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**ЛАБОРАТОРНЫЕ РАБОТЫ  
И ДОМАШНИЕ ЗАДАНИЯ  
ПО ОБЩЕЙ ХИМИИ**

**LABORATORY WORKS  
AND HOME TASKS  
IN GENERAL CHEMISTRY**

Практикум

*4-е издание*



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## **PREFACE**

This book contains home tasks and laboratory works for every lesson in “General chemistry” for students who study dentistry (D) and general medicine (M), as well as for every lesson in the first term of the “General and inorganic chemistry” for students who study pharmacy (P). Each laboratory work in this book is designated by corresponding symbols (D, M or P) showing which students should perform it.

All the test questions must be answered directly in the book. All the problems and chemical equations must also be written by students as a part of their homework.

The data acquired during laboratory works must be written in empty spaces of the protocols.

The authors are looking forward to receive any feedback from colleagues and students regarding the content of this book.

# CHAPTER 1

## INTRODUCTION TO THE TITRATION ANALYSIS

The titration analysis is based on the exact determination of the amount of the reactant used for the reaction with the defined substance. This kind of analysis is named *volumetric* because the most wide-spread practical way of quantitative determination is the exact measurement of the volume of the solution with known concentration which was used for the reaction with the defined substance.

Quantitative study of a solution means that we want to find out 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 that we can make. First, let us examine the most common units of concentration: percent by mass (mass fraction or mass percentage), mole fraction (percent by mole or mole percentage), molarity, molality, normality, titer.

**Percent by mass, mass percentage, mass fraction ( $\omega$ ).** The percent by mass (also called the percent by weight or the weight percent) is defined as

$$\omega = \text{mass fraction of a solute} = m(\text{solute}) / m(\text{solution}).$$

The percent by mass shows how many grams of a solute are there in 100 grams of a 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<sub>2</sub>O).

The mass fraction has no units because it is a ratio of two similar quantities, while mass percentage is measured in percent (%).

**Mole fraction, mole percentage, percent by mole ( $\chi$ ).** The mole fraction of a component in a solution, say, component A, is written as  $\chi_A$  and is defined as

$$\chi_A = \text{mole fraction of a solute} = n(\text{solute}) / n(\text{solution}).$$

The mole fraction has no units, since it is a ratio of two similar quantities, mole percentage is measured in percent (%).

**Molality ( $C_m$ ).** Molality is the number of moles of a solute (S) dissolved in 1 kg (1000 g) of a solvent.

$$C_m = n(\text{solute}) / m(\text{solvent}).$$

Thus molality is measured in mol/kg.

For example, to prepare a 1 mol/kg sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) 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 higher or lower than 1000 mL. It is also possible, but very unlikely, that the final volume could be equal to exactly 1000 mL.

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

$$C = n(\text{solute}) / V(\text{solution}).$$

Thus, molarity is measured in mol/L or M.

**Titer (T).** Titer is defined as a mass of a solute in 1 milliliter of a solution; that is,

$$T = m(\text{solute}) / V(\text{solution}).$$

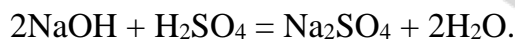
Thus, titer is measured in g/mL.

**Normality (C<sub>N</sub>).** Normality is defined as the number of moles of the equivalent of a solute (n<sub>eq</sub>) in 1 liter of a solution; that is,

$$C_N = n_{\text{eq}}(\text{solute}) / V(\text{solution}).$$

Thus, normality is measured in mol/L or N.

In chemical reactions the molar ratio of reacting substances is not always 1:1. It is determined by stoichiometric coefficients. For example, in the reaction written below the molar ratio between base and acid will be 2:1.



The coefficients can be replaced by equivalence factors: actually, for the base you need to divide number one (1) by the coefficient before acid, for the acid you need to divide number one by the coefficient before base. So, in the abovementioned reaction the equivalence factor for NaOH is 1, while for H<sub>2</sub>SO<sub>4</sub> it is equal to 1/2.

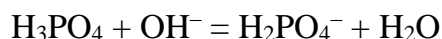
As substances behave differently in the complex formation reactions, chemists avoid using the notion of equivalent for them and use only molar masses instead. Thus, in this textbook the notion of equivalent will be used only for the substances taking part in oxidation-reduction and acid-base reactions.

Let's consider the following reactions:

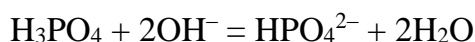
- a)  $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$ ; d)  $2\text{H}^+ + \text{S}^{2-} = \text{H}_2\text{S}$ ;  
b)  $\text{H}^+ + \text{NH}_3 = \text{NH}_4^+$ ; e)  $3\text{OH}^- + \text{H}_3\text{PO}_4 = \text{PO}_4^{3-} + 3\text{H}_2\text{O}$ ;  
c)  $\text{H}_2^0 - 2\text{e}^- = 2\text{H}^+$ ; f)  $\text{Al}^{3+} + 3\text{e}^- = \text{Al}^0$ .

In acid-base reactions (a, b, d, e) 1 OH<sup>-</sup> ion, 1 NH<sub>3</sub> molecule, 1/2 S<sup>2-</sup> ion, 1/3 of H<sub>3</sub>PO<sub>4</sub> molecule are equivalent to one H<sup>+</sup> ion. In oxidation-reduction reactions (c, f) 1/2 of H<sub>2</sub> molecule, 1/3 of Al<sup>3+</sup> ion are equivalent to one electron. The enumerated particles are considered as equivalents of substances taking part in these reactions.

From another point of view *the equivalent is some real or hypothetical particle which interacts with the carrier of one elementary charge in the ion exchange or oxidation-reduction reactions.* For example, in the reaction



the H<sub>3</sub>PO<sub>4</sub> molecule is the same as the equivalent because it reacts with just one OH<sup>-</sup> ion. But in the reaction



the H<sub>3</sub>PO<sub>4</sub> molecule reacts with two OH<sup>-</sup> ions, thus the equivalent of phosphoric acid is equal to 1/2 of H<sub>3</sub>PO<sub>4</sub> molecule.

Equivalence factor  $f_{\text{eq}}(X)$  is the number indicating which part of the real particle of substance  $X$  is equivalent to one hydrogen ion in the given acid-base reaction or to one electron in the oxidation-reduction reaction. This value is dimensionless and is calculated on the basis of stoichiometric coefficients of a definite reaction.

Equivalence factor is often written as  $1/z$  ratio, where  $z$  is the overall charge of ions from a molecule taking part in the given exchange reaction or the number of electrons which are gained or lost by a molecule (an atom) of the substance in oxidation-reduction reaction;  $z$  is always a positive integer and the equivalence factor is less or equal to 1:

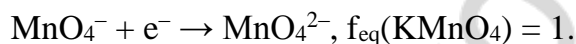
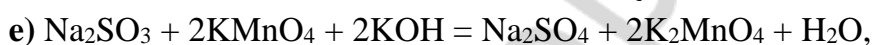
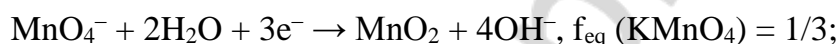
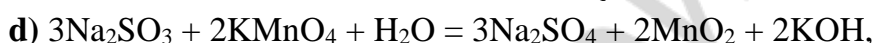
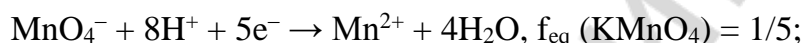
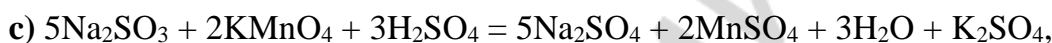
$$f_{\text{eq}}(X) = 1/z \leq 1.$$

Equivalence factor of the same substance can have different values in different reactions. Let's consider this using the following examples.

In acid-base reactions  $\text{Na}_2\text{CO}_3$  can be neutralized by an acid until the formation of an acidic salt or until the emission of  $\text{CO}_2$ :



In oxidation-reduction reactions  $\text{KMnO}_4$  is always an oxidizing agent:



The oxidation state of manganese in the products of the reaction (c-e) is determined by the pH level of the solution: the lower the acidity (and the higher the pH) of the medium, the weaker the oxidizing ability of permanganate.

As we can see from these examples equivalent and equivalence factor are different for different reactions of the same substance.

### THE LAW OF EQUIVALENCE

A chemical *equivalent* is a real or hypothetical particle of a substance which can interact with one hydrogen atom (proton) 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:  $M(\text{H}_2\text{O}) = 18$  g/mol,

$M(\text{HCl}) = 36.5$  g/mol,

$M(\text{NaOH}) = 40$  g/mol.

The mass of one mole of chemical equivalent is defined as equivalent molar mass ( $M_{\text{eq}}$ ), g/mol.

The equivalent molar mass relates to the molar mass of a substance as follows:

$M_{\text{eq}} = M \cdot f_{\text{eq}}$ , where  $f_{\text{eq}}$  is the factor of equivalence.

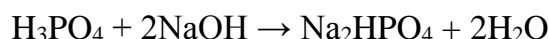
For substances involved in ion exchange reactions the equivalent factors can be calculated according to following formulas:

For acids:  $f_{\text{eq}} = 1 / \text{the number of H}^+$  ions

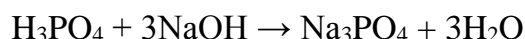
For monoprotic (monobasic) acids (HCl, HNO<sub>3</sub> and others) the equivalence factor is equal to one ( $f_{\text{eq}} = 1$ ); for diprotic (dibasic) acids (H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>CO<sub>3</sub> and others) the equivalence factor may take the values of 1 and 1/2 ( $f_{\text{eq}} = 1$  and 1/2); for triprotic (tribasic) acids (H<sub>3</sub>PO<sub>4</sub>) the equivalence factor takes the values 1, 1/2 or 1/3 ( $f_{\text{eq}} = 1, 1/2$  or 1/3).

For example:  $\text{H}_3\text{PO}_4 + \text{NaOH} \rightarrow \text{NaH}_2\text{PO}_4 + \text{H}_2\text{O}$

$$f_{\text{eq}} = 1 \quad f_{\text{eq}} = 1$$



$$f_{\text{eq}} = 1/2 \quad f_{\text{eq}} = 1$$



$$f_{\text{eq}} = 1/3 \quad f_{\text{eq}} = 1$$

For bases:  $f_{\text{eq}} = 1 / \text{the number of OH}^-$  ions.

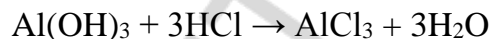
For bases with a single hydroxyl group — monoacidic bases (NaOH, KOH and others) the equivalence factor is equal to one ( $f_{\text{eq}} = 1$ ); for bases with two hydroxyl groups — diacidic bases (Ca(OH)<sub>2</sub>, Ba(OH)<sub>2</sub> and others) the equivalence factor may take the values 1 or 1/2 ( $f_{\text{eq}} = 1$  or 1/2); for bases with three hydroxyl groups — triacidic bases (Al(OH)<sub>3</sub> and others) the equivalence factor takes the values 1, 1/2 or 1/3 ( $f_{\text{eq}} = 1, 1/2$  or 1/3).

For example:  $\text{Al(OH)}_3 + \text{HCl} \rightarrow \text{Al(OH)}_2\text{Cl} + \text{H}_2\text{O}$

$$f_{\text{eq}} = 1 \quad f_{\text{eq}} = 1$$



$$f_{\text{eq}} = 1/2 \quad f_{\text{eq}} = 1$$



$$f_{\text{eq}} = 1/3 \quad f_{\text{eq}} = 1$$

For salts:  $f_{\text{eq}} = 1 / (\text{the number of metal cations} \times \text{the charge of the cation})$ .

For example:  $f_{\text{eq}}(\text{NaCl}) = 1$ ,  $f_{\text{eq}}(\text{Na}_2\text{SO}_4) = 1/2$ ,  $f_{\text{eq}}(\text{Ca}_3(\text{PO}_4)_2) = 1/6$ .

The equivalence factor for oxidizing and reducing agents in redox reactions is calculated as:  $f_{\text{eq}} = 1/Z$ , where Z is an amount of electrons gained or lost by one mole of a substance.

For example:  $\text{MnO}_2 + 4\text{HCl} \rightarrow \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$

$$f_{\text{eq}} = 1/2 \quad f_{\text{eq}} = 1$$

oxidizer: $\text{Mn}^{+4} + 2\bar{e} \rightarrow \text{Mn}^{+2}$	2	2	1
reducer: $2\text{Cl}^- - 2\bar{e} \rightarrow \text{Cl}_2^0$	2		1

The law of equivalence: the masses of chemical substances which are involved in a reaction and the masses of its products are directly proportional to their equivalent molar masses.

For a hypothetical reaction  $aA + bB = cC + dD$  the amounts of equivalents for reactants and products are identical:

$$n_{\text{eq}}(\text{A}) = n_{\text{eq}}(\text{B}) = n_{\text{eq}}(\text{C}) = n_{\text{eq}}(\text{D}),$$

where  $n_{\text{eq}}$  is the amount of an equivalent, mol.

The unit of the amount of equivalent is the mole. Along with the molar mass of the substance  $M(\text{X})$  we widely use the *molar mass of the equivalent of a substance*  $M_{\text{eq}}(\text{X})$ .

Molar mass of the equivalent of a substance  $\text{X}$  is the mass of one mole of the equivalents of this substance. It is equal to the product of equivalence factor of the substance (in the given reaction) and the molar mass of the substance  $\text{X}$ :

$$M_{\text{eq}}(\text{X}) = f_{\text{eq}}(\text{X}) \cdot M(\text{X}).$$

To illustrate the ways of writing down the calculation using the given formula let's calculate the molar masses of  $\text{Na}_2\text{CO}_3$  and  $\text{KMnO}_4$  equivalents in the reactions mentioned above:

- a)  $M_{\text{eq}}(\text{Na}_2\text{CO}_3) = 1 \cdot 106.0 = 106.0 \text{ g/mol};$
- b)  $M_{\text{eq}}(\text{Na}_2\text{CO}_3) = 1/2 \cdot 106.0 = 53.0 \text{ g/mol};$
- c)  $M_{\text{eq}}(\text{KMnO}_4) = 1/5 \cdot 158.0 = 31.60 \text{ g/mol};$
- d)  $M_{\text{eq}}(\text{KMnO}_4) = 1/3 \cdot 158.0 = 52.67 \text{ g/mol};$
- e)  $M_{\text{eq}}(\text{KMnO}_4) = 1 \cdot 158.0 = 158.0 \text{ g/mol}.$

The amount of equivalent is the number of moles of the equivalent of a substance for a given reaction.

$$n_{\text{eq}}(\text{X}) = m(\text{X})/M(\text{X}) \cdot f_{\text{eq}}(\text{X}).$$

For example, it is necessary to calculate the amount of the equivalent of sodium carbonate with the mass of 5.3 g in the reaction with  $\text{HCl}$  (see reaction equation b). Then, according to the equation written above we have:

$$n_{\text{eq}}(\text{Na}_2\text{CO}_3) = m(\text{Na}_2\text{CO}_3) / M(\text{Na}_2\text{CO}_3) \cdot f_{\text{eq}}(\text{Na}_2\text{CO}_3) = 5.3/106 \cdot 1/2 = 0.1 \text{ mole}.$$

On the basis of the two equations it is easy to get the equation for calculation the mass of the substance from the amount of the equivalent and the equivalence factor of the substance:

$$m(\text{X}) = n_{\text{eq}}(\text{X}) \cdot f_{\text{eq}}(\text{X}) \cdot M(\text{X}).$$

In the titration analysis both molar concentration (molarity) and molar concentration of the equivalent (normality) are used to express the content of the solution.

Molar concentration is equal to the amount of substance (in moles) in one liter of the solution. It is defined as  $C(\text{X})$  sometimes as  $C$  and is calculated as a ratio of the amount of the dissolved substance  $\text{X}$  and the volume  $V$  of the solution in liters:

$$C(\text{X}) = n(\text{X}) / V = m(\text{X}) / M(\text{X}) \cdot V.$$

When referring to the molar concentration we can use, for example, the following forms: a solution with molar concentration of  $\text{HCl}$  equal to 0.1 mol/L or  $C(\text{HCl}) = 0.1 \text{ mol/L}$ ; 0.1 M  $\text{HCl}$  solution (a decimolar solution of  $\text{HCl}$ ). M is the abbreviation of mol/L. All these forms mean that one liter of the solution contains 0.1 mole of  $\text{HCl}$ .



Similarly, 0.01M is a centimolar solution, 0.001 M is a millimolar solution and 0.015M is a fifteen-millimolar solution.

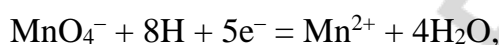
The molar concentration of the equivalent (normality) is equal to the amount of the equivalent (in moles) in one liter of the solution. It is defined as  $C_N$  (sometimes N) and is calculated as a ratio of the amount of the equivalent of the dissolved substance X to the volume of the solution in liters:

$$C_N(X) = n_{\text{eq}}(X) / V.$$

Having expressed in the denominator the molar mass of the equivalent through the molar mass of the substance and its equivalence factor in the reaction we get:

$$C_N(X) = m(X) / (f_{\text{eq}}(X) \cdot M(X) \cdot V).$$

When writing down the molar concentration of the equivalent, for example, for  $\text{KMnO}_4$  in half-reaction:



we use such forms:  $C_N(\text{KMnO}_4) = 0.1 \text{ mol/L}$  or 0.1N  $\text{KMnO}_4$  solution (decinormal solution of  $\text{KMnO}_4$ ).

The quantitative connection between the molar concentration of the substance and the molar concentration of the equivalent is the following:

$$C(X) / C_N(X) = f_{\text{eq}}(X) \quad \text{or} \quad C_N(X) = C(X)/f_{\text{eq}}(X).$$

The amount of substance X and, consequently, its mass in the volume V (L) of the solution can be calculated both on the basis of molar concentration of the solution and on the basis of its normality.

The solution with the precisely known concentration is called a **titrant** and the process of its slow addition to the analyzed probe is called **titration**. The moment of the completion the reaction between the titrant and the defined substance is called stoichiometric point (or equivalence point).

We can use the law of equivalents for the reactions taking place in stoichiometric relations. That's why if the reaction is conducted up to the completion, the amount of equivalents of one reactant is equal to the amount of equivalents of another reactant.

For example, at the equivalence point of titration of  $\text{H}_2\text{SO}_4$  solution by base solution ( $\text{H}_2\text{SO}_4 + 2\text{NaOH} = \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$ ) the equivalent amounts of  $\text{H}_2\text{SO}_4$  and NaOH are equal:

$$n_{\text{eq}}(\text{H}_2\text{SO}_4) = n_{\text{eq}}(\text{NaOH}).$$

If the normalities and the volumes of two solutions at which the equivalence point is reached are known, we can calculate the equivalent amounts of the acid and the base:

$$n_{\text{eq}}(\text{H}_2\text{SO}_4) = C_N(\text{H}_2\text{SO}_4) \cdot V(\text{H}_2\text{SO}_4),$$

$$n_{\text{eq}}(\text{NaOH}) = C_N(\text{NaOH}) \cdot V(\text{NaOH}),$$

where  $C_N$  (normality) mol/L; V (volume) L.

Combining these two equations together we get the most important expression of the equivalence principle for the titration analysis:

$$C_N(\text{H}_2\text{SO}_4) \cdot V(\text{H}_2\text{SO}_4) = C_N(\text{NaOH}) \cdot V(\text{NaOH}).$$

In general, for any kind of titration this ratio is the following:

$$C_N(X) \cdot V(X) = C_N(T) \cdot V(T),$$

where  $C_N(X)$  and  $C_N(T)$  are the normalities of the solution of the analyzed substance X and the titrant T;  $V(X)$  and  $V(T)$  are the volumes of the analyzed solution and the titrant respectively.

If we know the volume of the analyzed solution, then it is possible to calculate its normality:

$$C_N(X) = C_N(T) \cdot V(T) / V(X).$$

Having calculated the normality of the analyzed solution using the titration results we can determine the mass of the substance in any volume of the solution:

$$m(X) = C_N(X) \cdot M(X) \cdot f_{eq}(X) \cdot V.$$

To conduct successfully the titration analysis you should:

1) know the exact concentration of the titrant (the notion “exact concentration” is relative as we have to deal with approximate experimental data; “exact concentration” is the one having 4 significant digits in numerical expression (e. g.: 1.523; 0.01264; 0.3000).

2) know the exact solution volumes of the reacting substances, i. e. of the titrant and the analyzed solution.

3) choose correctly the reaction and the method of the equivalence point determination.

Let's consider in detail the tasks mentioned above.

The solution of exact concentration can be prepared only in that case when the **primary standard**, i. e. the substance which is used for the solution preparation corresponds to the whole number of requirements: it has a well-known composition that is described perfectly by its own chemical formula; it is stable at storage, easily dissolved in water, it has a big molar mass (the higher the molar mass of the given initial substance, the smaller the mistake at weighing). Only several substances can entirely or partially satisfy these requirements and that's why the number of substances suitable for primary standards is so limited.

In some cases we have to use less pure substances instead of primary standards. The grade of such secondary standard must be established by a very careful analysis.

The usage of special standard solutions or portions (in glass ampoules or plastic containers) produced industrially reduces the time loss for the preparation of standard solutions. Standards contain the amount of the substance known exactly. Dissolving or dilution of the standard solution in a volumetric flask allows getting the standard solution immediately.

To measure liquid volumes accurate within 0.01–0.03 ml it is necessary to use special measuring devices: a volumetric flask, a pipette, a burette.

We cannot use any chemical reaction for the titration analysis. There are some specific requirements for reactions suitable for titration analysis.

1) the reaction must be almost irreversible;

2) the reaction must go directly according to the chemical equation without formation of subproducts;

3) the reaction must occur rather quickly;

4) there must be a method for determination of the end of the reaction, i. e. of the equivalence point fixation.

It is obvious that in the titration analysis only the reactions in which the equivalence point is easily detected are used. This can happen in case of the appearance or disappearance of the colored products, precipitation and so on. The problem of choice of the method of the equivalence point fixation is always solved with regard to the particular technique.

If the reaction doesn't satisfy at least one of the mentioned requirements, it can't be used in the titration analysis.

### TITRATION TECHNIQUES

Titration method is a technique which allows the usage of a certain chemical reaction in practice. If the chosen reaction corresponds to all requirements mentioned above we should use direct titration.

*Direct titration* consists in the drop by drop addition of the titrant directly into the solution of analyzed substance until the equivalence point.

$$C_N(X) \cdot V(X) = C_N(T) \cdot V(T).$$

If the reaction, which is necessary for determination, doesn't correspond to all the requirements then this circumstance can be eliminated by using special titration methods — back and indirect titration.

*Back (reverse) titration* is the addition of the exactly known excess of the titrant to the analyzed substance with the further determination of its remainder (which hasn't reacted) with the help of the second titrant. In this case the equivalence principle establishes the ratio between the amounts of equivalents of the three substances and is written down in the formula:

$$C_N(T_1) \cdot V(T_1) = C_N(X) \cdot V(X) + C_N(T_2) \cdot V(T_2).$$

The first (added in excess) and the second titrant are indicated by 1 and 2 subscripts.

The name "indirect titration" is not the best but it has rooted in analytical practice. You can meet the synonyms "remainder titration" or "determination with two titrants" and so on.

*Indirect (substitute) titration* is the addition of the excess of the reactant to the solution of the analyzed substance with further determination of the amount of the product of the first reaction by the way of titration.

In case of the indirect titration the equivalence principle is written down in the same way as for the direct titration.

### TITRATION CURVES

The titration curve is the graph that shows the dependence of a certain characteristic of the solution (which reflects the degree of the completeness of the reaction) on the volume of

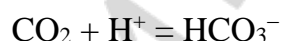
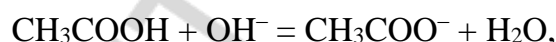
the added titrant (or the titration degree). For example, for the reactions of acid-base interaction such characteristic is the pH level.

The experimental titration curves result from measuring some system characteristic in the process of titration (optical density, strength of diffusion, etc.) which changes depending on the volume of the added titrant. In the corresponding graph we mark the amount of the added titrant on the X-axis and the values of the quantities which change directly with the decrease in concentration of one of the reactants or with the increase of concentration of one of the products (electrical conductivity, optical density, etc.) on the Y-axis. The values on the Y-axis may be converted to the logarithmic scale if it is helpful. For example, pH is the negative decimal logarithm of the concentration of  $H^+$  ions.

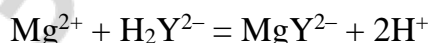
### METHODS OF THE TITRATION ANALYSIS

In titration analysis we use the reactions of different types (acid-base interaction, redox reaction, complexation reactions, etc.). Separate titration methods have been named according to the type of the main reaction occurring during titration or the name of the titrant (e. g. in argentometric methods the titrant is  $AgNO_3$  solution, in permanganometric methods —  $KMnO_4$  solution and so on). According to the method of equivalence point fixation we can classify titration methods into those using color indicators, potentiometry, conductometry, photometry, etc. When classifying the methods on basis of the type of the main reaction occurring at titration it is possible to separate them into the following methods of titration analysis:

1) *methods of acid-base titration* based on the reactions of proton transfer:



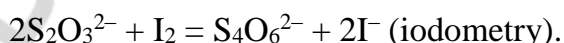
2) *complexation methods* which use the reaction of coordination compound formation (chelometry):



3) *precipitation methods* based on the reactions of the formation of insoluble compounds:



4) *oxidation-reduction titration methods* based on oxidation-reduction reactions (oxidimetry):



#### Main questions of the topic:

1. Titration analysis, its methods and tasks.
2. Classification of titration analysis methods.

3. Requirements to the methods used in titration analysis.
4. Standard solutions. Primary standards and requirements made to them.
5. Calculations in titration analysis.
6. The importance of titration analysis in medical and biological research and clinical analysis.

### LABORATORY WORK (M, D, P)

#### “MEASURING VOLUMES OF SOLUTIONS IN THE TITRATION ANALYSIS”

**The aim of the work:** to study the measures used in the titration analysis and to get some skills of the work with them.

**Tasks:**

- 1) to learn the names of laboratory equipment;
- 2) to fill in the graduated flask with water till the mark;
- 3) to measure 10.00 mL by Mohr's pipette;
- 4) to measure: a) 6.2 mL; b) 3.7 mL of water by graduated pipettes;
- 5) to measure the volume of one drop pouring out from a burette.

**Laboratory ware:** graduated flasks, Mohr's pipettes, graduated pipettes, rubber pumps, burettes, funnels; beaker, cylinders, measuring test-tubes, microburette.

To make precise measurements of volumes in titration analysis we use graduated flasks, pipettes and burettes. For approximately precise measurements we use cylinders, beakers and graduated test-tubes.

When measuring the volume you should remember that the experimenter's eye should be at the same level with the meniscus of the measured liquid while the volume of the transparent liquids should be measured on the lower edge of the meniscus and the volume of the intensively coloured ones, e. g.  $\text{KMnO}_4$  solution, on the upper edge.

The labware used in a chemical analysis must be chemically pure. Before the work the pipettes and the burettes should be washed carefully with a detergent, e. g. with a “chrompic” mixture ( $\text{K}_2\text{Cr}_2\text{O}_7$  solution in concentrated  $\text{H}_2\text{SO}_4$ ), with an alcoholic solution of an alkali or with an aqueous soda solution pouring it in the burette with the help of a funnel and filling the pipette with a rubber pump. Then they are carefully washed with tap and distilled water. Having persuaded in the fact that water wets inner walls with an even layer (if droplets still form on the walls, the washing should be continued) a pipette or a burette is washed 2–3 times with the same solution which we will use to fill in the burette or which we will take with the pipette.

#### Graduated flasks

Graduated flasks are used for the preparation of standard solutions and for the dilution of the solutions till the indicated volumes. These are the flat-bottom flasks with a long narrow neck and a circular mark applied on it; the nominal volume of the solution which

can be prepared (or measured) with the help of the given flask at the definite temperature is written on its wall. Graduated flasks can be of different capacity ranging from 25 mL to 2 L.

Dry weights (including the content of standards) are introduced into the graduated flask through a funnel and afterwards the rest of the substance is washing away from the funnel and ampoule with distilled water. Last steps of the solution preparation (when you need to fill the flask exactly until the mark) should be done carefully and the last drops of the liquid should be added with the help of an eye pipette. If the liquid appears to be poured above the mark then the primary standard solution is considered to be spoiled (you will have to try to make it again).

After the filling of the flask till the mark (the lower edge of the meniscus should be on the same level as the mark) the flask is closed with a cork and the solution is carefully mixed by the way of turning the flask with its bottom up.

### Pipettes

Pipettes are used for measuring precise volumes of the analyzed solution or the solution of the reactant. They can be of two types: graduated (with the volume of 1, 2, 5, 10, 25 mL) and simple ones with just one mark which are usually called Mohr's pipettes. Mohr's pipettes are narrow tubes with a wider part in the middle for the increase of the volume; the upper narrow part has a circular mark and an inscription about the volume of the liquid which can be measured with the help of the given pipette at a definite temperature. In biochemical research and clinical analysis we often use both graduated and ungraduated micropipettes of 0.1 and 0.2 ml. To store the pipettes a special support stand is used.

To take water with a pipette you should do the following:

1. Put the pipette till the bottom of a container with water and with the help of a rubber pump fill in the pipette with water up to 3–4 cm above the mark.

2. Remove the rubber pump and immediately close the upper end of the pipette with the index finger. Having taken the pipette out of the water you should remove the water drops from its outer surface with a piece of filter paper.

3. Having reduced the tension of the index finger and having lifted it a little let the liquid flow slowly into the container with water till the moment when the lower meniscus of water reaches the mark of the pipette. Once again close the end of the pipette and carefully carry it into a prepared vessel (e. g. a titration flask).

4. Keeping the pipette vertically remove the finger and let the water flow freely. When all the liquid flows away from Mohr's pipette place the lower part of the pipette to the wall or the bottom of the flask and wait for some 20–30 seconds for the rest of the liquid to flow out.

**Notice.** *Blowing out the rest of the liquid from the end of pipette is prohibited as its volume is taken into the account during their calibration and it isn't included into the volume of the liquid measured by the pipette!*

When working with the graduated pipettes in order to prevent mistakes you should determine carefully the type of the pipette. With the help of the pipettes of the first type the maximum volume appropriate for this pipette is measured in the same way as by Mohr's pipette. Pipettes of the second type have ungraduated nonworking volume and you can work with it only in the region of the graduated scale.

### Burettes

Usually laboratory burettes are looking like graduated glass tubes. In their lower end there is a glass tap or a rubber tube with a ball shutter or with a clamp. Burettes are used for measuring the volume of the titrant. To measure it carefully one should add it to the flask with analyzed solution in the drop by drop manner. A single drop can be poured from the burette by the way of pushing the rubber tube around the ball. This action leads to the deformation of rubber tube and the appearance of a narrow open space between the ball and the tube. So, liquid will find its way out. Your purpose is to make just a single drop (stop pushing when the drop has already poured). According to their capacity the burettes can be classified into macroburettes (10–100 ml) and microburettes (1–5 ml). You should titrate with the burette very slowly at constant mixing of the solution in the flask for titration in order to find out which drop of the titrant will be the final one. To reach high precision of the titration you should be able to make correct measurements on the burette and to know the volume of one drop pouring out of the burette. In order not to make a mistake you should begin each titration from the zero point on the burette scale and watch carefully for the air bubbles (they must not be created in the burette especially below the ball or a clamp).

To fill the burette with water you should do following:

1) fill in the burette with water through a funnel lifting it a little in order to enhance the process;

2) remove the air bubbles from the lower part of the burette; in order to do it you should bend the rubber tube in the U-form (the end of the burette should look up) and push the ball until air bubbles will escape the burette;

3) add some water into the burette, remove the funnel and set the water level at the zero mark of the scale (the lower edge of the meniscus should be on the mark);

4) pour out 100 water drops from the burette and determine their volume  $V(100)$  according to the burette scale in milliliters; determine the volume  $V(100)$  two more times and calculate the arithmetic average of the three obtained results;

Volume 1 \_\_\_\_\_ Volume 2 \_\_\_\_\_ Volume 3 \_\_\_\_\_

The average volume: \_\_\_\_\_

5) calculate the volume of one water drop pouring out from the burette dividing the obtained average volume of 100 drops  $V(100)$  by 100.

Schematically draw flask for titration, volumetric flask, graduated pipette, Mohr's pipette and burette.

The conclusion on the results of the laboratory work can be formulated as follows: "The rules of working with apparatus for measuring volumes used at titration analysis are learned. The volume of one water drop pouring out of the burette is determined; it is equal to ..... ml."

**TEST SELF-CHECK**  
(with a single correct answer)

**1. Indicate the unit of quantity of a substance:**

a) kilogram; b) molar mass; c) cubic centimeter; d) mole; e) liter.

**2. 100 mL of human blood contain 55.8 mg of iron. How many iron atoms does it contain?**

a)  $6 \cdot 10^{26}$ ; b) 1; c)  $6 \cdot 10^{17}$ ; d)  $10^{-3}$ ; e)  $6 \cdot 10^{20}$ .

**3. What value can the equivalence factor of  $\text{HNO}_3$  take in acid-base ion-exchange reactions?**

a) 1/2; b) 1/5; c) 1; d) 1/3; e) 1/8.

**4. Which amount of equivalents is there in 98 g of phosphoric acid (in the reaction of neutral salt formation)?**

a) 3; b) 2; c) 1/2; d) 1; e) 1/3.

**5. In which of the reactions given below the equivalence factor of  $\text{H}_2\text{SO}_4$  is equal to 1/8?**

- a)  $\text{H}_2\text{SO}_4 + 2\text{KOH} = \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O}$ ;
- b)  $\text{H}_2\text{SO}_4 + \text{KOH} = \text{KHSO}_4 + \text{H}_2\text{O}$ ;
- c)  $\text{H}_2\text{SO}_4 + \text{Cu} \rightarrow \text{CuSO}_4 + \text{SO}_2 + \text{H}_2\text{O}$ ;
- d)  $\text{H}_2\text{SO}_4 + \text{Zn} \rightarrow \text{ZnSO}_4 + \text{S} + \text{H}_2\text{O}$ ;
- e)  $\text{H}_2\text{SO}_4 + \text{HI} \rightarrow \text{I}_2 + \text{H}_2\text{S} + \text{H}_2\text{O}$ .

**6. Mass fraction of NaCl in a (physiologic) saline solution is 0.85 %. What mass of NaCl should be taken to prepare 1 kg of the saline?**

a) 85 g; b) 8.5 g; c) 0.85 g; d) 85 mg; e) 850 mg.



7. As a primary standard at titration analysis the following substance can be used:

- a)  $\text{KMnO}_4$ ; b)  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ; c)  $\text{I}_2$ ; d)  $\text{H}_2\text{SO}_4$ ; e)  $\text{NaOH}$ .

8. How many milliliters of 0.1 M solution of  $\text{AgNO}_3$  will be used to titrate 5 mL of 0.2M solution of  $\text{NaCl}$ ?

- a) 5 mL; b) 1 mL; c) 2.5 mL; d) 10 mL; e) 100 mL.

### PROBLEMS

1. How many grams of iodine and how many milliliters of ethyl alcohol (density is 0.80 g/mL) should be taken to prepare 200 g of iodine solution with the mass fraction of iodine equal to 5 %.

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*The answer:*

2. How many grams of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and milliliters of water should be taken to prepare 400 mL of the solution with the mass fraction of  $\text{Na}_2\text{SO}_4$  equal to 10 % (density is 1.065 g/mL)?

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*The answer:*

3. There is a solution with the mass fraction of  $\text{H}_2\text{SO}_4$  equal to 10 % (density is 1.07 g/mL). Calculate: a) molar concentration; b) normality if  $f_{\text{eq}}(\text{H}_2\text{SO}_4) = 1/2$ ; c) mole fraction of  $\text{H}_2\text{SO}_4$  in this solution.

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*The answer:*

4. 250 g of  $\text{NaOH}$  were dissolved in 1 kg of water. The density of the obtained solution is 1.219 g/mL. Calculate: a) the mass fraction of  $\text{NaOH}$ ; b) molar concentration; c) normality; d) molality of the alkaline solution.

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*The answer:*

5. 500 mL of the solution are obtained from 1.59 g of  $\text{Na}_2\text{CO}_3$  to carry out the reaction  $\text{Na}_2\text{CO}_3 + \text{HCl} = \text{NaHCO}_3 + \text{NaCl}$ . Calculate the normality of the solution.

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*The answer:*

6. Which volume of the solution with the mass percentage of  $\text{H}_2\text{SO}_4$  equal to 80 % (density 1.75 g/mL) should be taken to prepare 500 mL 0.1 N solution? ( $f_{\text{eq}}(\text{H}_2\text{SO}_4) = 1/2$ ).

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*The answer:*

7. To titrate 20.00 mL of 0.1985M of HCl solution we used 16.33 mL of the KOH solution. Calculate the molar concentration of the alkaline solution.

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*The answer:*

8. To titrate 0.2156 g of a chemically pure sodium carbonate  $\text{Na}_2\text{CO}_3$  we used 22.35 mL of sulphuric acid solution. Calculate the normality of the acid solution taking into account that  $f_{\text{eq}}(\text{Na}_2\text{CO}_3) = f_{\text{eq}}(\text{H}_2\text{SO}_4) = 1/2$ .

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*The answer:*

9. What mass of  $\text{KMnO}_4$  should be taken to prepare 2L of the solution with  $C_N(\text{KMnO}_4) = 0.02 \text{ mol/L}$ ? ( $f_{\text{eq}}(\text{KMnO}_4) = 1/5$ ).

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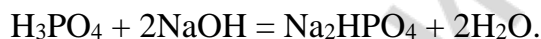
*The answer:*

## STANDARDS OF PROBLEM SOLUTIONS

### Preparation of solutions and the ways to express their composition

**Problem 1.** There is a solution with the mass fraction of  $\text{H}_3\text{PO}_4$  equal to 40 % (density 1.254 g/mL). Calculate the molar concentration and normality of this solution in neutralization reaction that goes up until the formation of sodium hydrogen phosphate.

*Solution.* Let's write the reaction equation:



Let's find the mass of the dissolved substance  $m(\text{H}_3\text{PO}_4)$  in the definite volume of the solution ( $V(\text{solution})$ ). Mass fraction of  $\text{H}_3\text{PO}_4$  is 40 %. This means that in 100 g of the solution there are 40 g of  $\text{H}_3\text{PO}_4$ . Knowing the density of the solution ( $\rho = 1.254 \text{ g/mL}$ ) we can find the volume of 100 g of the solution in litres:

$$V_{(\text{solution})} = 100 / (\rho \cdot 1000) = 1 / (\rho \cdot 10) = 1 / (10 \cdot 1.254) = 0.08 \text{ (L)}.$$

Molar concentration and normality (or molar concentration of the equivalent) of phosphoric acid solution can be calculated using respective formulas. Molar concentration:

$$C(\text{H}_3\text{PO}_4) = m(\text{H}_3\text{PO}_4) / M(\text{H}_3\text{PO}_4) \cdot V = 40 / 98 \cdot 0.08 = 5.10 \text{ (mol/L)}.$$

Normality of the solution:

$$C_N = m(\text{H}_3\text{PO}_4) / M(\text{H}_3\text{PO}_4) \cdot f_{\text{eqv}}(\text{H}_3\text{PO}_4) \cdot V = 40 / 98 \cdot 1/2 \cdot 0.08 = 10.20 \text{ (mol/L)}$$

or

$$C_N = C / f_{\text{eqv}} = 5.1 / 1/2 = 10.2 \text{ (mol/L)}.$$

*The answer:* 5.1 mol/L; 10.2 mol/L.

**Problem 2.** Mass percentage of acetic acid in the aqueous solution is 60 %. Determine the molarity and the mole fraction of the acid in the solution.

*Solution.* Knowing the mass fraction of  $\text{CH}_3\text{COOH}$  in the solution, we determine that in 100 g of the solution there are 60 g of  $\text{CH}_3\text{COOH}$  and 40 g of water. Let's find the amount of the dissolved acid and the solvent:

$$n(\text{CH}_3\text{COOH}) = m(\text{CH}_3\text{COOH}) / M(\text{CH}_3\text{COOH}) = 60 / 60 = 1 \text{ (mol)},$$

$$n(\text{H}_2\text{O}) = m(\text{H}_2\text{O}) / M(\text{H}_2\text{O}) = 40 / 18 = 2.22 \text{ (mol)}.$$

Let's find molality of  $\text{CH}_3\text{COOH}$  in the solution using the formula:

$$C_m(\text{CH}_3\text{COOH}) = n(\text{CH}_3\text{COOH}) / m(\text{H}_2\text{O}) = 1 / 0.04 = 25 \text{ (mol/kg)}.$$

Mole fraction of  $\text{CH}_3\text{COOH}$  in the solution we'll determine using the formula:

$$\chi(\text{CH}_3\text{COOH}) = n(\text{CH}_3\text{COOH})/n(\text{solution}) = 1/(1 + 2.22) = 0.31 \text{ (31 \%)}.$$

*The answer: 25 mol/kg; 31 %.*

**Problem 3.** There are 0.5884 g of  $\text{K}_2\text{Cr}_2\text{O}_7$  in 200 mL of the solution. Calculate molar concentration and normality of the solution. The equivalence factor of potassium dichromate is  $1/6$ .

*Solution.* Let's find:

$$C(\text{K}_2\text{Cr}_2\text{O}_7) = m(\text{K}_2\text{Cr}_2\text{O}_7) / (M(\text{K}_2\text{Cr}_2\text{O}_7) \cdot V) = 0.5884/294.2 \cdot 0.2 = 0.01 \text{ (mol/L)},$$

$$C_N(\text{K}_2\text{Cr}_2\text{O}_7) = m(\text{K}_2\text{Cr}_2\text{O}_7) / (M(\text{K}_2\text{Cr}_2\text{O}_7) \cdot f_{\text{eq}}(\text{K}_2\text{Cr}_2\text{O}_7) \cdot V) = \\ = 0.5884 / 294 \cdot 1/6 \cdot 0.2 = 0.06 \text{ (mol/L)}$$

or  $C_N(\text{K}_2\text{Cr}_2\text{O}_7) = C(\text{K}_2\text{Cr}_2\text{O}_7) / f_{\text{eq}}(\text{K}_2\text{Cr}_2\text{O}_7) = 6 \cdot 0.01 = 0.06 \text{ (mol/L)}.$

*The answer: 0.01 mol/L; 0.06 mol/L.*

**Problem 4.** How many millilitres of the solution with the mass fraction of  $\text{H}_2\text{SO}_4$  equal to 40 % (density 1.30 g/mL) should be taken to prepare 500 mL of the 0.1N  $\text{H}_2\text{SO}_4$  solution? The equivalence factor of  $\text{H}_2\text{SO}_4$  is  $1/2$ .

*Note:* molar concentration of the equivalent (normality) is indicated by the following symbols:  $C_N(\text{X})$ ,  $N(\text{X})$ . Together with these symbols there is also an indication of equivalence factor of the substance ( $f_{\text{eq}}$ ).

*Solution.* Normality of the concentrated solution of  $\text{H}_2\text{SO}_4$ :

$$C_N(\text{H}_2\text{SO}_4) = n_{\text{eq}}(\text{H}_2\text{SO}_4) / V = m(\text{H}_2\text{SO}_4) / M(\text{H}_2\text{SO}_4) \cdot f_{\text{eq}}(\text{H}_2\text{SO}_4) \cdot V,$$

where  $m(\text{H}_2\text{SO}_4) = 40 \text{ g}$  and  $m(\text{H}_2\text{O}) = 60 \text{ g}$ ,  $m(\text{solution}) = 100 \text{ g}$ , as  $\omega(\text{H}_2\text{SO}_4) = 40 \%$ .

The volume of 100 g of  $\text{H}_2\text{SO}_4$  solution with the mass fraction of 40 % is

$$V(\text{solution}) = m(\text{solution}) / \rho = 100 / 1.30 = 76.9 \text{ (mL)} \text{ or } 0.0769 \text{ L};$$

$$C_N(\text{H}_2\text{SO}_4) = 40/98 \cdot 1/2 \cdot 0.0769 = 10.62 \text{ (mol/L)}.$$

When dilute solution is prepared, the mass of the dissolved substance stays the same, i. e.  $C_{N1}V_1(\text{conc.}) = C_{N2}V_2(\text{diluted})$  where  $C_{N1}$  and  $C_{N2}$  are the normalities (N) of two solutions and  $V_1$  and  $V_2$  are the volumes of the solutions. Using this formula, let's calculate the volume of the concentrated solution which should be taken to prepare 500 mL of 0.1N  $\text{H}_2\text{SO}_4$  solution.

$$V_1(\text{conc.}) = C_{N2} \cdot V_2(\text{diluted}) / C_{N1}(\text{conc.}) = (0.1 \cdot 500) / 10.62 = 4.71 \text{ (mL)}.$$

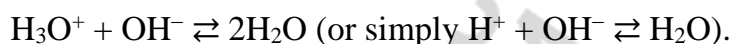
*The answer: 4.71 mL.*

## CHAPTER 2

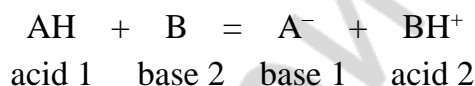
### ACID-BASE TITRATION

**Application of the method.** The field of practical application of acid-base titration in medical-biological research is extremely wide. In biochemical research the method of acid-base titration is used for the determination of acidity of the stomach juice, alkaline reserve of blood and plasma. In toxicology this method is used to determine ammonia, acetic and cyanic acid and others. In sanitation practice the method of acid-base titration can help to evaluate the acidity of different food products (milk, cottage cheese, bread, water and so on). In pharmacy in order to determine the range of medicines of acidic and basic character we use acid-base titration both in water and in mixed aqueous-organic and non-aqueous solvents.

Methods of acid-base titration are based on the usage of the neutralization reaction between acids and bases:



According to the protolytic theory of acids and bases this reaction in general form can be presented by the following equation:



where  $\text{A}^-$  and  $\text{BH}^+$  are the conjugate base and the conjugate acid.

Depending on the titrant we can differentiate the methods of acidimetric and alkalimetric titration. In acidimetry we use 0.01–0.1 N solutions of strong acids (usually HCl or  $\text{H}_2\text{SO}_4$ ) as titrants. In alkalimetry the titrants are 0.01–0.1 N solutions of alkalis such as NaOH, KOH,  $\text{Ba}(\text{OH})_2$ .

Methods of acid-base titration allow the determination of the concentrations of solutions (and, consequently, the amounts of substances in mixtures) of organic and inorganic acids and bases and some salts undergoing hydrolysis or reacting with acids and bases.

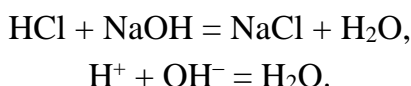
Acidimetric titration is used for the determination of concentrations for strong and weak bases and some salts of weak acids, e. g. NaOH,  $\text{NH}_4\text{OH}$ , amines, aniline,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$  and so on.

Alkalimetric titration is used for the determination of concentrations of strong and weak acids and some salts of weak bases, e. g. HCl,  $\text{H}_3\text{BO}_3$ ,  $\text{CH}_3\text{COOH}$ , phenols, salts of very weak organic bases used as medicines and so on.

#### EQUIVALENCE POINT FIXATION IN ACID-BASE TITRATION

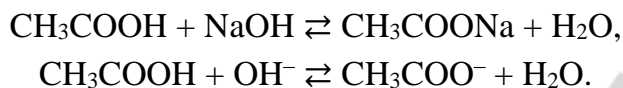
In acid-base titration the reaction of the medium at the equivalence point can be neutral, acidic or basic depending on the nature of the acid and the base taking part in the neutralization reaction. Let's consider this using the following examples.

The products of the reaction between a strong acid and a strong base are the salt, which is not undergoing hydrolysis, and water:



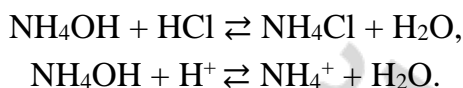
In this case the solution in the equivalence point has a neutral reaction, i. e.  $\text{pH}_{\text{eq.p.}} = 7$ .

Neutralization of a weak acid by a strong base results in the formation of the salt undergoing hydrolysis by its anion, i. e. in this case the reaction is reversible.



As a result of the hydrolysis by anion the reaction of the medium at the equivalence point becomes slightly basic, i. e.  $\text{pH}_{\text{eq.p.}} > 7$ .

If a weak base is titrated by a strong acid the salt undergoing hydrolysis by cation is formed:



The reversibility of this reaction determines the acidic reaction of the solution at the equivalence point, i. e.  $\text{pH}_{\text{eq.p.}} < 7$ .

If a polybasic acid or its salt is titrated, e. g.  $\text{H}_3\text{PO}_4$  or  $\text{Na}_2\text{CO}_3$ , then there will be several equivalence points during titration:

- a)  $\text{Na}_2\text{CO}_3 + \text{HCl} = \text{NaHCO}_3 + \text{NaCl}$ ,
- b)  $\text{NaHCO}_3 + \text{HCl} = \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$ .

The equivalence point of the first reaction (a) corresponds to the  $\text{pH} = 8.34$  due to the hydrolysis of hydrocarbonate; and the equivalence point of the second reaction (b) corresponds to the  $\text{pH} = 4.00$  due to the formation of the saturated saline solution of carbon dioxide.

Equivalence point fixation in acid-base titration is performed with the help of chemical indicators or physical-chemical methods. Physical-chemical methods are based on the analysis of changes of solution properties in the process of titration, for example, changes of the  $\text{pH}$  of the medium in potentiometric method, of electric conductivity of the solution in conductometric method, of optical properties in photometry and spectrophotometry, of current strength of electricity passing through the solution in amperometric method and so on.

### ACID-BASE INDICATORS

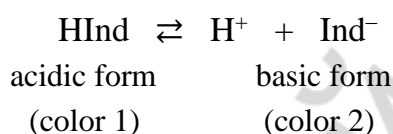
Indicators of acid-base titration are complex organic substances able to change their color at certain levels of  $\text{pH}$  of the solution. More than 200 acid-base indicators related to different groups of organic substances are known. The most wide-spread of them are the indicators of tritane group (phenolphthalein, thymolphthalein, phenol red, crystal violet, etc.) and azocompounds (methyl-orange, methyl red, etc.). Mixed indicators (which are

mixtures of two, three and more indicators) can also be used in titration since they produce more clear changes in color at different pH levels of solutions.

### PHYSICAL AND CHEMICAL CHARACTERISTICS OF ACID-BASE INDICATORS

The process of color change happens at certain definite interval of pH values called the interval of coloring change ( $\Delta\text{pH}$  of the indicator). Each indicator has its own interval of coloring change which depends on the specific features of its structure and its ability to be ionized. Besides  $\Delta\text{pH}$  indicators can be characterized by titration indicator (pT). Titration indicator is the pH value in the range of coloring change at which the most drastic change of the color is observed.

Let's write the formula for the determination of the solution pH at which there is a visible change in color of the indicator and take the indicator with the properties of a weak acid as an example:



As we can see from the expression for the ionization constant K (dissociation constant) of the indicator:

$$K = \frac{[\text{H}^+] \cdot [\text{Ind}^-]}{[\text{HInd}]},$$

the pH of the solution determines the quantitative ratio between the acidic and basic forms of the indicator and, consequently, the color of the indicator in the solution:

$$[\text{H}^+] = \frac{K \cdot [\text{HInd}]}{[\text{Ind}^-]},$$

hence,

$$\text{pH} = \text{pK} + \lg\left(\frac{[\text{Ind}^-]}{[\text{HInd}]}\right). \quad (5.1).$$

It is stated that the distinguishable change in color of the indicator occurs only when the concentration of one form of the indicator exceeds the concentration of the other form approximately 10 times, i. e.

$$\frac{[\text{Ind}^-]}{[\text{HInd}]} = 1/10; \quad \frac{[\text{Ind}^-]}{[\text{HInd}]} = 10/1.$$

Let's substitute these values in the equation (5.1) and get the expression determining the interval of the color change for an indicator:

$$\Delta\text{pH} = \text{pK} \pm 1.$$

For the majority of acid-base indicators the interval of the color transfer is approximately 2 units of pH:

from  $\text{pH}_1 = \text{pK} - 1$  till  $\text{pH}_2 = \text{pK} + 1$ .

The titration indicator pT is usually equal to the pH of the solution at which the concentrations of both colored forms of the indicator are equal, i. e.  $[\text{HInd}] = [\text{Ind}^-]$ . Consequently, as we can see from the equation:

$$\text{pT} = \text{pH} = \text{pK} + \lg(1/1) = \text{pK}$$

in chemical reference books we can usually find the color of acidic and basic forms of the indicator, the values of the color transfer intervals and the methodology of preparation of indicator solution.

In table 1 there are several characteristics of some acid-base indicators.

Table 1

Some acid-base indicators

Indicator	Group of indicators	Colouring of indicator forms		$\Delta\text{pH}$	pT
		acidic form	basic form		
crystal violet:	tritanine				
transfer I		yellow	green	0–0.1	0.5
transfer II		green	violet	1.0–2.6	1.8
thymol blue	sulfophthalein				
transfer I		red	yellow	1.2–2.8	2.0
transfer II		yellow	blue	8.0–9.6	8.0
methyl yellow	azoindicator	Red	yellow	2.9–4.0	3.2
<b>methyl orange</b>	azoindicator	Red	yellow	3.1–4.4	4.0
bromocresol green	sulfophthalein	yellow	blue	3.8–5.4	4.9
methyl red	azoindicator	Red	yellow	4.2–6.2	5.0
<b>litmus</b>	phthalein	Red	blue	5.0–8.0	7.0
phenol red	sulfophthalein	yellow	red	6.4–8.0	7.0
<b>phenolphthalein</b>	phthalein	colourless	red	8.2–10.0	9.0
thymolphthalein	phthalein	colourless	blue	9.4–10.6	10.0

Note: the names of the indicators widely used in laboratory practice are underlined.

Indicators are used either in the form of solutions (a few drops of them are added to the test solution) or in the form of indicator reactive paper, i. e. pieces of filter paper saturated with indicator solution and dried. For the pH determination we place several drops of the test solution on the indicator paper and match that color with the known color scale for the given indicator.

Different indicators change their color at different pH values and that helps to choose the appropriate indicator or indicator paper in the whole range of pH scale. More often we use universal indicators which are the mixtures of indicators getting different colors at several pH values, which helps to judge approximately about the pH value in the whole range of the pH scale. Universal papers have a comparative colored scale of pH values on their covers.

### **CURVES OF ACID-BASE TITRATION. HOW TO CHOOSE THE INDICATOR**

As it was shown above, the pH value in the equivalence point is determined, first of all, by the nature of the acid and the base reacting in the given titration experiment. For example, the titration of a strong acid by a strong base should be finished in a neutral medium ( $\text{pH}_{\text{eq.p.}} = 7.0$ ). From the indicators listed above in table 1 only litmus and phenol red, which drastically change their color in the neutral medium ( $\text{pT} = 7.0$ ), are suitable for



pH = 7.0 fixation. Meanwhile, the experiment doesn't prove it: not only these two indicators but all others having pT ranging from 4.0 till 10.0 give almost the same results.

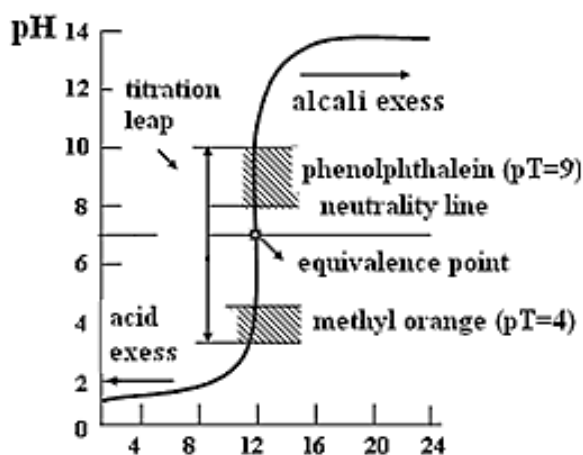


Fig. 1. The curve of titration of 10 ml of 0.1 N solution of a strong acid by a solution of a strong base

The explanation of the experiment can be given with the help of quantitative methods of indicator choice. One of those methods is the method of titration curve construction.

Curves of acid-base titration show the dependence of pH on the volume of the titrant added in the process of titration. Now we can make the following conclusions which are important for the choice of the indicator.

1. In the process of the titration of a strong acid by a strong base (fig. 1) the equivalence point is in the neutrality point (pH = 7.0) and the branches of the titration curve are symmetrical relative to neutrality lines.

2. Closer to the equivalence point we can observe a drastic leap (jump) of pH. Its value depends on the concentration of the titrated solution and the titrant and the temperature. With the increase of the concentration of reactants the value of the pH jump on the titration curve increases and with its decrease the value decreases too. Really, if  $C(\text{HCl}) = C(\text{NaOH}) = 1 \text{ mol/L}$ , then with the help of the same calculations it's easy to demonstrate that the value of pH jump on the titration curve is 8 pH units. But if  $C(\text{HCl}) = C(\text{NaOH}) = 0.01 \text{ mol/L}$ , then its value is just 4 pH units. With the increase of temperature the value of the pH jump on the titration curve decreases as the ion product of water increases (at 298K  $K_d = 1.0 \cdot 10^{-14}$  and at 373K  $K_d = 5.9 \cdot 10^{-14}$ ).

3. To fix the equivalence point in acid-base titration we can use any indicator with the interval of color change situated somewhere within the borders of the pH jump on the titration curve.

So, to determine the equivalence point in the abovementioned case we can use any acid-base indicator with the interval of color change in the range of the pH 4...10 (see table 1 and chemical reference books). The difference in the titration results in case of using methyl orange (pT = 4) and phenolphthalein (pT = 9) is no more than 0.02 or 0.2 %.

During titration of a weak acid by a strong base (fig. 2) the equivalence point is shifted from the neutrality line to the basic area due to the hydrolysis of the salt formed in the equivalence point. The titration jump narrows. The weaker the titrated acid, the more narrow will be the jump. In this case only phenolphthalein can be used from all above mentioned indicators.

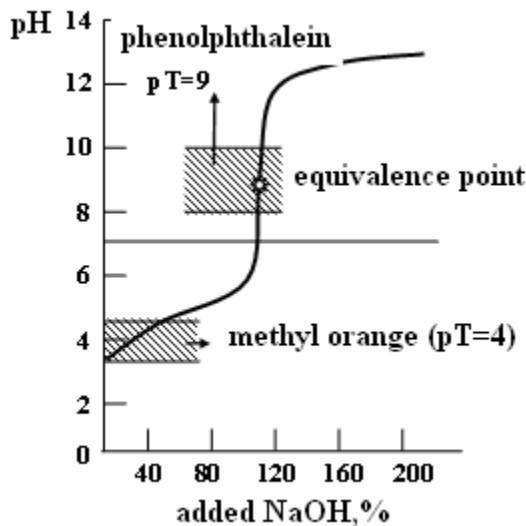


Fig. 2. Titration curve of 0.1 M of acetic acid solution by 0.1 M of alkali solution

During titration of a weak base by a strong acid (fig. 3) after the end of the reaction the salt is hydrolyzed by the cation; the equivalence point is shifted to the acidic area. To fixate the equivalence point we can use methyl orange, and phenolphthalein is out of use.

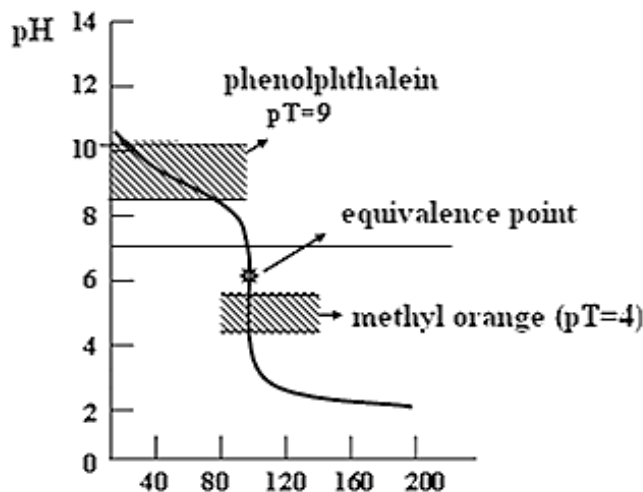


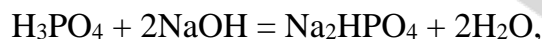
Fig. 3. Titration curve 0.1 M of ammonia solution by 0.1 M of hydrochloric acid solution

When we titrate a weak acid by a weak base the change of the pH occurs gradually during the whole process of titration so the area of pH jump on the titration curve is absent and it's impossible to determine the equivalence point. That is why the solutions of weak acids and bases are not used as titrants in acid-base titration.

In accordance with the stepwise ionization of polybasic acids their neutralization occurs also gradually. For example, the titration of  $\text{H}_3\text{PO}_4$  solution by an alkali includes the following reactions:

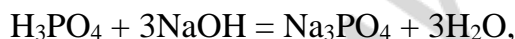


In accordance with these data the titration curve of  $\text{H}_3\text{PO}_4$  by an alkali has three equivalence points instead of one and only two clear pH jumps (for the reactions 1 and 2). The first equivalence point can be determined with the help of methyl orange (or methyl red), the second — with the help of phenolphthalein (thymolphthalein to be more exact). In the presence of methyl orange  $\text{H}_3\text{PO}_4$  is titrated as a monobasic acid, i. e. according to the first equation. In this case the equivalence factor is equal to 1. In contrast to this, phosphoric acid is titrated with phenolphthalein according to the following equation:



i. e. it behaves as a dibasic acid ( $f_{\text{eqv}} = 1/2$ ).

We can't titrate  $\text{H}_3\text{PO}_4$  directly as a tribasic acid, i. e. using the equation:



because the third ionisation constant of phosphoric acid is very small ( $K_3 = 2.2 \cdot 10^{-13}$ ) and that leads to the disappearance of the third pH jump from the titration curve.

The titration of salts of weak polybasic acids (e. g.  $\text{Na}_2\text{CO}_3$ ) and mixtures of acids which differ greatly in their strength (e. g. strong hydrochloric acid and weak acetic acid) also leads to the appearance of several equivalence points on the titration curve. The correct choice of the indicator in each definite case allows getting precise results of the analysis.

#### STANDARDIZATION OF TITRANTS IN METHODS OF ACID-BASE TITRATION

Standard solutions of strong acids and alkali can't be prepared immediately using the exact weight or volume of a more concentrated solution. That's why at first we prepare the solutions of approximate concentration and then we standardize them. The primary standard solution is titrated by a titrant. We know the exact normal concentration of the primary standard and the exact volume of its solution. In the standardization process we determine the volume of a titrant necessary to reach the equivalence point. After that the normal concentration of a titrant is calculated using the law of the equivalence.

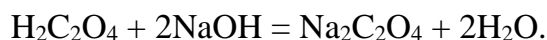
As primary standards for acid solutions we use sodium tetraborate  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  (borax), sodium carbonate  $\text{Na}_2\text{CO}_3$  or its decahydrate  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ .

The following reactions are happening during the standardization of HCl:



During both titrations we use methyl orange as an indicator because in the equivalence point a saline solution of a weak acid (the medium is weakly acidic) is obtained.

The standardization of alkali solutions is performed using oxalic acid dihydrate  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ; they are titrated in the presence of phenolphthalein because the medium is weakly basic in the equivalence point:



Using the results of the titration we calculate the normality of the prepared solution of a titrant.

If there are any standard solutions containing 0.1 mole of NaOH, HCl,  $\text{H}_2\text{SO}_4$  then the titrants are prepared from them. Dry weights of the primary standards mentioned above can also be used.

**Main questions of the topic:**

1. The main ideas and the methods of acid-base titration. Standard solutions.
2. Stoichiometric (equivalence) point in acid-base titration. Acid-base indicators.
3. Acid-base titration curves. The choice of the indicator.
4. The use of acid-base titration in medical-biological research.

**EXPERIMENTAL WORKS**

**LABORATORY WORK (P) “THE PREPARATION OF SOLUTIONS USING THE DRY WEIGHT AND THE STANDARD SOLUTION”**

**Task 1: The preparation of the oxalic acid solution using its dry dihydrate.**

**The aim of the task:** to learn how to make solutions of the needed volume and concentration using the dry substance.

**Reactants and equipment:** oxalic acid dihydrate  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , electric weighing scales, volumetric flask for 100 ml, funnel, distilled water, eye pipettes, the paper for weighing.

You need to use a certain mass of oxalic acid dihydrate ( $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) to make \_\_\_\_\_ ml of oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) solution with the normality (the molar concentration of the equivalent) of  $\text{H}_2\text{C}_2\text{O}_4$  \_\_\_\_\_ mol/L.

**Calculations:**

*Find the number of moles of  $\text{H}_2\text{C}_2\text{O}_4$  equivalents that is necessary to make the needed volume of the solution:*

$$n_{eq} = C_{eq} \cdot V = \text{_____} \cdot \text{_____} = \text{_____} \text{ mol}$$

*Since the number of moles of equivalents is always higher (or equal) to the number of moles of units, calculate the number of moles of units using the factor of equivalence (it is equal to  $1/2$  in this case):*

$$n = n_{eq} \cdot f_{eq} = \text{_____} \cdot 1/2 = \text{_____} \text{ mol}$$

*Since the number of moles of the oxalic acid is equal to the number of moles of its dry hydrate calculate the mass of the hydrate:*

$$m = n \cdot M = \text{_____} \cdot \text{_____} = \text{_____} \text{ g}$$

Measure the calculated weight of the dry dihydrate of the oxalic acid using the electric weighing scales. Don't forget to use the paper for weighing. Put the measured mass of the substance into the volumetric flask using the funnel. Wash the funnel with the distilled water (the water should run into the flask to avoid the loss of the substance). Then fill half the flask with the distilled water. Mix the flask by the way of careful rotation. Continue the fulfillment until the lower edge of the meniscus will be on the same level as the line on the neck of the flask (last drops should be added by the eye pipette). Mix the resulting solution. Now it is ready for the usage.

Write the conclusion: "I prepared the solution of oxalic acid with the normality of \_\_\_\_\_ mol/L using its dry dihydrate".

### **Task 2: The preparation of the solution using the standard solution.**

**The aim of the task:** to learn how to prepare solutions using the standard solutions.

**Equipment:** standard solutions, funnel, distilled water, glass scratchers, eye pipettes.

*The standard solution may be delivered as the closed glass or plastic container with the solution containing the exact amount of a certain substance. The standard solution is usually concentrated. You need to dissolve it in the designated volume of distilled water to prepare the solution of the molarity written on the sticker.*

Before the usage of the standard solution remove the sticker from the wall of the container and wash the container with the distilled water to avoid possible contamination of the resulting solution.

Put the funnel into the volumetric flask of the needed volume (usually 0.5 or 1 L) and open up the container with the standard solution. If you deal with the glass container: make a hole in the bottom of it by the scratcher (the liquid will not flow away), put it in the funnel and make the second hole in the glass (then liquid will flow in the flask), wash the glass container by distilled water into the flask. If you deal with the plastic container: cut the top of the container and pour the standard solution into the funnel; wash the container by distilled water into the flask. Usually you need the volume of the distilled water for washing the container that is six times higher than the volume of the container itself. Mix the flask by the way of careful rotation. Continue the fulfillment until the lower edge of the meniscus will be on the same level as the line on the neck of the flask (last drops should be added by the eye pipette). Mix the resulting solution. Now it is ready for the usage.

Write the conclusion: "I prepared the solution of \_\_\_\_\_ with the molarity of \_\_\_\_\_ mol/L using the \_\_\_\_\_ container with the standard solution".

## LABORATORY WORK (M, D, P)

### “THE PREPARATION OF TITRANTS BY THE DILUTION OF A CONCENTRATED SOLUTION”

**Task:** to prepare \_\_\_\_\_ ml of a titrant (HCl solution) with a molar concentration of \_\_\_\_\_ mol/L.

**The aim of the work:** to learn how to prepare solutions by diluting, that is to get the skills how to work with: areometers, labwares (graduated pipettes, graduated flasks) and acid solutions; to learn how to calculate the volume of the concentrated solution needed to prepare the dilute solution of a certain concentration.

**Reactants:** hydrochloric acid with the mass percentage of HCl in the interval of 10–20 %.

**Devices and equipment:** the set of areometers, the reference table “Density of aqueous solutions of some acids and alkalis”; graduated flasks and pipettes.

**You should do the following:**

– measure the density of the concentrated HCl solution with the help of the areometer. Then find the corresponding mass percentage of HCl in the reference table “Density of aqueous solutions of some acids and alkalis”;

– calculate how many millilitres of the concentrated HCl solution should be taken to obtain the solution with the specified molar concentration  $C(\text{HCl}_{\text{diluted}})$  by the way of its dilution with distilled water in the graduated flask (the volume of the graduated flask is equal to the volume of the diluted HCl solution, i. e.  $V(\text{flask}) = V(\text{HCl}_{\text{diluted}})$ ).

To make the calculations at first you should find the molar concentration of the initial concentrated solution of the acid  $C(\text{HCl}_{\text{conc}})$ .

As the amount of the dissolved substance is unchanged after the dilution, we can use the law of the equivalence to find the volume of the concentrated HCl solution:

$$C_1V_1 = C_2V_2,$$

where  $C_1$  and  $C_2$  are the normalities or molar concentrations of solutions, because  $f_{\text{eqv}}(\text{HCl}) = 1$ .

We need to prepare \_\_\_\_\_ mL of the HCl solution with  $C =$  \_\_\_\_\_ mol/L.

1. The density of the concentrated HCl solution equals \_\_\_\_\_ g/mL.
2. The mass fraction of HCl solution according to the reference table “Density of aqueous solutions of some acids and alkalis” is \_\_\_\_\_ %.
3. Now you need to convert the mass percentage into the molarity. To make it in an easy way we suggest you to imagine that you have exactly 100 g of the solution.

In 100 g of the solution we have \_\_\_\_\_ g of HCl.

The number of moles of HCl is:

$$n(\text{HCl}) = m/M = \text{_____ g} / \text{_____ g/mole} = \text{_____ mole}.$$

The volume of the solution can be calculated using its density.

$$V(\text{HCl solution}) = m(\text{solution}) / \rho(\text{solution}) = 100 \text{ g} / \text{_____ g/ml} = \text{_____ ml}.$$

Then calculate the molarity:

$$C(\text{HCl}) = n(\text{HCl}) / V(\text{HCl solution}) = \text{_____ mole} / \text{_____ L} = \text{_____ mol/L.}$$

4. Using the law of the equivalence calculate the volume of the concentrated solution:

$$C(\text{conc.}) \cdot V(\text{conc.}) = C(\text{diluted}) \cdot V(\text{diluted})$$

$$V(\text{conc.}) = (C(\text{diluted}) \cdot V(\text{diluted})) / C(\text{conc.}) =$$

$$= (\text{_____ mol/L} \cdot \text{_____ mL}) / \text{_____ mol/L} = \text{_____ mL.}$$

5. Pour distilled water in the graduated flask till the middle of its volume. With the help of the rubber pump you should fill in the graduated pipette with the concentrated HCl solution and place the previously calculated volume of the concentrated HCl solution into the graduated flask.

6. Mix the solution in the flask by circular rotations.

7. Add water till the mark (the mark should be on the lower edge of the meniscus). The last drops should be added with an eye pipette.

8. Close the flask with a cork and carefully mix the solution turning the flask bottom up several times.

**Conclusion.** “By the way of the dilution of a concentrated solution we have prepared HCl solution with the volume of \_\_\_\_\_ mL and the molar concentration of \_\_\_\_\_ mol/L”.

### LABORATORY WORK (M, D)

#### “STANDARDIZATION OF A TITRANT WITH THE SOLUTION OF A PRIMARY STANDARD”

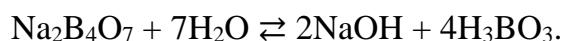
**Task:** to standardize the titrant — HCl solution.

**The aim of the work:** to learn how to standardize titrants with their primary standard using the technique of direct titration; to get the skills of working with the Mohr’s pipettes and burettes; to learn how to choose the appropriate indicator for definite cases of acid-base titration; to learn how to make the calculations based on the titration results.

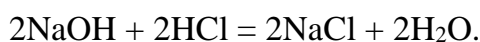
**Reactants:** titrant — HCl solution with the approximate concentration value in the interval from 0.05 to 0.2 mol/L; the solution of the primary standard — 0.10 N Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>; indicators — solutions of methyl orange and phenolphthalein.

**Measures:** burettes with the volume of 25 mL; Mohr’s pipettes; titration flasks (3 units); funnels.

The anion of borax is greatly hydrolyzed in water with the formation of a very weak boric acid (pH = 9.24):



During the titration by the hydrochloric acid the equilibrium of the hydrolysis is shifted almost entirely to the right because the alkali being formed during hydrolysis is used for the reaction with the acid:



Taking together the last two equations we get the general equation of the reaction taking place during titration:



where

$$f_{\text{eq}}(\text{Na}_2\text{B}_4\text{O}_7) = 1/2, f_{\text{eq}}(\text{HCl}) = 1, M(\text{HCl}) = 36.5 \text{ g/mol}.$$

Then you should choose the indicator. The solution in the equivalence point contains NaCl and free boric acid which makes the medium slightly acidic ( $\text{pH}_{\text{eq.p.}} = 5.1$ ). Among these two suggested indicators — methyl orange ( $\text{pT} = 4$ ) and phenolphthalein ( $\text{pT} = 9$ ) — more precise results will be provided by methyl orange.

Then you should describe the following definite moments of the work:

1. Which solution should be poured in the burette?

---

2. Which solution and which volume should be measured by Mohr's pipette into the titration flasks?

---

3. What color change should take place in the equivalence point?

---

Then you should titrate the solution and stop when its initial \_\_\_\_\_ color will turn to \_\_\_\_\_.

To reduce the possibility of an accidental mistake you should do 3–4 parallel titrations and at correct fulfilment of the operations the volumes of the titrants at parallel experiments shouldn't differ more than  $\pm 0.1$  ml.

Finally, you should do the titration and write down the results.

The first titration has mostly tentative character. You should add the titrant from the burette to the flask for titration in the drop by drop manner and mix that flask constantly. The titration should be finished when the permanent change of color happened. The results of the titration should be immediately written down with the accuracy from 0.03–0.05 ml.

The second and the following titrations should be conducted more precisely. You may add the volume of the titrant that is less than 0.5–1.0 ml than the volume determined during the first tentative titration very quickly. Then the titrant must be added in the drop by drop manner. The titration should be stopped when obvious change in color has just taken place after the addition of the one last drop of the titrant.

Titration should be repeated till you get three similar results. All the results should be written down in the table:

Titration number	Primary standard $\text{Na}_2\text{B}_4\text{O}_7$		Titrant HCl
	$C_{\text{N}}(\text{Na}_2\text{B}_4\text{O}_7)$ , mol/L	$V(\text{Na}_2\text{B}_4\text{O}_7)$ , mL	$V(\text{HCl})$ , mL
1	0.10	10.0	
2	0.10	10.0	
3	0.10	10.0	



HCl volume used for the titration can be calculated as the arithmetic average of three similar results:

$$V(\text{HCl}) = (V_1 + V_2 + V_3) / 3 = (\underline{\hspace{1cm}} + \underline{\hspace{1cm}} + \underline{\hspace{1cm}}) / 3 = \underline{\hspace{1cm}}$$

(V(HCl) is calculated with the precision up to 0.01 mL).

Using the titration results and the equivalence principle we can calculate the normality of HCl solution:

$$C_N(\text{HCl}) \cdot V(\text{HCl}) = C_N(\text{Na}_2\text{B}_4\text{O}_7) \cdot V(\text{Na}_2\text{B}_4\text{O}_7).$$

$$\text{Hence, } C_N(\text{HCl}) = (C_N(\text{Na}_2\text{B}_4\text{O}_7) \cdot V(\text{Na}_2\text{B}_4\text{O}_7)) / V(\text{HCl}) = \\ = (\underline{\hspace{1cm}} \cdot \underline{\hspace{1cm}}) / \underline{\hspace{1cm}} = \underline{\hspace{1cm}}$$

The value of C(HCl) should be calculated with the precision up to the fourth significant digit (e. g.  $C_N(\text{HCl}) = 0.1036 \text{ mol/L}$ ).

**Conclusion:** “By the method of acid-base titration, by the technique of direct titration with the usage of  $\text{Na}_2\text{B}_4\text{O}_7$  as a primary standard we have established the normality of the titrant — HCl solution:

$$C_N(\text{HCl}) = \underline{\hspace{1cm}} \text{ mol/L}”.$$

**Notice:** standardized HCl solution can be used as a secondary standard solution for standardization of alkali solution.

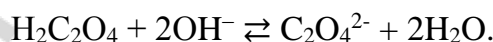
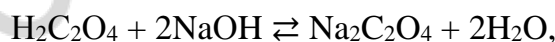
### LABORATORY WORK (P) “DETERMINATION OF THE NORMALITY OF THE OXALIC ACID SOLUTION BY THE WAY OF TITRATION”

**The aim of the work:** to learn how to determine the concentration of a substance in the solution using the acid-base titration.

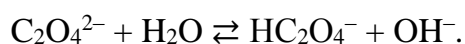
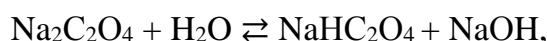
**Reactants:** the solution of oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) with unknown concentration; the titrant — 0.1 N solution of NaOH, the indicator — phenolphthalein.

**Equipment:** the burette (25 ml), the Mohr’s pipette (10 ml), flasks for titration (3 flasks), funnels.

Determination of the concentration of oxalic acid is the example of the titration of weak acids by strong bases. Reactions (complete and short ionic) of the process are as follows:



Remember that the resulting solution will be basic even in the case if you will not overtitrate it. Sodium oxalate is partially hydrolyzed. In this process  $\text{OH}^-$  ions are produced:



To determine the point of equivalence that is in the basic medium you need the indicator which changes its color in the basic medium. In this work it is phenolphthalein.

You need to fulfill your burette with the titrant (NaOH solution) using the funnel. Fill the burette until the point that is some higher than “0”. Then remove the bubbles of air from the end of the burette (you need to put the ending of the burette up and push the ball). After this operation set the level of titrant into the “0” line.

Wash three flasks for titration using distilled water. Pour 10 ml of the analyzed oxalic acid solution into each of these flasks using the Mohr’s pipette. Add two drops of phenolphthalein in each of these flasks.

Put the flask under the capillary of the burette and titrate the solution. Each drop of the titrant will cause a local pink coloring of the solution. That coloring will disappear after the mixing. Continue titration until the drop of the titrant will make the colorless solution permanently slightly pink. After that write the volume of the titrant spent for this titration (use the bottom of the meniscus).

Repeat the titration two times more. Keep in your mind that 3 results should be within the range of  $\pm 0.2$  ml. If they are not so close to each other, repeat the procedure again.

Write the results of three tries in the table below:

The number of the try	C (NaOH), mol/L	V(NaOH), ml	V(H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ), ml
1	0.1000		10.0
2	0.1000		10.0
3	0.1000		10.0

Calculate the average volume of NaOH:

$$V_{\text{av}}(\text{NaOH}) = (V_1 + V_2 + V_3) / 3 = (\underline{\quad} + \underline{\quad} + \underline{\quad}) / 3 = \underline{\quad} \text{ ml.}$$

Using the law of equivalence calculate the normality of the oxalic acid solution:

$$C(\text{NaOH}) \cdot V(\text{NaOH}) = C(1/2 \text{ H}_2\text{C}_2\text{O}_4) \cdot V(\text{H}_2\text{C}_2\text{O}_4).$$

$$\text{It means that: } C(1/2 \text{ H}_2\text{C}_2\text{O}_4) = (C(\text{NaOH}) \cdot V(\text{NaOH})) / V(\text{H}_2\text{C}_2\text{O}_4) = \\ = \underline{\quad} \text{ mol/L.}$$

**The conclusion:** “I estimated the normality of the oxalic acid solution using the acid-base titration method. It is equal to:  $\underline{\quad}$  mol/L”.

### TEST SELF-CHECK

(with multiple responses “correct-incorrect”)

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

**1. In the method of acid-base titration the titrants are the following:**

- a) NH<sub>4</sub>OH; b) H<sub>2</sub>SO<sub>4</sub>; c) H<sub>3</sub>BO<sub>3</sub>; d) NaOH.

**2. As primary standards in the method of acid-base titration we use the following substances:**

- a) H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> · 2H<sub>2</sub>O; b) Na<sub>2</sub>CO<sub>3</sub> · 10H<sub>2</sub>O; c) Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> · 10H<sub>2</sub>O; d) Na<sub>2</sub>SO<sub>4</sub> · 10H<sub>2</sub>O.

3. Four water solutions with the volume of 1 liter have been prepared from the substance weights (or gas volume) indicated below. What are the cases when the molar concentration of the equivalent of the obtained solution is equal to 0.1 mol/L?

- a) 4.0 g NaOH; c) 4.9 g  $\text{H}_2\text{SO}_4$  ( $f_{\text{eq}} = 1/2$ );  
b) 2.24 L HCl (norm.cond.); d) 5.6 g KOH.

4. The concentration of solutions or the amount of which substances in the mixture can be determined by the method of acid-base titration?

- a) NaCl; b)  $\text{Na}_2\text{CO}_3$ ; c)  $\text{Na}_2\text{Cr}_2\text{O}_7$ ; d) HCl.

5. Which factors determine the choice of the indicator in the acid-base titration?

- a) interval of color transition of the indicator; c) pH in the equivalence point;  
b) area of pH jump on the titration curve; d) volume of the titrated solution.

6. Which indicators can be used to titrate ammonia solution by a standard  $\text{HNO}_3$  solution?

- a) bromphenol blue,  $\Delta\text{pH} = 3.0 \dots 4.6$ ; c) methyl orange,  $\Delta\text{pH} = 3.1 \dots 4.4$ ;  
b) neutral red,  $\Delta\text{pH} = 6.8 \dots 8.0$ ; d) phenolphthalein,  $\Delta\text{pH} = 8.2 \dots 10.0$ .

7. In water solutions of which salts litmus ( $\text{pT} = 7$ ) will become blue?

- a)  $\text{CaCl}_2$ ; b)  $\text{Al}_2(\text{SO}_4)_3$ ; c)  $\text{NaNO}_3$ ; d)  $\text{Na}_2\text{CO}_3$ .

8. To titrate 10.0 mL of NaOH solution we used 12.0 mL of 0.10 M HCl solution. Which of the following concentrations corresponds to the composition of the analyzed alkali solution?

- a) 0.00480 g/mol; b)  $7.2 \cdot 10^{22}$  NaOH units/L; c) 0.12 mol/L; d) 12 g/L.

9. To titrate 10.0 mL of  $\text{H}_3\text{PO}_4$  solution in the presence of methyl orange we used 5.0 mL 0.2 M of NaOH solution. What are the mass and the amount of  $\text{H}_3\text{PO}_4$  in 1 litre of the analyzed solution?

- a) 4.9 g; b) 9.8 g; c) 0.05 mol; d) 0.1 mol.

10. In the final volume of 1 liter 22.4 mL of a gaseous HCl (norm.cond.) were dissolved. What are the pH and pOH of the obtained solution?

- a)  $\text{pH} = 3$ ; b)  $\text{pH} = 1$ ; c)  $\text{pOH} = 11$ ; d)  $\text{pOH} = 13$ .

## PROBLEMS

1. How many grams of KOH should be taken to prepare 500 mL of 0.05 M alkali solution.

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Answer: \_\_\_\_\_

2. What volume of hydrochloric acid with the mass fraction of HCl equal to 20 % (density 1.10 g/mL) should be taken to prepare 500 mL of 0.1 M HCl solution.

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Answer: \_\_\_\_\_

3. How many grams of  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  should be taken to prepare 250 mL of its 0.1N solution ( $f_{\text{eqv}} = 1/2$ ,  $M(\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}) = 381 \text{ g/mol}$ )?

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Answer: \_\_\_\_\_

4. What mass of oxalic acid dihydrate should be taken in order to use 20 mL of 0.1 M NaOH solution in the titration ( $M(\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}) = 126 \text{ g/mol}$ )?

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Answer: \_\_\_\_\_

5. Calculate the content of hydrochloric acid and general acidity of human gastric juice sample (in mol/L) if to titrate 10.0 mL of the juice with methyl orange we used 3.10 mL of 0.098 M NaOH solution and with phenolphthalein — 6.0 mL of the alkali.

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Answer: \_\_\_\_\_

6. 9.7770 g of concentrated solution of  $\text{HNO}_3$  were diluted by water to get 1 L of the solution in the volumetric flask. To titrate 25.0 mL of the obtained solution we used 23.40 mL of 0.1040 M NaOH solution. Determine the mass fraction of nitric acid in its concentrated solution.

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Answer: \_\_\_\_\_

7. To titrate 5.0 mL of sulphuric acid solution we used 4.12 mL of 0.102 M NaOH solution. Calculate the normality of the acid solution.

Answer: \_\_\_\_\_

8. To titrate 0.286 g of  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  in the presence of methyl orange we used 24.10 mL of HCl solution. Calculate the molarity of HCl solution.

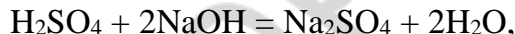
Answer: \_\_\_\_\_

## STANDARDS OF PROBLEM SOLUTIONS

### Calculations based on the results of direct titration

**Problem 1.** To titrate 10.0 mL of 0.10 N  $\text{H}_2\text{SO}_4$  solution we used 9.72 mL of NaOH solution. Calculate the normality of the solution of alkali.

*Solution.* The chemical reaction is the following:



where

$$f_{\text{eq}}(\text{NaOH}) = 1, \quad f_{\text{eq}}(\text{H}_2\text{SO}_4) = 1/2.$$

According to the equivalence principle,

$$n_{\text{eq}}(\text{H}_2\text{SO}_4) = n_{\text{eq}}(\text{NaOH}),$$

so

$$C_{\text{N}}(\text{H}_2\text{SO}_4) \cdot V(\text{H}_2\text{SO}_4) = C_{\text{N}}(\text{NaOH}) \cdot V(\text{NaOH}).$$

Let's find the normality of the alkaline solution:

$$C_{\text{N}}(\text{NaOH}) = (C_{\text{N}}(\text{H}_2\text{SO}_4) \cdot V(\text{H}_2\text{SO}_4)) / V(\text{NaOH}) = (0.10 \cdot 10) / 9.72 = 0.1029 \text{ (mol/L)}.$$

Answer: 0.1029 mol/L.

**Problem 2.** To titrate the solution containing 0.2490 g of  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  we used 12.60 ml of hydrochloric acid. Calculate the normality of HCl solution.

*Solution.* The chemical reaction is the following:



where

$$f_{\text{eq}}(\text{Na}_2\text{B}_4\text{O}_7) = 1/2 \text{ and } f_{\text{eq}}(\text{HCl}) = 1.$$

According to the equivalence principle  $n_{\text{eq}}(\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}) = n_{\text{eq}}(\text{HCl})$ .

Let's write the amounts of equivalents for  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  and  $\text{HCl}$  taking into account the terms of the task:

$$n_{\text{eq}}(\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}) = m(\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}) / (M(\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}) \cdot f_{\text{eq}}) = n_{\text{eq}}(\text{HCl}) = \\ = C_{\text{N}}(\text{HCl}) \cdot V(\text{HCl}),$$

$$m(\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}) / (M(\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}) \cdot f_{\text{eq}}) = C_{\text{N}}(\text{HCl}) \cdot V(\text{HCl}),$$

where  $V(\text{HCl})$  is expressed in litres.

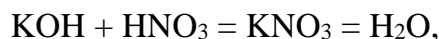
$$0.249 / (381 \cdot 1/2) = C_{\text{N}}(\text{HCl}) \cdot 0.0126,$$

$$C_{\text{N}}(\text{HCl}) = 0.1037 \text{ (mol/L)}.$$

*Answer:* 0.1037 mol/L.

**Problem 3.** How many grams of  $\text{KOH}$  are in 250 ml of the solution if we used 18.40 ml of 0.09234 M  $\text{HNO}_3$  solution to titrate 20.00 ml of this solution?

*Solution.* The chemical reaction is the following:



where

$$f_{\text{eq}}(\text{KOH}) = f_{\text{eq}}(\text{HNO}_3) = 1.$$

According to the equivalence principle

$$C(\text{KOH}) = (C(\text{KNO}_3) \cdot V(\text{KNO}_3)) / V(\text{KOH}) = (0.09234 \cdot 18.40) / 20.00 = 0.08495 \text{ (mol/L)}.$$

Let's find the mass of  $\text{KOH}$  in 250 mL (0.25L) of the solution:

$$m(\text{KOH}) = C(\text{KOH}) \cdot M(\text{KOH}) \cdot V(\text{KOH}) = 0.08495 \cdot 56.1 \cdot 0.25 = 1.19 \text{ g}.$$

*Answer:* 1.19 g.

**Problem 4.** Calculate the mass of  $\text{Na}_2\text{CO}_3$  in the solution if we used 22.35 mL of 0.1820 N  $\text{H}_2\text{SO}_4$  solution to titrate it in presence of methyl orange.

*Solution.* The chemical reaction of this titration in presence of methyl orange ( $\text{pT} = 4$ ) is as follows:



$$\text{So, } f_{\text{eq}}(\text{Na}_2\text{CO}_3) = f_{\text{eq}}(\text{H}_2\text{SO}_4) = 1/2.$$

In accordance with the equivalence principle:

$$n_{\text{eq}}(\text{H}_2\text{SO}_4) = n_{\text{eq}}(\text{Na}_2\text{CO}_3)$$

or

$$C_{\text{N}}(\text{H}_2\text{SO}_4) \cdot V(\text{H}_2\text{SO}_4) = m(\text{Na}_2\text{CO}_3) / (M(\text{Na}_2\text{CO}_3) \cdot f_{\text{eq}}(\text{Na}_2\text{CO}_3)),$$

where  $V(\text{H}_2\text{SO}_4)$  is expressed in liters.

Consequently, we can find  $m(\text{Na}_2\text{CO}_3)$ :

$$m(\text{Na}_2\text{CO}_3) = C_{\text{N}}(\text{H}_2\text{SO}_4) \cdot V(\text{H}_2\text{SO}_4) \cdot M(\text{Na}_2\text{CO}_3) \cdot f_{\text{eq}}(\text{Na}_2\text{CO}_3) = \\ = 0.182 \cdot 0.02235 \cdot 106 \cdot 1/2 = 0.2156 \text{ g}.$$

*Answer:* 0.2156 g.

## CHAPTER 3

### OXIDATION-REDUCTION TITRATION

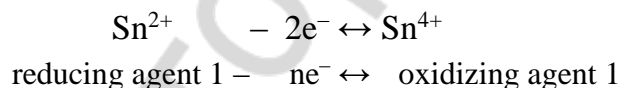
**Main postulates of the electron theory of oxidation-reduction processes.** A lot of titrimetric methods used in quantitative analysis are based on the oxidation-reduction reactions (redox reactions). They are commonly named as oxidimetry (redox) methods.

With the help of oxidimetry used in clinical and biochemical research one can determine the catalase and peroxidase activity, the presence of ascorbic acid, sugar in blood and other biological liquids, uric acid in urine, urea in blood and urine, calcium ions in blood serum and so on.

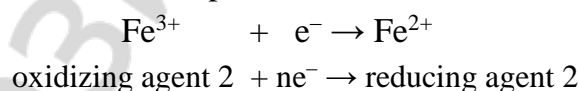
With the help of oxidimetry methods used in hygiene and sanitary investigations one can determine the oxidability of water, the content of active chlorine in drinking water, dissolved oxygen and organic admixtures in the water and so on.

The redox reactions include a partial or a complete electron transfer from one group of atoms or ions to another group. These transfers are resulted in the change of oxidation states of the atoms of certain elements.

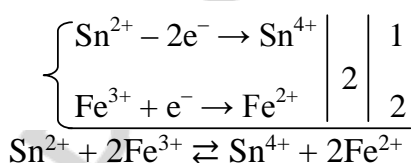
According to the electron theory of oxidation-reduction processes, oxidation is the process of the loss of electrons. The substance which has lost electrons is called a reducing agent (reducer). Reducer transforms into its oxidized form in the course of the reaction. Each reduced formed is, actually, the oxidizing agent that is coupled with the initial reducing agent. For example,



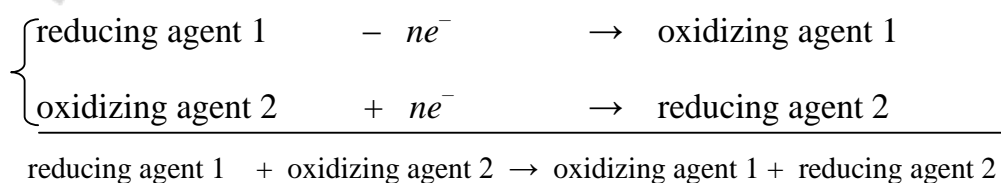
Reduction is the process of the gain of electrons. The substance taking the electrons in redox reactions is called the oxidizing agent. Oxidizer transforms into its coupled reduced form during the redox reaction. For example,



The processes of oxidation and reduction occur simultaneously and they should be considered inseparably, besides, the total number of electrons lost by the reducing agent is equal to the total number of the electrons gained by the oxidizing agent. For example,



or in general:



So, any redox reaction is the combination of two coupled processes — so-called half-reactions: oxidation of the reducing agent and the reduction of the oxidizing agent.

### WRITING THE EQUATIONS OF OXIDATION-REDUCTION (REDOX) REACTIONS

There are at least two methods which are used for the balancing of redox reactions: the method of electron balancing and the method of electron-ion balancing.

The method of electron balancing should be well-known from the pre-university chemistry course. That method can be used to balance any redox reaction. However, since the method of electron-ion balancing has been developed for redox processes taking place in water solutions, the method of electron balancing is recommended for redox reactions taking place in gaseous and solid phases.

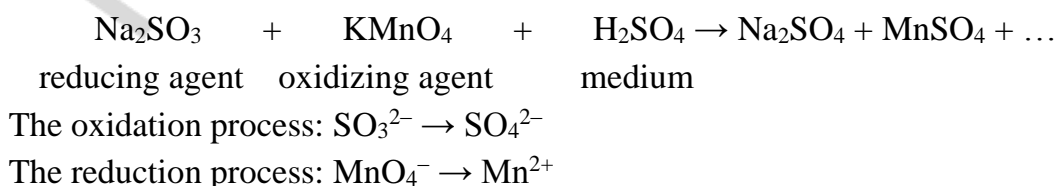
*The electron-ion method* is used not just for balancing, but also for writing redox reactions occurring in water solutions. It is based on the two half-reactions: for oxidation of the reducing agent and for the reduction of the oxidizing agent. In those half-reactions we use particles which really exist in water solutions (ions and molecules, sometimes, units of insoluble ionic substances). Oxidation states of the elements are not used.

In half-reactions we should use the general rules of ionic equations writing: weak electrolytes, gases and insoluble (according to the solubility chart) substances are written completely (they are not separated into ions). Strong acids, strong bases and soluble salts are written separately (in form of ions).

Usually formulas of oxidized and reduced forms have different numbers of oxygen atoms. For example, nitrate ion ( $\text{NO}_3^-$ ) has one additional oxygen atom relative to nitrite ion ( $\text{NO}_2^-$ ). Each half-reaction should have the same number of atoms of each element in the left and the right sides. So, one has to add water molecules,  $\text{H}^+$  or  $\text{OH}^-$  ions to the left and the right side of the half-reaction to make it balanced. Such technique is based on the fact that in the acidic medium there is an excess of  $\text{H}^+$  ions, in the basic medium there is an excess of  $\text{OH}^-$  ions, and, obviously, water molecules are always present in each water solution.

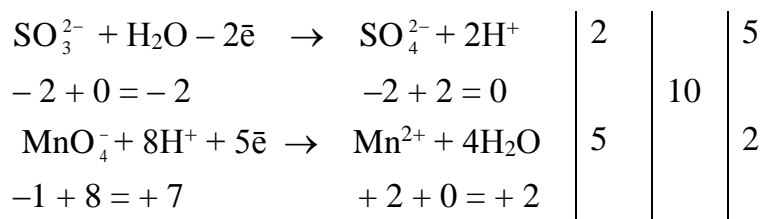
If the reaction takes place **in the acidic medium**, *only water molecules and  $\text{H}^+$  ions can be included in the half-reaction as reactants*. To “remove” one oxygen atom from the molecule or ion we add two  $\text{H}^+$  ions: they will form one water molecule. To “add” one oxygen atom to the molecule or ion we add one water molecule: there will be two  $\text{H}^+$  ions among the products.

For example, let's write the equation of oxidation reaction of sodium sulphite by potassium permanganate in the presence of sulphuric acid:





Half – reactions:



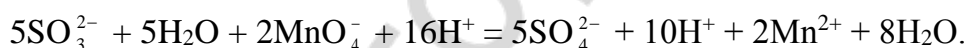
In these half-reactions you should calculate the sum of all charges of ions in the left side and compare it to the sum of all charges of ions in the right side. Then add or remove certain number of electrons to (from) the left side to make the total charges for reactants and products equal to each other.

The algorithm of balancing redox reactions:

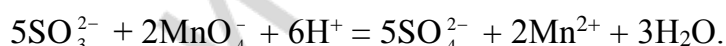
1. Write the half-reactions for the oxidation and reduction processes taking into account the pH of the medium: both the mass and the total charge should be the same in the right and the left side of each half-reaction.

2. Find the lowest common multiple of the number of electrons in the oxidation and reduction half-reactions (in the given case it is 10) and additional multipliers (coefficients) for the first ( $10 : 2 = 5$ ) and the second ( $10 : 2 = 5$ ) half-reaction.

3. Multiply the half-reactions by their additional multipliers (coefficients) and sum up the right side of the first part of the first half-reaction and the right side of the second half-reaction, as well as the left sides of both half-reactions, respectively. As the result we'll get ionic equation of a redox reaction:



After the crossing out of similar members the ion equation will have the following short form:



The obtained short ionic equation shows which particles take part in the reaction and are formed in it. After that write a complete reaction by the way of the addition of cations and anions that were not included into the half-reactions:



If the reaction occurs **in the basic medium**, then only water molecules and OH<sup>-</sup> ions can be included into the half-reactions as reactants. To “add” one oxygen atom we should add two OH<sup>-</sup> ions: one water molecule will appear among products. To “remove” one oxygen atom we should add one water molecule: two OH<sup>-</sup> ions will appear among products.

For example, let's use the plan mentioned above to write the equation for the oxidation reaction of sodium sulphite by potassium permanganate in the basic medium:

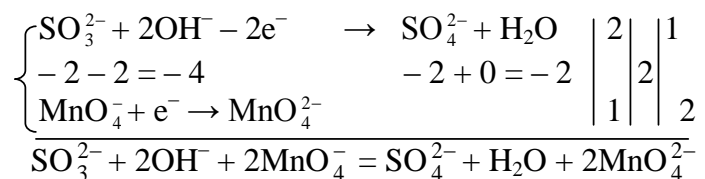


reducing agent      oxidizing agent      medium

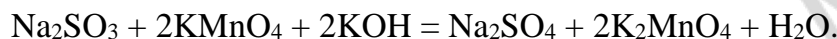
The oxidation process:  $\text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-}$

The reduction process:  $\text{MnO}_4^- \rightarrow \text{MnO}_4^{2-}$

Half-reactions:

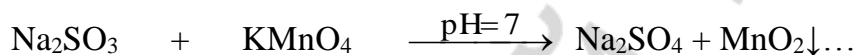


Complete equation of the reaction:



If the reaction occurs **in neutral medium** then we should add only water molecules to the left part. To “add” or “remove” one oxygen atom to (from) the left part of the half-reaction it’s necessary to add one water molecule: in the right part there will be two  $\text{H}^+$  ions or two  $\text{OH}^-$  ions, respectively.

For example, let’s write the equation of oxidation reaction of sodium sulphite by potassium permanganate in the neutral medium:

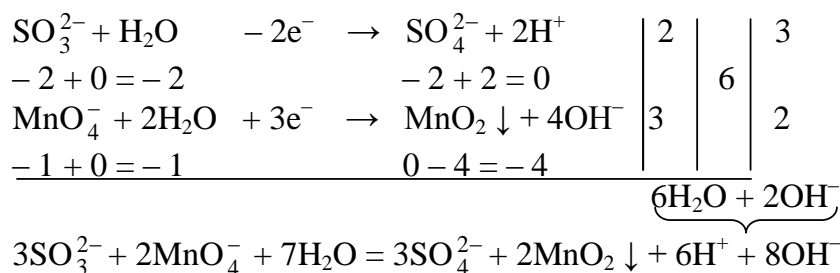


reducing agent    oxidizing agent

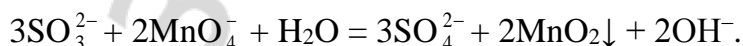
The oxidation process:  $\text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-}$

The reduction process:  $\text{MnO}_4^- \rightarrow \text{MnO}_2 \downarrow$

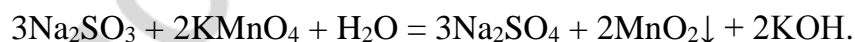
Half-reactions:



Short ionic equation:



Complete equation of the reaction:



### CLASSIFICATION OF THE REDOX TITRATION METHODS

Oxidation-reduction reactions are in the basis of a number of titrimetric analysis methods which has the common name “oxidimetry”. Titrants in these methods must be either strong oxidizers or strong reducers.

Oxidimetry methods are named according to the name of the corresponding titrant:

1) permanganometry: the main titrant is  $\text{KMnO}_4$  solution; solutions of iron sulphate  $\text{FeSO}_4$  and  $\text{H}_2\text{C}_2\text{O}_4$  are usually used together with it;

2) iodometry: titrants are solutions of iodine and sodium thiosulfate  $\text{Na}_2\text{S}_2\text{O}_3$ ;

3) dichromatometry: the main titrant is the solution of potassium dichromate  $\text{K}_2\text{Cr}_2\text{O}_7$ ;

4) bromatometry: titrant is the solution of potassium bromate  $\text{KBrO}_3$ ;

5) nitritometry: titrant is the solution of sodium nitrite  $\text{NaNO}_2$ .

Concentrations of various reducing agents (compounds of iron (II), tin (II), sulphites, arsenites, oxalates, hydrogen peroxide and others) can be determined with the help of strong oxidizers. With the help of reducing agents we can determine concentrations of various oxidizing agents: dichromates, chlorine, hypochlorites, chlorites, bromine, bromates, iodine, iodates, hydrogen peroxide and so on.

Permanganometric and iodometric titrations which will be discussed below are widely used in clinical, hygiene and sanitary and forensic research.

The requirements to the reactions used in oxidimetry are as follows: the reaction should be fast and irreversible; the products should have definite composition; there should not be any side reactions; there should be a method to fix the end of the reaction. The number of reactions which satisfy these criteria is very small. The difference between redox potentials of two substances ( $E = e_{\text{oxid}}^0 - e_{\text{red}}^0$ ) should be higher than 0.4 to make the process almost irreversible. Otherwise, there will be no drastic redox potential jump at the equivalence point.

There are different methods to fix the equivalence point in oxidimetry. For example, in permanganometry the titrant ( $\text{KMnO}_4$ ) has its own color which is disappearing in the solution with the excess of a reducer. At the equivalence point the color of  $\text{KMnO}_4$  doesn't disappear. In iodometry the equivalence point is fixed with the help of starch which reacts specifically with iodine. Special redox indicators (e.g. diphenylamine) can also be used in oxidimetry: they change their color at the certain ratio between concentrations of reducers and oxidizers in the solution.

### **DIRECTION OF SPONTANEOUS REDOX REACTIONS**

In any redox reaction reducer turns to oxidizer and oxidizer turns to reducer. There is a way to determine which of the redox reactions (the forward or the backward one) is spontaneous in standard conditions.

According to the second law of thermodynamics only the processes which are accompanied by the decrease of Gibb's free energy ( $\Delta G < 0$ ) are spontaneous. This happens when the pair of weaker oxidizer and the weaker reducer is formed from the pair of stronger oxidizer and stronger reducer.

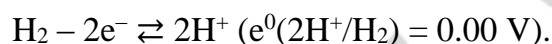
The strength of oxidizing and reducing agents depends on their ability to accept or lose electrons: the higher the ability to accept electrons, the stronger the oxidizing agent and, vice versa, the stronger reducing agent is more prone to lose electrons than the weaker reducing agent. There is an inverse relation between the strengths of coupled oxidizing and reducing agents: the stronger is the oxidizing agent in the couple, the weaker is the reducing agent coupled to it and, vice versa, the weaker oxidizing agent corresponds to the stronger reducing agent.

## OXIDATION-REDUCTION (REDOX) POTENTIAL AS A MEASURE OF OXIDATION AND REDUCTION ABILITY OF SUBSTANCES

The qualitative characteristics of the strength of different redox pairs are the values of their oxidation potentials which are measured in the galvanic element.

To measure absolute values of redox potentials is practically impossible. That's why all redox pairs in the galvanic element are compared to the same standard pair which is a normal hydrogen electrode, the potential of which for convenience is taken as 0:  $e^0(2H^+/H_2) = 0.00 \text{ V}$ .

A normal hydrogen electrode is a platinum plate covered by a layer of spongy platinum which is immersed in HCl or H<sub>2</sub>SO<sub>4</sub> solutions with the active H<sup>+</sup> ion concentration equal to 1 mol/L. Hydrogen under the pressure of 101.3 kPa (1 atm) is constantly added to the solution. The equilibrium state in this system is described by the equation of the half-reaction:



The second (analyzed) electrode in the galvanic element is either a metallic electrode immersed into the solution of the salt of this metal or an inert platinum electrode immersed into the solution containing coupled oxidized and reduced forms. The value of standard potential ( $e^0$ ) of redox system can be calculated in standard conditions, i. e. at the temperature of 298 K and pressure of 1 atmosphere and at active concentrations of oxidized and reduced forms equal to 1 mol/L. If H<sup>+</sup> or OH<sup>-</sup> ions participate in the half-reaction of reduction or oxidation, then their activity should be equal to 1 mol/L.

Let's see some examples.

1. To measure  $e^0(Zn^{2+}/Zn)$  a zinc plate should be immersed into ZnSO<sub>4</sub> solution where  $[Zn^{2+}] = 1 \text{ mol/L}$ .

2. To measure  $e^0(Fe^{3+}/Fe^{2+})$  a platinum electrode should be immersed into the solution containing a mixture of salts FeCl<sub>3</sub> and FeCl<sub>2</sub> where  $[Fe^{3+}] = [Fe^{2+}] = 1 \text{ mol/L}$ .

3. To measure the redox potential of KMnO<sub>4</sub> in the acidic medium ( $MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$ ) a platinum electrode should be immersed into the solution containing KMnO<sub>4</sub>, MnSO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>, where  $[MnO_4^-] = [Mn^{2+}] = 1 \text{ mol/L}$  and  $[H^+] = 1 \text{ mol/L}$ .

EMF (E) of the galvanic element is equal to the difference in potential between two components: a cathode and an anode.

$$E = e^0_{\text{cathode}} - e^0_{\text{anode}}$$

In a pair with a strong oxidation system the standard hydrogen electrode is an anode and with a strong reduction system it becomes a cathode. For example,

$$E_1 = e^0(2H^+ / H_2) - e^0(Zn^{2+} / Zn) = 0.76V,$$

$$E_2 = e^0(Fe^{3+} / Fe^{2+}) - e^0(2H^+ / H_2) = 0.77V,$$

$$E_3 = e^0(MnO_4^- / Mn^{2+}) - e^0(2H^+ / H_2) = 1.51V.$$

The measured value of EMF of the galvanic element numerically is equal to the standard redox potential of the analysed system as  $e^0(2\text{H}^+ / \text{H}_2) = 0.00\text{V}$ :

$$e^0(\text{Zn}^{2+} / \text{Zn}) = -0.76 \text{ V},$$

$$e^0(\text{Fe}^{3+} / \text{Fe}^{2+}) = +0.77 \text{ V},$$

$$e^0(\text{MnO}_4^- / \text{Mn}^{2+}) = +1.51 \text{ V}.$$

The obtained experimental values of standard potentials of some redox systems are shown in table 2.

Table 2

Standard potentials of redox systems relative to the standard hydrogen electrode

Oxidized form	+ ne <sup>-</sup>	Reduced form	e <sup>0</sup> , B
F <sub>2</sub>	+ 2e <sup>-</sup>	2F <sup>-</sup>	+2.87
H <sub>2</sub> O <sub>2</sub> + 2H <sup>+</sup>	+ 2e <sup>-</sup>	2H <sub>2</sub> O	+1.77
MnO <sub>4</sub> <sup>-</sup> + 8H <sup>+</sup>	+ 5e <sup>-</sup>	Mn <sup>2+</sup> + 4H <sub>2</sub> O	+1.51
Cl <sub>2</sub>	+ 2e <sup>-</sup>	2Cl <sup>-</sup>	+1.36
Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> + 14H <sup>+</sup>	+ 6e <sup>-</sup>	2Cr <sup>3+</sup> + 7H <sub>2</sub> O	+1.33
Br <sub>2</sub>	+ 2e <sup>-</sup>	2Br <sup>-</sup>	+1.06
NO <sub>3</sub> <sup>-</sup> + 3H <sup>+</sup>	+ 2e <sup>-</sup>	HNO <sub>2</sub> + H <sub>2</sub> O	+0.94
O <sub>2</sub> + 4H <sup>+</sup> (pH 7)	+ 4e <sup>-</sup>	2H <sub>2</sub> O	+0.82
Fe <sup>3+</sup>	+ e <sup>-</sup>	Fe <sup>2+</sup>	+0.77
O <sub>2</sub> + 2H <sup>+</sup>	+ 2e <sup>-</sup>	H <sub>2</sub> O <sub>2</sub>	+0.69
MnO <sub>4</sub> <sup>-</sup> + 2H <sub>2</sub> O	+ 3e <sup>-</sup>	MnO <sub>2</sub> + 4OH <sup>-</sup>	+0.59
MnO <sub>4</sub> <sup>-</sup>	+ e <sup>-</sup>	MnO <sub>4</sub> <sup>2-</sup>	+0.57
I <sub>2</sub>	+ 2e <sup>-</sup>	2I <sup>-</sup>	+0.54
H <sub>2</sub> SO <sub>3</sub> + 4H <sup>+</sup>	+ 4e <sup>-</sup>	S + 3H <sub>2</sub> O	+0.45
SO <sub>4</sub> <sup>2-</sup> + 8H <sup>+</sup>	+ 6e <sup>-</sup>	S + 4H <sub>2</sub> O	+0.36
Cu <sup>2+</sup>	+ 2e <sup>-</sup>	Cu	+0.34
SO <sub>4</sub> <sup>2-</sup> + 4H <sup>+</sup>	+ 2e <sup>-</sup>	H <sub>2</sub> SO <sub>3</sub> + H <sub>2</sub> O	+0.20
S <sub>4</sub> O <sub>6</sub> <sup>2-</sup>	+ 2e <sup>-</sup>	2S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	+0.08
2H <sup>+</sup>	+ 2e <sup>-</sup>	H <sub>2</sub>	+0.00
O <sub>2</sub> + 2H <sub>2</sub> O	+ 2e <sup>-</sup>	H <sub>2</sub> O <sub>2</sub> + 2OH <sup>-</sup>	-0.076
CrO <sub>4</sub> <sup>2-</sup> + 4H <sub>2</sub> O	+ 3e <sup>-</sup>	Cr(OH) <sub>3</sub> + 5OH <sup>-</sup>	-0.13
Pyruvate	+ 2e <sup>-</sup>	Lactate	-0.185
Cystine	-	Cysteine	-0.33
2H <sup>+</sup> (pH 7)	+ 2e <sup>-</sup>	H <sub>2</sub>	-0.414
S	+ 2e <sup>-</sup>	S <sup>2-</sup>	-0.508
Zn <sup>2+</sup>	+ 2e <sup>-</sup>	Zn	-0.76
Al <sup>3+</sup>	+ 3e <sup>-</sup>	Al	-1.67

To determine oxidative abilities of the system we should use the following rules:

1) the higher is the value of redox potential of the pair, the stronger is the oxidized form of the given pair as an oxidizing agent and the weaker is the reduced form as a reducing agent;

2) the lower is the value of redox potential of the pair, the weaker is the oxidized form as an oxidizing agent and the stronger is the reduced form as a reducing agent.

For example, in case of the three pairs mentioned above we can conclude that the strongest reducing agent is in the pair  $\text{Zn}^{2+}/\text{Zn}$  (metallic zinc) and the strongest oxidizing agent is in the pair  $\text{MnO}_4^-/\text{Mn}^{2+}$  (this is  $\text{MnO}_4^-$  ion).

In the table of standard redox potentials the pairs are usually arranged in the order of the decrease of their potentials (see table 2). In case of such arrangement, the substance situated in the left column of the higher pair can be an oxidizing agent for the substance situated in the right column of the lower pair. For example,  $\text{MnO}_4^-$  ions in the acidic medium ( $e^0 = 1.51$  V) can be an oxidizing agent for  $\text{Cl}^-$  ions ( $e^0 = 1.36$  V) converting them into  $\text{Cl}_2$  and forming  $\text{Mn}^{2+}$  ions.

A stronger oxidizing agent can be found in the left column of the upper part of the table and a stronger reducing agent — in the right column of the lower part of the table.

The values of redox potentials of different pairs depend not only on the nature of oxidized and reduced forms but also on their concentration (activity) and the pH of the solution. This dependence is expressed by Nernst–Peters' equation:

$$e = e^0 + \frac{RT}{nF} \ln \frac{[\text{oxid.}]}{[\text{red.}]}$$

where  $e$  — is the redox potential of the given pair, V;  $e^0$  — standard redox potential of the same pair, V;  $R$  — universal gas constant equal to 8.314 J/mol·K;  $T$  — absolute temperature, K;  $n$  — number of electrons in the half-reaction of the transfer of oxidized form into the reduced one;  $F$  — Faraday's number, i. e. charge of 1 mole of electrons that is equal to 96 500 coulomb/mol;  $[\text{oxid.}]$ ,  $[\text{red.}]$  — active concentrations of oxidized and reduced forms, mol/L.

As we can see from equation, the higher is the temperature, the higher is the concentration of the oxidized form and the lower is the concentration of the reduced form in the solution, the higher is the redox potential value and the higher is the oxidation ability of the system.

In standard conditions  $[\text{oxid.}] = [\text{red.}]$  and  $\ln[\text{oxid.}]/[\text{red.}] = 0$ . Then  $e = e^0$ .

If we substitute the numerical values of the constants in equation (6.1) and pass from natural to decimal logarithms ( $\ln N = 2.303 \log N$ ), then for the temperature of 298 K we'll get:

$$e = e^0 + \frac{0.059}{n} \log \frac{[\text{oxid.}]}{[\text{red.}]}$$

For all three half-reactions described earlier this equation can be written in the following way:

$$e(\text{Zn}^{2+} / \text{Zn}) = -0.76 + \frac{0.059}{2} \log [\text{Zn}^{2+}],$$

$$e(\text{Fe}^{3+} / \text{Fe}^{2+}) = +0.77 + \frac{0.059}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]},$$

$$e(\text{MnO}_4^- / \text{Mn}^{2+}) = +1.51 + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-] \cdot [\text{H}^+]^8}{[\text{Mn}^{2+}]}.$$

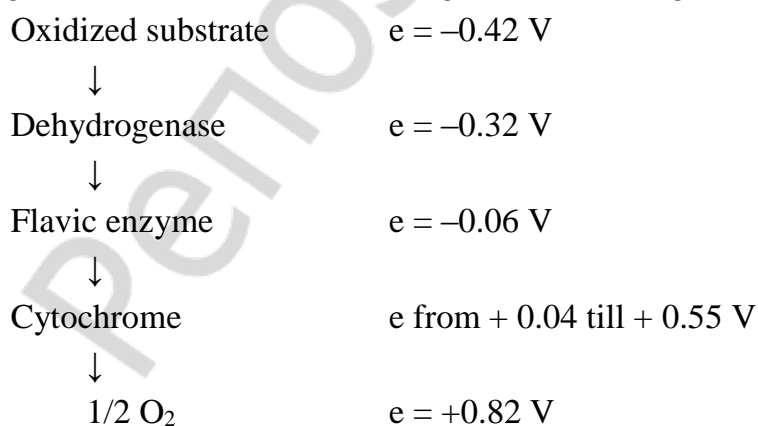
In non-standard conditions hydrogen electrode potential can be calculated on the basis of the following equation:

$$e(2\text{H}^+/\text{H}_2) = 0.00 + \frac{0.059}{1} \log [\text{H}^+] = -0.059 \cdot \text{pH}.$$

To solve the question with the direction of redox reaction in non-standard conditions we should at first calculate the redox potentials according to the Nernst's equation (in which actual concentrations of oxidized and reduced forms are included). In the spontaneous redox reaction the role of an oxidizing agent is played by an oxidized form with a higher value of the redox potential from the pair and the role of a reducing agent is played by a reduced form with a smaller value of the redox potential in the pair.

The higher is the difference of redox potentials of two pairs ( $E = e \text{ oxid.} - e \text{ red.}$ ), the more negative is the value of  $\Delta G$  of the redox reaction. That's why if there are several reducing agents in the solution (e. g.  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ), the added oxidizing agent (e. g. acidic solution of  $\text{KMnO}_4$ ) will react with the strongest reducer first, i. e. it will react with  $\text{I}^-$  ions oxidizing them to free iodine ( $E = 1.51 - 0.54 = 0.97 \text{ V}$ , see tab. 2). After the completion of that reaction the interaction of the remaining  $\text{KMnO}_4$  with  $\text{Br}^-$  ions ( $E = 1.51 - 1.06 = 0.45 \text{ V}$ ) starts. The reaction between  $\text{KMnO}_4$  and  $\text{Cl}^-$  ions begins ( $E = 1.51 - 1.36 = 0.15 \text{ V}$ ) only when there are no more  $\text{Br}^-$  ions.

This circumstance explains why the transfer of electrons and protons in the chain of biological oxidation occurs according to the following scheme:



The strict enzyme sequence in the oxidation chain avoids the drastic difference between the potentials of two interacting systems and this prevents gradual emission of

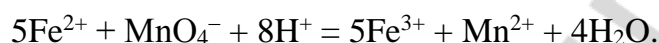
oxidation energy. Such peculiarity of biological oxidation allows the organism to regulate the production and the usage of energy more precisely.

### CURVES OF OXIDIMETRIC TITRATION

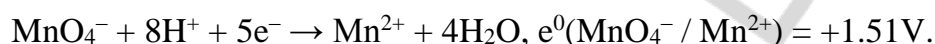
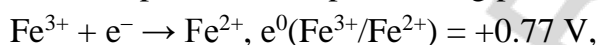
In oxidimetric titration the concentrations of the substances or ions taking part in the reaction are constantly changing together with the redox potential of the solution.

The curves of oxidimetric titration show the dependence of the redox potential of the solution on the volume of the titrant added.

For example, let's consider the curve of iron (II) salt titration by potassium permanganate in the acidic medium:



The values of standard redox potentials for pairs taking part in the reaction are equal to:



In any of the titration moments the solution usually contains two oxidation-reduction pairs:  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and  $\text{MnO}_4^-/\text{Mn}^{2+}$ . The value of the oxidation potential of the titrated solution at different titration moments can be calculated using Nernst–Peter's equation. In the excess of  $\text{Fe}^{2+}$  ions, i. e. before reaching the equivalence point, it's convenient to use the following equation for the calculations:

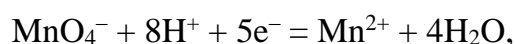
$$e = 0.77 + \frac{0.059}{1} \lg \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}.$$

In the excess of  $\text{MnO}_4^-$  ions in the solution, i.e. after the equivalence moment, it's necessary to do the calculations using the equation:

$$e = 1.51 + \frac{0.059}{5} \lg \frac{[\text{MnO}_4^-] \cdot [\text{H}^+]^8}{[\text{Mn}^{2+}]}.$$

### PERMANGANOMETRY

**The essence of the method.** The method of permanganometry is based on the oxidation of different substances by potassium permanganate. The oxidation is conducted in a strongly acidic medium where permanganate ion demonstrates the strongest oxidation properties. The standard redox potential of  $\text{MnO}_4^-/\text{Mn}^{2+}$  pair is 1.51V. Because of such high value of the redox potential potassium permanganate can react with the majority of reducing agents. The product of  $\text{KMnO}_4$  reduction in the acidic medium is an almost colorless ion  $\text{Mn}^{2+}$ :



which is very convenient for the equivalence point fixation. During titration the pink color of  $\text{MnO}_4^-$  ion stops disappearing in the titrated solution due to just one excessive drop of  $\text{KMnO}_4$  and no special indicator is required.

To create a strongly acidic medium we use  $\text{H}_2\text{SO}_4$  solutions. The use of hydrochloric or nitric acids is prohibited as hydrochloric acid besides its acid properties also exhibits



reducing properties and is able to react with  $\text{KMnO}_4$  with the production of chlorine gas. Nitric acid besides its acidic properties exhibits oxidative properties and can react with numerous reducing agents.

The method of permanganometry is widely used in practice to determine the reducing and oxidizing agents and also the substances which don't exhibit oxidizing and reducing properties (e. g. to determine  $\text{Ca}^{2+}$  ions in the materials of both biological and nonbiological origin).

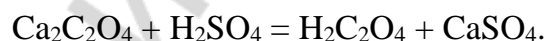
To determine reducing agents we use, as a rule, methods of direct titration, to determine oxidizing agents we use methods of back titration and to determine indifferent substances methods of both back and substitute titration are used.

For example, to determine hydrogen peroxide, iron (II) ions and other reducing agents we carry out direct titration of their solutions by a standardized  $\text{KMnO}_4$  solution.

To determine oxidizing agents such as  $\text{K}_2\text{Cr}_2\text{O}_7$  and others we use methods of back titration. The idea of such methods is the following: we add an excessive volume of the additional solution (for example,  $\text{FeSO}_4$ ) to the solution of the oxidizing agent. Then the rest of  $\text{FeSO}_4$  which hasn't reacted with the determined oxidizing agent is titrated by the  $\text{KMnO}_4$  solution. So, to determine the concentration of an oxidizer by the permanganometry we need both titrant and the additional solution.

To determine concentrations of indifferent substances, e. g.  $\text{Ca}^{2+}$  ions, we can use just one titrant  $\text{KMnO}_4$  (substitute titration) or two titrants ( $\text{KMnO}_4$  and  $\text{H}_2\text{C}_2\text{O}_4$ ) in the back (reverse) titration.

During the substitutive titration the analyzed solution containing  $\text{Ca}^{2+}$  ions is treated by some soluble oxalate, e. g.  $\text{Na}_2\text{C}_2\text{O}_4$ , in such a way that all  $\text{Ca}^{2+}$  ions precipitate in the form of insoluble  $\text{CaC}_2\text{O}_4$ . The precipitate then is filtrated, washed and dissolved in sulphuric acid:



Oxalic acid in the obtained solution is titrated by  $\text{KMnO}_4$  solution. It's obvious that

$$n_{\text{eq}}\text{KMnO}_4 = n_{\text{eq}}\text{H}_2\text{C}_2\text{O}_4 = n_{\text{eq}}\text{Ca}^{2+}.$$

On the basis of this equation we can calculate the mass of  $\text{Ca}^{2+}$  ions in the analyzed sample.

When applying the method of back titration to the analyzed solution containing  $\text{Ca}^{2+}$  ions we add an excess of the standard  $\text{H}_2\text{C}_2\text{O}_4$  solution. The obtained precipitate  $\text{CaC}_2\text{O}_4$  is then separated and thrown away. The rest of unreacted  $\text{H}_2\text{C}_2\text{O}_4$  is titrated by the  $\text{KMnO}_4$ . In this case

$$n_{\text{eq}}(\text{Ca}^{2+}) = n_{\text{eq}}(\text{H}_2\text{C}_2\text{O}_4) - n_{\text{eq}}(\text{KMnO}_4).$$

On the basis of the written equation we can calculate the amount or the mass of  $\text{Ca}^{2+}$  ions in the analyzed sample.

## TITRANT STANDARDIZATION IN PERMANGANOMETRY

We can't prepare a primary standard solution from the crystalline  $\text{KMnO}_4$  which is sold in the pharmacy because even the mark of "cp" (chemically pure) type doesn't satisfy the requirements necessary for the initial substances. It usually contains traces of  $\text{MnO}_2$  in the form of admixtures which can catalyze the reaction of water oxidation by permanganate:

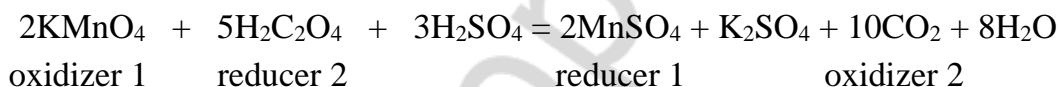


which is usually accompanied by the change in concentration of  $\text{KMnO}_4$  solution. Besides, during the dissolving of even the purest  $\text{KMnO}_4$  in water a part of it is used for the reaction with admixtures of organic substances which are always present in distilled water. Moreover, light can also influence the stability of  $\text{KMnO}_4$  solution.

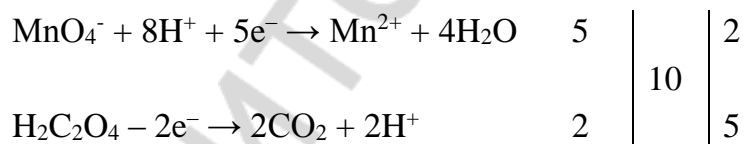
According to the principles indicated above, we should prepare  $\text{KMnO}_4$  solution with the concentration approximately equal to the required one (usually 0.02 or 0.05 mol/L) and leave it for some days till the complete precipitation of  $\text{MnO}_2$ . After that  $\text{KMnO}_4$  solution is taken by the siphon in such a way that  $\text{MnO}_2$  precipitate is left at the bottom.

As primary standards to determine the concentration of  $\text{KMnO}_4$  solution we use anhydrous sodium oxalate  $\text{Na}_2\text{C}_2\text{O}_4$  or oxalic acid dihydrate  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ . These substances after all the preparations satisfy the requirements needed for primary standards and can be used for the preparation of standard solutions.

In a strongly acidic medium  $\text{KMnO}_4$  is reduced by oxalic acid:



Half-reactions:



( $\text{H}_2\text{C}_2\text{O}_4$  is a weak electrolyte that exists in the form of molecules in the strongly acidic medium).

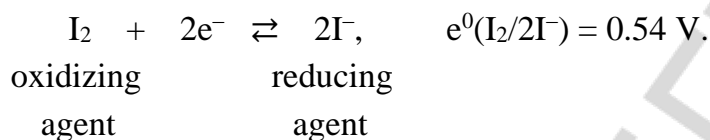
Although reducing properties of oxalate-ions are quite strong ( $e^0(2\text{CO}_2/\text{C}_2\text{O}_4^{2-}) = -0.49 \text{ V}$ ) the reaction between them and  $\text{MnO}_4^-$  ions at the beginning (the first drops of  $\text{KMnO}_4$  solution) occurs very slowly, the following drops of  $\text{KMnO}_4$  solution lose their color very quickly. It is connected with the fact that the considered reaction is autocatalytic and is catalyzed by one of the reaction products, i. e. by  $\text{Mn}^{2+}$  ions.

To speed up the disappearance of the color of first portions of  $\text{KMnO}_4$  the reacting mixture in the titration flask is heated till 80–90 °C (it mustn't be boiled to avoid the decomposition of  $\text{H}_2\text{C}_2\text{O}_4$ ). After the production of the sufficient amount of the catalyst —  $\text{Mn}^{2+}$  ions — the reaction becomes autocatalytic and proceeds at a very high speed so that the following portions of  $\text{KMnO}_4$  solution during titration are losing their color immediately.

KMnO<sub>4</sub> solution with the established concentration in its turn can be a secondary standard solution for the standardization of the reducing agent such as FeSO<sub>4</sub>. This titration is carried out in a cold place because heating of the solution speeds up the side reaction of Fe<sup>2+</sup> ion oxidation by oxygen from the air.

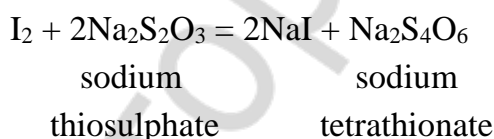
### IODOMETRY

**The idea of the method.** The method of iodometry is based on oxidation-reduction reactions connected with the transformation of I<sub>2</sub> into I<sup>-</sup> ions and vice versa:

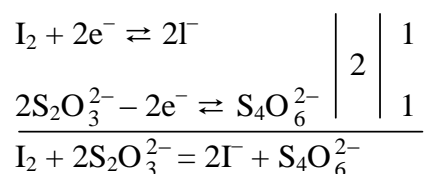


Special features of iodometry exist due to good reversibility of the half-reaction written above and low value of the standard redox potential of the pair I<sub>2</sub>/2I<sup>-</sup>. The value of the redox potential of the pair is intermediate between the values of the potential for typical strong oxidizing and reducing agents and characterizes iodine as the oxidizer of average strength, and I<sup>-</sup> ion as the reducer of average strength. That's why iodometric methods are used for determination of both oxidizing and reducing agents.

The titrants in iodometry are the standard solutions of I<sub>2</sub> (the oxidizer of the method) and sodium thiosulphate Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (the reducer of the method). The main titrimetric reaction in this method is the interaction of iodine solution and solution of sodium thiosulphate:



Half-reactions and ionic equation of the reaction:



As an indicator in iodometry we use water solution of starch which forms iodine-starch compound of blue color with molecular iodine. When the reducing agent is titrated by the solution of iodine the equivalence point is determined by the appearance of the intensive-blue color. When iodine is titrated by the solution of sodium thiosulphate the end of the reaction is determined by the disappearance of the blue color after the addition of one final drop of sodium thiosulphate solution.

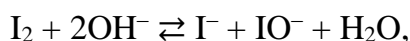
Starch should be added at the very end of titration when there is low concentration of iodine and the solution becomes pale yellow. The starch added to the solution with high iodine concentration becomes black. In such conditions starch will be destroyed. This side reaction will introduce significant mistake in the determination of the equivalence point. Because of the very high sensitivity of starch to iodine and the drastic color change of

the solution in the equivalence point, we can use lower concentrations of titrants (0.01–0.05 N) in this method, relatively to other methods of oxidimetry.

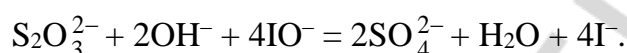
Many iodometric reactions are reversible and proceed till the end only in certain conditions:

1) titration should be conducted in a cold place because: iodine is a volatile substance, at higher temperature starch sensitivity to iodine decreases;

2) pH of the solution mustn't exceed 9 because in the basic medium iodine reacts according to the equation:



and  $\text{IO}^-$  that is a stronger oxidizer than  $\text{I}_2$  oxidizes thiosulphate-ion up to sulphate-ion:

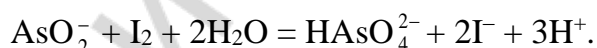
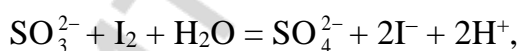


The greatest advantage of iodometric method is the availability of a very sensitive (and reversible) indicator. The disadvantages of the method are low stability of iodine solution and reversible nature of the reaction between iodine and many reducing agents.

### EXAMPLES OF IODOMETRIC DETERMINATIONS

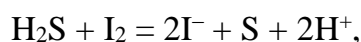
Iodometric determination of reducers is carried out using the method of direct or back titration. Oxidizing agents are determined by the substitutive titration.

The solution of iodine is used for the determination of reducing agents concentrations by the method of direct titration. This method determines arsenic (III), antimony (III), tin (II) compounds; thiosulphates, small amounts of  $\text{H}_2\text{S}$  (e. g. in mineral water), sulphides and sulphites. The examples of reactions taking place during the direct titration of reducing agents by iodine are the following:

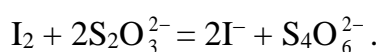


In those cases when direct titration is more complicated (e. g. the reducer is volatile or the reaction occurs very slowly) we use the method of back (reverse) titration to determine reducing agents.

To do this we need two solutions: solutions of iodine and sodium thiosulphate. We add an excess of iodine solution to the flask with the solution of the reducer. The reaction between iodine and the reducing agent occurs. Then the remaining iodine is titrated by sodium thiosulphate solution. For example, to determine  $\text{H}_2\text{S}$  concentration we need the following reactions:



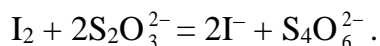
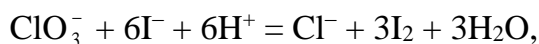
excess



remaining part

This method helps to determine high concentrations of H<sub>2</sub>S, sulphides and sulphites, metals in the form of powder (e. g. zinc), some organic compounds.

To determine oxidizing agents by the method of substitutive (indirect) titration we should do the following. We should add the oxidizing agent (e. g. KClO<sub>3</sub> solution of the known volume but unknown concentration) to the excess of acidic KI solution. Then the iodine produced in that reaction is titrated by sodium thiosulphate:



The number of moles of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> equivalents is equal to the number of moles of iodine equivalents, the latter being equal to the number of moles of the determined oxidizing agent (KClO<sub>3</sub>) equivalents. So, although the determined oxidizing agent and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> don't react directly, the amounts of their equivalents are identical. That's why we can use an ordinary formula used in direct titration to do the calculations:

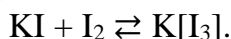
$$C_N(\text{KClO}_3) \cdot V(\text{KClO}_3) = C_N(\text{Na}_2\text{S}_2\text{O}_3) \cdot V(\text{Na}_2\text{S}_2\text{O}_3).$$

Using this method we can determine many oxidizing agents, e. g. Cl<sub>2</sub>, Br<sub>2</sub>, KMnO<sub>4</sub>, KClO<sub>3</sub>, CaOCl<sub>2</sub>, nitrites, H<sub>2</sub>O<sub>2</sub>, salts of Fe(III), Cu(II), arsenic compounds.

#### TITRANT STANDARDIZATION IN IODOMETRY

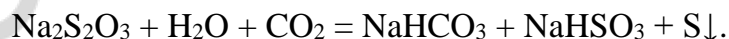
Crystalline iodine usually contains moisture and admixtures of chlorine and bromine compounds. Due to its volatility crystalline iodine can't be the initial substance and is rarely used as a primary standard. More often we prepare iodine solution with the concentration approximately equal to the required one and then the exact solution concentration is established with the help of the standardized solution of sodium thiosulphate.

**Molecular iodine is poorly dissolved in water.** To prepare the solution we use such property as good solubility of iodine in KI solution and, as a result, the formation of a complex compound:

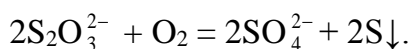


Triiodide-ion I<sub>3</sub><sup>-</sup> and molecular iodine in redox reactions behave in the same way. Because of this we can write I<sub>2</sub> in chemical reactions but mean I<sub>3</sub><sup>-</sup> ion.

Sodium thiosulphate solution is prepared from Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> · 5H<sub>2</sub>O crystalline hydrate of the variable composition. Besides, when sodium thiosulphate is dissolving in water it is partially decomposed by CO<sub>2</sub>:



On the other hand, thiosulphate ions react very slowly with molecular oxygen from the air:



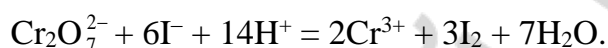
Due to sulphur precipitation the solution becomes turbid and a white precipitate appears on the bottom. To decrease the rate of thiosulphate ion decomposition we should use freshly boiled and cooled water to prepare the solution. The prepared solution is left for

8–10 days and after that we should determine its concentration using the primary standard of the method.

As primary standards for the determination of  $\text{Na}_2\text{S}_2\text{O}_3$  solution concentration we use potassium dichromate  $\text{K}_2\text{Cr}_2\text{O}_7$  or potassium iodate  $\text{KIO}_3$ .

It should be noted that sodium thiosulphate is a strong reducing agent ( $e^0(\text{S}_4\text{O}_6^{2-}/2\text{S}_2\text{O}_3^{2-}) = +0.08 \text{ V}$ ). It reacts quickly and stoichiometrically with triiodide-ions with the formation of tetrathionate-ions. With many other oxidizing agents, e. g.  $\text{MnO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{BrO}_3^-$ ,  $\text{IO}_3^-$  and so on, thiosulphate-ions react nonstoichiometrically. This excludes the possibility to use direct titration of oxidizing agents by  $\text{Na}_2\text{S}_2\text{O}_3$  solution. That's why the determination of exact concentration of  $\text{Na}_2\text{S}_2\text{O}_3$  solution using potassium dichromate or iodate as primary standards is based on the method of substitute (indirect) titration.

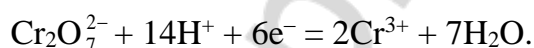
Potassium dichromate in the acidic medium reacts stoichiometrically with soluble iodates with the formation of the equivalent amount of molecular iodine:



The formed molecular iodine is titrated by sodium thiosulphate solution (we need to determine the exact concentration of that solution). It's obvious that

$$n_{\text{eq}}(\text{K}_2\text{Cr}_2\text{O}_7) = n_{\text{eq}}(\text{I}_2) = n_{\text{eq}}(\text{Na}_2\text{S}_2\text{O}_3),$$

as reduction reaction of dichromate-ions corresponds to the half-reaction:



We use the excess of KI (to be sure that all the dichromate ions really reacted) and  $\text{H}_2\text{SO}_4$  solution to increase the oxidation potential of the pair  $\text{Cr}_2\text{O}_7^{2-}/2\text{Cr}^{3+}$  and to be sure that dichromate ions will not form chromate ions, as they always do in neutral and basic medium.

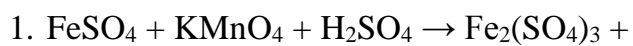
$\text{Na}_2\text{S}_2\text{O}_3$  solution with the established concentration in its turn can serve as a secondary standard solution for iodine solution standardization by the method of direct titration.

### **Main questions of the topic:**

1. Writing redox reactions using the electron-ion method.
2. The method of permanganometry.
3. The method of iodometry.
4. Prediction of the direction of the redox reaction using standard redox potentials.

### **Writing equations of redox reactions and determination of their direction.**

**I.** Using electron-ion method, write down the equations of the reactions listed below; in each reaction indicate the oxidizing and reducing agents and determine the equivalence factor for them.



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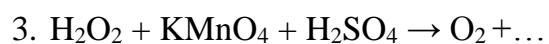
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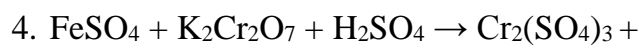
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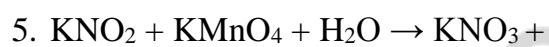
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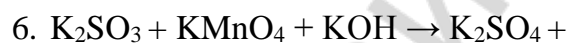
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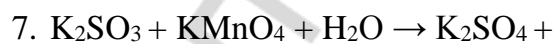
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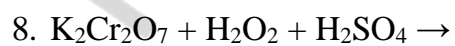
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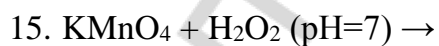
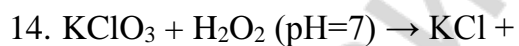
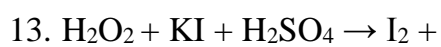
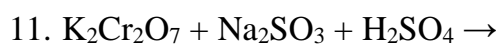
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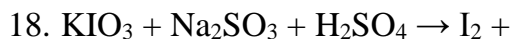




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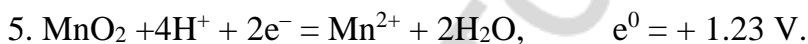
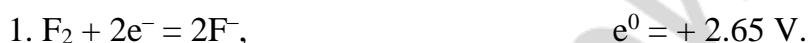


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**II.** On basis of the values of standard redox potentials listed below, determine which of the negatively charged ions  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$  can be oxidized to free halogens by manganese dioxide  $\text{MnO}_2$  in the acidic medium (in standard conditions).



Using the method of electron-ion balancing write the equations of possible redox processes.

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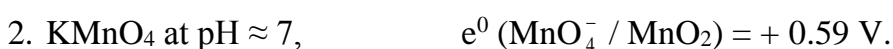
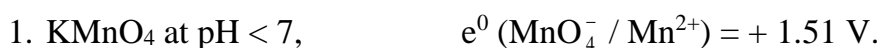
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**III.** Using the values of standard redox potentials, determine which oxidizing agents from those listed below can oxidize  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  if  $e^0(\text{Fe}^{3+}/\text{Fe}^{2+}) = + 0.77 \text{ V.}$



3.  $\text{H}_2\text{O}_2$  at  $\text{pH} > 7$ ,  $e^0 (\text{H}_2\text{O}_2 / 2\text{OH}^-) = + 1.17 \text{ V}$ .

4.  $\text{KIO}_3$  at  $\text{pH} > 7$ ,  $e^0 (\text{IO}_3^- / \text{I}^-) = + 0.26 \text{ V}$ .

### LABORATORY WORK (P)

#### “THE INFLUENCE OF DIFFERENT FACTORS ON REDOX REACTIONS”

**The aim of the work:** to study redox properties of certain substances and the influence of different factors on redox reactions.

**Equipment:** Graduated tubes; chemical tubes; ethanol stoves; porcelain cups; chemical glasses; tripods; glass sticks; holders.

**Reactants:** Dry ammonium dichromate; 0.5 N sodium sulfite solution; dilute and more concentrated sulfuric acid solutions; potassium dichromate solution; potassium dichromate solution; potassium hydroxide solution; sodium hydroxide solution; potassium iodide solution; 3 % hydrogen peroxide solution; 0.2 % starch solution.

#### The color of manganese compounds

The oxidation state of manganese	Precipitates or ions	Samples of compounds	The color
+7	$\text{MnO}_4^-$	$\text{KMnO}_4$ , $\text{NaMnO}_4$	From pink to purple and violet (with the increase of concentration)
+6	$\text{MnO}_4^{2-}$	$\text{K}_2\text{MnO}_4$ , $\text{Na}_2\text{MnO}_4$	green
+4	$\text{MnO}_2$ (insoluble)	$\text{MnO}_2$	brown
+2	$\text{Mn}^{2+}$	$\text{MnSO}_4$ , $\text{MnCl}_2$	From colorless to pale pink (with the increase of concentration)

#### Task 1. The influence of pH on the oxidative properties of potassium permanganate.

Pour approximately 1 ml of 0.5 N  $\text{KMnO}_4$  solution in each of the three tubes. Add 1 ml of 2 N  $\text{H}_2\text{SO}_4$  solution to the first tube; 1 ml of distilled water to the second tube and 1 ml of 0.5 M sodium hydroxide solution to the third one. Then add to each of these tubes 0.5 N solution of sodium sulfite in the drop by drop manner until the color of the solution will change. Write chemical reactions happened in these three tubes, balance them with the method of ionic half-reactions and indicate the factor of equivalence for  $\text{KMnO}_4$  in each of the three cases.

Reaction 1: \_\_\_\_\_

Gain of electrons: \_\_\_\_\_

Loss of electrons: \_\_\_\_\_

Reaction 2: \_\_\_\_\_

Gain of electrons: \_\_\_\_\_

Loss of electrons: \_\_\_\_\_

Reaction 3: \_\_\_\_\_

Gain of electrons: \_\_\_\_\_

Loss of electrons: \_\_\_\_\_

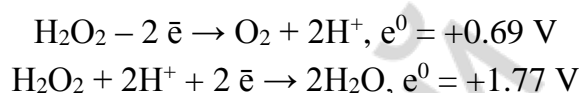
Calculate standard EMF levels for each of the three processes using the table with standard redox potentials.

EMF 1: \_\_\_\_\_ EMF 2: \_\_\_\_\_ EMF 3: \_\_\_\_\_

KMnO<sub>4</sub> has the highest oxidative properties in \_\_\_\_\_ medium.

### **Task 2. Reductive and oxidative properties of hydrogen peroxide.**

Hydrogen peroxide can play the role of both oxidizer and reducer. When H<sub>2</sub>O<sub>2</sub> reacts with a stronger oxidizer it forms oxygen (O<sub>2</sub>). When H<sub>2</sub>O<sub>2</sub> reacts with a stronger reducer it forms water. This substance can also spontaneously disproportionate into both O<sub>2</sub> and H<sub>2</sub>O. Redox potentials (in the acidic medium) for the corresponding half-reactions are written below.



**Experiment 1.** *The reaction between hydrogen peroxide and potassium permanganate in the acidic medium.*

Pour about 1 ml of potassium permanganate solution into the tube and add approximately equal volume of sulfuric acid solution. Then add approximately the same volume of the hydrogen peroxide solution to the same tube. Describe the results. Write the equation of chemical reaction and balance it with two half-reactions. Calculate the EMF level.

Reaction: \_\_\_\_\_

Gain of electrons: \_\_\_\_\_

Loss of electrons: \_\_\_\_\_

EMF: \_\_\_\_\_

**Experiment 2.** *The reaction between hydrogen peroxide and potassium iodide in the acidic medium.*

Pour about 1 ml of the potassium iodide solution in the tube. Add approximately the same volume sulfuric acid solution to that tube. Then add approximately the same volume of the hydrogen peroxide solution to the same tube together with several drops of the starch solution. Write the equation of chemical reaction and balance it with two half-reactions. Calculate the EMF level.

Reaction: \_\_\_\_\_

Gain of electrons: \_\_\_\_\_

Loss of electrons: \_\_\_\_\_

EMF: \_\_\_\_\_

Explain why hydrogen peroxide can demonstrate properties of both reducer and oxidizer. What factor determines whether it will be a reducer or an oxidizer?

\_\_\_\_\_

\_\_\_\_\_

**Task 3. The decomposition of ammonium dichromate (volcano) as an example of redox reaction between the atoms from the same compound.**

Put a portion of the ammonium dichromate ( $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ ) in the porcelain cup. Heat the end of the glass stick in the flame of the ethanol stove and then put it in the middle of the ammonium dichromate portion. Remove the stick only after the start of the intensive reaction. Then cover the porcelain cup with the large chemical glass. Describe your observations. Why the walls of the glass have been covered with water drops? Write the equation of chemical reaction and balance it with two half-reactions.

Reaction: \_\_\_\_\_

Gain of electrons: \_\_\_\_\_

Loss of electrons: \_\_\_\_\_

**Task 4. Reactions of disproportioning and conproportioning.**

**Experiment 1.** *The disproportioning of iodine in the basic medium.*

Pour about 1 ml of sodium hydroxide solution into the tube. Heat that tube in the flame of the ethanol stove but don't boil it. Add approximately the same volume of iodine solution to that tube with a hot alkali. Keep the resulting mixture for the next experiment. Describe your observations. Write the equation of chemical reaction and balance it with two half-reactions.

Reaction: \_\_\_\_\_

Gain of electrons: \_\_\_\_\_

Loss of electrons: \_\_\_\_\_

**Experiment 2.** *The conproportioning of sodium iodate and sodium iodide in the acidic medium.*

Add approximately the same volume of the sulfuric acid solution to the tube from the previous experiment. Describe your observations. Why the color appeared after the addition of sulfuric acid? Write the equation of chemical reaction and balance it with two half-reactions.

Reaction: \_\_\_\_\_

Gain of electrons: \_\_\_\_\_

Loss of electrons: \_\_\_\_\_

Which substances are able to participate in dis- and conproportioning reactions?

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**Conclusion:** *“I studied redox properties of certain substances and the influence of different factors on redox reactions”.*

**LABORATORY WORK (M, D) “DETERMINATION OF THE MASS OF A SUBSTANCE IN THE GIVEN VOLUME OF THE ANALYZED SOLUTION”**

**The task:** to determine the mass of  $\text{Fe}^{2+}$  ions in \_\_\_\_\_ ml of the iron (II) sulfate solution  $\text{FeSO}_4$ .

**The aim of the work:** to learn how to use permanganometric titration for quantitative determination of reducing agents by the method of direct titration.

**Reactants:** the solution of  $\text{FeSO}_4$  with unknown concentration; the solution of  $\text{KMnO}_4$  with the known concentration (0.05N); 1M solution of  $\text{H}_2\text{SO}_4$ .

**Labware:** burettes; Mohr’s pipettes; graduated cylinders for  $\text{H}_2\text{SO}_4$  solution; flasks for titration; funnels; rubber pumps.

We should fill in the burette with  $\text{KMnO}_4$  solution (the exact concentration of that solution is to be established in this work). As  $\text{KMnO}_4$  solution has a dark color, zero mark on the burette should be established using the upper edge of meniscus.

We should pour 10 mL of 1M  $\text{H}_2\text{SO}_4$  solution into the flask by the graduated cylinder. Then we should add 10.00 mL of the analyzed  $\text{FeSO}_4$  solution (by the Mohr’s pipette) into the same flask.

The content of the flask should be titrated in a cold place until the appearance of pale-rosy color that is stable for 30 seconds. The results of the three titration experiments should be close to each other (the difference must not be higher than 0.1 mL).

Using the results of the titration we should calculate the normality of the analyzed solution of iron (II) salt and the mass of  $\text{Fe}^{2+}$  in the given volume of the solution.

Write the results of three tries in the table below:

The number of the try	$C_{\text{eq}}(\text{KMnO}_4)$ , mol/L	$V(\text{KMnO}_4)$ , ml	$V(\text{FeSO}_4)$ , ml
1			10.0
2			10.0
3			10.0

Calculate the average volume of  $\text{KMnO}_4$  solution:

$$V_{\text{av}}(\text{KMnO}_4) = (V_1 + V_2 + V_3) / 3 = \underline{\hspace{1cm}} + \underline{\hspace{1cm}} + \underline{\hspace{1cm}} = \underline{\hspace{1cm}} \text{ ml}$$

Using the law of equivalence calculate the normality of the  $\text{FeSO}_4$  solution:

$$C_{\text{eq}}(\text{KMnO}_4) \cdot V(\text{KMnO}_4) = C_{\text{eq}}(\text{FeSO}_4) \cdot V(\text{FeSO}_4).$$

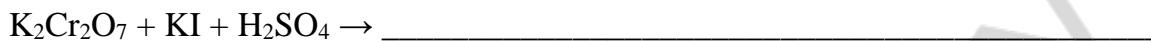
It means that:

$$C_{\text{eq}}(\text{FeSO}_4) = (C_{\text{eq}}(\text{KMnO}_4) \cdot V(\text{KMnO}_4)) / V(\text{FeSO}_4) = \underline{\hspace{1cm}} \text{ mol/L}.$$



the  $K_2Cr_2O_7$  solution (with the help of Mohr's pipette). Three flasks prepared in this way should be kept for 20 minutes in the dark place (to let the reaction between  $K_2Cr_2O_7$  and KI go up to the completion and avoid the degradation of  $I_2$  induced by the light).

Balance the chemical reaction of the described process using the ion-electron balancing.



The gain of electrons:  $\underline{\hspace{10cm}}$

The loss of electrons:  $\underline{\hspace{10cm}}$

After 20 minutes start the titration of the solution in the flask with the  $Na_2S_2O_3$  from the burette. The reddish solution soon will start its drift towards more yellow color. When the color will become approximately the same as that in the flask with the initial  $K_2Cr_2O_7$  solution add two drops of the starch in the flask and continue titration. After the addition of starch the yellow solution should turn to blue. Next drops of the titrant should be added slowly: each of the drops may convert blue solution into the almost colorless one. When your solution will become colorless, stop the titration and measure the volume of the titrant spent for it.

Write the results of three tries in the table below:

The number of the try	$C_{eq}(Na_2S_2O_3)$ , mol/L	$V(Na_2S_2O_3)$ , ml	$V(K_2Cr_2O_7)$ , ml
1			10.0
2			10.0
3			10.0

Calculate the average volume of  $Na_2S_2O_3$  solution:

$$V_{av}(Na_2S_2O_3) = (V_1 + V_2 + V_3) / 3 = \underline{\hspace{2cm}} + \underline{\hspace{2cm}} + \underline{\hspace{2cm}} = \underline{\hspace{2cm}} \text{ ml}$$

Balance the chemical reaction of the described process using the ion-electron balancing.



The gain of electrons:  $\underline{\hspace{10cm}}$

The loss of electrons:  $\underline{\hspace{10cm}}$

On the basis of the results of the titration we should calculate the normality of the  $K_2Cr_2O_7$  solution.

$$C_{eq}(K_2Cr_2O_7) \cdot V(K_2Cr_2O_7) = C_{eq}(Na_2S_2O_3) \cdot V(Na_2S_2O_3).$$

It means that:

$$C_{eq}(K_2Cr_2O_7) = (C_{eq}(Na_2S_2O_3) \cdot V(Na_2S_2O_3)) / V(K_2Cr_2O_7) = \underline{\hspace{2cm}} \text{ mol/L}$$

The mass of  $K_2Cr_2O_7$  in the suggested weight should be calculated by the following formula in which  $V_0$  is the volume of the graduated flask (in L):

$$m(K_2Cr_2O_7) = C_{eq}(K_2Cr_2O_7) \cdot V_0 \cdot M(K_2Cr_2O_7) \cdot f_{eq}(K_2Cr_2O_7) = \\ = \underline{\hspace{2cm}} \cdot \underline{\hspace{2cm}} \cdot \underline{\hspace{2cm}} \cdot \underline{\hspace{2cm}} = \underline{\hspace{2cm}} \text{ g}$$

**The conclusion:** "I estimated the mass of  $K_2Cr_2O_7$  in the given weight using iodometry titration method. It is equal to:  $\underline{\hspace{2cm}}$  g".

## TEST SELF-CHECK

You have a list of questions (phrases) and a list of answers indicated by the letters. In each question there is just one correct answer. The letter designating the answer can be used once, several times or may be not used at all.

Questions	Answers
<p><b>Choose the equivalence factor of the oxidizing agent in the following transformations:</b></p> <p>1. <math>\text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+}</math>                      3. <math>\text{MnO}_4^- \rightarrow \text{MnO}_2</math></p> <p>2. <math>\text{NO}_3^- \rightarrow \text{NO}_2^-</math>                              4. <math>\text{BrO}_3^- \rightarrow \text{Br}^-</math></p>	<p>a) 1/2. b) 1/5 c) 1/3 d) 1/6 e) 1/4</p>
<p><b>Choose the primary standards for the standardization of the following titrants:</b></p> <p>5. <math>\text{KMnO}_4</math>    7. <math>\text{Na}_2\text{S}_2\text{O}_3</math></p> <p>6. <math>\text{NaOH}</math>    8. <math>\text{H}_2\text{SO}_4</math></p>	<p>a) <math>\text{MgSO}_4</math> b) <math>\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}</math> c) <math>\text{Na}_2\text{CO}_3</math> d) <math>\text{NaCl}</math> e) <math>\text{K}_2\text{Cr}_2\text{O}_7</math></p>
<p><b>Which titrants can be used to titrate the following substances in the method of direct titration:</b></p> <p>9. <math>\text{Na}_2\text{C}_2\text{O}_4</math>                                      11. <math>\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}</math></p> <p>10. <math>\text{NaCl}</math>    12. <math>\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}</math></p>	<p>a) <math>\text{KMnO}_4</math> b) <math>\text{CH}_3\text{COOH}</math> c) <math>\text{I}_2</math> d) <math>\text{HCl}</math> e) <math>\text{AgNO}_3</math></p>
<p><b>Which pairs of titrants should be used for the determination of the following substances by the method of reverse titration:</b></p> <p>13. <math>\text{CaCO}_3</math>                                        15. <math>\text{Na}_2\text{SO}_3</math></p> <p>14. <math>\text{K}_2\text{Cr}_2\text{O}_7</math>                                      16. <math>\text{NH}_4\text{Cl}</math></p>	<p>a) <math>\text{HCl}</math> and <math>\text{NaOH}</math>. b) <math>\text{I}_2</math> and <math>\text{Na}_2\text{S}_2\text{O}_3</math>. c) <math>\text{CH}_3\text{COOH}</math> and <math>\text{NH}_4\text{OH}</math>. d) <math>\text{I}_2</math> and <math>\text{FeSO}_4</math>. e) <math>\text{KMnO}_4</math> and <math>\text{FeSO}_4</math>.</p>
<p><b>Which indicator should be used to fix the equivalence point during the following titrations:</b></p> <p>17. <math>\text{H}_2\text{O}_2</math> by the solution <math>\text{KMnO}_4</math> in acidic medium</p> <p>18. <math>\text{CH}_3\text{COOH}</math> by the <math>\text{KOH}</math> solution</p> <p>19. Iodine by the <math>\text{Na}_2\text{S}_2\text{O}_3</math> solution</p> <p>20. Ammonia solution by the <math>\text{H}_2\text{SO}_4</math> solution</p>	<p>a) <math>\text{K}_2\text{CrO}_4</math> b) methyl orange (pT = 4.0) c) phenolphthalein (pT = 9.0) d) starch e) indicator is not needed</p>



## PROBLEMS

### Permanganometry

1. Calculate the molar masses of the equivalents: a)  $\text{Fe}^{2+}$ ; b)  $\text{Na}_2\text{C}_2\text{O}_4$ ; c) KI in reactions with  $\text{KMnO}_4$  in the acidic medium.

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Answer: \_\_\_\_\_

2. To titrate 0.0244 g of  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  we used 19.5 mL of  $\text{KMnO}_4$  solution. Calculate the normality of  $\text{KMnO}_4$  solution.

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Answer: \_\_\_\_\_

3. To titrate 25.0 mL of 0.0500 N  $\text{KMnO}_4$  solution in the acidic medium we used 10.2 mL of sodium nitrite solution. How many grams of  $\text{NaNO}_2$  are in 100 mL of its solution?

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Answer: \_\_\_\_\_

4. 2.50 g of hydrogen peroxide solution were diluted by water till 200 mL. To titrate 5.0 mL of the obtained solution in the acidic medium we used 20.0 mL of 0.05N  $\text{KMnO}_4$  solution. Calculate the mass fraction of  $\text{H}_2\text{O}_2$  in the initial concentrated solution.

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Answer: \_\_\_\_\_

5. We added 20.0 mL of 0.1N  $\text{FeSO}_4$  solution to 10.0 mL of the analyzed solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution (in the presence of sulfuric acid). To titrate the excess of  $\text{FeSO}_4$  we used 28.0 mL of 0.0500 N  $\text{KMnO}_4$  solution. Calculate how many grams of  $\text{K}_2\text{Cr}_2\text{O}_7$  are in 200 mL of the analyzed solution.

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Answer: \_\_\_\_\_

6. To determine the content of calcium in blood serum it is precipitated in the form of  $\text{CaC}_2\text{O}_4$  by the addition of ammonium oxalate to 0.50 mL of the serum. The precipitate is filtered, washed and dissolved in sulfuric acid. The obtained solution is titrated by 0.0100 N  $\text{KMnO}_4$  solution until the appearance of rosy color. Calculate the amount of calcium in milligrams per 100 mL of the serum if we used 0.25 mL of  $\text{KMnO}_4$  solution to titrate it.

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Answer: \_\_\_\_\_

### Iodometry

7. How many grams of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  ( $f_{\text{eq}} = 1$ ) should be taken to prepare 2 L of 0.02 N sodium thiosulfate solution?  $M(\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}) = 248 \text{ g/mol}$ .

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Answer: \_\_\_\_\_

8. To titrate 20.0 mL of 0.0195 N sodium thiosulfate solution we used 20.1 mL of iodine solution. Determine the normality of iodine solution.

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Answer: \_\_\_\_\_

9. To titrate the solution containing 2.5 g of technical sodium thiosulfate we used 81.5 mL of 0.1N iodine solution. Calculate the mass fraction of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in that technical sample.

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Answer: \_\_\_\_\_

10. We dissolved 2.60 g of potassium dichromate in water and prepared 1L of the solution. Calculate the molar concentration and normality of the obtained solution if the equivalence factor of  $\text{K}_2\text{Cr}_2\text{O}_7$  is  $1/6$ .

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Answer: \_\_\_\_\_

11. 0.0980 g of chemically pure  $K_2Cr_2O_7$  is treated by potassium iodide solution (in the acidic medium). To titrate the formed iodine we used 25.5 mL of sodium thiosulfate solution. Calculate the normality of  $Na_2S_2O_3$  solution.

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Answer: \_\_\_\_\_

12. We added 20.0 mL of 0.1133 N  $KMnO_4$  solution to the potassium iodide solution (in the acidic medium) and the formed iodine was titrated by 25.9 mL of sodium thiosulfate solution. Calculate the normality of sodium thiosulfate solution.

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Answer: \_\_\_\_\_

13. To determine the content of active chlorine we dissolved 2.5615 g of lime white in a volumetric flask of 250 mL. To titrate 5.0 mL of the solution after its treating with KI and  $H_2SO_4$  we used 17.4 mL of 0.02N sodium thiosulfate solution. Calculate the mass fraction of active chlorine in lime white.

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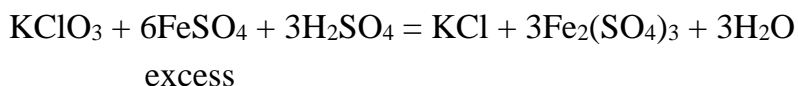
Answer: \_\_\_\_\_

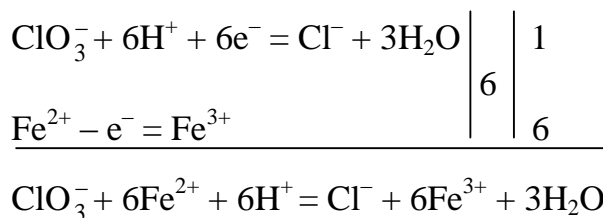
## STANDARDS OF PROBLEM SOLUTIONS

### Calculations based on the results of back titration

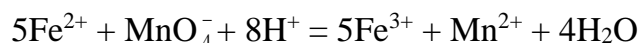
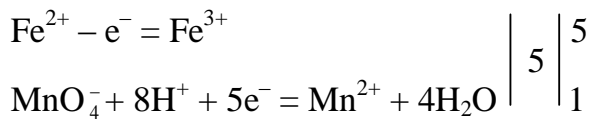
**Problem 1.** We added 20.00 mL of 0.1050 N  $FeSO_4$  solution to 10 mL of the analyzed  $KClO_3$  solution (in the acidic medium). To titrate the excess of  $FeSO_4$  we used 12.48 mL of 0.076 N  $KMnO_4$  solution. How many grams of  $KClO_3$  are there in 250 mL of the analyzed solution?

*Solution.* In the task we used the method of back titration for the quantitative determination of  $KClO_3$  by the permanganometry. The solutions: 0.1050 N  $FeSO_4$  and 0.076 N  $KMnO_4$ . The equations of chemical reactions:





the remaining portion



(When writing down these equations in a complete form all members of the ion equation should be multiplied by 2 because two  $\text{Fe}^{3+}$  ions are included in the composition of  $\text{Fe}_2(\text{SO}_4)_3$ ).

From the half-reactions we can see that  $f_{\text{eq}}(\text{KClO}_3) = 1/6$ ,  $f_{\text{eq}}(\text{FeSO}_4) = 1$ ,  $f_{\text{eq}}(\text{KMnO}_4) = 1/5$ .

The equivalence principle for this given case of the indirect titration is the following:

$$n_{\text{eq}}(\text{FeSO}_4) = n_{\text{eq}}(\text{KClO}_3) + n_{\text{eq}}(\text{KMnO}_4).$$

$$N(\text{FeSO}_4) \cdot V(\text{FeSO}_4) = N(\text{KClO}_3) \cdot V(\text{KClO}_3) + N(\text{KMnO}_4) \cdot V(\text{KMnO}_4).$$

Hence,

$$\begin{aligned} N(\text{KClO}_3) &= (N(\text{FeSO}_4) \cdot V(\text{FeSO}_4) - N(\text{KMnO}_4) \cdot V(\text{KMnO}_4)) / V(\text{KClO}_3) = \\ &= (0.1050 \cdot 20.00 - 0.07600 \cdot 12.48) / 10.00 = 0.1152 \text{ (mol/L)}. \end{aligned}$$

The mass of  $\text{KClO}_3$  in 250 mL (0.25 L) of the solution can be calculated in the following way:

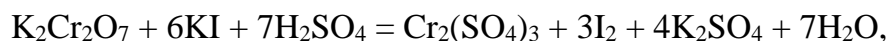
$$\begin{aligned} m(\text{KClO}_3) &= N(\text{KClO}_3) \cdot M(\text{KClO}_3) \cdot f_{\text{eq}}(\text{KClO}_3) \cdot V(\text{KClO}_3) = 0.1152 \cdot 122.5 \cdot 1/6 \cdot 0.25 = \\ &= 0.588 \text{ (g)} \end{aligned}$$

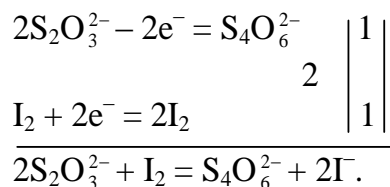
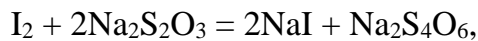
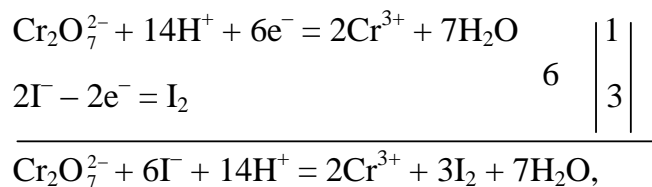
*Answer:* 0.588 g

### Calculations based on the results of substitutive titration

**Problem 2.** To the solution containing the excess of KI (in the acidic medium) we added 25.00 mL of 0.05 N  $\text{K}_2\text{Cr}_2\text{O}_7$  solution. To titrate the formed iodine we used 22.80 mL of sodium thiosulfate solution. Calculate the normality of  $\text{Na}_2\text{S}_2\text{O}_3$ .

*Solution.* In the task we used the method of substitutive titration of  $\text{K}_2\text{Cr}_2\text{O}_7$  to standardize the main titrant of iodometric method —  $\text{Na}_2\text{S}_2\text{O}_3$  solution. The chemical reactions are:





As we can see from the half-reactions,  $f_{\text{eq}}(\text{I}_2) = 1/2$ ,  $f_{\text{eq}}(\text{K}_2\text{Cr}_2\text{O}_7) = 1/6$ ,  $f_{\text{eq}}(\text{Na}_2\text{S}_2\text{O}_3) = 1$ .

According to the equivalence principle, in the substitutive titration the amount of iodine formed is equivalent to the amount of  $\text{K}_2\text{Cr}_2\text{O}_7$  and to the amount of  $\text{Na}_2\text{S}_2\text{O}_3$ :

$$n_{\text{eq}}(\text{K}_2\text{Cr}_2\text{O}_7) = n_{\text{eq}}(\text{I}_2) = n_{\text{eq}}(\text{Na}_2\text{S}_2\text{O}_3).$$

Consequently,

$$N(\text{K}_2\text{Cr}_2\text{O}_7) \cdot V(\text{K}_2\text{Cr}_2\text{O}_7) = N(\text{Na}_2\text{S}_2\text{O}_3) \cdot V(\text{Na}_2\text{S}_2\text{O}_3).$$

Using this expression we can find the normality of  $\text{Na}_2\text{S}_2\text{O}_3$  solution:

$$\begin{aligned}
 N(\text{Na}_2\text{S}_2\text{O}_3) &= (N(\text{K}_2\text{Cr}_2\text{O}_7) \cdot V(\text{K}_2\text{Cr}_2\text{O}_7)) / V(\text{Na}_2\text{S}_2\text{O}_3) = (0.05 \cdot 25.0) / 22.8 = \\
 &= 0.05482 \text{ (mol/L)}.
 \end{aligned}$$

*Answer: 0.05482 mol/L.*

## CHAPTER 4

### CHEMICAL THERMODYNAMICS

#### **Main questions of the topic:**

1. Subject and aims 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 processes. Enthalpy.
3. Hess law and its consequences. Standard enthalpies of formation and combustion. 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 components of food and some food products. Energy consumption during 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. The concept of chemical equilibrium. The constant of the chemical equilibrium. The interconnection between the constant of chemical equilibrium and the Gibbs free energy. Equations of isothermal and isobaric curves of a chemical reaction.

#### **LABORATORY WORK (M, D, P)**

##### **“DETERMINATION OF THE HEAT EFFECT OF NEUTRALIZATION REACTION”**

**The aim of the work:** to fix the change in temperature occurring during the neutralization reaction and calculate the value of the heat effect of that reaction.

**Devices and reactants:** thermometer; calorimeter; 1N NaOH solution; 1N HCl solution.

We should put 125 mL of 1N NaOH ( $\rho = 1.037$  g/mL) solution into the calorimetric glass (that has already been weighted). 125 mL of 1N HCl ( $\rho = 1.014$  g/mL) solution should be poured into the other glass. Then we should measure the temperature of both solutions using the thermometer. The glass with NaOH solution should be put into the calorimeter. After that HCl solution should be poured in the glass with NaOH under the control of thermometer. During this operation the resulting solution should be mixed. The temperature in the resulting solution will start to rise quickly, while after several minutes it will decrease to the previously established level. Your aim is to notice the maximal temperature in the experiment.

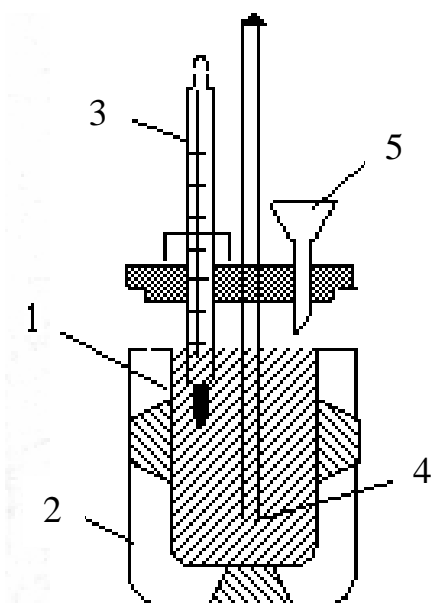


Fig. 1. The scheme of the calorimeter:  
 1 — the weighted glass with the NaOH solution (later it will play the role of the reaction chamber); 2 — thermal isolation; 3 — thermometer; 4 — mixer (a glass stick); 5 — funnel (HCl solution should be poured through it)

The results of the experiment must be written down below.

The mass of a calorimetric glass:  $m_1 =$  \_\_\_\_\_ g

NaOH solution concentration:  $C(\text{NaOH}) =$  \_\_\_\_\_ mol/L

HCl solution concentration:  $C(\text{HCl}) =$  \_\_\_\_\_ mol/L

The volume of NaOH solution:  $V(\text{NaOH}) =$  \_\_\_\_\_ mL

The volume of HCl solution:  $V(\text{HCl}) =$  \_\_\_\_\_ mL

The initial temperature of NaOH solution:  $t_{\text{alkali}} =$  \_\_\_\_\_ °C

The initial temperature of HCl solution:  $t_{\text{acid}} =$  \_\_\_\_\_ °C

The average initial temperature:  $t_1 = 0.5 \cdot (t_{\text{alkali}} + t_{\text{acid}}) =$  \_\_\_\_\_ °C

The maximal temperature during the neutralization:  $t_2 =$  \_\_\_\_\_ °C

The difference between the maximal and the average initial temperature is the key number in this experiment:

$\Delta t = t_2 - t_1 =$  \_\_\_\_\_ - \_\_\_\_\_ = \_\_\_\_\_ °C

The total mass of both solutions:  $m_2 = (\rho_{\text{alkali}} \cdot V_{\text{alkali}} + \rho_{\text{acid}} \cdot V_{\text{acid}}) =$   
 $=$  \_\_\_\_\_ · \_\_\_\_\_ + \_\_\_\_\_ · \_\_\_\_\_ = \_\_\_\_\_ g.

The total heat capacity of the system (the glass and the resulting solution in our case) equals to the sum of the products of heat capacities of the elements of the system and their masses.

$C = m_1 C_1 + m_2 C_2 =$  \_\_\_\_\_ · \_\_\_\_\_ + \_\_\_\_\_ · \_\_\_\_\_ =  
 $=$  \_\_\_\_\_ J/°C

$C_1 = 0.752 \text{ J/g} \cdot \text{°C}$  — the specific heat capacity of a glass;

$C_2 = 4.184 \text{ J/g} \cdot \text{°C}$  — the specific heat capacity of a solution;

Now we can calculate the heat effect of neutralization using the formula written below:

$Q = (\Delta t \cdot C) / (N \cdot V)$

$Q = ($  \_\_\_\_\_ · \_\_\_\_\_  $) / ($  \_\_\_\_\_ · \_\_\_\_\_  $) =$  \_\_\_\_\_ J/mol.

N — the concentration of the final solution (0.5 N).

V — the total volume of the final solution (0.25 L).

Then write the thermochemical equation of the neutralization reaction:



Then we calculate the absolute and the relative errors of the experiment.

The theoretical heat effect of this reaction ( $\Delta H_{\text{theoretical}}$ ) is equal to  $-57.0 \text{ kJ/mol}$ .

The absolute error =  $|\Delta H_{\text{theoretical}} - \Delta H| = \text{_____} - \text{_____} = \text{_____} \text{ kJ/mol}$ .

The relative error, % =  $(\text{the absolute error} / \Delta H_{\text{theoretical}}) \cdot 100 \% =$   
 $= (\text{_____} / \text{_____}) \cdot 100 \% = \text{_____} \%$ .

**Conclusion:** “I calculated the heat effect of the neutralization reaction, that is equal to \_\_\_\_\_  $\text{kJ/mol}$ ”.

### TEST SELF-CHECK

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

**1. A closed system is the system which:**

- a) participates only in the exchange of substance with the environment;
- b) participates only in the exchange of energy with the environment;
- c) participates in the exchange of both substance and energy with the environment;
- d) does not participate in the exchange of neither substance nor energy with the environment;

**2. A homogeneous system is a:**

- a) solution of sugar in water;
- b) precipitate of barium sulfate in contact with water solution;
- c) the mixture of nitrogen and oxygen at  $0 \text{ }^\circ\text{C}$ ;
- d) the mixture of water and ice at  $0 \text{ }^\circ\text{C}$ .

**3. We can experimentally determine the values of the following thermodynamic parameters:**

- a) mass; b) internal energy; c) enthalpy; d) absolute entropy.

**4. There is a thermodynamic process in the system if:**

- a) the volume of the system decreases;
- b) the temperature in the system is increased by  $1 \text{ }^\circ\text{C}$ ;
- c) the chemical composition of the substance in the system is changed;
- d) the system is moving in the environment.

**5. Which parameters can play the role of the function of the state of the system:**

- 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 in which the energy transferred 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 true:**

a) the absolute value of the enthalpy of a system can be experimentally determined with the help of a calorimeter;

b)  $\Delta H$  has a positive value for any endothermic reaction;

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

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

**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 of a chemical reaction taking place in isochoric or isobaric conditions depends on:**

a) the nature of reacting substances;

b) the amounts of reacting substances;

c) the state (solid, liquid or gaseous) of the reactants and the products of the reaction;

d) the concrete pathway (the number of steps and the nature of intermediate substances) of the reaction.

**11. Indicate the formula corresponding to the mathematical expression of the second law of thermodynamics for the thermodynamically reversible processes:**

a)  $Q = \Delta U + p \Delta V$ ;

c)  $\Delta S = Q/T$ ;

b)  $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$ ;

d)  $\Delta S > Q/T$ .

**12. If some spontaneous processes are going on in the isolated system, the entropy of the system:**

a) decreases;

c) increases;

b) first increases and then decreases;

d) doesn't change.

**13. Without any calculations indicate the processes in which the entropy of the system increases:**

a)  $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$ ;

c)  $\text{C}(s) + \text{CO}_2(g) \rightarrow 2\text{CO}(g)$ ;

b)  $\text{H}_2(g) + 0.5\text{O}_2(g) \rightarrow \text{H}_2\text{O}(g)$ ;

d)  $2\text{KClO}_3(s) \rightarrow 2\text{KCl}(s) + 3\text{O}_2(g)$ .

**14. Indicate the chemical reactions which are accompanied by the decrease of enthalpy and the increase of entropy:**

- a)  $\text{KClO}_3(\text{s}) \rightarrow \text{KCl}(\text{s}) + 1.5\text{O}_2(\text{g}) \quad \Delta H < 0;$
- b)  $\text{H}_2(\text{g}) + 0.5\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) \quad \Delta H < 0;$
- c)  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}^+(\text{aq.}) + \text{OH}^-(\text{aq.}) \quad \Delta H > 0;$
- d)  $0.5\text{C}(\text{s}) + 0.5\text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g}) \quad \Delta H < 0.$

**15. Any isobaric isothermal process is nonspontaneous if:**

- 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 is spontaneous at any temperature:**

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

**17. Indicate the inequality of any 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 decreases;
- b) the enthalpy of the system increases;
- c) the Gibbs free energy of the products of the reaction is lower than that of the initial substances;
- d) the Gibbs free energy of the products of the reaction is higher than that of the initial substances.

**19. In chemical equilibrium:**

- a)  $\Delta G = 0;$  c) the rates of the direct and reverse reactions are equal to each other;
- b)  $\Delta G < 0;$  d)  $\Delta G > 0.$

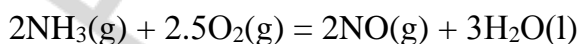
**20. Spontaneous chemical reaction is accompanied by the decrease in the enthalpy of the system. How does the constant of chemical equilibrium of this reaction change with the increase in temperature:**

- a) increases; b) decreases; c) doesn't change.

## PROBLEMS

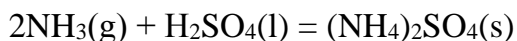
Use the data from the Table below for each of the problems.

1. Calculate  $\Delta G^0$  of the reaction. Is it spontaneous in standard conditions?



Answer: \_\_\_\_\_

2. Calculate the change of entropy ( $\Delta S^0$ ) in the reaction:



Answer: \_\_\_\_\_

3. Calculate  $\Delta H^0$  of the reaction:  $\text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g}) = \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$

Answer: \_\_\_\_\_

4. According to the equation of the chemical reaction:  $\text{H}_2\text{S}(\text{g}) + 1.5\text{O}_2(\text{g}) = \text{H}_2\text{O}(\text{l}) + \text{SO}_2(\text{g})$  calculate the enthalpy of  $\text{H}_2\text{S}$  formation, if  $\Delta H^0$  of the reaction =  $-562.45 \text{ kJ/mol}$

Answer: \_\_\_\_\_

5.  $\Delta H^0$  of the reaction =  $-101.2 \text{ kJ/mol}$ ;  $\Delta S^0$  of the reaction =  $-182.82 \text{ J/mol}\cdot\text{K}$ . The reaction is:  $2\text{HCl}(\text{g}) + 1/2\text{O}_2(\text{g}) = \text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$ . Calculate  $\Delta G^0$  of the reaction and write is it spontaneous in standard conditions

Answer: \_\_\_\_\_

**The table with thermodynamical parameters of the substances from the problems**

Formula	$\Delta H^0_f, \text{kJ/mol}$	$S^0, \text{J}/(\text{mol}\cdot\text{K})$	$\Delta G^0_f, \text{kJ/mol}$
$\text{NH}_3 (\text{g})$	-45.9	192.8	-16.4
$\text{NO} (\text{g})$	91.3	210.8	87.6
$\text{H}_2\text{O} (\text{l})$	-285.8	70.0	-237.1
$\text{H}_2\text{SO}_4 (\text{l})$	-814.0	156.9	-690.0
$(\text{NH}_4)_2\text{SO}_4 (\text{s})$	-1180.9	220.1	-901.7
$\text{CO} (\text{g})$	-110.5	197.7	-137.2
$\text{CO}_2 (\text{g})$	-393.5	213.8	-394.4
$\text{H}_2\text{S} (\text{g})$	-20.15	205.8	-33.4
$\text{SO}_2 (\text{g})$	-296.8	248.2	-300.1
$\text{HCl} (\text{g})$	-92.3	186.9	-95.3
$\text{H}_2\text{O} (\text{g})$	-265.8	188.7	-228.6

## CHAPTER 5

### THE ELEMENTS OF CHEMICAL KINETICS

#### Main questions of the topic:

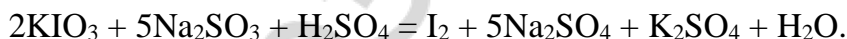
1. Main concepts of chemical kinetics. Elementary (one-step) and nonelementary (multiple step), homogeneous and heterogeneous reactions. The rate of homogeneous chemical reactions and methods of its measuring.
2. The main postulate of chemical kinetics. The order of the reaction and the reaction rate constant. The Law of mass action for the rate of the reaction and its applications.
3. Kinetic equations for the reactions of zero, first and second order. The period of semi-transformation. Molecularity of the reaction.
4. Theory of active collisions. Arrhenius' equation. Energy of activation. Vant-Hoff's rule. Temperature coefficient ( $Q_{10}$ ) of the reaction rate for enzymatic processes.
5. The concept of the theory of the transition state complex. 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, specific features of their action.

#### LABORATORY WORK (M, D, P) "THE INFLUENCE OF SODIUM SULFITE CONCENTRATION ON THE RATE OF THE SULFITE OXIDATION REACTION BY POTASSIUM IODATE IN THE ACIDIC MEDIUM"

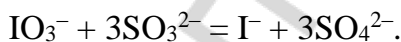
**The aim of the work:** to check the influence of the concentration of reactant on the rate of a chemical reaction.

The main idea of the work is to measure the time that is necessary for the complete sodium sulfite oxidation by potassium iodate in the acidic medium. Three different concentrations of sodium sulfite will be prepared.

The chemical equation of the reaction is the following:



This reaction has several steps. In the first step iodate ion is reduced to iodide ion and sulfite ion is oxidized to sulfate ion according to the equation:



In the same time iodate ions oxidize iodide ions formed in the result of the first reaction. Finally, free iodine is produced:



However, the interaction of iodate ions with iodide ions (with the emission of free iodine) will take place only after the complete sulfite oxidation. Indeed, the difference in redox potentials for the first reaction is 1.33 times higher than that for the second reaction.

That's why it will take several seconds for free iodine to be formed. The presence of  $\text{I}_2$  can be easily determined with the help of starch.

Fill in the table with results.

№ of the tube	Volumes of solutions (mL)				Final sulfite concentration, mol/L	Time of the reaction (before the solution turns to blue), sec	The average rate of the reaction, mol/L·s.
	Na <sub>2</sub> SO <sub>3</sub> 0.01M	H <sub>2</sub> O	Starch	KIO <sub>3</sub> 0.01M			
1	1.00	–	0.25	1.00			
2	0.50	0.50	0.25	1.00			
3	0.25	0.75	0.25	1.00			

Put sodium sulfite solution in three different tubes. The volume of sodium sulfite solution for each tube can be found in the table. Then add water to the tubes № 2 and № 3 according to the instructions from the table. After that put 0.25 ml of starch in each of those three tubes. Put 1.00 ml of potassium iodate solution in each clean tube from the next set of three tubes.

Then you should pour together the first tube from the first set and the first tube from the second set. Measure the time interval from the moment of pouring together the solutions until the moment when the solution becomes blue. Repeat that measurement for the second and the third pair of tubes.

To calculate the final sulfite concentration you can use the formula given below.

$$C_{\text{Na}_2\text{SO}_3} = \frac{0,01 \cdot V_{\text{Na}_2\text{SO}_3}}{V_{\text{total}}}$$

To calculate the average rate of the reaction you need to use another simple formula.

$$\bar{V} = \frac{C_{\text{Na}_2\text{SO}_3}}{t}$$

**Conclusion:** “The average rate of the reaction between sodium sulfite and potassium iodate shows \_\_\_\_\_ dependence on the concentration of sodium sulfite”.

### TEST SELF-CHECK

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

a) mol/L · s<sup>-1</sup>; b) L · mol<sup>-1</sup>; c) s · mol<sup>-1</sup>; d) mol · L<sup>-1</sup> · min<sup>-1</sup>?

**2. Indicate the kinetic equation for the one-step reaction A(s) + B(l) = AB(s):**

a) V = k[A]; b) V = k[A][B]; c) V = k[B]; d) V = k.

**3. How many times should we increase the pressure in order to make the rate of the one-step reaction 2A(g) + B(g) → A<sub>2</sub>B(s) 8 times faster:**

a) 2; b) 3; c) 4; d) 5?

**4. How many times will the rate of the one-step reaction A(s) + 2B(g) → D(s) decrease with the 4 times decrease in pressure:**

a) 8; b) 16; c) 4; d) 2?

**5. How will the rate of the reaction change due to the 20 °C decrease in temperature if the temperature coefficient ( $Q_{10}$ ) is equal to 3:**

- a) will decrease 3 times;                      c) will increase 3 times;  
b) will decrease 9 times;                      d) will increase 9 times?

**6. What value of the energy of activation corresponds to the chemical reaction which proceeds slower (if other conditions are identical):**

- a) 30 kJ/mol; b) 100 kJ/mol; c) 90 kJ/mol; d) 40 kJ/mol?

**7. Which temperature coefficient ( $Q_{10}$ ) corresponds to the highest value of the energy of activation?**

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

**8. The rate of the chemical reaction increased 9 times due to the 20 °C temperature increase. Choose the temperature coefficient ( $Q_{10}$ ):**

- 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 grows faster with the increase of temperature?

### PROBLEMS

1. A one-step reaction between substances A and B is expressed by an equation:  $A + 2B \rightarrow C$ . The initial concentrations of reactants are:  $[A]_0 = 0.3 \text{ mol/L}$ ,  $[B]_0 = 0.5 \text{ mol/L}$ . The reaction rate constant is equal to 0.4. Find the initial rate of the reaction and the rate of the reaction when the concentration of substance A has become 0.1 mol/L lower.

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Answer: \_\_\_\_\_

2. Find the value of the rate constant of a one-step reaction  $A + B \rightarrow AB$  if the rate of the reaction is 0.005 mol/L·s when concentrations of A and B substances equal to 0.5 and 0.1 mol/L respectively.

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Answer: \_\_\_\_\_

## STANDARDS OF PROBLEM SOLUTIONS

**Problem 1.** The rate constant of the reaction  $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$  at  $505^\circ\text{C}$  is equal to  $0.16 \text{ L/mol}\cdot\text{s}$ . The initial concentrations of the reacting substances were  $[\text{H}_2]_0 = 0.04 \text{ mol/L}$  and  $[\text{I}_2]_0 = 0.05 \text{ mol/L}$ . Calculate the initial reaction rate and its rate when hydrogen concentration will be equal to  $0.03 \text{ mol/L}$ .

We have:

*Solution:*

$$k = 0.16 \text{ L/mol}\cdot\text{s}$$

$$[\text{H}_2]_0 = 0.04 \text{ mol/L}$$

$$[\text{I}_2]_0 = 0.05 \text{ mol/L}$$

$$[\text{H}_2]_t = 0.03 \text{ mol/L}$$

$$V_0 = ? \quad V_t = ?$$

The rate of the reaction  $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$  according to the law of mass action is equal to:  $V = k[\text{H}_2] \cdot [\text{I}_2]$ .

The value of the initial reaction rate is:

$$V_0 = k[\text{H}_2]_0 \cdot [\text{I}_2]_0 = 0.16 \cdot 0.04 \cdot 0.05 = 0.00032 \text{ (L/mol}\cdot\text{s)}.$$

When  $\text{H}_2$  concentration becomes equal to  $0.03 \text{ mol/L}$ , it means that there was the decrease of  $\text{H}_2$  concentration equal to  $0.01 \text{ mol/L}$ . According to the equation of chemical reaction,  $\text{I}_2$  concentration will also become  $0.01 \text{ mol/L}$  lower (it will be equal to  $0.04 \text{ mol/L}$ ). At this moment the reaction rate will be:

$$V_t = k[\text{H}_2]_t \cdot [\text{I}_2]_t = 0.16 \cdot 0.03 \cdot 0.04 = 0.000192 \text{ mol/L}\cdot\text{s}.$$

*Answer:*  $0.00032$  and  $0.000192 \text{ mol/L}\cdot\text{s}$ .

**Problem 2.** The kinetic equation of the reaction  $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$  is the following:  $V = k \cdot [\text{NO}]^2 \cdot [\text{O}_2]$ . How will the rate of this reaction change in case of:

- a) 3 times pressure increase;
- b) 3 times volume decrease;
- c) 3 times increase of  $\text{NO}$  concentration?

*Solution.* The increase in pressure leads to the corresponding increase in concentrations of reactants. So, we can write the following:

$$V = k(3[\text{NO}]_0)^2(3 \cdot [\text{O}_2]_0) = 27k[\text{NO}]_0^2 \cdot [\text{O}_2]_0.$$

The rate of the reaction will increase 27 times:  $V_1 = 27 \cdot V_0$ .

The decrease in volume means the increase in pressure. So, again the reaction rate will increase 27 times.

In case of the increase of just  $\text{NO}$  concentration (3 times), the rate of the reaction will be:

$$V_2 = k(3[\text{NO}]_0)^2 \cdot [\text{O}_2]_0 = 9k[\text{NO}]_0^2 \cdot [\text{O}_2]_0.$$

The rate of the reaction will increase 9 times:  $V_2 = 9 V_0$ .

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

## CHAPTER 6

### COLLIGATIVE PROPERTIES OF SOLUTIONS

#### Main questions of the topic:

1. Thermodynamics of solution formation.
2. Osmosis 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 osmosis in biological processes.
5. The vapor pressure upon the solution of nonvolatile solutes. Raoult's first law.
6. Boiling and freezing points of solutions. Raoult's second law. Cryoscopy. Ebullioscopy.
7. Colligative properties of the solutions of electrolytes. Isotonic coefficient.

#### LABORATORY WORK (M, D, P)

##### “HEMOLYSIS OF ERYTHROCYTES IN HYPOTONIC SOLUTION”

**The aim of the work:** to determine which of the suggested solutions is isotonic to blood plasma.

#### Reactants and equipment:

- Solutions of sodium chloride with the mass fraction of NaCl 0.85 % and 0.3 %, the sample of blood, distilled water.
- Graduated centrifuge tubes, a glass stick, latex gloves;
- Centrifuge.

Pour 10 ml of the solution with the mass fraction of NaCl 0.85 % in the first tube and 10 ml of NaCl solution with the mass fraction of 0.3 % in the second tube.

Put 2 drops of the blood sample in each of the tubes. Then mix the solutions with a glass stick (clean up the stick before you start mixing the second solution). Wait for 10 minutes and try to notice any differences between two solutions. Then put two tubes in the centrifuge (in front of each other) and centrifuge them for 10 minutes at the rate of 1500 rotations per minute.

№ of the tube	Contents of the tube	Observations	
		Before centrifugation	After centrifugation
1	10 mL of NaCl solution with the mass fraction of 0.85 % + 2 drops of the blood sample		
2	10 mL of NaCl solution with the mass fraction of 0.3 % + 2 drops of the blood sample		

Write your observations in the table: notice the color of the solution, the presence of precipitate, the transparency of the solution.

**Conclusion:** “I approved the fact that \_\_\_\_\_ % NaCl solution is isotonic to blood plasma. Hemolysis of red blood cells happens in the \_\_\_\_\_ % NaCl solution”



## TEST SELF-CHECK

### 1. Indicate the true statements:

- a) the pressure of the saturated vapor upon the solution will decrease with the increase of the mole fraction of the solvent;
- b) the boiling temperature of pure liquids and solutions depends on the outer pressure;
- c) with the increase of the number of particles of the nonvolatile solute in a unit of the mass of the solvent the freezing temperature of the solution will decrease;
- d) water solutions of nonvolatile electrolytes and nonelectrolytes with the same molality have different boiling temperatures (in the same conditions);
- e) water solutions of nonvolatile electrolytes and nonelectrolytes with the same molar concentration have the same osmotic pressure (at the same temperature).

### 2. Indicate the osmolarity (mol/L) of 0.15M 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 water solutions with the molality of 0.05 mol/kg. Choose the solution with the highest freezing point in the same conditions:

- a)  $\text{MgSO}_4$ ; b)  $\text{CaCl}_2$ ; c)  $\text{C}_6\text{H}_{12}\text{O}_6$ ; d)  $\text{AlCl}_3$ ; e)  $\text{NaCl}$  ?

### 4. Which of the water solutions mentioned below has the highest boiling point in the same conditions:

- a)  $\text{C}_6\text{H}_{12}\text{O}_6$  solution with  $C_m = 0.5$  mol/kg;
- b)  $\text{MgSO}_4$  solution with  $C_m = 0.5$  mol/kg;
- c)  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  solution with  $C_m = 1.0$  mol/kg;
- d)  $\text{NaCl}$  solution with  $C_m = 0.5$  mol/kg;
- e)  $\text{CaCl}_2$  solution with  $C_m = 0.5$  mol/kg.

### 5. There are 5 different water solutions with the molar concentration of 0.05 mol/L at the same temperature. Which of these solutions are isotonic to each other:

- a)  $\text{CaCl}_2$ ; b)  $\text{NaCl}$ ; c)  $\text{C}_6\text{H}_{12}\text{O}_6$ ; d)  $\text{MgSO}_4$ ; e)  $\text{AlCl}_3$ ?

### 6. Which of the following water solutions are isotonic to the blood plasma (the solutions are compared at 37 °C):

- a) 0.15 M  $\text{KCl}$  solution;
- b) 5 %  $\text{C}_6\text{H}_{12}\text{O}_6$  solution;
- c) 0.85 %  $\text{NaCl}$  solution;
- d) 5 %  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  solution;
- e) 0.15 M  $\text{CaCl}_2$  solution?

### 7. Which of the following water solutions at 37 °C are hypotonic to the physiologic solution (saline):

- a) 0.15M  $\text{CaCl}_2$  solution;
- b) 0.1M  $\text{MgSO}_4$  solution;
- c) 0.15M  $\text{C}_6\text{H}_{12}\text{O}_6$  solution;
- d) 0.3M  $\text{KCl}$  solution;
- e) 0.3M  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  solution ?

Suggest the correct answers to the questions:

**8. Which components of the blood determine the distribution of water between the vessels and the extravascular space (intercellular liquid)?**

a) potassium cations and coupled anions;

b) urea;

c) proteins;

d) sodium cations and coupled anions;

e) glucose.

**9. Which components make the main impact into the osmotic pressure of the intracellular liquid?**

**10. Which components make the main impact into the maintenance of the osmolality of blood?**

### PROBLEMS

1. Calculate the vapor pressure upon the solution containing 13.68 g of sucrose  $C_{12}H_{22}O_{11}$  in 90 g of water at 65 °C if the pressure of saturated vapor upon water at the same temperature is 25.0 kPa.

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Answer: \_\_\_\_\_

2. The osmotic pressure of the solution containing 2.8 g of high molecular compound

i

n

2

Answer: \_\_\_\_\_

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

f

o

Answer: \_\_\_\_\_

4. Calculate the difference in boiling point temperature (relative to that for the pure water) if we dissolve 9 g of glucose  $C_6H_{12}O_6$  in 100 g of water?

n

e

Answer: \_\_\_\_\_

5. A

t

w

h

a

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

Answer: \_\_\_\_\_

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

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

Answer: \_\_\_\_\_

7. Apparent degree of dissociation of potassium chloride in its 0.1 M solution is 0.80.

C

a

l

c

Answer: \_\_\_\_\_

l

8. The solution containing 0.53 g of sodium carbonate in 200 g of water freezes at the temperature of  $-0.13\text{ }^{\circ}\text{C}$ . Calculate the apparent dissociation degree of the salt (in %) if

\_\_\_\_\_

t

h

Answer: \_\_\_\_\_

9. We dissolved in the same portions of water: 0.5 mole of sucrose and 0.2 mole of  $\text{CaCl}_2$ . The freezing temperatures of both solutions are equal. Determine the apparent degree of dissociation of  $\text{CaCl}_2$  (in %).

o

t

i

Answer: \_\_\_\_\_

10. A mixture containing 0.1 g of PAS (the medicine to fight tuberculosis — para-

p

r

e

s

s

u

r

o  
f

P

Answer: \_\_\_\_\_

S

11. The freezing temperature of the blood plasma is  $-0.56\text{ }^{\circ}\text{C}$ . Calculate the molality of salts in the blood taking all salts as binary strong electrolytes. The presence of nonelectrolytes in the blood plasma shouldn't be taken into consideration.

t

h

Answer: \_\_\_\_\_

### STANDARDS OF PROBLEM SOLUTIONS

**Problem 1.** At the temperature of  $0^{\circ}\text{C}$  the osmotic pressure of 0.05M potassium carbonate solution is 272.6 kPa. Determine the apparent dissociation degree of the salt.

We have:

n

$$P_{\text{osm}} = 272.6 \text{ kPa}$$

$$C = 0.05 \text{ mol/L}$$

$$\alpha_{\text{app}} = ?$$

S

For electrolyte solutions:  $P_{\text{osm}} = iCRT$ .

l

u

We calculate the isotonic coefficient:

$$i = \frac{P_{\text{osm}}}{CRT} = \frac{272.6}{0.05 \cdot 8.31 \cdot 273} = 2.4$$

r

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

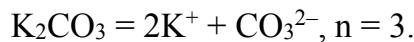
a

t

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

where  $\alpha_{\text{app}}$  — the apparent degree of dissociation,  $n$  — the number of ions, into which the electrolyte dissociates:

e



$$\text{Then, } \alpha_{\text{app}} = (2.4 - 1) / (3 - 1) = 0.7$$

o

f

A

n

P

a) to decrease the freezing point by one degree?

b) to increase the boiling point by one degree?

b

l

e

m

We have:

$$m(\text{H}_2\text{O}) = 270 \text{ g} = 0.27 \text{ kg}$$

$$\Delta t_{\text{freez.}} = 1^\circ$$

$$\Delta t_{\text{boiling.}} = 1^\circ$$

K

$$E(\text{H}_2\text{O}) = 0.52(\text{kg} \cdot \text{degree}/\text{mol})$$

$$M(\text{C}_6\text{H}_{12}\text{O}_6) = 180 \text{ g/mol}$$

$$\text{a) } m(\text{C}_6\text{H}_{12}\text{O}_6) = ?$$

$$\text{b) } m(\text{C}_6\text{H}_{12}\text{O}_6) = ?$$

S

$$\text{a) } \Delta t_{\text{freez.}} = C_m \cdot K(\text{H}_2\text{O}),$$

where  $C_m$  — molality (mol/kg);  $K(\text{H}_2\text{O})$  — cryoscopic constant of water

$$C_m = n(\text{C}_6\text{H}_{12}\text{O}_6) / m(\text{H}_2\text{O})$$

$$n(\text{C}_6\text{H}_{12}\text{O}_6) = m(\text{C}_6\text{H}_{12}\text{O}_6) / M(\text{C}_6\text{H}_{12}\text{O}_6)$$

$$\text{Hence: } \Delta t_{\text{freez.}} = \frac{K(\text{H}_2\text{O}) \cdot m(\text{C}_6\text{H}_{12}\text{O}_6)}{m(\text{H}_2\text{O}) \cdot M(\text{C}_6\text{H}_{12}\text{O}_6)}, \text{ then}$$

$$m(\text{C}_6\text{H}_{12}\text{O}_6) = \frac{\Delta t_{\text{freez.}} \cdot m(\text{H}_2\text{O}) \cdot M(\text{C}_6\text{H}_{12}\text{O}_6)}{K(\text{H}_2\text{O})} = (1 \cdot 0.27 \cdot 180) / 1.68 = 26.15 \text{ g.}$$

$$\text{b) } \Delta t_{\text{boiling.}} = E(\text{H}_2\text{O}) \cdot C_m,$$

where  $E(\text{H}_2\text{O})$  — ebullioscopic constant of water,  $\Delta t_{\text{boiling.}}$  — the difference in the boiling p

$$\text{Hence: } m(\text{C}_6\text{H}_{12}\text{O}_6) = \frac{\Delta t_{\text{boil.}} \cdot m(\text{H}_2\text{O}) \cdot M(\text{C}_6\text{H}_{12}\text{O}_6)}{E(\text{H}_2\text{O})} = (1 \cdot 0.27 \cdot 180) / 0.52 = 93.54 \text{ g.}$$

A

**Problem 3.** A solution containing 1.2 g of aspirin  $\text{HOOC}_6\text{H}_4\text{OCOCH}_3$  in 20 g of

w

e

We have:

$$m(\text{aspirin}) = 1.2 \text{ g}$$

$$m(\text{dioxan}) = 20.0 \text{ g} = 0.02 \text{ kg}$$

$$t_{\text{freeze}}(\text{solution}) = 10.43^\circ\text{C}$$

$$t_{\text{freeze}}(\text{dioxan}) = 12.0^\circ\text{C}$$

$$M(\text{aspirin}) = 180 \text{ g/mol}$$

$$K(\text{dioxan}) = ?$$

S

Dioxan is the solvent, aspirin is the solute.

1

$$= 12.00 - 10.43 = 1.57^\circ.$$

$$\Delta t_{\text{freez}} = K(\text{dioxan}) \cdot m(\text{aspirin}) / m(\text{dioxan}) \cdot M(\text{aspirin}),$$

where  $K(\text{dioxan})$  — a cryoscopic constant of dioxan ( $^\circ\text{C} \cdot \text{kg}/\text{mol}$ ).

ε

Hence:

$$K(\text{dioxan}) = \Delta t_{\text{freez}} \cdot m(\text{dioxan}) \cdot M(\text{aspirin}) / m(\text{aspirin}) = 1.57 \cdot 0.02 \cdot 180 / 1.2 = 4.7^\circ\text{C kg/mol.}$$

Answer:  $K(\text{dioxan}) = 4.7^\circ\text{C kg/mol.}$

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

ν

.

5

4

We have:

$$N = 10^{18} \text{ molecules}$$

$$mL = 10^{-3} \text{ L}$$

$$T = 298\text{K}$$

The osmotic pressure of dilute nonelectrolyte solutions is calculated using the equation  $P_{\text{osm}} = CRT$ . We should find the amount of substance and its molar concentration first.

$$P_{\text{osm}} \text{ — ?}$$

$$1. n(\text{substance}) = \frac{N}{N_A} = \frac{10^{18}}{6 \cdot 10^{23}} = 1.66 \cdot 10^{-6} \text{ mol.}$$

$$2. C_M = \frac{n(\text{substance})}{V(\text{solution})} = \frac{1.66 \cdot 10^{-6}}{10^{-3}} = 1.66 \cdot 10^{-3} \text{ mol/L.}$$

$$3. P_{\text{osm}} = CRT = 1.66 \cdot 10^{-3} \cdot 8.314 \cdot 298 = 4.12 \text{ kPa.}$$

A

**Problem 5.** How many grams of glucose  $C_6H_{12}O_6$  must be in 0.5 L of the glucose solution to make its osmotic pressure (at the same temperature) equal to the one in glycerin solution that has 9.2 g of glycerin  $C_3H_5(OH)_3$  in 1 L.

We have:

$$m(\text{glycerin}) = 9.2 \text{ g}$$

$$V(\text{glycerin solution}) = 1 \text{ L}$$

$$V(\text{glucose solution}) = 0.5 \text{ L}$$

$$M(\text{glycerin}) = 92 \text{ g/mol}$$

$$T_1 = T_2$$

$$P_{\text{osm } 1} = P_{\text{osm } 2}$$

*Solution:*

Use the equation  $P_{\text{osm}} = CRT$ .

If at the same temperature

$$P_{\text{osm } 1} = P_{\text{osm } 2}, \text{ then } C_1 = C_2,$$

where  $P_{\text{osm } 1}$  — osmotic pressure of glycerin solution;

$P_{\text{osm } 2}$  — osmotic pressure of glucose solution;  $C_1$  — molar concentration of glycerin;  $C_2$  — molar concentration of

m

$$1. C_1 = n(\text{glycerin}) / V(\text{glycerin solution}) = m(\text{glycerin}) / M(\text{glycerin}) \cdot V(\text{glycerin}$$

g

$$2. C_2 = m(\text{glucose}) / M(\text{glucose}) \cdot V(\text{volume of glucose solution}) = C_1 = 0.1 \text{ mol/L.}$$

$$3. m(\text{glucose}) = C_2 \cdot M(\text{glucose}) \cdot V(\text{volume of glucose solution}) = 0.1 \cdot 180 \cdot 0.5 = 9 \text{ g.}$$

A

**Problem 6.** At 315K the pressure of saturated vapor upon water is 8.2 kPa. Calculate the difference in the vapor pressure if we dissolve 36 g of glucose  $C_6H_{12}O_6$  in 540 g of water?

We have:

$$T = 315\text{K}$$

$$P = 8.2 \text{ kPa}$$

$$m(\text{H}_2\text{O}) = 540 \text{ g}$$

$$m(\text{C}_6\text{H}_{12}\text{O}_6) = 36 \text{ g}$$

S

Use the formula:  $\Delta P = P_0 - P$ ,

where  $P_0$  — the pressure of saturated vapor upon the solvent;

$P$  — the pressure of saturated vapor upon the solution.

t

$$\Delta P \text{ — ?}$$

The first variant of solution:

For solutions of nonvolatile nonelectrolytes the pressure of saturated vapor upon the solution is equal to the pressure of saturated vapor upon the solvent multiplied by the mole fraction of the solvent:

$$P = P_0 \cdot \chi_{\text{solv}} = \frac{P_0 \cdot n_{\text{solv}}}{(n_{\text{sub}} + n_{\text{solv}})}$$

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

$$n_{\text{sub}} = \frac{m(\text{C}_6\text{H}_{12}\text{O}_6)}{M(\text{C}_6\text{H}_{12}\text{O}_6)} = \frac{36}{180} = 0.2 \text{ mol.}$$

$$\chi_{\text{solv}} = \frac{n_{\text{solv}}}{(n_{\text{sub}} + n_{\text{solv}})} = 30/(30 + 0.2) = 0.9934.$$

P

$$\Delta P = P_0 - P = 8.2 - 8.146 = 0.054 \text{ kPa.}$$

The second variant of solution:

The difference of the pressure of saturated vapor upon the solution and the pure solvent is equal to the pressure of saturated vapor upon the solvent multiplied by the mole fraction of the solute:

$$\Delta P = P_0 \cdot \chi_{\text{sub}} = \frac{P_0 \cdot n_{\text{sub}}}{(n_{\text{sub}} + n_{\text{solv}})}$$

$$n_{\text{solv}} = \frac{m(\text{H}_2\text{O})}{M(\text{H}_2\text{O})} = \frac{540}{18} = 30 \text{ mol.}$$

$$n_{\text{sub.}} = \frac{m(\text{C}_6\text{H}_{12}\text{O}_6)}{M(\text{C}_6\text{H}_{12}\text{O}_6)} = \frac{36}{180} = 0.2 \text{ mol.}$$

$$\chi_{\text{sub}} = \frac{n_{\text{sub}}}{(n_{\text{sub}} + n_{\text{solv}})} = 0.2 / 30.2 = 0.006623.$$

$$\Delta P = P_0 \cdot \chi_{\text{sub}} = 0.0066232 \cdot 8.2 = 0.054 \text{ kPa.}$$

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2  
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0  
.  
9  
9  
3  
4  
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w  
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r  
:  
0  
.  
0  
5  
4  
k  
P

## CHAPTER 7

### THE pH LEVEL OF WATER SOLUTIONS

#### Main questions on the topic:

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

#### LABORATORY WORK (P) "PROPERTIES OF ACIDIC AND BASIC SALTS"

**The aim of the work:** to study the processes of production of hydroxides and salts (basic and acidic ones), to study the properties of main types of inorganic compounds.

**Reactants:** ZnO, HCl (water solution), NaOH (concentrated water solution), CaO, Na<sub>2</sub>CO<sub>3</sub>, Ca(OH)<sub>2</sub>, CuSO<sub>4</sub>, NaOH (dilute water solution), phenolphthalein, methyl orange, NiCl<sub>2</sub>, CH<sub>3</sub>COONa, Mg, Zn, Cu, MnSO<sub>4</sub>, CaCO<sub>3</sub>, ZnSO<sub>4</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Cr(NO<sub>3</sub>)<sub>3</sub>, Ca(OH)<sub>2</sub>, CoSO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> (concentrated water solution).

#### Part 1. The properties of amphoteric hydroxides.

Put a small portion of zinc oxide into two tubes. Add 10–15 drops of an acid solution to the first tube and several drops of an alkali solution to the second one. Shake both tubes until the solid substance will be dissolved. Write the equations of chemical reactions and make the conclusion about the nature of the studied oxide.

Reaction in tube 1: \_\_\_\_\_

Reaction in tube 2: \_\_\_\_\_

Conclusion: \_\_\_\_\_

#### Part 2. Production of bases.

##### Task 1: Production of alkalis.

Put a small portion of CaO in the tube and add 15–20 drops of water to it. Mix the tube with a glass stick and add 2–3 drops of phenolphthalein. Write the equation of chemical reaction and mention the color of the solution.

Reaction: \_\_\_\_\_

Conclusion: \_\_\_\_\_



Add  $\text{Ca}(\text{OH})_2$  solution in the drop by drop manner to the tube with several drops of  $\text{Na}_2\text{CO}_3$  solution until the precipitate will be formed. Mention the color of the precipitate. What kind of solution has been formed (upon the precipitate)? Write the equation of chemical reaction.

Reaction: \_\_\_\_\_

Conclusion: \_\_\_\_\_

**Task 2: Production of insoluble salts.**

Add the excess of sodium hydroxide solution to the tube with copper (II) sulfate solution. Repeat the same operation with solutions of iron (III) and manganese (II) salts. Mention the colors of precipitates. Write the equations of chemical reactions and made the conclusion about the ways to produce alkalis and insoluble bases.

Reaction 1: \_\_\_\_\_

Reaction 2: \_\_\_\_\_

Reaction 3: \_\_\_\_\_

Conclusion: \_\_\_\_\_

**Part 3. The properties of bases.**

**Task 1. Characteristic properties of alkalis.**

Add two drops of phenolphthalein and methyl orange into two tubes both containing sodium hydroxide solution ( $\text{NaOH}$ ). Write down your observations.

Conclusion: \_\_\_\_\_

Pour several drops of alkali water solution into the tube and add two drops of phenolphthalein to it. Add hydrochloric acid solution ( $\text{HCl}$ ) to this tube in the drop by drop manner (mix it by a glass stick every time) until the color of the solution will disappear. Write the chemical equation of the neutralization reaction.

Reaction: \_\_\_\_\_

Conclusion: \_\_\_\_\_

**Task 2. The properties of insoluble bases.**

Add the excess of  $\text{NaOH}$  solution to the solution (2–3 drops) of a nickel (II) salt. Add some drops of an acid to the tube with the precipitate. Describe your observations. Write the equation of chemical reaction.

Precipitation: \_\_\_\_\_

The dissolving of a precipitate: \_\_\_\_\_

Conclusion: \_\_\_\_\_

**Part 4. Production and properties of amphoteric hydroxides.**

Add several drops of a zinc salt into two tubes. Then add  $\text{NaOH}$  solution to the both tubes (don't forget to shake the tubes) until the precipitate will be formed. Add the solution of an acid to the first tube and the solution of an alkali to the second tube. Admit

the dissolving of a precipitate. Repeat these operations with salts of aluminum and chrome (III). Write the equations of chemical reactions of precipitation and disappearance of precipitates.

Precipitation reaction 1: \_\_\_\_\_

The addition of an acid: \_\_\_\_\_

The addition of a base: \_\_\_\_\_

Precipitation reaction 2: \_\_\_\_\_

The addition of an acid: \_\_\_\_\_

The addition of a base: \_\_\_\_\_

Precipitation reaction 3: \_\_\_\_\_

The addition of an acid: \_\_\_\_\_

The addition of a base: \_\_\_\_\_

Conclusion: \_\_\_\_\_

### **Part 5. Production and properties of acids.**

#### **Task 1: Production of acids.**

Put several crystals of sodium acetate ( $\text{CH}_3\text{COONa}$ ) into the tube and add several drops of  $\text{H}_2\text{SO}_4$ . Determine which substance has been formed using your own sense of smell. Write the equation of chemical reaction.

Reaction: \_\_\_\_\_

Conclusion: \_\_\_\_\_

#### **Task 2. The common properties of acids.**

Add the solution of hydrochloric acid into two tubes. Then add two drops of phenolphthalein to the first tube and two drops of methyl orange to the second tube. Describe your observations.

Conclusion: \_\_\_\_\_

Add dilute sulfuric acid to two tubes (one of them contains zinc, another one contains copper). Write the equation of the possible chemical reaction. Make the conclusion about the possibility of the reaction between a metal and dilute sulfuric acid.

Reaction: \_\_\_\_\_

Conclusion: \_\_\_\_\_

Add a small portion of magnesium oxide ( $\text{MgO}$ ) to the first tube and a small portion of zinc oxide ( $\text{ZnO}$ ) to the second tube. Add 12–15 drops of dilute sulfuric acid to each of those tubes. Carefully heat these tubes and describe your observations. Write equations of chemical reactions.

Reaction 1: \_\_\_\_\_

Reaction 2: \_\_\_\_\_

Conclusion: \_\_\_\_\_

Produce copper (II) and manganese (II) hydroxides in two different tubes using solutions of salts of Cu (II) and Mn (II), as well as solution of sodium hydroxide (NaOH). Then add dilute sulfuric acid to the both tubes. Write equations of chemical reactions and your observations.

Precipitation reaction 1: \_\_\_\_\_

The dissolving of the precipitate: \_\_\_\_\_

Precipitation reaction 2: \_\_\_\_\_

The dissolving of the precipitate: \_\_\_\_\_

Conclusion: \_\_\_\_\_

Put the piece of calcium carbonate ( $\text{CaCO}_3$ ) in the tube. Then add the solution of hydrochloric acid to it in the drop by drop manner. Describe your observations. Write the equation of chemical reaction.

Reaction: \_\_\_\_\_

Conclusion: \_\_\_\_\_

### Part 6. Production of acidic salts.

**Task 1.** Pour several drops of concentrated calcium hydroxide solution into the tube. Add dilute orthophosphoric acid solution to that tube in the drop by drop manner until the precipitate will be formed. Mention the color of the precipitate. Add to the tube the excess of  $\text{H}_3\text{PO}_4$  until the precipitate will be dissolved (don't forget to mix the solution by a glass stick). Write equations of chemical reactions of the production of insoluble neutral salt and the production of  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  — soluble dihydrogen phosphate (acidic salt). Keep the solution of the acidic salt for the next task.

Precipitation reaction: \_\_\_\_\_

The dissolving of the precipitate: \_\_\_\_\_

Conclusion: \_\_\_\_\_

**Task 2.** Add the solution of calcium hydroxide to the tube from the previous task until the precipitate will appear again. Write the equation of chemical reaction.

Reaction: \_\_\_\_\_

Conclusion: \_\_\_\_\_

### Part 7. Production of basic salts.

**Task 1.** Pour the solution of NaOH into the solution of cobalt (II) sulfate in the drop by drop manner until the blue precipitate will appear. Write the equation of chemical reaction of the basic salt ( $(\text{CoOH})_2\text{SO}_4$ ) formation. Keep the tube for the next task.

Reaction: \_\_\_\_\_

Conclusion: \_\_\_\_\_

**Task 2.** Divide the precipitate from the previous task into two parts and put it into two tubes. Add the solution of alkali into the first tube until the color will be changed. Add

the solution of sulfuric acid into the second tube until the disappearance of the precipitate. Write the equations of chemical reactions of the conversion of the basic salt into the base  $\text{Co}(\text{OH})_2$  and the conversion of the basic salt into the neutral salt  $\text{CoSO}_4$ .

Reaction 1: \_\_\_\_\_

Conclusion: \_\_\_\_\_

Reaction 2: \_\_\_\_\_

Conclusion: \_\_\_\_\_

### LABORATORY WORK (P) "HYDROLYSIS OF SALTS IN WATER SOLUTIONS"

**The aim of the work:** to study hydrolysis reactions and factors influencing these reactions.

**Reactants and equipment:** dry salts: sodium acetate ( $\text{CH}_3\text{COONa}$ ), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3$ ), tin (II) chloride ( $\text{SnCl}_2$ ), ammonium acetate ( $\text{CH}_3\text{COONH}_4$ ), potassium chloride ( $\text{KCl}$ ); water solutions: sodium carbonate (0.5 N); sodium sulfite (0.5 N); antimony (III) chloride (0.5 N); hydrochloric acid (2 N); the indicator paper, phenolphthalein; ethanol stoves.

#### Task 1. The pH levels in water solutions of salts.

Pour distilled water into 5 tubes (fill approximately 1/3 of their volumes). Keep the first tube as the control one. Add 0.05 g of the following salts to each of the four remaining tubes: sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), ammonium sulfate ( $\text{Al}_2(\text{SO}_4)_3$ ), ammonium acetate ( $\text{CH}_3\text{COONH}_4$ ), potassium chloride ( $\text{KCl}$ ). Mix the solutions until the complete dissolving of crystals (use a new glass stick for each tube).

Using the indicator paper check the pH level in each of the five tubes. Fill the table.

Salt	The color of the indicator paper	The medium	pH level (pH < 7, pH = 7, pH > 7)	Hydrolysis (yes or no)
–				
$\text{Na}_2\text{CO}_3$				
$\text{Al}_2(\text{SO}_4)_3$				
$\text{CH}_3\text{COONH}_4$				
$\text{KCl}$				

Write complete and short ionic equations of hydrolysis reactions in the stepwise manner (if it is possible).

#### Tube with $\text{Na}_2\text{CO}_3$

Step I: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

Step II: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

**Tube with  $\text{Al}_2(\text{SO}_4)_3$** 

Step I: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

Step II: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

Step III: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

**Tube with  $\text{CH}_3\text{COONH}_4$** 

Chemical reaction: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

**Tube with  $\text{KCl}$** 

Chemical reaction: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

**Task 2. The influence of the nature of salts on the degree of their hydrolysis.**

Pour about 1ml of  $\text{Na}_2\text{SO}_3$  solution in the first tube and about 1 ml of  $\text{Na}_2\text{CO}_3$  in the second tube (their molar concentrations are the same: 0.5 mol/L). Add one drop of phenolphthalein to each of these tubes. Describe your observations. Compare the intense of color in two tubes. Which of these salts has a higher hydrolysis degree? Write chemical reactions and ionic equations of hydrolysis for  $\text{Na}_2\text{SO}_3$  (for hydrolysis of  $\text{Na}_2\text{CO}_3$  see the previous task).

**Tube with  $\text{Na}_2\text{SO}_3$** 

Step I: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

Step II: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

Calculate constants of hydrolysis ( $K_{\text{hydrolysis}}$ ) and degrees of hydrolysis ( $h_{\text{hydrolysis}}$ ) for both salts. You can ignore the second step of hydrolysis in these calculations.

$$K_{\text{hydrolysis}} = K_{\text{H}_2\text{O}} / K_{\text{dissociation of a weak acid (the last step)}}$$

$$h_{\text{hydrolysis}} = \sqrt{\frac{K(\text{hydrolysis})}{C(\text{salt})}}$$

Fill in the table:

The salt	Dissociation constant of the weak acid (for the second step) $K_{\text{diss II}}$	$K_{\text{hydrolysis}}$	$h_{\text{hydrolysis}}$	pH
$\text{Na}_2\text{SO}_3$	$6.4 \cdot 10^{-8}$			
$\text{Na}_2\text{CO}_3$	$4.7 \cdot 10^{-11}$			

Which of the salts has been hydrolyzed better? Explain your answer.

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**Task 3. The influence of temperature on the degree of hydrolysis.**

Pour about 3 ml of distilled water in the tube and add 0.05 g of sodium acetate  $\text{CH}_3\text{COONa}$ . Mix the solution until the crystals will be completely dissolved. Add one drop of phenolphthalein to this tube. Notice the color of the solution.

Heat the tube using the ethanol stove almost until the boiling point. Describe your observations. Write the hydrolysis reaction, complete and short ionic equations.

Chemical reaction: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

How the increase in temperature influenced the dissociation degree of the acetic acid?

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How the increase in temperature influenced the degree of the hydrolysis?

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**Task 4. The influence of dilution on the degree of the hydrolysis.**

Pour 2–3 drops of the antimony (III) chloride to the tube and indicate its pH with the indicator paper. Is this salt hydrolyzed in the concentrated solution?

Add water to the tube in the drop by drop manner. Notice the changes. Stop when a white precipitate of  $\text{SbOCl}$  will appear.

Write chemical reactions, complete and short ionic forms of them.

Step I: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

Step II: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

Decomposition of  $\text{Sb(OH)}_2\text{Cl}$ : \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

Make the conclusion about the influence of dilution on the hydrolysis degree of a salt.

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**Task 5. The influence of the acid on the hydrolysis of a salt.**

Pour 8–10 drops of distilled water in the tube. Then dissolve 0.05 g of dry tin (II) chloride in that tube. Mix the solution with a glass stick until the complete dissolving of crystals.

Notice the formation of white precipitate ( $\text{SnOHCl}$ ). Write the hydrolysis reaction (just the first step).

Step I: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

How the addition of acid ( $\text{H}^+$  ions) will influence the hydrolysis? Add HCl solution to the tube in the drop by drop manner. Write the chemical reaction between  $\text{SnOHCl}$  and HCl. What happened to the white precipitate?

Chemical reaction: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

How the addition of acid influences the degree of the hydrolysis of  $\text{SnCl}_2$ ?

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**Conclusion:** “*I studied hydrolysis of salts in water solutions*”.

**LABORATORY WORK (M, D, P)**

**“DETERMINATION OF ACTIVE ACIDITY OF BIOLOGICAL FLUIDS”**

**The aim of the work:** to learn how to determine the active acidity of fluids by calorimetric and potentiometric methods.

**Devices and reagents:** two solutions with biological fluids; two glasses with the capacity of 50 mL; a glass stick; the test-paper; pH-meter; distilled water; filter paper.

**Task 1.** Determination of pH in the solutions № 1 and № 2 with the help of the test-paper.

You need to put the tip of the glass stick in the solution and then quickly but carefully put that tip on the test-paper. The color of the paper will be changed. Match the color of the paper with the pH scale. Wash, clean and dry the glass stick. Then repeat that procedure with the second solution. Write down the results in the table.

**Task 2.** Determination of pH in the solutions № 1 and № 2 with the help of pH-meter.

The analyzed solution is poured into a clean glass. That glass is used for pH measuring. We should put the electrodes into the solution and read the results on the screen

of the pH-meter. Some pH-meters will show the exact pH in the solution. Other devices will show the value of the electromotive force. In the last case you will have to convert it into the pH using specific instructions. Before the determination of pH of the second solution the electrodes must be carefully washed up with the distilled water. Water drops must be dried out with a filter paper. The obtained results are written down in the table. We should calculate the active acidity of these solutions using the formula:  $[H^+] = 10^{-pH}$ .

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

**Conclusion:** “The accuracy of the pH measuring is \_\_\_\_\_ when we use pH-meter instead of test-paper”.

### TEST SELF-CHECK

**1. How will the dissociation constant of acetic acid change in case of 4 times dilution of its solution:**

- a) will increase 2 times;
- b) will decrease 2 times;
- c) will not change;
- d) will decrease 4 times?

**2. Which of the 0.1M solutions has the lowest concentration of  $H^+$  ions:**

- 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 true 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 to the solution.

**4. How will the dissociation degree of propionic acid change after 4 times dilution of its solution?**

- a) will increase 2 times;
- b) will not change;
- c) will decrease 2 times;
- d) will increase 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 increases;
- c) in 0.1 M NaCl solution the ionic force is lower than in 0.1M  $MgSO_4$  solution;
- d) ionic force of saline is 0.15 mol/L.



**6. Choose the true statements: ion activity coefficient in the solution:**

a) shows the deviation of properties of a real solution from the properties of an ideal solution;

b) depends on the ionic force of the solution;

c) is lower if the ion charge is higher;

d) is higher if the electrolyte concentration in the solution is higher.

**7. The coefficient of ion activity in the solution of HCl will decrease:**

a) with the addition of NaCl;

c) with the decrease of temperature;

b) with the dilution of the solution;

d) with the increase of temperature.

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

a)  $\text{NH}_3 + \text{HOH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ ;

b)  $\text{CH}_3\text{COOH} + \text{HOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$ ;

c)  $\text{RNH}_2 + \text{HOH} \rightleftharpoons [\text{RNH}_3]^+ + \text{OH}^-$ ;

d)  $\text{PO}_4^{3-} + \text{HOH} \rightleftharpoons \text{HPO}_4^{2-} + \text{OH}^-$ .

**9. In 10 L of the solution there are 3.7 g of  $\text{Ca}(\text{OH})_2$ . 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 0.01M NaOH solution are diluted with water until the volume of 10 L. pH is equal to:**

a) 10; b) 13; c) 1; d) 4?

**11. To titrate 5 ml of  $\text{H}_2\text{SO}_4$  solution we used 4.10 ml of 0.1020M NaOH solution. pH in the initial acid solution is:**

a) 1.38; b) 2.0; c) 2.08; d) 1.08?

**12. Active acidity of the stomach juice is 0.04 mol/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;

c) overall acidity;

b) potential acidity;

d)  $\text{H}^+$  ion concentration.

## PROBLEMS

1. Calculate the pH and pOH of sulfuric acid solution, if in 1 L of this solution there are 0.049 g of  $\text{H}_2\text{SO}_4$ .

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Answer: \_\_\_\_\_

2. Calculate the pH of 0.001 M acetic acid solution, if its dissociation degree is 0.0134.

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Answer: \_\_\_\_\_

3. How will the pH of the medium change after the addition of 30 ml of 0.2 M sodium hydroxide solution to 300 ml of water? Density is 1 g/ml.

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Answer: \_\_\_\_\_

4. How many times the hydrogen ion concentration in blood is higher than the one in the cerebrospinal fluid? ( $\text{pH}(\text{blood}) = 7.36$ ,  $\text{pH}(\text{cerebrospinal fluid}) = 7.53$ ).

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Answer: \_\_\_\_\_

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

## STANDARDS OF PROBLEM SOLUTIONS

**Problem 1.** Calculate  $[H^+]$  and pH of 0.003 M HCl solution at the temperature of 25 °C.

We have:

$$C(\text{HCl}) = 0.003 \text{ mol/L}$$

pH — ?

$[H^+]$  — ?

*Solution:*

Hydrochloric acid is a strong electrolyte which is almost completely dissociated into ions in the water 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 :

$$[H^+] = C(\text{HCl}).$$

1. Let's determine  $[H^+]$  :  $[H^+] = C(\text{HCl}) = 0.003 \text{ mol/L}$ .

2. Let's determine pH:  $\text{pH} = -\log[H^+] = -\log 0.003 = 2.52$ .

*Answer:*  $[H^+] = 0.003 \text{ mol/L}$ ;  $\text{pH} = 2.52$ .

**Problem 2.** Calculate pH of 0.01 M  $\text{NH}_4\text{OH}$  solution at 298K, if the dissociation degree of ammonium hydroxide is 0.042.

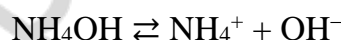
We have:

$$C(\text{NH}_4\text{OH}) = 0.01 \text{ mol/L}$$

$$\alpha = 0.042$$

pH — ?

*Solution:*



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

$$[\text{OH}^-] = C \cdot \alpha = 0.01 \cdot 0.042 = 4.2 \cdot 10^{-4} \text{ mol/L}.$$

$$2. \text{pOH} = -\log [\text{OH}^-] = -\log 4.2 \cdot 10^{-4} = 3.38.$$

$$3. \text{pH} = 14 - \text{pOH} = 14 - 3.38 = 10.62.$$

*Answer:*  $\text{pH} = 10.62$ .

**Problem 3.** Calculate the dissociation degree of lactic acid  $[H^+]$  and pH of 0.1 M lactic acid solution at 298K if the dissociation constant of lactic acid ( $K_a$ ) is  $1.38 \cdot 10^{-4}$ .

We have:

$$C(\text{acid}) = 0.1 \text{ mol/L}$$

$$K_a(\text{acid}) = 1.38 \cdot 10^{-4}$$

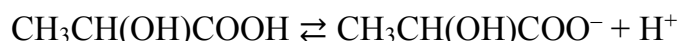
$\alpha$  — ?

$[H^+]$  — ?

pH — ?

*Solution:*

Lactic acid is a weak monoatomic acid which dissociates according to the following scheme:



We determine the dissociation degree:

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

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

$$\text{Hence, } \alpha = \sqrt{\frac{1.38 \cdot 10^{-4}}{0.1}} = 3.7 \cdot 10^{-2} = 0.037.$$

$$2. \text{ We determine } [H^+] : [H^+] = C \cdot \alpha = 0.1 \cdot 0.037 = 0.0037 \text{ mol/L.}$$

3

*Answer:*  $\alpha = 0.037$ ,  $[H^+] = 0.0037 \text{ mol/L}$ ,  $\text{pH} = 2.43$ .

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**Problem 4.** Calculate the dissociation degree, the concentration of acetic acid and the hydrogen ion concentration in the solution of acetic acid with  $\text{pH} = 2.87$ . Dissociation constant of acetic acid at 298 K is equal to  $1.75 \cdot 10^{-5}$ .

We have:

$$\text{pH} = 2.87$$

$$K_a = 1.75 \cdot 10^{-5}$$

$$[H^+] = ?$$

$$C = ?$$

$$\alpha = ?$$

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Let's determine  $[H^+]$ :

$$[H^+] = 10^{-\text{pH}} = 10^{-2.87} = 1.318 \cdot 10^{-3}$$

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2. We determine C: Acetic acid dissociates according to the scheme:



The dissociation constant is expressed as the ratio:

H

:

$$K_a = \frac{[H^+] \cdot [CH_3COO^-]}{[CH_3COOH]}$$

$[H^+] = [CH_3COO^-]$  and  $[CH_3COOH]$  in a dilute solution of a weak binary electrolyte

can be taken as C.

H

$$\text{Then: } K_a = [H^+]^2 / C.$$

$$\text{Hence: } C = [H^+]^2 / K_a = (1.318 \cdot 10^{-3})^2 / 1.75 \cdot 10^{-5} = 0.09926.$$

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3. Let's determine  $\alpha$ . For dilute solutions of weak binary electrolytes we can use

$$\text{the formula: } \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.75 \cdot 10^{-5}}{0.09926}} = 0.013.$$

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## CHAPTER 8

### BUFFER SYSTEMS

#### Main questions of the topic:

1. Buffer systems, their classifications.
2. Calculation of pH in acidic and basic buffer solutions.
3. Mechanism of action of buffer systems.
4. Buffer capacity.
5. Main buffer systems of the organism. Acidosis. Alkalosis.
6. Bicarbonate buffer system, mechanism of action.
7. Hemoglobin buffer system, mechanism of action.
8. Hydrogen phosphate buffer system, mechanism of action.
9. Protein buffer system, mechanism of action.

#### LABORATORY WORK (M, D, P): “PREPARATION OF BUFFER SOLUTIONS AND INVESTIGATION OF MECHANISM OF THEIR ACTION”

**The aim of the work:** to learn how to prepare buffer solutions; how to calculate pH in buffer solutions; to study the mechanism of buffering after the addition of water or a small amount of acid.

#### Devices and reactants.

- tubes, flasks with the volume of 100 ml, graduated pipettes
- solutions of acetic acid ( $C = 0.1 \text{ mol/L}$ ), sodium acetate ( $C = 0.1 \text{ mol/L}$ ), hydrochloric acid ( $C = 0.1 \text{ mol/L}$ )
- indicators: indicator paper, phenolphthalein, methylorange.

**Task 1.** We prepare the solutions according to the attached scheme, then calculate the pH level using the equation:  $\text{pH} = \text{pK}_a(\text{acid}) + \log \frac{[\text{salt}]}{[\text{acid}]}$  and determine it experimentally. The obtained results are written down in the table.

№ of the tube	1	2	3
Number of ml of 0.1 M CH <sub>3</sub> COOH solution	18	10	2
Number of ml of 0.1 M CH <sub>3</sub> COONa solution	2	10	18
pH calculated			
pH experimental			

pH in the tube № 1 =  $4.75 + \log\left(\frac{\quad}{\quad}\right) = \underline{\quad}$

pH in the tube № 2 =  $4.75 + \log\left(\frac{\quad}{\quad}\right) = \underline{\quad}$

pH in the tube № 3 =  $4.75 + \log\left(\frac{\quad}{\quad}\right) = \underline{\quad}$

Experimental determination of pH.

A strip of 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 test-paper by a clean glass stick. Then we should match the color of the paper with the pH scale and write the results in the table.

**Task 2.** To check the buffering properties of solutions.

a) The influence of dilution. In two tubes we pour 4 ml of buffer solution № 2. Then in the first tube we add 4 ml of water and in the second one we add 8 ml of water. Solutions are mixed. Then we determine pH levels in two tubes with the help of test paper. The results should be 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) The influence of acid addition. We pour 2 ml of the buffer solution № 3 in one tube and 2 mL of distilled water into another tube. After that we determine the initial pH in both tubes and write it down in the table. Then we add 2 drops of 0.1 M HCl solution into both tubes, mix them carefully and determine the pH once again. The results should be written down in the table.

Systems	Initial value of pH	pH after the addition of 2 drops of 0.1 M HCl
Buffer solution № 3		
H <sub>2</sub> O		

**Conclusion:** “Experimentally determined pH of buffer systems is \_\_\_\_\_ to the theoretically calculated one. Buffer systems are \_\_\_\_\_ to the addition of water and small amounts of acids”

### TEST SELF-CHECK

**1. Choose the pairs of water solutions of substances which can form a buffer system being poured together (pay attention to the products of the possible reactions between them):**

- a) 200 ml of 0.2M NH<sub>4</sub>OH solution;
- b) 200 ml of 0.3M NH<sub>4</sub>Cl solution;
- c) 100 mL of 0.3M NaH<sub>2</sub>PO<sub>4</sub> solution;
- d) 100 mL of 0.3M HCl solution;
- e) 100 mL of 0.3M NaOH solution;
- f) 200 mL of 0.2M K<sub>2</sub>HPO<sub>4</sub> solution;
- g) 200 mL of 0.1M NaOH solution.

**2. What factors influence the pH value of a buffer system:**

- a) addition of  $C_6H_{12}O_6$ ;
- b) dissociation constant of an acid (a base);
- c) temperature;
- d) the ratio of components' concentrations?

**3. What factors influence the value of buffer capacity:**

- a) ratio of components' concentrations;
- b) addition of  $C_6H_{12}O_6$ ;
- c) components' concentrations;
- d) dilution?

**4. Ratio of components' concentrations  $[Na_2HPO_4]/[NaH_2PO_4]$  in a phosphate buffer solution is 2:1. Choose the true statement for the given solution:**

- a) addition of a small amount of NaOH in the buffer solution will cause a little increase of the pH;
- b) after the 100 times dilution of the solution its pH will increase by 2 pH units;
- c) buffer solution has the maximum possible buffer capacity;
- d) after the dilution the buffer capacity of the solution will decrease.

**5. 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 true statements for these solutions:**

- a) the pH of the first solution is 1 unit higher than the pH of the second solution;
- 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 higher than that of the second solution;
- d) the concentration of hydrogen ions in the first solution is approximately equal to the concentration of hydrogen ions in the second solution.

**6. What is the pH of a buffer solution? There are 0.1 mol of  $CH_3COOH$  and 0.5 mol of  $CH_3COOK$  in 10 L of that solution,  $pK$  of  $CH_3COOH$  is 4.75 (here and in the further calculations it's necessary to consider ion activity coefficients to be equal to 1 and the temperature to be equal to 298 K):**

- a) 5.45; b) 4.75; c) 3.75; d) 4.05?

**7. We add 0.01 mol of NaOH in 1 L of a buffer solution containing 0.1 mol of  $NH_3 \cdot H_2O$  and 0.1 mol of  $NH_4Cl$ . 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?

**8. 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) of this solution, if after the addition of 10 mL of 1M NaOH solution the pH of the buffer has become 9.33:**

- a) 0.125; b) 1.25; c) 1250; d) 0.0107?

**9. Which buffer solutions can effectively maintain the constant pH of the solution with pH = 4:**

- a) acetate buffer,  $pK(\text{CH}_3\text{COOH}) = 4.75$ ; c) phosphate buffer,  $pK(\text{H}_2\text{PO}_4^-) = 6.8$ ;  
b) ammonia buffer,  $pK(\text{NH}_4\text{OH}) = 4.75$ ; d) formiate buffer,  $pK(\text{HCOOH}) = 3.75$ .

**10. Which buffer systems maintain the constant pH of human blood:**

- a) phosphate; d) protein;  
b) bicarbonate; e) hemoglobin and oxyhemoglobin ?  
c) acetate;

**11. Which of the buffer systems makes the main impact into the buffer capacity of erythrocytes:**

- a) phosphate; d) protein;  
b) bicarbonate; e) hemoglobin and oxyhemoglobin ?  
c) acetate;

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

- 12. Electrolytes and nonelectrolytes (total amount of dissolved particles):** a) ion force;  
b) overall acidity;  
**13. Electrolytes:** c) osmotic pressure;  
d) reserve alkalinity;  
**14.  $\text{HCO}_3^-$  ions:** e) oncotic pressure.

### PROBLEMS

1. Calculate the pH of a buffer solution. 1 L of the solution contains 18.4 g of formic acid and 68 g of sodium formiate,  $pK_a(\text{HCOOH}) = 3.75$ . How will the pH change after the 50 times dilution of the solution? \*

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Answer: \_\_\_\_\_

2. Calculate the pH of the acetate buffer solution which is made up of 100 ml of 0.1M  $\text{CH}_3\text{COOH}$  solution and 200 ml of 0.2M  $\text{CH}_3\text{COONa}$  solution, if  $K_a(\text{CH}_3\text{COOH}) = 1.75 \cdot 10^{-5}$ . How will the pH of this buffer solution change after the addition of 30 ml of 0.2 M NaOH solution?

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Answer: \_\_\_\_\_



3. Calculate the pH of the solution of formic acid, half neutralized by the alkali ( $pK(\text{HCOOH}) = 3.75$ ).

Answer: \_\_\_\_\_

4. To change the pH of 100 ml of blood from 7.36 until 7.00 we have to add 36 ml of 0.05M HCl solution. Calculate the buffer capacity of blood relatively to acid (mol/L · pH unit).

Answer: \_\_\_\_\_

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

### STANDARDS OF PROBLEM SOLUTIONS

**Problem 1.** We add 49.2 g of  $\text{CH}_3\text{COONa}$  to 2 L of 0.1 M  $\text{CH}_3\text{COOH}$  solution. Calculate pH level of the obtained buffer solution ( $K_a(\text{CH}_3\text{COOH}) = 1.75 \cdot 10^{-5}$ ).

We have:

$$V(\text{solution}) = 2 \text{ L}$$

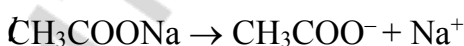
$$C(\text{CH}_3\text{COOH}) = 0.1 \text{ mol/L}$$

$$m(\text{CH}_3\text{COONa}) = 49.2 \text{ g}$$

$$K_a(\text{CH}_3\text{COOH}) = 1.75 \cdot 10^{-5}$$

$$pH = ?$$

S



Let's calculate the concentration of sodium acetate in the solution:

$$C(\text{CH}_3\text{COONa}) = m(\text{CH}_3\text{COONa}) / (M(\text{CH}_3\text{COONa}) \cdot V) = 49.2 / (82 \cdot 2) = 0.3 \text{ mol/L.}$$

Let's calculate the pH of acetate buffer solution:

$$pH = -\log K_a + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]} = -\log(1.75 \cdot 10^{-5}) + \log(0.3/0.1) = 4.75 + 0.48 = 5.23.$$

Answer: pH = 5.23

**Problem 2.** What is the pH level of the buffer solution? In 1 L of the solution there are 0.1 mol of  $\text{NH}_4\text{OH}$  and 0.1 mol of  $\text{NH}_4\text{Cl}$  ( $pK_b(\text{NH}_4\text{OH}) = 4.75$ ). How will the pH change after the 10 times dilution of the solution by water?

We have:	S
$C(\text{NH}_4\text{OH}) = 0.1 \text{ mol/L}$	ϕ. Let's calculate $\text{pH}_1$ of the initial solution:
$C(\text{NH}_4\text{Cl}) = 0.1 \text{ mol/L}$	ϑ
$V(\text{solution}) = 1 \text{ L}$	⊗ $14 - 4.75 - \log(0.1/0.1) = 9.25$
$\text{p}K_b(\text{NH}_4\text{OH}) = 4.75$	ϑ
$\text{pH}_1 - ? \text{ pH}_2 - ?$	K

Let's calculate the  $\text{pH}_2$  of the solution after the dilution. After the 10 times dilution of the solution the concentrations of the salt and the base also decrease 10 times:

$$\text{pH}_2 = 14 - 4.75 - \log(0.01/0.01) = 9.25^*$$

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Notice: in the reality, the value of pH after dilution slightly changes. In our case pH becomes approximately 0.07 units higher. Dilution causes the growth of the ion activity coefficient because of the decrease of the ion force of the solution.

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**Problem 3.** In order to make the pH level 1 unit higher we have to add 0.52 ml of 1M NaOH solution to 10 ml of acetate buffer solution. Find the buffer capacity of the given solution against the addition of alkali (mol/L·pH unit).

We have:	Solution	p
$\Delta\text{pH} = 1$	The buffer capacity against the addition of the alkali	ϑ
V	can be determined using the formula:	1
$C(\text{NaOH}) = 1 \text{ mol/L}$	$B_{\text{base}} = \frac{C(\text{NaOH}) \cdot V(\text{NaOH})}{\Delta\text{pH} \cdot V(\text{b.s.})}$	=
⊗	$(1 \cdot 0.52 \cdot 10^{-3}) / (1 \cdot 0.01) = 0.052 \text{ mol/L} \cdot \text{pH unit.}$	
$B_{\text{base}} - ?$	Answer: 0.052 mol/L·pH unit	

**Problem 4.** We have added 40 ml of 0.04 M  $\text{NaH}_2\text{PO}_4$  solution into 16 ml of 0.1 M  $\text{Na}_2\text{HPO}_4$  solution. Determine:

- pH of the obtained buffer solution, if  $K_a(\text{H}_2\text{PO}_4^-) = 6.2 \cdot 10^{-8}$ ;
- how will pH of this solution change after the addition of 6 ml of 0.1 M HCl solution;
- is it possible to prepare phosphate buffer solution with the  $\text{pH} = 8.5$ .

We have:	S	H
$C(\text{Na}_2\text{HPO}_4) = 0.1 \text{ mol/L}$	a) Let's calculate the pH of the phosphate buffer	ϑ
$V(\text{of Na}_2\text{HPO}_4 \text{ solution}) = 16 \text{ ml}$	l	
$C(\text{NaH}_2\text{PO}_4) = 0.04 \text{ mol/L}$	In the phosphate buffer solution the role of an acid is	ϑ
$V(\text{of NaH}_2\text{PO}_4 \text{ solution}) = 40 \text{ ml}$	performed by $\text{H}_2\text{PO}_4^-$ ion which dissociates according	
$C(\text{HCl}) = 0.1 \text{ mol/L}$	to the following scheme:	9
$V(\text{of HCl solution}) = 6 \text{ ml}$	$\text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-}$	.
$K_d(\text{H}_2\text{PO}_4^-) = 6.2 \cdot 10^{-8}$	As the dissociation constant of this process is law, we	
a) pH - ? b) $\Delta\text{pH} - ?$	can consider the concentration of $\text{H}_2\text{PO}_4^-$ to be equal	

to the  $\text{NaH}_2\text{PO}_4$  concentration, and the  $\text{HPO}_4^{2-}$  concentration to be equal to the  $\text{Na}_2\text{HPO}_4$  concentration.

$$\text{Then: } \text{pH} = -\log K_a (\text{H}_2\text{PO}_4^-) + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

It is necessary to take into account that after the mixing of two solutions the initial concentrations of both components decrease. New concentrations can be calculated with the following formula:  $C_{\text{init.}} \cdot V_{\text{init.}} = C_{\text{final.}} \cdot V_{\text{final.}}$

Then the new concentration of  $\text{NaH}_2\text{PO}_4$  will be:

$$[\text{NaH}_2\text{PO}_4] = \frac{C(\text{NaH}_2\text{PO}_4)_{\text{init.}} \cdot V(\text{solution NaH}_2\text{PO}_4)}{V(\text{buffer solution})}$$

The final concentration of  $\text{Na}_2\text{HPO}_4$  will be:

$$[\text{Na}_2\text{HPO}_4] = \frac{C(\text{Na}_2\text{HPO}_4)_{\text{init.}} \cdot V(\text{solution Na}_2\text{HPO}_4)}{V(\text{buffer solution})}$$

$$C(\text{NaH}_2\text{PO}_4)_{\text{init.}} \cdot V(\text{of NaH}_2\text{PO}_4 \text{ solution}) = n (\text{NaH}_2\text{PO}_4) = 0.040 \cdot 0.04 = 0.0016 \text{ mol.}$$

$$C(\text{Na}_2\text{HPO}_4)_{\text{init.}} \cdot V(\text{of Na}_2\text{HPO}_4 \text{ solution}) = n (\text{Na}_2\text{HPO}_4) = 0.016 \cdot 0.1 = 0.0016 \text{ mol.}$$

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

$$\text{Hence: } \text{pH} = -\log 6.2 \cdot 10^{-8} + \log \frac{n(\text{Na}_2\text{HPO}_4)}{n(\text{NaH}_2\text{PO}_4)} = 7.21 + \log(0.0016/0.0016) =$$

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b) Let's calculate the change of pH after the addition of HCl solution to the buffer solution. After the addition of 6 ml of 0.1 M HCl solution (0.0006 mol), the added acid will react with 0.0006 mol of  $\text{Na}_2\text{HPO}_4$  and form 0.0006 mol of  $\text{NaH}_2\text{PO}_4$ :

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+ Then the amount of  $\text{Na}_2\text{HPO}_4$  will become 0.0006 mol lower:

$$n (\text{Na}_2\text{HPO}_4) = 0.0016 - 0.0006 = 0.0010 \text{ mol.}$$

1 The amount of  $\text{NaH}_2\text{PO}_4$  will become 0.0006 mol higher:

o

H

g H

O

e Δ

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n c) It is impossible to prepare the phosphate buffer solution with the  $\text{pH} = 8.5$  because the borders of the effective action of a buffer system is within  $\pm 1$  pH unit from the  $\text{pK}$  of an acid. For the phosphate buffer solution  $\text{pK}_a = 7.21$  and the borders of the effective buffer action is in the pH interval from 6.21 to 8.21.

e

p

Answer : a)  $\text{pH} = 7.21$ ; b) will decrease in 0.35 pH units; c) impossible.

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## CHAPTER 9

### HETEROGENEOUS EQUILIBRIA

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**Main questions of the topic:**

1. Thermodynamic ( $K_s^0$ ) and concentration ( $K_s$ ) solubility constants of a process in heterogeneous equilibrium.
2. Relationships between the solubility  $S$  of a slightly soluble strong electrolyte and its  $K_s^0 \approx K_s$ .
3. Conditions of the 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 metabolism of human organism. Conditions of calcium phosphate formation in slightly basic solutions.
7. The pathology of bone tissue (influence of  $\text{Be}^{2+}$  and  $\text{Sr}^{2+}$ ) and physical chemistry of lithiasis.

**LABORATORY WORK (M, D, P) “OBTAINING OF HETEROGENEOUS SYSTEMS  
«PRECIPITATE-SOLUTION» AND THE SHIFT OF EQUILIBRIUM IN HETEROGENEOUS  
SYSTEMS «PRECIPITATE-SOLUTION»”**

**The aim of the work:** to make heterogeneous systems ‘precipitate-solution’ and to conduct the experimental investigations of the equilibrium shifts in such systems.

**Task 1.** To study the conditions of precipitation in case of slightly soluble strong electrolyte formation.

Pour 2 ml of 0.01 M  $\text{CaCl}_2$  solution in 2 tubes. Add 2 ml of  $\text{Na}_2\text{C}_2\text{O}_4$  solution in one of the tubes, and 2 ml of  $\text{Na}_2\text{SO}_4$  solution into the other one (the concentration of each of the solutions must be 0.01 mol/L). Then notice the changes occurring in the tubes.

Ion conc. (mol/L)	Ion conc. (mol/L)	Ion conc. after mixing	The product of ion concentrations after mixing	$K_s^0$	Observations (is there a precipitate or no)
$\text{Ca}^{2+}$ 0.01	$\text{C}_2\text{O}_4^{2-}$ 0.01			$2.3 \cdot 10^{-9}$	
$\text{Ca}^{2+}$ 0.01	$\text{SO}_4^{2-}$ 0.01			$2.35 \cdot 10^{-5}$	

Write complete and ionic equations of the corresponding reactions:

Tube 1 (with  $\text{Na}_2\text{C}_2\text{O}_4$ )

Complete form: \_\_\_\_\_

Ionic form: \_\_\_\_\_

Tube 2 (with  $\text{Na}_2\text{SO}_4$ )

Complete form: \_\_\_\_\_

Ionic form: \_\_\_\_\_

**Task 2.** To study the influence of concurrent equilibria on the heterogeneous equilibrium in the system “precipitate – solution”.

**Experiment 1.** The shift of the heterogeneous equilibrium towards the formation of the less soluble compound (concurrent equilibria of the same type).

Pour 2–3 drops of the KCl solution in the tube. Then add 2–3 drops of the AgNO<sub>3</sub> solution in the same tube. Write the reaction in complete and ionic form. Notice the color of the precipitate.

Complete form: \_\_\_\_\_

Ionic form: \_\_\_\_\_

Pour 2–3 drops of the KI solution in the same tube with AgCl precipitate. Notice the change in color. Write the complete and ionic equation of the reaction.

Complete form: \_\_\_\_\_

Ionic form: \_\_\_\_\_

Why the heterogeneous equilibrium has been shifted towards the formation of AgI? The solubility product for AgCl is  $1.77 \cdot 10^{-10}$  at room temperature, while for AgI this value is  $8.3 \cdot 10^{-17}$ .

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**Experiment 2.** The shift of heterogeneous equilibrium due to the formation of complex compounds (concurrent equilibria of the different types).

Prepare AgCl precipitate in one tube (according to the instructions from the previous experiment) and AgI precipitate in another tube. Then add 2–3 drops of ammonia (NH<sub>3</sub>) solution in each of the tubes. Mix each solution by a glass stick. Notice that one of the precipitates has been dissolved. Write the reaction of that process in the complete and ionic form.

Complete form: \_\_\_\_\_

Ionic form: \_\_\_\_\_

Why AgI cannot be dissolved in the solution of NH<sub>3</sub>?

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**Experiment 3.** The shift of heterogeneous equilibrium towards the formation of a weak acid.

Prepare two tubes with the precipitate of calcium oxalate (CaC<sub>2</sub>O<sub>4</sub>). Use 2–3 drops of the CaCl<sub>2</sub> solution and 2–3 drops of the (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution. Add 2–3 drops of 2M HCl solution into the first tube and see how the precipitate will be dissolved. Write this chemical reaction in complete and ionic form.

Complete form: \_\_\_\_\_

Ionic form: \_\_\_\_\_

Add 2–3 drops of 2M acetic acid solution to the second tube. Notice that the precipitate has not been dissolved. Why calcium oxalate has been dissolved in HCl and has not been dissolved in CH<sub>3</sub>COOH? pK<sub>a</sub> of CH<sub>3</sub>COOH is 4.75, pK<sub>a</sub> of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> is 1.25 for the 1<sup>st</sup> step of dissociation and 4.14 for the 2<sup>nd</sup> step.

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**Conclusion:** “I studied heterogeneous equilibria and factors which can shift them”.

### LABORATORY WORK (P) “PROPERTIES OF COMPLEX COMPOUNDS”

**The aim of the work:** to study how to produce complex compounds of different types, to study the properties of complex compounds and double salts.

**Reactants:** zinc in granules; solutions of AgNO<sub>3</sub> (0.1M), NaCl (2M), NH<sub>3</sub> (2M), CuCl<sub>2</sub> (0.5N), Hg(NO<sub>3</sub>)<sub>2</sub> (0.5N), KI (saturated), Bi(NO<sub>3</sub>)<sub>3</sub> (0.5N), FeCl<sub>3</sub> (0.5 N), KOH (0.2M), H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (0.5 M), KNCS (0.5 M), NH<sub>4</sub>Fe(SO<sub>4</sub>)<sub>2</sub> (0.1M), K<sub>3</sub>[Fe(CN)<sub>6</sub>] (0.1M), HNO<sub>3</sub> (2M).

#### Part 1. Production of complex compounds.

##### Task 1. Production of complex cations.

Pour several drops of AgNO<sub>3</sub> solution into the tube and add some drops of NaCl solution there. Dissolve the white precipitate by the way of ammonia solution addition to the tube.

Explain why the precipitate has been dissolved and write complete and short ionic equations of chemical reactions (coordination number of Ag<sup>+</sup> is equal to 2). Give the name to the complex compound.

Precipitation reaction: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

Complexation reaction: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

Add several drops of KOH solution into the tube with CuCl<sub>2</sub> solution until the precipitate will form. Then add the excess of ammonia solution to the same tube. Don't forget to shake it.

Compare the color of Cu<sup>2+</sup> in the initial and the final solutions. Which ions make the color of the resulting solution different? Write complete and short ionic equations of chemical reactions (coordination number of Cu<sup>2+</sup> is equal to 4). Give the name to the complex compound.

Precipitation reaction: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

Complexation reaction: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

Which base is stronger: copper (II) hydroxide or the corresponding complex base?  
Try to explain why it is so.

\_\_\_\_\_

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**Task 2. Production of complex anions.**

Pour several drops of mercury (II) nitrate (be careful because it is poison) into the tube and add KI solution to that tube until the precipitate ( $\text{HgI}_2$ ) will be formed. Then continue addition of KI solution until the disappearance of the precipitate.

Write complete and short ionic equations of chemical reactions (coordination number of  $\text{Hg}^{2+}$  is equal to 4). Give the name to the complex compound.

Precipitation reaction: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

Complexation reaction: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

Add several drops of KI into the tube with  $\text{Bi}(\text{NO}_3)_3$  solution until the precipitate ( $\text{BiI}_3$ ) will be formed. Then add some more KI solution until the complete dissolving of the precipitate.

Mention the color of the obtained solution. What is the cause of such color? Write complete and short ionic equations of chemical reactions (coordination number of  $\text{Bi}^{3+}$  is equal to 4). Give the name to the complex compound.

Precipitation reaction: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

Complexation reaction: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

**Task 3. Production of a chelate compound**

Mix together the same volumes of iron (III) chloride and KOH solutions and notice the precipitation. Then add the same volume of oxalic acid solution to that tube. Notice the changes happened in the tube. *Keep the tube for the next task.*

Write complete and short ionic equations of chemical reactions (coordination number of  $\text{Fe}^{3+}$  is equal to 6,  $\text{C}_2\text{O}_4^{2-}$  is a didentate ligand). Give the name to the complex compound.

Precipitation reaction: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

Complexation reaction: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

Draw the structural formula of the complex anion. Each oxalate anion makes two coordination bonds with the  $\text{Fe}^{3+}$  cation.

How many oxalate ions are involved in the complex? \_\_\_\_\_

## Part 2. The properties of complex compounds.

### Task 4. *Dissociation of complex compounds and double salts.*

Pour several drops of concentrated KNCS solution into the tube from the task 3 and the tube with  $\text{FeCl}_3$  solution. Describe the results.

Explain why the color in the tube from the task 3 did not change? Write equations of electrolytic dissociation for the complex compound from the first tube and for  $\text{FeCl}_3$ . Explain why in the first case reaction did not start.

Write complete and short ionic reactions for the process took place in the second tube.

Complexation reaction: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

Write the instability constant equation for the resulting complex anion and name the whole complex compound.

Add the same volume of KOH solution to the tube with the double salt solution ( $\text{NH}_4\text{Fe}(\text{SO}_4)_2$ ) and to the tube with complex compound solution ( $\text{K}_3[\text{Fe}(\text{CN})_6]$ ). Describe the changes. Why the precipitate has been formed just in the first tube? What is the difference in dissociation of double and complex salts of iron? Write equations of their electrolytic dissociation.



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Write complete and short ionic equations of the reaction happened in the second tube.

Precipitation reaction: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

Explain the results of this task.

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**Task 5.** *Destruction of complex compounds.*

Prepare  $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$  solution and add it to three different tubes. Add a piece of zinc in the first tube. Describe the consequences. Write the complete and the short ionic equation of the destruction of the initial complex and production of the new complex (coordination number of  $\text{Zn}^{2+}$  is equal to 4).

Complete reaction: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

Explain why such process is possible, if  $K_{\text{I}}[\text{Ag}(\text{NH}_3)_2]^+ = 5.9 \cdot 10^{-8}$ ;  $K_{\text{I}}[\text{Zn}(\text{NH}_3)_4]^{2+} = 8.3 \cdot 10^{-12}$

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Add dilute  $\text{HNO}_3$  into the second tube until the white precipitate will be formed. Write complete and short ionic equations of the reaction of complex compound destruction.

Complete reaction: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

Explain why the destruction of complex cation happened, if  $K_{\text{I}}[\text{Ag}(\text{NH}_3)_2]^+ = 6.8 \cdot 10^{-8}$ ;  $K_{\text{I}}\text{NH}_4\text{NO}_3 = 6.0 \cdot 10^{-10}$ .

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Add  $\text{KI}$  solution to the third tube until the formation of yellow precipitate. Explain the possibility of this reaction.

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Write complete and short ionic equations of the reaction of complex compound destruction.

Complete reaction: \_\_\_\_\_

Complete ionic form: \_\_\_\_\_

Short ionic form: \_\_\_\_\_

Explain how complex compounds can be destroyed.

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**Conclusion:** “I studied complexation reactions and chemical properties of complex compounds”.

### TEST SELF-CHECK

**1. What units should we use to express the solubility of a slightly soluble strong electrolyte:**

a) mol/dm<sup>3</sup>; b) mol/L; c) dm<sup>3</sup>/L; d) g/L?

**2. For saturated water solutions of which salts  $K_s^0$  can be used:**

a) silver chloride; b) silver nitrate; c) silver sulfate; d) sodium bromide?

**3. We have the equilibrium equation:  $K_{ch.e.} = \frac{a(Ag^+) \cdot a(I^-)}{a(AgI)_s}$ . Choose correct**

**consequences of the given 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 slightly soluble strong electrolyte  $Ag_2CrO_4$  the value of the thermodynamic ( $K_s^0$ ) solubility constant is expressed as:**

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

b)  $K_s^0 = 2a(Ag^+) \cdot a(CrO_4^{2-})$ ; 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 slightly soluble electrolyte  $Ca_3(PO_4)_2$  is:**

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

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

**6. In a heterogeneous system  $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ ,  $K_s^0(AgCl) = 1.8 \cdot 10^{-10}$ .**

**The precipitate is formed when we have 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 water solutions using the value of  $K_s^0$ :**

- a)  $\text{BaSO}_4$ ,  $\text{Ba}_3(\text{PO}_4)_2$ ,  $\text{Ag}_2\text{CO}_3$ ;      c)  $\text{MgCl}_2$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{FeCl}_2$ ;  
 b)  $\text{AgCl}$ ,  $\text{CaCO}_3$ ,  $\text{SrSO}_4$ ;      d)  $\text{PbS}$ ,  $\text{PbSO}_3$ ,  $\text{PbSO}_4$ ?

**8. We gradually added  $\text{CaCl}_2$  solution to the solution containing 0.01 mol of  $\text{Na}_2\text{SO}_4$ , 0.01 mol of  $\text{Na}_2\text{CO}_3$  and 0.01 mol of  $\text{Na}_2\text{C}_2\text{O}_4$ . Indicate the sequence of precipitation of salts from the solution if  $K_s^0(\text{CaSO}_4) = 6.1 \cdot 10^{-5}$ ,  $K_s^0(\text{CaCO}_3) = 4.8 \cdot 10^{-9}$ ,  $K_s^0(\text{CaC}_2\text{O}_4) = 2.6 \cdot 10^{-9}$ :**

- a)  $\text{CaCO}_3$ ,  $\text{CaC}_2\text{O}_4$ ,  $\text{CaSO}_4$ ;      c)  $\text{CaC}_2\text{O}_4$ ,  $\text{CaSO}_4$ ,  $\text{CaCO}_3$ ;  
 b)  $\text{CaC}_2\text{O}_4$ ,  $\text{CaCO}_3$ ,  $\text{CaSO}_4$ ;      d)  $\text{CaSO}_4$ ,  $\text{CaC}_2\text{O}_4$ ,  $\text{CaCO}_3$ .

**9. The general expression of the dependence between solubility (S) and constant of solubility ( $K_s$ ) of a slightly soluble strong electrolyte ( $\text{A}_m\text{B}_n$ ) is expressed by the equation:**

a)  $S = \sqrt[m \cdot n]{\frac{K_s}{m^m + n^n}}$ ;    b)  $S = \sqrt[m \cdot n]{\frac{K_s}{m^m \cdot n^n}}$ ;    c)  $S = \sqrt[m \cdot n]{\frac{K_s}{m^m + n^n}}$ ;    d)  $S = \sqrt[m \cdot n]{\frac{K_s}{m^m \cdot n^n}}$ .

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

- a)  $\text{Ag}_2\text{SO}_4$  ( $K_s^0 = 7.7 \cdot 10^{-5}$ );      c)  $\text{PbI}_2$  ( $K_s^0 = 8.7 \cdot 10^{-9}$ );  
 b)  $\text{PbCl}_2$  ( $K_s^0 = 1.7 \cdot 10^{-5}$ );      d)  $\text{PbF}_2$  ( $K_s^0 = 3.7 \cdot 10^{-8}$ ).

**11. In order to dissolve the  $\text{Mg}(\text{OH})_2$  precipitate, it's necessary:**

- a) to increase the concentration of  $\text{Mg}^{2+}$  ions or  $\text{OH}^-$  ions;  
 b) to decrease the concentration of  $\text{Mg}^{2+}$  ions or  $\text{OH}^-$  ions;  
 c) to add  $\text{HCl}$ ;  
 d) to add  $\text{NaOH}$ .

**12. Together with heterogeneous equilibria we can observe the following kinds of equilibria:**

- a) acid-base;      c) formation of complex compounds;  
 b) oxidation-reduction;      d) there is no correct answer.

**13. The solubility of  $\text{AgI}$  in 1 L of water at 25 °C is  $2.35 \cdot 10^{-6}$  gram. What is the concentration solubility constant of  $\text{AgI}$ :**

- a)  $1 \cdot 10^{-8}$ ;    b)  $1 \cdot 10^{-16}$ ;    c)  $1 \cdot 10^{-4}$ ;    d)  $1 \cdot 10^{-12}$ ?

**14.  $K_s^0(\text{CaC}_2\text{O}_4) = 2.6 \cdot 10^{-9}$ . What is the molar concentration of  $\text{C}_2\text{O}_4^{2-}$  ions in a saturated water 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)  $\text{Ca}_3(\text{PO}_4)_2$ ;    b)  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ;    c)  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ;    d)  $\text{CaHPO}_4$ .

## PROBLEMS

1. Will there be a precipitate of AgCl if we pour together equal volumes of 0.001 M AgNO<sub>3</sub> and 0.002 M NaCl solutions?  $K_s(\text{AgCl}) = 1.8 \cdot 10^{-10}$ .

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2. Will there be a precipitate of AgI if we pour together equal volumes of saturated AgCl solution and 0.002 M KI solution?

$$K_s(\text{AgCl}) = 1.8 \cdot 10^{-10}; K_s^0(\text{AgI}) = 8.3 \cdot 10^{-17}.$$

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3. In 2.5 L of a saturated Ag<sub>2</sub>CrO<sub>4</sub> solution there are 0.0625 g of the salt. Calculate the concentration solubility constant of Ag<sub>2</sub>CrO<sub>4</sub> at this temperature.

$$M(\text{Ag}_2\text{CrO}_4) = 332 \text{ g/mol}.$$

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4. The concentration solubility constant of PbSO<sub>4</sub> at 25 °C is equal to  $1.6 \cdot 10^{-8}$ . Calculate the solubility (S) of PbSO<sub>4</sub> in mol/L and g/L.

$$M(\text{PbSO}_4) = 303 \text{ g/mol}.$$

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5. Calculate the mass of SrSO<sub>4</sub> in 2 L of a saturated solution of this salt at 25 °C.

$$K_s(\text{SrSO}_4) = 3.2 \cdot 10^{-5}, M(\text{SrSO}_4) = 184 \text{ g/mol}.$$

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## STANDARDS OF PROBLEM SOLUTIONS

**Problem 1.** After the precipitation of BaSO<sub>4</sub> which was used in X-ray gastroscopy we have 1.5 L of a saturated solution at 25 °C. Calculate the mass of BaSO<sub>4</sub> in this solution.

*Solution.* There is an equilibrium in a saturated solution:



Let's say that «x» is the Ba<sup>2+</sup> ions concentration:

$$C(\text{Ba}^{2+}) = C(\text{SO}_4^{2-}) = x \text{ mol/L}.$$

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

$$K_s = C(\text{Ba}^{2+}) \cdot C(\text{SO}_4^{2-}) = x^2 C(\text{Ba}^{2+}) = C(\text{SO}_4^{2-}) = \sqrt{K_s(\text{BaSO}_4)}.$$

As we can find in the reference book  $K_s(\text{BaSO}_4) = 1.1 \cdot 10^{-10}$ .

The amount of substance of BaSO<sub>4</sub> can be calculated as follows:

$$n(\text{BaSO}_4) = C(\text{Ba}^{2+}) \cdot V \text{ solution},$$

and mass  $m = n \cdot M$ , so

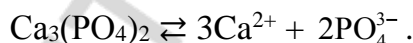
$$m(\text{BaSO}_4) = C(\text{Ba}^{2+}) \cdot V \text{ solution} \cdot M(\text{BaSO}_4).$$

Let's substitute the values and get:  $m = \sqrt{1.1 \cdot 10^{-10}} \cdot 1.5 \cdot 233 = 3.7 \cdot 10^{-3}(\text{g})$ .

*Answer:*  $m(\text{BaSO}_4) = 3.7 \cdot 10^{-3} \text{ g}$ .

**Problem 2.** The concentration of Ca<sup>2+</sup> ions in the solution is 0.001 mol/L. Calculate the minimal PO<sub>4</sub><sup>3-</sup> ions concentration in the solution that will cause the precipitation of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.

*Solution.* The equilibrium established in the saturated solution above the solid Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> is written below:



The solubility constant of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> is calculated according the following equation:

$$K_s(\text{Ca}_3(\text{PO}_4)_2) = [\text{Ca}^{2+}]^3 \cdot [\text{PO}_4^{3-}]^2$$

hence:

$$[\text{PO}_4^{3-}] = \sqrt{\frac{K_s}{[\text{Ca}^{2+}]^3}}$$

As we can find in the reference book  $K_s^0(\text{Ca}_3(\text{PO}_4)_2) = 2 \cdot 10^{-29}$ .

As the ion concentration in the solution is low, let's assume that  $K_s^0 = K_s$ .

$$\text{Then, } [\text{PO}_4^{3-}] = \sqrt{\frac{2 \cdot 10^{-29}}{(0.001)^3}} = 1.41 \cdot 10^{-10} \text{ mol/L}.$$

*Answer:* the precipitate will form at  $[\text{PO}_4^{3-}] > 1.41 \cdot 10^{-10} \text{ mol/L}$ .

**Problem 3.** Will the precipitate of CaC<sub>2</sub>O<sub>4</sub> be formed, if we add the equal volume of Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution with the concentration of  $1 \cdot 10^{-7} \text{ mol/L}$  to the saturated solution of CaSO<sub>4</sub>?

*Solution.* The equilibrium scheme in a saturated solution above the solid  $\text{CaSO}_4$  is written below:



Let's take "x" as the concentration of each of the ions  $[\text{Ca}^{2+}] = [\text{SO}_4^{2-}] = x$  mol/L, then  $K_s(\text{CaSO}_4) = x^2$ ,  $[\text{Ca}^{2+}] = \sqrt{K_s(\text{CaSO}_4)}$  mol/L.

If we mix two solutions of the identical volumes, the total volume of the final solution becomes 2 times higher than the initial one. The concentration of ions in the final solution is two times lower than in each of the initial ones. Let's find the product of ion concentrations of  $\text{Ca}^{2+}$  and  $\text{C}_2\text{O}_4^{2-}$  and compare it to the solubility constant of calcium oxalate.

The condition of the precipitation of  $\text{CaC}_2\text{O}_4$  is:  $[\text{Ca}^{2+}] \cdot [\text{C}_2\text{O}_4^{2-}] > K_s$ .

As we can find in the reference book  $K_s^0(\text{CaSO}_4)$  and  $K_s^0(\text{CaC}_2\text{O}_4)$ ;

$$K_s^0(\text{CaSO}_4) = 2.5 \cdot 10^{-5}; K_s^0(\text{CaC}_2\text{O}_4) = 2.6 \cdot 10^{-9}.$$

In dilute solutions  $K_s^0 = K_s$ ;  $[\text{Ca}^{2+}] = \frac{\sqrt{2.5 \cdot 10^{-5}}}{2}$ ;  $[\text{C}_2\text{O}_4^{2-}] = \frac{1 \cdot 10^{-7}}{2}$ ;

$$[\text{Ca}^{2+}] \cdot [\text{C}_2\text{O}_4^{2-}] = 1.25 \cdot 10^{-10}.$$

*Answer:* the precipitate will not be formed because  $1.25 \cdot 10^{-10} < 2.6 \cdot 10^{-9}$ .

**Problem 4.** The solubility of  $\text{PbI}_2$  at 25 °C is 0.581 g/L. Calculate  $K_s(\text{PbI}_2)$  at 25 °C.  $M(\text{PbI}_2) = 461$  g/mol.

*Solution.* The scheme of the equilibrium established in a saturated solution above the precipitate is:



The concentration solubility constant of  $\text{PbI}_2$  is:

$$K_s(\text{PbI}_2) = [\text{Pb}^{2+}] \cdot [\text{I}^-]^2 \quad (2)$$

Let's establish the connection between  $K_s$  and the solubility of  $\text{PbI}_2$  (S mol/L). As we can see from the equation (1), from 1 mole of  $\text{PbI}_2$  we have 1 mole of  $\text{Pb}^{2+}$  cations and 2 moles of  $\text{I}^-$  anions. So, if S mol/L of  $\text{PbI}_2$  are dissolved, then in a saturated solution:  $[\text{Pb}^{2+}] = S$  mol/L;  $[\text{I}^-] = 2S$  mol/L.

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

$$K_s(\text{PbI}_2) = S \cdot (2S)^2 = 4S^3 \quad (3)$$

Let's express the solubility of  $\text{PbI}_2$  in mol/L. As the molar mass of  $\text{PbI}_2$  is equal to 461 g/mol, then the solubility of  $\text{PbI}_2$  expressed in mol/L is equal to:

$$S = \frac{0,581}{461} = 1.26 \cdot 10^{-3} \text{ mol/L}.$$

Using the equation (3) we can find  $K_s(\text{PbI}_2)$ :  $K_s(\text{PbI}_2) = 4 \cdot (1.26 \cdot 10^{-3})^3 = 8 \cdot 10^{-9}$ .

*Answer:*  $K_s(\text{PbI}_2) = 8 \cdot 10^{-9}$ .

**Problem 5.** The solubility constant of  $\text{Cr(OH)}_3$  is  $5.4 \cdot 10^{-31}$  at  $20^\circ\text{C}$ . Calculate the solubility of  $\text{Cr(OH)}_3$  (in mol/L and in g/L) at  $20^\circ\text{C}$ .  $M(\text{Cr(OH)}_3) = 103 \text{ g/mol}$ .

*Solution.* The scheme of equilibrium in a saturated solution above the solid  $\text{Cr(OH)}_3$  is written below:



The concentration solubility constant of  $\text{Cr(OH)}_3$  is:

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

Let's establish the connection between  $K_s$  and the solubility of  $\text{Cr(OH)}_3$  ( $S \text{ mol/L}$ ). As we can see from equation (1), from 1 mole of  $\text{Cr(OH)}_3$  we have 1 mole of  $\text{Cr}^{3+}$  cations and 3 moles of  $\text{OH}^-$  anions. So, if  $S \text{ mol/L}$  of  $\text{Cr(OH)}_3$  are dissolved, then in a saturated solution:

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

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

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

$$\text{Hence: } S = \sqrt[4]{\frac{K_s \text{Cr(OH)}_3}{27}} = \sqrt[4]{\frac{5,4 \cdot 10^{-31}}{27}} = \sqrt[4]{2 \cdot 10^{-32}} = 1.19 \cdot 10^{-8} \text{ mol/L}.$$

The molar mass of  $\text{Cr(OH)}_3$  is  $103 \text{ g/mol}$ . The solubility of  $\text{Cr(OH)}_3$  expressed in g/L will be:

$$1.19 \cdot 10^{-8} \cdot 103 = 1.22 \cdot 10^{-6} \text{ g/L}.$$

*Answer:*  $1.19 \cdot 10^{-8} \text{ mol/L}$ ;  $1.22 \cdot 10^{-6} \text{ g/L}$ .

## CHAPTER 10

### ELECTRIC CONDUCTIVITY OF ELECTROLYTE SOLUTIONS

#### Main questions on the topic:

1. Fluids and tissues of the human body as the type II conductors of electricity.
2. Absolute ion movement rate and factors determining it. 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, its dependence on the absolute ion movement rate and the dilution (concentration).
5. Molar electric conductivity at the infinite dilution. Kohlrausch's law.
6. Electric conductivity of biological fluids and tissues.
7. Conductometry, conductometric determination of the degree and the constant of dissociation of weak electrolytes. Curves of conductometric titration.

#### LABORATORY WORK (M) "CONDUCTOMETRIC DETERMINATION OF THE DISSOCIATION DEGREE AND THE CONSTANT OF ACETIC ACID DISSOCIATION"

**The aim of the work:** to learn how to determine the electric conductivity of water solutions and how to use the data of conductometric measurements for the calculations of the dissociation degree and the constant of dissociation for weak electrolytes.

**Task 1.** To determine the constant of the equipment ( $K_v$ ) with 0.01M KCl solution.

The glass in which the electrodes are omitted should be taken away and washed twice with a small volume (20 ml) of 0.01M KCl solution. After that we should fill half the volume of the glass with that KCl solution, put it under the electrodes and carefully omit them into the solution. Do not let the electrodes touch the walls of the glass or its bottom. Write down the value of the electric conductivity  $L$  from the screen of the conductometer, as well as the temperature. Using the table below find  $\kappa_{KCl}$  at the given temperature and calculate  $K_v$  using the formula written below:

$$K_v = \kappa_{KCl} / L = \underline{\hspace{2cm}} / \underline{\hspace{2cm}} = \underline{\hspace{2cm}}$$

#### The dependence of the specific electric conductivity of 0.01M KCl on the temperature

Temperature	Specific electric conductivity $\kappa$ , $S \cdot m \cdot cm^{-1}$
18°	0.001225
19°	0.001251
20°	0.001278
21°	0.001305
22°	0.001332
23°	0.001359
24°	0.001386
25°	0.001413





## TEST SELF-CHECK

**1. The factors that determine the ion mobility in the water solution are:**

- a) the viscosity of the solvent;
- b) the temperature;
- c) the value of the ion charge;
- d) the size of the hydrodynamic radius of the ion?

**2. Indicate the formulas expressing Kohlrausch's law:**

- a)  $\lambda_m^0 = F(\omega_{an} + \omega_{cat})$ ; b)  $\alpha = \lambda_m / \lambda_m^0$ ; c)  $\lambda_m^0 = U_{cat} + U_{an}$ ; d)  $\lambda_m = \alpha / C$ .

**3. The values of the absolute ion movement rates in water solutions in the row  $\text{Na}^+$ ,  $\text{Rb}^+$ ,  $\text{OH}^-$ ,  $\text{H}^+$**

- a) decrease; b) stay the same; c) increase?

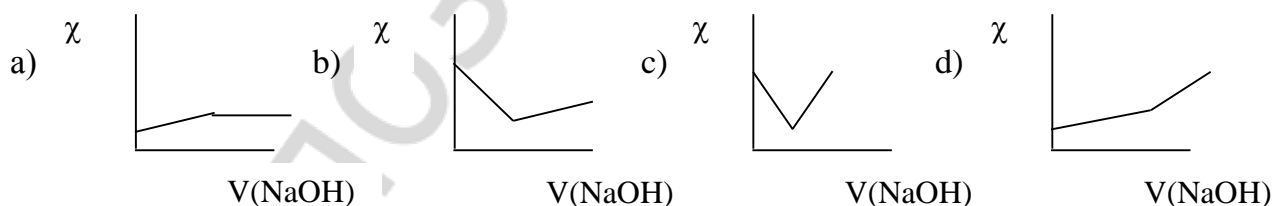
**4. How will the molar electric conductivity of electrolyte solutions change with the change in temperature:**

- 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 0.1M  $\text{H}_2\text{SO}_4$  and 0.1M  $\text{Na}_2\text{SO}_4$  solutions:**

- a)  $\text{Na}_2\text{SO}_4$  has a higher conductivity;
- b)  $\text{Na}_2\text{SO}_4$  has a lower conductivity;
- c) they are equal;
- d)  $\text{H}_2\text{SO}_4$  has a higher conductivity.

**6. Which of the diagrams represents the curve of the conductometric titration of  $\text{CH}_3\text{COOH}$  solution by  $\text{NaOH}$  solution?**



**7. Calculate the absolute  $\text{OH}^-$  ions movement rate if their mobility is  $198.5 \cdot 10^{-4} \text{ Sm} \cdot \text{m}^2 \cdot \text{mole}^{-1}$  ( $F = 96485 \text{ C/mol}$ ):**

- a)  $19.15 \cdot 10^2 \text{ m}^2 \cdot \text{v}^{-1} \cdot \text{sec}^{-1}$ ;
- b)  $20.6 \cdot 10^{-8} \text{ m}^2 \cdot \text{v}^{-1} \cdot \text{sec}^{-1}$ ;
- c)  $486.15 \cdot 10^4 \text{ m}^2 \cdot \text{v}^{-1} \cdot \text{sec}^{-1}$ ;
- d)  $486.15 \cdot 10^{-4} \text{ m}^2 \cdot \text{v}^{-1} \cdot \text{sec}^{-1}$ .

**8. Calculate the specific electric conductivity of the propionic acid solution ( $\text{Sm} \cdot \text{m}^{-1}$ ) with the concentration of 1.34 mol/L if the molar electric conductivity of this solution is  $7.8 \cdot 10^{-4} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ :**

- a)  $2.68 \cdot 10^{-5}$ ; b)  $2.68 \cdot 10^{-2}$ ; c)  $2.29 \cdot 10^{-5}$ ; d)  $2.29 \cdot 10^{-2}$ .

9. Calculate the degree of electrolytic dissociation of the propionic acid if the  $H^+$  ions mobility is  $349.8 \cdot 10^{-4} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1}$  and the propionate-ions mobility is  $40.9 \cdot 10^{-4} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ , molar electric conductivity of propionic acid is  $7.8 \cdot 10^{-4} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ :

- 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  $0.277 \text{ Sm} \cdot \text{m}^{-1}$  and the molar electric conductivity is  $1.385 \cdot 10^{-2} \text{ Sm} \cdot \text{m}^2 \cdot \text{mole}^{-1}$ .

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2. Molar electric conductivity of 0.1M  $\text{CH}_3\text{COOH}$  solution at 298K is  $5.2 \cdot 10^{-4} \text{ Sm} \cdot \text{m}^2 \cdot \text{mole}^{-1}$ . Calculate the dissociation constant of  $\text{CH}_3\text{COOH}$  and the pH of the solution.

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### STANDARDS OF PROBLEM SOLUTIONS

**Problem 1.** Determine the molar electric conductivity of 0.1M  $\text{AgNO}_3$  solution at 298K if its specific electric conductivity is  $1.097 \text{ Sm} \cdot \text{m}^{-1}$ .

We have:

$$C(\text{AgNO}_3) = 0.1 \text{ mol/L}$$

$$\kappa = 1.097 \text{ Sm} \cdot \text{m}^{-1}$$

$$\lambda_m = ?$$

Solution:

Specific and molar electric conductivities are connected by  $C$  (the molar concentration of the solution measured in  $\text{mol/m}^3$ ).

So, we can use the following formula  $\lambda_m = \kappa / C(\text{AgNO}_3) \cdot 1000 = 1.097 / (0.1 \cdot 1000) = 1.097 \cdot 10^{-2} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ .

*Answer:*  $1.097 \cdot 10^{-2} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ .

**Problem 2.** Are the specific and molar electric conductivities of 0.1M CH<sub>3</sub>COONa and CH<sub>3</sub>COOH solutions and 0.01M KCl and HCl solutions equal to each other? Will these values change with the increase in temperature?

*Solution:*

a) Sodium acetate is a strong electrolyte. It means that the number of ions in 0.1M CH<sub>3</sub>COONa solution is higher than that in the solution of acetic acid of the same concentration. Consequently,  $\alpha$  and  $\lambda_m$  are higher in CH<sub>3</sub>COONa solution than in the solution of a weak acid.

b) Electric conductivity of 0.01M HCl solution is higher than that of 0.01M KCl solution as the movement rate of H<sup>+</sup> ions is faster than the movement rate of K<sup>+</sup> cations.

c) With the increase in temperature the ion movement rate increases and the dissociation degree of weak electrolytes increases too. Consequently,  $\alpha$  and  $\lambda_m$  are increasing with increase in temperature.

**Problem 3.** Calculate the molar electric conductivity of potassium iodide at the infinite dilution ( $\lambda_m^0$ ) and at 298K if we know that the mobility of potassium cations is  $73.5 \cdot 10^{-4} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1}$  and the mobility of iodide anions is  $76.9 \cdot 10^{-4} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ .

We have:

$$U(\text{K}^+) = 73.5 \cdot 10^{-4} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1}$$

$$U(\text{I}^-) = 76.9 \cdot 10^{-4} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1}$$

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$$\lambda_m^0(\text{KI}) = ?$$

*Solution:*

According to the Kohlrausch's law:

$$\begin{aligned} \lambda_m^0(\text{KI}) &= U(\text{K}^+) + U(\text{I}^-) = 73.5 \cdot 10^{-4} + 76.9 \cdot 10^{-4} = \\ &= 150.4 \cdot 10^{-4} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1} \end{aligned}$$

*Answer:*  $\lambda_m^0(\text{KI}) = 150.4 \cdot 10^{-4} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ .

**Problem 4.** Determine the degree and the constant of dissociation of NH<sub>4</sub>OH in its 0.01M water solution at 298K. The molar electric conductivity of this solution is  $11.2 \cdot 10^{-4} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1}$  and the maximal molar electric conductivity is  $271.2 \cdot 10^{-4} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ .

We have:

$$C(\text{NH}_4\text{OH}) = 0.01 \text{ mol/L}$$

$$\lambda_m(\text{NH}_4\text{OH}) = 11.2 \cdot 10^{-4} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1}$$

$$\lambda_m^0(\text{NH}_4\text{OH}) = 271.2 \cdot 10^{-4} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1}$$

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$$\alpha = ? \quad K_d = ?$$

*Solution:*

Using the equation  $\alpha = \frac{\lambda}{\lambda_m^0}$  and  $K_d = \frac{\alpha^2 C}{1 - \alpha}$  we

determine the degree and the constant of dissociation of NH<sub>4</sub>OH in its 0.01M of solution.

$$1) \alpha = \frac{11.2 \cdot 10^{-4} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1}}{271.2 \cdot 10^{-4} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1}} = 0.0413.$$

$$2) K_d = \frac{(0.0413)^2 \cdot 0.01 \text{ mol/L}}{1 - 0.0413} = 1.78 \cdot 10^{-5} \text{ mol/L}.$$

*Answer:*  $\alpha = 0.0413$ ;  $K_d = 1.78 \cdot 10^{-5} \text{ mol/L}$ .

**Problem 5.** Specific electric conductivity of 0.02M KCl solution at 298K is  $0.277 \text{ Sm} \cdot \text{m}^{-1}$  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:

$$T = 298\text{K}$$

$$C(\text{KCl}) = 0.02 \text{ mol/L}$$

$$\kappa(\text{KCl}) = 0.277 \text{ Sm} \cdot \text{m}^{-1}$$

$$R(\text{KCl}) = 431.80 \text{ ohm}$$

$$R(\text{CH}_3\text{COOH}) = 750 \text{ ohm}$$

$$\kappa(\text{CH}_3\text{COOH}) = ?$$

*Solution:*

Specific electric conductivity of the acetic acid solution can be determined with the formula:

$$\kappa(\text{CH}_3\text{COOH}) = \frac{K_v}{R(\text{CH}_3\text{COOH})}, R = 1/L,$$

where  $K_v$  is the constant of the equipment which is calculated using the results of conductometric measurements for KCl solution.

$$1) K_v = \kappa(\text{KCl}) \cdot R(\text{KCl}) = 0.277 \text{ Sm} \cdot \text{m}^{-1} \cdot 431.8 \text{ ohm} = 119.608 \text{ m}^{-1}.$$

$$2) \kappa(\text{CH}_3\text{COOH}) = \frac{K_v}{R(\text{CH}_3\text{COOH})} = \frac{119,608 \text{ m}^{-1}}{750 \text{ ohm}} = 0.159 \text{ Sm} \cdot \text{m}^{-1}.$$

*Answer:*  $0.159 \text{ Sm} \cdot \text{m}^{-1}$ .

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

$$\lambda_m^0(\text{HCl}) = 426.1 \cdot 10^{-4} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1};$$

$$\lambda_m^0(\text{NaCl}) = 126.4 \cdot 10^{-4} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1};$$

$$\lambda_m^0(\text{CH}_3\text{COONa}) = 91.0 \cdot 10^{-4} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1}.$$

We have:

$$T = 298\text{K}$$

$$\lambda_m^0(\text{HCl}) = 426.1 \cdot 10^{-4} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1}$$

$$\lambda_m^0(\text{NaCl}) = 126.4 \cdot 10^{-4} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1}$$

$$\lambda_m^0(\text{CH}_3\text{COONa}) = 91.0 \cdot 10^{-4} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1}$$

$$\lambda_m^0(\text{CH}_3\text{COOH}) = ?$$

*Solution:*

Using Kohlrausch's law assuming the independent ion mobility we can write down the equation:

$$\begin{aligned} \lambda_m^0(\text{HCl}) + \lambda_m^0(\text{CH}_3\text{COONa}) &= \\ &= \lambda_m^0(\text{CH}_3\text{COOH}) + \lambda_m^0(\text{NaCl}) \end{aligned}$$

Hence:

$$\begin{aligned} \lambda_m^0 \text{CH}_3\text{COOH} &= \lambda_m^0(\text{HCl}) + \lambda_m^0(\text{CH}_3\text{COONa}) - \lambda_m^0(\text{NaCl}) = \\ &= (426.1 + 91.0 - 126.4) \cdot 10^{-4} = 390.7 \cdot 10^{-4} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1} = 3.907 \cdot 10^{-2} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1}. \end{aligned}$$

*Answer:*  $3.907 \cdot 10^{-2} \text{ Sm} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ .

## CHAPTER 11

### POTENTIOMETRY

#### Main questions of the topic:

1. Electrode and oxidation-reduction (redox) potentials, the mechanism of their appearance and the dependence of their values on different factors. Nernst–Peters' equation for the calculation of electrode potential values.
2. Galvanic elements (chemical and concentration-based): the mechanism of action, the calculation of EMF. The measurement of electrode and redox potentials.
3. Reversible electrodes of the first and the second type (hydrogen and silver chloride). Ion-selective electrodes (glass electrode). Structure and the mechanism of potential origin.
4. Electrodes for comparison (standard electrodes) and electrodes for measurement (ion sensitive electrodes) used in potentiometry.
5. The essence of the potentiometric determination of pH.
6. Potentiometric titration, its essence and its usage in quantitative analysis and medical and biological investigations.

#### LABORATORY WORK (M, D)

##### “DETERMINATION OF A WEAK ACID SOLUTION CONCENTRATION AND ITS DISSOCIATION CONSTANT BY THE POTENTIOMETRIC TITRATION”

**The aim of the work.** To learn how to determine the concentration of a weak acid in the water solution and how to calculate its constant of dissociation by the method of potentiometric titration.

**Devices and reactants.** Ion meter (pH meter), magnetic stirrer, burette for titration, Mohr's pipette (10 ml), the glass for titration, acetic acid solution of unknown concentration, 0.1000 M solution of sodium hydroxide.

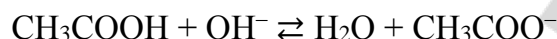
**Task 1.** To determine the concentration of acetic acid in the solution.

Pour 10 ml of the acetic acid solution (by the Mohr's pipette) and 20 ml of water into the glass for titration. With the help of a magnetic stirrer mix the solution and measure the value of pH of the initial solution using the ion meter (pH meter). Titrate the acid solution by an alkali from the burette by the portions written in the table below:

Number	The volume of each portion of the titrant, ml	General volume of the titrant, 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	

Number	The volume of each portion of the titrant, ml	General volume of the titrant, ml	pH of the solution
7.	0.2	9.4	
8.	0.2	9.6	
9.	0.2	9.8	
10.	0.2	10.0	
11.	0.2	10.2	
12.	0.2	10.4	

The chemical reaction during the titration:



You should measure pH level of the solution after the addition of each new portion of the titrant. The results of the measurements should be written down in the table. Using the data from the table draw a curve of the dependence of the pH level on the total volume of the added titrant.

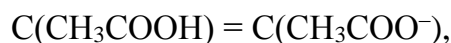


Using the curve of the potentiometric titration determine the equivalent volume of the titrant. Draw a perpendicular line from the middle of the titration jump down to the X-axis. According to the law of equivalents calculate the concentration of acetic acid:

$$C(\text{CH}_3\text{COOH}) = \frac{C(\text{NaOH}) \cdot V(\text{NaOH})}{V(\text{CH}_3\text{COOH})} = (0.1 \cdot \underline{\hspace{2cm}}) / \underline{\hspace{2cm}} = \underline{\hspace{2cm}} \text{ mol/L}$$

**Task 2.** The calculation of the constant of acetic acid dissociation.

Pour 10 ml of the acetic acid solution (with the Mohr's pipette) and 20 ml of water in the same glass. Then pour half the volume of the sodium hydroxide (the titrant from the burette) used for the titration in the first task. Measure the pH level. In this case 50 % of the acid have reacted. So, the amount of acid is equal to the amount of salt now.



then from the equation  $K_d = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$  it follows that

$$K_d = [\text{H}^+]$$

$$\text{pK} = \text{pH} = \underline{\hspace{2cm}}$$

$$\text{Hence, } K_d = 10^{-\text{pK}} = 10^{-\text{pH}} = 10^{-\underline{\hspace{2cm}}} = \underline{\hspace{2cm}}$$

**Conclusion:** "I performed the potentiometric titration and then calculated the constant of the acetic acid dissociation that is equal to  $\underline{\hspace{2cm}}$ "

### TEST SELF-CHECK

**1. The value of the electrode potential occurring on a metallic plate omitted into the solution of the salt of the same metal depends on:**

- the value of the charge of the metal cation;
- the value of the charge of the anion from the solution;
- the activity of the metal cation in the solution;
- temperature.

**2. The equation for the calculation of the redox potential is the following:**

$$\begin{array}{ll} \text{a) } \varphi = \varphi_{\text{ox/red}}^0 - \frac{RT}{nF} \ln \frac{a_{(\text{ox})}}{a_{(\text{red})}} ; & \text{c) } \varphi = \varphi_{\text{ox/red}}^0 + \frac{RT}{nF} \ln \frac{a_{(\text{ox})}}{a_{(\text{red})}} ; \\ \text{b) } \varphi = \varphi_{\text{ox/red}}^0 - \frac{RT}{nF} \ln \frac{a_{(\text{red})}}{a_{(\text{ox})}} ; & \text{d) } \varphi = \varphi_{\text{ox/red}}^0 + \frac{RT}{nF} \ln \frac{a_{(\text{red})}}{a_{(\text{ox})}} . \end{array}$$

**3. Indicate the scheme of the hydrogen electrode:**

- (Pt)  $\text{H}^+ | \text{H}_2$ ; b) Pt  $| \text{H}_2, 2\text{H}^+$ ; c)  $\text{H}_2 | 2\text{H}^+$ ; d) (Pt)  $\text{H}_2 | 2\text{H}^+$ .

**4. The electrode of the following scheme Ag  $|$  AgCl, KCl is:**

- type I electrode; c) the electrode for comparison;
- type II electrode; d) the electrode for measurement.

**5. The standard potential of the nickel electrode Ni  $|$  Ni<sup>2+</sup> is -0.23V. Exact nickel electrode potential Ni  $|$  Ni<sup>2+</sup> at 298K if the nickel ions activity in the solution is 0.1 mol/L should be equal to:**

- 0.2005V; b) -0.171V; c) -0.289V; d) -0.2595V.

**6. Indicate the processes occurring on the electrodes in the galvanic element made from cadmium and zinc ( $\varphi_{\text{Cd}^{2+}/\text{Cd}}^0 = -0.45\text{V}$ ):**

- Cd - 2e<sup>-</sup> → Cd<sup>2+</sup>; c) Zn - 2e<sup>-</sup> → Zn<sup>2+</sup>;
- Cd<sup>2+</sup> + 2e<sup>-</sup> → Cd; d) Zn<sup>2+</sup> + 2e<sup>-</sup> → Zn.



7. Which of the indicated chemical galvanic elements has the greatest EMF in standard conditions:

- a)  $\text{Zn} | \text{Zn}^{2+} || \text{Fe}^{2+} | \text{Fe}$ ;                      c)  $\text{Cu} | \text{Cu}^{2+} || \text{Ag}^+ | \text{Ag}$ ;  
b)  $\text{Zn} | \text{Zn}^{2+} || \text{Cu}^{2+} | \text{Cu}$ ;                      d)  $\text{Zn} | \text{Zn}^{2+} || \text{Ag}^+ | \text{Ag}$ .

8. Standard potential of the copper electrode  $\text{Cu} | \text{Cu}^{2+}$  is +0.34V. Standard potential of the silver electrode  $\text{Ag} | \text{Ag}^+$  is +0.8V. Standard EMF of the galvanic element made from silver and copper  $\text{Cu} | \text{Cu}^{2+} || \text{Ag}^+ | \text{Ag}$  in standard conditions is:

- a) 0.46V; b) -0.46V; c) 1.14V; d) -1.14V.

9. Standard potential of the silver electrode  $\text{Ag} | \text{Ag}^+$  is +0.8V. The EMF of the concentration-based galvanic element  $\text{Ag} | \text{Ag}^+ (0.1 \text{ mol/L}) || \text{Ag}^+ (1 \text{ mol/L}) | \text{Ag}$  at 25 °C is :

- a) -0.059V; b) 0.0295V; c) 0.059V; d) -0.0295V.

10. The potential of the hydrogen electrode omitted into the digestive juice is -0.106 V at 25 °C. The pH level of the digestive juice is:

- a) -1.8; b) 1.9; c) 1.8; d) -1.9.

### PROBLEMS

1. Calculate the pH level of urine if the potential of the hydrogen electrode omitted in that solution is 0.354 V at 25 °C.

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2. The standard potential of the silver chloride electrode is +0.24V. Calculate the potential of the silver chloride electrode omitted into HCl solution with the activity of  $\text{H}^+$  ions equal to 0.01 mol/L at 25 °C.

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3. The standard potential of the redox system  $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + \bar{e}$  is +0.77V. Calculate the redox potential of the electrode  $\text{Pt} | \text{Fe}^{3+}, \text{Fe}^{2+}$  at 298K, if the activity of  $\text{Fe}^{3+}$  ions is 0.1 mol/L and the activity of  $\text{Fe}^{2+}$  ions is 0.01 mol/L.

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4. The standard redox potential of the system  $\text{KMnO}_4 + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$  is +1.52V. Calculate the redox potential of this system at 298K, if the concentration of  $\text{KMnO}_4$  is 0.1 mol/L (the activity coefficient should be taken as 1).

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5. There is a chain of two hydrogen electrodes omitted into solutions of hydrochloric acid with different pH levels. Calculate the EMF of the chain  $(\text{Pt})\text{H}_2 \mid 2\text{H}^+(\text{C}_1) \parallel 2\text{H}^+(\text{C}_2) \mid \text{H}_2(\text{Pt})$  at 298K, if the pH of the first solution is 3, and the pH of the second solution one is 1.

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### STANDARDS OF PROBLEM SOLUTIONS

**Problem 1.** Calculate the potential of the copper electrode if a copper plate is omitted into the solution of blue vitriol with the copper ion activity equal to 0.02 mol/L at 25 °C. The standard potential of copper electrode is +0.34V.

We have:

$$a_{\text{Cu}^{2+}} = 0.02 \text{ mol/L}$$

$$\varphi_{\text{Cu}^{2+}/\text{Cu}}^0 = +0.34\text{V}$$

$$\varphi_{\text{Cu}^{2+}/\text{Cu}} = ?$$

*Solution:*

For the calculation of the value of the electrode potential appearing on the border between metal and solution we use Nernst's equation.

$$\varphi_{\text{Me}^{n+}/\text{Me}} = \varphi_{\text{Me}^{n+}/\text{Me}}^0 + \frac{2.3RT}{nF} \lg a_{\text{Me}^{n+}}$$

The scheme of the copper electrode is  $\text{Cu} \mid \text{Cu}^{2+}$ . The process taking place on the electrode is  $\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}$ . So, the number of electrons corresponding to 1 copper atom is two ( $n = 2$ ). At 298K the multiplier  $\frac{2.3RT}{F} = 0.059$  and the equation will be the following :

$$\varphi_{\text{Cu}^{2+}/\text{Cu}} = \varphi_{\text{Cu}^{2+}/\text{Cu}}^0 + \frac{0.059}{n} \log a_{\text{Cu}^{2+}}$$

Hence, we find that

$$\varphi_{\text{Cu}^{2+}/\text{Cu}} = +0.34 + \frac{0.059}{2} \lg 0.02 = +0.34 + 0.0295 \cdot \log(2 \cdot 10^{-5}) =$$

$$= 0.34 + 0.029 \cdot (-1.7) = 0.34 - 0.05 = 0.29\text{V}$$

*Answer: 0.29V.*

**Problem 2.** Calculate the EMF of the galvanic element at 25 °C. The galvanic element consists from silver and lead electrodes, the metal plates are omitted into 0.1 M silver nitrate solution and 0.25 M lead (II) nitrate solution (we should take the activity coefficient as 1 in both cases). The values of standard electrode potentials of silver and lead are the following: +0.80V and -0.13V.

We have:

$$C(\text{AgNO}_3) = 0.1 \text{ mol/L}$$

$$C(\text{Pb}(\text{NO}_3)_2) = 0.25 \text{ mol/L}$$

$$\varphi_{\text{Ag}^+/\text{Ag}}^0 = +0.80\text{V}$$

$$\varphi_{\text{Pb}^{2+}/\text{Pb}}^0 = -0.13\text{V}$$

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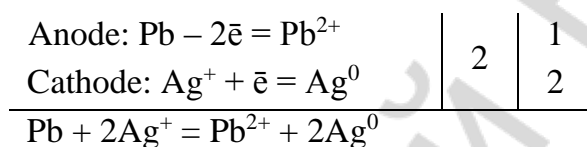

$$E = ?$$

*Solution:*

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



We write down the equations of the reactions occurring on the electrodes:



The EMF of the galvanic element is:  $E = \varphi_{\text{cathode}} - \varphi_{\text{anode}}$  or in our case

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

1. At 25 °C the potential of a silver electrode is:  $\varphi_{\text{Ag}^+/\text{Ag}} = \varphi_{\text{Ag}^+/\text{Ag}}^0 + \frac{0.059}{n} \lg a_{\text{Ag}^+}$ ,

where  $a_{\text{Ag}^+} = C \cdot f_a$ , hence  $\varphi_{\text{Ag}^+/\text{Ag}} = 0.8 + \frac{0.059}{1} \log 0.1 \cdot 1 = 0.8 + 0.059 \cdot (-1) = 0.741\text{V}$ .

2. For the lead electrode:

$$\begin{aligned} \varphi_{\text{Pb}^{2+}/\text{Pb}} &= \varphi_{\text{Pb}^{2+}/\text{Pb}}^0 + \frac{0.059}{n} \lg a_{\text{Pb}^{2+}} = -0.13 + \frac{0.059}{2} \log 0.25 \cdot 1 = -0.13 + 0.0295 \cdot (-0.6) = \\ &= -0.3 - 0.0177 = -0.3177\text{V}. \end{aligned}$$

3.  $EMF = 0.741 - (-0.3177) = 1.0587\text{V}$ .

*Answer:* 1.0587V.

**Problem 3.** Determine the EMF of the concentration-based galvanic element at 25 °C. The galvanic element is composed of two silver electrodes omitted into the solutions of silver nitrate with the silver ion activities of 1 mol/L and 0.5 mol/L. The standard electrode potential of the silver electrode is +0.80V.

We have:

$$a_1(\text{Ag}^+) = 0.5 \text{ mol/L}$$

$$a_2(\text{Ag}^+) = 1.0 \text{ mol/L}$$

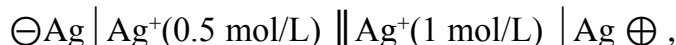
$$\varphi_{\text{Ag}^+/\text{Ag}}^0 = +0.80\text{V}$$

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$$EMF \text{ — ?}$$

*Solution:*

We write down the scheme of the galvanic element:



The EMF of the concentration galvanic element is:

$$E = \frac{2.3RT}{nF} \lg \frac{a_2}{a_1}, \text{ where } n = 1, a_2 > a_1$$

$$\text{At } 25\text{ }^\circ\text{C} \quad E = \frac{0.059}{1} \lg \frac{1}{0.5} = 0.059 \lg 2 = 0.059 \cdot 0.3 = 0.0177\text{V}.$$

*Answer: 0.0177V*

**Problem 4.** The standard redox potential of the system  $\text{KMnO}_4 + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$  is + 1.52V. Calculate the redox potential of this system if the pH of the solution is 5.

We have:

$$\varphi^0_{\text{MnO}_4^- / \text{Mn}^{2+}} = +1.52\text{V}$$

$$\text{pH} = 5$$

$$\varphi_{\text{MnO}_4^- / \text{Mn}^{2+}} = ?$$

*Solution:*

Peters' equation for the calculation of the redox potential of the given system is the following:

$$\varphi_{\text{MnO}_4^- / \text{Mn}^{2+}} = \varphi^0_{\text{MnO}_4^- / \text{Mn}^{2+}} + \frac{2.3RT}{nF} \lg \frac{a_{\text{MnO}_4^-} \cdot a_{\text{H}^+}^8}{a_{\text{Mn}^{2+}}}, \text{ where } n = 5.$$

There is just one difference with the standard conditions in our case: the active concentration of  $\text{H}^+$  ions changed.

As  $\text{pH} = 5$ , then  $a_{\text{H}^+} = 10^{-5}$  mol/L. That's why

$$\begin{aligned} \varphi_{\text{MnO}_4^- / \text{Mn}^{2+}} &= \varphi^0_{\text{MnO}_4^- / \text{Mn}^{2+}} + \frac{0.059}{5} \lg \frac{1 \cdot (10^{-5})^8}{1} = 1.52 + 0.0118 \cdot \log 10^{-40} = \\ &= 1.52 - 0.472 = 1.048\text{V}. \end{aligned}$$

*Answer: 1.048V.*

## CHAPTER 12

### PHYSICAL CHEMISTRY OF SURFACE PHENOMENA

#### **Main questions on the topic:**

1. Special features of the energy state of the surface (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 the surface tension of liquids.
3. Adsorption on the surface of liquid in the system made from liquid and gas and in the system made from two liquids which cannot be mixed together. Gibbs' equation and its analysis. The orientation of molecules in the surface layer; the structure of the bilipid layer of biological membranes.
4. Adsorption on the interface of solid substance in the systems "solid-gas" and "solid-liquid". Langmure's and Friendlikh's adsorption isotherms. Langmure's and Friendlikh's equations, their analysis.
5. The importance of surface phenomena in biology and medicine. The usage of adsorption in medicine and medical-biological research.

#### **LABORATORY WORK (D) "DETERMINATION OF THE DEPENDENCE OF THE SURFACE TENSION OF SOLUTIONS ON THE LENGTH OF THE HYDROCARBON CHAIN"**

**The aim of the work:** to study the influence of the length of the hydrocarbon chain of SAS on the value of the surface tension.

The methodology of the work is to calculate the number of drops of the investigated SAS solution and water which outflow from the same volume. We use Traube's stalagmometer to determine the surface tension. That's why the method has the name of stalagmometry. The main idea of the method is as follows: you should put the investigated liquid into the small glass, omit the end of the stalagmometer into the solution and then pump the liquid into the stalagmometer using the rubber pump. You should lift the level of liquid above the highest mark and stop pumping it in. The liquid will drop from the stalagmometer back into the glass. You should start counting the drops from the moment when the level of liquid crosses the first mark of the stalagmometer (before its wider part) and stop counting the drops when the level of liquid crosses the second mark (after the wider part).

The drops flow out of the capillary and fall down under the influence of the gravity of its own mass. The surface tension tries to prevent the falling of the drop as its formation is connected with the increase of the surface of the liquid.

The higher is the surface tension, the higher must be the mass of the falling drop in order to overcome the surface tension and to fall down. So, the surface tension  $\sigma$  is proportional to the density  $\rho$  and inversely proportional to the number of drops that has dropped from the same volume.

The surface tension is determined using the following formula:

$$\frac{\sigma}{\sigma_{\text{H}_2\text{O}}} = \frac{\rho \cdot n_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}} \cdot n}; \sigma = \sigma_{\text{H}_2\text{O}} \frac{\rho \cdot n_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}} \cdot n}, \quad (1)$$

where  $\sigma$  and  $\sigma_{\text{H}_2\text{O}}$  are the surface tensions of the studied liquid and water respectively,  $\rho$  and  $\rho_{\text{H}_2\text{O}}$  are the densities of the studied liquid and water;  $n$  and  $n_{\text{H}_2\text{O}}$  are the number of drops of the studied liquid and water.

For diluted water solutions with the density close to 1 g/ml the formula can be simplified:

$$\sigma = \sigma_{\text{H}_2\text{O}} \frac{n_{\text{H}_2\text{O}}}{n}, \quad (2)$$

where  $\sigma_{\text{H}_2\text{O}} = 72.8 \text{ mJ/m}^2$  at  $20^\circ\text{C}$ .

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.

At first we should determine the number of water drops and calculate the number of drops of 0.1M water solutions of the following alcohols in the indicated order:  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{C}_3\text{H}_7\text{OH}$ ,  $\text{C}_4\text{H}_9\text{OH}$ ,  $\text{C}_5\text{H}_{11}\text{OH}$ . Then we should calculate the surface tension of these alcohols using the formula (2).

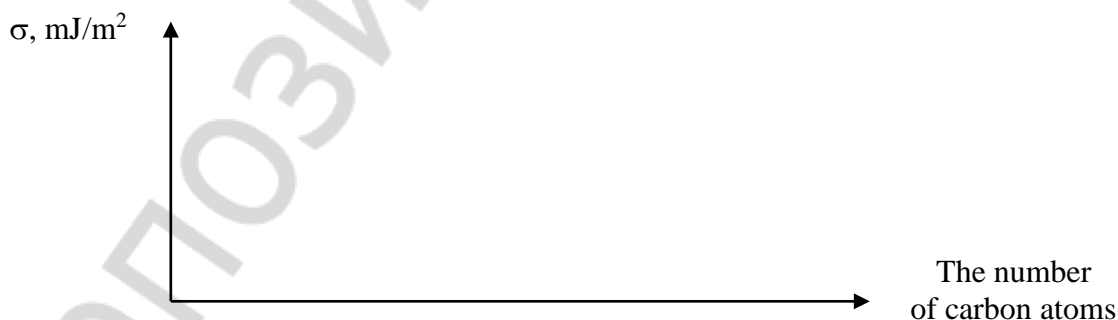
$$\sigma(\text{C}_2\text{H}_5\text{OH}) = \left( \frac{\quad}{\quad} / \frac{\quad}{\quad} \right) \times 72.8 \text{ mJ/m}^2 = \underline{\hspace{2cm}}$$

$$\sigma(\text{C}_3\text{H}_7\text{OH}) = \left( \frac{\quad}{\quad} / \frac{\quad}{\quad} \right) \times 72.8 \text{ mJ/m}^2 = \underline{\hspace{2cm}}$$

$$\sigma(\text{C}_4\text{H}_9\text{OH}) = \left( \frac{\quad}{\quad} / \frac{\quad}{\quad} \right) \times 72.8 \text{ mJ/m}^2 = \underline{\hspace{2cm}}$$

$$\sigma(\text{C}_5\text{H}_{11}\text{OH}) = \left( \frac{\quad}{\quad} / \frac{\quad}{\quad} \right) \times 72.8 \text{ mJ/m}^2 = \underline{\hspace{2cm}}$$

We should build the curve of the dependence of  $\sigma$  on the number of carbon atoms in alcohol molecules ( $n$  atoms of C).



**Conclusion:** "The surface tension shows \_\_\_\_\_ dependence on the length of the hydrocarbon chain of alcohols".

**LABORATORY WORK (M) “THE STUDY OF THE ADSORPTION OF A SUBSTANCE  
FROM THE SOLUTION ON THE SURFACE OF A SOLID ADSORBENT”**

**The aim of the work:** to study the adsorption of acetic acid on the activated coal.

The essence of the work is to adsorb acetic acid of different concentrations on the coal of the same mass and determine the concentration of acetic acid in these solutions after the adsorption. The amount of the substance adsorbed from the solution is determined using the difference in concentrations before and after the adsorption. Knowing the mass of coal we can get the data on the specific adsorption of acetic acid from solutions of a different concentration. Using these data we can draw the adsorption isotherm. In the present work the adsorption isotherm should be close to the one from the Langmuire’s theory of adsorption.

**The results of the experiment on acetic acid adsorption on the surface of coal**

№ of the flask	Concentration of		The volume of NaOH solution used for titration, mL	The equilibrium concentration of CH <sub>3</sub> COOH in the filtrate, mol/L	The adsorption of CH <sub>3</sub> COOH, mmol/g
	CH <sub>3</sub> COOH in the initial solution, mol/L	the titrant (NaOH), mol/L			
1	0.1	0.2			
2	0.2	0.2			
3	0.3	0.2			
4	0.4	0.2			

Pour 25 mL of the acetic acid solution of each concentration into the specific flask (you can use the same volumetric cylinder for this operation — start from the lower concentration). Then put 0.5 g (one small spoon) of the activated carbon into each of the four flasks. The contents of the flasks then should be stirred with circular motions for 10 minutes. Then the solutions must be filtered through dry paper filters into new flasks. With the help of the pipette take 10 mL of the filtrate of the lowest concentration and put it into the flask for titration. Add 2 drops of phenolphthalein indicator into the tube and titrate it with the solution of sodium hydroxide (until a slightly rosy color will appear). The results of the titration should be written down in the table. Repeat the titration for three more flasks. Calculate the equilibrium concentration of acetic acid using the formula:

$$C_{eq.} = (C_{NaOH} \times V_{NaOH}) / V_{acetic\ acid},$$

where  $V_{acetic\ acid}$  is the volume taken for titration (25 mL).

Calculate acetic acid adsorption using the formula:

$$A = \frac{(C_{init} - C_{eq.}) \cdot V_{init} \cdot 1000}{m} \text{ (mmol/g)}, \quad (4)$$

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 (equilibrium concentration),

mol/L,  $V_{\text{init.}}$  is the volume of acetic acid solution taken for adsorption (in our case 0.025 L),  $m$  is the mass of coal (in our case it is 0.5 g).



In order to get the adsorption isotherm we should put the initial concentrations  $C_{\text{init.}}$  on the X-axis and the adsorption values (A) corresponding to them on Y-axis.

**Conclusion:** “The value of adsorption shows \_\_\_\_\_ dependence on the concentration of acetic acid”.

### TEST SELF-CHECK

**1. In which units can we measure surface tension (according to SI):**

- a)  $\frac{\text{N} \cdot \text{m}^2}{\text{mol}}$ ; b)  $\frac{\text{J} \cdot \text{m}}{\text{mol}}$ ; c)  $\text{J}/\text{m}^2$ ; d)  $\text{N}/\text{m}$ .

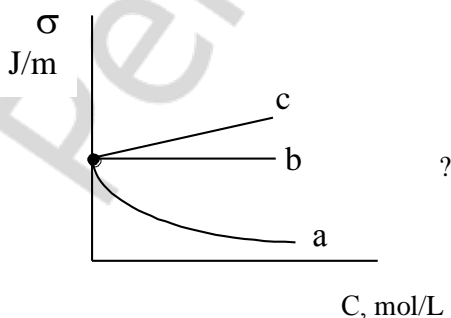
**2. Which factors influence the value of the surface tension of a liquid:**

- a) the nature of the liquid; c) the volume of the liquid ( $p, T$  — const);  
b) the nature of the solute; d) temperature ?

**3. Indicate the formulas of surface active substances (SAS):**

- a)  $\text{C}_3\text{H}_7\text{COONa}$ ; b)  $\text{NaHCO}_3$ ; c)  $\text{C}_2\text{H}_5\text{OH}$ ; d)  $\text{C}_2\text{H}_5\text{NH}_2$ ; e)  $\text{NH}_2 - \text{CH}_2 - \text{COOH}$ .

**4. Which curve reflects the dependence of the surface tension of the water solution on the concentration of acetic acid:**





5. In which row of substances, the formulas of which are written below, the surface tension of the solution first increases and then decreases:

- a)  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{C}_3\text{H}_7\text{OH}$ ;                      c)  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{C}_3\text{H}_7\text{OH}$ ,  $\text{CH}_3\text{OH}$ ;  
 b)  $\text{C}_3\text{H}_7\text{OH}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ ;                      d)  $\text{CH}_3\text{OH}$ ,  $\text{C}_3\text{H}_7\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ ?

6. Which solution has the highest surface tension:

- a) 0.5M  $\text{HOOC} - \text{CH}_2 - \text{NH}_2$ ;                      c) 0.1M  $\text{C}_5\text{H}_{11}\text{COONa}$ ;  
 b) 1M  $\text{HOOC} - \text{CH}_2 - \text{NH}_2$ ;                      d) 2M  $\text{C}_5\text{H}_{11}\text{COONa}$  ?

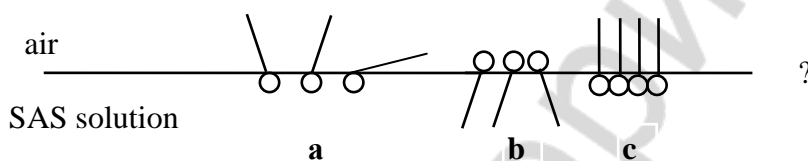
7. If the number of drops of the water solution flown from the stalagmometer is higher than the number of water drops, the dissolved substance is:

- a) SAS; b) SIS; c) SNA.

8. Choose true statements:

- 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) the surface tension is the surface energy of a unit of surface area;  
 c) the free surface energy is changing due to adsorption.

9. How can molecules of SAS be oriented in the surface layer of the water solution:



10. Which substances, the formulas of which are written below, have negative adsorption on the surface of water solution:

- a)  $\text{NH}_4\text{NO}_3$ ; b)  $\text{C}_3\text{H}_7\text{NH}_2$ ; c)  $\text{C}_6\text{H}_{13}\text{SO}_3\text{Na}$ ; d)  $\text{Na}_2\text{SO}_3$ ?

11. Indicate the Gibbs' equation:

- a)  $A = \frac{n}{m}$ ; b)  $A = K \cdot C^{1/n}$ ; c)  $A = -\frac{\Delta\sigma}{\Delta C} \cdot \frac{C}{RT}$ .

12. Adsorption of a non-volatile solute on the surface of its solution depends on:

- a) the nature of the solute and the solvent;  
 b) temperature;  
 c) pressure;  
 d) the concentration of a solute.

13. Choose the units of adsorption for a substance on a solid surface:

- a) mol/g; b) mol/m<sup>2</sup>; c) mol/L; d) J/m<sup>2</sup>?

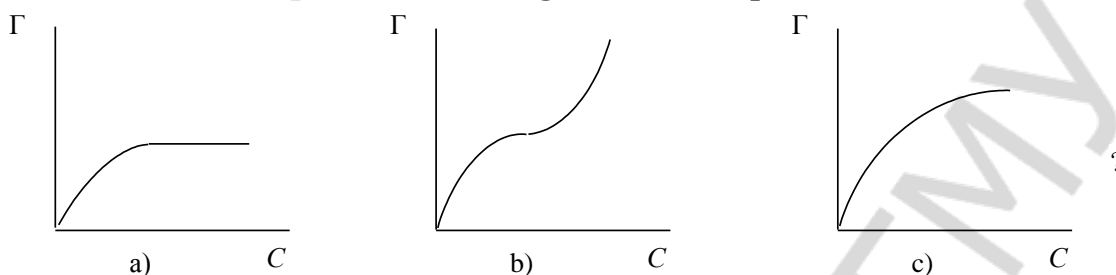
14. Choose true statements:

- a) physical adsorption occurs due to Van-der-Vaal's forces;  
 b) chemical adsorption can be irreversible;  
 c) adsorption doesn't depend on temperature.

15. The Langmuire's equation for the dilute solution is:

a)  $A = A_{\infty}$ ; b)  $A = A_{\infty} \cdot \frac{C}{K}$ ; c)  $A = A_{\infty} \cdot \frac{C}{K+C}$  ?

16. Which curve represents the Langmuire's adsorption isotherm:



17. Freundlich's adsorption equation is:

- a) true for solutions with average concentrations of the adsorptive;
- b) true for solutions with high concentrations of the adsorptive;
- c) empirical.

18. Adsorption of gases on the solid surface depends on:

- a) pressure;
- b) temperature;
- c) the nature of adsorbent and adsorbate;
- d) the area of the surface.

19. In which row substances are arranged in the order of the increase of their adsorption from water solution on the surface of activated carbon:

- a)  $\text{CH}_3\text{COOH}$ ;  $\text{CH}_3\text{COONa}$ ;  $\text{C}_2\text{H}_5\text{OH}$ ;  $\text{C}_3\text{H}_7\text{OH}$ ;
- b)  $\text{C}_3\text{H}_7\text{OH}$ ;  $\text{C}_2\text{H}_5\text{OH}$ ;  $\text{CH}_3\text{COOH}$ ;  $\text{CH}_3\text{COONa}$ ;
- c)  $\text{CH}_3\text{COONa}$ ;  $\text{CH}_3\text{COOH}$ ;  $\text{C}_2\text{H}_5\text{OH}$ ;  $\text{C}_3\text{H}_7\text{OH}$ ;
- d)  $\text{CH}_3\text{COONa}$ ;  $\text{C}_3\text{H}_7\text{OH}$ ;  $\text{CH}_3\text{COOH}$ ;  $\text{C}_2\text{H}_5\text{OH}$ ?

20. The adsorption of the solute from the solution on the surface of a solid adsorbent depends on:

- a) the nature of adsorbent and solute;
- b) temperature;
- c) the nature of the solvent;
- d) concentration of a solute.

21. 1.5 g of activated carbon are mixed with 20 mL of 0.4N  $\text{CH}_3\text{COOH}$  solution. Determine the concentration of the acid after the establishment of the adsorption equilibrium. 10 mL of the filtrate have been titrated with 18 mL of 0.2N NaOH solution:

- a) 0.36 mol/g; b) 0.36 mol/L; c) 0.18 mol/g; d) 0.18 mol/L?

22. We added 3 g of activated coal in 100 ml of  $\text{CH}_3\text{COOH}$  solution with the concentration of 400 mmol/L. After some period of time  $\text{CH}_3\text{COOH}$  concentration decreased to 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 of the cations shows the best adsorbance on the negatively-charged surface from the water solution:**

a)  $K^+$ ; b)  $Na^+$ ; c)  $Li^+$ ; d)  $Cs^+$ .

**24. Indicate, which ions will be adsorbed on the surface of silver iodide first:**

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. Calculate the surface tension of the water solution of amyl alcohol if the number of the drops of this solution flown from the stalagmometer is 72 and the number of water drops is 60? The surface tension of water at 293K is  $72.8 \cdot 10^{-3} \text{ J/m}^2$  (the density of the solution is equal to 1 g/ml).

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2. At 20 °C the surface tension of 0.2M water solution of SAS is  $55 \cdot 10^{-3} \text{ J/m}^2$ . Calculate the value of adsorption for that SAS (the surface tension of water at 20 °C is  $72.75 \cdot 10^{-3} \text{ J/m}^2$ ).

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3. The maximal adsorption value of propionic acid on coal is  $3.0 \cdot 10^{-3} \text{ mol/g}$ ; the coefficient K is  $6.0 \cdot 10^{-2} \text{ mol/L}$ . What mass of propionic acid has been adsorbed from the solution if the concentration of acid is 0.1 mol/L? The adsorbent mass is 1 g.

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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. Determine the value of adsorption 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

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### STANDARDS OF PROBLEM SOLUTIONS

**Problem 1.** Determine the adsorption value of the acid ( $C_8H_{17}COOH$ ) on the surface of the water solution at  $10\text{ }^\circ\text{C}$ , 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  $57.0 \cdot 10^{-3} \text{ J/m}^2$  respectively.

We have:

$$\omega C_8H_{17}COOH = 0.005 \%$$

$$\sigma_{H_2O} = 74.22 \cdot 10^{-3} \text{ J/m}^2$$

$$\sigma_{C_8H_{17}COOH} = 57.0 \cdot 10^{-3} \text{ J/m}^2$$

$$T = 283\text{K}$$

$$A = ?$$

*Solution:*

1. To calculate the adsorption (A) on the surface of solution we use Gibbs' equation:

$$A = -\frac{\Delta\sigma}{\Delta C} \cdot \frac{C}{RT} = -\frac{\sigma_2 - \sigma_1}{C_2 - C_1} \cdot \frac{C}{RT}$$

In Gibbs' equation the value of  $C_2$  means the molar concentration of the acid,  $C_1 = 0$  (pure water).

2. Considering that the density of the dilute acid solution is  $\approx 1 \text{ g/mL}$  (i. e. the same as the one for pure 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:

$$C = \frac{m_{\text{sub}}}{M_{\text{sub}} \cdot V_{\text{solution}}} = \frac{0.05}{158 \cdot 1} = 3.16 \cdot 10^{-4} \text{ (mol/L)}.$$

3. In Gibbs' equation we use the necessary data:

$$A = -\frac{57.0 \cdot 10^{-3} - 74.22 \cdot 10^{-3}}{3.16 \cdot 10^{-4} - 0} \cdot \frac{3.16 \cdot 10^{-4}}{8.314 \cdot 283} = 7.3 \cdot 10^{-6} \text{ (mol/m}^2\text{)}.$$

Answer:  $7.3 \cdot 10^{-6} \text{ mol/m}^2$ .

**Problem 2.** The maximal adsorption value of SAS ( $M = 60 \text{ g/mol}$ ) is  $5.0 \cdot 10^{-3} \text{ mol/g}$ . The value of  $K$  is  $0.06 \text{ mol/L}$ . How many grams of the substance have been adsorbed by two grams of the adsorbent from the solution if the concentration of SAS is equal to  $0.1 \text{ mol/L}$ ?

We have:

$$A_{\infty} = 5.0 \cdot 10^{-3} \text{ mol/g}$$

$$M_{\text{SAS}} = 60 \text{ g/mol}$$

$$K = 0.06 \text{ mol/L}$$

$$C_{\text{eq.}} = 0.1 \text{ mol/L}$$

$$m(\text{adsorbent}) = 2 \text{ g}$$

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$$M_{\text{SAS}} \text{ — ?}$$

*Solution:*

1. Calculate the SAS adsorption value using the Langmure's equation:  $A = A_{\infty} \frac{C}{K+C}$ ;

$$A = 5.0 \cdot 10^{-3} \frac{0.1}{0.06+0.1} = 3.125 \cdot 10^{-3} \text{ mol/g.}$$

2. The quantity of the substance adsorbed on the adsorbent with the mass of 2 g will be two times higher:

$$n_{\text{SAS}} = 3.125 \cdot 10^{-3} \text{ mol/g} \cdot 2 \text{ g} = 6.25 \cdot 10^{-3} \text{ mol.}$$

3. The mass of the adsorbed substance will be:

$$m_{\text{SAS}} = n \cdot M = 6.25 \cdot 10^{-3} \cdot 60 = 0.375 \text{ (g).}$$

*Answer:* the mass of the adsorbed SAS is 0.375 g.

**Problem 3.** We added 2 g of the adsorbent to 60 mL of the acetic acid solution with the concentration of  $0.1 \text{ mol/L}$ . After some period of time the sample of the solution with the volume of 10 ml was titrated by the solution of sodium hydroxide with the concentration of  $0.05 \text{ mol/L}$ . We used 15 mL of the titrant (NaOH solution) for the titration. Calculate the adsorption of acetic acid.

We have:

$$V_{\text{init}}(\text{CH}_3\text{COOH}) = 60 \text{ mL} = 0.06 \text{ L}$$

$$C_{\text{init.}}(\text{CH}_3\text{COOH}) = 0.1 \text{ mol/L}$$

$$M_{\text{SAS}} = 60 \text{ g/mol}$$

$$m(\text{adsorbent}) = 2 \text{ g}$$

$$V(\text{CH}_3\text{COOH for titration}) = 10 \text{ mL}$$

$$V(\text{NaOH}) = 15 \text{ mL}$$

$$C(\text{NaOH}) = 0.05 \text{ mol/L}$$

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$$A(\text{CH}_3\text{COOH}) \text{ — ?}$$

*Solution:*

1. Let's find the equilibrium concentration of the acetic acid solution using the results of the titration:

$$C_{\text{eq.}}(\text{CH}_3\text{COOH}) = \frac{C(\text{NaOH}) \cdot V(\text{NaOH})}{V(\text{CH}_3\text{COOH})};$$

$$C_{\text{eq.}}(\text{CH}_3\text{COOH}) = \frac{0.05 \cdot 15}{10} = 0.075 \text{ (mol/L).}$$

2. Let's calculate the adsorption value for the acetic acid using the formula:

$$\begin{aligned} A(\text{CH}_3\text{COOH}) &= \frac{n(\text{CH}_3\text{COOH})}{m \text{ adsorbent}} = \frac{(C_{\text{init.}} - C_{\text{eq.}}) \cdot V_{\text{init}}}{m} = \frac{(0.1 - 0.075) \cdot 0.06}{2} = \\ &= 7.5 \cdot 10^{-4} \text{ mol/g} = 0.75 \text{ mmol/g.} \end{aligned}$$

*Answer:*  $A(\text{CH}_3\text{COOH}) = 0.75 \text{ mmol/g}$ .

## CHAPTER 13

### PHYSICAL CHEMISTRY OF DISPERSED SYSTEMS

#### Main questions on the topic:

1. Dispersed systems, their properties and classification.
2. Kinetic properties of colloid systems. Sedimentation.
3. Optical properties of colloid systems. Opalescence.
4. Structure of colloid particles.
5. Methods of obtaining and purification of colloid systems. Peptization.
6. Structure and mechanism of action of the double electric layer on particles of sol.
7. Electrokinetic and electrothermodynamic potentials, their appearance, mechanism and factors determining them.
8. Electrokinetic phenomena in colloid solutions.
9. Types and factors of the colloid system stability.
10. Coagulation of colloid solutions, the factors causing coagulation.
11. Coagulation of colloid solutions by the addition of electrolytes. The threshold of coagulation.
12. Coagulation processes during the purification of drinking water and sewage.
13. Colloid protection and its importance.

#### LABORATORY WORK (M,D)

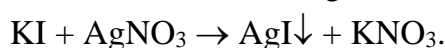
##### “THE PREPARATION OF COLLOID SOLUTIONS BY THE METHOD OF CONDENSATION AND THE INVESTIGATION OF THEIR OPTICAL PROPERTIES”

**The aim of the work:** to learn how to obtain colloid solutions by the method of condensation and to study the optical properties of colloid solutions

**Reactants and devices:** Tyndale's apparatus, tubes, 0.01N KI, AgNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, K<sub>4</sub>[Fe(CN)<sub>6</sub>], CuSO<sub>4</sub>, colophony solution in alcohol, water.

**Task 1.** To obtain colloid solutions by the methods of physical and chemical condensation.

**Experiment 1.** The obtaining of the sol of silver iodide. Pour 1/2 of the tube with KI solution. Add 2 drops of AgNO<sub>3</sub> solution in that tube. See the yellow precipitate of AgI. Then shake the tube until the moment when that precipitate will be dissolved. Notice the opalescence (a light luminous feculence) of the AgI sol:



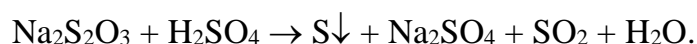
Write the scheme of the micelle of the obtained sol:

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**Experiment 2.** The obtaining of sulphur sol.

Pour 1/2 of the tube with the solution of  $\text{Na}_2\text{S}_2\text{O}_3$ . Add 4–5 drops of  $\text{H}_2\text{SO}_4$  solution. Shake the tube. Then wait for several minutes and notice opalescence.



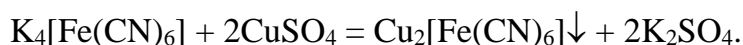
Write the scheme of the micelle of the obtained sol:

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**Experiment 3.** The obtaining of sol of copper (II) hexacyanoferrate.

Pour 1/2 of the tube with the solution of  $\text{K}_4[\text{Fe}(\text{CN})_6]$ . Add 2–3 drops of  $\text{CuSO}_4$  solution to that tube and shake it. See the formation of a sol with a brick-red color.



Write the scheme of the micelle of the obtained sol:

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**Experiment 4.** The obtaining of colophony sol by the method of solvent substitution.

Pour 1/2 of the tube with water. Then add 1–2 drops of alcohol solution of colophony to that tube and shake it. See the formation of a milk-white sol. Indeed, colophony is insoluble in water.

**Task 2.** To study the optical properties of the obtained colloidal solutions.

Put the tube with KI solution into the black box with a source of light (a simplified Tyndale's apparatus without a focusing lens). See how the light is going through the solution. Notice that there is no noticeable beam of light in the real solution. Then put each of the four colloid solutions into the black box and notice the Tyndale's effect. If there is a colloid solution in the tube, we can see a bright luminous ray or beam of light (Tyndale's cone) that reminds a spotlight. Write the obtained results in the table below.

Tube	The method of sol obtaining and the type of chemical reaction	The color of sol, the presence of opalescence	The presence of Tyndale's cone
Electrolyte solution (KI)			
Sol of silver iodide			
Sulphur sol			
Sol of copper hexacyanoferrate			
Colophony sol			

**Conclusion:** “I studied several methods for making colloid solutions. The main properties of colloid solutions are: \_\_\_\_\_”.

**LABORATORY WORK (M, D): “THE INVESTIGATION OF THE COAGULATING EFFECT OF ELECTROLYTES ON THE SOL AND THE DETERMINATION OF THE CHARGE SIGN OF SOL PARTICLES. THE CONFIRMATION OF THE PROTECTIVE EFFECT OF GELATIN”**

**The aim of the work:** to learn how to determine the coagulation thresholds of electrolytes for the given sol, how to determine the charge sign of the sol using the values of coagulation threshold; to prove experimentally that the protein solution (gelatin) increases the coagulation threshold, i.e. possesses protective properties.

**Reactants and devices:** sol of iron hydroxide, 0.7M KCl solution, 0.01M K<sub>2</sub>SO<sub>4</sub> solution, 0.001M K<sub>3</sub>PO<sub>4</sub> solution, 0.1 % solution of gelatin, flasks for titration, burettes, Mohr’s pipettes.

**Task 1.** To determine the coagulation thresholds of the given electrolytes for the sol of iron (III) hydroxide.

Put 10 ml of the solution of iron (III) hydroxide sol in three flasks for titration with the help of Mohr’s pipette. Each of the three flasks (with the sol solution) should be titrated by the solution of KCl, K<sub>2</sub>SO<sub>4</sub> and K<sub>3</sub>PO<sub>4</sub> respectively. You should stop titration when the feculence and the brightening of the solution color appear. Feculence can be noticed only if you compare the initial sol with the titrated solution. The intense of feculence must be the same in all three flasks.

We calculate the coagulation threshold  $\gamma$  for each electrolyte using the following formula:

$$\gamma = \frac{V \cdot C \cdot 1000}{V_0},$$

where C is the concentration of an electrolyte solution, mol/L; V is the volume of the electrolyte solution used for titration, mL; V<sub>0</sub> is the volume of sol solution, mL;  $\gamma$  is the threshold of coagulation, mmol/L.

The data of the experiment and the results of the calculations should be written down in the table below.

Electrolyte solution used for titration	The volume of the sol, mL	The concentration of the electrolyte solution, mol/L	The volume of the electrolyte solution used for titration, mL	The threshold of coagulation, mmol/L
KCl	10	0.7		
K <sub>2</sub> SO <sub>4</sub>	10	0.01		
K <sub>3</sub> PO <sub>4</sub>	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 for the given electrolytes obtained in Task 1. On the basis of the obtained data make the conclusion about the charge sign of particles of iron (III) hydroxide sol.

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**Task 3.** To check the protective properties of gelatin.

Put 10 ml of the solution of iron (III) hydroxide sol in the flask. Add 0.1 ml of 0.1 % gelatin solution to that flask using the Mohr's pipette. Titrate the obtained solution by KCl solution. Calculate the coagulation threshold of KCl for the sol protected by gelatin.

$$\gamma = \frac{V \cdot C \cdot 1000}{V_0} = (\text{_____} \cdot \text{_____} \cdot 1000) / 10 = \text{_____} \text{ mmol/L.}$$

How many times the coagulation threshold increased after the addition of gelatin?

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**Conclusion:** *"I determined the sign of the charge of iron (III) hydroxide sol particles and confirmed the protective effect of gelatin on the stability of sols against the addition of electrolytes".*

### TEST SELF-CHECK

**1. Choose true statements:**

- a) we can prepare colloid solution from KCl and water
- b) colloid solutions are thermodynamically unstable;
- c) dispersed system is a heterogeneous system which consists of a dispersed phase and a dispersion medium;
- d) the size of particles of a dispersed phase of a sol (a colloid solution) cannot exceed 100 nanometers.

**2. Indicate the properties of colloid solutions:**

- a) low osmotic pressure;
- b) diffusion of light;
- 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 in temperature;
- b) decrease in temperature;
- c) increase in size of particles;
- d) decrease of the viscosity.

**4. Indicate which of the following systems (if the mass percentage of the substance is the same in each of them) has the lowest osmotic pressure:**

- a) sodium chloride solution;                      c) sol of iron (III) hydroxide;  
b) glucose solution;                                  d) aluminum chloride solution.

**5. Indicate the factors that determine the sedimentation rate:**

- a) the size of particles of the dispersed phase;  
b) the viscosity of the dispersion medium;  
c) the density of the dispersion medium;  
d) the density of the dispersed phase.

**6. The most characteristic optical property of colloid solutions is:**

- a) reflection; b) absorption; c) diffraction; d) light diffusion.

**7. The aggregate of a colloidal particle (micelle) is made from microcrystals of:**

- a) a soluble electrolyte; b) an insoluble electrolyte;

**and on the surface of the aggregate there is the adsorption layer of ions from the electrolyte taken:**

- c) in excess; d) in deficiency.

**8. The sol of calcium carbonate is obtained by the way of mixing equal volumes of calcium nitrate and potassium carbonate solutions. Indicate what is the charge of sol granules if the concentration of  $\text{Ca}(\text{NO}_3)_2$  was higher than that of  $\text{K}_2\text{CO}_3$ :**

- a) positive; b) negative; c) neutral.

**9. The sol of barium carbonate is obtained by the mixing of the excess of barium chloride solution with the solution of ammonia carbonate. For the micelle of the obtained sol:**

A. Aggregate consists of microcrystals made from:

- a)  $\text{BaCl}_2$ ; b)  $(\text{NH}_4)_2\text{CO}_3$ ; c)  $\text{NH}_4\text{Cl}$ ; d)  $\text{BaCO}_3$ .

B. The potential determining ions are:

- a)  $\text{CO}_3^{2-}$ ; b)  $\text{Cl}^-$ ; c)  $\text{Ba}^{2+}$ ; d)  $\text{NH}_4^+$ .

C. The scheme of the nucleus is the following:

- a)  $[\text{mBaCO}_3] \cdot n\text{CO}_3^{2-}$ ;                      c)  $[\text{mBaCO}_3] \cdot 2n\text{NH}_4^+$ ;

- b)  $[\text{mBaCO}_3] \cdot 2n\text{Cl}^-$ ;                      d)  $[\text{mBaCO}_3] \cdot n\text{Ba}^{2+}$ .

D. The opposite ions are:

- a)  $\text{Ba}^{2+}$ ; b)  $\text{Cl}^-$ ; c)  $\text{CO}_3^{2-}$ ; d)  $\text{NH}_4^+$ .

E. The scheme of the adsorption layer is:

- a)  $n\text{Ba}^{2+}$ ;    d)  $2n\text{Cl}^- \cdot (n-x)\text{Ba}^{2+}$ ;

- b)  $2n\text{Cl}^-$ ;    e)  $n\text{CO}_3^{2-} \cdot (2n-x) \cdot \text{NH}_4^+$ ;

- c)  $n\text{Ba}^{2+} \cdot (2n-x)\text{Cl}^-$ ;                      f)  $n\text{CO}_3^{2-}$ .

F. The scheme of the granule is the following:

- a)  $\{[m\text{BaCO}_3] \cdot n\text{Ba}^{2+} \cdot (2n - x)\text{Cl}^-\}^{x+}$ ;
- b)  $\{[m\text{BaCO}_3] \cdot 2n\text{Cl}^- \cdot (n - x)\text{Ba}^{2+}\}^{2x-}$ ;
- c)  $\{[m\text{BaCO}_3] \cdot n\text{Ba}^{2+} \cdot (2n - x)\text{Cl}^-\}^{x-}$ ;
- d)  $\{[m\text{BaCO}_3] \cdot n\text{CO}_3^{2-} \cdot (2n - x)\text{NH}_4^+\}^{x-}$ .

G. The charge of the granule is:

- a) positive; b) negative; c) neutral.

H. The diffuse layer consists of the ions:

- a)  $\text{Ba}^{2+}$ ; b)  $\text{NH}_4^+$ ; c)  $\text{Cl}^-$ ; d)  $\text{CO}_3^{2-}$ .

I. The scheme of micelle is:

- a)  $\{[m\text{BaCO}_3] \cdot 2n\text{Cl}^- \cdot (n - x)\text{Ba}^{2+}\}^{2x-} \cdot x\text{Ba}^{2+}$ ;
- b)  $\{[m\text{BaCO}_3] \cdot n\text{CO}_3^{2-} \cdot (2n - x)\text{NH}_4^+\}^{x-} \cdot x\text{NH}_4^+$ ;
- c)  $\{[m\text{BaCO}_3] \cdot n\text{Ba}^{2+} \cdot (2n - x)\text{Cl}^-\}^{x-} \cdot x\text{Cl}^-$ ;
- d)  $\{[m\text{BaCO}_3] \cdot n\text{Ba}^{2+} \cdot (2n - x)\text{Cl}^-\}^{x+} \cdot x\text{Cl}^-$ .

**10. After the mixing of equal volumes of silver nitrate and sodium chloride solutions a sol of silver chloride with the positively charged particles has been formed. The concentrations of the initial electrolytes can be described like:**

- a) the concentration of  $\text{AgNO}_3$  solution was higher;
- b) the concentration of  $\text{NaCl}$  solution was higher;
- c) the concentration of  $\text{NaCl}$  solution was lower;
- d) the concentrations of both solutions were equal to each other.

**11. We need the following conditions to obtain a stable colloid solutions (sol):**

- 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) the presence of a stabilizer (a small excess of electrolyte).

**12. Indicate the dispersion methods for obtaining colloid solutions:**

- a) methods of solvent substitution; c) chemical oxidation;
- b) peptization; d) mechanic cracking.

**13. Indicate which of the ions plays the role of a peptizing agent when we add a small amount of nitric acid to the freshly prepared precipitate of aluminum hydroxide:**

- a)  $\text{AlO}^+$ ; b)  $\text{OH}^-$ ; c)  $\text{H}^+$ ; d)  $\text{NO}_3^-$ .

**14. Which of the properties mentioned below can be used to purify colloid solutions:**

- a) the size of particles of a dispersed phase is bigger than the size of ions and solvent particles;
- b) the concentration of particles of a dispersed phase is higher than the concentration of other particles from a solution;

- c) particles of a dispersed phase can diffuse through a membrane;
- d) small particles from a solution can diffuse through a membrane.

**15. The value of electrothermodynamic potential of sol particles is determined by:**

- a) the quantity of potential-determining ions in the adsorption layer;
- b) the quantity of opposite ions only in the diffuse layer;
- c) the quantity of opposite ions only in the adsorption layer;
- d) the general amount of opposite ions in the adsorption and the diffuse layers.

**16. Electrokinetic potential of particles in colloid solution exists:**

- a) between the potential-determining ions of the adsorption layer and all opposite ions;
- b) between ions of adsorption layer and opposite ions of diffuse layer;
- c) between the aggregate and potential-determining ions of the adsorption layer;
- d) between the granule and the diffuse layer.

**17. Choose the true statements:**

- a) the value of the charge of the granule can change because opposite ions of the diffuse layer can move to the adsorption layer and vice versa;
- b) the higher is the number of opposite ions in the diffuse layer, the higher is the charge size of the granule;
- c) electroosmosis is the movement of molecules of the dispersion medium relative to dispersed phase in the electric field;
- d) the potential of leaking appears when you push the sol through the capillary under pressure.

**18. Equal volumes of 0.008 M AgNO<sub>3</sub> solution and 0.0096 M NaCl solution have been poured together. A sol of silver chloride has been formed. The micelle structure scheme of that sol is the following:**

- a)  $\{[m\text{AgCl}] \cdot n\text{Cl}^- \cdot (n - x) \cdot \text{Na}^+\}^{x-} \cdot x\text{Na}^+$ ;
- b)  $\{[m\text{AgCl}] \cdot n\text{Na}^+ \cdot (n - x) \cdot \text{Cl}^-\}^{x+} \cdot x\text{Cl}^-$ ;
- c)  $\{[m\text{AgCl}] \cdot n\text{Ag}^+ \cdot (n - x) \cdot \text{NO}_3^-\}^{x+} \cdot x\text{NO}_3^-$ ;

**and during electrophoresis the granule of the sol mentioned above:**

- d) moves to the cathode;
- e) moves to the anode;
- f) remains immobile.

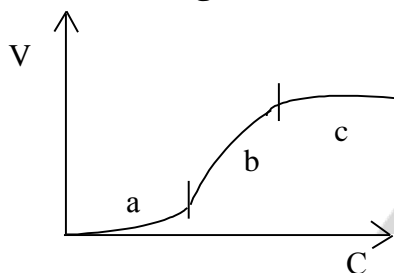
**19. Kinetic stability of colloid solutions will decrease:**

- 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 the particles of dispersed phase.

**20. Indicate the factors of aggregative stability of dispersed systems:**

- a) the presence of the ion shell of the particles;
- b) the presence of the diffuse layer of particles;
- c) the presence of solvation (hydration) sphere of particles;
- d) the high dispersion degree of the particles of a dispersed phase.

**21. Indicate which section of the kinetic curve of the colloid solution coagulation by electrolyte corresponds to the visible coagulation:**



**22. Indicate which electrolyte should we take in excess to make a sol with positively charged granules. We pour together solutions of  $\text{Ba}(\text{NO}_3)_2$  and  $\text{Na}_2\text{SO}_4$ :**

- a)  $\text{Ba}(\text{NO}_3)_2$ ; b)  $\text{Na}_2\text{SO}_4$ ;

**The coagulation of the above mentioned sol can be caused by the ions:**

- c)  $\text{Cl}^-$ ; d)  $\text{Al}^{3+}$ .

**23. To cause the coagulation we added 1 ml 0.005M potassium sulfate to 5 ml of a sol of iron (III) hydroxide. The coagulation threshold for the given electrolyte is:**

- a) 0.001 mmol/L; b) 0.001 mmol/L; c) 1.0 mmol/L; d) 1.0 mmol/L.

**24. Indicate which of the electrolytes will have the lowest coagulation threshold for the sol of  $\text{Fe}(\text{OH})_3$  with positively charged grains:**

- a)  $\text{KNO}_3$ ; b)  $\text{MgSO}_4$ ; c)  $\text{AlCl}_3$ ; d)  $\text{K}_3\text{PO}_4$ .

**25. Indicate the sign of the charge of the sol granules. The sol has been obtained by mixing  $\text{CuSO}_4$  and  $(\text{NH}_4)_2\text{S}$  solutions. The coagulation thresholds of this sol by electrolytes  $\text{KCl}$ ,  $\text{MgCl}_2$ ,  $\text{AlCl}_3$  are the following: 50; 0.72; 0.093 mmol/L:**

- a) positive; b) negative.

**26. Calculate the protective effect of gelatin for to the sol of aluminum hydroxide ( $\gamma_{\text{gel}}/\gamma$ ). We used 2.3 ml of 0.01M  $\text{K}_2\text{SO}_4$  solution to titrate 10 ml of the sol without gelatin, and 5.0 ml of 0.01M  $\text{K}_2\text{SO}_4$  solution to titrate 10 ml of the same sol with gelatin:**

- a) 0.005; b) 0.0023; c) 2.17; d) 0.46.

## PROBLEMS

1. Solutions of  $\text{AlCl}_3$  and  $\text{NaOH}$  have been mixed together. The sol of  $\text{Al}(\text{OH})_3$  with positively charged granules has been obtained. Determine which electrolyte was taken in excess, write down the scheme of the structure of a micelle of that sol.

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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. The sol of  $\text{Fe}(\text{OH})_3$  was formed. Write the scheme of a 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?

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3. The sol of iron sulfide is obtained by the way of mixing together equal volumes of  $(\text{NH}_4)_2\text{S}$  and  $\text{FeCl}_2$  solutions. In the electric field granules of that sol moved to the cathode. Which electrolyte has been taken in excess? Write down the scheme of a micelle.

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4. A sol of  $\text{Ag}_2\text{CrO}_4$  with negatively charged granules is formed after the pouring together  $\text{AgNO}_3$  and  $\text{K}_2\text{CrO}_4$  solutions. Determine which electrolyte has been taken in excess, write down the scheme of a micelle structure of this sol. Arrange in the row according to the increase of their coagulation thresholds for the given sol the following electrolytes:  $\text{MgSO}_4$ ,  $\text{Al}(\text{NO}_3)_3$  and  $\text{K}_4[\text{Fe}(\text{CN})_6]$ .

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5. Coagulation thresholds for  $\text{KCl}$ ,  $\text{MgCl}_2$  and  $\text{AlCl}_3$  electrolytes for a sol are the following: 50; 0.72; 0.093 mmol/L. Which ions — cations or anions — of the mentioned salts caused the coagulation of the given sol? What was the charge of the granules of that sol?

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6. We poured 100 ml of  $\text{Fe}(\text{OH})_3$  sol in three flasks. To cause a visible sol coagulation we added 10.5 ml of 1M KCl solution to the first flask, 62.5 ml of 0.01M  $\text{Na}_2\text{SO}_4$  solution to the second one and 37.0 ml of 0.001M  $\text{Na}_3\text{PO}_4$  to the third one. Calculate the coagulation thresholds of these electrolytes for the sol of iron (III) hydroxide and determine the sign of a charge of sol particles.

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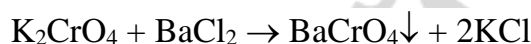


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## STANDARDS OF PROBLEM SOLUTIONS

**Problem 1.** Sol of silver chromate is obtained by the way of mixing equal volumes of 0.005M  $\text{K}_2\text{CrO}_4$  solution and 0.012M  $\text{BaCl}_2$  solution. Write down the scheme of micelle and indicate the sign of a charge of its granules.

*Solution.* The chemical reaction is as follows:

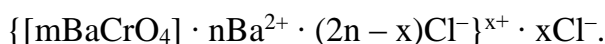


Since  $C(\text{BaCl}_2) > C(\text{K}_2\text{CrO}_4)$ , then (if the volumes are the same) the amount of  $\text{BaCl}_2$  is higher than the amount of  $\text{K}_2\text{CrO}_4$  ( $0.012 \cdot V > 0.005 \cdot V$ ). So,  $\text{BaCl}_2$  has been taken in excess.

The aggregate of the sol micelle is formed by microcrystals of insoluble  $\text{BaCrO}_4$ . According to Panette-Faience rule the potential-determining ions are those ions which are similar to the substance of aggregate from those which are present in excess in the solution. Such ions will be adsorbed on the aggregate surface. In our case they are  $n\text{Ba}^{2+}$  ions.

Opposite ions are those which are also present in excess ( $2n\text{Cl}^-$ ). They will be distributed in the following way:  $(2n - x)\text{Cl}^-$  will be situated in the adsorption layer and the rest of  $\text{Cl}^-$  will form the diffuse layer.

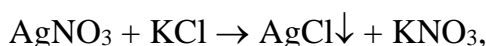
The scheme of the micelle structure of the sol will look like this:



The granule of micelle (written in brackets) has a positive charge, i. e. it has the sign of a charge of potential-determining ions  $\text{Ba}^{2+}$ .

**Problem 2.** Granules of silver iodide sol obtained by the way of mixing  $\text{AgNO}_3$  and KCl solutions have a negative charge. Which of the given electrolytes has been taken in excess? Write the formula of micelle.

*Solution.* Sol is obtained according to the following equation of chemical reaction:

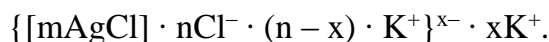


from which we can see that the aggregate is an insoluble silver chloride  $\text{AgCl}$ .

As the granule has a negative charge, then the potential-determining ions, according to the Panette-Faience rule, will be negatively charged ions which are the same as ions of

the aggregate, i. e.  $\text{Cl}^-$  ions. Consequently, the solution of KCl containing these ions has been taken in excess.

The formula of micelle is the following:



**Problem 3.** The charge of iron (III) hydroxide sol granules is positive. Which of the electrolytes – KCl,  $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{CaCl}_2$ ,  $\text{AlCl}_3$  – will have the lowest coagulation threshold for this sol?

*Solution.* As granules have a positive charge, then, according to Shultze–Gardi rule, the coagulation of that sol can be caused by ions with an opposite sign of charge, i. e. by anions of electrolytes ( $\text{Cl}^-$  or  $\text{SO}_4^{2-}$ ). The higher the size of a charge of an ion-coagulant, the stronger the coagulation effect of the electrolyte and the lower the coagulation threshold. Consequently, the lowest coagulation threshold will be for  $\text{Fe}_2(\text{SO}_4)_3$ , because the charge of sulfate-ion is higher than that of chloride-ion.

**Problem 4.** Electrolytes KCl,  $\text{K}_2\text{SO}_4$ ,  $\text{K}_3\text{PO}_4$  have the following thresholds of coagulation for the iron (III) hydroxide: 7.1; 0.099 and 0.01 mmol/L. What sign of charge do the sol granules have?

*Solution.* According to the problem the coagulation thresholds of these electrolytes KCl,  $\text{K}_2\text{SO}_4$ ,  $\text{K}_3\text{PO}_4$  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 of a different size of charge. In our case:  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ . As the coagulation is caused by anions, the sign of a charge of sol granules is positive.



## CHAPTER 14

### PHYSICAL CHEMISTRY OF SOLUTIONS OF BIOPOLYMERS

#### **Main questions of the topic:**

1. Macromolecular compounds (MMC). Their classification and chemical structure. The importance of biopolymers.
2. Formation of MMC solutions and their properties. Differences between MMC solutions and sols. Common properties of MMC solutions and sols.
3. Thermodynamics of the formation of MMC solutions.
4. Mechanisms of swelling and dissolving MMC. Limited and unlimited swelling. The influence of different factors on swelling and dissolving of MMC. The swelling degree. Medical and biological significance of MMC swelling.
5. Stability of MMC solutions and the ways of extraction of biopolymers from their solutions. Denaturation.
6. Osmotic pressure of MMC solutions. Osmometric method for calculation of the molar mass of MMC. Galler's equation.
7. The significance of MMC solutions viscosity for medical and biological investigations.
8. Proteins as polyelectrolytes. Isoelectric state and isoelectric point of proteins. The influence of the pH level in the solution on the charge of proteins.
9. Electrophoresis of the solutions of proteins.
10. The significance of electrophoresis and electroosmosis in medical and biological investigations and physiotherapeutic practice.

#### **LABORATORY WORK (M, D)**

##### **“DETERMINATION OF THE SWELLING DEGREE OF GELATIN AT DIFFERENT pH LEVELS”**

**The aim of the work:** to find out which of the solutions has the level of pH that is closer to the isoelectric point of gelatin.

**Equipment:** four solutions with different pH levels; dry gelatin; four graduated tubes.

Put 0.5 ml of dry gelatin powder in each of the four graduated tubes. Then fill in the same tubes up to the level of 10 ml with the following solutions: 0.1M hydrochloric acid solution (tube 1),  $1 \cdot 10^{-5}$  M HCl solution (tube 2),  $1 \cdot 10^{-5}$  M NaOH solution (tube 3), 0.1M NaOH solution (tube 4). The contents of the test tubes should be mixed with a glass stick (that stick should be washed after each agitation with distilled water). After 30 minutes you should determine the volume of swollen gelatin and calculate the swelling degree (the ratio between the final volume of gelatin and its initial volume). The obtained data should be written down in the table below.

### The results of the experiment

System	pH of the medium	The volume of the gelatin		Swelling degree
		Initial ( $V_0$ )	After the swelling ( $V$ )	
0.1M HCl solution				
$1 \cdot 10^{-5}$ M HCl solution				
$1 \cdot 10^{-5}$ M NaOH solution				
0.1M NaOH solution				

Draw a diagram of the dependence between the swelling degree (Y-axis) on the pH level of the solution (X-axis).



**Conclusion:** “isoelectric point of gelatin is close to \_\_\_\_\_”.

### TEST SELF-CHECK

**1. Indicate, which MMC are biopolymers:**

a) proteins; b) starch; c) natural rubber; d) glycogen

**2. Indicate the factors that can influence the overall charge of a protein:**

- a) hydrogen ( $H^+$ ) ion concentration in the solution;
- b) the total number of carboxylic and amine groups in the protein;
- c) the nature of the solvent;
- d) concrete pK level for each functional group.

**3. In the isoelectric point the protein has the minimum values of:**

- a) electrophoretic mobility;
- b) total charge;
- c) hydration degree;
- d) swelling degree.

**4. The 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 sols and MMC solutions:**

- a) low osmotic pressure;
- b) homogeneity;
- c) solutions are formed spontaneously;
- d) light diffusion.

**6. The process of MMC 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) the change of the pH of the solution closer to the 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 MMC solution viscosity:**

- a) temperature;
- b) MMC concentration;
- c) relative molecular mass of the polymer;
- d) the shape and the volume of a macromolecule

**11. Indicate the methods with the help of which the molecular mass of MMC can be determined:**

- a) cryoscopic;
- b) osmometric;
- c) the method of light diffusion;
- d) viscosimetric.

**12. Indicate the factors that influence the characteristic viscosity:**

- a) the nature of the polymer;
- b) the relative molecular mass of the polymer;
- c) the concentration of polymer in the solution;
- d) the rate of reciprocal movement of liquid layers.

**13. Indicate the right statements:**

- a) in water solutions amino acids exist in the form of bipolar ions;
- b) the total charge of amino acid 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) the separation of amino acids and proteins by the method of electrophoresis is based on their ability to change the sign of the charge depending on the pH medium;  
 d) in the electric field at the pH equal to pI the protein moves to the cathode.

**14. In the basic medium amino acids behave in the following way:**

- a)  $\text{NH}_3^+ - \text{R} - \text{COO}^- + \text{OH}^- \rightleftharpoons \text{NH}_3^+ - \text{R} - \text{COOH}$ ;  
 b)  $\text{NH}_3^+ - \text{R} - \text{COO}^- + \text{OH}^- \rightleftharpoons \text{NH}_2 - \text{R} - \text{COO}^- + \text{H}_2\text{O}$ ;  
 c)  $\text{NH}_3^+ - \text{R} - \text{COO}^- + \text{OH}^- \rightleftharpoons \text{NH}_2 - \text{R} - \text{COOH}$ ;

**the total charge of the abovementioned acid is:**

- d) negative; e) positive; f) neutral.

**15. For diaminomono-carboxylic amino acid the value of pI is in the:**

- a) slightly acidic medium; b) neutral medium; c) slightly basic medium.

**16. We separate proteins by the method of electrophoresis in the buffer solution with the pH = 4.9 ( $\alpha$ -globulin has pI = 4.8, albumin has pI = 4.64,  $\gamma$ -globulin has pI = 6.4). Indicate the proteins which will move to the anode:**

- a)  $\alpha$ -globulin; b) albumin; c)  $\gamma$ -globulin;

**indicate, which of the proteins mentioned above will migrate to the longer distance during electrophoresis:**

- d)  $\alpha$ -globulin; e) albumin; f)  $\gamma$ -globulin.

**17. Gelatin with pI equal to 4.7 is placed into a solution where the concentration of  $\text{H}^+$  ions is 100 times higher than in the pure water. During electrophoresis in this solution gelatin molecules will move to:**

- a) a cathode; b) an anode; c) won't move.

### PROBLEMS AND EXERCISES

1. pI of three proteins are 3.8, 4.6 and 5.1. Which of the proteins will have the highest swelling degree in a buffer solution with the pH 4.7?

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2. In which of the solutions of the following salts — NaI,  $\text{Na}_2\text{SO}_4$ , NaCNS, NaCl — if their molar concentrations are equal to each other the swelling degree of proteins should show the highest level?

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3. Myosin has the  $pI = 5.0$ . That protein has been placed into the solution with the concentration of  $H^+$  ions 100 times higher than that in the pure water. What charge will this protein have in that solution?

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4. Which electrode will the protein with  $pI = 4.0$  move to during the electrophoresis if the  $pH$  of the solution is 7.0?

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5. Egg albumin with the isoelectric point equal to 4.8 is placed into the solution where the concentration of  $OH^-$  ions is 100 times lower than that in water. Indicate the charge of albumin in the solution. Which electrode (anode or cathode) will albumin move to in the electric field?

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6. Isoelectric points of  $\alpha$ -,  $\beta$ - and  $\gamma$ -globulins from 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 highest charge?

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7. There are two proteins with the isoelectric points equal to 4.7 and 8.8. Which electrode will they move to during the electrophoresis in the buffer solution with the  $pH = 7.9$ . Which of the mentioned proteins (if they have the same molecular mass) will migrate to the longer distance to the corresponding electrode?

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8. Pepsin (with  $pI = 2.0$ ) is dissolved in the buffer solutions with the  $pH$  1.9; 4.75 and 9.24. In which of these solutions pepsin should show the better resistance to the salting out?

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9. We added equal volumes of 1M  $CH_3COONa$ ,  $NaCNS$ ,  $Na_2SO_4$  and  $NaNO_3$  solutions to four different tubes with the same amount of gelatin solution. Which of the electrolytes will have the best salting-out action?

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10. We added 1 ml of protein solution with the isoelectric point of 9.2 and the same volume of acetone 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. In which of the test tubes there will be the maximum protein coagulation?

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11. We added equal volumes of KI, CH<sub>3</sub>COOK, KCNS and K<sub>2</sub>SO<sub>4</sub> solutions with the same concentration in four different tubes containing equal volumes of protein solution. In which of the tubes the gelatinization of the protein solution will happen first?

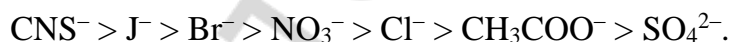
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### STANDARDS OF PROBLEM SOLUTIONS

**Problem 1.** In four tubes with 1M CH<sub>3</sub>COOK, KCNS, K<sub>2</sub>SO<sub>4</sub> and KCl solutions we placed 0.5 g of a polar polymer. In which of the electrolyte solutions there will be the highest swelling degree of the given polymer?

*Solution.* The influence of electrolyte ions on the swelling of MMC is connected to their ability to bind water molecules. According to their ability to decrease the swelling degree the anions are arranged in the row (if they are supplied together with the same cation):



As CNS<sup>-</sup> ions increase the swelling and SO<sub>4</sub><sup>2-</sup> ions decrease it, there will be the highest swelling degree in the KCNS solution and in the solution of K<sub>2</sub>SO<sub>4</sub> it will be the lowest.

**Problem 2.** The isoelectric point of pepsin is at pH = 2.0. What sign of the charge will this enzyme demonstrate in the buffer solution with the pH = 8.5.

We have:

$$\text{pI} = 2.0$$

$$\text{pH} = 8.5$$

The sign of the charge of pepsin?

*Solution:*

When pepsin is placed in the solution with the pH of the medium higher than pI, carboxylic and amino groups are deprotonated. Deprotonated amino groups have no charge, while deprotonated carboxylic groups have negative charge. The whole molecule acquires the negative charge.

**Problem 3.** Gelatin is placed in the buffer solution with the  $\text{pH} = 3$ . Determine the sign of the charge of gelatin. The isoelectric point of protein is 4.7.

We have: $\text{pI} = 4.7$ $\text{pH} = 3.0$	<i>Solution:</i> When gelatin is placed in the solution with the $\text{pH}$ of the medium that is lower than its $\text{pI}$ , the carboxylic groups become protonated (and so they will have no charge), amino groups also become protonated (and so they will have positive charge). The whole molecule gets a positive charge.
The sign of the charge of gelatin?	

**Problem 4.** The isoelectric point of albumin is 4.9. The protein is placed in the buffer solution with the hydrogen ion concentration equal to  $10^{-6}$  mol/L. Determine the direction of the migration of albumin during electrophoresis.

We have: $\text{pI} = 4.9$ $[\text{H}^+] = 10^{-6}$ mol/L	<i>Solution:</i> If hydrogen ion concentration is $10^{-6}$ mol/L, then the $\text{pH}$ of the medium is 6 because $\text{pH} = -\log[\text{H}^+]$ .
Direction of protein migration during electrophoresis?	As the $\text{pH}$ of the medium $>$ $\text{pI}$ ( $6 > 4.9$ ), then the protein gets a negative charge and during electrophoresis it migrates to the anode.

**Problem 5.** Pepsin ( $\text{pI} = 2.0$ ) is placed into a buffer solution in which the concentration of  $\text{H}^+$  ions is 1000 times higher than that in the pure water. Which electrode will the protein move to during the electrophoresis?

*Solution.* The concentration of  $\text{H}^+$  ions in water is  $10^{-7}$  mol/L. Consequently, in the given solution  $[\text{H}^+] = 10^{-7} \cdot 1000 = 10^{-4}$  mol/L. Hence,  $\text{pH}$  of the medium  $= -\log 10^{-4} = 4$ .

As  $\text{pH}$  of the medium is higher than  $\text{pI}$  ( $4 > 2$ ), the protein in the given medium has a negative charge.

Protein with a negative charge will migrate to the anode in the electric field.

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ПО ОБЩЕЙ ХИМИИ**

**LABORATORY WORKS AND HOME TASKS  
IN GENERAL CHEMISTRY**

Практикум

На английском языке

*4-е издание*

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