

Ministry of Health Protection of Ukraine
Higher State Educational Institution of Ukraine
“Ukrainian Medical Stomatological Academy”

Department of Medical, Bioorganic and Biological Chemistry

Methodical Instructions
in Medical Chemistry

for self-preparatory work of first-year students of dentistry
during preparation to practical classes and in class
Module «Basics of Medical Chemistry»

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The Methodical Instructions are prepared according to Program “Medical Chemistry” for students of dentistry at higher medical educational institutions of III – IV accreditation levels for speciality “Stomatology” (Kyiv, 2010).

The Methodical Instructions are structured in one module “Basics of Medical Chemistry”, that includes two thematical modules: “Homogeneous equilibriums in biological fluids” and “Heterogeneous equilibriums in biological fluids”. The booklet includes 18 laboratory-practical (2 hours) lessons and questions for the Summary Module Control. Importance of the subject, concrete aims, basic knowledge and skills necessary to study the subject, tasks for self-preparation for the lesson (theoretical questions, practical work) and materials for self-control (with questions and answers) are provided for every lesson.

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Module «Basics of Medical Chemistry»

Thematical module 1. Homogeneous equilibriums in biological fluids

Subjects 1-2. Safety and security in the laboratory. Biogenic elements in medicine and dentistry

1. Importance

Knowledge of electron structure and properties of biogenic *s*-, *p*-, *d*-elements explains their biological role in the organism.

Investigation of the relationship between the content of the biogenic elements in the human organism and their content in the environment renders it possible to understand causes and mechanisms of endemic diseases and their relationship with properties of biochemical provinces (regions with natural deficiency or excess of certain chemical elements in the lithosphere).

It elucidates problems of pollution of the biosphere by the toxic chemical compounds of technogenous origin.

Knowledge of chemistry of biogenic elements helps to produce gold, silver and copper alloys and amalgams and apply them in the dental practice. The following casting materials are widely applied: dental gypsum, filling materials: phosphate cements (zinc-phosphate, bactericidal, silicophosphate), zincpoly-carbonate, ionomeric cements.

2. Concrete aims

Explain the relationship of the biological role of biogenic *s*-, *p*-, *d*-elements and their state in the organism.

Analyze the relationship of the chemical properties of the compounds of biogenic *s*-, *p*-, *d*-elements and their application in the dental practice.

3. Basic knowledge and skills necessary to study the subject

It is necessary to know the Periodic System, be able to write electron formulas of chemical elements. The student has to be acquainted with *s*-, *p*-, *d*-elements and their chemical properties and be able to carry out qualitative reactions.

4. Tasks for self-preparation for the lesson

4.1 Theoretical questions for the lesson:

1. Biogenic elements:
 - a) organogens;
 - b) macroelements;
 - c) microelements.
2. Electron structure of biogenic *s*-, *p*-, *d*-elements.
3. Typical chemical properties of *s*-, *p*-elements and their compounds (reactions without change of oxidation state).

4. Typical chemical properties of *d*-elements and their compounds:
 - a) reactions with change of oxidation state;
 - b) formation of complexes.
5. Biological role of biogenic elements.
6. Relationship of location of *s*-, *p*-, *d*-elements in the Periodic table and their content in the organism.
7. Endemic diseases and their relationship with properties of biochemical provinces (regions with natural deficit or excess of certain chemical elements in the lithosphere).
8. Application of compounds of *s*-, *p*-, *d*-elements in dental practice.

4.2. Practical work (task) done by students in class

1. Acquaintance with safety and security rules in the chemical laboratory

While carrying out laboratory work students should follow the internal rules of the academy, as well as safety and security rules. Each student provides a signature in the register of safety after getting instructed about safety and security rules.

2. Acquaintance with rules for carrying out laboratory works and writing reports of the laboratory works

Students must learn the subject before the lesson using the plan in the book. It is necessary to write down the date, subject, aim of the lesson, procedure, results of experiments, reaction equations, calculations and conclusions.

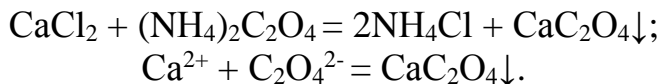
3. Acquaintance with rules for carrying out experiments in qualitative analysis

1. Do not put unused reagents back to their jars - reagents in the jars can be contaminated.
2. Take dry substances from a jar with a spatula.
3. Do not keep reagents open for a long time. Put corks and lids upside down on the table. Do not mix up corks of different jars.
4. Use only very clean glassware for experiments.
5. Strictly follow the procedure of analysis: conditions of the reaction, amounts and concentrations of reagents.
6. Work with concentrated acids only under the hood.
7. Do not leave obtained sediments in test tubes – dissolve them immediately in respective reagents and wash the test tubes.
8. If there is a need to leave a solution or sediment for a while, make a respective note on its glass.

4. Chemical properties of *s*-elements and their compounds (reactions without change of the oxidation state)

Qualitative reaction for Ca^{2+}

Add 1 mL of a calcium salt (chloride or nitrate) solution and 1 mL ammonium oxalate solution to a test tube. White crystals of calcium oxalate precipitate:



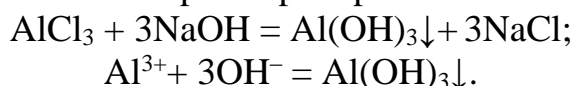
The reaction is used to determine calcium in the urine and blood.

Check, how the obtained precipitate reacts with a strong mineral acid and acetic acid. Write molecular and short ionic equations of the reaction of the precipitate dissolving in a strong mineral acid. Make a conclusion about conditions of opening the calcium cation by ammonium oxalate.

5. Chemical properties of *p*-elements and their compounds (reactions without change of the oxidation state)

Qualitative reaction for Al^{3+}

Add 1 mL of an aluminium salt solution to a test tube. Add by drops an alkali solution until a white amorphous precipitate is obtained.



Check, how strong mineral acids and alkalis react with the precipitate. Write molecular and short ionic equations of the reactions of the precipitate dissolving in a mineral acid and in excessive amount of alkali.

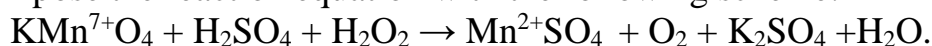
6. Chemical properties of *d*-elements and their compounds:

a) a reaction with a change of the oxidation state:

Qualitative reaction for permanganate ion. Reaction with hydrogen peroxide in an acidic medium

Add 1 mL of potassium permanganate solution, 2-3 drops of sulfuric acid solution and 5 drops of 10% hydrogen peroxide solution. The potassium permanganate solution becomes colorless.

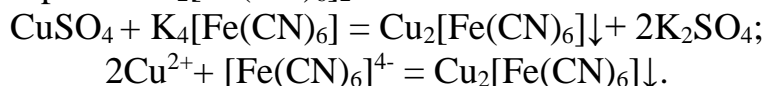
Compose the reaction equation with the following scheme:



b) a reaction of complexing:

Qualitative reaction for Cu^{2+}

Add 1 mL of a cupric salt solution to 1 mL of potassium ferrocyanate (II). A brownish precipitate $\text{Cu}_2[\text{Fe}(\text{CN})_6]_2$ is obtained.



Check, how strong mineral acids and alkalis react with the precipitate. Make a conclusion about conditions of opening the cuprous cation as copper hexacyanoferrate.

7. Writing a report of the laboratory work

Write the necessary reaction equations and conclusions to each experiment in your notebook.

Materials for self-control

1. Is carbon an organogenic element that forms structural components of the cell?
 - a) it is an organogenic element;
 - b) it is not an organogenic element;
 - c) it is only partially an organogenic element.
2. Choose the electron configuration of the magnesium atom:
 - a) $1s^2 2s^2 2p^6 3s^2$;
 - b) $1s^2 2s^2 2p^6$;
 - c) $1s^2 2s^2 2p^6 3s^1$;
 - d) $1s^2 2s^2 2p^7 3s^1$.
3. Choose the characteristic oxidation state of the *s*-elements of IIA group in their compounds:
 - a) +2;
 - b) -2;
 - c) +3;
 - d) +1.
4. Why is the valency of oxygen normally equal two?
 - a) oxygen is less electronegative than fluorine;
 - b) the oxygen atom does not have *d*-sublevels;
 - c) oxygen has non-metal properties;
 - d) the oxygen atom lacks two electrons to complete the outer electron shell.
5. Choose the ions of the *p*-elements of VA group that take part in physiological processes in the human organism.
 - a) NO_2^- ;
 - b) H_2PO_4^- ;
 - c) SbO^+ ;
 - d) As^{3+} .

Correct answers

1. The correct answer is a).

The specific position of carbon is stipulated by the properties of its atom. It only forms covalent bonds in all its compounds. The carbon atom can be an electron donor and electron acceptor in the same compound. From biochemical point of view it is important that the chemical bonds formed by carbon are rather strong and at the same time can be easily cleaved in biochemical reactions (labile bonds).
2. The correct answer is a).
3. The correct answer is a).

Atoms of IIA group normally do not have unpaired electrons. When the atom becomes excited one of the outer *s*-electrons moves to the *p*-sublevel and two

unpaired electrons are obtained, thus accounting for the oxidation level +2, that the elements have in their compounds.

4. The correct answer is b).

The atom of oxygen differs from atoms of the other elements of its subgroup by absence of the *d*-sublevel on the outer energy level. Increase of the number of unpaired electrons is only possible when one of electrons moves to the next energy level. The transition demands a great amount of energy which is not compensated by the energy released in the formation of new chemical bonds. That is why the oxygen atom can form not more than two covalent bonds with its unpaired electrons. Sulfur and the other elements of the subgroup can have a bigger number of unpaired electrons due to transition of *s*- and *p*- electrons on the *d*-sublevel on the outer energy level. Therefore the valencies of the elements are not only 2, but also 4 and 6.

5. The correct answer is b).

Dihydroorthophosphate ions H_2PO_4^- are in the phosphate buffer system of the blood, urine and extracellular fluid.

Subject 3. Ways of expression of quantitative composition of solutions

1. Importance

Blood plasma, saliva, gastric juice and other biological fluids in the organism are solutions. Processes of food assimilation and excretion are possible only in solutions. A great number of medical preparations are also solutions. Thus it is important for a doctor to know values that characterize quantitative composition of solutions.

2. Concrete aims

Be able to characterize quantitative composition of solutions.

3. Basic knowledge and skills necessary to study the subject

Know composition of solutions and values that characterize their quantitative composition.

Be able to calculate the amount of solute in a solution of given concentration.

4. Tasks for self-preparation for the lesson

4.1. Theoretical questions for the lesson:

1. Composition of solutions.
2. Classification of solutions.

3. Values that characterize quantitative composition of solutions.
 - 3.1. Mass, volume and mole fraction.
 - 3.2. Molarity.
 - 3.3. Normality (deci-, santi--, milli- and micromols).
 - 3.4. Molality.
 - 3.5. Titr.

4.2. Practical work (task) done by students in class

Task № 1

0.040kg salt was dissolved in 0.200L water. Calculate the mass part of the salt in the solution, if the density of water is 1 kg/L.

Task № 2

Calculate the mass of 10% (by mass) CuSO_4 solution and the mass of water, which are needed to prepare 0.5 kg 2% (by mass) CuSO_4 solution.

Task № 3

Calculate the molarity of a sodium hydroxide solution with the mass fraction 0.2. The density of the solution is 1.29 kg/L.

Task № 4

Calculate the normality of a solution obtained by dissolving 0.0426 kg sodium sulfate in 0.3 kg water. The density of the solution is 1.12 kg/L.

Task № 5

Calculate the molality of a potassium chloride solution, if 0.5 kg of the solution contains 0.05 kg salt.

Materials for self-control

Task № 1

Concentration of sodium cations in blood plasma is 142 mmol/L. Calculate the titr of sodium cations in the plasma.

Task № 2

A water solution is obtained by dissolving 0.005 kg glucose ($M_r = 180$) in 0.095 kg water. It is isotonic to blood plasma. Calculate the mass fraction and mole fraction of glucose in the solution.

Task № 3

Calcium chloride ($M_r = 111$) solution is used for treatment of allergic and skin diseases. Its titr is 0.0999 g/ml. Calculate the molarity and normality of calcium chloride in the solution.

Task № 4

Calculate the molality of physiological saline with mass percent of sodium chloride 0.85%.

Correct answers

Task № 1

Titr (T) is the mass of solute in 1 mL of a solution. The mass is usually in grams (g).

Thus we have:

$$T(\text{Na}^+) = \frac{m(\text{Na}^+)}{V(\text{solution})} = \frac{\nu(\text{Na}^+) \cdot M(\text{Na}^+)}{V(\text{solution})}, \text{ where:}$$

$M(\text{Na}^+)$ – mass of sodium cations, g;

$V(\text{solution})$ – volume of the solution, mL;

$\nu(\text{Na}^+)$ – number of moles of sodium cations, mol;

$M(\text{Na}^+)$ – molar mass of the sodium cation, g/mol;

$$T(\text{Na}^+) = \frac{0.142 \text{ mol} \cdot 23 \text{ g/mol}}{1000 \text{ mL}} = 3.266 \cdot 10^{-3} \text{ g/mL}.$$

Task № 2

Mole fraction (χ) is the moles of solute (ν solute) in the moles of solution (ν solution).

$$\begin{aligned} \chi(\text{glucose}) &= \frac{\nu(\text{glucose})}{\nu(\text{glucose}) + \nu(\text{H}_2\text{O})} = \\ &= \frac{m(\text{glucose}) / M(\text{glucose})}{m(\text{glucose}) / M(\text{glucose}) + m(\text{H}_2\text{O}) / M(\text{H}_2\text{O})} = \\ &= \frac{5 \text{ g} / 180 \text{ g/mol}}{5 \text{ g} / 180 \text{ g/mol} + 95 \text{ g} / 18 \text{ g/mol}} = \frac{0.0278 \text{ mol}}{0.0278 \text{ mol} + 5.28 \text{ mol}} = \frac{0.0278 \text{ mol}}{5.3056 \text{ mol}} = \\ &= 0.00524 \text{ or } 0.524\% \end{aligned}$$

Mass fraction (ω) is the mass of the solute in the mass of the solution. It is expressed in percents, promille, etc.

$$\omega(\text{glucose}) = \frac{m(\text{glucose})}{m(\text{solution})} = \frac{5 \text{ g}}{5 \text{ g} + 95 \text{ g}} = 0.05 = 5\%.$$

Task № 3

Molarity (C) is the number of moles ν of a solute in the given volume V of a solution. Molarity is expressed in mol/L.

$$C_{CaCl_2} = \frac{\nu_{CaCl_2}}{V_{\text{solution}}},$$

$$C(CaCl_2) = \frac{n(CaCl_2)}{V(\text{solution})}$$

where

ν_{CaCl_2} is the number of moles of the solute $CaCl_2$

V_{solution} is the volume of the solution, L.

If $T(CaCl_2)$ equals $0.0999\text{g/mL} = 0.0999\text{ kg/L}$, then 1L of the solution contains 0.0999 kg salt.

Therefore, $V_{\text{solution}} = 1\text{ L}$, $m_{CaCl_2} = 0.0999\text{ kg}$.

$$\text{Then } \nu_{CaCl_2} = \frac{m(CaCl_2)}{M(CaCl_2)} = \frac{0.0999\text{ kg}}{111\text{ kg/kmol}} = 9 \times 10^{-4}\text{ kmol} = 0.9\text{ mol}.$$

$$\text{Thus : } C_{CaCl_2} = \frac{0.9\text{ mol}}{1\text{ L}} = 0.9\text{ mol/L}.$$

Normality (C_f) is the number of moles of equivalent of a solute ν_f present in the volume of solution. Normality is expressed in mol/L.

$$C_f = \frac{\nu_f}{V},$$

where ν_f is the number of moles of equivalent of the solute

V is the volume of the solution, L.

$$\nu_f = \frac{m}{M_f};$$

$$M_f = M \cdot f;$$

$$f = \frac{1}{n},$$

where n is the number of H^+ ions in the molecule of the acid,

or the number of OH⁻ ions in the molecule of the base,
 or the product of the valency of the metal and the number of metal
 atoms
 in the molecule of the salt.

The equivalent is the part of the substance (real or symbolic), which is equivalent to one mole of hydrogen atoms or one mole of hydrogen cations in reactions or one electron in redox reactions.

$$C_{f \text{ CaCl}_2} = \frac{V_{f \text{ CaCl}_2}}{V};$$

$$V_{f \text{ CaCl}_2} = \frac{m_{\text{CaCl}_2}}{M_{f \text{ CaCl}_2}};$$

$$M_{f \text{ CaCl}_2} = M_{\text{CaCl}_2} \cdot f = M_{\text{CaCl}_2} \cdot \frac{1}{n} = \frac{M_{\text{CaCl}_2}}{n} = \frac{111 \text{ g/mol}}{2} = 55.5 \text{ g/mol};$$

$$V_{f \text{ CaCl}_2} = \frac{0.0999 \text{ g}}{55.5 \text{ g/mol}} = 0.0018 \text{ mol};$$

$$C_{f \text{ CaCl}_2} = \frac{0.0018 \text{ mol}}{1 \text{ mL}} = \frac{0.0018 \text{ mol}}{0.001 \text{ L}} = 1.8 \text{ mol/L}.$$

Task № 4

Molality (C_m) is the number of moles of the solute in the mass of the solvent.

$$C_m = \frac{v_{\text{solute}}}{m_{\text{solvent}}},$$

where v_{solute} is the number of moles of the solute,
 m_{solvent} is the mass of the solvent, kg

0.85% solution contains 0.85 g of salt in 100 g of the solution.

$$v_{\text{NaCl}} = \frac{m_{\text{NaCl}}}{M_{\text{NaCl}}} = \frac{0.85 \text{ g}}{58.5 \text{ g/mol}} = 0.0145 \text{ mol};$$

$$m_{\text{H}_2\text{O}} = m_{\text{solution}} - m_{\text{salt}} = 100 \text{ g} - 0.85 \text{ g} = 99.15 \text{ g} = 0.09915 \text{ kg};$$

$$C_{m \text{ NaCl}} = \frac{0.0145 \text{ mol}}{0.09915 \text{ kg}} = 0.146 \text{ mol/kg.}$$

Subject 4. Preparation of solutions with known quantitative composition

1. Importance

Solutions with molecular and ionic dispersion of the solute – true solutions – are the most important components of biological liquids. Water solutions of electrolytes and low molecular substances ensure constant osmotic pressure, buffer properties of biological liquids, values of membrane potentials, enzyme activity etc.

Altered composition of solutions in the organism can cause various diseases. Therefore knowledge both of the theory of solutions and methods of their preparation render it possible to use solutions to treat various diseases.

2. Concrete aims

Learn the theory of solutions, learn to prepare solutions of given concentration.

3. Basic knowledge and skills necessary to study the subject

Know values that describe concentrations of solutions, be able to calculate concentrations of solutions, have a skill of weighing substances on technochemical and analytical scales.

4. Tasks for self-preparation for the lesson

4.1. Theoretical questions for the lesson:

1. Solutions in life.
2. Enthalpy and entropy factors of dissolution, their relationship with the mechanism of dissolution.
3. Solubility of gases in liquids and its dependence on various factors. Henry-Dalton's law.
4. Effect of electrolytes on the solubility of gases (Sechenov's law). Solubility of gases in blood. The caisson disease.
5. Solubility of liquids and solids. Distribution of substances between two immiscible liquids. Nernst's law and its importance for explanation of permeability of biological membranes.
6. Preparation of solutions of given concentrations.

4.2. Practical work (task) done by students in class

1. Preparation of solutions from fixanals.

To prepare a solution of a fixanal it is necessary to transfer the contents of the ampule into a volumetric flask completely and make the flask to the mark with distilled water. The procedure: remove the label off the ampule, wash the ampule thoroughly and rinse it with distilled water. Take a needed volumetric flask (1.0, 0.5, 0.25L), insert a 9-10 cm diameter funnel into it. Place a beater inside. Hold the ampule vertically and pierce it with the beater from one side. Use another beater to pierce the ampule from the other side and let the contents pour into the flask. Without changing the position of the ampule wash it thoroughly with distilled water. Take six or more volumes of water for the volume of the ampule. Then make the flask to the mark with distilled water and mix thoroughly.

2. Preparation of solutions of given concentrations.

Every student receives a card with a task to prepare a solution of a medical preparation with certain concentration and explanation of its application. The students make calculations and then prepare the solution after checking the results with the teacher.

Preparation of solutions with mass concentrations

Weigh out the calculated mass of substance on technochemical scales, place into a retort and add the calculated volume of water. Mix until completely dissolved.

Preparation of solutions with molarity and normality.

Weigh out the calculated mass of substance on analytical scales (pipet the liquids) and transfer carefully into a volumetric flask (first add some distilled water to the flask). Dissolve the substance in the water, next make to the mark with distilled water. Mix the solution.

3. Writing a report of the laboratory work

Complete necessary calculations in the notebook and describe the procedure of preparation of the solution according to the personal task.

Materials for self-control

1. When ammonia nitrate is being dissolved, the solution is colder than the air. When sulfuric acid is dissolved, the solution is hotter than the air. Why?
2. Why must a diver rise gradually and slowly, not fast from the big depth?
3. To measure concentration of potassium ions in the saliva with the flame photometry method it is necessary to prepare 0.25 L of a solution, which

contains 0.04 mmol/L potassium cation and 0.64 mmol/L sodium cation. How to prepare the needed solution, if there is a 1 mmol/L potassium chloride solution and 2 mmol/L sodium chloride solution.

4. Calculate the volume of 9.3% (by mass) sulfuric acid solution (density 1.06 kg/L), needed to prepare 0.05 L of 0.35 N sulfuric acid solution.

Correct answers

1. According to the theory of solutions two processes take place at dissolving: destruction of the primary structure (crystalline, amorphous, supermolecular) and formation of solvates of the destruction products and solvent molecules (those in water are called hydrates). The first process is endothermic (energy absorption), the other one is exothermic (energy release). Dissolving of ammonia nitrate takes place with a temperature depression. It means that the destruction of crystalline structure needs more energy than is released in the formation of hydrates. When sulfuric acid is dissolved, much more energy is released in the formation of hydrates than in the first process.
2. If a diver is at a great depth, nitrogen in the air with which he breathes becomes more soluble in the blood because of a pressure increase at depths. Solubility of gases increases with the pressure increase. When a diver is abruptly brought to the surface, nitrogen is released so fast that it can cause breaking or clogging blood vessels. Lethal outcomes are documented.
3. Calculate the amount of substance of potassium and sodium cations in 0.25 L solution.

$$v_{K^+} = C_{K^+} \cdot V = 0.04 \text{ mmol/L} \cdot 0.25 \text{ L} = 0.01 \text{ mmol};$$

$$v_{Na^+} = C_{Na^+} \cdot V = 0.64 \text{ mmol/L} \cdot 0.25 \text{ L} = 0.16 \text{ mmol}.$$

Calculate the volumes of the solutions (1) and (2):

$$V_1 = \frac{v_{K^+}}{C_{1 K^+}} = \frac{0.01 \text{ mmol}}{1 \text{ mmol/L}} = 0.01 \text{ L} = 10 \text{ mL};$$

$$V_2 = \frac{v_{Na^+}}{C_{2 Na^+}} = \frac{0.16 \text{ mmol}}{2 \text{ mmol/L}} = 0.08 \text{ L} = 80 \text{ mL}.$$

To prepare 0.25 L of the needed solution it is necessary to pipet 10 mL of the solution (1) and 80 mL of the solution (2) into a 0.25 L volumetric flask, make to the mark with distilled water and mix.

4. Calculate the amount of substance of equivalent of the acid in the needed solution:

$$V_{f \text{ H}_2\text{SO}_4} = C_{f \text{ H}_2\text{SO}_4} \cdot V = 0.35 \text{ mol/L} \cdot 0.05 \text{ L} = 0.0175 \text{ mol}.$$

Calculate the mass of the acid:

$$m_{\text{H}_2\text{SO}_4} = V_{f \text{ H}_2\text{SO}_4} \cdot M_{f \text{ H}_2\text{SO}_4} = 0.0175 \text{ mol} \cdot 49 \text{ g/mol} = 0.8575 \text{ g}.$$

Calculate the mass of the acid solution necessary for preparation of the needed solution:

$$m_{\text{solution}} = \frac{m_{\text{H}_2\text{SO}_4} \cdot 100\%}{\omega_{\text{H}_2\text{SO}_4}} = \frac{0.8575 \text{ g} \cdot 100\%}{9.3\%} = 9.22 \text{ g}.$$

Calculate the volume of the solution:

$$V = \frac{m_{\text{solution}}}{\rho} = \frac{9.22 \text{ g}}{1.06 \text{ g/mL}} = 8.7 \text{ mL}.$$

Thus, to prepare 0.05 L of 0.35 N sulfuric acid solution it is necessary to pipet 8.7 mL of 9.3% (by mass) sulfuric acid solution in a 50 mL volumetric flask and make it to the mark with distilled water.

Subject 5. Acid-base equilibrium and pH of biological fluids

1. Importance

The biological fluids of the organism – blood, lymph, gastric juice, urine, saliva etc. normally have different pH values. The pH of biological fluids effects activities of enzymes and hormones that regulate biochemical transformations in cells, tissues, organs. Changes of composition of biological fluids, including changes of pH, characterize abnormalities of organ functioning. Changes of blood pH disrupt structure and functioning of enzymes and hormones and therefore cause disruptions of metabolic regulation, accumulation of incompletely oxidized toxic products, poisoning and, ultimately, death. Monitoring pH helps to reveal pathologies and provide correct disease prevention and treatment.

The potentiometric method of pH measurement is widely applied in biology, medicine and pharmacy. Compared to the indicator method it is more accurate (the accuracy of measurements is 0.02 -0.05 pH units) and renders it possible to measure pH of multicomponent systems and colored solutions.

2. Concrete aims

Make conclusions about acidity of biological fluids with pH values.

3. Basic knowledge and skills necessary to study the subject

Understanding of acidic, neutral and alkaline medium. pH scale. Salt hydrolysis.

4. Tasks for self-preparation for the lesson

4.1. Theoretical questions for the lesson:

1. Equilibrium in electrolyte solutions. Ostwald's Law of dilution.
2. Water dissociation. Ionic product of water. pH of biological fluids.
3. Types of protolytic reactions. Neutralization, hydrolysis and ionisation reactions.
4. Salt hydrolysis.
5. Degree of hydrolysis, its dependence on concentration and temperature.
6. Hydrolysis constant.

4.2. Practical work (task) done by students in class.

Measurement of pH of biological fluids

Potentiometric measurement of pH is done with an ionometer EV-74.

8.1 Preparation of the instrument for work

The instrument is prepared as following:

- press the buttons “t” and “-1-19”, plug the instrument in and turn it on; warm it up for 30 minutes;
- compose a galvanic chain with a measurement electrode and a comparison electrode.

The measurement electrode is the glass electrode ESL – 43-07 with the hydrogen function. The comparison electrode is the chlorine silver electrode with a constant potential ($0.201 \pm 0.003V$). Fix the electrodes in the holder. Plug them in the respective sockets on the back of the instrument.

The ionometer is standartized with control buffer solutions according to the instruction manual.

8.2. Measurement of pH of biological fluids

A measurement of pH of a biological fluid is done as following:

- immerse electrodes in a cup with a biological fluid to create a galvanic circle;
- press the buttons “anions/cations”, “pX” and the general range “-1-19”. Do not press the button “X/X”, because the ions to be measured are monovalent;
- determine an approximate pH value on the general range scale;
- press the button of the range which corresponds to the approximate pH value and determine the exact pH value on the scale of the range.

8.3. Processing of results and writing a report of the laboratory work

1) Fill in Table 5 with the obtained values of pH of biological fluids.

2) Calculate the activity of hydrogen cations a_{H^+} with the values of pH:

$$pH = -\lg a_{H^+}$$

Table 5

№ of measurement	Biological fluid	pH	a_{H^+} , mol/L	K (H ₂ O)	a_{OH^-} , mol/L	pOH	Medium
1							
2							
3							

3) As far as in all water solutions (and biological fluids as well) the ionic product of water $K(H_2O)$ is constant, we can find the activity of hydroxyl ions with the formula (at the standard temperature):

$$K(H_2O) = a_{H^+} \cdot a_{OH^-} = 10^{-14},$$

$$a_{OH^-} = \frac{10^{-14}}{a_{H^+}}.$$

4) Calculate pOH with the formula:

$$pOH = -\lg a_{OH^-}$$

5) Fill in the chart with the results.

6) With the pH values make conclusions about the acidity of the medium in each of the biological fluids.

Materials for self-control

1. The relationship between pH and pOH in a solution is:

- a) $pH = pOH$; b) $pH + pOH = 14$; c) $pH \cdot pOH = 7$; d) $pH/pOH = 1$.

2. Effect of alteration of pH in biological fluids:

- a) depends on the fluid;
 b) with increased pH processes become faster;
 c) with increased pH processes become slower, with decreased pH processes become faster;
 d) altered pH can change the rate of a process or stop it completely.

3. Why does pH decrease in an inflammation zone?
- organic acids as products of non-complete oxidation are formed;
 - metabolic products are evacuated slower;
 - oxidation is suppressed and reduction is promoted;
 - pH does not change because it does not depend on the direction of metabolic processes.
4. Choose the group of salts that can be hydrolyzed upon dissolving in water.
- sodium chloride, ammonium sulfate;
 - potassium cyanide, sodium carbonate;
 - potassium nitrate, calcium acetate;
 - ammonium acetate, sodium sulfate.
5. Choose the correct ionic equation (short form) of the reaction of hydrolysis of sodium carbonate.
- $\text{Na}^+ + \text{H}_2\text{O} = \text{NaOH} + \text{H}^+$;
 - $\text{CO}_3^{2-} + 2\text{H}^+ = \text{H}_2\text{CO}_3$;
 - $\text{Na}^+ + \text{OH}^- = \text{NaOH}$;
 - $\text{CO}_3^{2-} + \text{H}_2\text{O} = \text{HCO}_3^- + \text{OH}^-$.
6. What type of medium is obtained in dissolving of zinc sulfate in water?
- acidic;
 - basic;
 - neutral;
 - depends on the salt concentration.
7. Explain the effects of temperature and salt concentration on hydrolysis degree.
- hydrolysis degree does not depend of temperature and concentration;
 - hydrolysis degree increases with increase of temperature and concentration;
 - hydrolysis degree decreases with increase of temperature and concentration;
 - hydrolysis degree decreases with increase of concentration and increases with increase of temperature.

Correct answers

1. The correct answer is b).

As far as $\text{pH} = -\lg[\text{H}^+]$, and $\text{pOH} = -\lg[\text{OH}^-]$, when we logarithm the equation of the ionic product of water, we obtain:

$$[\text{H}^+] \cdot [\text{OH}^-] = 10^{-14};$$

$$\lg[\text{H}^+] + \lg[\text{OH}^-] = \lg 10^{-14};$$

$$\lg[\text{H}^+] + \lg[\text{OH}^-] = -14;$$

$$\text{or: } -\lg[\text{H}^+] + (-\lg[\text{OH}^-]) = 14;$$

$$\text{pH} + \text{pOH} = 14.$$

2. The correct answer is d).
pH of the medium affects physiological processes so much, that even a slight change in pH can alter the rate of a process significantly or even stop it. It happens because enzymes are proteins, and structure and functioning of proteins depend on pH. Alteration of the structure of the enzyme inhibits their catalytic activity. For example, salivary amylase, that catalyses starch hydrolysis, is most active at pH 6.7. Pepsin in gastric juice is most active at pH 1.5-2.5. Change of pH inactivates the enzymes.
3. The correct answer is a).
Organic substrates are normally oxidized to carbon dioxide and water. At inflammation anaerobic (without oxygen) oxidation is intensified, when organic acids (lactic acid etc) are produced. They decrease pH in the inflammation zone.
4. The correct answer is b).
Only the salts that are formed by a strong acid and an alkali, are not hydrolyzed. The answer b) only does not contain such salts. All the other answers contain such salts (sodium chloride, potassium nitrate, sodium sulfate).
5. The correct answer is d).
Sodium carbonate is a salt that is formed by a weak acid and an alkali. The hydrolysis is anionic.

$$\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} = \text{NaHCO}_3 + \text{NaOH};$$

$$\text{CO}_3^{2-} + \text{H}_2\text{O} = \text{HCO}_3^- + \text{OH}^- .$$
6. The correct answer is a).
Zinc sulfate is a salt that is formed by a strong acid and a weak base. The hydrolysis is cationic: $\text{Zn}^{2+} + \text{H}_2\text{O} = (\text{ZnOH})^+ + \text{H}^+$.
 H^+ ions obtained in the hydrolysis decrease pH of the solution of zinc sulfate, the medium becomes more acidic.
7. The correct answer is d).

Subject 6. Titrimetric analysis. Method of acid-base titration

1. Importance

Diagnostics of diseases is often based on the data of clinical, biochemical and physico-chemical methods of analysis. Titrimetric analysis is one of the

most important methods of chemical analysis. It includes the neutralization method in its two divisions: alkalimetry and acidimetry. The neutralisation method is used for measurement of acidity of gastric juice, urine and other biological fluids, as well as measurement of chlorides in blood plasma. In the sanitary analysis the neutralisation method is used for analysis of drinking water, measurement of acidity of food. The student needs basic understanding of the theory and methods of titrimetric analysis to study biochemistry, pharmacology, hygiene.

2. Concrete aims

1. Analyze the principles of the titrimetric methods.
2. Analyze concentrations of acids and bases in solutions with methods of acid-base titration.

3. Basic knowledge and skills necessary to study the subject

Know the principle of neutralization reaction.

Have skills of using indicators.

Be able to use the formulas of mass fraction, molarity and normality for calculations.

4. Tasks for self-preparation for the lesson

4.1. Theoretical questions for the lesson:

1. Basics of titrimetric analysis.
2. Methods of acid-base titration.
3. Acid-base indicators and principles of their selection.

4.2. Practical work (task) done by students in class

1. Technique of volumetric analysis

Utmost accuracy is crucial for obtaining correct data. Make sure that you have all necessary clean glassware at hand before you have started. Learn the analysis procedure and prepare your notebook for writing the data.

Filling the burette with work solution.

First rinse the burette with distilled water, then with work solution. Fill the burette with the work solution a bit higher than the mark. Remove the air bubble from the burette by lifting its end slightly and pressing the other end. After the lower end is completely filled with the solution and the funnel is removed make the solution to the zero mark. Pressing the clip, remove excess solution in drops until the lower part of the meniscus of a colorless solution or the upper part of the meniscus of a colored solution is level with the zero mark. Make sure your eye is level with the meniscus while doing that.

Measuring solutions with pipettes.

Use chemical pipettes to take precise quantity of a necessary solution. First rinse the pipette with the solution. Then fill the pipette with the solution slightly higher than the mark. Quickly close the upper end of the pipette with

your forefinger and take the pipette out. Releasing the finger let the excessive solution drop out until the meniscus is level with the mark. Carefully move the pipette to a flask. Hold the pipette vertically and let the solution out. The end of the pipette must not touch the flask. Do not shake the pipette or blow into it to get the rest of the solution out.

A solution to be titrated often contains additional components that create certain medium or react with a certain substance transforming it into a state necessary for the titration. Solutions of those components are also measured with pipettes or measuring cylinders.

Titration procedure

Place a conical flask with a solution to be titrated on white paper under the burette. The burette end must be level with the neck of the flask. Press the clip to let the work solution drop into the flask. Shake the flask continuously to mix the solution. The titration is nearly at end, when the solution in the flask obtains the necessary color in the place where the drops fall. Then add the work solution only by separate drops. Immediately after a steady color change is obtained, cease the titration and determine the used amount of the work solution. Repeat the titration procedure at least three times.

2. Measurement of the mass percent of the acetic acid.

Pipet 10.0 mL acetic acid solution into a 50-100 mL conical flask, add two to three drops of phenol phtalein and titrate from the burette with a work solution of NaOH until pink. Mark on the burette scale the volume of the work solution which was used for the titration. Repeat the titration two more times and calculate the average volume of NaOH used for the titration:

$$V_{\text{average}}(\text{NaOH}) = \frac{V_1 + V_2 + V_3}{3},$$

where V_1, V_2, V_3 are volumes of the NaOH solution in the parallel titrations, mL.

Calculation of the mass part of acetic acid:

1. Calculate the normality of acetic acid in the solution:

$$C_f(\text{CH}_3\text{COOH}) = \frac{C_f(\text{NaOH}) \cdot V_{\text{average}}(\text{NaOH})}{V(\text{CH}_3\text{COOH})},$$

where $C_f(\text{NaOH})$ is the molarity of NaOH solution, mol/L,

$V(\text{CH}_3\text{COOH})$ is the volume of the acetic acid that was used for the titration, mL.

2. Calculate the mass of acetic acid in one liter of the solution:

$$m(\text{CH}_3\text{COOH}) = C_f(\text{CH}_3\text{COOH}) \cdot M_f(\text{CH}_3\text{COOH}) \cdot V,$$

where $M_f(\text{CH}_3\text{COOH})$ is the molar mass of equivalent CH_3COOH , g/mol;
 $V = 1\text{L}$ – the volume of the acetic acid solution.

3. Calculate the mass part of acetic acid in the weighed portion of concentrated acetic acid that had been used for preparation of 1L of the analyzed solution.

$$\omega(\text{CH}_3\text{COOH}) = \frac{m(\text{CH}_3\text{COOH}) \cdot 100\%}{m(\text{weighed portion})}.$$

3. Writing a report of the laboratory work

Write the necessary calculations and conclusions in the notebook.

Materials for self-control

- Select a group of substances, amount of which can be measured with alkalimetry.

a) HCl, NaOH, K_2CO_3 ;	c) KOH, NH_3 , CaSO_4 ;
b) HCl, CH_3COOH , NaHCO_3 ;	d) $(\text{NH}_4)_2\text{SO}_4$, NH_4Cl , NaCl.
- Select an indicator for a measurement of concentration of a strong acid in a solution with an alkalimetric titration (color change intervals are given in brackets).

a) phenol phtalein (8.2 - 10.0);	c) litmus (4.4 – 6.4);
b) methyl orange (3.1 - 4.4);	d) methyl red (4.4 – 6.2).
- Select an indicator for measurement of the substances that create weak acidity of biological liquids, if the leap on the alkalimetric titration curve was 7.8 – 10.9 pH (intervals of indicator color change are given in brackets).

a) phenol phtalein (8.2 - 10.0);	c) methyl red (4.4 – 6.2);
b) methyl orange (3.1 - 4.4);	d) naphtylphtalein (7.4 – 8.6).
- Select a group of acids which are used as work solutions in acidimetry.

a) HCl, H_2SO_4 , CH_3COOH ;	c) H_3PO_4 , H_2S , H_3BO_3 ;
b) CH_3COOH , $\text{H}_2\text{C}_2\text{O}_4$, H_3PO_4 ;	d) HCl, HNO_3 , H_2SO_4 .
- 25.05 mL 0.1244 N HCl solution was titrated against 25.0 mL NH_3 solution. Calculate the mass of NH_3 in 1 liter of the solution.

Correct answers

- The correct answer is b).
 The alkalimetric method renders it possible to measure strong and weak acids, acidic salts and acidic substances in solutions and biological fluids.

2. Any of the indicators, because the intervals of the color change of all the indicators are within the pH leap on the titration curve of a strong acid.

3. The correct answer is a).

Only phenolphthalein has the interval of color change, which is within the pH leap on the titration curve. That is why it will provide the most accurate fixation of the equivalence point.

4. The correct answer is d).

Work solutions in acidimetry are those of strong acids that enable a great leap on the titration curve and application of most acid-base indicators within the interval of the color change in an acid medium.

5. Calculate the normality of the NH_3 solution:

$$C(\text{NH}_3) = \frac{C(\text{HCl}) \cdot V(\text{HCl})}{V(\text{NH}_3)} = \frac{0.1244 \text{ mol/L} \cdot 25.05 \text{ mL}}{25 \text{ mL}} = 0.1246 \text{ mol/L}.$$

Calculate the mass of NH_3 in 1 L of the solution:

$$m = \tilde{N}(\text{NH}_3) \cdot M(\text{NH}_3) = 0.1246 \text{ mol/L} \cdot 17 \text{ g/mol} = 2.12 \text{ g/L}.$$

Subject 7. Properties of buffer solutions

1. Importance

Constant pH is crucial for proper functioning of the organism. Constant pH is maintained through buffer systems and physiological mechanisms. Buffer systems regulate concentrations of hydrogen and hydroxide ions and pH-dependent reactions. It is important to know properties and composition of buffer systems in studying biochemistry, physiology and clinical sciences.

2. Concrete aims

Explain the mechanism of action of buffer systems.

3. Basic knowledge and skills necessary to study the subject

Understand strong and weak electrolytes, power of hydrogen, pH scale.

Be able to measure pH of solutions.

4. Tasks for self-preparation for the lesson

4.1. Theoretical questions for the lesson:

1. Classification of buffer solutions.
2. Mechanisms of action of buffer solutions.
3. pH of buffer solutions (Henderson – Hasselbach equation).

4.2. Practical work (task) done by students in class.

1. Effect of dilution on pH of a buffer solution

Take two test tubes. Add 6 mL of a buffer solution to a test tube. Add 2 ml of the same solution and 4 mL distilled water to the other test tube. Add 2 drops of methyl red indicator to each of the tubes. Shake each tube and compare the color.

2. Effect of acids and alkalis on pH of a buffer solution

Take three test tubes. Add 4 ml of a buffer solution with known pH to each of the test tubes. Add 2 drops of 0.1 N HCl solution to one test tube. Add 2 drops of 0.1 N NaOH solution to the second tube. Add 2 drops of distilled water to the third tube. Add 2 drops of methyl red to each tube. Shake the tubes and compare the color.

3. Writing a report of the laboratory work

From the observations make conclusions about effect of acids, alkalis and dilution on pH of buffer solutions.

Materials for self-control

1. Choose the correct formula to calculate pH of a HCN – NaCN buffer system:

a) $\text{pH} = \text{p}K_{\text{HCN}} + \lg \frac{[\text{NaCN}]}{[\text{HCN}]}$; c) $\text{pH} = 14 - \text{p}K_{\text{HCN}} + \lg \frac{[\text{NaCN}]}{[\text{HCN}]}$;

b) $\text{pH} = \text{p}K_{\text{HCN}} + \lg \frac{[\text{HCN}]}{[\text{NaCN}]}$; d) $\text{pH} = 14 + \text{p}K_{\text{HCN}} - \lg \frac{[\text{HCN}]}{[\text{NaCN}]}$.

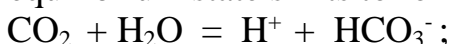
2. Calculate pH of a buffer solution, prepared from 0,040 L 0.15M ammonia solution and 0,020 L 0.25 M ammonia chloride. $\text{p}K_{\text{NH}_4\text{O}^1} = 4.74$.

a) 4.67; b) 6.42; c) 9.33; d) 10.12.

3. Why does not pH of the hydrocarbonate buffer system change when a small amount of a strong acid is added to it?

a) dissociation of sodium hydrocarbonate increases;

b) equilibrium state shifts to formation of hydrogen cations:



c) carbonic acid decomposes under influence of strong acids;

d) the strong acid is replaced by an equivalent amount of weak carbonic acid.

4. Which factors effect pH of a buffer system?

a) identity of the weak electrolyte (acid or base);

- b) ratio of the buffer system components;
- c) concentration of the weak electrolyte (acid or base);
- d) concentration of salt.

Correct answers

1. The correct answer is a).

Henderson-Hasselbach equation for the system is as following:

$$\text{pH} = \text{p}K_{\text{HCN}} + \lg \frac{[\text{NaCN}]}{[\text{HCN}]}.$$

2. The correct answer is c).

The solution belongs to base buffer systems. The following equation is necessary to calculate its pH :

$$\begin{aligned} \text{pH} &= 14 - \text{p}K_{\text{NH}_4\text{O}i} - \lg \frac{[\text{NH}_4\text{Cl}]}{[\text{NH}_4\text{OH}]} = 14 - \text{p}K_{\text{NH}_4\text{OH}} - \lg \frac{\nu(\text{NH}_4\text{Cl})/V(\text{buffer solution})}{\nu(\text{NH}_4\text{OH})/V(\text{buffer solution})} = \\ &= 14 - \delta\hat{E}_{\text{NH}_4\text{OH}} - \lg \frac{\nu(\text{NH}_4\text{Cl})}{\nu(\text{NH}_4\text{OH})}; \end{aligned}$$

$$\nu(\text{NH}_4\text{Cl}) = C(\text{NH}_4\text{Cl}) \cdot V(\text{NH}_4\text{Cl}) = 0.25 \text{ mol/L} \cdot 0.02 \text{ L} = 0.005 \text{ mol};$$

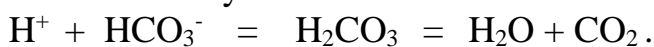
$$\nu(\text{NH}_4\text{OH}) = C(\text{NH}_4\text{OH}) \cdot V(\text{NH}_4\text{OH}) = 0.15 \text{ mol/L} \cdot 0.04 \text{ L} = 0.006 \text{ mol};$$

$$\text{pH} = 14 - 4.74 - \lg \frac{0.005}{0.006} = 9.26 - \lg 0.833 = 9.33$$

Therefore, pH of the buffer solution is 9.33.

3. The correct answer is d).

When a strong acid is added to the hydrocarbonate buffer solution, it reacts with sodium hydrocarbonate:



Thus the strong acid is substituted by an equivalent amount of weak carbonic acid and does not effect the pH value.

4. The correct answers are a) and b).

pH of a buffer system depends on the identity of the weak electrolyte (pK)

and the ratio of its components: $\left(\lg \frac{[\text{salt}]}{[\text{acid}]} \text{ or } \lg \frac{[\text{salt}]}{[\text{base}]} \right).$

Subject 8. Role of buffer solutions in biological systems

1. Importance

Blood, urine, saliva, extracellular fluid and other fluids of the human organism contain buffer systems to maintain stable pH. Certain disorders cause pH shift to acidic (acidosis) or alkaline (alkalosis). Buffer capacity is an important parameter of a buffer system because it shows how much acid or base can be neutralized by the buffer system. Potentiometric measurement of pH change is used to calculate buffer capacity.

2. Concrete aims

Explain the role of buffer systems in the maintenance of acid-base equilibrium in biological systems.

3. Basic knowledge and skills necessary to study the subject

Know classification and mechanism of action of buffer systems. Know pH scale and normal pH values of biological fluids. Be able to measure pH of solutions with potentiometric method.

4. Tasks for self-preparation for the lesson

4.1. Theoretical questions for the lesson:

1. Buffer systems of blood:
 - a) hydrogencarbonate (bicarbonate) buffer system;
 - b) phosphate buffer system;
 - c) protein buffer systems.
2. Buffer capacity and factors, that influence it.
3. Acid-base state of blood.

4.2. Practical work (task) done by students in class.

Potentiometric measurement of buffer capacity of blood plasma

The potentiometric measurement of buffer capacity of blood plasma is carried out with the ionometer EV-74, precalibrated with standard buffer solutions.

1. Preparation.

Press the buttons “t” and “-1 / 19”. Leave for 30 min.

Compose a galvanic circle with a measurement electrode and a comparison electrode. The measurement electrode is a glass electrode with H^+ function, the comparison electrode is a chlorinesilver electrode with constant potential 0.201V. Plug the electrodes in the sockets on the back side of the machine. Fix the electrodes over the magnet mixer. Titration is to be carried out in a 50 cm³ cup with a magnet inside.

Press the buttons ”anions / cations”, “pX” and the pH range button “4 / 9”.

2. Measurement of acid buffer capacity (B_{acid})

Pipet 20 mL of blood plasma into a cup with a magnet inside. Fill the burette with a titrated solution of HCl. Measure initial pH_0 . While mixing, add the acid until pH is changed for approximately 1 unit. Determine exact pH with the machine scale and exact volume of acid with the burette.

Calculate buffer capacity with the formula:

$$B_{\text{acid}} = \frac{C(\text{HCl}) \cdot V(\text{HCl})}{V(\text{plasma}) \cdot |\text{pH}_1 - \text{pH}_0|},$$

where $C(\text{HCl})$ is the normality of HCl solution (mol/L),
 $V(\text{HCl})$ is the volume of HCl solution, mL,
 $V(\text{plasma})$ is the volume of blood plasma, mL,
 $|\text{pH}_1 - \text{pH}_0|$ is the difference between pH data.

3. Measurement of alkali buffer capacity (B_{alkali})

Pipet 20 mL of blood plasma to a cup with a magnet inside. Fill the burette with a titrated solution of NaOH. Titrate as in the previous experiment. Register the obtained pH of blood plasma and used volume of NaOH.

Calculate with the formula:

$$B_{\text{acid}} = \frac{C(\text{NaOH}) \cdot V(\text{NaOH})}{V(\text{plasma}) \cdot |\text{pH}_1 - \text{pH}_0|},$$

where $C(\text{NaOH})$ is the normality of HCl solution (mol/L),
 $V(\text{NaOH})$ is the volume of HCl solution, mL,
 $V(\text{plasma})$ is the volume of blood plasma, mL,
 $|\text{pH}_1 - \text{pH}_0|$ is the difference between pH data.

4. Writing a report of the laboratory work

Calculate the acid and alkali buffer capacities, compare the obtained values and write down the conclusions.

Materials for self-control

1. Choose the group of buffer systems, which consists only of those of the human organism:
 - a) acetate, bicarbonate, phosphate;
 - b) protein, phosphate, amino acid;
 - c) ammonia, acetate, phosphate;
 - d) bicarbonate, phosphate, ammonia.
2. Explain the mechanism of buffering action of the phosphate buffer system:
 - a) phosphoric acid is an electrolyte of medium strength;
 - b) the salts, which form the phosphate buffer system, completely dissociate into ions;
 - c) dihydrophosphate ions dissociate like a weak acid;

- d) the salts that form phosphate buffer system are hydrolyzed, thus regulating pH.
3. Which factors effect buffer capacity:
- concentration, pH, nature of a buffer system;
 - concentration, ratio of components;
 - pH, temperature;
 - temperature, ratio of components, nature of the buffer system.
4. Change of acid-base balance caused by prolonged hypoventilation is called:
- respiratory acidosis;
 - respiratory alkalosis;
 - metabolic acidosis;
 - metabolic alkalosis.
5. Choose the pair of electrodes, which can be used to create a galvanic circle for potentiometric measurement of buffer capacity:
- chlorine silver and platinum;
 - glass and platinum;
 - hydrogen and hydrogen;
 - glass and chlorine silver.

Correct answers

1. The correct answer is b)
Among the given buffer systems only acetate and ammonia do not belong to buffer systems of the human organism. They are not present only in the answer b).
2. The correct answer is c)
Phosphate buffer system consists of two acidic salts: dihydrophosphate and hydrophosphate, which are related by the equation:

$$\text{H}_2\text{PO}_4^- = \text{H}^+ + \text{HPO}_4^{2-}.$$
Thus, the dihydrophosphate ion H_2PO_4^- is a weak acid and the hydrophosphate ion HPO_4^{2-} is the anion of the acid. Therefore, the action mechanism of the system corresponds to the one of a weak acid and its salt of a strong base.
3. The correct answer is b)
Buffer capacity shows ability of a system to maintain constant pH when alkalis and acids are added. It depends on concentration and ratio of components. The bigger the concentration of components, the more acids and alkalis can the buffer system neutralize without substantial shifts in pH.

4. The correct answer is a)

Hypoventilation results in increased CO_2 concentration in blood. It will cause decrease of pH. The phenomenon is called acidosis. It is caused by a respiration disorder and is called respiratory acidosis.

5. The correct answer is d)

A galvanic cell must consist of a measurement electrode, whose potential will depend on pH and a comparison electrode with a constant potential. The only correct pair is a glass electrode and a chlorine silver electrode. The glass electrode is the measurement electrode, the chlorine silver electrode is the comparison electrode.

Subject 9. Colligative properties of solutions

1. Importance

Colligative properties of solutions (diffusion, osmosis) are vital for the organism. Osmosis stipulates distribution of water and nutrients among different organs and tissues of the organism. Osmosis depends on the nature of membranes. Transportation of nutrients is possible due to selective permeability of membranes. Inside the cell osmotic pressure is bigger than in the extracellular fluid. Osmometric, criometric, and ebulliometric methods are used to study biological liquids, to measure their osmolality, average molecular mass of proteins and other physiologically active compounds.

2. Concrete aims

Analyze relationship of colligative properties and concentration of solutions.

3. Basic knowledge and skills necessary to study the subject

Know the theory of solutions.

Understand concentrations of solutions.

Know solutions of electrolytes and non-electrolytes, the theory of electrolytic dissociation, dissociation degree and dissociation constant.

Know structure of membranes.

Be able to draw schemes of diffusion and plasmolysis.

4. Tasks for self-preparation for the lesson

4.1. Theoretical questions for the lesson:

1. Colligative properties of diluted solutions of non-electrolytes:

a) Relative depression of the saturated vapor pressure of the solvent over the solution. Raoult's law;

b) Boiling point elevation and freezing point depression of solutions compared to pure solvents. Criometry, ebulliometry.

c) Osmosis. Osmotic pressure. Van't Hoff's law. Hemolysis and plasmolysis.

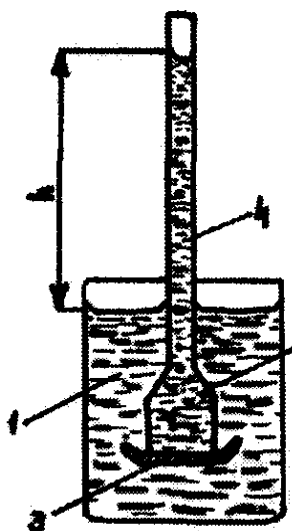
2. Colligative properties of diluted solutions of electrolytes. Isotonic coefficient. Hypo-, hyper- and isotonic solutions in medical practice.

3. Role of osmosis in biological systems. Osmotic pressure of blood plasma. Oncotic pressure.

4.2. Practical work (task) done by students in class

1. Measurement of osmotic pressure.

The simplest osmometer consists of a flask with distilled water (1) and a glass immersed in it (2). The glass (2) has a semipermeable membrane for the bottom (3). A capillary pipe (4) is attached to the top of the glass. Fill the glass with 1.5 M solution of sucrose. Add red color to the solution for better observation. Immerse the glass (2) in the water vessel (1) so that water levels in the flask and the capillary tube are the same.



The solution level in the capillary will go up due to osmosis. It will stop when a dynamic equilibrium is attained (when rates of water movement into the glass and out of the glass are equal). The column of the liquid in the capillary creates an additional hydrostatic pressure. Measure the height of the column in the capillary (h) from the level of the distilled water in the flask.

Calculate the osmotic pressure, which equals the hydrostatic pressure of the column of the liquid:

$$P_{\text{osm}} = P_{\text{hydr.}} \quad P_{\text{hydr.}} = \rho \times g \times h$$

where

ρ – density of the sucrose solution, kg/m^3 ;

g – acceleration of gravity, m/c^2 ;

h – height of the column of the liquid in the capillary, m.

Picture 1. Osmometer

Fill in the Table:

$\rho, \text{kg/m}^3$	$g, \text{m/c}^2$	h, m	$P_{\text{osm}}, \text{Pa}$
$1,14 \times 10^3$	9,8		

2. Observation of hemolysis and plasmolysis of erythrocytes

Add 2 mL 0.9% sodium chloride solution to a first test tube, 2mL 10% sodium chloride solution to a second test tube, 2 mL distilled water to a third test tube. Add two drops of blood to each test tube, stir the mixture with a glass stick. Place a drop of the solution from each test tube on a glass plate, cover it with another glass. With a microscope observe whether erythrocytes change shape.



Picture 2.

Decide, which of the schemes corresponds to plasmolysis and which one corresponds to hemolysis of erythrocytes, draw them in the notebook (Picture 2). Decide which solution was hypotonic, hypertonic and isotonic to blood.

3. Writing a report of the laboratory work

Draw the osmometer in the notebook. Calculate the osmotic pressure and fill in the chart.

Draw the schemes of hemolysis and plasmolysis of erythrocytes. Make a conclusion which solution was hypotonic, hypertonic and isotonic to blood.

Materials for self-control

1. What stipulates the osmotic pressure of the blood plasma?
2. What is the isotonic coefficient?
3. Why do fresh water in a river and salty water in a sea affect diver's eyes differently?
4. When is the first solution hypertonic to the second one?
 - a) 5 M sucrose and 5 M urea;
 - b) 1 M glucose and 0.1 M sucrose;
 - c) 0.1 M sucrose and 0.08 M potassium nitrate;
 - d) 0.1 M potassium nitrate and 0.8 M calcium chloride.
5. Over which of the solutions is the pressure of the saturated water vapor the biggest and leads to the smallest boiling temperature of the solution?
 - a) 0.4 M calcium chloride;
 - b) 1 M potassium chloride;
 - c) 0.4 M urea;
 - d) 1.0 M sucrose.

6. 13 g camphor was dissolved in 400 g diethyl ether, which led to 0.453° boiling point elevation. Calculate the molar mass of camphor.

Correct answers

- Osmotic pressure of the blood plasma is stipulated by concentration of electrolytes, low molecular non-electrolytes and biopolymers. Electrolyte cations and anions are the most important. Osmotic pressure of human blood plasma at 37 C° is 0.74-0.78 MPa. Colloidal particles and biopolymers are less important – to 0.004 MPa (0.5%). Constancy of the osmotic pressure of the blood is regulated by water evaporation at breathing, perspiration, kidney activity.
- The isotonic coefficient renders it possible to calculate colligative properties of electrolyte solutions, where number of particles increases due to dissociation. When 1.0 mole electrolyte dissociates completely (dissociation degree $\alpha = 1.0$), it furnishes n moles of ions, which behave as separate particles in the solution (for diluted solutions). The isotonic coefficient is calculated with the formula

$$i = 1 + \alpha(n-1).$$
- Total concentration of solutes (mostly salts) in eye tissues is greater than their concentration in fresh water but smaller than that in sea water. Upon exposure to fresh water the eye tissue swells due to osmosis. Upon exposure to sea water the eye tissue shrinks.
- The correct answer is b).
1.0 M glucose solution is hypertonic to 0.1 M sucrose solution, because it contains greater number of particles and its osmotic pressure is higher. For c) and d) it is necessary to take into account the dissociation degrees of the salts, which are strong electrolytes. In these cases the first solutions are hypotonic to the second solutions.
- The correct answer is c). 0.4 M urea solution contains the smallest number of particles. That is why the pressure of the saturated water vapor is the biggest over the solution.
- From the consequence of Raoult's law ($\Delta T_K = K_{EB} \cdot C_m$) the boiling point elevation of a solution (ΔT_K) is proportional to the molality (C_m) of the solute. Convert the formula so as to calculate the molar mass of the solute.

$$M = \frac{\hat{E}_{EB} \cdot m_{\text{solute}} \cdot 1000}{\Delta \hat{O}_{\hat{E}} \cdot m_{\text{solvent}}},$$

M – molar mass of camphor, g/mol;

K_{EB} – ebullioscopy constant of the solvent, kg·K/mol;

m_{solute}	–	mass of the solute, kg;
m_{solvent}	–	mass of the solvent, kg.
1000	–	the coefficient to change kilograms to grams.

For diethyl ester: $K_{\text{EB}} = 2.12 \text{ kg} \cdot \text{K/mol}$.

Do the calculations:

$$\Delta T_{\text{K}} = 0.453 \text{ K}; \quad m_{\text{solute}} = 0.013 \text{ kg}; \quad m_{\text{solvent}} = 0.4 \text{ kg};$$

$$M = \frac{2.12 \frac{\text{kg} \cdot \hat{\text{E}}}{\text{mol}} \cdot 0.013 \text{ kg} \cdot 1000}{0.453 \hat{\text{E}} \cdot 0.4 \text{ kg}} = 152 \text{ g/mol}.$$

Problems

Problem № 1

A solution contains 18g of solute in 500 mL water. Its osmotic pressure is 0.0456 MPa at 0°C. Calculate the molar mass of the solute.

Problem № 2

Calculate the freezing temperature of a solution which contains 1 mole urea per 1 kg water.

Problem № 3

Freezing temperature of a solution of 1.7 g zinc chloride in 0.25L water is -0.23° C. Calculate the isotonic coefficient of the solution.

Problem № 4

The osmotic pressure of blood plasma at 37° C is 0.77 MPa. How much sucrose is needed to prepare 0.5L solution that is isotonic to blood.

Thematical Module 2. Heterogeneous equilibriums in biological fluids

Subject 10. Thermodynamic basics of biochemical processes

1. Importance

Bioenergetics studies transformations of energy in the organism. The chemical energy of food products is the main source of energy for the organism. It is used in the internal processes: breathing, blood circulation, metabolism, secretion, temperature control, as well in doing external work. Chemical thermodynamics is the theoretical base for bioenergetics despite lots of specific characteristics of energy metabolism in the organism. Thermochemistry renders

it possible to measure energy values of food products, which is important in nutritiology. Laws and methods of thermochemistry are used to study heat effects of biochemical reactions.

2. Concrete aims

Explain chemical and biochemical processes with regard to their heat effects.

Be able to use thermodynamical functions for evaluation of directions of processes, explain energy coupling in living systems.

3. Basic knowledge and skills necessary to study the subject

Understand heat effects of reactions, endothermal and exothermal reactions.

Know the role of ATP as the primary source of energy in the organism.

Be able to compose equations of chemical reactions.

Understand the neutralization reaction.

Be able to measure temperature of solutions with a thermometer.

Be able to calculate caloric values of food products with caloric values of proteins, fat and carbohydrates.

4. Tasks for self-preparation for the lesson

4.1. Theoretical questions for the lesson:

1. Chemical thermodynamics as a science. Basic ideas:
 - thermodynamic systems and their types;
 - parameters of the state of the system (extensive, intensive);
 - processes (reversible, irreversible).
2. The First Law of Thermodynamics. Internal energy.
3. Enthalpy. Standard enthalpies (heats) of formation and combustion.
4. Thermochemistry. Hess' Law. Thermochemical transformations.
5. Thermochemical calculations and their applications for finding energy characteristics of biochemical processes.
6. The Second Law of Thermodynamics.
7. Entropy and its change in spontaneous processes.
8. The Gibbs energy and its change as the criteria of the spontaneous process.
9. Macroergic compounds. ATP as the universal source of energy for biochemical processes. Properties of macroergic bonds.

4.2. Practical work (task) done by students in class

1. Calorimetric measurement of the heat effect of the neutralisation reaction.

Calorimeters are used to measure heat effects of reactions. The simplest calorimeter consists of two porcelain cups (internal and external). The layer of air between them is thermoisolating. Let's assume, that the neutralisation heat

will be used to warm the solution, formed in the reaction, and the internal cup, the mass of which is known (m_{cup}).

Add 100 mL 1 M NaOH solution to the internal cup. Immerse the thermometer in the solution and record the temperature (t_1) after one or two minutes. Quickly add 100 mL 1 M HCl solution to the cup, assuming that it has the same temperature. Measure the maximal temperature of the obtained solution (t_2) with the thermometer.

Assume, that the densities of the solutions both of NaOH and HCl are equal (1 g/mL). Then the mass of the solution in the cup is as following:

$$m_{\text{solution}} = (V_{\text{NaOH}} + V_{\text{HCl}}) \cdot \rho = (100 \text{ mL} + 100 \text{ mL}) \cdot 1 \text{ g/mL} = 200 \text{ g}.$$

Record the m_{cup} , t_1 and t_2 in Table 8:

Table 8

Parameter	Name	Value
1. Mass of the internal cup	m_{cup}	
2. Mass of the solution Маса розчину	m_{solution}	200 g
3. Heat capacity of the cup	C_{cup}	1.087 J/g · grad
4. Heat capacity of the solution	C_{solution}	4.1 J/g · grad
5. Initial temperature	t_1	
6. Final temperature	t_2	

Calculate the total heat capacity (ΣC) of the cup and the solution in it:

$$\Sigma C = C_{\text{cup}} \cdot m_{\text{cup}} + C_{\text{solution}} \cdot m_{\text{solution}}, \quad \text{J/grad.}$$

Calculate the amount of heat released in the experiment:

$$q = (t_2 - t_1) \cdot \Sigma C, \quad \text{J.}$$

Calculate the amount of heat, that corresponds to the reaction of 1 mole NaOH with 1 mole HCl, taking into account, that 100 mL NaOH and HCl solutions contain 0.1 mole of substance respectively.

$$Q = q \cdot \frac{1}{0.1} \cdot 10^{-3}, \quad \text{kJ.}$$

2. Compose thermochemical equation of neutralization reaction

Write the thermochemical equation of the neutralisation reaction in the molecular and short ionic forms with the thermodynamical system of symbols of heat effects, taking into account that $H = -Q$.

3. Writing a report of the laboratory work

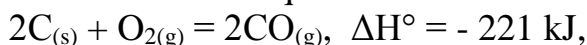
Write the necessary calculations of measurement of the heat effect of neutralization reaction in the notebook, fill out Table 8, write a thermochemical equation of the neutralization reaction in the molecular and short ionic forms.

Materials for self-control

- When the reaction is endothermal:
 - when the energy of products is equal to the energy of initial substances;
 - when the energy of products is higher than the energy of initial substances;
 - when the energy of products is lower than the energy of initial substances;
 - it is possible to determine only when it is known whether energy is absorbed or released.
- Choose thermochemical equations of exothermal reactions:
 - $\text{O}_2 + 1/2\text{O}_2 = \text{O}_3$; $\Delta H = 142 \text{ kJ}$;
 - $1/2\text{O}_2 + \text{H}_2 = \text{H}_2\text{O}(\text{g})$; $\Delta H = -242 \text{ kJ}$;
 - $\text{H}_2\text{O} + 1/2\text{O}_2 = \text{H}_2\text{O}_2$; $\Delta H = 98.2 \text{ kJ}$;
 - $\text{H}_2 + 1/2\text{O}_2 = \text{H}_2\text{O}(\text{l})$; $\Delta H = -285.8 \text{ kJ}$.
- Choose the substance with zero standard enthalpy of formation:
 - $\text{Br}_2(\text{g})$;
 - $\text{Br}_2(\text{l})$;
 - $\text{Br}_2(\text{s})$;
 - $\text{HBr}(\text{g})$.
- Calculate the heat effect of the reaction:
 $\text{C}(\text{s}) + 2\text{N}_2\text{O}(\text{g}) = \text{CO}_2(\text{g}) + 2\text{N}_2(\text{g})$,
if 22 g of N_2O take part in the reaction and the enthalpies of formation are:
 $\Delta H_{\text{f},298}^0(\text{N}_2\text{O}(\text{g})) = 81.55 \text{ kJ/mol}$; $\Delta H_{\text{f},298}^0(\text{CO}_2(\text{g})) = -393.51 \text{ kJ/mol}$:
 - 475.1 kJ;
 - 139.2 kJ;
 - 278.3 kJ;
 - 556.61 kJ.
- Decide about the change of entropy in the reactions:
 - $2\text{C}(\text{s}) + \text{O}_2(\text{g}) = 2\text{CO}_2(\text{g})$;
 - $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) = 2\text{H}_2\text{O}(\text{g})$.
 1. $\Delta S > 0$; 2. $\Delta S < 0$;
 1. $\Delta S < 0$; 2. $\Delta S > 0$;
 1. $\Delta S > 0$; 2. $\Delta S > 0$;
 1. $\Delta S < 0$; 2. $\Delta S < 0$.
- Calculate the caloric value of 200g margarine, that contains 0.3% protein, 82.3% fat and 1% carbohydrate, if 1g protein or 1g carbohydrate releases 17.18 kJ in the organism, and 1g fat releases 38.97 kJ in the organism.
- Decide about the changes of enthalpy and entropy, at which the reaction is spontaneous at any temperature:
 - $\Delta H > 0$, $\Delta S > 0$;
 - $\Delta H < 0$, $\Delta S < 0$;

- c) $\Delta H > 0$, $\Delta S < 0$;
 d) $\Delta H < 0$, $\Delta S > 0$.

8. Predict the temperature at which the process can happen spontaneously, if its thermochemical equation is as following:



and the standard entropies of the substances are as following:

$$S^\circ (\text{C}_{(s)}) = 5.74 \text{ J}/(\text{mol} \cdot \text{K});$$

$$S^\circ (\text{O}_{2(g)}) = 205.17 \text{ J}/(\text{mol} \cdot \text{K});$$

$$S^\circ (\text{CO}_{(g)}) = 197.68 \text{ J}/(\text{mol} \cdot \text{K});$$

- a) it is only possible at standard temperature;
 b) it takes place at any temperature;
 c) it is not possible at standard temperature;
 d) it is impossible at any temperature.

Correct answers

1. The correct answer is b).

The endothermic reaction is accompanied by an absorption of heat, that is why the energy of the products is higher than the energy of the reactants.

2. The correct answers are b) and d).

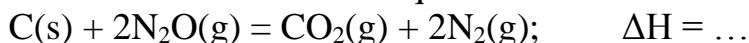
Exothermic reactions are accompanied by release of heat and for them the change of enthalpy is positive and the heat content in the system (enthalpy) decreases.

3. The correct answer is b).

The standard enthalpy (heat) of formation of a substance ($\Delta H_{f,298}^\circ$) is zero for simple substances, if they are stable at the standard conditions. Bromine is the only simple substance in the answers. Its stable state at the standard conditions is liquid, thus only for $\text{Br}_2(l)$ $\Delta H_{f,298}^\circ$ is zero.

4. The correct answer is b).

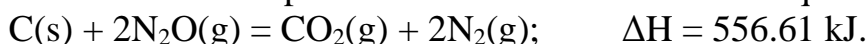
Write the thermochemical equation of the reaction:



Calculate the heat effect with the consequence of Hess' law. The standard enthalpies of formation of $\text{N}_2(g)$ and $\text{C}(s)$ are zero. We have:

$$\Delta H = \Delta H_{f,298}^\circ (\text{CO}_2(g)) - 2 \cdot \Delta H_{f,298}^\circ (\text{N}_2\text{O}(g)) = -393.51 - 2 \cdot (81.55) = -556.61 \text{ kJ}.$$

Therefore the complete form of the thermochemical equation is as following:



22 g N_2O is 0.5 mol ($M(\text{N}_2\text{O}) = 44 \text{ g/mol}$), four times less heat will be released.

$$\Delta H_1 = \frac{\Delta H \cdot 0.5 \text{ mol}}{2 \text{ mol}} = 1/4 \Delta H = \frac{-556.61 \text{ kJ}}{4} = -139.2 \text{ kJ}.$$

5. The correct answer is a).

The entropy of a substance depends on its aggregative state and decreases as following in the row: gas – liquid – solid. For an approximate qualitative assessment of the entropy change in the chemical reaction it is possible to compare the quantity of moles of gaseous substances before and after the reaction. The more moles of gas, the bigger the entropy. Thus in the first reaction we have 1 mole of gas in the right part of the reaction and 2 moles in the left part. Therefore $\Delta S > 0$. In the second reaction there will be less gas in the right part than in the left. Therefore $\Delta S < 0$ ($\Delta S = \Sigma S$ (products) – ΣS (reactants)).

6. Calculate the mass of protein, fat and carbohydrate in the margarine:

$$m(\text{protein}) = \frac{200 \text{ g} \cdot 0.3\%}{100\%} = 0.6 \text{ g} ;$$

$$m(\text{fat}) = \frac{200 \text{ g} \cdot 82.3\%}{100\%} = 164.6 \text{ g} ;$$

$$m(\text{carbohydrate}) = \frac{200 \text{ g} \cdot 1\%}{100\%} = 2.0 \text{ g}.$$

Calculate the total caloric value of 200 g margarine:

$$Q = (0.6 \text{ g} + 2.0 \text{ g}) \cdot 17.18 \text{ kJ/g} = 164.6 \text{ g} \cdot 38.97 \text{ kJ/g} = 44.67 \text{ kJ} + 6414.46 \text{ kJ} = 6459.13 \text{ kJ}.$$

Therefore the organism will receive 6459.13 kJ energy from complete oxidation of 200 g margarine.

7. The correct answer is d).

A reaction takes place spontaneously, if $\Delta G < 0$. The change of the Gibbs energy can be calculated with the equation:

$$\Delta G = \Delta H - T \cdot \Delta S$$

ΔG is negative regardless of temperature, if $\Delta H < 0$ and $\Delta S > 0$.

8. The correct answer is b).

The change of enthalpy of the reaction is known ($\Delta H = -221 \text{ kJ}$). Calculate the change of entropy. The change of entropy of the reaction ΔS° is calculated as the difference between the sum of the standard entropies of the products and the sum of the standart entropies of the reactants with their stoichiometric indices:

$$\Delta S = 2 \cdot S^\circ(\text{CO}_{(g)}) - 2 \cdot S^\circ(\text{C}_{(s)}) - S^\circ(\text{O}_{2(g)}) = 2 \cdot 197.68 - 2 \cdot 5.74 - 205.17 = 395.36 - 11.48 - 205.17 = 178.71 \text{ J}/(\text{mol} \cdot \text{K}) = 0.1787 \text{ J}/(\text{mol} \cdot \text{K}).$$

Calculate the change of the Gibbs energy of the reaction: ($\Delta G^0 = \Delta H^0 - T\Delta S^0$):

$$\Delta G^{\circ} = \Delta H^{\circ} - 298 \cdot \Delta S = -221 - 298 \cdot 0.1787 = -274.25 \text{ (kJ)}.$$

As far as $\Delta G^{\circ} < 0$, it can be concluded that the reaction takes place spontaneously at standard temperature (298 K). Nevertheless, as far as $\Delta H^{\circ} < 0$ and $\Delta S^{\circ} > 0$, the reaction is spontaneous at any temperature.

Subject 11. Kinetic basis of biochemical processes

1. Importance

Chemical kinetics is the basis for studying rates and mechanisms of biochemical reactions. Rates of biochemical reactions inform about enzymic activity, which is important for correct diagnosis and helps to use enzymes in treatment of diseases. Methods of chemical kinetics render it possible to measure rates of uptake and excretion of medical substances. It is important to know half life of substances to determine shelf life of medicines, accumulation of radionuclides, pesticides and other harmful substances in the environment. Methods of chemical kinetics help to choose optimal conditions for neutralization and utilization of pollutants as well as control pollution of the environment. Knowledge of theoretical basics of chemical kinetics aids students in study of biochemistry, pharmacology, hygiene.

2. Concrete aims

Analyze effects of concentration and temperature on the reaction rate.

Explain effect of activation energy on the reaction rate.

Analyze characteristics of catalyst action and explain the mechanisms of homogeneous and heterogeneous catalysis

Explain the mechanisms of action of enzymes and analyze effects of enzyme and substrate concentrations on rates of enzymatic processes.

3. Basic knowledge and skills necessary to study the subject

Write kinetic equations of simple and complex reactions, homogeneous and heterogeneous reactions.

Understand reaction rate, activation energy, catalysis and catalysts.

4. Tasks for self-preparation for the lesson

4.1. Theoretical questions for the lesson:

1. The rate of chemical reactions. The Law of mass action for rate of chemical reactions. The rate constant.
2. The order of a reaction. Reactions of first and second order. Reactions of zero order. The period of half-life.
3. Simple and complex reactions (subsequent, parallel, conjugated, reversible, chain). Photochemical reactions and their role in the life.

4. Effect of temperature on the reaction rate. The temperature coefficient. The Van't Hoff's rule. Characteristics of the temperature coefficient in biochemical processes.

5. The activation energy. The theory of active collisions and the theory of the transition state. The Arrhenius' equation.

6. Homogeneous and heterogeneous catalysis. Mechanism of catalytic action. Role of catalysis in the metabolic processes.

7. Enzymes as catalysts of biochemical reactions. Effects of enzyme and substrate concentration, temperature and pH on enzymic reactions.

4.2. Practical work (task) done by students in class

1. Determine the effect of the concentrations of reactants on the reaction rate

The experiment is based on the formation of sulfur insoluble in water. The equation of the reaction is as following:



1 N solutions are used.

Add sodium thiosulfate solution and distilled water to three retorts as shown in the table 11 below. Add 10 mL sulfuric acid solution to three test tubes. In turn add the contents of a test tube to each of the retorts and note the time (τ) from the moment of the mixing to the first signs of turbidity. Fill in the table. Calculate the symbolic reaction rate with the equation: $v = \frac{1}{\tau}$.

Table 11

Volume of solutions, mL			Time τ , s	Symbolic reaction rate v , s^{-1}
First series		Second series		
$\text{Na}_2\text{S}_2\text{O}_3$	H_2O	H_2SO_4		
10	20	10		
20	10	10		
30	–	10		

Make a conclusion about the effect of the concentrations of reactants on the rate of a homogeneous reaction.

2. Determine the effect of the temperature on the reaction rate

The equation of the reaction of formation of water insoluble sulfur is the same:



0.5 N solutions are used.

Add 5 mL sulfuric acid solution to three dry test tubes (the first series of solutions). Add 5 mL sodium thiosulfate to three other test tubes (the second series). Measure the temperature in the both sets of tubes with a thermometer (the

temperature of the both solutions is the same). Mix the contents of two test tubes from the both series and note the time (τ) from the moment of the mixing to the first signs of turbidity. Heat the rest of the test tubes in water until the temperature is 10 C° higher than the initial temperature. Repeat the procedure with two test tubes from the both series. Heat the last two test tubes 10 C° more and repeat the procedure again.

Fill in table 12 with the results and calculate the symbolic reaction rate for each temperature.

Table 12

Temperature $t, ^\circ\text{C}$	Time τ, s	Symbolic reaction rate ν, s^{-1}

Make a conclusion about the effect of temperature on the symbolic reaction rate.

3. Catalytic reduction of ferric thiocyanate

Add 3 mL KCNS or NH₄CNS solution and three drops of Fe(SCN)₃ solution to each of two test tubes. Add two drops of CuSO₄ solution to one of the test tubes. Then add 3ml sodium thiosulfate solution to each of the tubes. Compare the rate of decoloration in the both tubes and make a conclusion as to which substance is a catalyst and what kind of catalysis it is.

Balance the equation of the reaction:



4. Decomposition of hydrogen peroxide in the presence of a heterogeneous catalyst

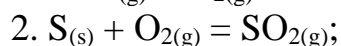
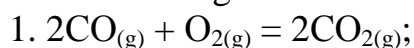
Add a small amount of PbO₂ or MnO₂ powder to two mL hydrogen peroxide solution. Watch the vigorous release of oxygen. Write an equation of the reaction of catalytic decomposition of hydrogen peroxide. Make a conclusion as to which substance is a catalyst and what type of catalysis it is.

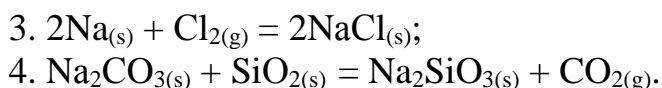
5. Writing a report of the laboratory work

Write necessary reaction equations in the notebook, fill in tables 11 and 12, write conclusions to each experiment.

Materials for self-control

1. Choose heterogenous reactions:





- a) 1, 2, 3;
- b) 2, 3, 4;
- c) 1, 3, 4;
- d) 1, 2, 4.

2. The rate constant depends on:

- a) temperature and concentrations;
- b) identity of reactants and concentrations;
- c) temperature and nature of reactants;
- d) identity of reactants, temperature and concentrations.

3. Choose the correct kinetic equation for the direct reaction:

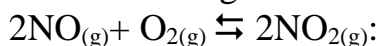


- a) $v = k \cdot [\text{CaCO}_3]$;
- b) $v = k \cdot [\text{CaO}] \cdot [\text{CO}_2]$;
- c) $v = k \cdot [\text{CO}_2]$;
- d) $v = k$.

4. Decide, how the rate of the direct reaction changes $2\text{NO}_{(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{NO}_{2(g)}$, if the volume of the reaction mixture decreases three times.

- a) 9 times decrease;
- b) 9 times increase;
- c) 27 times decrease;
- d) 27 times increase.

5. Determine the general order of the direct reaction:



- a) 5;
- b) 3;
- c) 2;
- d) 1.

6. Calculate, how many times the reaction accelerates with the temperature increase from 20 to 70C°, if the temperature coefficient of the reaction rate is 3.

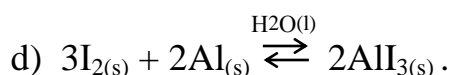
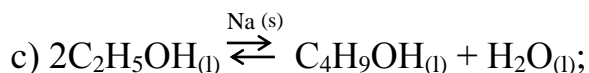
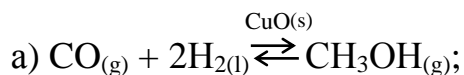
- a) 15;
- b) 81;
- c) 243;
- d) 729.

7. The reaction rate changes upon addition of a catalyst to the system, because:

- a) reaction products are formed;

- b) the temperature of the system increases;
- c) the activation energy of reactants decreases;
- d) concentration of reactants changes.

8. Choose equations of heterogeneous catalytic reactions:



9. Enzymes have specificity, because:

- a) they can accelerate only one specific reaction;
- b) they can accelerate reactions of a certain type (oxidation, hydrolysis);
- c) they can accelerate all reactions of the substrate;
- d) they can accelerate all reactions at certain pH.

10. Which of the following effects is caused by a significant temperature increase in activity of inorganic catalysts and enzymes?

- a) activity of inorganic catalysts increases, activity of enzymes decreases;
- b) activity of inorganic catalysts mostly increases, activity of enzymes ceases;
- c) activities of both inorganic catalysts and enzymes increase;
- d) activity of inorganic catalysts does not change, activity of enzymes first increases, than ceases.

11. How does activity of enzymes depend on the change of pH of the medium?

- a) change of pH does not affect activity of enzymes;
- b) decrease of pH increases activity of enzymes;
- c) change of pH causes inactivation of enzymes;
- d) change of pH can increase or decrease activity of an enzyme depending on its structure and nature.

Correct answers

1. The correct answer is b).

In heterogeneous reactions reactants belong to different phases. These are reactions between a gas and a liquid, a gas and a solid, two nonmiscible liquids, two solids.

2. The correct answer is c).

The rate constant always depends only on the identity of reactants and temperature. It equals the reaction rate when the concentrations equal one mol/L.

3. The correct answer is d).

Formal kinetic equations for heterogeneous reactions do not include concentrations of substances in condensed phases. The left part of the equation includes a solid substance only, and that is why the equation is $v = k$. From the formal point of view the rate of the reaction at constant temperature is constant.

4. The correct answer is d).

The kinetic equation for the reaction rate is:

$$v = k [\text{NO}]^2 \cdot [\text{O}_2].$$

Due to the volume decrease the concentrations of the gases rise 3 times. That is why the new rate is:

$$v_1 = k(3[\text{NO}])^2 \cdot 3[\text{O}_2] = 27k[\text{NO}]^2 \cdot [\text{O}_2] = 27v.$$

Therefore the reaction rate increases 27 times.

5. The correct answer is b).

The general order of a reaction is the sum of concentration indices in a kinetic equation (see the previous question). In this case it is $2 + 1 = 3$.

6. The correct answer is c).

According to the Van't Hoff's rule the change of concentration depends on the temperature change as following:

$$\frac{v_{\dot{0}_2}}{v_{\dot{0}_1}} = \gamma^{\frac{\dot{0}_2 - \dot{0}_1}{10}},$$

where:

T_1 and T_2 are initial and final temperatures;

$v_{\dot{0}_1}$ and $v_{\dot{0}_2}$ are the initial rate and the rate after the temperature change;

γ is the temperature coefficient of the reaction rate.

Calculate the equation with the given data, and you will have:

$$\frac{v_{70}}{v_{20}} = 3^{\frac{70-20}{10}} = 3^5 = 243, \quad \text{або} \quad v_{70} = 243 \cdot v_{20}.$$

Therefore the reaction rate will grow 243 times.

7. The correct answer is c).

A catalyst introduces a new way for a reaction (mostly because of the formation of an intermediate compound between the catalyst and one of the

reactants), for which the activation energy is significantly lower. It has been proved experimentally that 75.3 kJ/mol of energy is needed for the decomposition of hydrogen peroxide for hydrogen and oxygen without a catalyst. With colloidal platinum as a catalyst the activation energy decreases to 49.9 kJ/mol. Enzymatic catalysis lowers the energy to 23 kJ/mol.

8. The correct answers are a), c), d).

In heterogeneous catalysis the reactants and the catalyst are in different phases, there is a phase interface between them, and the reaction takes place on the surface. The reaction of homogeneous catalysis b) is in the gaseous phase and the reaction takes place in the whole volume.

9. The correct answer is a).

Catalysts are specific. They can only accelerate a single specific reaction. Enzymes are extremely specific. The enzyme that catalyzes sucrose hydrolysis does not catalyze starch hydrolysis despite of the fact that the both substances are carbohydrates and contain D-glucose. Different catalysts or enzymes catalyze formation of different products from the same initial substances. It is possible to obtain 40 different substances from ethyl alcohol. The human organism contains thousands of different enzymes. They are organized in complex enzymatic systems that ensure chains of subsequent changes. Lack of specification in enzymes would result in a complete disarray of metabolism.

10. The correct answer is b).

It has been proved, that activity of inorganic catalysts increases as temperature rises. Most of them work very well at high temperatures (500-1000°C). Enzymes can only work in a narrow temperature range, mostly 10-60°C. Optimal temperature for enzymes is 40°C. As the temperature increases, the activity of enzymes decreases. At more than 70°C enzymes are completely inactivated, mostly because of the denaturation of the protein structure.

11. The correct answer is c).

Enzymes are mostly proteins, therefore their structure depends on pH, and their activity in its turn depends on their structure. Enzymes are active in a rather narrow range of pH. For example, urease is active at pH = 6.7, pepsin is active at pH = 1.5 – 2.0, arginase is active at pH = 9.5 – 9.9. A significant change of pH inactivates enzymes.

Subject 12. Reactions of formation and dissolution of precipitates. Chemical equilibrium

1. Importance

Chemical equilibrium plays an important role in the homeostasis of the organism. Effect of different factors (concentrations of substances, pressure, temperature) can shift equilibrium state. To know the theory of chemical equilibrium is important for understanding conditions of formation and dissolution of precipitates, for instance, formation of kidney stones (nephrocalcinosis) or gallbladder stones. The knowledge renders it possible to define correct prophylaxis and treatment.

2. Concrete aims

Analyze chemical equilibrium and explain its conditions in the thermodynamic and kinetic aspects.

Explain effects of external factors on chemical equilibrium.

Analyze conditions of formation and dissolution of precipitates. Explain the role of heterogeneous equilibria with participation of salts in the total homeostasis of the organism.

3. Basic knowledge and skills necessary to study the subject

Be able to write equations of reversible reactions.

Know the Law of mass action for the rate of homogeneous and heterogeneous reactions.

Be able to write kinetic equations for reaction rate.

Know the definition of rate constant.

Know reactions of precipitation and dissolution.

Be able to write equations of dissociation of substances, dissociation constant and ionic product.

4. Tasks for self-preparation for the lesson

4.1. Theoretical questions for the lesson:

1. Chemical equilibrium. Thermodynamic conditions of equilibrium. Prediction of direction of spontaneous processes.

2. Exergonic and endergonic processes in the organism.

3. The Law of mass action. The constant of chemical equilibrium.

4. The Le Chatelier's principle. Prediction of shifts of chemical equilibrium.

5. The solubility product.

6. Conditions of formation and dissolution of precipitates.

Materials for self-control

1. Change of which of the factors can lead to a change of the equilibrium constant?

a) pressure;

- b) temperature;
 c) concentration;
 d) identity of reactants.
2. How will the rates of the direct and reverse reactions $2\text{SO}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{SO}_{3(g)}$ change, if the volume of the vessel, in which the reactions are in equilibrium, is decreased two times.
- a) the rates will be the same;
 b) the rate of the direct reaction will be two times bigger than the rate of the reverse reaction;
 c) the rate of the direct reaction will be two times smaller than the rate of the reverse reaction;
 d) the rate of the direct reaction will be 1.5 times bigger than the rate of the reverse reaction.
3. Which changes shift the equilibrium in the system to the left:
 $4\text{HCl}_{(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{Cl}_{2(g)} + 2\text{H}_2\text{O}_{(g)}$.
- a) increase of the concentration of oxygen;
 b) increase of the concentration of chlorine;
 c) increase of the general pressure;
 d) decrease of the volume of the vessel.
4. In which direction does the equilibrium shift in the system, if the general pressure is increased: $4\text{Fe}_{(s)} + 3\text{O}_{2(g)} \rightleftharpoons 2\text{Fe}_2\text{O}_{3(s)}$.
- a) to the left;
 b) to the right;
 c) no change.

Correct answers

1. The correct answers are b) and d).

The constant of the chemical equilibrium K_{eq} equals the rate constant of the direct reaction k_1 divided by the rate constant of the reverse reaction k_2 :

$$\hat{E}_{\text{eq}} = \frac{k_1}{k_2}.$$

As far as each of the rate constants depends only on the nature of the reactants and the temperature, the equilibrium constant also only depends on these factors. Changes of concentrations and pressure do not cause the change of the equilibrium constant, but can cause the shift of the equilibrium.

2. The correct answer is b).

In the equilibrium state the rates of the direct and reverse reactions were equal:

$$v_1 = v_2, \quad v_1 = k_1[\text{SO}_2]^2[\text{O}_2], \quad \text{a} \quad v_2 = k_2[\text{SO}_3]^2.$$

When the volume is two times decreased, the concentrations (or partial pressures) of the gases increases two times. Therefore the rate of the direct reaction increases eight times:

$$v_1' = k_1(2[\text{SO}_2])^2 \cdot 2[\text{O}_2] = 8k_1 [\text{SO}_2]^2 [\text{O}_2] = 8v_1,$$

The rate of the reverse reaction increases four times:

$$v_2' = k_2(2[\text{SO}_3])^2 = 4k_2[\text{SO}_3]^2 = 4v_2.$$

Therefore the rate of the direct reaction is two times bigger than the rate of the reverse reaction, and the equilibrium shifts to the right.

3. The correct answer is b).

According to the Le Chatelier's principle it is necessary to increase the concentration of the reaction products in order to shift the equilibrium to the right. The products are chlorine and water (gas). An increase of the concentration of oxygen shifts the equilibrium to the right. An increase of the general pressure or a decrease of the volume causes the equilibrium shift to the right, in the direction of the reaction products, because the amount of gaseous substances, which are responsible for the pressure in the system, is smaller on the right than on the left.

4. The correct answer is b).

It is a heterogeneous system and the pressure in it is caused only by the gaseous oxygen. According to the Le Chatelier's principle the increase of the pressure in the system causes a shift in the direction to smaller amount of gaseous substances. In this case it is to the right.

Subject 13. Formation of complexes in heterogeneous systems

1. Importance

Coordination compounds have specific structure and bond type. A great many compounds in nature are classified as coordination compounds because of their structure, properties and biological activity. Metal-containing enzymes, hemoglobin, myoglobin, vitamin B₁₂ are biologically active coordination compounds.

A specific group of compounds, that are able to form complexes with many cations, is widely used to dissolve stones in the kidneys and the gall bladder. They are used as stabilizers in blood conservation, because they bind the metal ions, which catalyze oxidation reactions. They are also used to remove ions of toxic metals and radioactive isotopes from the organism.

Knowledge of structure of coordination compounds is necessary in the study of biochemistry, pharmacology, hygiene and medical subjects.

2. Concrete aims

Explain principles of structure of coordination compounds.

Explain characteristics of structure of coordination compounds for their application in chelation therapy.

3. Basic knowledge and skills necessary to study the subject

To know the theory of structure of coordination compounds and their nomenclature.

To be able to write formulas of coordination compounds and equations of reactions of their formation and dissociation.

4. Tasks for self-preparation for the lesson

4.1. Theoretical questions for the lesson:

1. Modern theory of structure of coordination compounds.
2. Classification of coordination compounds by the identity of the ligands.
3. Classification of coordination compounds by the charge of the internal sphere.
4. Constants of instability and stability of coordination ions.
5. Internal coordination compounds.
6. Coordination compounds in biological systems. The structure of hemoglobin.
7. Complexons and their applications in medicine as antidotes in poisoning with heavy metals (chelation therapy).

4.2. Practical work (task) done by students in class

1. Obtaining of coordination compound $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$

Add an NH_4OH solution by drops to 1 mL of a CuSO_4 solution until a precipitate of cupric hydroxide is obtained. Dissolve the obtained precipitate in the excess of NH_4OH . A coordination compound is obtained, which contains the complex ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

Write an equation of the reaction of formation of the coordination compound. Name the compound.

2. Obtaining of coordination compound $\text{Na}_2[\text{Sn}(\text{OH})_4]$

Add a NaOH solution by drops to 1 mL of a SnCl_2 solution until a precipitate is obtained. Dissolve the obtained precipitate in the excess of NaOH . A coordination compound is obtained, which contains the complex ion $[\text{Sn}(\text{OH})_4]^{2-}$. Write an equation of the reaction of formation of the coordination compound. Name the compound.

3. Obtaining of coordination compound $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$

Add several drops of potassium ferrocyanate (II) $\text{K}_4[\text{Fe}(\text{CN})_6]$ to 1 mL of a FeCl_3 solution. A blue precipitate of "prussian blue" $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ is obtained. Write an equation of the reaction of formation of the coordination compound. Name the compound.

4. Obtaining of coordination compound $(\text{NH}_4)_2[\text{Co}(\text{SCN})_4]$

Add 1 mL of a CoSO_4 solution to 1 mL of ammonium thiocyanate NH_4SCN solution. A bright blue coordination compound $(\text{NH}_4)_2[\text{Co}(\text{SCN})_4]$ is obtained. Write an equation of the reaction, name the obtained coordination compound.

5. Writing a report of the laboratory work

Write the necessary reaction equations and names of coordination compounds in the notebook.

Materials for self-control

- Coordination number is:
 - the number of bonds of the ligands with the central atom;
 - number of sites, occupied by the ligands in the internal coordination sphere of the complex;
 - number of particles in one mole of a substance;
 - number of nuclons in the nucleus.
- Choose the central atom, its oxidation level, the coordination number and the charge of the coordination ion in the compound $\text{K}[\text{Cr}(\text{H}_2\text{O})_2(\text{CN})_4]$
 - K, +1, 4, -1;
 - Cr, +3, 6, -1;
 - H_2O , 0, 6, -1;
 - Cr, +2, 4, 0.
- The bond between the central atom and ligands in most coordination ions is:
 - ionic;
 - covalent;
 - hydrogen;
 - metallic.
- Instability constants (C_I) of cyanide complexes with certain metals are as following:
$$C_I[\text{Ag}(\text{CN})_2]^- = 1 \cdot 10^{-21};$$
$$C_I[\text{Hg}(\text{CN})_4]^{2-} = 3 \cdot 10^{-42};$$
$$C_I[\text{Cd}(\text{CN})_4]^{2-} = 7,7 \cdot 10^{-18};$$
$$C_I[\text{Fe}(\text{CN})_6]^{4-} = 1 \cdot 10^{-24}.$$
Decide, which of the metal cations forms the most stable cyanide complex:
 - Ag^+ ;
 - Cd^{2+} ;
 - Hg^{2+} ;
 - Fe^{2+} .

5. Which of the ions Fe^{2+} , Fe^{3+} , Cl^- , HCO_3^- , K^+ , Ca^{2+} , Na^+ , Cu^{2+} , Zn^{2+} are central atoms in coordination compounds in the enzymes.
- K^+ , Na^+ , Cl^- ;
 - K^+ , Ca^{2+} , Na^+ ;
 - Fe^{2+} , Fe^{3+} , Ca^{2+} , Cu^{2+} , Zn^{2+} ;
 - Cl^- , HCO_3^- .
6. Which of the functions is not characteristic for hemoglobin?
- binding of oxygen molecules with ferrous ions and transport of it from the lungs to the muscle;
 - transfer of oxygen to myoglobin molecules in the muscle;
 - binding of carbon dioxide and its transport to the lungs;
 - transport of electrons.

Correct answers

- The correct answer is a).
- The correct answer is b).
 Cr^{3+} is the coordination agent, the coordination number (number of ligands H_2O and CN^-) is 6, the charge of the coordination ion $[\text{Cr}^{3+}(\text{H}_2\text{O})_2^0(\text{CN})_4]^-$ is -1 :
 $+3 + 2 \cdot 0 + 4 \cdot (-1) = -1$.
- The correct answer is b).
 The most common chemical bond between a coordination agent and ligands is covalent, formed by the donor-acceptor mechanism. Ligands are mostly donors of electron pairs and the central atom is the acceptor.
- The correct answer is c).
 The instability constant (C_I) of a coordination ion is its dissociation constant. If the constant is small, it means that the coordination ion dissociates to lesser degree and is therefore more stable. The mercury cyanide ion $[\text{Hg}(\text{CN})_4]^{2-}$ has the smallest constant C_I ($3 \cdot 10^{-42}$) among the others given, so it is the most stable one.
- The correct answer is c).
 Ions of d-elements and of the s-element calcium are most common coordination agents in enzymes and other proteins.
- The correct answer is d).
 Unlike myoglobin, the only function of which is oxygen transport, hemoglobin has several functions. Beside oxygen transport, hemoglobin carries 3-10% of carbon dioxide from the tissues as the carbamine form, where carbon dioxide reacts with the N-terminus of the polypeptide chain of

globin. Release of oxygen by hemoglobin is stimulated by the elevated concentration of hydrogen ions, which react with hemoglobin. Therefore hemoglobin transports H^+ from tissues to the lungs. Binding of oxygen does not normally cause oxidation of Fe^{2+} to Fe^{3+} . That's why, unlike cytochromes, hemoglobin does not transport electrons. Hemoglobin, which contains ferric ion, loses the ability to transport oxygen.

Subject 14. Measurement of electrode potentials

1. Importance

Study of the mechanisms of formation of the electrode, diffusion, membrane and oxidation-reduction potentials, as well as their responses to various external factors renders it possible to understand mechanisms of most biochemical reactions. Measurement of biopotentials is applied in such important diagnostical methods as electrocardiography, electroencephalography and others. Concentrations of physiologically active ions (H^+ , K^+ , Na^+ , Ca^+ , Cl^- , NO_3^-) in biological fluids and tissues of the organism are measured with EMF values.

Electrochemical methods of analysis (polarography, potentiometric and amperometric titration) are widely applied in medical and biological research. Therefore doctors need the knowledge of the basics of electrochemistry for professional activities.

2. Concrete aims

Explain the mechanism of formation of the electrode potentials.

Analyze electrochemical processes in the mouth.

Analyze the principle of the potentiometry method and make conclusions about its applications in medical and biological research.

Be able to measure oxidation-reduction potentials and predict direction of oxidation-reduction reactions.

3. Basic knowledge and skills necessary to study the subject

Have understanding of the electrochemical cell, the electrode and the electrode potential.

To know the principle of the method and have skills of potentiometric measurements of pH of biological fluids with an ionometer.

To be able to compose equations of oxidation-reduction reactions.

4. Tasks for self-preparation for the lesson

4.1. Theoretical questions for the lesson:

1. Electrode processes and the mechanism of their formation.
2. The Nernst equation. The standard electrode potential.

3. The standard hydrogen electrode.
4. Electrochemical cells. Electrode processes in the mouth.
5. Measurement of electrode potential. Measurement electrodes. Comparison electrodes.
6. Oxidation-reduction electrode potentials. Mechanism of formation, biological importance. The Nernst-Peters equations.
7. Oxidation-reduction reactions in the organism. Prediction of their direction with the values of redox potentials.
8. Potentiometry, its application in medical and biological research.

4.2. Practical work (task) done by students in class

Measurement of redox potentials

Redox potentials of redox systems are calculated with EMF values, measured with an ionometer.

1. Preparation for work and measuring EMF.

- press the buttons "t" and "-1-19";
- plug the device in;
- warm up the device for 30 minutes;
- assemble a galvanic cell with the measurement electrode (the platinum electrode EPV-1) and the comparison electrode (the chlorinesilver electrode EVL-IM with the constant potential 0.201 ± 0.003 V);
- insert the electrodes in their sockets over the turntable and connect them to the device;
- immerse the electrodes in a solution of a redox system in a cup;
- press the button "mV" and the button of the needed measurement range and measure EMF value (E).

2. Calculations and writing a report of the laboratory work

1) Calculate practice values of redox potentials for the three redox systems with the formula:

$$\varphi_{pr} = E + \varphi_{comp},$$

where: E is EMF value, V (measured); $E = \varphi_{pr} - \varphi_{comp}$;

$\varphi_{comp} = 0.201$ V – the potential of the chlorinesilver electrode.

2) Calculate theoretical values of the redox potentials for the two redox systems with concentrations of reduced and oxydized forms with the equations:

$$1. \varphi_{I_2/2I^-} = 0.530 - \frac{0.059}{2} \lg \frac{[I_2]}{[I^-]^2};$$

$$2. \varphi_{Fe^{3+}/Fe^{2+}} = 0.771 + 0.059 \lg \frac{[Fe^{3+}]}{[Fe^{2+}]}.$$

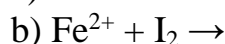
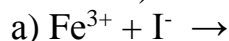
Concentrations are given in the table.

3) Fill in Table 15 with the results:

Table 15

№	Electrode	Composition of solutions	φ^0 , V	φ_{pr} , V	φ_{theor} , V	E , V
1	Pt I ₂ , 2I ⁻	KI (0.1 mol/L) I ₂ (0.001 mol/L)	0.530			
2	Pt Fe ³⁺ , Fe ²⁺	Fe ³⁺ (5·10 ⁻⁴ mol/L) Fe ²⁺ (5·10 ⁻² mol/L)	0.771			

4) With the standard reduction-oxidation potentials of the systems φ^0 (in the table) decide, whether the reactions can happen spontaneously:



with the formula: $E = \varphi_{ox.} - \varphi_{red.}$. A reduction-oxidation process proceeds spontaneously, if $\varphi_{ox.} > \varphi_{red.}$ and $E > 0$.

Materials for self-control

1. Explain the structure of the double electrical layer (DEL), that is formed when a piece of a metal is immersed in a solution of a salt of the metal:
 - a) distribution of charges between the inner and outer layers of the metal takes place due to movement of metal ions either into the solution or from the solution onto the metal and the DEL is formed;
 - b) the DEL consists of charges on the surface of the metal (ions or electrons) and in the adjacent layer of the solution (ions). It is formed due to the movement of metal ions from the metal into the solution and vice versa on the interface between the metal and the solution;
 - c) the DEL is formed due to the difference in cation concentrations in the whole volume of the solution and in the layer of the solution adjacent to the metal;
 - d) the DEL is formed due to the migration of the metal ions into the solution or from the solution. It consists of metal ions (electrons) on the surface of the metal and ions partly in the adjacent layer of the solution, partly at a distance from the interface.
2. What is the general equation of the equilibrium process on the zinc electrode Zn/Zn²⁺?
 - a) $\text{Zn} - 2e^- \rightleftharpoons \text{Zn}^{2+}$;
 - b) $\text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn}$;
 - c) $\text{Zn} + 2e^- \rightleftharpoons \text{Zn}^{2-}$;
 - d) $\text{Zn}^{2+} - 2e^- \rightleftharpoons \text{Zn}^{4+}$.

3. The Nernst equation for the nickel electrode at 298 K is:

a)
$$\varphi = \varphi^0 + \frac{0,059}{n} \lg [\text{Ni}^{2+}];$$

b)
$$\varphi = \varphi^0 - \frac{0,059}{n} \lg [\text{Ni}^{2+}];$$

c)
$$\varphi = \varphi^0 - 0,059 \lg [\text{Ni}^{2+}];$$

d)
$$\varphi = \varphi^0 + 0,059 \lg [\text{Ni}^{2+}].$$

4. The potential of a metal electrode is standard, if:

a) concentrations of all the substances taking part in the electrode process is one mole per liter;

b) concentrations of all the substances are equal;

c) the concentration of the metal cations equals one mole per liter, and temperature and pressure are standard;

d) it is measured against the standard hydrogen electrode.

5. Choose one best characteristic of the redox electrode:

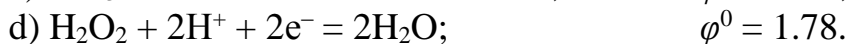
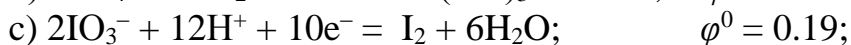
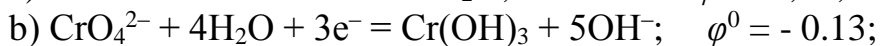
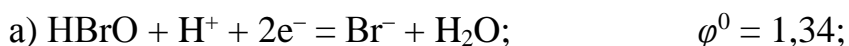
a) a metal immersed in an electrolyte solution and exchanging ions and electrons with it;

b) an inert metal immersed in an electrolyte solution and exchanging electrons with it;

c) an inert metal immersed in a reduction-oxidation system and conducting electrons only;

d) an inert metal immersed in a reduction-oxidation system and exchanging ions and electrons with it.

6. Choose a redox system, which oxidized form is the strongest oxidizing agent at standard conditions:



7. Choose a direction of the spontaneous reaction at standard conditions:



$$\varphi_{\text{Cl}_2|\text{2Cl}}^0 = 1,36 \text{ V}, \text{ and } \varphi_{\text{Fe}^{3+}|\text{Fe}^{2+}}^0 = 0,771 \text{ V};$$

a) from left to right;

b) from right to left;

c) the reaction will not take place;

- d) the reaction will go both ways.
8. Use the series of the standard electrode potentials and tell which of the reactions can take place at standard conditions:
- 1) $\text{Zn}^{2+} + \text{Cu} \rightarrow \text{Cu}^{2+} + \text{Zn}$;
 - 2) $\text{Mg} + \text{Sn}^{2+} \rightarrow \text{Sn} + \text{Mg}^{2+}$;
 - 3) $\text{Cd} + \text{Co}^{2+} \rightarrow \text{Cd}^{2+} + \text{Co}$;
 - 4) $2\text{Ag} + \text{Pb}^{2+} \rightarrow \text{Pb} + 2\text{Ag}^+$.
- a) 1, 2, 3;
 - b) 2, 3;
 - c) 4;
 - d) 2.
9. Choose the best oxidizing agent to transform the Fe^{2+} ion into Fe^{3+} ion at standard conditions, if the standard potential $\varphi_{\text{Fe}^{3+}|\text{Fe}^{2+}}^0 = 0.771 \text{ V}$, and the standard potentials of the oxidizing agents are given in brackets.
- a) KMnO_4 in an acidic medium ($\varphi^0 = 1.51 \text{ V}$);
 - b) KMnO_4 in a neutral medium ($\varphi^0 = 0.58 \text{ V}$);
 - c) HNO_2 ($\varphi^0 = 1.0 \text{ V}$);
 - d) CuSO_4 ($\varphi^0 = 0.153 \text{ V}$).
10. The pairs of electrodes that can be used in the galvanic cell for pH measurement are:
- 1) glass – quinhydrone;
 - 2) hydrogen – normal hydrogen;
 - 3) glass – chlorine silver;
 - 4) calomel – quinhydrone.
- a) 2, 3, 4;
 - b) 1, 3;
 - c) 1, 2, 3;
 - d) 1, 4.
11. Calculate the potential of the hydrogen electrode, immersed in a hydrochloric acid solution. 14.50 mL 0.1 M NaOH solution is used to titrate 10 mL of the hydrochloric acid solution.
- a) 0.0685 V;
 - b) -0.0435 V;
 - c) 0.0495 V;
 - d) -0.00985 V.

Correct answers

1. The correct answer is d).
According to the modern theory of the DEL, its structure differs from a charge distribution in a condenser, because charged particles in a solution (metal cations) belong to the condensed and diffuse parts of the DEL.
2. The correct answer is b).
Generally the process on a metal electrode is written as a reduction process: metal cations accept electrons and become non-charged atoms.
3. The correct answer is a).
The process on the nickel electrode can be written as: $\text{Ni}^{2+} + 2e^- \rightleftharpoons \text{Ni}$, thus the number of electrons (the n in the Nernst equation) is two.
4. The correct answer is c).
The standard potential of a metal electrode depends only on the nature of the metal. Therefore the pressure and the temperature must be standard, and the concentration of metal cations must equal one mole per liter. Under these conditions the potential of a metal electrode in the Nernst equation equals the standard potential.
5. The correct answer is c).
An inert metal (platinum, gold, palladium etc.) must be placed in a solution that is a reduction-oxidation system. The metal conducts electrons: it transfers electrons to the oxidized form in the solution from the external circuit, or accepts electrons from the reduced form and transfers them to the external circuit. The metal therefore does not exchange electrons or ions with the components of the solution.
6. The correct answer is d).
The oxidized form of the system with a bigger value of the redox potential is a stronger oxidizing agent.
7. The correct answer is b).
An oxidation-reduction process is spontaneous when its $\varphi_{\text{ox}} > \varphi_{\text{red}}$ and $\text{EMF} > 0$; ($\text{EMF} = \varphi_{\text{ox}} - \varphi_{\text{red}}$).
 Cl_2 is the oxidizing agent and Fe^{2+} is the reducing agent:
 $2\text{Fe}^{2+} + \text{Cl}_2 = 2\text{Cl}^- + 2\text{Fe}^{3+}$.
 $2\text{FeSO}_4 + \text{Cl}_2 + \text{Na}_2\text{SO}_4 \rightarrow 2\text{NaCl} + \text{Fe}_2(\text{SO}_4)_3$.
 $\text{EMF} = 1,36 - 0,771 = 0,589 \text{ V}$. Thus $\text{EMF} > 0$.
Therefore the reaction will go spontaneously from right to left.
8. The correct answer is b).

The reactions 2 and 3 will happen spontaneously under standard conditions, because those reactions only take place spontaneously where the metal with smaller potential is the reducing agent. Under standard conditions these are the metals that are on the left side in the series of standard electrode potentials. For example, the standard potential of magnesium (-2.363V) is smaller than the standard potential of tin (-0.136V); the standard potential of cadmium (-0.403V) is smaller than the standard potential of cobalt (-0.277V). The reactions 1) and 4) will not take place under standard conditions, because the standard potential of copper (0.337V) (it is the reducing agent) is bigger than the standard potential of zinc (-0.736V). The standard potential of silver (0.799V) (it is the reducing agent) is bigger than the standard potential of lead (-0.126V).

9. The correct answer is a).

The best oxidizing agent is the oxidized form of the redox system, which potential is to a greater extent bigger than 0.771 V . It is the system, the oxidized form of which is KMnO_4 in an acidic medium.

10. The correct answer is a).

A galvanic cell for pH measurement must consist of an electrode, which potential depends on the pH of a solution (measurement electrode) and an electrode which potential is constant and does not depend on the pH of a solution (comparison electrode). Among the four pairs of electrodes only the first pair can not be used for pH measurement, because it consists of two measurement electrodes. In the other pairs one of the electrodes is a measurement electrode (hydrogen, glass, quinhydrone respectively), and the other is a comparison electrode (normal hydrogen, chlorine silver and calomel respectively).

11. The correct answer is b).

First we calculate the normality of the acid from the titration results:

$$\tilde{N}(\text{HCl}) = \frac{C(\text{NaOH}) \cdot V(\text{NaOH})}{V(\text{HCl})} = \frac{0.1 \text{ mol/L} \cdot 14.5 \text{ mL}}{10 \text{ mL}} = 0.145 \text{ mol/L}.$$

Thus, the concentration (activity) of hydrogen cations (assuming that all the molecules of hydrochloric acid are dissociated) is: $[\text{H}^+] = 0.145 \text{ mol/L}$.

Then find the potential value (at standard temperature) from the Nernst equation for the hydrogen electrode:

$$\varphi_{\text{H}^+|\text{H}_2}^0 = 0.059 \lg [\text{H}^+] = 0.059 \cdot \lg 0.145 = 0.059 \cdot (-0.839) = -0.0495 \text{ V}.$$

Subject 15. Adsorption processes and ionic exchange in biosystems. Chromatography

1. Importance

Adsorption from solutions on solid surface is of great importance for the life of the organism. A lot of processes in the organism employ molecular adsorption from solutions. This is adsorption of substrates on the surface of enzymes, adsorption on cell membranes ($15\ 000\ \text{m}^2$ in the organism), adsorption of proteins on the surface of hydrophobic particles for their transport in blood and transport of oxygen by hemoglobin of erythrocytes.

Such solid adsorbents as activated carbon and ion-exchangers are used to remove foreign substances (xenobiotics, poisons, harmful metabolites, excessive medicines) from the organism. The surface area of the phase interface of a pill of activated carbon (0.25 g) is about $125\ \text{m}^2$. Enterosorbents are widely used in medical practice.

There are a variety of methods of adsorption therapy, that include hemosorption (removal of toxins from blood), plasmasorption, lymphosorption, liquorosorption (purification of the spine liquor), applicative sorption, enterosorption.

Adsorption on solid adsorbents is widely used to purify vitamins and antibiotics.

Immobilized preparations of enzymes, hormones, antibiotics on inorganic and organic polymers are used in medical practice.

Chromatography is a group of methods for separation and analysis of mixtures of gases, vapours, liquids or solutes with sorption processes. It is used for diagnostics, monitoring of treatment, control of detoxification of the organism at poisonings. It helps to make decisions about prophylaxis and treatment of diseases.

Chromatography is used in toxicological chemistry, forensic medicine, criminalistics and hygiene.

2. Concrete aims

Make conclusions about surface activity of substances from their structure.

Analyze characteristics of structure of the surface layer of surface-active compounds, explain principles of structure of biological membranes.

Analyze adsorption equations and limitations of their applications, distinguish monomolecular and polymolecular adsorption.

Explain principles of adsorption of substances from solutions on solid surfaces.

Explain physico-chemical principles of adsorption therapy.

Distinguish selective and ion-exchange adsorption of electrolytes.

Explain methods of chromatography analysis and their role in medical and biological research.

3. Basic knowledge and skills necessary to study the subject

Know properties of structure of biological membranes.

Understand hydrophilicity (polarity) and hydrophobicity (nonpolarity) of compounds.

Understand dissociation of substances.

Know adsorption, distribution of substances between two immiscible phases.

4. Tasks for self-preparation for the lesson

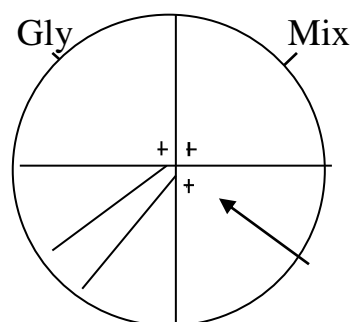
4.1. Theoretical questions for the lesson:

1. Surface activity. The Duclou-Traube rule.
2. The Gibbs equation. Orientation of molecules in the surface layer and structure of biological membranes.
3. The Langmuir equation.
4. Adsorption from solutions on the solid surface. The Freundlich equation.
5. Physico-chemical principles of the adsorption therapy.
6. Adsorption of electrolytes (selective and ion-exchange). The Paneth-Fajans rule.
7. Ionites and their application in medicine.
8. Classification of methods of chromatography by:
 - 1) aggregative phase;
 - 2) technique;
 - 3) mechanism of separation of components.Application of chromatography in medicine and biology.

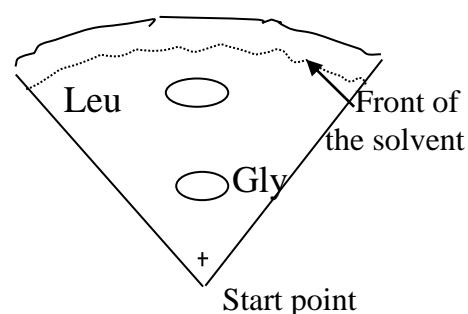
4.2. Practical work (task) done by students in class

Distributive chromatography of amino acids on paper.

Take a paper filter (diameter 12 cm), draw four sectors on it with a pencil. Mark the start points in three sectors at the distance 0.5 cm from the centre with a pencil. Cut out a narrow strip reaching almost to the centre in the fourth sector (see Picture 12). Mark the sectors on the edge: "Gly" – glycine, "Leu" – leucine, "Mix" – mixture.



Picture 12.



Picture 13. Chromatogram of amino acids

Place small drops (not bigger than 3-4 mm in diameter) of the corresponding solutions (glycine, leucine and their mixture) on the start points. Apply 3 to 4 drops one by one drying the previous drop before the next one.

Pour the solvent in a Petry dish, place the filter so, that the strip is immersed in the solvent. Cover the cup with another Petry dish and place it in the thermostate at temperature 45-50⁰C. When the solvent almost reaches the edge of the paper, take the paper out, dry it up and develop it with ninhydrin solution. Dry it up again until violet stains appear (see Picture 13).

With the chromatogram calculate the retention factors of leucine ($R_{f \text{ leucine}}$) and glycine ($R_{f \text{ glycine}}$). For this measure the distance from the start point to the middle of the stain of each of the amino acids and from the start point to the front of the solvent (see Picture 13).

Calculate the retention factors (R_f) of the amino acids with the formulas:

$$R_{f \text{ glycine}} = \frac{r_1}{r_\delta}, \quad R_{f \text{ leucine}} = \frac{r_2}{r_\delta},$$

where r_1 is the distance from the start point to the middle of the glycine stain, cm;

r_2 is the distance from the start point to the middle of the leucine stain, cm;

r_p is the distance from the start point to the front of the solvent, cm.

5. Writing a report of the laboratory work

Draw the chromatogram, write the results of calculations. Make a conclusion about distribution of amino acids depending on the polarity of their molecules.

Materials for self-control

1. From which solvent does activated carbon (non-polar adsorbent) adsorb a surface active compound better? The dielectric permeability of the solvents is given in brackets.
 - a) water (80);
 - b) ethanol (25.2);
 - c) acetone (20.7);
 - d) hexane (1.9).
2. Tell, whether the Duclou-Traube rule is true for adsorption of amphipatic molecules from solutions on a solid adsorbent:
 - a) not true;
 - b) true only for non-polar adsorbents;
 - c) true only for non-polar adsorbents in adsorption from polar solvents;
 - d) true only for non-polar adsorbents in adsorption from polar solvents and for polar adsorbents in adsorption from non-polar solvents.
3. Which factors effect adsorption of an ion on a solid adsorbent from a water solution?

- 1) ion charge;
 - 2) hydration degree of the ion;
 - 3) identity of the ion;
 - 4) nature of the adsorbent;
 - 5) mass of the adsorbent;
 - 6) total pressure.
- a) 1 – 4;
 - b) 1 – 6;
 - c) 1, 3, 4;
 - d) 1, 4, 5.
4. Which ions are able to adsorb on the surface of crystalline silver iodide according to the Paneth-Fajans rule?
- a) Ag^+ ;
 - b) I^- ;
 - c) NO_3^- ;
 - d) Na^+ .
5. Choose the ions that can be adsorbed by a cation exchanger in H^+ form with the mechanism of ion exchange adsorption:
- a) Cl^- ;
 - b) Ca^{2+} ;
 - c) NO_3^- ;
 - d) Na^+ .
6. Choose the processes on which chromatography methods are based:
- 1 – ion exchange;
 - 2 – dissolving in water;
 - 3 – adsorption;
 - 4 – evaporation;
 - 5 – crystallization;
 - 6 – distribution between two phases.
- a) 1, 3, 4;
 - b) 2, 3, 4, 6;
 - c) 1, 3, 6;
 - d) 2, 4, 5.
7. Which of the methods of chromatography are based on distribution of components of a mixture between two liquid phases:
- 1 – gas adsorption chromatography;
 - 2 – paper chromatography;
 - 3 – gel chromatography;
 - 4 – adsorption column chromatography;
 - 5 – thin layer chromatography;
 - 6 – ion exchange chromatography.

- a) 2, 5;
 - b) 4, 6;
 - c) 1, 3;
 - d) 1, 2.
8. Which of the substances is the stationary phase in paper chromatography:
- a) organic solvent;
 - b) water;
 - c) cellulose;
 - d) there is no stationary phase in paper chromatography.
9. Which parameters of paper chromatography must be standardized for exact measuring of retention factors of components in an analyzed mixture:
- 1 – temperature;
 - 2 – pressure;
 - 3 – amount of the mobile phase;
 - 4 – sort of the paper;
 - 5 – shape and dimensions of the paper;
 - 6 – type of the solvent.
- a) 3, 5;
 - b) 4, 6;
 - c) 1, 3;
 - d) 2, 4.
10. What is described by the retention factor in paper chromatography?
- a) ratio of solubilities of the components in the solvent;
 - b) ratio of solubilities of the components in the immobile phase;
 - c) ratio of velocities of the components;
 - d) ratio of velocities of a component and the solvent.
11. Choose the kind of chromatography which mechanism is similar to a method of obtaining purified or demineralized water.
- a) adsorption;
 - b) distributive;
 - c) ion exchange;
 - d) sedimentation.

Correct answers

1. The correct answer is a).
Carbon is a non-polar hydrophobic adsorbent. According to the Rebinder's rule of polarity equalization a surface active compound is better adsorbed on carbon from a polar solvent thus taking a place with an intermediate polarity between the solvent and the adsorbent. Water is the most polar of the given solvents.

2. The correct answer is c).

The Ducloux-Traube rule is only true for adsorption of surface active compounds on hydrophobic adsorbents from water solutions or solutions based on polar solvents. Adsorption of molecules of surface active compounds increases with an increase of the hydrocarbon radical (the hydrophobic portion of the amphipatic molecule). When surface active compounds are adsorbed on hydrophilic adsorbents from non-polar solvents, the results are opposite to the Ducloux-Traube rule: an increase of the hydrophobic chain of the amphipatic molecule leads to a decrease of adsorption.

3. The correct answer is a).

Ions with bigger charge and smaller hydration degree are adsorbed better. Adsorption is better when ions and the adsorbent are of similar nature. The mass of the adsorbent does not effect adsorption of ions, because the latter depends on the surface area of adsorbent. Pressure does not effect adsorption on the liquid-solid phase interface.

4. The correct answers are a), b).

According to the Panet's rule Ag^+ and I^- ions can complete the crystal lattice of AgI. Therefore only these ions are adsorbed on the surface of AgI crystals depending on which of the ions is in excessive amount.

5. The correct answers are b), d).

A cation exchanger in H^+ -form can exchange its mobile H^+ ions for cations in the solution. Therefore, if a solution with calcium or potassium cations is run through a layer of the cation exchanger, the cations can be completely exchanged for hydrogen cations.

6. The correct answer is c).

Dissolution, evaporation, crystallization do not belong to the processes, on which chromatography is based.

7. The correct answer is a).

The components of a mixture are distributed between the stationary phase and the solvent (mobile phase) only in the paper and thin layer methods. The solvent moves gradually from the point of start to the end of the paper or the adsorbent layer. The water in the paper is the stationary phase in paper chromatography. In thin layer chromatography the stationary phase is the liquid with which the adsorbent is soaked beforehand.

8. The correct answer is b).

The paper contains water, which is the stationary phase in paper chromatography. The special chromatography paper contains more than 20% water.

9. The correct answer is b).

Values of retention factors of components depend on the sort of the paper and the type of the solvent. The shape and dimensions of paper do not effect values of retention factors, as well as pressure and amount of the solvent (the solvent is always taken in excess). The temperature is not standardized. It must be slightly higher than the room temperature.

10. The correct answer is d).

11. The correct answer is c).

Like production of purified or demineralized water ion exchange chromatography is based on ion exchange between ions of the liquid phase (water, solution) and mobile ions of the ion exchange resin. Cationites (cation exchangers) or anionites (anion exchangers) are used separately in chromatography, and in water purification the water is successively run through both a cationite and an anionite. The resins exchange cations H^+ and anions OH^- for cations and anions in the water.

Subject 16. Obtaining, purification and properties of colloidal solutions

1. Importance

The cell of an organism is a heterogeneous colloidal system. Blood, cytoplasm, muscle cells, nerve cells, fibrils, genes, viruses are colloidal systems. Colloidal chemical processes are the basis of nutrition, growth and development of plants and animals as well as humans.

Research of properties of colloidal systems and methods of their obtaining helps to understand complex processes of life and design models of cells, biological membranes, nerve fibrils, oxygen transport etc.

Research of purification of dispersion systems has introduced such modern diagnostics and treatment methods as electrophoresis, compensatory dialysis, vivodialysis, “artificial kidney”.

The problem of protection of the environment is very important. The processes of purification and regeneration of wastewater, elimination of atmosphere pollutants and smokes are based on laws of physical and colloidal chemistry.

2. Concrete aims

Analyze principles of methods of formation and purification of dispersion systems.

Explain physical and chemical basis of hemodialysis.

3. Basic knowledge and skills necessary to study the subject

Have an understanding of solutions.

Know differences between homogeneous and heterogeneous systems.

Know main types of chemical reactions.

Reactions of metathesis and hydrolysis.

Know the principle of selective adsorption.

4. Tasks for self-preparation for the lesson

4.1. Theoretical questions for the lesson:

1. Dispersion systems and their classification.
2. Obtaining and purification of colloidal solutions. Dialysis and electro dialysis, ultrafiltration. "Artificial kidney".
3. Molecular-kinetic properties of colloidal systems (Brownian movement, diffusion, osmotic pressure).
4. Optical properties of colloidal systems. Ultramicroscopy.
5. Structure of colloidal particles.
6. Electrokinetical potential of colloidal particles. Electrophoresis, its application in medicine and medical and biological research. The Helmholtz – Smoluchowski equation.

4.2. Practical work (task) done by students in class

1. Obtaining of a sol by the solvent replacement method

Add 1 mL of an alcohol solution of sulfur (obtained by long-term infusion) to 10 mL distilled water in a test tube. Sulfur forms a real solution in an alcohol, but can not dissolve in water thus creating a colloidal system.

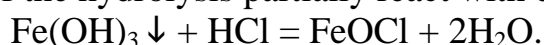
2. Obtaining of a ferric hydroxide sol by the method of hydrolysis

Add 50 mL distilled water to a conical flask and boil it. Measure out 5 mL 5% FeCl₃ (with a measuring test tube) and add it gradually to the boiling water.

At high temperature complete hydrolysis of ferric chloride takes place (III) and ferric hydroxide is obtained:

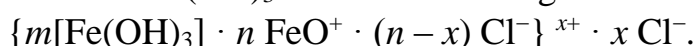


The products of the hydrolysis partially react with each other:



The obtained oxoferrous chloride (FeOCl) stabilizes colloidal particles.

The micelle formula of the Fe(OH)₃ sol is as following:



A clear reddish-brown sol is obtained.

3. Obtaining of a Prussian blue sol by the method of double metathesis

Add 10 mL 0.10 % potassium ferrocyanide $\text{K}_4[\text{Fe}(\text{CN})_6]$ and 1-2 drops of 2 % ferric chloride. A clear blue colloidal solution of Prussian blue $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ is obtained.

Write the reaction between potassium ferrocyanide and ferric chloride.

Write the micelle formula of the obtained sol, taking into account that the granule has a negative charge.

4. Obtaining a ferric hydroxide sol by the method of peptization.

Add 50 mL distilled water to a flask. Add 2 mL 5 % FeCl_3 solution. Add gradually 5 % ammonia solution until a strong ammonia smell is felt. A brown precipitate $\text{Fe}(\text{OH})_3$ is obtained in the reaction.

After sedimentation carefully decant off the upper layer of the liquid. Add about 30 mL distilled water to the sediment, shake well, leave to sedimentate and decant again. Repeat the procedure three times. Take two small portions of the washed precipitate (about 1 mL) and place in two test tubes. Add 10 mL water to the first test tube and 3 mL water and 2 mL 5 % FeCl_3 to the second test tube.

Write the reaction of formation of the ferric hydroxide precipitate. Write a micelle formula of the sol obtained with peptization in the second test tube.

Materials for self-control

1. Choose one best description of colloidal solutions:
 - a) dispersion systems with different dispersion media;
 - b) dispersion systems with the particle size in the dispersed phase $10^{-9} - 10^{-7}$ m.
 - c) dispersion systems with a solid dispersed phase;
 - d) dispersion systems that belong to homogeneous systems because of the particle size of the dispersed phase.
2. What ions are adsorbed on the surface of the aggregate in the micelle formation?
 - a) the ions, which charge is opposite to the charge of the aggregate;
 - b) the ions, concentration of which is the biggest in the solution;
 - c) the ions, which are not components of the aggregate;
 - d) the ions which are able to complete the crystal lattice of the aggregate.
3. Write a formula of the micelle of a sol, obtained by mixing 15 mL 0.025 M KCl solution and 85 mL 0.005 M AgNO_3 solution. Explain your reasoning.
4. Explain, on which processes peptization is based.
 - a) hydrolysis of peptide bonds in the dispersion medium;

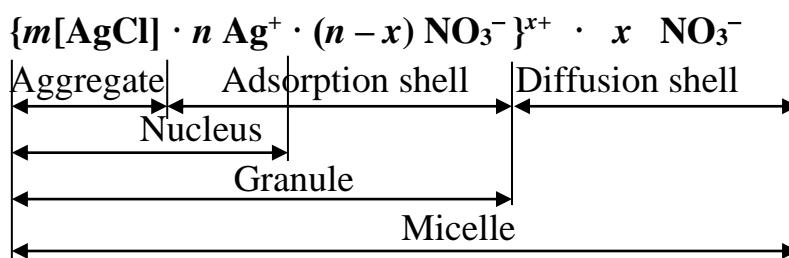
- b) chemical dissolution of the precipitate due to a reaction with the added electrolyte;
 - c) formation of colloidal particles because of the adsorption of electrolyte ions on the particles of the precipitate;
 - d) washing of the precipitate with the solvent.
5. Choose one best method to remove electrolytes from a colloidal solution:
- a) filtration;
 - b) dialysis;
 - c) electrodialysis;
 - d) vividialysis.
6. What method of purification of colloidal solutions is used in the apparatus “the artificial kidney”?
- a) ultrafiltration;
 - b) dialysis;
 - c) electrodialysis;
 - d) compensatory dialysis.

Correct answers

1. The correct answer is b).
According to the classification of dispersion systems colloidal solutions are highly dispersed systems with $10^{-9} - 10^{-7}$ m particle size of the dispersed phase.
2. The correct answer is d).
According to the rule of selective adsorption only the ions can adsorb on the surface of the aggregate that are able to complete its crystal lattice (the Paneth-Fajans rule). These are the ions that are components of the aggregate, or those isomorfic to them, or the ions that contain the same elements as in the crystal lattice of the aggregate. The ions are called potential-determining and determine the charge of the granule in the colloidal particle.
3. First decide which of the reactants is in excess.

$$\text{AgNO}_3 + \text{KCl} = \text{AgCl}\downarrow + \text{KNO}_3.$$
Number of moles of KCl $\nu = CV = 0.025 \text{ mol/L} \cdot 0.015 \text{ L} = 0.000375 \text{ mol} = 0.375 \text{ mmol}.$
Number of moles of AgNO₃ $\nu = CV = 0.005 \text{ mol/L} \cdot 0.085 \text{ L} = 0.000425 \text{ mol} = 0.425 \text{ mmol}.$
Thus AgNO₃ is in excess. Therefore, Ag⁺ cations are adsorbed on the surface of the aggregate, thus making the granula positive. Nitrate ions will be the counterions. The micelle is electroneutral.

The micelle formula is as following:



4. The correct answers are c) and d).

Peptization is a transformation of a freshly obtained precipitate into a colloidal state. It can take place when an electrolyte is added, that contains ions able to be adsorbed on the particles of precipitate according to the rule of selective adsorption (adsorptive peptization). Sometimes peptization is possible when the precipitate is washed by the solvent, if the precipitate contained significant concentration of one of the reactants because of insufficient washing.

5. The correct answer is c).

As the admixtures are electrolytes, electro dialysis is the best option.

6. The correct answer is d).

The apparatus “artificial kidney” works with the principle of compensatory vivodialysis. The blood of the patient flows through pipes with semipermeable walls. The walls are washed with a physiological saline that contains vital substances that must not leave the blood.

Subject 17. Colloidal solutions, their coagulation. Coarse dispersion systems (aerosols, suspensions, emulsions)

1. Importance

All biological fluids of the organism: blood, intracellular fluid, lymph, urine etc. are complex dispersion systems. Their stability depends on constancy of pH and the electrolyte and protein composition. Their alteration can lead to onset of coagulation of the colloidal phase, sedimentation of erythrocytes and proteins.

Coagulation also takes place in blood clotting – a complex of enzymic reactions that ensure minimal blood loss on one hand and formation of clots in blood vessels on the other hand.

Blood clotting (coagulation hemostasis) is routinely analyzed in clinical laboratories; the measurement of the rate of sedimentation of erythrocytes is included to the general clinical analysis of blood.

Knowledge of characteristics of coagulation processes is important in blood preservation and storage, applications of modern thromboresistant materials.

Colloidal protection is of great importance for the normal functioning of the organism. Proteins, polysaccharides and other natural polymers are adsorbed on the surface of colloidal hydrophobic particles, thus increasing their hydrophilicity. The polymers promote stability of the particles because they protect them from the coagulating action of electrolytes. Particles of lipids, cholesterol, insoluble calcium phosphates, urates and oxalates exist in the body fluids in the protected state. The protective action of proteins increases concentration of insoluble compounds: for instance, proteins of blood plasma increase solubility of calcium carbonate almost fivefold, the high concentration of calcium phosphate in milk is also ensured by the protective action of proteins. Certain pathological processes as well as aging alter concentrations and protective properties of proteins and polysaccharides. It causes formation of cholesterol plaques on the blood vessel walls as well as formation of stones in the kidneys, gallbladder and bladder.

The phenomenon of colloidal protection is used in the manufacturing of medicines. Sols of silver (protargol, collargol), gold, mercury and radioactive isotopes protected with albumins, gelatin, pectins and dextrin are widely applied in medicine.

2. Concrete aims

Explain physical and chemical basis of coagulation of colloidal solutions and measurement of the coagulation threshold.

3. Basic knowledge and skills necessary to study the subject

To be able to write formulas of micelles of sols.

To understand electrolytic dissociation.

To know characteristics of ions (charge, radius, hydrate shell).

To know structure of proteins and polysaccharides as natural polymers.

To know adsorption on the phase interface.

To know coarse dispersions (aerosols, suspension, emulsions).

4. Tasks for self-preparation for the lesson

4.1. Theoretical questions for the lesson:

1. Kinetic and aggregative stability of liosols. Stability factors.
2. Coagulation. Mechanism of coagulation action of electrolytes.
3. Coagulation threshold, its determination.
4. The Schultze-Hardy rule.
5. Coagulation processes in purification of drinking water and waste waters.
6. Colloidal protection, its biological role.

7. Coarse dispersion systems:
 - 1) Aerosols. Obtaining and properties. Medical applications.
 - 2) Suspensions. Obtaining and properties. Medical applications.
 - 3) Emulsions. Obtaining and properties. Medical applications.
8. Semicolloid soaps. Formation of micelles in solutions of semicolloids.

4.2. Practical work (task) done by students in class

Measurement of the coagulation threshold of a ferric hydroxide sol with an electrolyte KCl

1. Preparation of diluted solutions of electrolyte KCl

Take five test tubes. Add 10 mL of electrolyte solution KCl to the first test tube. Add 9 mL of distilled water to the other four test tubes. Normality of the KCl solution in the first test tube is 2.0 mol/L. Transfer 1 mL of the solution from the first test tube into the second, mix well. Then transfer 1 mL of the solution from the second test tube to the third and so on. Pour out 1 mL of the solution from the fifth test tube. Thus you have five solutions of the electrolyte, with tenfold concentration decrease in each.

2. Carrying out coagulation

Add 1 mL ferric hydroxide sol to all the electrolyte solutions, mix well. After five minutes mark the test tubes, where coagulation took place (the solutions became foggy or a precipitate is formed).

Note the smallest concentration of the electrolyte solution that has caused the coagulation.

3. Calculation of the coagulation threshold of an electrolyte.

Calculate the coagulation threshold for each electrolyte with the formula:

$$\tilde{N}_{\text{thr}} = \frac{V_{\text{el}} \cdot \tilde{N}_{\text{min}}}{V_{\text{sol}} + V_{\text{el}}},$$

where

C_{thr} – coagulation threshold, mmol/L;

V_{el} – volume of the electrolyte solution, mL;

C_{min} – minimal normality of the electrolyte, mmol/L;

V_{sol} – volume of the sol, mL.

Fill in Table 20 with the results of the experiment and the calculations.

Table 20

Electrolyte	Initial concentration, mmol/L	Test tubes, where coagulation took place	C _{min} , mmol/L	C _{thr} , mmol/L
KCl	2000			

Materials for self-control

1. Which of the factors ensure stability of colloidal solutions?
 - 1 – charge sign of the particle;
 - 2 – charge value of the particle;
 - 3 – thickness of the diffuse shell;
 - 4 – kind of ions in the diffuse shell;
 - 5 – Brownian motion of colloidal particles;
 - 6 – value of the electrokinetic potential.
 - a) 1, 2, 3, 6;
 - b) 2, 3, 5, 6;
 - c) 1, 2, 4, 5;
 - d) 1, 3, 4, 5.
2. Which of the factors cause coagulation of a sol?
 - 1 – change of temperature;
 - 2 – addition of the solvent;
 - 3 – change of pressure;
 - 4 – addition of an electrolyte;
 - 5 – addition of dehydrating agents.
 - a) 1, 2, 3;
 - b) 1, 3, 4;
 - c) 1, 4, 5;
 - d) 2, 3, 5.
3. Which of the factors effect the coagulation threshold and the coagulating ability of ions?
 - a) concentration of the ion;
 - b) hydration of the ion;
 - c) charge of the ion;
 - d) temperature.
4. Choose the electrolyte with the minimal coagulation threshold for a sol with negatively charged particles:
 - a) Na_2CO_3 ;
 - b) K_3PO_4 ;
 - c) CaCl_2 ;
 - d) $\text{Al}(\text{NO}_3)_3$.
5. To which electrode will sol particles move in electrophoresis, if the coagulation thresholds of the sol are as following for the electrolytes (mmol/L):
 $\text{K}_3\text{PO}_4 - 0.02$; $\text{MgSO}_4 - 1.50$; $\text{FeCl}_3 - 201.30$.
 - a) to the cathode;
 - b) the particles do not move;

- c) to the anode;
 - d) it is not possible to decide.
6. Choose one best characteristic of the antagonism of ions in the coagulation:
- a) impossibility for ions to exist simultaneously in the same solution because of a reaction between them;
 - b) a decrease of solubility of ions when they are present at the same time in the same solution;
 - c) a decrease of coagulation thresholds of ions in the mutual coagulation;
 - d) a decrease of coagulating ability of ions in the mutual coagulation.
7. Choose the substances which have the colloidal protection action in the human body:
- a) electrolytes;
 - b) cholesterol;
 - c) proteins;
 - d) polysaccharides.
8. Choose one best explanation of the protective action of high-molecular compounds:
- a) molecules of high-molecular compounds are adsorbed on the surface of the colloidal particle and increase its dimensions, thus increasing stability of the colloidal system;
 - b) the molecules are adsorbed simultaneously on several particles and promote formation of bigger aggregates;
 - c) the molecules adsorb electrolyte ions on their surface, thus preventing the colloidal system from coagulation;
 - d) the molecules are adsorbed on the surface of the colloidal particle and promote formation of a bigger hydrated shell.
9. When a small amount of a high-molecular compound which is not sufficient to cause colloidal protection effect is added to a colloidal solution, its stability decreases and the disperse phase eventually sedimentates. How is the phenomenon called?
- a) sedimentation;
 - b) flocculation;
 - c) flotation;
 - d) mutual coagulation.

Correct answers

1. The correct answer is b).

The stability of colloidal solutions depends on the factors of the aggregative stability: the charge value, the thickness of the diffuse layer (hydrated shell), the value of the electrokinetic potential and on the factor of the kinetic

stability: Brownian motion of particles. The stability of colloidal solution does not depend on the charge sign of the particle or the nature of ions.

2. The correct answer is c).

The change of temperature, an addition of electrolytes or dehydrating agents, and intensive mechanical mixing can effect factors of stability of colloidal systems and promote coagulation. An alteration of pressure almost does not influence stability of liquid systems. An addition of the solvent mostly increases the stability of the colloidal system, because it decreases concentration of the disperse phase.

3. The correct answers are b) and c).

The coagulation threshold is the number of mmol-equiv of an electrolyte that causes coagulation of 1L of a sol. The coagulating ability is inverse to the coagulation threshold. Therefore the both values do not depend on concentrations of ions in a solution. The coagulating strength of an ion depends on its charge and hydration (the radius of the hydrated ion). The bigger the charge and smaller the hydration, the smaller is the coagulation threshold and bigger the coagulating ability. Temperature equally effects coagulating ability of all ions.

4. The correct answer is d).

As far as sol particles are negatively charged its coagulation is caused by cations. The cation with the maximum charge has the smallest coagulation threshold. It is the aluminium cation, therefore aluminium nitrate has the smallest coagulation threshold for the sol.

5. The correct answer is a).

Let us assume that the coagulation is caused by cations. Then potassium phosphate would have had the maximum coagulation threshold (cation charge is +1) and ferric chloride (cation charge is +3) – the minimum. The assumption does not correspond to the obtained data and is therefore rejected. Then we assume that coagulation is caused by anions. Then potassium phosphate would have the minimum coagulation threshold (anion charge is – 3) and ferric chloride (anion charge is –1) – the maximum one. The assumption corresponds to the obtained data. Therefore coagulation is caused by anions and the sol particles are charged positively. The particles move to the cathode (the negatively charged electrode) in electrophoresis.

6. The correct answer is d).

When the coagulation thresholds of ions in the mutual coagulation are bigger than in the separate coagulation and the coagulating ability is respectively smaller, the phenomenon is called antagonism of ions.

7. The correct answers are c) and d).

Such high-molecular compounds as proteins and polysaccharides, have a protective effect in the human body. They are adsorbed on hydrophobic particles of calcium phosphate and calcium carbonate, lipids and other substances sparingly dissolvable in water, thus increasing their hydrophilicity and, respectively, stability.

8. The correct answer is d).

Hydrophilic molecules of high-molecular compounds are adsorbed on the surface of colloidal particles, for instance, protein molecules on the lipid particles in blood. The newly formed particle becomes bigger and more stable due to the presence of a thick hydrated shell. The shell prevents adhesion of the colloidal particles, when they gravitate to each other. The hydrophobic sol becomes hydrophilic.

9. The correct answer is b).

When small (not sufficient for the protective effect) amounts of certain kinds of high-molecular compounds (mostly polyelectrolytes with linear molecules) are added to colloidal solutions, a phenomenon of flocculation is observed. The ends of the macromolecules are adsorbed on several colloidal particles thus forming bigger aggregates, causing sedimentation.

Subject 18. Physical chemistry of biopolymer solutions

1. Importance

Such high-molecular compounds as proteins, polysaccharides and nucleic acids are vital for functioning of the living organism. Biopolymers perform important functions in the body. They catalyze biochemical processes, preserve and transfer genetic information, perform protective and structural functions, take part in blood coagulation, are storage forms of nutrients, maintain oncotic pressure of blood plasma.

pH alterations of the blood make proteins lose their charge (isoelectric state) thus impairing their structure and functioning.

Proteins do not come with the diet at starvation; synthesis of blood plasma proteins is deficient in liver diseases; proteins are lost with urine in kidney diseases. It causes decrease of protein concentration in blood and lowering of oncotic pressure of blood plasma. Therefore the water from the blood vessels moves to the tissues causing edema.

Artificial and synthetic polymers are of great importance in medicine and pharmaceuticals. They are used in production of artificial blood vessels, prosthetic teeth and bones. They are also used in the “artificial kidney” apparatus etc.

Polymers are used in production of modern medicines, prolongation of action of medicines in the organism.

2. Concrete aims

Explain physical and chemical characteristics of proteins as structure components of all tissues of the organism.

Make conclusions about the charge of dissolved biopolymers from their isoelectric point.

3. Basic knowledge and skills necessary to study the subject

To know high molecular compounds (polymers).

To know the structure of proteins.

To be able to explain formation of charge of the protein as an amphoteric polyelectrolyte.

4. Tasks for self-preparation for the lesson

4.1. Theoretical questions for the lesson:

1. Characteristics of solutions of high molecular compounds.
2. Mechanism of turgescence and solubility of high molecular compounds. Effect of various factors on turgescence and solubility of high molecular compounds. Role of turgescence in physiology of organisms.
3. Isoelectric point of the protein (pI) and methods of its measurement.
4. Jellification of solutions of high molecular compounds. Properties of jellies.
5. Anomalous viscosity of solutions of high molecular compounds. Viscosity of blood.
6. Osmotic pressure of solutions of biopolymers. The Galler equation. Oncotic pressure of blood plasma.

4.2. Practical work (task) done by students in class

Measurement of the isoelectric point of gelatin with the maximum precipitation.

Add such amounts of acetic acid (CH_3COOH) and sodium acetate (CH_3COONa) to five test tubes, that make 10 mL buffer solution with certain pH in each test tube (see Table 22). Add 0.5 mL 1% gelatin solution to each test tube, mix. Then add 2 mL ethanol to each test tube, mixing vigorously. Leave the tubes for ten minutes. Mark the test tube and the pH, where the solution is the most turbid. The pH will correspond to the isoelectric point of gelatin. Fill in Table 22 with the results.

Table 22

№	Volumes of solutions, mL		pH	№ test tube with the maximum turbidity	pH of the solution with the maximum turbidity	pI
	0.2 M CH ₃ COOH	0.2 M CH ₃ COONa				
1	9.75	0.25	3.17			
2	8.90	1.10	3.85			
3	5.35	4.65	4.70			
4	1.70	8.30	5.45			
5	0.25	9.75	6.35			

Materials for self-control

- Choose the correct characteristics of solutions of high molecular compounds:
 - 1 – homogeneous,
 - 2 – heterogeneous,
 - 3 – real,
 - 4 – coarse dispersion,
 - 5 – have molecular structure,
 - 6 – have micellar structure.
 - a) 1, 3, 5;
 - b) 2, 4, 6;
 - c) 1, 3, 6;
 - d) 2, 4, 5.
- Choose one best description of the isoelectric point (pI) of the protein:
 - a) it is the state of the protein macromolecule, when it is not charged;
 - b) it is the pH of the solution when the protein molecule is positively charged;
 - c) it is the pH of the solution when the resulting charge of the protein molecule equals zero;
 - d) it is the pH of the solution when the protein molecule is negatively charged.
- How do the volume of a polymer sample and the general volume of the polymer-solvent system change in turgescence?
 - a) the volume of the sample and the general volume of the system decrease;
 - b) the volume of the sample and the general volume of the system increase;
 - c) the volume of the sample increases, the general volume of the system decreases;
 - d) the volume of the sample decreases, the general volume of the system increases.
- Which pH values of the solution cause the smallest turgescence of the protein.
 - a) pH > pI;
 - b) pH < pI;

- c) $\text{pH} = \text{pI}$;
- d) $\text{pH} = 7$.

Correct answers

1. The correct answer is a).
From the contemporary point of view solutions of polymers are mostly homogeneous systems, where the disperse phase is made by polymer macromolecules. The molecules have large size, but their surface does not make interface between phases. The solutions belong to real solutions.
2. The correct answer is c).
3. The correct answer is c).
At the first stage of the turgescence molecules of the solvent penetrate the polymer structure. The polymer does not change its dimensions, and the general volume of the solution does not change much. At the second stage of turgescence the volume of the polymer greatly increases (the distance between polymer molecules grows), and the general volume of the system greatly decreases (“contraction”).
4. The correct answer is c).
Protein molecules are amphoteric polyelectrolytes, that can obtain a greater or smaller number of positive ($-\text{NH}_3^+$) or negative ($-\text{COO}^-$) charges depending on pH of the solution. If $\text{pH} < \text{pI}$, the resulting charge of the protein molecule is positive. If $\text{pH} > \text{pI}$, the resulting charge is negative. When $\text{pH} = \text{pI}$, the resulting charge of all charged groups in the protein molecule is zero. Charged molecules are hydrated better, therefore hydration and, respectively, turgescence are the smallest in a solution where $\text{pH} = \text{pI}$.

Subject 19 – 20. Summary control of the module “Basics of medical chemistry”

Subject 19. Summary control of the module “Basics of medical chemistry”.List of theory questions for the summary module control of knowledge in the subject

Thematical module 1. Homogeneous equilibriums in biological fluids

1. Electron structure of biogenic elements. Typical chemical properties of the elements and their compounds (reaction without change of the oxidation state, reactions with change of the oxidation state). Correlation of place of *s*-, *p*-, *d*-

elements in the Periodic system and their content in the organism. Application of compounds of *s*-, *p*-, *d*-elements in dentistry practice.

2. Solutions in life. Enthalpy and entropy factors of dissolution and their relationship to the mechanism of dissolution.

3. Nitrogen forms several oxides. One of the oxides is produced in blood vessels for vasodilation, the other is used for narcosis. Name the oxides.

4. What halogens are found in the organisms as hydrated ions?

5. Which ion is the central nervous system the most sensitive to?

6. Solubility of gases in liquids and its dependence on various factors. The Henry-Dalton law. Effect of electrolytes on solubility of gases. Solubility of gases in the blood.

7. Solubility of solids and liquids. Distribution of substances between two immiscible liquids. The Nernst law of distribution and its importance for permeability of biomembranes.

8. Equilibrium in solution of electrolytes. The Ostwald's law of dilution.

9. Dissociation of water. The ionic product of water. pH of biological liquids.

10. The product of solubility. Conditions of formation and dissolution of precipitates.

11. Types of protolytic reactions. Neutralization, hydrolysis and ionization reactions.

12. Salt hydrolysis. Hydrolysis degree, its dependence on concentration and temperature. The hydrolysis constant.

13. Basics of titrimetric analysis. Methods of acid-base titration. Acid-base indicators and their selection.

14. Buffer systems, their classification. pH of buffer solutions.

15. Action mechanism of buffer solutions.

16. Buffer capacity and the factors that effect it. Buffer systems of blood.

17. Colligative properties of diluted solutions: depression of freezing temperature, elevation of boiling temperature. The Raoult's laws. Criometry and ebulliometry.

18. A colligative property of diluted solutions: osmosis. Osmotic pressure. The Van't Hoff's law. Plasmolysis and hemolysis.

19. Colligative properties of diluted solutions of electrolytes. The isotonic coefficient. Hypo-, hyper- and isotonic solutions in medical practice. Role of osmosis in biological systems.

20. Is it possible to calculate osmotic pressure of a solution with cryoscopy and ebullioscopy data? Write an example of calculation.

21. How can molar mass of a substance be calculated with cryoscopy data? Which of solvents, with bigger or smaller cryoscopy constant should be used for a more exact measurement of molar mass?

Thematical module 2. Heterogeneous equilibriums in biological fluids

1. Macroergic compounds. ATP as a universal source of energy for biochemical reactions. Characteristics of macroergic bonds.
2. The First Law of Thermodynamics. Internal energy. Enthalpy. Heat of the isobaric and isochoric processes. Standard heats of formation and combustion of substances.
3. Thermochemistry. The Hess' law. Thermochemical transformations.
4. Thermochemical calculations and their application for evaluation of energy metabolism in biochemical processes.
5. The Second Law of Thermodynamics. Entropy. The Gibb's energy.
6. Chemical equilibrium. Thermodynamic conditions of equilibrium. Prediction of direction of spontaneous processes. Exergonic and endergonic processes in the organism.
7. The Law of working masses. The constant of chemical equilibrium. The Le Schatellier's principle. Prediction of shifts of chemical equilibrium.
8. The rate of chemical reactions. The Law of working masses for rate of chemical reactions. The rate constant.
9. Simple and complex reactions (subsequent, parallel, conjugated, reversible, chain). Photochemical reactions and their role in the life.
10. The order of a reaction. Reactions of first and second order. Reactions of zero order. The period of half-life.
11. Effect of temperature on the reaction rate. The temperature coefficient. The Van't Hoff's rule. Characteristics of the temperature coefficient of biochemical processes.
12. The Arrhenius' equation. The energy of activation. The theory of active collisions and the theory of the transition state.
13. Homogeneous and heterogeneous catalysis. Mechanism of catalytic action. Role of catalysis in the metabolic processes.
14. Enzymes as catalysts of biochemical reactions. Effects of enzyme and substrate concentration, temperature and pH on enzymic reactions.
15. Solutions of coordination compounds. Modern theories of structure of coordination compounds.
16. Classification of coordination compounds (by the nature of ligands and the charge of the inner sphere).

17. Constants of unstability and stability of coordination ions. Intercoordination compounds. Coordination compounds in biological systems. Structure of hemoglobin.
18. Which coordination compounds belong to aquacomplexes?
19. What type of bonds is characteristic for coordination compounds?
20. Electrode processes and the mechanism of their formation. The Nernst equation. The standard electrode potential.
21. The standard hydrogen electrode.
22. Measurement of electrode potential. Measurement electrodes. Comparison electrodes.
23. Oxidation-reduction electrode potentials. Mechanism of formation, biological importance. The Nernst-Peters equations.
24. Oxidation-reduction reactions in the organism. Prediction of their direction with the standard values of Gibb's energy and values of redox potentials.
25. Galvanic cells. Electrode processes in the oral cavity.
26. Potentiometric titration, its application in medical and biological research.
27. Characteristics of solutions of high molecular compounds. Mechanism of turgescence and solubility of high molecular compounds. Effect of various factors on turgescence and solubility of high molecular compounds. Role of turgescence in physiology of organisms.
28. Isoelectric point of the protein (pI) and methods of its measurement.
29. Jellification of solutions of high molecular compounds. Properties of jellies.
30. Anomalous viscosity of solutions of high molecular compounds. Viscosity of blood and other biological fluids. Osmotic pressure of solutions of biopolymers. Oncotic pressure of blood plasma and blood serum.
31. Donnan's membrane equilibrium.
32. Surface activity. The Traube's rule. The Gibbs' equation. Orientation of molecules in the surface layer and structure of biological membranes.
33. The Langmure's equation.
34. Adsorption from solutions on the solid surface. The Freundlich's equation.
35. Physico-chemical principles of the adsorption therapy.
36. Adsorption of electrolytes (selective and ion-exchange). The Panet's rule.
37. Ionites and their application in medicine.
38. Classification of methods of chromatography by distribution of substances, aggregative phase and technique. Application of chromatography in medical and biological research.

39. Dispersion systems and their classification. Obtaining and purification of colloidal solutions. Dialysis and electro dialysis, ultrafiltration. “Artificial kidney”.
40. Molecular-kinetic properties of colloidal systems (Brownian movement, diffusion, osmotic pressure).
41. Optical properties of colloidal systems. Ultramicroscopy. Structure of colloidal particles.
42. Electrokinetical potential of colloidal particles. Electrophoresis, its application in medicine and medical and biological research.
43. Kinetic and aggregative stability of liosols. Stability factors. Mechanism of coagulation action of electrolytes.
44. Coagulation threshold, its determination. Coagulation processes in purification of drinking water and waste waters. Colloidal protection, its biological role.
45. Coarse dispersion systems (aerosols, suspensions, emulsions). Obtaining and properties. Medical application. Semicolloids.

Subject 20. Summary control of the module “Basics of medical chemistry”. Control of practical skills. Test tasks

Refer to paragraph 4.2 and materials for self-control in every practical lesson.

Recommended literature

1. Medical Chemistry: textbook / V.O. Kalibabchuk, V.I. Halynska, V.I. Hryshenko et al. – Kyiv: “Medicine”, 2010 – 224 p.

