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Department of Physical and Colloid Chemistry

KOZMA A.A., GOLUB N.P., ROBASHCHUK A.V., GOLUB Ye.O.

MEDICAL CHEMISTRY

METHODICAL INSTRUCTIONS
for the laboratory workshop
for students of the Medical Faculty №2
of the Master's degree program
(specialty 222-i Medicine)

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Authors:
Kozma Anton Antonovych, Candidate of Chemical Sciences (Ph. D. in Chemistry), Associate Professor at the Department of Physical and Colloid Chemistry, Educational and Research Institute of Chemistry and Ecology, Uzhhorod National University;
Golub Nelya Petrivna, Candidate of Chemical Sciences (Ph. D. in Chemistry), Associate Professor, Head of the Department of Physical and Colloid Chemistry, Educational and Research Institute of Chemistry and Ecology, Uzhhorod National University;
Robashchuk Antonina Vitaliivna, Assistant of the Department of Physical and Colloid Chemistry, Educational and Research Institute of Chemistry and Ecology, Uzhhorod National University;
Golub Yevheniy Olehovych, Senior Lecturer of the Department of Pharmaceutical Disciplines, Faculty of Medicine, Uzhhorod National University.

Reviewers:
Lendiel Vasyl Heorhiiovych, Doctor of Chemical Sciences, Professor, Director of the Educational and Research Institute of Chemistry and Ecology at Uzhhorod National University;
Kalii Vasyl Vasylovych, Doctor of Medicine, Professor, Dean of the Medical Faculty №2 of Uzhhorod National University.

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PREFACE

The discipline "Medical Chemistry" is one of the fundamental disciplines in higher medical education. This subject allows you to form a highly professional specialist in the specialty 222-i "Medicine". Such knowledge is essential in the practical work of a doctor. Knowledge of the theoretical foundations of "Medical Chemistry", which is based on a symbiosis of educational material from physical, colloidal and inorganic chemistry, is necessary for a deeper understanding and mastery of professional medical disciplines. While studying Medical Chemistry, students integrate knowledge of bioinorganic chemistry, medical and biological physics, and medical biology. This lays important foundations for their subsequent study of biochemistry, pharmacology, physiology, internal medicine, pathophysiology, as well as endocrinology, medical genetics, clinical pharmacology, clinical immunology and allergology, occupational diseases, hygiene disciplines and many others.

The "Methodical instructions for the laboratory workshop on the course "Medical Chemistry" for students of the Medical Faculty №2 of the Master's degree program (specialty 222-i Medicine) are developed in full accordance with the work program for the course "Medical Chemistry". This manual includes laboratory works for two Modules of this discipline. For all 14 topics of the program educational material of the course "Medical Chemistry", the authors of these guidelines have prepared 39 laboratory works. Within each topic, several different methods of experimental work are presented. This allows the teacher to choose the experimental works, to organize individual work for each student well, and to implement a differentiated approach to the educational process. At the same time, the educational material is presented logically and consistently.

Each topic is followed by a list of theoretical questions. Next, there are laboratory activities that involve performing experimental studies and making relevant physical and chemical calculations. Each methodology begins with a list of necessary equipment, the specific purpose of the work, and the learning objectives that students must solve. Each experimental work is accompanied by theoretical information, including basic concepts, laws, and calculation formulas. This is followed by a description of the experimental procedure and calculations. At the end of the methodology, tables with the necessary reference values and a sample of the final table with the results are presented.

The developed methodological guidelines will help to improve the training of students of the Medical Faculty №2 of Uzhhorod National University in the specialty 222-i "Medicine" in accordance with modern requirements.

The developed guidelines will also be useful for researchers and teachers of medical, chemical and related natural sciences.

RULES OF WORK AND SAFETY IN THE LABORATORY OF MEDICAL CHEMISTRY

Successful completion of the Laboratory workoratory workshop is possible only if you comply with the rules of work in the Laboratory workoratory, safety and health requirements.

1. During all work, be extremely careful, remembering that carelessness, inattention, insufficient familiarity with the devices and properties of substances can cause an accident.

2. Carry out chemical reactions only with such quantities and concentrations of acids, in such dishes and under such conditions as specified in the Laboratory workoratory work methodology (instructions).

3. During the work, observe cleanliness, silence, order and safety rules. Do not engage in extraneous conversations, work thoughtfully, and be careful. It is strictly forbidden for unauthorized persons to visit students working in the Laboratory workoratory or to distract them with other work. After completing the work, put the workplace in order and hand it over to the Laboratory workoratory supervisor (or Laboratory workoratory assistant).

4. It is strictly forbidden to pour residues of concentrated acids, alkalis, odorous and flammable organic liquids into the sink, throw paper, cotton wool, matches, pour sediments and other solids into the sink. Use specially designed utensils for this purpose.

5. When heating and boiling liquids in a test tube, point the opening in the opposite direction from the person working and from neighbors. Do not look into the test tube or flask, as accidents may result from the possible release of the heated substance. It is strictly forbidden to heat any vessels that are sealed.

6. Heat flammable liquids (ether, petroleum ether, gasoline, acetone, benzene, alcohol, etc.) only in a water bath, not over an open fire. Do not light a fire in the immediate vicinity of these substances. It is strictly forbidden to place glasses with flammable and combustible substances near a lit burner.

7. When working with acids, remember the rules for mixing sulfuric (sulfuric) acid with water: pour **sulfuric acid into water in small portions**, not vice versa (!). Do not suck up concentrated acids and alkalis with pipettes. Use a rubber syringe for this purpose. Take care not to get your face or clothes wet.

8. To avoid an explosion, metal sodium and potassium scraps must never be thrown down the sink. They must be collected in special glasses with kerosene.

9. Wear safety goggles when working with alkali metals, caustic alkalis, acids, explosives or mixtures thereof, as well as in all other work involving eye hazards.

10. Do not taste any substances in the Laboratory workoratory. When determining the odor, do not inhale the vapors that are released. Smell carefully,

without inhaling deeply, but only directing vapors or gases toward you with a slight movement of the hand.

11. It is strictly forbidden to work in the Laboratory workoratory alone in the absence of a Laboratory workoratory assistant, engineer or teacher.

ELIMINATION OF ACCIDENTS AND FIRST AID

In the event of a fire, immediately extinguish alcohol and gas burners, turn off electrical and electric heating appliances, remove all combustibles and vials with combustibles, quickly cover the fire with sand or a woolen blanket. Extinguish large fires with a fire extinguisher. Water can be used to extinguish Laboratory workoratory furniture (tables, shelves, stools, cabinets, etc.). It is strictly forbidden to pour water on ether, gasoline, benzene, and metallic sodium.

If the worker's clothing catches fire, immediately put a woolen blanket, coat or jacket over it and pour water on it very well.

In the event of a thermal burn, immediately apply cotton wool moistened with ethyl alcohol, a 5% solution of potassium permanganate or a 5% solution of tannin to the affected area, then apply a wet bandage made from the same solution. In case of very severe burns, cover the affected area with cotton wool moistened with linseed oil or burn ointment after treatment with alcohol.

In case of burns with acids or caustic alkalis, first rinse the burned area well with plenty of tap water, then, in case of acid burns, rinse with a 3% sodium bicarbonate solution, and when alkali gets on the skin, rinse with a 2% acetic acid solution. In case of severe skin burns with acids or alkalis, after rinsing with water, apply a bandage moistened with a solution of potassium permanganate or tannin, or lubricate with burn ointment or petroleum jelly.

If acid gets into the eyes, rinse them with plenty of water and then with a 3% sodium bicarbonate solution. In case of alkali in the eyes, first rinse them with plenty of water, and then with a saturated solution of boric acid, and then instill a drop of castor oil in the eyes.

In case of bromine skin burns, immediately wash off the bromine with plenty of water or alcohol and lubricate the burned area with a burn ointment or wipe it with glycerin. Phenol should be washed off the skin with alcohol or gasoline.

In case of chlorine or bromine poisoning, it is necessary to inhale alcohol or ammonia vapors and then go out into the fresh air.

In case of glass cuts, it is imperative to remove the remnants of the glass from the wound, lubricate the wounded area with a 3% alcohol solution of iodine and apply a bandage.

In all cases of injuries, burns and poisoning, after first aid, the victim is immediately sent to a clinic or hospital.

PROCESSING AND REGISTRATION OF LABORATORY RESULTS

Making a report

When preparing a report of the results of a Laboratory workoratory test, the student is obliged to comply with certain recording requirements.

In particular, the report on each Laboratory workoratory work is drawn up according to the following scheme:

1. Date of the Laboratory workoratory class.
2. Number of the Laboratory workoratory report.
3. The topic of the Laboratory workoratory class.
4. The name of the Laboratory workoratory work.
5. List of equipment required for the Laboratory workoratory work.
6. The purpose of the work.
7. Method of execution (write down the entire sequence of the experiment, draw a diagram of the installation, indicate the output of the calculation formulas).
8. Results of experiments and their processing (presented in the form of tables, relevant calculations and graphs of Laboratory workoratory work).
9. Conclusion of the Laboratory workoratory work.

Expressing measurement results in the form of tables and graphs

To analyze the results of research, experimental and calculated values are recorded in a table and displayed in graphs. As a rule, the experimental data are summarized in tables, then the corresponding mathematical equations are written down and calculations are made based on them. Then, graphs are drawn (if necessary). Next, the conclusion of the work is clearly formulated.

Making tables

Any measurement has at least two variables, one of which is specified (the independent variable - *the argument*), and the other or others are the dependent variable or variables (*the functions*).

In tables, the argument and functions should be placed horizontally, each in its own column. Each column should be given a title and units of measurement.

Building graphs

When processing experimental data, graphical methods are widely used to provide a visual illustration of the relationship between the quantities under study.

As a rule, a rectangular coordinate system is used to graphically represent measurement results. The graphs are drawn using graph paper (if necessary, special types of coordinate paper, such as logarithmic paper, etc.). If possible, the results of the experiment can be drawn up on a computer using graphic programs.

Selecting the scale

1. When drawing graphs, the scale is chosen so that the coordinates of any point can be easily and quickly determined. It is most convenient to choose a scale so that 1 cm is taken for 1, 10, 100...10n units or for one, two or five units.

2. The scale should be chosen so that the curve on the graph occupies almost all the free space between the coordinates (abscissa (x) and ordinate (y) axes). If there are several curves, the scale must be calculated so that all of them fit in the coordinate system field.

3. When applying the scale, specify the dimension of the values.

4. When choosing a scale, it is not necessary to start from a zero value. Sometimes the scale can start with such rounded values that all measured values are in the interval between these values. The points on the graphs should be drawn carefully and clearly, either by marking them with crosses or by circling them with circles, squares, triangles, etc. Points that belong to the same measurement group (for the same curve) are Laboratory workeled the same way, points from different groups are Laboratory workeled differently. The curve through the marked points should be drawn so that it is smooth and passes as close to all the points as possible, but does not necessarily intersect all the points.

Practical tips

Each work in the Laboratory workoratory goes through the following *stages*:

1. theoretical preparation of the student for the experiment (passing a colloquium on theoretical issues of the topic and the methodology of the Laboratory workoratory work);

2. preparation of the research object and the setup for the experiment and the experiment itself (i.e., the experimental part of the Laboratory workoratory work);

3. theoretical processing of the results of the experiment, graphing, evaluation of the accuracy of the results of the experiment, formulation of the conclusion of the Laboratory workoratory work.

In theoretical preparation for the experiment, using appropriate textbooks and lecture notes, you should

a) master the basic theoretical provisions of this Laboratory workoratory work;

b) master the laws that underlie the phenomenon under study, consciously and accurately formulate them and be able to apply them;

c) to work out well the mathematical equations that give a quantitative characterization of the phenomena and establish a certain mathematical relationship between the studied quantities;

d) study the structure of the devices and installations on which the experimental study will be carried out; using literary sources, you should provide diagrams of these devices (principle of operation), familiarize yourself with them in the Laboratory workoratory, know the name and purpose of each part;

e) when preparing for work in the Laboratory workoratory, one should think over the methodology of the experiment as best as possible;

f) prepare in advance the forms of tables where the results of measurements during the experiment will be recorded.

TOPIC 1. CHEMICAL THERMODYNAMICS AND BIOENERGY

Theoretical questions:

Thermodynamics, its content, basic concepts. Thermodynamic system: homogeneous, heterogeneous, open, closed, isolated. State parameters: extensive, intense. Thermodynamic processes: reversible and irreversible, equilibrium and non-equilibrium. Living organisms as open thermodynamic systems. Irreversibility of life processes. Internal energy and enthalpy. Warmth and work. And the law of thermodynamics, its mathematical expression, its conclusions. Application of the Law of Thermodynamics to Chemical and Biological Systems. Thermochemistry. Thermal effects of chemical reactions. Thermochemical equations. Standard heat (enthalpy) formation, neutralization, combustion, dissolution. Hess's law, conclusions from it. Energy characteristics of biochemical processes. Thermochemical calculations to assess the caloric content of food and compile rational and therapeutic diets. II law of thermodynamics, its wording and analytical expression. Entropy. United beginning of thermodynamics. Statistical character of the II beginning of thermodynamics. III law of thermodynamics and the existence of a natural beginning of temperature reference. Characteristic functions and thermodynamic potentials. Differential equations for thermodynamic potentials. Criteria for equilibrium and directionality of processes in chemical and biochemical systems. Application of the basic positions of thermodynamics to living organisms. ATP as a source of energy for biochemical reactions. Macroergic compounds. Energy conjugation in living systems: exergonic and endergonic processes in the body.

Laboratory work

1.1. DETERMINATION OF THE HEATING VALUE OF GASES USING A JUNKERS CALORIMETER

For work you need: Junkers calorimeter; dry alcohol; contact thermometer; barometer; technical scales; measuring cylinder for 1 - 2 liters; stopwatch.

The purpose of this work is to determine the calorific value of solid, liquid and gaseous combustibles. For this purpose, a calorimeter of the Junkers system, the so-called manual calorimeter, is used, which is shown in Fig. 1.

It can burn gases (methane, ethane, propane, butane), liquids (alcohols), and solids (sugar, dry alcohol, etc.). In each case, a special device is made at the inlet of the calorimeter to burn the substance: either in a gas burner (as shown in Figure 1), or in a spirit burner (liquid substances), or on a special stand to burn solids (they are placed on a metal mesh covered with asbestos). Depending on the aggregate state of the substance whose caloric value is being determined, the calorific value is either per unit volume (gaseous substances) or per unit mass

(liquid and solid substances). The amount of gas burned is measured using a gas meter, while the amount of liquid or solid that was burned during the experiment is determined by the difference in mass at the beginning and end of the experiment. In the latter case, the spirit bottle is weighed before the experiment and after the experiment (with the alcohol) and the difference in mass of the evaporated and burned liquid alcohol is found. In the case of a solid substance (dry alcohol), several cubes of the substance are weighed before the experiment, then placed on a stand at the entrance to the calorimeter and set on fire. After a certain time, the flame is extinguished, and after the residual mass of dry alcohol has cooled, it is weighed. The difference in weight is used to determine the mass of dry alcohol that was burned during the experiment (namely, in the process of heating 1 kg of water to a certain temperature).

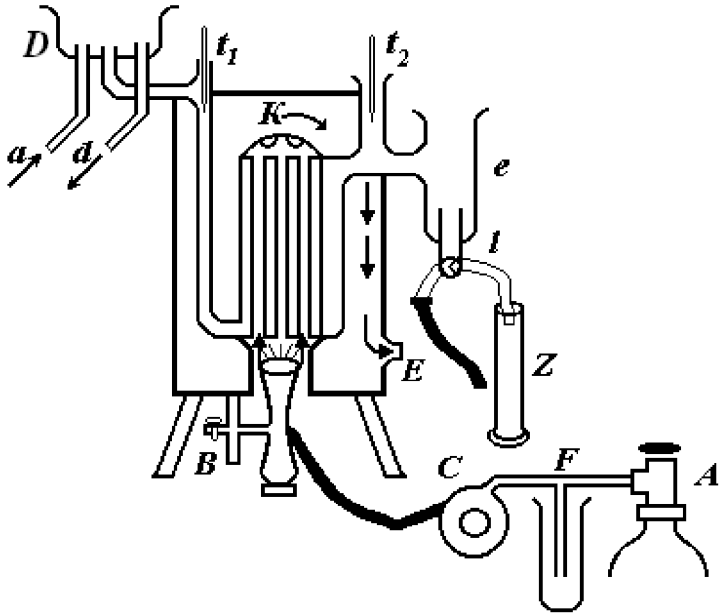


Figure 1. Junkers calorimeter.

A distinction is made between the higher and lower calorific value of a fuel. The higher calorific value is the amount of heat released during the combustion of organic matter to form liquid water (i.e., the heat released during water condensation is also taken into account).

The lower calorific value of a substance is the heat of combustion with the formation of vaporized water (when part of the heat is carried away with the combustion products in the form of water vapor).

The purpose of this work is to determine the higher calorific value of a substance. The calorific value of solids and liquids is determined in a calorimetric bomb at a constant volume, while the calorific value of gaseous substances is determined in a Junkers calorimeter at a constant pressure.

However, this calorimeter can also be used to measure the caloric value of solids and liquids with a little modification.

The principle of operation of such an installation is as follows: gas from the cylinder enters the device *C*, from where it passes into the burner, which is fixed in the lower part of the calorimeter *K*, where it burns. In the case of solids, instead of a burner, a special stand is placed on which the substance under test (dry alcohol) is placed. Water is circulated through the calorimeter throughout the experiment. From the tap through the tube a, the water is directed to the cup *D*, from where it enters the middle of the calorimeter under a constant pressure, exits into the cup *e*, and can be discharged through the tap 1 into the ebb or measuring cylinder. Excess water from the cup *D* is drained to the sump via the tube *d*.

The combustion products rise through the tubes in the calorimeter body and give off heat to the circulating water. As a result, the temperature of the water passing through the calorimeter rises. The cooled combustion products descend and exit through the outlet tube *E*. The temperature of the inlet and outlet water is measured using thermometers t_1 and t_2.

For proper operation of the unit, it is important that it is in a vertical position. This is controlled by the level on the outer wall of the calorimeter.

The mass of the substance that is burned is determined by the difference between the initial mass m_o and the final mass of the fuel m_t: $\Delta m = m_o - m_t$.

Work progress

Turn on the tap and let the water flow into the calorimeter. Using the mark on the tap *l*, turn it so that the water leaves the calorimeter at low tide.

Set fire to dry alcohol (unweighted) and within 10-15 minutes achieve a constant temperature of the inlet and outlet water, all the while observing the burning of dry alcohol. The temperature of the inlet and outlet water is observed on both thermometers and recorded every minute (for 5 minutes). From the data obtained, the average temperatures of the incoming and outgoing water are found separately. After the temperature of the cold and heated water has stabilized, the weighed dry alcohol is ignited under the calorimeter. Then the tap head is quickly turned so that the water flows into the 1 liter cylinder *Z*. When exactly 1 liter of water flows into the cylinder, the tap is turned off. The calorific value of the substance is calculated from the mass of dry alcohol that burned when exactly 1 liter of water was heated and the mass of water that was poured into the cylinder (1000 g) and the difference in thermometer readings. For the calculations, you also need to know the barometric pressure, the elasticity of water vapor at a given temperature, and the room temperature.

The amount of heat (in J) consumed to heat water during the combustion of a given mass of fuel is calculated by the formula

$$g = cm(T_2 - T_1),$$

where
m is the mass of water, g;
c is the heat capacity of water, J/g;
T_1 is the temperature of water at the inlet of the calorimeter, K;
T_2 is the temperature of water at the outlet of the calorimeter, K.

The caloric value of dry alcohol per 1 kg of fuel is calculated by the formula

$$Q = \frac{g}{\Delta m} 10^3.$$

The experiment is performed at different water flow rates and the average calorific value of dry alcohol is calculated. The mode of operation is specified by the instructor. The results are recorded in Table 1:

***m* =** ***h* =**
***g* =** ***T, K* =**
***H* =** ***Q* =**

Table 1

The initial mass m_0, kg	The final mass m_t, kg	The mass Δm_r, kg	Water temperature T, K		Average water temperature T, K	
			incomin	outgoin	incomin	outgoin

The elasticity of water vapor as a function of temperature is shown in Table 2.

Table 2

T, K	h, mm Hg	T, K	h, mm Hg
287,0	11,987	292,5	16,99
287,5	12,382	293,0	17,535
288,0	12,783	293,5	18,085
288,5	13,205	294,0	18,650
289,0	13,634	294,5	19,231
289,5	14,076	295,0	19,827
290,0	14,530	295,5	20,440
290,5	14,997	296,0	21,068
291,0	15,477	296,5	21,714
291,5	15,971	297,0	22,377
292,0	16,477	298,0	23,765

Laboratory work
1.2. DETERMINATION OF THE HEAT OF DISSOLUTION AND HEAT OF SALT HYDRATION

For work you need: calorimeter; Beckman thermometer; stirrer; salt test tube; distilled water; stopwatch; dissolving salt; current source; ammeter; voltmeter; electric heater.

Objective:

1. Determination of the heat capacity of the calorimetric system by the method of electric heating.
2. Determination of the specific heat capacity of salt dissolution.
3. Determination of the integral heat of dissolution, i.e. the thermal effect of dissolving one mole of salt in such an amount of solvent when Q is constant - Qint.
4. Determination of the heat of hydration of salt - specific and referred to one mole of salt.

The thermal effect of dissolving a salt in a large amount of water is equal to two thermal effects: a change in the heat capacity of the salt when the crystal lattice is destroyed Q_1, which is associated with heat absorption, and a change in the heat capacity when the particles dissolve in the solvent, which is associated with heat release Q_2:

$$Q = Q_1 + Q_2 .$$

Depending on the ratio of the respective effects, the thermal effect of dissolution can be positive or negative. The thermal effect of dissolving salts in water is mostly endothermic, i.e., the dissolution process is accompanied by heat absorption and the solution temperature decreases. The exothermic thermal effect is very rarely observed. The heat of dissolution of the salt under study in a given solvent can vary by changing the amount of salt and solvent taken.

By determining the heat of dissolution of salts, the heat of hydration of the salt can be determined. The heat of hydration is the amount of heat that a system must receive to form one gram-mole of solid crystallohydrate from a solid anhydrous salt and a corresponding amount of water. If you determine the heat of dissolution of a solid anhydrous salt and the heat of dissolution of a crystalline hydrate in sequence, you can find the heat of hydration of the salt from their difference

$$Q_{hydr.} = Q_{D.} - Q_{C.},$$

where

$Q_{D.}$ is the heat effect of dissolving an anhydrous salt;

$Q_{C.}$ is the thermal effect of dissolution of a crystalloid from a water molecule.

To determine the heat of dissolution, a calorimeter with an electric heater is used. When determining the heat capacity of a system, it is assumed that a certain amount of heat is provided to the system by electric heating Q_{theor} and the corresponding temperature change is calculated Δt.

Work progress

To conduct the experiment, assemble the device (calorimeter) (Fig. 1). Place 300 g of distilled water in a beaker (i.e., pour 300 ml, given that the density of water at the temperature of the experiment is approximately 1). The beaker with the stirrer is placed in the calorimeter and closed with a lid. A heating coil is attached to the calorimeter lid. Weigh a certain amount of salt (on a technical balance), pour it into a dry test tube and insert it into the calorimeter through the hole in the lid so that the salt takes on the temperature of the calorimeter. (The salt and the weight of salt are specified by the classroom teacher). When the calorimeter is assembled, the Beckman thermometer is set up. The thermometer is immersed in water through the hole in the lid and the level of mercury in the capillary is observed. The mercury level should be at the bottom of the scale. (The thermometer should not touch the coil, beaker walls, test tube, or stirrer.) If the mercury level is higher than one degree or the entire capillary is filled with mercury, it means that there is a lot of mercury in the lower reservoir and the excess must be poured into the upper reservoir.

To do this, the thermometer is placed obliquely so that the lower reservoir is higher than the upper reservoir, and heated slightly (by touching the lower reservoir with your hand). When some of the mercury has passed into the upper reservoir, the mercury column is broken. To do this, hold the lower end of the thermometer in your hand and tap the mercury in the capillary with a light tap on the Table. The transfusion is performed until the mercury stops in the middle of the Beckman thermometer scale under these conditions. If the mercury is below the scale divisions or does not fill the capillary at all, it means that under these conditions there is not enough mercury and it needs to be transferred from the upper to the lower reservoir. Then quickly turn the thermometer over with the upper reservoir down and connect the mercury. Then carefully turn the thermometer over, holding it tilted so that the reserve reservoir is above the main reservoir. When the required amount of mercury has passed from the upper reservoir to the lower reservoir, the mercury column is broken as described above.

The adjusted thermometer is inserted into the device and the electrical circuit is assembled (Fig. 1). The current source is switched on only after the electrical circuit has been checked by the classroom teacher.

After that, the experiment is started. Stirring the liquid in the calorimeter, turn on the stopwatch and start reading the temperature on the Beckman thermometer. The temperature changes due to heat exchange with the external environment. The countdown is carried out every half minute for 5 minutes – this

is the initial period. After recording the time and thermometer readings of the last reading of the initial period, then turn on the current for 3 minutes and continue to read the temperature every half minute. At the same time, the water in the glass is stirred to ensure uniform heating. Starting from the moment the current is turned on, there is an uneven temperature change – this is the main (main) period. Then the current is turned off and a uniform temperature drop is recorded over the next 5 minutes (every half minute) – this is the final period.

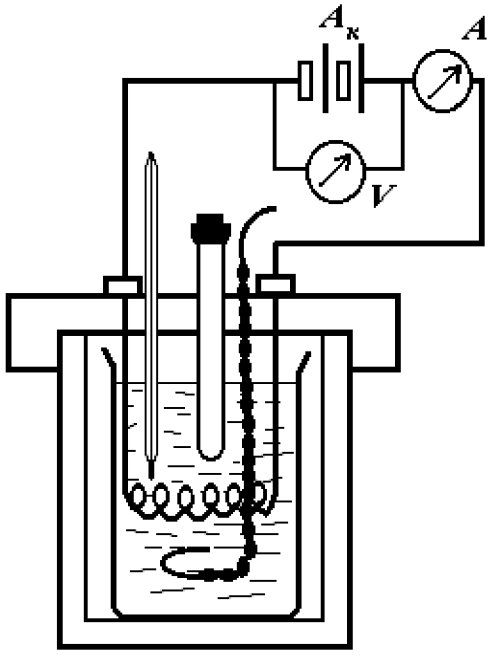


Fig. 1.

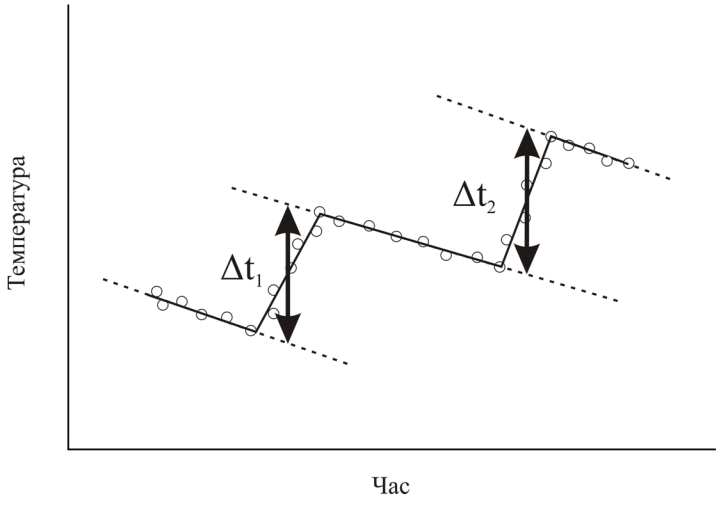


Fig. 2.

The current is turned on and off three times and the readings are recorded each time. After the third time the current is turned off, while continuing to read the temperature, quickly pour the salt from the test tube into a beaker of water

and mix vigorously. The salt will dissolve quickly. For a more accurate determination of Δt heating and Δt dissolution, the results of three periods and four cycles of continuous reading of temperature change over time (three cycles and one cycle of salt dissolution) are plotted on a graph (Fig. 2).

Time is plotted on the abscissa axis and temperature (i.e., Beckman thermometer readings) on the ordinate axis. The lines of the initial and final periods are extrapolated, i.e., extended to the middle of the graph. The time interval of the main period is divided in half and from this point a line parallel to the ordinate axis is drawn until it intersects both extrapolated lines. The interval between the two intersection points corresponds to the temperature increase Δt for a given cycle. Similarly, Δt is found for all cycles of the experiment.

The actual temperature Δt_{heat} is found as an arithmetic mean

$$\Delta t = \frac{\Delta t_1 + \Delta t_2 + \Delta t_3}{3}.$$

The Δt of salt dissolution is determined in the same way. If, after heating, the change in the dissolution temperature of the salt cannot be measured further on the thermometer scale, then the experiment is stopped after heating. The thermometer is adjusted to the appropriate scale divisions and a salt dissolution cycle is performed.

Knowing the Δt of heating, calculate the amount of heat received by the water during its heating

$$Q_{\text{exp}} = cm \cdot \Delta t_{heat},$$

where c is the specific heat capacity of water, which is taken as a unit;
t is the mass of water (corresponding to its volume of 300 ml), i.e. 300 g.

Substituting these values, we obtain

$$Q_{\text{exp}} = 300 \cdot \Delta t_{heat}.$$

This amount of heat is less than Qtheoretical due to heat absorption by the system. Qtheoretical can be calculated based on the Joule–Lenz law.

$$Q_{theor} = I \cdot U \cdot t \text{ (J)}.$$

Measuring the current I in amperes, the voltage U in volts, and the time of current transit t in seconds, the amount of heat in Joules is determined.

The amount of heat obtained experimentally is subtracted from the calculated theoretical amount of heat, and the difference is converted to 1 K. This will be the amount of heat absorbed by all parts of the calorimeter, Ck.

It is calculated based on the proportion

$$\Delta t_{heat} - (Q_{theor} - Q_{exp}),$$

$$1K - C_k,$$

$$C_K = \frac{Q_{theor} - Q_{exp}}{\Delta t_{heat}}.$$

The total heat capacity of the system is equal:

$$C_{syst} = C_{liq} + C_к,$$

where

$C_{liq.}$ is the heat capacity of the calorimetric fluid, which is equal to:

$$C_{liq.} = cm \cdot 1K,$$

C is the specific heat capacity of the solution, approximately equal to one.

The mass of the solution is taken to be equal to a volume of 300 ml, i.e. 300 g.

Then $C_{liq.}$ can be taken as 1293.6 J, hence

$$C_{syst.} = 1293,6 + C_к.$$

Using the graph $\Delta t_{calc.}$ and calculating the heat capacity of the calorimetric system, the thermal effect of dissolving a given salt sample is found:

$$Q_{sol.} = C_{syst} \cdot \Delta t_{sol.}.$$

The thermal effect of dissolution per gram of dissolved substance corresponds to the specific heat of dissolution:

$$Q_{spec.} = Q_{sol.} / g,$$

where g is the weight of salt, g.

The molar heat of dissolution of a salt is equal to:

$$Q_M = Q_{spec.} M,$$

where M is the molar mass of the salt, g/mol.

To determine the molar heat of hydration, find the molar heat of dissolution of an anhydrous salt and the crystalline salt hydrate. The difference of the molar heats obtained is the heat of hydration

$$Q_{hydr.} = Q_{мб.} - Q_{мк.}.$$

The crystalloid is not dissolved in 0.3 kg of water, but in an amount less than the amount contained in the crystalloid itself.

The correctness of the results is checked by the classroom teacher.

The results of the experiment are recorded in Tables 1 and 2:

Table 1

Amount of salt, 10^{-3} kg	Mol. mass of salt, kg/kmol	Weight of crystal., 10^{-3} kg	Mol. Mass of crystalohydrate, kg/kmol	Solvent volume, 10^{-6} m^3	Amperage, A	High-voltage, V	Current flow time, s	Q theor., J	Temperature change when heated, K	Average Temperature change when heated, K	Q practical, J	Heat capacity of system, J
					I_1= I_2= I_3= I_{av}=	U_1= U_2= U_3= U_{av}=	t_1= t_2= t_3=		Δt_1= Δt_2= Δt_3=			

Table 2

Change dissolutin temperature, K		Heat of dissolution, J						Warmth hydration, J		
		Salt			Crystallohydrate					
Salt	Crystal	Q	Q_T	Q_M	Q	Q_T	Q_M	Q	Q_T	Q_M

Laboratory work
1.3. DETERMINATION OF THE CONCENTRATION (NORMALITY) OF A STRONG ACID WHEN NEUTRALIZED WITH A STRONG ALKALI

For work you need: calorimeter; Beckman thermometer; acid vessel; stirrer; 0.2 N acid solution; 0.2 N alkali solution; distilled water; stopwatch; solutions of unknown acid; 500 ml beaker.

Objectives:

1. Familiarization with methods for determining the heat capacity of a calorimetric system
2. Determination of the thermal effect of the acid neutralization reaction with alkali
3. Determination of the thermal effect of dilution
4. Calculation of acid concentration by heat of neutralization.

It is known that the neutralization of one gram equivalent of any strong acid with a strong alkali in dilute solutions releases 137000 calories of heat. The stability of the heat of neutralization for these acids and alkalis is explained by the fact that in dilute solutions, the neutralization reaction is reduced only to the formation of water from H^+ and OH^- ions.

For example:

$$H^+ + Cl^- + Na^+ + OH^- = Na^+ + Cl^- + H_2O + Q_{neutr}$$

or

$$H^+ + OH^- = H_2O$$

That is, regardless of the nature of the acid anion and alkali cation, the process proceeds with the formation of water molecules from the ions.

When a weak acid is neutralized by a strong alkali or vice versa, the thermal effect of the reaction depends on the nature of the substances that react. The degree of dissociation of such acids and alkalis is insignificant, so the neutralization process is accompanied by a single process of dissociation of the weak acid or alkali into ions.

Since the thermal effect of dissociation can be positive or negative, the total effect of the reaction will be greater or less than 13700 calories.

The work begins with determining the heat capacity of the calorimetric system, which depends on the heat capacity of the liquid in the calorimeter (acid and alkali) and on the heat capacity of the calorimeter components (calorimeter, stirrer, acid vessel, thermometer). The heat capacity of the calorimetric system is equal to:

$$C_{syst.} = AC_1 + C$$

where

$C_{syst.}$ is the heat capacity of the system;

A is the weight of the calorimetric liquid;

C_1 is the specific heat capacity of the liquid; C is the heat capacity of the calorimetric system without liquid.

The thermal effect of the neutralization reaction carried out in this calorimeter is equal to:

$$Q = \Delta t \cdot C_{syst.}$$

where

Δt is the temperature change of the calorimetric liquid during the experiment.

In our case, the temperature increase is due to the heat released during neutralization. $C_{syst.}$ is the amount of heat required to heat the calorimetric system by 1 °C.

So, to find the thermal effect of the reaction, you need to determine the heat capacity of the system and the corresponding value of Δt.

Work progress

The practical part of the work is to determine the value of Δt. When determining the heat capacity of a system, it is assumed that a certain amount of heat is supplied to the system (a neutralization and dilution reaction is carried out with HCl 0.2 N, NaOH 0.1 N) and the temperature change Δt is recorded.

This method is the most appropriate in the Laboratory workoratory.

Therefore, if we take a certain amount of a strong acid of a precisely defined concentration and a strong alkali for neutralization, we will obtain a certain thermal effect. This thermal effect will be less than the theoretically calculated one, due to the fact that part of the heat released is used for heat exchange with the external environment.

The difference between the amount of heat calculated theoretically and obtained in the experiment represents the heat absorbed by the system when it is heated by Δt.

To calculate the heat capacity of a system, the resulting heat difference must be converted to one degree Celsius. Thus, to determine the heat capacity of a system, you need to do the following:

- carry out a neutralization reaction in a calorimeter with 150 ml of 0.1 N NaOH and 75 ml of 0.2 N HCl;
- carry out the process of diluting the acid with an alkali solution;
- find $\Delta t_{neutral}$ and $\Delta t_{dissolved}$ from the graph;
- calculate the amount of heat released during the reaction; it is equal to the product of Δtneutr. by the number of ml of liquid involved in the neutralization

$$Q_{neut.} = V_{liq} \cdot \Delta t_{neut.}$$

- calculate the heat of dilution of an acid with an alkali solution; it is equal to $\Delta t_{dil.}$ multiplied by the number of ml of liquid involved in the reaction:

$$Q_{diss.} = V_{liq.} \cdot \Delta t_{diss.}$$

The specific heat capacity of solutions is taken to be unity because solutions of concentration

$$Q_{\exp.} = Q_{neut.} - Q_{diss.} = V_{liq.}\left(\Delta t_{neut.} - \Delta t_{diss.}\right)$$

- calculate the amount of heat that should be released during the neutralization of a given amount of acid, based on the equation:

$$HCl + NaOH = Na^{+} + Cl^{-} + H_2O + 13700cal$$

$$Q_{theor.} = \frac{0{,}0365 \cdot 0{,}2 \cdot 75 \cdot 13700}{36{,}5} = 205{,}5cal$$

- the amount of heat obtained practically is subtracted from the amount of heat calculated theoretically; this difference gives the amount of heat spent on heat exchange with the environment

$$Q_{sorp.} = Q_{theor.} - Q_{pract.} = 205{,}5cal - Q_{pract.}$$

- the difference is calculated by $1^{o}C$ to obtain the heat capacity of the system, except for the heat capacity of the liquid

$$\Delta t - \left(Q_{theor.} - Q_{pract.}\right)$$

$$1^{0} - C$$

then

$$C = \frac{Q_{theor.} - Q_{pract.}}{\Delta t}$$

where

C is the heat capacity of the calorimetric system without liquid;

$C_{syst.}$ is the heat capacity of all parts of the system, taking into account the heat capacity of the liquid, which is equal to

$$C_{syst.} = V_{liq} C_1 + C$$

The heat capacity of a calorimetric liquid is taken to be equal to the volume of the liquid, since the specific heat capacity of the liquid is considered equal to unity.

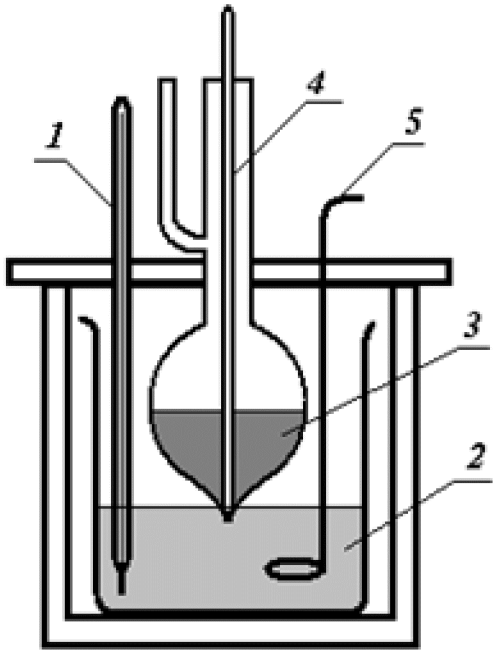


Fig. 1.

The neutralization reaction is carried out as follows: the required amount of alkali is poured into a glass beaker located in the calorimeter, a vessel with the required amount of acid, a stirrer and a Beckman thermometer are inserted there, as shown in Fig. 1.

On the meadow, which is poured into the calorimeter, the Beckman thermometer is set so that the mercury is in the lower part of the scale, because during the neutralization reaction, an increase in temperature should be expected. The method of setting the Beckman thermometer is given in the work "Determination of heat of dissolution and heat of hydration of salt". In order for the thermometer to warm up to the ambient temperature, the assembled unit is left for 5-10 minutes. Only after that, they begin to count the temperature using a thermometer, recording readings every half minute. In order to calculate the heat exchange of the calorimeter with the external environment and determine the actual temperature change during the process, the entire calorimetric experiment is divided into three periods:

1. The initial period, which lasts 5 minutes (10 counts of a constant temperature value or a uniform change in temperature).

2. The main (main) period, that is, the time of the neutralization reaction in the calorimeter.

3. The final period, which lasts 5 minutes (10 counts of a constant temperature value or a uniform change in temperature).

When 10 measurements of uniform temperature change are made in the initial period, we carry out the neutralization reaction. For this, the glass rod 4, which serves as a shutter in the vessel 3 for acid, is removed and all the acid is

allowed to flow into a glass with alkali. The solution is vigorously stirred. As in the initial period, the recording of thermometer readings continues. At the end of the main and the beginning of the final period, the first reading of the uniform temperature change, which is set again, is taken. In the final period, as in the initial period, 10 temperature readings are also taken (within 5 minutes).

When an acid solution is poured into an alkali solution, in addition to the neutralization reaction, the acid dilution process occurs simultaneously when it is poured into the alkali solution and the alkali is diluted by the acid. Since the volume of alkali is large and changes little when acid is poured into it, this process of alkali dilution is not taken into account. However, the process of acid dilution with alkali must be taken into account. The resulting effect can be determined by pouring a given volume of acid into a volume of pure water (dist. H_2O) equal to the volume of the alkali solution. In practice, this is done as described for the neutralization reaction. In this case, the effect of neutralization is excluded and the change in temperature characterizes only the effect of dilution.

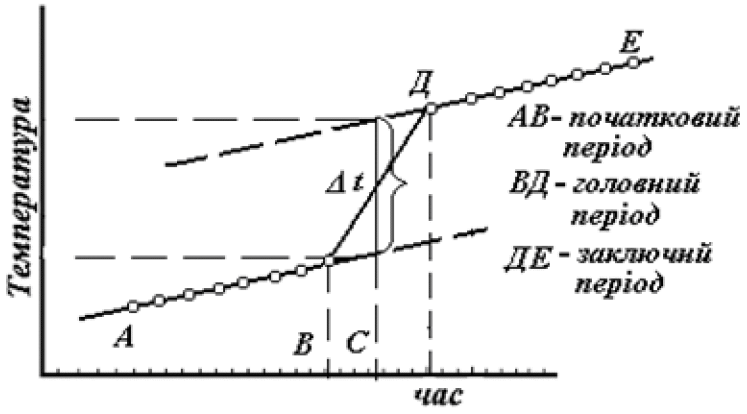


Fig. 2.

To calculate the amount of temperature increase, a graph is constructed, where the temperature is plotted on the ordinate axis, and time in minutes is plotted on the abscissa axis (Fig. 2).

Since during the reaction there is a constant heat exchange between the calorimeter and the external environment, it is necessary to make a correction for the temperature change obtained during the reaction. For this, the lines of the initial and final periods are graphically extrapolated on the diagram, that is, both lines continue to the middle of the diagram. Points B and D are determined on the diagram, which indicate the end of the uniform temperature change before the experiment and the beginning of a new uniform temperature change after mixing.

The time interval between these periods is divided in half (point C) and a straight line parallel to the ordinate axis is drawn through the resulting point C to

the intersection with both extrapolated straight lines. The segment Δt between the two crossing points is the real temperature rise. Thus, Δt is found for the neutralization reaction and for the dilution process.

Knowing Δt, calculate the heat capacity of the C system, as indicated above. The amount of acid, the concentration of which needs to be determined, and the amount of alkali are taken according to the instruction of the class leader.

The amount of acid and alkali is taken in such a way that the total volume of the calorimetric liquid is equal to 225 ml. When we know the heat capacity of the system and $\Delta t_{neutral.}$, $\Delta t_{dil.}$, we can calculate the amount of heat released during the neutralization reaction and the dilution process using the formulas:

$$Q_{neut.} = C_{syst.} \cdot \Delta t_{neut.}$$

$$q_{diss.} = C_{syst.} \cdot \Delta t_{diss.}$$

Knowing Q and q, you can determine the normality of the tested acid using the formula:

$$N = \frac{(Q - q) \cdot 1000}{13700 \cdot V}$$

where N is the normality of the acid; Q - heat of neutralization; q - heat of dilution; 13700 – thermal effect of neutralization of 1 gram-equivalent; V is the volume of acid taken for neutralization.

Having determined the concentration of the tested acid, it is possible to calculate the weight of the acid involved in neutralization (a). The thermal effect of acid neutralization, attributed to 1 gram-equivalent, is calculated by the formula:

$$\Delta H = \frac{\Delta t_{neut.} \cdot C_{syst.} \cdot N}{a}$$

where N is the gram-equivalent of the acid; a is concentration of acid.

The obtained results of the experiment and the calculated data are recorded in Table 1.

Table 1

Δt_{neutr}	Δt_{solv}	Volume of acid, V	Heat of neutralization, Q	Dilution heat, q	Heat capacity of system, $C_{syst.}$	Normality of acid, N	Acid concentration, a	Thermal effect, ΔH

QUESTIONS FOR SELF-CONTROL:

1. What do "thermodynamics" and "chemical thermodynamics" study? Explain their content, formulate the basic concepts.
2. What is called a "thermodynamic system"? What are the types of thermodynamic systems? Give examples.
3. What is called a "thermodynamic process"? What are the types of thermodynamic processes? Give examples.
4. Define the concept of "system state parameters" and give their classification. What properties belong to them? Give examples.
5. Write the equation of state of a thermodynamic system, explain it.
6. What is the "internal energy" of the system? Describe it.
7. Define what is the "enthalpy" of a thermodynamic system? Describe it. How does it differ from the "internal energy" of the system?
8. What is called the "heat" of a thermodynamic system, how is it denoted? Describe its types.
9. Formulate what is the "work" of the system, how is it designated? Describe its types. How does it differ from the "heat" of the system?
10. What is called the "heat capacity of substances"? What are the types of heat capacity? Write down the appropriate calculation formulas for the heat capacity of a substance.

11. What is the name of the first law of thermodynamics? Give its basic formulation. Write the mathematical expression of the first law of thermodynamics.
12. Formulate conclusions from the first law of thermodynamics.
13. Describe living organisms as open thermodynamic systems.
14. Describe the irreversibility of life processes from the standpoint of the laws of chemical thermodynamics.
15. Define the concepts of "reversible", "irreversible", "equilibrium" and "non-equilibrium" processes. Explain them and give examples.
16. Write the calculation formulas for the work and heat of different types of processes. Give a graphical representation of the corresponding work of the thermodynamic process.
17. What is "thermochemistry", "thermal effect of a chemical reaction" and "thermochemical equation"? What are the types of thermal effects of chemical reactions, give. Write down the formulas for theoretical calculation of the thermal effects of chemical reactions.
18. Define the concepts: "heat of formation", "heat of combustion", "heat of dissolution", "integral heat of dissolution", "heat of neutralization" and their designation in thermochemistry.
19. Formulate Hess's law and its conclusions. Write down the corresponding calculation formulas.
20. Write the equation of Konovalov. Explain it and its practical use in thermochemistry.
21. How is the dependence of the thermal effect of chemical reactions on temperature?
22. How is the caloric value of food and the preparation of rational and therapeutic diets based on thermochemical calculations?
23. What is the name of the second law of thermodynamics? Give its basic formulation. Write the mathematical expression of the second law of thermodynamics.
24. What is the "entropy"?
25. Write down the unified beginning of thermodynamics. What is its practical significance? Explain the statistical nature of the second beginning of thermodynamics.
26. What is the name of the third law of thermodynamics? Give the main formulations of the third law of thermodynamics and the existence of the natural beginning of the temperature reference.
27. What is called "characteristic functions"? What values belong to them?
28. What are thermodynamic potentials? What quantities belong to them and why?
29. Write the differential equations for the thermodynamic potentials of the system.

30. Formulate and write down the criteria for the direction of processes in chemical and biochemical systems.
31. What are the general conditions of equilibrium and their expression through characteristic functions?
32. How to apply the basic principles of thermodynamics to living organisms?
33. Describe ATP as a source of energy for biochemical reactions.
34. What are the “macroergic compounds”?
35. Explain the energy conjugation in living systems?
36. How do exergonic and endergonic processes occur in the body?

TOPIC 2. SURFACE PHENOMENA AND ADSORPTION

Theoretical questions:

Surface phenomena and their significance in biology and medicine. Surface tension as a specific surface energy at the boundary of the partition of two phases. Units of surface tension measurement. Factors affecting the surface tension of pure fluid. Surfactants and surfactants, their characteristics. Features of the structure of their molecules, examples. Surface tension isotherms. Rule Traube - Duklo. Methods for determining surface tension. Basic concepts of sorption. Gibbs equation. Surface activity. Positive and negative adsorption. Understanding the structure of biological membranes. Physico-chemical basis of adsorption therapy (hemosorption, plasmosorption, lymphosorption, enterosorption, application therapy). Immunosorbents. Langmür's monomolecular theory. Conclusions from it. Henry's equation. Freindlich's equation. Their practical application. Adsorption from electrolyte solutions. Paneta-Fajans rule. Ion exchange. Nikolsky equation. The use of zeolites of Transcarpathia as natural sorbents. The role of adsorption and ion metabolism in the processes of plant life and or organisms. Chromatography. Classification of chromatographic methods of analysis based on the aggregate state of phases, technique of execution and distribution mechanism. Adsorption, ion exchange and distribution chromatography. Application of chromatography in biology and medicine.

Laboratory work

2.1. DETERMINATION OF THE SURFACE TENSION OF SOLUTIONS BY THE DROP COUNTING METHOD (STALAGMOMETRIC METHOD)

For work you need: stalagmometer; pycnometer; glass beaker for 50 ml.

The aim of the work is to learn how to determine the value of surface tension for the studied solutions and parachor for individual substances using the stalagmometric method.

The free surface energy, that is, the excess of free energy per unit area of the surface layer at the liquid-air interface, is called surface tension, and at the liquid-liquid interface, it is called the boundary tension σ.

The units of measurement of surface tension in the modern SI International System of Units can be N/m in the case when it is considered as the excess free energy of the interface of two phases, which accumulates on this surface due to

uncompensated intermolecular forces. And also in J/m^2 if it is considered as the work of forming a new unit of surface area.

There are several methods of determining surface tension.

The most widespread method is the stalagmometric method (method of counting drops).

The basis of the method is the experimentally established proposition that the weight of a drop, which is slowly detached under the influence of the earth's gravity from the tip of the vertical tube of the stalagmometer, will be greater, the greater the surface tension of the liquid at the interface with air.

It is assumed that the force of surface tension F, acting vertically along the circumference of the tube, is approximately equal to $F = 2\pi r\sigma$. It supports the drop, balancing its weight P. At the moment of separation of the drop, these forces can be considered equal:

$$F = 2\pi r\sigma = P, \qquad (1)$$

$$P = mg, \qquad (2)$$

where

F is the surface tension force;

P is the weight of the drop;

σ is the proportionality factor that relates the force of surface tension to the perimeterσ (in this case, with the length of the circle of the capillary from which the liquid flows).

At $2\pi r$ = 0,01 m the proportionality factor is equal to the force of surface tension, i.e. $F = \sigma$.

Determination of the radius of the capillary is associated with some difficulties, and therefore the surface tension is practically determined relative to a standard liquid with a known surface tension. The standard liquid can only be such a liquid that forms drops close in volume to the drops of the liquid (or solution) under investigation.

When a drop is formed, the force of the surface tension of the substance under investigation is equal to $F=2\pi\ r\sigma_0$ (if the measurement is carried out in the same stalagmometer)

The force of surface tension is difficult to determine, therefore, in experimental studies, the weight of a drop is determined, which at the moment of separation is approximately equal to the force of surface tension.

The weight force of one drop of the liquid under study is

$$P = mg = \frac{V_p \rho g}{n}, \qquad (3)$$

where

V_p is the volume of liquid flowing out of the stalagmometer;

ρ is the density of the studied liquid;

n is the number of drops of the studied liquid in the volume;
g is the acceleration of the earth's gravity.

A similar expression for the same volume of the device can be written for a standard liquid (for example, dist. H_2O)

$$P_o = \frac{V\rho_o g}{n_o}. \qquad (4)$$

Then take the ratio of these equations

$$\frac{P}{P_o} = \frac{\frac{V_\rho \rho g}{n}}{\frac{V_o \rho_o g}{n_o}} = \frac{n_o \rho}{n \rho_o}. \qquad (5)$$

and so how

$$\frac{F}{F_o} = \frac{P}{P_o}, \qquad (6)$$

then

$$\frac{\sigma}{\sigma_o} = \frac{n_o \rho}{n \rho_o}. \qquad (7)$$

Solving this equation with respect to the surface tension of the substance under study, we obtain the calculation formula:

$$\sigma = \sigma_o \frac{n_o \rho}{n \rho_o}, \qquad (8)$$

where
σ_o, ρ_o are the surface tension and density of the standard liquid.

If distilled water is used as the standard liquid, then σ_o, which is taken from the Table 2 at the end of the description.

When studying dilute solutions (for example, isoamyl alcohol solutions), the density ρ can also be taken as 1.

The density of concentrated solutions of sodium chloride is taken from the Table 4, and the density of distilled water depending on the temperature – from Table 3.

Work progress

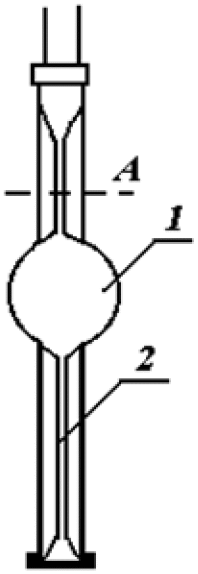


Fig. 1.

When studying individual (pure) liquids, their density must be determined.

For this, n, n_o are the number of drops of the standard and test liquid, are also determined using a stalagmometer. Figure 1 schematically shows a stalagmometer. It is a glass pipette that has an expanded part 1 and a capillary 2. The liquid flowing from the stalagmometer takes the form of a drop hanging on the lower, flat, well-polished end of the stalagmometer. The droplet detaches from the surface of the disk at the moment when the force of its weight slightly exceeds the force of surface tension that holds the droplet. Determination of surface tension is reduced to counting the number of drops flowing out of the capillary. Through the rubber tube located in the upper part of the stalagmometer, the liquid is drawn in above the mark A. Counting of drops begins when the lower meniscus of the liquid touches the mark. Count the number of drops of liquid from the mark to its last drop. First, measurements are made with a standard liquid. If it is water, then there is no need to dry the stalagmometer when switching to aqueous solutions. After distilled water (as a standard liquid), subsequent determinations of the number of drops are carried out, starting with the most diluted solutions, successively moving to more concentrated ones.

For each solution, the number of drops is determined at least three times and their average number of drops is found. Based on the obtained data, according to equation (8), the surface tension is calculated for solutions of surface-active and surface-inactive substances. Next, a surface tension isotherm is constructed in the coordinates $\sigma = f(C)$.

The results of the experiment and calculated data are recorded in the Table 1.

Table 1

In order	Name and concentration of the test substance	Number of drops	Average number of drops	Density, kg/m^3	Surface tension, N/m·10^{-2}
1					
2					
3					

Table 2

The surface tension of water depending on the temperature

T, K	Surface tension of water, N/m·10^{-2}
273	75,64
283	74,22
293	72,75
303	71,18
313	69,56
323	67,91
333	66,18

Table 3

The density of water depending on the temperature

T, K	Density, kg/m^3	T, K	Density, kg/m^3	T, K	Density, kg/m^3
277	1000,00	286	999,40	295	997,80
278	999,99	287	999,30	296	997,65
279	999,97	288	999,13	297	997,32
280	999,93	289	998,97	298	997,07
281	999,88	290	998,80	299	996,81
282	999,81	291	998,62	300	996,54
283	999,73	292	998,43	301	996,26
284	999,63	293	998,23	302	995,97
285	999,52	294	998,02	303	995,67

Table 4

The density of NaCl solutions at 293 K

Concentration, N	Density solutions, kg/m^3
0,10	994,7
0,25	1003,1
0,50	1018,5
1,00	1032,8

Laboratory work

2.2. DETERMINATION OF THE AREA AND LENGTH OF A SURFACTANT MOLECULE

For work you need: stalagmometer; rubber bulb; 50 ml glass beaker; distilled water; individual liquids; surfactant solutions to be tested.

The aim of this work is to determine and calculate the size of the area and length of the molecule of the studied surfactant using the stalagmometric method.

To perform the work, it is necessary to determine the surface tension of several solutions of surfactants of different molar concentrations (as instructed by the teacher). Surface tension measurements are carried out by the stalagmometric method, as described above (see Laboratory work 2.1).

To determine the value of Gibbs adsorption, the difference in surface tension σ_2 and σ_1 measured for two adjacent solutions of different molar concentrations $C_2(X)$ and $C_1(X)$ is found. Then this difference $\sigma_2 - \sigma_1 = \Delta\sigma$ i $C_2(X) - C_1(X) = \Delta C(X)$ is substituted into the Gibbs equation:

$$\Gamma = -\frac{C}{RT}\frac{\Delta\sigma}{\Delta C},$$

where
Γ is the value of Gibbs adsorption, mol/m^2;
$C(X)$ is the equilibrium molar concentration of the surface-active substance, mol/m^3;
R is the gas constant, which is equal to 8,314 J/mol·K;
T is the absolute temperature of the solution, K;
σ is the surface tension of the solution, J/m^2.

Work progress

In this case, $C(X)$ is taken as the arithmetic mean $\frac{C_1(X)+C_2(X)}{2}$. Then calculate $C_{aver.}(x)$ and plot a graph $\frac{C_{cee.}(X)}{\Gamma}$ of dependence (ordinate axis) on $C_{aver.}(x)$ (abscissa axis). A straight line is drawn, the value of Γ is found by the tangent of the angle.

The obtained data are recorded in the Table. 1.

Then, based on the data obtained, the area (S) and length (l) of the molecule of the surfactant under study are calculated according to the formula:

$$S_o = \frac{1}{\Gamma_{\max} \cdot N} = \frac{\Gamma_{\max} \cdot M(X)}{\rho},$$

where

N is the Avogadro constant ($6{,}02 \cdot 10^{23}$ molecules/mol);

Γ_{max} is the value of the limiting adsorption, mol/m^2;

$M(X)$ is the molar mass of the surfactant under study, kg/mol;

ρ is the density of the surfactant, kg/m^3.

Table 1

No.	C(X), mol/m^3	σ, J/m^2	$C_{cep.}$(X), mol/m^3	ΔC(X), mol/m^3	Δσ, J/m^2	Γ, mol/m^2	$C_{aver.}$(X)/Γ

Laboratory work
2.3. ADSORPTION OF ACETIC ACID ON ACTIVATED CARBON

For work you need: stalagmometer; rubber bulb; 50 ml glass beaker; distilled water; activated carbon; 0.4 mol/l acetic acid solution; 0.1 mol/l NaOH alkali solution; paper filter; flasks; phenolphthalein indicator.

The aim of this work is to determine the adsorption of acetic acid on activated carbon and the constants for the Freundlich equation describing this process in the region of average concentrations using the stalagmometric method.

Adsorption isotherms of surface-active substances from a solution on the surface of a solid body (adsorbent) in the region of average concentrations are described by the empirical Freundlich equation:

$$\frac{X}{m} = K \cdot C^{\frac{1}{n}}, \qquad (1)$$

where

X is the amount of adsorbate, mmol;
m us the adsorbent mass, kg;
$\frac{X}{m}$ are the adsorption value, kmol/kg;
K and $\frac{1}{n}$ are the empirical coefficients (constants) that depend on the nature of the adsorbent and adsorbate;
C is the equilibrium molar concentration of the adsorbate, mol/m^3.

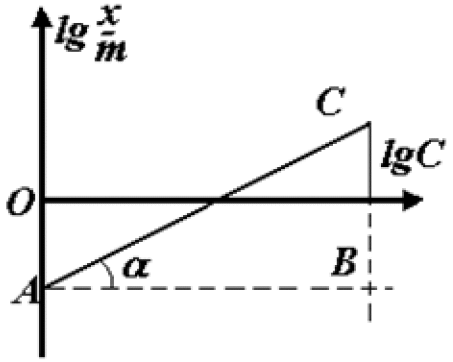
The amount of adsorption $\frac{X}{m}$ (or a) is calculated by the formula:

$$a = \frac{(c_o - c)\cdot V}{m}. \qquad (2)$$

After prologarithming equation (1), we obtain a mathematical dependence of a linear character of the type $y=a+in$:

$$lg\frac{X}{m} = lg\,K + \frac{1}{n}lg\,c. \qquad (3)$$

The resulting equation (3) is the equation of a straight line.



To determine the K and $\frac{1}{n}$ constants, the logarithms of the C concentration and adsorption values $\frac{X}{m}$ are found using a graphical method. Next, a graph is constructed, at the same time putting lgC on the abscissa axis, and the value $\lg\frac{X}{m}$ on the ordinate axis. The value of the segment AO cut off on the ordinate axis corresponds to the value of lg$K$. According to its value, the constant K is found. The value of the constant $\frac{1}{n}$ corresponds to the tangent of the angle of inclination of the straight line tgα (or the ratio of the lengths of the segments CB and AB, i.e. $\frac{1}{n} = \frac{CB}{AB}$.

Work progress

1 g of activated carbon is added to four cones and 25 ml of acetic acid solutions of different molar concentrations (0.05, 0.1, 0.2, 0.4 mol/l) are poured using a burette. The cones are periodically shaken for about 20 minutes. The solutions are then filtered through paper filters into dry cones, discarding the first 3–5 ml of filtrate (to avoid errors due to acid adsorption on the filter). The equilibrium molar concentration of the acid in the filtrate is determined by titrating 5 ml of acetic acid solution with NaOH alkali solution (C(NaOH) = 0.1 mol/l) in the presence of the phenolphthalein indicator. Each acid solution is titrated 2–3 times. Then, according to formula (2), the amount of adsorption of acetic acid on activated carbon is calculated, and the values of lgC and $\lg\frac{X}{m}$ are also found.

The obtained results are recorded in Table 1.

Table 1

C_o, mol/m^3	C, mol/m^3	X/m, kmol/kg	lgC	lgX/m	K	1/n

Using the data in Table 1, the acetic acid adsorption isotherm is then constructed. At the same time, the equilibrium molar concentration C is placed on the abscissa axis, and the value $\frac{X}{m}$ is on the ordinate axis. The constants K and $\frac{1}{n}$ in the Freundlich's equation are determined, as mentioned, from the graph of the dependence of $\lg\frac{X}{m}$ on lg$c$.

Laboratory work
2.4. STUDY OF ADSORPTION OF COLORED SUBSTANCES FROM SOLUTIONS

For work you need: 0.02% solutions of the dyes under study: methylene blue, potassium bichromate $K_2Cr_2O_7$, ferric (III) chloride $FeCl_3$, ash $Fe(OH)_3$, congo red, aqueous fuchsin solution and 1 ml of an alcoholic fuchsin solution, measuring pipettes; activated carbon; flasks; filter paper.

The aim of the work is to investigate the adsorption of the studied colored substances from solutions on the surface of activated carbon.

Work progress

1 ml of a solution with a mass fraction of 0.02% of the studied colored substances is placed in a row of test tubes: methylene blue, potassium dichromate $K_2Cr_2O_7$, ferric chloride (III) $FeCl_3$, sol $Fe(OH)_3$, Congo red, an aqueous solution of fuchsin and 1 ml of an alcoholic solution of fuchsin. Then add 0.2 g of activated carbon to all test tubes, mix for 2–3 min and filter. Observe the change in the color of the substances under study. Further, the results of the work are recorded in Table 1.

Then one should draw a conclusion about the nature of the adsorption of the substance under study and explain the essence of the phenomenon of adsorption, which is observed at the same time.

Table 1

The name of the investigated solution							
Color of the solution before adsorption							
Color of the solution after adsorption							
Conclusion on the nature of adsorption of the substance under study							

Laboratory work
2.5. STUDY OF ADSORPTION OF ISOAMYL ALCOHOL FROM SOLUTION USING ACTIVATED CARBON

For work you need: 0.1 mol/l isoamyl alcohol solution; stalagmometer; tripod with test tubes; activated carbon.

The aim of this work is to investigate the process of adsorption of isoamyl alcohol from solution onto the surface of activated carbon using the stalagmometric method.

Work progress

The surface tension of the studied solution of isoamyl alcohol is determined by the stalagmometric method described in work 2.1. Then place 10 ml of this solution in a test tube, add 0.2 g of activated carbon and stir for 2-3 minutes. Next, the studied solution of isoamyl alcohol is filtered and its surface tension is determined again. Based on the obtained data, a conclusion should be drawn about the nature of the change in the surface tension of the studied surfactant and the essence of this phenomenon should be explained.

Laboratory work
2.6. DETERMINATION OF THE TOTAL EXCHANGE CAPACITY OF CATIONITE

***For work you need*:** 0.1 mol/l NaOH solution; 0.1 mol/l HCl solution; 250 ml measuring flask; studied cationite; indicator.

The aim of this work is to determine the value of the total ion exchange capacity of the studied cationite.

Ion exchange capacity (IEC) is a value that expresses the number of g-equivalents (or mmol) of a substance ion from a solution that is exchanged in the process of ion exchange for the corresponding ion of a unit mass (1 g) of ionite.

Work progress

For research, 1 g of cationite is placed in a 250 ml flask, then 100 ml of 0.1 mol/l alkali solution is added, mixed and left for 1 hour. After that, take 25 ml of the solution with a pipette and transfer it to a flask for titration. Then 1–2 drops of the indicator are added to the sample and titrated with a 0.1 mol/l solution of HCl acid until the color of the indicator changes.

Next, the value of the ion exchange capacity of the studied cationite is calculated according to the following formula:

$$IEC = 100 \cdot C_{NaOH} - 4V_{HCl} \cdot C_{HCl} .$$

Laboratory work
2.7. DETERMINATION OF THE CONTENT OF A DRUG SUBSTANCE (CALCIUM GLUCONATE) IN A SOLUTION BY ION-EXCHANGE ADSORPTION

For work you need: medical substance calcium gluconate; N-cationite; 0.1 mol/l NaOH alkali solution; the indicator is methyl orange.

The aim of the work is to determine the content of the drug substance under study (calcium gluconate) in solution by ion-exchange adsorption.

WARNING! When working with the column, air penetration into the ionite is not allowed. The level of the test liquid should not fall below the upper level of the ionite.

Work progress

20 ml of the test solution, which contains calcium gluconate, is slowly passed through the column with H-cationite. Then the column is washed with 25 ml of distilled water, collecting it in the same flask. The entire collected filtrate is titrated with 0.1 mol/l NaOH alkali solution in the presence of methyl orange indicator. The content of calcium gluconate is calculated according to the formula:

$$\omega = \frac{N_{NaOH} \cdot V_{NaOH} \cdot E_{глюк.Ca} \cdot 100}{1000 \cdot V_{пипетки}} .$$

Laboratory work
2.8. DESALINATION OF WATER USING IONITES

For work you need: N-cationite; OH-anionite; ammonium oxalate solution; argentum nitrate solution; pipette; tripod with test tubes; methyl orange indicator.

The aim of this work is to study the process of water desalination using ionites.

Work progress

To desalinate water, you need to take tap water. Further, with the help of qualitative reactions, the presence of chlorine ions (by qualitative reaction with $AgNO_3$ solution) and calcium ions (by qualitative reaction with ammonium oxalate $(NH_4)_2C_2O_4$ should be confirmed in the tested water.

Next, 25 ml of tap water is slowly passed through the column with H-cationite. Then it is washed with 25 ml of distilled water. A few drops of the resulting solution are taken with a pipette into two test tubes. In the 1st of them, the presence of the content of Ca^{2+} ions is checked (by a qualitative reaction with a solution of ammonium oxalate $(NH_4)_2C_2O_4$, and in the 2nd tube – the presence of H^+ ions (using the methyl orange indicator).

Then, a sample of 25 ml is taken from the obtained preliminary solution and passed through a column with OH-anionite. Then it is washed with 25 ml of distilled water. After that, a few drops of the solution are taken into a test tube and checked for the presence of $C1^-$ ions in it. On the basis of the received data, they draw the appropriate conclusion.

Laboratory work
2.9. SEPARATION OF Fe^{3+}, Cu^{2+},Co^{2+} IONS BY CHROMATOGRAPHY ON ALUMINUM OXIDE

***For work you need*:** Al_2O_3; metal tripod; solutions of $CuSO_4$, $FeCl_3$ and $CoCl_2$ salts.

The aim of this work is to investigate the process of separation of a mixture of Fe^{3+}, Cu^{2+}, and Co^{2+} ions from solutions of their salts by chromatographic method using aluminum oxide as a sorbent.

Work progress

The column with the adsorbent ($A1_2O_3$) is fixed in the leg of the tripod. Next, 1 ml of the test mixture consisting of equal volumes of salt solutions: $CuSO_4$, $FeCl_3$ and $CoCl_2$ with a mass fraction of 0.1% is passed through the column with the adsorbent. Then carefully observe the change in the color of the solution. After that, in the protocol of this Laboratory workoratory work, the layers of the adsorbent should be drawn in the appropriate colors and a conclusion should be drawn.

QUESTIONS FOR SELF-CONTROL:

1. Describe the surface tension as the free surface energy at the interface between two phases. Explain the causes of surface tension.
2. Write down the calculation formulas for surface tension. What are the units of its measurement?
3. Describe the factors that affect the value of surface tension.
4. What is called a "surfactant"? What are the features of the structure of its molecules? Give examples and draw the corresponding isotherms of surface tension.
5. State the Traube-Duclo rule. Give examples and draw the corresponding graphical dependencies.
6. What is called a "surface-inactive substance"? What are the features of the structure of its molecules? Give examples and draw the corresponding surface tension isotherms.
7. Formulate the basic concepts of sorption, its qualitative and quantitative characteristics.
8. Write the Gibbs equation, explain it and describe its practical application.
9. Explain what is "positive adsorption"?
10. What is the essence of "negative adsorption?
11. What are the methods of determining surface tension? Describe their essence.
12. What laws are these methods based on? Write down the appropriate calculation formulas for determining surface tension.

TOPIC 3. SOLUTIONS OF NON-ELECTROLYTES

Theoretical questions:

The general concept of solution, its practical importance in the life of organisms. Factors affecting solubility of solid, liquid and gaseous substances. Henry-Dalton law. The Sechenov equation. Solubility of gases in the blood. Caesarean disease. Concentration of solution and methods of its expression. Preparation of solutions with a given quantitative composition. Fundamentals of thermodynamics of solutions. Perfect and real solutions. Laws of Raul. Deviation from Raoul's laws in real solutions. Ebulioscopy. Cryoscopy. Osmosis. Osmotic pressure solutions. Van Goff's Law. Oncotic pressure. The biological role of osmosis. Turgor, plasmolysis. Isotonic, hypertensive and hypotonicDiseases, their practical use in medicine. Konovalov's laws. Azeotropic mixtures. Fractional distillation, its application in chemical and pharmaceutical production. Mutual solubility of liquids. Lower and upper critical temperatures. The distribution of substance between two non-mixing liquids. The The distribution Nernst's Law and its significance in the phenomenon of permeability of biological membranes. Extraction, its importance for medicine and pharmacy.

Laboratory work

3.1. DETERMINATION OF THE MOLECULAR WEIGHT OF A DISSOLVED SUBSTANCES BY THE CRYOSCOPIC METHOD

For work you need: cryoscope (see Fig. 1); test tube for solution with a stirrer; Beckman thermometer; porcelain cup; ice; salt; substance and solutions for research.

The purpose of the work: Determine the molar mass of an unknown dissolved substance using the cryoscopic method and calculate its corresponding physicochemical parameters.

In this work, the student must complete the following tasks:
1. Determine the molar mass of the unknown dissolved substance.
2. Determine the molar concentration of the non-electrolyte solution.
3. Determine the "visible" degree of dissociation of the electrolyte.

Based on the modern theory of dilute solutions, the dependence of the decrease in the freezing temperature of the solvent on the concentration of the substance dissolved in it has been established:

$$\Delta T = \frac{K_{cryo} \cdot g}{g_o \cdot M},$$

where
K_{cryo} is the cryoscopic constant;
g is the mass of dissolved substance, kg;
g_o is the weight of the solvent, kg;
M is the molar mass of the dissolved substance.

This equation is valid for dilute solutions that do not dissociate into ions, as well as non-associated solutions.

Having solved this equation with respect to the molar mass M, experimentally determining the values included in it, it is possible to calculate the molar mass of the solute-non-electrolyte:

$$M = \frac{K_{cryo} \cdot g}{g_o \cdot \Delta T},$$

where
g_o is the weight of the solvent, kg (it can also be taken in volumetric units, knowing the density of the solvent).

For water, the density is approximately equal to 1.

Determining experimentally the decrease in the freezing temperature of a non-electrolyte solution, it is possible to calculate its molality, based on the fact that the cryoscopic constant K_{cryo} is the molal decrease in the freezing temperature of the solvent, that is, the temperature decrease that is observed when 1 mol of a substance is dissolved in 1 kg of solvent.

The concentration of a non-electrolyte solution is determined by the formula:

$$m = \frac{\Delta T}{K_{cryo}}.$$

The value of the cryoscopic constant depends on the properties of the solvent and is expressed by the equation:

$$K_{cryo} = \frac{R \cdot T_{freez}^2 \cdot M_o}{\lambda_{freez}} = \frac{R \cdot T_{freez}^2}{l_{freez}},$$

where
R is the universal gas constant;
T is the absolute freezing temperature of the pure solvent;
M_o is the molar mass of the solvent;
λ_{freez} is the molar heat of freezing of the solvent;

$l_{freez.}$ is the deputy is the specific heat of freezing of the solvent.

The freezing temperatures of some solvents, as well as cryoscopic steels, are given in the Table 2, which is at the end of the description. In the case of electrolytes, the number of molecules and ions is u times greater than the number of initially taken molecules:

$$i = 1 + \alpha(n-1),$$

where
i is the is the Vant Hoff's coefficient;
α is the degree of dissociation;
n is the number of ions formed from one electrolyte molecule.

Therefore, the equation for reducing the freezing temperature of the solution in the case of electrolytes can be written in the following form:

$$\Delta T = \frac{K_{cryo} \cdot g}{g_o \cdot M} \cdot i.$$

For electrolytes whose molar mass is unknown, solving this equation yields:

$$M = \frac{K_{cryo} \cdot g}{g_o \cdot \Delta T} \cdot i.$$

In the case of electrolytes, with a known molar mass, it is possible to calculate the Van't Hoff coefficient (ie, the isotonic coefficient):

$$i = \frac{g_o \cdot \Delta t \cdot M}{g \cdot K_{cryo}}.$$

Knowing the value of and, the "visible" degree of dissociation of the electrolyte is then calculated:

$$\alpha = \frac{i-1}{n-1}.$$

Work progress

The device for cryoscopic measurements, shown in fig. 1. It consists of the following parts: test tube 1, which is fixed to the cork in a metal dish 2, which plays the role of an air jacket. Beaker 3, in which the cooling mixture is placed, and which is closed with a lid 4 with two holes, in one of which a cork for a test tube 1 is inserted, and in the second – a stirrer 5.

Before starting work, it is necessary to familiarize yourself with the Beckman thermometer (Fig. 2).

The special feature of this thermometer is the long scale length (approximately 5 cm per 1°C) and the presence of a spare reservoir with mercury in the upper part of the thermometer, which makes it possible to change the amount of mercury in the working part of the thermometer. The large length of the scale allows you to take readings with the accuracy required for measurements, and the reserve tank makes it possible to set the thermometer to different temperature intervals.

The scale of the thermometer is divided into 5°C, each degree is divided into tenths, and each tenth is in turn divided into hundredths; thousandths can be roughly calculated using a magnifying glass.

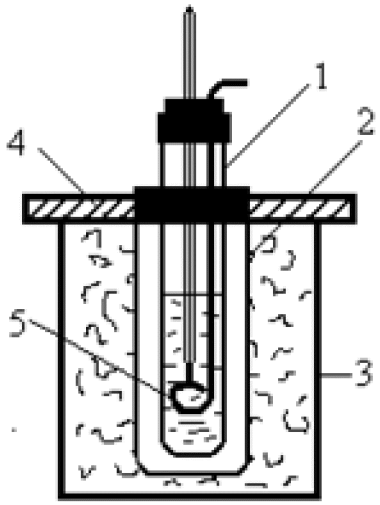


Fig. 1.

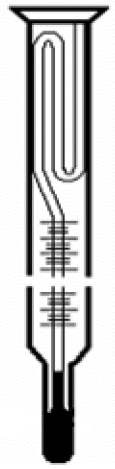


Fig .2.

The thermometer for cryoscopic measurements is adjusted so that at the freezing temperature the mercury level is between the third and fifth degrees. Before adjusting the thermometer, its readings are checked under the conditions necessary for work. If the mercury level in the capillary will not be set between 3°C and 5°C, the thermometer must be adjusted. This should be done as follows: the lower mercury tank is clamped by hand, that is, it is heated and connected to the column of mercury in the upper tank. If there was an excess of mercury in the lower tank, that is, the mercury rose above the fifth degree in the previous experiment, then after connecting both tanks, it is necessary to transfer part of the mercury to the upper tank.

For this, the thermometer is turned with the upper tank down. If the mercury in the previous experiment dropped below zero, that is, there is not enough mercury in the lower tank, then part of the mercury must be poured from the upper to the lower tank. For this, the upper and lower tanks are connected, then the lower tank is cooled in a mixture of ice and water. After the mercury moves in a certain amount in the desired direction, the column of mercury in the capillary is broken.

The lower tank is clamped in the palm of the hand and a light tap of one hand on the other (or hand on the Table) breaks the column of mercury. In the event that the mercury does not stop in the required temperature range, the settings are repeated. The adjusted thermometer is left in a glass with ice and the next step is started. The solvent is poured into the test tube in such an amount that after immersing the Beckman thermometer in it, the liquid level is 2–3 cm higher than the upper part of the lower reservoir, and the lower part of the reservoir should not reach the bottom by 1–2 cm. In most cases, 25–40 ml of solvent. Then prepare a cooling mixture of water, ice and salt with a temperature 3-4°C below the freezing point of the pure solvent. Beaker 3 is filled with a cooling mixture, an approximate determination of the freezing point of the solvent is carried out. To do this, a test tube with a solvent and a thermometer inserted into it is placed directly into the cooling mixture. While stirring the liquid, observe the readings of the Beckman thermometer. As a result of supercooling, the temperature drops below the freezing point of the liquid. At the moment when the crystallization of the liquid into a solid phase begins, due to the release of the heat of crystallization, the temperature begins to rise. The thermometer determines the maximum temperature, which is taken as the approximate freezing temperature. It is considered approximate because the experiment is conducted in conditions that do not exclude cooling irregularities.

After an approximate determination of the freezing point of the pure solvent, the test tube is removed from the cooling mixture and the formed crystals are melted by immersing the test tube in water at room temperature. Then put the test tube in the air jacket 2 of the device. To speed up the cooling process, the liquid in test tube 1 is stirred with a stirrer 5. When the temperature is set approximately 0.5°C higher than the previously found approximate crystallization temperature, mixing is stopped and the liquid is supercooled by 0.2–0.5°C below the approximate temperature. Stirring the supercooled solvent causes its crystallization. The crystallization process is accompanied by the release of latent heat of fusion, which, in turn, leads to an increase in temperature. The maximum temperature observed during crystallization is noted using a magnifying glass with an accuracy of 0.002°C and recorded as the freezing point of the solvent. The measurement of the freezing point for the pure solvent is repeated several times. After each determination, test tube 1 is removed from the device, the formed crystals are melted, as indicated above. The arithmetic mean of individual measurements is taken as the actual value of the freezing temperature of the solvent. Graphical error should not exceed 0.005°C. Next, the freezing temperatures of the studied solutions of non-electrolytes and electrolytes are similarly determined. At the same time, to determine the molar mass of the substance under study, take a g scale (0.2–0.3 g) with a weighing accuracy of up to 0.0001 g and dissolve it in this solvent. The approximate crystallization temperature is determined in the same way as for the

solvent. Determination is carried out 3 times for each tested solution. The average value of three measurements is taken as valid.

The results of the experiment and the obtained calculation data are recorded in the following form:

Volume of solvent V =

Mass of solvent g_o =

Mass of solute g =

Electrolyte for determining the "visible" degree of dissociation –

The volume taken to study the molal concentration V_k =

Mass of solvent g_o =

Mass of solute g =

Experimental data and those calculated on their basis are recorded in Table 1.

Table 1

	Themperature of crystallization, °C	Average temperature of crystallization, °C	Decrease temperature of crystallization, °C	Results
1. Clean solvent				
2.Solution for determination molar mass				
3. Solution for determination molar concentration				
4. Solution for determination visible degree				

Table 2

Solvent	$T_{sol.}$, K	Calculated $K_{krit.}$	Experimentally determined $K_{krit.}$
Water	273,2	1,862	1,86
Nitrobenzene	278,8	6,83	6,90
Benzene	278,9	5,12	5,10
Phenol	313,2	7,80	7,80
Camphor	451,2	48,20	49,00

Laboratory work
3.2. DETERMINATION OF THE CRITICAL TEMPERATURE OF MUTUAL DISSOLUTION OF LIQUIDS

For work you need: device for determining the critical temperature; electric tile; technical scales; pipette graduated to 5-10 ml; stand with test tubes; phenol; water.

The aim of this work is to determine the critical temperature of mutual solubility of substances.

When the mutual solubility of two liquids is limited in a certain concentration region, there is always an equilibrium between two solutions of different composition. Obviously, when the temperature changes, this equilibrium will shift in one direction or another. All of these relationships can be depicted graphically in temperature-composition diagrams.

The temperature above or below which liquids are mutually soluble in all ratios is called the critical temperature of mutual dissolution of liquids. There are upper and lower critical dissolution temperatures for liquids.

Examples of temperature-composition diagrams of systems with upper and lower critical dissolution temperatures are shown in Fig. 1 (a-c).

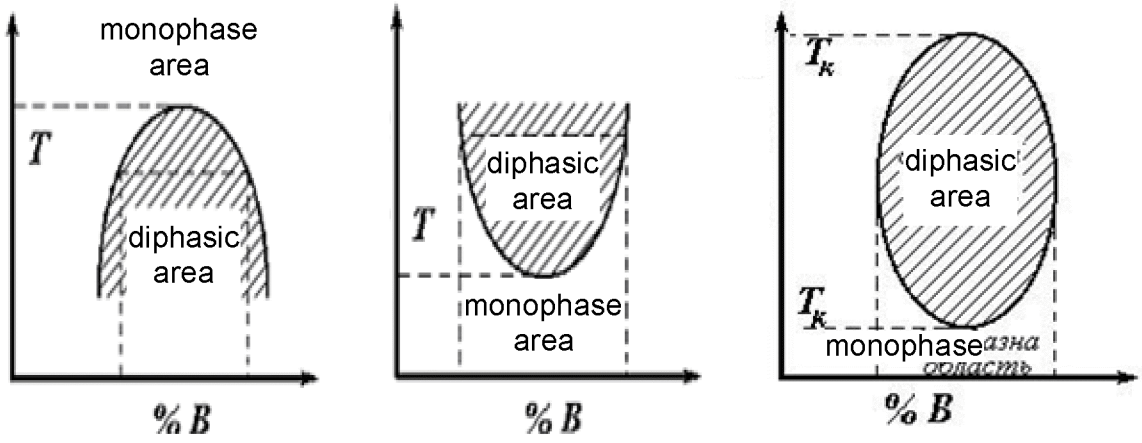


Fig.1. a) The system of the upper critical temperature of dissolution (phenol–water),
b) the system with the lower critical temperature of dissolution (alifaminy–water),
c) the system of the upper and lower critical temperature of dissolution (nicotine–water).

The easiest way to find the mutual solubility curve of two liquids is to determine the temperature at which the second phase disappears or forms. To determine this temperature, it is convenient to use the device shown in Fig. 4.

Flask 1 serves as a water or oil bath, test tube 2 contains the mixture under study, a thermometer 3 and a stirrer 4 are placed in it on the cork.

Based on the total weight and percentage content, the weight amounts for the test mixtures are calculated.

If the second component is a liquid, it can be taken in volumetric units. To do this, you need to know the density of the liquid. The density of water at the test temperature is assumed to be unity.

Work progress

Two substances that are poorly soluble in each other are used for the study, for example, the phenol-water system.

Prepare several mixtures with different percentages, which are specified by the instructor. The total weight of the mixture should not exceed 5-6 g.

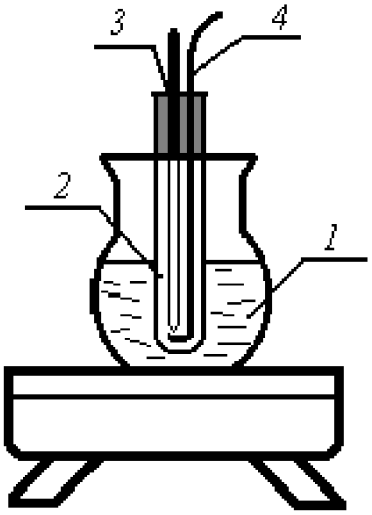


Fig. 2.

First, weigh the required amount of phenol, then measure the required amount of water to obtain a mixture of a certain percentage composition.

Place the test tube in the critical temperature apparatus (Fig. 2) and note two temperature points: the homogenization temperature (the transition of the system to one phase) and the heterogenization temperature (the separation of the system into two phases).

To obtain accurate data, the temperature should be changed slowly, with continuous stirring of the mixture in the test tube to avoid overheating or overcooling.

When working with phenol, make sure that it does not get on the skin, as phenol causes burns.

Then, based on the data obtained, a temperature-composition diagram is constructed to determine the critical temperature of mutual dissolution of liquids and to control the percentage composition by the temperature of mutual dissolution. The results of the experiments are recorded in Table 1:

Table 1

No. tubes	1	2	3	4	5	6	7	8	9	10	11	12
% Phenol												
Sample phenol, g												
Sample water, g												
Homogenization temperature, ^{0}C												
Heterohenizatsiyi temperature, ^{0}C												
Average temperature, ^{0}C												

TOPIC 4. SOLUTIONS OF ELECTROLYTES

Theoretical questions:

The nature of electrical conductivity in conductors I and II kinds. Theory of Arrhenius electrolytic dissociation. Degree of dissociation. Electrolytes in the human body. Water-electrolyte balance is a necessary condition for homeostasis. Theory of acids and bases. Types of protolytic reactions: neutralization, hydrolysis and ionization reactions. Hydrolysis of salts. The degree of hydrolysis, its dependence on concentration and temperature. Hydrolysis constant. The role of hydrolysis in biochemical processes. Total, specific and equivalent electrical conductivity, their definition, units of measurement. Factors affecting the electrical conductivity of strong and weak electrolytes. Ostwald's breeding law. Colrausch's Law. Theory of strong electrolytes Debai-Hückel. Ionic atmosphere. The ionic force of the solution. Activity, activity coefficient. The essence of conductometric titration. Patterns of titration of strong, weak and mixture of acids with a strong base. Practical application of electrical conductivity and conductometry in medicine and pharma.

Laboratory work

4.1. DETERMINATION OF ELECTROLYTE CONDUCTIVITY AND CALCULATION OF THE DEGREE OF DISSOCIATION

For work you need: rheochord ABC; sound generator SG; headphones T or oscilloscope; dishes for determining electrical conductivity and platinum electrodes B; 50-100 ml measuring flask; measuring pipettes; measuring flasks; electrolyte solutions; resistance magazine.

The aim of the work is to determine the values of the total, specific, and equivalent electrical conductivities of the solutions of the studied electrolytes and to calculate their degree of dissociation.

Since electrical conductivity is inversely proportional to resistance, its determination is reduced to measuring resistance. The electrical circuit used to measure the resistance is shown in Fig. 1.

From the source, the current flows into A, branches, and goes through ABC and ADS. By moving the contact C along the wire AB, you can find a position at which there will be no current on the segment DC. This happens when

$$\frac{R_{AC}}{R_{CB}} = \frac{R_{mag.}}{R_{sol}},$$

hence

$$R_{sol} = R_{mag} \frac{R_{CB}}{R_{AC}}.$$

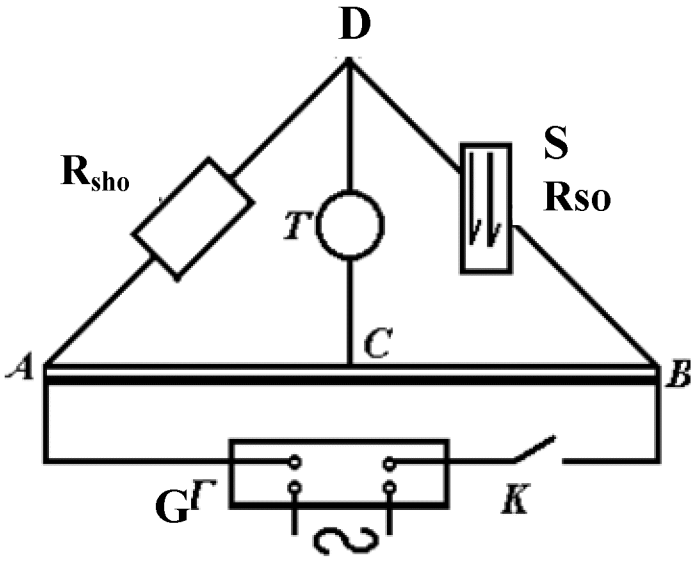


Fig. 1. Electric scheme for conductometric titration.

When determining electrical conductivity, weak high-frequency currents are used. A sound generator is used as a current source; headphones or an oscilloscope are used as a zero instrument. The equilibrium point is determined by the position of the contact C, at which no sound is heard at all or is minimal in the headphones, or a clear bright spot is seen on the oscilloscope screen.

The device for determining electrical conductivity is shown in Fig. 2. This is a glass vessel with tubes A and B lowered into it.

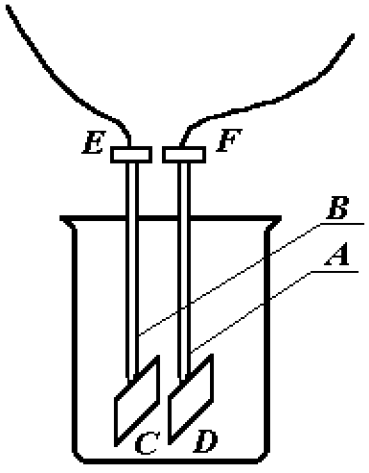


Fig. 2. A device for determining electrical conductivity (Arrhenius vessel).

Platinum electrodes C and D are soldered to the lower ends of the tubes. To prevent polarization, the surface of the electrodes is increased along with the use

of weak high-frequency alternating currents. For this purpose, the electrodes are paid.

Work progress

The work begins with the preparation of solutions with a known specific electrical conductivity and those whose specific electrical conductivity is to be determined. The concentration is set by the teacher.

From 1 n. solution of KCl or NaCl, prepare the solutions specified by the instructor by dilution. Do not prepare all solutions directly from 1 n., as errors in measuring its volume lead to a large error in the concentration of the prepared solution. For dilution, use a solution of a previous concentration.

After all the solutions are prepared, draw up a circuit. The current source is not turned on until the circuit is checked by the class instructor or laboratory assistant. If the circuit works, the resistance measurements are started. Resistance measurements start with distilled water, the most dilute solutions, and move on to concentrated solutions. The measurement procedure is as follows. The vessel for determining the electrical conductivity and the electrodes are thoroughly rinsed with distilled water. After that, 20-25 ml of distilled water is poured into the vessel (since the measurement starts with water).

Wearing headphones, or by scanning the oscilloscope screen, the contact is placed approximately in the middle of the ruler (0.25-0.30 m). After turning on the current, the resistance meter selects the resistance at which the sound in the headphones will be minimal (dot on the screen). It is recommended to use a single cascade when selecting the resistance. It should be remembered that the more dilute the solution, the lower its overall electrical conductivity, i.e., the higher the resistance. So, in order for the compensation to be in the middle of the range, obviously, you need to use larger resistances on the magazine. As the concentration increases, the resistance selected on the magazine decreases. Having reached the minimum sound in the headphones, more precise compensation is carried out by means of a movable contact on the rheochord.

Without pouring out the solution, change the resistance of the magazine by 10% up and down and determine the position of the contact for these cases, i.e. for each solution, three determinations are made to find the average of the resistance values. If at any position of the contact there is no minimum sound or dots on the oscilloscope screen, then it is necessary to check the correctness of the connections in the general circuit, in each branch separately.

Using the results of the experiment, you can calculate the resistance and electrical conductivity of solutions, the resistance capacity of the vessel, the specific and equivalent electrical conductivity, the degree of dissociation, and the dissociation constant. Calculate the values specified in the problem.

The specific electrical conductivity of aqueous solutions of KCl and NaCl at 298 K is given in Table 1.

Table 1

Concentration, mol·equiv/m^3	χ, m · Om^{-1}	
	KCl	NaCl
0,5	0,0005940	0,0004681
0,2	0,0002484	0,0002034
0,1	0,0001288	0,0001067
0,5	0,00006668	0,00005553
0,02	0,00002767	0,00002315
0,01	0,00001413	0,00001185
0,005	0,000007177	0,000006032
0,002	0,000002526	0,000002112
0,001	0,000001496	0,000001237

The resistance of solutions or water is calculated using the expression:

$$\frac{R_{AC}}{R_{CB}} = \frac{R_{mag.}}{R_{sol}},$$

hence

$$R_{sol} = R_{mag} \frac{R_{CB}}{R_{AC}}$$

From the average values of resistances, their average electrical conductivities are calculated

$$W_{sol} = \frac{1}{R_{sol}}$$

Using the dependence of the specific electrical conductivity on the total $\chi = KW$, where χ is the specific electrical conductivity, which can be calculated if the proportionality coefficient K is known, which is a constant (resistance capacity) of the vessel in which the measurements are performed. Its value depends on the area of the electrodes, the distance between them, the shape of the vessel, and other factors.

According to the formula $K = S / l$, where S is the electrode area, l is the distance between them. The constant K is calculated using equation (3), taking into account the correction for the electrical conductivity of the solution prepared with distilled water.

The electrical conductivity of water is calculated using formulas (1), (2). If the value W_{H_2O} is very small compared to W_{sol}, then it is neglected when calculating the value of K.

Then

$$K = \frac{\chi_{sol}}{W_{sol}}$$

To use formula (3), you need to know the value of the specific electrical conductivity χ. To do this, the total electrical conductivity is determined from the experiment, and the specific conductivity is taken from the Table data.

To determine the conductivity (K), three solutions of KCl or NaCl are used. Their concentrations are specified by the teacher. The specific conductivity for these solutions is taken from the Tables.

Knowing the constant of the vessel, you can calculate the specific conductivity of any solution whose total conductivity is determined in this vessel:

$$\chi_{sol} = KW_{sol}$$

Knowing the specific electrical conductivity, the equivalent λ_{sol} is calculated using the formula for their relationship

$$\lambda_{sol} = \frac{\chi_{sol} \cdot 1000}{C}$$

where C is the concentration of the solution expressed in mol-eq./l.

The equivalent electrical conductivity at dilution λ_{∞} is determined in a similar way. The concentration of 0.0001 n. of the solution is taken as the infinite dilution.

Knowing λ_{∞} and λ at this dilution, calculate the degree of dissociation

$$\alpha = \frac{\lambda}{\lambda_{\infty}}.$$

Using Ostwald's dilution law, we can calculate the dissociation constant of a weak electrolyte by substituting (6)

$$K_{dis.} = \frac{\alpha^2 \cdot C}{1-\alpha}$$

The value α of weak acids and bases in not very dilute solutions is very small, and it can be neglected in the denominator of (7), taking it to be 1. Then we get:

$$K_{dis} = \alpha^2 c$$

or

$$\alpha = \sqrt{(K_{dis}/c)}$$

This equation makes it possible to calculate the degree of electrolytic dissociation of a weak electrolyte in a solution of a known concentration if the constant Kdis is known.

The above laws are applicable to weak electrolytes. However, at low concentrations, they are also applicable to strong ones.

Determination of the electrical conductivity of electrolytes and calculating the degree of dissociation begin to measure the resistance values of solutions using reohord bridge P38.

The front panel bridge is shown in Fig. 3:

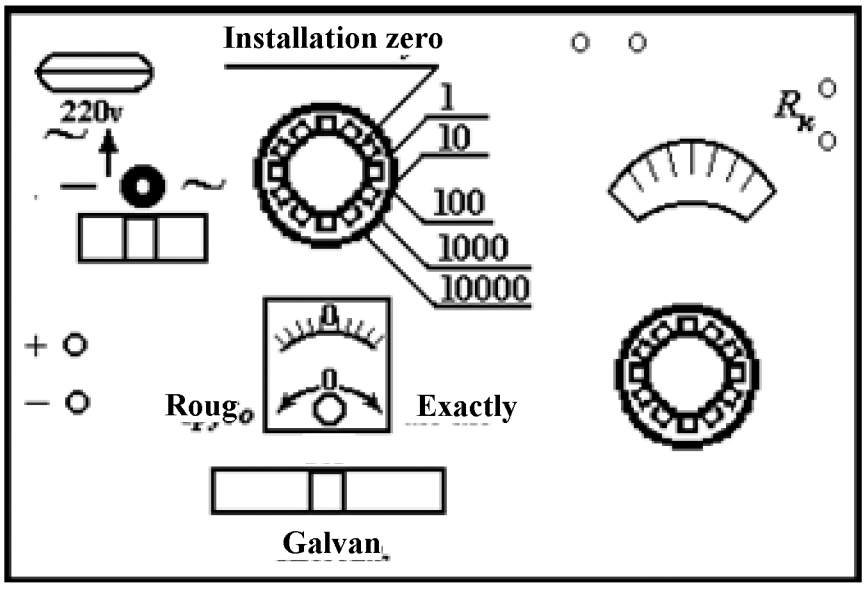


Fig. 3. The front panel bridge P 38.

Operation at alternating current

1. Connect 220 V with a frequency of 50 Hz to the sockets of the device and set the "Power" switch to the "~" position.
2. Set the comparison lever switch to the "Zero setting" position and set the "Galvanic" switch to the "Exact" position by rotating the corrector on the galvanometer, setting the arrow to the zero position.
3. Set the "Galvanometer" switch to the "Coarse" position and balance the bridge by rotating the handles of the comparison lever and the rheochord, then set the "Galvanometer" switch to the "Fine" position and balance the bridge by rotating the rheochord handle.
4. Measurement of electrolytes at an increased frequency up to 500 Hz is performed in the same way as at a frequency of 50 Hz.

The results of the experiment and calculations are recorded in Table 2:

Table 2

Concentration, kmol·eq./m³	Resistance of the solution, Om	Average resistance of the solution, Om	Average electrical conductivity of the solution, Om^{-1}	Resistance capacity of the vessel, m	χ, $Om^{1} \cdot m^{1}$	λ, $\frac{Om^{-1} \cdot m^{-1}}{kg \cdot eq.}$	α	K_{dis}
1	2	3	4	5	6	7	8	9

Based on the data obtained, graphical dependencies $\chi = \varphi(c)$ and $\lambda = f(C)$ are constructed.

Laboratory work
4.2. DETERMINATION OF ACID CONCENTRATION BY CONDUCTOMETRIC TITRATION

For work you need: 1 N; 0.1 N NaOH solutions; acid control solution; 20-25 ml pipette; micropipette; electrical conductors - 5 pcs.

The aim of the work is to determine the concentration of the acid solution based on the measurement of the electrical conductivity of the acid solution using the conductometric titration method.

In volumetric analysis, color indicators are used to determine the end of the titration. These indicators should not be used when titrating colored or cloudy solutions, as it is impossible to determine the color change of the indicator against the background of these solutions.

In such cases, especially in the neutralization of weak acids and alkalis, the electrical conductivity of solutions is often used as an indicator.

Measurement of the electrical conductivity of solutions has found wide practical application. One of them is conductometric titration. The essence of the method is that during the titration process, some ions in the solution are replaced by others with different mobility, and the electrical conductivity of the solution changes accordingly.

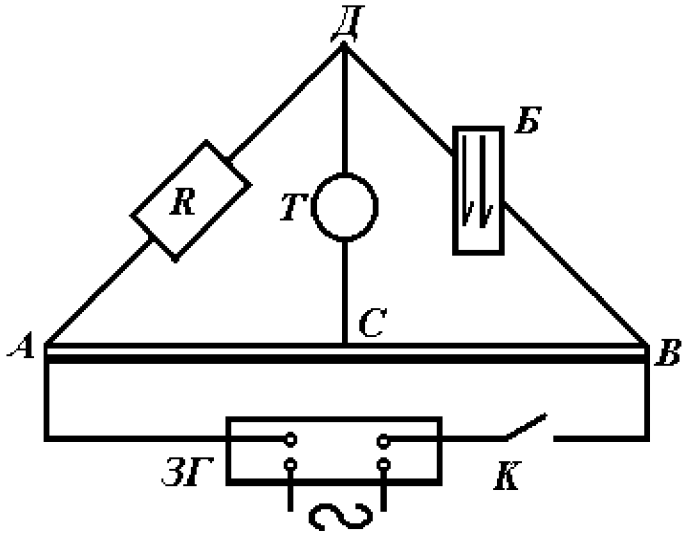


Fig. 1. Electrical circuit for conductometric titration.

By determining the electrical conductivity of a solution, you can calculate its concentration.

Since electrical conductivity is the inverse of resistance, it is sufficient to find the resistance of the solution to the current passing through it. The resistance is determined by the compensation method using the Kohlrausch bridge, the scheme of which is shown in Fig. 1, where ABC is a rechord; R is a resistance

store; T is headphones or an oscilloscope; B is a container with an electrolyte solution whose electrical conductivity is to be determined; SG is a sound generator; K is a key.

When the circuit is closed with a key, the current from the current source branches out, forming 4 resistance branches: R_{AC}, R_{CB}, R_{sol}, R_{mag}.

A sound is heard in the headphones and a line is observed on the oscilloscope screen. When the contact is moved along the reochord in one and the other direction, the sound is amplified or weakened, and the line on the screen changes in size.

At the moment when $\frac{R_{AC}}{R_{CB}} = \frac{R_{mag.}}{R_{sol}}$, there is no current in the SD bridge, which is manifested by the complete disappearance of sound in the headphones, the oscilloscope screen will show a dot.

Based on the above equation, we can determine the resistance of the solution

$$R_{sol} = R_{mag} \frac{R_{CB}}{R_{AC}} \ .$$

Knowing the resistance of the solution, calculate the conductivity by the formula

$$W_{sol} = \frac{1}{R_{sol}}$$

Work progress

When determining electrical conductivity, weak high-frequency currents are used: a sound generator is used for this purpose.

The vessel into which the solution (whose electrical conductivity is to be determined) is poured is a beaker with platinum electrodes (Fig. 2). To avoid polarization, the surface of the electrodes is increased along with the use of high-frequency currents. For this purpose, the electrodes are plated.

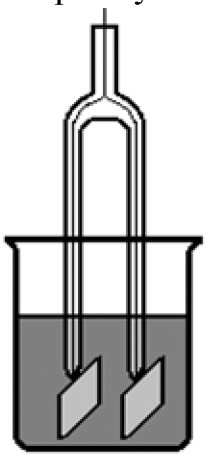


Fig. 2.

Pour 20-25 ml of a control solution of acid into a beaker of acid solution is poured into the beaker and the electrodes are immersed in the acid. After placing the the movable contact at divisions of 0.25-0.3 m on the rheochord, turn on the current using the K key.

In this position, use the resistance magazine to select the resistance at which the current does not pass through the headphones, i.e., the sound in the headphones is absent or becomes minimal, or a dot lights up on the oscilloscope screen. Leaving the resistance of the magazine constant for all subsequent measurements, a micropipette is used to add NaOH

solution in portions. (The amount of solution and the concentration of the NaOH solution is specified by the instructor).

Stir the solution in the beaker and find the minimum sound with a moving contact.

The minimum sound is again found with the moving contact.

The minimum sound or dot on the screen shifts to the left with the addition of each portion of alkali until the acid is completely neutralized. After the neutralization point, the electrical conductivity of the solution increases, and therefore the moving contact must be shifted to the right on the ruler.

The experiment is considered complete when 5-6 measurements are obtained after the neutralization point.

The measurement results are recorded in the following Table:

Table 1

Acid quantity, ml	Concentration NaOH, mol-equivalent/l	Quantity NaOH, m	Resistance, Om	Reohord data, m		Solution resistance, Om	Solution electrical conductivity, Om^{-1}
				AC	CB		

Using the data in the Table, plot the electrical conductivity of the solution against the amount of alkali used to titrate the acid. From the graph, find the amount of NaOH solution required to neutralize the amount of acid taken and use the formula $N_1V_1 = N_2V_2$ to find the concentration of the control acid solution

$$N_1 = \frac{N_2V_2}{V_1}$$

where

N_1 is the unknown concentration of acid;

V_1 is the volume of acid taken for the experiment;

N_2 is the concentration of the alkali solution;

V_2 is the volume of alkali required to titrate the acid.

Laboratory work
4.3. DETERMINATION OF THE SOLUBILITY OF POORLY SOLUBLE COMPOUNDS

For work you need: silver chloride, ABC rheochord; sound generator ZG; headphones T or oscilloscope; dishes for determining electrical conductivity; platinum electrodes B; 50-100 ml measuring flask; measuring pipettes; measuring flasks; resistance magazine.

The aim of this work is to determine the solubility of poorly soluble compounds based on the electrical conductivity of their aqueous solutions.

Work progress

It is very convenient to use silver chloride to perform this work. For this purpose, a small amount (2-5 g) of well-pounded salt is transferred to a flask and decanted with distilled water. After rinsing, distilled water is added again carefully (without shaking) until the solution is clear and the resistance of the solution is measured.

Since AgCl salt is very poorly soluble, the degree of its ionization in aqueous solution is close to unity, i.e., the molar conductivity of a saturated solution of this salt is practically the same as the ultimate electrical conductivity:

$$\lambda_c = \lambda_{\max},$$

$$\lambda_c = \frac{\chi}{1000 \cdot C} = \frac{\chi}{1000 \cdot S},$$

where

S is the solubility of silver chloride,

$$S = \frac{\chi}{1000 \cdot \lambda_{\max}}$$

It has been experimentally established that the specific electrical conductivity of a saturated solution of silver chloride is $3{,}40 \cdot 10^{-4}$ cm·m^{-1}. Since water itself is a weak electrolyte, its own contribution to the electrical conductivity of the solution should be taken into account
(χ of water is $1{,}60 \cdot 10^{-4}$ cm·m^{-1}).

Thus,

$$\chi_{AgCl} = 3{,}40 \cdot 10^{-4} - 1{,}60 \cdot 10^{-4} = 1{,}80 \cdot 10^{-4} \left(sm \cdot m^{-1}\right)$$

Using the Table below, determine the value of the ultimate molar conductivity of silver chloride:

$$\lambda_{\max}^{AgCl} = \lambda^{Ag+} + \lambda^{Cl-} = 61{,}9 \cdot 10^{-4} + 76{,}35 \cdot 10^{-4} = 138{,}25 \cdot 10^{-4} \left(s \cdot mol^{-1} \cdot m^2\right)$$

then the solubility of silver chloride

$$S = \frac{1{,}80 \cdot 10^{-4}}{1000 \cdot 138{,}25 \cdot 10^{-4}} = 1{,}30 \cdot 10^{-5} \left(mol/l\right)$$

Table 1

Electrolytic mobility of ions in aqueous electrolyte olutions at 298 K (λ^i, $sm \cdot mol^{-1} \cdot m^2$)

Cation	$\lambda^+ \cdot 10^4$	Anion	$\lambda^- \cdot 10^4$
H_3O^+	349,81	OH^-	198,30
Li^+	38,68	F^-	55,40
Na^+	50,10	Cl^-	76,35
K^+	73,50	Br^-	78,14
Ag^+	61,90	I^-	76,88
NH_4^+	73,50	NO_3^{2-}	71,46
Mg^{2+}	53,05	HCO_3^-	44,50
Ca^{2+}	59,50	CH_3COO^-	40,90
Ba^{2+}	63,63	SO_4^{2-}	80,02
Cu^{2+}	56,60	$HCOO^-$	54,60
Zn^{2+}	52,80	$C_6H_5COO^-$	32,30
Al^{3+}	63,00	$C_2H_4^{2-}$	74,10

Since silver chloride is a binary electrolyte, then [Ag^+] = [Cl^-]. Knowing the concentration of ions, we can determine the solubility product *SP*:

$$SP = \left[Ag^+\right] \cdot \left[Cl^-\right] = 1{,}30 \cdot 10^{-5} \cdot 1{,}30 \cdot 10^{-5} = 1{,}69 \cdot 10^{-10} \left(mol/l\right).$$

Similarly, the solubility and solubility product of other hardly soluble compounds are determined.

The results of the experiment and calculations are recorded in Table 2:

Table 2

Concentration	Resistance of the solution, Om	Medium resistance, Om	Average electrical conductivity of the solution	Resistance capacity of the vessel	χ	λ	SP

Laboratory work
4.4. DETERMINATION OF THE IONIC PRODUCT OF WATER

For work you need: rheochord ABC; sound generator ZG; headphones T or oscilloscope; dishes for determining electrical conductivity and platinum electrodes B; 50-100 ml measuring flask; measuring pipettes; resistance magazine.

The aim of this work is to determine the ionic product of water based on its electrical conductivity.

Work progress

The aim of this work is to determine the ionic product of water based on its electrical conductivity.

To perform this work, the equation is used

$$S = \frac{\chi}{1000 \cdot \lambda_{\max}}$$

For example, at 291 K, the specific electrical conductivity of pure water is $4.41 \cdot 10^{-6}$ cm·m^{-1}. According to the Table given in the previous work, we find

$$\lambda_{\max}^{H_2O} = 315 \cdot 10^{-4} + 171 \cdot 10^{-4} = 468 \cdot 10^{-4} \left(sm \cdot mol^{-1} \cdot m^2\right)$$

Having obtained the concentration of H^+ and OH^-

$$S = \frac{4{,}41 \cdot 10^{-6}}{1000 \cdot 486 \cdot 10^{-4}} = 9{,}07 \cdot 10^{-8}$$

determine the ionic product of water at 291 K:

$$H_W = \left[H^+\right] \cdot \left[OH^-\right] = 9{,}07 \cdot 10^{-8} \cdot 9{,}07 \cdot 10^{-8} = 0{,}823 \cdot 10^{-14}$$

The value of the ionic product of water at other temperatures is determined in a similar way. The results of the experiment and calculations are recorded in Table 1:

Table 1

Concentration	Resistance of the solution, Om	Medium resistance, Om	Average electrical conductivity of the solution	Resistance capacity of the vessel	χ	λ	SP

Laboratory work
4.5. DETERMINATION OF THE CONTENT OF THE DRUG SUBSTANCE IN A SOLUTION

For work you need: AC bridge; thermostat ($298 \pm 0{,}1$K); conductometric cell with platinum electrodes (cell constant is known); 4–5 100 ml measuring flasks; 4–5 glasses of the same capacity; solutions of strong electrolytes used in pharmacy: hydrochloric acid, benzoate, salicylate, sodium bicarbonate; magnesium sulfate or calcium chloride, distilled water; analytical balance; HCl acid solution with a concentration of $2 \cdot 10^{-2}$ mol/l; 4–5 conical flasks with stoppers; test objects: amidopyrine, streptocide or sodium benzoate in the form of pure pharmacopoeial preparations and tablets.

The purpose of the work is to determine the content of a drug substance in a solution based on the value of specific electrical conductivity.

In this work, the student must perform the following tasks:
1) measure the resistance of the reagent solution system;
2) add an accurate weight of the substance under study;
3) measure the resistance of the solution;
4) calculate the specific electrical conductivity and its change;
5) obtain a calibrated graph or its equation;
6) determine the composition of the substance in the original tablet.

Direct conductometric determination of the drug content in weak electrolytes is practically impossible. The absolute values of χ of weak

electrolytes are small, and the dependence $\chi = f(c)$ is nonlinear. The addition of a test substance to a solution of a reagent that interacts with it causes a change in the specific electrical conductivity of the solution, which under certain conditions is proportional to the concentration of this substance. This method is called direct conductometry with chemical influence on the system.

Here is an example of direct conductometric analysis of weak bases. As a reagent, a solution of a weak acid HA of known concentration cp is used; its specific electrical conductivity is $10^{-3}\chi_{нач.} = c_p\lambda_{HA}$. After the addition of a weak base, BON with a concentration of c_o under the condition $c_o < c_p$ is neutralized according to the reaction

$$HA + BOH \Leftrightarrow BA + H_2O$$

The resulting solution contains the formed salt of BA in a concentration of co and an excess of reagent HA in a concentration of $c_p - c_o$. Based on additivity, we find the specific electrical conductivity of the resulting solution (χ):

$$\chi = \chi_{BA} + \chi_{surplus\cdot HA}$$

$$\chi \cdot 10^{-3} = c_o\lambda_{BA} + (c_p - c_o)\lambda_{YHA}$$

According to the reaction equation, instead of the strong acid HA, an equivalent mass of the salt BA is formed, so the concentration of the solution does not change, the difference in ionic equivalent electrical conductivities $(\lambda_{H^+} - \lambda_{B^-})$ is constant, and the change in the specific electrical conductivity of the solution is directly proportional to the concentration of the weak base under study in equation (2).

In practice, certain masses of the test substance are added to the reagent solution, each time determining $\Delta\chi$. A linear graph $m = f(\Delta\chi)$ is plotted, where m is the mass of the substance, or the equation is obtained

$$m = a\Delta\chi - b\,.$$

The coefficients a and b are found using the least squares method.

Direct conductometry with chemical influence on the system takes into account the speed of the direct conductometric method with the capabilities of conductometric titration. This method can be used not only for neutralization reactions, but also for precipitation, salt displacement, and complexation. Impurities of a foreign electrolyte (up to 3–4%) interfere with the analysis to a lesser extent than in the classical version of direct conductometry.

For a successful analysis, the interaction must be fast and complete, and the reaction products and reagent must have as different equivalent electrical conductivities as possible. The ratio of the concentrations of the substance to be determined and the reagent should be in the range of 0,5–0,95, as the analysis error increases due to a decrease in $\Delta\chi$.

Work progress

Accurate masses of the pure drug are placed in 4–5 conical flasks, and 50 ml of HCl of the determined concentration is added from the burette. The masses are calculated so that the ratio of the concentration of the substance to be determined and the reagent is within 0,50–0,95. The solutions are mixed and the resistance of the pure reagent HCl and all solutions at T = 298 K. The tablet of the unknown composition is weighed, then crushed to a powder and added to a pure reagent solution (50 ml), completely dissolved (turbidity of insoluble impurities is allowed). Sometimes it is necessary to heat the solution in a water bath. Measure the resistance of the resulting solution.

Processing the results of the experiment

For each solution, calculate the resistance $R = \rho \frac{l}{S}$ and the change in specific electrical conductivity $\Delta\chi$ according to Equation (1), build a dependence $m = f(\Delta\chi)$, and calculate the coefficients a and b of Equation (3) using the least squares method. Calculate χ and $\Delta\chi$ in the tablet experiment and use the calibrated graph or Equation (3) to find the mass of the substance in the tablet to be analyzed. Estimate the error of the analysis by substituting $\Delta\chi$ into Equation (3) and comparing the taken weights with those calculated from the equation.

The results of the experiment and calculations are recorded in Table 1.

Table 1

No.	Weighing weight m, kg	Resistance R, Om	Specific electrical conductivity χ, $Om^{-1} \cdot m^{-1}$	Change in specific electrical conductivity $\Delta\chi$, $Om^{-1} \cdot m^{-1}$

QUESTIONS FOR SELF-CONTROL:

1. What is the nature of electrical conductivity in conductors of the I and II kind?
2. What is the essence of the theory of electrolytic dissociation of Arrhenius?
3. What is the "degree of dissociation" of an electrolyte?

4. What is the role of electrolytes in the human body?
5. Describe the hydrolysis of salts.
6. What is the role of hydrolysis in biochemical processes?
7. Define the concepts: “total”, “specific” and “equivalent” electrical conductivity, their definitions, units of measurement.
8. What factors affect the electrical conductivity of strong and weak electrolytes? Explain the essence and mechanism of action.
9. Formulate Ostwald's dilution law and write it down.
10. Formulate the law of Kohlrausch and write it down.
11. Explain the essence of the theory of strong electrolytes Debye-Hückel.
12. What is the “ionic atmosphere” and “ionic strength of a solution”?
13. What is the activity and activity coefficient of a solution?
14. What is the essence of conductometric titration?
15. Describe the patterns of titration of strong, weak and mixture of acids with a strong base.
16. What are the practical applications of conductivity and conductometry in medicine and pharmaceutical analysis?

TOPIC 5. ELECTRODE POTENTIALS AND GALVANIC CELLS

Theoretical questions:

Electrode potential and mechanism of its occurrence on the edge of a metal solution of its salt. The dependence of the value of the potential on the nature of the metal, the concentration of the metal ions in the solution and the temperature. The Nernst equation. Classification of electrodes. Electrodes I kind. Normal hydrogen electrode, its structure and the emergence of potential. Normal potentials. A number of voltages. Standard electrodes, determination of electrodes, comparison electrodes. Electrodes of the second kind. Oxidation-reduction electrodes. Calomel electrode. Hingidron electrode. Glass electrode. Application of ionselective electrodes in medicine and pharma. Galvanic elements, their classification. Chemical, concentration and oxidation-reduction galvanic elements. Their structure, examples. Reversible and irreversible galvanic elements. Batteries. Weston element, its structure and application. Diffusion potential. Membrane potential. Biological role of diffusion and membrane potentials. Damage potential. The potential for calm. Action potential. The role of oxidative-restorative reactions in the processes of life. Oxidation-reduction potential as a measure of oxidative and restorative capacity of systems. Peters equation. Normal redox potential. Forecasting the direction of oxidative-reduction reactions by the quantities of oxidative-reduction potentials. The equivalent of an oxidizer and a restorer. The value of oxidative-reduction potentials in the mechanism of biological oxidation processes.

Laboratory work
5. MEASUREMENT OF ELECTROMOTIVE FORCES OF GALVANIC CELLS AND DETERMINATION OF ELECTRODE POTENTIALS OF INDIVIDUAL ELECTRODES

For work you need: battery for 1,2 V is A_k; galvanometer is Γ; normal Weston element is *En*; element with unknown EMF is *Ex*; rheochord *AB*; switching key *K*; switch for six terminals *P*; current conductors; solutions of $CuSO_4$, $ZnSO_4$; saturated solution KCl.

The aim of the work is to determine the value of the EMF of the studied galvanic elements and the electrode potentials of individual electrodes by the compensation method.

A device that converts chemical energy into electrical energy is called a galvanic cell. It can be represented by the diagram

$$(+)Me_1 \left| \begin{matrix} salt \\ solution \\ Me_1^{n+} \end{matrix} \right\| \left. \begin{matrix} salt \\ solution \\ Me_2^{n+} \end{matrix} \right| Me_2(-)$$

In most cases, the EMF of such an element is measured by two methods: by connecting a sensitive voltmeter to the circuit or by the compensation method. The first of these methods has some disadvantages associated with the passage of electric current through the device. These disadvantages are eliminated when determining the EMF by the compensation method, when no current passes through the element.

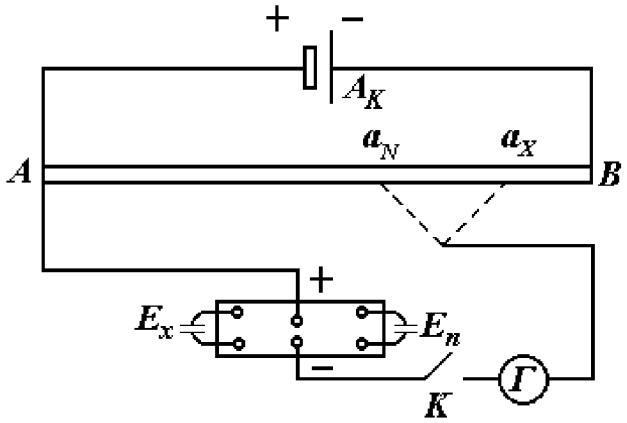


Fig. 1. Scheme of installation for measuring EMFcompensation method.

The principle of the compensation method is that another element with an unknown emf is connected to an element with an opposite emf (current source). This results in mutual compensation of the two electromotive forces – the element under test and the current source.

The installation scheme for the compensation method is shown in the figure. The battery *AK* is closed through the wire *AB*, which is stretched along the scale of the rechord with a length of 1 m. The wire along the entire length of the rechord is uniform and has the same cross-section, so the voltage drop per unit length is also the same and equal to , and the voltage drop along the entire length of the rechord is equal:

$$E_a = Ir\,, \qquad (1)$$

where
I is amperage;
r is resistance per unit length of wire (resistivity).

If an element with an unknown emf is included in the circuit towards the battery, then by moving the slider *C* along the ruler *AB*, you can find a position at which the galvanometer *Г* arrow reaches zero.

This is due to the fact that the emf of the galvanic cell E_x is exactly compensated by the potential difference between points A and B. If this potential difference is greater than the emf of the cell, the galvanometer arrow deviates to one side. If the emf of the galvanic cell is greater than the potential difference on the ruler, the galvanometer arrow will deviate in the opposite direction.

It is necessary to know these two positions, then reduce the interval between them until the galvanometer arrow reaches the zero position.

If the galvanometer is in the zero position and the slider is at distance ah, then

$$E_x = a_x \cdot Ir \text{, a } E_{AK} = Ir .$$

From the ratio

$$\frac{E_x}{E_{AK}} = \frac{a_x \cdot Ir}{Ir},$$

find

$$E_x = E_{AK} a_x . \qquad (2)$$

However, the emf of the battery is unknown, and even more so, it can change during operation. Therefore, before compensating for E_x, a normal Weston element E_N, whose emf is known, is included in the electrical circuit instead of the element under study.

When compensating for E_N and the battery emf, we obtain a certain position of the contact a_N, then

$$E_N = a_N \cdot Ir . \qquad (3)$$

From the ratio

$$\frac{E_{AK}}{E_N} = \frac{Ir}{a_N \cdot Ir},$$

find

$$E_{AK} = \frac{E_N}{a_N} . \qquad (4)$$

Substituting Equation (4) into equation (2), we find the EMF of the element under study:

$$E_x = E_N \frac{a_x}{a_N} . \qquad (5)$$

Work progress

According to the above scheme, the normal Weston element is compensated first, then the copper-zinc element, and only then the calomel-zinc

element. From the data obtained, the EMFs of the elements under study are calculated using formula (5).

From the value of the emf of the calomel-zinc element, the potential of the zinc electrode is calculated. The potential of the calomel electrode in relation to the zinc electrode will be positive. Its values depending on the temperature are given in work 6.1.

The value of the zinc electrode potential is calculated based on the following relation:

$$E_{кал/Zn} = П_{кал} - \left(- П_{Zn/Zn^{+2}}\right), \text{ hence } - П_{Zn/Zn^{+2}} = E_{кал/Zn} - П_{кал}. \qquad (6)$$

The experimental results and estimates recorded in the Table:

Table 1

Element	Indicationson line	EMF	Electrode potential
Norm. element Weston			
$Cu^{+} / CuSO_4 \| ZnSO_4 / Zn^{-}$			
$(Pt)Hg^{+} / \frac{Hg_2Cl_2}{KCl} \| ZnSO_4 / Zn^{-}$			$П_{Zn^{2+}/Zn} =$

QUESTIONS FOR SELF-CONTROL:

1. Describe the electrode potential and the mechanism of its occurrence at the metal-salt solution interface.
2. The dependence of the potential value on the nature of the metal, the concentration of ions of a given metal in solution and on temperature.
3. Nernst's equation.
4. Classification of electrodes.
5. Electrodes of the first kind. Normal hydrogen electrode, its structure and potential.
6. Normal potentials. A number of voltages. Standard electrodes, determination electrodes, comparison electrodes.
7. Electrodes of the second kind.
8. Redox electrodes.
9. Calomel electrode.
10. The quinhydrone electrode.
11. Glass electrode.

12. Application of ion-selective electrodes in medicine and pharmaceutical analysis.
13. Galvanic elements, their classification.
14. Chemical, concentration and redox galvanic elements. Their structure, examples.
15. Reversible and non-reversible galvanic cells. Batteries.
16. Weston's element, its structure and application.
17. Diffusion potential. Membrane potential. Biological role of diffusion and membrane potentials.
18. Damage potential. Resting potential. Action potential.
19. The role of redox reactions in life processes.
20. Redox potential as a measure of oxidation and reduction capacity of systems.
21. Normal redox potential.
22. Prediction of the direction of redox reactions by the values of redox potentials.
23. What is the equivalent of an oxidizing and reducing agent?
24. What is the importance of redox potentials in the mechanism of biological oxidation?

TOPIC 6. HYDROGEN INDEX. BUFFER SYSTEMS

Theoretical questions:

Water as a weak electrolyte. Electrolytic dissociation of water. Ionic product of water, its practical value. Concentration of hydrogen ions, hydrogen indicator, their relationship. pH scale. Methods of pH measurement. Buffer mixtures, their properties. Classification of buffer systems, examples. Mechanism of action of buffer systems. Buffer capacity and factors that determine it. Alkaline blood reserve. Biological role of buffer systems. Valeur of hydrogen pH for various biological fluids of the human body in normal and pathology. Potentiometric titration and its value for the analysis of biological fluids and medicinal substances.

Laboratory work
6.1. DETERMINATION OF THE HYDROGEN INDEX BY THE POTENTIOMETRIC METHOD

For work you need: potentiometer; battery; Weston's normal cell; chinhydrone-calomel cell; galvanometer; conductors; quinhydrone; test solutions.

The aim of the work is to determine the value of the hydrogen pH of the studied buffer systems by potentiometric titration based on the measurement of the EMF of the studied galvanic cells.

Work progress

To determine the pH using a quinhydrone electrode, a quinhydrone-calomel chain is used:

$$^{(-)}Hg\left|Hg_2Cl_2,\ KCl\right\|H^+, quinhydrone\left|Pt^+\right.$$

The EMF of this circuit is measured using a potentiometer. The pH of the solution is calculated based on the equation for the dependence of the potential of the quinhydrone electrode on the concentration of hydrogen ions:

$$P_{\text{quin}} = P_{\text{Oquin}} + 2{,}303\frac{RT}{F}lgC_{H^+},\ pH = -lgC_{H^+}$$

or

$$P_{quin} = P_{Oquin} - 2{,}303\frac{RT}{F}pH\ .$$

The EMF of the chinhydron-calomel element takes the form:

$$E_{quin/cal} = P_{quin} - P_{cal}.$$

Substituting the values of P_{quin} and P_{cal} into this equation, we obtain:

$$E_{quin/cal} = P_{Oquin} - 2{,}303\frac{RT}{F}pH - P_{cal}.$$

This is where we get the calculation formula:

$$pH = \frac{P_{Oquin} - P_{cal} - E_{quin/cal}}{2{,}303\frac{RT}{F}}.$$

The values of the normal potential of the chinhydrone electrode is P_{Oquin}, the potential of the saturated calomel electrode is P_{cal}, depending on the temperature, as well as the value of the coefficient $2{,}303\frac{RT}{F}$ is taken from the Tables at the end of the description.

To determine the emf of the quinhydrone-calomel element, connect the following to the corresponding terminals on the potentiometer: a quinhydrone-calomel element, a normal Weston element, a galvanometer, and a current source. Remember that the current source is connected last when assembling the electrical circuit. Prepare the quinhydrone electrode as follows.

Pour the test solution into a glass dish; add the quinhydrone to the same dish until saturation.

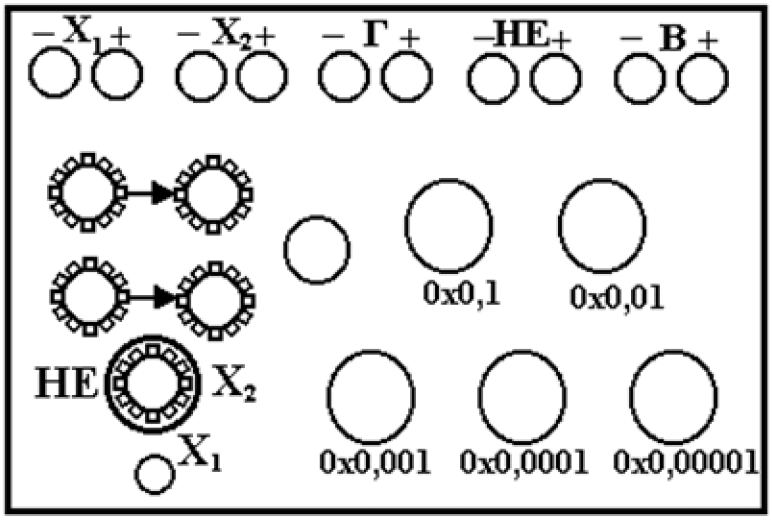


Fig. 1. The compensation scheme potentiometer.

The solution is thoroughly mixed and the platinum electrode is lowered. The prepared chinhydrone electrode is connected to the calomel electrode by means of salt bridges.

The finished chinhydrone-calomel element is connected to the device shown in the figure.

If measurements are performed with a chinhydrone electrode, the calomel electrode is connected to the minus terminal, and with a hydrogen electrode – to the plus terminal. Before measuring the emf of the quinhydrone-calomel circuit, the potentiometer is first adjusted to the normal element. To do this, the switch knob is placed in the "NC" position, and the rheostats mounted on the left side of the device are used to select the resistance, starting with a rough setting and ending with a smoother one until the galvanometer arrow shows no current. Then begin to determine the emf of the element under study. To do this, the switch knob is placed in the "X" position and the rheostats mounted on the right side of the device (starting with the knob 0.1 and ending with 0,001 V) are used to select such a resistance at which the galvanometer arrow shows no current, i.e., it will reach zero.

The total value of the readings of each rheostat corresponds to the value of the emf of the chinhydron-calomel element. Given the value of the emf of the quinhydrone-calomel electrode, the value of the hydrogen index is calculated using the calculation formula.

The results of the experiment are recorded in Table 1.

Table 1

Test solution	Potentiometer readings, V	$P_{o\ quin}$, V	P_{cal}, V	$2{,}303\frac{RT}{F}$	pH

The results are checked by teacher.

The value of the potential of a saturated calomel electrode at different temperatures are shown in Table 2.

Table 2

Tempera-ture, K	Potential, V	Tempera-ture, K	Potential, V	Tempera-ture, K	Potential, V
286	0,32	289	0,2517	292	0,2425
287	0,2525	290	0,2509	293	0,2488
288	0,2517	291	0,2503	294	0,2458

The value of the normal capacity quinhydrone electrode at a temperature of 281 K to 301 K are given in the Table 3.

Table 3

Temperature, K	$P_{o\ hin}$, V	Temperature, K	$P_{o\ hin}$, V
281	0,6866	292	0,6948
282	0,6874	293	0,6955
284	0,6888	294	0,6970
285	0,6896	295	0,6977
286	0,6903	296	0,6985
287	0,5911	297	0,6992
288	0,6918	298	0,6999
289	0,6925	299	0,7007
290	0,6933	300	0,7011
291	0,6940	301	0,7022

The values $2{,}303\frac{RT}{F}$ for different temperatures are shown in Table 4.

Table 4

T, K	$\mathbf{2{,}303\frac{RT}{F}}$	T, K	$\mathbf{2{,}303\frac{RT}{F}}$
283	0,0561	294	0,0583
284	0,0563	295	0,0585
285	0,0565	296	0,0587
286	0,0567	297	0,0589
287	0,0569	298	0,0591
288	0,0571	299	0,0593
289	0,0573	300	0,0595
290	0,0575	301	0,0597
291	0,0577	302	0,0599
292	0,0579	303	0,0601
293	0,0581	–	–

Laboratory work
6.2. POTENTIOMETRIC pH DETERMINATION, CALCULATION DISSOCIATION CONSTANT OF A WEAK ACID

For work you need: solutions of weak acid; 50 ml chemical beaker; glass electrode; pH meter.

The purpose of the work is to determine the value of the hydrogen pH of the studied solutions of a weak acid and to calculate its dissociation constant.

Work progress

The potentiometric method of determining the pH of a weak acid solution makes it possible to calculate the dissociation constant. If we take a weak acid for the experiment, we know the mathematical expression of Ostwald's dilution law:

$$K = \frac{\alpha^2 \cdot c(x)}{1-\alpha}$$

can be replaced by the equation: $K \cong \alpha^2 \cdot c(x)$,

where

K is the dissociation constant of the acid;

α is the degree of dissociation;

$c(x)$ is the molar concentration of the acid.

The molar concentration of hydrogen ions in a solution of a weak acid is related to the degree of dissociation and the dissociation constant by the following relation:

$$[H^+] = \alpha \cdot c(x) = \sqrt{K \cdot c(x)}$$

Logarithmizing the equality $[H^+] = \sqrt{K \cdot c(x)}$, we get

$$pH = \frac{1}{2} pK - \frac{1}{2} lg\, c(x).$$

Hence

$$\frac{1}{2} pK = pH + \frac{1}{2} lg\, c(x); \; pK = 2\left(pH + \frac{1}{2} lg\, c(x) \right).$$

The task is to determine the pH of a solution of a weak acid with a known molar concentration. For measurements, it is recommended to take solutions with a molar concentration of 0,01 mol/l to 0,5 mol/l.

Pour 20-30 ml of the test solution of a weak acid into a 50 ml chemical beaker. Carefully immerse the electrodes in the solution so that the glass

electrode ball is completely submerged. Measure the pH of the solution using a pH meter and calculate the pK using the formula $pK = 2\left(pH + \frac{1}{2} lg\, c(x)\right)$.

Then use the antilogarithmic Table to determine the dissociation constant. Compare this value with the Table. Determine the absolute and relative error.

Laboratory work
6.3.STUDY OF BUFFER PROPERTIES OF SOLUTIONS AND DETERMINATION OF THEIR BUFFER CAPACITY

For work you need: distilled water; 0.1 N solution of CH_3COOH; 0.1 N solution of CH_3COONa; 0.1 N solution of NaOH; indicator; measuring pipettes; chemical beaker; chemical flasks; titration burette.

The aim of the work is to determine the buffer capacity of the buffer system under study.

To quantitatively characterize the buffering properties of solutions, a value called buffering capacity is introduced.

The buffering capacity is equal to the number of gram equivalents of acid or alkali that must be added to 1 liter of buffer solution to change its value by one.

To experimentally determine the buffering capacity, a certain amount of acid (or alkali) in gram equivalents is added to 1 liter of buffer system. Determine before the addition of the acid (or alkali) and take this value as , and after the addition as . The change in value is calculated using the formula:

$$\Delta pH = pH_K - pH_0. \qquad (1)$$

The value of the buffer capacity B is calculated by the formula:

$$B = \frac{b}{\Delta pH}, \qquad (2)$$

where

b is the amount of alkali (or acid) in gram equivalents, for example $NaOH$, added to 1 liter of the test solution.

The value of the buffer capacity depends on the concentration of the components of the buffer system and on the concentration of the alkali or acid solutions introduced into the system. The highest buffering capacity is achieved in solutions in which the concentration of a weak acid (or weak base) is equal to the concentration of its salt in the buffer mixture.

Work progress

Prepare solutions of 0.1 N of CH_3COOH and 0.1 N of CH_3COONa. Then, using pipettes, take 50 ml of each and mix to obtain a buffer mixture.

Take 25 ml of this mixture and dilute with water in a ratio of 1:1 and 1:2. In separate samples, determine the pH of the original buffer solution and both diluted solutions. Next, the effect of dilution on the pH of the buffer solution under test is determined.

Next, determine the buffer capacity of each of the three solutions under test. To do this, take 25 ml of sample, add a universal indicator and titrate with 0.1 N NaOH solution. Next, determine the pH of each solution after titration using the potentiometric (or electrometric) method (see Procedure 6.1).

Calculate the buffer capacity of the buffer system under study using the formula:

$$B = \frac{C_{NaOH} \times V_{NaOH} \times 40}{1000 \times (pH_0 - pH_K)}, \qquad (3)$$

where

C_{NaOH} and V_{NaOH} are, respectively, the concentration (in g-eq/l) and volume (in ml) of the solution used for titration;

pH_0 and pH_K are the values of the solution before and after titration, respectively.

QUESTIONS FOR SELF-CONTROL:

1. Describe water as a weak electrolyte.
2. Electrolytic dissociation of water.
3. Ionic product of water, its practical significance.
4. Concentration of hydrogen ions, hydrogen index, their relationship.
5. The pH scale. Methods of measuring pH.
6. Buffer mixtures, their properties.
7. Classification of buffer systems, examples.
8. The mechanism of action of buffer systems.
9. Buffer capacity and factors that determine it.
10. What is the “alkaline blood reserve” and “BCC”?
11. What is the biological role of buffer systems and their types in the human body?
12. The value of hydrogen pH for different biological fluids of the human body in normal and pathological conditions.
13. What is the essence of potentiometric titration and what is its significance for the analysis of biological fluids and drugs?

TOPIC 7. KINETICS OF CHEMICAL REACTIONS AND CATALYSIS

Theoretical questions:

Chemical kinetics as a basis for studying the velocities and mechanism of biochemical reactions. Its importance for medicine, life of living organisms, pharmacy and practice. Reaction speed and methods of its expression. The law of active masses, the reaction velocity constant. Factors affecting the rate of chemical reaction. Influence of temperature on the rate of chemical reaction. Van Goff rule. Temperature limits of life. Features of temperature coefficient of reaction rate for biochemical processes. The concept of the mechanism of reaction. Molecularity and reaction order. Kinetic equations of first, second and zero order. The half-transformation period is a quantitative characteristic of the change in the concentration of radionuclides, pesticides, etc. Complex reactions (parallel, sequential, reversible, conjugated). Chain and photochemical reactions. The concept of photosynthesis, antioxidants. Free radical reactions in the living organism. Catalysis and catalysts. Features of the action of catalysts. Inhibitors, promoters, catalytic poisons. Homogeneous and heterogeneous catalysis. Acid-base and enzymatic types of catalysis. Autocatalysis.

Activation energy. Theory of active co-strikes. Arrhenius equation. The concept of transition state theory (activated complex). The idea of the kinetics of enzymatic reactions. Enzymes as biological catalysts. Features of enzymes action: selectivity, efficiency, dependence of enzymatic action on temperature and reaction of the medium. The concept of the mechanism of action of enzymes. Dependence of the speed of enzymatic processes on the concentration of enzyme and substrate. Activation and inhibition of enzymes. Influence of environmental factors on the kinetics of enzymatic reactions. Use of catalysts in medicine, pharmaceutical industry.

Laboratory work

7.1. DETERMINATION OF THE DECOMPOSITION RATE OF HYDROGEN PEROXIDE BY THE GASOMETRIC METHOD

For work you need: installation (Fig. 1), hydrogen peroxide, thermostat.

The aim of this work is to determine the rate of homogeneous or heterogeneous decomposition of hydrogen peroxide and to calculate the corresponding kinetic parameters of the process using the gasometric method.

Hydrogen peroxide in aqueous solutions decomposes slowly according to the equation:

$$H_2O_2 \rightarrow H_2O + 0{,}5O_2$$

The decomposition of hydrogen peroxide is significantly accelerated in the presence of cations and anions of some organic substances, as well as a number of solids. Therefore, this reaction in aqueous solutions can be a homogeneous or heterogeneous catalytic reaction, depending on the catalyst used.

The progress of the reaction is monitored by the change in the volume of oxygen released at different intervals from the start of the reaction.

Work progress

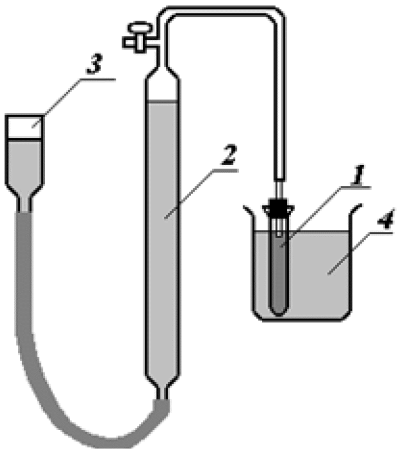


Fig. 1.

Fill the reaction vessel 1 with the catalyst solution so that the height of the air space between the liquid level and the crust does not exceed 2 cm and place it in the thermostat 4 at a certain set temperature. Fill the equalization beaker 3 and the burette 2 with water. Set the water level in the burette to the level of the upper tap.

After 30 minutes of thermostatting, pour a certain amount of hydrogen peroxide into the reaction vessel. Stir the solution thoroughly with a glass rod and close the reaction vessel with a cork.

Keep the top tap open for 1-2 min (to expel the air released by the oxygen from the reaction vessel), then close it, thus connecting the reaction vessel to the gas burette. Set the liquid levels in the burette and the equalization beaker to the same level, make the first measurement, and record the level on the burette and the time. Each subsequent change is recorded in this way, and the liquid level in the burette and the leveling beaker is kept the same. The liquid level in the burette is recorded after 2-5 minutes (the higher the temperature, the shorter the time between measurements). After the reaction has almost stopped, the reaction vessel is placed in a boiling water bath and kept in it until the hydrogen peroxide is completely decomposed (about 30 minutes). The reaction is considered complete when the gas level in the burette stops changing. During the boiling in the water bath, the volumetric beaker is held in the highest position.

After complete decomposition of hydrogen peroxide, cool the reaction vessel to the temperature of the thermostat, keep it there for 25-30 minutes, and measure the level of liquid in the burette and the equalization beaker at the same level.

When processing the experimental data, take the third or fourth measurement as the beginning of the reaction (i.e., measurements under steady-state conditions). Determine the time interval from the start of the reaction to each subsequent measurement τ and the volume of oxygen released during these intervals a_{τ}..

Using the data obtained, draw dependence graphs:

1.Equality of oxygen volumes versus time (time in minutes):

$$[a_\infty - a_\tau] = f(\tau)$$

2. The equation $\lg v = f(\lg C)$ by which the order of the reaction is found.

3. the logarithm of the reaction rate at different intervals from the logarithm of the difference in the volume of oxygen released $\lg v_\tau = [\lg(a_\infty - a_\tau)]$.

Next, the value of the reaction rate constant is calculated by E_q:

$$K = \frac{2{,}303}{t}\lg\frac{C_o}{C_\tau} = \frac{2{,}303}{t}\lg\frac{a_\infty}{a_\infty - a_\tau}.$$

where

a_∞ is the volume of oxygen released after the decomposition of hydrogen peroxide (defined as the difference in levels in the ballot at the moment taken as the beginning of the reaction and after boiling H_2O_2 until complete decomposition).

Present the results in the form of 4 graphs and a Table 1.

Temperature of the experiment _____

Catalyst _____

Amount of hydrogen peroxide _____

Table 1

No. of measurements	Measurement time, s	Time from the beginning of the reaction, s	The liquid level in the in the burette, ml	The volume of gas that released, m^3	Reaction speed	$\lg(\alpha_\infty - \alpha_\tau)$	$\lg v_\tau$	$K = \frac{2,3}{t}\lg\frac{\alpha_\infty}{\alpha_\infty - \alpha_\tau}$	K

Laboratory work
7.2. PHOTOCHEMICAL DECOMPOSITION OF H_2O_2

For work you need: unit (Fig. 1), hydrogen peroxide.

The aim of this work is to determine the rate of photochemical decomposition of hydrogen peroxide and to calculate the corresponding kinetic parameters of the process using the gasometric method.

The photochemical decomposition of H_2O_2 is a typical chain process, the mechanism of which can be represented as follows:

$H_2O_2 + h\gamma \rightarrow 2OH\cdot$ – chain nucleation reaction;
$OH\cdot + H_2O_2 \rightarrow H_2O + HO_2$ – regeneration cycle;
$HO_2 + 2H_2O_2 \rightarrow H_2O + H_2O_4$
$H_2O_4 + h\gamma \rightarrow 2OH\cdot + O_2$ – branching reaction;
$OH\cdot + OH\cdot = H_2O_2$ – chain break reaction.

Oxygen is released as a result of the reaction of

$$H_2O_4 \rightarrow H_2O_2 + O_2$$

This reaction is a chain reaction with "degenerate branching". In this process, the branching is carried out photochemically by supplying energy from the outside. A relatively stable intermediate is the free radical $OH^{\bullet}$. The kinetics of this reaction is expressed by E_q:

$$v = A\left(e^{\varphi\tau} - 1\right),$$

where
φ is the growth constant characterizing the branching rate;
τ is time.

Its logarithmization gives $\ln v = \ln A + \varphi\tau$. This is the equation of a straight line in the coordinate system $\ln v - \tau$. Before starting the work, it is necessary to calculate the thermal effects of the elementary stages of the reaction using thermodynamic functions and assess the feasibility of their implementation. The work is carried out on the installation, the scheme of which is shown in Fig. 1.

Work progress

The apparatus consists of a quartz flask 1 transmitting ultraviolet rays, a reflux condenser 5, a graduated gas burette 3, a balancing beaker 4, and a mercury-quartz lamp 2. Connect the quartz flask 1 with the H_2O_2 solution to the reflux condenser 5 and place it against the opening 6 and the protective shield 7. Open the tap 8 and set the liquid level in the burette 3 to zero using the leveling beaker 4.

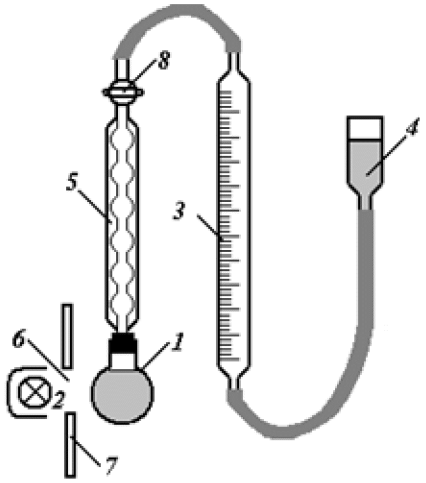


Fig. 1. Schematic of the setup for studying the kinetics of photochemical decomposition of H_2O_2

Pour water into the refrigerator and wait until the liquid level in the gas burette is established with the tap 8 closed.

The changed liquid level in the burette should be established by opening the tap 8. This ensures that the pressure is constant and equal to atmospheric pressure.

After equalization of the levels with the valve 8 closed, the mercury-quartz lamp and stopwatch are turned on simultaneously. The first count is recorded after 1.0-1.5 cm^3 of oxygen is released, then after 3 minutes, when the gas release rate reaches 1 cm3/min, counts are made every minute. When calculating the volume of gas, it is necessary to equalize the levels of liquids in the equalizing beaker and gas burette.

Stop the experiment when 75–100 cm^3 of gas is released. Record the experimental data in the Table 1:

Table 1

No. of measu-rement	The time from start reaction, s	Fashion burette	Volume O_2, which separated, m^3	The reaction rate, m/s	lg *v*

When processing the experimental data, plot the graph in the coordinate system . This relationship is necessary to calculate the velocity. The velocity at different times is determined by $v = \frac{\alpha_{\tau_2} - \alpha_{\tau_1}}{\tau_2 - \tau_1}$.

Take the time interval $\tau_2 - \tau_1$ equal to 2 minutes. The analytical dependence of the velocity on time is expressed by the equation $v = At^{\varphi\tau}$ which is in logarithmic form $\lg v = \lg A + \varphi\tau$.

To find the empirical constants *A* and φ, plot the dependence of *v* and τ and, following the increasing curve, take the value of *v* at different points in time and draw a graph in the coordinate system $\ln v - \tau$.

The value of φ is defined as the tangent of the angle of inclination of the resulting line to the τ axis, and is the segment cut off by the line on the axis at the value of $\tau = 0$.

7.3. DETERMINATION OF THE DECOMPOSITION RATE THIOSULFURIC ACID

For work you need: 0.1 mol/l $Na_2S_2O_3$ solution; 1 mol/l H_2SO_4 solution; rack with test tubes; burette; stopwatch.

The aim of this study is to investigate the influence of various factors on the decomposition rate of thiosulfuric acid.

Thiosulfuric acid is formed by the reaction of sodium thiosulfate with sulfuric acid:

$$Na_2S_2O_3 + H_2SO_4 = Na_2SO_4 + H_2S_2O_3$$

$$S_2O_3^{2-} + 2H^+ = H_2S_2O_3$$

The reaction is very fast. The decomposition of thiosulfuric acid is relatively slower:

$$H_2S_2O_3 \rightarrow H_2O + SO_2 + S$$

7.3.1. Dependence of the decomposition rate of thiosulfuric acid on its molar concentration

Work progress

Pour a $Na_2S_2O_3$ solution with a molar concentration 0.1 mol/l and distilled water in the volumes indicated in Table 1 into three test tubes. Pour 0.005 l of the solution ($C(H_2SO_4)$ = 1 mol/l) from the burette into the second three test tubes. Pour the prepared solutions of $Na_2S_2O_3$ and H_2SO_4, mix and note the time (t) from the moment of pouring the solutions until the turbidity due to the appearance of sulfur precipitate.

The molar concentration of sodium thiosulfate $C_2(Na_2S_2O_3)$ and the initial molar concentration of sulfuric acid $C(H_2S_2O_3)$ in the prepared mixtures are calculated by the formula:

$$C_2(Na_2S_2O_3) = C(H_2S_2O_3) = \frac{C_1(Na_2S_2O_3) \cdot V(Na_2S_2O_3)}{V_{(mixture)}}$$

where

$V(Na_2S_2O_3)$ is the volume of sodium thiosulfate solution added, l;

$V_{(mixture)}$ is the volume of the mixture under study, l.

Next, conclusions are drawn about the effect of the molar concentration of thiosulfuric acid on the reaction rate by comparing the time from the moment the solutions are poured until turbidity due to the formation of sulfur precipitate.

Table 1

No. of experiment	Solution volumes, 10^{-3} m^3			$C(H_2S_2O_3)$ in the mixture under study, kmol/m^3	t, s
	$Na_2S_2O_3$	H_2O	H_2SO_4		
1.	0,001	0,004	0,005	0,01	
2.	0,003	0,002	0,005	0,03	
3.	0,005	0,000	0,005	0,05	

7.3.2. Dependence of the decomposition rate of thiosulfuric acid on the temperature

Work progress

Pour 0.005 l of a solution with a molar concentration of $c(Na_2S_2O_3) = 0,1$ mol/l into three test tubes, and 0.005 l of a H_2SO_4 solution with $c = 1$ mol/l into the other three. Place all the tubes in a beaker of water and after 5 minutes, measuring the temperature of the water in the beaker, pour out the contents of one pair of tubes with solutions H_2SO_4 and $Na_2S_2O_3$, note the time t from the moment the solutions are poured out until they become cloudy due to the appearance of sulfur precipitate. Then pour some hot water into the beaker to raise the temperature by about 10 K. Keep the solutions at this temperature for 5 minutes and pour out the contents of the second pair of tubes with solutions: H_2SO_4 and $Na_2S_2O_3$, noting the time from the moment the solutions are poured out until they become cloudy due to the appearance of sulfur precipitate. The experiment with the last pair of tubes is carried out at a temperature approximately 20 degrees above the initial temperature.

The results are recorded in Table 2.

Table 2

No.	Temperature, K	t, s
1		
2		
3		

Next, you need to draw a conclusion about the effect of temperature on the rate of the chemical reaction by plotting the dependence $v = f(T)$.

Laboratory work
7.4. CATALYTIC EFFECT OF FERRIC IONS ON THE RATE OF OXIDATION OF HYDROCHLORIC ACID BY AMMONIUM PERSULFATE

For work you need: 0.5 mol/L solutions of KI, H_2SO_4, $CuSO_4$, $FeSO_4$, $(NH_4)_2S_2O_8$; thermostat; refrigerator; distilled water; starch solution; 250 ml conical flasks; pipette.

The aim of this work is to investigate the catalytic effect of Fe^{2+} and Cu^{2+} ions on the rate of HI oxidation by ammonium persulfate.

The oxidation reaction of hydrochloric acid with ammonium persulfate can be described by the equation:

$$(NH_4)_2S_2O_8 + 2HI \rightarrow 2NH_4HSO_4 + I_2$$

This reaction is slow. In the presence of a catalyst – copper and iron ions – this reaction is significantly accelerated.

In this work, we experimentally determine the effect of iron and copper ions on the oxidation rate.

Work progress

Prepare 300 ml of aqueous solutions: 1) 0,12 N KI; 2) 0,025 N H_2SO_4; 3) 0,0005 N $CuSO_4$ (0,062 g/l $CuSO_4$); 4) 0,0005 N $FeSO_4$ (0,07 g/l $FeSO_4 \cdot 7H_2O$); 5) 0,1 N $(NH_4)_2S_2O_8$. All these solutions with distilled water are placed in a thermostat with a temperature of 298 K.

At the same time, distilled water is placed in a refrigerator or in snow.

Using pipettes, the reaction mixtures are prepared as shown in Table 1.

In all three cases, potassium iodide is added to the solution last. The moment the potassium iodide is added (resulting in the formation of HI) is considered the beginning of the reaction. The mixture in each flask is quickly stirred and placed in a thermostat.

Table 1

Composition of the reaction mixture

No. of reaction mixture	Volume of solution in the mixture, 10^{-6} m^3					
	Distilled water	$(NH_4)_2S_2O_8$	H_2SO_4	$CuSO_4$	$FeSO_4$	KI
1	100	50	50	-	-	50
2	50	50	50	50	-	50
3	50	50	50	-	50	50

After 3, 6, 10, 20, 40, and 60 min, take 20 ml of the mixture, pour it into a 250 ml conical flask, add approximately 100 ml of cooled water, and titrate with 0.01 n. sodium thiosulfate solution in the presence of starch. The time of sample collection is noted exactly by the clock. The titration allows you to determine the amount of iodine formed during the reaction.

The titration results are recorded in Table 2.

Based on the experiment data, a graph is plotted in the coordinates: volume of sodium thiosulfate solution used for titration (ml), time (min), which is used to evaluate the catalytic effect of copper and ferrous ions.

Table 2

Titration results

No. of solution	The volume of $Na_2S_2O_8$ solution used to titrate the sample, ml, taken after a certain time, s					
	180	360	600	1200	2400	3600

Laboratory work
7.5. STUDY OF STARCH HYDROLYSIS IN THE PRESENCE OF HYDROCHLORIC ACID

For work you need: 10 % HCl solution; 10 % NaOH solution; starch; 1 % $CuSO_4$ solution; glucose; rack with test tubes; 250 ml flasks; alcohol.

The aim of this work is to investigate the catalytic effect of hydrochloric acid on the rate of starch hydrolysis.

Work progress

Pour 30 ml of 1 % starch solution into a reflux flask, add 15 ml of 10 % hydrochloric acid solution, bring to a boil, and boil for 10 minutes. Carefully cool the flask with running water. Perform the following reactions with the contents of the flask (hydrolyzate): a) starch; b) glucose (Tromer's reaction).

a) Take 10 drops of hydrolyzate into a clean test tube and add 1-2 drops of iodine. The appearance of blue color indicates the presence of starch (positive reaction), the absence of blue color indicates that starch has been hydrolyzed and hydrolysis products – maltose – have been formed (negative reaction).

b) Pour 5 drops of hydrolyzate into a test tube, add 8 drops of 10 % NaOH solution and copper sulfate $CuSO_4$ (1 % solution) until a blue copper (II) hydroxide precipitate appears. Heat the test tube over a burner flame. The

appearance of a yellow color turning to red indicates the presence of starch hydrolysis products – maltose and glucose.

Laboratory work
7.6. INVESTIGATION OF STARCH HYDROLYSIS IN THE PRESENCE OF ENZYMES AND HYDROCHLORIC ACID AT 310 K

For work you need: starch solution; enzyme solutions; water bath; test tube rack; iodine alcohol solution; hydrochloric acid solution.

The aim of this work is to investigate the catalytic effect of enzymes and hydrochloric acid on the rate of starch hydrolysis.

Work progress

Pour 2 ml of starch solution into 5 test tubes. Add 1 ml of saliva (or other enzyme) diluted 2-fold to 1 test tube, 4-fold to 2, 8-fold to 3, 1 ml of hydrochloric acid to 4, and 1 ml of water to 5 (test tube 5 serves as a control). Put all the tubes in a water bath at 310 K for 10 minutes. After cooling, pour the contents of each tube into 2 clean test tubes and perform the starch-iodine reaction and the Tromer reaction, similar to (a) and (b).

The results of the studies are recorded in Table 1.

Table 1.

No. p/n	Substrate	Catalyst	Temperature, K	Reaction to starch	Tromer's reaction	Does hydrolysis occur?

QUESTIONS FOR SELF-CONTROL:

1. Describe chemical kinetics as a basis for studying the rates and mechanisms of biochemical reactions.
2. What is its importance for medicine, the life of living organisms, pharmacy and practice?
3. Reaction rate and methods of its expression.
4. Law of active masses, reaction rate constant.
5. Factors affecting the rate of chemical reaction.
6. The effect of temperature on the rate of chemical reaction. Van't Hoff's rule.

7. Temperature limits of life. Features of the temperature coefficient of reaction rate for biochemical processes.
8. The concept of the reaction mechanism.
9. Molecularity and order of the reaction.
10. Kinetic equations of the first, second and zero order.
11. Half-life - quantitative characterization of changes in the concentration of radionuclides, pesticides, etc. in the environment.
12. Complex reactions (parallel, sequential, reversible, conjugated).
13. Chain and photochemical reactions.
14. The concept of photosynthesis, antioxidants.
15. Free radical reactions in a living organism.
16. Catalysis and catalysts.
17. Features of the action of catalysts.
18. Inhibitors, promoters, catalytic poisons.
19. Homogeneous and heterogeneous catalysis.
20. Acid-base and enzymatic types of catalysis.
21. Autocatalysis.
22. Activation energy. The theory of active collisions. Arrhenius equation.
23. The concept of the theory of the transition state (activated complex).
24. Concept of the kinetics of enzymatic reactions.
25. Enzymes as biological catalysts.
26. Features of enzyme action: selectivity, efficiency.
27. Dependence of enzymatic action on temperature and reaction of the medium.
28. The concept of the mechanism of action of enzymes.
29. Dependence of the rate of enzymatic processes on the concentration of enzyme and substrate.
30. Activation and inhibition of enzymes.
31. How do environmental factors affect the kinetics of enzymatic reactions?
32. Describe the use of catalysts in medicine and pharmaceutical industry.

TOPIC 8. PHYSICO-CHEMISTRY OF DISPERSE SYSTEMS

Theoretical questions:

Classification of disperse systems (DS) by aggregate state. Classification of DS by interaction between disperse phase and dispersion medium. General characteristics of lyophobic colloidal systems. General characteristics of lyophilic colloidal systems. Classification of DS by topographic characteristic. Classification of DS by the intensity of interaction between particles of disperse phase (by structure). Classification of DS by phase difference (suspensoids and molecular colloids). General description of methods for obtaining DS.Dispergative methods. Condensation methods, basic conditions. Physical condensation. Structure of micelles of lyophobic ash. Methods of chemical condensation. Peptizing methods. Methods of cleaning colloidal solutions: dialysis, electrodialysis, ultrafiltration, compensatory dialysis, vividialysis. Hemodialysis and artificial kidney apparatus.

Laboratory works

8.1. METHODS OF PREPARING COLLOIDAL SOLUTIONS

The aim of this work is to obtain colloidal solutions using various methods.

A colloidal solution or sol is a system consisting of particles of the dispersed phase with a size of 10^{-9}–10^{-7} m and a dispersion medium.

Particles of the dispersed phase can be solid (crystalline or amorphous), liquid and gaseous.

To date, it has been established that any substance can be obtained in the form of a colloidal solution if appropriate experimental conditions are chosen.

8.1.1. PREPARATION OF BERLIN AZURE SOL

For work you need: solutions of $K_3[Fe(CN)_6]$ (concentrations of 0.1 g/l and 20 g/l); 2% $FeCl_3$; 50 ml flasks - 2 pcs.; measuring pipettes.

Work progress

Prepare 20 ml of a diluted solution of potassium hexacyanoferrate $K_3[Fe(CN)_6]$ with a concentration of 0.1 g/l and add 1–2 ml of a 2% solution of iron (III) chloride dropwise.

For comparison, prepare 20 ml of a solution of potassium hexacyanoferrate conc. concentration of 20 g/l and add 10–20 ml of a 2% iron (III) chloride solution.

Conclusions and observations are recorded in a journal.

8.1.2. PREPARATION OF ROSIN OIL

For work you need: 2% rosin solution in ethyl alcohol; distilled water; 100-250 ml flask.

Work progress

Prepare a 2% solution of rosin in ethyl alcohol. Pour it dropwise into a large volume of distilled water (at the rate of 5 ml of rosin alcohol solution per 50 ml of water) with vigorous stirring (shaking). A transparent, highly opalescent lyophobic rosin-in-water sol is formed.

Rosin particles in this solution are negatively charged.

8.1.3. PREPARATION OF SULFUR HYDROZOL

For work you need: 2% sulfur solution in alcohol; distilled water; 50-100 ml flask.

Work progress

A solution of sulfur in ethyl alcohol is prepared in advance by periodically shaking the sulfur in the alcohol. The remaining sulfur that has not dissolved is filtered off.

Sulfur hydrosol is obtained by adding 5 ml of its alcohol solution dropwise to 20 ml of distilled water. The structure of the sulfur micelle in this solution is unknown. Sulfur particles are negatively charged.

8.1.4. PREPARATION OF IRON HYDROXIDE SOL

For work you need: 2 % solution; 30 and 200 ml measuring cylinders; 250 ml flask; 8 25 ml flasks; K2SO4 salt solution; $K_3[Fe(CN)_6]$ salt solution.

Work progress

This method is mainly used to produce heavy metal hydroheavy metal hydroxides. Its essence is as follows: in a flask, 200 mL of distilled water is heated to a boil

200 ml of distilled water is heated to a boil in a flask and 30 ml of a 2% solution of $FeCl_3$ is added in separate portions. First, ferric (III) oxide hydrate is obtained according to the scheme (reaction equation):

$$FeCl_3 + 3H_2O \Leftrightarrow Fe(OH)_3 + 3HCl$$

The $Fe(OH)_3$ molecules enter into chemical interaction with HCl:

$$Fe(OH)_3 + HCl \Leftrightarrow FeOCl + 2H_2O$$

The FeOCl molecules dissociate into ions:

$$FeOCl \rightarrow FeO^+ + Cl^-$$

On the surface of a colloidal particle, those ions that are similar in nature to the nucleus are adsorbed from the solution. Then the structure of a colloidal particle of ferric hydroxide (III) ash can be schematically represented as follows:

$$\{m[Fe(OH)_3]nFeO^+(n-x)Cl^-\}^{+x} \cdot xCl^-$$

Laboratory work
8.2. DETERMINATION OF THE CHARGE SIGN OF A COLLOIDAL PARTICLE (CAPILLARY ANALYSIS)

For work you need: distilled water; colloidal solution; chemical beaker; chemical stand; filter paper.

The purpose of the work is to determine the charge of micelle granules of the studied colloidal solutions.

Work progress

The electric charge sign of colloidal particles or macromolecules can be determined by capillary analysis. The preferred method is to use loose filter paper with sufficiently wide pores.

When the paper is immersed in water, the cellulose walls of the capillaries become negatively charged due to the selective adsorption of OH- ions, while the water is positively charged.

If a strip of paper is not completely immersed in water, the water will rise through the capillary forces (surface tension). The negatively charged particles of the colloidal solution will rise with the water, resisting the forces of attraction. Positively charged particles will be attracted to the negatively charged walls of the capillaries, so their height of rise will be lower. A significant difference in the height of the ash can be used to determine the charge sign or to separate colored ash.

Pour the colored iron(III) hydroxide and Prussian blue ash into small beakers to the same height and dip identical narrow strips of filter paper into them. The upper edges of the strips of paper are glued to a bar that is fixed horizontally in a tripod. After 30-60 minutes, the height of the rise is measured

and a conclusion is made about the charge sign of the ash. The results of the observations are recorded in a journal.

8.3. COLLOIDAL SOLUTION DIALYSIS

For work you need: distilled water; 1% solution of purified gelatin or freshly prepared ash; sodium chloride; colloidal dialysis bag; silver nitrate solution; 10% tannin solution; chemical beaker; chemical rack with test tubes.

The aim of the work is to purify a colloidal solution from electrolyte ions using the dialysis method.

Work progress

A 1% solution of purified gelatin is poured into a colloidal dialysis bag, to which a small amount of sodium chloride is added. The bag with the solution is immersed in distilled water.

After a certain period of time (3-4 hours), a separate portion of water from an external vessel is analyzed for chloride ions with silver nitrate and gelatin with a 10% tannin solution.

QUESTIONS FOR SELF-CONTROL:

1. What does the subject of colloidal chemistry study and what is its importance for living organisms and medicine?
2. Basic concepts of colloidal chemistry.
3. The body as a complex set of dispersed systems.
4. Classification of dispersed systems (DS) by particle size (by dispersion).
5. Classification of DS by aggregate state.
6. Classification of DS by the interaction between the dispersed phase and the dispersion medium.
7. General characteristics of lyophobic colloidal systems.
8. General characteristics of lyophilic colloidal systems.
9. Classification of DS on a topographic basis.
10. Classification of DS by the intensity of interaction between particles of the dispersed phase (by structure).
11. Classification of DS by phase difference (suspensions and molecular colloids).
12. General characteristics of methods for obtaining DS. Dispersion methods.
13. Condensation methods, basic conditions. Physical condensation.
14. The structure of the micelle of lyophobic sol.

15. Methods of chemical condensation.
16. Describe the methods of peptidization.
17. What is the essence of the methods of purification of colloidal solutions: dialysis, electrodialysis, ultrafiltration, compensatory dialysis, vividialysis? What is their difference?
18. Explain the essence of hemodialysis and the principle of operation of the "artificial kidney".

TOPIC 9. ELECTRICAL SURFACE PROPERTIES OF DISPERSE SYSTEMS

Theoretical questions:

Formation and structure of a double electric layer (PES). Basic PES theories. Electrokinetic phenomena. Electrokinetic phenomena: electroosmosis, electrophoresis, potentials of flow and sedimentation. Helmholtz–Smolukhovsky equation. Practical use of electrokinetic phenomena in medicine, pharmacy, biology, in research and clinical and Laboratory workoratory practice, etc. Electrophoregrams.

Electrokinetic potential of ξ. The concept of the isoelectric state of ash. Factors affecting electrokinetic potential. Influence of indifferent electrolytes on the magnitude of electrokinetic potential. Influence of non-indifferent electrolytes on the magnitude of electrokinetic potential. Influence of pH-medium on the magnitude of electrokinetic potential. Influence of other factors on electrokinetic potential.

Causes of hydrophilic and amphoteric properties of the protein molecule. Influence of hydrogen ion concentration of H^+ on protein dissociation. Isoelectric state. The influence of electrolytes on the position of the isoelectric point of casein. Features of the isoelectric state of lyophilic ash. Changes in the properties of a protein molecule at an isoelectric point.

Laboratory work
9.1. DETERMINATION OF THE ELECTROKINETIC POTENTIAL VALUE BY ELECTROPHORESIS

For work you need: a device for electrophoresis; voltmeter; iron hydroxide sol (III); 0.001 n. NaOH solution.

The aim of this work is to determine the value of the electrokinetic potential using the electrophoresis method and to investigate the influence of various factors on it.

Work progress

The magnitude of the electrokinetic potential can be determined using electrophoresis is the movement of microscopic particles suspended in water under the influence of direct current. This phenomenon was first observed in 1807 by Prof. F.F. Reiss.

The device for electrophoresis is a U-shaped glass tube (see figure) with two taps 1 and 2. From below, this tube is connected by tap 3 to tube 6, which goes into the watering can. The device is filled with a colloidal solution through

a funnel with the taps open, after which the funnel is closed with a lid, all the taps are turned and the excess colloidal solution is drained from both elbows of the U-shaped tube. Then a transparent uncolored electrolyte (side liquid) is poured into both knees, the electrical conductivity of which should be equal to the electrical conductivity of the colloidal solution. Next, taps 1 and 2 are opened and tap 3 is slowly opened. At the same time, the colloidal solution rises above the taps, and the electrolyte solution rises until electrodes 4 are immersed in it. Then tap 3 is closed. A clear border should be established between the painted sol and the electrolyte. Turn on the source of direct current 8 and observe the movement of the boundary of the colored sol on the scale 5, accurately noting the time of the beginning and end of the experiment and the corresponding path of movement of the sol S.

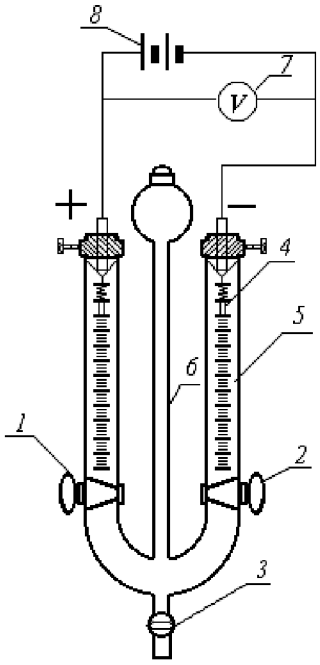


Fig. 1. Device for electrophoresis.

With the help of a flexible wire, the distance (average) between the electrodes is measured and the average value of the potential gradient is calculated

$$H = \frac{U}{l}. \qquad (1)$$

The value of U is determined using a voltmeter 7.

ξ-potential is calculated by the formula:

$$\xi = \frac{k\pi\eta}{D} \cdot U \cdot 300^2, \qquad (2)$$

where

D is the dielectric constant of the liquid;

η is liquid viscosity, N·s/m^2;
k is a constant that depends on the shape of the particles;
U is the electrophoretic speed, which is equal to the path (m) that the particles travel in 1 s at a potential gradient H with a value of B per 0.01 m.

For sols of iron hydroxide and Berlin blue, the value k = 4 (for globular particles).

The value of the electrophoretic speed U is determined by the formula

$$U = \frac{s}{\tau \cdot H}, \qquad (3)$$

where
S is path, m, traveled by the particles during time τ, s.

A battery of galvanic cells with a voltage of 60–80 V is used as a source of direct current. You can use alternating current, connected whose rectifier.

For experiments, iron hydroxide sol is prepared in advance and dialyzed they call it, ammonium chloride solution with a concentration of 1 g/l is used as a side liquid.

The prepared hydroxide sol is poured into 4 vessels of 25–50 ml each and 0.001 N is added to the first one. caustic soda solution, 10 ml in the second, 5 ml in the third.

Instead of iron hydroxide sol, you can use any dye flax sol (for example, Berlin blue).

If the device is used with only one tap (without taps 1 and 2 U-shaped tube), then the colloidal solution is poured into the device with the tap closed so that the thin tube and the funnel are filled with it. 10^{-2} m from the upper edges of the U-shaped tube. Then pour 6–10 ml of lateral liquid into the U-shaped tube, insert the platinum electrodes so that they are at a distance of 5–6 Then carefully open the tap a little so that the sol slowly flows into the U-shaped tube. At the same time, a clear boundary between the colored sol and the side liquid should be maintained. When the lateral liquid reaches 1/2–3/4 of the platinum electrodes, the tap is closed.

The results of experiments are recorded in the following Table:

Table 1

No. of solution	Duration electrophoresis, s	The path that passed the border of colored ash, 10^{-3} m	High-voltage , V

Laboratory work
9.2. DETERMINATION OF THE ISOELECTRIC POINT OF PROTEINS

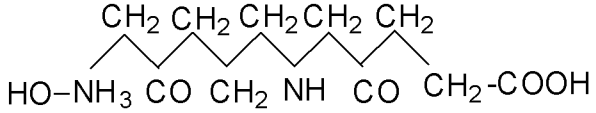
For work you need: solutions: 0.01 N of CH_3COOH; 0.1 N of CH_3COOH; 1 N of CH_3COOH; 0.1 N of CH_3COONa; casein solution in 0.1 N of CH_3COONa; methyl orange indicator; a pipette graduated for 10 ml; tripod with sample kami.

The aim of this work is to determine the isoelectric point of protein (casein).

Proteins, which make up the basis of protoplasm, have a number of properties arising from their specific chemical nature.

Protein molecules are long polymer-type chains consisting of many amino acids.

A simplified diagram of the structure of a protein molecule can be presented as follows:

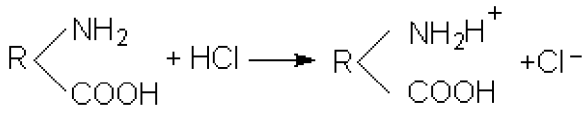


The scheme shows that the protein molecule, along with the hydrocarbon radical, contains a significant number of polar hydrophilic groups: –COOH; –NH_2; =CO; =NH.

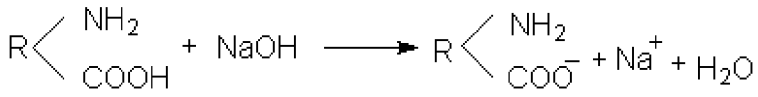
In this regard, proteins have highly hydrophilic properties. The presence of the basic –NH_2 group and acidic –COOH condition the amphoteric properties of the protein molecule, which has basic properties when trans- the influence of the amino group prevails, and acidic, when the influence prevails carboxyl group.

In aqueous solutions, proteins exhibit the properties of weak electrolytes. In this case, dissociation of both the basic and acidic groups takes place.

In an acidic environment, the dissociation of carboxyl groups is reduced by hydrogen ions, which are present in excess. At the same time, the protein molecule is positively charged. For example, in the presence of hydrochloric acid, pro- the reaction is:



In an alkaline environment, due to an excess of OH–ions, the dissociation of the main group –NH_2 decreases and the protein molecule is negatively charged tively



Therefore, at a certain concentration of hydrogen ions (that is, at a certain pH value of the medium), the number of ionized basic groups and the total charge of the particle will be zero, that is, the system will be in an isoelectric state.

The concentration of hydrogen ions, expressed by the value of the hydrogen indicator pH, at which the protein molecule is in the isoelectric triple state is called the isoelectric point. For each protein, there is a certain pH value at which it is see in the isoelectric state. For most proteins, their isoelectric point lies in an acidic environment at pH<7.

This is explained by the fact that the surface of the protein molecule is dominated by acidic groups, the dissociation constant of which is much greater than the dissociation constant of basic groups. Since at the isoelectric point there is an equal number of oppositely charged bases along the entire length of the molecule new and acid groups, then as a result of electrostatic attraction forces, the protein molecule twists into a ball, becomes more compact, and its density increases. The properties associated with the shape and charge of the macromolecule change. So, for example, in the isoelectric state, the viscosity, swelling, and solubility of proteins decrease. The method of determining isoelectricity is based on a decrease in the solubility of proteins in the isoelectric state. triple point of casein. When performing the practical part of the work, they take a tripod for 18 pro- Laboratory workels - two rows of 9 test tubes.

Work progress

According to the Table below, in all 18 test tubes using the a blown pipette is filled with distilled water, 0.01 N; 0.1 N; 1 N dis- of acetic acid. 1 ml of freshly prepared casein in 0.1 N is added to the test tubes of the first row. sodium acetic acid solution. Add 1 ml of 0.1 N to the tubes of the second row. sodium acetic acid solution and methyl orange indicator. At the same time, buffer mixtures with different pH values are obtained, and the composition of the buffer mixtures is the same in both rows of test tubes. The solubility of casein depends on the pH of the medium and is lowest in the isoelectric state. This is observed in the greatest turbidity of the solution.

Therefore, the pH value in the test tube, where the turbidity of the casein solution is greatest, corresponds to the isoelectric point of casein. Obviously, the transition of the color of methyl orange from orange to red of it in the tubes of the second row should coincide with the tube of the greater turbidity in the first row.

Table 1

Warehous esolutions	Number of tubes								
	1	2	3	4	5	6	7	8	9
Distilled water, ml	8,3	7,8	8,7	8,5	8,0	7,0	5,0	1,0	7,4
0,01 N CH_3COOH, ml	0,7	1,2	–	–	–	–	–	–	–
0,1 N CH_3COOH, ml	–	–	0,3	0,5	1,0	2,0	4,0	8,0	–
1 N CH_3COOH, ml	–	–	–	–	–	–	–	–	1,6
pH value	5,2	5,6	5,3	5,0	4,7	4,4	4,1	3,8	3,5

The second row of tubes is a control. The transition of the color of the indicator from a basic to an acidic medium should lie within the isoelectric point of casein. For methyl orange, this transition lies within pH = 2.7 – 4.7.

After 5-10 minutes. in a number of test tubes containing casein, the degree of turbidity is indicated. The absence of turbidity is indicated by the sign "–", its presence ness - with a "+" sign. The degree of turbidity is indicated by a different number of plus or minus signs (up to three). In the second row of test tubes, note the color of methyl orange - "o"; color transition - "p"; red - "h".

The results of the work are checked by the class leader. The pH value corresponding to the isoelectric point of casein is recorded.

QUESTIONS FOR SELF-CONTROL:

1. Explain the mechanisms of formation and structure of the double electric layer (DEL).
2. What is the essence of the basic theories of the DLS?
3. Electrokinetic phenomena.
4. Electroosmosis, electrophoresis.
5. Potentials of flow and sedimentation.
6. Helmholtz–Smoluchowski equation.
7. Practical use of electrokinetic phenomena in medicine, pharmacy, biology, research and clinical laboratory practice, etc.
8. Electrophoregrams.

9. Electrokinetic potential ξ. The concept of the isoelectric state of ash.
10. Factors affecting the electrokinetic potential.
11. The influence of indifferent electrolytes on the value of the electrokinetic potential.
12. Effect of nonindifferent electrolytes on the value of electrokinetic potential.
13. The effect of pH on the value of the electrokinetic potential.
14. Influence of other factors on the electrokinetic potential.
15. Causes of hydrophilic and amphoteric properties of a protein molecule.
16. Effect of hydrogen ion concentration H^+ on the dissociation of proteins.
17. The isoelectric state of the protein.
18. Effect of electrolytes on the position of the isoelectric point of casein.
19. What are the features of the isoelectric state of lyophilic sols?
20. How do the properties of a protein molecule change at the isoelectric point?

TOPIC 10. STABILITY AND COAGULATION OF DISPERSE SYSTEMS

Theoretical questions:

Aggregative and sedimentation (kinetic) stability of DS, causes of their coagulation. Factors of stability. Coagulation. Effect of electrolytes on coagulation of lyophobic ash. The threshold of coagulation. Schulz-Hardy rule. Basic theories of DS stability. Theory of DLFO. Effect of electrolytes on coagulation of lyophobic ash. Coagulation under the action of a mixture of electrolytes. Coagulation kinetics. Factors affecting it. Influence of dilution and temperature on DC coagulation. Heterocoagulation (mutual coagulation). Ash aging. Influence of physical factors on coagulation. Coagulation processes in the treatment of drinking water and wastewater. Colloid protection. Protective effect of lyophilic substances. The phenomenon of peptization. The value of stabilization of colloidal systems for preparation of drugs.

Laboratory work
10. COAGULATION OF COLLOIDAL SOLUTIONS WITH ELECTROLYTES

For work you need: ferric hydroxide (III) ash; K_2SO_4 solution; $K_3[Fe(CN)_6]$ solution; 0.5% gelatin solution; pipette.

The aim of the work is to investigate the effect of electrolytes on the coagulation of ferric hydroxide (III) ash and the protective stabilizing effect of gelatin on the ash under study.

Work progress

The obtained and cooled to room temperature ferric hydroxide sol (III) is poured into 8 cones of 20 ml each.

The sol $Fe(OH)_3$ in the first two cones is titrated with a K_2SO_4 solution, the sol in the other two cones is titrated with a solution until coagulation begins, observing until the sol $K_3[Fe(CN)_6]$ becomes cloudy.

10 drops of a 0.5% solution of gelatin are poured into the next four cones and also titrated with K_2SO_4 and $K_3[Fe(CN)_6]$. In this case, there is more electrolytes. This indicates that gelatin increases the stability of colloids, showing a protective effect.

The titration results are recorded in the following Table:

Table 1

	Number of cones	K_2SO_4, ml	Number of cones	$K_3[Fe(CN)_6]$, ml
Without gelatin	1 2		3 4	
With gelatin	5 6		7 8	

QUESTIONS FOR SELF-CONTROL:

1. What is the essence of aggregative and sedimentation (kinetic) stability of DS, what are the causes of their coagulation?
2. Describe and explain the mechanism of action of stability factors on DS.
3. The main theories of stability of DS.
4. The theory of DLFO.
5. Coagulation. The effect of electrolytes on the coagulation of lyophobic sols.
6. The threshold of coagulation.
7. The Schultz-Hardy rule.
8. Coagulation under the influence of a mixture of electrolytes.
9. Kinetics of coagulation. Factors affecting it.
10. Effect of dilution and temperature on DS coagulation.
11. Heterocoagulation (mutual coagulation).
12. The phenomenon of aging of ash.
13. Influence of physical factors on coagulation.
14. Coagulation processes in living organisms and in the treatment of drinking water and wastewater.
15. Colloidal protection. Protective effect of lyophilic substances.
16. Explain the phenomena and methods of peptidization.
17. What is the essence and significance of stabilization of colloidal systems for the preparation of drugs and the vital activity of living organisms?

TOPIC 11. OPTICAL, MOLECULAR-KINETIC PROPERTIES ANS STRUCTURAL FORMATION PHENOMENA IN DISPERSE SYSTEMS

Theoretical questions:

General characteristics of optical properties of disperse systems (DS). Rayleigh's theory. Factors affecting light scattering. Optical methods of DS research: nephelometry, turbidimetry, ultramicroscopy. General characteristic of molecular-kinetic properties of DS. Diffusion in DS. Fick's Law. Einstein's equation. Einstein–Smolukhovsky equation. Osmotic pressure of colloidal solutions.

Condensation and crystallization structures. Thixotropy. Synerezis. IUD solutions and their characteristics. Highly molecular compounds are the basis of living organisms. Globular and fibrillar structure of proteins. Comparative characteristics of solutions of high-molecular compounds, true and colloidal solutions. The difference between fragile gels from studs (dragles). Swelling of the IUD (limited and unlimited), dissolution of polymers. Swelling mechanism. Degree of swelling of the IUD. Pressure and heat of swelling of the IUD. Influence of pH medium, temperature and electrolytes on swelling. The role of swelling in the physiology of the body. Dragging of IUD solutions. Dragging mechanism. Influence of pH of the medium, temperature and electrolytes on the drag rate. Diffusion in drags. Isolation of biopolymers from solutions. Coacervation and its role in biological systems. Osmotic pressure of the IUD. Isoelectric state of the IUD. Isoelectric point and methods of its definition. Ionic state of biopolymers in aqueous solutions. Ionic state of biopolymers in aqueous solutions. Viscosity DS. Abnormal viscosity of IUD solutions. Viscosity of blood. Donnan's membrane equilibrium. Rheological models: Hook, Newton, Maxwell, Kelvin.

Laboratory work
11.1. SWELING OF GELS

For work you need: gelatin; 0.1 N of CH_3COOH solution; 0.1 N of CH_3COONa solution; tripod with test tubes; pipette, graduated on 10 ml.

The aim of this work is to investigate the effect of the pH of the medium on the swelling process of gels and to determine the appropriate degrees of swelling.

Absorption of liquid by jelly or gel, accompanied by a significant increase in its volume, is called swelling.

The swelling process is a characteristic property of gels in such high-molecular compounds such as gelatin, agar-agar, rubber, called elas- tic gels, as opposed to non-swelling - inelastic gels, which mainly include inorganic gels of

the type SiO_2, SnO_2, TiO_2. Such gels can absorb the liquid wetting them. However, their volume does not change.

A characteristic feature of high-molecular compounds is the asymmetry of the shape of thread-like macromolecules with large chain sizes.

The property of the elastic gel is related to the elasticity of the chains of macromolecules that make up the base of the gel. The elasticity of macromolecules depends lives from the nature of the atoms that make up macromolecules, from the character distribution of these atoms, from the length of the chain, the size of the intermolecular cular forces and temperature.

The swelling process can be imagined as the penetration of low-energy molecules molecular solvent into the space between the molecules of a high-molecular compound. When the free space is filled with liquid, the molecules dissolve nyc begin to expand the links of the polymer chain, forming new those that are refilled with a low molecular weight liquid. In this you- then, when the swollen gel then spontaneously turns into a solution at the same temperature, unlimited swelling takes place.

Thus, natural rubber swells in water, and then goes into solution, forming a solution of a high-molecular compound. In this case, the process see extension of polymer chains.

Gelatin and agar-agar gels at normal temperature swell in water to a certain limit and do not pass into the solution. Extension of chains of passage child only in some areas, the last part of the chain remains connected to each other. In this case, limited swelling takes place at this temperature. An increase in temperature often leads to the fact that limited swelling jellies begin to dissolve, as observed swears in the case of gelatin. However, an increase in temperature does not always lead to dissolution, for example, the dissolution of volcanic rubber This is explained by the presence of "bridge bonds" between the molecules, which make it difficult for macromolecules to pass into the solution. In the presence of a large number of such "bridge bonds", such as ebonite, the spatial network of the polymer becomes rigid, the chains lose their elasticity and the polymer loses its ability to swell.

The initial stage of swelling is characterized by significant heat release - swelling heat and swelling pressure. The sum of the volumes of the dry gel and the liquid absorbed by it is greater than the volume of the swollen gel. This phenomenon is called contraction. It is observed mainly in water-swelling gels (gelatin, agar-agar, starch) and is explained by a relatively higher density of oriented bound water molecules. Swelling in organic solvents occurs without noticeable contraction. The amount of liquid absorbed by one gram of gel is called the degree of swelling. With unlimited swelling, the amount of liquid absorbed can be very large and exceed ten times the volume of the gel taken for swelling.

The swelling process takes place at a certain speed, depending on live naturally swelling gel and solvent. Swelling occurs as a first-order reaction. A

large group, which have a number of peculiarities during swelling, pre- put gels of protein substances in water and aqueous solutions. In these conditions, when measuring the degree of swelling, it is necessary to take into account the pH of the medium.

At a certain concentration of hydrogen ions from the protein macromolecule, ions corresponding to both acidic and basic dissociation are grafted ciation Only at a certain pH value does such a state occur, which is charac- is weighed by the presence of an equal number of positive and negative charges; the protein becomes electroneutral.

Such a state is called isoelectric, and the pH of the solution at which this state occurs is called the isoelectric point. The curve of dependence of the degree of swelling on pH has a minimum in iso- electric point The reason for the influence of hydrogen and hydroxyl ions on the degree of swelling lies in the fact that in the isoelectric state, the particles of macromolecules connect into more complex and large complexes. This process is caused by some desolvation of polymer chains in the isoelectric state.

Work progress

To perform the work in test tubes, prepare 6 buffer solutions (see Table 1).

Pour 0.1 g of dry gelatin powder into graduated test tubes, accurately note the volume of dry matter in the tubes. Then 5 ml of one of the prepared solutions with the appropriate pH value is poured into each of the tubes. After an hour, measure the volume of gelatin after swelling. The degree of swelling is calculated by the formula:

$$\alpha = \frac{V - V_o}{V_o}$$

Table 1

Composition of solutions	Number of tubes					
	1	**2**	**3**	**4**	**5**	**6**
0,1 N CH_3COOH, ml	9	7	5	3	1	–
0,1 N CH_3COONa, ml	1	3	5	7	9	–
distillate H_2O, ml	–	–	–	–	–	10
pH value	3,8	4,4	4,7	5,0	5,6	7

The data of experiment and calculation results recorded in the Table 2.

Table 2

	Number of tubes					
	1	2	3	4	5	6
pH of buffer solution	3,8	4,4	4,7	5,0	5,6	7,0
Gelatin volume before swelling V_o, ml						
Gelatin volume after swelling V, ml						
Swelling degree, α						

QUESTIONS FOR SELF-CONTROL:

1. Give a general description of the optical properties of dispersed systems (DS).
2. What is the essence of Rayleigh's theory? What factors affect the scattering of light?
3. Optical methods of studying DS: nephelometry, turbidimetry, ultramicroscopy.
4. General characteristics of molecular kinetic properties of DS.
5. Diffusion in DS. Fick's law.
6. Einstein's equation. Einstein-Smoluchowski equation.
7. Osmotic pressure of colloidal solutions.
8. Condensation and crystallization structures.
9. Contractions. Thixotropy. Syneresis.
10. Navy solutions and their characteristics.
11. High molecular weight compounds - the basis of living organisms.
12. Globular and fibrillar structure of proteins.
13. Comparative characteristics of solutions of high molecular weight compounds, true and colloidal solutions.
14. The difference between fragile gels and jelly (dragons).
15. Swelling of the IMS (limited and unlimited), dissolution of polymers.
16. The mechanism of swelling.
17. The degree of swelling of the IUD.
18. Pressure and heat of swelling of the Navy.
19. Effect of pH, temperature and electrolytes on swelling.
20. The role of swelling in the physiology of the body.
21. Dragelling of IV solutions.
22. The mechanism of dragling.
23. Effect of pH, temperature, and electrolytes on the rate of dragling.

24. Diffusion in pellets. Drying of biopolymers from solutions.
25. Coacervation and its role in biological systems.
26. Osmotic pressure of the Navy.
27. Isoelectric state of the Navy.
28. Isoelectric point and methods of its determination.
29. Ionic state of biopolymers in aqueous solutions.
30. Viscosity in DS.
31. Abnormal viscosity of solutions of the Navy. Viscosity of blood.
32. What is the “Donnan membrane equilibrium”, its essence?
33. Describe the rheological models of DS: Hooke, Newton, Maxwell, Kelvin.

TOPIC 12. BIOGENIC ELEMENTS. s-ELEMENTS

Theoretical questions:

General information about biogenic elements. Qualitative and quantitative content of biogenic elements in the human body. Macroelements, microelements and impurity elements. Organogens. The concept of the teaching of V.I. Vernadsky about the biosphere and the role of living matter (living organisms). Electronic structure of s-elements. Typical chemical properties of s-elements and their compounds. The relationship between the location of s-elements in the Periodic Table and their content in the body. s-Elements of the main subgroup of group I, occurrence in nature, extraction methods, physical and chemical properties. Biological role of group I s-elements and their compounds, use in medicine. s-Elements of the main subgroup of the II group, occurrence in nature, extraction methods, physical and chemical properties. Biological role of II group s-elements and their compounds, practical application in medicine.

Laboratory work
12.1. QUALITATIVE REACTIONS TO s-ELEMENT IONS

The aim of the work is to conduct a qualitative analysis of chemical compounds for the ions of the studied s-elements.

Among the s-elements, biometals include sodium, potassium, magnesium and calcium. Their ions are part of the buffer systems of the body, provide the necessary osmotic pressure, participate in the formation of membrane potentials, in the transmission of nerve impulses (Na^+, K^+), structure formation (Mg^{2+}, Ca^{2+}). Such s-elements as beryllium and barium have very toxic properties. Knowledge of the physico-chemical bases of s-elements and their compounds is important in the diagnosis, prevention and treatment of diseases caused by an excess or lack of s-elements in the body.

12.1.1. DETERMINATION OF Na^+ IONS BY THE COLOR OF THE FLAME

Work progress

The platinum (or nichrome) wire cleaned by washing in a concentrated solution of hydrochloric acid and roasting on the colorless flame of an alcohol still is immersed in a solution of sodium chloride, and then introduced into the colorless flame of an alcohol still. The color of the fire flame is observed to be yellow.

The color of the flame of fire, that is, the ability of atoms to be excited and emit light quanta of the appropriate wavelength when mineral salts are heated on fire, is used in the method of flame photometry to determine sodium ions in blood plasma, erythrocytes, urine and tissues.

12.1.2. DETERMINATION OF K^+ IONS BY THE COLOR OF THE FLAME

Work progress

A drop of potassium salt solution is placed on the tip of a platinum wire (the wire is previously cleaned with concentrated hydrochloric acid and heated) into the colorless flame of an alcohol still and the change in color of the flame to purple is observed. This is how the presence of potassium ions in biological fluids and tissues is determined. The flame color effect is used in the photometric method.

12.1.3. THE REACTION OF Mg^{2+} ION WITH SODIUM HYDROGEN PHOSPHATE Na_2HPO_4 IN THE PRESENCE OF AN AQUEOUS SOLUTION OF AMMONIA AND AMMONIUM CHLORIDE

Work progress

Pour 0.5 ml of magnesium salt solution into the test tube, and then add 0.5 ml of the following solutions: NH_4Cl, NH_3OH and Na_2HPO_4 in the indicated sequence. At the same time, a white fine crystalline precipitate of the double salt $MgNH_4PO_4$ falls out:

$$MgCl_2 + Na_2HPO_4 + NH_3 = MgNH_4PO_4 + 2\ NaCl$$

$$Mg^{2+} + HPO_4^{2-} + NH_3 = MgNH_4PO_4$$

The presence of NH_4Cl in the solution is necessary to prevent the formation of magnesium hydroxide according to the reaction equation:

$$Mg^{2+} + 2NH_3 + 2H_2O = Mg(OH)_2 + 2NH_4^+ ,$$

an increase in NH_4^+ shifts this equilibrium to the left and Mg^{2+} ions, thanks to this, remain in solution.

Divide the resulting precipitate into two parts and check its solubility in hydrochloric and acetic acids. The reactions proceed according to the equations:

$$MgNH_4PO_4 + 3HCl = MgCl_2 + NH_4Cl + H_3PO_4$$

$$MgNH_4PO_4 + 3H^+ = Mg^{2+} + NH_4^+ + H_3PO_4$$

or

$$MgNH_4PO_4 + 2CH_3COOH = Mg(CH_3COO)_2 + NH_4H_2PO_4$$

$$MgNH_4PO_4 + 2CH_3COOH = Mg^{2+} + NH_4^+ + 2CH_3COO^- + H_2PO_4^-$$

The reaction of $MgNH_4PO_4$ formation is used in biochemical analysis to determine Mg^{2+} ions in blood and tissues.

12.1.4. Reaction of Ca^{2+} ion with ammonium oxalate $(NH_4)_2C_2O_4$

Work progress

Pour 0.5 ml of calcium salt solution and the same amount of $(NH_4)_2C_2O_4$ solution into the test tube. A white crystalline precipitate is formed:

$$CaCl_2 + (NH_4)_2C_2O_4 = CaC_2O_4 + 2\ NH_4Cl$$

$$Ca^{2+} + C_2O_4^{2-} = CaC_2O_4$$

The sediment is divided into two parts and tested for solubility in hydrochloric and acetic acids. In which acid will the precipitate dissolve? Write down the chemical reaction equation. The considered reaction is used to determine the total content of calcium ions in blood, urine and tissues.

12.1.5. Reaction of Ba^{2+} ion with potassium chromate K_2CrO_4

Work progress

Pour 0.5 ml of barium salt solution and 0.5 ml of potassium chromate solution into a test tube. A yellow crystalline precipitate of barium chromate falls out:

$$BaCl_2 + K_2CrO_4 = BaCrO_4 + 2KCl$$

$$Ba^{2+} + CrO_4^{2-} = BaCrO_4$$

The resulting precipitate must be divided into two parts and its solubility in hydrochloric and acetic acid must be checked. In hydrochloric acid, the precipitate dissolves according to the equation

$$2\ BaCrO_4 + 2HCl = BaCl_2 + BaCr_2O_7 + H_2O$$

$$2\ BaCrO_4 + 2H^+ = Cr_2O_7^{2-} + H_2O$$

The considered reaction is used to determine the total content of barium ions in biological materials.

12.1.6. Reaction of Sr^{2+} ion with sulfuric acid H_2SO_4

Work progress

0.5 ml of sulfuric acid solution is poured into 1 ml of strontium salt solution, if the precipitate does not fall out immediately, then it is necessary to let the precipitate stand.

The corresponding reaction equations have the form:

$$SrCl_2 + H_2SO_4 = SrSO_4 + 2HCl$$

$$Sr^{2+} + SO_4^{2-} = SrSO_4$$

The considered reaction is used to determine the total content of strontium ions in blood erythrocytes and other biological materials.

QUESTIONS FOR SELF-CONTROL:

1. What are "nutrients"? Describe them.
2. What is the qualitative and quantitative content of nutrients in the human body?
3. Macronutrients, trace elements and impurity elements.
4. Organogens. The concept of Vernadsky's doctrine of the biosphere and the role of living matter (living organisms).
5. Electronic structure of s-elements.
6. Typical chemical properties of s-elements and their compounds.
7. The relationship between the location of s-elements in the Periodic Table and their content in the body.
8. s-Elements of the main subgroup of group I, occurrence in nature, methods of extraction, physical and chemical properties.
9. What is the biological role of s-elements of group I and their compounds, their use in medicine?
10. Describe the s-elements of the main subgroup of group II, occurrence in nature, methods of extraction, physical and chemical properties.
11. What is the biological role of s-elements of group II and their compounds and their practical use in medicine?

TOPIC 13. BIOGENIC ELEMENTS. p-ELEMENTS

Theoretical questions:

Electronic structure and electronegativity of p-elements. Typical chemical properties of p-elements and their compounds. The relationship between the location of p-elements in the Periodic Table and their content in the body. Properties of p-elements of the III group, their biological role and application in medicine. Properties of p-elements of the IV group, their biological role and application in medicine. Properties of p-elements of group V, their biological role and application in medicine. Properties of p-elements of group VI, their biological role and application in medicine. Properties of p-elements of the VII group, their biological role, application of them and their compounds in medicine. Properties of p-elements of group VIII, their biological role, application of them and their compounds in medicine. The relationship between the content of biogenic elements in the human body and their content in the environment. Endemic diseases, their connection with the features of biogeochemical provinces (areas with a natural deficiency or excess of certain chemical elements in the lithosphere). Problems of pollution and purification of the biosphere from toxic chemical compounds of p-elements of man-made origin.

Laboratory work
13.1. QUALITATIVE REACTIONS TO p-ELEMENT IONS

The aim of the work is to conduct a qualitative analysis of chemical compounds for the ions of the studied p-elements.

Among all p-elements, five elements are organogenic (the so-called "elements of life"). These include: Carbon (C), Nitrogen (N), Oxygen (O), Phosphorus (P) and Sulfur (S), which form the basis of biologically important molecules. Chlorine and iodine are also biogenic elements, while boron, fluorine and bromine are present in living organisms in trace amounts. Compounds of lead and arsenic have very toxic properties. As a rule, in a living organism, p-elements are part of complex organic macromolecules or ions OH^-, Cl^-, HCO_3^-, $H_2PO_4^-$, HPO_4^{2-}, SO_4^{2-}, F^-. They form the basis of the buffer system of the blood, provide the necessary osmo- pressure, contained in gastric juice and other biological environments. Many compounds of p-elements are used as medicines.

13.1.1. Reaction to Boron ions (III) according to the color of the flame

Work progress

The 5–6 drops of borax solution are evaporated in a porcelain cup. After cooling, add 4–5 drops of concentrated H_2SO_4 solution and 5–6 drops of ethyl alcohol to the dry residue. The mixture is stirred with a glass rod and ignited. The flame of burning alcohol colored turns green. This coloration is due to the volatile ethyl ether of boric acid $B(OC_2H_5)_3$. It is obtained by the action of sulfuric acid and ethyl alcohol on sodium tetraborate:

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O = 4H_3BO_3 + Na_2SO_4$$

$$H_3BO_3 + 3C_2H_5OH = B(OC_2H_5)_3 + 3H_2O,$$

With the help of these reactions, the content of such drugs as boric acid and its salts is checked.

13.1.2. Reaction to CO_3^{2-} ions with dilute acids

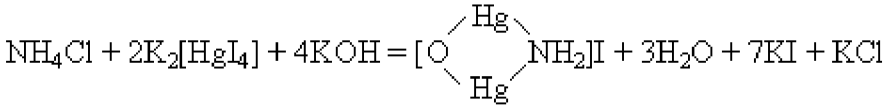
Work progress

0.5 ml of Na_2CO_3 or K_2CO_3 solution is poured into the test tube and 1–2 drops of acid solution are added. What is observed at the same time? Write the reaction equation in molecular and ionic form. This reaction is used in sanitary and hygienic practice for the determination of such components as CO_3^{2-} and HCO_3^- in natural and wastewater.

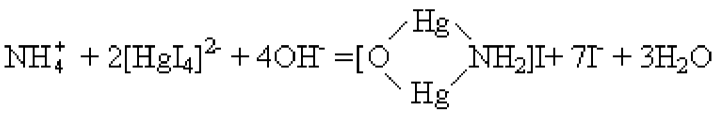
13.1.3. Reaction to ions with Nessler's reagent

Work progress

One drop of NH_4Cl solution and Nessler's reagent are applied to the glass slide at a distance of 0.5–1 cm from each other. Connect the drops using a glass rod – a reddish-brown precipitate falls out:



$$NH_4Cl + 2K_2[HgI_4] + 4KOH = [O(Hg)_2NH_2]I + 3H_2O + 7KI + KCl$$



$$NH_4^+ + 2[HgI_4]^{2-} + 4OH^- = [O(Hg)_2NH_2]I + 7I^- + 3H_2O$$

With very small amounts of ammonium salts, a yellow solution is formed instead of a precipitate. This effect is used in the colorimetric method of analysis

to determine the content of total and residual nitrogen in blood, urea, in sanitary and hygienic practice - in the analysis of water, air, and food products.

13.1.4. Reaction of NO_3^- ions with ferric sulfate (II) in the presence of concentrated sulfuric acid

Work progress

A drop of sodium nitrate solution is applied to the slide. A small crystal $FeSO_4 \cdot 7H_2O$ is placed inside the drop. One drop of concentrated hydrochloric acid is applied to it (using a dropper). A brown color appears around the crystal:

$$3\ FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 4H_2O + 2NO$$

$$3Fe^{2+} + NO_3^- + 4H^+ = 3Fe^{3+} + 2H_2O + NO$$

$$FeSO_4 + NO = [\ Fe(NO)]SO_4$$

$$Fe^{2+} + NO + SO_4^{2-} = [Fe(NO)]SO_4$$

13.1.5. Reaction to NO_2^- ions with potassium iodide

Work progress

A drop of potassium or sodium nitrite solution is diluted with water to 3 ml, and then one drop of KI solutions, sulfuric acid and a few drops of starch solution are added. What is observed at the same time?

Reaction equation:

$$2NaNO_2 + 2NaI + 2H_2SO_4 = 2NO + I_2 + 2H_2O + 2Na_2SO_4$$

$$2NO_2^- + 2I^- + 4H^+ = 2NO + I_2 + 2H_2O$$

This reaction is used to check the pharmacopoeial drug $NaNO_2$.

13.1.6. Reaction to PO_4^{3-} ions with ammonium molybdate

Work progress

Pour 0.5 ml of Na_2HPO_4 solution and 0.5 ml of $(NH_4)_2MoO_4$ solution into the test tube. The mixture is heated. What is observed during cooling?

Reaction equation:

$$12(NH_4)_2MoO_4 + Na_2HPO_4 + 23HNO_3 = (NH_4)_3H_4[P(Mo_2O_7)_6] +$$

$$+ NaNO_3 + 10H_2O + 21NH_4NO_3$$

The specified reaction is used to determine the phosphorus content in orthophosphates, which are dissolved in industrial waste waters.

To determine phosphorus in biological fluids, a reaction with molybdic acid in the presence of a reducing agent is used.

13.1.7. Analytical reaction to arsenic ions (III)

This reaction is based on the production of arsenic hydrogen (III), which reduces argentum salts to metallic silver.

Work progress

Pour 0.5 ml of diluted sulfuric acid solution and a drop of arsenic salt solution into the test tube. Close the test tube tightly with filter paper moistened with 1–2 drops of argentum nitrate solution. Then, lifting the paper a little, put a piece of granulated zinc into the test tube and again quickly close the opening of the test tube. After a few minutes, a characteristic yellow, brown or black spot appears on the inside of the filter paper, depending on the concentration of Arsenic in the solution:

$$2Na_3AsO_3 + 6Zn + 9H_2SO_4 = 2AsH_3 + 6ZnSO_4 + 3Na_2SO_4 + 6H_2O$$

$$AsO_3^{3-} + 3Zn + 9H^+ = AsH_3 + 3Zn^{2+} + 3H_2O$$

$$AsH_3 + 6AgNO_3 + 3H_2O = H_3AsO_3 + 6Ag + 6HNO_3$$

$$AsH_3 + 6Ag^+ + 3H_2O = H_3AsO_3 + 6Ag + 6H^+$$

This reaction is used to determine Arsenic in biological materials and waters contaminated with industrial waste.

13.1.8. Reaction of Bi^{3+} ions with potassium iodide

Work progress

2–3 drops of KI solution are added to 0.5 ml of bismuth salt solution. A black-brown precipitate of bismuth iodide falls out:

$$Bi(NO_3)_3 + 3KI = BiI_3 + 3KNO_3$$

$$Bi^{3+} + 3I^- = BiI_3$$

An excess of KI solution is added to the resulting precipitate and shaken. The precipitate dissolves with the formation of an orange-colored complex salt:

$$BiI_3 + KI = K[BiI_4]$$

$$BiI_3 + I^- = [BiI_4]^-$$

The reaction is used to check the pharmacopoeial drug $BiONO_3$.

13.1.9. Reaction to SO_4^{2-} ions with barium chloride solution

Work progress

Pour 5 ml of solution: K_2SO_4, Na_2SO_4 or H_2SO_4 and 1 ml of $BaCl_2$ solution into the test tube. Write the reaction equation. Make sure that the precipitate that forms is insoluble in HNO_3 and HCl.

The reaction is used to determine SO_4^{2-} ions in natural, drinking and waste water.

13.1.10. Reaction of SO_3^{2-} ions with mineral acid solution

Work progress

0.5 ml of K_2SO_3 or Na_2SO_3 solution, 1 ml of HCl solution are poured into the test tube and heated. Sulfuric gas with a characteristic smell is released. Write the equation for this reaction.

13.1.11. Reaction of $S_2O_3^{2-}$ ions with mineral acid solution

Work progress

Pour 0.5 ml of $Na_2S_2O_3$ solution and 1 ml of HCl solution into the test tube. Warm up a little. Record the results of observations. The reaction equations have the form:

$$Na_2S_2O_3 + 2HCl = S + SO_2 + H_2O$$

$$S_2O_3^{2-} + 2H^+ = S + SO_2 + H_2O$$

This reaction is the basis of the existing method of treatment of skin diseases.

13.1.12. Reaction to $S_2O_3^{2-}$ ions with iodine solution

Work progress

Pour 0.5 ml of $Na_2S_2O_3$ solution and a few drops of iodine solution into the test tube. The iodine solution is discolored.

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$$

$$S_2O_3^{2-} + I_2 = S_4O_6^{2-} + 2I^-$$

With the help of this reaction, pharmacopoeial preparations of iodine and thiosulfate are established.

13.1.13. Reaction of Cl– ions with a solution of argentum nitrate

Work progress

Pour 1 ml of NaCl or KCl solution and a few drops of argentum nitrate solution into the test tube. The formation of a white precipitate is observed. Write the reaction equation. Make sure that the precipitate that forms is insoluble in HNO_3 and H_2SO_4.

The reaction is used to determine Cl^- ions in natural, drinking, wastewater, biological fluids, and pharmacopoeial drugs.

13.1.14. Quantitative determination of the content of Cl- ions ions in drinking water by the Folgard method

In drinking water, chlorine ions are in the form of salts: NaCl, KCl, $CaCl_2$, $MgCl_2$.

Work progress

To determine the quantitative content of chloride ion in drinking water, transfer 10 ml of the tested water to a titration flask with a pipette, add 10 ml of a titrated solution of argentum nitrate, 1 ml of a saturated solution of ferrumammonium alum and titrate with NH_4CSN solution until a pink color appears. The titration is repeated three times.

The content of chloride ion is calculated according to the formula:

$$\rho = \frac{[C(AgNO_3) \cdot V(AgNO_3) - C(NH_4CNS) \cdot V(NH_4CNS) \cdot M(Cl^-)]}{V(H_2O)},$$

where

$\rho(Cl^-)$ is the mass concentration of chloride ion, mg/l;

$M(Cl^-)$ is the molar mass of chlorine ions, mg/mol;

$V(H_2O)$ is the volume of the tested water, l;

$C(AgNO_3)$ is the molar concentration of $AgNO_3$ solution, mol/l;

$C(NH_4CNS)$ is the molar concentration of the NH_4CNS solution, mol/l;

$V(AgNO_3)$ is the volume of titrated $AgNO_3$ solution, l;

$V(NH_4CNS)$ is the volume of the titrated NH_4CNS solution, l.

This method gives positive results and is used for the quantitative determination of chloride ion in natural, drinking or waste water, if the content of Cl^- ion does not exceed 2–3 g in 1 ml of the tested water.

QUESTIONS FOR SELF-CONTROL:

1. Describe the electronic structure and electronegativity of p-elements.
2. Explain the typical chemical properties of p-elements and their compounds.
3. Analyze the relationship between the location of p-elements in the Periodic Table and their content in the body.
4. Properties of p-elements of group III, their biological role and application in medicine.
5. Properties of p-elements of group IV, their biological role and application in medicine.
6. Properties of p-elements of group V, their biological role and application in medicine.
7. Properties of p-elements of group VI, their biological role and application in medicine.
8. Properties of p-elements of group VII, their biological role, application of them and their compounds in medicine.
9. Properties of p-elements of group VIII, their biological role, application of them and their compounds in medicine.
10. Explain the relationship between the content of nutrients in the human body and their content in the environment.
11. Endemic diseases, their connection with the features of biogeochemical provinces (areas with a natural deficit or excess of certain chemical elements in the lithosphere).
12. What are the causes and essence of the problems of pollution by p-elements?
13. Describe the methods of purification of living organisms?
14. Describe the methods of cleaning the environment and the biosphere from toxic chemicals of man-made origin.

TOPIC 14. BIOGENIC ELEMENTS. d-ELEMENTS

Theoretical questions:

Electronic structure of d-elements. Typical chemical properties of d-elements and their compounds. The relationship between the location of d-elements in the Periodic Table and their content in the body. Properties of d-elements of groups I and II, occurrence in nature, methods of extraction, physical and chemical properties. Biological role of d-elements of groups I and II and their compounds, application in medicine. d-Elements of III and IV groups (subgroups of scandium and titanium), physical and chemical properties, application in medicine. d-Elements of groups V, VI and VII (subgroups of vanadium, chromium and manganese), physical and chemical properties, application in medicine. d-Elements of VIII group, occurrence in nature, physical and chemical properties. Biological role of d-elements and their compounds, application in medicine. The toxic effect of compounds of d-elements on the human body. Problems of pollution and cleaning of the biosphere from toxic chemical compounds d-elements of man-made origin.

14.1. QUALITATIVE REACTIONS TO d-ELEMENT IONS

The aim of the work is to perform a qualitative analysis of chemical compounds for the ions of the studied d-elements.

When compared with the previously discussed s-elements, d-elements are contained in the body in much smaller quantities. However, their role in physiological and pathological processes is very large and important. Currently, there is a debate whether to consider chromium and vanadium as biometals. Biometals are indispensable trace elements that have a catalytic effect on numerous biochemical reactions and activate the activity of enzymes. In macro quantities, they are poisonous. Mercury compounds pose a particular threat.

14.1.1. Reaction to the Cr^{2+} ion

Work progress

Pour 1–2 ml of $Cr_2(SO_4)_3$ salt solution into the test tube, add 3–5 ml of NaOH solution and add 3–4 drops of H_2O_2 solution. Then it is heated until a yellow color appears. Write the equations of the corresponding reactions.

14.1.2. Reaction to the Mn^{2+}

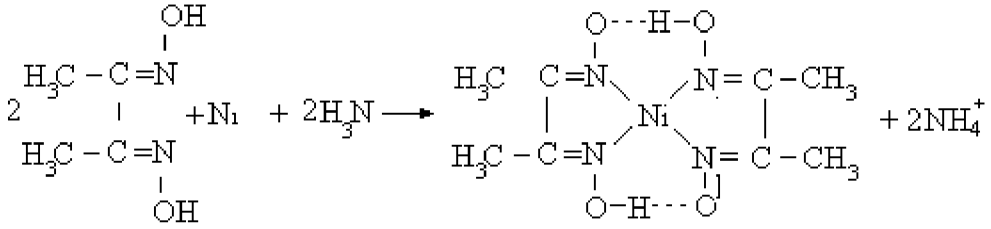
Work progress

1–2 drops of a very dilute solution of $MnSO_4$, 1–2 drops of $AgNO_3$ (catalyst), 1 ml of NaOH solution with c(NaOH) = 2 mol/l and 1 ml of $Na_2S_2O_8$ solution are poured into the test tube. The contents of the test tube are heated. The solution turns a characteristic red-violet color. Write the reaction equations. Is it possible to use this reaction to determine Ag^+ ions?

14.1.3. Reactions of Ni^{2+} ion with dimethylglyoxime

Work progress

Pour a drop of nickel (II) nitrate salt solution into the test tube, add 3–6 drops of an aqueous ammonia solution and 2–3 drops of an alcoholic solution of dimethylglyoxymate. A bright red precipitate of nickel dimethyl glyoxymate (internally complex compound) is observed.



The reaction is very sensitive and is used to detect Ni^{2+} ions in industrial wastewater.

14.1.4. Reactions of the Co^{2+} ion with potassium nitrate

Work progress

Pour 2–3 drops of cobalt nitrate (II) solution into a test tube, add a few drops of CH_3COOH solution to pH=3 (test with a universal indicator) and 1–2 drops of potassium nitrate solution. A yellow crystalline precipitate of $K_3[Co(NO_2)_6]$ falls out.

$$Co(NO_3)_2 + 7KNO_2 + 2CH_3COOH = K_3[Co(NO_2)_6]\downarrow + NO +$$
$$+ 2KNO_3 + 2CH_3COOK + H_2O$$

$$Co^{+2} + 7NO_2^- + 3K^+ + 2CH_3COOH = K_3[Co(NO_2)_6]\downarrow + NO + 2CH_3COO^- + H_2O$$

14.1.5. Reaction of Hg^{2+} ion with $SnCl_2$

Work progress

$SnCl_2$ solution is added dropwise to 0.5 ml of mercury (II) chloride solution (sulemia) in a test tube. A white precipitate of calomel (Hg_2Cl_2) is formed, which gradually turns black.

$$a)\ 2HgCl_2 + SnCl_2 = Hg_2Cl_2\downarrow + SnCl_4$$
$$2HgCl_2 + Sn^{2+} = Hg_2Cl_2\downarrow + Sn^{4+} + 2Cl^-$$
$$b)\ Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4$$
$$Hg_2Cl_2 + Sn^{2+} = 2Hg + Sn^{4+} + 2Cl^-$$

14.1.6. Reaction of Pb^{2+} ions with potassium iodide

Work progress

Add the same amount of potassium iodide solution to a few drops of the Plumbum salt solution. A yellow precipitate of lead iodide falls out.

$$Pb(NO_3)_2 + 2KI = PbI_2 + 2KNO_3$$

$$Pb^{2+} + 2I^- = PbI_2$$

1 ml of acetic acid is added to the resulting precipitate. The resulting mixture is heated to boiling. Then the solution is slowly cooled. At the same time, lead iodide precipitates again in the form of golden crystals.

QUESTIONS FOR SELF-CONTROL:

1. Explain the electronic structure of d-cells.
2. Describe the typical chemical properties of d-elements and their compounds.
3. Analyze the relationship between the location of d-elements in the Periodic Table and their content in the body.
4. Properties of d-elements of groups I and II, occurrence in nature, methods of extraction, physical and chemical properties.
5. What is the biological role of d-elements of groups I and II and their compounds, application in medicine?
6. d-Elements of groups III and IV (subgroups of scandium and titanium), physical and chemical properties, application in medicine.
7. d- Elements of groups V, VI and VII (subgroups of vanadium, chromium and manganese), physical and chemical properties, use in medicine.
8. d-Elements of group III, occurrence in nature, physical and chemical properties.

9. What is the biological role of d-elements and their compounds, their use in medicine?
10. Describe the toxic effects of d-element compounds on the human body.
11. What is the essence and mechanism of the problems of pollution and purification of the biosphere from toxic chemical compounds of d-elements of man-made origin?

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