STUDY GUIDE

On self-preparation for lesson and performance of laboratory operations

ON GENERAL CHEMISTRY

For 1-st course students of stomatological faculty

Vitebsk,
2018
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K 91 Study guide on self-preparation for lesson and performance of laboratory
operations on general chemistry for the 1-st course students of stomatological:

«Study guide on self-preparation for lesson and performance of laboratory operations
on general chemistry for the 1-st course students of stomatological faculty» prepared
according to the curriculum for the academic discipline on general chemistry for the students
of stomatological faculty of higher education institutions.
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About this study guide.

The present study guide are made in view of the educational program on general chemistry for the students of treatment-prophylactic department of Vitebsk state medical university and are intended for rendering assistance to the students in self-preparation for lesson and performance of laboratory operations.

In study guide are included: the methodical paper to each lesson, are given general purposes and problems of a sectional course of chemistry, ground rules of operation and laboratory safety guidelines in chemical laboratory, literature, methodical paper for laboratory work, reference on self-preparation of the students in lesson. In the extremity the list of knowledge, skills and skills is resulted which should the students get during study of a course of general chemistry, and also reference on self-preparation for examination.

On each lesson are resulted: the methodical indicatings and references, which acquaint the students with a theme and purpose of lesson, brief substantiation of the medicobiological importance of a theme for the student, program questions and question for self-preparation with the indicating of the literature. The methodical paper on performance of laboratory work are given.

We consider, that the submitted study guide will appear to rather useful students and will facilitate by him preparation for lesson, and the performance of the references will serve as a pledge of successful study.

The purpose and problems of a course

Formation and development at the students of systemic knowledge about a role of relative connection between the physical and chemical shapes of a motion of a substance in biological processes in norm and pathological states; development of skills and skills of application of theoretical positions and experimental methods of chemistry at study of medicobiological disciplines and in medical practice.

Before to initiate with operation in a laboratory practical work, the students should study rules of operation in chemical laboratory and laboratory safety guidelines.

How to Succeed in General Chemistry

General chemistry has been described by many students as one of the hardest courses that they took in university. There are many reasons for this generalization: among them are the large amount of vocabulary that is learned, the quantitative nature of the material and the many concepts that are learned in the short period of time. However, many students take and do quite well in general chemistry, so what is the secret to
success? The key to success in general chemistry is the proper balance of study habits and time invested in the course. Some suggestions towards achieving this balanced are offered. First, you must actively participate in the course to succeed. Many instructors believe that a student in general chemistry should spend about three to five hours working on the course for every hour of lecture. Second, you should not fall behind, because, the pace of a university general chemistry class is fast, and it is very difficult to catch up once you get behind.

**Before lectures**, read the sections of the text and study guide that pertain to the lecture topics; in this reading, you are not striving for understanding, but general notions of what topics are to be covered. Pay attention to figures and equations and what they pertain to.

**During the lecture**, take notes. It is important that you not only write down selected portions of the lecture, but also jot down questions about what may not be clear. You should develop a compact way of taking notes.

**After the lecture**, review your notes and work homework problems. Some students find it helpful to copy over their lecture notes. In reviewing your lecture notes, check for accuracy by comparing the definitions and equations with those in your text and study guide. Go through sample problems solved in the lecture to make sure that the method is clear to you. Reread the text and study guides, much more thoroughly than you did before the lecture, paying special attention to the sample problems. You should also work many of the problems in your text, even those which are not assigned as homework. A significant portion of your grade will be determined on how accurately you can solve problems and the only way to get better is by practice.

**Before an exam**, you should re-read your text and your notes. Review your homework sets, and perhaps a few extra problems which gave you trouble during the homework. Your instructor may also post a sample examination, which may help you determine something of the test’s style.

**Rules of operation and behaviour in chemical laboratory**

1. Each student is obliged to come in laboratory for 4-5 minutes before class and take your constant workplace.
2. The student should test cleanliness of a workplace and presence of all necessary equipment and reagents for carrying out of laboratory work.
3. Before each laboratory work to study a theoretical material, concerning this theme. The practical operation can be begun after careful study of a procedure of its performance.
4. Each student should know, where are found the running water tape, medicine chest agent of a quenching of fire.
5. During practical operation to contain a workplace in cleanliness.
6. To not spend reagents it is more than the specified quantity.
7. To not carry away devices and reagents of general usage on the your workplace.
   Each subject or reagent to put on its place immediately after its use.
8. Don’t exchange the stoppers at different vessels, pipets, and measuring cylinders for different reagents.
9. It is categorically forbidden to put vessels, flask with reagents on the books, copybooks methodical materials.
10. After finishing the work to wash up ware to put reagents on its places, to clean the workplace, to close running water tape.
11. To time of class is nominated on duty, which tracks the order and cleanliness in laboratory, behind keeping by the students of rules of safety.
12. In an operating time in laboratory each student is obliged:
   a) to keep silence and order;
   b) carefully to fall into to material values: to the books and manuals, to laboratory property (benches, chairs, devices and ware etc.);
   c) to keep safety measures.

**Laboratory safety guidelines.**

By operation in laboratory it is necessary to be especially attentive and to keep exclusive care. Poor acquaintance to devices and properties of substances or the negligence in operation can cause accidents (damage of an eye, skin of hand and person, mucosas of a nose, throat and bodies of respiration, cuts etc.). You should have read and understood the safety section in that manual. Safety in the laboratory cannot be overemphasized. Therefore we present here an abbreviated list of safety rules.
1. Safety glasses or safety goggles must be worn at all times when you are in the laboratory. Even if you are performing an experiment that is using no potentially dangerous chemicals, you are still in a laboratory where numerous potential hazards exist.
2. Unless your instructor indicates otherwise, contact lenses are not to be worn in the laboratory.
3. You should know where to find and how to use first aid equipment.
4. Your instructor will show you where the eye wash is located. If a corrosive chemical gets in your eyes, immediately wash the affected area with large quantities of water from the eye wash. Notify the instructor of the accident.
5. Your instructor will show you where the safety shower is located. If a corrosive chemical gets on your skin or clothes, immediately wash the affected area with large quantities of water. If your clothing catches fire or if a large quantity of chemicals is
spilled on your clothing, then use the safety shower. Notify the instructor of the accident.

6. Never taste anything in the laboratory. Smoking, chewing, eating, or drinking in the laboratory under any circumstances is strictly prohibited.

7. Never directly smell the source of vapor, but rather bring a small quantity of the vapor to your nose with your cupped hand.

8. Reactions involving malodorous, noxious, or dangerous chemicals should be performed in the hood.

9. You should know the location of and know how to use a fire extinguisher. A small fire, such as a liquid burning in a beaker, can be extinguished by covering the beaker to remove the source of oxygen.

10. No unauthorized experiments are to be performed.

11. Clean up broken glassware immediately.

12. When pouring one liquid into another, do so slowly and cautiously. To dilute an acid, pour the acid into the water: never pour water into acid.

13. When heating a test tube, make certain that the open end is pointed away from you and your fellow students. Then, if overheating causes the contents to bump out, they will not splash anyone.

14. Do not rub your eyes while in the laboratory, as your hands might have chemicals on them.

15. In case of any accident, immediately notify the instructor. In the event that your instructor is not available, notify the stockroom personnel.

**Conducting a laboratory magazine**

The laboratory journal is a report of the student on the executed research work (RW). The conducting it is obligatory.

Each student conducts a laboratory journal, where the course of performance and results of experimental operation is featured.

For a laboratory journal most approaches copybook in a cell. The record in a journal is conducted only by ink, how the records in a laboratory journal are conducted, it is possible to judge the attitude of the student to operation and to quality of its performance.

Each operation should be begun with new pages. On pages of copybook it is necessary to leave fields for calculations, of the padding notes etc. Student should learn to apply for the records the natural and precise formulations, to explain results of experiment and to make conclusion.

**The provisional plan of veneering laboratory operation (RW)**

1. The number and name of research work (RW). Date of performance.
2. The purpose of reseach work.
3. A course of operation (brief transfer of consecutive operations 1, 2, 3..., operation, necessary for performance,).
4. Results of experiment: quantitative sectional are reduced in the table; the quality observations are numbered 1, 2 .., or also are reduced in the table. Is resulted chemical reactions (molecular and ionic equations of reactions).
5. Calculations: 1) complete calculation of result; 2) calculation of an error.
6. A deduction: the achievement of the purpose of experiment, performance of the put problem RW is reflected.

**The note: (attention!)**

1) the protocol of laboratory work on items 1-3 is made at home on the eve of lesson and is a part of the home work.
2) on item 4 of a house the shape of the table for the experimental data is made.
3) on lesson the students carry out experiment, fill in items 4-6. Amend in other items of the protocol.

Each operation executed by the student, is protected at the teacher. The protection consists in the answers to questions, bound with a principle of the executed operation, substance of the apparent phenomena and received results.

The operation is considered executed, if it proofs by the student and is signed by the teacher. Without presentation of the protocols or, if the protocols will not answer the showed demands, the operation of the student on sectional partition will not be marks.

The students successfully executed all laboratory operations, gain offset and it are supposed to a passing examinations on chemistry.

**LESSON 1. Introduction in a practical work. Rules and laboratory safety guidelines in chemical laboratory. Introduction in chemistry of biogenic elements and qualitative analysis. Chemistry of biogenic s-elements.**

**Medicobiological value:** the s-elements are present in human body in the form cations in hydrated state, and more often - as central atoms of complexes compaunds. Such s- elements, as hydrogenium, sodium, potassium, magnesium, calcium are major biogenic macroelements. The change of the content of ions of these elements in an organism result in the usturbance of biochemical and physiological processes, therefore study of a biological role of each s- element is important. In medicine the medicinal drugs are widely applied, which composition enter the s- elements. The knowledge of a biogenic role of s- elements and their bonds will be used further at study of a course of biological chemistry, pharmacology, normal and pathological physiology and clinical disciplines.
The students get acquainted with ecological aspects of activity of mineral substances (carbon oxide and nitrogen, oxide, nitrates and nitrites, compounds lead etc.), at study of a sectional theme. All this predetermines importance of study of p- elements and their compounds. The knowledge, obtained on lesson, will be used at study of series of problems of biology, physiology, hygiene, toxicology.

**To lesson it is necessary:**


**Literature:**


**Research work:**

«Some properties and analytical reactions of ions, formed s – elements»

**Properties the ammonium cation.**

**Experience 1. Interaction between ammonium salts with alkalis.** Select in a test tube 5 drops of a solution salt of ammonium (NH₄Cl), add 5 drops of a solution KOH and slightly heat. Spot on a smell, with what is made the gas.

Take above a test tube a wet display paper (generalpurpose, or litmus). How discolour of a display paper? Explain an apparent appearance.

**Experience 2. Identify of ammonium ion in a solution with the help of Nessler's reagent.** 1 drop of a solution salt of ammonium locate on hour (or subject) glass. Series
locate 1 drop of Nessler’s reagent. Connect to the help of a glass stick both drops. What observe? Note observation and equation of reaction.

**Properties the sodium cation.**

**Experiment 1. Assay of a staining of a flame.** To a flame of a gas burner bring on a loop from an iron wire in 1 drop of a sodium chloride solution Watch colour of a flame. Note and sketch an apparent appearance.

**Properties the potassium cation.**

**Experiment 1.** *Formation the potassium hydrogentartras.* To 2-3 drops of a strong solution of a potassium salt add as much of drops of a solution of a sodium hydrogentartras NaHC₄H₄O₆. Rub on a wall of a test tube by glass stick and give slightly to stand. The white crystalline deposit КНС₄Н₄О₆ is formed. For checkout of a requirement of course of reaction shake up a obtained admixture and divide into three test tubes. Add 3 - 4 drops of a molar solution H₂SO₄ in the first test tube, in second - 4-5 drops of a solution NaOH (c = 2 mol/l), and in a third – 4 - 5 drops of distilled water and warm up on a water bath. What observed? Note the observations, equations of deposit formation and its dissolution.

**Experiment 2. Assay of a staining of a flame.** To a flame of a gas burner bring in 1 drop of a potassium salt solution. Note and sketch colour of a flame.

**Properties the magnesium cation.**

**Experiment 1.** *Formation the magnesium hydroxide.* Add 2 - 3 drops of an ammonia solution to 2 - 3 drops of a magnesium salt solution. Study the relation of the formed deposit Mg(OH)₂ to activity of acids, alkalis, salts of ammonium. Explain apparent appearances. Give the equations of reactions.

**Experiment 2.** *Formation the ammonium - magnesium phosphas.* Add 2 - 3 drops of ammonia buffer solution and 2 - 3 drops of a sodium hydrogenphosphas solution to 2 - 3 drops of a solution of magnesium salt. If the deposit has not dropped out rub on a test tube walls by glass stick. Add there hydrochloric, sulfuric and acetic acids to the deposit. Note observations and equations of reactions.

**Properties the calcium cation.**

**Experiment 1.** *Formation the calcium sulfas.*


b) Locate on subject glass 1 drop of a solution of calcium salt and add to it 1 drop of a solution H₂SO₄ (c = 1 mol/l). Cautiously heat glass to occurrence on edges of a drop hardly noticeable white border. Locate glass on a subject table of a microscope and
consider the shape and process of formation of crystal of calcium of sulfas under a microscope. Sketch the shape of crystal and note the equation of reactions.

**Experiment 2.** *Formation the calcium oxalatas.* Add in one test tube 2-3 drops of ammonium oxalatas to 2-3 drops of a calcium salt solution, and in another - as much oxalic acids. Note observation and equation of formation of a deposit of calcium oxalatas. Add acetic and hydrochloric acids to the deposit.

**Properties the barium cation.**
**Experiment 1.** *Reaction with sulfases.* Select till 3-4 drops of a barium chloride solution in three test tubes. Add 2-3 drops of a saturated solution of strontium sulfas in the first test tube, in second - 2-3 drops of gypsum water, in a third - 2-3 drops of a molar solution $\text{H}_2\text{SO}_4$. Compare results. Being grounded on results of the previous experience, make a conclusion about solubility change in series of sulfases of s-elements IIA group.

**Experiment 2.** *Formation the barium oxalatas.* Select till 3-4 drops of a solution $\text{BaCl}_2$ in two test tubes. Add 2-3 drops of an oxalic acid solution in the first test tube, in second - 2-3 drops of an ammonium oxalatas solution. Compare results among themselves and to results of similar experience with calcium cation. Make a conclusion about likeness and difference of properties of callcium and barium oxalatas.

**Experiment 3.** *Assay of a staining of a flame.* Do experience and note observations, as is described in operation for potassium salts.

**Problems for discussion:**

1. How solubility, acid-base properties of compaunds of s-elements in group and in a period are changed?
2. Write the electrons formulas of s-elements atoms (ions), define a possible oxidation state, compare nuclear parameters and reducibility of metals on a position of s-elements in Periodic table
3. Make the equation of oxidation-reduction reaction with participation of hydrogene peroxyde.
4. What value pH (= 7, > 7, < 7) have the solutions: a) of sodium chloride and calcium chloride; b) of a carbonate and hydrocarbonate. Pruve the answer by the ionic equations of reactions.
5. Write down the equations of reactions, with which help it is possible to detect ions, $\text{K}^+$, $\text{Na}^+$, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{Ba}^{2+}$, $\text{NH}_4^+$. What properties of received compaunds allow to detect these ions?
6. What types of bonds (ionic, covalent) are characteristic for compaunds of s-elements?
7. On what properties of $\text{H}_2\text{O}_2$ its wide application in medicine and chemical analysis is based?

8. A carbonate of magnesium, hydrocarbonate of a sodium and magnesium oxide are used at disease of a stomach. What the aim of appling of these substances? What from these drugs is more effective?

9. Potassium acetate salt is applied as a diuretic remedy at edemas, bounded with infringement of a circulation, thus 30g $\text{CH}_3\text{COOK}$ dissolve in 200 ml of water. Define a mass share of these solution and daily dose of a drug, if it is accepted by 5 times per day on 1 restaurant to a spoon (20g).

10. The energy expenditures of an organism at parenteral power supply of the patients in a postoperative period coat with intravenous introduction 1.5 l per day of a solution for hiperalimentation: a glucose 400g/l, $\text{KCl}$ – 5.0 g/l, $\text{NaCl}$ – 2.1 g/l, $\text{CaCl}_2$ – 1.0 g/l, $\text{KH}_2\text{PO}_4$ – 0.2 g/l. Define a mass share (%) of potassium chloride in this solution. What quantity (mmol) of ions $\text{Ca}^{2+}$ will be injected to the patient? (density a 1.2 g/ml).

**LESSON 2. Chemistry of biogenic d-elements.**

**Medicobiological value:** the d-elements are mainly microelements in an organism of the man. Alongside with enzymes, hormonums, vitamins and others biologically active substances the microelements participate in process of exchange of nucleic acids, protein, adepeses and carbohydrates; body height; reproduction etc. Such d-elements as iron, cobalt, copper, zinc and molibden play an important role in an organism. The biological functions of microelements in an alive organism are connected primarily with processes of a complexing between amino acids, protein, nucleic acids and ions of the relevant metals. The compaunds of d-elements are used as medicinal preparations; in excess concentrations. They are toxic in excess concentrations.

The sectional theme includes a basis of knowledge about a role of cations of d-elements in origin of series of diseases, their influence to course of biological processes in healthy and patient an organism, that serves theoretical datum(basis) for study of biochemistry, pharmacology, therapy etc. clinical disciplines.

**To lesson it is necessary:**


**Literature:**

**Research work:**

«Some properties and analytical responses d-elements ions»

**Experiment 1.** A hydrolysis cations of d-elements. Prepare for performance of experience 10 pure microtest tubes in a support. Note in a laboratory journal the table under the following shape:

<table>
<thead>
<tr>
<th>Test tube</th>
<th>explored cation</th>
<th>Colouring of a solution</th>
<th>colouring of a display paper</th>
<th>pH of a solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Cr^{3+}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Mn^{2+}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Fe^{2+}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>Fe^{3+}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>Co^{2+}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>Ni^{2+}</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Select till 3 - 4 drops of solutions of salts of the indicated cations in test tubes 1, 2, 4 - 6. Prepare a solution of Mohr's salt in a test tube 3. Note colouring of solutions in the table. Dip a glass stick in a solution in a test tube 1 and moisten with a wet stick a general purpose display paper. Compare colouring a paper to a colour scale linking colouring with pH of a solution. Note colour of a paper and value pH in the table. Wash a glass stick by water and iterate experience with a solution salt in a test tube 2 etc.

At the analysis of observations of experience 1 mark, at what cations the degree of a hydrolysis is more, what - have less. What cation – Fe^{2+} or Fe^{3+} - is hydrolyzed in the greater degree? Why? Try to formulate conclusion about dependence a degree of hydrolysis cations of d-elements on a nature of cation and charge. Write the ionic equation of reaction of a hydrolysis of cations (better from a point of view of the protolytic theory of acids and bases.)
**Experiment 2.** *Formation the hydroxides of d-elements cations and study of their properties.* Prepare the table for record of observations under the shape:

<table>
<thead>
<tr>
<th>Test tube</th>
<th>cation</th>
<th>reagent</th>
<th>KOH, disadvantage</th>
<th>KOH, excess</th>
<th>H₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Cr³⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Mn²⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Fe²⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>Fe³⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>Co²⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>Ni²⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>Cu²⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>Zn²⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Select till 3 - 4 drops of solutions of salts indicated in the table of cations in test tubes. Pose test tubes in a support according to the numbers. Then add till 1 - 2 drops of a solution KOH (or NaOH) c = 2 mol/l (KOH, disadvantage) in each test tube. Mark in the table colour of the formed deposits of hydroxides. Pay attention, that the colouring of oxides Mn (II), Fe (II) varies in the course of time.

Then add till 2-3 drops of a solution KOH c = 6 mol/l (strong solution of alkali, excess) in the same test tubes. Marks, what deposits were dissolved a lot of alkali. Then add till 8 - 10 of drops of a solution H₂SO₄ (c = 3 mol/l) in the same test tubes. Note observations.

Wash up test tubes upon termination of experience and filling of the table of observations. Prepare test tubes for performance of experiment 3.

At the analysis of observations explain, why was discoloured of hydroxides iron (Π) and manganese (Π). What hydroxides have noticeable acid properties? Write in a general view of reaction of formation of nonsoluble hydroxides.

Write the equation of reaction of dissolution of zinc and chromium hydroxides in a lot of alkali.

**Experiment 3.** *Equilibrium the chromate ↔ dichromat.* Select 2 - 3 drops of a solution K₂Cr₂O₇ in a test tube. Note, what colour has a solution. Add 1 drop of a solution KOH (c = 2 mol/l) to it. How discolour of a solution? Then add 2 - 3 drops of a solution H₂SO₄ in the same test tube. What is observed? Do the same experience with a solution of potassium chromate as a starting solution. Note observations and equations of apparent transmutations.

**Experiment 4.** *Deriving thyocyanates complexes of iron (III) and cobalt (II).*

The ions Fe³⁺ with thiocyanates - ions form iron (III) thiocyanide:
Fe(H₂O)₆³⁺ + nNCS⁻ ↔ [Fe(H₂O)₆₋ₙ(NCS)ₙ]³⁻₋ₙ + nH₂O

The composition of a generated complex is nonconstant. And it can be oscillate from [Fe(H₂O)₆(NCS)]²⁺ up to [Fe(NCS)₆]³⁻ depending on concentration Fe³⁺, NCS⁻. The reaction can be used for quantitative definition by a colorimetric method.

The cobalt II) forms with thiocyanides - ions a complex of blue colour extracted in a layer of amyl alcohol.

Add 2 - 3 drops of a solution of a potassium (or ammonium) thiocyanate to 2 - 3 drops of an iron (III) salt solution. Note observations.

**Experiment 5. Interaction between cations Cu²⁺, Zn²⁺, Hg²⁺, Hg²⁺ with iodines ions.**

The copper (II) easily reduces iodide - ions. The formed ions of copper (I) with ions I⁻ give a nonsoluble in water deposit of copper (I) iodide:

\[ 2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2 \]

The ions Zn²⁺ do not react with ions I⁻, and the ions Hg²⁺ form ion with excess of iodides - ions:

\[ Hg^{2+} + 2I^- \rightarrow HgI_2 \leftrightarrow [HgI_4]^{2-} \text{ Orange deposit} \]

The deposit - mercuri (I) iodide HgI₂ of dirty - green colour is formed at interaction KI with compounds of mercury (I). A deposit is dissolved in a lot of reagent with formation of a potassium tetraiodidmercurate (II) and black deposit of metal mercury.

\[ HgI_2 (s) + 2KI \rightarrow K_2[HgI_4] + Hg (l) \]

The mild formation complex of tetraiodidmercurate (II) ion proves softness of cation of mercuri (II).

Select till 1 - 2 drops of solutions of salts of the indicated cations and add to them till 1 - 2 drops of a solution KI in four test tubes. Note, that observe in each of test tubes. Then add in the same test tubes till 3 - 4 drops of a solution KI (excess). Note new observations. The yellow colour of an admixture in a test tube with copper is explained by allocating diiode. Add 1 drop of a solution of a sodium thiosulfatas in this test tube. What observe (note)? Then add 3 - 4 drops of a solution Na₂S₂O₃. Observe, what appearances thus happen. Results note.

Analyzing datas of experiment, formulate a conclusion about ability of cations of d-elements to a complexing. Mark reactions, which, in your opinion, it is possible to recommend as specific qualitative tests for the relevant cations. Write the equations of these reactions, using the formulas of generated deposits, addused in exposition of experience.
Problems for discussion:
1. Write down electron formulas for atoms of manganese, iron, cobalt, zinc, mercury. Why are these elements related to as d-elements?
2. How are basic atoms characteristics of d-elements (radius of atom, potential of ionization, affinity to electron) changed in group and period?
3. Write down chemical formulas for major compounds (oxide, hydroxide, salt - simple and complex) of copper, silver, zinc, mercury, manganese, iron, cobalt. Formulate legitimacy - how acid-base properties of compounds are changed with the increase of oxidation state.
4. Give examples of the use of potassium permanganate for different purposes. What is in the basis of its use?
5. As you see by performed experiments, there are 2 characteristic oxidation states for copper: +1 and +2. Can copper catalyze reactions with electrons transfer?
6. Can zinc catalyze oxidation-reduction reactions?
7. Copper sulfate is used as a remedy vomitive in medicine. Describe analytical effects, which will be observed with adding:
   a) a abundance of concentrated ammonium solution;
   b) a barium chloridem solution in weak alkaline medium.
   to this substance. Write down the equations of chemical reactions.
8. Solution of AgNO₃ is used in medicine:
   a) what is pH for this solution?
   b) What has oxidation-reduction properties silver ion has? How is explained the germicidal activity of silver nitrate solution?
9. Mercury compounds have a strong antiseptic effect. Why are not its preparations used for the treatment of human inner infectious diseases? What is the mechanism of toxic effect of mercury compounds?
10. What is biological role of iron and cobalt compounds for human organism? In what oxidation states cobalt is fond in living compounds?

LESSON 3 Chemistry of biogenic p-elements.

Medicobiological value: From 6 organogens being the basic building material of protein, adipose, carbohydrates and nucleic acids, 5 are p- elements. It is carboneum, nitrogen, oxygenium, phosphorous and sulfur. The majority p- elements-nonmetals are biogenic. From p- elements-metals to biogenic refer aluminum and tin. From low molecular weight compounds of p- elements the ions – CO₃²⁻ have greatest value in vital activity of an organism. It is a lot of compounds of p- elements are used as remedies.

The students get acquainted with ecological aspects of activity of mineral substances (carbon oxide and nitrogen, oxide, nitrates and nitrites, compounds lead etc.), at study of a sectional theme. All this predetermines importance of study of p- elements.
and their compounds. The knowledge, obtained on lesson, will be used at study of series of problems of biology, physiology, hygiene, toxicology.

**To lesson it is necessary:**

1. **STUDY** chemistry of p-block elements. Presence the p-elements in a nature. Electron frames of atoms and ions. Change the radiuses of atoms and ions; potential of ionization in the groups. Feature of acid-base, oxidation-reduction and complexing properties of compounds IIIA - VIIA. A biological role the p- elements and application of their compounds in medicine.

**Literature:**

**Research work:**

«Some properties and analytical reactions of ions, formed p – elements»

**Experiment 1.** A hydrolysis of cations: Al$^{3+}$, Sn$^{2+}$ and Pb$^{2+}$. Reaction with alkalis. Select till 2-3 drops of cations salts solutions in three test tubes. Spot reaction of medium in solutions with the help of a display paper. Note observations and make a conclusion about acid-base properties of cations.

Add till 1-2 drops of a solution KOH to solutions. What observe? Add till 2-3 drops of a solution KOH (excess) up to alkaline reaction to the dropped out deposits of hydroxides. Note observations.

**Experiment 2.** Reaction the cations Al$^{3+}$, Sn$^{2+}$ and Pb$^{2+}$ with sulfides. Add till 3-4 drops of a solution of a sulfide to 2-3 drops of explored cations salts solutions. What is observed? H$_2$S is emited in a test tube with a solution of aluminium salt. It can be detected on a smell or with the help of a display paper - strias of a filter paper imbued by a solution salt Pb(II). Bring this paper to a test tube. H$_2$S at contact to a paper paint it in black colour (same, as colour of a deposit in a test tube, where there reaction Pb$^{2+}$ with S$^2-$ ions transited).

Note observations. Test activity for the dropped out deposits of alkalis and acids.

**Experiment 3.** Formation the lead iodide. Add 2-3 drops of a solution KI to 2-3 drops of a lead salt solution. What thus watch? Note the equation of reaction.

Take a part of the dropped out deposit, add 5-7 drops of distilled water and 2 mol/l of solution of an acetic acid and heat. What happens to a deposit? Make conclusion. It is specific response to cation lead.
Identification limit - 15 mcmol of lead ions.

**Experiment 4. The oxidation - reduction properties of nitrites.**

a) an Oxidizing of nitrites of a potassium by permanganate. Add 2-3 drops dilute H₂SO₄ and 5-6 drops of a solution NaNO₂ to 2-3 drops of a solution KMnO₄. Note and explain an apparent appearance.

b) Reaction of reduction of a potassium iodide add 2-3 drops dilute H₂SO₄. Add 2-3 drops of a solution KI to 2-3 drops of a solution of a sodium nitrite. What is watched? Add 1 drop of a solution of amyllum to this admixture. Explain a discoloration of a solution.

**Experiment 5. A salification heteropolimolybdenophasnak acid.** Add 1-2 drops HNO₃ to 4-5 drops of a solution of molybdate ammonium and a mixture warm up. Add 1-2 drops of a solution Na₂HPO₄ and a little crystalls NH₄NO₃ to a mixture.

A yellow crystalline deposit of triammonium tetrahydrogendetacamolybdate (VI) monophosphas (V) a bit later falls out:

\[
\text{Na}_2\text{HPO}_4 + 12(\text{NH}_4)_2\text{MoO}_4 + 23\text{HNO}_3 \rightarrow (\text{NH}_4)_3\text{H}_4[\text{P(Mo}_2\text{O}_7)_6]\downarrow + 21\text{NH}_4\text{NO}_3 + 10\text{H}_2\text{O} + 2\text{NaNO}_3.
\]

The deposit is not dissolved in hydrogen nitrate, but is dissolved much Na₂HPO₄, diabrotic alkalis, in a solution of ammonia. Therefore it is necessary take the abundance of solution (NH₄)₂MoO₄.

**Experience 6. Properties of sulfitas - anion.** Reduction the potassium permanganate. Add 3-4 drops of a solution of sulfuric acid to 1-2 drops of a solution KMnO₄ and then on drops - solution of a sodium sulfitas up to a decolorization permanganate. Note observations, equation of reaction, conclusions.

**Problems for discussion:**

1. Compare: a) change of atoms radius, potential of ionization; b) change of oxidation-reduction properties of p-elements in the group and period.
2. Consider a structure of a molecule of carbon oxide (II) and justify the mechanism of its interaction with a hemoglobin. Why on fresh air or at use an oxygen cushion the toxic activity of carbon oxide (II) can be reduced?
3. The cation of aluminum exposes in a solution to a strong hydrolysis. Whether its presence at an organism as aquacomplexe is possible?
4. The sodium nitrite is used in medicine as an antispasmodic. Describe analytical effects, which will watch at adding to this substance: a) dilute sulfuric acid? b) potassium permanganate in acidic medium. Write the equations of reactions.
5. How to distinguish in a solution: a) nitrites and nitratas? b) sulfate and sulfite? c) to detect an ion of ammonium?

7. A sodium sulfas is applied as antidote at a poisoning with salts of lead and barium. What chemical interaction is cause of the medical effect in this case?

8. Both zinc sulfas and copper are used as antiseptic and astringents. What is medium in their aqueous solutions?

9. What chemical property explains antiseptic properties of lime chloride?

10. Chloride of ammonium is used in medicine as an expectorant. What is medium in its aqueous solution (pH < 7, pH > 7, pH = 7)?

11. Sodium thiosulfatum in an admixture with a hydrochloric acid is applied to treatment of dermal diseases. Thus there is a chemical reaction, which yields render medical effect. Write the equations of this reaction.

12. What oxide of nitrogen is used for a narcosis? What its properties (write the equations of reaction)? How would be reflected in a state of the patient, if it was acid oxide?

13. Hydroxide of aluminum is applied at heightened gastric acidity, peptic ulcer of a stomach and duodenal intestine. The drug neutralizes a hydrochloric acid: 1 g neutralize about 250 ml 0,1M solution HCl. Calculate, what quantity HCl is neutralized 50g Al(OH)₃, received as 4% of a suspension.

**LESSON 4 Properties of biogenic s-, p-, d-elements, they analytical reactions (final lesson).**

**The purpose of lesson:** the check, fastening and systematization of knowledge on chemistry of biogenic elements; their biological role in an organism, toxic activity of some elements ions and bionomics in connection with contaminations by mineral substances; the check and fastening of practical skills of analytical definition of ions of biogenic elements in a solution.

**The control operation includes:**
1. Control test on a theme.
2. Control-analytical problem on a mixture of cations s- and d-elements.

**The purpose.** Define the cationic composition of the solution.

**For preparation for control operation it is necessary:**
1. TO ITERATE investigated on lesson №1 - 3 a program material; analytical reactions s-, p-, d-elements.
2. **TO GET READY** for performance of the control-analytical problem "The analysis of a mixture of ions".

**Literature:** see lessons №1-3.

**General references:** the analysis of an admixture of cations will carry out in the basic so-called fractional method, i.e. the cations unclose in separate assays of a solution. Prior to the beginning discovery of separate cations it is necessary to lead some prestress observations and trials.

1. **Score colour of the examinee of a solution.** On colouring a solution make the prestress inferences about presence or absence in a solution of this or that cations (tab. 1).

<table>
<thead>
<tr>
<th>Colour of a solution</th>
<th>Colour of the solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue</td>
<td>Cu$^{2+}$</td>
</tr>
<tr>
<td>Yellow</td>
<td>Fe$^{3+}$</td>
</tr>
<tr>
<td>Violet (dark)</td>
<td>Cr$^{3+}$</td>
</tr>
<tr>
<td>Pink</td>
<td>Co$^{2+}$</td>
</tr>
<tr>
<td>Light green</td>
<td>Ni$^{2+}$</td>
</tr>
<tr>
<td>Yellow-green</td>
<td>Cu$^{2+}$ and Fe$^{3+}$ is simultaneous</td>
</tr>
</tbody>
</table>

If the solution is not painted, in a nem there are cations, marked in tab. 1 giving in water painted aquacomplexes.

2. **Test a decomposed solution for a staining of a flame.** To a unpigmented flame of a gas burner import on an iron wire 1 drop of a decomposed solution, note result of observation and prestress deduction about presence (or absence) in a solution of this or that cation (tab. 2).

If the flame remains to unpigmented in a solution miss indicated in tab. 2 (and some other, giving a painted flame) cations.

At positive response to a flame the guessed cation then is unclosed in a solution by carrying out of the relevant qualitative tests.
3. **Define reaction of a solution.** The alkaline reaction of a solution testifies to presence at a decomposed solution of cations of the strong bases: $K^+$, $Na^+$, $Ca^{2+}$, $Ba^{2+}$. In an alkaline condition there are cations $Mg^{2+}$ and majority of $d$-devices, as in these requirements they form nonsoluble in water oxyhydroxides. At pH $> 7$ can not exist and ion of ammonium.

The acidic reaction points presence at a solution of free acids (cation $H_3O^+$) or cations of mild bases.

4. **Test activity of diabrotic alkalis.** If the solution has acidic or neutral reaction, select 2 - 3 drops of a solution in a test tube and add 2 - 3 drops of a solution $KOH$. Note result of observation (colour of the dropped out deposit or its absence) and conclude presence (absence) in a solution of those or other cations:

<table>
<thead>
<tr>
<th>The colour of the dropping out deposit</th>
<th>white</th>
<th>white, is prompt dark on air</th>
<th>Dark green</th>
<th>Light brown</th>
<th>blu</th>
<th>Light green</th>
<th>blu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation</td>
<td>$Mg^{2+}$</td>
<td>$Mn^{2+}$</td>
<td>$Fe^{2+}$</td>
<td>$Fe^{3+}$</td>
<td>$Co^{2+}$</td>
<td>$Ni^{2+}$</td>
<td>$Cu^{2+}$</td>
</tr>
</tbody>
</table>

The cations $Hg^{2+}$ form yellow, and cations of hydrargyrum (I) and silver - black deposit of oxides.

5. **Test activity of a potassium hexacyanoferate (II) and (III).** Reaction usually will carry out by a trickling method. On a filter paper put 1 drop of a decomposed solution and 1 drop of a solution of reagent. Pay attention to colour of the formed deposits (if the deposits are formed), note result of observation and make conclusions, were guided tab. 3.

If at activity on a decomposed solution of the indicated reagents of a deposit and brown staining is not formed, and at interaction with diabrotic alkalis the white deposit falls out, the solution contains cation of magnesium.
After carrying out of trial tests conclude presence (absence) in a solution of this or that cations and will carry out the padding analyses once more not unclosed cations.

At carrying out of the analysis in basic will use characteristic reactions investigated in the previous operations. But it is possible to use and other known reactions. So, the cation Cu\(^{2+}\) can be unclosed in a solution not only the activity of excess of an aqueous solution of ammonia (at presence Cu\(^{2+}\) occurs bright - dark blue colouring), but also reaction of displacement of copper by iron: Cu\(^{2+}\) + Fe\(^0\) → Fe\(^{2+}\) + Cu\(^0\). On an iron wire dropped in a solution, there is a red scurf of copper.

<table>
<thead>
<tr>
<th>Cation</th>
<th>(K_4[Fe(CN)_6])</th>
<th>(K_3[Fe(CN)_6])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(^{3+})</td>
<td>white deposit Mn(_2)[Fe(CN)(_6)]</td>
<td>brown deposit Mn(_3)[Fe(CN)(_6)](_2)</td>
</tr>
<tr>
<td>Fe(^{3+})</td>
<td>white deposit K(_2)Fe[Fe(CN)(_6)]</td>
<td>dark blue deposit KFe[Fe(CN)(_6)]</td>
</tr>
<tr>
<td>Fe(^{3+})</td>
<td>dark blue deposit KFe[Fe(CN)(_6)]</td>
<td>a brown staining</td>
</tr>
<tr>
<td>Cr(^{3+})</td>
<td>a deposit does not give.</td>
<td>-</td>
</tr>
<tr>
<td>Co(^{2+})</td>
<td>greenish deposit Co(_2)[Fe(CN)(_6)]</td>
<td>a brown-red deposit Co(_3)[Fe(CN)(_6)](_2)</td>
</tr>
<tr>
<td>Ni(^{3+})</td>
<td>greenish deposit Ni(_2)[Fe(CN)(_6)]</td>
<td>yellow-brown deposit Ni(_3)[Fe(CN)(_6)](_2)</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>a dark red deposit Cu(_2)[Fe(CN)(_6)]</td>
<td>red-brown deposit Cu(_3)[Fe(CN)(_6)](_2)</td>
</tr>
<tr>
<td>Zn(^{2+})</td>
<td>white deposit K(_2)Zn(_3)[Fe(CN)(_6)](_2)</td>
<td>brown-yellow deposit Zn(_3)[Fe(CN)(_6)](_2)</td>
</tr>
</tbody>
</table>

Example of the solution and veneering of a control-analytical problem.

For the analysis the solution №1 is obtained.

Prestress observations, trials and conclusions.

1. **Appearance and colour of the solution** - transparent colourless fluid. The conclusion. In a decomposed solution there are cations Cr\(^{3+}\), Fe\(^{3+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\).

2. **A staining of a flame**. The flame is coloured in violet colour. The conclusion. In a decomposed solution, except for the marked above cations, there are cations Na\(^+\), Ca\(^{2+}\). Probably, there is a cation K\(^+\).


Conclusion. In a solution I am present cations of d-devices, which, exposing a hydrolysis, give acidic response of medium.

4. **Activity of diabrotic alkalis**. The white deposit, буреющий on air falls out. Conclusion. Except for the listed above cations, in a decomposed solution miss Fe\(^{2+}\), Hg\(^{2+}\), Hg\(^{2+}\). Probably, are present Mn\(^{2+}\) and Mg\(^{2+}\).

5a. **Activity \(K_4[Fe(CN)_6]\)**. The white deposit falls out.

Conclusion. In a decomposed solution, probably, there are cations Mn\(^{2+}\), Zn\(^{2+}\).

5b. **Activity \(K_3[Fe(CN)_6]\)**. The brown-yellow deposit falls out.
**Deduction.** At a solution there can be cations Mn$^{2+}$ and Zn$^{2+}$.

*General conclusion on the basis of trial tests.* In a decomposed solution, probably, there are cations K$^+$, Mg$^{2+}$, Mn$^{2+}$, Zn$^{2+}$.

Then discovery of cations will spend with the help of specific reactions.

**LEGITIMACIES OF COURSE**

**CHEMICAL REACTIONS**

**LESSON 5 Chemical thermodynamics and bioenergetics.**

**Medicobiological value:** the thermodynamics is the theoretical basis of a modern bioenergetics - science which study legitimacy of accumulation, keeping and using of energy by alive systems.

Since the change of energy does not depend on way of process, but only from an initial and final state of system, therefore there is no necessity to know true mechanism of reactions occurring in alive organisms (cells). It is possible to simulate them outside of an organism. So, it was possible to establish on model experience, with the help of thermodynamic calculations, that at multiphase process of an oxidizing of nutritious substances in an organism the same quantity of energy precipitates out, as well as at their immediate burning outside of an organism. It allows to establish connection between a calorific of nutrition and serviceability of an organism. These connection is a base of scientific dietology. The model operation of various biochemical processes can be carried out at various temperatures distinguished from that, at which they proceed in an organism, and using the relevant equations of thermodynamics it is possible to count change of energy in substantial requirements.

The thermochemical investigation of processes of an oxidizing of various products in alive organisms are necessary not only for study of mechanisms of transformation of various substances in energy. The comparison of energetics healthy and patients of cells allows to develop early diagnostics of various diseases and check behind their current. The diseases of the man are always accompanied by change of values of thermodynamic parameters describing a sectional organism in norm. So, occurrence and the course of diseases is accompanied by increasing of entropy system. The increasing of entropy is marked also at development of processes of neogenesis and embryogenesis.

The application of the basic laws of thermodynamics allows to establish specific features of an alive nature, to prognosticate a direction of spontaneous course of processes in an organism and their depth depending on requirements, to predict an possibility of participation of this or that medicinal substance in the necessary reaction proceeding in biological medium, and relevant bioenergy changes.
Knowledge of thermodynamic legitimacies and skill to apply them for decision of concrete practical questions it is necessary for study of the following chapters of these course (chemical kinetics and equilibrium, theory of solutions, electrochemistry, fizico-chemistry of surface phenomenas), and also for study of biochemistry, physiology both other medicobiological and clinical disciplines.

To lesson it is necessary:
TO STUDY the following program questions: a subject and problems of chemical thermodynamics. Interrelation between processes of a metabolism and energy in an organism. Chemical thermodynamics is a theoretical basis of a bioenergetics.

The basic concepts of thermodynamics. Internal energy. Work and heat - two shapes of power transmission. Types of thermodynamic systems and processes.


Measure of a direction of spontaneous processes.

Literature:

Research work:
«Definition the heat of neutralization reaction»

Starting sectional

Mass of an interior glassful of a calorimeter m1, g ……………………………
Volumes of solutions of reactants V, ml ………………………………………
Concentration of solutions C, mol/l ……………………………………………
Density of solutions ρ, g/ml ……………………………………………………
Specific heat of water Cm (H2O) - 4,184 J / (g · K)
Specific heat of glass Cm (gl) - 0,753 J / (g · K)
1. By measuring graduates measure till 30 ml of solutions of a strong acid and strong basis.
2. Measure temperature of one of solutions, for example basis, is immediate in the cylinder by the thermometer. After that wash the thermometer by distilled water and again insert into a calorimeter.
3. Add a solution of an acid through a funnel to an interior glassful of a calorimeter and also write down its temperature.
4. Add the alkali liquor prompt in a calorimeter to a solution of an acid and intermix.
5. Within several seconds observe for level of mercury in the thermometer and write down the highest indication.
6. The obtained experimental data write down in the table under the shape:

<table>
<thead>
<tr>
<th>The measured and calculated quantities</th>
<th>reactants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature of a solution of an acid $T_a$</td>
<td></td>
</tr>
<tr>
<td>Temperature of a solution of the basis $T_b$</td>
<td></td>
</tr>
<tr>
<td>Reference temperature of experience $T_1 = 0.5(T_a + T_b)$</td>
<td></td>
</tr>
<tr>
<td>Best temperature after mixture $T_2$</td>
<td></td>
</tr>
<tr>
<td>$\Delta T = T_2 - T_1$</td>
<td></td>
</tr>
<tr>
<td>$Q$, kJ</td>
<td></td>
</tr>
<tr>
<td>$\Delta H_c$, kJ/mol</td>
<td></td>
</tr>
</tbody>
</table>

Processing of results of experiment

For evaluation under the experimental data of reaction heat of neutralization calculate:
1) Blanket calorific capacity of a calorimeter $C_m$, taking into account a calorific capacity of a solution and calorific capacity of an interior glassful:

$$C_m = C_m(gl) \cdot m(gl) + C_m(H_2O) \cdot m(sol).$$

Where: $m(sol)$ - mass of a solution in a calorimeter calculated on volume of a solution and density (Density can be accepted peer 1 g/ml).

2) Calculate the heat, allocated in a calorimeter:

$$Q = C_m \cdot \Delta T$$

This heat gradually in accordance with alignment of temperature is transmitted in a surrounding medium and can be accepted peer on absolute value to change of enthalpy of system (calorimeter) - $\Delta H_c$:

$$\Delta H_c = -Q$$

3) For calculation of reaction heat $\Delta H_r$, the found value of heat count on 1 of a mol reacting acid or basis that corresponds 1 of mol generated water:

$$\Delta H_r = \frac{\Delta H_c}{n} = \frac{\Delta H_c}{C \cdot V}$$
Where: \( n \) – chemical quantity of one of substances participating in reaction.

**Problems for discussion:**

1. What is: a) an exothermic reaction, b) an endothermic reaction? Give two examples of each.
2. Discuss some different forms of energy and give examples of their conversions.
3. What is meant by a system in thermodynamics?
4. Define enthalpy change for a system.
5. What is the difference, if any, between enthalpy of formation and enthalpy of reaction?
6. What is the difference, if any, between \( \Delta H_f \) and \( \Delta H'_f \)?
7. Write an equation relating the heat of a reaction and the heats of formation of the reactants and the products of the reaction.
8. For the metabolism of sugar, \( \text{C}_{12}\text{H}_{22}\text{O}_{11}, \) in the body, \( \Delta H = -5645 \text{ kJ mol}^{-1}. \) How many kilocalories (Ccal) of energy would your body gain from the sugar in a candy bar that has the mass of 150.0 g and contains 60.0 percent sugar and no other nutrients?
9. The combustion of benzene is represented by the equation
   \[
   \text{C}_6\text{H}_6(\ell) + 7 \frac{1}{2} \text{O}_2(\ell) \rightarrow 6\text{CO}_2(\ell) + 3\text{H}_2\text{O}(\ell)
   \]
   Using the standard data to four significant figures, calculate the standard enthalpy of combustion of benzene.
10. The combustion of octane occurs according to the equation
    \[
    2\text{C}_8\text{H}_{18}(\ell) + 25\text{O}_2(\ell) \rightarrow 16\text{CO}_2(\ell) + 18\text{H}_2\text{O}(\ell)
    \]
    The standard enthalpy for this reaction as written is \(-1.094 \times 10^4 \text{ kJ} \). Using the Standard data, calculate the standard enthalpy of formation of octane.
11. What is a «spontaneous process»? Give examples of some spontaneous and of some nonspontaneous prosesses.
12. What is entropy? Give examples of some systems of law entropy and others of higher entropy.
13. State the second law of thermodynamics.
14. In thermodynamics, what is a «reversible» process?
15. What is the Gibb’s free energy? Write an equation for the Gibb’s free energy of a system in terms of the change, the entropy change, and the temperature of the system.
16. What is the relationship between the free energy change of a reaction and the spontaneously of the reaction?
17. Write an equation for calculating the standard free energy change for a reaction from the values of the standard free energies of formation for the reactants and products.
18. Show how you would calculate the standard free energy change for a reaction from given values of standard enthalpies of formation and standard absolute entropies for the reactants and the products.
19. Predict the sign of $\Delta S$ for each of the following reactions and give a reason for each prediction:
(a) $\text{AgCl(s)} \rightarrow \text{Ag}^+(aq) + \text{Cl}^-(aq)$;
(b) $2\text{Na(s)} + \text{Cl}_2(g) \rightarrow 2\text{NaCl(s)}$;
(c) $\text{H}_2(g) + \text{I}_2(g) \rightarrow 2\text{HI}(g)$;
(d) $\text{H}_2(g) + \text{I}_2(s) \rightarrow 2\text{HI}(g)$;
(e) $2\text{H}_2\text{O}_2(l) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$.

**LESSON 6**

A chemical equilibrium. The chemical kinetics and catalysis. Peculiarities of catalytic activity the enzymes.

**Medicobiological value:** many biochemical processes in a human organism are reversible. Among them such vital processes, as interaction of haemoglobin with oxygen, transport of carbon dioxide and transport role of protein, the hydrolysis of ATP etc. Knowing an equilibrium constant is possible to give a quality estimation of a direction of many biochemical transmutations in an human organism for medical diagnostics. According to a Le Chatelier's principle it is possible to prognosticate many infringements in an organism caused by change of temperature, pressure and concentration of metabolites; to adjust many biochemical and physiological processes. In particular, to understand influence of changes of partial pressure of oxygen on process of transport it in a human organism; shift of equilibriums of buffer systems on a constancy pH of biological fluids and tissues; allocation of ions till both parties of biological membranes. Action of a radioactive ion strontium, bound with equilibrium process of replacement of calcium - basic builder of an osteal tissue - on strontium. The sharp shift of chemical equilibriums in a human organism can cause death.

The study of these theme is necessary for the future doctor for successful mastering of many questions of biochemistry, pharmacology, physiology, therapy. The study of the rates and mechanisms of chemical reaction is known as chemical kinetics. Chemical kinetics has major practical value (for studing of chemical reactions proceeds in alive organisms). On the basis of legitimacies of chemical kinetics and thermodynamics it is possible to prognosticate course in time of biochemical transmutations. All biochemical reactions are composite. Practically all processes of a metabolism are consecutive reactions (for example, metabolism of a glucose etc.). Photochemical reactions are the processes underlying activities of the visual evaluator and at formation of sunburn of a skin. It is important to know an influence of various exterior actions on rate of metabolic transmutations. For example, is similar to reactions proceeding in a lifeless nature, at rising temperature of a human body as a result of any of disease the rate of biochemical transmutations in a human body strongly increases.

The special interest for medicine represents study of kinetics of enzymatic reactions, as practically all reactions in a human organism proceed with participation of
biological catalytic agents - enzymes; besides the ferment drugs will be used in therapy of many diseases.

The rate of reactions transiting in an organism, substantially causes activity of various medicinal substances. At a keeping of medicinal preparations the chemical reactions proceed, which rate defines a period of validity of medicines. The medical discipline «pharmacokinetics» studies legitimacies of an adsorption of medicinal substances in a blood, allocation them on bodies and tissues, metabolism and removing from an organism. With this purpose through particular time slices determine the content of medicinal preparations and their metabolites in various biological fluids and organs of an organism. On the basis of these data a dose and regimen of assignment, and also toxic activity of medicinal substances and others biologically active substances are determined.

To lesson is necessary:

1. TO STUDY the following program questions: a chemical equilibrium. Reversible and nonreversible reaction. A constant of a chemical equilibrium and ways of its expression: $K_p$, $K_c$, $K_a$. The isotherm of chemical reaction equation. To predict a shift of a chemical equilibrium, according to a Le Chatelier principle. Concept about a homeostasis and stationary state of an alive organism. a subject and basic concepts of chemical kinetics. Chemical kinetics as a basis for study of rates and mechanisms of biochemical processes. Reactions simple and composite, homogeneous and heterogeneous.


Literature:
Research work:
«Quality experience on a chemical equilibrium»

Purpose of operation: To study experimentally direction of shift of a chemical equilibrium at change of concentration of reagents and temperature.

Performance of experiment

Experiment 1. Study of shift of a chemical equilibrium at change of concentration of reagents.

For experience we shall take advantage a reaction of formation iron (III) thiocyanide:

\[
FeCl_3 + 3KSCN \leftrightarrow Fe(SCN)_3 + 3KCl
\]

Iron (III) thiocyanide is intensively painted in red colour, solution FeCl_3 - in yellowish, and the solutions KSCN and KCl are colourless. At change of concentration Fe(NCS)_3 colourings of a solution change, that allows visually to establish a direction of shift of equilibrium.

In a laboratory magazine for record and analysis of observations prepare the table under the following shape:

<table>
<thead>
<tr>
<th>The test tube</th>
<th>added substance</th>
<th>observation - change of intensity of colour</th>
<th>a direction of shift of equilibrium (finger to the right or to the left)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>FeCl_3(l)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>KSCN(l)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>KCl(s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. To four test tubes bring till 5-7 drops 0.0025 mol/l of solutions FeCl_3 and KNCS. Solutions stir by a glass rod and put in a support.
2. The fourth test tube with a received solution leave for comparison of results of experience. In other test tubes add the following reagents: in first - 1 drop of a saturated solution FeCl_3, in second - 1 drop of a saturated solution KNCS, in a third - a little crystals KCl.
3. Compare intensity of colouring of received solutions to intensity of colouring of a solution in 4-th test tube and bring sectional in the table.

Experiment 2. Study of shift of a chemical equilibrium at change of temperature.
1. To two test tubes bring till 4-5 mls of a solution of amyllum and add there till 3-4 mls of a solution I_2. Write down observations (colour of the formed solution).
2. Heat up one of test tubes in a glassful with hot water. The second test tube leave for comparison. Observe change of colouring. How the colouring of a solution in a heated test tube changes in comparison with cold?

3. Write down observations in a laboratory magazine.

4. Cool a heated test tube under a jet of cold water. What occurs? Write down the equation of the investigated equilibrium:

\[ I_2 + \text{Amylum} \leftrightarrow [I_2 \cdot \text{Amylum}] \]

yellow colourless dark blue

5. Being grounded on results of observations, make a conclusions about a direction of shift of equilibrium in system at warming and cooling. Using a Le Chatelier's principle, answer a question – exo- or endothermic the reaction of formation \([I_2 \cdot \text{Amylum}]\) and reaction of its dissociation is.

In the report on laboratory operation write down also expressions of the mass action law for the investigated equilibriums.

**Problems for discussion**

1. What is meant by the «position» of an equilibrium?

2. What is meant by a «shift» of an equilibrium?

3. What is a «reaction quotient»?

4. Write an expression for \(K_c\) for each of the following gaseous equilibria:
   (a) \(3\text{O}_2(g) \rightleftharpoons 2\text{O}_3(g)\),
   (b) \(\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI} (g)\),
   (c) \(2\text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)\),
   (d) \(4\text{NH}_3(g) + 3\text{O}_2(g) \rightleftharpoons 6\text{H}_2\text{O}(g) + 2\text{N}_2(g)\),
   (e) \(2\text{H}_2\text{S}(g) + 3\text{O}_2(g) \rightleftharpoons 2\text{H}_2\text{O}(g) + 2\text{SO}_2(g)\)

5. Write an expression for the equilibrium constant, \(K_c\), for each of the following reactions:
   (a) \(\text{Fe}(s) + 5\text{CO}(g) \rightleftharpoons \text{Fe}(	ext{CO})_5 (g)\),
   (b) \(\text{C}(s) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + \text{H}_2(g)\),
   (c) \(2\text{HgO}(s) \rightleftharpoons 2\text{Hg}(l) + \text{O}_2(g)\),
   (d) \(\text{HC}_2\text{H}_3\text{O}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{C}_2\text{H}_5\text{O}_2^-(aq)\),
   (e) \(\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)\),
   (f) \(2\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)\).

6. For the reaction \(\text{SO}_2(g) + \text{NO}_2(g) \rightleftharpoons \text{SO}_3(g) + \text{NO}(g)\) at 973 K the equilibrium constant, \(K_c\), is 9.00. Calculate the equilibrium concentrations of all the species present when:
   (a) 1.00 mol of \(\text{SO}_2\) and 1.00 mol of \(\text{NO}_2\) are injected into a 1.00-L container at 973 K;
   (b) 1.00 mol of \(\text{SO}_2\) and 1.00 mol of \(\text{NO}_2\) are injected into a 2.00-L container at 973 K;
(c) 1.00 mol of SO$_3$ and 1.00 mol of NO are injected into a 1.00-L container at 973 K.

7. For the reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

the value of $K_p$ is 0.050 at 2473 K. If the equilibrium partial pressures of $N_2$ and NO in this system are 0.20 and 0.045 atm, respectively, what is the partial pressure of $O_2$?

8. At 1000 K, $K_p$ for the reaction $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$ is 158. When a certain mixture of these reactants and products is at equilibrium at 1000 K, the partial pressure of NO is 0.50 atm and the partial pressure of O is 0.30 atm. Calculate the partial pressure of NO$_2$ in this equilibrium mixture.

9. Formulate the Law of chemical equilibrium (Guldberg and Waage).

10. Formulate the Le Chatelier’s principle.

11. Write an equation relating $K_p$ to $K_c$. Show how this equation can be rearranged to solve for either of these equilibrium constants from the known value of the other.

12. In the following system at equilibrium $4NH_3(g) + 3O_2(g) \rightleftharpoons 6H_2O(g) + 2N_2(g)$ how is the amount of nitrogen present affected by each of the following changes?
   a) The volume of the container is doubled;
   b) the volume of the container is decreased;
   c) more water vapor is introduced;
   d) more ammonia is introduced;
   e) some oxygen is removed from the system;
   f) temperature is increased (the forward reaction in this system is exothermic);
   g) the pressure of the system is increased by introducing helium gas;
   h) a catalyst is added.

14. For the gaseous equilibrium mixture

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \quad \Delta H^o = +180 \text{ kJ}$$

State the effect on the equilibrium of each of the following changes:
   a) more oxygen gas is introduced;
   b) some nitrogen is removed;
   c) the temperature is increased;
   d) the volume of the container is decreased without allowing any of the gas to escape;
   e) the pressure is increased on the system by introducing helium gas;
   f) a catalyst is added. Explain your reasoning in each case.

14. Consider the Haber process for making ammonia:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H^o = -46 \text{ kJ}$$

Complete the following table to state the effects (increased, decreased, unchanged) the indicated changes will have on the concentrations of the components at equilibrium:
<table>
<thead>
<tr>
<th>Change</th>
<th>Concentration of N₂</th>
<th>Concentration of H₂</th>
<th>Concentration of NH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increasing pressure by decreasing the volume of the reaction vessel</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Increasing temperature</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Increasing the amount of N₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adding neon gas</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adding a catalyst</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

15. List three factors that can affect reaction rates.
16. What is a rate law? Write the general form of the rate law for the reaction
   \[ A \rightarrow B \] and for the reaction \[ A + B \rightarrow C + D. \]
17. What is meant by the order of a reaction? Considering the general form of the rate expression you wrote in question 2 for the reaction \[ A + B \rightarrow C + D, \] what is the order of this reaction in:
   (a) reactant A;
   (b) reactant B?
   (c) what is the overall order of the reaction?
18. Write an equation for a first-order reaction that relates the initial concentration of a reactant A with its concentration at time \( t \), the rate constant, \( k \), and time \( t \).
19. What is the meaning of "half-life"?
20. Write a modified form of the equation in question 7 so that the equation contains \( t_{1/2} \) instead of \( t \). What is the numerical value of the product \( kt_{1/2} \) in this equation? Show that you can obtain this number on your calculator.
21. Write the general and the logarithmic form of the Arrhenius equation. Identify all the symbols used in the equation, and explain how, according to this equation, the value of the rate constant, and consequently the reaction rate, is affected by varying \( T \).
22. Explain the term "activation energy."
23. What is: (a) collision theory;
   (b) transition state theory?
24. What is the molecularity of a reaction? Illustrate this.
25. The decomposition of hydrogen peroxide to water and oxygen is a first-order reaction with a rate constant of \( 5.0 \times 10^{-6} \text{ s}^{-1} \) at a certain temperature. How long will it take at that temperature for a 0.820 M solution of \( \text{H}_2\text{O}_2 \) to decrease to 0.500M?
26. The reaction \( \text{SO}_2\text{Cl}_2(\text{l}) \rightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g}) \) is a first-order reaction with a rate constant of \( 2.2 \times 10^{-5} \text{ s}^{-1} \) at 320°C. What percent of \( \text{SO}_2\text{Cl}_2 \) is decomposed after heating the substance at 320°C for 1.0 h?
LESSON 7 Solubility of substances. Expedients of expression concentration of a solution.

Medicobiological value of dissolution: the formation of solutions is connect to dissolution of various substances in the relevant dissolvents. Such dissoivent is the water in alive organisms. The water is the basic constituent of all cells and tissues of organisms. It provides processes of an adsorption, movement of nutritious substances and products of metabolism in an organism. Besides the formation of water as final product of an oxidizing of substances is accompanied by excretion of a great quantity of energy (29 kJ/mol). Total volume of liquid (aqueous) mediums of an organism makes 60 % from mass. From them volume invascular liquid - 5 %, endocellular - 40 %, and intercellular - 15 %. The important biological and biochemical role of water is connect with peculiarities of its structure and properties.

Knowledge of legitimacies of dissolution of gases it is necessary for study of such vital processes as transport of oxygen and product of an oxidizing nutritious substances - CO₂ by a blood. A quantitative basis of a solubility of gases - the Henry’s and Dalton’s, Sechenov’s laws have major value not only in chemistry, but also in medicine, as the infringement of a solubility of gases in a blood can be caused pathological changes. The Henry’s law, in particular, allows to open a pathology of diseases at the divers, pilots, which operation is connect to prompt transferring on medium with sharply distinguished atmospheric pressure. On the basis of the Henry’s law the treatment in pressure chamber (hyperbaric oxygenation) - inhale of oxygen at abnormal higt pressure (at treatment gangren, anemia, at poisonings etc. diseases). will be carried out. According to the Sechenov’s law, not only electrolytes, but also protein and the lipids, which content in a blood can change, render influence on a solubility in it O₂ and CO₂.

In physiological, biochemical, sanitary - hygienic, pharmacological and other laboratories solutions of precise concentration is used for studing of product metabolism, of metabolism drags, definition chemical composition biological liquids and etc. Samples of substances, the various assays for carrying out of the analysis, including clinical, usually transfer in a solution.

To lesson it is necessary:
Ways of expressing of composition of a solution: percent by mass, molarity, molality, molar concentration of an equivalent, mole fraction.
Dissolution prosses: dissolving solids in liquids; dissolving liquids in liquids; solubility of gases in liquids and its dependence on the various factors. Henry’s and Dalton’s. laws Influence of electrolytes on a solubility of gases. The Sechenov’s. law A solubility of gases in a blood.
Literature:

Research work:
«Preparation of solutions of given concentration»

The task 1. Preparation of a solution of a given percent by mass (w, %).
Having received from the teacher the individual task.
1) calculate what quantity of solid substance and the waters are necessary for taking for its preparation.
2) give on weights the designed shot of solid substance.
3) transfer a shot to a chemical glass.
4) add necessary quantity of water, having measured its cylinder.
5) intermix contents before complete dissolution by circular motions.
6) transfer in a measuring cylinder the prepared solution. Spot density of a solution areometer (under the check of the teacher).
7) on quantity of found density, using the relevant table (see is lower), establish a true percent by mass (, %) in a solution.

The note: If the measured value of density will appear between two values in the table, a mass share (, %) find by a method of interpolation.

For example, density of your solution is peer 1247 kg / m³. The densities 1241 and 1263 kg / m³ are specified in the table to which there correspond(meet) (%) 22 % and 24 %. Hence, to change on 2 % there corresponds(meets) change of density on 1263-1241=22. Your solution differs on density from 1241 on quantity 6.
Let's make a proportion:

22 - 2 %
6 - x of %

\[ x = \frac{6 \cdot 2}{22} = 0.54\% .\]

The percent by mass (%) of your solution will be peer: 22 % + 0.54 % = 22.54 %.

The task 2. Preparation of a solution of a given percent by mass by a dilution of a starting solution.
1) calculate necessary quantity of a solution and water.
2) measure necessary volumes by the cylinder (or pipet) in a chemical glass.
3) spot density of a solution by an areometer and under the table establish a true percent by mass of a solution (see task 1, item 6 and further).
4) calculate absolute errors and relative errors.

### Densities (kg/m$^3$) of aqueous solutions of salts (20° C)

<table>
<thead>
<tr>
<th></th>
<th>Na$_2$CO$_3$</th>
<th></th>
<th>NaCl</th>
<th></th>
<th>KCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega, %$</td>
<td>$\rho, \text{kg/m}^3$</td>
<td>$\omega, %$</td>
<td>$\rho, \text{kg/m}^3$</td>
<td>$\omega, %$</td>
<td>$\rho, \text{kg/m}^3$</td>
</tr>
<tr>
<td>1.62</td>
<td>1015</td>
<td>2.0</td>
<td>1012</td>
<td>2.0</td>
<td>1011</td>
</tr>
<tr>
<td>2.10</td>
<td>1020</td>
<td>4.0</td>
<td>1029</td>
<td>4.0</td>
<td>1024</td>
</tr>
<tr>
<td>3.05</td>
<td>1030</td>
<td>6.0</td>
<td>1041</td>
<td>6.0</td>
<td>1037</td>
</tr>
<tr>
<td>4.03</td>
<td>1040</td>
<td>8.0</td>
<td>1056</td>
<td>8.0</td>
<td>1050</td>
</tr>
<tr>
<td>6.00</td>
<td>1060</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Densities (kg / m$^3$) of aqueous solutions of salts (20° C)

<table>
<thead>
<tr>
<th></th>
<th>K$_2$Cr$_2$O$_7$</th>
<th></th>
<th>CuSO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega, %$</td>
<td>$\rho, \text{kg/m}^3$</td>
<td>$\omega, %$</td>
<td>$\rho, \text{kg/m}^3$</td>
</tr>
<tr>
<td>2.0</td>
<td>1012</td>
<td>2.0</td>
<td>1019</td>
</tr>
<tr>
<td>3.0</td>
<td>1019</td>
<td>3.0</td>
<td>1030</td>
</tr>
<tr>
<td>4.0</td>
<td>1026</td>
<td>4.0</td>
<td>1040</td>
</tr>
<tr>
<td>5.0</td>
<td>1033</td>
<td>5.0</td>
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</tr>
<tr>
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<td>6.0</td>
<td>1062</td>
</tr>
<tr>
<td>7.0</td>
<td>1048</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>1055</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Problems for discussion:

1. What is meant «solution»?
2. What is: (a) a saturated solution; (b) supersaturated solution?
3. What is meant by the general statement «like dissolves like»?
4. Why are low – molecular- weight alcohols soluble in water, but high – molecular – weight alcohols insoluble or only sparingly soluble?
5. How does an increase in temperature generally affect the solubility of: (a) solids in liquids; (b) liquids in liquids; (c) gases in liquids?
6. What effect, if any, does an increase in pressure have on the solubility of: (a) solids in liquids; (b) liquids in liquids; (c) gases in liquids?
7. What is Henry’s law? Write a mathematical expression for Henry’s law and define the symbols used.
8. What is «molality»?
9. What is the molarity of a sodium chloride solution that contains 6.82 g of NaCl in 450 ml of solution?
10. Which of the following compounds would you expect to be water soluble? (a) (NH₄)₃PO₄; (b) H₂S; (c) CCl₄; (d) C₆H₆; (e) HCOOH; (f) CH₃OH; (g) NH₃; (h) HCl; (i) Ca(NO₃)₂.
11. Explain why Na₂SO₄ is soluble in water but BaSO₄ is not.
12. Predict how an increase in temperature might affect the solubility of each of the following substances in water (a) KNO₃; (b) C₁₂H₂₂O₁₁; (c) SO₂; (d) O₂.
13. How does the concentration of dissolved oxygen in water in a river at sea level compare with that in a mountain brook? Explain.
14. What is the molality of a solution that contains 1.2 mol of a solute per 4.0 L of water? Assume that the density of water is 1.0 g mL⁻¹.
15. How many grams of potassium hydrogen phthalate, KHC₈H₄O₄, must be used to make 250.0 mL of 0.400 M solution?

**LESSON 8 Colligative properties of solutions.**

**Medicobiological value:** Colligative properties of solutions are: the decrease in the vapor pressure of a solvent above a solution, boiling point elevation, freezing point depression, osmosis. The osmotic phenomena are most important for biology and medicine. It is caused by that the travel of nutritious substances and yields of an exchange occurs first of all by means of a diffusion and osmosis. In too time a diffusion and osmosis in alive organisms are adjusted by a function state of tissues of an organism and depend on their structure. The change of physicochemical properties of phases till both parties of biological membranes results in change of rate of an osmosis, and intensity of metabolic processes.

Due to an osmosis entering water in cells and intercellular frames is adjusted. The osmotic pressure, incipient at it, provides elasticity of cells (turgor), elastance of tissues and shape of bodies, the water-salt exchange etc. All this is necessary for normal current of manifold physical and chemical processes in an organism: reactions of a hydrolysis, oxidizing, hydration, dissociation etc. It explains a constancy of osmotic pressure (osmotic homeostasis) blood and other biological fluids. The basic body of an osmoregulation at the human, are the kidneys. The osmotic pressure of a blood at the man is supported at a level 740-780 kPa. The drugs for injection should be isotonic to biomediums (except for hypertonic salt solutions - for example, 25 % a solution of magnesium sulfas at hypertonic crises). The introduction of hypotonic salt solutions can give in fracture of erythrocytes shells and yield of a haemoglobin in plasma (hemolysis). Eye drops should be isotonic necessarily. All solutions used as blood substitutes, are also isotonic with the blood.
With the help of drugs it is possible to change locally osmotic pressure. It is used for intensifying a uropoiesis at acute poisonings, at acute renal failure, at various edemas. The activity of saline purgative drugs also depends on osmotic pressure.

The knowledge of the numbered phenomena and properties has direct application in therapeutic and surgical practice, scientific - medical examinations. This knowledge is necessary for study of separate questions of biochemistry, physiology, pharmacology.

To lesson it is necessary:
1. TO STUDY the following program questions: Colligative properties of dilute solutions. An osmosis and osmotic pressure. A Van't Hoff law. Osmolarity and osmolality of biological fluids and perfused solutions. Hyper-, hypo- and isoosmotic solutions. Concept about osmotic homeostasis. A role of an osmosis and osmotic pressure in biological systems. A plasmolysis and cytolisis.

Vapor pressure of a solution. A Raoult's law and consequences from it: freezing point depression, boiling point elevation of a solution. A cryometry and ebulyometry.

Colligative properties of dilute solutions of electrolytes. An Van't Hoff's isotinic coefficient.

Literature:

Research work:
«Definition of osmotic concentration and isotonic coefficient of a solution»

Performance of experiment
1. Receive from the laboratory assistant the device for cryometric definitions. The device (fig. 1) consists of a wide glass test tube 1, stoppered, into which are inserted the thermometer 2 and metal stirrer 3. The test tube is placed in a thick-walled glassful 4, in which there is a cooling mixture.
2. Prepare a cooling mixture from 3 parts of snow or ice and 1 parts NaCl and place it in a vessel 4.
3. Measure by the thermometer temperature of a cooling mixture. It should be about –5°C. The cooling mixture should fill in a glassful approximately on 3/4 of its volume.
4. In a test tube 1 add such volume of distilled water completely to cover the tank of the thermometer, close a test tube by a fuse with the thermometer and stirrer and place a test tube in a glassful with a cooling mixture.
5. Stirring the water by a stirrer 3 (try to not concern by an stirrer of the thermometer), track change of temperature. Track, that the thermometer did not concern bottom and walls of a test tube 1. Usually temperature falls little bit below than freezing point of water, then the crystallization begins, the energy and level of mercury rises upwards
sharply and then stiffens on value of temperature of a crystallization of water (about 0°C). Note freezing temperature of water, write down it in a magazine with accuracy, which allows to fix the thermometer, used by you. Take out a test tube from a cooling mixture and, warming up it by an hand, completely dissolve the formed crystals of ice. Again sink a test tube in a cooling mixture and iterate definition of freezing temperature of water.

6. Receive from the teacher a flask with a decomposed solution and write down in a magazine dates about a solution. Wash a test tube 1, fill it by a solution the same as at measuring freezing temperature of water. Close a test tube by a fuse, insert into it the thermometer and stirrer (previously and that and another should be washed by a decomposed solution).

7. Spot temperature began of freezing of a solution, as determined freezing temperature of water. All measurements write down in a laboratory magazine.

![Fig. 1. A simple apparatus for cryometry measurements](image)

**Processing of experiment results**

a) Calculate molality of a decomposed solution.
b) On the experimentally found freezing point depression of a solution in comparison with freezing temperature of water calculate an isotonic coefficient of a solution and real osmotic ion concentration in a solution.

**Problems for discussion:**

1. What is Raolt’s law? Write a mathematical expression for Raolt’s law and define the symbols used.
2. Explain why the vapor pressure of a solution of a solid in a liquid is lower than the vapor pressure of the pure solvent.
3. Show how Raolt’s law can be used to calculate the vapor pressure of a solution of two liquid components, assuming ideal behavior.
4. Explain why the boiling point of a solution of a solid in a liquid is higher than that of the pure solvent.
5. What different types of data are needed to determine the molar mass of a nonvolatile nonelectrolyte in a given solvent? Show how you would calculate the molar mass from these data.

6. Explain why the boiling point elevation of a 0.01 m solution of sodium chlorite is nearly twice that for a 0.01 m solution of sucrose, and the boiling point elevation for a 0.01 m solution of sodium sulfate is nearly three times that for a 0.01 m solution of sucrose.

7. What is interionic attraction theory? How does that theory explain the fact that the boiling point elevation for a dilute sodium chlorite solution is nearly twice, the boiling point elevation for an equally dilute sucrose solution?

8. How does the freezing point depression of a 0.01 m solution of acetic acid compare with: (a) the freezing point depression of a 0.01 m solution of sucrose; (b) the freezing point depression of a 0.01 m solution of sodium chloride? Explain the difference.

9. What is osmosis, and what is the meaning of osmotic pressure? Give some examples of the importance of osmosis in nature.

10. Explain which of the following 0.100 m aqueous solutions has the highest and which has the lowest vapor pressure at 25°C: (a) sucrose; (b) sodium chloride; (c) magnesium chloride.

11. What is the vapor pressure of water over the solution prepared by dissolving 100 g of glucose, C₆H₁₂O₆, in 1.00 L of water (the density of water is 1.00 g mL⁻¹) at 25°C is 23.8 torr.

12. Calculate the boiling point and the freezing point of a solution containing 12.5 g of benzoic acid (C₇H₆O₂) in 110 g of benzene (C₆H₆). The freezing point of benzene is 5.48°C and its Kf is 4.90°C m⁻¹. Benzoic acid is a very weak acid in water but does not ionize in benzene.

13. A 0.0100 m acetic acid solution freezes at –0.0194°C. Calculate the percent dissociation of acetic acid in this solution.

14. Calculate the osmotic pressure of a 0.100 m glucose solution at 22.0°C.

15. Human blood serum freezes at –0.56°C. Calculate the osmotic pressure of blood at 0.0°C and at 37°C, assuming that 1.0 ml of the blood serum contains 1.0 g of water.

LESSON 9 Protolytic equilibriums and processes. Acid-base equilibriums. Buffer solutions.

Medicobiological value: biological fluids and the tissues contain many various weak and strong electrolytes: NaCl, KCl, HCl, CaCl₂, KH₂PO₄, NaHCO₃ etc. The biochemical and physiological function of separate ions was studied on lesson N 1 - 3. On this lesson the role of electrolytes at their combined action in solutions is discussed. The electrolytes play a huge role in vital activity of an organism. In particular:
The presence of electrolytes defines osmotic pressure of all biological fluids of an organism and the constant ionic homeostasis. In a blood plasma the average 154 mmol/L of cations (in the basic ions of a sodium, potassium, calcium, magnesium) should be for normal functioning of an organism. The content of anions makes too 154 mmol/L. Among them sodium chlorid and hydrocarbonate-ions, and also amphiions of protein play a determining role.

The electrolytes influence a solubility biological HMC. For example, the concentration of electrolytes in biological fluids of an organism defines a solubility in them of a haemoglobin, carboxyhemoglobin.

The acid-alkaline equilibrium in a blood and other biofluids is defined by the content of weak and strong electrolytes (NaH_2PO_4, Na_2HPO_4, H_2CO_3, NaHCO_3 etc.).

The presence of electrolytes causes an electrical conductance of fluids and tissues of an organism (carrying out of nervous impulses, cutting of heart, motion of scetetal muscles etc.).

The rate of many biochemical reactions depends on a nature and concentration of the ions, present in biomediums.

The physicochemical properties of biological fluids can correctly be estimated only in view of all legitimacies in solutions of electrolytes. So, at performance of series of biochemical investigations, at carrying out of experience on isolated bodies and tissues it is necessary to take into account ionic strength of fluids. The ionic strength of the majority of biological fluids is peer 0.15.

The role of a hydrolysis in biochemical processes is difficult for overestimating. First of all in an organism the enzymatic hydrolysis takes place, due to which fats, protein and the carbohydrates of nutrition in a gastrointestinal path is splitted by water on more shallow fragments since to be inhausted in an intestine the rather small molecules are capable only. So, for example, the polysaccharides are acquired only after their hydrolysis by enzymes up to monosaccharides. Energy necessary for body height and normal functioning, is escaped both the expense of multiphase process of an oxidizing of nutrition - protein, fats, carbohydrates, and expense of a hydrolysis of some esters, peptides and glycosides. However, a main energy source for many biological processes such as biosynthesis of protein, transport of ions, cutting of muscles, electrical conductance of nervous cells etc. is ATP. The energy is escaped owing to a hydrolysis ATP.

The activity of many pharmaceuticals is bound to their acid-alkaline properties and ability to be hydrolyzed, that it is necessary to take into account at the solution of a question on an admissibility of simultaneous assignment of medicines at treatment. the normal vital activity of an organism is impossible without supported of constant caracteristics (temperature, osmotic pressure, concentration of substances) in endocellular and tissues fluids of an organism. One of the constant caracteristics an organism is the value pH of all liquid mediums of an organism (isohydrya). The conservation of a constancy pH of liquid mediums has for an organism the vital value, as
all biochemical and physiological processes with participation of hormons and enzymes proceed only in a particular interval of values pH. Besides the hydronium ion are catalytic agents of many biochemical processes, and even the small changes of an concentration $\text{H}^+$ ion in a blood and intertissues fluids strongly influence on value of osmotic pressure in these biofluids. The diversion pH of a blood from norm (7.36) is results in infringement of processes of vital activity of an organism. The restricted constancy pH in various mediums of our organism is supported first of all by physicochemical way - buffer systems.

In chemical, toxicological, sanitary - hygienic and clinical laboratories the buffer solutions are applied to support of a constancy pH of medium, for example, at study of properties of protein, enzymes, hormons and others biologically active substances; at excretion of toxins from a biological material and their analysis; for preparation injectionly of solutions, blood substitutes and stabilization of series of medicinal substances. The definition pH of series of biological fluids (urine, gastric juice) is the important diagnostic test, as the various diseases are accompanied by infringement of acid - alkaline equilibrium in an organism. It is a subject of study of clinical disciplines.

To lesson it is necessary:

Protolytic equilibriums and processes. The protolytic theory of acids and bases. Molecular and ionic acids and basis. A conjugate protolytic steam of an ampholyte. Protolytic reactions of ionization, neutralization, hydrolysis. A role of reactions of a hydrolysis in biochemical processes. A constant of an acidity ($K_a$) and basicity ($K_b$). A hydrolysis ATP as a universal energy source in an organism. Autoionization of water and $K_w$. pH and $\text{pOH}$


Literature:
**Research work:**
«Properties of buffer solutions»

**Experiment 1.** An establishment of dependence pH of buffer solutions from a relation of concentrations of constituents and from delution

**Course of operation:**

1. Prepare 3 buffer solutions with the following relations of concentrations \(\text{CH}_3\text{COOH}\) and \(\text{CH}_3\text{OONa}\): 9/1; 5/5; 1/9. Each prepared solution intermix.
2. Prepare 3 buffer solutions with the same relation of concentrations but more dilute. For this purpose take on 1 ml prepared before buffer solutions and add to everyone on 8 ml of water. Each weak solution intermix.
4. Compare on a white background colouring of solutions and write down. Calculate pH of the prepared solutions. An ionization constant of an acetic acid \(K_a\) = 1.85 \times 10^{-5}.
5. Results of observations and calculations present to the table:

<table>
<thead>
<tr>
<th>№ of a test tube</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relation of concentration CH(_3)COOH/CH(_3)COONa</td>
<td>9/1</td>
<td>5/5</td>
<td>1/9</td>
</tr>
<tr>
<td>Colour of a solution after addition of lackmoid</td>
<td>1’</td>
<td>2’</td>
<td>3’</td>
</tr>
<tr>
<td>№ of a test tube with a dilute buffered solution</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relation of concentrations CH(_3)COOH/CH(_3)COONa in dilute solution</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Colour of a solution after addition of lackmoid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH Calculations</td>
<td>(\text{pH}_1 = )</td>
<td>(\text{pH}_2 = )</td>
<td>(\text{pH}_3 = )</td>
</tr>
</tbody>
</table>

6. Make conclusions on the basis of comparison of colouring in 1, 2, 3 test tubes, and also 1 and 1’; 2 and 2’; 3 and 3’ also explain obtained conclusions.

**Experience 2.** Finding - out of the relation of buffer solutions to addition of small quantities of strong acids and bases

1. Prepare 2 identical buffered solutions, merging on 4 ml 0.1 M of a solution \(\text{CH}_3\text{COOH}\) and 6 ml 0.1 M of solution \(\text{CH}_3\text{COONa}\).
2. In both test tubes add till 3 drops of an alcohol solution of lackmoid. Solutions intermix.
3. In one test tube add 5 drops 0.1 M of solution HCl; in the second 5 drops 0.1 M of solution NaOH. Solutions in both test tubes intermix and write down their colouring.
4. Results present as the table and explain them.

<table>
<thead>
<tr>
<th>Buffered solution</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colouring after addition of 0.1 M HCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Colouring after addition of lackmoid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Colouring after addition of 0.1 M NaOH</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Problems for discussion:**

1. Write an equation to illustrate a Brønsted acid – base reaction. Specify each of the reactants and products in your equation as a Brønsted acid or base. Identify the two conjugate acid-base pairs.
2. Write two equations to illustrate the amphiprotic properties of water.
3. Write an equation for the reaction of ammonia with water, and the expression for $K_b$.
4. Write an equation for the dissociation of a weak acid, HA, and the expression for $K_a$ for the acid.
5. How does base strength of conjugate bases vary with the strength of their respective acids? Give some examples that illustrate your answer.
6. In each of the following reversible reactions, identify the Brønsted acids and bases:
   (a) $\text{H}_2\text{SO}_4(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HSO}_4^-(\text{aq})$
   (b) $\text{CH}_3\text{COOH}(\ell) + \text{HBr}(\text{g}) \rightleftharpoons \text{CH}_3\text{COOH}_2^+ (\text{aq}) + \text{Br}^-(\text{aq})$
   (c) $\text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\ell)$
7. In each of the reactions in question 6 identify the conjugate acid-base pairs.
8. The $K_a$ for hypochlorous acid is $3.0 \cdot 10^{-8}$. What is the value of $K_b$ for hypochlorite ions?
9. The $K_b$ for ammonia is $1.8 \cdot 10^{-5}$. What is the value of $K_a$ for ammonium ions?
10. Classify the aqueous solutions of each of the following salts as acidic, neutral, or alkaline: (a) NaCl; (b) NaF; (c) Na$_2$S; (d) NaClO$_4$; (e) NH$_4$NO$_3$; (f) Cr(NO$_3$)$_3$; (g) KNO$_3$.
11. Write the formula of the conjugate base for each of the following substances: (a) HNO$_3$; (b) HSO$_4$; (c) NH$_3$; (d) H$_2$O.
12. Write the formula of the conjugate acid for each of the following substances: (a) H$_2$O; (b) NH$_3$; SO$_4^{2-}$; (d) OH$^-$; (e) H$_3$PO$_4$; (f) HPO$_4^{2-}$.
13. Write a chemical equation for the autoionization of water and a mathematical equation for $K_w$. 

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14. What is: (a) pH; (b) pOH?
15. What is a buffer solution? Give an example of an acid buffer solution and an alkaline buffer solution.
16. What is meant by «buffer capacity»?
17. Briefly explain how an acid buffer solution resists a change in pH when a small amount of hydrochloric acid is added.
18. Explain how you would choose a buffer system that is effective at a given pH.
19. Use the Henderson – Hasselbalch equation to explain how the [base]/[acid] ratio of a buffer solution affects the pH of the solution.
20. What are the hydronium ion concentration and hydroxide ion concentration of a 0.15M solution of nitric acid?
21. What are the hydronium ion concentration and hydroxide ion concentration of: (a) a 0.080M solution of potassium hydroxide; (b) a 0.0035M solution of barium hydroxide?
22. What are the pH and pOH of: (a) a 0.010M solution of nitric acid; (b) a 0.25M solution of hydrochloric acid?
23. What are the pH and pOH of: (a) a 0.010M solution of sodium hydroxide; (b) a 0.25M solution of potassium hydroxide; (c) a 0.0056M solution of barium hydroxide?
24. The pH of a solution is 5.70. What are the pOH, the hydronium ion concentration, and the hydroxide ion concentration of the solution?
25. If you dissolve 1.58 g of solid potassium hydroxide in water to make 850 ml of solution, what is the pH of the solution?
26. Calculate the pH of 100 ml of 2.00M solution of nitric acid. What is the pH of this solution after it is diluted with water to 450 ml?
27. Calculate the hydronium ion concentration, hydroxide ion concentration, pH, and pOH of a 0.40M solution of HCN.
28. Calculate the hydronium ion concentration of (a) 0.0400M HCN; (b) 0.0040M HCN.
29. What volume of 0.50M sodium benzoate must be added to 500 ml of 2.0M benzoic acid solution to prepare a solution of pH 4.00?
30. Calculate the $[\text{HCO}_3^-]/[\text{H}_2\text{CO}_3]$ ratio of blood that has pH 7.40.

**LESSON 10 Equilibriums in solutions of coordination complexes. Heterogeneous equilibriums and processes.**

**Medicobiological value:** the coordination complexes carry out various biological functions. So, for vital activity of a human organism the unique value has a coordination complex of iron ions with protein - haemoglobin exercising transport of oxygen from lung to tissues. In life of plants the important role is played chlorophyll - complex of magnesium, due to which the plants transmute carbone dioxide and water into composite...
organic matters (amylum, saccharum, etc.). The ion Cu$^{2+}$ is the component of several important enzymes - participants of a biological oxidizing. The coordination complexes of cobalt considerably raise intensity of protein metabolism, regulate composition of a blood. Metalenzymes is the coordination complexes with high specificity of ions of metals, among them, except for mentioned above, is more often than others there are ions of zinc, molybden, manganese. In the whole cations almost of all metals are in alive organisms as coordination complexes.

Pollution by transition metals and their compounds: mercury, lead, cadmium, chromium, nickel - can result into a poisoning. The toxicity of such compounds in many cases is explained to that these ions supersede ions of biogenic metals (Fe, Zn, Cu, W) from coordination complexes with a bioorganic ligand (for example, porphyrin). The stability of coordination complexes, formed at it, usually is higher, they collect in an organism, therefore the normal vital activity of an organism is broken and the toxicosis begins.

The coordination complexes will be used in medical practice. Various metals (macrolelements) introduce to the organism as coordination complexes. The complex drugs of platinum will be used as anticancerogenic drugs. However the efficiency of many medicinal preparations in an organism changes, as they form stable coordination complexes with protein of a blood.

Property of ions of metals to form stable bonds with sulfurcontaining ligands will be used at selection of medicines used at poisonings. Such medicines are called - antidotes. For example, unithiolum will be used at a poisoning with an arsenic, mercury, cadmium, lead, chromium, cobalt and some radioelements. As antidotes will be used in medical practice also a coordination complex in which the metal ion is coordinated to one or more chelating ligands – chelate. (for example disodium salt of ethylenediaminetetraacetic acide Na$_2$H$_2$EDTA). The activity of this compound is grounded that acting in roles of ligands they form more stable coordination complexes with ions of metals, than complexes of the same ions with sulfurcontaining groups of protein, enzymes, amino acids. The generated complexes in an organism are not blasted and are easily output through kidneys. Chelate will be used also as stabilizers at preservation of a blood, for dissolution of stones in kidneys, liver and cholic bubble.

Chelate will be used for quantitative definition of cations of many metals, including biological objects$^\text{9}$.

The knowledge, obtained on lesson will be used at the further study of chemistry, pharmacology, therapy, toxicology etc. The formation of an bone tissue, which inorganic basis is calcium hydroxidephosphate - a typical example of heterogeneous process in an organism. The study of legitimacies of a heterogeneous equilibrium is important for medicine, as at collateral presence of ions at biological fluids the formation of slightly soluble compounds is possible (at infringement of their concentration or some functions of an organism).
For example the formation of gall - stones, deposition of a cholesterin and calcium in walls of vessels (atherosclerosis and calcification) and salts in joints.

On the basis of solubility product constant $K_{sp}$ it is possible to prognosticate, at what ion concentrations in a solution the slightly soluble salt begins presipitate at absence or presence of other electrolytes. Knowing, for example, ion concentration of calcium – ions and oxalate - ions in a blood and, using tabulated values of solubility product constant of calcium oxalate, it is possible to solve whether there are requirements for formation of slightly soluble deposit of calcium oxalate (at a gout). It is similarly possible to test an efficiency of various medicinal preparations at treatment of diseases, bound with formation slightly soluble salts in various biological fluids and tissues of an organism. Fixed also, that there is a close interrelation between a solubility of compounds in water and toxic activity of series elements ions. For example, the excess of aluminium ions in an organism results in a rachitis, owing to formation of slightly soluble aluminium phosphate.

The reactions of precipitation underlie a method of precipitation, which is used in a quantitative analysis of medicinal preparations. The method of precipitation is applied also in the clinical analysis of chlorides in urine, gastric juice, blood, in sanitary - hygienic practice - at the analysis of drinking water.

To lesson it is necessary:

Literature:
Research work:
«Reception of complexes»

Experiment 1. Reception of chelate iron oxalate (III)
To 2 test tubes bring till 3 drops of an iron (III) chloride solution. One of test tubes leave as control. In the second test tube add 3 drops of sodium hydroxide. To the formed deposit add 12 - 15 drops of a solution of an oxalic acid H₂C₂O₄. What is observed? In both test tubes add 1 - 2 drops of a solution of potassium thiocyanate KCNS. What is observed? Write down the equations of reactions:

a) Formation of iron hydroxide (III);

b) Formations of chelate iron (III) oxalate, which has the following structure:

c) Formations of iron (III) thiocyanate (has blood-red colour).

Answer the questions:
1. In what test tube the iron (III) thiocyanate was not formed? Why?
2. What complex Fe(CNS)₃ or Fe(HC₂O₄)₃ - stronger?
3. The constant of what instability from these complexes is less?

Experiment 2. Reception hexaamminenickel (II) sulfate
To 3 drops of a solution of nickel (II) sulfate add some drops a solution of ammonia before dissolution of precipitating basic salt.
Write down the equations of reactions:

a) Formation hexaamminenickel (II) sulfate.
b) Dissociation of complex.

Write expression of a constant of instability of a sectional complex.

«Study of heterogeneous equilibriums and processes»

Experiment 1. Select in a test tube 5 drops of a solution Pb(NO₃)₂ with concentration 0.5 mol / l and 15 drops of a solution NaCl (c = 1 mol / l). The dropped out heavy deposit of lead chloride promptly settles at the test tubes bottom. Test completeness of precipitation of a deposit: add 1-2 drops a solution HCl with concentration 2 mol / l to a fluid above a deposit. In case of complete precipitation of lead as PbCl₂ the solution above a deposit is not turbid. Precipitation of PbCl₂ should be
complete. Remove a solution from a deposit. A light solution divide into 2 parts. To one add 1-2 drops of a solution Na₂SO₄ (c = 1 mol / l). Whether the formation of a deposit of lead sulfate is observed? Having compared $K_{sp}(\text{PbCl}_2)$ with $K_{sp}(\text{PbSO}_4)$, explain the apparent phenomenon. To other part of a saturated solution PbCl₂ add a solution KI (c = 1 mol / l). What is observed? Explain observations, using solubility product constant of PbCl₂ and PbI₂. Write the chemical equation.

**Experiment 2.** Measure in a test tube 10 drops of a solution CaCl₂ (c = 0.5 mol/l), add to it 10 drops of a solution Na₂C₂O₄ of the same concentration. The deposit of calcium oxalate is formed. Divide contents of a test tube together with a deposit into two parts. To one add 5 drops of a solution HCl (c = 1 mol / l), and to another - 5 drops of a solution of an acetic acid of the same concentration. Whether in both test tubes the deposit of calcium oxalate was dissolved? Explain result of experience, using solubility product constant of calcium oxalate, and also $K_a$ of acetic and oxalic acids. Write the chemical equation.

**Experiment 3.** Select in a test tube 5 drops of iron (II) sulfate (c = 0.1mol / l), and in second - same volume of a solution of copper (II) sulfate of the same concentration. Add in both test tubes till 5 drops of solutions of a sodium sulfide (c = 0.01 mol / l). What is observed? Write the chemical equation.

Remove solutions from deposits and add some 2mol / l of a solution of a hydrochloric acid to deposits FeS and CuS. Whether both deposits were dissolved? Write down the equation of reaction. Explain difference in a solubility of deposits, using solubility product constant.

**Problems for discussion**

1. What is: (a) a ligand; (b) a coordination sphere?
2. Write a formula to illustrate a complex compound that is composed of: (a) monatomic cations and negatively charged coordination spheres; (b) positively charged coordination spheres and monatomic anions; (c) neutral molecules that are coordination spheres; (d) positive coordination spheres and negative coordination spheres.
3. What is meant by «coordination number» in a coordination complex?
4. Give the formula of: (a) a monodentate ligand; (b) a bidentate ligand.
5. Explain how you can determine the oxidation states of the central metal ion in a coordination sphere from the formula of the complex.
6. A coordination compound of chromium contains 1 mol of chromium, 3 mol of chlorine, and 5 mol of ammonia per mole of the compound. Treatment of 0.5 mol of this compound with silver nitrate gives an immediate precipitate of 1 mol of silver chloride. Write the formula of the compound and indicate the coordination sphere in brackets. What are the oxidation states of chromium in this compound?
7. What are the oxidation states of the central metal in each of the following coordination complexes? (a) Ag(NH₃)₂⁺; (b) FeCl₄⁻; (c) Fe(CN)₆³⁻; (d) K₄[Fe(CN)₆]; (e) [Cr(H₂O)₆Cl₂]⁺; (f) [Co(NH₃)₆Cl₂]⁺; (g) [Co(NH₃)₆]Br₃.

8. Which of the following species can act as ligands and which cannot? (a) H₂; (b) CH₄; (c) Be²⁺; (d) F⁻; (e) AlH₃; (f) PH₃; (g) NH₄⁺.

9. Classify each of the following ligands as monodentate, bidentate, terdentate, and so on: (a) H₂O; (b) CN⁻; (c) H₂NCH₂CH₂NHCH₂CH₂NH₂; (d) Cl⁻.

10. Which of the following ligands can act as chelating agents? (a) OH⁻; (b) EDTA⁴⁻; (c) Br⁻.

11. Name each of the following: (a) Ag(NH₃)₂⁺; (b) Cu(H₂O)₄²⁺; (c) Fe(CN)₆³⁻; (d) Fe(CN)₆⁴⁻; (e) Co(NH₃)₆Br₃⁻; (f) [Cr(H₂O)₆Cl₂]NO₃⁻; (g) K₂[PtCl₆]; (h) Na₂[Zn(OH)₄]; (i) Al(OH)₄⁻; (j) [Cu(NH₃)₄]²⁺.

12. Write a formula for each of the following: (a) tetraamminecopper (II) ion; (b) tetraaquadichlorocromium (III) ion; (c) tetrahydroxozincate ion; (d) sodium tetrahydroxozincate; (e) tetraamminedichlorocobalt (III) chloride; (f) trisethylenediaminencobalt (II) bromide; (g) diamminesilver (I) hexacyanoferrate (II); (h) aquapentaammineruthenium (III) ion.

13. Define “molar solubility” and the “solubility product constant” for a sparingly soluble salt.

14. Assuming that the molar solubility of a sparingly soluble salt is x, show how can be calculated from the Ksp for each of the following types of salt: (a) AB; (b) AB₂; (c) A₂B; (d) AB₃; (e) A₂B₃.

15. Given the following sulfides and their respective Ksp values: Cu₂S, 6.3 × 10⁻³⁶; PbS, 8.2 × 10⁻²⁸; MnS, 1.4 × 10⁻¹⁵; Hg₃S₂, 1.0 × 10⁻⁵⁰; and Zn₂S, 1.1 × 10⁻²¹. (a) Which of these sulfides is most soluble in water? (b) Which has the smallest [S²⁻] in its saturated solution?

16. Calculate the molar solubility of silver bromide. What are [Ag⁺] and [Br⁻] in a saturated solution of silver bromide.

17. Calculate the solubility of barium chromate in moles per liter and in grams per liter of water.

18. How many grams of lead (II) sulfate can be dissolved in 3.0 l of water to make a saturated solution of lead (II) sulfate?

19. The solubility of silver chloride is 1.25 × 10⁻⁵ mol per liter. Calculate Ksp for silver chloride.

20. Solubility of manganese (II) hydroxide is 3.2 × 10⁻³ g per liter of water. Calculate: (a) the pH of a saturated solution of manganese (II) hydroxide; (b) Ksp for of manganese (II) hydroxide.

21. Write a net ionic equation for the reaction that occurs when solution of each of the following pairs of substances are mixed: (a) sodium chloride and silver nitrate; (b) barium nitrate and sodium sulfate; (c) lead (II) nitrate and hydrochloric acid; (d) potassium chromate and lead (II) nitrate (e) magnesium chloride and sodium
hydroxide; (f) calcium chloride and sodium phosphate; (g) iron (II) nitrate and sodium sulfide; (h) silver nitrate and sodium chromate.

22. Will a precipitate of mercury (I) chloride form when a 0.20 M solution of mercury (I) nitrate, Hg₂(NO₃)₂, is made 0.010 M in sodium chloride? If a precipitate forms, what are the molar concentrations of Hg₂²⁺ and Cl⁻ ions remaining in the solution?

23. The solubility of calcium fluoride is 1.6 · 10⁻² g L⁻¹. Calculate the solubility product constant for calcium fluoride. Ignore the hydrolysis of fluoride ions.

24. The solubility product constant for lead sulfate is 1.6 · 10⁻⁸. Calculate the molar solubility of lead sulfate in water. How many grams of lead sulfate dissolves in 1.0 L of water?

25. Calculate the molar solubility of silver chloride in 0.20 M solution of sodium chloride. What is the Ag⁺ ion concentration in a saturated solution of AgCl that is also 0.20 M in NaCl?


**Medicobiological value:** The titrimetric analysis is one of prime and accessible expedients of reception of the chemical information. It is applied in clinical biochemistry to diagnostics of series of pathological states. In biochemical, physiological, sanitary - hygienic and etc. laboratories for definition of chemical composition and quantitative content of separate builders of bodies and tissues, study of a metabolism, metabolism of medicines, the definitions of composition of water, ground, air and etc. will widely be used methods of analytical chemistry. Diagnostics of the majority of diseases includes study of the clinical analyses which are carried out with use of methods quantitative and qualitative analysis.

In medicobiological investigations the methods of acid-base titration will widely be used, they allow to solve many problems incipient at chemical analysis of biological fluids as at statement of the diagnosis, and at treatment of the patients (for definition of an acidity of gastric contents, alkaline reserve of a blood and plasma). In sanitary - hygienic practice the methods of acid-base titration allow to estimate quality of various foodstuff.

The laboratory part of lesson a sectional theme is extremely important, as during performance of laboratory operation the practical skills of operation with analytical ware, technique of performance of measure analysis on an example of a method of acid-base titration are shaped.

**To lesson it is necessary:**

1. TO STUDY the following program questions: devices of a quantitative analysis. The titrimetric analysis. A chemical equivalent of a substance. The equivalent’s

**Literature:**

**Research work:**
«Preparation of a solution of a sodium tetraborate and standardization of its concentration on HCl»

**Experiment 1.** Preparation of a reference solution of a sodium tetraborate (50.0 mls of a solution of a sodium tetraborate, \( c(\frac{1}{2} \text{Na}_2\text{B}_4\text{O}_7) \sim 0.1 \text{ mol/l} \) to within three significant digits)

**Performance of experiment.** Before a cut-in familiarize with the device analytical balance with the instructions on their operation. Prepare a measuring flask and dry funnel. Calculate mass of a shot of a sodium tetraborate necessary for preparation of a given solution. The designed shot of a sodium tetraborate weigh on counter balance. As container use test tube. For record of results of weighing on analytical balance in a laboratory magazine beforehand prepare under the shape the following records:

| Mass test tube with \( \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} \) | … | … | … |
| Mass test tube with oddments of substance | … | … | … |
| Mass of \( \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} \) | … | … | … |

Then test tube with a shot weigh on analytical balance. On a scale pan at once establish a load relevant to result of prestress weighing. Write down the indications of analytical balance and, having taken off test tube from a scale pan, is cautious add a shot through a dry funnel in a measuring flask. Test tube cant above slowly by funnel and do not suppose a diffusion and pulverization of substance. Test tube with oddments of substance on walls immediately again weigh on analytical balance and write down result. After that take off from weights all load and close doors.

Add heat distilled water in a test tube. A flask charge with distilled water approximately on 2/3 volumes, dissolve all substance, cool a solution up to ambient temperature and add by distilled water up to a score. Intermix a solution in a flask. A flask close by a fuse and paste a label with the name of a solution and surname.

**Experiment 2.** An establishment of precise concentration of a hydrochloric acid on a reference solution of a sodium tetraborate
**Performance of experiment.** Prepare ware necessary for carrying out of the titrimetric analysis. A burette, pipet and flasks wash by distilled water. A laboratory magazine prepare for record of results of the analysis:

Volume of a solution \( \text{Na}_2\text{B}_4\text{O}_7 \) – 5.00 mls
\[
c(1/2\text{Na}_2\text{B}_4\text{O}_7) = \ldots \text{ mol} / \text{l}
\]
\[V (\text{HCl}): \quad 1 \text{ titration} \quad \ldots
\]
\[2 \quad « \quad \ldots
\]
\[3 \quad « \quad \ldots
\]
\[V (\text{HCl}): \text{ medial value} \quad \ldots
\]

In a burette fill by a working solution HCl. Measuring pipet by containment 5 mls wash by a solution of a sodium tetraborate. Then in flasks for titration select by the pipet till 5.00 mls of a solution \( \text{Na}_2\text{B}_4\text{O}_7 \) and 1 drop of a solution of the indicator. The solution becomes yellow. Assay in a flask titrate by a solution HCl before transferring colouring in light pink. (Sometimes for rising accuracy of titration will use a flask - witness. The witness plot, measuring off in a flask 5.0 mls of water, 1 drop of an acid and 1 drop of the indicator. Assay titrate before occurrence of the same colouring, as in a flask - witness). The pink colouring in an endpoint of titration means presence in a flask of excess of an acid about 1 drop. (Therefore in separate experience it is necessary to spot volume of one drop of a solution for a sectional burette). Having concluded titration, wash a flask usual, and then distilled water also lead titration some more time before reception not less than four results concurrent in limits 0.04 mls.

Flasks for titration and pipet wash by distilled water. Flasks with solutions clean(remove) in a table or case for performance of other laboratory operations.

Processing results of experiment. From plurality of separate results of titration reject misses and find medial of concurrent results. From medial value take away volume of one drop of a sectional burette. On obtained volume of an acid calculate concentration of HCl. Spot also error of the analysis.

Formulate a deduction describing basic result of operation: specify concentration of a working solution HCl to within three significant digits.

**Problems for discussion.**

1. In an acid – base titration, what is the meaning of each of the following words? «Neutralization», «equivalence point», and «end-point».
2. How many milliliters of 0.200 M sodium hydroxide is required to neutralize 40.0 ml of 0.0500 M HCl solution?
3. How many milliliters of 0.200 M sodium hydroxide is required to completely neutralize: (a) 40.0 ml of 0.0500 M \( \text{H}_2\text{SO}_4 \); (b) 40.0 ml of 0.0500 M \( \text{H}_3\text{PO}_4 \)?
4. Write down the mathematical form of equivalence’s law.
5. What demands are showed to reactions used in the titrimetric analysis?
6. What titrants apply in an acidimetry and alkalimetries?
7. What molarity and titr of a solution HCl, if on titration 25 mls of it at the presence of phenolphthalein 19.75 mls 0.1 M of a solution NaOH are spent.
8. Calculate molar mass of an equivalent for the following substances: NaOH, H₃PO₄, CaCl₂

LESSON 12 Reactions with transport of electrons in a quantitative analysis
Oxidimetry. Permanganatemetry.

Medicobiological value: the oxidation-reduction reactions widely wide-spread in a nature. The majority of chemical reactions underlying processes of vital activity, are oxidation-reduction. On the oxidation-reduction mechanism the numerous enzymes - cytochromes, catalase,, haemoglobin etc. work

In the biochemical and clinical analysis, medical and sanitary - hygienic investigations the analytical methods based on oxidation-reduction reactions (for example, definition of an acetone, quinone and hydroquinone, urinary acid in urine, saccharum in a blood, ions of calcium in serum of a blood etc.) are widely applied.

Oxidimetry will use for quality surveillance of pharmaceuticals, in sanitary - hygienic investigations. So, with the help of an oxidimetry determine the content of fissile chlorine in potable water dissolved oxygen and organic impurities in natural water. In medicine and biology widely apply a method of permanganatemetry.

To lesson it is necessary:

Literature:

Research work:
«Definition of the content Fe²⁺ in a solution of its salt»
The ions Fe²⁺, acidifying, lose 1 electron. Therefore molar mass of an equivalent Fe²⁺ is peer to molar mass Fe²⁺.

For definition of the content Fe²⁺ in a control solution is necessary to find concentration of a solution and its volume.
Concentration of a solution Fe²⁺ is possible to spot with the help of a standard solution KMnO₄ by a method of the titrimetric analysis.
**Equipment.** A measuring flask by containment 50 mls, funnel, burette, measuring pipets by containment 2 mls, and 5 ml, flask for titration, measuring pipet for a solution H$_2$SO$_4$.

**Reagents.** A standard solution KMnO$_4$, solution H$_2$SO$_4$ by concentration 1mol/l, distilled water.

**Performance of experiment.** A burette wash out by a standard solution KMnO$_4$, anchor it in a support and then fill by its standard solution KMnO$_4$. Prepare clean pipet by containment 2 mls and a flask for titration.

Write down in a laboratory magazine molarity of an equivalent of a standard solution of a potassium permanganate.

Receive from the teacher a test tube with a control solution salt Fe$^{2+}$ and write down in a magazine the number of a control solution (test tube). Then add a control solution in a measuring flask containment 50мл (use by a funnel). In a test tube fill by water and this water also add in a measuring flask. Iterate this operation once again. Thus, all control solution will be quantitatively transferred in a measuring flask on 50 ml. Then add in a measuring flask of distilled water up to a score also intermix a obtained solution.

For definition of concentration of a control solution select 5,00мл it in a flask for titration, add in a flask from a pipet 2 ml of a solution H$_2$SO$_4$ and titrate by a standard solution KMnO$_4$ before occurrence of not disappearing pink colouring of a titrated solution. Write down in a magazine volume of a solution of KMnO$_4$, spent on an oxidizing Fe$^{2+}$.

Iterate operation of titration until receive series concurrent in limits of 0,04 mm of results.

All obtained results write down in the booklet of operating conditions. If will consider necessary, comment on this or that result. For example:

\[ V_1 = 2.71 \text{ ml} \]
\[ V_2 = 2.66 \text{ ml concurrent results} \]
\[ V_3 = 2.70 \text{ ml} \]

\[ V = \frac{V_1 + V_2 + V_3}{3} \]

It is necessary also to pay attention that a decomposed control solution salt Fe$^{2+}$ should not long adjoin to air in order to prevent a partial oxidizing of ions Fe$^{2+}$ oxygen. Therefore try all operation to lead promptly.

**Processing results of experiment.** By results of the analysis find medial volume of a working solution KMnO$_4$, spent on titration 5 ml of a control solution salt Fe$^{2+}$. Using the equivalents’ law

\[ c(1/5\text{KMnO}_4) \cdot V(\text{KMnO}_4) = c(\text{Fe}^{2+}) \cdot V(\text{Fe}^{2+}) , \]

calculate concentration of a control solution c(Fe$^{2+}$) in mol/l.

Taking into account volume of a decomposed solution (50 ml = 0.5 l), calculate amount (mol) Fe$^{2+}$ in a control solution and its mass.
Report to the teacher result of the analysis of a control solution salt Fe$^{2+}$ and find out from the teacher numerical values of the true content Fe$^{2+}$-ions in a control solution. Calculate a terrain clearance and relative diversion of result of the analysis from a true value. Analyse a probable radiant of an experimental error. Write down the equation of reaction.

**Problems for discussion:**
1. What the oxidation state should have sulfur, nitrogen, chlorine, that they showed properties only: a) of an oxidizing agent; b) of reducer.
2. To calculate molar mass of an equivalent: a) Fe$^{2+}$, b) KI in reaction with KMnO$_4$ in acidic medium.
3. How many grams KMnO$_4$ are necessary for preparation 1.5 l of a solution with concentration $c(1/5\text{KMnO}_4) = 0.2$ mol/l?
4. Calculate a shot dry FeSO$_4$·7H$_2$O for preparation 100 ml of a solution FeSO$_4$ with molarity of an equivalent 0.05 mol/l, which will be used in oxidation-reduction titration.
5. In what the substance of a permanganatemetry consists? For what definition of substances it can be used?
6. 21.6 ml of a solution KMnO$_4$ with concentration $c(1/5\text{KMnO}_4) = 0.09$ mol / l are spent for titration of a solution FeSO$_4$. How many grammes FeSO$_4$ contained in a solution?
7. Spot the content of calcium in mg on 100 ml of serum of a blood, if 0.25 ml of a solution KMnO$_4$ with concentration $c(1/5\text{KMnO}_4) = 0.1$ mol/l. are spent for titration
8. Make the equations of the given below reactions. Specify an oxidizing agent and reducer.
   
   \[
   \begin{align*}
   \text{HCl} + \text{KMnO}_4 + \text{H}_2\text{SO}_4 & \rightarrow \text{Cl}_2 + ... \\
   \text{H}_2\text{O}_2 + \text{KMnO}_4 + \text{H}_2\text{SO}_4 & \rightarrow \text{O}_2 + ... \\
   \text{K}_2\text{SO}_3 + \text{KMnO}_4 + \text{H}_2\text{SO}_4 & \rightarrow \text{K}_2\text{SO}_4 + ... \\
   \text{KNO}_2 + \text{KMnO}_4 + \text{H}_2\text{SO}_4 & \rightarrow \text{KNO}_3 + ... \\
   \text{K}_2\text{SO}_4 + \text{KMnO}_4 + \text{H}_2\text{O} & \rightarrow \text{K}_2\text{SO}_4 + ... \\
   \text{H}_2\text{C}_2\text{O}_4 + \text{KMnO}_4 + \text{H}_2\text{SO}_4 & \rightarrow \text{CO}_2 + ... \\
   \end{align*}
   \]

**LESSON 13 Properties of solutions (control work).**

**Medicobiological value:** see appropriate items to lessons 7-12.

The purpose of lesson: generalization, fastening and ordering of knowledge a program material on chapter «The doctrine about solutions»; development of skills of application of theoretical knowledge for the decision of tasks and exercises.
To lesson it is necessary:
1. TO REPEAT program questions and decision of sample tasks to lessons 7-12

**LESSON 14 Physico-chemistry of surface phenomenas. A chromatography.**

**Medicobiological value:** the surface phenomenas observe on a phase boundary (in heterogeneous systems) and are caused by difference of physico-chemical properties of different phases. The alive organisms are the systems with the very much advanced interfaces (dermal integuments, wall of blood vessels and nervous terminations, of cell’s membrane etc.). So, for example, the surface area of erythrocytes of all blood of the man makes approximately 3800 m², surface of a skeleton - about 200 km².

All vital processes in an organism occur on a surface of biological membranes, therefore for comprehension of their mechanism and pathological changes, bound to a permeability of cell’s membranes, it is important to know legitimacies, to which the surface phenomenas submit. The surface tension, on a phase boundary in biological fluids, is one of diagnostic tests at some diseases (anaphylactic shock, cancer etc.). The surface tension plays a considerable role in such phenomena as division of cells, englobement, changes of a permeability of a cell’s membranes. From process of an adsorption - spontaneous change of concentration of substances in surface layer, the process of an adsorption of nutritious and medicinal substances, infiltration of toxins into cells and tissues of an organism begins. On the phenomenon of an adsorption the application of adsorbents for interlinking poisons, toxins in a gastrointestinal path and adsorption of gases in an intestine.

The study of features of surface layer and orientation to a nem of surface-active substances plays a major role in development of the doctrine about structure of biological membranes, that is one of questions investigated on a lesson. Important acquaintance with legitimacies of an adsorption of ions is also. The selectivity of an adsorption of ions allows to make a conclusion, that the selectivity takes place and in an alive nature. So, the toxins of microbes selectively amaze bodies and tissues of an organism. The immune proteins and enzymes have very major selectivity. The knowledge of theoretical bases of an ionic adsorption is necessary for study of the following chapter of a course - for physico-chemistry of disperse systems.

The major value has and ionexchanges adsorption, investigated on a lesson. The ionexchanges adsorption is used for preparation of injections solutions; at clearing both excretion of antibiotics and amino acids. The ionites apply to erasion of ions Ca^{2+} from a blood before its preservation, for correction of infringements of gastric acidity etc.

The various sorption processes underlie such important method of physicochemical investigations, as a chromatography.

To lesson it is necessary:

Adsorptive equilibriums on fixed phase boundarys. Physical adsorption and chemosorption. An adsorption of gases on solids. An adsorption from solutions. The Lengmyur’s and Freindlikh’s equation. Dependence of quantity of an adsorption on the various factors. Selective and an ion-exchanges adsorption. Value of adsorptive processes for vital activity (adsorptive therapy, hemosorption), application in medicine of ionites. Chromatography is one of the most commonly used methods of separation and analysis of chemical compounds due to its high sensitivity and resolving power. Manifold methods of a chromatography are effectively applied to separation and identification of many builders of tissues and biological fluids (lipids, amino acids, carbohydrates); establishment of primary structure of proteins; for quantitative definition of vitamins, hormonums and other biologically active substances. The chromatography is the irreplaceable instrument at diagnostics of acute poisonings by phosphoroorganoc substances of household chemistry, narcotic agents, strongly effective medicinal preparations, substitutes of ethanol etc. a chromatography. Classification of chromatographic methods by the dominant mechanism of separation of substances. Application of thin-layer, paper, gas-fluid, high performance fluid, molecular-screen chromatography in medicobiological investigations.

Literature:

Research work:
«Chromatography»

Performance of experiment.
Experience 1. Separation of copper and iron ions. Accurately cut a stria of breadth 2-3 sm and length 8-10 sm from a chromatographic paper. Apart 1 sm from the inferior edge lead by a pencil on a ruler a thin line (line of start). Place a solution containing cations Cu$^{2+}$ and Fe$^{3+}$ in center of a line with the help of a thin capillary. The diameter of a stain should not exceed 3-4 mm. Dry up a paper on air.

Fix the paper with the help of two elastics between two glass stiks and sink it in a glassful with distilled water. Bed of water in a glassful should be peer 1-1.5 cm, depth of submergence of a stria of a paper should by 2-3 mm. Take out a stria from a glassful
after a raising of water on height 6-7 sm and note a line of uprise of a dissolvent (line of front). Dry up a chromatogram on air.

Moisten a stria for detection of divided cations zones in a solution of potassium hexacyanoferrate (II). Note number of zones. Measure distance from center of each zone up to a line of start. Write down all done manipulations and results in a laboratory magazine.

**Processing results of experiment.**

For each zone calculate value $R_f$ as the relation of a distance from it center up to a start line to a distance from a line of start up to a front line. Tot results of experience as the table under the shape:

<table>
<thead>
<tr>
<th>Method of chromatography</th>
<th>Object of investigation</th>
<th>Chemical nature of stationary(non-moving) phase</th>
<th>Chemical nature of moving phase</th>
<th>Description of a chromatogram</th>
</tr>
</thead>
<tbody>
<tr>
<td>By the technique</td>
<td>By the dominant mechanism</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Number of zones (color and conformity to ions)
$R_f$ (Fe$^{3+}$)
$R_f$ (Cu$^{2+}$)

Give drawing of chromatogram.

**Problems for discussion:**

1. What is meant «adsorption»?
2. Give a definition of “surface tension”.
3. Give examples of most frequently used adsorbents, in a practice.
4. What is meant surface active and surface inactive substances.
5. Write down the Gibb’s equation for definition of adsorption? Identify each of symbols.
6. Dependence of quantity of an adsorption on the various factors.
7. Write down the Lengmyur’s equation. Identify each of symbols.
8. Formulate the Thraube’s rule.
9. Describe the structure of the surface active substances.
10. Write down the Freindlikh’s equation. Identify each of symbols.

LESSON 15 Reception, clearing and properties of colloidal solutions. A coagulation and peptization of sols.

Medicobiological value: the colloidal systems play an important role in human life. In biological fluids of an organism series of substances are in a colloidal state, which features are studied in a sectional theme. In medical practice series of drugs in a colloidal degree of dispersion will be used. Such drugs have prolonged activity, as are more slowly output from an organism. On this lesson are studied series of properties of colloids, which take place and in biological systems: disability of colloid particles to transit through a membrane (dialysis), and research methods (ultracentrifugation and ultramicroscopy; electrophoresis and electroosmosis). In particular, in a basis of clearing of a blood from products of metabolism the principle of a dialysis lays. By a principle of a dialyzer works kettle «a synthetic kidney», which can temporarily replace function of the patients of kidneys at such disease, as acute renal failure as a result of poisonings, at serious combustions and others. For investigation of biological fluids will widely be used vivodialysis, with which help in a blood it is possible to find out, for example, not bound with protein medicinal substances.

The ultracentrifuges are an irreplaceable agent for separation and excretion of fractions of protein, nucleic acids, viruses. A ultramicroscopy apply at a blood analysis, lymph, vaccines, to the check of cleanliness ijectional of solutions, water and air medium. With the help of a ultramicroscope it is possible to spot the shape and size of colloid particles.

The electrophoretic analysis of serum proteins will widely be used in medicobiological investigations with the purpose of the diagnosis of diseases. At the healthy people electrophoreagrams have the approximately same pattern. At various diseases electrophoreagrams change. For example, at inflammatory processes a fraction of γ-globulins grows sharply; at nephritises - the bands α- and β- globulins are increased and almost fractions of a γ-globulin and albumin disappear. With the help of electrophoresis into an organism inlet various medicinal substances and determine cleanliness of medicinal preparations. The method of an immunoelctrophoresis will be used for detection of antigenes specific to sectional antibodies. The method of electroosmosis is applied to elimination of water from medical cotton and draing of medicinal preparations. The study of processes of a coagulation and peptization has an important value, since the colloids of cells and biological fluids of an organism are subject to a coagulation. The formation of thrombuses in blood vessels, sticking of erythrocytes is the processes similar coagulations. One of the reasons of above named pathological changes can be electrolytes. As the colloids of all cells of an organism are in constant
contact to electrolytes and slightest change of a constancy of an ion concentration or quality composition them can give in infringement of aggregate stability of colloids - coagulation. In an organism: the phenomenon of accustoming (to alcohol, narcotics and some medicinal preparations); activity of an admixture of electrolytes or multicomponent medicinal preparations take place. In hygiene and the sanitations apply intercoagulation - to clearing drinking and waste water. The substance of these phenomena and legitimacies of the coagulation by electrolytes you will study on sectional lesson.

The peptization plays an essential role in boosted dissolving power of serum of a blood in relation to series slightly soluble in water of substances; in dissolution of fresh deposit of thrombuses under activity of medicines - anticoagulants.

At preparing series of medicinal substances representing colloidal solutions, it is necessary to protect them from a possible coagulation, for example, colloidal drugs a silver - collargol and protargolum.

To lesson it is necessary:

1. TO STUDY the following program questions: classification of disperse systems by a degree of dispersion; on a nature of phases; on force of an intermolecular interaction between a dispersed phase and dispersion medium.


Literature:

Research work:
«Reception, clearing and properties of colloidal solutions»

The experiment 1. Reception of sol of a colophonium. In a test tube measure 5 ml of distilled water and add 2 drops of 1% an alcohol solution of a colophonium, and intermix. Note colour of a obtained solution and specify a method of reception of sol.

The experiment 2. Reception of sol of iron (III) hexacyanoferrate (II). In a test tube measure 3 ml 0,005 M of solution K₄[Fe(CN)₆] and add 1ml 0,005M of a solution FeCl₃. Gain sol painted in dark blue colour. Specify, by what method sol was received, what electrolyte is the stabilizer. Write the chemical reaction and formula of a micelle.

The experiment 3. Reception of sol of iron (III) hydroxide. Measure in a flask by the cylinder 25 ml of distilled water and heat up to boil, add promptly 5 ml 2% of a solution FeCl₃. The received sol has red - brown colour. Specify a method of reception of sol and stabilizer. Write the chemical reaction and formula of a micelle. Obtained sol use for a dialysis (experience 4).

The experiment 4. Clearing of sol by a dialysis. In a test tube measure 1 ml of sol Fe(OH)₃, obtained in experience 3. A hole of a test tube closey) by cellophane, fix by rubber ring. A test tube with cellophane bottom insert into a hole of a cardboard circle and sink in a glassful with distilled water (10 ml). In 15 minutes from a glassful in a test tube select sample of water (1 ml), carry out a qualitative test on ions of chlorine (reaction with AgNO₃). Explain absence in a glassful with water of a red - brown staining and presence there of ions of chlorine.


«Definition of a critical coagulation concentration. A peptization»

The experiment 1. Definition of critical coagulation concentration

Carry out consistently two experience with solutions of electrolytes Na₂SO₄ and K₄[Fe(CN)₆] with concentration Cₐ(X) = 0.0025 N. Prepare starting electrolyte solutions of various concentrations, admixing in five test tubes measured with the help of burettes starting electrolyte solution and distilled water in relations specified in the table.
In 5 well washed up test tubes measure from a burette till 5.0 ml of iron (III) hydroxyde sol. In all test tubes with sol add prepared electrolyte solutions and immediately intermix. Observe of changes in test tubes. Through 10 mines note, in what test tubes the opacification or sedimentation is observed. Effects of observations write down in the table: is familiar «+» note presence of a coagulation, is familiar «−» absence.

**Processing effects of experiment.** Calculate critical coagulation concentration of sol and coagulable ability (C.A.). For each electrolyte, using such equations:

$$C.C.C = \frac{C_N(X) \cdot V_{min} \cdot 1000}{V_{sol}}$$

$$C.A = \frac{1}{C.C.C(X)}$$

Where $C_N(X)$ - molarity of an equivalent of electrolyte solution, mol/l;

$V_{min}$ - least volume of starting electrolyte solution causing a coagulation of sectional volume of sol, ml;

$V_{sol}$ - cooperative volume of sol, starting electrolyte solution and water, ml.

Least volume of starting electrolyte solution causing a coagulation of sol, find as medial value on the equation

$$V_{min} = \frac{V_i + V_{i+1}}{2}$$

Where $V_i$ - volume of starting electrolyte solution in a test tube, in which there was a coagulation, ml;

$V_{i+1}$ - volume of starting electrolyte solution in the next test tube, in which the coagulation has not taken place (see table).

Formulate a deduction, scoring, whether there are experimental data according to Shults-Gardi’s - rule.

**Experiment 2.** A peptization of a iron (III) hexacyanoferrate (II) deposit.
1. Receive a deposit of iron (III) hexacyanofferrate (II): in a test tube to 1 ml of a saturated solution FeCl₃ add 0.1 ml of a saturated solution of K₄[Fe(CN)₆].
2. Transfer a little deposit by a glass rod on the impregnated-paper filter.
3. On the filter add 3 ml 0.1 M of solution of an oxalic acid (peptizator).
4. Note, that thus is observed. Explain a method of a peptization. Write the formula of a micelle of received sol by peptization method.

**Problems for discussion:**
1. How classify disperse systems on the size of particles of a dispersed phase?
2. What systems are called colloidal?
3. What is meant “dispersed phase” and “dispersion medium”?
4. What methods of clearing of colloidal solutions from impurities do you know?
5. Give an example of using of dialysis.
6. What is Tyndall effect?
7. 12 ml 0.02 M of solution of copper (II) sulfas and 10 ml 0.05 M of solution of potassium hexacyanoferrate (II) are immixed. To write the formula of a micelle of the formed sol and to designate its constituents.
8. What volume 0.05 M of solution of silver nitrate needs to be added to 25 ml 0.01 M of solution KCl to receive negative sol of silver chloride? To write the formula of its micelle.
9. At intermixturing 12 ml 0.02 M of solutions of iron (III) chloride whith 100 ml 0.005 M of solutions of potassium hexacyanoferrate (II) sol was formed. Write the formula of a micelle of sectional sol. To what electrode at electrophoresis the particles of dispersed phase are transferred?
11. What phenomenon is termed as a coagulation? What the visual attributes of the coagulation do you know?
12. What factors are cause a coagulation of lyophobe sols?
13. What is meant “critical coagulation concentration”. Write down the mathematical expression of C.C.C
14. What is meant «coagulable ability» of electrolyte? On what factors the C.A. depends on?
16. The coagulation 10 ml of Fe(OH)₃ sol has come at addition to it 2 ml of a solution Na₂SO₄ with molarity of an equivalent 0.0025 mol•l⁻¹. Calculate a critical coagulation concentration and coagulable ability of that electrolyte.
17. What volume of a solution K₄Cr₂O₇ with concentration 0.01 mol•l⁻¹ can be added to 1 l of sol to cause its coagulation, if it is known, what the critical coagulation concentration is peer 0,6 mol•l⁻¹?
18. What volume of aluminium sulfate solution of concentration 0.01 mol/l is required for a coagulation 10⁻³ m³ of silver chloride sol? The critical coagulation concentration is peer 96 • 10⁻⁶ mmol/l;
In 2 flasks is added on 100 cm$^3$ of iron (III) hydroxide sol. To cause an obvious coagulation of this sol it was required to add 62.5 cm$^3$ of a 0.01 M sodium sulfate solution in one flask, and in second - 67 cm$^3$ 0.001 M of sodium phosphate solution. To calculate critical coagulation concentration and to define a sign of a charge of particles of this sol. To write the formula of a micelle of this sol in an isoelectric state.

LESSON 16 Solutions of high-molecular compounds (HMS).

Medicobiological value: HMS, to which the fissile substances concern biologically: the protein, nucleic acids and glycogen, are the basic building material of a protoplasm and kerns of cells. These compounds play the important role during vital activity of organisms. For example, the protein protect hydrophobic colloids in a blood and other biological fluids from a coagulation, provide a buffer effect, oncotic pressure, allocation of water both mineral substances between a blood and tissues. At change of the content of protein in a blood and infringement of their protective functions the various pathological changes in an organism are observed which will be surveyed at study patophysiology, therapy, surgery and other disciplines.

The knowledge of the basic legitimacies of a bloating and deaquation of protein is necessary for comprehension of physiological and biochemical processes at an anogenesis, combustions, formation of edemas, centers of an inflammation and aging of an organism. In the diagnostic purposes everyone are more widely implanted immunological examinations, which will be carried out in jellies, which properties and substance of an immunodiffusion are studied on sectional lesson.

Important the study of process of salting-out and isoelectric state of protein is, as these questions underlie excretion of protein with the purpose of their study and preparation of medical serums. The method of a staining of cells of a tissue is based also on knowledge I.E.P. at histochemical examinations.

In medicine the tretment-diagnostic devices from polymers are widely used: catheters, sondes, squirt guns, system for a capture, transfusion and preservation of a blood, kettles for replacement of functions of bodies (heart, liver, kidney) etc.

Some polymers have properties to prolong activity of medicinal substances in an organism, to represent itself as blood substitutes (vinyl alcohol, dextran, gelatine etc.). On any other business modified cellulose apply to manufacturing bandage and cotton with antimicrobial properties.

For successful application of polymers in medical practice, activities of biological medium to know exceptions of their side effect, it is important of the best acclimatization them to as physicochemical properties of used polymers, and biopolimers of our organism.
The purpose of lesson: formation of systemic knowledge about legitimacies of process of dissolution HMS, properties of their solutions and role in vital activity of an organism; purchase of skills of experimental definition of quantity of a bloating and isoelectric point of protein.

To lesson it is necessary:
1. TO STUDY the following program questions: features of dissolution HMS as a consequence of their frame. The shape of macromolecules. The mechanism of a swelling and dissolution of HMS. Dependence degree of swelling on the various factors. Abnormal viscosity of HMS solutions. The Staudinger equation. Viscosity of a blood and other biological fluids. Osmotic pressure of solutions of biopolymers. The Haller equation. Polyelectrolytes. An isoelectric point (IP) and methods of it definition. Membrans Donnan equilibrium.
2. TO BE PREPARED for performance of research work.

Literature:
1. Colloid chemistry

Research work:
«Influence pH and electrolytes on degree of swelling of gelatin»

Experiment 1. Study of influence pH on degree of swelling and definition of the isoelectric point of gelatine.

Performance of experiment:
1. To 3 test tubes bring on 0.5 g of a powder of gelatine. With the help of a ruler of a paper measure height of bed of dry gelatine (h₀).
2. In test tubes add accordingly: in the first 6 ml 0.1M HCl; in the second 6 ml 0.1M NaOH; in a third - 3 mls 0.1M CH₃COOH (K=1.8 • 10⁻⁵) and 3 ml 0.1M CH₃COONa.
3. Contents of test tubes intermix and leave on 20 minutes.
4. Through 20 minutes measure height of swelling gelatine (h), calculate a degree of swelling and pH of solutions.
5. Observed datas bring in the table.
6. Explain apparent dependence of the degree of swelling gelatine from pH.
7. For definition isoelectric point (IP) of gelatine construct the graph of dependence h = f(pH). IP find, havinginked from valleys on the curve a perpendicular on an abscissa axis.
<table>
<thead>
<tr>
<th>№ of a test tube</th>
<th>The added fluid</th>
<th>height of dry gelatine layer ((h_o))</th>
<th>height of swelling gelatine ((h))</th>
<th>a degree of swelling</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>3</td>
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</tbody>
</table>

**Problems for discussion**

1. What mechanism of dissolution HMS? What the features of dissolution HMS in comparison with dissolution LMS are bound?
2. Give and analyse the graph of dependence the degree of swelling HMS on pH.
3. How it is possible to increase a degree of swelling? Pose halogenids - ions in lyotropic series on their ability to strengthen process of a swelling.
4. For what in medicine is defined IP of protein? Term methods of its definition. Explain substance of each method.
5. At pH = 4.64 albuminums of serum of a blood are in an isoelectric state. To what electrode albuminum will move, if it to place in a buffered solution prepared from 5ml 0.1M of solutions of ammonia and 5 ml 0.1M of ammonia chloride solutions. The ionization constant of ammonia is \(\text{peer } 1.8 \cdot 10^{-5}\).
6. Pose cations of alkali metals on ability them to accelerate jellification. Explain, why the various ions render unequal influence on rate of jellification.
7. Give the graph and write the formulas used at viscosimetric a method of definition \(M\) of polymers.
8. Calculate molecular weight of protein, if the characteristic viscosity of its solution is peer 0.105. Constants of the Staudinger equation: \(K=1.7 \cdot 10^{-5}\), \(\alpha = 0.69\).
9. Write and analyse the equation for evaluation of osmotic pressure of biopolmers. Compare to the similar equation for LMS.
10. Than the abnormal viscosity of solutions HMS is explained?
11. In what the biological role of the phenomenon of colloidal protection consists?

**LESSON 17 Control work 2: Physico-chemistry of surface phenomenas. Preparation, purification and properties of colloidal solutions. Solutions of high-molecular compounds. Suspensions, emulsions, aerosols.**

To lesson it is necessary: TO REPEAT program questions and decision of sample tasks to lessons 14 – 16.

**The literature:** see appropriate chapters of lessons №№14-16.
LESSON №18 Electrochemical processes. Potentiometric definition of the pH.

Potentiometry. Potentiometric titration.

Medicobiological value: Potentiometry is the physicochemical method based on the relation between the electrode potential and the composition of a solution in which the electrode is immersed. Potentiometric studies require the assembly of a galvanic cell consisting of a reference electrode immersed in the solution being studied and an indicator electrode, after which the e.m.f. of this cell is measured. Here it is essential to strictly observe the correspondence of the composition of the indicator electrode to that of the analyte substance in the solution. To groups of potentiometric studies are distinguished, namely, direct potentiometric analysis and potentiometric titration. The former is used when only processes that are strictly reversible relative to the analyte ions in the solution can occur on the indicator electrode, and no side reactions are possible. The determination of the acidity of solution – the hydrogen ion concentration (pH) – is one of the main applications of direct potentiometry. Here indicator electrodes are used that are reversible relative to H⁺ or OH⁻ ions, i.e. that exchange H⁺ or OH⁻ ions with a solution. Potentiometry will widely be used for definition pH of biological liquids, for example, blood, blood plasma, gastric juice, solutions of medicinal substances etc.; at study of a permeability of biological membranes in relation to electrolytes; for studies redox potentials of a various sort of biological systems, that is the important condition at an establishment of a direction, sequence and power of oxidation-reduction processes proceeding in an organism. Potentiometry - irreplaceable in many cases a method of definition concentration of physiologically active ions (H⁺, K⁺, Ca²⁺, NH₄⁺, Cl⁻, J⁻ etc.) in biomediums of an organism. Potentiometric titration is widely applied at definition of concentration of a various sort of biological active materials in biological objects, and also at the analysis of medicinal substances, when the application of usual indicators labored.

To lesson it is necessary:

2. TO SOLVE tasks:
   a) Calculate the potential of a zinc electrode at temperature 25°C, if the φ°(Zn²⁺/Zn) = -0,76 V, and the concentration of a ZnSO₄ solution is 0,05mol/l;
   b) Calculate the potential silver-silver chloride electrode at temperature 25°C, if φ°(Ag/AgCl, Cl⁻) = 0,222 V, c(KCl) = 0,001 mol/l.
c) Calculate e.m.f. of a galvanic element consisting of two hydrogen electrodes, omitted: one in a solution with pH = 3, and second - with pH = 8, at temperature 25°C.

3. TO BE PREPARED for performance of research work.

Research work (RW):
«Definition of the pH solutions with the help of a glass electrode. Indication of an equivalence point by potentiometric method»

The purpose of work. To determine the pH of liquids and their concentration by potentiometric method.

Task 1. Definition the pH of a solution with the help of a glass electrode.

Performance of work:

1. In a laboratory magazine prepare the table for results of definitions under the form:

<table>
<thead>
<tr>
<th>The code of a investigated solution</th>
<th>Approximately value of the pH on a scale - 1÷19</th>
<th>an interval of gaugings</th>
<th>the indications on a scale of chosen interval</th>
<th>exact value of the pH</th>
</tr>
</thead>
</table>

2. Prepare the pH meters for work. Include it in a network and warm up 15 minute.

3. In the table write down the code of a researched solution, fill by it in a glass, omit in it the necessary electrodes and measure approximate value of the pH.

For this purpose:
4. Press keys "pX", "anions and cations" and "1÷19".

5. Remove the indications pH on a scale and write down result in the table.

6. For exact definition of pH press a key of that narrow measuring range, which includes approximate value of the pH, and remove the indication on a scale. For readout pH on this scale to initial value of the chosen range add the indication of a finger.

7. Write down in a magazine exact (up to two marks after a point) value pH of a solution.

8. Verify at the teacher result of gauging pH.

9. The electrodes omit in a glass with distilled water.

Task 2. Indication of an equivalence point by potentiometric method (potentiometric titration).
1. Connect pH-meter to a network of an alternating current and warm up "15 minutes.
2. In a glass add 10 mls of a solution of a researched acid also are shipped by electrodes (reference electrode and indicator electrode) and measure pH.
3. Add from a burette in a glass with acid 1 ml of 0,1M solution of NaOH also mix a solution. Measure pH.
4. Add in the same way till 1 ml of alkali and determine pH. When total amount adding of alkali reaches 6-7 ml, the alkali should be added till 0,5 mls.
5. At approach to an equivalent point (pH = 7) titration carry out, adding on 0,2 - 0,1 mls of NaOH.
6. It is possible to judge an end point of titration on appreciable ascending pH at addition of small quantity of alkali (0,2-0,1 mls).
7. After a closing-up electrodes carefully wash out by distilled water and leave shipped in water.
8. The data bring in the table.
9. On the basis of the received data construct the curve potentiometric titration of an acid, postponing on an axis of ordinates pH, and on an axis abscissa - volume of alkali, ml.
10. Determine an equivalent point and under the law of equivalents calculate normality of an acid (molarity of an equivalent).

Problems for discussion:
1. What electrodes will be used for definition pH by potentiometric method?
2. Describe the device of a glass electrode.
3. Write down the circuit of a galvanic cell made for gauging of the pH.
4. In what the advantage of the potentiometric titration consists in comparison with other methods of analysis?
5. Represent the curve of the potentiometric titration of a strong acid by the strong base. How with the help of the curve of titration to determine of an equivalence point?
6. Calculate electrode potential of a copper electrode omitted in 0,02M solution of the coppers (II) salt at 300°C. if the \( \phi'(\text{Cu}^{2+}/\text{Cu}) = 0,345 \) V.
7. Calculate the pH of urine, if the potential of a hydrogen electrode omitted in it is - 0,342V at 25°C.
8. To calculate the pH of a blood, if e.m.f. of a galvanic cell made from hydrogen and calomel electrodes at 25°C is 0,686V. \( \phi' \) calomel electrode is 0,25V.
9. Result examples of the ionselective electrodes.
10. What potential electrodes can be used for gauging pH?
11. What by itself represents an internal reference electrode?
12. On what border undressed in a glass electrode there is a potential dependent from pH of a solution?
13. Why the glass electrode should necessarily be in water?
14. In this connection before gauging pH the device should be adjusted on a standard buffered solution?
15. Why before gauging pH the device is necessary for adjusting on certain temperature?
16. For definition of gastric acidity have lead by potentiometric titration 5 mls it 0,01M by alkali liquor. On a point of equivalence is found, that 10 mls of alkali liquor are spent. Calculate total acidity of gastric juice.

LESSON 19 Final lesson

1. To final lesson the students who are not having of debts on laboratory work are supposed.
2. The student should have notebook for laboratory work with the made out protocols of works.
STUDY GUIDE
On self-preparation for lesson and performance of laboratory operations
ON GENERAL CHEMISTRY
For 1-st course students of stomatological faculty

Study guide

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