**STATE MEDICAL EDUCATIONAL INSTITUTION
OF MINISTRY OF HEALTH OF UKRAINE**

“UKRAINIAN MEDICAL STOMATOLOGICAL ACADEMY”

M E T H O D I C A L I N S T R U C T I O N S

FOR SELF-PREPARATORY WORK OF FIRST-YEAR STUDENTS OF THE MEDICAL FACULTY IN MEDICAL CHEMISTRY

Poltava – 2010

Українська медична стоматологічна академія

Кафедра медичної, біологічної і біоорганічної хімії

Методичні вказівки до самостійної роботи з медичної хімії для студентів 1 курсу медичного факультету

Полтава - 2010 р.

The booklet contains methodical instructions in self-preparatory work in medicinal chemistry for first-year students of the medicinal faculty. The Methodical instructions in medicinal chemistry (Module 1-2) for self-preparatory work of first-year students of higher medicinal educational institutions of the IV accreditation level are prepared in accordance with the program "Medicinal chemistry" from 2005. The methodical instruction of each lesson contains the subject of the lesson, aim of studying, necessary skills and knowledge. Plans for self-preparation and self-assessment tasks are included. At the end of the booklet there is a list of recommended literature. Integration of chemistry with other subjects of study is accounted for.
The booklet also contains methodical instructions for self-preparatory independent work in order to help students to learn the topics which are not included in the class work.
Theoretical knowledge and practical skills in bioinorganic, physical and colloidal chemistry are important in studying biochemistry, hygiene, pharmacology, physiology and specialized medical and dentistry subjects.

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Збірник містить методичні вказівки до самостійної роботи з медичної хімії для студентів першого курсу медичного факультету. Методичні вказівки складені відповідно до Програми з навчальної дисципліни "Медична хімія" (Київ, 2005 р.).
У методичних вказівках до кожного заняття зазначені: обгрунтування теми і мета заняття, перелік знань, умінь і навичок, якими повинен оволодіти студент. Для кращої підготовки студентів до заняття складена орієнтовна картка з основними питаннями теми, запропоновані питання і завдання для самостійного опрацювання з відповідями. Наведений список необхідної літератури. У вказівках врахована інтеграція викладання хімії з іншими навчальними дисциплінами.
У збірнику містяться також методичні рекомендації для самостійної позааудиторної роботи студентів з тих тем програми, що винесені на самостійне опрацювання. Вони допоможуть студентам краще засвоїти цей матеріал.
Теоретичні знання та практичні навички з цих розділів курсу будуть необхідні студентам при подальшому вивченні біохімії, гігієни, фармакології, фізіології, спеціальних медичних дисциплін.
Матеріали збірника допоможуть студентам краще оволодіти знаннями та вміннями, набути необхідних практичних навичок.

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Module 1.

ACID-BASE EQUILIBRIUM AND FORMATION OF COMPLEXES IN BIOLOGICAL LIQUIDS

Lesson № 1

1.SUBJECT. **Introduction to the practical course. Safety precautions in the laboratory. Biogenic *s*-elements of the IA and IIA groups: biological role, applications in medicine.**

2.IMPORTANCE. Sodium, potassium, calcium and magnesium create (together with chlorine) basic electrolyte composition of the organism. The metals comprise 99% (by mass) of all the metals in the organism. They perform important functions in the organism. For example, calcium is found in bone and dental tissues, participates in blood coagulation and muscle contraction. Sodium, potassium, calcium and magnesium are uniformly distributed in all the tissues of the organism, but K^+ and Mg^{2+} ions are inside cells, and Na^+ and Ca^{2+} are extracellular ions. Some compounds of the elements are used as medicines.
Knowledge of structure and biological functions of *s*-elements is important in understanding metabolic processes and their medical correction (biochemistry, physiology, pharmacology, clinical sciences).

3.AIM OF STUDYING: Create understanding of biogenic elements, their qualitative and quantitative content in the human organism (macroelements, microelements, organogenes) and in the biosphere. Learn about *s*-elements, their structure, properties, role in metabolism, applications of compounds of *s*-elements in medicine. Learn to carry out analytic reactions for cations of *s*-elements in solutions and biological fluids.

Necessary knowledge:
- "biogenic elements", "macroelements", "microelements", "organogenes";
- "biosphere" and the role of the living matter;
- the correlation between the content of biogenic elements in the environment and in the human organism;
- the correlation between endemic diseases and biogeochemical provinces;
- position in the Periodic system, electron structure, oxidation level, valency, electronegativity of *s*-elements;
- rules of change of physical and chemical properties of *s*-elements and their compounds;
- biological role of *p*-elements in the organism, consequences of excess or deficiency of the elements;
- applications of compounds of *s*-elements in medicine;
- characteristic analytic reactions of potassium, sodium, calcium, magnesium and barium cations.

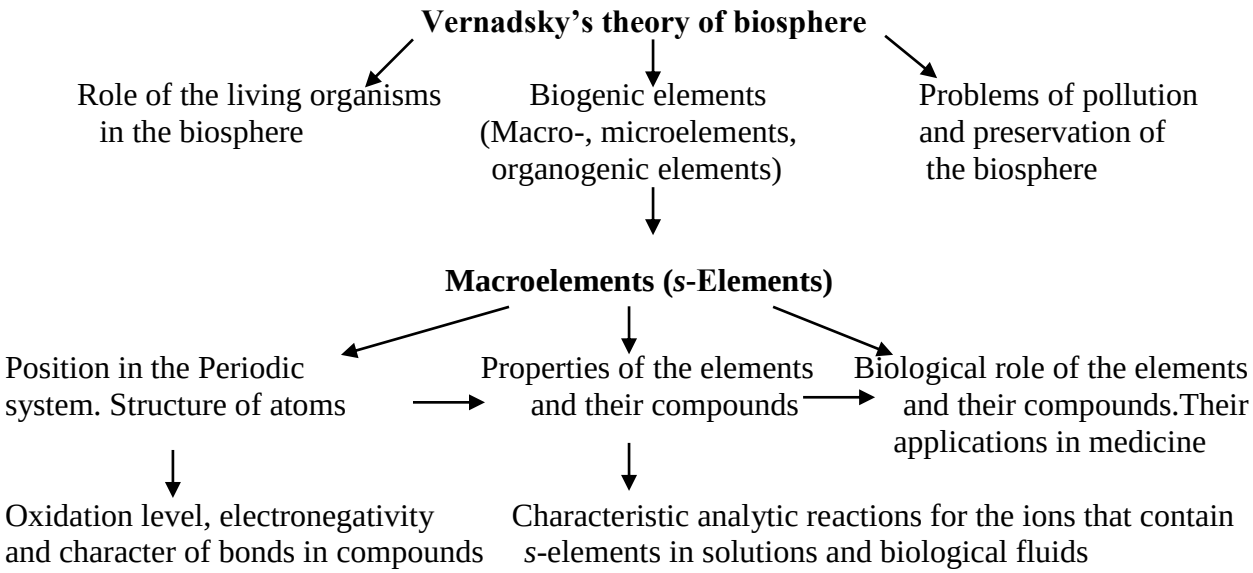
Necessary skills:
- write electron formulas of atoms and ions of *s*-elements;
- carry out analytic reactions for the potassium, sodium, calcium, magnesium and barium cations;
- write equations of analytic reactions for the *s*-elements.

Skills to obtain:
- opening of the cations of the *s*-elements in solutions and biological fluids.

4. BASIC KNOWLEDGE:

1) Vernadsky's theory of biosphere.
2) Macro- and microelements.
3) Writing electron formulas.
4) The Periodic System (high school course and previous classes).

5. LOGICAL STRUCTURE



6. STUDYING PLAN (for self-preparation)

Studying actions	Guidelines for studying actions
1. The man and the biosphere.	1.1. Vernadsky's theory of the biosphere. 1.2. Role of the living matter in the biosphere. 1.3. Protection of the environment. 1.4. Correlation of endemic diseases with biogeochemical provinces.
2. Biogenic elements	1.1. Organogens. 1.2. Macroelements. 1.3. Microelements. 1.4. Trace elements.
3. *s*-elements.	3.1. Position in the Periodic Table, the structure of the atoms. 3.2. Electronegativity, oxidation level, character of bonds. 3.3. Properties of *s*-elements and their compounds. 3.4. Correlation between the position of the *s*-elements in the Periodic Table and their content in the organism.
4. Biological role of the *s*-elements and their applications in medicine.	4.1. Biological role of sodium and potassium in the human organism. 4.2. Applications of sodium and potassium compounds in medicine. 4.3. Biological role of calcium, barium and magnesium in the human organism. 4.4. Applications of compounds of the elements of IIA group in medicine.

5. Analytic reactions for the cations of the *s*-elements in solutions and biological fluids.	5.1. Analytic reaction for the potassium ion. 5.2. Analytic reaction for the sodium ion. 5.3. Analytic reaction for the calcium ion. 5.4. Analytic reaction for the barium ion. 5.5. Analytic reaction for the magnesium ion.

7. SELF ASSESSMENT TASKS

1) Choose the correct electron formula for the valency electrons for the *s*-elements of IA group:
a) ns^1; b) ns^2; c) $2ns^1$; d) $2ns^2$.

2) Why are properties of the elements of IA group very similar?
a) the structure of the outer electron shell is the same;
b) the structure of the previous electron shell is the same;
c) the atomic radii increase;
d) the ionization potentials decrease.

3) What oxidation-reduction properties are characteristic for the elements of IA group?
a) reductive; b) oxidative;
c) reductive and oxidative;
d) no oxidation-reduction properties.

4) Choose the characteristic oxidation level of the *s*-elements of IA group in their compounds:
a) –1; b) +1; c) +2; d) –2.

5) In which state are potassium and sodium in the human organism?
a) free;
b) in coordination compounds with proteins;
c) as hydrated ions.

6) Choose the correct electron formula for the valency electrons for the *s*-elements of IIA group:
a) ns^1; b) $2ns^1$; c) ns^2; d) $ns^1(n-1)$.

7) Choose the characteristic oxidation level of the *s*-elements of IIA group in their compounds:
a) +2; b) -2; c) +3; d) +1.

8) Choose the correct electron formula for the magnesium atom:
a) $1s^22s^22p^63s^2$; b)$1s^22s^22p^6$; c) $1s^22s^22p^63s^1$; d) $1s^22s^22p^73s^1$.

9) In which state is magnesium in the human organism?
a) free;
b) as hydrated ions;
c) in coordination compounds with proteins;

10) Concentrations of potassium, sodium and calcium cations in the blood normally are 16-19 mg%, 8,2-11,6 mg%, 1,9-2,2 mg% respectively.
Calculate concentrations of the ions in the blood in g/L and mol/L.
The density of blood is assumed to be 1 g/L.

Answers

1) The correct answer is a).
s-Sublevel of the outer energy level is filled in atoms of *s*-elements of IA group.

2) The correct answers are a), b).
The great similarity of properties of elements of IA group is explained by the similar structure of their outer and previous electron shells of their atoms (except lithium). Atoms of alkaline metals have one electron in the outer energy level. The lithium atom has 2 e^- on the previous energy level, atoms of the other metals have 8 e^-.

3) The correct answer is a).
Atoms of *s*-elements of IA group give their valence electrons, thus having reducing properties. The reducing properties increase due to the decrease of the ionization potential from top to bottom.

4) The correct answer is b).
Atoms of *s*-elements of IA group have similar structure of their electron shells. They have only one electron, that can participate in formation of a chemical bond and their oxidation level is constant and equals +1.

5) The correct answer is c).

6) The correct answer is a).
The elements of IIA group contain two valence electrons on the *s*-sublevel of the outer energy level.

7) 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.

8) The correct answer is a).

9) The correct answers are b), c).
Magnesium is represented both by Mg^{2+} cations and compounds with proteins in biological liquids. Magnesium is a cofactor in certain enzymes.

10) 1. Calculate the masses of potassium, calcium and magnesium cations in 1 L of the blood:

$m_{(K^+)} = 160 \div 190$ mg or $(160 \div 190) \cdot 10^{-3}$ g/L
$m_{(Ca^{2+})} = 82 \div 116$ mg or $(82 \div 116) \cdot 10^{-3}$ g/L
$m_{(Mg^{2+})} = 19 \div 22$ mg or $(19 \div 22) \cdot 10^{-3}$ g/L

2. Calculate the molarity of the cations in the blood:

$$C_{(K^+)} = \frac{m(K+)}{M(K+)} = \frac{(160 \div 190) \cdot 10^{-3}}{39} = (4{,}1 \div 4{,}9) \cdot 10^{-3} \text{ mol/L} = 4{,}1 \div 4{,}9 \text{ mmol/L}$$

$C_{(Ca^{2+})} = \frac{m(Ca^{2+})}{M(Ca^{2+})} = \frac{(82 \div 116) \cdot 10^{-3}}{40} = (2{,}05 \div 2{,}9) \cdot 10^{-3}$ mol/L = 2,05 ÷ 2,9 mmol/L

$C_{(Mg^{2+})} = \frac{m_{(Mg^{2+})}}{M_{(Mg^{2+})}} = \frac{(19 \div 22) \cdot 10^{-3}}{24} = (7{,}9 \div 9{,}1) \cdot 10^{-4}$ mol/L = 0,79 ÷ 9,1 mmol/L

8. PRACTICUM

Tips for:

a) self-preparation

- learn the subject before the lesson using the plan in the book

b) lab work report

- write down the date, subject, object of the lesson, procedure, results of experiments, reaction equations and conclusions

c) experiments

- use only clean glassware for experiments
- do not return excess reagents back into bottles
- do not mix up corks from different bottles. Put corks on the table only upside down.
- work with concentrated acids only under the hood

do not keep any unnecessary things on the work table

8.1. Guidelines to procedure of analytic experiments

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 CLEAN glassware for experiments.
5) Strictly follow the procedure of analysis: conditions of the reaction, amounts and concentrations of reagents.
6) Do not leave obtained sediments in test tubes – dissolve them immediately in respective reagents and wash the test tubes.
7) If there is a need to leave a solution or a sediment for a while, make a respective note on its glass.

8.2 Analytic reaction for the potassium cation. Reaction with sodium hydrotartrate $NaHC_4H_4O_6$

Add 1 mL of a potassium salt solution and 1 mL sodium hydrotartrate solution to a test tube. Rib carefully the inner surface of the test tube with a glass stick. White crystals of potassium hydrotartrate precipitate.

$$KNO_3 + NaHC_4H_4O_6 = KHC_4H_4O_6\downarrow + NaNO_3$$

$$K^+ + HC_4H_4O_6^- = KHC_4H_4O_6\downarrow$$

Check, how the obtained precipitate reacts with a strong mineral acid, acetic acid and an alkali. Write molecular and short ionic equations of the reactions of the precipitate dissolving in a strong mineral acid and in an alkali.
Make a conclusion about conditions of opening the potassium cation.

8.3 Analytic reaction for the sodium cation. Reaction with potassium hydroxyantimonate (V) $K[Sb(OH)_6]$.

Add 1 mL of a sodium salt solution and 1 mL potassium hexahydroxoantimonate (V) $Na[Sb(OH)_6]$ to a test tube. Rib carefully the inner surface of the test tube with a glass stick and cool the solution. White crystals of sodium hexahydroxoantimonate precipitate. The reaction is

used to precipitate sodium ions from blood plasma in measurement of sodium concentration in blood.

$$NaNO_3 + K[Sb(OH)_6] = Na[Sb(OH)_6]\downarrow + KNO_3$$
$$Na^+ + [Sb(OH)_6]^- = Na[Sb(OH)_6]\downarrow$$

Check, how the obtained precipitate reacts with a strong mineral acid and an alkali. Write molecular and short ionic equations of the reactions of the precipitate dissolving in an alkaline medium and degradation of the reagent in an acidic medium with formation of white amorphous precipitate of metastibnic acid $HSbO_3$.
Make a conclusion about conditions of opening the sodium cation.

8.4 Analytic reaction for the calcium cation. Reaction with ammonia oxalate $(NH_4)_2C_2O_4$.
Add 1 mL of a calcium salt (chloride or nitrate) solution andd 1 mL ammonium oxalate solution to a test tube. White crystals of calcium oxalate precipitate.

$$CaCl_2 + (NH_4)_2C_2O_4 = 2NH_4Cl + CaC_2O_4\downarrow$$
$$Ca^{2+} + C_2O_4^{2-} = CaC_2O_4\downarrow$$

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.

8.5 Analytic reaction for the barium cation. Reaction with sodium sulfate or sulfuric acid
Add 1 mL of a barium salt solution and 1 mL of sodium sulfate or sulfuric acid to a test tube. A white crystalline precipitate is obtained.

$$BaCl_2 + Na_2SO_4 = BaSO_4\downarrow + 2NaCl$$
$$Ba^{2+} + SO_4^{2-} = BaSO_4\downarrow$$

Check, how the obtained precipitate reacts with a strong mineral acid.
Make a conclusion about conditions of opening the barium cation.

8.6 Analytic reaction for the magnesium cation. Reaction with sodium hydrophosphate Na_2HPO_4.
Add 1 mL of a magnesium salt solution to a test tube. Add 4-6 drops of hydrochloric acid solution (1 : 1) and 1 mL Na_2HPO_4 solution to the test tube (hydrochloric acid prevents formation of amorphous sediment $MgHPO_4$). Add by drops ammonia solution, mixing the contents after each drop. First ammonia neutralizes hydrochloric acid:

$$NH_3 \cdot H_2O + H^+ = NH_4+ + H_2O$$

Then a characteristic crystalline sediment of magnesium-ammonia phosphate is formed.

$$MgCl_2 + NH_3 \cdot H_2O + Na_2HPO_4 = MgNH_4PO_4\downarrow + NaCl + H_2O$$
$$Mg^{2+} + NH_3 \cdot H_2O + HPO_4^{2-} = MgNH_4PO_4\downarrow + H_2O$$

Presence of NH_4^+ in the solution prevents formation of magnesium hydroxide precipitate. Formation of $MgNH_4PO_4$ precipitate can be accelerated by ribbing the inner surface of the test tube with a glass stick.
The reaction of formation of magnesium-ammonia orthophosphate is used to determine magnesium in the blood plasma.
Check, how the obtained precipitate reacts with a strong mineral acid and acetic acid.
Write a reaction equation of the precipitate dissolving in an acidic medium.
Make a conclusion, how pH of the medium effects the possibility to open magnesium as magnesium-ammonia orthophosphate.

Write down the results. Check them with the teacher

Lesson № 2

1. SUBJECT. **Biogenic p-elements: biological role, applications in medicine.**

2.IMPORTANCE. The organogenic elements carbon, nitrogen, oxygen, phosphorus and sulfur, that build the major organic compounds of the organism – proteins, lipids, carbohydrates, polynucleotides, belong to *p*-elements. The *p*-element chlorine takes part in formation of the electrolyte balance of the organism, the microelements selenium and iodine participate in regulatory and transportation processes. Compounds of many *p*-elements are used as medicines. Therefore it is important to learn structure and biological functions of *p*-elements in order to understand metabolic processes and their medical correction (biochemistry, physiology, pharmacology, clinical sciences).

3. AIM OF STUDYING: Create understanding of *p*-elements, their structure, properties, role in metabolism, applications of their compounds in medicine. Master the skill to carry out analytic reactions for ions of *p*-elements in solutions and biological fluids.

Necessary knowledge:

- position in the Periodic system, electron structure, oxidation level, valency, electronegativity of *p*-elements;
- rules of change of physical and chemical properties of *p*-elements and their compounds;
- biological role of *p*-elements in the organism, consequences of excess or deficiency of the elements;
- applications of compounds of *p*-elements in medicine;
- characteristic analytic reactions of aluminium and ammonium cations, carbonate, nitrite, sulfate, thiosulfate anions.

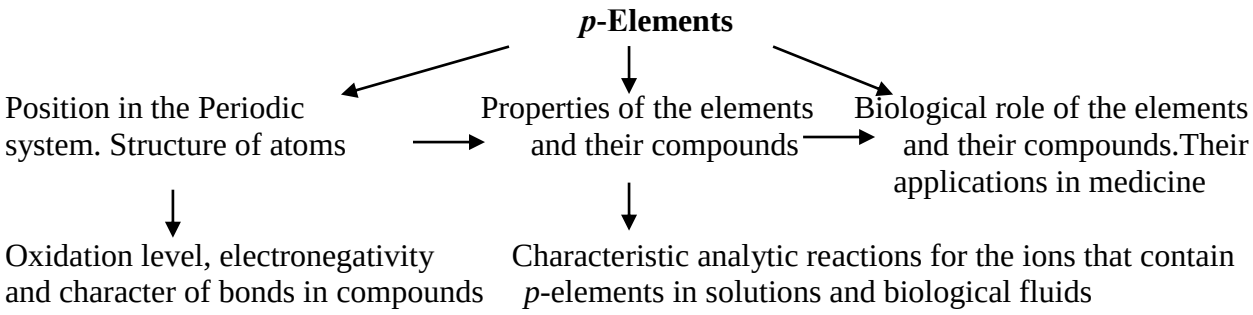
Necessary skills:

- write electron formulas of atoms and ions of *p*-elements;
- carry out analytic reactions for the aluminium and ammonium cations, carbonate, nitrite, sulfate, thiosulfate anions;
- write equations of analytic reactions for the *p*-elements.

Skills to obtain:

- opening of the ions, that contain the *p*-elements, in solutions and biological fluids.

4. LOGICAL STRUCTURE



5. STUDYING PLAN (for self-preparation)

Studying actions	Guidelines for studying actions
1. *p*-Elements	1.1. Position in the Periodic Table, the structure of the atoms. 1.2. Electronegativity, oxidation level, character of bonds. 1.3. Acid-base and oxidation-reduction properties of *p*-elements and their compounds.
2. Biological role of *p*-elements and their applications in the medicine.	2.1. Biological role of *p*-elements of IIIA and IVA groups in the human organism. 2.2. Biological role of *p*-elements of VA group in the human organism. 2.3. Biological role of *p*-elements of VIA and VIIA groups in the human organism. 2.4. Application of compounds of *p*-elements in the medicine.
3. Analytic reactions for the ions of the *p*-elements in solutions and biological fluids	3.1. Analytic reaction for the aluminium cation (IIIA group). 3.2. Analytic reaction for the ion, that contains carbon (IVA group). 3.3. Analytic reaction for the ions, that contain nitrogen (VA group). 3.4. Analytic reaction for the ions, that contain sulfur (VIA group).

6. SELF ASSESSMENT TASKS

1. Choose the correct electron formula for the valency electrons for the *p*-elements of IIIA group.
   a) $2ns^2 2p^2$; b) ns^2np^1; c) ns^3np^4; d) ns^1np^5.

2. Choose the correct electron formula for the valency electrons for the *p*-elements of IVA group.
   a) ns^2np^2; b) $ns^1 2p^2$; c) ns^3np^1; d) ns^2np^0.

3. Choose the correct electron formula for the valency electrons for the *p*-elements of VA group.
   a) ns^2np^4; b) ns^1p^3; c) ns^2np^3; d) ns^2.

4. Choose the correct electron formula for the valency electrons for the *p*-elements of VIA group.
   a) ns^2np^4; b) $ns^1 2p^3$; c) ns^2np^5; d) ns^2np^2.

5. Choose the correct electron formula for the valency electrons for the *p*-elements of VIIA group.
   a) ns^2np^5; b) $ns^1 2p^4$; c) ns^2np^6; d) ns^0np^6.

6. Choose the cause of amphoterity of compounds of the elements of IIIA group.
   a) character of the chemical bond;
   b) change of the ionic radii;
   c) change of the atomic radii;
   d) change of oxidation-reduction potentials.

7. Why can the analogues of nitrogen have bigger valencies than the maximum valency of nitrogen?

a) their atoms have valency *d*-orbitals;
b) their atomic radii are bigger than that of the nitrogen atom;
c) the first ionization potentials of their atoms decrease;
d) the charges of the nuclei increase.

8. 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.

9. Decide, whether carbon is an organogenic element that forms structural components of the cell.
a) it is; b) it is not; c) to some extent.

10. 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+}.

Answers

1. The correct answer is b).
Atoms of the elements of IIIA group: boron, aluminium, gallium, thallium have three valency electrons on the outer energy level: two of them are on the *s*-sublevel and one is on the *p*-sublevel.

2. The correct answer is a).
Carbon, silicon, germanium, tin and lead are *p*-elements of IVA group. Atoms of the elements have four valency electrons: two of them are on the *s*-sublevel and two are on the *p*-sublevel of the outer energy level (s^2p^2).

3. The correct answer is c).
Atoms of nitrogen, phosphorus, arsenic, stibium and bismuth have five valency electrons on the outer energy level: two of them are on the *s*-sublevel and three are on the *p*-sublevel.

4. The correct answer is a).
Atoms of oxygen, sulfur, selen, tellur have six valency electrons on the outer energy level: two of them are on the *s*-sublevel and five are on the *p*-sublevel.

5. The correct answer is a).
Atoms of halogens have seven valency electrons: two of them are on the *s*-sublevel and five are on the *p*-sublevel of the outer energy level (s^2p^5).

6. The correct answer is d).
It is not possible to draw a line between ionic and covalent character of bonds in compounds of the elements of IIIA group. Due to its high ionization potential boron forms covalent bonds in its compounds, but it also can form crystalline modifications that are able to conduct electric current. Aluminium has a big difference between ionization potentials of the $3p^1$ electron (5,8 eV) and $3s^2$ (I_2= 18,82 eV, I_1 = 28,44 eV) and therefore forms covalent bonds. Its ionic compounds are short-living and can exist only at high temperatures (about 1000^0C). Compounds of thallium are similar to those of aluminium. Nevertheless the s^2 pair of electrons of gallium, indium and thallium becomes more difficult to excite and the difference between ionization potentials of np^1-electron and ns^2-electrons increases

significantly. At the same time the radius of the 3+ ion increases from gallium to thallium. Therefore thallium (III) hydroxide has predominantly basic properties and thallium (I) hydroxide is similar to sodium hydroxide.

7. The correct answer is a).

Properties of nitrogen are significally different from those of phosphorus, arsenic, stibium, bismuth (like all the first elements of A groups). It is explained by the small dimensions of the atom, small number of electrons and absence of *d*-orbitals. The other elements of VA group have *d*-orbitals, and *s*- and *p*-electrons can move to the *d*-orbitals. Therefore the other elements of VA group can have higher valency.

8. The correct answer is b).

The atom of oxygen differs from atoms of the other elements of its subdroup 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.

9. The correct answer is a).

The specific position of carbon is explained 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.

10. The correct answer is b).

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

8. PRACTICUM

8.1 Analytic reaction for the aluminium cation. Reaction with an alkali

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.

$$AlCl_3 + 3\ NaOH = Al(OH)_3\downarrow + 3\ NaCl$$

$$Al^{3+} + 3\ OH^- = Al(OH)_3\downarrow$$

Check, how strong mineral acids and alkalis react with the solution.

Write molecular and short ionic equations of the reactions of the precipitate dissolving in a mineral acid and in excessive amount of alkali.

8.2 Analytic reaction for the carbonate ion. Reaction with mineral acids

Add 1 mL sodium carbonate solution and 2 mL hydrochloric acid solution to a test tube. Quickly close the test tube with a funnel cork (with a pipe for gas funneling). Place one end of the pipe in a test tube with lime water or barite water. Note the changes.

a) $Na_2CO_3 + 2\ HCl = 2\ NaCl + H_2CO_3 \nearrow CO_2\uparrow$, $\searrow H_2O$

$$CO_3^{2-} + 2\ H^+ = CO_2\uparrow + H_2O$$

b) $Ca(OH)_2 + CO_2 = CaCO_3\downarrow + H_2O$

$$Ca^{2+} + 2\ OH^- + CO_2 = CaCO_3\downarrow + H_2O$$

c) $CaCO_3\downarrow + CO_2 + H_2O = Ca(HCO_3)_2$

$$CaCO_3\downarrow + CO_2 + H_2O = Ca^{2+} + 2\ HCO_3^-$$

8.3 Analytic reaction for the ammonium cation. Reaction with an alkali

Add 0.5 mL of an ammonium salt solution and 0.5 mL of a concentrated alkali solution to a test tube. Heat the mixture. Hold a wet phenol phtalein paper over the test tube. The appearing color proves presence of ammonia ions in the solution.

In the test tube: $NH_4^+ + OH^- \leftrightarrows NH_3 \cdot H_2O \leftrightarrows NH_3\uparrow + H_2O$,

On the paper: $NH_3 + H_2O \leftrightarrows NH_3 \cdot H_2O \leftrightarrows NH_4^+ + OH^-$

8.4 Analytic reaction for the nitrite ion. Reaction with potassium permanganate solution

Add 1 mL sodium nitrite solution to a test tube. Add 1 mL 2 *M* sulfuric acid and a $KMnO_4$ solution by drops. The solution of potassium permanganate becomes colorless.

$$NO_2^- - 2e^- + H_2O \rightarrow NO_3^- + 2\ H^+ \quad | \quad 5$$
$$MnO_4^- + 5e^- + 6\ H^+ \rightarrow Mn^{2+} + 4\ H_2O \quad | \quad 2$$
$$5\ NO_2^- + 2\ MnO_4^- + 6\ H^+ = 5\ NO_3^- + 2\ Mn^{2+} + 3\ H_2O$$
$$5\ KNO_2 + 2\ KMnO_4 + 3\ H_2SO_4 = 5\ KNO_3 + 2\ MnSO_4 + K_2SO_4 + 3\ H_2O$$

8.5 Analytic reaction for the sulfate ion. Reaction with barium chloride solution

Add 1 mL sodium or potassium sulfate solution to a test tube. Add a solution of barium chloride until small white crystals of barium sulfate precipitate.

$$Na_2SO_4 + BaCl_2 = BaSO_4\downarrow + 2\ NaCl$$
$$Ba^{2+} + SO_4^{2-} = BaSO_4\downarrow$$

Check, how sulfuric or nitric acid reacts with the precipitate. Make a conclusion about conditions of opening of the sulfate-ion.

8.6 Analytic reaction for the thiosulfate ion. Reaction with mineral acids

Add 1 mL sodium thiosulfate solution to a test tube. Add 1 mL 2 *M* hydrochloric acid. Heat the mixture slightly and observe formation of yellowish precipitate of free sulfur.

$$Na_2S_2O_3 + 2\ HCl = S\downarrow + H_2SO_3 + 2\ NaCl$$
$$S_2O_3^{2-} + 2\ H^+ = S\downarrow + H_2SO_3$$

Write down the results. Check them with the teacher.

Lesson № 3

1. SUBJECT. **Biogenic *d*- elements: biological role, applications in medicine.**

2.IMPORTANCE. The biological role of *d*-elements is stipulated by their ability to participate in ligand-metathetical, heterogeneous and protolytic reactions. Understanding of structure and properties of the *d*-elements and their compounds is important for students of medicine in learning biochemistry, pharmacology, physiology, clinical sciences. Therefore it is important to learn structure and biological functions of *d*-elements and their simple compounds in order to understand metabolic processes and their medical correction.

3. AIM OF STUDYING: Create understanding of *d*-elements, their structure, properties, role in metabolism, applications of their compounds in medicine. Master the skill to carry out analytic reactions for ions of *d*-elements in solutions and biological fluids.

Necessary knowledge:

- position in the Periodic system, electron structure, oxidation level, valency, electronegativity of *d*-elements;
- rules of change of physical and chemical properties of the *d*-elements and their compounds;
- biological role of *d*-elements in the organism, consequences of excess or deficiency of the elements;
- applications of compounds of *d*-elements in medicine;
- characteristic analytic reactions for cations of *d*-elements.

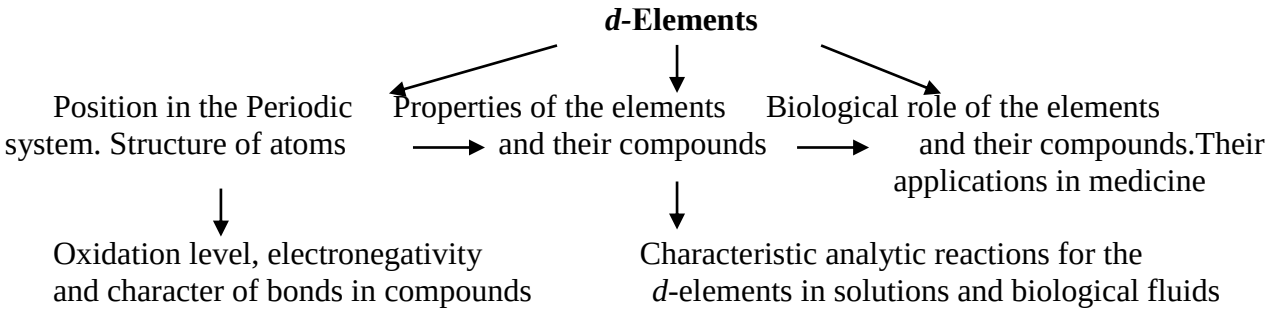
Necessary skills:

- write electron formulas of atoms and ions of *d*-elements;
- carry out analytic reactions for silver, copper, zinc, iron cations, permanganate ion;
- write equations of analytic reactions for *d*-elements.

Skills to obtain:

- opening of the ions of the *d*-elements in solutions and biological fluids.

4. LOGICAL STRUCTURE



5. STUDYING PLAN (for self-preparation)

Studying actions	Guidelines for studying actions
1. *d*-Elements.	1.1 Position in the Periodic Table, the structure of the atoms. 1.2. Electronegativity, oxidation level, character of bonds. Coordination numbers. 1.3. Acid-base and oxidation-reduction properties of compounds of the elements compared to those of the A groups.
2. Biological role of d-elements and their applications in the medicine.	2.1. Biological role of *d*-elements in the human organism. 2.2. Application of compounds of *d*-elements in medicine.
3. Analytic reactions for the ions of the *d*-elements in solutions and biological fluids.	3.1. Analytic reaction for the silver cation. 3.2. Analytic reaction for the copper cation. 3.3. Analytic reaction for the zinc cation. 3.4. Analytic reaction for the permanganate anion. 3.5. Analytic reaction for the ferric cation.

6. SELF ASSESSMENT TASKS

1) Choose the correct electron formula for the valency electrons of the chromium atom.

a) $3d^5\ 4s^2$ c) $3d^4\ 4s^2$

b) $3d^5\ 4s^1$ d) $4d^4\ 4s^2$

2) Choose the most characteristic oxidation levels of the elements of IB group in their compounds with increase of the nucleus charges.

a) +1, +2, +3 c) +2, +3, +3

b) +2, +1, +3 d) +1, +1, +1

3) Choose the most characteristic oxidation levels of zinc, cadmium and mercury.

a) +2, +2, +1 c) +2, +2, 0

b) +2, +2, +2 d) +2, 0, 0.

4) What is the character of the bond in the crystals of chlorides of metals of IIB group?

a) polar covalent; c) ionic;

b) nonpolar covalent; d) metal.

5) In which state is copper in the human organism?

a) free;

b) as hydrated ions Cu^{2+};

c) in coordination compounds with proteins, where oxidation levels of copper are +1 and +2;

d) in coordination compounds with proteins, where oxidation level of copper is +2.

6) When ammonia solution is added to a precipitate of copper hydroxide, it dissolves and the solution becomes bright blue. Why?

a) pH of the solution becomes basic;

b) $[Cu(OH)_4]^{2-}$ ions are formed;

c) $[Cu(NH_3)_4]^{2+}$ ions are formed;

d) $[Cu(H_2O)_6]^{2+}$ ions are formed.

7) What are the most characteristic oxidation numbers of iron, cobalt and nickel in their compounds?

a) +3,+2,+3 c) +3,+3,+2

b) +3,+2,+2 d) +2,+3,+3

8) What are oxidation numbers of elements of the family of iron in their coordination compounds with proteins in the organism?

a) +2; b) +3; c) +2 and +3; d) +1,+2,+3.

9) What oxidation state is characteristic for manganese compounds in the organism?

a) 0; b) +2; c) +4; d) 7.

Answers

1. The correct answer is b).

Chromium is situated in VIB group in period 4, that is why 3*d*-sublevel is being filled in its atom. The number of valence electrons (*s* and *d*) must be six. As far as in the chromium atom there is a transition of one electron from 4*s*-sublevel to 3*d*-sublevel, it has a stable half-filled 3*d*-sublevel.

2) The correct answer is b).

3) The correct answer is c).
In IIB group the ionization potentials increase from zinc to mercury. Tendency to oxidation and therefore stability of cations decrease. Thus the most common oxidation level of zinc is +2, but mercury is most stable when its oxidation level is 0. Strong oxidizing agents only can transform mercury into a soluble state and the mercury cations Hg^{2+} and Hg_2^{2+} are easilly reduced to free metal.

4) The correct answer is a).
Zinc, cadmium and mercury chlorides are salts with polar covalent bonds. The polarity of the bond decreases in the row. Presence of molecular structures has been proven for $HgCl_2$ crystals. The property of the bond can be explained by high ionization energies of the atoms due to the stable state of completed $(n-1)d^{10}ns^2$ atomic orbitals.

5) The correct answer is c).
In the organism copper is found in coordination compounds with proteins. The oxidation numbers of copper in the complexes are +1 and +2. The coordination compounds are found mostly in enzymes oxidoreductases. The copper-containing enzymes transfer electrons from the substrate by changing the oxidation states of copper atoms from +2 to +1.

6) The correct answer is c).
Copper hydroxide forms a coordination compound in a surplus amount of ammonia solution. The compound is water-soluble and bright blue.
$Cu(OH)_2 + 4 (NH_3 \cdot H_2O) = [Cu(NH_3)_4](OH)_2 + 4H_2O$
$Cu(OH)_2 + 4(NH_3 \cdot H_2O) = [Cu(NH_3)_4]^{2+} + 2OH^- + 4H_2O$

2) The correct answer is b).
The stability of compounds with the lowest positive oxidation level grows from iron to nickel. Oxidation level +3 is the most characteristic for iron, but compounds of cobalt (III) have strong oxidative properties. Compounds of nickel (III) are so unstable, that virtually do not exist in water solutions. They can be obtained only in reactions of nickel (II) compounds with strong oxidizing agents. Therefore the most characteristic oxidation level for iron is +3, and for cobalt and nickel is +2.

8) The correct answer is c).

9) The correct answer is b).

8. PRACTICUM

8.1 Analytic reaction for the silver cation. Reaction with a chloride solution or with hydrochloric acid.

Add 1 mL of a solution of salt of silver. Add 1 mL of hydrochloric acid or its salt. A white precipitate of silver salt is obtained.

$$AgNO_3 + NaCl = AgCl\downarrow + NaNO_3$$
$$Ag^+ + Cl^- = AgCl\downarrow$$

Check solubility of the precipitate in strong mineral acids and ammonia solution.
Write equation of the reaction of dissolution of the precipitate in ammonia solution. Make a conclusion about conditions of opening Ag^{1+} ion as silver chloride.

8.2. Analytic reaction for the cupric cation. Reaction with potassium ferrocyanate (II) $K_4[Fe(CN)_6]$.
Add 1 mL of a cupric salt solution to 1 mL of potassium ferrocyanate (II). A brownish precipitate $Cu_2[Fe(CN)_6]_2$ is obtained.

$$2CuSO_4 + K_4[Fe(CN)_6]) = Cu_2[Fe(CN)_6]\downarrow + K_2SO_4$$
$$2Cu^{2+} + [Fe(CN)_6]^{4-} = Cu_2[Fe(CN)_6]\downarrow$$

Divide the contents of the test tube into two parts. Add hydrochloric acid to one of the test tubes. Add alkali to the other test tube. Write reaction equations of dissolving of the precipitate. Make a conclusion about conditions of opening Cu^{2+} ion by potassium ferrocyanate (II).

8.2 Analytic reaction for the zinc (II) cation. Reaction with an alkali

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

$$ZnSO_4 + 2NaOH = Zn(OH)_2\downarrow + Na_2SO_4$$
$$Zn^{2+} + 2OH^- = Zn(OH)_2\downarrow$$

Divide the contents of the test tube into two parts. Add hydrochloric acid to one of the test tubes. Add excessive amount of alkali to the other test tube. Write reaction equations of dissolving of the precipitate in acids and alkalis. Make a conclusion about conditions of opening Zn^{2+} ion as a hydroxide.

8.4. Analytic reaction for the ferric cation. Reaction with ammonium rhodanide NH_4CNS.

Add 1 mL ammonia rhodanide or potassium rhodanide to 1 mL of a Fe(III) salt solution. The mixture becomes blood-red.

$$Fe_2(SO_4)_3 + 6NH_4CNS = 2Fe(CNS)_3 + 3(NH_4)_2SO_4$$
$$Fe^{3+} + 3CNS^- = Fe(CNS)_3$$

Check, how strong acids and alkalis react with ferric rhodanide. Write a reaction equation of degradation of rhodanides in an alkaline medium. Make a conclusion about conditions of opening Fe^{3+} ion by the rhodanide ion.

8.5. Analytic reaction for permanganate anion. A reaction with hydrogen peroxide in an acidic medium

Add 1 mL of potassium permanganate in the test tube, add 2-3 drops of sulfuric acid solution and 5 drops of 10% hydrogen peroxide solution. The solution of potassium permanganate loses color.

Balance the reaction equation:

$$KMnO_4 + H_2SO_4 + H_2O_2 \rightarrow MnSO_4 + O_2 + K_2SO_4 + H_2O$$

Write down the results. Check them with the teacher.

Lesson № 4

1. SUBJECT. **Formation of complexes in biological systems.**

2.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 B_{12} 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 from the organism, in the sanitary analysis, to measure microelements in biological liquids

3.AIM OF STUDYING: Create understanding of structure and properties of coordination compounds, their role in the organism, learn basics of methods, in which coordination compounds are obtained.

Necessary knowledge:

- structure and bonding of coordination compounds
- classification of coordination compounds
- role of coordination compounds in metabolic processes
- basics of metal and ligand homeostasis
- complexones and their applications in medicine

Necessary skills:

- write formulas of coordination compounds, determine their parts (ligands, complex ion)
- write dissociation equations of coordination compounds
- write equations of reactions that characterise properties of coordination compounds

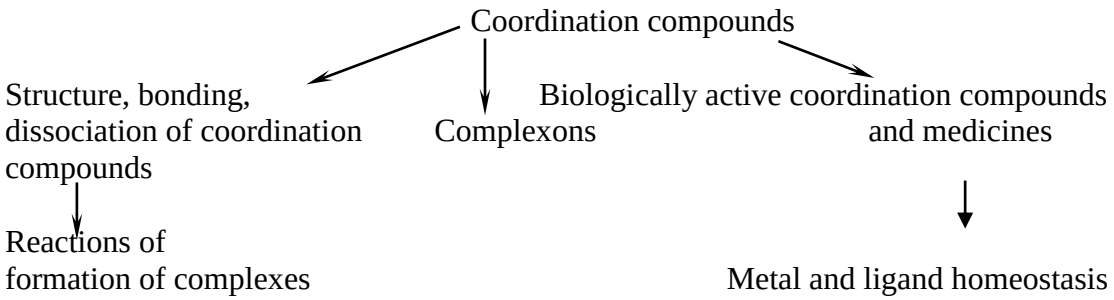
Skills to obtain:

- carrying out reaction of formation of complexes.

Basic knowledge:

- theory of coordination compounds

4. LOGICAL STRUCTURE



5. STUDYING PLAN (for self-preparation)

Studying actions	Guidelines for studying actions
1. Structure of coordination compounds	1.1. Theory of structure of coordination compounds 1.2. Identity of chemical bonds in coordination compounds 1.3. Dissociation of coordination compounds. Unstability constant of the complex ion.
2. Classification of coordination compounds	2.1. Classification by the charge of the internal sphere. 2.2. Classification by the nature of ligands. 2.3. Intercoordination compounds. 2.4. Polynuclear complexes.
3. Biologically active natural complexes.	3.1. Iron-, cobalt-, copper, zinc-containing biocomplex compounds. 3.2. Metal and ligand homeostasis and its deviations.
4. Complexons and their applications in medicine	4.1 Properties and applications of Trilon B (Complexon III).
5. Reactions of formation of complexes.	5.1 Formation of amino-, aqua- and hydroxycomplexes. 5.2 Obtaining of coordination compounds by the metathesis reaction. 5.3 Effect of solvent on stability of coordination compounds.

6. SELF ASSESSMENT TASKS

1. Coordination number is:
a) the number of bonds of the ligands with the complex former;
b) number of sites, occupied by the ligands in the internal coordination sphere of the complex;
c) number of particles in one mole of a substance;
d) number of particles in the nucleus.

2. Choose the coordination agent, its oxidation level, the coordination number and the charge of the coordination ion in the compound $K[Cr(H_2O)_2(CN)_4]$

a)	K, +1, 4, -1	c)	H_2O, 0, 6, -1
b)	Cr, +3, 6, -1	d)	Cr, +2, 4, 0

3. The bond between the coordination agent and ligands in most coordination ions is

a)	ionic	c)	hydrogen
b)	covalent	d)	metallic

4. Instability constants (C_u) of cyanide complexes with some metals are as following:
C_u $[Ag(CN)_2]^-$ = 1 x 10^{-21}, C_u $[Cd(CN)_4]^{2-}$ = 7.7 x 10^{-18},
C_u $[Fe(CN)_6]^{4-}$ = 1 x 10^{-24}, C_u $[Hg(CN)_4]^{2-}$ = 3 x 10^{-42}.

Decide, which of the metals forms the most stable cyanide complex:
a) Ag^+ b) Cd^{2+} c) Hg^{2+} d) Fe^{2+} .

5. Which of the ions Fe^{2+}, Fe^{3+}, Cl^-, HCO_3^-, K^+, Ca^{2+}, Na^+, Cu^{2+}, Zn^{2+} can form coordination compounds in the enzymes.
a) K^+, Na^+, Cl^-; b) K^+, Ca^{2+}, Na^+; c) Fe^{2+}, Fe^{3+}, Ca^{2+}, Cu^{2+}, Zn^{2+}; d) Cl^-, HCO_3^-.

6. Which of the functions is not characteristic for hemoglobin?
a) binding of oxygen molecules with ferrous ions nad transport of it from the lungs to the muscle;
b) transfer of oxygen to myoglobin molecules in the muscle;
c) binding of carbon dioxide and its transport to the lungs;
d) transport of electrons.

Answers

1. The correct answer is a).

2. The correct answer is b).
Cr (III) is the coordination agent, the coordination number (number of ligands H_2O and CN^-) is 6, the charge of the coordination ion is –1: 4 x (-1) + (+3) + 2 x (0) = -1

3. The correct answer is b).
The most common bonding between a coordination agent and ligands is covalent, formed by the donor-acceptor mechanism. Ligands are mostly donors of electron pairs and the complex former is the acceptor.

4. The correct answer is c).
The instability constant of a coordination ion is its dissociation constant. If the constant is big, it means that the coordination ion dissociates to greater degree and is therefore less stable. Mercury cyanide has the smallest constant among the other given, so it is the most stable one.

5. The correct answer is c).
Ions of d-elements are most often complex formers in enzymes and other proteins. Calcium and potassium are more often found as free ions than in compounds with proteins.

6. 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+} (hemoglobun, which contains ferric ion, loses ability to transport oxygen). That's why, unlike cytochromes, hemoglobin does not transport electrons.

8. PRACTICUM

8.1. Obtaining of an ammonia-containing coordination compound of copper.

Add 1 mL of a copper (II) salt solution to a test tube. Add an ammonia solution by drops until a precipitate of a basic salt is obtained. Add an excessive amount of ammonia solution until a bright blue transparent solution is obtained.

1) $2CuSO_4 + 2NH_3 \cdot H_2O = (CuOH)_2SO_4\downarrow + (NH_4)_2SO_4$
   $2Cu^{2+} + SO_4^{2-} + 2NH_3 \cdot H_2O = (CuOH)_2SO_4| + 2NH_4^+$
2) $(CuOH)_2SO_4 \downarrow + 10NH_3 \cdot H_2O = 2[Cu(NH_3)_4](OH)_2 + (NH_4)_2SO_4 + 8H_2O$
   $(CuOH)_2SO_4\downarrow + 8NH_3 \cdot H_2O = 2[Cu(NH_3)_4]^{2+} + SO_4^{2-} + 2OH^- + 8H_2O$

Name the obtained coordination compound. Check, how strong acids react with the solution, that contains the tetraammine copper cation. Write a reaction equation of degradation of the complex in an acidic medium.

8.2 Obtaining of a hydroxy salt of tin.

Add 1 mL of a tin Sn^{2+} salt solution to a test tube. Add an alkali solution by drops until a precipitate is obtained.

$$SnSO_4 + 2NaOH = Sn(OH)_2\downarrow + Na_2SO_4$$
$$Sn^{2+} + 2OH^- = Sn(OH)_2\downarrow$$

Dissolve the obtained precipitate in the excess of alkali. A coordination compound is obtained, which contains the complex ion $[Sn(OH)_4]^{2-}$.
Write an equation of the reaction of formation of a coordination compound. Name the compound.

8.3 Obtaining of coordination compound with a metathesis reaction.

Add 1 mL of a ferric salt solution to 1 mL of potassium ferrocyanate (II). A blue precipitate of "prussian blue" $Fe_4[Fe(CN)_6]_3$ is obtained.

$$2Fe_2(SO_4)_3 + 3K_4[Fe(CN)_6] = Fe_4[Fe(CN)_6]_3\downarrow| + 6K_2SO_4$$
$$4Fe^{3+} + 3[Fe(CN)_6]^{4-} = Fe_4[Fe(CN)_6]_3\downarrow$$

Name the obtained compound. Check solubility of the sediment in strong acids and alkalis. Write a reaction equation of dissolving of the sediment.

8.4 Effect of solvent on the stability of coordination compound.

Add 1 mL of a cobalt salt solution to 1 mL of ammonium rhodanide NH_4SCN. A bright blue coordination compound $(NH_4)_2[Co(SCN)_6]$ is obtained. Write an equation of the reaction. Divide the solution into two parts. Add amyl alcohol to the first part and water to the other part. Compare the color of the obtained solutions and stability of the complexes in amyl alcohol and in water.

Write down the results. Check them with the teacher.

Lesson № 5

1.SUBJECT. **Quantitative composition of solutions.**

2.IMPORTANCE. Chemistry is crucial for proper medical education. Knowledge of solutions is a must for the doctor. Processes of food assimilation and excretion are possible only in solutions. Blood plasma, saliva, gastric juice and other biological liquids in the organism are solutions. A great number of medical preparations are also solutions. Thus it is important to know values that characterize quantitative composition of solutions, mixtures and systems.

3. AIM OF STUDYING: to understand classification of solutions and values that characterize quantitative composition of solutions, mixtures and systems. To learn safety precautions in the laboratory.

Necessary knowledge:
- safety precautions in the laboratory;
- values, that characterize quantitative composition of solutions;
- formulas for calculation of mass percent, molarity, normality, titr and molality;
- formulas for calculation of amount of substance, molar mass of equivalent, equivalency factor.

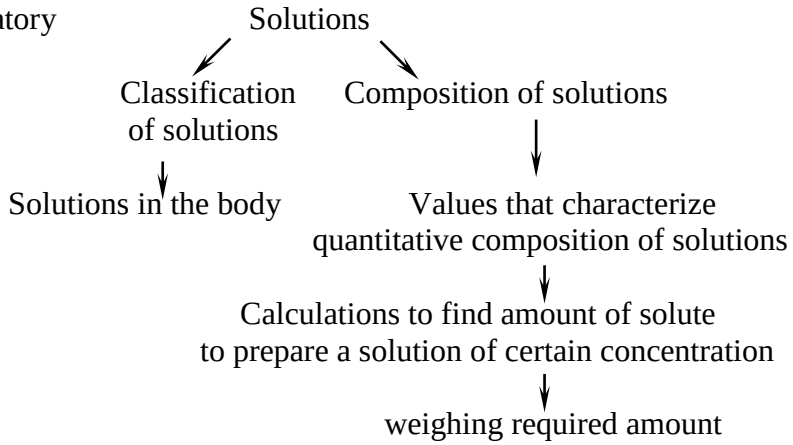
Necessary skills:
- calculations for preparing solutions of given concentration;
- calculations to transit from one form of concentration to another.

Skills to obtain:
- weighing on analytical and technical scales.

4. BASIC KNOWLEDGE:
1) solutions;
2) concentration of solutions: mass percent, molarity;
3) calculation of amount of dissolved substance to prepare solutions with certain mass percent and molarity (the high school course).

5. LOGICAL STRUCTURE

Safety precautions in the laboratory



6. STUDYING PLAN (for self-preparation)

Studying actions	Guidelines for studying actions
1.Classification of solutions:	1.1 Gaseous, solid and liquid solutions. 1.2 Saturated, unsaturated, oversaturated solutions.
2.Composition of solutions: (solutes and solvents)	
3.Values, that characterize quantitative composition of solutions.	3.1 Mass part, volume part and molar part (percent, promille). 3.2 Molarity. 3.3 Normality. 3.4 Molality. 3.5 Titr.

7. SELF ASSESSMENT TASKS

Step I

Calculate the molar masses of the following:

- (1) Ammonia (NH_3)
- (2) Calcium bromide ($CaBr_2$)
- (3) Sulphuric acid
- (4) Strontium bromide
- (5) Chlorine atoms
- (6) Chlorine molecules
- (7) Iodine molecules
- (8) Potassium chloride
- (9) Oxygen molecules

Step II

It is often necessary to calculate how many moles of a substance there are in a given mass of material. This can be done using the following expression:

Number of moles = Mass present / Molar Mass

Worked examples

Calculate the number of moles of material present in the following:-

- (1) 6.3 g of carbon
- (2) 12.5 g of magnesium chloride

Answers

- (1) Number of moles = Mass Present / Molar mass = 6.3 / 12 = 0.525 mol
- (2) Number of moles = Mass Present / Molar mass = 12.5 / 95.3 = 0.131 mol

Calculate the number of moles of material present in each of the following:-

- (1) 0.5 g of glycine (formula NH_2CH_2COOH)
- (2) 10 g of urea (formula $CO(NH_2)_2$)
- (3) 25g of disodium hydrogen phosphate (formula Na_2HPO_4)
- (4) 6.3 g of octane (formula C_8H_{18})
- (5) 0.003 g of scandium trichloride ($ScCl_3$)
- (6) 12 g of sodium hydroxide
- (7) 19 g of barium chloride.

Step III

Amounts in Solution

The **molar concentration** of a solution is the amount (which is normally in moles, but if in terms of a mass we can convert to moles) of a substance present in a given volume of solvent. Hence:-

Concentration = amount / volume

Normally we measure the amount in mol and the volume in dm^3(L). So the concentration of a substance is usually expressed in mol dm^{-3} or mol/L. *What, then, is 1 dm^3?*

1 dm = 0.1 m = 10 cm.

So **1 dm^3** = 10 cm x 10 cm x 10 cm = **1000 cm^3**

Hence 1 dm^3 = 1000 cm^3, 1 L = 1000 mL.

The number of moles of a substance that is dissolved in 1 dm^3 of solvent yields the concentration of that substance in mol dm^{-3} (which is verbally stated as moles per decimetre cubed).

Example

A solution of sodium chloride in water is prepared such that 11.7 g of solid is dissolved in 1.0 L of water. What is the concentration of the sodium chloride in mol/L?

One mole of NaCl may be calculated as 23 + 35.5 g = 58.5 g. So,

11.7 g = (11.7 / 58.5) moles of NaCl = 0.2 mol

So the solution has been prepared in such a way that 0.2 moles have been dissolved in 1 L of water. So, the concentration of the solution is 0.2 mol/L

Example

A solution of sodium chloride in water is prepared such that 6.5 g of solid is dissolved in 250 mL of water. What is the concentration of the sodium chloride in mol/L?

One mole of NaCl may be calculated as 23 + 35.5 g = 58.5 g. So,
6.5 g = (6.5 / 58.5) moles of NaCl = 0.111 mol
So the solution has been prepared in such a way that 0.111 moles have been dissolved in 250 mL of water. Now 250 mL represents 250/1000 L = 0.25 L.
So, the molarity of the solution is:
(0.111 / 0.25) mol/L = 0.444 mol/L.

- (1) A solution of disodium hydrogen phosphate (Na_2HPO_4) is prepared. If the solution contained 71.5 g of Na_2HPO_4 in 1 L of water , what is the concentration in mol/L?
- (2) What mass of material is there in each of the following:

  (a) 2.00 mol of SO_3. (b) 0.03 mol of Cl_2.

  (c) 9.00 mol of CuO (d) 0.15 mol of $MgSO_4.7H_2O$

- (3) The mass of one molecule of a compound is 2.19×10^{-22} g. What is the molar mass of the compound?
- (4) A solution is made containing 2.38 g of magnesium chloride ($MgCl_2$) in 500cm^3 of water. What is the concentration of $MgCl_2$ in this solution?

Step IV

Worked examples
1. Concentration of sodium cations in blood plasma is 142 mmol/L. Determine titr of plasma by sodium cations.

2. A water solution is obtained by dissolving 0.005 kg glucose (Mr = 180) in 0.095 kg water. It is isotonic to blood plasma. Determine mass part and molarity of glucose in the solution.

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

4. Calculate molality of physiological saline with mass part of sodium chloride 0.85%.

5. There are two sodium chloride solutions with mass parts 10% and 0.5%. Calculate, how much of each solution is necessary to take to prepare 0.5 L physiological solution with mass part 0.85% and density 1.003 kg/L.

Answers

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

Thus we have:

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

$m(Na^+)$ – mass of sodium cations, g;
V (solution) – volume of the solution, mL;
$n(Na^+)$ – amount of substance of sodium cations, mol;
$M (Na^+)$ – molar mass of the sodium cation, g/mol;

$T (Na^+) = \frac{0{,}142 \times 23}{1000} = 3{,}266 \times 10^{-3}$ g/mL

2. Mass percent (W) is the mass of the solute in the mass of the solution. It is expressed in percents, promille, etc.

$$W(glucose) = \frac{m(glucose)}{m(glucose)} = \frac{0{,}005}{0{,}005 + 0{,}095} = 0{,}05 = 5\% = 50‰ = 5 \times 10^4$$

Molar part (χ) is the amount of substance of solute in the amount of substance of solution.

$$\chi(glucose) = \frac{n(glucose)}{n(glucose) + n(H_2O)} = \frac{m(glucose) \div M(glucose)}{m(glucose) \div M(glucose) + m(H_2O) \div M(H_2O)} =$$

$$= \frac{0{,}005 \div 180}{0{,}005 \div 180 + 0{,}095 \div 18} = \frac{0{,}0000278}{0{,}0000278 + 0{,}00528} = \frac{0{,}0278}{5{,}3056} = 0{,}00524 \quad or \ 0{,}524\%$$

3. Molarity is the amount of the substance in the given volume V of a solution. Molarity is expressed in mol/m^3, mol/L, mmol/L.

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

where
$n(CaCl_2)$ is the amount of the substance $CaCl_2$, mol
V(solution) is the volume of the solution, L

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

V(solution) = 1L
$m(CaCl_2)$ = 0.0999kg

$$n(CaCl_2) = \frac{m(CaCl_2)}{M(CaCl_2)} = \frac{0.0999kg}{111kg/kmol} = 9x10^{(-4)}kmol = 0.9mol$$

Then:

$$C(CaCl_2) = \frac{0.9mol}{1L} = 0.9mol/L$$

Normality C_f is the amount of equivalent of the substance present in the volume of solution. Normality is expressed in mol/m^3, mol/L, or their subunits (mmol/L)

$$C_f = \frac{n_f}{V}$$

n(fX) is the amount of equivalent of the substance, mol
f is the equivalency factor
V is the volume of the solution, L

The equivalent is the part of a 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. The equivalency factor *f* expresses the part of the mole of the substance corresponding to its equivalent. For a substance X equivalency factor f expresses correspondence between the molar

$$f(X) = \frac{m(f)}{M}$$

mass of equivalent M(f) and the molar mass M of the substance.

e.g. for H_2SO_4 :

$$f(H_2SO_4) = \frac{M(\frac{1}{2}H_2SO_4)}{M(H_2SO_4)} = \frac{49g/mol}{98g/mol} = \frac{1}{2} = 0.5$$

$$C(1/2\ CaCl_2) = \frac{n(1/2\ CaCl_2)}{V}, \quad where: n(1/2CaCl_2) = \frac{m(CaCl_2)}{M(1/2CaCl_2)} =$$

$$= \frac{m(CaCl_2)}{1/2M(CaCl_2)} = \frac{2m(CaCl_2)}{M(CaCl_2)} = 2n(CaCl_2) = 2x0.9mol = 1.8mol$$

For $CaCl_2$:

$$C(1/2CaCl_2) = \frac{1.8mol}{1L} = 1.8mol/L$$

Then

or in general: **C = f ·C(fX)**

4. Molality of a substance *Cm* is the amount of the substance present in the mass of solvent.

$$Cm = \frac{n(solute)}{m(solvent)}, mol/kg$$

If the mass percent of sodium chloride in a solution equals 0.85%, it means, that 0.85g salt is dissolved in 99.15g water.

$$n(NaCl) = \frac{m(NaCl)}{M(NaCl)} = \frac{0.85}{58.5} = 0.0145mol$$

Thus:

$m(H_2O) = 99.15g = 0.09915kg.$

$$Cm(NaCl) = \frac{0.0145mol}{0.09915kg} = 0.146mol/kg$$

5. Let us assume, that

$W_1(NaCl) = 10\%$ $W_2(NaCl) = 0.5\%$ $W_x(NaCl) = 0.85\%$
$V_x(solution)=0.5L$ $\rho_x(solution)=1.003kg/L$
Determine the mass of the needed solution:
$m_x(solution) = V_x(solution) \times \rho_x(solution) = 0.5 \times 1.003 = 0.5015kg$

Calculate it according to the "criss-cross" rule:

$W_1(NaCl) \leftarrow m_1(solution) = W_x - W_2$

$W_x(NaCl)$

$W_2(NaCl) \leftarrow m_2(solution) = W_1 - W_x$

$m_x(solution) = m_1(solution) + m_2(solution)$

OR:

10% ← 0.35kg

0.85%

0.5% ← 9.15kg

$m_x(solution) = 9.5kg$
Calculate the necessary masses of the solutions.

$$m_1(solution) = \frac{m_x(solution)}{m_x'(solution)} \times m_1'(solution) = \frac{0{,}5015}{9{,}5} \times 0{,}35 = 0{,}0185\,kg = 18{,}5\,g$$

$$m_2(solution) = \frac{m_x(solution)}{m_x'(solution)} \times m_2'(solution) = \frac{0{,}5015}{9{,}5} \times 9{,}15 = 0{,}483\,kg = 483\,g$$

Result: it is necessary to take 18.5g solution with W_1 = 10% and 483g solution with W_2 = 0.5%.

8. PRACTICUM

8.1. Problems

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 1kg/L.

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.

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

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 1.29 kg/L.

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

8.2. Weighing on technochemical and analytical scales.

The scales should be adjusted and calibrated beforehand. Substances should be cooled to the room temperature before weighing. Special containers should be used for weighing. The substance to be weighed should be put on the left scale, weights beginning with the biggest – on the right scale. Weights must be not taken with hands or put on the table. They must be taken only with pincers. When it is necessary to weigh out exact mass of a substance, put the necessary weights on the right scale. Add the substance gradually on the left scale until the scales are balanced. Move the substance or the weights only when the scales are fixed (the handle is on the left, the beam is down).

To practice weighing, weigh out the following substances:
1.6g NaCl, 0.52g $CaCl_2$, 2.50g $NaHCO_3$, 0.15g $ZnSO_4$, 0.07g H_3BO_3.

Write down the results. Check them with the teacher.

Lesson № 6

1.SUBJECT. **Theory of solutions. Preparation of solutions.**

2.IMPORTANCE. Solutions with molecular and ionic dispersion of solute are the most important representatives of biological liquids. Water solutions of electrolytes and low molecular substances ensure constant osmotic pressure, buffer properties of biological liquids, enzyme activity etc. So a student must know basics of the theory of solutions and be able to prepare needed solutions in order to learn biological chemistry and pharmacology.

3.AIM OF STUDYING: Create understanding of the role of solutions in the body, learn basics of the theory of solutions, learn to prepare solutions of certain concentration.

Necessary knowledge:

- the theory of solutions;
- formulas to calculate amount and mass of the solute, relationship of mass and volume units;
- systematic and nonsystematic units of concentration.

Necessary skills:

- calculate the necessary amount of substance to prepare a solution with given concentration;
- use measuring glassware to prepare solutions.

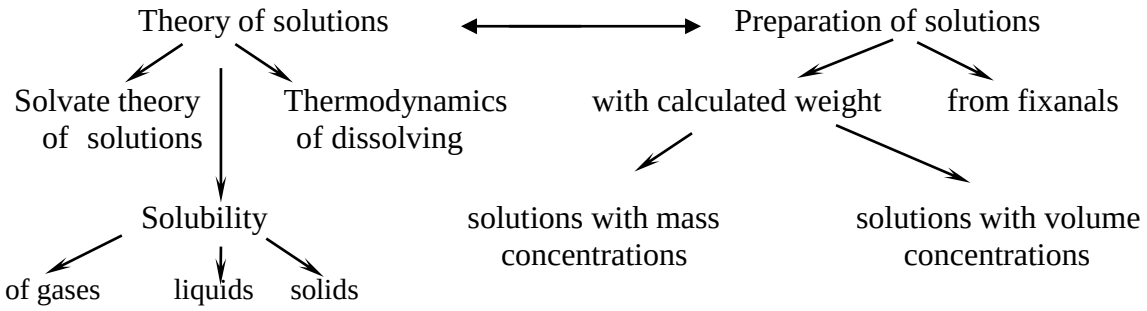
Skills to obtain:

- preparation of solutions of given concentrations (mass percent, molarity, normality).

4. BASIC KNOWLEDGE:

1) values, that characterize quantitative composition of solutions;
2) formulas to calculate concentrations of solutions;
3) using technochemical and analytical balance (the high school course and the previous lesson)

5. LOGICAL STRUCTURE



6. STUDYING PLAN (for self-preparation)

Studying actions	Guidelines for studying actions
1.Theory of solutions:	1.1 Solvate theory of solutions; 1.2 Thermodynamics of dissolving process.

2.Solubility of gases, liquids and solids	2.1 Dependence of gas solubility on pressure (Henry-Dalton's law), nature, temperature. Effect of electrolytes on solubility of gases (Sechenov's law), the caisson disease; 2.2 Solubility of liquids and solids. Nernst's law and its importance for explanation of permeability of biological membranes.
3. Preparation of solutions of given composition	3.1 Preparation of solutions of fixanals; 3.2 Preparation of solutions with calculated weight of solute.

7. SELF ASSESSMENT TASKS

1. When ammonia nitrate is being dissolved, the solution is hotter than the air. When sulphuric acid is dissolved, the solution is colder than the air. Why?

2. How does a water solution of sugar differ from a water solution of sodium chloride?

3. Why must a diver rise slowly, not fast from the big depth?

4. To measure potassium in 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 are 0.001 *M* potassium chloride solution and 0.002 *M* sodium chloride solution.

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

Answers

1. According to the theory of solutions two processes take place at dissolving: destruction of the primary structure (crystalline, amorphic, supermolecular) and formation of solvates of the destruction products and solvent molecules (those in water are called hydrates). The first process is endothermal (energy absorption), the other one is exothermal (energy release). Dissolving of ammonia nitrate takes place with a temperature depression. It means that the destruction of crystalline structure needs more energy than it is given off in the formation of hydrates. When sulphuric acid is dissolved, much more energy is released in the formation of hydrates than in the first process.

2. According to the theory the both solutions consist of molecules and associates of water: hydrates of sucrose molecules (sucrose solution) and hydrates of sodium cations, chloride ions (sodium chloride solution). The sucrose solution does not contain hydrated ions and the salt solution does not contain hydrated molecules.

3. If a diver is at a great depth, nitrogen in the air with which he breathes becomes more soluble in 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 releases so fast that it can cause breaking or clogging blood vessels.

4. Calculate the amount of substance of potassium and sodium cations in 0.25 L solution.

$n(K^+) = C(K^+) \cdot V = 0.04 \cdot 0.25 = 0.01$ mmol

$n(Na^+) = C(Na^+) \cdot V = 0.64 \cdot 0.25 = 0.16$ mmol

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

$V_1 = n(K^+) : C_1(K^+) = 0.01$mmol : 1 mmol/L = 0.01 L = 10 mL.

$V_2 = n(Na^+) : C_2(Na^+) = 0.16$mmol : 2 mmol/L = 0.08 L = 80 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.

5. Determine the amount of substance of equivalent of the acid in the needed solution:

$n(1/2H_2SO_4) = C(1/2H_2SO_4) \cdot V = 0.35 \cdot 0.05 = 0.0175$ mol.

Calculate the mass of the acid:

$m(H_2SO_4) = n(1/2H_2SO_4) \cdot M(1/2H_2SO_4) = 0.0175 \cdot 49 = 0.8575$ g.

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

$m(solution) = m(H_2SO_4) \cdot 100\% : W(H_2SO_4) = 0.8575 \cdot 100\% : 9.3\% = 9.22$g

Calculate the volume of the solution:

$V = m(solution) : \rho = 9.22 : 1.06 = 8.7$ 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 to the mark with distilled water.

8. PRACTICUM

8.1. 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 and make 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.

8.2. 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 given 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, then make to the mark with distilled water. Mix the solution.

Write down the results. Check them with the teacher

Lesson № 7

1.SUBJECT. **Basics of titrimetric analysis. Neutralization method. Alkalimetry. Measurement of mass percent of acetic acid.**

2.IMPORTANCE. 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 liquids. In the sanitary analysis the neutralisation method is used for analysis of drinking water, measurement of acid content of food products.

3.AIM OF STUDYING: Learn the theory of titrimetric analysis, neutralization method, master titration skills.

Necessary knowledge:

- basics of titrimetric analysis
- essentials of neutralization method
- indicator theory in neutralization method
- indicator selection to determine end of a titration with titration curves

Necessary skills:

- choose an indicator for a given titration
- mark the titration end in the neutralization method with indicators
- make calculations using the titrimetric analysis formulas

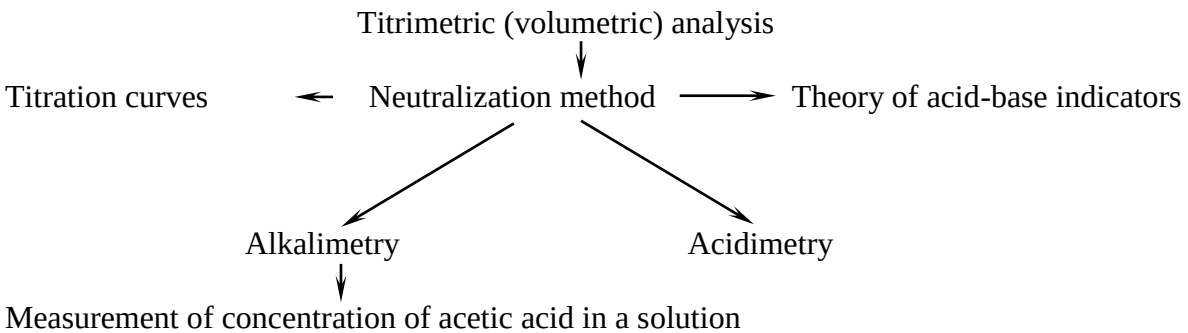
Obtained skills:

- using pipettes and burettes for titrations
- titration technique
- calculations with the neutralization method (alkalimetry) of quantity of acids in solutions and biological liquids

Basic knowledge:

1) essentials of neutralization reaction
2) molecular and ionic equations of neutralization reactions
3) solutions, concentrations of solutions
4) calculations of mass part, molar concentration, molar concentration of equivalent (from previous lessons)

5. LOGICAL STRUCTURE



6. STUDYING PLAN (for self-preparation)

Studying actions	Guidelines
1.Titrimetric analysis	1. Basics of titrimetric analysis; 2. Titration technique; 3. Calculations in titrimetric analysis.
2. Neutralization method	1. The most important reactions in the neutralization method; 2. Equivalence point in the neutralization method.
3. Acid-base indicators	1. One- and two-color indicators; 2. Interval of indicator color change.
4. Titration curves in neutralization method	1. Titration leap; 2. Indicator selection.
5. Application of acidimetry and alkalimetry	

7. SELF ASSESSMENT TASKS

1. Select a group of substances, amount of which can be measured by alkalimetry

a) HCl, NaOH, K_2CO_3 c) HCl, CH_3COOH, $NaHCO_3$

b) KOH, NH_3, $CaSO_4$ d) $(NH_4)_2SO_4$, NH_4Cl, NaCl

2. Select an indicator for measurement of concentration of a strong acid in a solution by an alkalimetric titration (color change intervals are given in brackets)

a) phenolphtalein (8.2 - 10.0) c) litmus (4.4 – 6.4)

b) methyl-orange (3.1 - 4.4) d) methyl-red (4.4 – 6.2)

3. 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) phenolphtalein (8.2 - 10.0) c) methyl-red (4.4 – 6.2)

b) methyl-orange (3.1 - 4.4) d) naphtylphtalein (7.4 – 8.6)

4. 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, $H_2C_2O_4$, H_3PO_4 d) HCl, HNO_3, H_2SO_4

5. 25.05 cm^3 (mL) 0.1244 *N* HCl solution was titrated against 25.0 cm^3 (mL) NH_3 solution. Calculate NH_3 content in the solution (g/L)

Answers

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

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 phenolphtalein has the interval of color change, which is within 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:

$$C_{(NH_3)} = \frac{C_{(HCl)} \times V_{(HCl)}}{V_{(NH_3)}} = \frac{0{,}1244 mol/L \times 25{,}05 mL}{25{,}00 mL} = 0{,}1246 mol/L.$$

Calculate the mass of NH_3 in 1 dm^3 (L) of the solution:

$$C = C_{(NH_3)} \times M_{(NH_3)} = 0{,}1246 mol/L \times 17 g/mol = 2{,}12 g/L.$$

8. PRACTICUM

8.1 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 continiously 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.

8.2 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 phenolphtalein and titrate from the burette with a work solution of NaOH until pale 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:

$$V_{av.(NaOH)} = \frac{V_1 + V_2 + V_3}{3}, \quad :V_1, V_2, V_3 - volumes\ of\ NaOH\ in\ \ parallel\ titrations,\ mL.$$

Calculation of the mass part of acetic acid:

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

$$N_{(CH_3COOH)} = \frac{N_{(NaOH)} \times V_{av.(NaOH)}}{V_{(CH_3COOH)}}, mol/L$$

where $N_{(NaOH)}$ is the normality of the NaOH solution, mol/L
$V_{(CH3COOH)}$ is the volume of acetic acid which was used for the titration.

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

$$m_{(CH_3COOH)} = N_{(CH_3COOH)} \cdot M_{(CH_3COOH)} \cdot V,\ g,$$

where V = 1L – the volume of the acetic acid solution
$M_{(CH_3COOH)}$ is the molar mass of equivalent CH_3COOH, g/mol

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

$$W_{(CH_3COOH)} = \frac{m_{(CH_3COOH)} \times 100\%}{m_{(weighed\ portion)}}, \%$$

Write down the results. Check them with the teacher.

Lesson № 8

1.SUBJECT. **Basics of titrimetric analysis. Chelatometry method. Measurement of general water hardness.**

2.IMPORTANCE. Titrimetric methods of analysis, based on the reaction of formation of coordination compounds of metal cations with complexons, are widely used in clinics and research. A specific group of compounds, called complexons, 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 from the organism. Complexons are used to measure concentrations of microelements in biological fluids, in analysis of medicinal preparations, in sanitary analysis, for example, to measure water hardness.

3.AIM OF STUDYING: Create understanding of the chelatometry method of titrimetric analysis, learn to measure total water hardness with chelatometry method.

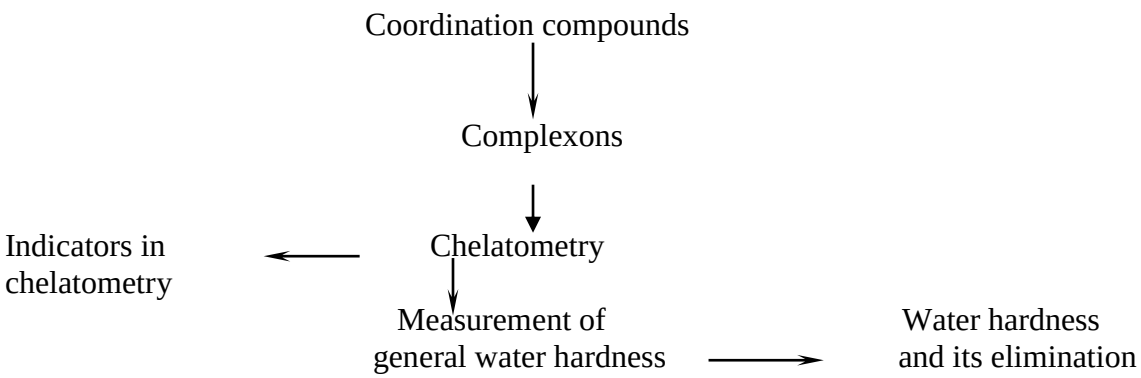
Necessary knowledge:
- the chelatometry method, applications of Trilon B and indicators
- types of water hardness, elimination of water hardness

Necessary skills:
- titrate liquids with a Trilon B solution
- make calculations in the chelatometry analysis

Obtained skills:
- measurement of general water hardness with the chelatometry method

Basic knowledge:
1) theory of coordination compounds
2) water hardness
3) theory of solutions, kinds of concentration of solutions
4) calculations in titrimetric analysis

4. LOGICAL STRUCTURE



5. STUDYING PLAN (for self-preparation)

Studying actions	Guidelines for studying actions
1. Chelatometry method	1. Reactions of the method; 2. Complexons; 3. Indicators in the chelatometry method; 4. Applications of the chelatometry analysis.
2. Measurement of general water hardness	1. General, temporary, constant water hardness; 2. Elimination of water hardness; 3. Measurement of general water hardness with the chelatometry method.

6. SELF ASSESSMENT TASKS

1. Two coordination compounds are formed in the chelatometric measurement of water hardness. Decide, which of them is more stable:

a) calcium ions and Trilon B
b) calcium ions and indicator
c) calcium ions and buffer solution
d) indicator and Trilon B

2. Which substances are used to eliminate water hardness:

a) soda, sodium hydroxide, sodium orthophosphate;
b) soda, slaked lime, sodium orthophosphate;
c) sodium hydroxide, slaked lime, ammonia solution;
d) hydrochloric acid, orthophosphoric acid, sulfuric acid.

3) Which medium is used for chelatometry measurements?

a) neutral; b) acidic; c) alkaline.

4) Calculate total water hardness (mmol-equiv/L), if 50mL of the water was titrated against 5.6 mL of 0.05*N* Trilon B solution.

a) 5; b) 50; c) 0,5; d) 5,5.

Answers

1. The correct answer is a).
In the chelatometric measurement of water hardness two coordination compounds are formed consecutively. First magnesium (calcium) ions form a wine-red complex with the indicator. When titrated with Trilon B calcium (magnesium) cations form a more stable complex with the colorless Trilon. The buffer solution creates an alkaline medium, in which the indicator becomes blue.

2. The correct answer is b).
Soda, slaked lime and sodium orthophosphate form non-soluble compounds with calcium and magnesium cations in hard water and thus decrease water hardness:

$Ca^{2+} + CO_3^{2-} = CaCO_3\downarrow$
(soda)
$3Ca^{2+} + 2PO_4^{2-} = Ca_3(PO_4)_2\downarrow$
(orthophosphate)
It is removal of permanent hardness.

$Ca^{2+} + 2HCO_3^- + Ca^{2+} + 2OH^- = 2CaCO_3\downarrow + 2H_2O$
(lime)
$Mg^{2+} + 2HCO_3^- + 2Ca^{2+} + 4OH^- = Mg(OH)_2\downarrow + 2CaCO_3\downarrow + 2H_2O$
(lime)
It is elimination of temporary hardness.

3) The correct answer is c). .

4) The correct answer is b).
Total water hardness (mmol-equiv/L) is calculated with the formula:

$$Water\ hardness = \frac{V_{Tr.B} \cdot C_{(1/2\,Tr.B)} \cdot 1000}{V_{water}}, mmol \cdot equiv/L$$

$V_{Tr.B}$ is the average volume of Trilon B, mL;
V_{water} is the volume of titrated water, mL;
$C_{(1/2\ Tr.\ B)}$ is the normality of Trilon B solution, mol/L .

$$Water\ hardness = \frac{56 \cdot 0{,}05 \cdot 1000}{50} = 56$$

8. PRACTICUM

<u>Measurement of general water hardness by chelatometry method.</u>
Each student receives a water sample from the teacher and analyses it (individual tasks).

Pipet 20.0 mL water into a flask for titration. Add 10 mL ammonia buffer solution (pH = 10) and 20 to 30 mg (on spatula tip) dry mixture of indicator chromogen black (eriochrome black T) and sodium chloride. The solution in the flask becomes wine-red. Fill the burette with work solution of Trilon B and titrate until blue. Repeat the procedure at least three times. Calculate the average volume of Trilon B used for the titration.

Calculate the general water hardness as following:

$$Water\ hardness = \frac{V_{Tr.B} \cdot C_{(1/2\,Tr.B)} \cdot 1000}{V_{water}}, mmol \cdot equiv/L$$

$V_{Tr.B}$ is the average volume of Trilon B, mL;
V_{water} is the volume of titrated water, mL;
$C_{(1/2\ Tr.\ B)}$ is the normality of Trilon B solution, mol/L .

Write down the results. Check them with the teacher.

Lesson № 9

1.SUBJECT. **Acid-base equilibrium in the organism. pH value. Potentiometric determination of pH with a glass electrode.**

2.IMPORTANCE. The vital liquids of the organism – blood, lymph, gastric juice, urine, saliva etc are water solutions. Their pH influences metabolism of cells, tissues, organs and the whole organism, because, first, hydrogen ions catalyse biochemical reactions, second, enzymes and hormones can only work within a certain range of pH, third, the ion concentration influences osmotic pressure of biological liquids. Stability of the pH value is maintained by physiological mechanisms and buffer systems. pH stability of the biological liquids is necessary for normal functioning of the organism. pH measurement helps to define pathologies.

3.AIM OF STUDYING: Create understanding of the role of pH, hydrolytic processes in the organism. Learn the basics of potentiometric measurements.
Learn basics of theory of salt hydrolysis. Create understanding of role of hydrolytic processes in metabolism and in action of medicines.

Necessary knowledge:

- pH and its importance for living organisms
- pH of the most important biological liquids in the organism
- causes of acid-base balance shifts
- hydrolysis process
- "degree of hydrolysis", "hydrolysis constant"
- role of hydrolysis in metabolic processes
- the main principles of ionometry, electrodes of measurement and comparison

Necessary skills:

- calculate pH values and H^+ concentrations
- write molecular and ionic reaction equations of hydrolysis
- evaluate pH of the medium in solutions of salts, that can be hydrolyzed

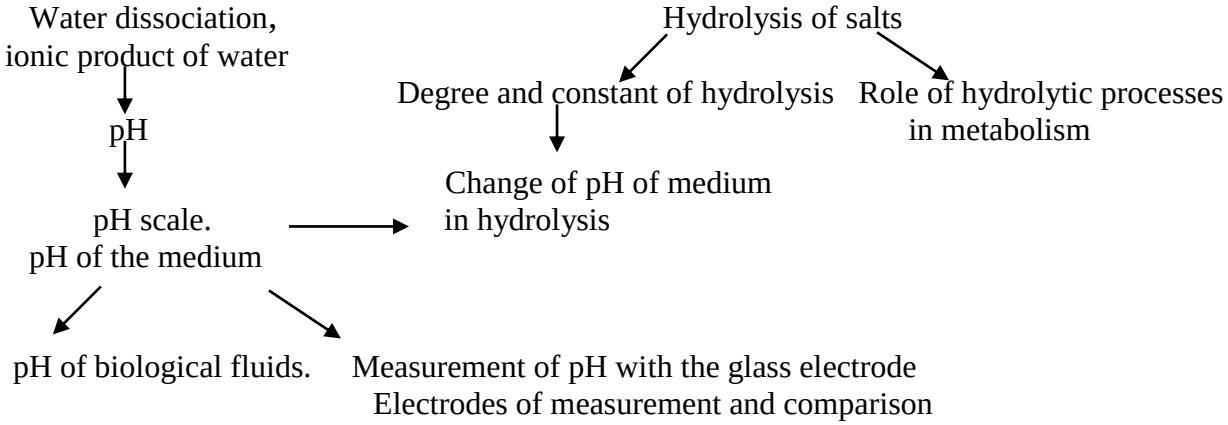
Obtained skills:

- potentiometric pH measurement of solutions and biological liquids with the glass electrode

Basic knowledge:

1) hydrolysis of salts
2) equations of hydrolysis of salts
3) acidic, neutral and alkaline environment, pH scale

5. LOGICAL STRUCTURE



6. STUDYING PLAN (for self-preparation)

Studying actions	Guidelines for studying actions
1. Dissociation of water	1.1 The constant of water dissociation. 1.2 Ionic product of water.
2. pH "power of hydrogen"	2.1 pH scale. 2.2 pH values of the liquids in the human body. 2.3 decrease of pH
3. Salt hydrolysis	3.1 Hydrolytic processes. Types of salts, that can be hydrolyzed 3.2 Degree of hydrolysis, effect of concentration and temperature 3.3 Hydrolysis constant 3.4 Effect of hydrolysis on pH medium 3.5 Role of hydrolytic processes in metabolism

7. SELF ASSESSMENT TASKS

1. The relationship between pH and pOH in a solution is:
a) pH = pOH b) pH+ pOH = 14 c) pH · pOH = 7 d) pH/pOH = 1

2. Effect of alteration of pH in biological liquids:
   a) depends on the liquid;
   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 a zone of inflammation?
   a) organic acids as products of non-complete oxidation are formed;
   b) metabolic products are evacuated slower;
   c) oxidation is supressed and reduction is promoted;
   d) 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.
a) sodium chloride, ammonium sulfate;
b) potassium cyanide, sodium carbonate;
c) potassium nitrate, calcium acetate;
d) ammonium acetate, sodium sulfate.

5. Choose the correct ionic equation (short form) of the reaction of hydrolysis of sodium carbonate.
a) $Na^+ + H_2O$ == NaOH + H^+ c) $Na^+ + OH^-$ == NaOH
b) $CO_3^{2-} + 2H^+$ == H_2CO_3 **d**) $CO_3^{2-} + H_2O$ == $HCO_3^- + OH^-$

6. What type of medium is obtained in dissolving of zinc sulfate in water.
a) acidic; b) basic; c) neutral; d) depends on the concentration of the salt.

7. Explain effect of temperature and salt concentration on hydrolysis degree.
a) hydrolysis degree does not depend of temperature and concentration;
b) hydrolysis degree increases with increase of temperature and concentration;
c) hydrolysis degree decreases with increase of temperature and concentration;
d) hydrolysis degree decreases with increase of concentration and increases with increase of temperature.

8. Explain the change of the hydrolysis constants of three salts that are formed with the same alkali and acids of different strength.
a) hydrolysis constant increases with increase of acid strength;
b) hydrolysis constant decreases with increase of acid strength
c) hydrolysis constant does not depend on acid strength;
d) hydrolysis constant is stipulated by dissociation constant of the base.

Answers

1. The correct answer is b).
As far pH = -lg[H^+], and pOH = -lg[OH^-], when we logarythm the equation of the ionic product of water, we obtain:
$[H^+] \cdot [OH^-] = 10^{-14}$, or: $-\lg[H^+] + (-\lg[OH^-]) = 14$
$pH + pOH = 14$
$\lg[H^+] + \lg[OH^-] = \lg 10^{-14}$,
$\lg[H^+] + \lg[OH^-] = -14$,

2. The correct answer is d).
pH of the medium effects physiological processes so much, that even a slight change in pH can alter the rate of a process significantly or even cease 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 catalytical 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.
$Na_2CO_3 + H_2O == NaHCO_3 + NaOH$
$CO_3^{2-} + H_2O == HCO_3^- + OH^-$

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.
$Zn^{2+} + H_2O == (ZnOH)^+ + H^+$.
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).

8. The correct answer is b).
The smaller the dissociation constant of an acid (the weaker the acid), the stronger hydrolysis of a salt of the acid. Therefore hydrolysis constant of a salt decreases with increase of strength of an acid or increase of its dissociation constant, because hydrolysis of the salts is anionic.

$An^- + H_2O == HAn + OH^-$, hydrolysis constant can be calculated with the formula:

$K_{hydr.} = \frac{K_{H_2O}}{K_{HAn}}$, *where*: K_{H_2O} is ionic product of water;

K_{HAn} is dissociation constant of the acid;

$K_{hydr.}$ is hydrolysis constant .

8. PRACTICUM

8.1 Preparation of the instrument to work.

Potentiometric measurement of pH is done with the ionometr EV-74. The instrument is prepared as following:

– press the buttons “t” and “-1-19", plug in the instrument 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 the constant potential (0,201±: 0,003V). Fix the electrodes in the holder. Plug them in the respective sockets on the back of the instrument.

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

8.2. Measurement of pH of biological liquids.

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

– immerse electrodes in a cup with a biological liquid 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. Write down the results.

1) Fill in the chart with exact values of pH of biological liquids.

№ of measurement	Biological liquid	pH	a_{H^+}, mol/L	K_w	a_{OH^-}, mol/L	pOH	environment

2) Calculate the activity of hydrogen cations a_{H^+} with the exact values of pH:
$pH = -\lg a_{H^+}$, or $\lg a_{H^+} = -pH$

3) As far as in all water solutions (and biological liquids as well) the ionic product of water K_w is constant, we can find the activity of hydroxyde ions with the formula (at standard temperature):

$$K_w = a_{H^+} \cdot a_{OH^-} = 10^{-14},\ a_{OH^-} = \frac{10^{-14}}{a_{H^+}}$$

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 liquids.

Write down the results. Check them with the teacher.

Lesson № 10

1. SUBJECT. **Buffer solutions.**

2.IMPORTANCE. Stable 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-depending reactions. It is important to know properties and composition of buffer systems in studying biochemistry, physiology and clinical sciences.

3.AIM OF STUDYING: Create an idea of buffer solutions and their action mechanism. Examine, how acids, bases and dilution effect pH of buffer solutions.

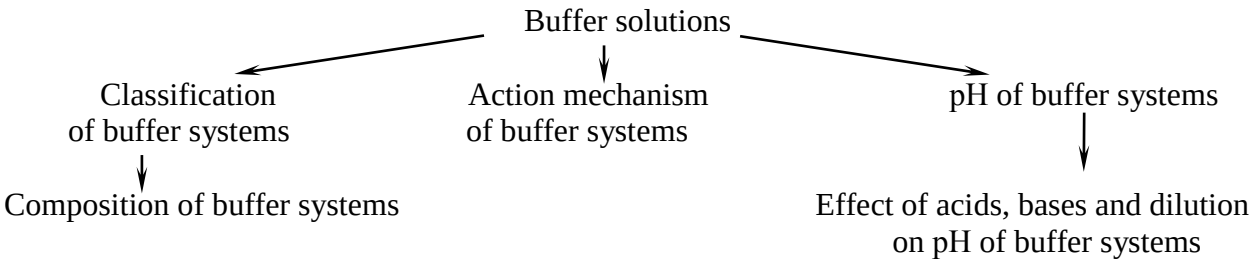
Necessary knowledge:
- general idea of buffer systems;
- classification of buffer systems;
- mechanism of buffering;
- composition of buffer systems;
- factors, that influence pH of buffer systems.

Necessary skills:
- writing reaction equations of buffering;
- calculations with Henderson – Hasselbach equation.

Skills to obtain:
- decide how acids, bases and dilution influence pH of buffer solutions.

4. BASIC KNOWLEDGE:
1) strong and weak electrolytes;
2) power of hydrogen and pH scale;
3) measuring pH in solutions.

5. LOGICAL STRUCTURE



6. STUDYING PLAN (for self-preparation)

Studying actions	Guidelines for studying actions
1. Buffer solutions	1.1 Classification of buffer solutions; 1.2 Action mechanism of buffer solutions.
2. pH of buffer solutions	2.1 Henderson-Hallelbach equation; 2.2 Effect of different factors on pH of buffer solutions.

7. SELF ASSESSMENT TASKS

1. How many main types of buffer solutions (by composition) do you know ?

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

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

a) $pH = pK_{HCN} + \lg\frac{C_{(NaCN)}}{C_{(HCN)}}$ b) $pH = pK_{HCN} + \lg\frac{C_{(HCN)}}{C_{(NaCN)}}$

c) $pH = 14 - pK_{HCN} + \lg\frac{C_{(NaCN)}}{C_{(HCN)}}$ d) $pH = 14 + pK_{HCN} - \lg\frac{C_{(HCN)}}{C_{(NaCN)}}$

3. Calculate pH of a buffer solution, prepared from 0,040 L 0.15*M* ammonia solution and 0,020 L 0.25 *M* ammonia chloride. pK ($NH_3 \cdot H_2O$) = 4.74

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

4. 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

$$CO_2 + H_2O = H^+ + HCO_3^-;$$

c) carbonic acid decomposes under influence of strong acids;
d) the strong acid is replaced by an equivalent amount of weak carbonic acid.

5. Which factors effect pH of a buffer system?

a) nature 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.

Answers

1. The correct answer is b)

Buffer systems fall into two types:

- weak acid and a salt of the weak acid and an alkali;
- weak base and a salt of the weak base and a strong acid.

2. The correct answer is a)

Henderson-Hasselbach equation for the system is as following:

$$pH = pK_{HCN} + \lg\frac{C_{(NaCN)}}{C_{(HCN)}}$$

3. The correct answer is c)

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

$$pH = 14 - pK_{NH_3 \cdot H_2O} - \lg\frac{C_{(NH_4Cl)}}{C_{(NH_3 \cdot H_2O)}} = 14 - pK_{NH_3 \cdot H_2O} - \lg\frac{n_{(NH_4Cl)}}{n_{(NH_3 \cdot H_2O)}}$$

$n_{(NH_4Cl)} = C_{(NH_4Cl)} \cdot V_{(NH_4Cl)} = 0{,}25 \cdot 0{,}02 = 0{,}005\,mol = 5\,mmol$

$n_{(NH_3 \cdot H_2O)} = C_{(NH_3 \cdot H_2O)} \cdot V_{(NH_3 \cdot H_2O)} = 0{,}15 \cdot 0{,}04 = 0{,}006\,mol = 6\,mmol$

$pH = 14 - 4{,}74 - \lg\frac{5}{6} = 9{,}26 - \lg 0{,}833 = 9{,}33$

Therefore, pH of the buffer solution is 9.33.

4. The correct answer is c)

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

$H^+ + HCO_3^- = H_2CO_3 = H_2O + CO_2$

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

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

pH of a buffer system depends on the nature of weak electrolyte (pK) and ratio of its components:

$\lg\frac{N_{salt}}{N_{acid}}$ *or* $\lg\frac{N_{salt}}{N_{base}}$

8. PRACTICUM

8.1. 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 methylred indicator to each of the tubes. Shake each tube and compare the colour.

8.2. Effect of acids and alkalis on pH of buffer solutions.

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 metylred to each tube. Shake the tubes and compare the colour.

Make a conclusion about influence of acids, alkalis and dilution on pH of buffer solutions.
Write down the results. Check them with the teacher.

Lesson № 11

1. SUBJECT. **Buffer systems in the human organism. Potentiometric measurement of buffer capacity of blood plasma.**

2.IMPORTANCE. Blood, urine, saliva, extracellular fluid and other liquids in 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.

3.AIM OF STUDYING: Create an idea of the most important buffer systems of the human organism, acid-base balance in the organism and its changes, buffer capacity of buffer systems. Master the potentiometric method of measurement of buffer capacity.

Necessary knowledge:

- main buffer systems of the human organism, their components, properties and importance;
- buffer capacity of buffer systems, its dependence on different factors;
- importance of acid – base balance in the human organism, acidosis and alkalosis;
- potentiometric titration and potentiometric measurement of buffer capacity.

Necessary skills:

- select electrodes to measure buffer capacity;
- calculate acid and alkali buffer capacity.

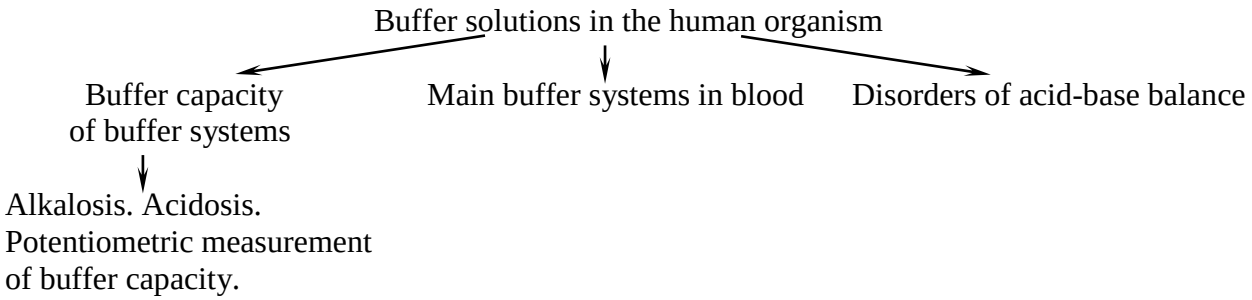
Skills to obtain:

- potentiometric measurement of blood plasma buffer capacity with glass and chlorine-silver electrodes.

4. BASIC KNOWLEDGE:

1) electrodes, galvanic circles, formation of the potential;
2) buffer solutions, mechanism of buffering, Henderson-Hasselbach equation;
3) potentiometric measurement of pH (from previous lessons).

5. LOGICAL STRUCTURE



6. STUDYING PLAN (for self-preparation)

Studying actions	Guidelines for studying actions
1. Buffer systems in the human organism.	1.1 Bicarbonate buffer system; 1.2 Phosphate buffer system; 1.3 Hemoglobin-oxyhemoglobin buffer sytem; 1.4 Protein (amino acid) buffer system.
2. Buffer capacity of buffer systems.	2.1 Effect of concentration and component ratio on buffer capacity; 2.2 Calculation of buffer capacity; 2.3 Potentiometric measurement of buffer capacity of the blood plasma.
3. Acid – base balance in the organism.	3.1 Major factors in acid – base balance of blood plasma (pH value, partial pressure of carbon dioxyde and concentration of bicarbonate); 3.2 Acidosis and alkalosis (metabolic and respiratory).

7. SELF ASSESSMENT TASKS

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 hydrolized, thus regulating pH.

3. Which factors effect buffer capacity:
    a) concentration, pH, nature of a buffer system;
    b) concentration, ratio of components;
    c) pH, temperature;
    d) temperature, ratio of components, nature of the buffer system.

4. Which ratio of an acid and its salt will create the greatest buffer capacity:
    a) 50 : 50;
    b) 30 : 70;
    c) 80 : 20;
    d) 20 : 80.

5. Change of acid-base balance caused by prolonged hypoventilation is called:
    a) respiratory acidosis;
    b) respiratory alkalosis;
    c) metabolic acidosis;
    d) metabolic alkalosis.

6. Choose the pair of electrodes, which can be used to create a galvanic circle for potentiometric measurement of buffer capacity:

a) chlorinesilver and platinum;
b) hydrogen and hinhydron;
c) glass and platinum;
d) glass and chlorinesilver.

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 connected by the equation: $H_2PO_4^- = H^+ + HPO_4^{2-}$.

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 concentration of components, the more acids and alkalis can the buffer system neutralize without substantial shifts in pH.

4. The correct answer is a)
When the ratio of components of a buffer system is 1 : 1, its buffer capacity for acid and for alkali will be the greatest compared to other variations. Influence of acid or alkali on pH will be the smallest with the ratio. For example, let us compare the three types of salt-acid ratio (mmol):

a) 50 : 50; b) 30 : 70; c) 80 : 20.

The results will be as following:

- addition of 10 mmol HCl will result in the change of the ratio:

a) 40 : 60; b) 20 : 80; c) 70 : 30,

and relative change of the ratio will be:

a) 0.67; b) 0.58; c) 0.58.

- addition of 10 mmole NaOH will change the ratio as following:

a) 60 : 40; b) 40 : 60; c) 90 : 10,

relative change of the ratio will be:

a) 1.50; b) 1.56; c) 2.25.

Thus we can make a conclusion, that any ratio other than 1 : 1 (50 : 50) causes greater change of pH of a buffer system.

5. The correct answer is a)
Hypoventilation results in increased CO_2 concentration in blood. It will cause decrease of pH. The phenomena is called acydosis. It is caused by a respiration disorder and is called respiratory acidosis.

6. The correct answer is d)
A galvanic circle must consist of a measurement electrode, which 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.

8. PRACTICUM

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

8.1. 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 0.201 V. Plug the electrodes in the sockets on the back side of the machine. Fix the electrodes over the magnete mixer. Titration is to be carried out in a 50 cm^3 cup with a magnete inside.

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

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

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

Calculate buffer capacity with the formula:

$$B_{acid} = \frac{N_{(HCl)} \cdot V_{(HCl)}}{V_{(plasma)} \cdot |pH_1 - pH_0|}, mol/L$$

$N_{(HCl)}$ - normality of HCl solution (mol/L),
$V_{(HCl)}$ - volume of HCl solution, mL,
$V_{(plasma)}$ – volume of blood plasma, mL,
($pH_1 – pH_0$) – difference between pH data.

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

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

Calculate with the formula:

$$B_{alkali} = \frac{N_{(NaOH)} \cdot V_{(NaOH)}}{V_{(plasma)} \cdot |pH_1 - pH_0|}, mol / L$$

$N_{(NaOH)}$ - normality of NaOH solution (mol/L),
$V_{(NaOH)}$ - volume of NaOH solution, mL,
$V_{(plasma)}$ – volume of blood plasma, mL,
($pH_1 – pH_0$) – difference between the pH data.

Write down the results. Check them with the teacher.

Lesson № 12

1.SUBJECT. **Colligative properties of solutions.**

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

3.AIM OF STUDYING: Create an idea of colligative properties of solutions and their importance for the organism. Carry out osmometric research, select hypo-, hyper- and isotonic solutions for blood erythrocytes.

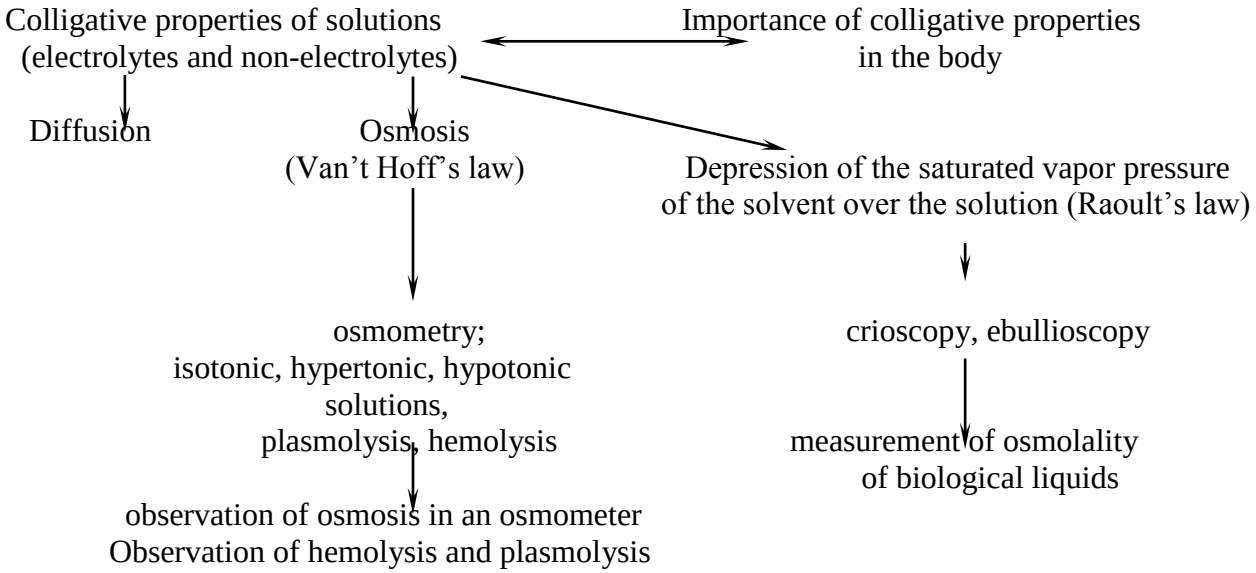
Necessary knowledge:
- colligative properties of solutions: diffusion, osmosis, depression of saturated vapor pressure of the solvent over the solution, boiling point elevation and freezing point depression;
- isotonic, hypertonic, hypotonic solutions;
- hemolysis, plasmolysis;
- osmometry, crioscopy and ebullioscopy.

Necessary skills:
- calculations with the Ostwald's and Raoult's equations, crioscopy and ebullioscopy formulas;
- comparison of solutions as isotonic, hypertonic and hypotonic.

Skills to obtain:
- simple osmometric testing of biological liquids;
- determination of hemolysis, plasmolysis.

4. BASIC KNOWLEDGE:
1) solutions of electrolytes and non-electrolytes;
2) theory of solutions;
3) concentration of solutions;
4) theory of electrolytic dissociation, strong and weak electrolytes, dissociation degree and dissociation constant (high school course).

5. LOGICAL STRUCTURE



6. STUDYING PLAN (for self-preparation)

Studying actions	Guidelines for studying actions
1.Colligative properties of diluted solutions of nonelectrolytes:	1.1 Diffusion; 1.2 Osmosis, osmotic pressure; 1.3 Osmosis in nature, biological importance of osmosis; 1.4 Relative depression of the saturated vapor pressure of the solvent over the solution. Raoult's law; 1.5 Consequences of Raoult's law. Crioscopy, ebullioscopy.
2. Colligative properties of solutions of electrolytes and biological liquids:	2.1 ***i***, the isotonic coefficient; 2.2 Hypo-, hyper- and isotonic solutions. Plasmolysis and hemolysis; 2.3 Osmotic pressure; 2.4 Role of electrolytes, non-electrolytes, biopolymers in osmotic pressure of biological liquids.

7. SELF ASSESSMENT TASKS

1. What stipulates the osmotic pressure of the blood plasma?
2. What is the isotonic coefficient?
3. 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.
4. 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
5. 13 g camphor was dissolved in 400 g diethyl ether, which led to 0.453º boiling point elevation. Calculate the molar mass of camphor.

Answers

1. 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 Cº 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.

2. 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 α = 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

$$\boldsymbol{i} = 1+\alpha(n-1).$$

3. 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.

4. 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.

5. From the consequence of Raoult's law $\Delta t_к = E \times C_{m\,t}$ the boiling point elevation of a solution ($\Delta t_к$) is proportional to the molality (C_m) of the solute. Convert the formula so as to calculate the molar mass of the solute.

$$M = \frac{E \times a \times 10^3}{\Delta t_k \times B},$$

M – molar mass of camphor, g/mol;
E – ebullioscopy constant of the solvent, kg·grad/mol;
a – mass of solute, kg;
B – mass of solvent, kg.

For diethyl ester E = 2,12 kg·grad/mol

Do the calculations

$\Delta t_к = 0{,}453^0$ a = 13×10^{-3} kg B = 0,4 kg

$$M = \frac{2{,}12\times13\times10^{-3}\times10^3}{0{,}453\times0{,}4} = 152\times10^{-3}\times10^3\ g/mol \quad or\ 152\,g/mol$$

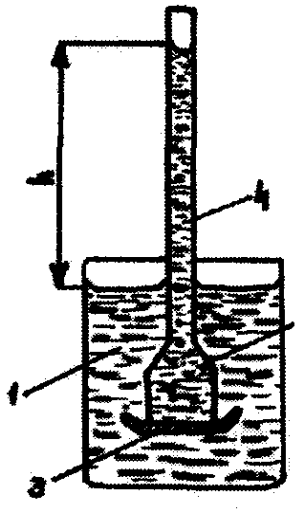
Problems

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

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

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

8. PRACTICUM



8.1. Measurement of osmotic pressure.

The simplest osmometer consists of a flask with distilled water and a glass immersed in it. The glass has a semi-permeable membrane for the bottom. A capillary pipe 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 in the water 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 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.

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

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.

Fill in the chart:

Solution concentration C, mol/m^3	ρ, kg/m^3	g, m/c^2	h, m	P_{osm}, Pa
$1{,}5 \times 10^3$	$1{,}14 \times 10^3$	9,8		

Write down the results. Check them with the teacher.

Lesson № 13

Summary control of Module 1
"ACID-BASE EQUILIBRIUM AND FORMATION OF COMPLEXES IN BIOLOGICAL LIQUIDS"

List of questions for the summary control of Module 1

Chemistry of biogenic elements. Formation of complexes in biological liquids.

1. Electron structure of biogenic elements. Typical chemical properties of the elements and their compounds (reactions without change of oxidation levels, with change of oxidation levels, formation of complexes). Correlation of position of *s*-, *p*-, *d*-elements in the Periodic Table and their content in the organism.

2. Solution of coordination compounds. Modern theories of structure of coordination compounds. Classification of coordination compounds (by the nature of ligands and the charge of the inner sphere).

3. Constants of unstability and stability of coordination ions. Basics of chelatometry.

4. Intercoordination compounds. Polynuclear complexes. Coordination compounds in biological systems. Structure of hemoglobin.

Acid-bace equilibrium in biological liquids.

1. Solutions in the life. Enthalpy and entropy factors of dissolving and their relation to the mechanism of dissolving.

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

3. Solubility of solids and liquids. Distribution of substances between two non-mixable liquids. The Nernst law of distribution and its importance for permeability of biomembranes.

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

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

6. The product of solubility. Conditions of formation and dissolving of precipitates. Concentrations of solutions.

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

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

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

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

11. Action mechanism of buffer solutions.

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

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

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

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

Module 2.

EQUILIBRIUM IN BIOLOGICAL SYSTEMS ON THE PHASE INTERFACE

Lesson № 1

1.SUBJECT. Thermal effects of chemical reactions in solutions. Directions of processes.

2.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. 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.

3. AIM: Create understanding of importance of thermodynamical approach in studying chemical and biochemical processes. Learn basic concepts of thermochemistry. Master technique of simple thermochemical research and calculations.

Necessary knowledge:

- the First and the Second Laws of Thermodynamics;
- Hess' law and its consequences;
- enthalpy, internal energy, enthropy, standard ethalpy (heat) of formation, standard ethalpy (heat) of combustion;
- writing thermochemical equations of reactions;
- Hess' law for direct and indirect calorimetry;
- thermodynamic criteria of spontaneous processes;
- macroergic bonds, macroergic compounds and their importance in the organism;
- endergonic and exergonic processes, energetic coupling in the organism.

Necessary skills:

- write termochemical equations for exo- and endothermal reactions;
- make calculations with thermochemical reactions;
- calculate thermal effects of reactions with standard enthalpies of formation and combustion;
- calculate energetic value of food products from energetic values of proteins, fats, carbohydrates;
- predict feasibility of a spontaneous process with the change of Gibb's energy or the changes of enthalpy and entropy.

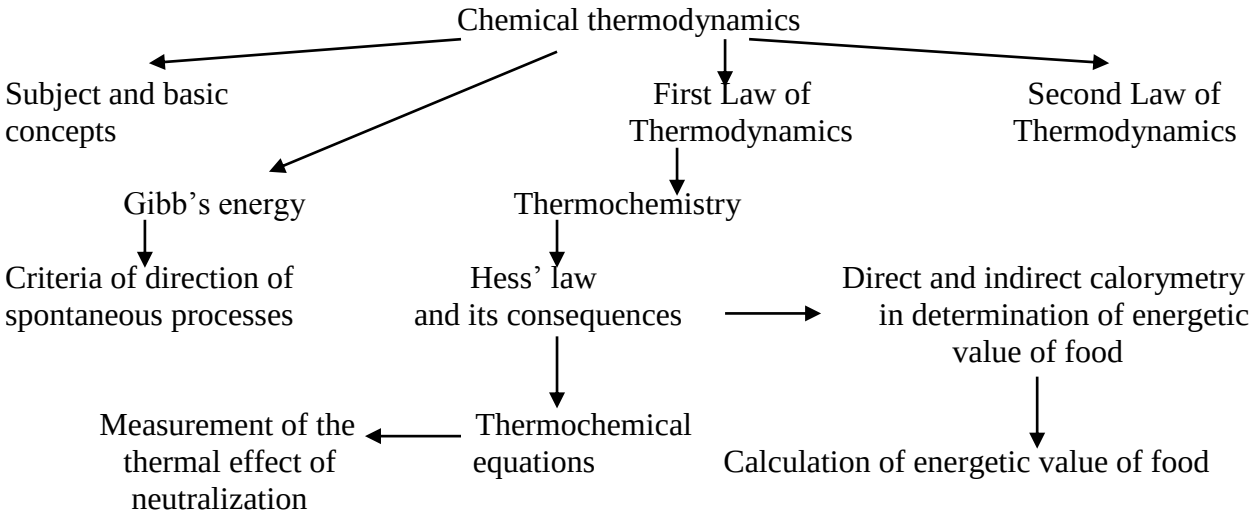
Skills to obtain:

- elementary thermochemical experiments and calculations.

4. BASIC KNOWLEDGE:

1) thermal effects of reactions, exo- and endothermal reactions;
2) writing equations of chemical reactions;
3) the neutralisation reaction.

5. LOGICAL STRUCTURE



6. STUDYING PLAN (for self-preparation)

Studying actions	Guidelines to studying actions
1. Chemical thermodynamics as a science	Systems, types of systems. Parameters of systems. Isobaric, isochoric, isothermal processes.
2. The First Law of Thermodynamics.	Heat and work as different forms of transformation of different kinds of energy. Internal energy, enthalpy.
3. Thermochemistry as the science about thermal effects of reactions.	Change of enthalpy as the thermal effect of the reaction. Thermochemical equations. Calculations with thermochemical equations.
4. The Hess' law and its consequences.	Application of the Hess' law in calculations. Standard enthalpies (heats) of formation and combustion and their application in calculations of thermal effects of reactions. Direct and indirect calorimetric measurement of energetic value of food products.
5. The Second Law of Thermodynamics.	Entropy and its change in spontaneous processes. Qualitative assessment of entropy change in chemical reactions.
6. Thermodynamics potentials: Gibb's energy.	6.1. Calculations of the change of Gibb's energy in the reaction with the standard values of Gibb's energy of the reactants and products.
7. Criteria of direction of spontaneous processes.	7.1. Enthalpy and entropy factors in chemical reactions. 7.2. Change of Gibb's energy as the criteria of the spontaneous process.

8. Thermodynamics of the organism as of the open system.	8.1. Macroergic compounds in the organism. ATP as the source of energy. 8.2. Energetic coupling of endergonic and exergonic processes in the organism.

7. SELF ASSESSMENT TASKS

1. When the reaction is endothermal:

a) when the energy of products is equal to the energy of initial substances;
b) when the energy of products is higher than the energy of initial substances;
c) when the energy of products is lower than the energy of initial substances;
d) it is possible to determine only when it is known whether energy is absorbed or released.

2. Choose exothermal reactions:

a) $O_2 + 1/2O_2 = O_3$, $\Delta H = 142$ kJ
b) $1/2O_2 + H_2 = H_2O$, $\Delta H = -242$ kJ
c) $H_2O + 1/2O_2 = H_2O_2$, $\Delta H = 98.2$ kJ
d) $H_2 + 1/2O_2 = H_2O$, $\Delta H = -285.8$ kJ

3. Choose the substance with zero standard enthalpy of formation:

a) Br_2 (g) b) Br_2 (l) c) Br_2 (s) d) HBr (g)

4. Calculate the change of enthalpy ΔH of the reaction which is not possible to carry out in an experiment: $H_2(g) + O_2(g) = H_2O_2(l)$, if the following thermochemical equations are known:

$H_2O_2(l) = H_2O(l) + 1/2O_2(g)$, $\Delta H = -98.2$ kJ (1)
$H_2(g) + 1/2O_2(g) = H_2O(l)$, $\Delta H = -284.2$ kJ (2)

a) –382.4 kJ b) –186.0 kJ c) 186.0kJ d) 382.4 kJ

5. Calculate the enthalpy of formation of acetylene, if it is known, that combustion of 1 mole releases 1300.84 kJ, and the enthalpies of formation are:

$\Delta H^0_{f,298}$ ($H_2O(l)$) = -285.84 kJ/mol $\Delta H^0_{f,298}$ ($CO_2(g)$) = -393.51 kJ/mol

a) 2373.7 kJ/mol b) 1980.19 kJ/mol c) 621.49 kJ/mol d) 227.98 kJ/mol

6. Calculate the enthalpy of the reaction: $C(s) + 2N_2O(g) = CO_2(g) + 2N_2(g)$
if 22 g of N_2O take part in the reaction and the enthalpies of formation are:
$\Delta H^0_{f,298}$ ($N_2O(g)$) = 81.55 kJ/mol $\Delta H^0_{f,298}$ ($CO_2(g)$) = -393.51 kJ/mol

a) 475.1 kJ b) 139.2 kJ c) 278.3 kJ d) 556.61kJ

7. Decide about the change of entropy in the reactions:

1. $2C(s) + O_2(g) = 2CO_2(g)$ 2. $2H_2(g) + O_2(g) = 2H_2O(g)$

a) 1. $\Delta S > 0$ b) 1. $\Delta S < 0$ c) 1 & 2 $\Delta S > 0$ d) 1 & 2 $\Delta S < 0$
2. $\Delta S < 0$ 2. $\Delta S > 0$

8. Calculate the energetic 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.

9. Decide about the changes of enthalpy and entropy, at which the reaction is spontaneous at any temperature.

a) $\Delta H>0$, $\Delta S>0$ b) $\Delta H<0$, $\Delta S<0$ c) $\Delta H>0$, $\Delta S<0$ d) $\Delta H<0$, $\Delta S>0$

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

$2\ C_{(s)} + O_{2\ (g)} = 2\ CO_{(g)},\ \Delta H° = -\ 221$ kJ,

and the standard entropies of the substances are as following:

$S^0_{298}(C_{(s)}) = 5.74$ J/mol · K; $S^0_{298}(O_{2(g)}) = 205.17$ J/mol · K;

$S^0_{298}(CO_{(g)}) = 197.68$ J/mol · 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.

Answers

1. The correct answer is b).
An endothermal reaction is accompanied by 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). Exothermal reactions are accompanied by release of heat and for them the change of enthalpy is positive.

3. The correct answer is b). The standard enthalpy of formation of a substance ($\Delta H^0_{f,298}$) is zero, if it is 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 Br_2 (l) $\Delta H^0_{f,298}$ is zero.

4. The correct answer is b). To get the thermochemical equation of the reaction
$H_2(g) + O_2(g) = H_2O_2(l)$, subtract the equation (1) from the equation (2) and subtract ΔH_1 from ΔH_2.

$H_2(g) + 1/2O_2(g) - H_2O_2(l) = H_2O(l) - H_2O(l) - 1/2O_2(g)$,

$\Delta H = \Delta H_2 - \Delta H_1$

or

$H_2(g) + 1/2O_2(g) + 1/2O_2(g) = H_2O_2(l)$

$\Delta H = -284.2 – (-98.2)$

Thus we receive:

$H_2(g) + O_2(g) = H_2O_2(l)$, $\Delta H = -186.0$ kJ.

5. The correct answer is d). First write the termochemical equation of combustion of 1 mole of acetylene C_2H_2:

$C_2H_2(g) + 5/2O_2(g) = 2\ CO_2 + H_2O(l)$, $\Delta H = -1300.84$ kJ.

To calculate the enthalpy of formation of acetylene use the consequence of the Hess' law, according to which the thermal effect of a reaction equals the difference between the sum of the

standard enthalpies of formation of products and the sum of the standard enthalpies of formation of the reactants taken with stoichiometric indices.
Thus we receive (the standard enthalpy of formation of $O_2(g)$ is zero):

$\Delta H = \Delta H^0_{f,298} (H_2O(l)) + 2 \times \Delta H^0_{f,298} (CO_2(g)) - \Delta H^0_{f,298} (C_2H_2(g))$

$\Delta H^0_{f,298} (C_2H_2(g)) = -285.84 + 2 \times (-383.51) – (-1300.84) = 227.98$ kJ/mol

227.98 kJ is absorbed in formation of 1 mole (26g) acetylene from simple substances at the standard conditions

6. The correct answer is b). Write the termochemical equation of the reaction:
$C(s) + 2N_2O(g) = CO_2(g) + 2N_2(g)$
Calculate the thermal effect with the consequence of Hess' law (see the previous task). The standard enthalpy of formation of $N_2(g)$ and C(s) is zero. We have:

$\Delta H = \Delta H^0_{f,298} (CO_2(l)) - 2 \times \Delta H^0_{f,298} (N_2O(g)) = -393.51 – 2 \times (81.55) = -556.61$ kJ

22 g N_2O is 0.5 mol ($M_{(N2O)}$ = 44g/mol), four times less heat will be released.

$\Delta H_1 = \Delta H \times 0.5$ mol/2mol = ¼ ΔH = - 139.2 kJ

7. 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 a rough 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).

8. Calculate the mass of protein, fat and carbohydrate in the margarine:
m(protein) = 200g x 0.3% : 100% = 0.6g
m(fat) = 200g x 82.3% : 100% = 164.6g
m(carbohydrate) = 200g x 1% : 100% = 2.0g

Calculate the total energetic value of the margarine:
Q = (0.6g + 2.0g) x 17.18 kJ/g = 164.6g x 38.97 kJ/g = 44.67 kJ + 6414. 46 kJ = 6459.13 kJ.
Therefore the organism will receive 6459 kJ energy from complete oxidation of 200g margarine.

9. The correct answer is d).
A reaction takes place spontaneously, if $\Delta G<0$. The change of the Gibb's 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 $\Delta S>0$.

10. The correct answer is b).

The change of enthalpy of the reaction is known (ΔH = -221 kJ). Calculate the change of entropy. The change of entropy of the reaction $\Delta S°$ 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 stoichiometric indices.

$\Delta S = 2 \cdot S^{O}_{298}(CO_{2(g)}) - 2 \cdot S^{O}_{298}(C_{(s)}) - 2 \cdot S^{O}_{298}(O_{2(g)}) = 2 \cdot 196,68 – 2 \cdot 5,74 – 205,17 =$
$= 395,36 – -11,48 – 205,17 = 178,71$ (J/K)

Calculate the change of the Gibb's energy of the reaction:

$\Delta G° = \Delta H° - 298 \cdot \Delta S = - 221 – 298 \cdot 0,1787 = - 274,25$ (kJ)

As far as $\Delta G°<0$, it can be concluded that the reaction takes place spontaneously at standard temperature. Nevertheless, if $\Delta H°<0$ and $\Delta S°>0$, the reaction is spontaneous at any temperature.

8. PRACTICUM

8.1. Measurement of the thermal effect of the neutralisation reaction.

Calorimeters are used to measure thermal 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:

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

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

Parameter	name	value
1. mass of the internal cup	m_{cup}	
2. mass of the solution	$m_{solution}$	200g
3. heat capacity of the cup	C_{cup}	1.087 J/g x grad
4. heat capacity of the solution	$C_{solution}$	4.1 J/g x 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:

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

Calculate the amount of heat released in the experiment:

$q = (t_2 - t_1) \cdot \Sigma C$, 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.

$Q = q \cdot 1 : 0.1 \cdot 10^{-3}$, kJ

2. Write the thermochemical equation of the neutralisation reaction in the molecular and short ionic forms with the thermodynamical system of symbols of thermal effects, taking into account that
H = -Q.
Write down the results. Check them with the teacher.

Lesson № 2

1.SUBJECT. **Chemical kinetics. Effect of concentration and temperature on reaction rate.**

2.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. Methods of chemical kinetics render it possible to measure rates of moving 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.

3. AIM. Learn general concepts of chemical kinetics as the basis for studying mechanisms and rates of chemical and biochenmical reactions. In the experiment prove effect of concentration and temperature on reaction rate.

Necessary knowledge:

- measurement of reaction rate;
- the Law of working masses for the reaction rate, its application for homogeneous and heterogeneous reactions, the rate constant;
- molecularity and the order of the reaction;
- activation energy, Arrennius' equation, the theory of transition state;
- examples of simple and complex reactions, chain reactions, antioxidants.

Necessary skills:

- write kinetic equations according to the Law of working masses for homogeneous and heterogeneous reactions;
- determine the formal general order of the reaction from its kinetic equation;
- determine the rate change from the change of concentration and pressure of reactants;
- make calculations with the Vant Hoff's rule.

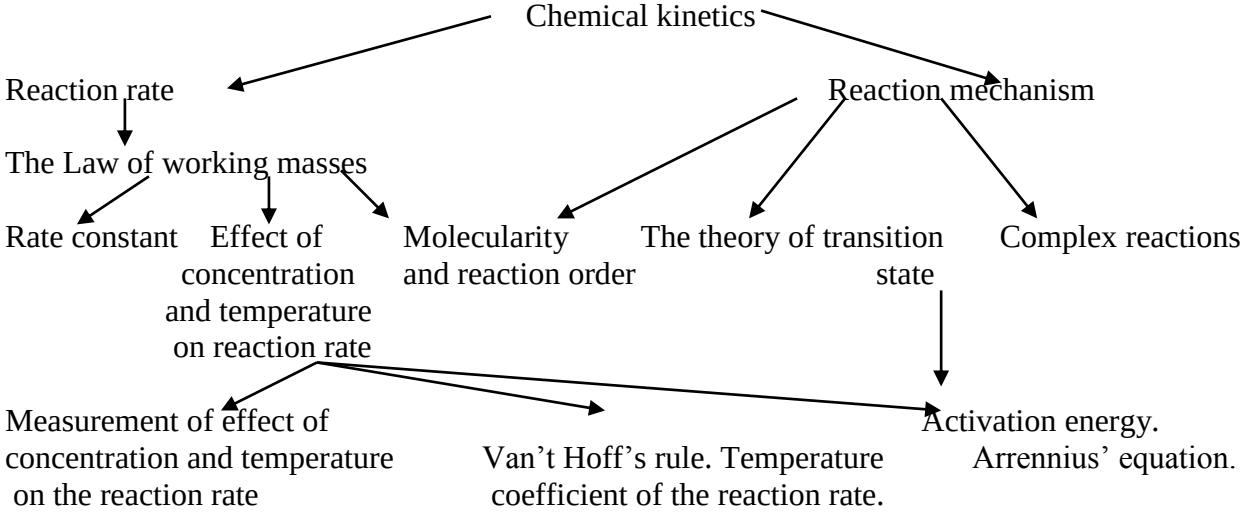
Skills to obtain:

- prove the effect of concentration and temperature on the reaction rate.

4. BASIC KNOWLEDGE:

1) homogeneous and heterogeneous reactions;
2) the average reaction rate.

5. LOGICAL STRUCTURE



6. STUDYING PLAN (for self-preparation)

Studying actions	Guidelines to studying actions
1.Rate of chemical reactions.	1.1 Average rate. 1.2 Momentary rate.
2. The Law of working masses for reaction rate	2.1 Application of the Law for homogeneous and heterogenous reactions. 2.2 The rate constant. 2.3 Effect of concentration, pressure, temperature on the reaction rate.
3. Molecularity and the order of reactions.	3.1 Zero order, first order and second order reactions. 3.2 Reaction mechanism, transition state theory.
4. Effect of temperature on the rate constant.	4.1 Energy of activation. 4.2 Arrennius' equation. 4.3 Vant Hoff's rule. The temperature coefficient of the reaction rate, its characteristics in biochemical processes.
5. Complex reactions	5.1 Parallel, subsequent, coupled reactions. 5.2 Chain reactions. Antioxidants

7. SELF ASSESSMENT TASKS

1. Choose heterogenous reactions:

1) $2CO(g) + O_2(g) = 2CO_2(g)$
2) $2Na(s) + Cl_2(g) = 2NaCl(s)$
3) $S(s) + O_2(g) = SO_2(g)$
4) $Na_2CO_3(s) + SiO_2(s) = Na_2SiO_3(s) + CO_2(g)$

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) nature of reactants and concentrations;
c) temperature and nature of reactants;
d) nature of reactants, temperature and concentrations.

3. Choose the correct kinetic equation for the reaction:

$CaCO_3(s) = CaO(s) + CO_2(g)$

a) $v = k[CaCO_3]$ b) $v = k[CaO][CO_2]$ c) $v = k[CO_2]$ d) $v = k$

4. Decide, how the rate of the reaction will change, if the volume of the reaction mixture decreases three times.

a) 9 times decrease c) 27 times decrease
b) 9 times increase d) 27 times increase

5. Determine the general order of the reaction:

$$2NO(g) + O_2(g) = 2NO_2(g)$$

a) 5 b) 3 c) 2 d) 1

6. Calculate, how many times will the reaction accelerate 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

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 non-mixable liquids, two solids.

2. The correct answer is c). The rate constant always depends only on the nature 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 concentration 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 is $v = k[NO]^2 [O_2]$. Due to the volume decrease the concentrations of the gases rise 3 times. That is why the rate is:
$v = k[3NO]^2 [3O_2] = 27k[NO]^2 [O_2] = 27v$. Therefore the reaction rate will grow 27 times.

5. The correct answer is b).
The general order of a reaction is the sum of concentration indices in a kinetic equation. 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:

$$\frac{v_{t2}}{v_{t1}} = \gamma^{t2-t1/10}$$, where

t_1 and t_2	are	initial and final temperatures
v_{t1} and v_{t2}	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 numbers, and you will have:

$v70°/v20° = 3^{(70-20)/10} = 3^5 = 243$. Therefore the reaction rate will grow 243 times.

8. PRACTICUM

8.1 Determine the effect of the powderisation of substances on the rate of a heterogeneous reaction.

Add dry crystals of $Pb(NO_3)_2$ and KI to a dry test tube. Mix slowly and note whether a colour change takes place. Then powder the mixture in a porcelain mortar. Note the colour change. Add several drops of distilled water to the powdered mixture and note the colour of the solution. Write an equation of the reaction and mark the substance which renders the colour to the solution. Make the conclusion about the effect of the powderisation of the substances on the reaction rate; compare the rates of homogeneous and heterogeneous reactions.

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

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

$$Na_2S_2O_3 + H_2SO_4 = Na_2\ SO_4 + S\downarrow + H_2SO_3$$

Use 1 *N* solutions.

Add sodium thiosulphate solution and distilled water to three retorts as shown in the chart below. Add 10 mL sulphuric 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 chart. Calculate the symbolic reaction rate with the equation: $v = I/\tau$.

Volume, mL			time, τ, s	the symbolic reaction rate, v, s^{-1}
$Na_2S_2O_3$	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.

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

The equation of the reaction is the same:

$$Na_2S_2O_3 + H_2SO_4 = Na_2\ SO_4 + S\downarrow + H_2SO_3$$

Use 0.5 *N* solutions.

Add 5 mL sulphuric acid solution to three test tubes (the first series). Add 5 mL sodium thiosulphate to three other test tubes (the second series). Measure the temperature in the both sets of tubes with a termometer (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 the chart with the results and calculate the symbolic reaction rate for each temperature.

Temperature, t, C°	time, τ, s	the symbolic reaction rate, v, s^{-1}

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

Write down the results. Check them with the teacher.

Lesson № 3

1. SUBJECT. **Chemical kinetics. Catalysis. Enzymic catalysis.**

2.IMPORTANCE. catalytic processes play a great role in the nature, industry, everyday life. Catalysts render it possible to accelerate reaction rates, obtain significant industry outputs. Enzymes are biological catalysts. They are much more active than inorganic catalysts. The absolute majority of biochemical reactions are catalyzed by enzymes. Cell metabolism is directed by enzymic processes. Measurement of enzymic activity is widely used for diagnostics of internal diseases. For example, measurement of aspartate aminotransferase (AST) activity in blood plasma ensures diagnostics of cardiac infarction with 96% accuracy. Enzymes, their activators and inhibitors are used in medical treatment (enzymotherapy) and to study pathogenesis of some diseases.

3. AIM OF STUDYING: to understand concepts and mechanism of action of catalysts and enzymes, characteristics of enzymic catalysis and its role in biochemical processes.

Necessary knowledge:

- definition of catalysis and catalysts;
- mechanism of catalytic action;
- mechanism of homogeneous catalysis;
- characteristics of heterogeneous catalysis;
- structure and action of enzymes;
- role of enzymes in the organism, diagnostics and medical treatment.

Necessary skills:

- write equations of catalytic reactions;
- explain the mechanism of catalytic action with energy graphs.

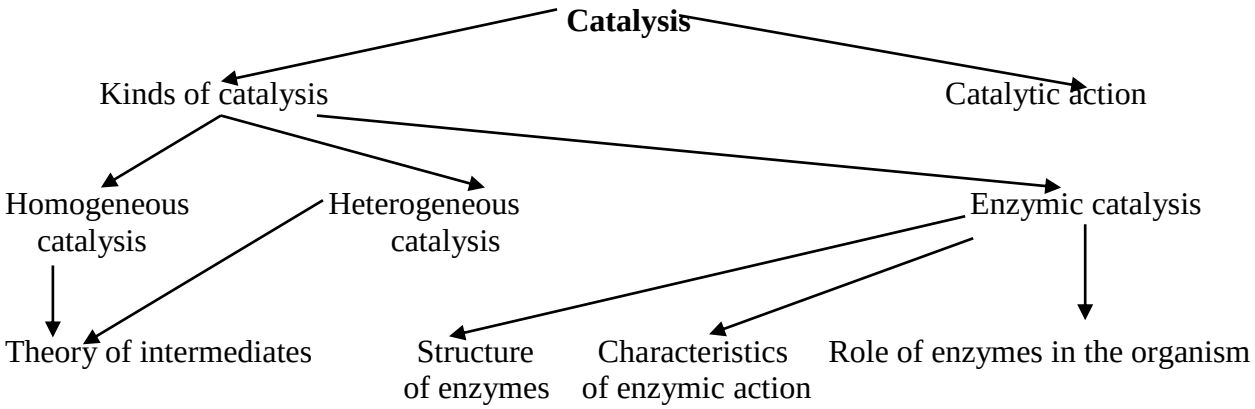
Skills to obtain:

- determination of the effect of catalysts on the reaction rate

4. BASIC KNOWLEDGE:

1) catalysis and catalysts;
2) homogeneous and heterogeneous catalysis;
3) reaction rate, energy of activation, simple and complex reactions;

5. LOGICAL STRUCTURE



6. STUDYING PLAN (for self-preparation)

Studying actions	Guidelines to studying actions
1. Mechanism and types of catalysis.	1.1. Types of catalysis: homogeneous, heterogeneous, enzymic (microheterogeneous). 1.2. The mechanism of catalysis. Reduction of energy of activation in catalytic process. 1.3. The theory of intermediate compounds in catalysis. 1.4. Characteristics of heterogeneous catalysis. 1.5. Autocatalysis.
2. Enzymes as biological catalysts.	2.1. Structure of enzymes. 2.2. Catalytic action of enzymes. 2.3. Effect of temperature and pH on enzymic activity. 2.4. Mechanism of enzymic action. 2.5. Role of enzymes in the organism and their application in diagnostics and treatment

7. SELF ASSESSMENT TASKS

1. The reaction rate changes with adding 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.

2. Choose the equations of heterogeneous catalytic reactions:

   a) $CO(g) + 2H_2(g) \xrightarrow{CuO(S)} CH_3OH(g)$
   b) $SO_2(g) + ½\ O_2(g) \xrightarrow{NO(g)} SO_3(g)$
   c) $2C_2H_5OH(l) \xrightarrow{Na(s)} C_4H_9OH(l) + H_2O(l)$
   d) $3I_2(s) + 2Al(s) \xrightarrow{H2O(l)} 2AlI_3(s)$
   e) $CH_3COH(g) \xrightarrow{I2(g)} CH_4(g) + CO(g)$

3. 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.

4. 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.

5. How does activity of enzymes depend on the change of pH of the medium:
   a) change of pH does not influence 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.

Answers

1. The correct answer is c).
From the contemporary point of view 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 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. Enzymic catalysis lowers the energy to 23 kJ/mol.
2. 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 reactions of homogeneous catalysis b) and e) are in gaseous phase and the reaction takes place in the whole volume.

3. The correct answer is a).
Catalysts are specific. They can accelerate only a single specific reaction. Enzymes are extremely specific. The enzyme catalysing saccharose hydrolysis does not catalyse starch hydrolysis despite of the fact that the both substances are carbohydrates and contain D-glucose. Different catalysts or enzymes catalyse formation of different products from the same initial substances. It is possible to obtain 40 different substances from ethyl alcohol. The human organism contains more than 1000 different enzymes. They are organized in complex enzymic systems, that ensure chains of subsequent changes. Lack of specification in enzymes could have caused complete disarray of metabolism.

4. 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 (500-1000ºC). Enzymes can only work in a narrow temperature range, mostly 10-60ºC. Optimal temperature for enzymes is 40ºC. As the temperature increases, the activity of enzymes decreases. At more than 70ºC enzymes are completely inactivated, mostly because of the denaturation of the protein structure.

5. The correct answer is c).
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. Enzymes are mostly proteins, therefore their structure depends on pH, and their activity in its turn depends on their structure.

8. PRACTICUM

8.1. Reduction of potassium permanganate in the presence of a catalyst.

Fill a test tube to a half with 30% (by mass) sulphuric acid solution, add three drops of 0.1 *N* $KMnO_4$ solution. Mix until rosy and divide into three test tubes. Add one drop of KNO_3 solution to the first test tube. Then add small pieces of zync to the first and the second tubes. Leave the third test tube for comparison.

Compare the speed of decoloration in the first and the second test tubes and make a conclusion as to which substance is a catalyst.

Write an equation of the reaction with the following scheme:

$$Zn + KMnO_4 + H_2SO_4 = ZnSO_4 + K_2SO_4 + MnSO_4 + H_2O$$

8.2. Catalytic reduction of ferric rhodanide.

Add 3 mL KCNS or NH_4CNS solution and three drops of $FeCl_3$ solution to each of two test tubes. Ferric rhodanide is formed in the reaction:

$$3KCNS + FeCl_3 = Fe(CNS)_3 + 3KCl$$

Add two drops of $CuSO_4$ 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.

Write an equation of the reaction with the following scheme:

$$Fe(CNS)_3 + Na_2S_2O_3 = Fe(CNS)_2 + Na_2S_4O_6 + NaCNS$$

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

Add a small amount of PbO_2 or MnO_2 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.

8.4. Autocatalytic reduction of potassium permanganate in an acidic medium.

Add 10 mL of 5% (by mass) oxalic acid $H_2C_2O_4$ and 5 mL 0.1 *M* H_2SO_4 to a conical flask. Pipet aliquots of 0.2-0.5 mL diluted solution of potassium permanganate and mark the time of decoloration for each aliquot. Compare the time of color loss of the first aliquot with the next and make a conclusion as to what the catalyst is.

Write an ionic equation of the reaction with the following scheme:

$$H_2C_2O_4 + MnO_4^- + H^+ = CO_2 + Mn^{2+} + H_2O$$

Write down the results. Check them with the teacher.

Lesson № 4

1. SUBJECT. **Chemical equilibrium. The Le Shatellier's principle**

2.IMPORTANCE. Life in the organism is based on lots of biochemical processes. Most of them are equilibrium reactions. Some steps of multi-step pathways are reversible reactions. To know the theory of chemical equilibrium is important for understanding chemical processes in the organism, action of medicines and harmful substances.

3. AIM OF STUDYING: Learn general concepts of equilibrium processes and possibilities of equilibrium shift in a desired direction.

Necessary knowledge:

- the theory of chemical equilibrium;
- the Law of the working masses for equilibrium state;
- the equilibrium constant;
- the Le Shatellier's principle;
- difference between an equilibrium state of a system and a stationary state of an open system.

Necessary skills:

- write formal equations to calculate the equilibrium constant for homogeneous and heterogeneous reactions;
- determine the direction of the equilibrium shift with changes of temperature, pressure and concentration of reactants;
- assess the equilibrium state of a system with the value of the equilibrium constant and the change of the Gibb's energy.

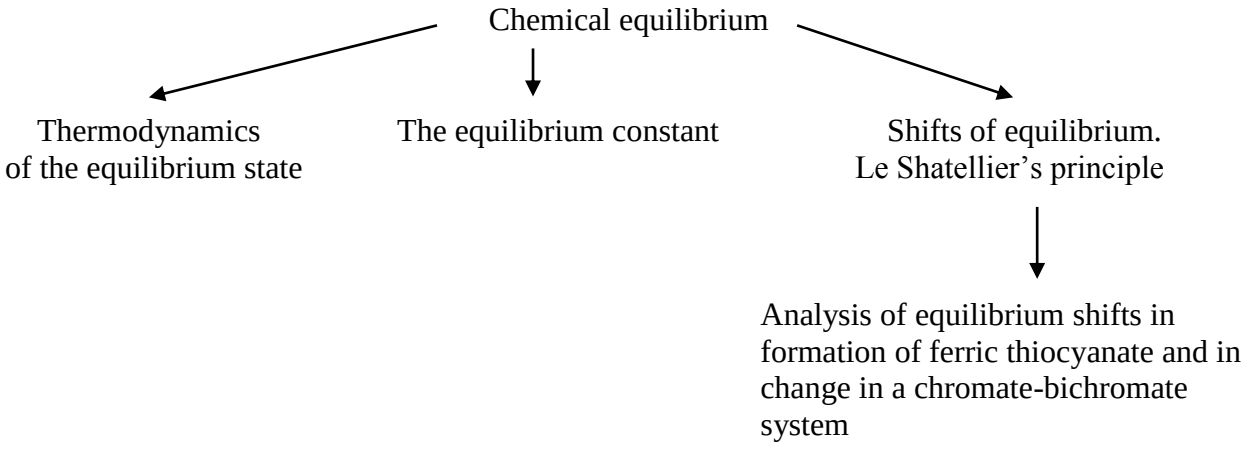
Skills to obtain:

- shift chemical equilibrium in a desired direction by change of concentration of reactants and temperature.

4. BASIC KNOWLEDGE:

1) reversible reactions;
2) the reaction rate, the rate constant;
3) the Law of the working masses for homogeneous and heterogeneous reactions.

5. LOGICAL STRUCTURE



6. STUDYING PLAN (for self-preparation)

Studying actions	Guidelines to studying actions
1. Chemical equilibrium as a state of reversible processes.	1.1. The Gibb's energy as the thermodynamic characteristics of reversible processes. 1.2. Dynamic nature of chemical equilibrium state.
2. The Law of working masses for chemical equilibrium state	2.1. The equilibrium constant. 2.2. The equilibrium constant as a characteristics of chemical equilibrium state
3. Shift of chemical equilibrium	3.1. Factors that effect shifts of equilibrium 3.2. Le Shatellier's principle and its application for shifts of equilibrium in a desired direction.

7. SELF ASSESSMENT TASKS

1. Change of which factors can lead to a change of the equilibrium constant?
a) pressure b) temperature c) concentration d) nature of reactants

2. How will the rates of the direct and reverse reactions change, if the volume of the vessel, in which the reactions are in equilibrium, is decreased two times.

$$2SO_2(g) + O_2(g) \leftrightarrow 2SO_3(g)$$

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 will shift the equilibrium in the system to the left:

$$4HCl(g) + O_2(g) \leftrightarrow 2Cl_2(g) + 2H_2O(g)$$

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 will the equilibrium shift in the system, if the general pressure is increased: $4Fe(s) + 3O_2(g) \leftrightarrow 2Fe_2O_3(s)$
a) to the left b) to the right c) will not change

5. Explain the change of the enthalpy of the equilibrial reaction, if the equilibrium constant increases with the temperature rise

$$H_2O(g) \leftrightarrow H{=}(g) + ½O_2(g)$$

a) $\Delta H > 0$ b) $\Delta H < 0$ c) $\Delta H = 0$

Answers

1) The correct answers are b) and d). The constant of the chemical equilibrium K equals the rate constant of the direct reaction k_1 divided by the rate constant of the reverse reaction k_2.
$K = k_1/k_2$
As far as each of the rate constants depends only on the nature of the reactants and the temperature, the equilibrium constant will also depend only on these factors. Changes of concentrations and pressure will 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:

$$v_1 = v_2, \qquad v_1 = k_1[SO_2][O_2], \qquad v_2 = k_2[SO_3]^2$$

When the volume is two times decreased, the concentrations (or partial pressures) of the gases will increase two times. Therefore the rate of the direct reaction will increase eight times:
$v'_1 = k_1(2[SO_2])^2(2[O_2]) = 8k_1[SO_2][O_2] = 8v_1$
The rate of the reverse reaction will increase two times:
$v'_2 = k_2(2[SO_3]^2) = 4v_2$
Therefore the rate of the direct reaction will be two times bigger than the rate of the reverse reaction, and the equilibrium will shift to the right.

3. The correct answer is b). According to the Le Shatellier'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 will shift the equilibrium to the right. An increase of the general pressure or a decrease of the volume will cause 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 Shatellier's principle the increase of the pressure in the system will cause a shift in the direction to smaller amount of gaseous substances. In this case it is to the right.

5. The correct answer is a). The equilibrium constant equals the rate constant of the direct reaction k_1 divided by the rate constant of the reverse reaction k_2. $K = k_1/k_2$. It shows how many times the rate constant of the direct reaction is bigger than the rate constant of the reverse reaction. An increase of the equilibrium constant means, that the rate of the direct reaction increases. It causes a shift of the equilibrium to the right. As far as the shift is caused by the temperature increase, the direct reaction is endothermal, and $\Delta H > 0$.
Therefore the thermochemical equation will be as following:

$$H_2O(g) \leftrightarrow H_2(g) + \tfrac{1}{2}O_2(g) \qquad \Delta H > 0$$

8. PRACTICUM

8.1. Determination of the effect of a change of the concentration of reactants on the shift of the chemical equilibrium.

Dependence of the reaction rate in the equilibrium state on a change of concentrations of the reactants and a direction of the shift of the equilibrium can be examined on the example of the reversable reaction between ferric chloride and ammonium rhodanide.
Mix 10 mL 0.002 *M* $FeCl_3$ solution and 10 mL 0.006 *M* NH_4CNS solution in a retort. Pour the obtained solution into four test tubes. Add 1 mL 0.25 *M* $FeCl_3$ solution to the first test tube, 1 mL 0.6 *M* NH_4CNS solution to the second test tube, 1 mL 3.0 *M* NH_4Cl solution to the third test tube. Leave the fourth test tube for control. Tabulate the changes of the colours of the solutions:

Added solution	role of the substance in the reaction	colour change	direction of the equilibrium shift
1. $FeCl_3$	reactant		
2. NH_4CNS	reactant		
3. NH_4Cl	reaction product		

Write an equation of the reversible reaction between ferric chloride and ammonium rhodanide. Write the formula for calculation the equilibrium constant according to the Law of working masses for equilibrium state. Make a conclusion about the direction of the equilibrium shift if the concentrations of reactants or reaction products are increased.

8.2. Determination of the effect of pH of a medium on the equilibrium state in the system “chromate ion – bichromate ion”.

In a solution which contains anionic forms of chromium (VI) an equilibrium between these forms exists:

$$2CrO_4^{2-} + 2H^+ \leftrightarrow Cr_2O_7^{2-} + H_2O$$

chromate ion dichromate ion

or

$$Cr_2O_7 + 2OH^- \leftrightarrow 2CrO_4^{2-} + H_2O$$

A change of the pH of the medium causes an equilibrium shift, which can be observed because the colour changes.

Add some 10 % (by mass) orange potassium dichromate solution $K_2Cr_2O_7$ to a 100 mL cup. Add an alkali solution by drops until yellow. Add several drops of sulfuric acid solution to the yellow chromate solution until orange.
Make a conclusion as to which anionic form of chromium (VI) is stable in acid medium and which is stable in alkaline medium.

8.3. Determination of the effect of temperature on the state of chemical equilibrium .

In a water solution of ammonia there is an equilibrium:

$$NH_3 + H_2O \leftrightarrow NH_3 \bullet H_2O \leftrightarrow NH_4^+ + OH^-$$

Add 30 mL distilled water to a conical flask, add several drops of concentrated ammonia solution and two to three drops of phenol phtalein solution. Heat the obtained rosy solution until colorless. Cool the hot solution with tap water until the rosy color reappears.

Make a conclusion about the direction of equilibrium shift in ammonia solution when heated and cooled.

Write down the results. Check them with the teacher.

Lesson № 5

1.SUBJECT. **Reduction-oxidation interaction and biological oxidation. Measurement of** redox potentials

2.IMPORTANCE. The process of biological oxidation is the primary source of energy in the organism. The main characteristics of the process are its multistep nature and the gradual increase of the potential of reducing agents. Knowledge of the basic concepts of reduction-oxidation processes, alterations of reduction-oxidation potentials and direction of electron (or hydrogen atom) transport is crucial for understanding biochemical reduction-oxidation processes. Values of redox potentials render it possible to predict a direction of biological oxidation and calculate an energy change.

3.AIM OF STUDYING: Create understanding of reduction-oxidation potentials and their role in the direction of reduction-oxidation processes. Learn to measure reduction-oxidation potentials.

Necessary knowledge:

- the theory of reduction-oxidation (redox) potentials, their role in reduction-oxidation processes;
- how to evaluate strength of reducing and oxidizing agents and predict the direction of a spontaneous reduction-oxidation process;
- the concept of the standard biochemical reduction-oxidation potential and its role in the processes of biological oxidation.

Necessary skills:

- calculate values of reduction-oxidation potentials with the Nernst-Peters equation;
- compare strengths of reducing and oxidizing agents;
- predict directions of spontaneous reduction-oxidation processes.

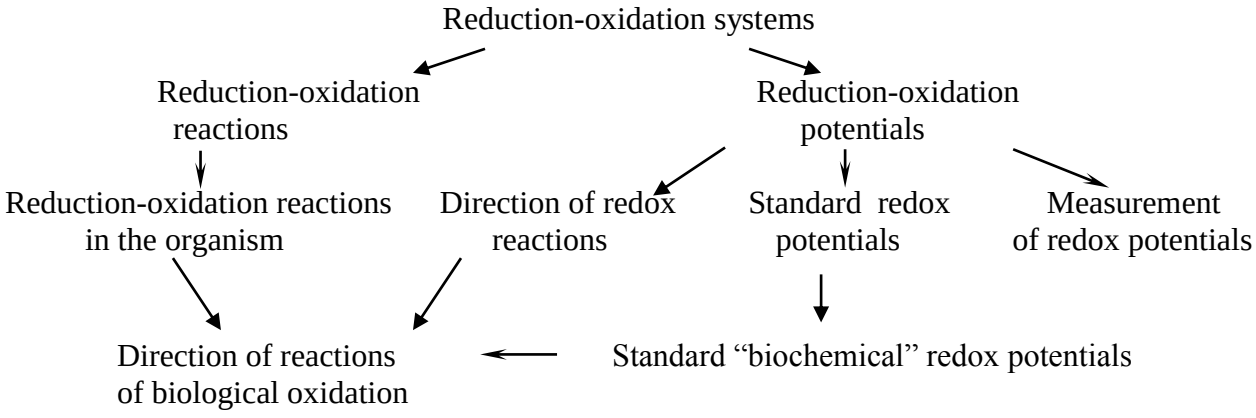
Obtained skills:

- measure spontaneous reduction-oxidation potentials of reduction-oxidation systems with the platinum electrode.

4. BASIC KNOWLEDGE:

1) The theory of reduction-oxidation reactions, balancing reduction-oxidation equations.
2) The theory of electrode potentials, the Nernst equation.
3) The concept of the galvanic chain and types of electrodes.

5. LOGICAL STRUCTURE



6. STUDYING PLAN (for self-preparation)

Studying actions	Guidelines to studying actions
1. Reduction-oxidation systems	1.1. Reactions in reduction-oxidation systems and their role. 1.2. Reduction-oxidation systems in the living organisms and their role.
2. The concept of redox potentials	2.1. Mechanism of formation of redox potentials. 2.2. The Nernst-Peter's equation and factors that effect values of redox potentials. 2.3. The standard (normal) redox potential. 2.4. Practical measurement of redox potentials with the platinum electrode.
3. Prediction of a direction of spontaneous redox reactions.	3.1. Comparison of strengths of reducing and oxidizing agents in general and at standard conditions. 3.2. Conditions of spontaneous redox reactions.
4. Reduction-oxidation reactions in the living organisms.	4.1. Characteristics of biological oxidation. 4.2. The concept of the standard "biochemical" redox potential. 4.3. Direction of reactions of biological oxidation.

7. SELF ASSESSMENT TASKS

1. Choose equations of reduction-oxidation reactions from the following:

1. $Al_2(SO_4)_3 + 6NaOH = 2Al(OH)_3 + 3\ Na_2SO_4$
2. $2Al + 2NaOH + 6\ H_2O = 2\ Na[Al(OH)_4] + 3\ H_2$
3. $AgNO_3 + NaI = NaNO_3 + AgI$
4. $Cl_2 + 2\ NaI = 2\ NaCl + I_2$

a) 1,2 b) 2,3 c) 3,4 d) 2,4

2. Choose one best characteristic of the redox electrode:

a) metal immersed in an electrolyte solution and exchanging ions and electrons with it;
b) inert metal immersed in an electrolyte solution and exchanging electrons with it;
c) inert metal immersed in a reduction-oxidation system and conducting electrons only;
d) inert metal immersed in a reduction-oxidation system and exchanging ions and electrons with it.

3. Choose a redox system, the potential of which depends on pH:

a) $Fe^{3+} + e^- = Fe^{2+}$
b) $MnO_4^- + e^- = MnO_4^{2-}$
c) $MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$
d) $S_4O_6^{2-} + 2e^- = 2\ S_2O_3^{2-}$

4. Choose a fraction under the logarythm in the Nernst-Peter's equation for the redox system:
$CrO_4^{2-} + 2\ H_2O + 3e^- = CrO_2^- + 4\ OH^-$

$a)\ \frac{[CrO_4^{2-}]}{[CrO_2^-]\cdot[OH^-]^4}$ $b)\ \frac{[CrO_2^-]\cdot[OH^-]^4}{[CrO_4^{2-}]}$ $c)\ \frac{[CrO_4^{2-}]}{[CrO_2^-]}$ $d)\ \frac{[CrO_2^-]}{[CrO_4^{2-}]}$

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

a) $HBrO + H^+ + 2e^- = Br^- + H_2O$ $\varphi° = 1.34$ V
b) $CrO_4^{2-} + 4\ H_2O + 3e^- = Cr(OH)_3 + 5\ OH$ $\varphi° = -0.13$ V
c) $2\ IO_3^- + 12\ H^+ + 10e^- = I_2 + 6\ H_2O$ $\varphi^o = 0.19$ V
d) $H_2O_2 + 2\ H^+ + 2e^- = 2\ H_2O$ $\varphi^o = 1.78$ V

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

$2\ NaCl + Fe_2(SO_4)_3 = 2\ FeSO_4 + Cl_2 + Na_2SO_4$, where
$\varphi^oCl_2/2Cl^- = 1.36$ V, and $\varphi^o_{Fe^{3+}/Fe^{2+}} = 0.771$ 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.

7. Choose the best oxidizing agent to transform the Fe^{2+}ion into Fe^{3+}ion at standard conditions< if the standard potential $\varphi_{Fe^{3+}/Fe^{2+}}$ is 0.771 V and the standard potentials of the oxidizing agents are given in brackets.

a) $KMnO_4$ ($\varphi° = 1.51$ V)
b) $KMnO_4$ in neutral medium ($\varphi° = 0.58$ V)
c) HNO_2 ($\varphi^0 = 1.0$ V)
d) $CuSO_4$ ($\varphi^0 = 0.153$ V)

8. How does the EMF of the galvanic chain $Pв/Pв^{2+}$ // Ag^+ /Ag change, if a small amount of hydrogen sulfide is added to the solution.

a) decrease;
b) increase;
c) no change;
d) the chain will be disrupted.

9. Which of the processes will take place on the electrode with a bigger potential in the reduction-oxidation galvanic chain:
a) depends on the nature of the electrode;
b) reduction;
c) oxidation;
d) reduction or oxidation.

Answers

1. The correct answer is d).
Reduction-oxidation reactions are accompanied by changes of oxidation levels in molecules of the reactants.

2. $Al + 2\ NaOH + 6\ H_2O = 2\ Na\ [Al(OH)_4] + 3\ H_2$

$Al + 4\ OH^- - 3e^- = [Al(OH)_4]^-$	2	oxidation
$2\ H_2O + 2e^- = H_2 + 2\ OH^-$	3	reduction

4. $Cl_2 + 2\ NaI = 2\ NaCl + I_2$

$Cl_2 + 2e^- = 2\ Cl^-$	1	reduction
$2\ I^- - 2e^- = I_2$	1	oxidation

The reactions 1 and 3 do not involve changes of oxidation levels of the reactants.

2. 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 internal circuit. The metal therefore does not exchange electrons or ions with the components of the solution.

3. The correct answer is c).
The equation contains $8H^+$, and the potential will depend on pH (T = 298 K)

$$\varphi = \varphi^0 + \frac{0.059}{5}\lg\frac{[MnO_4^-]}{[Mn^{2+}]} - 0.094\,pH$$

4. The correct answer is a).
The concentration of the oxidized form CrO_4^{2-} must be in the numerator, and the concentration of the reduced form CrO_2^- and OH^- must be in the denominator of the logarythm.

5. The correct answer is d).
The oxidized form of the system with a bigger value of redox potential is a stronger oxydizing agent.

6. The correct answer is b).
As far as the standard potential of the system of $Cl_2/2Cl^-$ is bigger, Cl_2 is the oxidizing agent and Fe^{2+} is the reducing agent. Therefore the reaction will go spontaneously from right to left.

$2\ FeSO_4 + Cl_2 + Na_2SO_4 = 2\ NaCl + Fe_2(SO_4)_3$, or $2\ Fe^{2+} + Cl_2 = 2\ Cl^- + + 2\ Fe^{3+}$

7. 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 acid medium.

8. The correct answer is b).
The EMF of the galvanic chain is calculated with the formula:

$$E = \varphi_{Ag^+/Ag} - \varphi_{Pb^{2+}/Pb} = \varphi^o{}_{Ag^+/Ag} + 0.059\lg[Ag^+] -$$

$$-(\varphi^o{}_{Pb^{2+}/Pb} + \frac{0.059}{2}\lg[Pb^{2+}]) = \varphi^o{}_{Ag^+/Ag} - \varphi^o{}_{Pb^{2+}Pb} +$$

$$+(0.059\lg[Ag^+] - \frac{0.059}{2}\lg[Pb^{2+}])$$

When hydrogen sulfide is added to the solution, that contains Pb^{2+} ions, the reaction takes place:

$Pb^{2+} + H_2S = PbS\downarrow + 2\ H^+$

Concentration of Pb^{2+} cations decreases because of the reaction.

The lg $[Pb^{2+}]$ decreases in the formula of EMF, and the difference in the brackets increases, thus leading to an increase of EMF.

9. The correct answer is b).
Reduction of the oxidized form takes place on the electrode with a bigger potential in the reduction-oxidation galvanic chain. The oxidized form is the reducing agent. The electrode is the anode and is always charged positively.

8. PRACTICUM

Redox potentials of redox systems are calculated with EMF values, measured by the ionometer EV-74.

8.1. Preparation for work and measuring EMF.

- press the buttons "t" and "-I-I9";
- plug the device in;
- warm up the device for 30 minutes;
- assemble a galvanic chain with the measurement electrode (the platinum electrode EPV1) 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;
- add a solution of a redox system to a glass and immerse the electrodes in it;
- press the button "mV" and the button of the needed measurement range and measure EMF value (E).

8.2. Calculations

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);

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

as far as $E = \varphi_{pr.} - \varphi_{comp.}$

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

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

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

$$3.\varphi_{Cr_2O_7^{2-}/2Cr^{3+}} = 1.333 + 0.01\lg\frac{[Cr_2O_7^{2-}]}{[Cr^{3+}]^2} - 0.138\,pH$$

Concentrations are given in the table.

3) Fill in the table with the results:

№	El.	Redox system	pH	Composition of solutions	$\varphi^{в}$, V	$\varphi_{pr.}$ V	$\varphi_{theor.}$ V	E, V
1	Pt	I_2, I^-		0.1 *M* KI 0.001 *M* I_2	0.530			
2	Pt	Fe^{3+}, Fe^{2+}		$5\cdot10^{-4}$ *M* Fe^{3+} $5\cdot10^{-2}$ *M* Fe^{2+}	0.771			
3	Pt	$Cr_2O_7^{2-}$, H^+,Cr^{3+}	1.86	$4.18\cdot10^{-2}$ *M* $Cr_2O_7^{2-}$ $1.67\cdot10^{-4}$ *M* Cr^{3+}	1.333			

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

a) $Fe^{3+} + I^- \rightarrow$

b) $Fe^{2+} + I_2 \rightarrow$

c) $Cr_2O_7^{2-} + Fe^{2+} \rightarrow$

with the formula: $E = \varphi_{ox.} - \varphi_{red.}$

A reduction-oxidation process will happen spontaneously, if $\varphi_{ox.} > \varphi_{red.}$ and $E > 0$.

Write down the results. Check them with the teacher.

Lesson № 6

1. SUBJECT. **Sorption of biologically active substances on the phase interface. Molecular adsorption from solutions on the solid surface. Adsorption of acetic acid on activated carbon.**

2.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 of amino acids on the surface of erythrocytes, adsorption on cell membranes, adsorption of proteins on the surface of hydrophobic particles in blood. Such solid adsorbents as activated carbon and ion-exchangers are used to remove foreign substances from the organism. Adsorption on solid adsorbents is widely used to purify vitamins, anaesthetics, antibiotics.

3. AIM OF STUDYING: to understand concepts and mechanism of adsorption of substances from solutions on solid surfaces. Obtain practical skills in carrying out adsorption from a solution with a solid adsorbent and in calculations with the Freundlich's adsorption equation.

Necessary knowledge:
- adsorption from solutions on solid adsorbents, the adsorption theory;
- molecular adsorption of non-electrolytes, the Rebinder's rule of polarity equalization;
- kinds and characteristics of adsorption of electrolytes from solutions, the Panet's rule;
- biological importance and practical applications of adsorption from solutions.

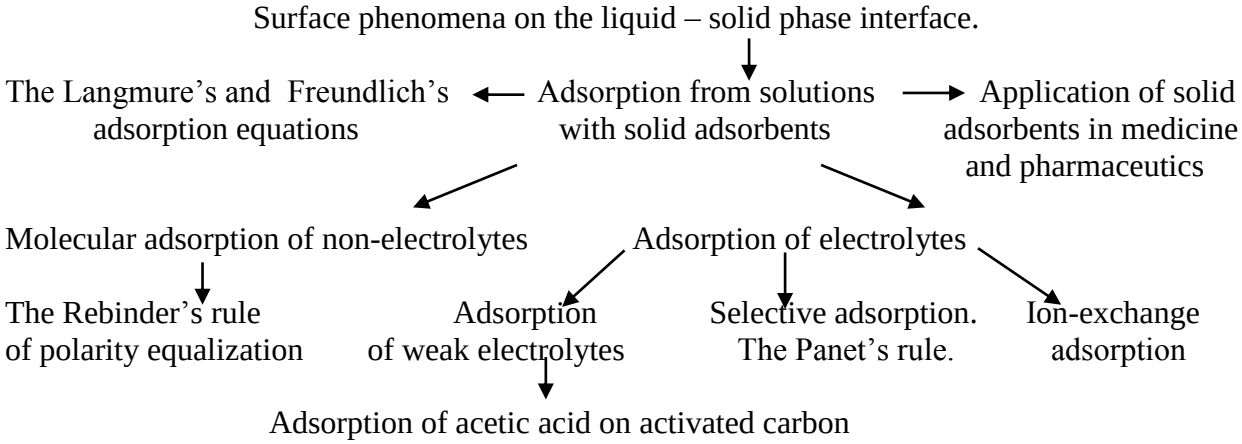
Necessary skills:
- make calculations with the Freundlich's and Langmure's adsorption equations;
- plot graphs of the adsorption isotherm and find constants in the Freundlich's equation by the calculatory-graphic method.

Skills to obtain:
- carrying out adsorption from a solution with a solid adsorbent and calculation of the adsorption value of a dissolved substance with the calculatory-graphic method.

4. BASIC KNOWLEDGE:

1) Polarities of molecules.
2) Homogeneous systems and phase equilibrium.
3) Basic concepts of adsorption.
4) Skills of acid-base titration. (Previous classes)

5. LOGICAL STRUCTURE



6. STUDYING PLAN (for self-preparation)

Studying actions	Guidelines to studying actions
1. Surface phenomena on the liquid – solid phase interface.	1.1. Active centres on the surface of adsorbent.
2. Adsorption from solutions with solid adsorbents.	2.1. Characteristics of adsorption from solutions. 2.2. The Freundlich and Langmure's adsorption equations, their application. 2.3. Application of solid adsorbents in medicine and pharmaceutics. Adsorption therapy.
3. Molecular adsorption from solutions.	3.1. Adsorption of nonelectrolytes. The Rebinder's rule of polarity equalization.
4. Adsorption from electrolyte solutions.	4.1. Selective adsorption. The Panet's rule. 4.2. Ion exchange adsorption. Cation and anion exchangers. 4.3. Adsorption of weak electrolytes.
5. Adsorption of acetic acid on activated carbon.	5.1. Method of analysis of adsorption of acetic acid and construction of adsorption isotherm; 5.2. Determination of coefficients in the Freundlich's equation for adsorption of acetic acid by the calculatory-graphic method.

7. SELF ASSESSMENT TASKS

1. Choose the factors that effect adsorption on the liquid-solid phase interface:

a) nature of the adsorbent, pressure, temperature;
b) nature of the adsorbent, nature of the liquid, pressure, temperature;
c) nature of the adsorbent, nature of the liquid, temperature;
d) pressure, temperature.

2. From which solvent does activated carbon (non-polar adsorbent) adsorb a surfactant better? The permitivity of the solvents is given in brackets.

a) water (80); b) ethanol (25.2); c) acetone (20.7); d) hexane (1.9).

3) Tell, whether the Traube's 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.

4) Which factors effect adsorption of an ion with a solid adsorbent from water solution?

1) ion charge, 2) hydration degree of the ion, 3) nature of the ion,
4) nature of the adsorbent, 5) mass of the adsorbent, 6) general pressure.

a) 1 – 4; b) 1 – 6; c) 1, 3, 4; d) 1, 4, 5.

5) Which ions are able to adsorb on the surface of crystalline silver iodide according to the Panet's rule?

a) Ag^+; b) I^-; c) NO_3^-; d) Na^+.

6) 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^+.

Answers

1) The correct answer is c).

Adsorption on the liquid-solid phase interface depends on the nature of adsorbent and adsorbate (liquid), temperature and does not depend on pressure, because liquids are practically non-compressed.

2) The correct answer is a).

Carbon is a non-polar hydrophobic adsorbent. According to the Rebinder's rule of polarity equalization a surfactant 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.

3) The correct answer is c).

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

4) The correct answer is a).

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

5) 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 what ion is in excessive amount.

6) 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.

8. PRACTICUM

8.1. Preparation of initial solutions of acetic acid.

Add 50 mL distilled water to four numbered flasks. Add 50 mL initial solution of acetic acid (approximately 0.8 mol/L). Mix and transfer 50 mL of the solution into the second flask and so on from second into the third and from the third to the fourth. Mix the solution in the fourth flask and pour 50 mL of it away. The concentration of every subsequent solution is two times smaller than the previous one.

8.2. Adsorption of acetic acid on carbon.

Add 1g activated carbon to each of the initial solutions. Leave the flasks for 20 minutes, mixing the content from time to time. Meanwhile adsorption of acetic acid on carbon takes place and adsorption equilibrium is established.

8.3. Measurement of exact concentration of acetic acid in the initial solutions.

First measure the exact concentration of acetic acid in the first solution. For that titrate 5 mL of the first solution against a titrant NaOH with phenol phtalein as the indicator. Calculate concentration of acetic acid in the first solution with the formula:

$$C_{first}(CH_3COOH) = \frac{V(NaOH)xC(NaOH)}{V(CH_3COOH)}$$, mol/L, where:

C (NaOH) – concentration of titrant NaOH, mol/L;
V (NaOH) – average titrant volume, mL;
V (CH_3COOH) – volume of the first solution of acetic acid, used for the titration, mL.

Calculate concentrations of acetic acid in each of the consequent initial solutions. Fill in the table with the results.

8.4. Measurement of equilibrium concentrations of acetic acid after the adsorption.

Prepare four clean dry flasks with funnels and dry filters. When the adsorption is finished, filter all the four solutions, discarding first portions of filtrates. Successively take 10 mL of each filtrate and titrate against a titrant NaOH with phenol phtalein as the indicator. Calculate the concentration of acetic acid C_i in each of the filtrates. Fill in the table with the results.

№	Initial concentration of acetic acid C_{0i}, mol/L	Equilibrium concentration of acetic acid C_{0i}, mol/L	Amount of adsorbed acetic acid, X_i, mol	Value of adsorption $\frac{Xi}{m}, \frac{mol}{kg}$	lgC_i	$\lg\frac{Xi}{m}$	Constants in the Freundlich equation	
							K	1/n
1 2 3 4								

8.5. Calculations.

Calculate the number of moles of the adsorbed acetic acid with the formula:

$$X_i = (C_{0i} - C_i)\cdot \frac{V}{1000}\ ,\ \text{mol}$$

where: C_{0i}, C_i – the initial and equilibrium concentrations of acetic acid respectively, mol/L;
V – volume of the acetic acid solution taken for the adsorption, mL

Calculate the adsorption value of acetic acid per 1kg of adsorbent with the formula:

$$\frac{Xi}{m} = \frac{Xi}{m(carbon)} \cdot 1000\ ,\ \text{mol/kg}$$

where: m – the mass of activated carbon taken for the adsorption, g;
m(carbon) = 1g.

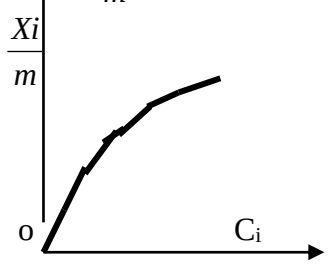
Calculate the value: $\lg C_i$ and $\lg\frac{Xi}{m}$.

Fill in the table with the results.

8.6. Plotting charts and calculations of constants in the Freundlich equation for acetic acid adsorption.

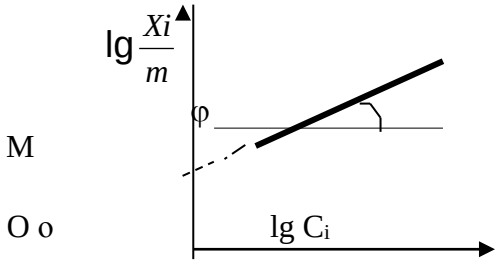
With the data of the experiment and calculations plot the charts of Freundlich's adsorption isotherm in the conventional (A, Picture 1) and linear (B, Picture 2) forms.

A: $\frac{Xi}{m} = \mathbf{K \cdot C_i^{1/n}}$



Picture 1

B: $\mathbf{\lg\frac{Xi}{m} = lgK + \frac{1}{n} lgC_i}$



Picture 2

To find K in the Freundlich's equation measure the OM segment (Picture 2), taking into account the scale on the axis of ordinates. Then calculate the antilogarithm of the length of the segment, because **lg K** = OM.

To find the constant **1/n**, determine **tg φ** (Picture 2), taking into account the scales on the both axes, because **1/n = tg φ.**

Write the constants **K** and **1/n** in the table and write the Freundlich equation for adsorption of acetic acid on carbon.

Write down the results. Check them with the teacher.

Lesson № 7

1.SUBJECT. **Ionic exchange. Chromatography.**

2.IMPORTANCE. Chromatography is widely used in research and laboratory practice. It can be applied to separate and identify amino acids, proteins, nucleic acids, lipids and other bioorganic compounds. Chromatography belongs to the most important methods of research in biology, medicine and pharmaceutical science. It is also a method of ecological control and monitoring.

3.AIM OF STUDYING: Get acquainted with kinds, characteristics and possibilities of chromatography, its applications in biochemical, laboratory and sanitary analysis. Obtain practical skills in distributive paper chromatography and adsorption chromatography on a solid adsorbent.

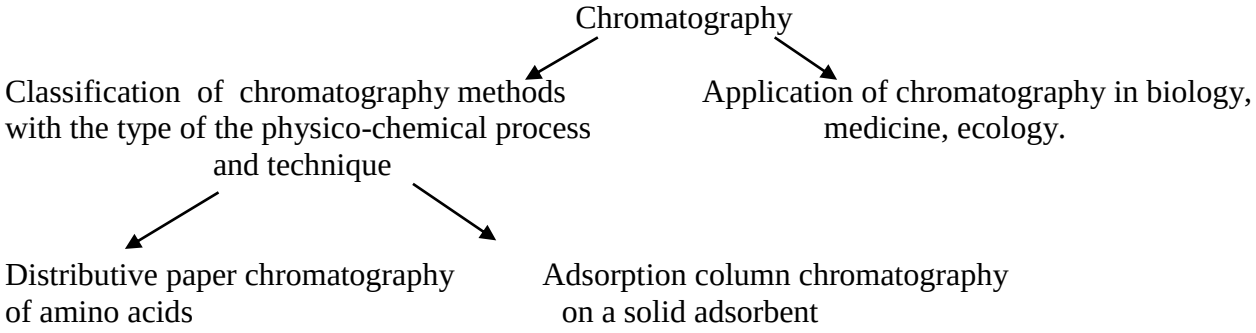
Necessary knowledge:
- basics of chromatography;
- classification of methods of chromatography with the type of the physico-chemical process;
- application of chromatography in biology, medicine, ecology.

Necessary skills:
- carry out qualitative column adsorption chromatography;

Skills to obtain:
separation and qualitative analysis of substances with distributive paper chromatography.

4. BASIC KNOWLEDGE:
1) Hydrophilic (polar) and hydrophobic (non-polar) compounds.
2) Adsorption and distribution of components between two nonmixable liquids.
3) Heterogeneous equilibrium on the interface between phases. (from the previous classes).

5. LOGICAL STRUCTURE



6. STUDYING PLAN (for self-preparation)

Studying actions	Guidelines to studying actions
1. Basics of chromatography.	1.1. Separation of mixtures and identification of components. Qualitative and quantatitive analysis.
2. Classification of methods of chromatography by the type of a physico-chemical process.	2.1. Adsorption chromatography. 2.2. Distributive chromatography. 2.3. Ion exchange chromatography. 2.4. Sedimentation chromatography. 2.5. Gel-filtration.

3. Methods of chromatography by the technique.	3.1. Gaseous and gaseous-liquid chromatography. 3.2. Paper and thin-layer chromatography. 3.3. Column chromatography.
4. Applications of chromatography in biology, medicine, ecology.	
5. Technique of separation of amino acids in the distributive paper chroma-tography.	

7. SELF ASSESSMENT TASKS

1) Choose the processes on which chromatography is based:
1 – ion exchange, 2 – dissolving in water, 3 – adsorption,
4 – evaporation, 5 – cristallization, 6 – distribution between two phases.

a) 1, 3, 4; b) 2, 3, 4, 6; c) 1, 3, 6; d) 2, 4, 5.

2) 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 – ionic exchange chromatography.

a) 2, 5; b) 4, 6; c) 1, 3; d) 1, 2.

3) Which of the substances is the immobile phase in paper chromatography:
a) organic solvent; b) water; c) cellulose;
d) there is no immobile phase in paper chromatography.

4) Which parameters of paper chromatography must be standartized 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-kind of the solvent.
a) 3,5; b) 4,6; c) 1,3; d) 2,4.

5) What is described by the retention factor in paper chromatography:
a) correlation of solubilities of the components in the solvent;
b) correlation of solubilities of the components in the immobile phase;
c) correlation of velocities of the components;
d) correlation of velocities of a component and the solvent.

6) Choose the kind of chromatography which mechanism is similar to a method of obtaining purified or demineralized water.
a) adsorption; b) distributive c) ionic exchange; d) sedimentation

Answers

1) The correct answer is c).
Dissolving, evaporation, cristallization do not belong to the processes, on which chromatography is based.

2) The correct answer is a).
The components of a mixture are distributed between the immobile 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 immobile phase in paper chromatography. In thin layer chromatography the immobile phase is the liquid with which the adsorbent is soaked beforehand.

3) The correct answer is b).
The paper contains water, which is the immobile phase in paper chromatography. The specific chromatography paper contains more than 20% water.

4) The correct answer is b).
Values of retention factors of components depend on the sort of the paper and the kind 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 standartized. It must be slightly higher than the room temperature.

5) The correct answer is d).

6) 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 exhange resin. Cationites (cation exchange) or anionites (anion exchange) 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.

8. PRACTICUM

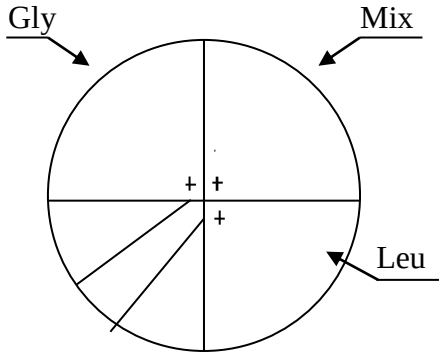
8.1. Adsorption chromatography of cations on aluminium oxide.

Separation of cations **Fe^{3+}** and **Cu^{2+}** is done with adsorption column chromatography. Prepare the chromatography column as following: take a dry glass pipe (length - 12-15 cm, diameter - 1 cm) with a narrow end. Place some cotton wool into the end. Fill the pipe with 4-5 cm of aluminium oxide powder, tapping the pipe gently to avoid gaps. Fix the prepared column in a stand. Take 3 mL ferric chloride solution and 3 mL cupric sulfate solution of the same concentration, mix them in a test tube. Pour carefully the obtained mixture into the column. Place an empty flask under the column.
After some time the upper layer of the adsorbent becomes yellow (Fe^{3+} cations). A blue layer is formed under it (Cu^{2+}cations).
After all the solution has gone through the column, wash the adsorbent with a small amount of water and then pour a developer into the column for better spectacularity. The developer is a diluted solution of potassium ferrocyanide **$K_4[Fe(CN)_6]$**. The top layer becomes dark blue, the bottom one becomes brown.

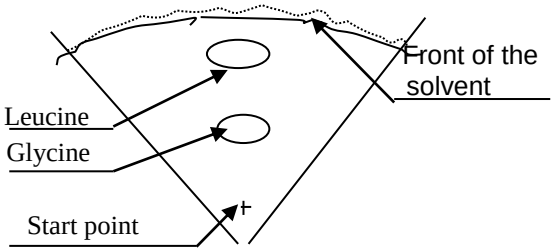
Make a conclusion about dependence of adsorbtion of cations on aluminium oxide on the charge of the cation. Draw the column with the coloured layers of the cations in the notebook.

8.2. 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 1). Mark the sectors on the edge: "Gly" – glycine, "Leu" – leucine, "Mix" – mixture.



Picture 1



Picture 2

Place small drops (not bigger than 3-4 mm in diameter) of the corresponding solutions (glycine, leucine and their mixture) on the start points.

Pour the solvent in a Petry dish, place the filter so, that the strip were immersed in the solvent. Cover the cup with another Petry dish and place in the thermostate at temperature 45-50^0C. 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.

With the chromatogram calculate the retention factors of leucine and 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 (Picture 2).

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

$$\mathbf{R_{f(glycine)} = r_1/r_s} \qquad \mathbf{R_{f(leucine)} = r_2/r_s,}$$

where $\mathbf{r_1}$ is the distance from the start point to the middle of the glycine stain, cm;
$\mathbf{r_2}$ is the distance from the start point to the middle of the leucine stain, cm;
$\mathbf{r_s}$ is the distance from the start point to the front of the solvent, cm.

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

Check the results with the teacher

Lesson № 8

1. SUBJECT. **Colloidal solutions: obtaining, properties and purification. Electrophoresis.**

2.IMPORTANCE. The living organism can be regarded as a complex entity of dispersion systems. Low molecular electrolytes and nonelectrolytes form real solutions in biological liquids; proteins, lipids, nucleic acids, polysaccharides form colloidal-dispersion solutions. Cells, blood cells, bacteria form coarse dispersion solutions. Alteration of the physico-chemical state of dispersion systems in the organism can lead to pathologies. Blood coagulation, transport of lipids and water-insoluble compounds, formation of cholesterol plagues in the blood vessels and other important processes are based on the properties of dispersion systems. Research of dispersion systems has introduced such modern diagnostics and treatment methods as electrophoresis, compensatory dialysis, vividialysis, "artificial kidney".

3. AIM OF STUDYING: to understand the methods of obtaining and purification of colloidal solutions, their properties and application in clinical, pharmaceutical and sanitary practice. Acquire practical skills in obtaining colloidal solutions and their purification with dialysis.

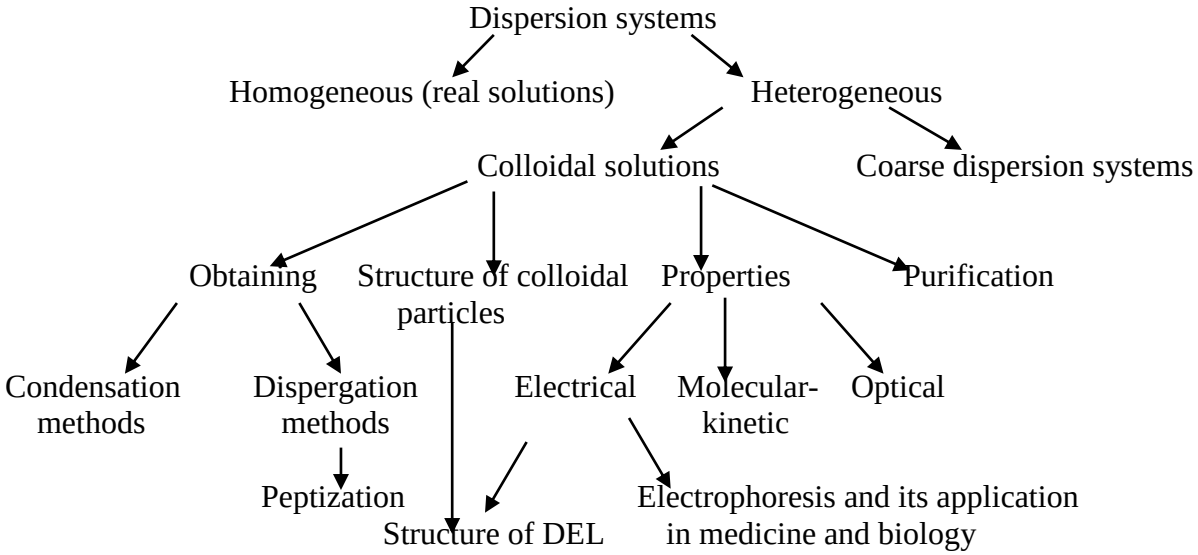
Necessary knowledge:
- cassification of dispersion systems by the aggregative state and by the size of the particles of the dispersed phase;
- principal methods of obtaining colloidal solutions;
- the micellar theory of the structure of hydrophobic sols;
- molecular-kinetic, electrical and optical properties of colloidal solutions;
- theory and practical applications of electrophoresis in medical and biological research;
- principal methods of purification of colloidal solutions.

Necessary skills:
- compare physico-chemical properties of dispersion systems;
- write formulas of micelles of hydrophobic colloidal sols;
- choose methods of purification of colloidal solutions depending on the kind of admixtures.

Skills to obtain:
- different methods of obtaining colloidal solutions in the laboratory (hydrolysis, double metathesis, solvent replacement, peptization);
- purification of colloidal solutions with dialysis.

4. BASIC KNOWLEDGE:
1) Properties of solutions.
2) Basic types of chemical reactions. Reactions of metathesis and hydrolysis (the high school course).
3) Homogeneous and heterogeneous systems.
4) Selective adsorption (previous chemistry classes).

5. LOGICAL STRUCTURE



6. STUDYING PLAN **(for self-preparation)**

Studying actions	Guidelines to studying actions
1.Dispersion systems and their classification	1.1 Composition of dispersion systems. Dispersed phase and disperse medium. 1.2 Classification according to the aggregative state. 1.3 Classification according to the size of the particles of the dispersed phase: real solutions, colloidal solutions, coarse dispersions.
2. Methods of obtaining colloidal solutions	2.1 Condensation methods. 2.2 Dispergation methods. 2.3 Peptization.
3. Methods of purification of colloidal solutions	3.1 Dialysis, electrodialysis, compensatory dialysis, vividialysis, the principle of "the artificial kidney". 3.2 Ultrafiltration 3.3 Filtration
4. Structure of the micelle as a base unit of the colloidal solution	4.1 The micelle nucleus and selective adsorption of ions on the nucleus. 4.2 Ions in the micelle structure. 4.3 Micelle as the electroneutral particle in a colloidal solution.
5. Properties of colloidal solutions	5.1 Molecular-kinetic properties: Brownian motion, diffusion, osmosis. 5.2 Optical properties: Tindal's effect. 5.3 Electrical properties. Structure of the DEL of the colloidal particle.

6. Electrophoresis and its applications in medical and biological research	6.1 Electrokinetic phenomena. 6.2 Electrokinetic potential. 6.3 Electrophoresis. Velocities of the particle movement in electrophoresis. 6.4 Applications of electrophoresis in medical research.

7. SELF ASSESSMENT TASKS

1) Choose one best description of colloidal solutions:
   a) dispersion systems with different disperse media;
   b) dispersion systems with the particle size in the dispersed phase from 1 to 100 nm.
   c) dispersion systems with 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 nucleus in the micelle formation?
   a) the ions, which charge is opposite to the charge of the nucleus;
   b) the ions, concentration of which is the biggest in the solution;
   c) the ions, which are not components of the nucleus;
   d) the ions which are able to complete the crystal lattice of the nucleus.

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* $\mathbf{AgNO_3}$ solution. Explain your reasoning.

4) Explain, on which processes peptization is based on.
   a) hydrolysis of peptide bonds in the disperse 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) formation of colloidal particles because of the adsorption of the ions which are formed in a reaction of a part of the precipitate with the electrolyte.

5) Choose one best method to remove glucose 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.

Answers

1) The correct answer is b).
According to the classification of dispersion systems colloidal solutions are microheterogenous systems with 1 – 100 nm 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 nucleus that are able to complete the crystal lattice of the nucleus. These are the ions that are components of the nucleus, or those isomorfic to them, or the ions that contain the same elements as in the crystal lattice of the nucleus. The ions are called potential-determining and determine the charge of the colloidal particle.

3) First decide which of the reactants is in excess.

$$\mathbf{AgNO_3 + KCl = AgCl\downarrow + KNO_3}$$

Number of moles of **KCl**: 0,015 L · 0,025 mol/L · 10^3 = 0,375 mmol

Number of moles of **$AgNO_3$**: 0,085 L · 0,005 mol/L · 10^3=0,425 mmol

$AgNO_3$ is in excess. Therefore, Ag^+ cations will adsorb on the surface of the nucleus, thus making the granula positive. Nitrate ions will be the counterions.

The micelle formula is as following:

$$\mathbf{\{[m\ AgCl] \cdot n\ Ag^+ \cdot (n - x)\ NO_3^-\}^{x+} \cdot x\ NO_3^-}$$

nucleus *adsorption layer of ions* *diffuse layer of ions*

granule

micelle

The micelle is electroneutral.

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

Peptization is a transition of a freshly formed precipitate into 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).

Peptization can also take place when a small amount of electrolyte is added, which can react with the surface of the particles of the precipitate, forming ions able to be adsorbed selectively (chemical peptization).

Sometimes peptization is possible when the precipitate is rinsed by the solvent, if the precipitate contained significant concentration of one of the reactants because of insufficient rinsing.

5) The correct answer is b).

As the admixtures are not electrolytes, simple dialysis is the best decision.

6) The correct answer is d).

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

8. PRACTICUM

8.1. 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.

8.2. 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% $FeCl_3$ (with a measuring test tube) and add it gradually to the boiling water.

At high temperature complete hydrolysis of ferric chloride takes place (III):

$$\mathbf{FeCl_3 + 3\ H_2O = Fe(OH)_3\downarrow + 3\ HCl}$$

The products of the hydrolysis partially react with each other.

$$\mathbf{Fe(OH)_3\downarrow + HCl + FeOCl + 2\ H_2O}$$

The obtained oxoferrous chloride (**FeOCl**) stabilizes colloidal particles.

The micelle formula of the **$Fe(OH)_3$** sol is as following:

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

A clear reddish-brown sol is obtained.

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

Add 10 mL 0.10 % potassium ferrocyanide **$K_4[Fe(CN)_6]$** and 1-2 drops of 2 % ferric chloride. A clear blue colloidal solution of Prussian blue **$Fe_4[Fe(CN)_6]_3$** is obtained.

Write the reaction between potassium ferrocyanide and ferric chloride.

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

8.4. 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 **$Fe(OH)_3$** 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 sediment (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 sediment. Write a micelle formula of the sol obtained with peptization in the second test tube.

8.5. Purification of a starch dispersion by the method of dialysis.

Add a small amount of 1 % starch solution and several drops of 2% sodium sulfate solution in a cellophane bag. Place the bag in a flask with distilled water so that the water level in the flask is slightly higher than the level of the liquid in the bag. After 20 minutes analyze the water for presence of sulfate ions and starch molecules. For this pour approximately 2 mL of the water in two test tubes. Add several drops of Lugol's solution (iodine in a water solution of KI) – qualitative reaction for presence of starch in water. Add 2-3 drops of barium chloride solution - qualitative reaction for presence of sulfate ions.

Explain, why the reaction is negative in the first test tube and positive in the other test tube. Explain the principle of dialysis.

Write down the results. Check them with the teacher.

Lesson № 9

1.SUBJECT. Measurement of the threshold of coagulation of a sol by electrolytes.

2.IMPORTANCE. All biological liquids of the organism (blood, intracellular liquid, lymph, urine etc) are complex dispersion systems. Their stability depends on constancy of pH and electrolyte and protein composition. Their alteration can lead to onset of coagulation of the colloidal phase, sedimentation of erythrocytes and proteins. A slight alteration of the electrolyte composition in the organism can lead to coagulation of colloidal components, because ions with different charges have different coagulation thresholds. Coagulation also takes place in blood clotting.

3.AIM OF STUDYING: Get acquainted with stability of colloidal systems, the coagulation mechanism and factors that cause coagulation. Understand importance of coagulation processes in the life of the organism and in medical practice.

Necessary knowledge:

- factors of stability of colloidal systems
- causes and mechanism of coagulation of colloidal solutions;
- characteristics of coagulation of colloidal systems by electrolytes;
- role of coagulation in biological systems;
- processes that accompany coagulation (alternation of coagulation zones, adaptation of sols, mutual coagulation).

Necessary skills:

- calculate coagulation threshold of electrolytes;
- assess coagulation stability of colloidal systems.

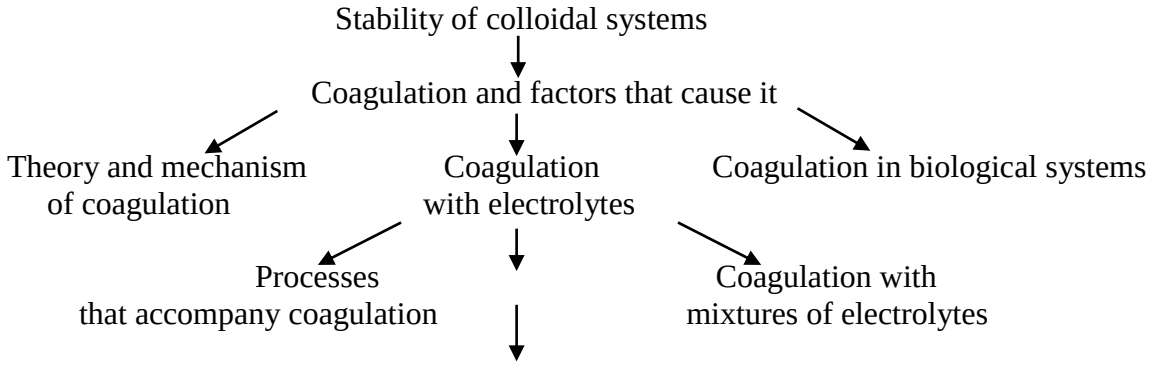
Skills to obtain:

- coagulation of colloidal systems by electrolytes.

4. BASIC KNOWLEDGE:

1) Properties of ions (charge, radius, hydrated shell) (the high school knowledge).
2) Structure of the micelle of a sol.
3) Surface energy of the phase interface in the heterogeneous system. (the previous classes).

5. LOGICAL STRUCTURE



6. STUDYING PLAN (for self-preparation)

Studying actions	Guidelines to studying actions
1. Stability of colloidal solutions	1.1. Kinetic (sedimentation) stability. 1.2. Aggregative stability.
2. Coagulation of colloidal solutions.	2.1. Factors that cause coagulation. 2.2. Kinetics of coagulation. 2.3. Coagulation in biological systems.
3. Coagulation by electrolytes	3.1. Concentrational and neutralizational coagulation by electrolytes. 3.2. Coagulation threshold and coagulation ability of electrolytes. 3.3. Dependence of coagulation threshold and coagulation ability on the charge and radius of a hydrated ion. Liotropic series of anions and cations. 3.4. Coagulation by electrolyte mixtures: additivity, synergism and antagonism of ions in coagulation.
	3.5. The phenomena concomitant to coagulation: alternation of coagulation zones, adaptation of sols, mutual coagulation.
4. Measurement of a coagulation threshold of a ferric hydroxide sol by electrolytes with different charges of the coagulating ions	

7. SELF ASSESSMENT TASKS

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 layer; 4 – kind of ions in the diffuse layer ;
   5 – Brownian motion of colloidal particles;
   6 - value of 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 the 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 coagulation threshold and coagulating ability of ions?

a) concentration of the ion; b) hydration of the ion;
в) charge of the ion; d) temperature.

4) Choose the electrolyte with minimal coagulation threshold for a sol with negatively charged particles:

a) Na_2CO_3; b) K_3PO_4; c) $CaCl_2$; d) $Al(NO_3)_3$.

5) To which electrode will sol particles move in electrophoresis, if coagulation thresholds of the sol are as following for the electrolytes (mmol/L):
K_3PO_4 – 0.02; $MgSO_4$ – 1.50; $FeCl_3$ – 201.3.

a) to the catode; b) the particles do not move;
c) to the anode; d) not possible to decide.

6) Choose one best characteristic of antagonism of ions in coagulation:

a) impossibility for ions to exist simultaneously in the same solution because of a reaction between them;
b) decrease of solubility of ions when they are present at the same time in the same solution;
c) decrease of coagulation thresholds of ions in mutual coagulation;
d) decrease of coagulating ability of ions in mutual coagulation.

Answers

1) The correct answer is b).

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

Change of temperature, addition of electrolyte or dehydrating agents, and intensive mechanical mixing can effect factors of stability of colloidal systems and promote coagulation. Alteration of pressure almost does not influence stability of liquid systems. Addition of the solvent mostly increases stability of 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. Coagulating strength of an ion depends on its charge and hydration (radius of the hydrated ion). The bigger the charge and smaller hydration, the smaller is the coagulation threshold and bigger coagulating ability. Temperature equally affects 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 maximum charge has the smallest coagulation threshold. It is the aluminium cation, therefore aluminium nitrate will have the smallest coagulation threshold.

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 will move to the catode (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. There is no sufficient theory to explain the phenomenon.

8. PRACTICUM

1. Preparation of diluted solutions of electrolytes

Prepare three series of five test tubes, that are needed to study coagulating action of electrolytes:

I series – 2.0 *N* **KCl** solution;

II series – 0.1 *N* $\mathbf{K_2CrO_4}$ solution;

III series – 0.01 *N* $\mathbf{K_4[Fe(CN)_6]}$ solution.

Prepare diluted solutions of the electrolytes:

Add 10 mL of an electrolyte solution to the first test tube. Add 4 mL of distilled water to other four test tubes. 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 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 coagulation.

3. Calculation of the coagulation threshold of an electrolyte.

Calculate the coagulation threshold for each electrolyte with the formula:

$$\mathbf{C_{thr}} = \frac{V \cdot C\,\mathrm{min} \cdot 1000}{Vs}, \text{ mmol/L;}$$

Where: $\mathbf{C_{thr.}}$ – coagulation threshold, mmol/L;

V - volume of the electrolyte solution, mL;

$\mathbf{C_{min}}$ - minimal normality of the electrolyte, mmol/L;

$\mathbf{V_s}$ - volume of the sol, mL.

4. Determination of the relationship between the ion charge and coagulation threshold.
Fill in the table with the results.

№ of the series	Electrolyte	Initial concentration, mol/L	Test tubes, where coagulation took place	C_{min}, mol/L	$C_{пор.}$, mmol/L	Charge of the coagulating ion
I	**KCl**	2.0				
II	$\mathbf{K_2CrO_4}$	0.1				
III	$\mathbf{K_4[Fe(CN)_6]}$	0.01				

Make conclusions about the kind of the coagulating ion (anion or cation) and about the relationship between the value of coagulation threshold and the charge of the coagulating ion.

Write down the results. Check them with the teacher.

Lesson № 10

1.SUBJECT. **Colloidal protection.**

2.IMPORTANCE. 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 hydrophylity. The polymers promote stability of the particles because they protect them from 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.

3.AIM OF STUDYING: create understanding of the mechanism of the protective action of high-molecular compounds, biological importance and applications of colloidal protection.

Necessary knowledge:
- the phenomenon of colloidal protection;
- the mechanism of the protective action of high-molecular compounds;
- biological importance and applications of colloidal protection in medicine.

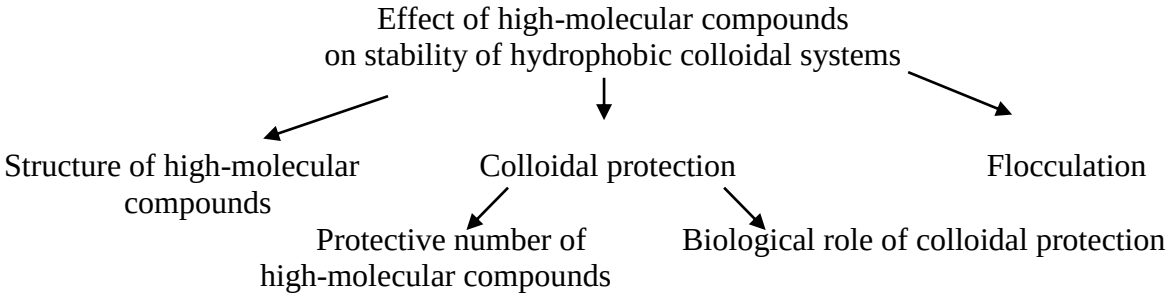
Necessary skills:
- calculate the protective number of a natural polymer.

Skills to obtain:
- measurement of the protective number of gelatine.

4. BASIC KNOWLEDGE**:**

1) Polymers. Proteins and polysaccharides as natural polymers (High school course).
2) Adsorption on the interface between phases.
3) Structure of the colloidal particle.
4) Coagulation of colloidal systems (Previous classes).

5. LOGICAL STRUCTURE



6. STUDYING PLAN (for self-preparation)

Studying actions	Guidelines to studying actions
6. High-molecular compounds (polymers)	Structure of high-molecular compounds. Polymers in the human body
7. Effect of high-molecular compounds on the stability of hydrophobic colloidal systems	Colloidal protection. Protective number of high-molecular compounds. Biological role of colloidal protection Flocculation.
8. Measurement of protective number of gelatin for ferric hydroxide sol – iron number of gelatin.	

7. SELF ASSESSMENT TASKS

1) 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.

2) Colloidal protection was observed, when 0.5 mL 0.5% solution of a protein (ρ = 1 g/mL) was added to 2 mL sol. Calculate the protective number of the protein.

a) 2.5 mg; b) 12.5 mg; c) 10.0 mg; d) 50.0 mg.

3) Choose the substances which have the protective action in the human body:

a) electrolytes; b) cholesterol; c) proteins; d) polysaccharides.

4) Choose the factors that effect the protective action of compounds:

1 – nature of the high-molecular compound, 2 – its polymerization degree;
3 – nature of colloidal solution; 4 – nature of the electrolyte that causes coagulation.

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

5) When a small amount of a high-molecular compound, which is not sufficient to cause protective 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.

Answers

1) The correct answer is d).

Hydrophylic molecules of high-molecular compounds, for instance, protein molecules on the lipid particles in blood, are adsorbed on the surface of colloidal particles. 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.

2) The correct answer is b).

First calculate the mass of the protein in the solution:

$$m_{protein} = \frac{m_{solution} \cdot W_{protein}}{100\%} = \frac{0.5 \cdot 1 \cdot 0.5\%}{100\%} = 0.0025 \text{ g} = 2.5 \text{ mg}$$

Then calculate the protective number (P.N). It is the mass (mg) of the protein, which protects 10 mL sol from coagulation:

$$\text{P.N.} = \frac{m_{protein} \cdot 10mL}{2mL} = \frac{2.5mg \cdot 10mL}{2mL} = 12.5 \text{ mg}$$

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

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

4) The correct answer is a).

The protective effect of high-molecular compounds depends on many factors. In the first place it is the nature of a polymer and the nature of a colloidal solution. They have the greatest influence on the adsorption process. The protective effect also depends on the polymerization degree of a high-molecular compound, dispersion degree of the particles in the disperse phase. pH of a colloidal solution influences the protective effect of proteins and polypeptides. The nature of an electrolyte that causes coagulation is a secondary factor which influences the process of coagulation but has no effect on the protective action of adsorbed molecules of high-molecular compounds.

5) 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 polymer macromolecules are adsorbed on different colloidal particles thus forming bigger aggregates. The stability of the aggregates is significantly smaller than that of separate colloidal particles. Therefore sedimentation of flocculates is observed.

8. PRACTICUM

8.1. Observation of the protective effect of gelatin.

Add 10 mL $Fe(OH)_3$ sol to two flasks. With a burette add gradually 0.02 *M* ammonium sulfate solution to the first flask until the first signs of coagulation (slight turbidity) are observed. Note the volume of the electrolyte used for the coagulation. Add 1 mL 0.5% gelatin solution and as much ammonium sulfate as was used for the first flask. See, if the solution becomes turbid, i.e. whether the coagulation takes place. Make a conclusion about the protective effect of gelatin.

8.2. Measurement of protective number of gelatin.

Prepare gelatin solutions in 7 test tubes. For this add 2 mL 1% gelatin solution to the first test tube and 1 mL distilled water to the other test tubes. Transfer 1 mL of the solution from the first test tube to the second one, mix and transfer 1 mL of the solution to the third test tube and so on. Mix the solution in the seventh test tube and pour 1 mL of it away. Thus concentrations of solutions decrease twice in each successive test tube.

Add 1 mL ferric hydroxide sol to each test tube. Mix and add 1 mL semisaturated KCl solution.

Mark the test tubes in which coagulation (turbidity or precipitation) happened and the test tubes, in which the protective action of gelatin (absence of turbidity) is observed. Fill in the chart with the results. Mark the presence of coagulation with "+" and its absence with "–".

Calculate the mass of gelatin in each test tube. Assume that density of the gelatin solution is 1 g/mL and calculate the mass of gelatin in the first test tube with the formula:

$$\text{m(gelatin)} = \frac{m_{solution} \cdot W_{gelatin} \cdot 1000}{100\%}, \text{ mg}$$

The mass of gelatin in each successive test tube is twice smaller than in the previous one.

Fill in the table with the results.

№ test tube	**1**	**2**	**3**	**4**	**5**	**6**	**7**
m(gelatin), mg							
Coagulation							
Colloidal protection							

Mark the smallest mass of gelatin that protects the sol from coagulation and calculate "the iron number" – protective number of gelatin for $Fe(OH)_3$ sol as the smallest mass of gelatin that protects 10 mL of the sol from coagulation.

$$\text{P.N.} = \frac{m_{gelatin} \cdot 10mL}{1mL}, \text{ mg,}$$

where: $m_{gelatin}$ is the smallest mass of gelatin, mg.

Write down the results. Check them with the teacher.

Lesson № 11

1.SUBJECT. **Properties of solutions of high-molecular compounds. Measurement of the pI of a protein.**

2.IMPORTANCE. Such high-molecular compounds as polypeptides, proteins, polysaccharides and nucleic acids are vital for functioning of the living organism. The natural polymers are constituents of dispersion systems in all organisms. Such processes as synthesis and degradation of natural high-molecular compounds, their turgescence and dissolving, formation of physiologically active supermolecular structures, create the molecular basis of life. Biopolymers perform important functions in the body. They catalyze biochemical processes, preserve and transfer genetic information, perform protective and structural functions.

Artificial and synthetic polymers are of great importance in medicine and pharmaceutics. They are used in production of artificial blood vessels, teeth etc.

3.AIM OF STUDYING: create understanding of formation and properties of solutions of high-molecular compounds, correlation of their dissolving and turgescence, effect of various factors on the turgescence process. Obtain practical skills in measurement of the pI of proteins.

Necessary knowledge:
- characteristics of structure of high-molecular compounds and biopolymers;
- formation and characteristics of solutions of high-molecular compounds;
- turgescence and its dependence on various factors;
- characteristics of structure of protein molecules as amphoteric polyelectrolytes;
- the isoelectric point (pI) of proteins;
- methods of measurement of the pI of proteins.

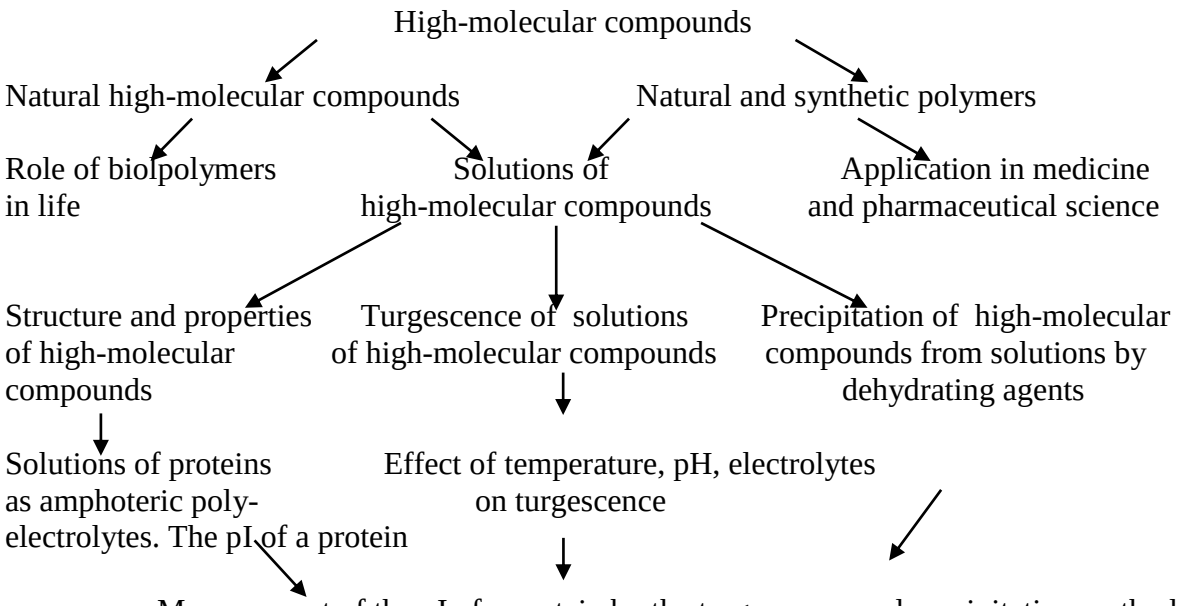
Necessary skills:
- evaluate the charge of a protein molecule depending on the pH of solution and the pI of the protein;
- prepare buffer solutions with certain pH values;
- measure the pI of a protein by the turgescence and precipitation methods.

Skills to obtain:
- measure pI of gelatin with the minimum of turgescence and maximum of precipitation from solutions.

4. BASIC KNOWLEDGE**:**

1) Solutions of electrolytes, pH.
2) High-molecular compounds, biopolymers and characteristics of their structure.
(the high school course, the previous lessons).
3) Buffer solutions.
4) Calculations of pH of buffer solutions (the previous lessons).

5. LOGICAL STRUCTURE



6. STUDYING PLAN (for self-preparation)

Studying actions	Guidelines to studying actions
1. High-molecular compounds (polymers)	1.1. Natural, artificial and synthetic polymers. 1.2. Role of biopolymers in life. 1.3. Application of polymers in medicine and pharmaceutical science.
2. Solutions of high-molecular compounds.	2.1. Structure and properties of solutions of high-molecular compounds. 2.2. Solutions of polypeptides and proteins as amphoteric electrolytes. The pI of proteins.
3. Turgescence of high-molecular compounds.	3.1. The mechanism of turgescence. Limited and unlimited turgescence. Degree of turgescence. 3.2. Effect of temperature, pH, nature of the solvent and the high-molecular compound on turgescence. 3.3. Effect of the electrolyte composition of the solution on turgescence. Liotropic series of anions and cations.
9. Precipitation of high-molecular compounds from solutions by dehydrating agents.	
5. Measurement of the pI of a protein.	5.1. Measurement of the pI of a protein with the turgescence method. 5.2. Measurement of the pI of a protein with the maximum precipitation from solution.

7. SELF ASSESSMENT TASKS

1) Which of the high-molecular compounds belong to natural polymers:

1 – glycogen, 2 – polyethylene, 3 – nylon,
4 – carboxymethylcellulose, 5 – DNA, 6 – starch.

a) 2, 3, 4; b) 4, 5, 6; c) 1, 4, 5; d) 1, 5, 6.

2) 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.

3) Choose one best description of the pI of the protein:

a) it is the state of the protein molecule, when it is not charged;
b) it is the pH of solution when the protein molecule is not charged;
c) it is the pH of solution when the resulting charge of the protein molecule equals zero;
d) it is the polymerization degree of the protein molecule, when its resulting charge equals zero.

4) 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 volumes 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.

5) Which pH values of the solution cause the smallest turgescence of the protein.

a) pH > pI; b) pH < pI; c) pH = pI; d) pH = 7.

6) Which pH values of the solution cause the greatest precipitation of a protein upon addition of a dehydrating agent?

a) pH > pI; b) pH < pI; c) pH = pI; d) pH = 7.

7) Choose one best cause of heat release at the beginning of turgescence.

a) exothermal chemical reaction between the solvent and the polymer;
b) solvation of polymer molecules by solvent molecules;
c) destruction of the structure of the polymer by solvent molecules;
d) break of bonds between molecules of the polymer and the solvent.

Answers

1) The correct answer is d).

Glycogen, DNA and starch are natural polymers. Carboxymethylcellulose is an artificial polymer (obtained by a chemical modification of the natural polymer cellulose). Polyethylene and nylon belong to synthetic polymers (they are obtained synthetically and do not exist in the nature).

2) 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 surface, but the surface does not make interface between phases. The solutions belong to real solutions.

3) The correct answer is c).

4) The correct answer is c).

At the first stage of 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").

5) The correct answer is c).

Protein molecules are amphoteric polyelectrolytes, that can obtain a greater or smaller number of positive ($-NH_3^+$) or negative ($-COO^-$) charges depending on pH of the solution.

If pH< pI, the resulting charge of the protein molecule is positive. If pH > pI, the resulting charge is negative. When pH = pI, the resulting charge of all charged qroups in the protein molecule is zero. Charged molecules are hydrated better, therefore hydration and, respectively, turgescence are the smallest in a solution where pH = pI.

6) The correct answer is c).

When dehydrating agents are added to a protein solution, molecules with a small charge are the first to lose solubility. When pH = pI, the protein molecule is at its isoelectric point, i.e its resulting charge equals zero. Therefore its solubility in a polar solvent (water) is the smallest. These molecules precipitate first when a dehydrating agent is added.

7) The correct answer is b).

Solvation (hydration for water) of fragments of the polymer by molecules of the solvent is the first stage of turgescence. Solvate (hydrate) shells are formed around polymer molecules. The phenomenon is accompanied by a release of heat (heat of hydration). At this stage the turgerscent polymer sample does not change its size (turgescence is not observed).

8. PRACTICUM

8.1. Determination of effect of pH of a solution on turgescence. Measurement of the pI of gelatin with the minimum turgescence.

Add such volumes of CH_3COOH and CH_3COONa to five test tubes, that make 10 mL acetate buffer solution with certain pH in each test tube (see the chart). Add 0.5 g gelatin to each test tube, mix and leave for 40-50 minutes, mixing from time to time. Then measure the layer of the turgescent gelatin in each test tube with a ruler. Mark the pH, when the minimum turgescence is observed.

Fill in the chart with the results. Make a conclusion about effect of pH on turgescence.

№	Volumes of solutions, mL		pH solution	Height of the gelatin layer, cm	pH of the solution with the minimum turgescence	pI
	0.2 *M* CH_3COOH,	0.2 *M* CH_3COONa,				
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			

8.2. Determination of effect of electrolytes on turgescence.

Add 10 mL of K_2SO_4, KCl, KBr, KCNS solutions of the same normality to four test tubes. Add 0.5 g gelatin to each test tube, mix and leave for 40-50 minutes, mixing from time to time. Then measure the layer of turgescent gelatin in each test tube with a ruler.

Fill in the chart with the results.

№ of test tube	1	2	3	4
Electrolytes	**K_2SO_4**	**KCl**	**KBr**	**KCNS**
Height of the gelatin layer, cm				
Sequence of turgescence increase (series of anions)				

With the place of the anions in the series make a conclusion about the effect of each ion on turgescence of gelatin.

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

Add such amounts of acetic acid and sodium acetate to five test tubes, that make 2 mL buffer solution with certain pH in each test tube (see the chart).

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 the chart with the results.

№	Volumes of solutions, mL		pH	№ test tube with the maximum turbidity	pH of the solution with the maximum turbidity	pI
	0.2 *M* CH_3COOH	0.2 *M* CH_3COONa				
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			

Compare the pI values of gelatin, obtained with the maximum precipitation and the minimum turgescence.

Write down the results. Check them with the teacher.

Lesson № 12

Summary control of Module 2

"EQUILIBRIUM IN BIOLOGICAL SYSTEMS ON THE PHASE INTERFACE"

List of questions for the summary control of Module 2

Thermodynamic and kinetical principles of processes

and electrokinetical phenomena in biological systems.

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

16. The standard hydrogen electrode.

17. Measurement of electrode potential. Measurement electrodes. Comparison electrodes.

18. Oxidation-reduction electrode potentials. Mechanism of formation, biological importance. The Nernst-Peters equations.

19. Oxidation-reduction reactions in the organism. Prediction of their direction with the standard values of Gibb's energy and values of redox potentials.

20. Oxidation-reduction titration (oxidimetry). The permanganatometry method.

21. The iodinemetry method.

22. Potentiometric titration, its application in medical and biological research.

23. Diffusion and membrane potentials, their role in formation of biological potentials. Ion-selective electrodes, their applications for measurement of H^+ ions (the glass electrode), K^+, Na^+, Ca^{2+} in biological fluids.

Physico-chemistry of surface phenomena.

Liophilic and liophobic dispersion systems.

1. 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.

2. Isoelectric point of the protein (pI) and methods of its measurement.

3. Jellification of solutions of high molecular compounds. Properties of jellies.

4. 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.

5. Donnan's membrane equilibrium.

6. Surface activity. The Traube's rule. The Gibbs' equation. Orientation of molecules in the surface layer and structure of biological membranes.

7. The Langmure's equation.

8. Adsorption from solutions on the solid surface. The Freundlich's equation.

9. Physico-chemical principles of the adsorption theory.

10. Adsorption of electrolytes (selective and ion-exchange). The Panet's rule.

11. Ionites and their application in medicine.

12. Classification of methods of chromatography by distribution of substances, aggregative phase and technique. Application of chromatography in medical and biological research.

13. Dispersion systems and their classification. Obtaining and purification of colloidal solutions. Dyalysis and electrodialysis, ultrafiltration. "Artificial kidney".

14. Molecular-kinetic properties of colloidal systems (Brownian movement, diffusion, osmotic pressure). Optical properties of colloidal systems. Ultramicroscopy.

15. Structure of colloidal particles.

16. Electrokinetical potential of colloidal particles. Electrophoresis, its application in medicine and medical and biological research.

17. Kinetic and aggregative stability of liosols. Stability factors. Mechanism of coagulation action of electrolytes.

18. Coagulation threshold, its determination. Coagulation processes in purification of drinking water and waste waters. Colloidal protection, its biological role.

19. Coarse dispersion systems (aerosols, suspensions, emulsions). Obtaining and properties. Medical application.

METHODICAL INSTRUCTIONS
for independent self-preparatory work of students

1.SUBJECT. ***Basics of titrimetric analysis.***

2. IMPORTANCE. Analytic chemistry is connected to a whole complex of medical sciences: physiology, microbiology, biochemistry and pharmacology. The chemical analysis is used to control quality of medical preparations and to diagnose diseases from composition of biological fluids (urine, blood, gastric juice, saliva).

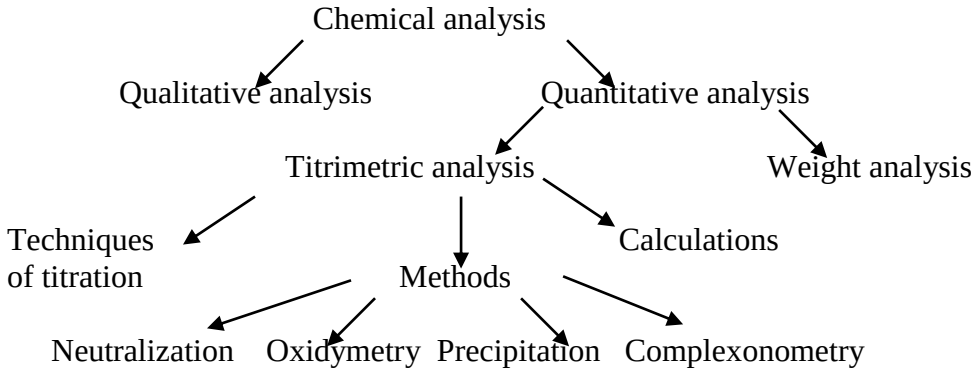
3. AIM OF STUDYING: Learn theory of titrimetric analysis

Necessary knowledge:
- essentials of titrimetric analysis;
- ideas of titration, titration end, equivalency point;
- methods of volumetric analysis;
- main techniques of titration.

Necessary skills:
- do calculations with the basic equation of titration

4. BASIC KNOWLEDGE:
1) Solutions, concentrations of solutions.
2) Normality of solutions.
3) Application of normality formulas for calculations (from the previous classes).

5. LOGICAL STRUCTURE



6. STUDYING PLAN (for self-preparation)

Studying actions	Guidelines for studying actions
1. Titrimetric analysis	1.1. The principle of titrimetric analysis. 1.2. Basic concepts of titrimetric analysis. 1.3. Glassware for volumetric analysis.
2. Methods of volumetric analysis.	2.1. Neutralization method. 2.2. Oxidymetry method. 2.3. Precipitation titration. 2.4. Complexonometry method.
3. Main techniques of titration	3.1. Direct titration. 3.2. Reverse titration (titration of the remainder). 3.3. Indirect titration (titration of the substitute).
4. Calculations in volumetric analysis	

7. SELF ASSESSMENT TASKS

TASK No.1.

25.5 mL sodium hydroxide solution was titrated against 10.20 mL 0.1 *N* sulfuric acid. Calculate the normality of the sodium hydroxide solution.

TASK No.2

0.1164 g of soda Na_2CO_3 was titrated against 20.35 mL hydrochloric acid solution. Calculate the normality of the hydrochloric acid solution.

TASK No.3

0.9225 g sodium hydroxide was dissolved in 200 mL of water. 15.0 mL of the solution was titrated against 17.60 mL 0.0976 *N* hydrochloric acid solution. Calculate the mass percent of sodium hydroxide in the weighed portion.

TASK No.4

0.9576 g sodium carbonate was titrated against 19.35 mL 0.9885 *N* hydrochloric acid solution in the presence of methyl orange. Calculate the mass percent of Na_2CO_3 in the weighed portion.

Answers

TASK No.1.

Calculate the normality of sodium hydroxide with the formula:

$$N(B) = \frac{N(A) \cdot V(A)}{V(B)}.$$

$$N(NaOH) = \frac{N(H_2SO_4)V(H_2SO_4)}{V(NaOH)} = \frac{0.1 \cdot 10.20}{25.5} = 0{,}04\,(mol/L).$$

TASK No.2.

Calculate the normality of HCl from the mass of the weighed portion and the volume of the titrant, with the formula:

$$N(B) = \frac{m(A) \cdot 1000}{Mequiv(A) \cdot V(B)}$$

$$N(HCl) = \frac{m(Na_2CO_3) \cdot 1000}{Mequiv(Na_2CO_3) \cdot V(HCl)} = \frac{0.1164 \cdot 100}{53 \cdot 20.35} = 0.1079 \quad (mol/L)$$

TASK No.3.

1. Calculate the normality of NaOH in the analyzed solution with the formula:

$$N(B) = \frac{N(A) \cdot V(A)}{V(B)}:$$

$$N(NaOH) = \frac{N(HCl) \cdot V(HCl)}{V(NaOH)} = \frac{0.0976 \cdot 17.6}{15.0} = 0.1145 \quad (mol/L)$$

TASK No.4.

1. Calculate the mass of sodium carbonate in the weighed portion with the formula:

$$m(B) = \frac{N(A) \cdot V(A) \cdot Mequiv(B)}{1000}$$

$$m(Na_2CO_3) = \frac{N(HCl) \cdot V(HCl) \cdot Mequiv(Na_2CO_3)}{1000} = \frac{0.9885 \cdot 16.75 \cdot 53}{1000} = 0.8775 \quad (g)$$

2. Calculate the mass percent of the analyzed substance with the formula:

$\omega(B) = \frac{M(B)}{q} \cdot 100$ where q is the weighed portion of the analyzed substance, g.

,

$$\omega(Na_2SO_3) = \frac{m(Na_2SO_3) \cdot 100}{q} = \frac{0.8775 \cdot 100}{0.9576} = 91.64\%$$

2. SUBJECT. ***Redox reactions. Permanganatometry method. Measurement of the mass percent of ferrous sulfate in technical ferrum vitriol***

2.IMPORTANCE. Redox reactions are of foremost importance in the organism. Some quantitative analysis methods, known as oxidimetry, are based on redox reactions. The methods are used fro determination of oxidizing and reducing agents in solutions, biological liquids, water. Permanganatometry is one of the oxidimetry methods (working solution – potassium permanganate). It can be used to determine the amount of uric acid in urine and blood, calcium ions, oxydizing enzyme catalase. It is also used in the sanitary analysis to examine drinking water and waste water. Potassium permanganate is also used as a disinfectant and bleaching agent in stomatology.

3.AIM OF STUDYING: Create understanding of applications of oxidation-reduction reactions in the quatitative analysis and acguire the skill of permanganatometry titration.

Necessary knowledge*:*

- basics of redox theory;
- essentials of oxydymetry methods;
- reactions of potassium permanganate in different conditions;
- redox reactions in the human body.
-

Necessary skills:

- balance redox reaction equations;
- perform permanganatometric titration;
- make calculations in perganatometric analysis.
-

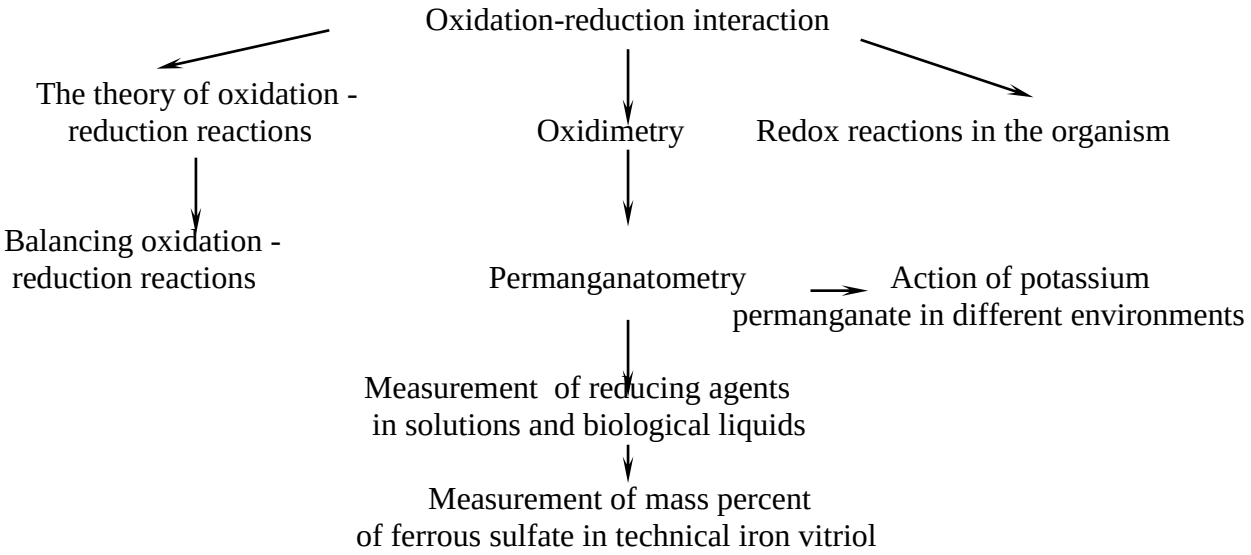
Obtained skills:

- detemination reducing agents in solutions and biological liquids with permanganatometric method.

4. BASIC KNOWLEDGE:

1) oxidation state of elements in compounds, oxidizing and reducing agents, redox reactions;
2) balancing typical redox equations;
3) technique of titrimetric analysis;
4) calculations in volumetric analysis.

5. LOGICAL STRUCTURE



6. STUDYING PLAN (for self-preparation)

Studying actions	Guidelines for studying actions
1. Oxidation-reduction interaction	1.1. Theory of oxidation-reduction reactions; 1.2. Classification of redox reactions (intramolecular, intermolecular, disproportional); 1.3. Balancing equations of redox reactions.
2. Oxidation-reduction reactions in the organism	
3. Oxidimetry	
4. Permanganatometry	4.1 Basics of the permanganatometry method. The titrant. Indicators of the method. 4.2 Oxidizing action of potassium permanganate depending on pH of the environment. 4.3. Characteristics of titration in permanganatometry. Autocatalysis.
5. Measurement of mass percent of ferrous sulfate in technical iron vitriol	5.1 Technique of titration. 5.2 Calculation of mass percent with results of the titration.

7. SELF ASSESSMENT TASKS

1) Tell which of the given substances are only oxidizing agents:

a) $K_2Cr_2O_7$ b) Cr_2O_3 c) Na_2CrO_4 d) $NaCrO_2$

2) In which of the following schemes does oxidation take place?

a) $NO_3 \rightarrow NH_3$ b) $CO \rightarrow CO_2$ c) $NO_2 \rightarrow NO$ d) $CO_2 \rightarrow CO_3^{2-}$

3) Write the complete molecular equation of oxidizing of manganese (II) sulfate by potassium permanganate in a neutral medium, if the ionic equation is as following:

$Mn^{2+} + MnO_4^- + H_2O = MnO_2 +$

The sum of the coefficients in the equation is:

a)21 b)32 c)10 d)15

4) Determine the molar mass of equivalent of potassium permanganate in perganatometric titration

a)31.61 b)52.68 c)79.02 d)158.04

5) Describe peculiarities of redox reactions in the living organisms

Answers

1) the correct answers are a) and c). In $K_2Cr_2O_7$ and Na_2CrO_4 chromium ON is maximal (+6), in the other compounds its ON is (+3). A compound with maximum ON can be only an oxidising agent.

2) The correct answer is b). Oxidation an increase in oxidation number.

a) $N^{+5}O_3^- \rightarrow N^{-3}H_3$ b) $C^{+2}O \rightarrow C^{+4}O_2$ c) $N^{+4}O_2 \rightarrow N^{+2}O$ d) $C^{+4}O_2 \rightarrow C^{+4}O_3^{2-}$

3) The correct answer is d). Let's use the half reaction method. The reaction takes place in the neutral media, that is why we only have H_2O in the left part of the half equations, and ions H^+ and OH^- in the right part.

Oxidation reaction: $Mn^{2+} + 2H_2O - 2e^- \rightarrow MnO_2 + 4H^+$ 6 | 3 |

Reduction reaction: $MnO^{4-} + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$ | 2 |

Let's balance the both half reactions with the number of gained and lost electrons:

$3Mn^{2+} + 2\ MnO_4^- + 10H_2O = 5MnO_2 + 12H^+ + 8OH^-$

Taking into account that $8H^+ + 8OH^- = 8H_2O$ we obtain the following equation:

There are $8H_2O$ in the both left and right parts, so:

$3Mn^{2+} + 2\ MnO_4^- + 2H_2O = 5MnO_2 + 4H^+$

It is the full ionic equation. The full molecular equation will be as following:

$3MnSO_4 + 2\ KMnO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2\ H_2SO_4$

The sum of all stechiometric indices is 15.

4) The correct answer is a). Permanganatometric titration should be held in acidic conditions, where its oxidising abilities are maximal and the end of the titration is easy to mark. The equation of reduction of potassium permanganate in acidic conditions is as following:

$MnO^{4-} + 8H^{+} + 5e^{-} \rightarrow Mn^{2+} + 4H_2O$

The molar mass of equivalent of potassium permanganate is calculated:

$M_{(1/5\ KMnO4)} = M_{(KMnO4)} : 5 = 158.04 : 5 = 31.61\ g/mol,$

because 1 mole $KMnO_4$ accepts 5 electrons.

5) In the living organism hydrogen in substrates is the main reducing agent, oxygen is the main oxidising agent. The redox processes in the body are of multistaged nature. The energy of the reactions transforms not into heat but into the energy of chemical bonds in ATP, ADP.

3.SUBJECT. ***Iodinemetry. Determination of the mass percent of formaldehyde in formalin.***

2.IMPORTANCE. Due to its simplicity and accuracy iodinemetry is the most popular method of oxidimetric titrations. It is used in the chemical, clinical and sanitary analysis to determine oxidising and reducing agents in solutions and biological liquids. For example it is used to determine peroxidase in blood, active chlorine in chlorine water. It is also used to determine aldehyde and ketone groups, acetone, chinone, hydrochinone.

3.AIM OF STUDYING: Learn the theory and possibilities of the iodinemetry method. Master the skills of reverse iodinemetric titration.

Necessary knowledge:

- basics of iodinemetry method
- direct and reverse titration to determine reducing agents
- substitution method to determine oxidising agents

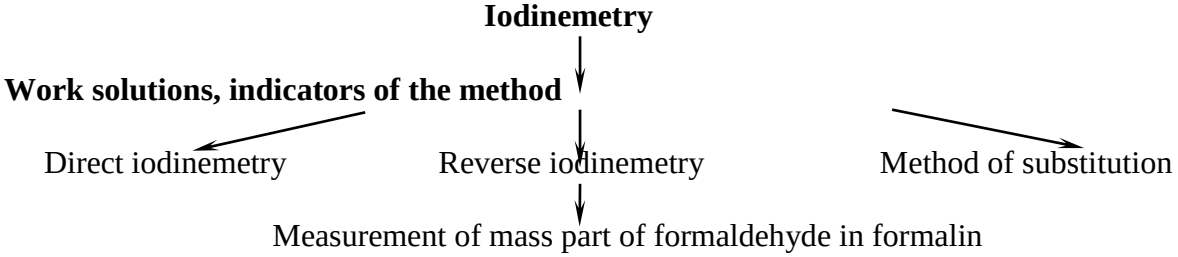
Necessary skills:

- balance redox reaction equations in iodinemetry titration
- make calculations in iodinemetric analysis

4. BASIC KNOWLEDGE**:**

1) theory of redox processes;
2) balancing redox equations;
3) technique of titrimetric analysis;
4) calculations in volumetric analysis.

5. LOGICAL STRUCTURE



6. STUDYING PLAN (for self-preparation)

Studying actions	Guidelines
1. Basics of the iodinemetry method	1.1 Reactions of the method. 1.2. Working solutions. 3. The indicator of the iodinemetry method.
2. Measurement of oxidizing agents with the iodinemetry method.	2.1 Direct titration. 2.2 Reverse titration.
3. Technique of quantitative measurement of mass percent of formaldehyde in formalin.	

7. SELF ASSESSMENT TASKS

1) the working solutions in iodinemetry are:
   a) iodine
   b) potassium iodide
   c) sodium thiosulfate
   d) starch

2) to determine formaldehyde in formaline reverse titration is used instead of direct. Why?
   a) slow reaction hinders determination of equivalency point in the direct titration
   b) the direct titration is chemically impossible
   c) starch cannot be used as an indicator in the direct titration
   d) reverse titration is faster

3) Calculate the molar mass of equivalent of formaldehyde in its reaction with iodine.
a) 30 b) 15 c) 10 d) 6

4) When is starch added in the reverse titration?
   a) at the beginning of the titration with thiosulfate
   b) immediately after adding iodine solution
   c) when very little iodine is left in the titration with thiosulfate
   d) when the yellow colour disappears in the titration with thiosulfate

Answers

1) the correct answers are a) and c). Work solutions in iodinemetry are iodine and sodium thiosulfate solutions. An additional titration is needed to determine their exact concentrations.

2) the correct answer is a). Formaldehyde slowly reacts with iodine in alkaline conditions, that is why the reaction cannot be used for titration.

3) the correct answer is b). Iodine reacts with formaldehyde as following:

$HCHO + 3NaOH + I_2 = HCOONa + 2NaI + 2H_2O$

The formaldehyde molecule is oxidised and loses two electrons:

$HCHO + 3OH^- - 2e^- \rightarrow HCOO^- + 2H_2O$

Thus the molar mass of equivalent of formaldehyde equals:

$$M_{(1/2HCHO)} = M_{(HCHO)} : 2 = 30g/mol : 2 = 15g/mol$$

4) the correct answer is c). Starch solution is added at the end of the titration when there is very little iodine in the titrated solution (it becomes pale yellow). If starch is added when the concentration of the iodine is still high, the iodine will be adsorbed on starch molecules and the reaction between starch and thiosulfate will be very slow.

4. SUBJECT. ***Control work "Solutions. Methods of quantitative analysis".***

2.AIM OF STUDYING. Strengthen understanding of the values that characterize quantitative composition of solutions and understanding of titrimetric analysis.

Necessary knowledge:
- the values that characterize quantitative composition of solutions;
- formulas to calculate mass percent, molarity, normality;
- formulas to calculate number of moles, number of moles of equivalent, equivalency factor;
- formulas of calculations in titrimetric analysis.

Necessary skills:
- calculate concentrations of solutions;
- calculate the mass and the number of moles of a solute in a solution;
- transform one form of concentration into another;
- make calculations with the formula of titrimetric analysis.

4. STUDYING PLAN (for self-preparation)

Studying actions	Guidelines for studying actions
1. Types of concentrations of solutions.	1.1. Mass, volume and molar parts. 1.2. Molarity. 1.3. Normality.
2. Calculations in volumetric analysis	2.1. The main formula of volumetric analysis. 2.2. Measurement of concentration of a substance in an analyzed solution. 2.3. Measurement of purity of a substance with volumetric analysis.

4. EXAMPLE OF THE TEST CARD

1) Glutamic acid is used in treatment of diseases of the central nervous system as a solution with mass percent 1% and density 1.12 g/mL. 25% (by mass) glucose solution is the solvent. Calculate the mass of glutamic acid that is needed to prepare 50 mL of the solution.

2) A solution of aluminium acetate is used in treatment of skin and mucosa inflammations. The solution is obtained by dissolving 8.7 g of the salt in 100 mL water. Calculate the molarity of aluminium acetate in the solution, if its density is 1.05 g/mL.

3) A 0.335% (by mass) ferric chloride solution in concentrated hydrochloric acid is used for the Obermayer's test in biochemical analysis. The density of the solution is 1.2 g/mL. Calculate the normality of ferric chloride in the solution.

4) 1.14 g of dihydrate of oxalic acid $H_2C_2O_4 \cdot 2H_2O$ was dissolved in water to make 200 mL of solution. 25.00 mL of the solution were titrated against 20.00 mL of 0.1 *N* NaOH solution. Calculate the mass percent of pure oxalic acid in the weighed portion.

Answers

Problem 1.

1) Calculate the mass of the solution of glutamic acid:

$m_{(solution)} = \rho \cdot V = 1.2\ g/mL \cdot 50\ mL = 56\ g$

2) Calculate the mass of glutamic acid in the solution:

$$m_{(acid)} = \frac{W_{(acid)} \cdot m_{(solution)}}{100\%} = \frac{1\% \cdot 56\,g}{100\%} = 0.56\,g$$

Problem 2.

1) Calculate the amount of the substance of aluminium acetate:

$$n_{(Al(CH_3COO)_3)} = \frac{m_{(Al(CH_3COO)_3)}}{M_{(Al(CH_3COO)_3)}} = \frac{8.7\,g}{204\,g/mol} = 0.0426 mol$$

2) Calculate the mass of the solution, taking into account that density of water is 1 g/mL:

$m_{(solution)} = m_{(Al(CH_3COO)_3)} + m_{(water)} = 8.7\ g + 100\ г = 108.7\ g$

3) Calculate the volume of the solution:

$$V_{(solution)} = \frac{m_{(solution)}}{\rho} = \frac{108.7\,g}{1.05\,g/mL} = 103.5 mL = 0.1035 L$$

4) Calculate the molarity of the salt:

$$C_{(Al(CH_3COO)_3)} = \frac{n_{(Al(CH_3COO)_3)}}{V_{(solution)}} = \frac{0.0426}{0.1035} = 0.4116 mol/L$$

Problem 3.

1) Assume, that the volume of the solution is 1L:

$V_{(solution)} = 1L = 1000mL$

2) Calculate the mass of 1 L of the solution:

$m_{(solution)} = V_{(solution)} \cdot \rho = 1000\ см^3 \cdot 1.2\ г/см^3 = 1200\ g$

3) Calculate the mass of ferric chloride:

$$m_{(FeCl_3)} = \frac{W_{(FeCl_3)} \cdot m_{(solution)}}{100\%} = \frac{0.335\% \cdot 1200\,g}{100\%} = 4.02\,g$$

4) Calculate the molar mass of equivalent of ferric chloride:

$$M_{(1/3 FeCl_3)} = \frac{M_{(FeCl_3)}}{3} = \frac{162.5}{3} = 54.167\,g/mol$$

5) Calculate the number of moles of equivalent of ferric chloride in 1 L of the solution, i.e the normality of the solution:

$$n_{(1/3FeCl_3)} = \frac{m_{(FeCl_3)}}{M_{(1/3FeCl_3)}} = \frac{4.02}{54.167\,g/mol} = 0.0742mol$$

$$Therefore, N_{(FeCl_3)} = 0.0742mol/L$$

Problem 4.

1) Calculate the normality of oxalic acid in the solution with the main equation of titration:

$$C_{(1/2H_2C_2O_4)} = \frac{C_{(NaOH)} \cdot V_{(NaOH)}}{V_{(H_2C_2O_4)}} = \frac{0.1 \cdot 20.00}{25.00} = 0.08\,mol/L$$

2) Calculate the mass of dihydrate of oxalic acid in one liter of the solution:

$$m_{(H_2C_2O_4 \cdot 2H_2O)} = C_{(1/2\,H_2C_2O_4 \cdot 2H_2O)} \cdot M_{(1/2\,H_2C_2O_4\,\cdot\,2H_2O)}, where:$$

$M_{(1/2H_2C_2O_4 \cdot 2H_2O)}$ -molar mass of equivalent of dihydrate of oxalic acid, g/mol:

$$M_{(1/2H_2C_2O_4 \cdot 2H_2O)} = \frac{M_{(H_2C_2O_4 \cdot 2H_2O)}}{2} = 63\,g/mol$$

$C_{(1/2H_2C_2O_4 \cdot 2H_2O)}$ - normality of dihydrate of oxalic acid, mol/L:

$$C_{(1/2H_2C_2O_4 \cdot 2H_2O)} = C_{(1/2H_2C_2O_4)} = 0.08mol/L$$

$$Therefore, \quad m_{(H_2C_2O_4 \cdot 2H_2O)} = 0.08 \cdot 63 = 5.04\,g/L$$

3) Calculate the mass of dihydrate of oxalic acid in 200 mL (0.2 L) of the solution:

$$m_{1(H_2C_2O_4 \cdot 2H_2O)} = m_{(H_2C_2O_4 \cdot 2H_2O)} \cdot 0.2\,L = 5.04 \cdot 0.2 = 1.008\,g$$

4) Calculate the mass percent of pure oxalic acid (dihydrate) in the weighed portion:

$$W_{(H_2C_2O_4 \cdot 2H_2O)} = \frac{m_{(H_2C_2O_4 \cdot 2H_2O)100\%}}{m_{(weighed\ portion)}} = \frac{1.008 \cdot 100\%}{1.14} = 88.42\%$$

LITERATURE

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