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Laboratory classes

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The laboratory classes are an integral part of the course "Principles of Chemical Engineering", taught as a normative discipline at chemical departments of Ukrainian classical universities. The manual describes in detail the methodology and procedure for performing laboratory works, provides reference materials necessary for processing the data obtained and understanding the results.

CONTENTS

INTRODUCTION

The laboratory classes are an integral part of the course "Principles of Chemical Engineering", taught as a normative discipline in the fourth year for the full-time and extramural students of the School of Chemistry. The manual describes in detail the methodology and procedure for performing laboratory works, provides reference materials necessary for processing the data obtained and understanding the results. Its continues the traditions of courses taught at the Materials Chemistry Department from the day it was founded.

The basis of these laboratory classes was laid at the Department for many years largely due to the efforts of associate professor R. S. Cheshko, professor V. N. Tolmachev, associate professor V. K. Yushko. This manual has absorbed some of the material from the previous guidelines for labs on classical methods for obtaining technological products and technical analysis.

Newer laboratory works are united by the topic "catalysis": "Comparison of various types of catalysis", " Main types of the nonlinear behavior of catalytic systems exemplified by the Belousov–Zhabotinsky reaction", "Polarimetric study of regularities of sucrose inversion and invertose reversion", "Catalytic hydrolysis of eter" . The appearance of these labs in the program is quite natural. On the one hand, more than 90% of modern chemical productions are essentially catalytic. On the other hand, the area of development of modern catalysts and catalytic processes (with the emphasis on nonlinear regimes) is one of the promising areas for professionals who have received a classical chemical education.

Compared with previous manuals, the style of presentation of the material has been changed. This was done in order to avoid a sequence of actions that requires a minimum of intellectual effort from the student: "take a sample ... → carry out the reaction ... → substitute the data into the formula → take the result to the teacher". With the accepted style of presentation, the student himself decides whether to process the obtained data on the basis of his own knowledge or refer to the "reference materials" section and find the necessary formulas there.

At the beginning of the description of each laboratory work, the main aspects of safety are emphasized, taking into account the peculiarity of the work. These are clarifications to the general instructions that students get acquainted with in the introductory lesson. Report forms are proposed that are designed to help you better imagine the work as a whole, but do not eliminate the need to maintain a laboratory journal.

COMPARISON OF VARIOUS TYPES OF CATALYSIS

PURPOSE Using the catalytic decomposition of hydrogen peroxide as an example, delve into the basic regularities of enzymatic, chemical and photochemical catalysis; compare the efficiency of these types of catalysis.

SAFETY

- Be careful when handling hydrogen peroxide to avoid skin irritation.
- Do not look at the UV lamp, the non-used part of the lamp must be covered with an opaque material.

WORKFLOW

The work includes the following main stages: study of the kinetics of the hydrogen peroxide decomposition catalyzed by

- enzyme catalase;
- Fe^{3+} ion;
- ultraviolet radiation;
- heterogeneous catalyst (MnO_2, Al_2O_3).

In all cases, the volumetric method is used.

Volumetric equipment

The kinetics of hydrogen peroxide decomposition is studied by the volume of released oxygen using a volumetric equipment, schematically shown in Fig.1.

The tightness of the system must be carefully checked before taking measurements. To do this, use a leveling bottle to set the liquid level in the burette to zero, close the valve, lower the leveling bottle and make sure that the liquid level does not change for at least 15 minutes. If the level "creeps", you need to find and fix the leak.

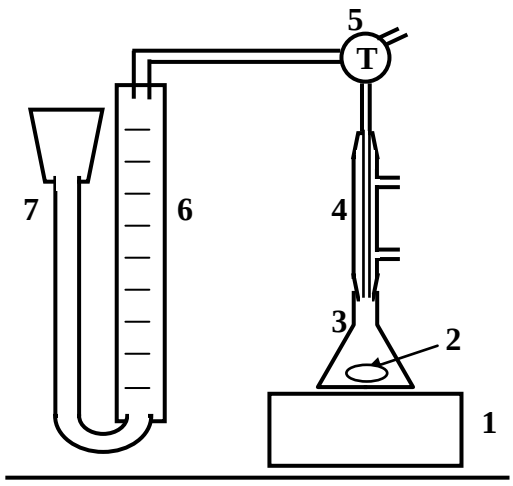


Fig. 1. Volumetric equipment: 1 – magnetic stirrer, 2 – anchor in Teflon, 3 – reaction flask, 4 – refrigerator, 5 – three-way valve, 6 – volumetric burette, 7 – equalizing bottle

All readings on the scale of the gasometric burette are made at the same level of liquid in the burette and equalizing bottle. To ensure this, at each reading, it is necessary to bring the bottle to the scale and achieve equalization of the levels. Since readings need to be done quickly, it is recommended to practice this before measurements are started.

The concentration of the original hydrogen peroxide may change during the semester. Therefore, it must be controlled perganatometrically or photometrically.

Catalase is the catalyst

The dependence of the reaction kinetics on the concentration of hydrogen peroxide is studied.

The concentration of solutions of catalase and hydrogen peroxide is indicated by the teacher. One of the possible options is described below as an example.

The concentration of the catalase in all experiments is unchanged - 1μmol/L.

For work, you need 25 ml of solution.
The initial concentration of catalase in the reacting system is also the same ~0.06 μmol/L

In total, 8 kinetic curves $V(t)$ need to be obtained. Concentrations and volumes of solutions are given in the table.

Experiment No	1	2	3	4	5	6	7	8
H_2O_2 concent (%)	0.5	1	2	3	4	15	30	4
V H_2O_2 (ml)	120	60	30	20	15	15	15	15
V catalase (ml)	8	4	2	1.3	1	1	1	1

1. Rinse the flask thoroughly with chromium mixture.
2. Check the tightness of the system.
3. Arrange everything you need to prepare hydrogen peroxide solutions of the required concentration.
4. Prepare a 6 mg/25 ml catalase solution. Catalase is taken from the freezer to prepare the solution; during weighing, it is stored on ice; immediately after weighing it is returned to the freezer. The prepared solution should be stored on ice or in the refrigerator.
5. Pour the first hydrogen peroxide solution into the flask. Quickly add catalase and set the liquid level in the buret to zero. Turn on the stopwatch. Measure the volume of released oxygen every minute until the volume of the burette (100 ml) is exhausted or until the reaction stops.
6. Do the same for dilutions No 2-7.
7. Place the rest of the catalase solution in a boiling water bath for 10 minutes. Cool to room temperature.
8. Conduct experiment number 8
9. For each of the experiments, calculate how many molecules of hydrogen peroxide is decomposed by one molecule of catalase in one second in the interval of 3-4 minutes. How many molecules of hydrogen peroxide decompose in one second in each of the experiments?
10. Plot all kinetic curves on one graph.
11. From the results of the experiments, calculate the Michaelis constant and v_{max} using the Lineweaver–Burk linearization in the range of substrate concentrations in which the Michaelis–Mentaigne equation is applicable.

UV radiation is the catalyst

The experiment is carried out in a quartz flask. A quartz flask is a fragile and expensive thing that requires careful handling!

The volumetric unit is assembled on a source of ultraviolet radiation.

1. Rinse the quartz flask with a chromium mixture and several times with distilled water.
2. Pour 120 ml of distilled water into the flask and connect it to the device.
3. Carefully check the tightness of the system.
4. Using a syringe, inject 4 ml of 30% H_2O_2 into the flask.
5. Set the liquid level in the buret to zero.
6. Turn on the UV lamp. Simultaneously with the ignition of the lamp, note the time.
7. The volume of released oxygen (V) should be measured every 5 minutes for 90 minutes. Record the results in a table.
8. Turn off the lamp and take readings every 5 minutes for another 20 minutes. These data are not included in the calculations.
9. Plot the $V(t)$ dependence.
10. Calculate how many molecules of hydrogen peroxide decompose in one second in the intervals of 5-10 and 60-65 minutes.
11. The kinetics of the chain reaction of the photochemical decomposition of hydrogen peroxide is described by the equation $\frac{\Delta V}{\Delta t} = kn_0 \exp(\varphi t)$, where φ is the growth constant, k is the reaction rate constant, and n_0 is the number of radicals generated per unit time. Determine φ and kn_0 from experimental data. To do this, the dependence should be approximated by a polynomial of an appropriate degree, differentiated and converted to logarithmic scale.

Fe^{3+} is the catalyst

The dependence of the reaction kinetics on the concentration of hydrogen peroxide and on pH is studied.

The initial concentration of Fe^{3+} in the reacting system is the same ~10^{-3} mol/L. Iron nitrate or perchlorate can be used.
Ions Cl^- and SO_4^{2-} form complexes with iron ions.

$Fe(NO_3)_3$ stock solution 40 mg/L is prepared once for the whole semester.

In total, it is necessary to obtain 6 kinetic curves $V(t)$.

The volumes of solutions are indicated in the table.

Experiment No	1	2	3
H_2O_2 concentration (%)	1	2	4
V H_2O_2 (ml)	60	30	15
V sol $Fe(NO_3)_3$ (ml)	4	2	1

1. Rinse the flask thoroughly
2. Check the tightness of the system.
3. Prepare everything you need to prepare hydrogen peroxide solutions of the required concentrations.
4. Pour the first hydrogen peroxide solution into the flask. Quickly add the $Fe(NO_3)_3$ solution and set the liquid level in the burette to zero. Turn on the stopwatch. Measure the volume of released oxygen every minute until the volume of the burette (100 ml) is exhausted or until the reaction stops.
5. Do the same for solutions #2-3.
6. Repeat the measurements, bringing the pH of the H_2O_2 solutions to 1 with concentrated nitric acid.
7. For each of the experiments, calculate how many molecules of hydrogen peroxide are decomposed by one iron ion in one second in the interval of 3-4 minutes. How many molecules of hydrogen peroxide are decomposed in one second?
8. Plot all kinetic curves on one plot
9. Check in which cases the reaction order on H_2O_2 is close to the first order; V_∞ calculate theoretically

Heterogeneous catalyst

The volumetric unit is assembled on a magnetic stirrer

The dependence of the reaction kinetics on the nature and dispersity of the heterogeneous catalyst is studied.

In total, it is necessary to obtain 6 kinetic curves $V(t)$

To carry out the reaction, such a volume of hydrogen peroxide is taken that produces at least 200 ml of O_2 in full decomposition. The concentration of the solution is indicated by the teacher.

1. Rinse the flask thoroughly.
2. Check the tightness of the system.

3. Prepare a hydrogen peroxide solution of the required concentration.
4. Sieved each of the two dispersed heterogeneous catalysts (for example, MnO_2 and Fe_2O_3) into three fractions using sieves indicated by the teacher.
5. The catalyst weight is the same in all experiments (indicated by the teacher). In total, you need to take six samples of catalysts.
6. Pour the hydrogen peroxide solution into the flask. Turn on the magnetic stirrer and set the speed low enough but still sufficient to keep the catalyst in suspension. Add the first batch of catalyst to the flask, quickly set the level to zero and start the stopwatch. Measure the volume of released oxygen every minute until the volume of the burette (100 ml) is exhausted or until the reaction stops.
7. Carry out similar measurements for the rest of the catalysts.
8. For each of the experiments, calculate how many molecules of hydrogen peroxide are decomposed in one second in the interval of 3-4 minutes and 15-17 minutes. Considering the catalyst particles to be spherical, estimate the surface area of the catalyst in each case.
9. Plot all kinetic curves on one plot

REFERENCE INFORMATION

The molecular weight of catalase is 250000

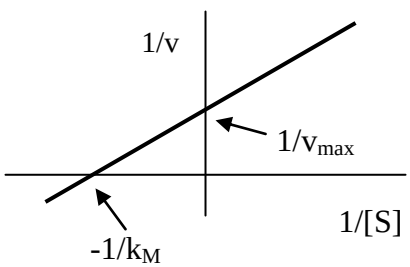
The catalase molecule consists of four subunits, each of which contains a heme associated with a polypeptide protein chain. Thus, as in hemoglobin, there are 4 iron atoms in the molecule.

Michaelis–Menten equation:

$$v = \frac{k_{catal}[E]_0[S]_0}{k_M + [S]_0}$$

Lineweaver–Burk linearization:

$$\frac{1}{v} = \frac{1}{k_{catal}[E]_0} + \frac{k_M}{k_{catal}[E]_0}\frac{1}{[S]_0} = \frac{1}{v_{\max}} + \frac{k_M}{v_{\max}}\frac{1}{[S]_0} \quad ;$$



At high concentrations of hydrogen peroxide, the reaction is inhibited by the substrate. The dependence of the rate on the substrate concentration in this case passes through a maximum, and the entire set of data is not described by the Michaelis–Mentaigne equation

The simplest scheme describing the inhibition includes the formation of a ternary complex enzyme-substrate-substrate:

$$\begin{array}{l} \mathrm{E}+\mathrm{S} \Leftrightarrow \mathrm{ES} \xrightarrow{k_{catal}} \mathrm{E}+\mathrm{P} \\ \quad \Updownarrow (+S) \\ \mathrm{ES}_2 \quad \xrightarrow{\alpha k_{catal}} \quad \mathrm{ES}+\mathrm{P}. \end{array}$$

The stage of formation of the second enzyme-substrate complex is also considered to be an equilibrium one with an equilibrium constant

$$K_S^i = \frac{[ES][S_0]}{[ES_2]}.$$

This scheme corresponds to the equation

$$v = \frac{\left(k_{catal} + \frac{\alpha k_{catal}[S]_o}{K_S^i}\right)[E]_o[S]_o}{k_M + [S]_o + \frac{[S]_o^2}{K_S^i}}.$$

At low substrate concentrations ($[S]_o << K_S^i$), it reduces to the Michaelis–Mentaigne equation. At high substrate concentrations ($[S]_o >> K_S^i$), the equation takes the form

$$v = \frac{k_{catal}[E]_o}{1+\frac{[S]_o}{K_S^i}}$$

It is linearized as

$$\frac{1}{v} = \frac{1}{v_{\max}} + \frac{1}{v_{\max} K_S^i} S_o,$$

which makes it possible to find the parameters $v_{\max}$ and K_S^i. At intermediate substrate concentrations, more complex difference methods have to be used [10]

One of the probable mechanisms of photochemical decomposition of H_2O_2:

1. $H_2O_2 \xrightarrow{h\nu} 2OH^{\bullet}$
2. $2OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O$
3. $HO_2^{\bullet} + H_2O_2 \rightarrow H_2O_4 + H^{\bullet}$
4. $H_2O_4 \rightarrow H_2O_2 + O_2$
5. $OH^{\bullet} + OH^{\bullet} + M \rightarrow H_2O_2 + M$
6. $OH^{\bullet} + HO_2^{\bullet} + M \rightarrow H_2O + O_2 + M$

One of the probable mechanisms of H_2O_2 decomposition catalyzed by Fe^{3+}. It includes reversible (1–3) and irreversible (4–10) stages. Irreversible stages: initiation (4), chain propagation (5–7), and chain termination (8–10). Depending on the conditions of the process, one or another stage of chain continuation / termination dominates

1. $Fe^{3+} + H_2O_2 \Leftrightarrow FeHO_2^{2+} + H^+$
2. $Fe^{3+} \Leftrightarrow FeHO^{2+} + H^+$
3. $HO_2^{\bullet} \Leftrightarrow H^+ + O_2^{\bullet -}$
4. $FeHO_2^{2+} \rightarrow Fe^{2+} + HO_2^{\bullet}$
5. $Fe^{2+} + H_2O_2 \xrightarrow{H^+} Fe^{3+} + OH^{\bullet} + H_2O$
6. $OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O$
7. $Fe^{3+} + O_2^{-} \rightarrow Fe^{2+} + O_2$
8. $Fe^{2+} + HO_2^{\bullet} \xrightarrow{H^+} Fe^{3+}\ H_2O_2$
9. $Fe^{2+} + OH^{\bullet} \xrightarrow{H^+} Fe^{3+}\ H_2O$
10. $HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$

This reaction belongs to ion-radical-chain reactions. The chain reaction mechanism is evidenced by the high sensitivity to impurities. Among the intermediate substances, Fe^{2+} ions are registered. The reaction rate depends on the ionic strength of the solution, which confirms the essential role of ions in the reaction mechanism

Despite the complex mechanism, the formal order of the reaction with respect to H_2O_2 is close to the first order in a fairly wide range of conditions, and the corresponding kinetic constant can be calculated from experimental data using the equation

$$k = \frac{1}{t} \ln \frac{V_\infty}{V_\infty - V_t}.$$

H_2O_2 concentration control

Permanganatometric method. Take 10 ml of the test solution. Dilute with distilled water in a volumetric flask to 100 ml. Take 10 ml and titrate with 0.1 N $KMnO_4$ solution until a pink color appears, which does not disappear within 30 s. Perform at least three titrations. $T_{KMnO_4/H_2O_2} = 0.001701$; $Э_{KMnO_4} = 31.608$.

Photometric method. For hydrogen peroxide ε=1.08 M^{-1} cm^{-1}; λ=300 nm.

TEST QUESTIONS

1. Main types of catalysis.
2. Basic concepts and distinctive features of enzymatic catalysis.
3. Scheme of a simple enzymatic reaction, Michaelis equation; complex reactions: ordered mechanism, disordered mechanism, "ping-pong" mechanism.
4. Main points of the theory of enzymatic catalysis.
5. Main stages of heterogeneous catalysis.
6. The main stages of chain reactions.
7. Reaction mechanism, mechanism matrix, transition to a system of differential equations.

Comparison of different types of catalysis

Full name
_____;
Group No _____;
date of the work _____; date of submission of the report _____.

Temperature in the laboratory:

All the results of volumetric measurements need to be presented in tabular form

In graphical form present:
• all dependencies $V(t)$;
• Lineweaver–Burk linearization results;
• results of data processing on photochemical decomposition
k_M =
k_{catal} =

φ =
kn =

One molecule of catalase decomposes for 1 s # H_2O_2 molecules

1	2	3	4	5	6	7	8

One Fe^{3+} ion decomposes for 1 s # H_2O_2 molecules

	1	2	3
pH=7			
pH=1			

The number of H_2O_2 molecules that decompose in one second
• enzymatic catalysis:
• UV catalysis:
• Fe^{3+}-catalysis:
• heterogeneous catalysis:

MAIN TYPES OF THE NONLINEAR BEHAVIOR OF CATALYTIC SYSTEMS EXEMPLIFIED BY THE BELOUSOV–ZHABOTINSKY REACTION

PURPOSE Using the Belousov–Zhabotinsky model reaction as an example, study the main types of nonlinear behavior observed in various catalytic systems.

SAFETY

- Concentrated sulfuric acid is used. If acid comes into contact with skin, rinse immediately with water.
- Sampling of liquids should only be done with a bulb.

WORKFLOW

The work includes the following main stages:
- study of the constancy of the oscillation period;
- study of the dependence of the oscillation period of on the intensity of mixing;
- study of the dependence of the oscillation period on the concentration of sulfuric acid (or ferroin);
- observation of traveling waves in a cylinder;
- observation of standing waves in a Petri dish.

The reaction is capricious, so the glassware used must be ideally clean.

Preparation of solutions

• Preparation of potassium bromate solution: dissolve 5 g of $KBrO_3$ in 105 mL of distilled water.

• Preparation of malonic acid solution: dissolve 1 g of $C_3H_4O_4$ in 10 mL of distilled water.

• Preparation of ferroin solution: dissolve 1 g of $FeSO_4*7H_2O$ and 0.5 g of o-phenanthroline in 100 mL of distilled water. *This solution is prepared once for the entire semester.*

• Solutions should stand for 30-40 minutes. The prepared solutions are designed for three experiments.

Starting a reaction

In a 50 mL flask, mix in the following order:

- 35 mL of $KBrO_3$ solution,
- 0.6 mL of concentrated sulfuric acid,
- 3 mL of malonic acid solution,
- 3 mL of ferroin solution.

Mix vigorously 4-5 times in a circular motion and place on a sheet of white paper. The solution is red. After the induction period, the duration of which depends on a number of factors and is approximately 1–5 min, the color of the solution will change to blue and quickly enough again to red (but not so bright). After that, oscillations in the color of the solution are established. They persist for 40-60 minutes.

Study the constancy of the oscillation period

- Color transition R-B (Red – Blue) is clearer than B-R. Therefore, the oscillation period is fixed as the time interval between two successive R-B color transitions.
- The oscillation period depends on the mixing speed. The contents of the flask should be poured into a beaker with a magnetic rod. Place the beaker on a magnetic stirrer and set the I stirring mode (the smallest stirring speed).
- After 5 minutes, use a stopwatch to measure at least 15 oscillation periods. Record the results in the table.

Study the dependence of the oscillation period on the intensity of mixing

- Set the stirring mode II on the magnetic stirrer (increase the stirring speed).
- After 5 minutes, measure the period of 5 oscillations.
- Set the stirring mode III on the magnetic stirrer (increase the stirring speed even more).
- After 5 minutes, measure the period of 5 oscillations.
- Record the results in the table.

Return the contents of the beaker to the flask and leave to stand. In the absence of mixing, the oscillations will soon stop (the reaction will "fall asleep"). At the end of the lab, make sure that if you “wake it up” with intensive short-term mixing (or return it to the magnetic stirrer), then the oscillations will resume with the same period.

Study the dependence of the oscillation period on pH

- Run the second Belousov-Zhabotinsky reaction in a flask as described above, taking 0.4 mL of concentrated sulfuric acid instead of 0.6 mL.
- Place it in the beaker on a magnetic stirrer, set the I stirring mode. After 5 minutes, measure 5 oscillation periods. Return the reaction back to the flask.
- Run the third Belousov-Zhabotinsky reaction in a flask as described above, taking 0.8 mL of concentrated sulfuric acid instead of 0.6 mL.
- Place it in the beaker on a magnetic stirrer, set the I stirring mode. After 5 minutes, measure 5 oscillation periods. Return the reaction back to the flask.
- Record the results in the table.

Observation of spatio-temporal structures

- Use the third reaction to observe spatio-temporal structures.
- Shake the contents of the flask vigorously and pour into a 25 ml cylinder, filling it almost to the top. Observe the occurrence of blue waves moving from bottom to top or from top to bottom.
- In the absence of mixing, the reaction "falls asleep". Therefore, for long-term observation of waves, the contents of the cylinder should be vigorously stirred from time to time (for example, by turning the cylinder 2-3 times after each wave has passed).
- After mixing the contents of the cylinder, pour it into a Petri dish. Place the dish on a sheet of white paper and observe the spatio-temporal structures.
- Return the contents to the flask. Make sure the oscillation period has not changed.

At the end of the work, "wake up" the sleeping reactions and make sure that their periods of oscillations have not changed.

REFERENCE INFORMATION

The study of various nonlinear regimes is currently one of the priority scientific directions in catalysis. In recent years, the main emphasis is on the control of these regimes; for example, the transfer of a heterogeneous catalytic reaction from a chaotic regime to a regime of periodic oscillations.

Five main types of nonlinear behavior are distinguished:

- bistability,
- oscillations (periodic and aperiodic),
- traveling waves,
- standing waves,
- dynamic chaos.

The famous Belousov–Zhabotinsky reaction makes it possible to observe three of them.

The skeletal FKN (Fields–Keresh–Noyse) mechanism describing the Belousov–Zhabotinsky reaction includes 9 stages:

R1. $3(Br^- + HOBr + H^+ \leftrightarrow Br_2 + H_2O)$
R2. $Br^- + HBrO_2 + H^+ \leftrightarrow 2HOBr$
R3. $Br^- + BrO_3^- + 2H^+ \leftrightarrow HOBr + HBrO_2$
R4. $2HBrO_2 \leftrightarrow HOBr + BrO_3^- + H^+$
R5. $2(HBrO_2 + BrO_3^- + H^+ \leftrightarrow 2BrO_2^\bullet + H_2O)$
R6. $4(BrO_2^\bullet + Fe^{2+} + H^+ \leftrightarrow Fe^{3+} + HBrO_2)$
R7. $CH_2(COOH)_2 \xleftrightarrow{H+} (HO)_2C{=}CHCOOH$
R8. $(HO)_2C{=}CHCOOH + Br_2 \rightarrow BrCH(COOH)_2 + H^+ + Br^-$
R9. $2Fe^{3+} + CH_2(COOH)_2 + BrCH(COOH)_2 \rightarrow 2Fe^{2+} + f\,Br^- +$ other products.

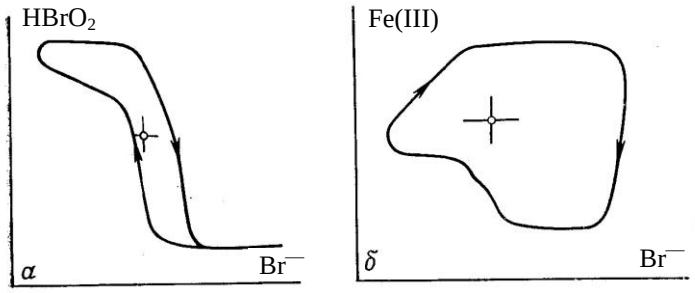
To simulate the nonlinear phenomena observed in this system, a simplified scheme is proposed, called the "oregonator":

1. A + Y → X + P corresponds to R3
2. X + Y → 2P corresponds to R2
3. A + X → 2X + Z corresponds to R5 + R6
4. 2X → A + P corresponds to R4
5. Z → fY corresponds to R9

$X=HBrO_2$, $Y=Br^-$, $A=BrO_3^-$, $P=HOBr$, $Z=Fe^{3+}$

This is the minimum set of equations that allows modeling the main regimes observed in the experiment

The figure shows two projections of the limit cycle corresponding to periodic oscillations in the system (from [16]):



TEST QUESTIONS

1. Main distinctive features and types of behavior of nonlinear systems.
2. The overall equation and the FKN mechanism of the reaction.
3. What causes oscillations in the system? What particles play the role of autocatalyst and feedback.
4. Oregonator.
5. Practical applications of the Belousov–Zhabotinsky reaction.
6. Examples of nonlinear behavior in heterogeneous catalysis.
7. Ideas about the qualitative analysis of nonlinear differential equations; phase portrait; parametric portrait.

Main types of the nonlinear behavior of catalytic systems exemplified by the Belousov–Zhabotinsky reaction

Full name _____;
Group No _____;
date of the work _____; date of submission of the report _____.

The results obtained are entered into tables

Measurement number	Oscillation period	Measurement number	Oscillation period
Stirring mode *I*		Stirring mode *II*	
1		1	
2		2	
3		3	
4		4	
5		5	
6		6	
7		7	
8		Average	
9		Stirring mode *III*	
10		1	
11		2	
12		3	
13		4	
14		5	
15		6	
Average		7	
		Average	

For mixing mode I, the dispersion is calculated _____

Measurement number	H_2SO_4 volume (mL)	
	0.4	0.8
1		
2		
3		
4		
5		
6		
7		
Average		

POLARIMETRIC STUDY OF REGULARITIES OF SUCROSE INVERSION AND INVERTOSE REVERSION

PURPOSE Using a polarimeter, determine the rate constant for acid sucrose inversion or invertose reversion under specified conditions.

SAFETY

- Acids are used in this work. If acid comes into contact with skin, rinse immediately with water.
- When working with thermometers, remember that they contain mercury.
- Before starting work, check the grounding. It is unacceptable to work with the polarimeter and the thermostat with wet hands.
- Care must be taken to ensure that no acid enters the inside of the polarimeter.

WORKFLOW

The work includes three main stages:

- familiarization with the device and its preparation for operation;
- measurement of the rotation angle in the absence of reaction;
- polarimetric study of reaction kinetics.

Before starting work with the polarimeter, turn on the thermostat and set the temperature to 45 ° C. This should be done at the beginning of the work, because it takes time for the thermostat to reach the mode.

Preparing the polarimeter for operation

Polarimeter is a device for measuring the rotation angle of the polarization plane by optically active transparent solutions and homogeneous liquids.

Fig. 1 shows a circular polarimeter, in which a scheme for equalizing the three parts of the field of view is implemented. A more detailed image and optical scheme are given in the "Reference materials" section.

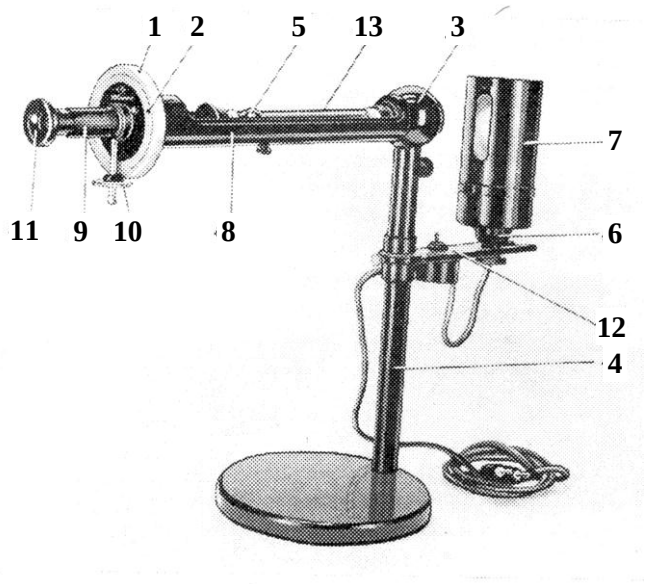


Fig. 1. Circular polarimeter

The main elements of the device:

1. **Fixed limb**. Clockwise on the limb is a degree scale from 0^o to 360^o.
2. **Nonius**. Inside the limb, two nonius are located diametrically on the movable sleeve. Each of them has 20 divisions. The value of one division of the nonius is 0.05^o. Two nonius are needed to take into account the eccentricity of the circle at large rotation angles.
3. **Polarizer**. Rigidly fixed in a certain position.
4. **Rack**.
5. **Cuvette for solution**. Made from glass. The bulge serves to collect air bubbles. At the ends there are metal tips, on which shells are screwed, pressing the cover glasses. Rubber gaskets between shells and cover glasses ensure tightness and at the same time prevent stresses in the glass. Too much tightening of the shells should be avoided. DO NOT LOSE THE COVER GLASSES WHEN RINSING THE CUVETTE!
6. **Light source**. When measuring angles within 10°, an ordinary frosted electric lamp (220 V, 40 W) can be used. ***Owing to the orange glass and polaroids, the maximum spectral distribution of the transmitted beam corresponds to the yellow sodium line***. At much larger angles, the middle part of the field of view is colored reddish or greenish. This makes it difficult to equalize the fields and reduces the measurement accuracy. In this case, a special sodium lamp is used.
7. **Illuminator**. Allows to move the lamp in different directions to ensure uniform illumination.
8. **Curtain**. Protects the test solution from extraneous light.

9. **Coupling**. Allows to set the eyepiece to sharpen the triple field image.
10. **Friction**. Serves for simultaneous smooth rotation of the analyzer, nonius and telescope. The analyzer is made of a polaroid film glued between two protective glasses.
11. **Eyepiece**. Used to observe the triple field. In the shell of the eyepiece there are two lenses that allow, without changing the position of the head, to count the angle of rotation of the nonius relative to the degree scale of the limb.
12. **Bracket**

- Turn on the device. Observe the photometric field through the eyepiece. It consists of three parts. An example is shown in fig. 2b.
- Move the sleeve to adjust the eyepiece so that you can see sharply the dividing lines.
- By turning the handwheel, make sure that the photometric equality of the three parts of the field can be achieved in two positions - in the light and in the dark areas. In the dark area, the photometric equality is much more sensitive to handwheel rotation. Therefore, three parts of the field should be equalized in the dark area.
- By moving the illuminator down, up, left, right, achieve the most uniform illumination of the field.
- The polarimeter is ready for use.

INVERSION OF SUCROSE

Measuring the angle of rotation in the absence of reaction

- Prepare 50 ml of sucrose solution of the prescribed concentration (e.g. 10%). Filter the solution.
- Remove the cuvette from the polarimeter and equalize three fields in the dark area. Notice the mutual situation of the scales of limbus and nonius (Fig. 2a). Equalization is repeated five times. The average value of the five readings is the instrument's zero reading (correction for zero).
- The cuvette and coverslips must be perfectly clean. The tube is cleaned by pushing a stopper of filter paper moistened with alcohol (gasoline in case of a greasy surface). The cover glasses are wiped with a cloth soaked in alcohol.
- Fill the polarimeter tube with sucrose solution. To do this, the tube is closed with a shell with a cover glass at one end and filled with a solution in a vertical position so that the upper meniscus of the liquid protrudes above the upper edge of the tube; the protruding meniscus is shifted by the cover glass; then the upper shell is twisted. The shells must not be tightened very tightly to avoid tension in the cover glasses that affects the correct reading. If a small

air bubble has formed, then it should be "driven away" into the expanded part of the tube. If a large air bubble forms, add the solution. Cover glasses must be thoroughly wiped from the outside.

- Place the polarimetric tube in the instrument, close the shutter. As a result, the photometric equality is violated (Fig. 2b). If the field of view is colored, it is necessary to slightly squeeze the cover glasses. You should also check the position of the illuminator.
- Adjust the sharpness with the clutch. By rotating the flywheel, restore the photometric equality. As a result, the relative position of the limbus and nonius will change (Fig. 2c). The reading is done as follows:
  - determine how many full degrees the zero of the nonius has shifted with respect to the limb (in Fig. 2c this value is 3 and corresponds to 3 degrees);
  - then determine which stroke of the nonius exactly coincides with the stroke of the limbus (in Fig. 2c this stroke is 6.5, which corresponds to 0.65^{o});
  - nonius reading is added to the reading on the limb, in this example we get 3.65^{o};
  - subtract the zero correction, in this example it is equal to 0.1^{o};
  - The result is 3.55^{o}.
- Take 5 readings, each time knocking down the previous reading. Record the results in the table ($2\alpha_0$). At the end of the measurements, the solution is poured into the sewerage.
- Using the reference data below, evaluate the purity of the starting reagent.

At this stage, it is necessary to master the work on the device well, because in making kinetic measurements readings will need to be taken quickly.

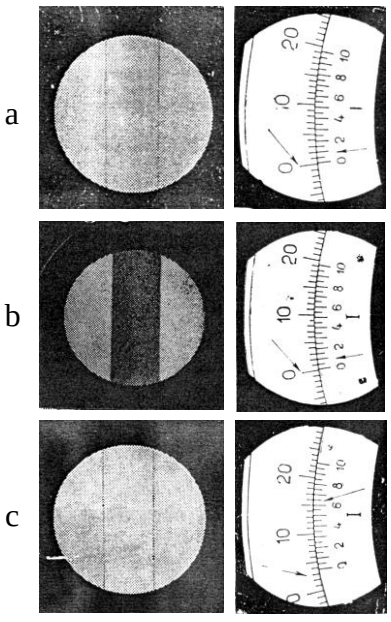


Fig. 2. An example of reading on the polarimeter scale

Polarimetric study of reaction kinetics

- Using 25 ml pipettes, mix in a flask 25 ml of sucrose solution and 25 ml of acid solution of the indicated concentration (e.g.1N HCl solution). Record the time immediately. This is the start time of the reaction. Record the ambient temperature.
- Fill the polarimetric tube with this solution after rinsing it with this solution. Place the tube into the polarimeter
- Pour the rest of the solution into another flask, close the stopper carefully and place in a thermostat.
- Make readings of the rotation angle at time intervals indicated in the table below. The time is counted from the beginning of the reaction. Make three readings. The readings must be made quickly enough, since the rotation angle change all the time. Record the results in the table (α).
- 20 minutes before the end of measurements, remove the solution from the thermostat and leave to cool. You can cool it down a bit under running water.
- After the last measurement, empty the solution from the polarimetric tube into a sewerage. Make sure that the cooled solution has reached room temperature (record the thermometer readings), and fill the polarimetric tube with this solution. Place the tube in the polarimeter and take five readings (if the work is done correctly, the angle will be negative). Record the results in the table (α_∞).
- Pour out the solution, thoroughly rinse the polarimetric tube with distilled water and dry with filter paper. (Acid corrodes the metal parts of the instrument.)
- Check the instrument zero again without the polarimeter tube. If it does not match the initial value, take the average value.
- Using the reference data below, draw a conclusion about the presence/absence of an adverse reaction.
- Make the necessary calculations. Plot $\ln\left(\frac{\alpha_0 - \alpha_\infty}{\alpha - \alpha_\infty}\right)$ against time. Process the data using the least squares method. Estimate the reaction rate constant.

REVERSION OF INVERTOSE

Invertose is an equimolar mixture of D-glucose and D-fructose, formed during the acid inversion of sucrose.
Operation with the polarimeter is described in detail in the previous section "Inversion of sucrose".

Measuring the rotation angle in the absence of reaction

- Prepare 30 ml of glucose and fructose solutions at the concentration indicated by the teacher (e.g. 50%). Filter the solutions.
- Zero the instrument.
- Fill the polarimeter tube with glucose solution. Place it in the polarimeter and take 5 readings. At the end of the measurements, save the solution (pour back into the flask).
- Fill the polarimeter tube with fructose solution. Place it in the polarimeter and take 5 readings. At the end of the measurements, save the solution (pour back into the flask with the fructose solution).
- Using the reference data below, evaluate the purity of the starting reagents.
- Mix 25 ml each of glucose and fructose solutions, mix thoroughly. Fill the polarimeter tube with this mixture and take 5 readings. After measurements, the solution is poured into the sewerage.

At this stage, it is necessary to master the work on the device well, because. when making kinetic measurements, readings will need to be taken quickly.

Polarimetric study of reaction kinetics

- Using 25 ml pipettes, mix in a flask 25 ml of a mixture of glucose and fructose solutions and 25 ml of an acid solution of the indicated concentration (e.g. 1N HCl solution). Immediately record the time; this is the start time of the reaction. Record the ambient temperature.
- Fill the polarimetric tube with this solution after rinsing it with this solution. Place the tube into the polarimeter.
- Pour the rest of the solution into another flask, close the stopper carefully and place in a thermostat..
- Make readings of the rotation angle at intervals of time indicated in the table. The time is counted from the beginning of the reaction. Make three readings. The readings should be made quickly enough, since the rotation angle change all the time. Record the results in the table (α).
- 20 minutes before the end of measurements, remove the solution from the thermostat and leave to cool. You can cool it down a bit under running water.
- After the last measurement, empty the solution from the polarimetric tube into a sewerage. Make sure that the cooled solution has reached room temperature (record the thermometer readings) and fill the polarimetric tube with this solution. Place the tube in the polarimeter and take five readings. Record the results in the table (α_∞).

- Pour out the solution, thoroughly rinse the polarimetric tube with distilled water and dry with filter paper. (Acid corrodes the metal parts of the instrument.)
- Check the instrument zero again without the polarimeter tube. If it does not match the initial value, take the average value.
- Using the reference data below, draw a conclusion about the presence/absence of an adverse reaction.
- Make the necessary calculations. Plot $\ln\left(\frac{\alpha_0-\alpha_\infty}{\alpha-\alpha_\infty}\right)$ against time. Process the data using the least squares method. Estimate the reaction rate constant.

REFERENCE INFORMATION

The length of the polarimetric tube d = 19 cm.

The error of the indication of the device is 0.05°.

Specific rotation of the plane of polarization:

	Sucrose	Glucose	Fructose
$[\alpha]_D^{20}$	+ 66.55	+52.7	-91.9

This value depends on the temperature, the wavelength of the polarized light, and the nature of the solvent. For a mixture of optically active substances, the rotation angle is equal to the sum of the rotation angles for each optically active substance. The data are given for aqueous solutions at a temperature of 20°C; wavelength is 589.3 nm (yellow line D of the sodium spectrum). In the temperature range of 20±5 °C, the temperature correction for the specific rotation of the polarization plane can be omitted.

For solutions, the rotation angle α of the polarization plane is directly proportional to the thickness of the solution layer d (decimeter) and the concentration of the active substance C (g/mL):

$$\alpha = [\alpha]_D^{20} \bullet d \bullet C.$$

Since fructose strongly rotates the polarization plane to the left, the reaction of acid hydrolysis of sucrose is accompanied by a rotation of the angle up to negative values. This is where the terms "inversion" and "reversion" come from.

In the technological or biotechnological processing of biomass, the inversion of di- and trisaccharides is a separate step. It follows pre-hydrolysis and main hydrolysis

and is sometimes referred to as post-hydrolysis. The inversion of di- and trisaccharides is isolated during the industrial hydrolysis of biomass in a separate stage in order to increase the yield of monosaccharides, because this requires conditions which differ significantly from those required for main hydrolysis. Under the conditions of main hydrolysis, reversion of monosaccharides is observed, which reduces their yield. As the volume of biomass hydrolysis increases and new (bio)technologies are developed in this area, interest in the features of the inversion stage and its conjugation with the main hydrolysis stage increases.

Optical activity. Light waves are transverse waves: oscillations occur in a plane perpendicular to the direction of the beam. In a natural beam, oscillations occur in all planes perpendicular to its direction. A polarized beam oscillates in only one plane. The plane perpendicular to it is called the plane of polarization. Substances that can rotate the plane of polarization are called optically active. Optically active are chiral molecules (having no mirror symmetry plane and inversion center). Their optical activity is related to the electronic polarizability, in particular, to the features of the electric and magnetic dipole moments induced in the molecule.

The optical scheme of the polarimeter is shown in Fig. 3.

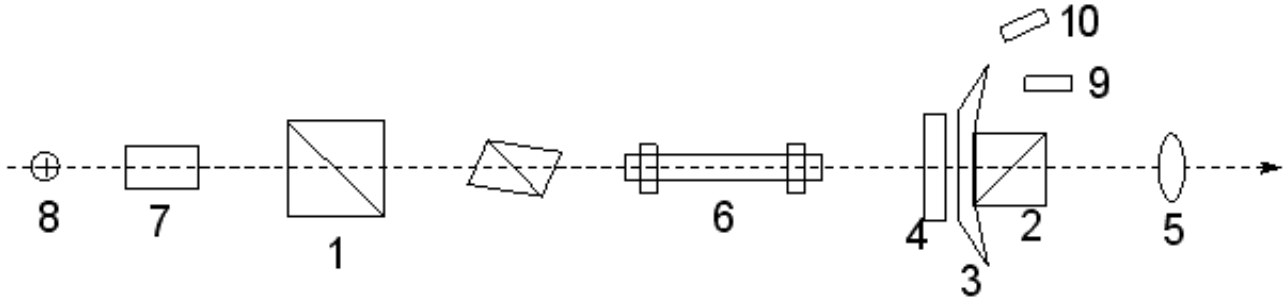


Fig. 3. Optical scheme of the polarimeter: 1 is polarizer, 2 is analyzer, 3 is pointer, 4 is limb, 5 is eyepiece, 6 is polarimetric tube, 7 is light filter, 8 is light source, 9 is magnifying glass, 10 is mirror

TEST QUESTIONS

1. Biomass as an organic raw material. Chemical and biotechnological processing of biomass.
2. Acid inversion of sugars as one of the stages of biomass processing.
3. Optically active substances.
4. Mechanism and kinetics of acid inversion of sucrose and reversion of invertose.
5. Basic principles of the polarimetric study of these reactions.

Polarimetric study of sucrose inversions

Full name _____;
Group No _____;
date of the work _____; date of submission of the report _____.

Concentration of sucrose solution _____ .

Acid _____ . Acid concentration _____ .

	Rotation angle					
Measurement # :	1	2	3	4	5	
Initial solution						$2\alpha_0 =$
Solution after thermostat						$\alpha_\infty =$

t, min	Rotation angle				$\alpha - \alpha_0$	$\frac{\alpha_0 - \alpha_\infty}{\alpha - \alpha_\infty}$	$\ln\left(\frac{\alpha_0 - \alpha_\infty}{\alpha - \alpha_\infty}\right)$	$\frac{1}{t}\ln\left(\frac{\alpha_0 - \alpha_\infty}{\alpha - \alpha_\infty}\right)$
	1	2	3	average (α)				
10								
20								
30								
40								
50								
70								
90								

Polarimetric study of the reversion of invertose

Full name _____;
Group No _____;
date of the work _____; date of submission of the report _____.

Concentration of glucose and fructose solutions _____ .

Acid _____ . Acid concentration _____ .

	Rotation angle					
Measurement # :	1	2	3	4	5	average
Initial glucose solution						
Initial solution of fructose						
Equimolar mixture						$2\alpha_0 =$
Solution after thermostat						$\alpha_\infty =$

t, min	Rotation angle				$\alpha - \alpha_0$	$\frac{\alpha_0 - \alpha_\infty}{\alpha - \alpha_\infty}$	$\ln\left(\frac{\alpha_0 - \alpha_\infty}{\alpha - \alpha_\infty}\right)$	$\frac{1}{t}\ln\left(\frac{\alpha_0 - \alpha_\infty}{\alpha - \alpha_\infty}\right)$
	1	2	3	average (α)				
10								
20								
30								
40								
50								
70								
90								

CATALYTIC HYDROLYSIS OF ETER

PURPOSE To study the kinetics of alkaline hydrolysis of methyl acetate at four different temperatures and to determine the activation energy of the reaction; for one of these temperatures, compare the kinetics of alkaline hydrolysis with the kinetics of acid hydrolysis

SAFETY

- Avoid contact with acid and alkali of the skin and mucous membranes.
- If acid or alkali comes into contact with the skin or mucous membranes, rinse immediately with water.
- Sampling of liquids should only be done with a bulb

WORKFLOW

The work includes two stages:

- alkaline hydrolysis;
- acid hydrolysis.

Alkaline hydrolysis

At the beginning of the work, it is necessary to have ice and distilled water free from carbon dioxide.

The study of the kinetics of alkaline hydrolysis of ester is carried out at temperatures of 20, 25, 30 and 35 ^{0}C. At 30 ^{0}C, the acid hydrolysis is studied in parallel.

At each temperature, alkaline hydrolysis is carried out as follows:

- Turn on the thermostat and set the temperature of the experiment.
- Ice is placed in a container to form a mixture of water and ice.
- 70 ml of a solution of ester in water (~0.01 N) are placed in a clean, dry flask.
- 70 ml of a solution of sodium hydroxide in water (~0.015 N) are placed in a clean, dry flask.
- The flasks are closed with paraffin stoppers (if not available, cork stoppers may be used) and placed with a load in a thermostat.

- 10 ml of distilled water free from carbon dioxide is poured into 4 flasks and placed in a cooling mixture.
- Two flasks are filled with 15 ml of carbon dioxide-free water and 5 ml of the initial alkali solution. Samples are titrated with 0.05 N hydrochloric acid in the presence of methyl orange (n_0). This can be done once; not necessarily at the beginning of the work.
- 10-15 minutes after placing the flasks in the thermostat, the alkali solution is poured into the ether solution, while the flask with the ether solution is not removed from the thermostat. **Mark the time**.
- Samples of 10 ml are taken after 10, 20, 40 and 70 minutes; two samples are taken each time.
- Samples are quickly transferred into flasks with cooled distilled water and titrated with 0.05 N hydrochloric acid in the presence of methyl orange (n_t).
- After processing the first and second samples, two flasks with distilled water (10 ml each) are placed in the cooling mixture to process the third sample, and after processing the third sample, two flasks are placed to process the fourth sample.
- **The remaining mixture of ether and alkali solutions is left until the next lesson**. The mixture remains outside the thermostat, but in order to obtain the last point at the next lesson, it need to be placed again in a thermostat at the temperature of the experiment and after 10-15 minutes the remaining alkali is titrated (n_∞).

Presentation of results

1. The results for each temperature T are entered in the table:

T=

t	n_t	n_t-n_∞	$\ln(n_t/(n_t-n_\infty))$	k

n_0 – the volume of acid used for titration of the initial alkali solution;

n_t – volume of acid used for titration of samples;

n_∞ –the volume of acid used to titrate the last sample after the completion of the reaction.

2. The value of the constant for each value of time t is calculated by the formula

$$k_t = \frac{1}{t}\frac{V}{n_\infty N}\ln\frac{n_t(n_0 - n_\infty)}{n_0(n_t - n_\infty)},$$

where N is the normality of the acid taken for titration, V is the volume of the sample.

3. Calculate the average value of the constant.
4. Plot $\ln(n_t/(n_t-n_\infty))$ against t; check its linearity; find the rate constant from the slope; compare it with the average calculated value.
5. The dependence of the found rate constants on temperature is presented in the form of a table

T	$1/T$	k	$\ln k$

and as a plot of $\ln k$ on $1/T$. From the plot, the activation energy E and the pre-exponential A are found.

6. If the experiment is not careful enough and it is not possible to draw a straight line, the activation energy is estimated for each pair of points using the formula

$$E = \frac{T_1 T_2}{T_1 - T_2} \cdot R \cdot \ln\frac{k_1}{k_2}$$

and the average is taken.

Acid hydrolysis

The study of the kinetics of acid hydrolysis of the ester is carried out at 30 ^{0}C in parallel with the study of alkaline hydrolysis. **Therefore, it is important to plan the work so that sampling and titration in two experiments do not overlap.**

Acid hydrolysis is carried out as follows:

- The thermostat is turned on and the experiment temperature is set.
- Ice is placed in a container.
- 70 ml of hydrochloric acid (~0.05 N) are placed in a clean, dry flask. The flask is closed with a paraffin stopper (if not available, cork stopper may be used) and placed in a thermostat, hanging the weight.
- 10 ml of distilled water free from carbon dioxide is poured into 6 flask and placed in a cooling mixture.

- Two flasks are filled with 15 ml of carbon dioxide-free water and 5 ml of the initial alkali solution. Samples are titrated with 0.05 N hydrochloric acid in the presence of methyl orange (n_0). This can be done once; not necessarily at the beginning of the work.
- After 10-15 minutes, 2 ml of ester is poured into the flask with hydrochloric acid, while the flask is not removed from the thermostat. **Mark the time**.
- The first two samples of 3 ml are taken immediately. Samples should be quickly transferred into flasks with cooled distilled water and titrated with 0.05 N sodium hydroxide solution in the presence of methyl orange (n_t).
- Then samples of 3 ml are taken after 10, 30, 60 and 120 minutes; two samples are taken each time.
- After processing the first, second and third samples, two flasks with distilled water (10 ml each) are placed in the cooling mixture to process the fourth sample, and after processing the fourth sample, two flasks are placed to process the fifth sample.
- The remaining mixture of ether and acid solutions is left until the next lesson. The mixture remains outside the thermostat, but in order to obtain the last point in the next lesson, it need to be placed again in a thermostat at the temperature of the experiment and after 10-15 minutes the remaining alkali is titrated (n_∞).

Presentation of results

1. The results are entered in the table:

t	n	Δ_t	Δ_∞-Δ_t	$\ln(\Delta_\infty$-$\Delta_t)$	k

n is the volume of sodium hydroxide solution used to titrate the corresponding sample,

$\Delta_t = n_t - n_0$,

$\Delta_\infty = n_\infty - n_0$.

2. The value of the constant for each value of time t is calculated by the formula

$$k = \frac{1}{t} \ln \frac{\Delta_\infty}{\Delta_\infty - \Delta_t}.$$

3. Calculate the average value of the constant.
4. Plot $\ln(\Delta_\infty-\Delta_t)$ against *t*; check its linearity; find the rate constant from the slope; compare it with the average calculated value.

REFERENCE INFORMATION

Derivation of calculation formulas

Alkaline hydrolysis

$CH_3COOCH_3 + NaOH \rightarrow CH_3OH + CH_3COONa$

is described by the second-order kinetic equation. For a schematic representation of the reaction

$E + A \rightarrow$ products

the equation for an excess of alkali has the form

$$k = \frac{1}{t}\left(\frac{1}{a_0 - e_0}\right)\ln\left(\frac{e_0(a_0 - x)}{(e_0 - x)a_0}\right),$$

where e_0 and a_0 are the initial concentrations of ether and alkali, respectively; *x* is the amount of decomposed ether.

The initial alkali concentration is

$$a_0 = n_0 N/V\ ,$$

where N is the normality of the acid taken for titration; n_0 (ml) is the volume of acid used for titration of the initial volume of alkali; *V* is the sample volume.

The concentration of alkali by the time *t* is equal to

$$(a_0 - x) = n_t N/V\ ,$$

where n_t (mL) is the volume of acid used for titration of the sample taken after time *t* after the start of the reaction. Two parallel samples are taken for control. The result of the first titration should be substituted into the equation, and its

reliability should be judged from the second result. With a strong discrepancy between the results, the second one can be used if, when processing the entire set of data, it becomes clear that the first one is erroneous and drops out.

The initial concentration of ether is

$$a_0 = (n_0 - n_\infty)N/V$$

where n_∞ is the volume of acid used for titration of the last sample (after the ultimate completion of the reaction).

The ether concentration by the time *t* is

$$(e_0 - x) = (n_t - n_\infty)N/V = \{[(n_0 - n_\infty)N - (n_0 - n_t)N]/V\}.$$

Finally, we obtain the calculation formula

$$k_t = \frac{1}{t}\frac{V}{n_\infty N}\ln\frac{n_t(n_0 - n_\infty)}{n_0(n_t - n_\infty)}.$$

Acid hydrolysis

According to the equation, the reaction of catalytic acid hydrolysis of ester

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

is a bimolecular reaction. Therefore, the equation should hold

$$-\frac{de}{dt} = k_1 ew,$$

where *e* and *w* are the current concentrations of ether and water, respectively. But since water, which also acts as a solvent, is in great excess, its consumption during the reaction can be neglected and the concentration of water can be included in the constant:

$$-\frac{de}{dt} = ke, \quad \text{where} \quad k = k_1 w.$$

Thus, the experimental results on the hydrolysis of an ester in the presence of an acid should be treated according to the first order kinetic equation

$$k = \frac{1}{t}\ln\left(\frac{e_0}{e_0 - x}\right),$$

where e_0 is the initial concentration of the ether, x is the concentration of the decomposed ether.

The initial concentration of ether is proportional to the value

$$\Delta_\infty = n_\infty - n_0,$$

where n_0 and n_∞ are the volumes of sodium hydroxide solution used for titration of the first and last samples, respectively. Two parallel samples are taken for control. The result of the first titration should be substituted into the equation, and its reliability should be judged from the second result. With a strong discrepancy between the results, the second one can be used if, when processing the entire set of data, it becomes clear that the first one is erroneous and drops out.

The concentration of ether hydrolyzed by time t is proportional to the value $\Delta_t = n_t - n_0$, where n_t is the volume of sodium hydroxide solution used for titration of the sample taken at time t.

Finally, we arrive at the calculation formula:

$$k = \frac{1}{t}\ln\frac{\Delta_\infty}{\Delta_\infty - \Delta_t}.$$

(In this calculation, it is not necessary to know the concentration of the alkali solution used for titration).

TEST QUESTIONS

1. Main types of catalysis.
2. Features of acid-base catalysis
3. Examples of catalysts.
4. Mechanism of basic hydrolysis.
5. Mechanism of acid hydrolysis.

Catalytic hydrolysis of ester

Full name _____;
Group No _____;
date of the work _____; date of submission of the report _____.

Tabular information:
Four tables of results for alkaline hydrolysis (20, 25, 30 and 35 ^{o}C)

T=

t	n_t	n_t-n_∞	$\ln(n_t/(n_t-n_\infty))$	k

Table of results for acid hydrolysis

t	n	Δ_t	Δ_∞-Δ_t	$\ln(\Delta_\infty-\Delta_t)$	k

Dependence of the found rate constants on temperature

T	$1/T$	k	$\ln k$

Graphic information:

four plots of $\ln(n_t/(n_t-n_\infty))$ against t,
plot of $\ln k$ against $1/T$,
plot of $\ln(\Delta_\infty-\Delta_t)$ against t .

E =

A =

PRODUCTION OF SODIUM HYDROXIDE AND CHLORINE BY ELECTROCHEMICAL METHOD

PURPOSE To study the main regularities of the electrochemical production of sodium hydroxide and chlorine on a model unit; to analyze the gas and liquid phases.

SAFETY

- Chlorine is poisonous. In particular, it can cause inflammation of the mucous membrane of the respiratory tract and poisoning the body. Therefore, electrolysis can only be carried out in a fume hood with ventilation turned on. During electrolysis, do not bend over the electrolytic bath.
- During electrolysis, hydrogen is released at the cathode. No open fire nearby.
- Sodium arsenite (used in the liquid phase analysis) is poisonous. Solutions containing this reagent can only be drained into a special bottle
- Sampling of liquid should be made only with the help of a bulb.

WORKFLOW

The work includes three main stages:

- carrying out electrolysis;
- gas phase analysis (during the electrolysis);
- liquid phase analysis (upon completion of electrolysis).

Electrolysis

The schematic representation of a laboratory unit with a bell-type electrolyzer for the electrochemical production of NaOH and Cl_2 is given in Fig. 1.

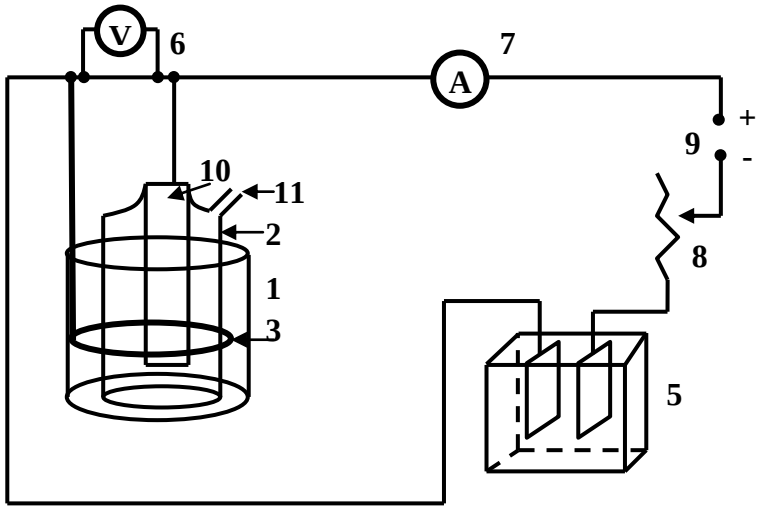


Fig. 1. Schematic representation of the model unit: 1 is electrolyzer; 2 is bell; 3 is iron cathode (ring); 5 is copper coulometer; 6 is voltmeter (5-10 V); 7 is ammeter (5 A); 8 is rheostat; 9 is electric rectifier; 10 is graphite anode; 11 is outlet for Cl_2

1. Clean and weigh the electrodes of the copper coulometer.
2. Assemble the unit in accordance with the above scheme. The teacher checks the correctness of the assembly.
3. Pour 250 ml of NaCl solution with a concentration of 305-310 g/L into the electrolyzer. The electrolyte level must be above the cathode.
4. Notice the time. Turn on the rectifier. Set the current strength in the range of 2–2.5 A (as directed by the teacher).
5. Every 15 minutes register the voltage on the cell (U_{pract}).
6. After 1.5 hours, analyze the gas phase.
7. The time of electrolysis is 2-3 hours (as directed by the teacher).
8. After turning off the current, filter the contents of the electrolyzer into a clean, dry container, record the volume, close tightly. Liquid phase analysis is carried out in the next lesson
9. Dry and weigh the coulometer electrodes.

Gas phase analysis

During the analysis of the gas phase, the content of Cl_2, CO_2 and O_2 is quantitatively determined. The schematic representation of the gas analyzer is shown in Fig. 2. In the leveling bottle 3 there is a blocking liquid; absorption vessels 6–9 contain, respectively, solutions of sodium thiosulfate, potassium iodide, potassium hydroxide, and alkaline solution of pyrogallol.

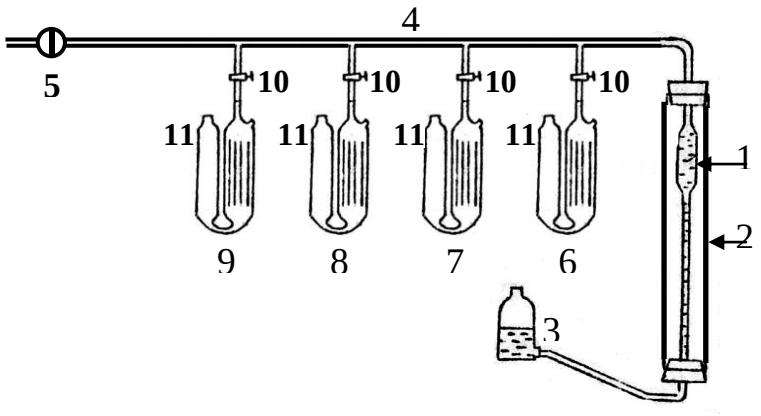


Fig. 2. Schematic representation of the gas analyzer: 1 is gas measuring burette; 2 is air jacket; 3 is leveling bottle; 4 is comb; 5 is three-way tape; 6–9 are absorption vessels; 10 are tapes; 11 are absorption vessels

1. Check the tightness of the system. With taps 10 open, switch tap 5 to atmosphere and, raising the leveling bottle, fill the burette with sealing liquid up to the upper mark. Then close tap 5 and lower the leveling bottle. If the system is sealed, the levels of liquids in the absorption vessels will first drop slightly and then will not change. Otherwise, the taps should be lubricated more thoroughly.
2. Set the levels in the absorption vessels. The liquid level in each absorption vessel must be brought to the mark. Close taps 10 of all absorption vessels. Set the leveling bottle on the level with the solution of the first absorbing vessel. Open tap 10 (other taps are closed). Lower the leveling bottle down. In this case, the level in the absorption vessel rises due to the vacuum in the burette. Close tap 10 and go to the next absorption vessel.
3. Switch tap 5 back to atmosphere and fill the burette with sealing liquid up to the upper mark.
4. Switch tap 5 to the electrolyzer and draw 100 mL of the test gas into the burette by lowering the leveling bottle. Close tap 5.
5. The sequence of solutions in the analysis of the gas phase: sodium thiosulfate - potassium iodide - potassium hydroxide - alkaline solution of pyrogallol.
6. Open tap 10 on the vessel with sodium thiosulfate. Raising and lowering the leveling bottle, transfer the test gas into the absorption vessel and back into the burette until the volume is constant. (Approximately this operation should be repeated 8-10 times). Bring the liquid level in the absorption vessel up to the mark, as described above. Record the volume of gas in the burette. To ensure the completeness of absorption, repeat all steps. Record the absorbed volume in the laboratory journal. (Please note that the measuring burette has

two scales: one indicates the absorbed volume, the second indicates the remaining volume).

7. Similarly, determine the volume of gas absorbed in the second, third and fourth absorption vessels. In the second vessel, residual chlorine is absorbed; in the third - carbon dioxide; in the fourth - oxygen.

Liquid phase analysis

The liquid phase is analyzed in the second lesson for NaOH, NaCl, NaClO и $NaClO_3$.

Determination of NaOH

- Pipette 2.5 ml of the analyzed liquid phase into a conical flask.
- Add 15-20 ml of distilled water.
- Add a few drops of 0.1 M $Na_2S_2O_3$ or H_2O_2 solution to remove NaClO to avoid the damage of the indicator.
- Titrate in the presence of methyl orange with 0.1 mol/L HCl until the color changes from yellow to faint pink.
- Calculate the concentration of NaOH in the liquid phase in g/L.

Determination of NaCl

- The concentration of NaCl is determined in the initial solution and in the liquid phase after electrolysis.
- Dilute the analyzed solution 40 times. Pipette 2.5 ml of the analyzed solution into a 100 ml volumetric flask and dilute with distilled water to the mark.
- Draw 5 ml into a conical flask and add
  - some distilled water;
  - 3-4 drops of 1 M HNO_3 (to neutralize alkali to pH 3-3.5);
  - 5-6 drops of saturated $NaHCO_3$ solution (to neutralize the excess of HNO_3 to pH ~ 7.5);
  - a few drops of H_2O_2 to break down the hypochlorite.
- Add 4 drops of 5% K_2CrO_4 solution and titrate (under constant shaking) with 0.05 M $AgNO_3$ solution until a persistent orange precipitate.
- Calculate the concentration of NaCl in g/L. 4 drops of K_2CrO_4 takes 0.2 ml of $AgNO_3$ solution.

Determination of NaClO

- Pipette 25 ml of the solution into a conical flask.
- Pour 50 ml of 0.01 M sodium arsenite solution from a burette and let stand for 10 minutes.
- Add 1-2 drops of phenolphthalein solution and neutralize with 30% acetic acid solution.
- Add 1 ml of saturated $NaHCO_3$ solution, 1 ml of starch and titrate with 0.01 mol/l iodine solution until a faint blue color.
- Calculate the concentration of NaClO in g/l.

Determination of $NaClO_3$

- Pipette 50 ml of test solution into a 500 ml conical flask.
- Add 3-5 ml H_2O_2, let stand for 5 minutes, then boil for 5 minutes.
- Add 25 ml of Mohr's salt solution 0.1 mol/l, boil for 10 minutes and cool quickly by pouring 200 ml of cold boiled distilled water into the flask.
- Add 10 ml of Reinhardt's mixture.
- Titrate the ferrous iron residue with 0.1 mol/l $KMnO_4$ solution until a pink color, which does not disappear within 30 s.
- Calculate the concentration of $NaClO_3$ in g/l.

The material balance for sodium ion makes it possible to evaluate the accuracy of the analytical control of the liquid phase. It is composed in the form of a table.

Arrival		Consumption		
Substance	Quantity Na, g	Substance	Quantity Na, g	% of original
NaCl		NaCl NaOH NaClO $NaClO_3$		

Calculation formulas. When processing the results of liquid phase analysis, the following formulas can be used.

$$c_{\mathrm{NaOH}} = \frac{V_1 \cdot 0.1 \cdot k \cdot 0.04}{V_2} 1000$$, where

V_1 is the volume of HCl solution used for titration, ml;
V_2 is the volume of solution taken for titration, ml;
0.1 is the HCl concentration, mol/l;
k is the correction factor for HCl concentration (if necessary);
0.04 is the milligram equivalent of NaOH [mg/mol].

$$c_{\mathrm{NaCl}} = \frac{k(V - 0.2) \cdot 0.05 \cdot 0.05846 \cdot 1000}{0.125}$$, where

V is the volume of $AgNO_3$ solution used for titration, ml;
0.2 is the volume of $AgNO_3$ solution bound by K_2CrO_4 (4 drops);
k is the correction factor (if necessary) for $AgNO_3$ concentration;
0.05846 is the milligram equivalent of NaCl;
0.125 is the volume of solution taken for titration (with the account of dilution).

$$c_{\mathrm{NaClO}} = \frac{0.074 \cdot 0.01(V_1 k_1 - V_2 k_2)}{V_3} 1000$$, where

V_1 is the volume of sodium arsenite solution, ml;
V_2 is the volume of iodine solution used for titration, ml;
V_3 is the volume of solution taken for analysis, ml;
0.01 is the concentration of solutions of iodine and sodium arsenite, mol/l;
k_1, k_2 are the correction factors for these concentrations (if necessary);
0.074 is the milligram equivalent NaClO; M(NaClO)=74.

$$c_{\mathrm{NaClO_3}} = \frac{0.01775 \cdot 0.1 \cdot (V_1 k_1 - V_2 k_2)}{V_3} 1000$$, where

V_1 is the volume of Mohr's salt solution, ml;
V_2 is the volume of potassium permanganate solution used for titration, ml;
V_3 is the volume of solution taken for analysis, ml;
0.1 is the concentration of solutions of Mohr's salt and potassium permanganate, mol/l;
k_1, k_2 is the correction factors for these concentrations;
0.01775 is the milligram equivalent of $NaClO_3$; M($NaClO_3$)=106.5
$6Fe^{2+}+ClO_3^-+6H^+ = 6Fe^{3+}+Cl^-+3H_2O$

CRITERIA FOR THE USE OF ELECTRIC ENERGY

The cathode current efficiency is calculated as the ratio of the mass of alkali formed during electrolysis to the mass of alkali predicted by Faraday's law:

$$\eta = \frac{M_{\mathrm{NaOH}}^{\mathrm{pract}}}{M_{\mathrm{NaOH}}^{\mathrm{theor}}} 100 .$$

The value in the numerator is calculated based on the results of the analysis of the liquid phase according to the formula

$$M_{\mathrm{NaOH}}^{\mathrm{pract}} = c_{NaOH} V ,$$

where V is the volume of the liquid phase. The theoretical value, according to Faraday's law,

$$M_{\mathrm{NaOH}}^{\mathrm{theor}} = Q E_{\mathrm{NaOH}} ,$$

where E_{NaOH} is the electrochemical equivalent of sodium hydroxide ($0.414 \cdot 10^{-3}$ g/C), Q is the amount of electricity passed through the electrolyzer. The amount of electricity, in principle, can be calculated as the product of current strength and time: $Q = I\tau$. However, such a calculation is inaccurate due to the occurrence of side processes, the instability of the current strength during electrolysis, and other factors. Much more accurate is the amount of electricity that has passed through the electrolyzer that is determined by the coulometer, because the current efficiency of copper in the coulometer is close to 100%:

$$Q = \frac{\Delta M_{\mathrm{Cu}}}{E_{\mathrm{Cu}^{2+}}} ,$$

where E_{Cu} is the electrochemical equivalent of copper ($0.3294 \cdot 10^{-3}$ g/C), ΔM_{Cu} is the mass of copper released on the cathode of the coulometer.

The cathodic current efficiency for industrial flow baths is usually higher due to less diffusion of OH^-–ions into the cathode space and the formation of fewer by-products.

The efficiency of anode current is approximately calculated based on the results of the gas phase analysis using the following formula:

$$A = 100 - \frac{100 \cdot 2 \cdot \left(c_{CO_2} + c_{O_2}\right)}{c_{Cl_2} + 2 \cdot \left(c_{CO_2} + c_{O_2}\right)},$$

in which the concentrations of gases are expressed in volume percent in terms of the airless gas phase. It is convenient to explain this recalculation with a particular case. For example, according to the results of the analysis of the gas phase, the following results were obtained: $c'_{Cl_2} = 90\%$, $c'_{CO_2} = 3\%$, $c'_{O_2} = 2\%$; in total – 95%. Accordingly, the proportion of nitrogen coming from the air is 5%. Part of the oxygen determined in the analysis of the gas phase also came from the air. Since there is approximately 4 times less oxygen in the atmosphere (by volume) than nitrogen, the fraction of atmospheric oxygen is 1.25%. Thus, the gas phase contains 5+1.25=6.25% of air. This means that the conversion factor for the airless phase is χ=100/(100-6.25). As a result of the recalculation, we get: $c'_{Cl_2} = \chi \cdot 90\% = 96.01\%$, $c'_{CO_2} = \chi \cdot 3\% = 3.19\%$, $c'_{O_2} = \chi \cdot (2 - 1.25)\% = 0.8\%$. Eventually A=92.32%.

The energy utilization factor is calculated as the ratio of the energy used usefully to the energy used actually:

$$\gamma = \frac{W_{usful}}{W_{fact}} = \frac{QU_{theor}\eta}{QU_{fact}} = \frac{U_{theor}\eta}{U_{fact}} \quad (\%).$$

Energy is calculated as the product of voltage and the amount of electricity passed through the electrolyzer. The amount of electricity is the same when calculating the numerator and denominator. When calculating the energy used actually, the voltage on the electrolyzer is used, which is found by averaging all the values recorded during the experiment (U_{fact}). Energy used usefully is calculated based on the previously found cathode current efficiency η and the theoretical decomposition potential of sodium chloride U_{theor} = 2.17 V.

From the above formula, the energy utilization factor is greater, the higher the current output and the lower the voltage on the bath. The ohmic resistance during electrolysis can be reduced by bringing the cathode and anode closer together, raising the temperature of the electrolyte, and eliminating current leakage with solutions (for example, by removing the catholyte drop by drop).

Energy consumption per unit of product is calculated by the formula

$$\omega = \frac{W_{\text{fact}}}{M^{\text{pract}}_{\text{NaOH}}}.$$

The values included in the formula were calculated above.

The balance of the amount of electricity makes it possible to estimate the losses associated with the reactions. Points of income and consumption are shown in the table below.

Calculations for points of income and consumption are carried out as follows.

The consumption of electricity for the main reaction is determined by the equation

$$2NaCl + 2H_2O + 2F = 2NaOH + Cl_2 + H_2.$$

The formation of 1 mole of sodium hydroxide consumes 1 faraday (96,500 coulombs) of electricity. The amount of hydroxide formed is calculated based on the results of the analysis of the liquid phase.

Sodium hypochlorite is formed by the reaction

$$Cl_2 + 2NaOH = NaCl + NaClO + H_2O.$$

The formation of 1 mole of hypochlorite consumes 2 moles of hydroxide (obtained with the cost of 2 F of electricity).

Income		Consumption		
	Q, C	Point of consumption	Q, C	% of original
The amount of electricity passed through the electrolyzer (by coulometer)		Main reaction		
		Side reactions: $NaClO$ $NaClO_3$ CO_2 O_2 Total:		
		Leakage current		

When calculating the amount of electricity spent on the formation of sodium chlorate, it is considered that all of it is formed by the reaction[1)]

$$2HClO + NaClO = NaClO_3 + 2HCl\ .$$

The formation of both starting substances is associated with the consumption of sodium hydroxide:

$$2\ Cl_2 + 2\ NaOH = 2NaCl + 2\ HClO;$$

the second equation is written above. In addition, sodium hydroxide is used to neutralize the HCl. As a result, the total consumption of NaOH for the formation of one mole of $NaClO_3$ is 6 moles and requires 6F of electricity.

Oxygen and carbon dioxide are formed due to the discharge of ions OH^-

$$4HO^- – 4e = 2H2O + O2$$

and subsequent interaction of oxygen with the anode material[1)]

$$C + O_2 = CO_2.$$

The formation of 1 mole of O_2 or CO_2 requires 4 F of electricity. The quantities of gases should be calculated in terms of the airless gas phase.

Current leakage through the elements of the experimental unit is usually small. In laboratory conditions, it can be ignored.

REFERENCE INFORMATION

Normal decomposition potentials at 18 ^oC.

Reaction	E^o, V
$Na^+ + e = Na$	– 2.714
$H_2O + e = OH^- + 0.5\ H_2$	– 0.415
$H_2O – 2e = 2H^+ + 0.5O_2$	+ 0.815
$2Cl^- -2e = Cl_2$	+ 1.359

In real conditions, due to overvoltage, the discharge of ions occurs at other potential values. The overvoltage depends on the material of the electrode and state of its surface, electrolyte temperature and concentration, current density,

etc. When the electrolysis of sodium chloride solutions is concerned it is possible, by varying these parameters, to obtain gaseous hydrogen or metallic sodium at the cathode, as well as gaseous chlorine or oxygen at the anode. Metallic sodium is released on a mercury cathode. Hydrogen is released on platinum and iron cathodes; on the iron cathode, the overvoltage is much higher. The evolution of oxygen usually proceeds with a large overvoltage at any electrode. On the contrary, for chlorine, the overvoltage on platinum is insignificant; on graphite it is noticeably higher. When carrying out the process on an industrial scale, for economic reasons, an iron (or mercury) cathode and a graphite anode are used.

Reinhardt mix: 67 g $MnSO_4 \bullet 4H_2O$ + 138 mL H_3PO_4 (ρ=1.1) + 138 mL H_2SO_4 (ρ=1.84) + 500 mL H_2O.

Arsenite method for the determination of hypochlorite

In an alkaline environment, hypochlorite oxidizes arsenite:

$$Na_3AsO_3 + NaClO = Na_3AsO_4 + NaCl\ .$$

The excess of arsenite is determined iodometrically. Iodine easily oxidizes arsenite in an alkaline medium, but it also reacts with sodium hydroxide:

$$J_2 + 2NaOH = NaJ + NaJO + H_2O\ .$$

Therefore, before iodometric titration of an excess of arsenite, it is necessary to neutralize the excess of sodium hydroxide. Acetic acid is used for this. An excess of hydrogen ions is unacceptable, because in an acidic medium iodine does not oxidize arsenite due to the fact that the potentials of the system AsO_4^{3-} / AsO_3^{3-} and $J_2/2J^-$ almost equal. In a neutral environment, they differ significantly and arsenite can be oxidized with iodine:

$$Na_3AsO_3 + J_2 + H_2O \leftrightarrow Na_3AsO_4 + 2HJ\ .$$

This reaction is reversible, and to bring it to the end, HJ needs to be bind:

$$NaHCO_3 + HJ = NaJ + H_2CO_3\ .$$

This forms a buffer mixture with pH of approximately 6-7.

TEST QUESTIONS

1. Reactions during electrolysis.
2. Faraday's laws. Inert and active electrodes; overvoltage; Nernst's law.
3. Reactions during gas phase analysis.
4. Determination of NaOH and NaCl in the liquid phase.
5. Arsenite method for the determination of hypochlorite.
6. Reactions used for the determination of chlorate.
7. Criteria for the use of electrical energy.
8. Industrial methods for obtaining sodium hydroxide. The use of sodium hydroxide.

Production of sodium hydroxide and chlorine by electrochemical method

Full name
_____;
Group No _____;
date of the work _____; date of submission of the report _____.

Amperage (A):

Voltage (V)												Average

Weight of coulometer electrodes (g)

	Before	After	Difference
Cathode			
Anode			

	Composition of the gas phase, %		
	Cl_2	CO_2	O_2
Experimental data			
Conversion to the airless phase			

Liquid phase volume:

Liquid phase composition, g/L			
NaCl	NaOH	NaClO	$NaClO_3$

Sodium ion balance

Income		Consumption		
Substance	Quantity Na, g	Substance	Quantity Na, g	% from initial
NaCl		NaCl NaOH NaClO $NaClO_3$		

Cathode current output: Anode current output:

Energy utilization rate: Energy consumption per unit of product:

Electricity balance

Income		Consumption		
	Q, C	Point of consumption	Q, C	% from initial
The amount of electricity passed through the electrolyzer (by coulometer)		Main reaction		
		Side reactions: NaClO $NaClO_3$ CO_2 O_2 Total:		
		Leakage current		

PRODUCTION OF SODIUM HYDROXIDE BY THE CAUSTIFICATION OF SODA WITH LIME

PURPOSE To study the main regularities of the chemical production of sodium hydroxide by the caustification of soda with lime, and also methods of analysis of initial raw materials and final product.

SAFETY

- Contact of the caustic alkaline solution with the body and especially with the eyes should be avoided. In case of contact, rinse immediately with plenty of water, then - if necessary - with a solution of boric acid and again with water.
- Observe safety when working with electrical units.

WORKFLOW

The work includes three main stages:

- analysis of initial substances;
- caustification process;
- product analysis.

Analysis of starting materials

The starting materials are technical soda and lime.

Lime analysis is carried out in order to determine the content of the active substance[1]

1. Take two weights of lime, 0.1 g each.
2. Transfer each sample to a conical flask, add 50 ml of distilled water and mix thoroughly.
3. Add a few drops of phenolphthalein solution and titrate with 0.1 mol/L HCl. Titrate slowly as lime is poorly soluble in water and goes into solution as it is titrated. The titration is complete if the pink color that has disappeared does not reappear within 3 minutes.

[1] When analyzing raw materials on an industrial scale, the first step of the analysis is grinding and taking an average sample by quartering and scooping methods. Quartering: the sample is poured in the form of a cone, the cone is turned into a circle with a wooden spatula, the circle is divided into four parts and one of them is taken for further work. After the sample has been reduced to 2 kg, the scooping method is used. The sample is placed as a uniform thin layer on a flat surface, divided by a special grid into 15-20 squares with a side of 50 mm, and the material is taken from each square with a spatula.

4. Calculate the content of the active substance in the sample in terms of $Ca(OH)_2$.

Next, you need to prepare 100 g of a 15% soda solution. The solution is prepared in a conical flask by heating. Further this solution will be used for the caustification process. Part of the prepared solution is taken and analyzed for the content of sodium carbonate and bicarbonate. Measure the volume of the remaining soda solution with a graduated cylinder.

1. Place 10 ml of the cooled solution into a 100 ml volumetric flask and make up to the mark with distilled water.
2. Take 10 ml of the solution into a titration flask.
3. Add some distilled water, a few drops of phenolphthalein solution and titrate with 0.1 mol/L HCl until the pink color disappears (V_1).
4. Add a few drops of methyl orange to the same flask and titrate until the color changes from yellow to pink (V_2).
5. Calculate the content of sodium carbonate and bicarbonate in the solution. Sodium carbonate is titrated in the presence of phenolphthalein:

$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl,$$

bicarbonate - in the presence of methyl orange:

$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2.$$

Calculate the amount of technical lime CaO_{techn} required for the caustification proceeding according to the equations:

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons 2NaOH + CaCO_3,$$
$$2NaHCO_3 + Ca(OH)_2 \rightleftharpoons 2NaOH + CaCO_3 + CO_2 + H_2O.$$

Process of caustification

The caustification reaction is reversible. Optimal conditions for it: temperature ~ 80 ° C and concentration of soda solution ~ 150 g / L.

1. Place the soda solution in a porcelain glass with a capacity of 300-500 ml.
2. Add the calculated amount of lime.
3. Place the beaker in a water bath (or thermostat). Dip the stirrer into the mixture.

4. Heat for 1 hour with constant stirring, maintaining the temperature inside the porcelain glass ~ 80 °C.
5. Cool the solution and filter on a Buchner funnel. Wash the precipitate 1-2 times with distilled water, add washing water to the filtrate and measure the total volume.

Product Analysis

1. Pipette 10 ml of the filtrate into a 100 ml volumetric flask and dilute to the mark with distilled water.
2. Pipette 10 ml of the this solution into a conical titration flask.
3. Add some distilled water, a few drops of phenolphthalein and titrate with 0.1 mol/L HCl until the pink color disappears (V_3).
4. Add a few drops of methyl orange to the same flask and titrate until the color changes from yellow to pink (V_4).
5. Calculate the content of sodium hydroxide and carbonate in the solution. In the presence of phenolphthalein, sodium hydroxide and sodium carbonate are titrated:

$$NaOH + HCl \rightarrow NaCl + H_2O,$$

$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl.$$

sodium bicarbonate is determined in the presence of methyl orange:

$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2.$$

6. Based on the results obtained, calculate the NaOH yield (as a percentage of theory).

REFERENCE INFORMATION

Calculation formulas. In processing the results of the analysis, the following formulas can be used.

The content of CaO in a sample of 0.1 g CaO_{tech} (%) is 2.8 V, where V is the volume of acid consumed for titration.

Analysis of the initial soda solution:

$c_{Na_2CO_3} = 0.0106 \cdot V_1$; g/ml

$c_{NaHCO_3} = 0.0084 \cdot (V_2 - V_1)$; g/ml, where

V_1 – volume of HCl solution used for titration with phenolphthalein

V_2 – volume of HCl solution used for titration with methyl orange

Product analysis:

$c_{NaOH} = 0.004 \cdot (V_3 - V_4)$, g/ml

$c_{Na_2CO_3} = 0.0106 \cdot V_4$, g/ml where

V_3 – the volume of HCl solution used for titration with phenolphthalein;

V_4 – volume of HCl solution used for titration with methyl orange.

Calculation formulas with the account of the dilution scheme.

Analysis of the initial soda solution:

$$C_{Na_2CO_3} = \frac{0.0106 \cdot V_1 \cdot V_{volumetric\ flask}}{V_{solution,taken\ into\ a\ volumetric\ flask} \cdot V_{solution,taken\ from\ a\ volumetric\ flask}}$$

where 0.0106 is 10^{-4} mol Na_2CO_3, the amount of Na_2CO_3 (g) corresponding to 1 mL of HCl (0.1 mol/L);

$$C_{NaHCO_3} = \frac{0.0084 \cdot (V_2 - V_1) \cdot V_{volumetric\ flask}}{V_{solution,\ taken\ into\ a\ volumetric\ flask} \cdot V_{solution,\ taken\ from\ a\ volumetric\ flask}},$$

where 0.0084 is 10^{-4} mol of $NaHCO_3$, the amount of $NaHCO_3$ (g) corresponding to 1 mL of HCl (0.1 mol/L).

Product analysis:

$$C_{NaOH} = \frac{0.004 \cdot (V_3 - V_4) \cdot V_{volumetric\ flask}}{V_{solution,taken\ into\ a\ volumetric\ flask} \cdot V_{solution,taken\ from\ a\ volumetric\ flask}},$$

where 0.004 is 10^{-4} mol of NaOH, the amount of NaOH (g) corresponding to 1 mL of HCl (0.1 mol/L);

$$C_{Na_2CO_3} = \frac{0.0106 \cdot V_4 \cdot V_{volumetric\ flask}}{V_{solution,taken\ into\ a\ volumetric\ flask} \cdot V_{solution,taken\ from\ a\ volumetric\ flask}}$$

where 0.0106 is 10^{-4} mol Na_2CO_3, the amount of Na_2CO_3 (g) corresponding to 1 mL of HCl (0.1 mol/L).

Lime analysis:

$$P_{Ca(OH)_2} = \frac{0.0037V}{0.1\left(M_{Ca(OH)_2}/M_{CaO}\right)}100 \quad (\%),$$

where
M – molar mass,
0.0037 is 0.5 10^{-4} mole of $Ca(OH)_2$, amount of $Ca(OH)_2$ (g) corresponding to 1 mL of 0.1 M HCl.
V is the volume of HCl used for titration

Solubility (g/100 g H_2O)

	20 ^oC	80 ^oC
Na_2CO_3	21.5	45.8
$NaHCO_3$	9.6	17.4

TEST QUESTIONS

1. Caustification reaction. Equilibrium constant.
2. Influence of reagent concentrations on the equilibrium of the caustification reaction.
3. Effect of temperature on the equilibrium of the caustification reaction.
4. Analysis of raw materials and products, selection of indicators.
5. Industrial methods for production of sodium hydroxide. The use of sodium hydroxide.

Production of sodium hydroxide by the caustification of soda with lime

Full name
_____;
Group No _____;
date of the work _____; date of submission of the report _____.

Lime analysis
$V1_{HCl}$ (mL): ; $V2_{HCl}$ (mL):
$Ca(OH)_2$ (g/100 g technical lime):

Soda analysis
$V_{HCl,phenolphthalein}$ (mL): ; $V_{HCl,methyl\ orange}$ (mL):
Na_2CO_3 (g/ mL):
$NaHCO_3$ (g / mL):

A sample of technical lime taken for caustification:

Product analysis
$V_{HCl,\ phenolphthalein}$ (mL): ; $V_{HCl,\ methyl\ orange}$ (mL):
NaOH (g / mL):
Na_2CO_3 (g / mL):

Product yield (%):

STEELOSCOPE ANALYSIS OF STEELS AND ALLOYS

PURPOSE Master the steeloscopic method of analysis and determine the chromium content in the proposed steel samples.

SAFETY

- The generator providing arcing and sparking provides voltage up to 1000 V. The device must be grounded. Do not touch live contacts.
- Do not touch the optical parts of the instrument or wipe them with a hard, scratchy cloth. The first condenser lens and eyepiece lenses are cleaned with a swab moistened with alcohol or sulfuric ether.
- After 800 hours of operation, clean the discs with fine sandpaper.

WORKFLOW

The work includes three main stages:

- study of the spectrum of iron;
- identification of characteristic lines of chromium in the spectra of alloys with known chromium content;
- analysis of an alloy with unknown chromium content.

Preparing the steeloscope for work

The steeloscope is a device specially adapted for visual observation of the spectra of metals and alloys. Allows to analyze steels for almost all impurities (except sulfur and phosphorus). The steeloscope enables to view the entire visible part of the spectrum from the violet to the red region.

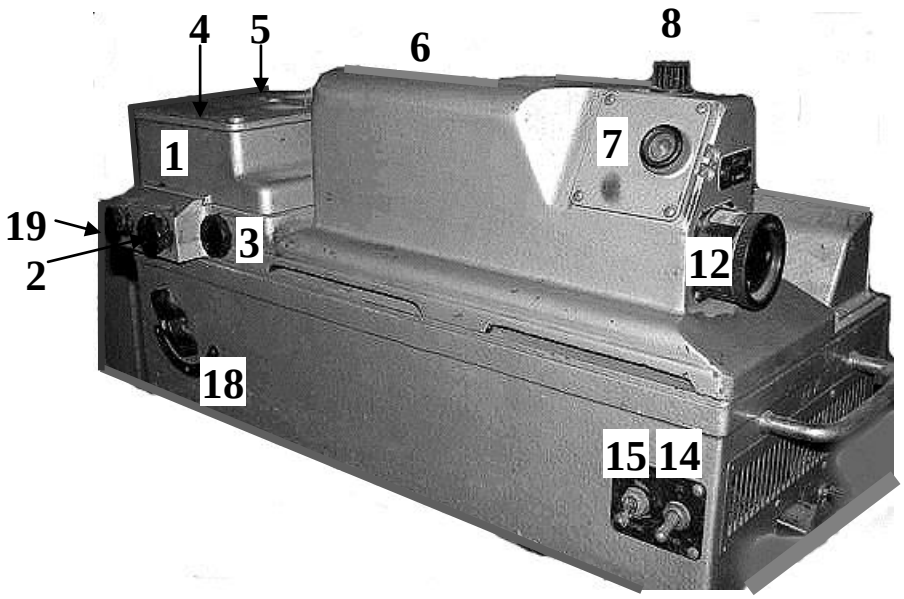


Fig. 1. Steeloscope SL-IIA

1. Remove table *1* by first unscrewing the bolt from behind.
2. Clean the reference electrode with a file or sandpaper by turning knob *2*. Place table *1* back, securing with the bolt.
3. Set the switch *18* to the "arc" position.
4. Set a distance of 3 mm between the electrodes according to the template. To do this, put the template in the slot *4* on the table *1* and use the handle *19* to bring the electrode disk to the template until it stops.
5. Clean the test sample with sandpaper and fix it on the table *1* with a spring clip *5*.
6. Use handle *3* to set the best direction of light beams into the monochromator.
7. Turn the wedge handle *8* to set the white dot against the number «13.5».
8. Set toggle switch *14* to position "2A" or "4A".
9. Check the grounding of the device (DO NOT POWER ON WITHOUT GROUNDING!).
10. Power on the device and put the toggle switch *15* in the "on" position.
11. Set the drum *12* to position "115" and rotate the eyepiece *7* to achieve a sharp image of the spectrum lines.

The steeloscope can be turned on for no more than 2–3 minutes, after which it must be turned off. Turn the circular electrode with handle *2* by one click and turn it on again.

Studying the spectrum of iron

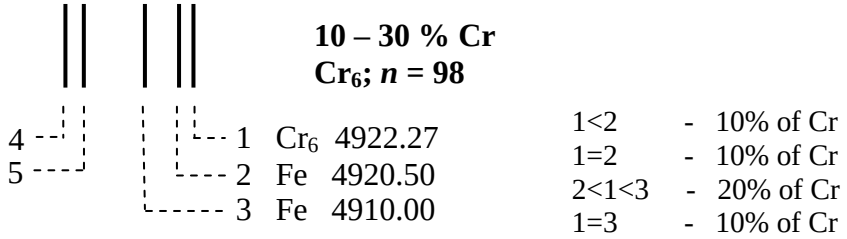
1. Clean the iron sample with sandpaper and place it on the steeloscope table.
2. Set drum *12* to zero position.
3. Rotate the drum to view the entire visible part of the spectrum. Identify the characteristic parts of the spectrum, record the readings of the drum *12* for the beginning and end of each such part.
4. Compare the spectrum with the atlas.

Finding characteristic lines of chromium in the spectra of alloys with a known chromium content

To perform this stage of work, samples with different known chromium content are needed: 1%, 10%, 30%.

Spectrum region Cr_6

- Place the sample containing 30% of chromium on the table.
- Set drum *12* to position n=98, turn on the steeloscope and find three characteristic lines (1–3) shown in the diagram (two more iron lines 4 and 5 are located on the left).



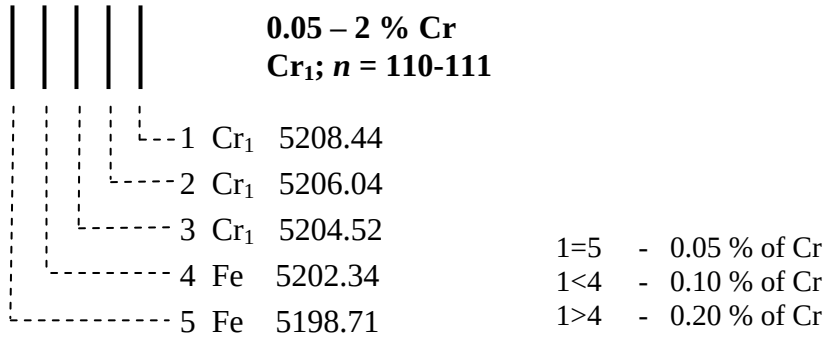
- Draw a line of chrome to the pointer and record the drum reading.
- Place a 1% chromium sample on the table and check that the chromium line disappears.

In this region of the spectrum, chromium lines are visible only at a chromium content of 10–30%.

Spectrum region Cr_1

- Place a low content chromium sample on the table.
- Set drum *12* to position n=110-111.

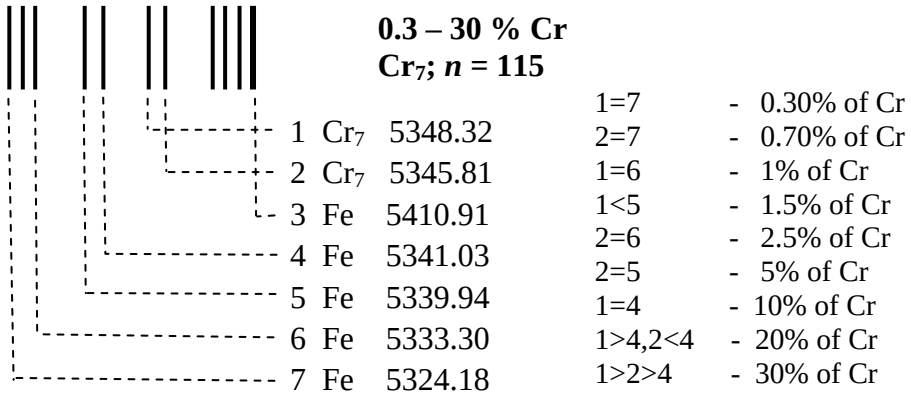
- Turn on the steeloscope and find the three indicated bright lines of chrome (they are located to the left of the pointer).
- Bring line 1 to the pointer and record the readings.



Spectrum region of Cr_7

In this region, two lines of chromium (1 and 2) are determined provided its content in the sample is 0.3–30%. To the right and to the left there are characteristic groups of iron lines.

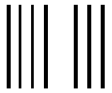
- Any of the samples is placed on the table.
- Position of drum *12* is n= 115.
- Bring line 1 to the pointer and record the readings.



Spectrum region Cr_4

In this region, one line of chromium (1) is determined when its content in the sample is 1–4%. It is located very close to the line of iron 2; sometimes they may seem to merge. To the right of these lines is iron line 3, then three more iron lines are situated. On the left is the line of iron 4.

- Place a sample containing 30% of chromium on the table.
- Position of drum *12* is n= 118.
- Bring line 1 to the pointer and record the readings.

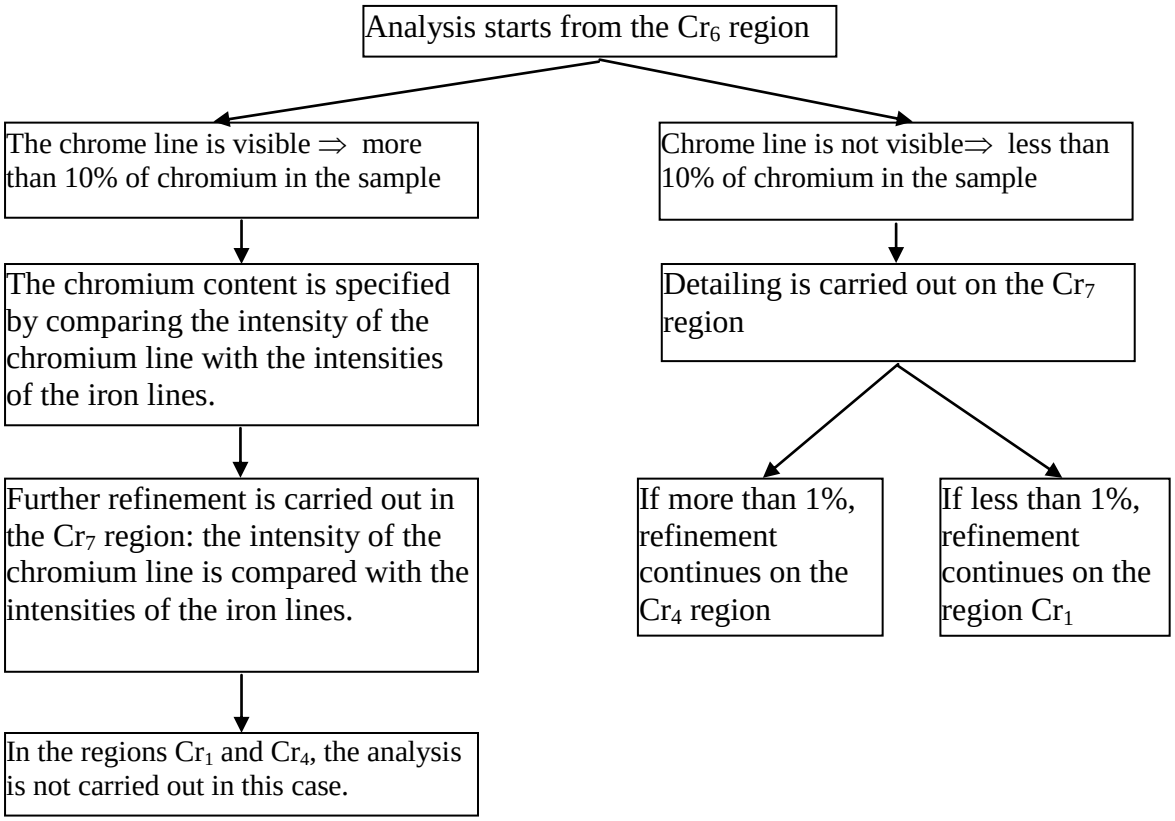


1 – 4 % Cr
Cr_4; *n* = 118

3 Fe 5415.21
2 Fe 5410.91
1 Cr_4 5409.79
4 Fe 5405.78

1=2 - 1.0 % of Cr
1=3 - 2.5 % of Cr
1>4 - 5.0 % of Cr

Analysis of samples with unknown chromium content



REFERENCE INFORMATION

The steeloscopic method belongs to the group of spectral methods of analysis.

The emission spectral analysis is based on two principles:

1. Atoms of each element are characterized by a certain set of spectral lines.
2. The intensity of the spectral line depends on the concentration of atoms in the plasma.

Emission spectra of the same sample can be obtained with different excitation sources:

- flame (~ 3000 °C);
- electric arc (~ 5000-6000 °C);
- high-voltage spark (~ 10000 °C).

These spectra differ from each other. Steeloscopic analysis uses an arc and a spark as sources of excitation.

Steeloscopic analysis is a semi-quantitative method with visual registration of results, based on the use of an internal standard.

The intensity of line due to the transition from level *i* to level *k* is determined by the relation

$$I_{ik} = N_i A_{ik} h \nu_{ik},$$

where N_i is the concentration of atoms in the excited state *i*; A_{ik} is the probability of a spontaneous transition; ν_{ik} is the radiation frequency; *h* is Planck's constant. The relation is valid for low self-absorption (reabsorption) and low stimulated emission.

A series of lines in the emission spectrum is a set of lines corresponding to the transition of an electron to a given level from higher levels. The brightest in each series are the first lines. They are most advantageous when determining small amounts of elements. But sometimes these lines are situated in hard-to-observe regions of the spectrum, and the analysis has to be designed using different lines. Also, the so-called last lines play an important role in the steeloscopic analysis. The last line is in the accessible region of the spectrum and disappears last with a decrease in the concentration of this element. Information on the latest lines are given in reference books.

Steeloscopic analysis is based on the use of an internal standard: the intensity of the line of the analyzed impurity is determined in comparison with the intensity of the line of the main component chosen as the comparison line. These two lines form an analytical pair. The ratio of their intensities is sufficiently stable to changes in the conditions for obtaining the spectrum with the same excitation source.

In steeloscopic analysis, the test sample is one of the arc electrodes. It is logical to use a dominating metal of the alloy as the second (so-called permanent) electrode. However, such an electrode may also contain impurities, which will distort the results of the analysis. Therefore, in most cases, preference is given

to electrolytic copper. In addition to a high degree of purity, the advantage of copper electrodes is their high thermal conductivity: copper electrodes heat up less, do not burn so much, and give a more contrast spectrum.

Optical scheme. The device is built according to an autocollimation scheme with a horizontal arrangement of elements (Fig. 2).

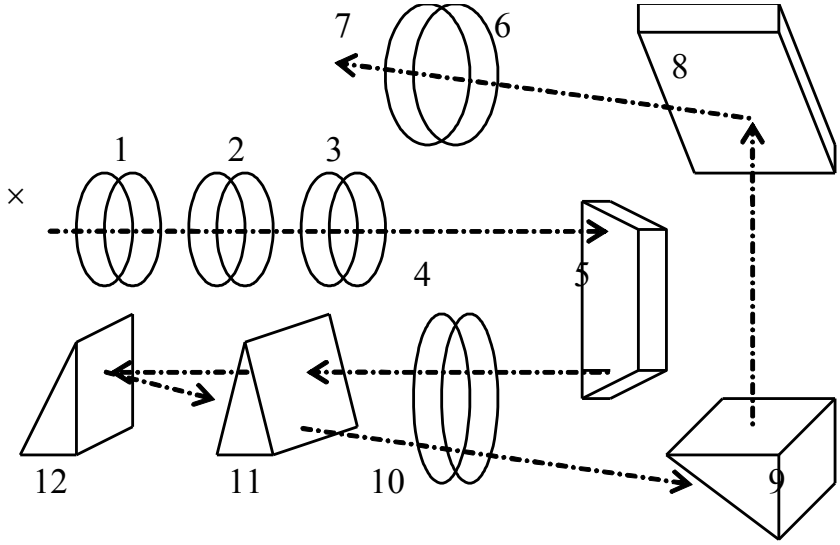


Fig. 2. Optical scheme of the steeloscope SL-11A

The light from the arc uniformly fills the slit *4* with the help of a three-lens scheme, the reflective prism *5* directs the beam onto the lens *10* (the slit is placed at the focus). The resulting parallel beam hits the dispersive prisms *11* and *12*. The large leg of prism *12* with a refractive angle of 30° is silver plated, so the rays are reflected from it, pass in the opposite direction through the prisms to the lens and fall on a rectangular prism *9* and mirror *8*, which direct them to the eyepiece *7*. A photometric wedge *6* is located in the focal plane of the eyepiece. The dispersing system consists of two prisms; the prism with a refractive angle of 60^0 is fixed on the bridge, and the prism with a refractive angle of 30^0, together with its bridge, can be rotated using drum *12* (Fig. 1). As a result the spectrum moves in the field of view of the eyepiece. When working on a steeloscope, the entire visible spectrum from the violet to the red region can be viewed. On the drum *12*, there is a uniform scale with a division value of 2^0 and a scale *11* with symbols of chemical elements. Symbols denote groups of spectral lines used in the analysis of steels for the corresponding elements (impurities).

TEST QUESTIONS

1. Origin of the emission spectra of atoms.
2. Sources of spectra excitation in emission spectral analysis.
3. Steeloscopic analysis. Logic scheme of steeloscopic analysis of impurities in steels.
4. Design and operation of steeloscope SL-11A.
5. Intensity of the spectral line; resonance lines, last lines, internal standard in steeloscopic analysis.

Steeloscope analysis of steels and alloys

Full name
_____;
Group No _____;
date of the work _____; date of submission of the report _____.

Samples with known chromium content

Spectrum region of Cr_6

Spectrum region of Cr_1

Spectrum region of Cr_7

Spectrum region of Cr_4

Samples with unknown chromium content

Spectrum region of Cr_6

Spectrum region of Cr_7

Spectrum region of Cr_4

Spectrum region of Cr_1

DETERMINATION OF IRON OXIDE IN MAGNESITES

PURPOSE Determine the content of iron oxide in the proposed sample of refractory magnesite.

SAFETY

- Acids are used in this work. In case of acid contact with skin, rinse immediately with water.
- The beaker with the sample in the sand bath can be heated only under fume hood. Carefully monitor that sulfuric acid vapor does not go beyond the glass.
- Liquids should only be sampled with a bulb.

WORKFLOW

The work includes the following steps:

- preparation of standard solutions;
- preparation of a sample for analysis;
- determination of the optical density of solutions.

The content of iron oxides in the sample is determined photocolorimetrically. The method is applicable when the content of oxides is up to 2.5% in terms of iron.

Preparation of standard solutions

- Using a 5 ml graduated pipette with a graduation value of 0.02 ml, take 5 aliquots of the standard solution* (as directed by the instructor; e.g. 1, 2, 3, 4 and 5 ml) and transfer each sample to a 50 ml volumetric flask.
- To each of these flasks add 3 ml of a 30% solution of sulfosalicylic acid.

* The initial standard solution is prepared once for the entire semester: 0.16 g of Fe_2O_3 is dissolved in 30 ml of HCl (specific weight 1.19) while heating in a water bath. The solution is cooled, transferred to a 1 L volumetric flask and diluted to the mark with water. The concentration (titer) of the resulting solution is 0.00016 g/mL.

- With the 25% ammonia solution create an alkaline medium with pH 9-11 in each flask (pH is checked with universal indicator paper).
- Solutions in flasks are made up to 50 ml with distilled water and mixed thoroughly.

Preparation of sample for analysis

- Take a sample of magnesite 0.2 g.
- Place it in a glass with a capacity of 200-300 ml, add 20 ml of distilled water and 10 ml of concentrated sulfuric acid.
- The beaker is heated (obligatory under fume hood!) in a sand bath until the sample dissolves and the water evaporates. Heating is stopped when white vapors of sulfuric acid begin to form in the beaker.
- The contents of the beaker are cooled and water (≈100 ml) is carefully poured along the walls.
- Silicic acid is filtered off, the solution is collected in a 200 ml volumetric flask, brought to the mark with distilled water and mixed thoroughly.
- Take 20 ml of the resulting solution into a 50 ml volumetric flask, add 3 ml of 30% sulfosalicylic acid, 25% ammonia solution to a stable yellow color, dilute to the mark with distilled water and mix thoroughly.

Determination of the optical density of solutions

- Determination of optical density is made with the КФК-2 photocolorimeter. The order of operation and the optical scheme of the device are given below.
- Use cuvettes 30–50 mm thick for weakly colored solutions and 1–3 mm thick for strongly colored solutions.
- Each solution is measured three times and the average value (A_i) is found. All results are summarized in a common table.
- The results for standard solutions are used to built the calibration graph as the dependence of optical density on concentration; the regression equation is determined by the least squares method.
- Using the calibration graph, determine the concentration of the test solution, based on the average value of the optical density. Then the percentage of Fe_2O_3 in magnesite is calculated.

Operation procedure on КФК-2

1. Switch on the colorimeter (220 V) 15 minutes before the measurements. The POWER ON toggle switch is located on the rear panel of the device. During warm-up, the sample compartment must be open. Note that the shutter in front of the photodetectors blocks the light beam. DO NOT TOUCH THE SHUTTER! (Photocells may fail).
2. Set the "SENSITIVITY" knob to «1» (on the black scale).
3. Move the “SETTING 100 ROUGH and FINE” knobs to the extreme left position.
4. To ensure the smallest error in determining the concentration, the right wavelength needs to be chosen, at which measurements will be performed. To do this, one of the prepared solutions should be measured with all light filters and plotted $A = f(\lambda)$, where λ are the wavelengths (nm) corresponding to different light filters (Fig. 1). On the resulting spectral curve, the region with the maximum optical density is chosen. When switching filters, the “SENSITIVITY” knob should be in the «1» position, and both “SETTING 100” knobs should be in the leftmost position (minimum sensitivity).

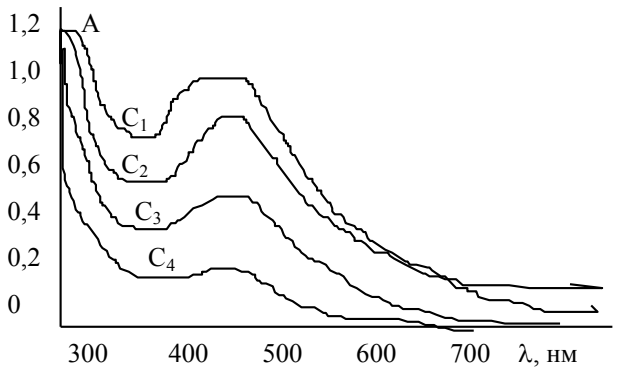


Fig. 1. Dependences of the optical density on the wavelength for different light filters

5. Optical density measurement:
   a) Fill the cuvette with water or a reference solution containing all components, except Fe^{3+} to be determined, wipe dry and place in the far section of the cuvette compartment.
   b) Place the cuvette with the test solution in the near section.
   c) Close the lid of the cuvette compartment.

d) Set the "SENSITIVITY" knob alternately to «1», «2», «3».
e) Turn the “SETTING 100 ROUGH AND FINE” knob to bring the arrow to the minimum value of *A* («0» on the lower scale of the colorimeter).
f) By moving the handle on the front panel of the device, put a cuvette with the test solution into the light beam and read the optical density A.
g) Similarly, the optical density of all prepared solutions is determined.

REFERENCE INFORMATION

Determination of the concentration of the test solution C_x (g / ml) using a calibration plot; A_x is the average value of the optical density:

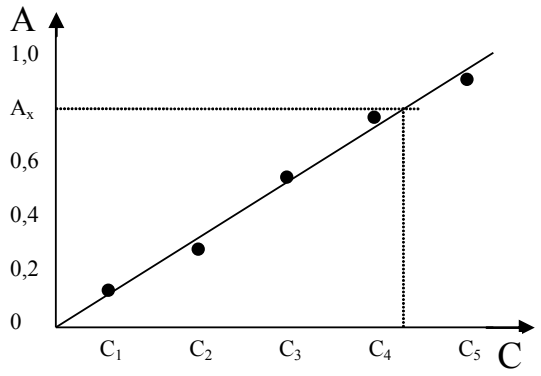


Fig. 2. Calibration plot

The percentage of Fe_2O_3 in magnesite can be calculated using the formula

$$C_{Fe\,O} = C_x \bullet v \bullet n \bullet 100 / q \text{ ,}$$

where C_x is the titer of the analyzed substance, g/ml;
v is its volume (50 ml);
n is the dilution of the analyzed solution (10);
q is the weighed portion of the analyzed substance, g.

Magnesite are refractory materials with a fire resistance of 2000 °C and higher.

Refractoriness is the ability of a material to withstand, without melting, the action of high temperatures. It is characterized by the temperature at which a standard sample in the form of a special trihedral pyramid softens so much that the height touches the base.

Refractory materials are usually divided into three groups:

- refractory 1580–1770 °C
- highly refractory 1770–2000 °C
- highest refractory > 2000 °C, ***including magnesites***

An example of the chemical composition of magnesite:

MgO	at least 91%
SiO_2	2 - 4%
Al_2O_3	1 - 3%
Fe_2O_3	0.5 - 3%
CaO	0.5 - 2%

The iron content of magnesite is one of the main factors determining their heat resistance.

Magnesite refractory units are widely used in the metallurgical industry for lining the floors and walls of open-hearth electric furnaces, for the manufacture of steel-pouring machines and ladles, etc.

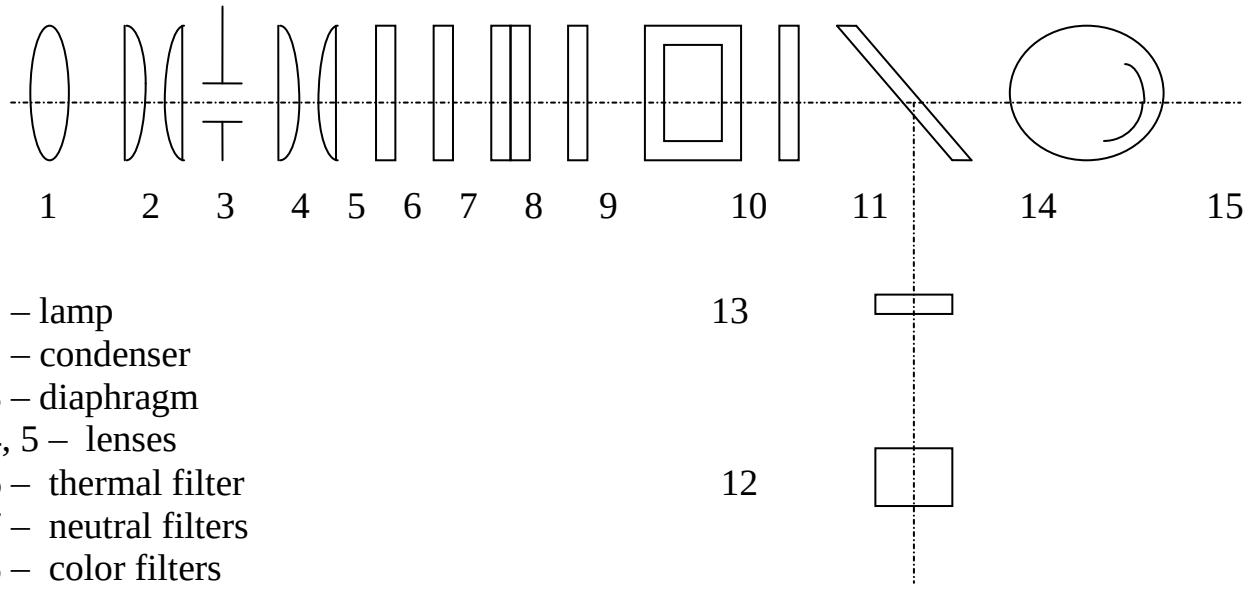
The photocolorimetric method for the determination of iron in refractory materials is based on the formation of a complex with sulfosalicylic acid. The composition of the iron complex with sulfosalicylic acid depends on the pH. Changes in the composition of the complex are accompanied by a change in its color. At pH 1.8–2.5, a brownish-pink $[Fe(Sal)]^+$ complex is formed. At pH 4–8, a brown complex $[Fe(Sal)_2]$ is formed. At pH 8–11, yellow iron trisulfosalicylate $[Fe(Sal)_3]^{3-}$ is formed. The last complex is the most stable. In a more alkaline environment (at pH $\geq$12), iron sulfosalicylate decomposes with the formation of a precipitate. In an alkaline medium, sulfosalicylic acid forms complexes not only with Fe^{3+} ions, but also with Al^{3+} and Cu^{2+}. However, since the complex with Al^{3+} is colorless and Cu^{2+} is absent in magnesite, sulfosalicylic acid can be used to determine iron in magnesites.

The relationship between the concentration of the dissolved substance, the thickness of the colored layer and the degree of attenuation of the intensity of monochromatic light is expressed by the Bouguer–Lambert–Beer law:

$$A = \lg(J_0 / J_t) = \varepsilon \bullet C \bullet l ,$$

where: J is the light intensity; C is the concentration of the colored solution, mol/l; A is the optical density; ε is the molar extinction coefficient, depending on the nature of the dissolved substance, temperature and wavelength; l is the thickness of the colored layer, cm.

The functioning of photocolorimeters is based on the equating the light fluxes incident on photocells using an adjustable slit diaphragm connected to a counting drum. The photocurrents of these elements have opposite directions. The photocurrent compensation is registered by a null galvanometer connected to the photocells in a differential circuit. The absolute measurement error is 1%.



1 – lamp
2 – condenser
3 – diaphragm
4, 5 – lenses
6 – thermal filter
7 – neutral filters
8 – color filters
9, 11 – protective glasses
10 – cuvette
12 – photodiode
13 – light filter
14 – light dividing plate
15 – photocell

Fig. 3. Optical scheme of the photocolorimeter

TEST QUESTIONS

1. Where are magnesites used? How does the iron content affect their properties?
2. The principle of operation of photocolorimeter. The Bouguer-Lambert-Beer law. The main reasons for the deviation from the Bouguer–Lambert–Beer law. Filter selection.
3. Iron complexes with sulfosalicylic acid. The choice of complex for analysis.
4. Fundamentals of technology for obtaining refractories.
5. Main properties of refractories.

Determination of iron oxide in magnesites

Full name
_____;
Group No _____;
date of the work _____; date of submission of the report _____.

Aliquot volumes of stock standard solution:

Sample weight of magnesite:

Results of photocolorimetric measurements

C_i (г/мл)	$A_{i(1)}$	$A_{i(2)}$	$A_{i(3)}$	A_i
C_1 C_2 C_3 C_4 C_5				
C_x				

A calibration chart must be attached to the report.

The equation of the calibration line:

The concentration of the analyzed solution:

Content of Fe_2O_3 in the sample:

ANALYSIS OF LUBRICATING OILS

PURPOSE Master the methods for determining the main characteristics of lubricating oils.

SAFETY

- Lubricating oils are products of oil refining and are classified as combustible materials.
- When lubricating oils ignite in small vessels, the flame can be extinguished by covering the crucible with a metal lid or asbestos plate.
- Burning oil must not be extinguished with water.

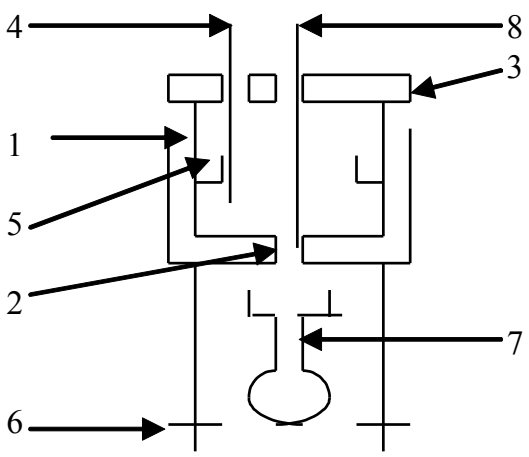
WORKFLOW

The work includes three stages:
- determination of specific viscosity;
- determination of flash and ignition temperature;
- determination of specific gravity.

Determination of specific viscosity

Viscosity is determined by the rate of flow of a certain volume of oil from the viscometer. When performing this work, the Engler viscometer (shown in the figure) is used.

The viscometer consists of a brass vessel (1) with three pins (5) on the inner surface of the walls, which indicate the oil level and at the same time serve to correctly install the device with screws (6). In the center of the bottom there is a platinum tube (2), which serves to drain the liquid. The vessel is closed with a lid (3), through which a wooden stick (8) passes, tightly fitting into the tube (2), and also a thermometer (4), which simultaneously serves as a stirrer for stirring the oil. The oil flows into the volumetric flask (7).



- Obtain an oil sample for analysis and verify the temperature at which the viscosity is determined. Depending on the type of oil tested, the viscosity is determined at 20, 50 or 100 °C.
- Oil is poured into the viscometer up to the level indicated by the pins.
- Heated to the specified temperature using a water bath.
- When the temperature has been established, lift the wooden stick (8) for a second to fill the platinum tube with oil, and lower it again.
- A volumetric flask (7) with a capacity of 200 ml is placed under the tube (2).
- Stir the oil with a thermometer (4), carefully rotating the lid and monitoring the temperature.
- After a five-minute exposure exactly at the set temperature, quickly remove the stick (8) and simultaneously start the stopwatch.
- When the flask is filled to the level, note the flow time.
- The experience is repeated two more times with a new portions of the same oil.
- In a separate experiment, determine the time of flow of the same volume of water at 20 °C (water number of the viscometer).
- Calculate the average oil flow time; discrepancies in values for parallel determinations should not exceed one second.
- Relative specific viscosity is expressed in degrees Engler as the ratio of oil flow time at a given temperature to water flow time at 20°C.

Determination of flash and fire points

The determination is carried out in a Marcusson apparatus in an open crucible.

- Oil is poured into a crucible with a diameter and a height of 4 cm, on the inner wall of which there are two marks. When testing oils with a low flash point (below 200°C), it is poured to the upper mark, when testing oils with a high flash point (above 200°C) - to the lower mark. This takes into account the expansion of the oil during heating: the oil level should not rise close to the edge of the crucible so that the burner flame does not get too close to the surface of the oil.
- The crucible is heated with a gas burner so that the temperature of the oil rises by 4-5°C per minute.
- From time to time, passing the flame of a small burner (rotating around a vertical axis) over the surface of the oil. The flame must not touch the surface of the oil to avoid local overheating.

- The temperature at which a flickering bluish flame appears on the surface of the oil, quickly extinguished when the burner is removed, is taken as the flash point. It characterizes the volatility of the oil and indicates the formation of a sufficient amount of vapor above the surface for a flash.
- Continue heating the oil and record the temperature at which the oil ignites over its entire surface and does not go out when the flame is removed. This is the ignition temperature. (As a rule, it is 20–50°C higher than the flash point).

Determination of the specific gravity

- The investigated oil is placed in a glass cylinder with a diameter of 5-6 cm and a height of 50 cm.
- A hydrometer graduated at 20°C with respect to water at 4°C is lowered into the cylinder.
- After 15 minutes, make a reading along the lower line of the meniscus. At the same time, the oil temperature is determined. In the case of dark oils, the reading is taken along the upper line of the meniscus and a correction is introduced by adding 0.0015 (if the hydrometer scale exceeds 16 cm) or 0.001 (if the scale is below 16 cm) to the hydrometer readings.
- To bring data to a temperature of 20°C subtract 0.00068 per each degree below 20°C or add 0.00068 per each degree above 20°C.

Example:	hydrometer reading at 19 °C	0.90550
	meniscus correction	0.00100
	temperature correction	0.00068
	specific gravity at 20°C	0.90582

REFERENCE INFORMATION

Mineral oils are one of the main products of oil refining. The corresponding distillates are obtained by distillation under vacuum of the fuel oil remaining after preceding distillation under atmospheric pressure of the products of oil cracking. The following classification of distillates according to distillation temperature is accepted:

- spindle distillate 230-250 ^{o}C;
- machine distillate 260-305 ^{o}C;
- light cylinder distillate 315-325 ^{o}C;
- heavy cylinder distillate 350-370 ^{o}C.

Along with this, synthetic oils are being used more and more, especially when it is necessary to ensure operation in specific conditions (very high or low temperatures, high vacuum, etc.). There are various types of synthetic oils: hydrocarbon, diester, polyalkylene glycol, fluorocarbon, silicone, etc.

The viscosity of the oil determines not only the quality of the liquid film in the friction units, but also the cooling of rubbing parts, the sealing of the piston rings in the cylinder, the ease of starting the engine, etc.

Dynamic (absolute) viscosity is the coefficient of internal friction. The SI unit of dynamic viscosity is Pascal-second = $N \cdot s/m^2$.

Kinematic viscosity is the ratio of dynamic viscosity to density at the same temperature. The SI unit of kinematic viscosity is m^2/s. (The kinematic viscosity of oils may be determined in a Pinkevich viscometer).

Relative viscosity is the ratio of oil flow time at a given temperature to water flow time at 20°C (Engler degrees).

The flash point depends on the device in which it is determined. The flash point can be determined in two types of devices - in a closed crucible and an open crucible. The test oil must be dehydrated to obtain correct results. In an open-type device, the flash point of oils is 20-30°C higher than in a closed-type device, due to the volatilization of part of the oil vapor. Low flash and ignition points indicate the flammability of the oil.

If the amount of oil to be tested is limited, its specific gravity is determined using a Westphal-Mohr balance.

According to their functional purpose, the following types of oils are distinguished: automotive, aviation, transmission, diesel, industrial, spindle, machine, cylinder, compressor, turbine, instrument oils for special purposes, etc.

TEST QUESTIONS

1. Mineral and synthetic lubricating oils.
2. Methods for cleaning and processing of the oil.
3. Various options for oil cracking.
4. Determination of the viscosity of lubricating oils.
5. Determination of the flash and ignition points of lubricating oils.

Analysis of lubricating oils

Full name
_____;
Group No _____;
date of the work _____; date of submission of the report _____.

Oil sample:

Viscosity determination temperature:

Oil flow time
1 measurement:
2 measurement:
3 measurement:
Average:

Water outflow time (20 °C):

Relative viscosity:

Flash point:

Ignition temperature:

Density:

WATER ANALYSIS IN THE CHEMICAL INDUSTRY

PURPOSE To master the methods of analysis of hardness and oxidizability of water used in the chemical industry.

SAFETY

- In case of skin contact with sulfuric acid solution, immediately wash the affected area with water, and then lubricate with 5% potassium permanganate solution or 10% sodium bicarbonate solution.
- For thermal burns, the burnt surface should be lubricated with burn ointment and bandaged with sterile material. The affected area can also be treated with a 5% solution of potassium permanganate or alcohol.

WORKFLOW

The work includes two stages:

- determination of water hardness;
- determination of water oxidizability.

Determination of water hardness

- Pipette 100 ml of test water into a 250 ml conical flask.
- Add 0.1 N HCl solution to remove bicarbonate ions. The point of neutralization is determined by indicator paper "Congo-rot" (to blue color).
- The sample is boiled for 5 minutes to remove CO_2, ammonia buffer is then added to the cooled solution to neutralize excess of HCl (until the congo-rot red color), then another 5 ml of ammonia buffer to create an alkaline environment.
- The solution is slowly titrated with a 0.05 N solution of Trilon-B in the presence of an acid chromium dark blue indicator (eriochrome) until the color of the solution changes from violet-red to blue.
- Calculate water hardness in mg-eq/l.

Determination of the oxidizability of water

1. Preparation of the flask:
   - Pour 100 ml of distilled water, 5 ml of 25% sulfuric acid and 8-10 ml of 0.01 N $KMnO_4$ solution into a 250 ml conical flask.
   - The mixture is heated to a boil, boiled for 5 minutes and poured 0.01 N solution of oxalic acid until discoloration. Then a 0.01 N solution of KMnO4 is added until a faint pink color appears.
   - The contents of the flask are poured out and the flask is not rinsed (!).

This preliminary operation serves to oxidize organic substances contained on the walls of the dishes, the presence of which would lead to erroneous results.

2. Determination of oxidizability:
   - Pipette 100 ml of test water into the prepared flask, add 5 ml of 25% sulfuric acid and 8 ml of 0.01 N $KMnO_4$ solution (V_1).
   - The contents of the flask are heated to a boil and boiled for 10 minutes from the moment the first bubble of steam appears.
   - If discoloration of the solution occurs, add a few more milliliters of $KMnO_4$ (V_2).
   - 10 ml of 0.01 N oxalic acid solution is poured from a burette (or pipette) to a hot liquid.
   - An excess of oxalic acid is titrated with 0.01 N $KMnO_4$ solution until a slightly pink color appears (V_3).

3. *Control of the concentration of potassium permanganate (potassium permanganate solution is very unstable, and each time it is necessary to determine the correction factor (K)*:
   - Into the flask, without pouring out the contents, pour 10 ml of 0.01 N oxalic acid solution.
   - Titrate with 0.01 N $KMnO_4$ until a faint pink color (V_4) appears.
   - Based on the results obtained (V_1, V_2, V_3, V_4) calculate the amount of oxidant consumed in terms of oxygen (mg O_2 / L H_2O).

REFERENCE INFORMATION

The use of water in the chemical industry is extremely diverse: as a solvent, for mechanical washing of gases and solid materials from impurities, for pulping bulk materials during their enrichment by flotation and other wet methods, etc.
Natural waters are usually divided into three types, which differ greatly in the presence of impurities:

1. Atmospheric water (rain, snow) containing dissolved oxygen, carbon dioxide, nitrogen and sulfur oxides, dust, etc.
2. Surface waters (river, sea, lake) contain, in addition to the impurities present in atmospheric water, diverse salts (bicarbonate, sulfate and chloride salts of calcium, magnesium, sodium, potassium, etc.).
3. Groundwater (spring, well, etc.) contains a variety of ions, like surface water, but usually they have less organic impurities and mineral suspensions.

Water containing less than 1 g of salts per 1 kg of water is called fresh, more than 1 g of salts per 1 kg of water is called salty.

The hardness of water is due to the compounds of magnesium and calcium dissolved in it. As the temperature rises, the salts of these metals precipitate and can form very hard deposits. Hardness largely determines the suitability of water for use in both industrial and domestic purposes.

Water hardness is divided into carbonate and non-carbonate.

Carbonate hardness is due to calcium and magnesium bicarbonates. When water is heated, dissolved bicarbonates decompose and carbonate hardness is significantly reduced. The amount of hardness by which it decreases after 10 minutes of boiling water is called "removable" or "temporary" hardness. Complete elimination of bicarbonate hardness during boiling does not occur due to the fact that calcium and magnesium carbonates are partially soluble in water. The hardness left after boiling water is called permanent hardness.

Non-carbonate (permanent) hardness is mainly due to sulfates and chlorides.

The sum of non-carbonate and carbonate hardness is the total hardness. The total hardness of water is expressed as the sum of mg-eq/l of calcium and magnesium ions contained in 1 liter of water. 1 mg-eq/l of hardness means the content of 20.04 mg/l of calcium ions or 12.16 mg/l of magnesium ions.

Water hardness is usually classified as follows:
- soft water - up to 3 mg-eq/l of calcium and magnesium ions;
- moderately hard (average) water – 3–6 mg-eq/l;
- hard water - more than 6 mg-eq/l.

The sensitivity of the trilonometric method for determining water hardness is 0.001 mg-eq/l. This method is applicable to waters of different salinity.

Trilon-B is the disubstituted sodium salt of ethylenediaminetetraacetic acid (abbreviated as Na_2H_2T). In an alkaline environment, it forms strong complexes with calcium and magnesium ions:

$$Na_2H_2T + Ca^{2+} \rightarrow Na_2CaT + 2H^+ ,$$

$$Na_2H_2T + Mg^{2+} \rightarrow Na_2MgT + 2H^+ .$$

Instability constants: for Ca – $2.7 \cdot 10^{-11}$; for Mg – $2.0 \cdot 10^{-9}$.

In trilonometric titration, the equivalence point is determined using the complexing properties of the indicator. It should be remembered that the color of the indicator also depends on the pH, which can change during the titration. To maintain pH = 10, a buffer consisting of NH_4OH and NH_4Cl is added to the solution. In a moderately alkaline environment, magnesium ions cause a particularly sharp change in the color of the indicator:

$$\underset{}{Mg^{2+}} + \underset{\text{blue}}{(HInd)^{2-}} \rightarrow \underset{\text{violet}}{(MgInd)^-} + H^+ .$$

After binding all calcium ions, Trilon-B extracts magnesium ions from their combination with an indicator:

$$\underset{\text{violet.}}{(MgInd)^-} + Na_2H_2T \rightarrow Na_2MgT + \underset{\text{blue}}{(HInd)^{2-}} + H^+ .$$

In this case, the color of the solution changes from violet-red to blue.

Calcium ions do not give such a clear change in the color of the indicator, so they can be determined trilonometrically only in the presence of magnesium ions, in total with them.

If the concentration of Trilon-B is exactly 0.05 N, each milliliter of solution corresponds to 0.05 mg-eq/l of calcium ion. The hardness of the analyzed water can be calculated by the formula

$$H = 0.05 \cdot K \cdot a \cdot 1000 / V \ \text{(mg-eq/l)},$$

where V is the volume of the analyzed water sample (100 ml); a is the volume of 0.05 N Trilon-B solution used for titration (mL); K is the correction factor for the normality of the Trilon-B solution.

1 мg/eq ~ 20.04 mg Ca^{2+} or 12.16 mg Mg^{2+}

The oxidizability of water is due to the presence in it of organic and easily oxidizable inorganic substances, such as Fe^{2+}, sulfites, nitrites, H_2S, etc. The integral characteristic of oxidizability is the amount of oxygen consumed for the oxidation of all impurities under certain conditions. It is expressed as the number of milligrams of oxygen consumed for the oxidation of impurities contained in 1 liter of water (mg O_2/L).

The concentration of $KMnO_4$ can be calculated by the formula

$$C_{KMnO} = C_{ox.acid} \cdot V_{ox.acid} / V_{KMnO} = 0.01 \cdot 10 / V_4.$$

The correction factor K can be calculated using the formula

$$K = C_{KMnO} / 0.01.$$

The value of oxidizability X can be calculated by the formula

$$X = (V_1 + V_2 + V_3 - 10) \cdot 10 \cdot K \cdot 0.08,$$

where 0.08 is the oxygen titer (1 mL 0.01n $KMnO_4$ ~ 0.08 mg O_2).

Water treatment for industrial processes depends on the degree of contamination. The main operations of water treatment are purification from suspended impurities and softening, in some cases also neutralization, degassing, disinfection.

Coarse softening (up to approximately 0.3 mg-eq/l) is carried out by adding lime or caustic soda and soda, while precipitating $CaCO_3$ and $Mg(OH)_2$. A more complete softening (up to approximately 0.03 mg-eq/l) is achieved by precipitation of impurities with sodium and magnesium phosphate ($Ca_3(PO_4)_2$ and $Mg_3(PO_4)_2$). With this reagent softening, silicon and iron compounds are also partially precipitated.

Natural water with low hardness is most effectively softened and desalinated using ion exchangers. For example, cation exchangers are used to absorb Ca^{2+}, Mg^{2+}, Fe^{3+} ions from water: sulfonated coal, various synthetic high-molecular resins containing sulfocarbonyl and other acidic groups.

The acceptability of water hardness for different needs depends on specific conditions. In drinking water, the taste threshold for calcium ion is in the range of 2–6 mg-eq/L, depending on the corresponding anion, and the taste threshold

for magnesium is much lower (in some cases, water with a hardness of 10 mg-eq/L is acceptable). Hard water has a bitter taste and negatively affects the digestive organs, the organoleptic properties of water correspond to a low level. However, soft water with a hardness of less than 2 mg-eq/L has a low buffer capacity and, depending on the pH value and other parameters, can adversely affect the corrosive activity of water conduits. Depending on the specific tasks, special chemical treatment of water is carried out in order to achieve an optimal and effective ratio between water hardness and its corrosiveness.

TEST QUESTIONS

1. Water in the chemical industry: main sources, areas of application, environmental problems.
2. Water hardness: removable, irremovable; carbonate, non-carbonate.
3. Trilonometric determination of hardness: chemical reactions, optimal pH values, interfering ions.
4. Oxidizability of water. Determination of the oxidizability of water.
5. Basic water treatment operations.

Water analysis in the chemical industry

Full name
_____;
Group No _____;
date of the work _____; date of submission of the report _____.

Water sample number _____

Volume of Trilon B used for titration _____

Volumes of $KMnO_4$:

V_1 =

V_2 =

V_3 =

V_3 =

Hardness of water:

Oxidizability of water:

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