_5 yielding compound **C**. The alkaline hydrolysis of **C** results in the formation of carboxylic acid **D**. In the neutralization reaction, the equivalent mass of **D** is equal to $114 \text{ g}\cdot\text{mol}^{-1}$. In the $^1\text{H-NMR}$ spectrum of acid **D** four signals are observed with the ratio of integral intensities 4 : 4 : 1 : 1.

1) **Determine** substances **A–D**.

2) **Propose** the mechanism of the transformation **B**→**C**.

Task 5. The wide absorption band near 1720 cm^{-1} is observed in the IR spectrum of compound **A**. Compound **A** is introduced in the reaction with magnesium amalgam suspended in benzene. The acidification of the reaction mass leads to the formation of compound **B**. Under the influence of concentrated H_2SO_4 , **B** is transformed into substance **C**. Under the influence of the warm alkaline I_2 solution, compound **C** is converted into compound **D** ($\text{C}_6\text{H}_{10}\text{I}_2\text{O}$). Being heated with the alkaline Cl_2 solution, compound **C** forms CHCl_3 and the salt of acid **E**. Under the action of Br_2 , the argentum salt of acid **E** is converted to compound **F** ($\text{C}_4\text{H}_9\text{Br}$). This compound demonstrates only one singlet in the $^1\text{H-NMR}$ spectrum.

- 1) **Determine** substances **A – F**.
- 2) **Give** the mechanisms of formation **B**, **C** and **E**.
- 3) **Explain** the different behavior of compound **C** in reactions with Cl_2 and I_2 .
- 4) **Sketch** the $^1\text{H-NMR}$ spectrum of substance **D** and **indicate** the relative peak areas.

Task 6. In 1918 Born proposed his well-known equation. According to this equation, the lattice energy of the ionic crystal (U) depends on the distance between ions in the crystal (r):

$$U = \frac{-N_A A e^2 z_1 z_2}{r} + \frac{B}{r^n}.$$

Here N_A is the Avogadro number, A is the Madelung constant, e is the charge of electron, z_1, z_2 are the charges of ions, n is the Born's exponent ($n \approx 9$), B is a constant.

- 1) **What** is meant by "the lattice energy of the ionic crystal"?
- 2) **Choose** the right statement about the Madelung constant A :
 a) $A < 0$; b) $A > 0$; c) $A < 1$; d) $A > 1$; e) A depends on the charges of ions;
 f) A depends on the type of the crystal lattice. Several correct answers are possible.
- 3) **Sketch** the plot of the lattice energy against the inter-ionic distance.

To calculate the lattice energy of crystalline NaCl the following experimental data ($\text{kJ}\cdot\text{mol}^{-1}$) are used:

the standard formation enthalpy of crystalline NaCl , $\Delta_f H^0 = -410,5$;
 the standard dissociation enthalpy of chlorine molecule, $\Delta H_{\text{dissociation}}^0 = 238$;
 the standard enthalpy of sodium sublimation, $\Delta H_{\text{sublimation}}^0 = 109$;
 the first ionization potential of sodium atoms, $I_1 = 496$;
 the electron affinity of chlorine atoms, $E_{\text{Cl}} = -360$.

- 4) Using the Born–Haber cycle, **determine** the lattice energy of NaCl (U_{NaCl}).

To estimate the lattice energy ($\text{kJ}\cdot\text{mol}^{-1}$) of crystals having the NaCl structure one can use equation

$$U = \frac{-242,6z_1z_2}{(r_{\text{cation}} + r_{\text{anion}})} \times \left(1 - \frac{0,0345}{r_{\text{cation}} + r_{\text{anion}}} \right),$$

proposed by Kapustinski in 1943. Here the ionic radii are measured in nm.

5) **Determine** U_{NaCl} , if the ionic radii are as follows: $r_{\text{Na}} = 0,098$ nm; $r_{\text{Cl}} = 0,181$ nm. **Compare** U_{NaCl} found by two methods and explain the discrepancy.

THE EXPERIMENTAL ROUND

Task 1. The reaction of benzaldehyde with 2,4-dinitrophenylhydrazine in the presence of the catalytic quantities of sulfuric acid

1) **Write the equation for the reaction.**

The reagents should be taken in the equimolar quantities, the yield of the reaction is about 95 %.

2) **Calculate the masses and the quantities (mol) of the reagents that are needed to synthesize 3,0 g of the product.** Show three significant figures.

The density of benzaldehyde is $1.045 \text{ g}\cdot\text{cm}^{-3}$.

3) **Calculate the volume of benzaldehyde.**

Compound	v, mol	m, g	V, ml
Benzaldehyde			
2,4-Dinitrophenylhydrazine			—

The solution of benzaldehyde in ethanol with the concentration 5 % is used. The density of solution is $0.789 \text{ g}\cdot\text{cm}^{-3}$.

4) **Calculate the volume of the benzaldehyde solution that is necessary for the synthesis.**

5) ***Procedure***

To the benzaldehyde solution in ethanol (the volume is calculated above) ethanol is added to reach the total volume 10 ml. The obtained solution is placed into the round-bottom flask (100 ml). Then the calculated amount of 2,4-dinitrophenylhydrazine, one drop of H_2SO_4 and boiling stones are added. The mixture is boiled with the reflux condenser for 20 min. After that the mixture is cooled to the ambient temperature. The precipitate is filtered off through a Shott filter and washed twice with water (5 ml). The dried product is weighed and the yield (as a percentage to the theoretical yield) is determined (show your calculations).

6) **Give the mechanism of reaction.**

Task 2. The identification of organic substances

Five test tubes are filled with toluene and aqueous solutions of glucose, ethanol, fructose and propanol-2.

You can use the following reagents: ZnCl_2 solution in concentrated HCl ; CrO_3 solution in concentrated H_2SO_4 ; resorcinol solution; aqueous solution of CH_2O ; aqueous NaOH solution; H_2SO_4 (concentrated); aqueous CuSO_4 solution; aqueous HCl solution (concentrated).

Determine the contents of each test tube and write equations of corresponding reactions.

Answers and Solutions

THE FIRST THEORETICAL ROUND

Task 1.

The task was proposed by Prof. V. Yatsimirsky (Taras Shevchenko Kiev National University, Head of the Physical Chemistry Department, yats@chem.univ.kiev.ua)

$$1) \bar{v} = \left(\frac{8 \cdot 1,38 \cdot 10^{-23} \cdot 298}{3,14 \cdot \frac{56 \cdot 10^{-3}}{2 \cdot 6,02 \cdot 10^{23}}} \right)^{1/2} = 475 \text{ (m}\cdot\text{s}^{-1}\text{)}.$$

$$2) \sigma = 3,14 \cdot 6,25 \cdot 10^{-20} = 1,96 \cdot 10^{-19} \text{ (m}^2\text{); } z = 9,3 \cdot 10^{-17} \text{ (m}^3 \cdot \text{s}^{-1}\text{)}.$$

$$3) 9,3 \cdot 10^{-17} \cdot 10^3 \cdot 6,02 \cdot 10^{23} = 5,6 \cdot 10^{10} \text{ (L/mol}\cdot\text{s)}.$$

4) $z_{\text{experimental}} \ll z_{\text{theoretical}}$.

5) The reactions for which $E_{\text{act}} \approx 0$, for instance, recombination of free radicals.

Task 2.

The task was proposed by Prof. Yu. Kholin (V.N. Karazin Kharkov National University, Head of the Technical Chemistry Department, kholin@univer.kharkov.ua)

The standard equilibrium constant

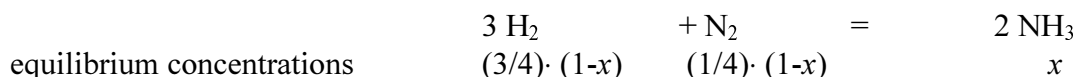
$$K_a = \prod_i \tilde{P}_i^{v_i} = \prod_i \left(\frac{P_i}{P_0} \right)^{v_i},$$

where P_i is the partial pressure of the i -th reagent,

v_i are the stoichiometric coefficients (+ for products, – for initial species).

Hence, $K_p = K_a \cdot (P_0)^{+\Delta v}$ [Pa].

Let us denote x the molar fraction of NH_3 at the equilibrium mixture.



The partial pressures are determined as follows:

$$P(\text{H}_2) = (3/4) \cdot (1-x) \cdot P, \quad P(\text{N}_2) = (1/4) \cdot (1-x) \cdot P, \quad P(\text{NH}_3) = x \cdot P,$$

where P is the total pressure.

$$\begin{aligned} K_p &= \{P(\text{NH}_3)\}^2 \times \{P(\text{H}_2)\}^{-3} \times P(\text{N}_2) = \\ &= \{x^2 \cdot P^2\} \times \{3^{-3} \cdot 4^3 \cdot (1-x)^{-3} \cdot P^{-3}\} \times \{4^1 \cdot (1-x)^{-1} \cdot P^{-1}\} = 256 \cdot x^2 / \{27 \cdot (1-x)^4 \cdot P^2\}, \\ & \quad x^2 / (1-x)^4 = 27 \cdot K_p \cdot P^2 / 256. \end{aligned}$$

By definition, $K_p = K_a \cdot (P_0)^{+\Delta v}$. Then

$$x^2 / (1-x)^4 = 27 \cdot K_a \cdot \tilde{P}^2 / 256,$$

where $\tilde{P} = P / P_0$.

This simply yields quadratic equation:

$$x / (1-x)^2 = 0,325 \cdot \tilde{P} \cdot (K_a)^{1/2}.$$

$$\mathbf{x \text{ for } P = 1 \text{ atm:}} \quad x / (1-x)^2 = 0,325 \cdot 1 \cdot (4,21 \cdot 10^{-3})^{1/2} = 0,021;$$

$$x = 2,03 \cdot 10^{-2} \text{ (2,03 \%)}.$$

$$\mathbf{x \text{ for } P = 100 \text{ atm:}} \quad x / (1-x)^2 = 0,325 \cdot 100 \cdot (4,21 \cdot 10^{-3})^{1/2} = 2,11; \quad x = 0,509 \text{ (50,9 \%)}.$$

Task 3.

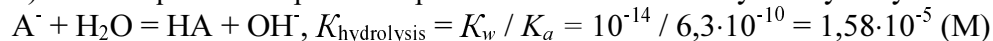
The task was proposed by **Yu. Korovkin** (Taras Shevchenko Poltava State Teacher's Training College) and **B. Chalyk** (V.N. Karazin Kharkov National University)

1) For a buffer solution containing a weak acid and its salt

$$\text{pH} = \text{p}K_a + \lg(C_{\text{salt}} / C_{\text{acid}}),$$

$$\text{p}K_a = \text{pH} - \lg(C_{\text{salt}} / C_{\text{acid}}) = 10,20 - \lg 10 = 9,20; K_a = 10^{-9,20} = 6,3 \cdot 10^{-10} \text{ (M)}.$$

2) At the equivalence point the pH value is determined by the hydrolysis of the anion:



c^0	A^-	$+$	H_2O	$=$	HA	$+$	OH^-	$,$	$K_{\text{hydrolysis}} = 1,58 \cdot 10^{-5}$
	c^0					0	0		
Δc	$-x$				x	x			
$[\]$	$c^0 - x$				x	x			

$$x^2 / (c^0 - x) = 1,58 \cdot 10^{-5},$$

at $\text{pH} = 11$ $[\text{OH}^-] = x = 10^{-3}$ M. Assuming $x \ll c^0$, one obtains the simplified equation, namely:

$$x^2 / c^0 = 1,58 \cdot 10^{-5},$$

$$c^0 = 0,063 \text{ (M)}.$$

$M(\text{HA}) = 1,73 \text{ g} / 0,063 \text{ M} = 27 \text{ g/mol}$. The molecular formula of HA is HCN, The tautomers are $\text{H}-\text{C}\equiv\text{N}$ and $\text{H}-\text{N}=\text{C}$.

3) $K_a = c^0 \cdot \alpha^2$ (α is the degree of dissociation).

The total concentration of HF in Solution 1

$$c^0 = 1,73 / (0,900 \cdot 27) = 0,071 \text{ (M)};$$

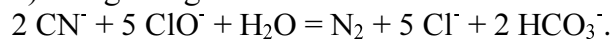
$$\alpha = (K_a / c^0)^{1/2} = 9,42 \cdot 10^{-5},$$

$$[\text{H}^+] = 9,42 \cdot 10^{-5} \times 0,071 = 6,69 \cdot 10^{-6} \text{ (M)},$$

$$\text{pH} = 5,17.$$

$$4) K_i = [\text{S}_2] / [\text{S}_1] = 0,005 / (1 - 0,005) \approx 5 \cdot 10^{-3}.$$

5) The gassing is observed.



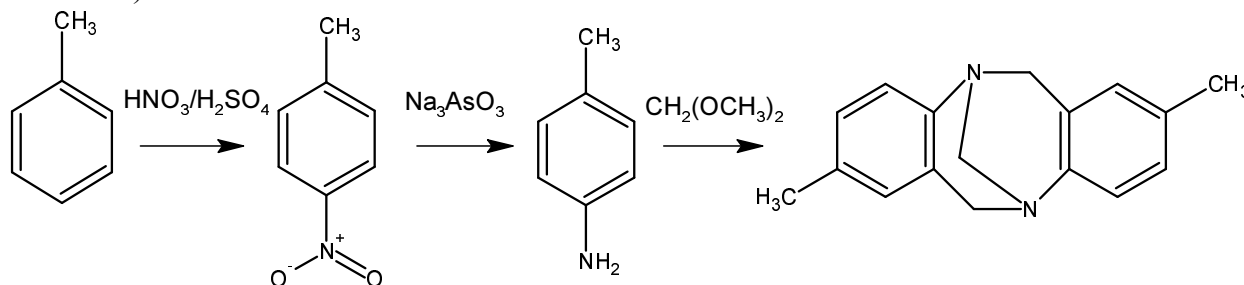
$$6) \text{CN}^- : \sigma_{\text{N}}^2 \sigma_{\text{z}}^2 \pi_{x,y}^4 \sigma_{\text{C}}^2.$$

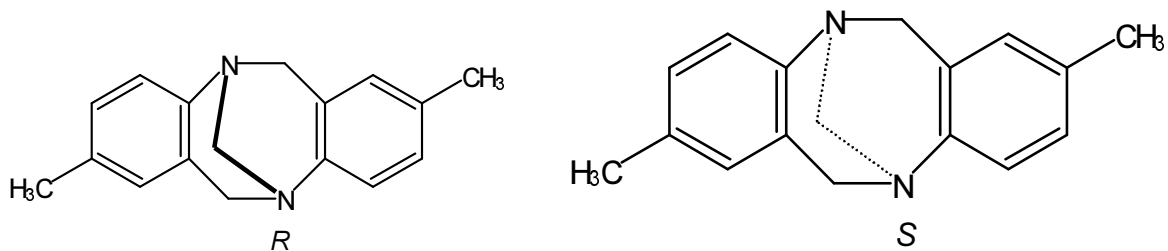
The ion is diamagnetic.

Task 4.

The task was proposed by **Ye. Ostapchuk** (Taras Shevchenko Kiev National University)

1-2)



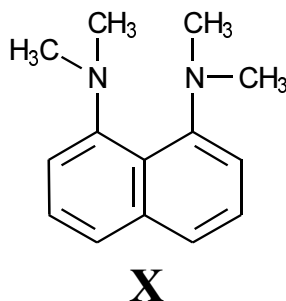


- 3) The stereo configuration is easily changed in the absence of the fourth group.
 4) For instance, $R_1R_2S=O$, $SR_1R_2R_3^+$, $PR_1R_2R_3$, $AsR_1R_2R_3$.
 5) The Treger base is too weak to form salts with the natural optically active acids, while in solutions of strong acids the racemisation takes place.

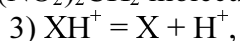
Task 5.

The task was proposed by Dr. V. Pivovarenko (Taras Shevchenko Kiev National University, Department of Organic Chemistry, pvg@mail.univ.kiev.ua)

1)



2) In compound **X** the lone pairs of electrons are shielded with the methyl groups. Hence, the interaction with acids is possible only in a case when protons are spatially accessible. In the $(NO_2)_2CH_2$ molecule the hydrogen atoms are blocked with two bulky nitro groups.



$$K_a = [X] \cdot [H^+] / [XH^+].$$

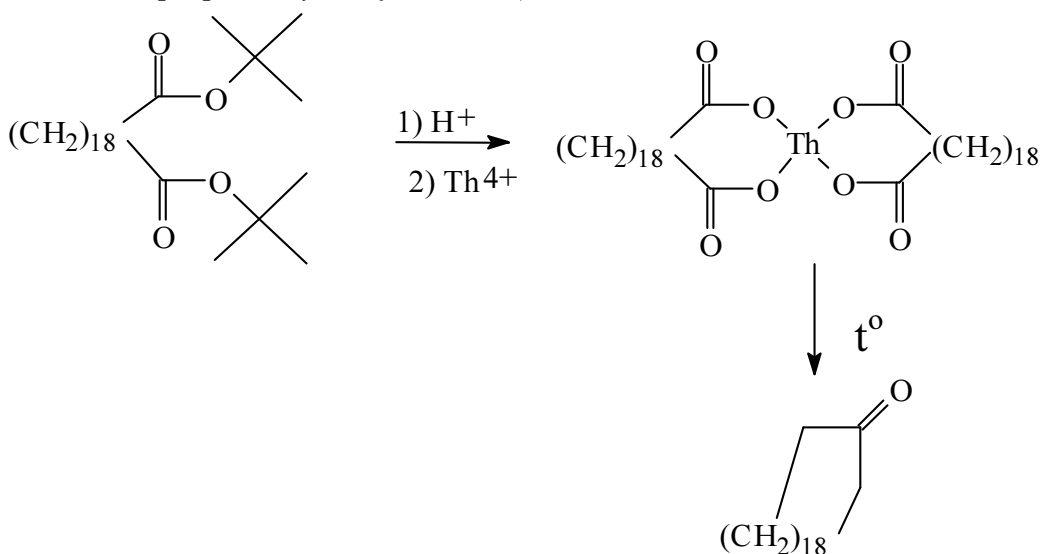
As $[X] = [XH^+]$, $K_a = [H^+]$,

$$[H^+] = 3 \cdot 10^{-11} \text{ (M)},$$

$$pH = -\lg(3 \cdot 10^{-11}) = 10,52.$$

Task 6.

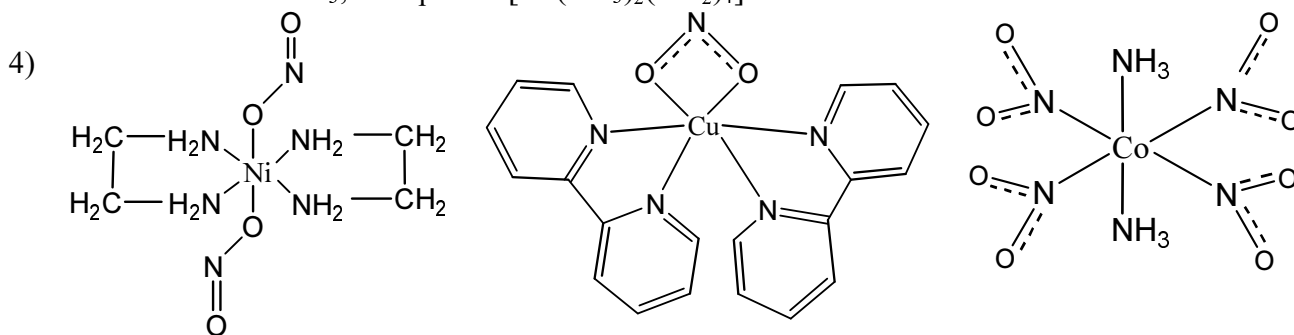
The task was proposed by S. Ryabukhin (Taras Shevchenko Kiev National University)



The similar analysis for complexes 2 and 3 reveals:

B = C₁₀H₈N₂, 1,10-phenanthroline, complex = [Cu(C₁₀H₈N₂)₂NO₂]⁺,

C = NH₃, complex = [Co(NH₃)₂(NO₂)₄]⁻.



Task 2.

The task was proposed by Dr. **O. Zhikol** (V.N. Karazin Kharkov National University, Department of Functional Materials, zhikol@xray.isc.kharkov.com)

1) This is a concentration cell. The electrodes are the amalgams of a certain metal. Just this metal forms metal sulfate. The quantitative composition of the solution remains unchanged.

2) According to proportion

$$\frac{96500 \text{ C} \cdot \text{mol}^{-1} - M \left(\frac{1}{z^*} \text{Me} \right) \text{ g} \cdot \text{mol}^{-1}}{144 \text{ C}} = \frac{48,8 \cdot 10^{-3} \text{ g}}{48,8 \cdot 10^{-3} \text{ g}}$$

the equivalent mass $M \left(\frac{1}{z^*} \text{Me} \right) = 32,7 \text{ g} \cdot \text{mol}^{-1}$. At $z^* = 2$ this value corresponds to Zn²⁺ ($M(\text{Zn}) = 65,4 \text{ g} \cdot \text{mol}^{-1}$).

3) The equation for the electromotive force of the cell may be written as

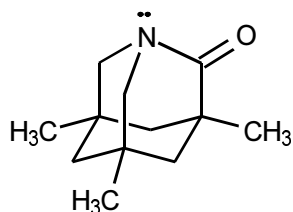
$$\Delta E = \frac{RT}{2F} \ln \left(\frac{c_{e2}(\text{Zn})}{c_{e1}(\text{Zn})} \right).$$

ΔE depends only on temperature and the zinc concentrations in the amalgams.

4) The galvanic cell does not operate when Na₂SO₄ is used instead of ZnSO₄.

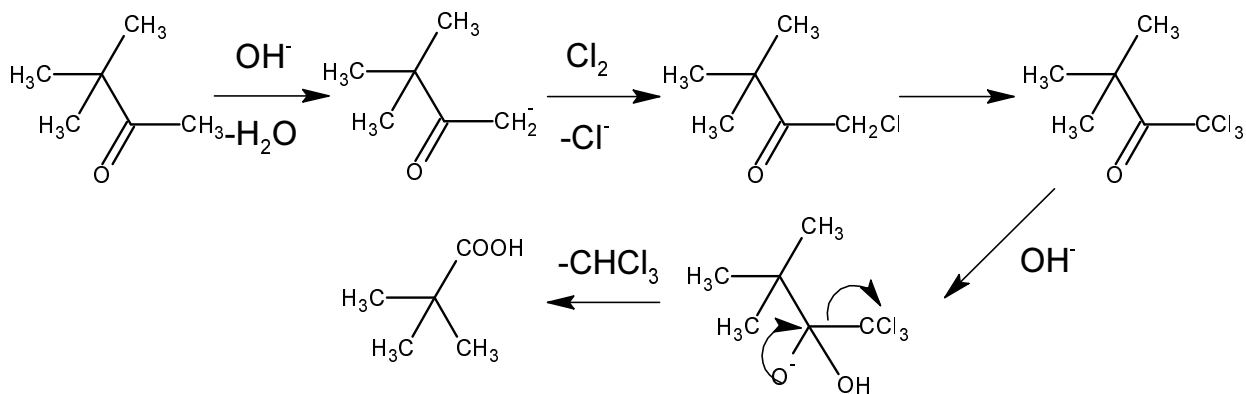
Task 3. The task was proposed by **P. Mikhailyuk** (Taras Shevchenko Kiev National University)

1)



A

2) Compound **A** resembles both amines and halogen anhydrides of carboxylic acids. Hence, as halogen anhydride it reacts with water, ammonia, amines, alcohols, thiols and so on. On the other hand, the reactions of acylation, alkylation and arylation are typical for compound **A** as well.



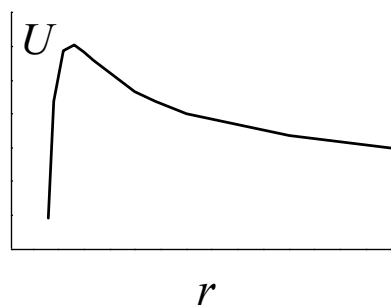
4) Two singlets in the strong and weak fields are observed. The ratio of areas is equal to 9:1.

Task 6. 1) The lattice energy is the positive quantity equal to work needed to move away ions from 1 mol of the crystal.

$U = -\Delta H^0_{\text{crystal}}$, where $\Delta H^0_{\text{crystal}}$ characterizes the formation of 1 mol of crystal from the gaseous ions.

2) b; d; f.

3) See figure.



$$4) \Delta_f H^0 = \Delta H_{\text{sublimation}}^0 + I_1 + 0,5 \cdot \Delta H_{\text{dissociation}}^0 + E_{\text{Cl}} + \Delta H^0_{\text{crystal}};$$

$$U_{\text{NaCl}} = -\Delta H^0_{\text{crystal}} = -\{\Delta_f H^0 - (\Delta H_{\text{sublimation}}^0 + I_1 + 0,5 \cdot \Delta H_{\text{dissociation}}^0 + E_{\text{Cl}})\} =$$

$$= -\{-410,5 - (109 + 496 + 119 - 360)\} = 774,5 \text{ (kJ} \cdot \text{mol}^{-1}\text{)}.$$

$$5) U_{\text{NaCl}} = \frac{242,6 \cdot 1 \cdot 1}{0,279} \times \left(1 - \frac{0,0345}{0,279}\right) = 762 \text{ (kJ} \cdot \text{mol}^{-1}\text{)}.$$

The Kapustinskii equation supposes the bond ionicity to be 100 %. For real crystals the bond ionicity is less. As a result, some disagreement between the calculated and the experimental U values is observed.