МИНИСТЕРСТВО ЗДРАВООХРАНЕНИЯ РЕСПУБЛИКИ БЕЛАРУСЬ

БЕЛОРУССКИЙ ГОСУДАРСТВЕННЫЙ МЕДИЦИНСКИЙ УНИВЕРСИТЕТ

КАФЕДРА ОБЩЕЙ ХИМИИ

РУКОВОДСТВО К ПРАКТИЧЕСКИМ ЗАНЯТИЯМ ПО ОБЩЕЙ ХИМИИ

GENERAL CHEMISTRY: PRACTICE

Практикум

2-е издание

Минск БГМУ 2012

Рекомендовано Научно-методическим советом университета в качестве практикума 30.05.2012 г., протокол № 8

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Издание содержит экспериментальные работы по химической термодинамике, кинетике и катализу, коллигативным свойствам растворов, растворам электролитов, по гетерогенным равновесиям, по кондуктометрии и потенциометрии, хроматографии, дисперсным системам и растворам высокомолекулярных соединений. Первое издание вышло в 2009 году.

Предназначено для студентов 1-го курса медицинского факультета с обучением на английском языке.

PREFACE

This students' guide is coming to you as our contribution to the effective teaching of practical chemistry for foreign first year students of the Byelorussian State Medical University on General chemistry, including some topics of Colloidal and Biophysical chemistry. In spite of the wide range of ability and ultimate achievement, students appear to manifest one common characteristic, and that is the high thirst for knowledge. The obvious corollary is the innate motivation and willingness to learn. Sometimes, however, the enthusiasm

to aquire knowledge is handicapped or misdirected. One of the several reasons for such disadvantage is the inability to obtain appropriate textbooks. Books for this level of learning must be able to arrange facts simply and logically. They should also possess the ability to present such facts systematically so as to assist students understand subject matter and recollect facts with ease.

This book attempts to organize and present «General Chemistry: Practice» in this light – simplicity, logicality and systematism. We are putting forward this book in the sincere hope that every student would find it very beneficial. The main questions on the topic, experimental works, tests self-check, standards of problem solutions make this book a most valuable practical chemistry manual for students.

What has been done by the authors in an attempt to make use of the theoretical achievements in the chemical science is possibly far from perfection. The authors will be gratefull for any constructive criticism and useful suggestions which will doubtless be taken into account in a subsequent edition.

I. ELEMENTS OF CHEMICAL THERMODYNAMICS

MAIN QUESTIONS ON THE TOPIC

1. Subject and tasks of chemical thermodynamics. Chemical thermodynamics as the basis of bioenergetics. Isolated, closed and open systems.

2. The first law of thermodynamics. Internal energy, heat and work. Isobaric and isochoric thermal processes. Enthalpy.

3. Hess's law and its corollaries. Standard formation and combustion heat. Thermochemical calculations and their usage for energetic characteristic of biochemical processes.

4. Interconnection between the processes of metabolism and energy exchange. Caloric value of main constituents of food and some food products. Energy consumption at different modes of moving activity.

5. Thermodynamically reversible and irreversible processes. The second law of thermodynamics. Entropy. Statistic and thermodynamic explanation of entropy. Standard entropy.

6. The Gibbs free energy (isobaric-isothermal potential). Enthalpy and entropy factors. Ex- and endergonic processes in the organism.

7. Thermodynamics of chemical equilibrium. Reversible and irreversible reactions. Concept of chemical equilibrium. Constant of the chemical equilibrium. The interconnection between the constant of chemical equilibrium and the Gibbs free energy. Equations of isotherm and isobaric curve of a chemical reaction.

EXPERIMENTAL WORKS

Work 1. Determination of heat of neutralization reaction.
Devices and reagents: 1. Calorimeter. 2. 1N NaOH solution. 3. 1N HCl solution.

Performance of the work. We should put 125 mL of 1N NaOH (p = 1,037 g/mL)solution into a weighted calorimetric glass. Then 125 mL of 1N HCl (p = 1,014 g/mL) solution are poured into the other glass. Then we should measure the temperature of both solutions. At working mixer we pour the solution of the acid with the help of a funnel into the calorimeter and watch the temperature change. Then we mark the maximum solution temperature.

The results of the experiment are written down in the table.

Mass of a calorimetric glass — m_1

Solution concentration NaOH

Solution concentration HCl

Solution volume NaOH, V, mL

Solution volume HCl, V, mL
Solution temperature NaOH — t_{alkali}
Solution temperature HCl — t_{acid}
Initial temperature $t_1 = 0{,}5(t_{alkali} + t_{acid})$
Temperature after the neutralization — t_2
Total mass of these solutions $m_2 = (\rho_{alkali}V_{alkali} + \rho_{acid}V_{acid})$
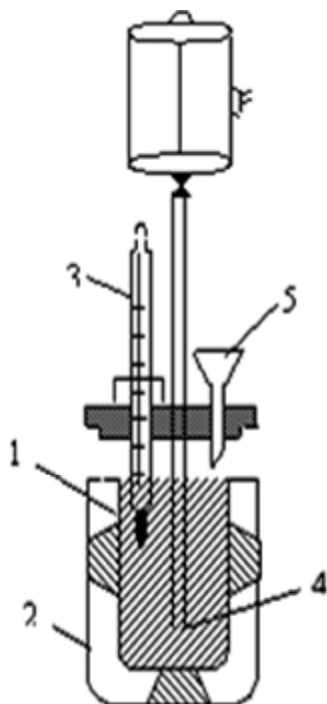

Fig. 1. The scheme of a calorimeter:
1 — vessel with the solution (reaction chamber);
2 — outer vessel; 3 — thermometer; 4 — mixer;
5 — funnel

We can calculate the neutralization heat using the formula:
$Q = \Delta t \cdot C / N \cdot V$, where: $\Delta t = t_2 - t_1$, C — total heat capacity of a calorimeter
$C = m_1C_1 + m_2C_2$.
$C_1 = 0{,}752$ J/g · °C — specific heat capacity of glass;
$C_2 = 4{,}184$ J/g · °C — specific heat capacity of a solution;
N — ending solution concentration (0,5 N);
V — total solution volume (0,25 L).
We write a thermochemical equation of the neutralization reaction:
$NaOH + HCl = NaCl + H_2O$; $\Delta H = ?$
Then we calculate the absolute and relative accuracies of the experiment if
$\Delta T_{theoretical.} = -57{,}0$ kJ/mol
Absolute error $= |\Delta H_{theoretical.} - \Delta H|$
Relative error, % $= |\Delta H_{theorelical.} - \Delta H| / \Delta H_{theoretical.} \cdot 100$ %

Work 2. Effect of temperature on the equilibrium position.
The reversible chemical reaction is under study:
I_2 + Starch Solution $\leftrightarrow$ [$I_2 \cdot$ Starch]
yellow   colourless   blue

Do an experiment in a following sequence of operations:

1. Pour distilled water into 250 mL-chemical glass and heat water up to the boiling point.

2. Take three test tubes and pour 4 mL of iodine solution and 3–4 drops of starch solution into each of them. Mark a colour of a prepared solutions.

3. Immerse one test tube into hot water and compare the colour of a solution after heating with its initial colour. Does the blue colour of starch-iodine complex deepened or fade after heating?

4. Immerse the same test tube into cold water and examine its color. Does the blue colour of starch-iodine complex deepened or fade after cooling?

5. Use experimental data to answer the following questions:

a) What reaction (forward or reverse) is favorable under heating and under cooling?

b) What reaction (forward or reverse) is exothermic or endothermic?

6. Make the conclusion.

TEST SELF-CHECK

For each question or an statement there are four different answers, one, two, three or even four of which can be correct.

1. A closed system is the system which:
a) exchanges with the environment only by the substance;
b) exchanges with the environment only by energy;
c) exchanges with the environment both by the substance and by energy;
d) exchanges with the environment by neither energy nor the substance.

2. A homogeneous system is a:
a) solution of sugar in water;
b) precipitate of barium sulfate contacting with water;
c) mixture of nitrogen and oxygen at 0 °C;
d) mixture of water and ice at 0 °C.

3. We can experimentally determine the value of the following thermodynamic parameters of the system condition:
a) mass;   b) internal energy;
c) enthalpy;   d) absolute entropy.

4. There is a thermodynamic process in the system if:
a) the system volume decreases;
b) the temperature in the system is increased by 1 °C;
c) the chemical composition the substance of the system is changed;
d) the system is moving in the environment.

5. The functions of the system condition are:

a) enthalpy;   b) heat;   c) work;   d) the Gibbs free energy.

6. Indicate the mathematical expression of the first law of thermodynamics for isochoric processes:
a) $Q = A$;   b) $Q = \Delta H$;   c) $Q = \Delta U$;   d) $A = -\Delta U$.

7. Indicate the kind of the process at which the energy conducted to the system in the form of heat is equal to the change of enthalpy of the system:
a) isothermal;   b) isochoric;   c) isobaric;   d) adiabatic.

8. Which of the following statements are right:
a) the absolute value of the system enthalpy can be experimentally determined with the help of a calorimeter;

b) ΔH is a positive value for an endothermic reaction;

c) the enthalpy of a compound formation is equal to the value but opposite in the sign to the enthalpy of decomposition of this compound;

d) the heat effect of a chemical reaction is equal to the sum of enthalpies of products combustion minus the sum of enthalpies of reactants combustion taking into account the stoichiometric coefficients of the reaction equation.

9. Indicate the inequality which characterizes the endothermic reaction:
a) $\Delta H > 0$;   b) $\Delta S > 0$;   c) $\Delta H < 0$;   d) $\Delta G > 0$.

10. The heat effect DH of a chemical reaction occurring in isochoric or in isobaric conditions depends on:
a) nature of reacting substances;
b) amount of reacting substances;
c) the state of aggregation of the reactants and the products of the reaction;
d) the way of converting the reactants into the products of the reaction.

11. Indicate the formula corresponding to the mathematical expression of the second law of thermodynamics for the reversible processes:
a) $Q = \Delta U + p\,\Delta V$;   b) $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$;
c) $\Delta S = Q/T$;   d) $\Delta S > Q/T$.

12. If in an isolated system there are some spontaneous processes, the entropy of the system:
a) decreases;   b) first increases and then decreases;
c) increases;   d) doesn't change.

13. Without any calculations indicate the processes at the occurrence of which the entropy of the system increases:
a) $H_2O(l) \rightarrow H_2O(g)$;   b) $H_2(g) + 0,5O_2(g) \rightarrow H_2O(g)$;
c) $C(s) + CO_2(g) \rightarrow 2CO(g)$;   d) $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$.

14. Indicate the chemical reactions where the conversion of the reactants into the products is accompanied by simultaneous enthalpy decrease and entropy increase:

a) $KClO_3(s) \rightarrow KCl(s) + 1,5O_2(g)$ $\Delta H < 0$;

b) $H_2(g) + 0,5O_2(g) \rightarrow H_2O(g)$ $\Delta H < 0$;

c) $H_2O(l) \rightarrow H^+(aq.) + OH^-(aq.)$ $\Delta H > 0$;

d) $0,5C(s) + 0,5O_2(s) \rightarrow CO(g)$ $\Delta H < 0$.

15. The criteria of fundamental impossibility of the spontaneous occurring of isobaric-isothermal process is the inequality:

a) $\Delta H > 0$;   b) $\Delta S < 0$;   c) $\Delta G < 0$;   d) $\Delta G > 0$.

16. In which of the following cases a chemical reaction can take place spontaneously 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) $\Delta H < 0, \Delta S < 0$.

17. Indicate the inequality which characterizes the endergonic reaction:

a) $\Delta H < 0$;   b) $\Delta H > 0$;

c) $\Delta G < 0$;   d) $\Delta G > 0$.

18. Which of the following statements characterizes the exoergonic reaction:

a) the enthalpy of the system in the course of the reaction decreases;

b) the enthalpy of the system increases;

c) the Gibbs free energy of the products of the reaction is less than that of the initial substances;

d) the Gibbs free energy of the products of the reaction is greater than that of the initial substances.

19. Chemical equilibrium in a reacting system can be reached provided:
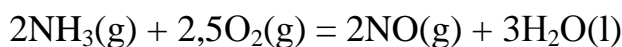
a) $\Delta G = 0$;

b) $\Delta G < 0$;

c) the speeds of the direct and reverse reactions are equal;

d) $\Delta G > 0$.

20. Spontaneously occurring chemical reaction is accompanied by the decrease in the enthalpy of the system. How does the chemical equilibrium constant of this reaction change with the increase in temperature:
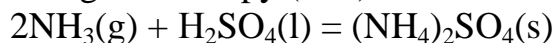
a) increases;

b) decreases;

c) doesn't change.

PROBLEMS

1. Calculate ΔG^0 of the reaction and determine the possibility to carry it out under standard conditions :
$$2NH_3(g) + 2{,}5O_2(g) = 2NO(g) + 3H_2O(l)$$
Answer: –505,56 kJ/mol

2. Calculate the change of entropy (ΔS^0) in the reaction:
$$2NH_3(g) + H_2SO_4(l) = (NH_4)_2SO_4(s)$$
Answer: –321,6 J/molK

3. Calculate ΔH^0 of the reaction: $H_2O(g) + CO(g) = CO_2(g) + H_2(g)$
Answer: –41,2 kJ/mol

4. According to the equation of the reaction: $H_2S(g) + 1{,}5O_2(g) = H_2O(l) + SO_2(g)$ calculate the enthalpy of the formation H_2S, if ΔH^0reaction = –563 kJ/mol
Answer: –19,7 kJ/mol

5. Using the data ΔH^0reaction = –101,2 kJ/mol and ΔS^0reaction = –182,82 J/molK, for the reaction: $2HCl(g) + 1/2O_2(g) = Cl_2(g) + H_2O(l)$, calculate ΔG^0 of the reaction and determine the possibility to carry it out under standard conditions
Answer: –46,9 kJ/mol

II. ELEMENTS OF CHEMICAL KINETICS

MAIN QUESTIONS ON THE TOPIC

1. Main concepts of chemical kinetics. Simple and complex, homogeneous and heterogeneous reactions. The speed of homogeneous chemical reactions and methods of its measuring.

2. The main postulate of chemical kinetics. The order of reaction and the reaction speed constant. The Law of mass action for the speed of the reaction and its sphere of application.

3. Kinetic equations of the reactions of zero, first and second order. Period of semi-transformation. Molecularity of the reaction.

4. Theory of active collisions. Arrhenius' equation. Energy of activation. Vant-Hoff's rule. Temperature coefficient of the reaction speed for enzymatic processes.

5. The concept of the theory of transition state. The main equation of the theory of transition state.

6. Catalysis and catalysts. The theories of catalysis. The mechanism of homogeneous and heterogeneous catalysis. Enzymes as biological catalysts, peculiarities of their action.

EXPERIMENTAL WORKS

Work 1. Effect of the reactants' concentrations on the reaction rate.

The aim of the experiment is to determine a linkage between reactants concentrations and the rate for the following chemical reaction:

$$Na_2S_2O_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2S_2O_3$$
$$H_2S_2O_3 \rightarrow H_2O + SO_2 + S \downarrow$$
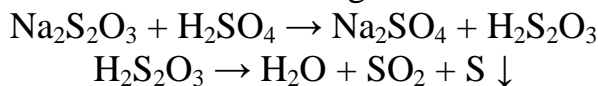
The end of the reaction is identified by evident appearance of sulphur precipitate. Fill 10 test tubes with solution of sodium thiosulphate, sulphuric acid and water according to the scheme, given in a table.

№ of a test tube	1	2	3	4	5	6	7	8	9	10
Initial solutions 1 M $Na_2S_2O_3$, mL	1		2		3		4		5	
Water, mL	4		3		2		1		0	
$Na_2S_2O_3$ concentration, mol/L	0.2		0.4		0.6		0.8		1.0	
1 M H_2SO_4, mL		5		5		5		5		5
Time after which sulfur precipitate appears, sec.										

Rate of a chemical reaction: $R = \pm\dfrac{dC}{dt}$; $\overline{V} = \pm\dfrac{\Delta C}{\Delta t}$.

Concentrations of solids (S(s)↓) are assumed to be 1 (constant) and they can be left out of the formulas. Than $\overline{V} = \dfrac{1}{\Delta t}$, where $\overline{V}$ is an average rate; Δt is the time after which sulphur precipitate appears.

Mix solutions of $Na_2S_2O_3$ and H_2SO_4, contained in test tubes 1 and 2, 3 and 4, 5 and 6, 7 and 8, 9 and 10 respectively. Mark the time of solutions mixing, and the time, when sulphur precipitate appears.

Calculate rates of a chemical reaction using formula $\overline{V} = \dfrac{1}{\Delta t}$ and represent the obtained data in a graph form (a plot of rates against $Na_2S_2O_3$ concentrations).
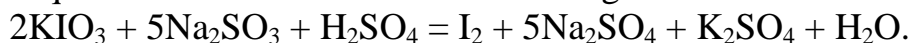
Make the conclusion.

Work 2. The influence of sodium sulfite concentration on the rate of the sulphite oxidation reaction by potassium iodate in the acid medium.
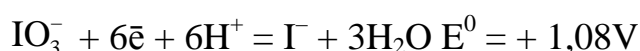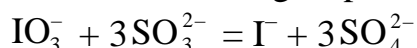
The aim of the work. To study the influence of the concentration of reacting substances on the rate of a chemical reaction.

The main idea of the work is to determine the rate of the reaction regarding the time which is necessary for the complete sodium sulphite oxidation
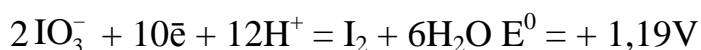by potassium iodate in the acid medium.

Total equation of the reaction is the following:
$$2KIO_3 + 5Na_2SO_3 + H_2SO_4 = I_2 + 5Na_2SO_4 + K_2SO_4 + H_2O.$$
This complex reaction occurs in different stages. In the first stage iodate-ion being an oxidizing agent is reduced to iodide-ion in the result of this reaction while oxidizing sulphite-ion to sulphate-ion according to the equation:

$$IO_3^- + 3SO_3^{2-} = I^- + 3SO_4^{2-}$$

$$IO_3^- + 6\bar{e} + 6H^+ = I^- + 3H_2O \quad E^0 = +1,08V$$

$$SO_3^{2-} - 2\bar{e} + 2H_2O = SO_4^{2-} + 2H^+ \quad E^0 = +0,20V$$

Along with it iodate-ion oxidizes iodide-ion formed in the result of this reaction with the emission of free iodine:

$$IO_3^- + I^- + 6H^+ = I_2 + 3H_2O$$

$$2IO_3^- + 10\bar{e} + 12H^+ = I_2 + 6H_2O \quad E^0 = +1,19V$$

$$I_2 + 2\bar{e} = 2I^- \quad E^0 = +0,53V$$

However, as we can see from standard values of redox potentials, the interaction of iodate-ion with iodide-ion with the emission of free iodine will take place only after the complete sulphite oxidation.

That's why the time interval from the beginning of the reaction till the appearance of free iodine, the presence of which can easily be determined when the solution turns blue at the presence of starch, will indicate the time necessary complete oxidation of sodium sulphite by potassium iodate.

Changing the concentration of one of the reagents, e.g. sodium sulphite, we can determine the dependence of the rate of the reaction on the concentration of reacting substances at constant temperature.

Order of work performance. Draw a table according to the pattern shown below:

№ of tubes	Volumes of solutions (mL)				Final sulphite concentration of sulfite C, mol/L	Time interval before the solution turns blue t, s	Average speed of the reaction $\overline{V_i}$. mol/L×s
	Na_2SO_3 0,01M	water	starch	KIO_3 0,01M			
1	1,00	–	0,25	1			
2	0,50	0,50	0,25	1			
3	0,25	0,75	0,25	1			

In three different test-tubes having the volumes of 1–2 mL with the help of a pipet we put 0,01M of sodium sulfite solution, water and 1 % solution of

starch in the volumes indicated in the table. In other three tubes we put 1 mL 0,01 M of solution of potassium iodate in 0,25 M of solution of sulphuric acid.

Then we pour together by pairs the solutions of sodium sulphite and potassium iodate measuring the time interval from the moment of pouring together the solutions till the moment when the solution becomes blue using the stop-watch or a second hand of the watch. Then we fill in the table with the results.

Using the experimental data we can calculate the initial molar concentration of sulphite taking into account its dilution while pouring together the solutions and the average rate of sodium sulphite oxidation at the measured time interval and its different concentrations:

$$C_{Na_2SO_3} = \frac{0,01 \cdot V_{Na_2SO_3}}{V_{total}}$$

$$\overline{V} = \frac{C_{Na_2SO_3}}{t}$$

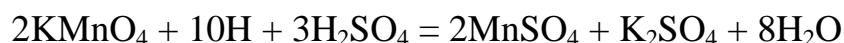Now we compare the change of the reaction rate to the change of sodium sulphite concentration.

We make the conclusions about the influence of concentration of reacting substances on the rate of a chemical reaction.

Work 3. The influence of catalysts on the rate of a chemical equation.

The aim of the work. To study the catalytic action of ions on the rate of chemical reactions.

Experiment 1. Catalytic action of NO_3^- ion on reduction reaction of potassium permanganate by atomic hydrogen.

The main reaction in this experiment is the reduction reaction of $KMnO_4$ by atomic hydrogen obtained in the result of interaction of zinc and sulphuric acid:

$$2KMnO_4 + 10H + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 8H_2O$$

or

$$2KMnO_4 + 5Zn + 8H_2SO_4 = 5ZnSO_4 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

This reaction occurs slowly but its rate increases greatly at adding $NaNO_3$. Catalytic action of $NaNO_3$ is explained by its participation in two successive reactions occurring quickly:

$$NaNO_3 + 2H = NaNO_2 + H_2O$$
$$5NaNO_2 + 2KMnO_4 + 3H_2SO_4 = 5NaNO_3 + 2MnSO_4 + K_2SO_4 + 3H_2O$$
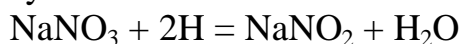
In the first reaction we can see the reduction of sodium nitrate to sodium nitrite by atomic hydrogen, in the second — the oxidation of the formed sodium nitrite back to sodium nitrate by potassium permanganate in the acid medium. As we can see from these reactions $NaNO_3$ participates in the

formation of the intermediate product — nitrite and is again regenerated in the second reaction.

Performance of the experiment. We pour equal volumes (3 mL) of solution of $KMnO_4$ acidated by sulphuric acid in three different test-tubes. Then
we add the reagents indicated below in the test tubes and compare the rate of permanganate decolouration:

Test-tube 1: Zn (dust or grains).
Test-tube 2: Zn and 3–5 drops of $NaNO_3$ solution.
Test-tube 3: 3–5 drops of $NaNO_2$ solution.

The result of the experiment in test-tube 3 confirms the mechanism of catalytic action of NO_3^- ion considered above: the decolouration of $KMnO_4$ by sodium nitrite in the acid medium occurs almost immediately.

Experiment 2. Catalytic action of Mn^{2+} ion on the reduction reaction of potassium permanganate by oxalic acid in the acid medium (autocatalysis).

The interaction of $KMnO_4$ and $H_2C_2O_4$ (in H_2SO_4 medium) at room temperature occurs very slowly. The catalyst in this reaction is its product — Mn^{2+} cations:

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O$$
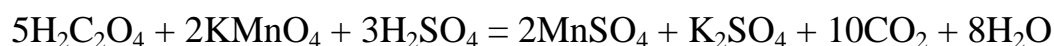
Performance of the experiment. We pour 2 mL of $H_2C_2O_4$ solution and $KMnO_4$ solution acidated by sulphuric acid in two different test-tubes. In one of the tubes we add several drops of salt solution Mn^{2+}. Then we compare the time which is necessary for the decolouration of $KMnO_4$ in both cases.

Work 4. Kinetic investigation of oxidation reaction of iodide-ion by hydrogen peroxide in acid medium.

Aim of the work. 1. To calculate the average rate of the reaction according to iodine.

2. To calculate the constants of the reaction rate according to I^--ion and H_2O_2.

In an aqueous solution in the acid medium the oxidation reaction of hydroiodic acid by hydrogen peroxide occurs according to the following equation:

$$H_2O_2 + 2H^+ + 2I^- \rightarrow I_2 + 2H_2O$$
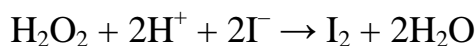
The reaction mechanism includes two stages. During the first stage we can see the formation of hypoiodous acid HIO: $H_2O_2 + I^- + H^+ \rightarrow HIO + H_2O$; the second stage of the reaction finishes with the emission of iodine:

$$HIO + H^+ + I^- \rightarrow I_2 + H_2O$$

The first stage is rather slow while the second one is quick. It is the first stage that determines the rate of total iodine emission and that's why the orders of the reactions according to I^--ion and H_2O_2 are equal to 1 and the total order of reaction is equal to 2. The second stage unites several quick reactions. And

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this is not the only one among the suggested mechanisms. Hydroiodic acid can be obtained by acting of sulphuric acid on KI or NaI when the reaction between them occurs almost immediately: $2KI + H_2SO_4 = K_2SO_4 + 2HI$.

The change of concentration of reacting substances is determined by methods of analytical chemistry (titration) or physical-chemical methods which investigate the changes of physical properties of mixtures in the course of the reaction (electroconductivity, viscosity, light absorption, etc.)

In the given work the concentration of emitted iodine is determined by measuring the light absorption using the calorimeter KFK-2 and the calibration diagram.

The order of work performance. In a dry test-tube we pour 2 mL 0,005 M of KI solution and 1 mL 1M of H_2SO_4 solution, then add 2 mL 0,005 M of H_2O_2 solution. At the very beginning of pouring in H_2O_2 we switch on the stop-watch. The reacting mixture is mixed up and is poured into a cuvette with the operating thickness of 5 mm. 5 minutes later and then every other minute we fix the absorption (A) of the emitted iodine at 440 nanometers. The concentration of emitted iodine can be determined using the calibration diagram (fig. 2.)
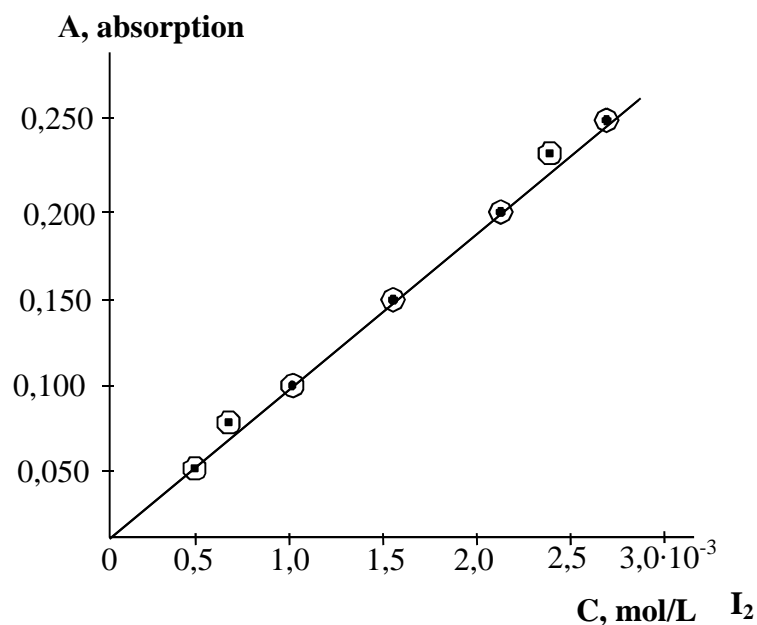
Fig. 2. Calibration diagram for determining iodine concentration
(absorption used to be called optical density and was denoted by the letter D)

Results of the experiments and design data are written down in the table

№ of experiment	Time from the beginning of the experiment,s	Absorption A	Iodine concentration, mol/L	Rate of the reaction according to iodine, $mol \times L^{-1} \times s^{-1}$	H_2O_2 concentration (equil), мol/L	I^-–ion concentration (equil), мol/L

1	300					
2	360					
3	420					
4	480					
5	540					
6	600					

Calculations. Concentrations of hydrogen peroxide $[H_2O_2]$ and iodide-ions $[I^-]$ before mixing up the solutions were $5 \cdot 10^{-3}$ mol/L. At the moment of mixing the solutions their concentration decreased 2,5 times and became $2 \cdot 10^{-3}$ mol/L. At interacting of hydrogen peroxide and hydroiodic acid with the emission iodine, the concentrations of the components change and can be calculated according to the following formulas:

$$[H_2O_2]_{equil.} = [H_2O_2]_{initial.} - [I_2]$$
$$[I^-]_{equil} = [I^-]_{initial} - 2\,[I_2]$$

Using the results of the experiments we can calculate the average rate of the reaction according to iodine on the following formula:

$$V_{I_2} = \frac{\Delta C}{\Delta t},$$

where ΔC is the change of iodine concentration, Δt is the time interval. The constants of the reaction rate according to hydrogen peroxide and iodide-ion can be calculated using these formulas respectively: for each time interval **t** with the precision till the fourth decimal digit:

$$k = \frac{2,303}{t} \lg \frac{[H_2O_2]initial}{[H_2O_2]equil} \qquad k = \frac{2,303}{t} \lg \frac{[I^-]initial}{[I^-]equil}$$

At very precise work the difference in values of the constants found for each time interval mustn't exceed several ten thousandth shares. This shows that the reaction rate constant investigated in this experiment doesn't depend on the concentration of H_2O_2 (or iodide-ion concentration) and, consequently, the order of the reaction on H_2O_2 (or on iodide-ion) is equal to 1. In both cases we calculate simple average value of rate constants.

In the conclusion we show the numerical values of the average reaction rate on iodine and the reaction rate constants on hydrogen peroxide and iodide-ion.

TEST SELF-CHECK

1. What units should we use to express the rate of a chemical reaction?

   a) $mol/L \cdot s^{-1}$;   b) $L \cdot mol^{-1}$;   c) $s \cdot mol^{-1}$;   d) $mol \cdot L^{-1} \cdot min^{-1}$.

2. Indicate the kinetic equation for the one-stage reaction A(s) + B(*l*) = AB(s):
   a) V = k[A];   b) V = k[A][B];   c) V = k[B];   d) V = k.

3. In how many times should we increase the pressure in order to increase the rate of the one-stage reaction 2A(g) + B(g) ® A$_2$B(s) in 8 times?
   a) 2;   b) 3;   c) 4;   d) 5.

4. How many times will the rate of the one-stage reaction A(s) + 2B(g) ® D(s) be decreased with the decrease of pressure in 4 times?
   a) 8;   b) 16;   c) 4;   d) 2.

5. How will the rate of the reaction change at cooling the reaction mixture at 20 ºC if the temperature coefficient g is equal to 3?
   a) will be decreased in 3 times;
   b) will be decreased in 9 times;
   c) will be increased in 3 times;
   d) will be increased in 9 times.

6. What value of energy of activation makes the chemical reaction proceed slower at other equal conditions?
   a) 30 kJ/mol;   b) 100 kJ/mol;
   c) 90 kJ/mol;   d) 40 kJ/mol.

7. At what temperature coefficient the activation energy is the greatest:
   a) 1;   b) 2;   c) 3;   d) 4.

8. If at heating the reaction mixture at 20 ºC the reaction rate has increased in 9 times, the temperature coefficient will be equal to:
   a) 2;   b) 3;   c) 4;   d) 5.

9. How does the positive catalyst influence the value of activation energy of a chemical process?
   a) increases;   b) decreases;   c) doesn't change.

10. The energies of activation of some reactions are respectively equal to:
   a) 20 kJ/mol;   b) 30 kJ/mol;
   c) 40 kJ/mol;   d) 50 kJ/mol.
The rate of which of these reactions depends greater on the temperature?

PROBLEMS

1. A simple reaction between substances A and B is expressed by an equation A + 2B → C. The initial concentrations of reagents are: [A$_2$]$_0$ = 0,3 mol/L, [B]$_0$ = 0,5 mol/L. The reaction rate constant is equal to 0,4. Find

the initial rate of the reaction and the rate of the reaction some time later when the concentration of substance A diminishes by 0,1 mol/L.

Answer: 0,03 and 0,0072 mol/L·s

2. Find the value of the rate constant of a simple reaction $A + B \rightarrow AB$ if, at concentrations of A and B substances equal to 0,5 and 0,1 mol/L respectively, the rate of the reaction is 0,005 mol/L·s.

Answer: 0,1 L/mol·s

STANDARDS OF PROBLEM SOLUTIONS

Problem 1. The constant of the reaction rate $H_2 + I_2 \rightarrow 2HI$ at 505 ºC is equal to 0,16 L/mole·s. The initial concentrations of the reacting substances were $[H_2]_0 = 0,04$ mol/L and $[I_2]_0 = 0,05$ mol/L. Calculate the initial reaction rate and its rate when hydrogen concentration will be equal to 0,03 mol/L.

We have:	*Solution*
$k = 0,16$ L/mol·s $[H_2]_0 = 0,04$ mol/L $[I_2]_0 = 0,05$ mol/L $[H_2]_t = 0,03$ mol/L $V_0 - ?\ V_t - ?$	The rate of the reaction $H_2 + I_2 \rightarrow 2HI$ according to the law of mass action is equal to: $V = k[H_2]\cdot[I_2]$ The value of the initial reaction rate can be obtained at substitution of initial concentrations of reagents in this equation: $V_0 = k[H_2]_0\cdot[I_2]_0 = 0,16\cdot0,04\cdot0,05 = 0,00032$ (L/mol·s)

When H_2 concentration becomes equal to 0,03 mol/L, i. e. is decreased at 0,01 mol/L, then according to the reaction equation I_2 concentration will also be decreased at 0,01 mol/L and will become equal to 0,04 mol/L. At this moment the reaction rate will be:

$$V_t = k[H_2]_t\cdot[I_2]_t = 0,16\cdot0,03\cdot0,04 = 0,000192 \text{ mol/L·s}$$

Answer: 0,00032 and 0,000192 mol/L·s

Problem 2. The kinetic equation of the reaction $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ is the following: $V = k \cdot [NO]^2 \cdot [O_2]$. How will the rate of this reaction change if:

a) we increase the pressure in the system in 3 times;
b) we decrease the volume of the system in 3 times;
c) we increase the concentration of NO in 3 times?

Solution. Before changing the pressure, volume of the system and NO concentration the reaction rate was expressed by the equation: $V = k[NO]_0^2\cdot[O_2]_0$, where $[NO]_0$ and $[O_2]_0$ are the initial concentrations of reagents. As a result of the increase of pressure in 3 times, the concentration of each of the reacting substances will also increase in 3 times. Consequently, now we have:

$$V_1 = k(3[NO]_0)^2(3\cdot[O_2]_0) = 27k[NO]_0^2\cdot[O_2]_0$$

Comparing the equations with V_0 и V_1, we find that the reaction rate will increase in 27 times: $V_1 = 27 \cdot V_0$

The decrease of the volume of the system in 3 times is equivalent to the increase of the pressure in the system in 3 times, consequently, the reaction rate will also increase in 27 times.

With the increase of NO concentration in 3 times the rate of the reaction will be:

$$V_2 = k(3[NO]_0)^2 \cdot [O_2]_0 = 9k[NO]_0^2 \cdot [O_2]_0$$

Comparing the equations with V_0 и V_2, we find that the rate of the reaction will increase in 9 times: $V_2 = 9\, V_0$

Answer: a) and; b) will increase in 27 times; c) will increase in 9 times.

III. THE EQUIVALENT LAW. DIFFERENT CONCENTRATION UNITS

A chemical equivalent *is a real or hypothetical particle of a substance which can interact with one Hydrogen atom in acid-base reactions or with one electron in Redox reactions.*

The mass of one mole of a substance is defined as **molar mass (M)**, g/mol.

For example: $M(H_2O) = 18$ g/mol
$M(HCl) = 36{,}5$ g/mol
$M(NaOH) = 40$ g/mol

The mass of one mole of chemical equivalent is defined as **equivalent molar mass (M_e)**, g/mol.

The equivalent molar mass relates to the molar mass of a substance as follows: $M_e = M \times f_e$, where f_e — **an equivalent factor**.

For substances involved *into ion exchange reactions the equivalent factors can be calculated* according to following formulas:

For acids: $f_e = \dfrac{1}{\textbf{a number of hydrogen atoms substituted in a molecule}}$

For monoprotic (monobasic) acids (HCl, HNO_3 and others) the equivalent factor is equal to one ($f_e = 1$); for diprotic (dibasic) acids (H_2SO_4, H_2CO_3 and others) equivalent factor takes the values 1 and 1/2 ($f_e = 1$ and 1/2); for triprotic (tribasic) acids (H_3PO_4) the equivalent factor takes the values 1, 1/2 and 1/3 ($f_e = 1$, 1/2 and 1/3).

For example: $H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O$
     $f_e = 1 \qquad f_e = 1$
     $H_3PO_4 + 2NaOH \rightarrow Na_2HPO_4 + 2H_2O$
     $f_e = 1/2 \qquad f_e = 1$

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$$H_3PO_4 + 3NaOH \rightarrow Na_3PO_4 + 3H_2O$$
$$f_e = 1/3 \quad f_e = 1$$
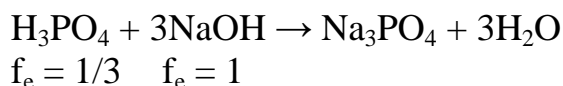
For bases: $f_e = \dfrac{1}{\textbf{a number of OH - groups substituted in a molecule}}$

For bases with one hydroxyl group — monoacid bases (NaOH, KOH and others) the equivalent factor is equal to one ($f_e = 1$); for bases with two hydroxyl groups — diacid bases ($Ca(OH)_2$, $Ba(OH)_2$ and others) equivalent factor takes the values 1 and 1/2 ($f_e = 1$ and 1/2); for bases with three hydroxyl groups — triacid bases ($Al(OH)_3$ and others) the equivalent factor takes the values 1, 1/2 and 1/3 ($f_e = 1$, 1/2 and 1/3).

For example: $Al(OH)_3 + HCl \rightarrow Al(OH)_2Cl + H_2O$
$$f_e = 1 \qquad f_e = 1$$
$$Al(OH)_3 + 2HCl \rightarrow AlOHCl_2 + 2H_2O$$
$$f_e = 1/2 \quad f_e = 1$$
$$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$$
$$f_e = 1/3 \quad f_e = 1$$
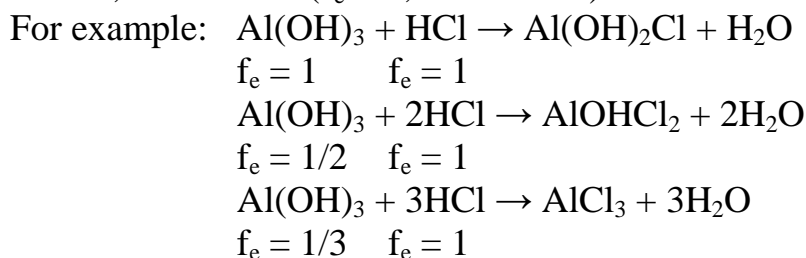
For salts: $f_e = \dfrac{1}{\textbf{a number of metal atoms} \times \textbf{oxidation number}}$

For example: $f_e (Na^+Cl^-) = 1$, $f_e (Na_2^+SO_4) = 1/2$, $f_e (Ca_3^{+2}(PO_4)_2) = 1/6$.

The equivalent factor for oxidizing and reducing agents in Redox reactions is calculated as: $f_e = 1/Z$, *where* Z *is an amount of electrons gained or lost by one mole of a substance.*

For example: $\overset{+4}{Mn}O_2 + 4HCl^- \rightarrow \overset{+2}{Mn}Cl_2 + Cl_2^0 + H_2O$
$$f_e = 1/2 \quad f_e = 1$$
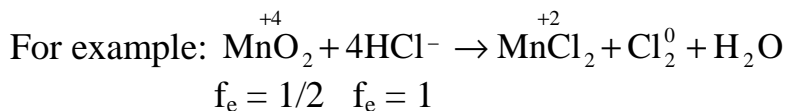
oxidant: $Mn^{+4} + 2\bar{e} \rightarrow Mn^{+2}$	2	2	1
reductant: $2Cl^- - 2\bar{e} \rightarrow Cl_2^0$	2		1

The Equivalent Law: *the masses of chemical substances which are involved into a reaction and masses of its products are directly proportional to their equivalent molar masses.*

For a hypothetical reaction **a A + b B = c C + d D** *the amounts of equivalents for reactants and products are identical:*
$$n_e(A) = n_e(B) = n_e(C) = n_e(D),$$
where n_e — **an amount of an equivalent, mol.**

For a substance the amount of an equivalent is a ratio of its mass and its equivalent molar mass:

$$n_e = \frac{m}{M_e}, \quad M_e = M \times f_e, \quad n_e = \frac{m}{M \cdot f_e},$$

where m — mass of a substance, g.

The Equivalent law is applied to do calculations in volumetric analysis.

Concentration Units

Quantitative study of a solution requires that we know its concentration, that is, the amount of solute present in a given amount of a solution. Chemists use several different concentration units, each of which has advantages as well as limitations. The choice of concentration unit is generally based on the kind of measurement made of the solution. First, though, let us examine the most common units of concentration: percent by mass (mass fraction), mole fraction (percent by mole), molarity, molality, normality, titer.

Solution = Solvent + Solutes

Sol = Solv + S

Types of Concentration Units

Percent by mass, mass fraction (ω). The percent by mass (also called the percent by weight or the weight percent) is defined as

$$\omega_S = \text{percent by mass of solute} = \frac{\text{mass of solute}}{\text{mass of solute} + \text{mass of solvent}} \times 100\,\%$$

or w_s = **mass fraction of solute** = $\dfrac{m_S}{m_S + m_{solv}} = \dfrac{m_S}{m_{sol}}$

The percent by mass shows how many grams of solute is in 100 grams of solution.

For example: we have 10 % water solution of NaCl.

It means that 10 g of NaCl is in 100 g of solution (in 90 g of H_2O).

$$w_{solv} = \text{percent by mass of solvent} = \frac{\text{mass of solvent}}{\text{mass of solution}} \times 100\,\%$$

or w_{solv} = **mass fraction of solvent** = $\dfrac{m_{solv}}{m_{sol}} = \dfrac{m_{solv}}{m_S + m_{solv}}$.

percent by mass = mass fraction × 100 %.

The percent by mass has no units because it is a ratio of two similar quantities.

Mole fraction, percent by mole (χ). The mole fraction of a component in a solution, say, component A, is written χ_A and is defined as

$$\text{mole fraction of component } A = \chi(A) = \frac{\text{moles of } A}{\text{sum of moles of all components}}$$

or $\chi_s = \dfrac{n_S}{n_{sol}}$; $\quad \chi_{solv} = \dfrac{n_{solv}}{n_{sol}}$; **mole fraction × 100 % = percent by mole.**

The mole fraction has no units, since it is a ratio of two similar quantities.

Molality (C_m). Molality is the number of moles of a solute (S) dissolved in 1 kg (1000 g) of solvent (Solv) — that is,

$$\text{molality} = C_m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} \qquad C_m = \frac{n_S}{m_{solv}}$$

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Thus molality has the units of mol/kg.

For example, to prepare a 1 mol/kg sodium sulfate (Na_2SO_4) aqueous solution, we need to dissolve 1 mole (142.0 g) of the substance in 1000 g (1 kg) of water. Depending on the nature of the solute-solvent interaction, the final volume of the solution will be either greater or less than 1000 mL. It is also possible, though very unlikely, that the final volume could be equal to 1000 mL.

Molarity (C_M). Molarity is defined as the number of moles of solute in 1 liter of a solution; that is,

$$\text{molarity} = C_M = \frac{\text{moles of solute}}{\text{liters of solution}}, \qquad C_M = \frac{n_s}{V_{sol}} = \frac{m}{M \cdot V_{sol}}$$

Thus, molarity has the units of mol/L or M.

Normality (C_N). Normality is defined as the number of equivalent moles of a solute in 1 liter of a solution; that is,

$$\text{normality} = C_N = \frac{\text{equivalent moles of solute}}{\text{liters of solution}}; \quad C_N = \frac{n_e}{V_{sol}} = \frac{m}{M_e \cdot V_{sol}} = \frac{m}{M \cdot f_e \cdot V_{sol}}$$

Thus, normality has the units of mol/L or N.

Titer (T). Titer is defined as a mass of a solute in 1 milliliter of a solution; that is, $\mathbf{Titer = T} = \dfrac{\text{mass of solute}}{\text{milliliters of solution}}; \qquad T = \dfrac{m_s}{V_{sol}(mL)}$

Thus, titer has the units of g/mL.

Concentration units are interconvertible.

$C_M = \text{molarity} = C_N \times f_e$

$C_N = \text{normality} = \dfrac{C_M}{f_e}$

$C_M = \text{molarity} = \dfrac{1000 \times T}{\text{molar mass of solute}}, \qquad C_M = \dfrac{1000 \cdot T}{M} \ (\dfrac{mol}{L})$

$C_N = \text{normality} = \dfrac{1000 \times T}{\text{equivalent molar mass of solute}},$

$C_N = \dfrac{1000 \cdot T}{M_e} = \dfrac{1000 \cdot T}{M \cdot f_e} \ (\dfrac{mol}{L})$

$C_M = \text{molarity} = \dfrac{10 \times \text{density of solution} \times \text{percent by mass}(\%)}{\text{molar mass of solute}},$

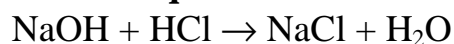$C_M = \dfrac{10 \cdot \rho_{sol} \cdot \omega_s}{M_s} \ (\dfrac{mol}{L})$

$$\omega_S = \text{percent by mass of solute}(\%) = \frac{\text{molarity} \times \text{molar mass of solute}}{10 \times \text{density of solution}},$$

$$\omega_S = \frac{C_M \cdot M_S}{10 \cdot \rho_{sol}} (\%)$$

$$\rho_{sol} = \text{density of solution} = \frac{\text{mass of solution}}{\text{volume of solution}}, \quad \rho_{sol} = \frac{m_{sol}}{V_{sol}} \left(\frac{g}{mL}\right)$$

The Equivalent Law:

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

1. $n_e(NaOH) = n_e(HCl) = n_e(NaCl) = n_e(H_2O)$
2. $C_N V(sol.NaOH) = C_N V(sol.HCl)$
3. $\dfrac{m(NaOH)}{M(NaOH) \cdot f_{\mathfrak{z}}(NaOH)} = C_N V(sol.HCl).$

PROBLEMS

1. An acid with mass of 9 g was neutralized by 8 g of sodium hydroxide NaOH. Calculate the equivalent molar mass of an acid.

Answer: 45 g/mol

2. A sample of potassium chloride (KCl) of 0,892 g is dissolved in 54,6 g of water. What is the percent by mass of KCl in a prepared solution?

Answer: 1,61 %

3. A chemist prepared a solution by adding 200 g of pure ethanol (C_2H_5OH) to 144 g of water. Calculate the mole fractions of these two components. The molar masses of ethanol and water are 46 g/mol and 18 g/mol, respectively.

Answer: 0,353 (35,3 %); 0,647 (64,7 %)

4. Calculate the molality of a sulphuric acid solution containing 24.4 g of sulphuric acid in 198 g of water. The molar mass of sulphuric acid is 98 g/mol.

Answer: 1,26 mol/L

EXERCISES FOR THE SELF-CONTROL

1. Calculate f_e and M_e for H_3PO_4 in the following reactions:

$$H_3PO_4 + NaOH = NaH_2PO_4 + H_2O$$
$$H_3PO_4 + 2\,NaOH = Na_2HPO_4 + 2\,H_2O$$
$$H_3PO_4 + 3\,NaOH = Na_3PO_4 + 3\,H_2O$$
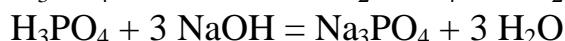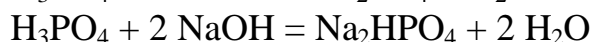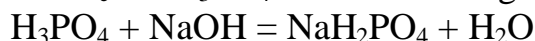
2. Calculate f_e and M_e for $Fe(OH)_3$ in the following reactions:

$$Fe(OH)_3 + HCl = Fe(OH)_2Cl + H_2O$$
$$Fe(OH)_3 + 2\,HCl = FeOHCl + 2\,H_2O$$

$$Fe(OH)_3 + 3\ HCl = FeCl_3 + 3\ H_2O$$
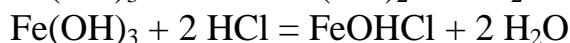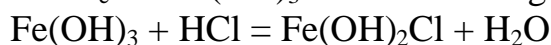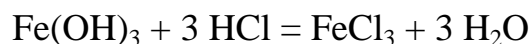
3. Calculate the percent by mass of the solute in each of the following aqueous solutions:

a) 5.5 g of NaBr in 78.2 g of solution;

b) 31 g of KCl in 152 g of water.

Answer: a) 7 %; b) 17 %

4. A solution is prepared by mixing 62.6 mL of benzene (C_6H_6) with 80.3 mL of toluene (C_7H_8). Calculate the mole fractions of these two components. The densities are: benzene, 0.879 g/cm^3; and toluene, 0.867 g/cm^3.

Answer: 48 %; 52 %

5. Calculate the molality of each of the following solutions:

a) 143 g of sucrose ($C_{12}H_{22}O_{11}$) in 676 g of water;

b) 7.2 mole of ethylene glycol ($C_2H_6O_2$) in 3546 g of water.

Answer: a) 0,62 mol/kg; b) 2,03 mol/kg

6. Calculate the molalities of each of the following aqueous solutions:

a) 1.22 M NaCl solution (density of solution = ρ = 1,12 g/mL);

b) 0.87 M NaOH solution (density of solution = ρ = 1,19 g/mL);

c) 5.24 M NaHCO$_3$ solution (density of solution = ρ = 1,19 g/mL).

Answer: a) 1,16 mol/kg ; b) 0,75 mol/kg; c) 6,99 mol/kg

7. The concentrated sulphuric acid we use in the laboratory is 98 percent H_2SO_4 by mass. Calculate the molality, molarity and normality of the acid solution. The density of the solution is 0,982 g/mL, $f_e(H_2SO_4)$ = 1/2.

Answer: 500 mol/kg; 9,82 M(mol/L); 19,64 N(mol/L)

IV. COLLIGATIVE PROPERTIES OF SOLUTIONS

MAIN QUESTIONS ON THE TOPIC

1. Thermodynamics of solution formation.
2. Osmose and osmotic pressure of solutions. Vant-Hoff's law.
3. Osmotic pressure, osmolarity and osmolality of some biological fluids. The concept of isotonic, hypertonic and hypotonic solutions.
4. The role of osmotic phenomena in biological processes.
5. The pressure of saturated vapor of solvent above the solution. Raoul's first law.
6. Boiling and freezing temperatures of solvents. Raoul's second law. Cryoscopy. Ebullioscopy.
7. Colligative properties of electrolyte solutions. Isotonic coefficient.

EXPERIMENTAL WORKS

Work 1. Cryoscopic determination of molecular mass of saccharose.

Aim of the work: To determine the molecular mass of saccharose and to compare it to the true molecular mass.

Devices and reagents:

– the investigated solution of saccharose (with the known mass share of saccharose in the solution), distilled water;

– a cooling mixture (crystalline sodium chloride, water and ice), a thick-wall glass (crystallizer), a glass stick, a laboratory thermometer for measuring the temperature of a mixture.

– the device for measuring the temperature of crystallization (the scheme of the device should be drawn in the laboratory copy book).

The order of work performance

1. Preparation of the cooling mixture.

In a thick-wall glass (crystallizer) we put finely ground ice, add some water and table salt into it filling approximately 2/3 of the glass. The mixture is stirred by a glass stick and using the thermometer we watch the temperature of the cooling mixture be approximately –5 °C during the experiment.

2. Determination of the freezing temperature of the solvent.

In a test-tube (1) we pour /10–15 mL of distilled water till the mark (4) and having closed the tube with the cork we immerse the thermometer (2) into the water so that the water level should be above the thermometer ball at approximately 1 cm (**fig.3**).
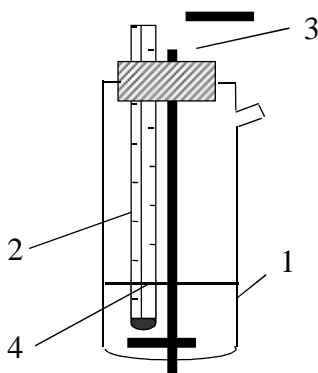
Fig. 3. The device for determination of the freezing temperature

The lower end of the thermometer must be higher from the bottom of the test-tube also at about 1 cm. The test-tube with water and the thermometer fixed in it is immersed into the cooling liquid. Stirring periodically the water in it with a mixer (3) we watch the changes in the temperature of water. When the temperature is lowered at approximately 1–1,5° below 0 (supercooled water) we actively stir water with the mixer (3). There begins the process of freezing of water with the emission of heat and the column of mercury

in the thermometer goes drastically up. We mark the maximum temperature (with the precision up to 0,05–0,1°) which is the freezing temperature of water. Then we put the test-tube into the glass with tap water (room temperature) and, stirring, we make the formed ice crystals dissolve. Then we repeat the determination of freezing temperature of water. The results of the experiment done twice are written down.

3. Determination of the freezing temperature of the saccharose solution.

In a dry test-tube we pour in the saccharose solution with the known mass percent of saccharose till the same mark. The test-tube is placed in the cooling mixture and, being stirred from time to time, the analyzed solution is supercooled till 3–3,5° below 0. We determine the freezing temperature of the solution according to the above mentioned scheme twice. The results are written down in the table.

Substance	Freezing temperature		
	Experiment 1 t¢	Experiment 2 t²	Average value
Solvent (water), t_0			
Saccharose solution, $t_{solution}$			

4. Calculations

According to Raoul's second law: $\Delta t_{freez.} = KC_m$, where

$$C_m = \frac{n_{sub}}{m_{solv.}}\,(mol/kg),\quad n_{sub} = \frac{m_{sub}}{M_{sub}},\quad C_m = \frac{m_{sub}}{M_{sub} \cdot m_{solv}},\quad \Delta t_{freez.} = \frac{K \cdot m_{sub}}{M_n \cdot m_{solv}}$$

Hence, the molar mass (g/mol) of saccharose found experimentally is the following:

$$M_{experimental} = \frac{K \cdot m_{sub}}{\Delta t_{freez} \cdot m_{solv}},$$

where $\Delta t_{freez.} = t_0 - t_{solution}$ (°C), m_{sub}(g), $m_{solvent}$ (kg), $K_{(H_2O)} = 1,86$ kg·°C ·mol^{-1};

The mass of the substance m_{sub} and the mass of the solvent $m_{solvent}$ can be calculated knowing the mass percent of the saccharose in the analyzed solution:

$$\omega = \frac{m_{sub}}{m_{sub} + m_{solv}} \cdot 100\,\%$$

The true molar mass of saccharose $C_{12}H_{22}O$ is 342 g/mol.

Relative accuracy is $\Delta X_{relat.} = \left|\dfrac{M_{theor.} - M_{exp.}}{M_{theor.}}\right| \cdot 100\,\%$.

Make the conclusions using the results of the work.

Work 2. The determination of isotonicity of sodium chloride solution and the blood serum using the reaction of erythrocytes.

Aim of the work: to determine which of the suggested solutions is isotonic to blood serum.

Reactants and equipment:

– Solutions of sodium chloride with the mass percent of NaCl 0,85 %, 0,7 %, 0,5 %, 0,3 %, erythrocytic mass, distilled water.

– Graduated centrifuge test-tubes, a glass stick, a pharmaceutical pipet, gauze napkins;

– Photoelectrocalorimeter, a centrifuge.

The order of work performance

It's necessary to prepare 4 numerated test-tubes. In the first one we pour 10 mL of the solution with the mass percent of NaCl 0,85 %, in the second one — 10 mL of NaCl solution with the mass percent 0,7 %, in the third one — 10 mL of NaCl solution with the mass percent 0,5 % and into the forth one — 10 mL of NaCl solution with the mass percent of 0,3 %.

In each of the four test-tubes we introduce 2 drops of erythrocytic mass with the help of a pharmaceutical pipet. The solutions are mixed with a glass stick (when passing from one solution to another we should clean up the stick with a gauze napkin). In 10 minutes the contents of the test-tubes are centrifuged for 10 min. in the mode of 1,5–2 thousand rotations per minute. (Pay attention to the correct arrangement of test-tubes in the centrifuge). The obtained centrifugates are calorimetered (see the instruction for using the photoelectrocalorimeter). The values of solution absorptions are written down in the table:

№ of the test-tube	Contents of the test-tube	Absorption, A
1	10 mL of NaCl solution with the mass percent of 0,85 % + 2 drops of erythrocytic mass	
2	10 mL of NaCl solution with the mass percent of 0,7 % + 2 drops of erythrocytic mass	
3	10 mL of NaCl solution with the mass percent of 0,5 % + 2 drops of erythrocytic mass	
4	10 mL of NaCl solution with the mass percent of 0,3 % + 2 drops of erythrocytic mass	

We build the dependence graph between the absorption value (A) and the mass percent of sodium chloride solution. On the ordinate axis we mark the values of absorption; on the abscissa axis we mark the mass percent of sodium chloride solution in %. Then we should make the conclusions based on the results of the work.

TEST SELF-CHECK

1. Indicate the right statements:

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a) the pressure of the saturated vapor above the solution will decrease with the increase of the mole fraction of the solvent;

b) the boiling temperature of liquids and their solutions depends on the outer pressure;

c) with the increase of the number of particles of the solute non volatile substance in a unit of mass of the solvent the freezing temperature of the solution will decrease;

d) at the same conditions aqueous solutions of non volatile electrolytes and non-electrolytes with the same molality have different boiling temperatures;

e) at the same temperature aqueous solutions of non volatile electrolytes and non-electrolytes with the same molar concentration have the same osmotic pressure.

2. Indicate the osmolarity (mol/L) 0,15 M of sodium chloride solution (here and in the following tests the apparent degree of salt dissociation should be taken as 1):

a) 0,1;   b) 0,15;   c) 0,3;   d) 0,45;   e) 0,75.

3. There are 5 different aqueous solutions with the molality of 0,05 mol/kg. The solution of which of the substances indicated below has the highest freezing temperature at the same conditions:

a) $MgSO_4$;   b) $CaCl_2$;   c) $C_6H_{12}O_6$;   d) $AlCl_3$;   e) $NaCl$?

4. Which of the aqueous solutions mentioned below has the highest boiling temperature at the same conditions:

a) $C_6H_{12}O_6$ solution with $C_m = 0,5$ mol/kg;

b) $MgSO_4$ solution with $C_m = 0,5$ mol/kg;

c) $C_{12}H_{22}O_{11}$ solution with $C_m = 1,0$ mol/kg;

d) $NaCl$ solution with $C_m = 0,5$ mol/kg;

e) $CaCl_2$ solution with $C_m = 0,5$ mol/kg.

5. There are 5 different aqueous solutions with the molar concentration 0,05 mol/L at the same temperature. Which of these solutions   are isotonic with respect to each other:

a) $CaCl_2$;   b) $NaCl$;   c) $C_6H_{12}O_6$;   d) $MgSO_4$;   e) $AlCl_3$?

6. Which of the following aqueous solutions are isotonic with respect to the blood serum (the solutions are compared at 37 ºC):

a) 0,15 M KCl solution;

b) 5 % $C_6H_{12}O_6$ solution;

c) 0,85 % $NaCl$ solution;

d) 5 % $C_{12}H_{22}O_{11}$ solution;

e) 0,15 M $CaCl_2$ solution?

7. Which of the following aqueous solutions at 37 ºC are hypotonic with respect to a physiologic solution (saline):

a) 0,15 M $CaCl_2$ solution;

b) 0,1 M $MgSO_4$ solution;
c) 0,15 M $C_6H_{12}O_6$ solution;
d) 0,3 M KCl solution;
e) 0,3 M $C_{12}H_{22}O_{11}$ solution ?

Suggest the right answers to the questions:

8. Which components of the blood serum determine to a greater extent the distribution of water between the blood stream and the extravascular space?

9. Which components make the main impact into the osmotic pressure of the intracellular fluid? Which components make the main impact into the maintenance of osmolality of blood serum?

a) potassium cations and coupled anions;
b) urea;
c) proteins;
d) sodium cations and coupled anions;
e) glucose.

PROBLEMS

1. At 65 °C calculate the vapor pressure above the solution containing 13,68 g of saccharose $C_{12}H_{22}O_{11}$ in 90 g of water if the the pressure of saturated vapor above water at the same temperature is 25,0 kPa.

Answer: 24,8 kPa

2. At 25 °C the osmotic pressure of the solution containing 2,8 g of high molecular compound in 200 ml of the solution is equal to 0,70 kPa. Find the relative molecular mass of the solute.

Answer: 49 530

3. Calculate the osmotic pressure of the solution containing 16 g of saccharose $C_{12}H_{22}O_{11}$ and 350 g of water at 293 K (density of the solution should be taken as 1g/cm^3).

Answer: 311 kPa

4. At how many degrees will the boiling temperature of the solution rise compared to the boiling temperature of water if we dissolve 9 g of glucose $C_6H_{12}O_6$ in 100 g of water?

Answer: at 0,26°

5. At approximately what temperature will the aqueous solution of ethyl alcohol with the mass percent of 20 % freeze if the freezing point of water is 0 °C?

Answer:at 10°C

6. How many grams of saccharose $C_{12}H_{22}O_{11}$ should be dissolved in 100 g of water in order to?
a) to lower the freezing temperature of the solution by one degree;
b) to increase the boiling temperature of the solution by one degree.

Answer: 18,4 g; 65,8 g

7. Apparent degree of dissociation of potassium chloride in 0,1 M of the solution is 0,80. What is the osmotic pressure of this solution at the temperature of 17 °C?

Answer: P_{osm} = 434 kPa

8. A solution containing 0,53 g of sodium carbonate in 200 g of water freezes at the temperature of –0,13 °C. Calculate the apparent dissociation degree of the salt (in %) if the freezing point of water is 0^0C.

Answer: 90 %

9. In the equal volumes of water we've dissolved: in the first case 0,5 мole of saccharose, in the second one — 0,2 mole of $CaCl_2$. The freezing temperatures of both solutions are equal. Determine the apparent degree of dissociation of $CaCl_2$ (in %).

Answer: 75 %

10. A mixture containing 0,1 g of PAS (antituberculous medicine — para-aminosalicylic acid) and 2 g of camphor melts at 165 °C. Find the relative molecular mass of PAS if the melting temperature of camphor is 178 °C and its cryoscopic constant is equal to 40 kg·К/mol.

Answer: 154 g/mol

11. The freezing temperature of the blood serum is –0,56 °C. Calculate the molality of salts in the blood taking all salts as binary ones and decaying completely into ions according to the scheme: $KA \rightarrow K^+ + A^-$. The presence of non-electrolytes in the serum shouldn't be taken into consideration.

Answer: 0,15 mol/kg

STANDARDS OF PROBLEM SOLUTIONS

Problem 1. At the temperature of 0 °C the osmotic pressure of 0,05 M of potassium carbonate solution is 272,6 kPa. Determine the apparent dissociation degree of the salt.

We have:	*Solution*
t = 0 ºC	For electrolyte solutions: $P_{osm} = iCRT$.
P_{osm} = 272,6 kPa	1. We calculate the isotonic coefficient:
C= 0,05 mol/L	
α_{app} – ?	

$$i = \frac{P_{osm}}{CRT} = \frac{272,6}{0,05 \cdot 8,31 \cdot 273} = 2,4$$

2. The apparent degree of dissociation is calculated using the formula:

$$\alpha_{app} = \frac{i-1}{n-1},$$

where α_{app} — the apparent degree of dissociation, n — number of ions, into which the electrolyte molecule is dissociated:

$$K_2CO_3 = 2K^+ + CO_3^{2-}, \; n = 3.$$

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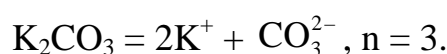
Then, $\alpha_{app} = \dfrac{2,4-1}{3-1} = 0,7$.

Answer: 0,7 or 70 %

Problem 2. How many grams of glucose should be dissolved in 270 g of water for?

a) decreasing of the freezing temperature by one degree;

b) increasing the boiling temperature by one degree.

We have:

m(H₂O) = 270 g = 0,27 kg
$\Delta t_{freez.} = 1^o$
$\Delta t_{boiling.} = 1^o$
K(H₂O) = 1,86 (kg ×degree/mol)
E(H₂O) = 0,52 (kg ×degree/mol)
M(C₆H₁₂O₆) = 180 g/mol

Solution

a) $\Delta t_{freez..} = C_m \cdot K(H_2O)$, where:
C_m — molality (mol/kg)
K(H₂O) — cryoscopic constant of water
$C_m = n\,(C_6H_{12}O_6)\,/\,m\,(H_2O)$
$n\,(C_6H_{12}O_6) = m\,(C_6H_{12}O_6)\,/\,M\,(C_6H_{12}O_6)$

a) m (C₆H₁₂O₆) – ?   б) m (C₆H₁₂O₆) – ?

Hence: $\Delta t_{freez.} = \dfrac{K(H_2O) \cdot m(C_6H_{12}O_6)}{m(H_2O) \cdot M(C_6H_{12}O_6)}$, then

$m(C_6H_{12}O_6) = \dfrac{\Delta t_{freez} \cdot m(H_2O) \cdot M(C_6H_{12}O_6)}{K(H_2O)} = \dfrac{1 \cdot 0,27 \cdot 180}{1,86} = 26,15$ g.

б) $\Delta t_{boiling.} = E\,(H_2O) \cdot C_m$, where: E (H₂O) — ebullioscopic constant of water, $\Delta t_{boiling.}$ — the rise in the boiling temperature of the solution compared to a pure solvent

Hence: $m(C_6H_{12}O_6) = \dfrac{\Delta t_{boil.}\, m(H_2O) \cdot M(C_6H_{12}O_6)}{E(H_2O)} = \dfrac{1 \cdot 0,27 \cdot 180}{0,52} = 93,54$ g.

Answer: 26,15 g; 93,54 g

Problem 3. A solution containing 1,2 g of aspirin $HOOCC_6H_4OCOCH_3$ in 20 g of dioxan freezes at 10,43 °C. Determine the cryoscopic constant of dioxan. The freezing temperature of dioxan is 12,0 °C.

We have:

m (aspirin) = 1,2 g
m(dioxan) = 20,0 g = 0,02 kg
t_{freeze} (solution) = 10,43 °C
t_{freeze} (dioxan) = 12,0 °C
M (aspirin) = 180 g/mol

K (dioxan) – ?

Solution

Dioxan is the solvent, aspirin is the solute.
1. $\Delta t_{freez} = t_{freez}$ (dioxan) $- t_{freez}$ (solution) =
= 12,00 – 10,43 = 1,57 град.
2. Δt_{freez} = K(dioxan.) · m(aspirin.)/ m(dioxan.) · M(aspirin.)
where K (dioxan) — a cryoscopic constant of dioxan (°C ·kg/mol).

Hence: K (dioxan) = Δt_{freez}· m(dioxan) · M(aspirin) / m(aspirin) = 1,57 × 0,02×180 / 1,2 = 4,7 °C kg/mol.

Problem 4. In 1 mL of the solution there are 10^{18} molecules of a dissolved non-electrolyte. Calculate the osmotic pressure of the solution at 298 K.

We have:	*Solution*
$N = 10^{18}$ molecules	The osmotic pressure of dilute non-electrolyte
$V(\text{solution}) = 1mL = 10^{-3}\,L$	solutions is calculated using the equation $P_{osm} =$
$T = 298\,K$	CRT. For this we should find the amount of
$P_{osm} - ?$	substance and its molar concentration first.

1. $n\,(\text{substance}) = \dfrac{N}{N_A} = \dfrac{10^{18}}{6 \cdot 10^{23}} = 1{,}66 \times 10^{-6}$ mole

2. $C_M = \dfrac{n(\text{substance})}{V(\text{solution})} = \dfrac{1{,}66 \cdot 10^{-6}}{10^{-3}} = 1{,}66 \times 10^{-3}$ mol/L

3. $P_{osm} = CRT = 1{,}66 \times 10^{-3} \times 8{,}314 \times 298 = 4{,}12$ kPa

Answer: 4,12 kPa

Problem 5. How many grams of glucose $C_6H_{12}O_6$ must be in 0,5 L of the glucose solution for its osmotic pressure (at the same temperature) to be equal to the osmotic pressure of glycerin solution, in 1 L of which there are 9,2 g of glycerin $C_3H_5(OH)_3$?

We have:	*Solution*
$m(\text{glycerin}) = 9{,}2$ g	When making the calculations use the equation
$V(\text{glycerin solution}) = 1$ L	$P_{osm.} = CRT$. If at the same temperature $P_{osm\,1} =$
$V(\text{glucose solution}) = 0{,}5$ L	$P_{osm\,2}$, then $C_1 = C_2$, where:
$M(\text{glycerin}) = 92$ g/mole	$P_{osm\,1}$ — osmotic pressure of glycerin solution
$T_1 = T_2$	$P_{osm\,2}$ — osmotic pressure of glucose solution
$P_{osm\,1} = P_{osm\,2}$	C_1 — molar concentration of glycerin
	C_2 — molar concentration of glucose

$m(\text{glucose}) - ?$

1. $C_1 = n(\text{glycerin})/V(\text{glycerin solution}) = m(\text{glycerin})/M(\text{glycerin}) \cdot V(\text{glycerin solution}) = 9{,}2/92 \cdot 1 = 0{,}1$ mol/L.

2. $C_2 = m(\text{glucose})/M(\text{glucose}) \cdot V(\text{volume of glucose solution}) = C_1 = 0{,}1$.

3. $m(\text{glucose}) = C_2 \cdot M(\text{glucose}) \cdot V(\text{volume of glucose solution}) = 0{,}1 \cdot 180 \cdot 0{,}5 = 9$ g.

Answer: 9 g

Problem 6. At 315K the pressure of saturated vapour above water is 8,2 kPa. How will the vapour pressure lower at the given temperature if we dissolve 36 g of glucose $C_6H_{12}O_6$ in 540 g of water?

We have:	*Solution*
$T = 315K$ $P = 8,2$ kPa $m(H_2O) = 540$ g $m(C_6H_{12}O_6) = 36$ g	The lowering of the pressure of saturated vapour of the solvent above the solution is calculated using the formula: $\Delta P = P_0 - P$, where: P_0 — the pressure of saturated vapour above the solvent; P — the pressure of saturated vapour above the solution

$\Delta P - ?$

1 variant of solution:

For the non-volatile non-electrolyte solutions the pressure of saturated vapour above the solution is equal to the pressure of saturated vapour above the solvent multiplied by the mole fraction of the solvent: $P = P_0 \cdot \chi_{solv} = \dfrac{P_0 \cdot n_{solv}}{(n_{sub} + n_{solv})}$.

$$n_{solv} = \frac{540}{18} = 30 \text{ mole}$$

$$n_{sub} = \frac{m(C_6H_{12}O_6)}{M(C_6H_{12}O_6)} = \frac{36}{180} = 0,2 \text{ mole}$$

$$\chi_{solv} = \frac{n_{solv}}{(n_{sub} + n_{solv})} = \frac{30}{(30 + 0,2)} = 0,9934$$

$P = P_0 \cdot \chi_{solv} = 8,2 \times 0,9934 = 8,146$ kPa

$\Delta P = P_0 - P = 8,2 - 8,146 = 0,054$ кPa

2 variant of solution:

The lowering of the pressure of saturated vapour of the solvent above the solution is equal to the pressure of saturated vapour above the solvent multiplied by the mole fraction of the solute: $\Delta P = P_0 \cdot \chi_{sub} = \dfrac{P_0 \cdot n_{sub}}{(n_{sub} + n_{solv})}$.

$$n_{solv} = \frac{m(H_2O)}{M(H_2O)} = \frac{540}{18} = 30 \text{ mole}$$

$$n_{sub} = \frac{m(C_6H_{12}O_6)}{M(C_6H_{12}O_6)} = \frac{36}{180} = 0,2 \text{ mole}$$

$$\chi_{sub} = \frac{n_{sub}}{(n_{sub} + n_{solv})} = \frac{0,2}{30,2} = 0,006623$$

$\Delta P = P_0 \cdot \chi_{sub} = 0,0066232 \times 8,2 = 0,054$ кPa

Answer: 0,054 kPa or54 kPa

V. ELECTROLYTE SOLUTIONS. ACIDITY
AND BASICITY OF AQUEOUS SOLUTIONS. pH

MAIN QUESTIONS ON THE TOPIC

1. The theory of weak electrolyte solutions. Main characteristics of a weak electrolyte: α, K_{ion}, pK_{ion}.
2. The theory of strong electrolyte solutions. Main characteristics of a strong electrolyte: a, f_a, I.
3. Protolytic (proton) theory of acids and bases.
4. The ion product of water. Hydrogen ion exponent pH.
5. Calculation of solution pH of weak and strong acids and bases.
6. Determination of hydrogen ion exponent.
7. Role of hydrogen ions in biological processes.

EXPERIMENTAL WORKS

Work 1. Determination of active acidity of biological fluids.
Aim of the work: to learn how to determine the active acidity of fluids by calorimetric and potentiometric methods.
Devices and reagents: the analyzed solutions № 1 and № 2; two glasses with the capacity of 50 mL; a glass stick; universal test-paper; a universal ion meter ЭВ-74 or laboratory ion meter И-176; distilled water; filter paper.
Order of work performance.
Task 1. Determination of pH of the solutions № 1 and № 2 with the help of a universal indicator.

A clean glass stick is immersed into the analyzed solution and then we touch a strip of test paper with it. We compare the colouring of the moist part of the test-paper to the calorimetric pH scale. Then we determine the pH of the analyzed solution and write down the results in the table. After the determination of pH of the solution № 1 the glass stick is washed and cleaned up with a piece of filter paper and we determine the pH of the solution № 2. We write down the obtained results in the table.

Task 2. Determination of pH of the solutions № 1 and № 2 with the help of an ionometer.

Before the beginning of the work it's necessary to read the application instructions. The analyzed solution is poured into a clean glass and we immerse the electrodes into the solution at 1,5 cm. The further order of work performance is described in «Directions for use of an ionometer». Before the determination of pH of the second solution the electrodes are carefully washed up with the distilled water and water drops are dried out with some filter paper.

The obtained results are written down in the table and then we calculate the ac-active acidity of these solutions using the formula: $[H^+] = 10^{-pH}$.

№ of solution	pH according to the universal test-paper	pH according to ionometer	$[H^+]$, моle/l
1			
2			

1) Make the conclusions about the character of the medium in the analyzed solutions.

Compare $[H^+]$ in both solutions.

2) Compare the precision of both methods.

TEST SELF-CHECK

1. How will the dissociation constant of acetic acid change at the dilution of the solution in 4 times?

a) will increase in 2 times;   b) will decrease in 2 times;

c) won't change;   d) will decrease in 4 times.

2. Using the values of pK of acids at 25 ºC determine in which of their 0,1 M solutions the concentration of H^+-ions is the lowest?

a) formic acid, pK = 3,75;   b) acetic acid, pK = 4,75;

c) oxalacetic acid, pK = 2,6;   d) lactic acid, pK = 3,9.

3. Choose the right statement:

Dissociation degree of a weak base in the solution;

a) depends on the nature of a weak base and a solvent;

b) will decrease with the increase of temperature;

c) will decrease with the increase of base concentration;

d) will increase with the addition of sodium hydroxide into the solution.

4. How will the dissociation degree of propionic acid change at the dilution of the solution in 4 times?

a) will increase in 2 times;

b) won't change;

c) will decrease in 2 times;

d) will increase in 4 times.

5. Which of the statements characterizing the ionic force of the solution are correct:

a) ionic force is the measure of ionic electrostatic interactions in the solutions of electrolytes;

b) with the increase of ionic force of the solution the value of ion activity coefficient in the solution will increase;

c) in 0,1 M of NaCl solution the ionic force is less than in 0,1 M of $MgSO_4$ solution;

d) ionic force of saline is 0,15 mole/kg.

6. Choose the right statements:
Ion activity coefficient in the solution
a) shows the deviation measure of properties of a real solution from the properties of an ideal solution;
b) depends on the ionic force of the solution;
c) is the lower, the higher is the ion charge;
d) is the greater, the greater is the electrolyte concentration in the solution.

7. The activity ion coefficient in the solution of HC1 will decrease at:
a) the addition of NaCl;
b) the dilution of the solution;
c) the lowering of temperature;
d) the rising of temperature.

8. From the point of view of protolytic theory of acids and bases determine in which of the reactions water plays the role of a base:

a) $NH_3 + HOH \rightleftarrows NH_4^+ + OH^-$;

b) $CH_3COOH + HOH \rightleftarrows CH_3COO^- + H_3O^+$;

c) $RNH_2 + HOH \rightleftarrows [RNH_3]^+ + OH^-$;

d) $PO_4^{3-} + HOH \rightleftarrows HPO_4^{2-} + OH^-$.

9. In 10 L of the solution there are 3,7 g of Ca(OH)₂. What is the pH of this solution (here and in the further calculations the activity ion coefficient is taken as 1 and the temperature is 298 K)?
a) 1;   b) 2;   c) 12;   d) 13.

10. 100 mL of 0,01 M NaOH solution are diluted with water till the volume of 10 L. What will be the pH of the obtained solution?
a) 10;   b) 13;   c) 1;   d) 4.

11. To titrate 5 mL of H₂SO₄ solution we've used up 4,10 mL of 0,1020 M NaOH solution. What will be the pH of the acid solution?
a) 1,38;   b) 2,0;   c) 2,08;   d) 1,08.

12. Active acidity of digestive juice is 0,04 мол/L. What is the pH of this liquid?
a) 1,4;   b) 1,8;   c) 2,6;   d) 4,0.

13. pOH of pancreatic juice is 5,4. What is the active acidity (mol/L) of this liquid?
a) $2,51 \cdot 10^{-9}$;   b) $10^{8,6}$;   c) $4,0 \cdot 10^{-6}$;   d) 5,4.

14. Within what limits does the pH of pancreatic juice change in the organism of a healthy person?

a) 5,0–8,0;   b) 0,9–2,0;   c) 8,6–9,0;   d) 7,36–7,44.

15. Using the pH value of a biological fluid we can determine:
a) active acidity;   b) potential acidity;
c) total acidity;   d) H^+-ion concentration.

PROBLEMS

1. Calculate the pH and pOH of sulphuric acid solution, if in 1 l of this solution there are 0,049 g of H_2SO_4.

Answer: pH = 3, pOH = 11

2. Calculate the pH of 0,001 M of acetic acid solution, if its dissociation degree is 0,0134.

Answer: pH = 4,89

3. How will the pH of the medium change at adding 30 mL of 0,2 M of sodium hydroxide solution to 300 mL of water?

Answer: will increase at 5,26 pH units

4. In how many times is the hydrogen atom concentration in blood greater compared to the cerebrospinal fluid? (pH (blood) = 7,36, pH (cerebrospinal fluid) = 7,53).

Answer: approximately in 1,5 times

* **Notice:** when solving the problem it's necessary to consider ion activity coefficients to be equal to 1 and the temperature — 298 K.

STANDARDS OF PROBLEM SOLUTIONS

Problem 1. Calculate $[H^+]$ and pH of 0,003 M of HCl solution at the temperature

We have:	*Solution*
C_M (HCl) = 0,003 mol/L	Hydrochloric acid is a strong electrolyte which is
pH – ? $[H^+]$ – ?	almost completely dissociated into ions in an aqueous solution.

As HCl concentration is low, the activity coefficient (f_a) is approximately equal to 1 and the activity (a) is equal to the concentration. Then, hydrogen ion activity ($a(H^+)$ or $[H^+]$) is equal to: $[H^+] = C_N$ (HCl).

1. Let's determine $[H^+]$ **:** $[H^+] = C_M(HCl) = 0,003$ mol/L
($C_M(HCl) = C_N$ (HCl))
2. Let's determine pH: pH = $-lg[H^+] = -lg0,003 = 2,52$.

Answer: $[H^+]$ = 0,003 mol/L; pH = 2,52

Problem 2. Calculate pH of 0,01 M of NH_4OH solution at 298 K, if the dissociation degree of ammonium hydroxide is 0,042.

We have:	*Solution*
C_M (NH_4OH) = 0,01 mol/L	

$\alpha = 0{,}042$

pH – ?

$NH_4OH \rightleftarrows NH_4^+ + OH^-$

1. In a dilute solution of a weak electrolyte the hydroxide-ion activity is equal to:

$[OH^-] = C_H \cdot \alpha = 0{,}01 \cdot 0{,}042 = 4{,}2 \cdot 10^{-4}$ mol/L

$C_N (NH_4OH) = C_M (NH_4OH)$

2. $pOH = -lg\,[OH^-] = -lg\,4{,}2 \cdot 10^{-4} = 3{,}38$

3. $pH = 14 - pOH = 14 - 3{,}38 = 10{,}62$

Answer: pH = 10,62

Problem 3. Calculate the dissociation degree of lactic acid $[H^+]$ and pH of 0,1 M of lactic acid solution at 298K if the dissociation constant of lactic acid (K_a) is $1{,}38 \cdot 10^{-4}$.

We have:

$C_M (acid) = 0{,}1$ mol/L

$K_a (acid) = 1{,}38 \cdot 10^{-4}$.

α – ? $[H^+]$ – ? pH – ?

Solution

Lactic acid is a weak monobasic acid and dissociates on the following scheme:

$CH_3CH(OH)COOH \rightleftarrows CH_3CH(OH)COO^- + H^+$

1. We determine the dissociation degree:

For dilute solutions of weak binary electrolytes we use the formula:

$\alpha = \sqrt{\dfrac{K_a}{C}}$ (a simplified expression of Ostwald's law of dilution)

Hence, $\alpha = \sqrt{\dfrac{1{,}38 \cdot 10^{-4}}{0{,}1}} = \sqrt{13{,}8 \cdot 10^{-4}} = 3{,}7 \cdot 10^{-2} = 0{,}037$

2. We determine $[H^+]$: $[H^+] = C_N \cdot \alpha = 0{,}1 \cdot 0{,}031 = 0{,}0037$ mol/L

$C_M (CH_3CH(OH)COOH) = C_N (CH_3CH(OH)COOH)$

3. We determine pH**:** $pH = -lg\,[H^+] = -lg\,0{,}0037 = 2{,}43$

Answer: a = 0,037, [H⁺] = 0,0037 mol/L, pH = 2,43

Problem 4. Calculate the dissociation degree, the concentration of acetic acid and the hydrogen ion concentration in the solution of acetic acid, pH of which is 2,87. Dissociation constant of acetic acid at 298 K is equal to $1{,}75 \times 10^{-5}$.

We have:

pH = 2,87

$K_a = 1{,}75 \cdot 10^{-5}$

$[H^+]$ – ? C_M – ? α – ?

Solution

1. Let's determine $[H^+]$: $[H^+] = 10^{-pH} = 10^{-2{,}87} = 1{,}318 \cdot 10^{-3}$

2. We determine C_M: Acetic acid dissociates on the scheme: $CH_3COOH \rightleftarrows CH_3COO^- + H^+$.

The dissociation constant is expressed by the ratio: $K_a = \dfrac{[H^+] \cdot [CH_3COO^-]}{[CH_3COOH]}$

$[H^+] = [CH_3COO^-]$ and $[CH_3COOH]$ in a dilute solution of a weak binary electrolyte can be taken as equal to C_M. Then: $K_a = \dfrac{[H^+]}{C_M}$

Hence: $C_M = \dfrac{[H^+]^2}{K_a} = \dfrac{(1{,}318 \cdot 10^{-3})^2}{1{,}75 \cdot 10^{-5}} = 0{,}09926.$

3. Let's determine α: for dilute solutions of weak binary electrolytes we can use the formula: $\alpha = \sqrt{\dfrac{K_a}{C}} = \sqrt{\dfrac{1{,}75 \cdot 10^{-5}}{0{,}09926}} = 0{,}013.$

Answer: $[H^+] = 1{,}318 \cdot 10^{-3}$ mol/L; $C_M = 0{,}09926$ mol/L; $a = 0{,}013$

VI. BUFFER SYSTEMS

MAIN QUESTIONS ON THE TOPIC

1. Buffer systems, their classifications.
2. Calculation of pH of acid and basic buffer solutions.
3. Mechanism of action of buffer systems.
4. Buffer capacity.
5. Basic buffer systems of the organism. Acidosis. Alkalosis.
6. Hydrocarbonate buffer system, mechanism of action.
7. Hemoglobin buffer system, mechanism of action.
8. Phosphate buffer system, mechanism of action.
9. Protein buffer system, mechanism of action.

EXPERIMENTAL WORKS

Work 1. Preparation of buffer solutions and investigation of mechanism of buffering.

Aim of the work: to learn to prepare buffer solutions; to calculate pH; to study the mechanism of buffering at adding water or a small amount of an acid.

Devices and reagents:

– Test-tubes, beaker flasks with the volume of 100 mL, graduated pipets of 10 and 2 mL.

– Solutions of acetic acid ($C_M = 0{,}1$ mol/L), sodium acetate ($C_M = 0{,}1$ mol/L), hydrochloric acid ($C_M = 0{,}1$ mol/L).

– indicators: a universal indicator, phenolphthalein, methyl orange.

Order of work performance

Task 1. We prepare the solutions according to the attached scheme, then we calculate the pH using the equation: $pH = pK_a(acid) + lg\dfrac{[salt]}{[acid]}$ and determine it experimentally. The obtained results are written down in the table.

№ of solution	1	2	3
Number mL 0,1 M of CH_3COOH solution	18	10	2
Number mL 0,1 M of CH_3COONa solution	2	10	18
pH calculated			
pH experimental			

Experimental determination of the pH of the solution

A strip of a universal test-paper is placed on the piece of filter paper. The solution prepared in the test-tube is carefully mixed and is applied on the strip of the universal test-paper with a clean glass stick then we compare the colouring with the pH scale. The value of pH should be written down in the table.

Task 2. To check the buffering of solutions.

a) Influence of dilution. In two test-tubes we pour 2 mL of buffer solution № 2, then in the first one we add 2 mL of water and in the second one — 4 mL of water. Solutions are mixed and we determine the pH with the help of a universal indicator. The results are written down in the table.

	Initial solution № 2	4 mL of solution № 2+4 mL of water	4 ml of solution № 2+8 mL of water
pH			

б) Influence of acid addition. We pour 2 mL of the buffer solution № 3 in one test-tube and 2 mL of water into the other one then determine the pH with the help of universal test-paper. Then we add 2 drops 0,1 M of HCl solution into both test-tubes, mix carefully and determine the pH once again. The results are written down in the table.

Systems	Initial value of pH	pH after the addition of 2 drops 0,1 M of HCl
Buffer solution № 3		
H_2O		

In the conclusions explain the reasons of the observed changes or their absence in the experiments a) and b).

Work 2. Determination of buffer capacity.

Aim of the work: to determine the buffer capacity of two acetate buffer solutions in relation to alkali.

Devices and reagents:

– A universal ionometer ЭВ-74 or a laboratory ionometer И-176.

– Glasses with the volume of 50 mL, graduated pipets, burets, filter paper, glass sticks.

– Solutions: acetic acid (C_M = 0,1 mol/L), sodium acetate (C_M = 0,1 mol/L), sodium hydroxide (C_M = 0,1 mol/L).

Order of work performance. In one of the glasses we pour 6 mL of CH_3COOH solution and 14 mL of CH_3COONa solution and mix the obtained solution with a glass stick. Then we measure the initial pH with the help of ionometer. The order of work performance is described in «Directions for use of an ionometer» (you should carefully wash the electrodes by distilled water and water drops are dried out with some filter paper before each determination of pH). Then we add 2 mL 0,1 M of NaOH solution from the burette into the glass, mix it and measure the pH.

Into the second glass we pour 14 mL of CH_3COOH solution and 6 mL of CH_3COONa solution, mix it and measure the pH. Then we add 2 mL 0,1 M of NaOH solution from the burette, mix and measure the pH. The results of all the measurements are written down in the table.

Buffer capacity is calculated by the formula.

$$B_{alk.} = \frac{C_N(NaOH)\, V(NaOH)}{(pH - pH_0)\, V(buffer\ solution)}$$

Ratio salt/acid	Initial value of pH_0	Value of pH after the addition of NaOH	DpH	V(mL) Volume of the added alkali	B (mol/L×units of pH)
14/6				2	
6/14				2	

Using the results of the work make the conclusions about the factors that can influence the pH of the buffer solution and the buffer capacity.

TEST SELF-CHECK

Choose the pairs of aqueous solutions of substances, at pouring out of which buffer systems will be formed (pay attention to the reaction products):

1. 200 mL 0,2M of NH_4OH solution. a) 200 mL 0,3M of NH_4Cl solution;

2. 100 mL 0,3M of NaH_2PO_4 solution. b) 100 mL 0,3M of HCl solution;

c) 100 mL 0,3M of NaOH solution;

d) 200 mL 0,2M of K_2HPO_4 solution;

e) 200 mL 0,1M of NaOH solution.

3. What factors influence the pH value of a buffer mixture?
a) addition of $C_6H_{12}O_6$;
b) dissociation constant of an acid (a base);

c) temperature;

d) ratio of component concentrations.

4. What factors influence the value of buffer capacity:

a) ratio of component concentrations;

b) addition of $C_6H_{12}O_6$;

c) component concentration;

d) dilution?

5. Ratio of component concentrations $[Na_2HPO_4]/[NaH_2PO_4]$ in a phosphate buffer solution is 2:1. Choose the right statement for the given solution:

a) at adding of a small amount of NaOH in the buffer solution the pH of the solution will slightly increase;

b) at diluting the solution in 100 times its pH will increase by 2 pH units;

c) buffer solution has the maximum buffer capacity;

d) at diluting the buffer capacity of the solution will decrease.

6. We have two ammonia buffer solutions: in the first one the concentrations of both components are equal to 1 mol/L; in the second one the concentrations of both components are equal to 0,1 mol/L. Choose the right statements for these solutions:

a) the pH of the first solution is greater than the pH of the second solution at 1 unit;

b) the first solution maintains the constant pH of the medium more effectively than the second one;

c) the buffer capacity of the first solution is greater than that of the second solution;

d) hydrogen ion concentration in the first solution is approximately equal to hydrogen ion concentration in the second solution.

7. What is the pH of a buffer solution, in 10 L of which there are 0,1 mole of CH_3COOH and 0,5 mole of CH_3COOK, if pK of (CH_3COOH) = 4,75 (here and in the further calculations it's necessary to consider ion activity coefficients to be equal to 1 and the temperatute –298 К)?

a) 5,45;   b) 4,75;   c) 3,75;   d) 4,05.

8. In 1 L of a buffer solution containing 0,1 mole of $NH_3 \cdot H_2O$ and 0,1 mole of NH_4Cl we add 0,01 mole of NaOH. What is the pH of the solution after the addition of the alkali (pK ($NH_3 \cdot H_2O$) = 4,75)?

a) 9,56;   b) 4,66;   c) 9,34;   d) 4,84.

9. Ammonia buffer solution with the concentration of each component equal to 0,1 mol/L has the pH equal to 9,25. What is the buffer capacity (mol/L×units of pH) for this given solution, if at adding 10 mL 1 M of NaOH solution the pH of the buffer will be 9,33?

a) 0,125;   b) 1,25;   c) 1250;   d) 0,0107.

10. Which buffer solutions can effectively maintain the constant pH of the medium for the solution, pH of which is 4:
   a) acetate buffer, pK(CH_3COOH) = 4,75;
   b) ammonia buffer, pK(NH_4OH) = 4,75;
   c) phosphate buffer, pK($H_2PO_4^-$) = 6,8;
   d) formate buffer, pK(HCOOH) = 3,75.

11. Which buffer systems maintain the constant pH of human blood?

12. Which of the buffer systems makes the main impact into the amount of buffer capacity of erythrocytes?

a) phosphate;
b) hydrocarbonate;
c) acetate;
d) protein;
e) hemoglobin and oxyhemoglobin.

Which blood plasma characteristic can be determined by the concentration of:

a) ion force;
b) general acidity;

13. Electrolytes and non-electrolytes (sum amount of dissolved particles)

c) osmotic pressure;
d) reserve alkalinity;
e) oncotic pressure.

14. Electrolytes

15. HCO_3^-–ions

PROBLEMS

1. Calculate the pH of a buffer solution, 1 L of which contains 18,4 g of formic acid and 68 g of sodium formate if pK_a(HCOOH) = 3,75. How will the pH change at diluting the solution in 50 times?[*]

Answer: pH = 4,15. Practically doesn't change

2. Calculate the pH of the acetate buffer mixture which is made up of 100 mL 0,1 M of CH_3COOH solution and 200 mL 0,2 M of CH_3COONa solution if K_a(CH_3COOH) = 1,75×10^{-5}. How will the pH of this buffer solution change at adding of 30 mL 0,2 M of NaOH solution?

Answer: pH = 5,36; pH will increase in 0,46 units

3. Calculate the pH of the solution of formic acid, half neutralized by the alkali (pK(HCOOH) = 3,75).

Answer: pH = 3,75

4. To change the pH of 100 ml of blood from 7,36 till 7,00 we have to add 36 mL 0,05 M of HCl solution. Calculate the buffer capacity of blood on acid (mol/L·units of pH).

Answer: 0,05 mol/L·un. pH

[*] **Notice:** when solving the problem it's necessary to consider ion activity coefficients to be equal to 1 and the temperature — 298 K.

STANDARDS OF PROBLEM SOLUTIONS

Problem 1. We added 49,2 g of CH_3COONa to 2 L 0,1 M of CH_3COOH solution. Calculate the pH of the obtained buffer solution ($K_a(CH_3COOH) = 1,75 \times 10^{-5}$).

We have:

$V(\text{solution}) = 2$ L
$C_M(CH_3COOH) = 0,1$ mol/L
$m(CH_3COONa) = 49,2$ g
$K_a (CH_3COOH) = 1,75 \cdot 10^{-5}$

pH – ?

Solution

$CH_3COOH \rightleftarrows CH_3COO^- + H^+$
$CH_3COONa \rightarrow CH_3COO^- + Na^+$
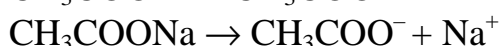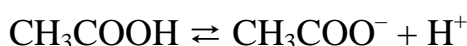
1. Let's calculate the concentration of sodium acetate in the solution:

$$C_M(CH_3COONa) = m(CH_3COONa)/M(CH_3COONa) \times V = 49,2 / 82 \times 2 = 0,3 \text{ mol/L}$$

2. Let's calculate the pH of acetate buffer solution:

$$pH = -\lg K_a + \lg \frac{[CH_3COONa]}{[CH_3COOH]} = -\lg 1,75 \cdot 10^{-5} + \lg \frac{0,3}{0,1} = 4,75 + 0,48 = 5,23.$$

Answer: pH = 5,23

Problem 2. What is the pH of the buffer solution, in 1 L of which there are 0,1 mole of NH_4OH and 0,1 mol of NH_4Cl ($pK_b (NH_4OH) = 4,75$)? How will the pH change at diluting of the solution with water in 10 times?

We have:

$C_M(NH_4OH) = 0,1$ mol/L
$C_M(NH_4Cl) = 0,1$ mol/L
$V(\text{solution}) = 1$ L
$pK_b (NH_4OH) = 4,75$

pH_1 – ? pH_2 – ?

Solution

1. Let's calculate pH_1 of the initial solution:

$pH_1 = 14 - pK(NH_4OH) - \lg\frac{[NH_4Cl]}{[NH_4OH]} = 14 - 4,75 - \lg\frac{0,1}{0,1} = 9,25$

2. Let's calculate the pH_2 of the solution after the dilution. At dilution of the solution in 10 times the concentrations of the salt and the base also decrease in 10 times: $pH_2 = 14 - 4,75 - \lg\frac{0,01}{0,01} = 9,25*$

Answer: $pH_1 = 9,25$; $pH_2 \approx 9,25$

* Notice: in reality, the value of pH at dilution slightly changes (in our case it increases in approximately 0,07 units, which depends on the change in the ion activity coefficient because of the decrease of ion force of the solution at dilution).

Problem 3. In order to change the pH to 1 we had to add 0,52 mL 1 M of NaOH solution into 10 ml of acetate buffer solution. Find the buffer capacity of the given solution on the alkali (mol/L·units pH).

We have:

Solution

$\Delta pH = 1$
$V(b.s.) = 10$ mL $= 0,01$ L
$C_M(NaOH) = 1$ mol/L
$V(alkali) = 0,52$ mL $=$
$0,52 \cdot 10^{-3}$ L

The buffer capacity on the alkali can be determined using the formula:

$$B_{base.} = C_N \frac{C_N(NaOH) \cdot V(NaOH)}{\Delta pH \cdot V(b.s.)} = \frac{1 \cdot 0,52 \cdot 10^{-3}}{1 \cdot 0,01} =$$

0,052 mol/L·units of pH;
$(C_N(NaOH) = C_M(NaOH))$

$B_{base.} - ?$

Answer: 0,052 mol/L·units of pH

Problem 4. We've added 40 mL 0,04 M of NaH_2PO_4 solution into 16 mL 0,1 M of Na_2HPO_4 solution. Determine:

a) pH of the obtained buffer solution $(K_a(H_2PO_4^-) = 6,2 \cdot 10^{-8}$;

b) how will pH of this solution change when adding of 6 mL 0,1 M of HCl solution;

c) if it's possible to prepare phosphate buffer solution with the pH = 8,5.

We have:
$C_M (Na_2HPO_4) = 0,1$ mol/L
$V(\text{of } Na_2HPO_4 \text{ solution}) = 16$ mL
$C_M (NaH_2PO_4) = 0,04$ mol/L
$V(\text{of } NaH_2PO_4 \text{ solution}) = 40$ mL
$C_M (HCl) = 0,1$ mol/L
$V (\text{of HCl solution}) = 6$ mL
$K_d (H_2PO_4^-) = 6,2 \cdot 10^{-8}$

a) pH – ? b) ΔpH – ?

Solution

a) Let's calculate the pH of the phosphate buffer solution.

In the phosphate buffer solution the role of an acid is performed by $H_2PO_4^-$ ion dissociating on the following scheme:
$H_2PO_4^- \rightleftarrows H^+ + HPO_4^{2-}$.
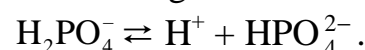
As the dissociation constant of this process is small, we can consider the concentration of $H_2PO_4^-$ to be equal to NaH_2PO_4 concentration and HPO_4^{2-} concentration to be equal to Na_2HPO_4 concentration.

Then: $pH = -\lg K_a(H_2PO_4^-) + \lg \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$.

It is necessary to take into account that at mixing of two solutions the initial concentrations of components change. New concentrations can be calculated by the formula:

$$C_{init.} \cdot V_{init.} = C_{final.} \cdot V_{final.}$$

Then the new concentration of NaH_2PO_4 will be:

$$[NaH_2PO_4] = \frac{C_M(NaH_2PO_4)_{init} \cdot V(\text{solution } NaH_2PO_4)}{V(\text{buffer solution})}$$

Final concentration of Na_2HPO_4 will be:

$$[Na_2HPO_4] = \frac{C_M(Na_2HPO_4)_{init} \cdot V(\text{solution } Na_2HPO_4)}{V(\text{buffer solution})}$$

$C_M (NaH_2PO_4)_{init.} \cdot V(\text{of } NaH_2PO_4 \text{ solution}) = n(NaH_2PO_4) = 0,040 \cdot 0,04 = 0,0016$ mol

$$C_M \text{ (Na}_2\text{HPO}_4)_{init.} \cdot V(\text{of Na}_2\text{HPO}_4 \text{ solution}) = n \text{ (Na}_2\text{HPO}_4) = 0{,}016 \cdot 0{,}1 = 0{,}0016 \text{ mol}$$

Then, $\dfrac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = \dfrac{n(\text{Na}_2\text{HPO}_4) \cdot V(\text{buffer sol.})}{n(\text{NaH}_2\text{PO}_4) \cdot V(\text{buffer sol.})} = \dfrac{n(\text{Na}_2\text{HPO}_4)}{n(\text{NaH}_2\text{PO}_4)}$

Hence: $\text{pH} = -\lg 6{,}2 \cdot 10^{-8} + \lg \dfrac{n(\text{Na}_2\text{HPO}_4)}{n(\text{NaH}_2\text{PO}_4)} = 7{,}21 + \lg \dfrac{0{,}0016}{0{,}0016} = $

$7{,}21 + \lg 1 = 7{,}21$.

b) Let's calculate the pH change at adding HCl solution to the buffer solution. At adding 6 mL 0,1 M of HCl solution (which is 0,0006 mole), the added acid will react with 0,0006 mole of Na_2HPO_4 with the formation of 0,0006 mole of NaH_2PO_4:

$$\text{Na}_2\text{HPO}_4 + \text{HCl} = \text{NaH}_2\text{PO}_4 + \text{NaCl}.$$
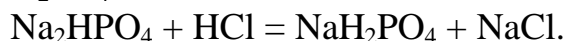
Then the amount of Na_2HPO_4 will decrease in 0,0006 mole:

$$n \text{ (Na}_2\text{HPO}_4) = 0{,}0016 - 0{,}0006 = 0{,}0010 \text{ mol}.$$

And the amount of NaH_2PO_4 will increase in 0,0006 mole:

$$n \text{ (NaH}_2\text{PO}_4) = 0{,}0016 + 0{,}0006 = 0{,}0022 \text{ mol}.$$

Hence: $\text{pH} = -\lg 6{,}2 \cdot 10^{-8} + \lg \dfrac{n(\text{Na}_2\text{HPO}_4)}{n(\text{NaH}_2\text{PO}_4)} = 7{,}21 + \lg \dfrac{0{,}0010}{0{.}0022} = 6{,}86$

$$\Delta \text{pH} = 7{,}21 - 6{,}86 = 0{,}35$$

c) To prepare the phosphate buffer solution with the pH = 8,5 is impossible because the zone of effective action of a buffer system is determined   by the ratio $\Delta \text{pH} = \text{pK} \pm 1$. For the phosphate buffer solution pK = 7,21 and the zone of effective buffer action lies in the interval of the pH $6{,}21 \div 8{,}21$.

Answer : a) pH = 7,21; b) will decrease in 0,35 un. pH; c) impossible

VII. HETEROGENEOUS EQUILIBRIA

MAIN QUESTIONS ON THE TOPIC

1. Thermodynamic (K_s^0) and concentration (K_s) solubitity constants of a heterogeneous process equilibrium.

2. Interconnection between the solubility S of a sparingly soluble strong electrolyte and its $K_s^0 \approx K_s$.

3. Conditions of formation and dissolution of precipitates in heterogeneous systems.

4. Competitive heterogeneous equilibria of the same type.

5. Competitive heterogeneous equilibria of different types (the formation of complex compounds, a slightly dissociated acid, oxidation or reduction of one of the ions of a slightly soluble compound).

6. Heterogeneous equilibria in the vital activity of the organism. Conditions of calcium phosphate formation in slightly alkaline solutions.

7. Pathology of bone tissue (influence of Be^{2+}, Sr^{2+}, Sr^{90}) and physico-chemistry of a pathological formation of calculus in the organism.

EXPERIMENTAL WORKS

Work 1. Obtaining of heterogeneous systems «precipitate-solution» and the shift of equilibrium in heterogeneous systems «precipitate-solution».

Aim of the work: to gain the skills of obtaining heterogeneous systems «precipitate-solution» and to conduct the experimental investigations of equilibrium shift in heterogeneous systems «precipitate-solution».

Task 1. To study the condition of precipitate formation of a sparingly soluble strong electrolyte.

In 2 test-tubes we pour 2 mL of salt solution Ca^{2+} with the concentration of 0,01 mol/L. In one of the test-tubes we add 2 mL of $Na_2C_2O_4$ solution, into the other one —— 2 mL of Na_2SO_4 solution (the concentration of each of the solutions is 0,01 mol/L). Then we mark the changes occurring in the test-tubes.

Ion concentr. (mol/L)	Ion concentr. (mol/L)	Ion concentration after mixing	Product of ion concentrations after mixing	K_s^0	Observations
Ca^{2+} 0,01	$C_2O_4^{2-}$ 0,01			$2,3 \cdot 10^{-9}$	
Ca^{2+} 0,01	SO_4^{2-} 0,01			$2,35 \cdot 10^{-5}$	

Write the equations of the corresponding reactions. Make up the conclusions about the conditions of precipitate formation of sparingly soluble strong electrolytes.

Task 2. To study the influence of competitive equilibria on the heterogeneous equilibrium «precipitate-solution».

Experiment 1. Shift of heterogeneous equilibrium in the direction of the formation of a less soluble compound.

In one of the two test-tubes we pour 2 mL of $BaCl_2$ solution with the concentration of 0,5 mol/L and 2 mL of the saturated solution of $CaSO_4$. Into the other one we pour 4 mL of the saturated solution of $CaSO_4$. Both test-tubes are heated almost till the temperature of heating. Fill in the table.

Electrolyte	K_s^0	After mixing	Product of ion	Observati

		$C(SO_4^{2-})$	$C(Ba^{2+})$	concentrations after mixing	ons
$CaSO_4$	$2,3 \cdot 10^{-5}$				
$BaSO_4$	$1,1 \cdot 10^{-10}$				

Write the corresponding reactions and make the necessary conclusions about the direction of heterogeneous equilibrium shift.

Experiment 2. The shift of heterogeneous equilibrium at the expense of the formation of complex compounds.

We pour in 2 test-tubes 10 drops of $CuCl_2$ and $CrCl_3$ with the concentration of 0,5 mol/L. In each test-tube we add several drops of a dilute solution
of КOH till the precipitate is formed trying to avoid the excess of alkali. Then to the obtained precipitate we add drop by drop the concentrated solution of КOH. We should notice how many drops we used in each case to dissolve the precipitate.

Write the equations of the corresponding reactions. Make the conclusions about the direction and the degree of heterogeneous equilibrium shift.

Experiment 3. The shift of heterogeneous equilibrium to the direction of the formation of a slightly dissociated acid.

We should determine the ratio of $BaSO_4$ and $BaCO_3$ to the acetic acid.

In two test-tubes we pour 5–6 drops of $BaCl_2$ solution and then we add in one test-tube 5–6 drops of Na_2SO_4 and into the other one — the same amount of Na_2CO_3. Then we pour in 10–12 drops of CH_3COOH solution to the contents of both test-tubes. We notice the difference in the behavior of the formed sparingly soluble barium salts in relation to the acetic acid.

Write the equations of the corresponding reactions. Make the necessary conclusions about the direction and the conditions of the heterogeneous equilibrium shift.

$K_{d.I} H_2CO_3 = 4,5 \cdot 10^{-7} \; K_d H_2SO_4 = 1,15 \cdot 10^{-2}$
$K_{d.II} H_2CO_3 = 4,7 \cdot 10^{-11} \; K_d CH_3COOH = 1,85 \cdot 10^{-5}$

TEST SELF-CHECK

1. What units should we use to express the solubility of a sparingly soluble strong electrolyte:
a) mol/dm^3;   b) mol/L;   c) dm^3/L;   d) g/L?

2. For the saturated aqueous solutions of which salts can we use K_s^0:
a) silver chloride;   b) silver nitrate;
c) silver sulphate;   d) sodium bromide?

3. We have the equation: $K_{ch.e.} = \dfrac{a(Ag^+) \cdot a(I^-)}{a(AgI)_S}$. What expressions are correct when calculating K_s^0 using this equation:

a) $a(AgI)_s = 1$;   b) $K_s^0 = K_{ch.e.} \cdot a(AgI)_s$;

c) $a(AgI)_s = K$;   d) $K_s^0 = a(Ag^+) \cdot a(I^-)$?

4. For a sparingly soluble strong electrolyte Ag_2CrO_4 the value of the thermodynamic solubitity constant is expressed:

a) $K_s^0 = C(Ag^+) \cdot C(CrO_4^{2-})$;   b) $K_s^0 = 2a(Ag^+) \cdot a(CrO_4^{2-})$;

c) $K_s^0 = a^2(Ag^+) + a(CrO_4^{2-})$;   d) $K_s^0 = a^2(Ag^+) \cdot a(CrO_4^{2-})$?

5. The ratio of K_s^0 and the product of ion activities in an unsaturated solution of a sparingly soluble electrolyte $Ca_3(PO_4)_2$ can be determined:

a) $a^3(Ca^{2+}) \cdot a^2(PO_4^{3-}) = K_s^0$;   b) $3a(Ca^{2+}) \cdot 2a(PO_4^{3-}) < K_s^0$;

c) $a^3(Ca^{2+}) \cdot a^2(PO_4^{3-}) > K_s^0$;   d) $a^3(Ca^{2+}) \cdot a^2(PO_4^{3-}) < K_s^0$?

6. In a heterogeneous system $AgCl(s) \rightleftarrows Ag^+(aq) + Cl^-(aq)$, K_s^0 (AgCl) $= 1,8 \times 10^{-10}$. The precipitate is formed under the following ion concentrations (mol/L):

a) $C(Ag^+) = 1 \cdot 10^{-7}$ and $C(Cl^-) = 1 \cdot 10^{-5}$;

b) $C(Ag^+) = 5 \cdot 10^{-7}$ and $C(Cl^-) = 5 \cdot 10^{-7}$;

c) $C(Ag^+) = 5 \cdot 10^{-7}$ and $C(Cl^-) = 5 \cdot 10^{-3}$;

d) $C(Ag^+) = 3 \cdot 10^{-5}$ and $C(Cl^-) = 3 \cdot 10^{-5}$?

7. For which row of salts (without any additional calculations) can we determine the sequence of precipitation from their saturated aqueous solutions using the value of K_s^0:

a) $BaSO_4$, $Ba_3(PO_4)_2$, Ag_2CO_3;

b) $AgCl$, $CaCO_3$, $SrSO_4$;

c) $MgCl_2$, Na_2SO_4, $FeCl_2$;

d) PbS, $PbSO_3$, $PbSO_4$?

8. To the solution containing 0,01 mole of Na_2SO_4, Na_2CO_3 and $Na_2C_2O_4$ each, we gradually added $CaCl_2$ solution. Indicate the sequence of anion precipitation from the solution if K_s^0 ($CaSO_4$) $= 6,1 \times 10^{-5}$, K_s^0 ($CaCO_3$) $= 4,8 \times 10^{-9}$, K_s^0 (CaC_2O_4) $= 2,6 \times 10^{-9}$:

a) $CaCO_3$, CaC_2O_4, $CaSO_4$;

b) CaC_2O_4, $CaCO_3$, $CaSO_4$;

c) CaC_2O_4, $CaSO_4$, $CaCO_3$;

d) $CaSO_4$, CaC_2O_4, $CaCO_3$.

9. The general view of the dependence between S and K_s of a sparingly soluble strong electrolyte of A_mB_n type is expressed by the equation:

a) $S = \sqrt[m \cdot n]{\dfrac{K_S}{m^m + n^n}}$;

b) $S = \sqrt[m+n]{\dfrac{K_S}{m^m \cdot n^n}}$;

c) $S = \sqrt[m+n]{\dfrac{K_S}{m^m + n^n}}$;

d) $S = \sqrt[m \cdot n]{\dfrac{K_S}{m^m \cdot n^n}}$.

10. Indicate the formula of the salt with the lowest solubility in water at 25 °C:

a) Ag_2SO_4 ($K_s^0 = 7{,}7 \cdot 10^{-5}$);

b) $PbCl_2$ ($K_s^0 = 1{,}7 \cdot 10^{-5}$);

c) PbI_2 ($K_s^0 = 8{,}7 \cdot 10^{-9}$);

d) PbF_2 ($K_s^0 = 3{,}7 \cdot 10^{-8}$).

11. In order to dissolve the precipitate $Mg(OH)_2$, it's necessary:
a) to increase the concentration of Mg^{2+} ions or OH^- ions;
b) to decrease the concentration of Mg^{2+} ions or OH^- ions;
c) to add HCl;
d) to add NaOH.

12. In the processes of competing equilibria together with heterogeneous equilibria we can observe the following kinds of the equilibria:
a) acid-base;
b) oxidation-reduction;
c) with the formation of complex compounds;
d) there is no correct answer.

13. The solubility of AgI in 1 L of water at 25 °C is $2{,}35 \times 10^{-6}$ gram. What is the concentration solubility constant of AgI:
a) $1 \cdot 10^{-8}$;   b) $1 \cdot 10^{-16}$;   c) $1 \cdot 10^{-4}$;   d) $1 \cdot 10^{-12}$?

14. K_s^0 (CaC_2O_4) = $2{,}6 \times 10^{-9}$. What is the molar concentration of $C_2O_4^{2-}$ ions in a saturated aqueous solution of this salt:
a) $5{,}1 \cdot 10^{-4}$;   b) $1{,}6 \cdot 10^{-4}$;   c) $5{,}1 \cdot 10^{-5}$;   d) $1{,}6 \cdot 10^{-5}$?

15. The main mineral component of bone tissue:
a) $Ca_3(PO_4)_2$;   b) $Ca(H_2PO_4)_2$;
c) $Ca_5(PO_4)_3OH$;   d) $CaHPO_4$.

PROBLEMS

1. Will AgCl precipitate at pouring together of equal volumes of 0,001 M of $AgNO_3$ solution and 0,002 M of NaCl solution? $K_s(AgCl) = 1{,}8 \cdot 10^{-10}$.

Answer: will precipitate; $C(Ag^+) \times C(Cl^-) = 5 \times 10^{-7} > 1{,}8 \times 10^{-10}$

2. Will AgI precipitate at pouring together of equal volumes of a saturated solution of AgCl and 0,002 M of KI solution? $K_s(AgCl) = 1,8 \cdot 10^{-10}$; $K_s^0(AgI) = 8,3 \cdot 10^{-17}$.

Answer: will precipitate; $6,7 \times 10^{-9} > 8,3 \times 10^{-17}$

3. In 2,5 L of a saturated solution of Ag_2CrO_4 there are 0,0625 g of salt at some temperature. Calculate the concentration solubility constant of Ag_2CrO_4. $M(Ag_2CrO_4) = 332$ g/mol.

Answer: $1,7 \times 10^{-17}$

4. The concentration solubility constant of $PbSO_4$ salt at 25 °C is equal to $1,6 \cdot 10^{-8}$. Calculate the solubility (S) of $PbSO_4$ in mol/L and g/L. $M(PbSO_4) = 303$ g/mol. *Answer: $1,26 \times 10^{-4}$ mol/L; $3,8 \times 10^{-2}$ g/L*

5. Calculate the mass of $SrSO_4$ in 2 L of a saturated solution of this salt at 25 °C. $K_s(SrSO_4) = 3,2 \cdot 10^{-5}$, $M(SrSO_4) = 184$ g/mol.

Answer: 2 g

STANDARDS OF PROBLEM SOLUTIONS

Problem 1. After the precipitation of $BaSO_4$ which was used at radioscopy we have 1,5 L of a saturated solution at 25 °C. Calculate the mass of $BaSO_4$ in this solution.

Solution. In a saturated solution there is an equilibrium:

$$BaSO_4 \rightleftarrows Ba^{2+} + SO_4^{2-}$$

Let's mark **x** as the ion Ba^{2+} concentration:

$$C(Ba^{2+}) = C(SO_4^{2-}) = x \text{ mol/L}.$$

As the salt is sparingly soluble, the ion concentration is small and, $f_a \approx 1$, $K_s^0 \approx K_s$

$$K_s = C(Ba^{2+}) \cdot C(SO_4^{2-}) = \mathbf{x^2} \quad C(Ba^{2+}) = C(SO_4^{2-}) = \sqrt{K_s(BaSO_4)}$$

As we can find in the reference book $K_s(BaSO_4) = 1,1 \cdot 10^{-10}$.

The amount of substance $BaSO_4$

$$n(BaSO_4) = C(Ba^{2+}) \cdot V\text{solution},$$

and mass m = nM,

$$m(BaSO_4) = C(Ba^{2+}) \cdot V \text{ solution} \cdot M(BaSO_4).$$

Let's substitute the values and get: m = $\sqrt{1,1 \cdot 10^{-10}} \cdot 1,5 \cdot 233 = 3,7 \cdot 10^{-3}$(g)

Answer: $m(BaSO_4) = 3,7 \times 10^{-3}$ g

Problem 2. We precipitate $Ca_3(PO_4)_2$ from 0,001 M of the salt Ca^{2+} solution. Calculate the minimum ion PO_4^{3-} concentration in the solution that is necessary to obtain this precipitate.

Solution. The equilibrium scheme in a saturated solution above the precipitate $Ca_3(PO_4)_2$:

$$Ca_3(PO_4)_2 \rightleftarrows 3Ca^{2+} + 2PO_4^{3-}$$
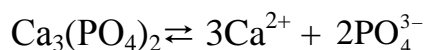
The solubility constant $Ca_3(PO_4)_2$:

$$K_s(Ca_3(PO_4)_2) = [Ca^{2+}]^3 \cdot [PO_4^{3-}]^2$$

hence:
$$[PO_4^{3-}] = \sqrt{\frac{K_s}{[Ca^{2+}]^3}} \, .$$

As we can find in the reference book $K_s^0(Ca_3(PO_4)_2) = 2 \cdot 10^{-29}$.

As the ion concentration in the solution is small, let's take $K_s^0 = K_s$.

Then,
$$[PO_4^{3-}] = \sqrt{\frac{2 \cdot 10^{-29}}{(0,001)^3}} = 1,41 \cdot 10^{-10} \text{ mol/L}$$

Answer: the precipitate will form at $[PO_4^{3-}] > 1,41 \times 10^{-10}$ mol/L

Problem 3. Will the precipitate CaC_2O_4 be formed, if we add the equal volume of $Na_2C_2O_4$ solution with the concentration of $1 \cdot 10^{-7}$ mol/L to the saturated solution of $CaSO_4$?

Solution. The equilibrium scheme in a saturated solution above the precipitate $CaSO_4$:

$$CaSO_4 \rightleftarrows Ca^{2+} + SO_4^{2-} \, .$$

Let's denote **x** to be the concentration of each of the ions $[Ca^{2+}] = [SO_4^{2-}] =$ x mol/L, then $K_s(CaSO_4) = x^2$, $[Ca^{2+}] = \sqrt{K_s(CaSO_4)}$ mol/L.

As at mixing up of the initial solutions the total volume of the solution is doubled, the ion concentration is halved. Let's find the product of ion concentrations of Ca^{2+} и $C_2O_4^{2-}$ and compare it to the solubility constant of calcium oxalate. The condition of the precipitate formation of CaC_2O_4 is: $[Ca^{2+}] \cdot [C_2O_4^{2-}] > K_s$

As we can find in the reference book K_s^0 $(CaSO_4)$ and K_s^0 (CaC_2O_4); K_s^0 $(CaSO_4) = 2,5 \cdot 10^{-5}$; K_s^0 $(CaC_2O_4) = 2,6 \cdot 10^{-9}$

In dilute solutions $K_s^0 = K_s$; $[Ca^{2+}] = \sqrt{\frac{2,5 \cdot 10^{-5}}{2}}$; $[C_2O_4^{2-}] = \frac{1 \cdot 10^{-7}}{2}$;

$[Ca^{2+}] \cdot [C_2O_4^{2-}] = 1,25 \cdot 10^{-10}$

Answer: the precipitate isn't formed because $1,25 \times 10^{-10} < 2,6 \times 10^{-9}$

Problem 4. The solubility of PbI_2 at 25 °C is 0,581 g/L. Calculate $K_s(PbI_2)$ at 25 °C. $M(PbI_2) = 461$ g/mol.

Solution. The scheme of equilibrium in a saturated solution above the precipitate

$$PbI_2 \rightleftarrows Pb^{2+} + 2I^- \tag{1}$$

The concentration solubility constant of PbI_2:

$$K_s(PbI_2) = [Pb^{2+}] \cdot [I^-]^2 \qquad (2)$$

Let's establish the connection between K_s and the solubility of PbI_2 (S mol/L). As we can see from the equation (1), at the dissolution of 1 mole of PbI_2, 1 mole of Pb^{2+} and 2 moles of I^- ions transfer into the solution. Consequently, if S mol/L of PbI_2 is dissolved, then in a saturated solution: $[Pb^{2+}] = S$ mol/L; $[I^-] = 2S$ mol/L.

Let's substitute these values into the equation (2) and obtain:

$$K_s(PbI_2) = S \cdot (2S)^2 = 4S^3 \qquad (3)$$

Let's express the solubility of PbI_2 in mol/L. As the molar mass (PbI_2) is equal to 461 g/mol, then the solubility of PbI_2 expressed in mol/L is equal:

$$S = \frac{0{,}581}{461} = 1{,}26 \cdot 10^{-3} \text{ mol/L}$$

Using the equation (3) let's find $K_s(PbI_2)$:

$$K_s(PbI_2) = 4 \cdot (1{,}26 \cdot 10^{-3})^3 = 8 \cdot 10^{-9}$$

Answer: $K_s(PbI_2) = 8{\times}10^{-9}$

Problem 5. The solubility constant of $Cr(OH)_3$ is $5{,}4 \cdot 10^{-31}$ at 20 °C. Calculate the solubility of $Cr(OH)_3$ (in mol/L and in g/L) at 20 °C. $M(Cr(OH)_3) = 103$ g/mol.

Solution. The scheme of equilibrium in a saturated solution above the precipitate $Cr(OH)_3$:

$$Cr(OH)_3 \rightleftharpoons Cr^{3+} + 3OH^- \qquad (1)$$

The concentration solubility constant $Cr(OH)_3$:

$$K_s(Cr(OH)_3) = [Cr^{3+}] \cdot [OH^-]^3 \qquad (2)$$

Let's establish the connection between K_s and the solubility of $Cr(OH)_3$ (S mol/L). As we can see from equation (1), at the dissolution of 1 mole of $Cr(OH)_3$, 1 mole of Cr^{3+} and 3 moles of OH^- ions transfer into the solution. Consequently, if S mol/L of $Cr(OH)_3$ is dissolved, then in a saturated solution:

$$[Cr^{3+}] = S \text{ mol/L}, \ [OH^-] = 3S \text{ mol/L}.$$

Let's substitute these values in the equation (2) and obtain:

$$K_s(Cr(OH)_3) = S \cdot (3S)^3 = 27S^4$$

Hence: $S = \sqrt[4]{\dfrac{K_s Cr(OH)_3}{27}} = \sqrt[4]{\dfrac{5{,}4 \cdot 10^{-31}}{27}} = \sqrt[4]{2 \cdot 10^{-32}} = 1{,}19 \cdot 10^{-8}$ mol/L.

As the molar mass of $Cr(OH)_3$ is 103 g/mol then the solubility of $Cr(OH)_3$ expressed in g/L will be: $1{,}19 \cdot 10^{-8} \cdot 103 = 1{,}22 \cdot 10^{-6}$ g/L

Answer: $1{,}19{\times}10^{-8}$ mol/L; $1{,}22{\times}10^{-6}$ g/L

VIII. THE ELECTRICAL CONDUCTIVITY OF ELECTROLYTE SOLUTIONS. CONDUCTOMETRY

MAIN QUESTIONS ON THE TOPIC

1. Fluids and tissues of the organism as conductors of type II.
2. Absolute ion movement rate and factors determining it. Dimensionality. Absolute movement rate of H^+ and OH^-. Ion mobility.
3. Specific electric conductivity and its dependence on the absolute ion movement rate, concentration (dilution), temperature.
4. Molar electric conductivity, its connection with the specific electric conductivity, the dependence on absolute ion movement rate and the dilution (concentration).
5. Molar electric conductivity at the infinite dilution. Kolraush's law.
6. Electric conductivity of biological fluids and tissues.
7. Conductometry, conductometric determination of degree and constant of dissociation of weak electrolytes.
8. Curves of conductometric titration.

EXPERIMENTAL WORK

Work № 1. Conductometric determination of dissociation degree and constant of acetic acid dissociation.

Aim of the work: to learn to determine the electric conductivity of conductors of type II and to use the data of conductometric measurements for the calculations of dissociation degree and constant of weak electrolytes.

Task 1. To determine the constant of the vessel K_v with 0,01 M of KCl solution.

An electrode vessel is washed twice with a small amount (20 ml) of 0,01 M of KCl solution. We measure and write down the value of electric conductivity L. Using table 1 we find $æ_{KCl}$ at the given temperature and calculate K_v by the formula:

$$K_v = æ_{KCl} / L.$$

Specific electric conductivity of 0,01 M of KCl depending on temperature

Temperature, º	Specific electric conductivity æ, Sm×cm⁻¹
18	0, 001225
19	0, 001251
20	0, 001278
21	0, 001305

22	0, 001332
23	0, 001359
24	0, 001386
25	0, 001413

Problem 2. To determine the dissociation degree and the dissociation constant of acetic acid.

Electrode vessel and electrodes are washed with the distilled water, then wash them with the 0,01 M of acetic acid solution and fill in the vessel with this solution till the mark. Electrodes must be completely covered with the solution. We make the measurement of the conductivity of acetic acid solution in the same way as we measured the conductivity of potassium chloride solution three times. Then we calculate λ_m, α and K_d using the equations:

$$æ(CH_3COOH) = K_v \cdot L;$$
$$\lambda_m = æ(CH_3COOH) / C(CH_3COOH);$$
$$\alpha = \lambda_m / \lambda_m^0;$$
$$K_d = \frac{\alpha^2 C}{1 - \alpha}.$$

The value of molar electric conductivity at the infinite dilution λ_m^0 for acetic acid is calculated using Kolraush's equation:

$$\lambda_m^0 = \lambda_c^0 + \lambda_a^0.$$

The values of mobility of H^+ and CH_3COO^- ions are taken from the table 2.

Ion mobility depending on the temperature

Temperature, º	Ion mobility U ($Sm \times cm^2 \times mole^{-1}$)	
	H^+	CH_3COO^-
18	315·	35·
19	320·	35,9·
20	324,8·	36,6·
21	329,8·	37,4·
22	334,7·	38,2·
23	339,7·	39,1·
24	345,0·	40,1·
25	349,8·	40,9·

The experimental value K_d is compared to the theoretical one and we calculate the experimental error in % ($K_d(CH_3COOH)_{theor.} = 1,75 \cdot 10^{-5}$).

TEST SELF-CHECK

1. What are the factors the ion mobility in the solution depend on?
a) the viscosity of the solvent;
b) the temperature;
c) the size of the ion charge;

d) the size of hydrodynamic radius of the ion.

2. Indicate the formulas expressing Kolraush's law:
a) $\lambda_m^0 = F(\omega_A + \omega_K)$;   b) $\alpha = \lambda_m / \lambda_m^0$;
c) $\lambda_m^0 = U_c + U_A$;   d) $\lambda_m = æ / C$.

3. How will the values of absolute ion rate in aqueous solutions in the row Na^+, Rb^+, OH^-, H^+ change?
a) will decrease;   b) won't change;   c) will increase.

4. How will the molar electric conductivity of electrolyte solutions change with the change of temperature:
a) will increase with the increase of temperature;
b) will increase with the decrease of temperature;
c) will decrease with the increase of temperature;
d) will decrease with the decrease of temperature?

5. Compare the electric conductivity of 0,1 M of H_2SO_4 and Na_2SO_4 solutions:
a) Na_2SO_4 has a higher conductivity;
b) Na_2SO_4 has a lower conductivity;
c) they are equal;
d) H_2SO_4 has a higher conductivity.

6. Which of the diagrams can explain the course of the curve of conductometric titration of CH_3COOH solution by NaOH solution?

V(NaOH)	V(NaOH)	V(NaOH)	V(NaOH)
a	**b**	**c**	**d**
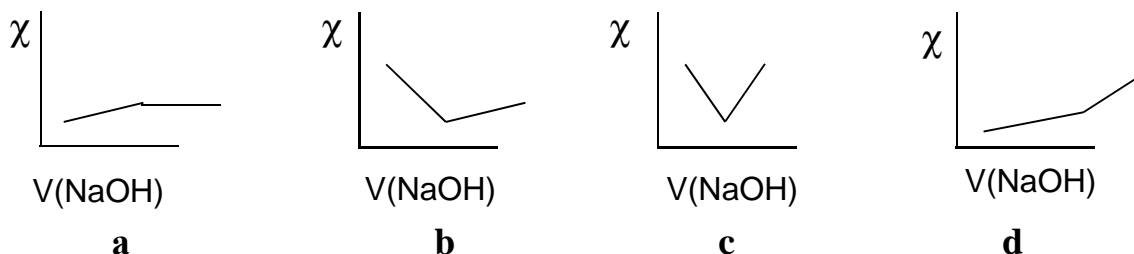
7. Calculate the absolute OH^--ion movement rate if their mobility is $198,5{\times}10^{-4}$ Sm×m²×mole⁻¹:
a) $19,15 \cdot 10^2$ m²·v⁻¹·sec⁻¹;
b) $20,6 \cdot 10^{-8}$ m²·v⁻¹·sec⁻¹;
c) $486,15 \cdot 10^4$ m²·v⁻¹·sec⁻¹;
d) $486,15 \cdot 10^{-4}$ m²·v⁻¹·sec⁻¹.

8. Calculate the specific electric conductivity of propionic acid solution (Sm×m⁻¹) with the concentration of 1/34 mol/L if the molar electric conductivity of this solution is $7,8 {\times}10^{-4}$ Sm×m²×mole⁻¹:
a) $2,68 \cdot 10^{-5}$;   b) $2,68 \cdot 10^{-2}$;   c) $2,29 \cdot 10^{-5}$;   d) $2,29 \cdot 10^{-}$.

9. Calculate the degree of electrolytic dissociation of propionic acid if the H^+ ion mobility is $349,8 \times 10^{-4}$ Sm$\times$m$^2\times$mole^{-1} and the propionate-ion mobility is $40,9 \times 10^{-4}$ Sm$\times$m$^2\times$mole^{-1}, molar electric conductivity of propionic acid is $7,8 \times 10^{-4}$ Sm$\times$m$^2\times$mole^{-1}:

a) $3,99 \cdot 10^{-2}$;　　　b) $2,52 \cdot 10^{-2}$;　　　c) $5,05 \cdot 10^{-2}$;　　　d) $1,99 \cdot 10^{-2}$.

10. In which row of biological fluids the specific electric conductivity decreases?

a) blood plasma, digestive juices, whole blood, urine;

b) digestive juices, urine, blood plasma, whole blood;

c) whole blood, digestive juices, blood plasma, urine;

d) urine, blood plasma, digestive juices, whole blood.

PROBLEMS

1. Calculate the molar concentration of HCl in the solution if the specific electric conductivity of the solution is $0,277$ Sm$\cdot$m^{-1} and the molar electric conductivity is $-1,385 \cdot 10^{-2}$ Sm$\cdot$m$^2\cdot$mole^{-1}.

Answer: 0,02 mole/L

2. Molar electric conductivity of $0,1$ M of CH_3COOH solution at 298 K is $5,2 \cdot 10^{-4}$ Sm$\cdot$m$^2\cdot$mole^{-1}. Calculate the dissociation constant of CH_3COOH solution and its pH.

Answer: $K_d = 1,79 \times 10^{-5}$ mole$\times$L^{-1}; pH= 2,88

STANDARDS OF PROBLEM SOLUTIONS

Problem 1. Determine the molar electric conductivity of $0,1$ M of $AgNO_3$ solution at 298 K if its specific electric conductivity is $1,097$ Sm$\cdot$m^{-1}.

We have:	*Solution*
$C_M(AgNO_3) = 0,1$ mol/L æ $= 1,097$ Sm$\cdot$m^{-1}	Specific and molar electric conductivities are connected where C is the solution concentration, mol/м^3 Consequently,
$\lambda_m = ?$	

$$\lambda_m = \text{æ}/C(AgNO_3) \cdot 1000 = \frac{1,097 \cdot \text{Sm} \cdot \text{m}^{-1}}{0,1 \text{mol/L} \cdot 1000} = 1,097 \cdot 10^{-2} \text{Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1}$$

Answer: $1,097 \times 10^{-2}$ Sm$\times$m$^2\times$mol^{-1}

Problem 2. Are the specific and molar electric conductivities of $0,1$ M of CH_3COONa and CH_3COOH solutions and $0,01$ M of KCl и HCl solutions equal? Will these values change with the increase in temperature?

Solution

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a) Sodium acetate is a strong electrolyte. This means that there are more ions (electricity carriers) in 0,1 M of CH_3COONa solution than in the solution of acetic acid of the same concentration. Consequently, æ and λ_m are greater in CH_3COONa solution.

b) Electric conductivity of 0,01 M of HCl solution is greater than that of 0,01 M of KCl solution as the H^+ ion movement rate is greater than the movement rate of K^+ cations.

c) With the increase in temperature the ion movement rate also increases and the dissociation degree of weak electrolytes is increased too. Consequently, with the increase in temperature æ and λ_m are increased too.

Problem 3. Calculate the molar electric conductivity of potassium iodide at the infinite dilution (λ_m^0) and at 298 K if we know that potassium cation mobility is $73,5\cdot10^{-4}$ $Sm\cdot m^2\cdot mol^{-1}$ and iodide anion mobility is $76,9\cdot10^{-4}$ $Sm\cdot m^2\cdot mol^{-1}$.

We have:	Solution
$U(K^+)= 73,5\cdot10^{-4}$ $Sm\cdot m^2\cdot mol^{-1}$	According to Kolraush's law we find:
$U(I^-) = 76,9\cdot10^{-4}$ $Sm\cdot m^2\cdot mol^{-1}$	$\lambda_m^0(KI) = U(K^+) + U(I^-) = 73,5\cdot10^{-4} +$
$\lambda_m^0(KI) - ?$	$76,9\cdot10^{-4} = 50,4\cdot10^{-4}$ $Sm\cdot m^2\cdot mol^{-1}$

Answer: λ_m^0 (KI) = 150,4×10^{-4} Sm×m^2×mol^{-1}

Problem 4. Determine the degree and constant of dissociation of NH_4OH in 0,01 M of solution at 298 K if the molar electric conductivity for this solution is $11,2\cdot10^{-4}$ $Sm\cdot m^2\cdot mol^{-1}$ and the limiting molar electric conductivity is $271,2\cdot10^{-4}$ $Sm\cdot m^2\cdot mol^{-1}$.

We have:	Solution
$C(NH_4OH) = 0,01$ mol/L	Using the equation $\alpha=\dfrac{\lambda}{\lambda_m^0}$ and $K_d=$
$\lambda_m (NH_4OH)= 11,2 \cdot10^{-4}$ $Sm\cdot m^2\cdot mol^{-1}$	
$\lambda_m^0 (NH_4OH)=271,2\cdot10^{-4}$ $Sm\cdot m^2\cdot mol^{-1}$	$\dfrac{\alpha^2 C}{1-\alpha}$ we determine the degree and the
$\alpha -?$ $K_d - ?$	constant of dissociation of NH_4OH in its 0,01M of solution.

1) $\alpha = \dfrac{11,2\cdot10^{-4}Sm\cdot m^2\cdot mol^{-1}}{271,2\cdot10^{-4}Sm\cdot m^2\cdot mol^{-1}} = 0,0413$

2) $K_d=\dfrac{(0,0413)^2\cdot0,01\,\text{mol/L}}{1-0,0413} = 1,78\cdot10^{-5}$ mol/L

Answer: a = 0,413; K_d = 1,78×10^{-5} mol/L

Problem 5. Specific electric conductivity of 0,02 M of KCl solution at 298 K is 0,277 $Sm\cdot m^{-1}$ and its resistance is 431,8 ohm. Calculate the specific electric conductivity of the acetic acid solution if its resistance in the same vessel is 750 ohm.

We have:	*Solution*
$T = 298K$	Specific electric conductivity of the acetic acid solution can be determined by the formula:
$C(KCl) = 0{,}02$ mol/L	
æ$(KCl) = 0{,}277$ Sm·m^{-1}	$æ(CH_3COOH) = \dfrac{K_v}{R(CH_3COOH)}$, $R = 1/L$,
$R(KCl) = 431{,}80$ ohm	
$R(CH_3COOH) = 750$ ohm	where K_v is the constant of the vessel which is
æ$(CH_3COOH) = ?$	calculated using the results of conductometric measurements for KCl solution.

1) $K_v = $ æ$(KCl) \cdot R(KCl) = 0{,}277$ Sm·m$^{-1} \cdot 431{,}8$ ohm $= 119{,}608$ m^{-1}

2) æ$(CH_3COOH) = \dfrac{K_v}{R(CH_3COOH)} = \dfrac{119{,}608 \text{m}^{-1}}{750 \text{ ohm}} = 0{,}159$ Sm·m^{-1}

Answer: 0,159 Sm·m^{-1}

Problem 6. Calculate the molar electric conductivity of acetic acid at the infinite dilution at 298 K if we know that the limiting molar conductivities are:

$$\lambda^0_m (HCl) = 426{,}1 \cdot 10^{-4} \text{ Sm·m}^2 \cdot \text{mol}^{-1};$$
$$\lambda^0_m (NaCl) = 126{,}4 \cdot 10^{-4} \text{ Sm·m}^2 \cdot \text{mol}^{-1};$$
$$\lambda^0_m (CH_3COONa) = 91{,}0 \cdot 10^{-4} \text{ Sm·m}^2 \cdot \text{mol}^{-1}.$$

We have:	*Solution*
$T = 298K$	Using Kolraush's law about the independent ion mobility we can write down the equality:
$\lambda^0_m (HCl) = 426{,}1 \cdot 10^{-4}$ Sm·m^2·mol^{-1}	
$\lambda^0_m (NaCl) = 126{,}4 \cdot 10^{-4}$ Sm·m^2·mol^{-1}	$\lambda^0_m (HCl) + \lambda^0_m (CH_3COONa) =$
$\lambda^0_m (CH_3COONa) =$	$= \lambda^0_m (CH_3COOH) + \lambda^0_m (NaCl)$
$= 91{,}0 \cdot 10^{-4}$ Sm·m^2·mol^{-1}	
$\lambda^0_m (CH_3COOH) -?$	

Hence:

$\lambda^0_m CH_3COOH = \lambda^0_m (HCl) + \lambda^0_m (CH_3COONa) - \lambda^0_m (NaCl) = (426{,}1 + 91{,}0 - 126{,}4) \cdot 10^{-4} = 390{,}7 10^{-4}$ Sm·m^2·mol$^{-1} = 3{,}907 \cdot 10^{-2}$ Sm·m^2·mol^{-1}

Answer: 3,907×10^{-2} Sm·m^2·mol^{-1}

IX. POTENTIOMETRY

MAIN QUESTIONS ON THE TOPIC

1. Electrode and oxidation-reduction (OR) potentials, the mechanism of their appearance and the dependence on different factors. Nernst-Peters' equation for calculating of potential values.

2. Galvanic elements (chemical and concentration): action mechanism and calculation of EMF. Measuring of electrode and OR-potentials.

3. Reversible electrodes of the first and the second type (hydrogen and silver chloride). Ion-selective electrodes (glass electrode). Structure and mechanism of potential origin.

4. Electrodes of comparison and electrodes of determination (indicating) used in potentiometry.

5. The essence of potentiometric determination of pH.

6. Potentiometric titration, its essence and its usage in quantitative analysis and medicobiological investigations.

EXPERIMENTAL WORK

Work 1. Determination of a weak acid solution concentration and its dissociation constant by the method of potentiometric titration.

Aim of work. To learn to determine the concentration of a weak acid in the solution and its dissociation constant by the method of potentiometric titration.

Devices and reagents. Ionometer, magnetic stirrer, burette for titration, 10 mL Mor's pipette, titration glass, acetic acid solution of unknown concentration, 0,1000 N solution of sodium hydroxide.

Task 1. To determine the concentration of acetic acid in the solution.

We measure 10 mL of investigated solution of acetic acid by Mor's pipette and 10 mL of water and pour them into the titration glass. With the help of a magnetic stirrer we mix the solution and measure the value of pH of the initial solution using ionometer and **strictly following the instruction**. Further we titrate the acid solution adding an alkali from the burette by portions, the volume of which is indicated in the table:

Sequence number	Volume of each portion of the added titrant, mL	General volume of the titrant using the burette, mL	pH of the solution
1.	0	0	
2.	4	4	
3.	2	6	
4.	2	8	
5.	1	9	
6.	0,2	9,2	
7.	0,2	9,4	
8.	0,2	9,6	
9.	0,2	9,8	

Sequence number	Volume of each portion of the added titrant, mL	General volume of the titrant using the burette, mL	pH of the solution
10.	0,2	10,0	
11.	0,2	10,2	
12.	0,2	10,4	

At the same time there occurs the reaction:

$$CH_3COOH + OH^- \rightleftarrows H_2O + CH_3COO^-$$
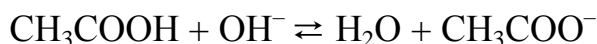
After adding of each portion of the titrant the solution is mixed and its pH is measured. The results of the measurements are written down in the above mentioned table. Using the data from the table we draw a curve of dependence of pH solution on the general volume of the added titrant solution.

Using the curve of potentiometric titration we determine the equivalent volume of the titrant drawing a perpendicular from the middle of the titration jump down to the abscissa axis. According to the law of equivalents we calculate the acid concentration:

$$C_N(CH_3COOH) = \frac{C_N(NaOH) \cdot V(NaOH)}{V(CH_3COOH)},$$

where V(NaOH) — the equivalent volume of the titrant.

Task 2. To determine the dissociation constant of acetic acid.

We measure 10 mL of acetic acid solution by Mor's pipette and add 10 mL of water then from the burette we pour in half of the volume of sodium hydroxide titrant used for titration in the first task for reaching the equivalent point. The solution is mixed up and its pH is measured. In this case 50 % of the acid have reacted and as a result the same amount of the salt has been formed, i. e.
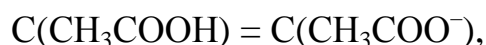
$$C(CH_3COOH) = C(CH_3COO^-),$$

then from the equation $K_d = \dfrac{[CH_3COO^-][H^+]}{[CH_3COOH]}$ it follows that $K_d = [H^+]$ or logarithming we get pH = pK. Hence, $K_d = 10^{-pK} = 10^{-pH}$.

Work 2. Glass electrode. Dependence of glass electrode potential on hydrogen ion concentration.

Aim of the work. To determine experimentally the dependence of glass electrode potential on hydrogen ion concentration.

Order of work performance. Into the solutions of hydrochloric acid with the concentration ranging from 0,00001 till 1 mol/L we immerse a glass electrode and the electrode of comparison (e. g. a silver chloride one) one by one and measure the pH and EMF of the chain for each of the indicated solutions beginning with the most diluted one. The obtained results are written down
in the table. Then we calculate the value of the glass electrode potential

in the hydrochloric acid solutions of different concentration using the formula: $\varphi_{gl.} = E - 0{,}055$ (V), where E is the value of EMF in the galvanic chain.

Using the calculated values $\varphi_{gl.}$ we draw a diagram of dependence of $\varphi_{gl.}$ on pH marking the values of pH on the axis of abscissa, and values of $gl_{T.}$ — on the axis of ordinate. Using the diagram we determine the value of the standard potential of the glass electrode ($\varphi^0_{gl.}$) as a segment cut by the line on the axis of ordinate.

Experimental results of the dependence of glass electrode potential on hydrogen ion concentration are written down in the table using the form

Equence number	C(HCl)mol/L	pH	E of chain, V	$j_{gl., v}$
1	0,00001			
2	0,0001			
3	0,001			
4	0,01			
5	0,1			
6	1,0			
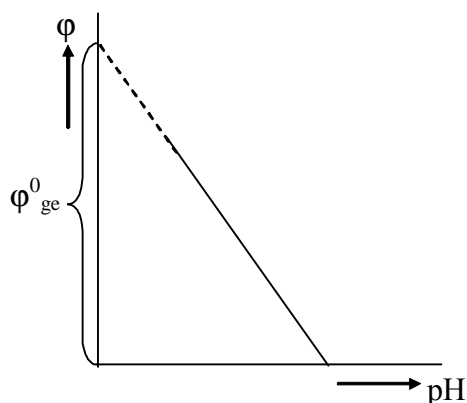
Fig. 3. Diagram of dependence of glass electrode potential on pH. We make the conclusions about the dependence of glass electrode potential on hydrogen ion concentration

TEST SELF-CHECK

1. The value of electrode potential at immersing of a metallic plate into the salt solution of this metal depends on:
a) the charge size of the metal cation;
b) the charge size of the salt anion;
c) the activity of metal cation in the solution;
d) temperature.

2. Equation for calculating OR-potential is the following:

a) $\varphi = \varphi^0_{ox/red} - \dfrac{RT}{nF} \ln \dfrac{a_{(ox)}}{a_{(red)}}$;   c) $\varphi = \varphi^0_{ox/red} + \dfrac{RT}{nF} \ln \dfrac{a_{(ox)}}{a_{(red)}}$;

b) $\varphi = \varphi^0_{ox/red} - \dfrac{RT}{nF} \ln \dfrac{a_{(red)}}{a_{(ox)}}$;   d) $\varphi = \varphi^0_{ox/red} + \dfrac{RT}{nF} \ln \dfrac{a_{(red)}}{a_{(ox)}}$.

3. Indicate the scheme of hydrogen electrode:
a) (Pt) $H^+ | H_2$;   b) $Pt | H_2, 2H^+$;   c) $H_2 | 2H^+$;   d) (Pt) $H_2 | 2H^+$.
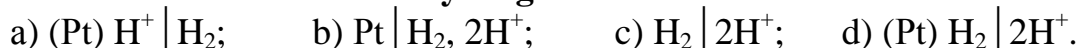
4. Electrode Ag ½AgCl, KCl is:
a) electrode of type I;   b) electrode of type II ;
c) electrode of comparison;   d) electrode of determination.

5. Standard potential of nickel electrode Ni½Ni^{2+} is –0,23 V. Nickel electrode potential Ni½Ni^{2+} at 298 K and nickel ion activity of 0,1 mol/L is:
a) –0,2005V;   b) –0,171V;   c) –0,289V;   d) –0,2595V.

6. Indicate the processes occurring on the electrodes in cadmium-zinc galvanic element ($j^0_{Cd^{2+}/Cd} = -0,45$ V):
a) $Cd - 2\bar{e} \rightarrow Cd^{2+}$;   b) $Cd^{2+} + 2\bar{e} \rightarrow Cd$;
c) $Zn - 2\bar{e} \rightarrow Zn^{2+}$;   d) $Zn^{2+} + 2\bar{e} \rightarrow Zn$.

7. Which of the indicated chemical galvanic elements at standard conditions have the greatest EMF :
a) $Zn | Zn^{2+} \| Fe^{2+} | Fe$;   b) $Zn | Zn^{2+} \| Cu^{2+} | Cu$;
c) $Cu | Cu^{2+} \| Ag^+ | Ag$;   d) $Zn | Zn^{2+} \| Ag^+ | Ag$.

8. Standard potential of copper electrode Cu½Cu^{2+} is +0,34 V. Standard potential of silver electrode Ag½Ag$^+$ is +0,8 V. Standard EMF of silver-copper galvanic element Cu½Cu$^{2+} \|$ Ag$^+$½Ag at standard conditions is:
a) 0,46V;   b) –0,46V;   c) 1,14 V;   d) –1,14V.

9. Standard potential of silver electrode Ag½Ag$^+$ is +0,8 V. EMF of concentrated galvanic element Ag½Ag$^+$ (0,1mol/L)$\|$Ag$^+$(1mol/L)½Ag at 25 ºC is:
a) –0,059V;   b) 0,0295V;   c) 0,059V;   d) –0,0295V.

10. Hydrogen electrode potential immersed into the digestive juice is minus 0,106 B at 25 ºC. pH of digestive juices is:
a) –1,8;   b) 1,9;   c) 1,8;   d) –1,9.

PROBLEMS

1. Calculate pH of urine if electrode potential of hydrogen immersed in it is 0,354 V at 25 ºC.   *Answer: pH = 6*

2. Standard potential of silver chloride electrode is +0,24 V. Calculate the potential of silver chloride electrode filled with HCl solution with the activity of H$^+$-ions of 0,01 mol/L at 25 ºC.

Answer: 0,358 V

3. Standard potential of OR-system $Fe^{2+} \rightleftarrows Fe^{3+} + \bar{e}$ is +0,77 V. Calculate OR potential of the electrode Pt $|Fe^{3+}, Fe^{2+}$ at 298 K, if the activity of Fe^{3+}-ions is 0,1 mol/L and Fe^{2+}-ions is 0,01 mol/L.

Answer: 0,829 V

4. Standard OR potential of the system $MnO_4^- + 8H^+ + 5\bar{e} \rightarrow Mn^{2+} + 4H_2O$ is +1,52B. Calculate the OR potential of this system at 298 K, if $KMnO_4$ concentration is decreased to 0,1 mol/L (the activity coefficient should be taken as 1).

Answer: 1,508 V

5. There is a chain of two hydrogen electrodes immersed into the solutions of hydrochloric acid with different pH values. Calculate EMF of the chain $(Pt)H_2 | 2H^+(C_1) \| 2H^+ (C_2) | H_2(Pt)$ at 298 K, if the pH of the first solution is 3, and of the second one is 1.

Answer: 0,118 V

STANDARDS OF PROBLEM SOLUTIONS

Problem 1. Calculate the potential of a copper electrode if a copper plate is immersed into the solution of blue vitriol with the copper ion activity of 0,02 mol/L at 25 ºC. Standard potential of copper electrode is +0,34 V.

We have:

$a_{Cu^{2+}} = 0,02$ mol/L
$\varphi^0_{Cu^{2+}/Cu} = +0,34$ V
$\varphi_{Cu^{2+}/Cu} - ?$

Solution

For calculating the value of the electrode potential appearing on the border «metal-solution» we use Nernst's equation. Passing in this equation from a natural logarithm to the common logarithm we get:

$$\varphi_{Me^{n+}/Me} = \varphi^0_{Me^{n+}/Me} + \frac{2,3RT}{nF} lg\, a_{Me^{n+}}$$

The scheme of copper electrode is $Cu|Cu^{2+}$ and on the electrode there is a process $Cu^{2+} + 2\bar{e} \rightleftarrows Cu$, hence n = 2. At 298 K the multiplier $\frac{2,3RT}{F} = 0,059$ and the equation will be the following :

$$\varphi_{Cu^{2+}/Cu} = \varphi^0_{Cu^{2+}/Cu} + \frac{0,059}{n} lg\, a_{Cu^{2+}}$$

Hence, we find that

$\varphi_{Cu^{2+}/Cu} = +0,34 + \frac{0,059}{2} lg\, 0,02 = +0,34 + 0,0295 \cdot lg2 \cdot 10^{-5} = 0,34 + 0,029 \cdot (-1,7) = 0,34 - 0,05 = 0,29$ V.

Answer: 0,29 V

Problem 2. Calculate EMF of the element at 25 ºC, which consists of a silver and a lead electrodes, the metal plates of which are immersed into the solution of silver nitrate with the concentration of 0,1 mol/L and the

solution of lead nitrate (II) with the concentration of 0,25 mol/L (we should take

the activity coefficient as 1 in both cases) if the values of standard electrode potentials of silver and lead are the following: +0,80V and –0,13V.

We have:

$C(AgNO_3) = 0,1$ mol/L

$C(Pb(NO_3)_2) = 0,25$ mol/L

$\varphi^0_{Ag^+/Ag} = +0,80$ V

$\varphi^0_{Pb^{2+}/Pb} = -0,13$ V

E = ?

Solution

As $\varphi^0_{Ag^+/Ag} > \varphi^0_{Pb^{2+}/Pb}$, then the cathode is the silver electrode and anode is the lead electrode. We write down the scheme of the galvanic element:

$$\ominus Pb \,|\, Pb^{2+} \,\|\, Ag^+ \,|\, Ag \oplus$$
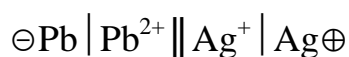
We write down the equations of the reactions occurring on the electrodes:

| Anode: $Pb - 2\bar{e} = Pb^{2+}$ | 2 | 1 |
| Cathode: $Ag^+ + \bar{e} = Ag^0$ | | 2 |

$$Pb + 2Ag^+ = Pb^{2+} + 2Ag^0$$
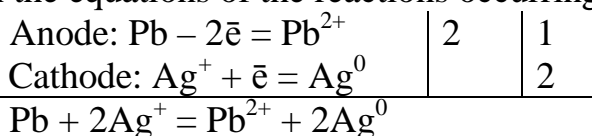
EMF of the galvanic element is: $E = \varphi_{cathode} - \varphi_{anode}$ or in our case

$$E = \varphi_{Ag^+/Ag} - \varphi_{Pb^{2+}/Pb}$$

1. At 25 °C the potential of a silver electrode is: $\varphi_{Ag^+/Ag} = \varphi^0_{Ag^+/Ag} + \dfrac{0,059}{n}\lg a_{Ag^+}$, where $a_{Ag^+} = C \cdot f_a$, hence $\varphi_{Ag^+/Ag} = 0,8 + \dfrac{0,059}{1}\lg 0,1 \cdot 1 = 0,8 + 0,059 \cdot (-1) = 0,741$ V.

2. For a lead electrode:

$\varphi_{Pb^{2+}/Pb} = \varphi^0_{Pb^{2+}/Pb} + \dfrac{0,059}{n}\lg a_{pb^{2+}} = -0,13 + \dfrac{0,059}{2}\lg 0,25 \cdot 1 = -0,13 + 0,0295 \cdot (-0,6) = -0,3 - 0,0177 = -0,3177$ B.

3. EMF = 0,741 – (–0,3177) = 1,0587 V.

Answer: 1,0587 V

Problem 3. Determine EMF of the concentration galvanic element at 25 °C which is composed of two silver electrodes immersed into the solutions of silver nitrate with the silver ion activity of 1 mol/L and 0,5 mol/L. Standard electrode potential of the silver electrode is +0,80 V.

We have:

$a_1(Ag^+) = 0,5$ mol/L

$a_2(Ag^+) = 1,0$ mol/L

$\varphi^0_{Ag^+/Ag} = +0,80$ V

EMF – ?

Solution

We write down the scheme of the galvanic element:

$$\ominus Ag \,|\, Ag^+(0,5 \text{ mol/L}) \,\|\, Ag^+(1 \text{ mol/L}) \,|\, Ag \oplus,$$
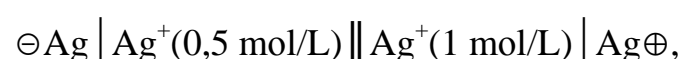
EMF of the concentration galvanic element is:

$$E = \frac{2,3RT}{nF}\lg\frac{a_2}{a_1}, \text{ where } n = 1, \text{ a } a_2 > a_1$$

At 25 °C $E = \dfrac{0,059}{1}\lg\dfrac{1}{0,5} = 0,059\lg 2 = 0,059 \cdot 0,3 = 0,0177$ V.

Problem 4. Standard OR potential of the system $MnO_4^- + 8H^+ + 5\bar{e} \rightarrow Mn^{2+} + 4H_2O$ is $+1,52V$. Calculate OR potential of this system with the increase of the pH of the solution till 5.

We have:

$\varphi^0_{MnO_4^-/Mn^{2+}} = +1,52$ V

pH = 5

$\varphi_{MnO_4^-/Mn^{2+}} - ?$

Solution

Peters' equation for calculating of OR potential of the given system is the following:

$$\varphi_{MnO_4^-/Mn^{2+}} = \varphi^0_{MnO_4^-/Mn^{2+}} + \frac{2,3RT}{nF} \lg \frac{a_{MnO_4^-} \cdot a^8_{H^+}}{a_{Mn^{2+}}},$$

where n = 5 V

In comparison with the standard conditions we see the changes only in the active concentration of H^+-ions: as pH = 5, then $a_{H^+} = 10^{-5}$ mol/L. That's why $\varphi_{MnO_4^-/Mn^{2+}} = \varphi^0_{MnO_4^-/Mn^{2+}} + \frac{0,059}{5} \lg \frac{1 \cdot (10^{-5})^8}{1} = 1,52 + 0,0118 \cdot \lg 10^{-40} = 1,52 - 0,472 = 1,048$ V.

Answer: 1,048 V

X. PHYSICO-CHEMISTRY OF SURFACE PHENOMENA. SURFACE ENERGY AND SURFACE TENSION

MAIN QUESTIONS ON THE TOPIC

1. Special features of the energy state of phase interfaces. Surface energy and surface tension.

2. Surface active and surface inactive substances. Surface tension isotherms. Ducklo-Traube rule. Stalagmometric method of measurement of surface tension in liquids.

3. Adsorption at the interface liquid-gas and liquid-liquid. Gibbs' equation and its analysis. Molecule orientation in the surface layer; the structure
of the lipid biolayer of biological membranes.

4. Adsorption on the interface solid-gas and solid-liquid. Langmure and Friendlikh's adsorption isotherms. Langmure's and Friendlikh's equations, their analysis.

5. Importance of surface phenomena in biology and medicine. Usage of adsorption in medicine and medical-biological research.

EXPERIMENTAL WORKS

Work 1. Determination of the dependence of solution surface tension on the length of the hydrocarbon chain and the concentration of surface active substances (SAS).

Aim of the work: to study the influence of the length of the hydrocarbon chain and the concentration of SAS on the value of solution surface tension.

The essence of the work is to calculate the number of drops of investigated SAS solutions and water which outflow from the same volume. To determine surface tension we use Traube's stalagmometer (see fig. 4). That's why the method bears the name stalagmometric. The main idea of the method is as follows: the liquid is sucked above the highest mark and as soon as its level lowers to this mark we should begin to calculate the number of drops outflowing from the tube until its level reaches the lowest mark.

Fig. 4. Scheme of stalagmometer

The drop flows out of the capillary and falls down under the influence of gravity of its own mass. But the surface tension tries to prevent the falling of the drop as its formation is connected with the increase of liquid surface.

The greater is the surface tension, the greater must be the mass of the falling drop in order to overcome the surface tension and to fall down. So, surface tension σ is proportional to the density ρ and inversely proportional to the number of drops outflowing from the same volume.

Surface tension is determined using the following formula:

$$\frac{\sigma}{\sigma_{H_2O}} = \frac{\rho \cdot n_{H_2O}}{\rho_{H_2O} \cdot n}; \ \sigma = \sigma_{H_2O} \frac{\rho \cdot n_{H_2O}}{\rho_{H_2O} \cdot n}, \quad (1)$$

where σ and σ_{H_2O} are the surface tensions of the studied liquid and water respectively, ρ and ρ_{H_2O} are the densities of the studied liquid and water; n and n_{H_2O} are the number of drops of the studied liquid and water.

For diluted aqueous solutions with the density nearly 1 the formula can be simplified:

$$s = \sigma_{H_2O} \frac{n_{H_2O}}{n}, \quad (2)$$

where $\sigma_{H_2O} = 72,8 \ mJ/m^2$ at 20 °C.

As we can see from the formula (2) it's enough to calculate the number of drops of the studied liquid and water in order to determine the surface tension.

Task 1. Determine the dependence of solution surface tension on the length of the hydrocarbon chain of SAS.

66

At first we should determine the number of water drops and calculate the number of drops of 0,1M of aqueous solutions of the following alcohols in the indicated order: C_2H_5OH, C_3H_7OH, C_4H_9OH, $C_5H_{11}OH$. Then we calculate the surface tension of these alcohols using the formula (2). We build the dependence curve σ on the number of carbon atoms in alcohol molecules (*n* atoms of C). Then we make conclusions about the dependence of surface tension of aqueous solutions on the length of hydrocarbon chain in alcohol molecules.

Task 2. Determine the dependence of the solution surface tension on SAS concentration.

Like in task 1 we should first calculate the number of water drops and the number of drops of the aqueous solution of amyl alcohol of the following concentrations: 0,01 M, 0,025 M, 0,05 M, 0,1 M, 0,2 M. The calculations should be started beginning with the solutions having the lowest concentrations.

We calculate the surface tension of aqueous solutions of amyl alcohol using the formula (2). This dependence of surface tension of alcohol aqueous solutions on its concentration can be represented graphically. We make conclusions about the dependence of surface tension of amyl alcohol solutions on its concentration.

Work 2. **The study of the adsorption of a substance from the solution on solid adsorbent.**

Aim of the work: to determine experimentally the adsorption value of acetic acid from the solution on coal (activated carbon).

The essence of the work is to establish the contact between the solutions of known concentration and the adsorbent. As soon as the adsorption equilibrium between them is created we should determine the concentration of the equilibrium solution. The amount of adsorbed substance from the solution is determined using the difference in concentrations before and after the adsorption. Determining this difference for the solutions of different concentrations and knowing the adsorbent mass we get the data about the specific
adsorption of a substance at different values of equilibrium concentrations. Using these data we draw the adsorption isotherm. In the present work the adsorption isotherm is satisfactorily described by Langmure's equation.

The order of work performance. Draw a table using the form shown below.

№	Concentration of	Volume	Equilibrium	Adsorption

of the test tube	CH₃COOH in the initial solution, mol/L	NaOH in the solution for titration, mol/L	of NaOH solution, mL	concentration of CH₃COOH in the filtrate, mol/L	of CH₃COOH, mmol/g
1	0,1	0,2			
2	0,2	0,2			
3	0,3	0,2			
4	0,4	0,2			

With the help of a graduated cylinder we pour 25 mL of acetic acid solution of the concentration indicated in the table into four dry test tubes. Then in each test tube we introduce simultaneously 0,5 g of the activated carbon previously ground. The contents of the test tubes are stirred by circular motions for 10 minutes. Then the solutions are filtered through dry folded filter into separate tubes. Then with the help of a pipet we take 10 mL from each filtrate and place them into the titration tubes and add 2 drops of phenolphthalein indicator and titrate each sample with the solution of sodium hydroxide (till the appearance of a slightly rosy colour). The titration results are written down in the table. We calculate the equilibrium concentration of acetic acid using the formula:

$$C_{eq.} = \frac{C_{NaOH} \cdot V_{NaOH}}{V_{CH_3COOH}}, \qquad (3)$$

where V_{CH_3COOH} is the volume taken for titration.

Calculate acetic acid adsorption by the formula:

$$\Gamma = \frac{(C_{init} - C_{eq}) \cdot V_{init} \cdot 1000}{m} \text{ (mmol/g)}, \qquad (4)$$

where $C_{init.}$ is the concentration of acetic acid solution before adsorption, mol/L, $C_{eq.}$ is the concentration of acetic acid solution after the adsorption or equilibrium concentration, mol/L, $V_{init.}$ is the volume of acid solution taken for adsorption (in our case 0,025 L), m is the adsorbent mass (in our case 0,5 g).

In order to get the adsorption isotherm we should mark the equilibrium concentrations $C_{eq.}$ on the X-axis and the corresponding them adsorption values (Γ) on Y-axis.

Make conclusions about the dependence of adsorption value of acetic acid from the solution with carbon on its equilibrium concentration.

TEST SELF-CHECK

1. **Indicate the units of measurements of surface tension in SI:**

a) $\dfrac{N \cdot m^2}{mol}$;   b) $\dfrac{J \cdot m}{mol}$;   c) J/m^2;   d) N/m.

2. Which factors influence the surface tension of a liquid?
a) nature of the liquid;   b) nature of adjacent phase;
c) volume of the liquid (p, T — $const$);   d) temperature.

3. Indicate the formulas of SAS:
a) C_3H_7COONa;   b) $NaHCO_3$;   c) C_2H_5OH;
d) $C_2H_5NH_2$;   e) $NH_2 - CH_2 - COOH$.

4. Which curve reflects the dependence of the surface tension of the aqueous solution on the acetic acid concentration:

5. In which row of substances, the formulas of which are written below, the surface tension of the solution firstly increases and then decreases?
a) $CH_3OH, C_2H_5OH, C_3H_7OH$;   b) $C_3H_7OH, CH_3OH, C_2H_5OH$;
c) $C_2H_5OH, C_3H_7OH, CH_3OH$;   d) $CH_3OH, C_3H_7OH, C_2H_5OH$.

6. Which solution has the greatest surface tension?
a) 0,5 M $HOOC - CH_2 - NH_2$;   b) 1 M $HOOC - CH_2 - NH_2$;
c) 0,1 M $C_5H_{11}COONa$;   d) 2 M $C_5H_{11}COONa$.

7. If the number of drops of the aqueous solution outflowing from the stalagmometer is greater than the number of water drops, the dissolved substance is:
a) SAS;   b) SIS;   c) SNA.

8. Indicate the statements which are correct:
a) the state of molecules in the surface layer of a liquid doesn't differ from that of molecules in the volume of a liquid;
b) surface tension is the surface energy of a unit of surface area;
c) adsorption is the method of changing the free surface energy.

9. How can the SAS molecules be orientated in the surface layer of the aqueous solution:

10. Which substances, the formulas of which are written below, have negative adsorption on the surface of the aqueous solution?

a) NH_4NO_3;   b) $C_3H_7NH_2$;   c) $C_6H_{13}SO_3Na$;   d) Na_2SO_3.

11. Indicate Gibbs' equation:

a) $\Gamma = \dfrac{n}{m}$;   b) $\Gamma = K \cdot C^{1/n}$;   c) $\Gamma = -\dfrac{\Delta\sigma}{\Delta C} \cdot \dfrac{C}{RT}$.

12. Adsorption of a non-volatile solute on the surface of its solution depends on:

a) nature of the solute and the solvent;   b) temperature;

c) pressure;   d) solute concentration.

13. What are the units of measurement for adsorption of a substance on a solid adsorbent?

a) mol/g;   b) mol/m^2;   c) mol/L;   d) J/m^2.

14. Indicate the correct statements:

a) physical adsorption occurs due to Van-der-Vaal's forces;

b) chemical adsorption can be irreversible;

c) adsorption doesn't depend on the temperature.

15. What will Langmure's equation look like at the description of adsorption from the solutions of small concentrations?

a) $\Gamma = \Gamma_\infty$;   b) $\Gamma = \Gamma_\infty \cdot \dfrac{C}{K}$;   c) $\Gamma = \Gamma_\infty \cdot \dfrac{C}{K+C}$.

16. Which curve is the Langmure's adsorption isotherm:
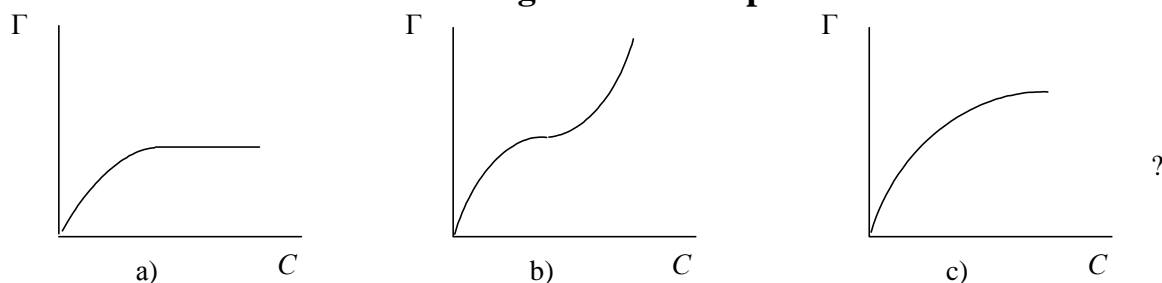
17. Friendlikh's adsorption equation is:

a) true of average concentrations of the adsorptive;

b) true of high concentrations of the adsorptive;   c) empirical.

18. Adsorption of gases on the solid adsorbent depends on:

a) pressure;   b) temperature;

c) nature of adsorbent and adsorbate;   d) specific surface area.

19. In which row there is the increase of substance adsorption from aqueous solutions on the activated carbon?

a) CH_3COOH; CH_3COONa; C_2H_5OH; C_3H_7OH;

b) C_3H_7OH; C_2H_5OH; CH_3COOH; CH_3COONa;

c) CH_3COONa; CH_3COOH; C_2H_5OH; C_3H_7OH;

d) CH_3COONa; C_3H_7OH; CH_3COOH; C_2H_5OH.

20. Adsorption of the solute from the solution on the surface of a solid adsorbent depends on:

a) nature of adsorbent and solute;   b) temperature;

c) nature of the solvent;   d) concentration of the solute.

21. 1,5 g of activated carbon are poured with 20 mL of 0,4 N of CH_3COOH solution. Determine the concentration of the acid after the establishment of adsorption equilibrium if to titrate 10 mL of filtrate we used 18 mL of 0,2 N NaOH solution:

a) 0,36 mol/g;   b) 0,36 mol/L;

c) 0,18 mol/g;   d) 0,18 mol/L?

22. In 100 ml of CH_3COOH solution with the concentration of 400 mmol/L we added 3 g of activated coal and agitated. After the state of equilibrium was reached the CH_3COOH solution concentration decreased till 160 mmol/L. Calculate the value of acetic acid adsorption on coal (in mmol/g):

a) 8000 mmol/g;   b) 8 mmol/g;   c) 16 mmol/g;   d) 80 mmol/g.

23. Indicate, which cation from the aqueous solution is best adsorbed on negatively-charged surface areas of the adsorbent:

a) K^+;   b) Na^+;   c) Li^+;   d) Cs^+.

24. Indicate, which ions from the aqueous solution can primarily be adsorbed on the surface of a crystalline silver iodide:

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

25. Indicate, which ions are adsorbed on the ionite in H^+-form:

a) K^+;   b) Na^+;   c) NO_3^-;   d) Cl^-.

PROBLEMS

1. What will be the surface tension of the aqueous solution of amyl alcohol if the number of the drops of this solution outflowing from the stalagmometer is 72 and the number of water drops is 60? The surface tension of   water at the temperature of the experiment 293 K is $72,8 \cdot 10^{-3}$ J/m^2 (the density of the solution is equal to 1 g/cm^3). To solve this task see experimental work 1.

Answer: $60,6 \times 10^{-3}$ J/m^2

2. At 20 ºC the surface tension of 0,2 M of SAS aqueous solution is $55 \cdot 10^{-3}$ J/m^2. Calculate SAS adsorption value (surface tension of water at 20 ºC is $72,75 \cdot 10^{-3}$ J/m^2).

Answer: $7,3 \times 10^{-6} mol/m^2$

3. It is determined experimentally that the maximum adsorption value of propionic acid on coal is $3,0 \cdot 10^{-3} mol/g$; K coefficient is $6,0 \cdot 10^{-2} mol/L$. What mass of propionic acid has been adsorbed from the solution if the equilibrium acid concentration is 0,1 mol/L? The adsorbent mass is 1 g.

Answer: 0,139 g

4. We have three solutions of acetic acid of different concentrations. We added 3 g of activated coal into 100 mL of each of the solutions. The acid quantity before and after adsorption was determined by the titration of 50 mL of each of the acid solutions by KOH solution with the concentration of 0,1 mol/L.

a) Determine the adsorption value for each solution using the following data:

Titrant volume (KOH) before adsorption, mL	5,50	10,60	23,00
Titrant volume (KOH) after reaching the equilibrium, mL	1,22	3,65	10,20

b) Analyze the change of acetic acid adsorption on coal with the increase of its concentration.

Answer: a) Γ_1 = 0,28 mmol/g; Γ_2 = 0,46 mmol/g; Γ_3 = 0,85 mmol/g;
b) with the increase of acetic acid concentration in the solution there is the increase of its adsorption value on coal.

STANDARDS OF PROBLEM SOLUTIONS

Problem 1. Determine the adsorption value of the acid $C_8H_{17}COOH$ on the surface of the aqueous solution at 10 °C, if the mass fraction of the acid in the solution is 0,005 %. The surface tension of pure water and the solution at this temperature are $74,22 \cdot 10^{-3}$ and $57,0 \cdot 10^{-3}$ J/m² respectively.

We have:	*Solution*
$\omega C_8H_{17}COOH = 0,005\%$	1. To calculate adsorption Γ on the solution
$\sigma H_2O = 74,22 \cdot 10^{-3}$ J/m²	surface we use Gibbs' equation:
$\sigma\ C_8H_{17}COOH = 57,0 \cdot 10^{-3}$ J/m²	$$\Gamma = -\frac{\Delta\sigma}{\Delta C} \cdot \frac{C}{RT} = -\frac{\sigma_2 - \sigma_1}{C_2 - C_1} \cdot \frac{C}{RT}$$
$T = 283K$	

$\Gamma - ?$

In Gibbs' equation the value C_2 means the molar concentration of the acid, $C_1 = 0$ (pure water).

2. Considering that the density of the diluted acid solution is $\approx$ 1 g/mL (i. e. the same as the one of water) and using $\omega\%$ of the acid we can find that in 100 mL of the solution there are 0,005 g of the acid. Consequently, in 1000 mL of the solution there are 0,05 g of the acid. The molar mass of the acid is 158 g/mol, that's why the molar concentration of the solution will be:

$$C_M = \frac{m_{sub}}{M_{sub} \cdot V_{solution}} = \frac{0{,}05}{158 \cdot 1} = 3{,}16 \cdot 10^{-4} \text{ (mol/L)}.$$

3. In Gibbs' equation we use the necessary data:

$$\Gamma = -\frac{57{,}0 \cdot 10^{-3} - 74{,}22 \cdot 10^{-3}}{3{,}16 \cdot 10^{-4} - 0} \cdot \frac{3{,}16 \cdot 10^{-4}}{8{,}314 \cdot 283} = 7{,}3 \cdot 10^{-6} \text{ (mol/m}^2\text{)}.$$

Answer: $7{,}3 \times 10^{-6} mol/m^2$

Problem 2. It is determined experimentally that the maximum adsorption value of SAS (M = 60 g/mol) in some way is $5{,}0 \cdot 10^{-3}$ mol/g. K value is 0,06 mol/L. How many grams of the substance have been adsorbed by two grams of the given adsorbent from the solution if SAS equilibrium concentration is equal to 0,1 mol/L ?

We have:

$\Gamma_\infty = 5{,}0 \cdot 10^{-3}$ mol/g
$M_{SAS} = 60$ g/mol
$K = 0{,}06$ mol/L
$C_{eq.} = 0{,}1$ mol/L
$m(\text{adsorbent}) = 2$ g

$M_{SAS} - ?$

Solution

1. Calculate the SAS adsorption value using Langmure's equation: $\Gamma = \Gamma_\infty \dfrac{C}{K + C}$;

$$\Gamma = 5{,}0 \cdot 10^{-3} \frac{0{,}1}{0{,}06 + 0{,}1} = 3{,}125 \cdot 10^{-3} \text{ (mol/g)}.$$

2. The quantity of the adsorbed substance on the adsorbent with the mass of 2 g will be twice greater:

$$n_{SAS} = 3{,}125 \cdot 10^{-3} \text{ mol/g} \cdot 2 \text{ g} = 6{,}25 \cdot 10^{-3} \text{ mol}.$$

3. The mass of the adsorbed substance will be:

$$m_{SAS} = n \cdot M = 6{,}25 \cdot 10^{-3} \cdot 60 = 0{,}375 \text{ (g)}.$$

Answer: m of the adsorbed SAS is 0,375 g

Problem 3. To 60 mL of acetic acid solution with the concentration of 0,1 mol/L we added 2 g of the adsorbent and agitated. After reaching the state of the equilibrium the sample of the solution with the volume of 10 ml was titrated by the solution of sodium hydroxide with the concentration of 0,05 mol/L. We used 15 mL of titrant for the titration. Calculate the adsorption value of acetic acid.

We have:

$V_{init}(CH_3COOH) = 60$ mL = 0,06 L
$C_{init.}(CH_3COOH) = 0{,}1$ mol/L
$M_{SAS} = 60$ g/mol
$m(\text{adsorbent}) = 2$ g
$V(CH_3COOH$ for titration$) = 10$ mL
$V(NaOH) = 15$ mL
$C(NaOH) = 0{,}05$ mol/L

Solution

1. Let's find the equilibrium concentration of acetic acid solution using the results of titration:

$$C_{eq.}(CH_3COOH) = \frac{C(NaOH) \cdot V(NaOH)}{V(CH_3COOH)};$$

$$C_{eq.}(CH_3COOH) = \frac{0{,}05 \cdot 15}{10} = 0{,}075 \text{ (mol/L)}$$

$\Gamma(CH_3COOH)$ – ?

2. Let's calculate the adsorption value of acetic acid using the formula:

$$\Gamma(CH_3COOH) = \frac{n\,(CH_3COOH)}{m\,\text{absorbent}} = \frac{(C_{init.} - C_{eq.}) \cdot V_{init}}{m} = \frac{(0{,}1 - 0{,}075) \cdot 0{,}06}{2} =$$
$$7{,}5 \cdot 10^{-4}\,(mol/g) = 0{,}75\,(mmol/g)$$

Answer: $\Gamma(CH_3COOH) = 0{,}75\,mmol/g$

XI. CHROMATOGRAPHY

MAIN QUESTIONS ON THE TOPIC

1. The essence of chromatography, the classification of chromatographic methods.

2. Gas and liquid chromatography.

3. Column and planar chromatography. Determination of retention index.

4. Elution chromatography, its mechanism and kinetics. The distribution coefficient and its connection with the retention index.

5. The essence of adsorption chromatography.

6. The essence of ion-exchange chromatography. Ionites and their classification and properties.

7. The usage of ionites for the purification of water.

8. The essence of exclusion chromatography and its usage in medicobiological investigations.

9. Principles of division, isolation and purification of different biopolymers with the help of affine chromatography.

EXPERIMENTAL WORKS

Work 1. Separation of blood serum lipids by the method of thin-layer chromatography (TLC)

Aim of the work*:* to get the chromatogram of blood serum lipid mixture and find out the presence of cholesterol and stearic acid in the extract.

The essence of work: the separation of blood serum lipids is based on their different solubility in a mobile organic solvent and in the immobile phase — water, fixed by a polar sorbent. In the result of a chromatographic process the mixture components are multiply and continuously rearranged between the mobile and immobile phases according to their distribution coefficients, which can be determined by the relation degree either to the immobile polar phase — water or to the nonpolar organic solvent — a mobile phase. That's why the mixture components move along the plate with different

rate and migrate at different distances from the place of their application (start line).

The order of work performance. The separation is carried out on the chromatographic plate «Silufol» which is an aluminum foil covered with a thin layer of silica gel with the admixture of starch.

At the distance of 2 cm from the lower edge of the plate we mark a start line with a pencil (we do it carefully in order not to damage the sorbent layer) and at the distance of 10 cm from the start line we mark the finish line. With the help of a thin capillary we apply two drops (0,02 mL) of the solutions of cholesterol and stearic acid (witnesses) and the mixtures of components at the same distance from each other on the start line (fig. 5). The plate is dried in the air and is placed into the desiccator with an organic solvent with the help of the pincers so that the solvent level should be lower the place of substance application. Then we close the dessicator and after the mobile phase rises along the plate at 12 cm (till the finish line) we take the plate out of the dessicator and dry it in the air till the complete disappearance of the solvent. For the appearance of the stains on the plate we should put it into the vessel with crystalline iodine. Then it is taken out and after the evaporation of iodine excess the plate is watered and dried in the air. Then we measure the distances passed   by the mixture substances (L_1, L_2, L_3), «witnesses» and the organic solvent ($L_{solv.}$). We calculate the retention indexes (R_1, R_2, R_3) using the formula $\mathbf{R} = \dfrac{\mathbf{L\,substance}}{\mathbf{L\,solvent}}$. Comparing R of «witnesses» to R_1, R_2, R_3 of the developed substances in the mixture we make conclusions about the presence or absence of cholesterol and stearic acid in the extract.
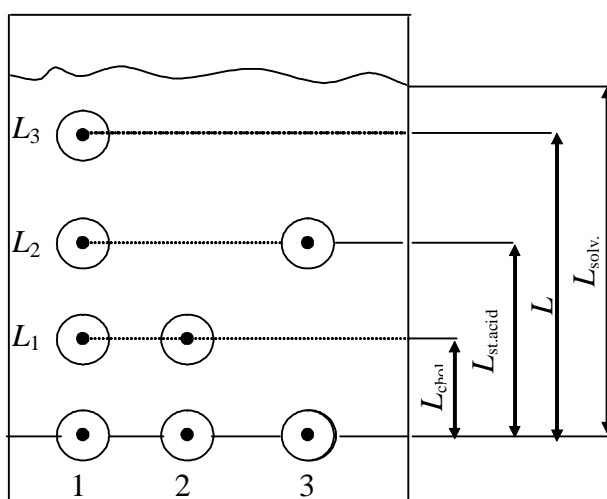
Fig. 5. Determination of the retention index (*R*) at chromatography in the thin layer:
1 — investigated mixture; 2 — cholesterol; 3 — stearic acid

In the conclusions using the values of the retention indexes R_1, R_2, R_3 of the separate components of the separated lipid mixture we compare their polarity.

Work 2. Determination of exchange capacity of cation.

Aim of the work: to determine the total exchange capacity of cation suggested by the teacher.

The essence of the work: the weighed sample of the cation is filled with the excess of sodium hydroxide solution and then its excess is titrated with the solution of hydrochloric acid, i. e. we use the method of reverse titration; all determinations are based on the following reactions:

$$R–An^-H^+ + NaOH \rightarrow R–An^-Na^+ + H_2O;$$
ionite   excess

$$NaOH + HCl \rightarrow NaCl + H_2O$$
residuum
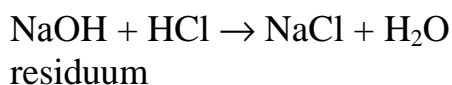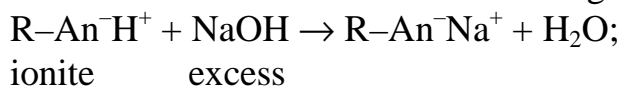
The order of work performance. With the help of a technical balance we measure 0,50 g of cation in the form of H^+, the weighed sample is quantitatively transferred into the flask with the volume of 100–150 mL and we pour
in 50 mL 0,1 M of sodium hydroxide solution. The contents of the flask are stirred from time to time for 1,5–2 hours. After that this equilibrium solution we should separate from ionite grains and titrate three portions (by 10 mL of the solution) 0,1 M of the solution of hydrochloric acid in the presence of 1–2 drops of methyl red. Then you get the humidity values of the ionite sample from the teacher and you should calculate its exchange capacity by the formula:

$$EC = [C(NaOH)·V(NaOH) – a·C(HCl)·V(HCl]/m(1–\omega) \text{ mmol/g},$$

where m is ionite weighed sample, g; $V(NaOH)$ is the volume of the working solution of the alkali added to the ionite weighed sample, mL; $V(HCl)$ is the average volume of the hydrochloric acid used for the titration of the cationite of the equilibrium solution, mL; $C(NaOH)$ and $C(HCl)$ is the solution concentration of alkali and acid, mol/L; ω — the mass fraction of water in cation;
a is the coefficient indicating in how many times the volume of the solution being in contact with ionite is greater than the volume of the cationite taken for the titration (in our case the coefficient a is 5).

After the end of the experiment ionite is taken into the container with the used ionite for the following regeneration.

Work 3. Gel-filtration.

Aim of the work*:* to purify the protein (albumine) from the admixture of ammonia sulphate with the help of sephadex *G*–10.

The essence of the work: at the base of the purification of high molecular compounds from low-molecular ones there is the principle of molecule separation according to their molecular weight and size.

The order of work performance. In a column filled with swollen sephadex we introduce 10 mL 0,005 M of sodium chloride solution and having opened the tap let the solution pour out. When in the column there remains a liquid layer of 0,3 cm high above the gel we close the tap. Then we check the presence of protein and NH_4^+ ion in the analyzed solution with the help of qualitative reactions. In particular, the presence of the protein can be determined using the biuret reaction. For this we pour into a test-tube 1 mL of the analyzed solution and add 0,1 mL of copper sulphate with its mass fraction of 4 % and 1 mL of sodium hydroxide with its mass fraction of 10 %. Then we shake the mixture. If the protein is present, the solution will have a violet colour. To determine NH_4^+ ions we pour 1 mL of the analyzed solution into the other test-tube and add 3 drops of Nessler's reagent. If NH_4^+ ions are present the solution will become yellow.

After that we introduce 1 mL of the analyzed solution into the column by a pipette and having opened the tap we pass the solution into the gel layer. After the gel absorbs the solution , we carefully pour in 30–40 mL 0,005 M of NaCl solution into the column trying not to stir up the gel. Then having opened the tap we gather 10 cuts by 2 mL of the flowing out solution into separate graduated and numerated test tubes. We close the tap and the contents of each test tube is halved (by 1 mL). now we have two rows of test tubes with 10 of them in each row. We carry out qualitative reactions: for the protein — in the test tubes of the first row and for NH_4^+ ion — in the second. The results are shown in the form of the table and a diagram.

Cut number	Test tubes with the solution									
	1	2	3	4	5	6	7	8	9	10
Protein										
NH_4^+ ion										

In the table in the column «cut number» we mark the intensity of the qualitative reaction on the protein or NH_4^+ ion in points using the signs «+» or «0». The maximum of colouring intensity is 5 points (5+), a weaker intensity is ranging from 4+ till 1+,
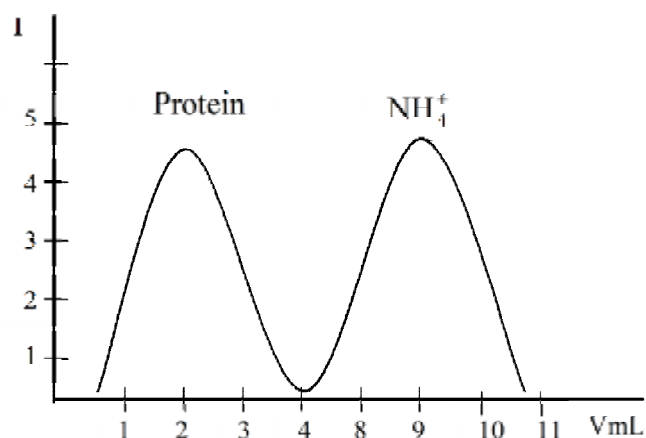
Fig. 6. Diagram of protein and ion NH_4^+ distribution on the sephadex G–10

absence of reaction is marked by «0».

Using the data from the table we draw a diagram. At the axis of abscissa we mark the numbers of cuts corresponding to milliliters of the solution and on the axis of ordinate we mark the coloring intensity in points (fig. 6).

Make the conclusions about the possibility of albumine purification from ammonia ions.

TEST SELF-CHECK

1. All chromatographic methods are based on:
a) multiple repetition of sorption and desorption processes of the separated substances;
b) the differences in the movement rates of separate components of mixture in the mobile phase;
c) the difference in the molecule size of separated substances;
d) the difference in the distribution degree of separated substances between the mobile and stationary phases.

2. According to the mechanism of interaction of sorbent and sorbate we differentiate the following types of chromatography:
a) ion-exchange;
b) affine;
c) exclusion;
d) thin layer chromatography.

3. The distribution degree of separated substances between the stationary and mobile phases (distribution coefficient) is quantitatively expressed by:
a) the ratio of transition rate of different components in the mobile phase;
b) the ratio of substance concentrations in stationary and mobile phases;
c) the substance concentration only in the mobile phase;
d) the substance concentration only in the immobile phase.

4. The retention index depends on:
a) the distribution coefficient;
b) the volume of the stationary phase;
c) the volume of the mobile phase;
d) affinity degree of the substance to the mobile or immobile phase.

5. In the mixture «water-phenol» the distribution coefficient $\left(\dfrac{C_{H_2O}}{C_{phenol}} \right)$ **of cysteine is greater than that of tyrosine. Indicate, which of the**

aminoacids will have the greater transition rate on the plate with silica-gel at thin-layer chromatography (at TLC)?
a) cysteine; b) tyrosine.

Which of the aminoacids is more polar:
c) cysteine; d) tyrosine.

6. Indicate the scheme of the reaction which occurs on the ionite at the separation of salt mixtures NaCl, KCl, CaCl$_2$, FeCl$_3$:

a) $R - Kt^+OH^- + MeAn \rightleftharpoons R - Kt^+An^- + MeOH$;

b) $R-An^-H^+ + MeAn \rightleftharpoons R-An^-Me^+ + HAn$;

c) $R - Kt^+OH^- + MeAn \rightleftharpoons R - Kt^+Me^+ + AnOH$;

d) $R-An^-H^+ + MeAn \rightleftharpoons R-An^-An^- + MeH$.
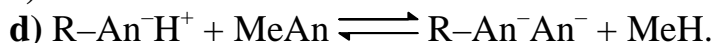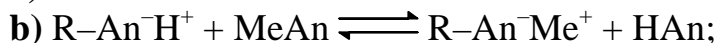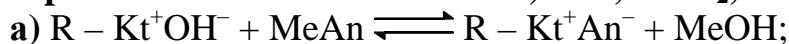
7. To titrate 0,4 g of anionite containing –OH$^-$ groups we used 20,8 mL 0,01 N of hydrochloric acid solution. Exchange capacity of anionite in mmol/g is:
a) 6,2; b) 0,52; c) 7,2; d) 0,62.

8. Indicate, in which working range of pH medium weak-acid cationite have the least ability to ion exchange:
a) weak-acid medium; b) strong-acid medium;
c) weak-alkali medium; d) strong-alkali medium.

9. What is the sequence of appearing of salt solutions NaCl, NaBr, NaI and Na$_2$SO$_4$ at washing out by NaOH solution from the column filled with anionite:
a) Na$_2$SO$_4$, NaCl, NaBr, NaI; b) NaBr, NaCl, NaI, Na$_2$SO$_4$;
c) NaCl, NaBr, NaI, Na$_2$SO$_4$; d) Na$_2$SO$_4$, NaI, NaBr, NaCl.

10. Indicate, what is the sequence of appearing of proteins: hemoglobin (Mr = 67000), cytochrome (Mr = 15500), fibrinogen (Mr = 330000) at washing out by the solvent from the column filled with sephadex *G–200*,
a) hemoglobin, cytochrome, fibrinogen;
b) fibrinogen, hemoglobin, cytochrome;
c) cytochrome, hemoglobin, fibrinogen;
d) hemoglobin, fibrinogen, cytochrome.

PROBLEMS

1. During the chromatography of the pigment of green leaves on the polar adsorbent Al$_2$O$_3$, the coloured layers are arranged top-down in the following way:
a) yellow-green – β-chlorophyll;
b) blue-green – α-chlorophyll;

c) yellow – xanthophylls;

d) red – carotene.

Make conclusions about the degree of polarity of the pigments of separate leaves.

2. In the column filled with a strong-acid cation exchanger (cationite) we introduced a solution containing Fe^{3+}, Ca^{2+}, Li^+ and K^+ cations. What is the sequence of appearing of these cations from the column at their washing out by the solution of 0,5 M of HCl?

3. 1,00 g of dry cation exchanger (cationite) in the form of H^+ was filled up with 100 mL 0,10 M of NaOH solution. To titrate 10 mL of equilibrium solution containing the excess of the alkali which hasn't reacted with the ionite we used 4,8 mL 0,10 M of HCl solution. Calculate the exchange capacity of cationite.

Answer: 5,2 mmol/g of ionite.

STANDARDS OF PROBLEM SOLUTIONS

Problem 1. At the separation of lipid mixture on the plate with silica-gel we obtained four stains, the distances from which to the start line are the following: a) 1,2 cm; b) 2,5 cm; c) 6,4 cm; d) 7,2 cm. The distance passed by the solvent is 11,6 cm. Identify the stains of cholesterol and stearic acid on the chromatogram if the retention index R of cholesterol and stearic acid in the mixture «water-mixed organic solvent» are the following: 0,103 and 0,560. Which of the components of the lipid mixture is more polar? Explain the answer.

We have:	*Solution*
$L_1 = 1,2$ cm	The retention index R is the ratio of the distance passed by the substance from the start line to the distance passed by the solvent. For each of the four stains we calculate R on the formula:
$L_2 = 2,5$ cm	
$L_3 = 6,4$ cm	
$L_4 = 7,2$ cm	
$L_{solvent.} = 11,6$ cm	
$R_{stearic\ acid} = 0,560$	
$R_{cholesterol.} = 0,103$	

To identify the stains of cholesterol and stearic acid on the chromatogram. Which of the components is more polar?

$$R = \frac{L\ substance}{L\ solvent}$$

$$R_1 = \frac{1,2}{11,6} = 0,103 \quad R_3 = \frac{6,4}{11,6} = 0,552$$

$$R_4 = \frac{7,2}{11,6} = 0,620 \quad R_2 = \frac{2,5}{11,6} = 0,216$$

When comparing the calculated values of the retention index to the retention indexes in the problem we can say that the stain with $R_1 = 0,103$ corresponds the value R of cholesterol and, consequently, belongs to it. By analogy the value $R_3 = 0,552$ belongs to the stain of stearic acid, the value R of which is 0,560 (this difference is not significant).

Silica-gel is a polar adsorbent and fixes the polar solvent — water (immobile phase). The polar substance dissolves better in a polar solvent than in
a nonpolar organic solvent which is a mobile phase and is characterized by a smaller value of R. In our case the value R of cholesterol is smaller because it's more polar compared to stearic acid.

Problem 2. Arrange the cations of $CaCl_2$, Na_2SO_4, KCl, $FeCl_3$, $LiNO_3$ salts into a row according to the increase in their ability to be absorbed by their H^+-form of cationite from aqueous solutions. How will this row change if the solvents are slightly polar?

Solution. Adsorption ability of ions depends on the charge size and the radius. The greater is the ion charge, the stronger it demonstrates its ability to ionic exchange. For ions of the same charge the maximum ionic exchange ability is demonstrated by those ions, the radius of which is smaller in the hydrated state. That's why the ability to be adsorbed by cationite from aqueous solutions increases along the row:

$$Li^+ < Na^+ < K^+ < Ca^{2+} < Fe^{3+}$$

In slightly polar solvents we have to take into account the radius of non-solvated ions, that's why the ability of ions to be adsorbed by cationite increases in the following row:

$$K^+ < Na^+ < Li^+ < Ca^{2+} < Fe^{3+}$$
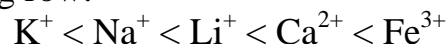
Problem 3. To titrate 0,50 g of air-dried strong-acid cationite with sulphate groups — SO_3H we used 25,5 mL 0,100 M of sodium hydroxide solution. Calculate the exchange capacity of cationite if the mass fraction of water in the sample is 8 %.

We have:	*Solution*
$m = 0{,}50$ g	Exchange capacity of ionites (EC) is characterized by the quantity of equivalents (mmol) of active groups (or counterions) contained in 1 g of dry ionite and able to exchange in the solution into the equivalent number of ions of the same sign.
$V(NaOH) = 25{,}5$ mL	
$C(NaOH) = 0{,}100$ M	
$\omega(H_2O) = 8$ %	

EC – ?

1. The ion exchange reaction occurs on the following reaction:
$$R\text{--}SO_3H + NaOH \rightleftharpoons R - SO_3Na + H_2O$$
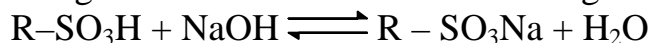
As we can see from this equation, the exchange takes place between H^+ and Na^+ in equivalent amounts. Consequently, the amount of NaOH is equal to the amount of H^+ ions contained in the dry cationite.

2. We find the mass of the dry cationite
m(dry cationite) = m(cationite) · ω(dry cationite) = 0,5 · 0,92 = 0,46 (g)

3. We calculate EC of cationite using its definition:

$$OE = \frac{n(H^+)}{m(\text{dry cationite the})} = \frac{C(NaOH) \cdot V(NaOH)}{m(\text{dry cationite the})} = \frac{25{,}5 \cdot 0{,}100}{0{,}46} = 5{,}54 (\text{mmol/g})$$

Answer: 5,54 mmol/g.

XII. PHYSICO–CHEMISTRY OF DISPERSION SYSTEMS

MAIN QUESTIONS ON THE TOPIC

1. Dispersion systems, their peculiarities and classification.
2. Molecular-kinetic properties of colloidal systems. Sedimentation.
3. Optical properties of colloidal systems. Opalescence.
4. Structure of colloid particles.
5. Methods of obtaining and purification of colloidal systems. Peptization.
6. Structure and mechanism of double electric layer of sol particles.
7. Electrokinetic and electrothermodynamic potentials, their appearance, mechanism and factors determining them.
8. Electrokinetic phenomena in colloidal solutions.
9. Electrophoresis of colloidal solutions. Factors determining the rate of electrophoresis.
10. Proteins as polyelectrolytes. Isoelectric state and isoelectric point of proteins. The influence of pH of the solution on the ionization character of proteins.
11. Electrophoresis in the solutions of proteins.
12. The significance of electrophoresis and electroosmosis in medical-biological investigations and physiotherapeutic practice.
13. Kinds and factors of colloidal system stability.
14. Coagulation of colloidal solutions and factors causing it.
15. Coagulation of colloidal solutions by electrolytes. Coagulation threshold.
16. Kinetics and coagulation mechanism of colloidal solutions.
17. Coagulation processes at purification of drinking water and sewage.
18. Colloid protection and its importance.

EXPERIMENTAL WORKS

Work 1. **The obtaining of colloidal solutions by the condensation method and the investigation of their optical properties.**

Aim of the work: to learn to obtain colloidal solutions by the condensation method and to study the optical properties of colloidal solutions

Reactants and devices: Tindal's apparatus, a stand with test tubes, 0,01 N of KI, $AgNO_3$, H_2SO_4, $Na_2S_2O_3$, $K_4[Fe(CN)_6]$, $CuSO_4$ solutions, colophony solution in alcohol, water.

Task 1. To obtain colloidal solutions by the methods of physical and chemical condensation (for sols obtained by the method of chemical condensation you should write the schemes of micelle structure).

Experiment I. The obtaining of sol of silver iodide.In a test tube we pour 1/2 of KI solution and shaking it we add by drops $AgNO_3$ solution till the formation of opalescent sol AgI (a light luminous feculence):

$$KI + AgNO_3 \rightarrow AgI\downarrow + KNO_3$$
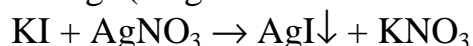
Experiment II. The obtaining of sulphur sol.

To the solution of $Na_2S_2O_3$ (1/2 of the test tube) we add 4–5 drops of H_2SO_4 solution. When this solution remains immobile we can see a *slow* formation of opalescent sol of sulphur:

$$Na_2S_2O_3 + H_2SO_4 \rightarrow S\downarrow + Na_2SO_4 + SO_2 + H_2O$$
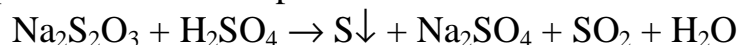
Experiment III. The obtaining of sol of copper (II) hexacyanoferrate.

To the solution of $K_4[Fe(CN)_6]$ (1/2 of the test tube) we add it by drops $CuSO_4$ solution and shake it till the formation of sol of brick-red colour:

$$K_4[Fe(CN)_6] + 2CuSO_4 = Cu_2[Fe(CN)_6]\downarrow + 2K_2SO_4$$
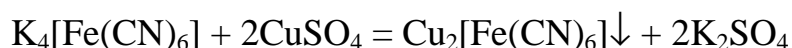
Experiment IV. The obtaining of colophony sol by the method of solvent substitution.

To water (1/2 of the test tube) we add 1–2 drops of alcohol solution of colophony and shake vigorously the test tube. We can see the formation of milk-white sol as colophony is insoluble in water.

Make conclusions about the methods of sol obtaining in experiments I–III and in the experiment IV.

Task 2. To study the optical properties of the obtained colloidal solutions. A prepared test tube with water or with electrolyte solution, for example, KI and also the test tubes with the obtained colloidal solutions are by turns placed through the upper aperture into a black box with a source of light (a simplified Tindal's apparatus without a focusing lens). If there is a colloidal solution in the test tube, we can see a bright luminous ray (Tindal's cone) through the lateral aperture. The obtained results are written down in the form of the following table.

System	Method of obtaining and type of reaction	External form of the sol (colour, opalescence)	Presence of Tindal's cone	Conclusions
Electrolyte solution				
Sol of silver iodide				
Sulphur sol				
Sol of copper				

hexacyanoferrate				
Colophony sol				

On the basis of investigations of optical properties of obtained solutions we make conclusions whether they are colloidal or not and why.

Work 2. Investigation of coagulating action of electrolytes on the sol and determination of the charge sign of sol particles. Testing of protective forces of gelatin.

Aim of the work: to learn to determine experimentally the coagulation threshold for electrolytes in relation to the given sol and also the charge sign of the sol using the values of coagulation threshold; to prove experimentally that the protein solutions (gelatin) increase the coagulation threshold, i. e. possess protective actions.

Reactants and devices: sol of iron hydroxide, 0,7 M of KCl solution, 0,01 M of K_2SO_4 solution, 0,001 M of K_3PO_4 solution, 0,1 % solution of gelatin, flasks for titration, burettes, Mor's pipettes with the volume of 10 mL.

Task 1. To determine the coagulation thresholds for the given electrolytes in relation to the sol of iron (III) hydroxide.

In three flasks for titration (one for each electrolyte) we introduce 10 ml of the solution of iron (III) hydroxide sol with the help of Mor's pipette. Each flask with the sol solution we titrate by the solution of the following electrolytes KCl, K_2SO_4, K_3PO_4 till the appearance of feculence or till the brightening of the solution colouring. Feculence can be seen compared to the initial sol and must be the same in all three flasks.

We calculate the coagulation threshold γ for each electrolyte using the formula:

$$\gamma = \frac{V \cdot C \cdot 1000}{V_0},$$

where C is the electrolyte concentration, mol/L; V is the volume of electrolyte solution, mL; V_0 is the volume of sol solution, mL; γ is coagulation threshold, mmol/L.

The data of the experiment and the results of the calculations are written down in the form of the table.

Number of experiment	Electrolyte solution for titration	Sol volume, mL	Electrolyte concentration, mol/L	Volume of electrolyte, mL	Coagulation threshold, mmol/L
1	KCl	10	0,7		
2	K_2SO_4	10	0,01		
3	K_3PO_4	10	0,001		

Task 2. To determine the charge sign of particles of iron (III) hydroxide sol using the values of coagulation threshold.

Find the ratio of coagulation thresholds of the given electrolytes obtained in Task 1. On the basis of the obtained data we make conclusions about the charge sign of ion-coagulant and indicate the charge sign of particles of iron (III) hydroxide sol.

Task 3. To check the protective properties of gelatin.

In a flask we introduce 10 mL of sol solution and 0,1 mL of 0,1 % gelatin solution with Mor's pipette. We titrate the obtained solution by KCl solution comparing the feculence degree with the same solution in Task 1. Then we calculate the coagulation threshold of KCl solution in respect to the sol of iron hydroxide after adding gelatin (γ_g) and determine, in how many times the coagulation threshold will increase after adding gelatin.

On the basis of the change in coagulation threshold at adding gelatin we make conclusions about the protective properties of gelatin and explain the mechanism of it protective action.

Work 3. Electrophoresis of aminoacids on the paper.

Aim of the work: to separate the mixture of aminoacids by the method of electrophoresis on the paper, on the basis of electrophoregram to determine the charge sign of aminoacids in the given medium.

Reactants and devices: the device for electrophoresis of aminoacids, strips of chromatographic paper of *FN*–15 type, buffer solution with the pH = 9,24, solutions of aspartic acid and arginine, Barolie's colouring solution, a drying box.

The order of work performance foresees several stages.

1. In the middle of a strip of chromatographic paper we draw a light transverse line (a mark) with a pencil and on both sides of it at the distance of ~7 cm we put the signs «+» and «–».

2. In Petri dish we pour the buffer solution with the pH 9,24 and moisten a paper strip in it so that its ends should remain dry. The excess of the buffer can be removed from the paper having been dried with some filter paper.

3. With the help of a pipette we apply 0,05 mL (1 drop) of aminoacid mixture on the paper strip in the form of a thin line.

4. In the device for electrophoresis we place a paper strip on the stand in such a way that the charge signs on the device coincide with the signs on the strip. Then we check that the dry ends of the paper should be completely moistened by the buffer solution. *Then we close the device with a cover and work further strictly following the instruction* for the given device taking care because it works under high voltage

5. On completion of electrophoresis (~25 min) we switch off the device, take off the paper and, having cut off the wet ends, we place it on the stand into a drying box for 5–7 min at 80 ºC.

6. The dried paper is again moistened by a colouring solution poured into Petri dish and without blotting we dry it for 5–10 min till the coloured stripes: violet (asparagine) and pink (arginine) appear.

7. The obtained electrophoregram is pasted into the copy book with the indications of the name of each aminoacid.

On the basis of the obtained electrophoregram we make conclusions about the charge signs of arginine and asparagine in the given medium and also indicate which of the aminoacids has the greatest rate of electrophoresis and why.

Work 4. Determination of charge sign of sol particles and the value of x-potential by the method of electrophoresis.

Aim of the work: to learn to determine the charge sign of sol particles and to measure the value of ξ-potential by the method of colloidal solution electrophoresis.

Reactants and devices: the device for electrophoresis of colloidal solutions; 0,01 M of KI solution, 0,01 M of $AgNO_3$ solution, a ruler, a flask.

The order of work performance. To get a colloidal solution AgI we mix 20 mL 0,01 M of KI solution and 14 mL 0,01 M of $AgNO_3$ solution in a cone flask. Electrophoresis is carried out in a glass device which is a intercommunicating vessel composed of a U-shaped tube and connected to it funnel *B* with tap 1 (fig. 7). With the tap open we fill in the vessel with water till the level of the tap. Then we switch off the tap and pour the prepared sol along the wall of the vessel into the funnel so that no air bubbles should get into the tube. Then we carefully open the tap for the sol to fill in both elbows of the device up to 1/3 of its volume and close the tap. Water at the same time will occupy the upper part of the U-shaped tube.

We should watch the border line between the sol and water be rather distinct. This can be reached at very slow adding of sol through the tap. The sol border (2) is marked with a pencil on the glass of both elbows and put in the electrodes so that their ends should be in the water layer at 3–4 cm above the interface. The electrodes are attached to the clips of direet current source *according to the instruction* for the device. When the border moves at 1–1,5 cm regarding the initial position the device is switched off and we mark the time of electrophoresis in seconds.
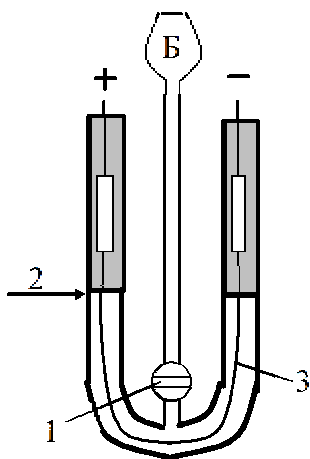
Fig. 7. The device for eletrophoresis

We write down the direction of bounda-boundary displacement of sol and using it determine the charge of sol particles.

With a flex we mark the distance between two electrode ends immersed into the solution along the line 3 and using voltmeter we determine the voltage on the clips. The obtained data we write down in the form of the table and calculate the electrophoretic mobility:

shift of sol border S, m:

time of electrophoresis t, s:

distance between electrodes L, m:

voltage on the clips E, volt:

linear speed of shift of sol border V, m/s ($V = S/t$)

field density H, volt/m ($H = E/L$)

electrophoretic mobility m^2/sec·volt ($u = V/H$)

Then we calculate the electrokinetic potential x, V:

$$x = \frac{u \cdot k \cdot \pi \cdot \eta}{\varepsilon} \cdot B$$

where $k = 6$; η (water) $= 1 \cdot 10^{-3}$ H·s/m^2; ε (water) $= 81$ at 20 ºC; $B = \dfrac{1}{9 \cdot 10^9}$,

B — coefficient for interconversion of electrostatic units into SI units.

TEST SELF-CHECK

1. Indicate the right statements:

a) at dissolving sodium chloride in water we can obtain a colloidal solution;

b) a colloidal solution is a thermodynamically unstable system;

c) a dispersed system is a heterogeneous system which consists of a dispersed phase and a dispersion medium;

d) the sizes of particles of a dispersed phase of a sol (a colloidal solution) are greater than 100 nanometers.

2. Indicate the properties characterizing colloidal solutions:

a) low osmotic pressure;

b) light diffusion;

c) sedimentation is characteristic for the dispersed phase particles;

d) low diffusion rate of the dispersed phase particles.

3. Indicate the factors decreasing the diffusion rate:

a) increase of temperature;

b) decrease of temperature;

c) increase of particle size;

d) decrease of solution viscosity.

4. Indicate in which of the following systems at the same mass concentration of the substance the osmotic pressure is lower:

a) sodium chloride solution;

b) glucose solution;

c) sol of iron (III) hydroxide;

d) aluminum chloride solution.

5. Indicate the factors, which the segmentation rate depends on:

a) particle size of the dispersed phase;

b) viscosity of the dispersion medium;

c) density of the dispersion medium;

d) density of the dispersed phase.

6. Colloidal solutions have the most characteristic optical property which is:

a) reflection;   b) absorption;

c) diffraction;   d) light diffusion.

7. The basis (aggregate) of a colloidal particle (micelle) are the microcrystalls of:

a) a slightly soluble electrolyte;

b) a quickly soluble electrolyte;

and on the surface of the aggregate there is the adsorption of the ions of the electrolyte taken :

c) in excess;   d) in deficiency.

8. Sol of calcium carbonate is obtained by the method of mixing of equal volumes of calcium nitrate and potassium carbonate solutions. Indicate what is the charge of sol grains if the concentration of $Ca(NO_3)_2$ is higher than that of K_2CO_3:

a) positive;   b) negative;   c) neutral.

9. Sol of barium carbonate is obtained by the interaction of the excess of barium chloride solution with the solution of ammonia carbonate. For the micelle of the obtained sol:

A. aggregate consists of microcrystalls:

a) $BaCl_2$;   b) $(NH_4)_2CO_3$;   c) NH_4Cl;   d) $BaCO_3$.

B. the potential determining ions are:

a) CO_3^{2-};   b) Cl^-;   c) Ba^{2+};   d) NH_4^+.

C. the scheme of the nucleus is the following:

a) $[mBaCO_3] \cdot n\,CO_3^{2-}$;   b) $[mBaCO_3] \cdot 2nCl^-$;

c) $[mBaCO_3] \cdot 2n\,NH_4^+$;   d) $[mBaCO_3] \cdot nBa^{2+}$.

D. counterions are the ions:

a) Ba^{2+};   b) Cl^-;   c) CO_3^{2-};   d) NH_4^+.

E. the scheme of the adsorption layer is:

a) nBa^{2+};   b) $2nCl^-$;   c) $nBa^{2+} \cdot (2n-x)Cl^-$;

d) $2nCl^- \cdot (n-x)Ba^{2+}$;   e) $nCO_3^{2-} \cdot (2n-x) NH_4^+$;   f) nCO_3^{2-}.

F. the scheme of the grain is the following:

a) $\{[mBaCO_3] \cdot nBa^{2+} \cdot (2n-x)Cl^-\}^{x+}$;

b) $\{[mBaCO_3] \cdot 2nCl^- \cdot (n-x)Ba^{2+}\}^{2x-}$;

c) $\{[mBaCO_3] \cdot nBa^{2+} \cdot (2n-x)Cl^-\}^{x-}$;

d) $\{[mBaCO_3] \cdot nCO_3^{2-} \cdot (2n-x) NH_4^+\}^{x-}$.

G. the charge of the grain is:

a) positive;   b) negative;   c) neutral.

H. the diffuse layer consists of the ions:

a) Ba^{2+};   b) NH_4^+;   c) Cl^-;   d) CO_3^{2-}.

I. the scheme of micelle is:

a) $\{[mBaCO_3] \cdot 2nCl^- \cdot (n-x)Ba^{2+}\}^{2x-} \cdot xBa^{2+}$;

b) $\{[mBaCO_3] \cdot nCO_3^{2-} \cdot (2n-x) NH_4^+\}^{x-} \cdot xNH_4^+$;

c) $\{[mBaCO_3] \cdot nBa^{2+} \cdot (2n-x)Cl^-\}^{x-} \cdot xCl^-$;

d) $\{[mBaCO_3] \cdot nBa^{2+} \cdot (2n-x)Cl^-\}^{x+} \cdot xCl^-$.

10. At mixing of equal volumes of silver nitrate and sodium chloride solutions a sol of silver chloride with the positively charged particles is formed. The concentration of the initial electrolytes is:

a) greater in $AgNO_3$ solution;   b) greater in NaCl solution;

c) lower in NaCl solution;   d) equal.

11. To obtain stable colloidal solutions (sols) we need the following conditions:

a) the particle size of the dispersed phase is 1–100 nanometers;

b) good solubility of the dispersed phase in the dispersion medium;

c) weak solubility of the dispersed phase in the dispersion medium;

d) presence of stabilizer (a small excess of electrolyte).

12. Indicate the dispersion methods of obtaining colloidal solutions:

a) methods of solvent substitution;   b) peptization;

c) chemical oxidation;   d) mechanical cracking.

13. Indicate which of the ions plays the role of peptizing agent when we add a small amount of nitric acid to the freshly prepared precipitate of aluminum hydroxide:

a) AlO^+;   b) OH^-;   c) H^+;   d) NO_3^-.

14. Which of the properties mentioned below are the basis for purification of colloidal solutions:

a) particle sizes of a dispersed phase are greater than those of admixture particles;

b) the particle concentration of a dispersed phase is greater than the concentration of admixture particles;

c) diffusion of particles of a dispersed phase through a membrane;

d) diffusion of admixture particles through a membrane.

15. The value of electrothermodymanic potential of sol particles is determined by:

a) the quantity of potential-determining ions in the adsorption layer;

b) the quantity of counteions only in the diffuse layer;

c) the quantity of counterions only in the adsorption layer;

d) the general amount of counterions in the adsorption and diffuse layers.

16. Electrokinetic potential of colloidal solution particles appears:

a) between the potential-determining ions of the adsorption layer and all counterions;

b) between ions of adsorption layer and counterions of diffuse layer;

c) between the aggregate and potential-determining ions of the adsorption layer;

d) between the grain and the diffuse layer.

17. Indicate the right statements:

a) the charge size of the grain can change because counterions of the diffuse layer can move to the adsorption layer and vice versa;

b) the more counterions are in the diffuse layer, the greater is the charge size of the grain;

c) electroosmosis is the movement of molecules of dispersion medium relative to dispersed phase in the electric field;

d) the potential of leaking appears at pushing the sol through the capillary under pressure.

18. The electrophoresis rate of colloidal solution particles increases with:

a) the increase of value of zeta-potential;

b) the decrease of value of zeta-potential;

c) the decrease of dispersion medium viscosity;

d) the increase of electric (field) intensity.

19. When pouring together equal volumes of 0,008 M of AgNO₃ solution and 0,0096 M of NaCl solution a sol of silver chloride is formed, the micelle structure scheme of which is the following:

a){[mAgCl]·nCl^-·(n–x)·Na^+}$^{x-}$·xNa^+;

b)$\{[mAgCl] \cdot nNa^+ \cdot (n-x) \cdot Cl^-\}^{x+} \cdot xCl^-$;

c)$\{[mAgCl] \cdot nAg^+ \cdot (n-x) \cdot NO_3^-\}^{x+} \cdot xNO_3^-$;

and at electrophoresis the grain of the sol mentioned above:

d) move to the cathode;

e) move to the anode;

f) remain immobile.

20. Indicate the right statements:

a) in aqueous solutions aminoacids are in the form of bipolar ions;

b) total charge of aminoacid in the solution depends on the ratio of the number of amino-and carboxylic groups in a molecule and the pH of the medium;

c) separation of aminoacids, proteins by the method of electrophoresis is based on their ability to change the charge sign depending on the pH medium;

d) in the electric field at the pH equal to pI the protein moves to the cathode.

21. In the alkali medium an aminoacid takes part in the conversion:

a) $NH_3^+ - R - COO^- + OH^- \rightleftarrows NH_3^+ - R - COOH$;

b) $NH_3^+ - R - COO^- + OH^- \rightleftarrows NH_2 - R - COO^- + H_2O$;

c) $NH_3^+ - R - COO^- + OH^- \rightleftarrows NH_2 - R - COOH$;

and at the same time the total charge of the above mentioned acid is:

d) negative;   e) positive;   f) neutral.

22. For diaminomonocarboxylic aminoacid the value of pI corresponds to:

a) weak-acid medium;   b) neutral medium; c) weak-alkali medium.

23. At separation of proteins (a-globulin with pI = 4,8, albumin with pI = 4,64, g-globulin with pI = 6,4) by the method of electrophoresis we used the buffer solution with the pH = 4,9. Indicate the proteins which moved to the anode:

a) α-globulin;   b) albumen;   c) γ-globulin;

indicate, which of the proteins mentioned above will have a greater rate of electrophoresis:

d) α-globulin;   e) albumen;   f) γ-globulin.

24. Gelatin with pI equal to 4,7 is placed into a solution where the H$^+$ion concentration is 100 times greater than in water. At electrophoresis in this solution gelatin molecules will move to:

a) a cathode;   b) an anode;   c) won't move.

25. Kinetic stability of colloidal solutions will decrease:

a) with the decrease of temperature;

b) with the increase of dispersion medium viscosity;

c) with the increase of temperature;

d) with the decrease of dispersion degree of dispersed phase particles.

26. Indicate the factors of aggregative stability of dispersed systems:
a) presence of ion shell of the particles;
b) presence of diffuse layer at the particles;
c) presence of solvation (hydrated) sphere of particles;
d) dispersity degree of the particles of a dispersed phase.

27. Mechanism of coagulation of colloidal solutions by electrolytes is connected to:
a) the compression of ion shell of the dispersed phase particles;
b) the increase of the thickness of the diffuse layer of particles;
c) the decrease of the value of zeta-potential of particles;
d) the increase of the value of particle charge.

28. Indicate which section of the curve of coagulation kinetics of the colloidal solution by electrolyte corresponds to manifest coagulation:
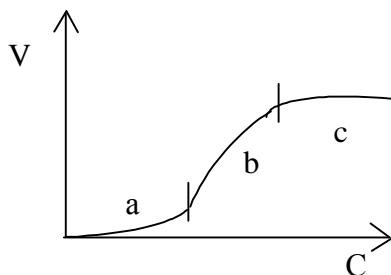
29. Indicate, which electrolyte we should take in excess at pouring together the solutions of $Ba(NO_3)_2$ and Na_2SO_4 to obtain the sol of barium sulfate with positively charged grains:
a) $Ba(NO_3)_2$;   b) Na_2SO_4;
and the coagulation of the above mentioned sol can be caused by the ions:
c) Cl^-;   d) Al^{3+}.

30. To cause coagulation we had to add 1 mL 0,005 M of potassium sulfate to 5 mL of sol of iron (III) hydroxide. Coagulation threshold of the given electrolyte in respect to the sol of $Fe(OH)_3$ is:
a) 0,001 mmol/L;   b) 0,001 mmol/L;
c) 1,0 mmol/L;   d) 1,0 mmol/L.

31. Indicate, which of the electrolytes will have the lowest coagulation threshold in respect to the sol of $Fe(OH)_3$ with positively charged grains:
a) KNO_3;   b) $MgSO_4$;   c) $AlCl_3$;   d) K_3PO_4.

32. Indicate, which charge sign the sol grains obtained by mixing of $CuSO_4$ and $(NH_4)_2S$ solutions have, if the coagulation thresholds of this

sol by electrolytes KCl, MgCl$_2$, AlCl$_3$ are the following: 50; 0,72; 0,093 mmol/L:

a) positive;   b) negative.

33. Calculate the protective action of gelatin in respect to the sol of aluminum hydroxide (g$_{gel}$/g), if to titrate 10 mL of the sol without gelatin before the appearance of feculence it takes 2,3 mL 0,01 M of K$_2$SO$_4$ solution and with gelatin — 5,0 mL of the same solution:

a) 0,005;   b) 0,0023;

c) 2,17;   d) 0,46.

34. To increase the stability of hydrosol we can add:

a) glucose;   b) protein;

c) dextrine;   d) calcium nitrate.

PROBLEMS

1. At interaction of the solutions of AICI$_3$ and NaOH we obtain the sol of Al(OH)$_3$ with positively charged grains. Determine, which electrolyte is taken in excess at its obtaining and write down the structure scheme of sol micelle.

2. A fresh precipitate of iron (III) hydroxide was treated with a small amount of hydrochloric acid which was not enough to dissolve it completely. At the same time the sol of Fe(OH)$_3$ is formed. Write the formula of micelle of iron hydroxide sol taking into account that in the electric field sol particles move to the cathode. What method has been used to obtain this sol?

3. Sol of iron sulfide is obtained by mixing of equal volumes of (NH$_4$)$_2$S and FeCl$_2$ solutions. In the electric field grains moved to the cathode. Will the concentration of the initial electrolyte solutions be the same? Write down the scheme of micelle structure and name its constituent parts.

4. Egg albumen with the isoelecric point equal to 4,8 is placed into the solution where the concentration of OH$^-$-ions is in 100 times less than in water. How is albumen charged in the solution? Which electrode: anode or cathode will the protein move to in the electric field?

5. Isoelectric points α-, β- and γ-globulins of blood are the following: 4,8; 5,2 and 6,4. Which charge do these proteins have in the blood of a healthy person? Which of these globulins has the greatest charge size? Explain the answer.

6. In the solution there are two proteins, the isoelectric points of which are 4,7 and 8,8. Which electrode will they move to at the electrophoresis in the buffer solution with the pH = 7,9. Which of the mentioned proteins (at other equal conditions) will move quicker to the corresponding electrode and why?

7. At the interaction of $AgNO_3$ and K_2CrO_4 solutions a sol of Ag_2CrO_4 with negatively charged grains is formed. Determine, which electrolyte is taken in excess at its obtaining and write down the scheme of micelle structure of this sol. Arrange in row of increasing of coagulation thresholds the following electrolytes: $MgSO_4$, $Al(NO_3)_3$ and $K_4[Fe(CN)_6]$ in relation to this sol.

8. Coagulation thresholds for KCl, $MgCl_2$, $AlCl_3$ electrolytes in relation to a sol are the following: 50, 0,72; 0,093 mmole/L. Which ions — cations or anions — of the mentioned salts cause the coagulation of the given sol? What charge sign do the sol grains have?

9. In three flasks we pour 100 mL of $Fe(OH)_3$ sol. To cause a manifest sol coagulation we had to add 10,5 mL 1 M of KCl solution into the first flask, 62,5 mL 0,01 M of Na_2SO_4 solution into the second one and 37,0 mL 0,001 M of Na_3PO_4 into the third one. Calculate the coagulation thresholds for these electrolytes in relation to the sol of iron (III) hydroxide and determine the charge sign of sol particles.

10. Calculate the rate and the electrophoretic particle mobility of colloidal platinum if zeta-potential of particles is 60 mV, the potential drop between the electrodes is 240 V, the distance between the electrodes is 20 cm, viscosity is $1 \cdot 10^3$ N·s/m^2, dielectric constant is 81. The form of sol particles is cylindrical.

STANDARDS OF PROBLEM SOLUTIONS

Problem 1. Sol of silver chromate is obtained by mixing of equal volumes of 0,005 M of K_2CrO_4 solution and 0,012 M of $BaCl_2$ solution. Write down the scheme of micelle structure and indicate the charge sign of its grains.

Solution. Make up a reaction equation which is the base for sol obtaining:
$$K_2CrO_4 + BaCl_2 \rightarrow BaCrO_4\downarrow + 2KCl$$
$$\text{As } C(BaCl_2) > C(K_2CrO_4),$$
then at equal volumes of solutions the amount of $BaCl_2$ is greater than the amount of K_2CrO_4 (0,012·V > 0,005·V). Consequently, $BaCl_2$ is in excess.
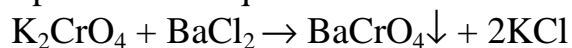
The aggregate of sol micelle is formed by microcrystalls of slightly soluble $BaCrO_4$. According to Panette-Faience rule the potential-determining ions relative to the aggregate substance and being present in excess in the solution will be adsorbed on the aggregate surface. In our case they are nBa^{2+} ions.

Counterions are those also being present in excess $2nCl^-$, which will be distributed in the following way: $(2n–x)Cl^-$ will be situated in the adsorption layer and all the rest Cl^- — in the diffuse layer.

The scheme of micelle structure of the sol will look like this:
$$\{[mBaCrO_4] \cdot nBa^{2+} \cdot (2n–x)Cl^-\}^{x+} \cdot xCl^-.$$
Micelle grain in the braces has a positive charge, i. e. charge sign of potential-determining ions Ba^{2+}.
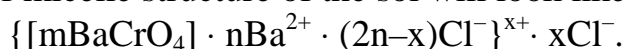
Problem 2. Grains of silver iodide sol obtained by mixing of $AgNO_3$ and KCl solutions have a negative charge. Which of the given electrolytes is taken in excess? Write the micelle formula.

Solution. Sol is obtained according to the following reaction equation:

$$AgNO_3 + KCl \rightarrow AgCl\downarrow + KNO_3,$$
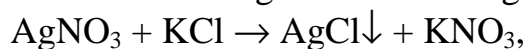
from which we can see that the aggregate is a slightly soluble silver iodide AgCl.

As the grain has a negative charge, then the potential-determining ions, according to Panette-Faience rule, will be negative ions being a part of the aggregate, i. e. Cl^--ions. Consequently, the solution of KCl containing these ions is taken in excess.

Micelle formula will be the following:

$$\{[mAgCl] \cdot nCl^- \cdot (n–x) \cdot K^+\}^{x-} \cdot xK^+.$$
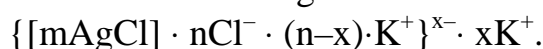
Problem 3. The particle charge of iron (III) hydroxide sol is positive. Which of the electrolytes — KCl, $Fe_2(SO_4)_3$, $CaCl_2$, $AlCl_3$ — will have the lowest coagulation threshold in relation to this sol?

Solution. As particles have a positive charge, then, according to Shultze-Gardi rule, sol coagulation can be caused by ions having an opposite charge sign, i. e. anions of electrolytes (Cl^- or SO_4^{2-}). And the greater is the charge size of ion-coagulant, the greater is the coagulating action of the electrolyte and the coagulation threshold is lower. Consequently, the lowest coagulation threshold will be at $Fe_2(SO_4)_3$, because the charge of sulfate-ion is greater than that of chloride-ion.

Problem 4. Electrolytes KCl, K_2SO_4, K_3PO_4 in relation to iron (III) hydroxide have the following coagulation thresholds: 7,1; 0,099 and 0,01 mmol/L. What charge sign do the sol particles have?

Solution. According to the problem the coagulation thresholds of these electrolytes KCl, K_2SO_4, K_3PO_4 are in the following ratio: $\gamma_1 : \gamma_2 : \gamma_3 = 7,1 : 0,099 : 0,01 = 740 : 10 : 1$.

This ratio is close to the theoretical ratio of coagulation thresholds (730 : 11 : 1). Consequently, the coagulation is caused by the ions *of the same sign but different charge size*. In our case these are Cl^-, SO_4^{2-}, PO_4^{3-}. As the coagulation is caused by anions, the charge sign of sol particles is positive.

Problem 5. Pepsin of digestive juice (pI = 2,0) is placed into a buffer solution in which the H^+-ion concentration is in 1000 times greater than in pure water. Which electrode will the protein move to at the electrophoresis in this solution?

Solution. Concentration of H^+-ions in water is 10^{-7} mol/L. Consequently, in the given solution $[H^+] = 10^{-7} \cdot 1000 = 10^{-4}$ mol/L. Hence, pH of the medium $= -\lg 10^{-4} = 4$.

As pH of the medium is greater pI $(4 > 2)$, the protein molecule in the given medium obtains a negative charge according to the following equation:

$$\overset{+}{H_3}N - \underset{\underset{R}{|}}{CH} - COO^- + OH^- \rightleftharpoons H_2N - \underset{\underset{R}{|}}{CH} - COO^- + H_2O$$
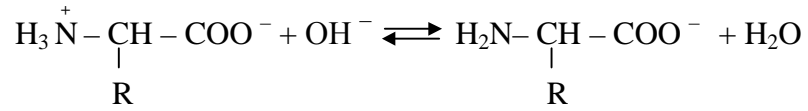
Protein, having a negative charge, in the electric field will move to the anode.

XIII. COARSELY DISPERSED SYSTEMS

MAIN QUESTIONS ON THE TOPIC

1. Classification and general properties of coarsely dispersed systems.
2. Suspension, its obtaining and properties. Pastes.
3. Emulsions, their classification, properties and methods of obtaining.
4. Emulsifiers, their nature and mechanism of action.
5. Methods of determining the type of emulsions.
6. Biological importance of emulsions.
7. Aerosols, their obtaining and properties. Powders.

EXPERIMENTAL WORKS

Work 1. The obtaining of emulsions and investigation of their properties.

Aim of the work: to learn to obtain stable emulsions and determine their type; to investigate the conversion of emulsion phases.

Reactants and devices: oil (liquid), water, 1 % solution of K_2CO_3 and $CaCl_2$, the solution of sudan (III), solution of methylene blue, a microscope, test-tubes, microscope slide.

Task 1. To obtain the emulsion by the method of dispersion.

Experiment 1. Obtaining of emulsion without emulsifier.

We pour 5 mL of distilled water in the test tube, add 5–6 drops of oil and shake it vigorously till the formation of white feculence. The test tube with the obtained emulsion is placed into a stand for further observations.

Experiment 2. Obtaining of the emulsion with emulsifier.

We pour 5 mL of distilled water in the test tube, add 5–6 drops of oil and 5–6 drops of 1 % solution of K_2CO_3. We shake the test tube vigorously till the formation of the milk-white emulsion. *We leave the test tube in the stand for other tasks.*

Using the results of the experiment 1 and 2 we can make a conclusion which of the obtained solutions is more stable and why. We confirm the conclusion by the description of the physical form of the obtained emulsions.

Task 2. To determine the emulsion type.

Experiment 3. Determination of the emulsion type by the method of dilution.

A. With the help of a glass stick an emulsion drop from experiment 2 and a drop of water are placed side by side on the microscope slide. The microscope slide should be bent so that the drops should contact. Then we write down the observed effect and on the basis of it we make conclusions about the emulsion type.

B. We pour 0,5 mL of oil, 5 drops of water and 5 drops of 1 % solution of CaCl$_2$ into the test tube. We shake it vigorously till the formation of the emulsion. A drop of the obtained emulsion and a drop of water are placed side by side on the microscope slide and bend it. Then we write down the effect and make a grounded conclusion about the emulsion type.

Experiment 4. Determination of emulsion type by the method of colouring.

We pour 3 drops of oil, 2 mL of distilled water, 2 drops of 1 % solution of K$_2$CO$_3$, into the test tube and shake it vigorously till the formation of the emulsion. Then we add one drop of the solutions of sudan (III) and methylene blue. After vigorous shaking of the test-tube for 1–2 minutes a drop of the obtained emulsion is placed on the microscope slide with a glass stick and is studied under the microscope. Make a sketch of the emulsion indicating the distribution of dyes and on the basis of it determine the type of the emulsion. *We conserve the emulsion to fulfill task 3.*

Task 3. To study the conversion of emulsion phases.

Experiment 5. We pour off a half of the emulsion obtained in experiment 4 into another test tube and add 3 drops of oil, 4 drops of CaCl$_2$ into it. After vigorous shaking of the test tube for 1–2 minutes we examine the drop of the obtained emulsion under the microscope. Make a sketch and determine the emulsion type.

On the basis of experiment 4 and 5 we make conclusions about the cause of change of emulsion type. The conclusion is confirmed by the corresponding reaction equations of the formation of hydrophilic emulsifier and its transformation into a hydrophobic one.

TEST SELF-CHECK

1. Indicate the properties which are characteristic of coarsely dispersed systems:
a) intensive Brownian motion of the dispersed phase particles;
b) opalescence;
c) thermodynamic instability;
d) sedimentation.

2. Indicate the coarsel dispersed systems with liquid dispersion medium:
a) suspensions;   b) dust;   c) emulsions;   d) fog.

3. Indicate the properties which are characteristic of suspensions but not of true solutions:
a) transparency;   b) thermodynamic stability;
c) heterogeneity;   d) turbidity.

4. Indicate the properties which are characteristic of aerosols:
a) low viscosity of the dispersion medium;
b) high viscosity o f the dispersion medium;
c) high rate of diffusion and sedimentation of the dispersed phase particles;
d) aggregative instability.

5. Indicate, which of the pairs of substances mentioned below at mixing can form an emulsion:
a) acetic acid and water;
b) anilin and water;
c) water and barium sulfate;
d) water and sunflower-seed oil.

6. Indicate, which of the following emulsions are concentrated:
a) emulsions of type I formed by mixing 5 mL of corn oil and 5 mL of water;
b) emulsions of type II formed by mixing 0,08 mL of water and 99,92 mL of oil;
c) emulsions of type II formed by mixing 0,055 mL of benzol and 79,945 mL of water;
d) emulsions of type I formed by mixing 40 mL of water and 60 mL of kerosene.

7. Type of the obtained emulsion depends first of all on:
a) the nature of dispersed phase and dispersion medium;
b) nature of stabilizer (emulsifier);
c) the concentration of dispersed phase particles;
d) the order of mixing of liquids forming the emulsion.

8. Choose the hydrophilic emulsifiers:
a) $R - COOK$;   b) $(R - COO)_2Ca$;
c) chalk powder;   d) caoutchouc.

9. Emulsion is obtained at shaking 5 mL of sunflower-seed oil and 10 mL of water in the presence of $CaCl_2$. Determine the type of this emulsion:
a) oil/water;   b) water/oil;
c) type I;   d) type II.

10. Determine, if the emulsion drop obtained in test 9 interflows with a drop of water:
a) yes;   b) no;
Indicate what will be the electric conductivity of the given emulsion compared to the electric conductivity of water:
c) higher;   d) lower.

11. When analyzing under the microscope a drop of the emulsion obtained at shaking 25 mL of corn oil and 10 mL of water in the presence of such dyes as methylene blue and sudan III we observe red drops on the blue background. Indicate, which substances could have been used as emulsifiers to obtain this emulsion:

a) cholesterol;　　　b) gelatin;　　c) graphite;　　d) chalk powder.

12. A medical product is a reverse emulsion (water/oil). This medicine is prescribed for:

a) the external use;　　　b) for the intravenous introduction.

PROBLEMS

1. This emulsion is obtained by mixing equal volumes of oil and water with the addition of K_2CO_3 solution. Determine the type of this emulsion and indicate, what emulsion type we would obtain in the presence of $CaCl_2$ solution.

2. This emulsion is obtained by shaking equal volumes of sunflower-seed oil and water in the presence of calcium chloride. Indicate, if the emulsion drop will combine with water drop. Explain the answer.

3. When shaking equal volumes of olive oil and water in the presence of an electrolyte we obtain a stable milk-white emulsion, the drops of which interflows with a water drop on the microscope slide. Indicate, which electrolyte — $CaCl_2$ or K_2CO_3 was taken to obtain this emulsion. Explain the answer.

4. This emulsion is obtained by shaking equal volumes of oil and water with the addition of emulsifier. This emulsion is mixed with the solution of methylene blue (a hydrophilic dye) and sudan III (hydrophobic red dye). Determine the types of the emulsifier and emulsion if under the microscope it can
be seen that the dispersion medium is coloured red and the dispersed phase is coloured blue.

STANDARDS OF PROBLEM SOLUTIONS

Problem 1. This emulsion is formed by mixing 25 mL of water and 75 mL of anilin in the presence of chalk powder. Will the obtained emulsion be concentrated?

Solution. As chalk powder is a hydrophilic emulsifier, we've obtained emulsion of type I, i. e. oil/water. The volume fraction of the dispersed phase (anilin) in the obtained emulsion is:

$$\varphi = \frac{V(\text{anilin})}{V(\text{anilin}) + V(\text{water})} = \frac{75}{75 + 25} = 0{,}75 \ (75\ \%).$$

Answer: the obtained emulsion is not concentrated but strongly concentrated as the volume fraction of the dispersed phase is greater than 74 %.

XIV. PHYSICO-CHEMISTRY OF SOLUTIONS OF BIOPOLYMERS

MAIN QUESTIONS ON THE TOPIC

1. The concept of a high-molecular compound (HMC). Their classification and chemical structure. The importance of biopolymers.

2. Formation and solution properties of HMC. Difference of HMC solutions from colloidal solutions. General properties of HMC solutions and colloidal solutions. Specific properties of HMC solutions.

3. Thermodynamics of the formation of HMC solutions.

4. Mechanism of swelling and dissolving of HMC. Limited and unlimited swelling. The influence of different factors on swelling and dissolving of HMC. The swelling degree. Medical-biological significance of swelling processes.

5. Stability of HMC solutions and the ways of extraction of biopolymers from their solutions. Denaturation.

6. Osmotic pressure of HMC solutions. Osmometric method of determining of HMC molar mass. Galler's equation.

7. Viscosity of HMC solutions. Viscosimetric method of determining of the relative molecular mass of HMC. Staudinger's equation. Mark-Hauwink-Kun's equation.

8. The significance of determining of viscosity for medical-biological investigations.

9. Proteins as polyelectrolytes. Methods of determining of isoelectric point of proteins.

EXPERIMENTAL WORKS

Work 1. Analysis of physical-chemical properties of biopolymers.

Aim of the work: to prove experimentally the dependence of the swelling degree of HMC on the nature of solvent and the pH of the medium; to learn to determine the isoelectric point of the protein; to study the influence of electrolytes on the protein solubility.

Task 1. To determine the swelling degree of rubber in water, benzine and turpentine.

We weigh three rubber pieces (each of the separately) and place the first one into the weighing bottle with water, the second — into the weighing bottle with benzene, the third — into the weighing bottle with turpentine. In 30 minutes we take the pieces out of the solvents, dry them with some filter paper

and weigh them once again. Then we calculate the swelling degree using the formula. The obtained data are written down in the form of the table.

| Solvent | Polymer mass | | Swelling degree |
	Initial	Swollen	
Water			
Turpentine			
Benzine			

Make the conclusions about the dependence of rubber swelling on the nature of the polymer and the solvent.

Task 2. To determine the swelling degree of gelatin at different values of pH of the medium.

Into dry graduated test tubes with the volume of 10 mL we introduce 0,5 mL of gelatin powder and fill in the test tubes till the upper marker with the following solutions: into the first one — 0,1 M of hydrochloric acid solution, into the second one — the buffer solution with the pH 4,7, into the third one — distilled water, into the fourth one — 0,1 M of sodium hydroxide solution. The contents of the test tubes we mix with a stick which should be washed after each agitation with distilled water. In 30 minutes we determine the volume of swollen gelatin and calculate the swelling degree using the formula. The obtained data are written down in the form of the table.

| System | pH of the medium | Volume of the polymer | | Swelling degree |
		Initial (V_0)	Swollen (V)	
0,1M of HCl solution				
$1 \cdot 10^{-5}$M of HCl solution				
Water				
$1 \cdot 10^{-5}$M of NaOH solution				
0,1M of NaOH solution				

Draw a diagram of the dependence of swelling degree on the pH of the medium and make conclusions about the influence of pH of the medium on the swelling of gelatin.

Task 3. To determine the isoelectric point of the protein.

In each of the five centrifugal test tubes we pour 1 mL of acetate buffer with the pH = 3,2; 4,1; 4,7; 5,3; 6,2. We add 0,5 mL of protein solution (gelatin) with its mass fraction ranging from 0,5 till 1 % and add 1 mL of acetone. The contents of the test tubes is carefully mixed, we notice the degree of turbidity of the test samples on the dark background and evaluate it qualitatively using a five-point scale. In case of a slightly visible turbidity we introduce 0,5 mL of acetone in each of the test tubes. The maximum of turbidity corresponds to the maximum coagulation of the protein which can be seen in the test tube with the solution, the pH of which is equal to pI of the protein.

For a more vivid detection of maximum protein coagulation we place the test tubes into the centrifuge and centrifugate them for 2–3 minutes at the speed of rotation 3000 turns/min. At the bottom of the test tubes we will see the precipitate. The supernatant is poured out by a quick overturn of the test tubes. Then we add 2 mL of biuret reactant (mixture of solutions of copper sulphate and sodium-potassium tartrate) to the precipitate. The intensity of the violet colouring in the test samples is proportional to the amount of the precipitated protein. The intensity of colouring is evaluated visually using a five-point scale or measure the optical density of solutions with the help of a photocalorimeter (we use a cuvette with the layer thickness of 10 mm and a yellow light filter). The results should be written down in the table using the following sample:

pH	3,2	4,1	4,7	5,3	6,2
Degree of turbidity					
The intensity of colouring (using a five-point scale or measuring the adsorption (A)					

On the basis of the fulfilled work we determine the isoelectric point of gelatin.

Task 4. To carry out the precipitation of gelatin from the solution by the method of salting-out.

To the protein solution in the test tube we add a saturated solution of ammonia sulphate till the precipitation of the protein. Then, adding water into the test tube we obtain complete dissolution of the precipitate. In the conclusions we analyze the mechanisms explaining the protein precipitation and its dissolution.

Work 2. Determination of the relative molecular mass of polygluchin by the viscosimetric method.

Aim of the work: to determine the relative molecular mass of polygluchin by the viscosimetric method.

Devices and reactants: a viscosimeter, a stop-watch, solutions of polygluchin with its mass tractions 0,03, 0,04, 0,05, 0,06 respectively.

The essence of the work is concluded in the precise determination of time of outflow of equal volumes of pure solvent (water) and the investigated solutions in viscosimeter. On the basis of experimental and calculated data we determine the relative molecular mass of polygluchin.

Polygluchin is the product of acid hydrolysis of native dextran ($C_6H_{10}O_5)_n$ which is a polysaccharide of bacterial origin. The solution of polygluchin with its mass fraction 6 % and relative molecular mass ranging from 40 000 till 60 000 thousand in a physiological solution of sodium chloride is used as blood substitutes.
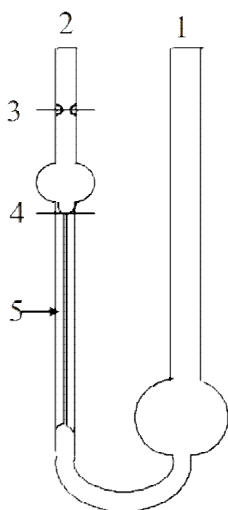
Fig. 8. Osvald's viscosimeter

The order of work performance is the following. A dried Ostwald's viscosimeter (fig. 8) is placed strictly vertically in a water bath at definite temperature. In a wide elbow (1) of the viscosimeter we pour 10 mL of `distilled water (solvent). With the help of a rubber syringe we transfer the water into a narrow elbow (2) at 1–2 cm higher than the upper mark (3) and let the water pass freely into the wide elbow of the viscosimeter. As soon as the water level lowers till the upper mark, we switch on the stop-watch. When the water level lowers till the bottom mark (4), we switch off the stop-watch and write down the time of water outflow through a capillary (5). The measurement should be repeated not less than 3 times. Then water is poured out through a wide elbow and the viscosimeter is washed out by the most diluted solution of polygluchin. We determine the time of polygluchin solution outflow through the viscosimeter capillary beginning with the solution with the lowest concentration. We should take the measurements for each solution not less than 3 times. For the calculations we take the average outflow time, calculated from three measurements.

We calculate the relative, specific and reduced viscosites of solutions using the formulas. We draw a dependence diagram of $\eta_{sp.}/C$ on concentration C. The segment severed by the line on the axis of ordinate corresponds to the characteristic viscosity $[\eta]$.

We calculate the relative molecular mass of polygluchin substituting the found value $[\eta]$ in Mark-Hauwink-Kun equation. For aqueous solutions of polygluchin the constants K and α are $9,66 \cdot 10^{-2}$ cm^3/g and 0,5 respectively.

All the results of the measurements and calculations are written down in the table.

C, g/cm^3	Outflow time, s				h$_{relat.}$	h$_{sp.}$	h$_{reduc.}$ cm^3/g
	t$_1$	t$_2$	t$_3$	T$_{aver.}$			

In the conclusion we should mark the possibility of application of polygluchin solution as blood substitute based on the found value of the relative molecular mass.

TEST SELF-CHECK

1. Indicate, which HMC are biopolymers:
a) proteins;   b) starch;   c) natural rubber;   d) glycogen.

2. Indicate the factors that can influence the charge of a protein molecule:
a) hydrogen H^+ ion concentration in the solution;
b) number of carboxylic and amine groups;
c) nature of the solvent;
d) ionicity of functional groups.

3. In the isoelectric point the protein has the minimum values of:
a) electrophoretic mobility;
b) total charge of macromolecules;
c) hydration degree;
d) swelling degree.

4. Protein solution in the isoelectric point has the maximum values of:
a) osmotic pressure;
b) viscosity;
c) coagulation rate;
d) gelatinization rate.

5. Indicate the properties which are common for both colloidal solutions and HMC solutions:
a) a small value of osmotic pressure;
b) homogeneity;
c) solutions are formed spontaneously;
d) light diffusion.

6. The process of HMC formation is accompanied by:
a) limited swelling;
b) unlimited swelling;
c) the decrease of the Gibbs free energy;
d) the increase of the Gibbs free energy.

7. Indicate, which factors increase the swelling degree:
a) addition of sodium sulphate into the protein solution;
b) addition of sodium rodanide into the protein solution;
c) decrease of temperature;
d) change of the pH of the solution in relation to pI of the protein.

8. Indicate, which factors can speed up the process of gelatinization of polymer solution:
a) increase of temperature;
b) decrease of temperature;
c) increase of polymer concentration in the solution;
d) addition of potassium iodide into the polymer solution.

9. Indicate, which methods are used for purification and extraction of proteins:
a) denaturation;   b) salting-out;
c) electrophoresis;   d) gel-filtration.

10. Indicate the factors which influence the value of HMC solution viscosity:
a) temperature;
b) HMC concentration;
c) relative molecular mass of the polymer;
d) form and volume of polymer macromolecule.

11. Indicate the methods of determining of relative molecular mass of HMC:
a) cryoscopic;
c) method of light diffusion;
b) osmometric;
d) viscosimetric.

12. Indicate, which equations are used for determining of relative molecular masses of polymers:
a) Vant-Hoff;
b) Galler;
c) Staudinger;
d) Mark-Hauwink-Kun.

13. Indicate the assumption made by Staudinger while deducing his equation:
a) linear macromolcules behave as rough rods in the solution;
b) macromolcules are rolled up into a ball in the solution;
c) flexible macromolcules in the solution are close to a sphere by form;
d) reduced viscosity doesn't depend on HMC solution concentration.

14. Indicate the factors that influence the characteristic viscosity:
a) nature of the polymer;
b) relative molecular mass of the polymer;
c) polymer concentration in the solution;
d) rate of reciprocal movement of liquid layers.

15. Indicate, which viscosity helps to judge about conformational changes of a HMC macromolcule:
a) specific;   b) reduced;
c) characteristic;   d) relative.

PROBLEMS AND EXERCISES

1. The time of water outflow in Ostavald's viscosimeter is 50 s and in the polygluchin solution with its mass fraction 2 % is 72 sec. Calculate the reduced viscosity of the solution.

Answer: 22 cm³/g

2. The time of outflow of polymer solution with its mass fraction 1 % in the viscosimeter is twice greater than that of a pure solvent. Calculate the relative molecular mass of the polymer if the constant K in Staudinger's equation is $2 \cdot 10^{-3}$ cm³/g (polymer macromolecules in the solution are in the form of rigid sticks).

Answer: 50 000

3. Calculate the relative molecular mass of myoglobin protein if its characteristic value in an aqueous solution is 3,1 cm³/g. Constants K and α in the equation of Mark-Hauwink-Kun are equal to $2,32 \cdot 10^{-2}$ cm³/g and 0,5.

Answer: 17850

4. pI of three proteins are 3,8, 4,6 and 5,1. Which of the proteins will swell most of all and which — least of all in a buffer solution with the pH 4,7? Explain the answer.

5. In which of the solutions of the following salts — NaI, Na_2SO_4, NaCNS, NaCl — at their equal molar concentration the swelling degree of biopolymers is the greatest and in which — the smallest? Why?

6. Five samples of protein with pI 5,1 were poured over with the solutions with the pH 1,0; 4,0; 5,0; 6,5; 8,0. Draw a graphic dependence of the swelling degree of the given protein on the pH of the medium.

7. Myosin of the muscles with pI 5,0 is placed into the solution with the concentration of H^+-ions is 100 times greater than in pure water. What charge will the protein have in this solution?

8. Which electrode will the protein particles move to at the electrophoresis with pI 4,0 and the pH of the solution is 5,0?

9. Pepsin of the digestive juice with pI 2,0 is dissolved in the buffer solutions with the pH 1,9: 4,75 and 9,24. At what value of the pH the protein stability is the greatest?

10. In four different test tubes, each containing 10 mL of gelatin we added equal volumes 1 M of CH_3COONa, NaCNS, Na_2SO_4 and $NaNO_3$ solutions. Explain, which of the electrolytes will have the greatest salting-out action and which — the lowest?

11. In five test tubes, each containing 1 mL of ammonia buffer with the pH 8,2: 9,1; 9,7; 10,3 and 11,2, we added 1 mL of protein solution with the isolelectric point 9,2 and the same volume of acetone. In which of the test tubes shall we see the maximum protein coagulation and why?

12. In four different test tubes containing equal volume of protein solution we added equal volumes of KI, CH_3COOK, KCNS and K_2SO_4 solutions with

the same concentration. In which of the test tubes the gelatinization of the pro-
protein solution will be the quickest?

STANDARDS OF PROBLEM SOLUTIONS

Problem 1. Calculate the relative molecular mass of polyvinyl alcohol
if the constants in the equation of Mark-Hauwink-Kun for the solution of
polyvinyl alcohol in water are equal to: $K = 4,53 \cdot 10^{-5}$ cm^3/g, $\alpha = 0,74$;
characteristic viscosity $[\eta] = 0,15$ cm^3/g.

We have:	*Solution*
$K = 4,53 \cdot 10^{-5}$ cm^3/g	Let's substitute the values K, α and $[\eta]$ in the equation
$\alpha = 0,74$	$[\eta] = KM^{\alpha}$
$[\eta] = 0,15$ cm^3/g.	$0,15 = 4,53 \cdot 10^{-5} \cdot M^{0,74}$ or
M – ?	

$$M^{0,74} = \frac{0,15}{4,53} \cdot 10^5 = 3,311 \cdot 10^{-2} \cdot 10^5 = 3,311 \cdot 10^3, \text{ i. e. } M^{0,74} = 3311.$$

Let's find the logarithm of this equality: $0,74 \lg M = \lg 3311$. The value
$\lg 3311$ can be found in the table of logarithms.

$\lg M = \dfrac{3,5198}{0,74} = 4,757$, i. e. $\lg M = 4,757$. In the table of antilogarithms we find

the value M. It is 57 150.

Answer: 57 150

Problem 2. Staudinger's constants in the equation of Mark-Hauwink-Kun
for amylosis solution in dimethyl-sulphoxide are : $K = 3,06 \cdot 10^{-2}$ cm^3/g,
$\alpha = 0,68$. Using the following experimental data calculate the relative
molecular mass of amylose.

C, g/100cm^3	Relative viscosity
0,15	1,09
0,20	1,12
0,30	1,19
0,40	1,26
0,50	1,34

We have:

$K = 3,06 \cdot 10^{-2}$ cm^3/g

$\alpha = 0,64$

_____

$M_{amylase} - ?$

Solution

Let's calculate the specific and reduced viscosities by the formulas ($\eta_{spec.} = \eta_{red..} - 1$; $\eta_{red.} = \dfrac{\eta_{spec.}}{C}$). Then we draw a dependence diagram of $\eta_{red.}/C$ on the concentration. By extrapolation of the line on the axis of ordinate we get a segment corresponding to the limited value of the reduced viscosity $[\eta]$. The results of the calculations are written down in the form of a table.

C, g/cm^3	h$_{relative}$	h$_{specific}$	h$_{specific}$/C, cm^3/g	[h], cm^3/g
0,0015	1,09	0,09	60	
0,0020	1,12	0,12	60	
0,0030	1,19	0,19	63	56
0,0040	1,26	0,26	65	
0,0050	1,34	0,34	68	

We calculate the relative molecular mass of amylose using the equation $[\eta] = KM^\alpha$ 56 = $3,06 \cdot 10^{-2}$ M^{0,64} or M^{0,64} = $56/3,06 \cdot 10^{-2}$ = 1830.

We find the logarithm of the last equality: 0,64 lgM = lg1830. The value lg1830 is found in the table of logarithms. (lg = 1830 = 3,2625) Hence, lgM = 3,2625/0,64 or lgM = 5,098. Using the table of antilogarithms we find the value M. M = 125300.

Answer: 125 300

Problem 3. Calculate the relative molcular mass of the myoglobin protein if the constants in the equation of Mark-Hauwink-Kun for the solution of the given protein in water are: $K = 2,32 \cdot 10^{-2}$ cm^3/g, $\alpha = 0,5$; characteristic value $[\eta] = 3,1$ cm^3/g.

We have:

$K = 2,32 \cdot 10^{-2}$ cm^3/g

$\alpha = 0,5$

$[\eta] = 3,1$ cm^3/g.

_____

$M_{myoglobin} - ?$

Solution

For the calculations we use the equation $[\eta] = KM^\alpha$

$3,1 = 2,32 \cdot 10^{-2}$ M^{0,5}

$M^{0,5} = \dfrac{3,1 \cdot 10^2}{2,32} = 1,336 \cdot 10^2 = 133,6$, i. e. M^{0,5} = 133,6.

We raise both parts of the equality to the second power and get the relative molecular mass:

$$M = (133,6)^2 = 17849.$$

Answer: 17 849

Problem 4. In four test-tubes with 1 M of CH_3COOK, KCNS, K_2SO_4 and KCl solutions we placed 0,5 g of a polar polymer. In which of the electrolyte

solutions the swelling of the polymer will be the greatest and in which — the smallest? Why?

Solution. The influence of electrolyte ions on HMC swelling is connected to their ability to hydrate. According to their ability to decrease the swelling the anions are arranged in the row (at the same cation):

$$CNS^- > J^- > Br^- > NO_3^- > Cl^- > CH_3COO^- > SO_4^{2-}$$
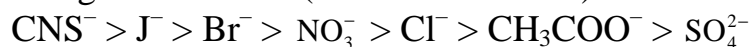
As CNS^- ions increase the swelling and SO_4^{2-} ions hinder it, the swelling is the greatest in KCNS solution and in the solution of K_2SO_4 it is minimal.

Problem 5. The isoelectric point of pepsin of digestive juice is at pH 2,0. What charge sign will the enzyme macromolecules have when placed in the buffer solution with the pH 8,5.

We have:	Solution
ИЭТ = 2,0 pH = 8,5	When pepsin is placed in the solution with the pH of the medium greater than pI, aminoacid dissociation is inhibited and enzyme macromolecules get a negative charge.

Charge sign of pepsin
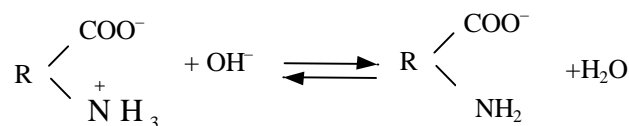
Problem 6. Gelatin is placed in the buffer solution with the pH 3. Determine the charge sign of gelatin particles, if the isoelectric point of protein is 4,7.

We have:	Solution
pI = 4,7 pH = 3	When gelatin is placed in the solution with the pH of the medium less than pI, the carboxylic group dissociation is inhibited and gelatin particles get a positive charge:

Charge sign of gelatin?
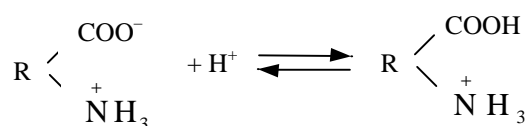
Problem 7. The isoelectric point of albumin protein is 4,9. The protein is placed in the buffer mixture with the hydrogen ion concentration 10^{-6} mol/L. Determine the direction of movement of protein particles at electrophoresis.

We have:	Solution
pI = 4,9 $[H^+] = 10^{-6}$ mol/L	If hydrogen ion concentration is 10^{-6} mol/L, then the pH of the medium is 6 because $pH = -lg[H^+]$.

Direction of
particles ?

As the pH of the medium > pI (6 > 4,9), then according to the following equation the protein gets a negative charge and at electrophoresis moves to the anode:

$$\overset{+}{H_3N} - \underset{\underset{R}{|}}{CH} - COO^- + OH^- \rightleftarrows H_2N - \underset{\underset{R}{|}}{CH} - COO^- + H_2O$$
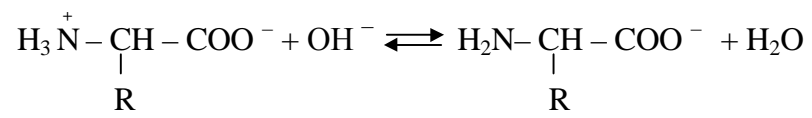
ANSWERS

Chapter I. Elements of Chemical Thermodynamics

1	2	3	4	5	6	7	8	9	10
b	a, b	a, d	a, b, c	a, d	c	c	b, c	a	a, b, c
11	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
c	c	a, c, d	a, d	d	b	d	c	a, c	b

Chapter II. Elements of Chemical Kinetics

1	2	3	4	5	6	7	8	9	10
a, d	c	a	b	b	b	d	b	b	d

Chapter IV. Colligative properties of solutions

1	2	3	4	5	6	7	8	9	10
b, c, d	c	c	e	b, d	a, b, c	b, c	c	a	d

Chapter V. Electrolyte solutions. Acidity and basicity of aqueous solutions. pH.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
c	b	a, b	a	a, b, d	a, b, c	a	b	c	a	d	a	a	a	a, d

Chapter VI. Buffer solutions

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
a, b	d, e	b, c, d	a, c, d	a, d	b, c, d	a	c	b	a, d	d	b,e	c	a	c

Chapter VII. Heterogeneous equilibria

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
a, b, d	a, c	a, b, d	d	d	c, d	b, d	b	b	c	b, c	a, b, c	b	c	c

Chapter VIII. The electrical conductivity of electrolyte solutions. Conductometry

1	2	3	4	5	6	7	8	9	10
a, b, c, d	a, c	c	a, d	b, d	d	b	d	d	d

Chapter IX. Potentiometry

1	2	3	4	5	6	7	8	9	10
a, c, d	c	d	b, c	d	b	d	a	c	c

Chapter X. Physico-chemictry of surface phenomena. Surface energy and surface tension

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
c, d	a, b, d	a, c, d	a	b	b	a	b, c	a, c	a, d	c	a, b, d	a, b	a, b	b

16	17	18	19	20	21	22	23	24	25
a	a, c	a, b, c, d	c	a, b, c, d	b	b	d	b, c	a, b

Chapter XI. Chromatography

1	2	3	4	5	6	7	8	9	10
a, b, d	a, b, c	b	a, b, c, d	b, c	b	b	b	c	b

Chapter XII. Physico-chemistry of Dispersion systems

1	2	3	4	5	6	7	8	9A	9B
b, c	a, b, c, d	b, c	c	a, b, c, d	d	a, c	a	d	c

9C	9D	9E	9F	9G	9H	9I	10	11	12
d	b	c	a	a	c	d	a	a, c, d	b, d

13	14	15	16	17	18	19	20	21	22
a	a, d	a	b, d	a, b, c, d	a, c, d	a, e	a, b, c	b, d	c

23	24	25	26	27	28	29	30	31	32	33	34
a, b, f	b	a, d	a, b, c	a,c	b, c	a,c	b, d	d	b	c	b, c

Chapter XIII. Coarsely dispersed systems

1	2	3	4	5	6	7	8	9	10	11	12
c, d	a, c	c, d	a, c, d	b, d	a, d	b	a, c	b, d	b, d	b, d	a

Chapter XIV. Physico-chemistry of solutions of biopolymers

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
a, c	a, b, c, d	a, b, c, d	c, d	a, d	b, c	b, d	b, c	b, c, d	a, b, c	a, b, c, d	a, b, d	a	a, b	c

PERIODIC TABLE OF THE ELEMENTS

1A 1	2A 2		3B 3	4B 4	5B 5	6B 6	7B 7	8B 8	8B 9	8B 10	1B 11	2B 12	3A 13	4A 14	5A 15	6A 16	7A 17	8A 18
1 H Hydrogen 1.00794																		2 He Helium 4.00260
3 Li Lithium 6.941	4 Be Beryllium 9.01218												5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.0067	8 O Oxygen 15.9994	9 F Fluorine 18.998403	10 Ne Neon 20.1797
11 Na Sodium 22.98977	12 Mg Magnesium 24.305												13 Al Aluminum 26.98154	14 Si Silicon 28.0855	15 P Phosphorus 30.97376	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078		21 Sc Scandium 44.9559	22 Ti Titanium 47.88	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.9380	26 Fe Iron 55.847	27 Co Cobalt 58.9332	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.61	33 As Arsenic 74.9216	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62		39 Y Yttrium 88.9059	40 Zr Zirconium 91.224	41 Nb Niobium 92.9064	42 Mo Molybdenum 95.94	43 Tc Technetium [98]	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.9055	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.82	50 Sn Tin 118.710	51 Sb Antimony 121.757	52 Te Tellurium 127.60	53 I Iodine 126.9045	54 Xe Xenon 131.29
55 Cs Cesium 132.9054	56 Ba Barium 137.327	57 *La Lanthanum 138.9055	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.2	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.9665	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.9804	84 Po Polonium [209]	85 At Astatine [210]	86 Rn Radon [222]
87 Fr Francium [223]	88 Ra Radium 226.0254	89 †Ac Actinium 227.0278	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [263]	107 Bh Bohrium [262]	108 Hs Hassium [265]	109 Mt Meitnerium [268]	110 [269]	111 [272]	112 [277]							

*Lanthanide Series

58 Ce Cerium 140.115	59 Pr Praseodymium 140.9077	60 Nd Neodymium 144.24	61 Pm Promethium [145]	62 Sm Samarium 150.36	63 Eu Europium 151.965	64 Gd Gadolinium 157.25	65 Tb Terbium 158.9254	66 Dy Dysprosium 162.50	67 Ho Holmium 164.9303	68 Er Erbium 167.26	69 Tm Thulium 168.9342	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967

† Actinide Series

90 Th Thorium 232.0381	91 Pa Protactinium 231.0359	92 U Uranium 238.0289	93 Np Neptunium 237.048	94 Pu Plutonium [244]	95 Am Americium [243]	96 Cm Curium [247]	97 Bk Berkelium [247]	98 Cf Californium [251]	99 Es Einsteinium [252]	100 Fm Fermium [257]	101 Md Mendelevium [258]	102 No Nobelium [259]	103 Lr Lawrencium [260]

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MOLAR MASS OF INORGANIC SUBSTANCES

	OH^-	O^{2-}	Cl^-	Br^-	I^-	S^{2-}	SO_3^{2-}	SO_4^{2-}	NO_3^-	PO_4^{3-}	CO_3^{2-}	SiO_3^{2-}
H^+	18	18	36.5	81	128	34	82	98	63	98	62	78
NH_4^+	35	-	53.5	98	145	68	116	132	80	149	96	112
Na^+	40	62	58.5	103	150	78	126	142	85	164	106	122
K^+	56	94	74.5	119	166	110	158	174	101	212	138	154
Mg^{2+}	58	40	95	184	278	56	104	120	148	262	84	100
Ca^{2+}	74	56	111	200	294	72	120	136	164	310	100	116
Ba^{2+}	171	153	208	297	391	169	217	233	261	601	197	213
Al^{3+}	78	102	133.5	267	408	150	294	342	213	122	234	282
Cr^{3+}	103	152	158.5	292	433	200	344	392	238	147	284	332
Zn^{2+}	99	81	136	225	319	97	145	161	189	385	125	141
Mn^{2+}	89	71	126	215	309	87	135	151	179	355	115	131
Fe^{2+}	90	72	127	216	310	88	136	152	180	358	116	132
Fe^{3+}	107	160	162.5	296	437	208	352	400	242	151	292	340
Cu^{2+}	98	80	135	224	318	96	144	160	188	382	124	140
Ag^+	125	232	143.5	188	235	248	294	312	170	419	276	292
Pb^{2+}	241	223	278	367	461	239	287	303	331	811	267	283

SOLUBLE OF INORGANIC SUBSTANCES IN WATER

Cations	Anions												
	OH^-	F^-	Cl^-	Br^-	I^-	S^{2-}	SO_3^{2-}	SO_4^{2-}	NO_3^-	PO_4^{3-}	CO_3^{2-}	SiO_3^{2-}	CH_3COO^-
NH_4^+	—	s	s	s	s	—	s	s	s	s	s	—	s
Na^+ K^+	s	s	s	s	s	s	s	s	s	s	s	s	s
Mg^{2+}	L	in	s	s	s	s	in	s	s	in	in	in	s
Ca^{2+}	L	in	s	s	s	L	in	L	s	in	in	in	s
Ba^{2+}	s	L	s	s	s	s	in	in	s	in	in	in	s
Al^{3+}	in	L	s	s	s	—	—	s	s	in	—	in	L
Cr^{3+}	in	in	s	s	s	—	—	s	s	in	—	in	s
Zn^{2+}	in	L	s	s	s	in	in	s	s	in	in	in	s
Mn^{2+}	in	L	s	s	s	in	in	s	s	in	in	in	s
Co^{2+} Ni^{2+}	in	s	s	s	s	in	in	s	s	in	in	in	s
Fe^{2+}	in	in	s	s	s	in	in	s	s	in	in	in	s
Fe^{3+}	in	in	s	s	s	—	—	s	s	in	in	in	s
Cd^{2+}	in	s	s	s	s	in	in	s	s	in	in	in	s
Hg^{2+}	—	—	s	L	n	in	in	s	s	in	in	—	s
Cu^{2+}	in	in	s	s	s	in	in	s	s	in	in	in	s
Ag^+	—	s	in	in	in	in	in	L	s	in	in	in	s
Sn^{2+}	in	s	sp	s	s	in	—	s	—	in	—	—	s
Pb^{2+}	in	in	L	L	in	in	in	in	s	in	in	in	s

where **s** – Soluble

in – Insoluble

L – Soluble, but it is low.

Standard Enthalpies of Formation ΔH_f^0, Entropies S^0 and Gibbs Energies of Formation ΔG_f^0 of Selected Substances at 298K

Substance	ΔH_f^0 kJ/mol	S^0 kJ/mol	ΔG_f^0 kJ/mol
C(graphite)	0	5.7	0
CH_4 (g)	−74.9	186.2	−50.8
C_2H_6 (g)	−89.7	229.5	−32.9
C_2H_4 (g)	52.28	219.4	68.11
C_6H_6 (l)	82.9	269.2	129.7
C_2H_5OH (l)	−277.5	160.7	−174.8
$C_6H_{12}O_6$ (glucose)	−1260	288.9	−919.5
CO (g)	−110.5	197.5	−137.1
CO_2 (g)	−393.5	213.7	−394.4
H_2 (g)	0	130.5	0
H_2O (g)	−241.8	188.7	−228.6
H_2O (l)	−285.8	70.1	−237.3
H_2S (g)	−21.0	205.7	−33.8
H_2SO_4 (l)	−821.3	156.9	−690.1
Cl_2 (g)	0	223.07	0
N_2 (g)	0	191.5	0
NH_3 (g)	−46.11	192.45	−16.45
NO (g)	90.37	210.6	86.57
NO_2 (g)	33.89	240.4	51.84
HCl (g)	−92.307	186.91	−95.3
NH_4Cl (s)	−314.43	94.6	−202.87
$(NH_4)_2SO_4$ (s)	−1179.0	220.3	−900.8
S_2 (g)	129.0	228.18	—
S (s)	0	31.6	0
SO_2 (g)	−296.9	248.1	−300.2
SO_3 (g)	−395.2	256.1	−370.4
OH^- (aq)	−228.9	—	—
O_2 (g)	0	205.0	0
O_3 (g)	142.3	238.8	163.2
Pb (s)	0	64.81	0
$PbCl_2$ (s)	−359.41	136.0	−314.1
CCl_4 (l)	−139.3	214.4	−68.2

CONTENTS