MINISTRY OF HEALTH OF UKRAINE

ODESSA NATIONAL MEDICAL UNIVERSITY

Faculty of Pharmacy

Department of Pharmaceutical Chemistry and Drug Technology

APPROVED by

Vice-rector for scientific and pedagogical work

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_____, 202_

METHODOLOGICAL DEVELOPMENT
TO THE LECTURES ON THE EDUCATIONAL DISCIPLINE

Faculty, course Pharmaceutical, II course

Educational discipline Analytical chemistry

(the name of the educational discipline)

Approved:

The meeting of the department Pharmaceutical chemistry and Drug technology

Odesa National Medical University

Minutes № _dated _____

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Developers:

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Lecture No. 1

Topic: Theoretical foundations of analytical chemistry. Analytical chemistry as a science. The subject and tasks of analytical chemistry. Chemical analysis and its types. Analytical properties of substances, analytical reactions and requirements for them.

Relevance of the topic: Analytical chemistry is a science that develops theoretical foundations and practical methods of chemical analysis. Therefore, it is relevant to solve the problems facing analytical chemistry with the help of physical, chemical and physicochemical methods used for the analysis of medicinal products.

Purpose: to acquaint students with the subject, content and history of the development of analytical chemistry, to form students' knowledge of the use of various chemical and physicochemical methods for qualitative and quantitative analysis of medicinal substances.

Basic concepts: analytical chemistry, qualitative analysis, quantitative analysis, chemical method of analysis, physical method of analysis, physicochemical method of analysis, microanalysis, microanalysis, semi-microanalysis, ultramicroanalysis, analytical reaction, analytical effect, analytical reagent

Plan and organizational structure of the lecture:

1. 1. The subject of analytical chemistry, its place and role among other chemical disciplines
2. Methods of analytical chemistry
3. Qualitative analysis. Analytical reactions
4. Qualitative analysis of cations

Content of lecture material (lecture text):

1. The subject of analytical chemistry, its place and role among other chemical disciplines

Analytical chemistry is a fundamental chemical science about methods of determining the qualitative and quantitative composition of compounds and their mixtures, as well as establishing the chemical structure of substances. The subject

of analytical chemistry is the study of the theoretical foundations of analysis methods, the development of analytical methods and the practical performance of analyzes.

The main tasks of analytical chemistry:

1. Development of the theory of chemical processes, calculation of complex chemical systems on the basis of thermodynamic and quantum chemical ideas using algorithms and computer technology.

2. Study of the relationship between the structure of substances and their chemical-analytical properties: creation of methods of chemical analysis based on analytical properties and analytical reactions of substances; increasing the accuracy and correctness of the results of analytical determinations and developing methods for assessing their accuracy and correctness

3. Study of the structure of the most important biologically active compounds, development of bioanalytical chemistry.

4. Development of instrumental methods of analysis; solving the problem of chemical metrology - development and improvement of measurement units, their reproducibility in the form of standards, use of standard samples of the chemical composition of substances and materials.

5. Chemical and technological control of production at all its stages

Analytical chemistry is closely related not only to chemical sciences, but also to other sciences: physics, biology, geochemistry, metallurgy, medicine, agrochemistry, etc. So, for example, no conclusion about the value of a mineral deposit or the quality of metal alloys can be made without preliminary chemical analysis. What would the study of the Moon be worth without a thorough study of the chemical composition of its soil?

Analytical chemistry plays an important role in those branches of industry and transport, where constant and thorough control of the chemical composition of raw materials, semi-finished products and finished products is necessary. We will give only one of many examples, close to your chosen profession.

1. Methods of analytical chemistry

The main method of analytical chemistry is analysis.

Chemical analysis is a set of actions that result in obtaining information about the chemical composition of an object. Means of chemical analysis — reagents, devices, standard samples, etc.

The analysis method is a universal and theoretically grounded way of determining the composition, which is based on the relationship between the composition and the property being determined.

Methodology of analysis – application of the method of analysis to a specific identified object with a detailed description of all analytical operations.

The analysis methodology may include the following stages:

• Sampling

• Sample preparation

• Obtaining an analytical signal

• Processing and interpretation of results

To better understand the difference between the above concepts, consider an example. Let's imagine that the preparation calcium chloride 10% for injections has arrived for analysis. The chemical analysis consists in posing a general question - to qualitatively and quantitatively prove that there is 10% CaCl2 in the ampoules.

The analysis method we use:

1. for the qualitative determination of: calcium cations in the solution - test tube reaction with carbonate ion, oxalate ion, potassium hexacyanoferrate (II); chloride anions - test tube reaction with silver cations.

2. titrimetric methods of analysis can be used for the quantitative determination of calcium chloride in the solution: argentometry and complexonometry.

In the method, we always give specific values: add 2 ml of ammonium oxalate solution to 1 ml of calcium chloride solution. We observe the formation of a white crystalline precipitate.

Analysis methods are classified by:

1) measurable properties of the analyzed substance: chemical, physical and physico-chemical;

2) methods of solving this or that task - qualitative analysis (identification and detection) and quantitative analysis.

3) mass of the substance taken for analysis

4) the object of analytical control and the purpose of the analysis: labeling, rapid or express analyses, arbitration analyses;

According to the method, chemical, physical and physico-chemical methods of analysis are determined.

In chemical methods of qualitative analysis, an element is determined or an ion is converted into a compound by a chemical method, which has certain properties, on the basis of which it can be established that this particular compound was formed. A chemical transformation is called an analytical reaction, and the substance that caused it is called a reagent. An example of an analytical reaction can be the reaction of the interaction of chloride ions with silver cations, resulting in the formation of a white cheesy AgCl ↓ precipitate. At the same time, we can say that chlorides are a reagent for silver cations, and vice versa.

$$Cl^- + Ag^+ = AgCl\downarrow$$

Physical methods of analysis are methods that allow you to determine the composition of a substance without resorting to the use of chemical reactions. Physical methods are based on the measurement of any parameters of the system (optical, electrical, magnetic, thermal), which are a function of the composition. Physical methods of analysis include spectral, luminescent, X-ray structural, and mass spectrometric methods of analysis. For example, spectral analysis examines radiation spectra that occur when a substance is introduced into the flame of a burner, electric arc, etc. Based on the presence of lines characteristic of these elements in the spectrum, the presence of these elements in the substance under investigation is judged, and the brightness of the lines indicates their quantitative content.

Physico-chemical methods of analysis are based on the study of physical phenomena that occur during chemical reactions. For example, colorimetry - uses the phenomenon of changing the color of the solution during the chemical process. reactions, conductometry - change in electrical conductivity, etc. It is not always possible to draw a strict boundary between physical and physicochemical methods. Sometimes they are combined under the general name "instrumental" methods, since "instruments" are needed to perform certain measurements - devices that allow you to measure the values of certain parameters characterizing certain properties of a substance with great accuracy.

Depending on the quantities of substances used in performing analytical reactions, the following are distinguished: macro-, semi-micro-, micro- and ultra-micro methods of qualitative analysis.

In macroanalysis, relatively large amounts of substances (0.5-1 g) or 20-50 ml of solutions are examined. Reactions are carried out in ordinary test tubes (with a capacity of 10-20 ml), chemical beakers.

In microanalysis, we usually deal with approximately 100 times smaller amounts of the substance under investigation, that is, with several milligrams of a solid substance or with several tenths of a milliliter of a solution. At the same time, highly sensitive reactions are used, which allow to detect the presence of individual components even with a small content of them in the substance under investigation. Reactions are performed by the microcrystalloscopic or droplet method.

The analysis of this or that substance is carried out in order to establish its qualitative or quantitative chemical composition. Accordingly, a distinction is made between qualitative and quantitative analysis. The tasks of qualitative analysis are diverse, but they all boil down to qualitative discovery (discovery).
So, with the help of qualitative analysis, it is found from the atoms of which elements, ions, groups of atoms, including functional groups of organic compounds, and molecules (crystals) that make up the analyzed object.

Quantitative analysis allows you to establish quantitative (mass or volume) ratios between constituent parts of chemical compounds or mixtures of substances. When studying the composition of an unknown substance, qualitative analysis always precedes quantitative analysis, since the choice of the method of quantitative determination of the components of the analyzed substance depends on the results of qualitative analysis.

Qualitative and quantitative chemical analysis unites the fact that, firstly, they are necessarily based on the so-called analytical reaction, and secondly, that the performance of relevant determinations, as a rule, does not require complex measuring devices (instruments).

2. Qualitative analysis. Analytical reaction

In qualitative analysis, depending on the composition of the studied mixture, the following are distinguished:

• analysis of inorganic substances, including determination of cations and anions;

• analysis of organic substances, which includes elemental analysis and functional analysis;

• molecular analysis – analysis of individual chemical compounds.

In chemical methods of analysis, characteristic qualitative analytical reactions are used. A substance that is used to carry out a qualitative analytical reaction is called a reagent.

Analytical reactions – reactions used in qualitative analysis and based on the transformation of the substance under investigation as a result of interaction with an analytical reagent with the formation of products with characteristic analytical features (effects) (formation of precipitates, colored compounds, dissolution of precipitates, release of gases, formation of crystals of a characteristic shape, appearance or quenching of luminescence, coloration of the flame of a gas burner, etc.).

The reaction used in qualitative analysis must meet the following requirements:

- run quickly, almost instantly;

- to be accompanied by an external effect: the formation of a characteristic sediment, gas or the appearance of color;

- to be practically irreversible, i.e. to run mainly in one direction;

- be as specific as possible and have high sensitivity.

The sensitivity of reactions is determined by the following parameters:

The limit of detection (mmin or Cmin) is the smallest mass or concentration of a substance that can be distinguished from the signal of a control experiment with a given confidence probability.

The minimum (limit) concentration (Smin) is the smallest concentration of ions or substances at which this reaction still allows them to be detected in a small volume of solution (0.01-0.03 cm3).

$$C_{мін} = \frac{1}{V}, г/см^3$$

where V is the volume of the solvent, cm3, which is per 1 g of the substance or ions to be determined.

The limiting dilution (W) is the inverse of the minimum concentration

$$W = \frac{1}{C_{\min}}, см^3 / г$$

The relationship between these indicators is defined as follows:

$$m = C_{\min} \cdot V_{\min} \cdot 10^6$$

where: m is the opening minimum, μg;

C_{min}— limit concentration, g/cm^3;

W— limit dilution;

V_{min}— the minimum volume of the solution required for the determination of the studied ions, cm^3.

Conditions affecting the sensitivity of the analytical reaction:

1) sufficient concentration of the reagent and the analyzed substance in the solution being analyzed;

2) the presence of an appropriate pH value of the environment;

3) compliance with the temperature regime;

4) the volume of the aliquot (the volume of the sample of the analyzed substance) taken for one analysis;

5) sequence of adding reagents.

Ways to increase the sensitivity of the analytical reaction:

1) the increase in concentration is determined by the substance in the solution being analyzed and the reagent being added;

2) creation of conditions for acceleration of sediment formation (cooling of the solution, introduction of crystallization centers, addition of organic solvent, etc.);

3) reducing the solubility of sediment by adding organic non-electrolytes, for example, ethanol, ether;

4) use of masking of interfering ions.

Masking is the elimination of the impact of interfering ions by binding them into complex compounds with the help of complexons, tartaric acid, fluoride ion, chloride ion.

Analytical reactions can be performed "dry" and "wet". In the first case, the substance under study and reagents are taken in a solid state and the reaction is usually carried out by heating them to a high temperature; in the second case, the interaction of the investigated substance and the corresponding reagents in the solution is observed.

Reactions carried out dryly include flame coloring reactions with metal salts, as well as float coloring reactions obtained by heating a substance with potassium tetraborate or sodium phosphate in the ear of a platinum wire.

Most analytical reactions are carried out wet, i.e. in solutions, and in the process of dissolution many substances disintegrate (dissociate) into ions - positively and negatively charged particles, so they are written in the abbreviated ionic form**:**

• for strong electrolytes, only the ions that react to form a sparingly soluble compound, a weak electrolyte, or a gaseous product are recorded, e.g.:

$$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4\downarrow$$

• weak electrolytes, sparingly soluble and gaseous substances are written in molecular form, e.g:

$$BaCO_3 + 2CH_3COOH \rightarrow Ba^{2+} + 2CH_3COO^- + H_2O + CO_2\uparrow$$

Methods of the technique of performing characteristic reactions by the wet method:

1) Test-tube - the deposition reaction is carried out in centrifuge tubes, which place a few drops of the test solution and add a few drops of the reagent, stir with a glass rod.

Tubeless:

a) dropwise - by mixing a drop of the test solution and a reagent on a porcelain (ceramic or glass) plate with depressions, on glass or on filter paper or in a drop tube

b) microcrystalloscopic - apply 1-2 drops of the solution under study and 1-2 drops of the reagent, which gives the characteristic formation of crystals, which are examined under a microscope

c) extractive.

In analytical chemistry, such reactions as characteristic, specific and group are widely used.

Characteristic reactions are those reactions in which products with particularly pronounced external features are formed with this type of ions: a pronounced crystal structure of the precipitate or the color of the precipitate; distinct change in the color of the solution; gassing.

Specific reactions are reactions that allow one or another substance (ion) to be detected in the presence of other substances (ions).

Selective reactions are analytical reactions of a reagent with a limited number of ions. The smaller the number of ions that react with a given reagent, the more selective this reaction and reagent are.

Group reactions are analytical reactions of a reagent with a certain group of ions, which allow to separate this group from other ions.

Group reagents must meet certain requirements:

• quantitatively separate ions according to their analytical groups (residual concentration in the solution should not exceed 10-6 mol/l);

• an excess of group reagent should not interfere with the detection of ions remaining in the test sample;

• the precipitate obtained should be easily soluble in certain reagents for further analysis.

4. Qualitative analysis of cations

In most cases, when analyzing cations, the presence of some ions interferes with the determination of others, because specific reactions exist only for individual ions. In this regard, detection of ions is most often carried out using a systematic course of analysis. There are two methods of analysis: fractional and systematic.

- Systematic - separation of a mixture of ions using group reagents into groups and subsequent detection of ions using selective reactions.
- Fractional – detection of each ion in the presence of others using specific reactions or carrying out reactions under conditions that exclude the influence of other ions.

Depending on the used group reagent, the following classifications of systematic analysis are distinguished: hydrogen sulfide (sulfide), ammonia-phosphate, and acid-base. Hydrogen sulfide is based on the solubility of sulfide cations, ammonia-phosphate - on the different solubility of phosphate cations, and acid-base - on the different solubility of hydroxides and some salts formed by cations and strong acids. The most widely used classification is the acid-base classification in which cations are divided into 6 groups.

Group	Cations	Group reagent	Analytical effect
I	Na^+, K^+, NH_4^+	Absent	Absent
II	Ag^+, Hg_2^{2+}(I), Pb^{2+}	Solution HCl (2 M)	White precipitates
III	Ca^{2+}, Sr^{2+}, Ba^{2+}	Solution H_2SO_4 (1	White precipitates,

		M) (+C_2H_5OH)	insoluble in acids and bases
IV	Zn^{2+}, Al^{3+}, Sn^{2+}, Sn^{4+}, Cr^{3+}, As^{3+},As^{5+}	Solution NaOH (6M) in the presence 3% H_2O_2	Precipitates soluble in an excess of group reagent
V	Mg^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Sb^{3+}, Sb^{5+}, Bi^{3+}	Excess solution NH_4OH	Precipitates not soluble in an excess of group reagent
VI	Cu^{2+}, Co^{2+}, Hg^{2+} (II), Ni^{2+}	Excess solution NH_4OH	Precipitates soluble in an excess of group reagent

General material and bulk-methodological support of the lecture:

- ✓ computer presentation;
- ✓ illustrative materials;
- ✓ examples of solving typical tasks or performing typical tasks;
- ✓ multimedia projector.

Questions for self-control:

1. Subject, problems of analytical chemistry.
2. What is the difference between method and technique of analysis.
3. What is an analytical reaction? What are the requirements for it?
4. What is the sensitivity of the reaction? What are its characteristics?
5. Methods of performing an analytical reaction (dry and wet). A brief description of each of the methods.
6. What is a systematic analysis? What is the fractional method?
7. What are the classifications of cations depending on the group reagent?
8. Characterize groups of cations by acid-base classification.

References:

General:

1. Analytical chemistry: handbook / V. V. Bolotov, O. A. Yevtifeyeva, L. Yu. Klimenko, T. A. Kostina, T. V. Zhukova, E. Yu. Ahmedov , O. A. Brizicky; edited by V. V. Bolotov.— Kharkiv: NUPh; Original, 2012.
2. Analytical chemistry (Qualitative analysis). Part I / O. A. Ievtifieieva, V. V. Bolotov, T. A. Kostina, O. M. Svechnikova, T. I. Yuschenko, N. I. Kaminska, A. E. Kosareva, L. V. Slobodyanyuk, O. P. Yashchuk ; edited by O. A. Ievtifieieva. – Kharkiv : Publishing house the CLL «Generous farmstead plus», 2014. – 168 p.
3. Analytical chemistry. Part II. Quantitative analysis: the manual for foreign students of pharmaceutical higher schools and pharmaceutical departments of medical higher schools of the III – IV accreditation levels / V. V. Bolotov, O. M. Svechnikova, T. A. Kostina et al. – Kharkiv: NUPh, 2010. – 160 p.
4. Analytical chemistry: textbook [the textbook for students of higher schools] / I.S. Grytsenko, V. V. Bolotov, L.Yu. Klimenko et al.; ed. by I.S. Grytsenko – Kharkiv: NUPh, Golden Pages, 2019. – 600 p.

Lecture No. 2

Topic: The main provisions of the theory of strong electrolytes. The law of active masses and its application to different types of ionic equilibria in analytical chemistry. Application of the law of active masses to equilibria in heterogeneous systems and its significance in analytical chemistry.

Relevance of the topic: Analytical chemistry is a science that develops theoretical foundations and practical methods of chemical analysis. Therefore, it is relevant to solve the problems facing analytical chemistry with the help of physical, chemical and physicochemical methods used for the analysis of medicinal products.

Purpose: generalize students' knowledge of the theory of electrolytic dissociation, familiarize students with the concepts of total and active concentration of ions, activity coefficient. To study the law of active masses and its application to various types of ionic equilibria in analytical chemistry, including in heterogeneous systems.

Basic concepts: analytical chemistry, electrolyte, non-electrolyte, dissociation constant, total and active concentration of ions, activity coefficient, solubility product, solubility, solubility constant, salt effect.

Plan and organizational structure of the lecture:

1. Theory of strong electrolytes. Total and active concentration of ions, relationship between them, activity coefficient.
2. The law of active masses and its application to various types of ionic equilibria in analytical chemistry.
3. Heterogeneous systems, solubility constant. Conditions of sediment formation and dissolution.
4. Ionic strength of the solution. Salt effect.

Content of lecture material (lecture text):

1. Theory of strong electrolytes. Total and active concentration of ions, relationship between them, activity coefficient.

All substances are divided into electrolytes and non-electrolytes according to their ability to conduct electricity.

Electrolytes are substances capable of conducting electric current.

According to electrical conductivity and characteristics of electric current transmission, substances are divided into conductors of the first kind (Purposely and their alloys), in which electricity is transferred due to the movement of electrons, and conductors of the second kind, where electricity is transferred with the help of ions.

Substances that do not conduct electricity either in a molten or dissolved state are called non-electrolytes.

Let's recall the main provisions of Arrhenius' theory of electrolytic dissociation.

1. The dissolution of the electrolyte is accompanied by its breakdown into positively and negatively charged ions, which undergo solvation (or hydration, if the solvent is water). The solvated ions are in a state of disordered thermal motion and move in different directions in the solution.

2. When an electric current is passed through a solution or melt of an electrolyte, ions acquire a directional movement: positively charged ions move to the cathode (that is why they got the name cation), and negatively charged ones - to the anode, so they are called anions.

3. Electrolytic ionization is a reversible process, that is, simultaneously with the breakdown of molecules into ions, the reverse process occurs - the combination of ions into molecules - the so-called association.

4. Electrical conductivity and some other general properties of electrolyte solutions are proportional to the total concentration of molecules and ions.

5. Quantitative characteristics of the dissociation process are the degree and constant of dissociation.

The degree of dissociation is the ratio of the concentration of the electrolyte disintegrated into ions to its total concentration in the solution:

$$\alpha = C_{дис}/C_{заг}$$

where $C_{дис}$ і $C_{заг}$ – respectively, the molar concentration of that part of the electrolyte that has broken down into ions, and its total concentration, mol/l.

Depending on the ability of the electrolyte to dissociate and, as a result, on the degree of dissociation in dilute solutions, all electrolytes are divided into separate groups: strong, medium and weak.

Strong electrolytes are those for which the degree of dissociation in dilute solutions has sufficiently high values: $\alpha > 0.3 (\alpha > 30\%)$, which is explained by almost complete dissociation.

Electrolytes of medium strength, for which the degree of dissociation in diluted solutions ranges from $0.02 < \alpha < 0.3$ (or $2\% < \alpha < 30\%$).

Weak electrolytes, which even in dilute solutions dissociate to a very small degree and have low values of the degree of dissociation ($\alpha < 0.02$ or $\alpha < 2\%$).

The fundamental difference between strong electrolytes and weak electrolytes is that the dissociation equilibrium of strong electrolytes is completely shifted to the right, so the equilibrium (dissociation) constant is an undefined value. The modern theory of strong electrolytes, the greatest contribution to the

development of which was made by P. Debye, takes into account the electrostatic interaction between ions.

The main ideas of the theory of strong electrolytes can be reduced to several basic propositions:

1. 1. Strong electrolytes in dilute solutions (C < 0.01 mol/l) undergo a complete irreversible process of dissociation, therefore they are not subject to the law of active masses and the law of Ostwald dilution. Since the dissociation is complete, one would expect the degree of dissociation to be equal to unity (α=1). However, when studying the properties of solutions of strong electrolytes, the value of α turns out to be smaller.

The magnitude of the degree of dissociation of strong electrolytes, determined experimentally, is called the apparent degree of dissociation.

2. The deviation in the value of the degree of dissociation from unity (α<1) is described by the model of ionic atmospheres. Its essence is that despite the presence around each ion of a solvate (hydrate) shell formed by solvent molecules, the forces of electrostatic interaction between ions force them to coordinate in a certain way. As a result, a peculiar layer appears around each ion - the so-called ionic atmosphere, consisting of solvent molecules and ions of the opposite sign. The charge of the ionic atmosphere is opposite in absolute value to the charge of the central ion. Any ion that is part of the ionic atmosphere of a given central ion, in turn, can be considered as another central ion, which also has its own ionic atmosphere. Therefore, such a simplified definition can be given:

An ionic atmosphere is a layer of equally charged ions that surround a certain central ion that has a charge of the opposite sign and tend to approach it due to electrostatic attraction.

3. 3. The electrostatic interaction of ions of the opposite sign takes place taking into account the influence of the ionic atmosphere. As a result of the action of interionic interaction forces, the electrolyte behaves as if

its concentration is lower than the real one. Therefore, the concept of concentration is replaced by the concept of active concentration, or activity.

Activity (*a*) is the effective concentration at which the electrolyte manifests itself in action. The term activity is understood as the value, when substituted into the thermodynamic equations, the calculated values coincide with the experimentally determined ones.

Activity, like molar concentration, has the dimension [mol/l] and the dependence associated with it:

$$a = fC,$$

where f – activity coefficient, a dimensionless quantity by which the concentration must be multiplied to obtain the activity value. The activity coefficient formally takes into account all types of interactions between particles that lead to deviations from the properties of an ideal solution. Therefore, the activity coefficient is determined experimentally.

If $\boldsymbol{f < 1}$, ions in the solution are under mutual influence and then the active concentration is less than the real one (a< **C**), if $\boldsymbol{f \sim 1}$, then the interaction between the ions is practically absent, and the activity is equal to the concentration: a~ **C**.

In studies and calculations that do not require high accuracy, the apparent degree of dissociation α can be used for calculations instead of the activity coefficient *f*:

$$a = f \cdot C = \alpha \cdot C_a$$

The activity coefficient increases with increasing temperature and decreasing concentration of the solution. In addition, the value of the activity coefficient depends on the nature of the electrolyte and the ionic strength of the solution.

The ionic strength of a solution μ is a value determined by the half-sum of the product of the concentrations of all ions in the solution by the square of the charge of each ion *($C_i \cdot z_i^2$):*

$$\mu = \frac{1}{2}(C_1 \cdot z_1^2 + C_2 \cdot z_2^2 + \cdots + C_n \cdot z_n^2)$$

In particular, for dilute aqueous solutions of strong electrolytes at C < 0.01 mol/l, the activity coefficient is related to the ionic strength dependence

$$lgf = -0{,}5117 \cdot z_1 \cdot z_2 \cdot \sqrt{\mu}$$

At a higher concentration, the relationship between the activity coefficient f and the ionic strength of the solution μ is determined using the Debye-Hückel equation:

$$lgf = -\frac{0{,}5117 \cdot z_1 \cdot z_2 \cdot \sqrt{\mu}}{1 + \sqrt{\mu}}$$

The theory of strong electrolytes satisfactorily explains the behavior of dilute solutions, but cannot describe concentrated solutions. Its other drawback is that it does not take into account the chemical processes occurring in solutions of strong electrolytes: the phenomenon of solvation and the possible change in this activity of the solvent, which is a component of the solution.

2. The law of active masses and its application to various types of ionic equilibria in analytical chemistry

Reversible chemical reactions were studied by the Russian scientist M.M. Beketov (1865), who established the influence of the concentration of reactants on the direction and speed of a chemical process. Thus, Beketov came close to formulating the law of active masses. This formulation in a more general form was given later by Gulberg and Waage (1867): the rate of a chemical reaction is directly proportional to the acting masses. Active masses are the concentrations of substances that participate in reactions.

If we denote the concentrations of substances A and B by [A] and [B], then the rate of a chemical reaction according to the law of active masses can be written in the form of equationsя:

$$V = k\,[A][B],$$

where k – the rate constant of a chemical reaction, which shows the fate of the starting substances reacting per unit of time.

Such reactions are very common, in which several molecules of the same substance participate in the elementary act, for example:

$$mA + nB \longrightarrow pAB.$$

In this case, the reaction rate is written by the general formula:

$$V = k\,[A]^{m}\,[B]^{n}\,.$$

As you can see, in the presented version, the concentration is included in the rate equation in a degree that is equal to the numerical coefficient of the chemical equation of the reaction. Thus, the given equations are a mathematical expression of the law of active masses.

The quantitative characteristic of the state of dynamic equilibrium can be expressed through the so-called constant of chemical equilibrium, which can be easily deduced from such considerations. For the reverse chemical reaction type

$$mA + nB\ pC + qD$$

the rate of direct reaction according to the law of active masses

$$V_1 = k_1\,[A]^m\,[B]^n,$$

and the rate of the reverse reaction

$$V_2 = k_2\,[C]^p\,[D]^q$$

At the moment of chemical equilibrium, $V_1 = V_2$, i.e

$$k_1\,[A]^m\,[B]^n = k_2\,[C]^p\,[D]^q$$

By transforming the equation, it is possible to write down for any chemical reaction that occurs in solutions or in a gaseous medium, the expression of the equilibrium constant:

$$K = \frac{k_1}{k_2} = \frac{[C]^p[D]^q}{[A]^m[B]^n}$$

Thus, the chemical equilibrium constant K is a value that is numerically equal to the ratio of the product of the active masses of the reaction products to the product of the active masses of the starting reactants. Moreover, the stoichiometric coefficients are indicators of the degree at the corresponding effective masses.

The chemical equilibrium constant is a characteristic value for each chemical reaction. As the experiment shows, it does not depend on the concentration of reactants, but changes with temperature.

Since the constant of chemical equilibrium, as follows from equation (82), is equal to the ratio of the rate constants of the forward and reverse reactions, it

shows how many times the forward reaction is faster than the reverse under the given conditions and at a given product of the concentrations of the reactants, which is equal to one. If K > 1, then the forward reaction is faster, and, conversely, if K < 1, the reverse reaction is faster.

3. 3. Heterogeneous systems, solubility constant. Conditions of sediment formation and dissolution.

In analytical chemistry, heterogeneous systems - "sediment - saturated solution" are of great importance.

It should be remembered that absolutely insoluble substances do not exist, so if a precipitate has formed in the solution, then the liquid above the solution is a saturated solution of this sparingly soluble electrolyte. A solution that is in dynamic equilibrium with the corresponding solid phase is called saturated.

Strong electrolytes dissociate almost completely in aqueous solution. Among these electrolytes there are highly soluble and poorly soluble substances in water. The solubility of substances corresponds to the concentration of saturated solutions. If a strong electrolyte is poorly soluble in water, its saturated solution will be very dilute. In a saturated salt solution, there is always a certain amount of solid matter in the form of a precipitate. Between the A+ and B- ions of the sparingly soluble strong electrolyte AB and its sediment at a constant temperature, a state of heterogeneous ionic equilibrium is established*:*

$$A^+ + B^- \leftrightarrow AB\downarrow$$

saturated solution precipitate

Applying the law of active masses to heterogeneous sediment - saturated solution systems, the equilibrium in them can be characterized by the equilibrium constant, which in this case is called the solubility product *SP:*

$$SP = [A^+]\cdot[B^-] = \text{const}$$

The solubility product of a poorly soluble strong electrolyte is the product of the equilibrium molar concentrations of cations and anions of this electrolyte in a saturated aqueous solution.

For an electrolyte with a more complex composition A_aB_b, the solubility product is expressed as follows:

$$A_aB_b \leftrightarrow aA^{b+} + bB^{a-}$$

$$SP = [A^{b+}]^a \cdot [B^{a-}]^b$$

Example.1. For silver chloride:

$$AgCl\downarrow \leftrightarrow Ag^+ + Cl^-;$$

$$SP = [Ag^+] \cdot [Cl^-] = 1{,}8 \cdot 10^{-10} \text{(Reference data)}$$

2. For calcium orthophosphate:

$$Ca_3(PO_4)_2\downarrow \leftrightarrow 3Ca^{2+} + 2PO_4^{3-};$$

$$SP = [Ca^{2+}]^3 \cdot [PO_4^{3-}]^2 = 1{,}0 \cdot 10^{-25} \text{ (Reference data)}$$

If the electrolyte concentration in the solution is higher than the SP value, then an excessive amount of the substance precipitates. Therefore, the condition for precipitation of AB electrolyte will be the ratio:

$$C_A^+ \cdot C_B^- > SP \text{ (sediment falls out)}$$

where C_A^+i C_B^-- concentrations of A^+ and B^- ions in the electrolyte solution (obtained by mixing solutions containing arbitrary concentrations of A+ and B- ions, respectively).

If the precipitation condition is not met, ie

$$C_A^+ \cdot C_B^- < SP$$

then the precipitate of sparingly soluble substance is not formed.

Like any other equilibrium constant, the value of SP depends on the temperature, i.e. the solubility of a substance (the concentration of a saturated solution) changes when the temperature increases or decreases.

For sparingly soluble strong electrolytes, the solubility of which increases with increasing temperature, the solubility product increases with increasing temperature**.**

Since SP characterizes the solubility of a substance, knowing its value, it is possible to determine the concentration of ions of a given electrolyte in its saturated solution, i.e. Its solubility (S) in mol/dm^3.

There is a relationship between the solubility product and the solubility of a poorly soluble electrolyte. For AB electrolyte, it has the following mathematical expression:

$$AB\downarrow \leftrightarrow A^+ + B^-;$$

$$SP = [A^+]\cdot[B^-]$$

$$[A^+] = [B^-] = s$$

$$SP = [A^+]\cdot[B^-] = s^2 \text{ або } s = \sqrt{SP}$$

Example. The solubility of silver chloride at 25^0C is:

$$AgCl\downarrow \leftrightarrow Ag^+ + Cl^-;\ SP = [Ag^+]\cdot[Cl^-] = 1{,}8\cdot10^{-10}$$

$$s = \sqrt{SP} = \sqrt{1{,}8\cdot10^{-10}} = 1{,}3\cdot10^{-5}\ \text{mol/dm}^3$$

It is obvious that the concentration of both types of ions $[A^+]$ and $[B^-]$ is also equal to $1.3\cdot10^{-5}$ mol/dm^3.

4. Ionic strength of the solution. Salt effect.

A change in the concentration of one of the electrolyte ions affects the solubility of the substance. If the concentration of one of its ions is artificially increased in a saturated electrolyte solution, then, according to the constancy of the SP value, the concentration of another type of ion must decrease, which means that the solubility of the electrolyte decreases and part of it precipitates out of the solution.

Example. If a saturated solution of calcium sulfate

$$CaSO_4\downarrow \leftrightarrow Ca^{2+} + SO_4^{2-};\ SP = [Ca^{2+}]\cdot[SO_4^{2-}]$$

some well-soluble sulfate (K_2SO_4, Na_2SO_4) is added, then the concentration of sulfate ions SO_4^{2-} increases, and therefore the concentration of Ca^{2+} ions should decrease due to precipitation of $CaSO_4$ in the sediment. Therefore, the solubility of $CaSO_4$ decreases. Adding another well-soluble calcium salt ($CaCl_2$,$Ca(NO_3)_2$) to a saturated solution of $CaSO_4$ causes the same effect - a decrease in the solubility of $CaSO_4$.

If another salt is introduced into the saturated solution of $CaSO_4$, which does not change the concentration of Ca^{2+} and SO_4^{2-} (KCl, $NaNO_3$) ions, then the solubility of $CaSO_4$ will not change.

Summarizing the above, it can be stated that the introduction of ions of the same name (cations or anions) reduces the solubility of a sparingly soluble strong electrolyte.

Therefore, the solubility of such an electrolyte will be greatest if its cations and anions are in the solution in a stoichiometric ratio. If the concentration of one of the ions is artificially increased (by introducing ions of the same name), the solubility of the electrolyte decreases.

Reducing the solubility of a sparingly soluble electrolyte by adding ions of the same name is often used in analytical chemistry.

Example. To exclude the loss of silver cations due to the, albeit small, but still present in AgCl solubility, sodium chloride NaCl solution is added to the solution containing Ag^+ ions (that is, an excess of Cl^- ions is introduced), for example, to a concentration of 0.5 mol/dm3. After precipitation of AgCl, not $1.3 \cdot 10^{-5}$ mol/dm^3 of Ag^+ ions will remain in the solution, but five orders of magnitude less:

$$AgCl\downarrow \leftrightarrow Ag^+ + Cl^-;\ SP = [Ag^+] \cdot [Cl^-] = 1{,}8 \cdot 10^{-5}$$

$$[Ag^+] = SP / [Cl^-] = 1{,}8 \cdot 10^{-5} / 0{,}5 = 3{,}6 \cdot 10^{-10}\ \text{mol/dm}^3$$

Because $s_{AgCl} = [Ag^+]$, then the solubility of AgCl in the presence of an excess of Cl^- ions turns out to be very small, and the results of a quantitative analysis (weighing the sediment) will be slightly more accurate than in the case of an analysis without an excess of chloride ions..

General material and bulk-methodological support of the lecture:

- ✓ computer presentation;
- ✓ illustrative materials;
- ✓ examples of solving typical tasks or performing typical tasks;
- ✓ multimedia projector.

Questions for self-control:

1. Define the terms "electrolyte" and "non-electrolyte".
2. Basic provisions of Arrhenius' theory of electrolytic dissociation.
3. What is activity and activity ratio?

4. Formulate the law of active masses. What is the chemical equilibrium constant?

5. What are saturated and unsaturated solutions?

6. Define the terms solubility product and solubility.

7. How do the ions of the same name affect the solubility of sediments?

References:

General:

1. Analytical chemistry: handbook / V. V. Bolotov, O. A. Yevtifeyeva, L. Yu. Klimenko, T. A. Kostina, T. V. Zhukova, E. Yu. Ahmedov , O. A. Brizicky; edited by V. V. Bolotov.— Kharkiv: NUPh; Original, 2012.
2. Analytical chemistry (Qualitative analysis). Part I / O. A. Ievtifieieva, V. V. Bolotov, T. A. Kostina, O. M. Svechnikova, T. I. Yuschenko, N. I. Kaminska, A. E. Kosareva, L. V. Slobodyanyuk, O. P. Yashchuk ; edited by O. A. Ievtifieieva. – Kharkiv : Publishing house the CLL «Generous farmstead plus», 2014. – 168 p.
3. Analytical chemistry. Part II. Quantitative analysis: the manual for foreign students of pharmaceutical higher schools and pharmaceutical departments of medical higher schools of the III – IV accreditation levels / V. V. Bolotov, O. M. Svechnikova, T. A. Kostina et al. – Kharkiv: NUPh, 2010. – 160 p.
4. Analytical chemistry: textbook [the textbook for students of higher schools] / I.S. Grytsenko, V. V. Bolotov, L.Yu. Klimenko et al.; ed. by I.S. Grytsenko – Kharkiv: NUPh, Golden Pages, 2019. – 600 p.

Lecture No. 3

Topic: Application of the law of active masses to acid-base equilibria. Equilibrium in aqueous solutions of acids and bases. Calculation of pH in different systems. Buffer solutions.

Relevance of the topic: Analytical chemistry is a science that develops theoretical foundations and practical methods of chemical analysis. Therefore, it is relevant to

solve the problems facing analytical chemistry with the help of physical, chemical and physicochemical methods used for the analysis of medicinal products.

Purpose: generalize students' knowledge of modern concepts of acid-base interaction, familiarize students with the concepts of equilibrium in aqueous solutions of acids and bases. Learn how to calculate pH in different systems

Basic concepts: analytical chemistry, electrolyte, non-electrolyte, dissociation constant, total and active concentration of ions, activity coefficient

Plan and organizational structure of the lecture:

1. Protolytic theory of acids and bases
2. Application of the law of active masses to water ionization equilibrium. Ionic product of water.
3. Calculation of pH of solutions of acids, bases, salts, and ampholytes.
4. Mechanism of buffer action.

Content of lecture material (lecture text):

1. Protolytic theory of acids and bases

At the end of the 19th century Swedish chemist Svante Arrhenius created the theory of acids and bases, which is called classical. It was based on the idea of electrolytic dissociation of substances in aqueous solutions. Acids were substances that formed H^+ ions upon dissociation, and substances that formed hydroxide ions OH^- upon dissociation were considered bases. The division into acids and bases was based on the behavior of substances in aqueous solutions.

The processes of ionization and dissociation of substances in solutions are explained by the interaction of the dissolved substance with the molecules of the solvent. As a result of this interaction, compounds of solute ions with solvent ions or molecules are formed. The classical theory of acids and bases cannot explain a number of phenomena that occur when a given substance is dissolved in various solvents. For example, ammonium chloride dissociates into NH_4^+ and Cl^-, that is, it behaves like a salt, but at the same time, ammonium chloride dissolved in liquid ammonia exhibits all the typical properties of acids, up to the ability to dissolve

Purposeles with the release of hydrogen, although H^+ ions in these solutions , obviously, it cannot be.

Urea (carbamide), which is neutral in aqueous solutions, exhibits acid properties in liquid ammonia, and bases in anhydrous acetic acid. Very strong in aqueous solutions, nitric acid dissolved in liquid hydrogen fluoride or anhydrous H_2SO_4 behaves as a base. Similar facts that contradict electrolytic dissociation can be cited a lot.

In 1923, Brønsted and Lowry proposed the protolytic theory of acids and bases, according to which acids include those substances that can split off protons. Substances capable of attaching protons are called bases. This division of substances into acids and bases is not related to the use of any solvent (in the case of the classical theory, such a solvent was water). If we conventionally denote a proton with the sign H+, then the relationship between this acid and its corresponding base can be represented by the equation::

$$\text{Acid} \leftrightarrow \text{Base} + H^+.$$

Thus, the concept of an acid-base pair arises. This definition is broader than the definition of acids and bases according to the classical theory. For example, acetic acid will also be an acid according to the Brønsted theory, since it is able to split off protons:

$$\underset{\text{acid}}{CH_3COOH} \Leftrightarrow \underset{\text{base}}{CH_3COO^-} + H^+.$$

Ammonia will be the basis according to Brønsted's theory, as it is able to attach protons:

$$\underset{\text{base}}{NH_3} + H^+ \Leftrightarrow \underset{\text{acid}}{NH_4^+}.$$

But according to Brønsted, acids are not only molecules, but also ions that can split off protons:

$$NH_4^+ \Leftrightarrow NH_3 + H^+;$$

$$H_2SO_4^- \Leftrightarrow SO_4^{2-} + H^+.$$

From the given examples, we are convinced that neutral molecules, as well as ions, can exhibit protonation properties. Therefore, acids are sometimes divided into molecular, cationic and anionic acids. Molecular acids include, for example, HCl, HNO_3, CH_3COOH, H_2CO_3, H_2O; to cationic ones – H_3O^+, NH_4^+, $[Zn(OH_2)_4]^{2+}$, and to anionic ones – HCO_3^-, $H_2PO_4^-$, HPO_4^{2-}, HS–, etc. Similarly, bases are divided into molecular NH_3, cationic $[Zn(OH)(H_2O)_3]^+$ and anionic Cl^-, NO_3^-, CH_3COO^-, HCO_3^-, OH^-.

Some protolytes (H_2O, HCO_3^-) have both proton-donor and proton-acceptor properties. Such protolytes are called amphiprotic or amphiprotic. Amphiprotic solvents are water, alcohols, carboxylic acids, liquid ammonia, anhydrous sulfuric acid:

$$NH_3 + NH_3 \Leftrightarrow NH_4^+ + NH_2^-;$$

$$H_2O + H_2O \Leftrightarrow H_3O^+ + OH^-;$$

$$H_2SO_4 + H_2SO_4 \Leftrightarrow H_3SO_4^+ + HSO_4^-;$$

$$C_2H_5OH + C_2H_5OH \Leftrightarrow C_2H_5OH_2^+ + C_2H_5O^-.$$

If when two molecules of the amphiprotic solvent HSolv collide, one of the molecules exhibits proton-donor properties (acid) and the other has proton-acceptor properties (base), then a protolytic reaction takes place, which is called an autoprotolysis reaction, and equilibrium is established:

$$HSolv + HSolv \Leftrightarrow H_2Solv^+ + Solv^-.$$

Ions of the H_2Solv^+ type are called lionium ions (when H_3O^+-hydroxonium, $H_3SO_4^+$-sulfonium, $H_2NO_3^+$-nitronium, $C_2H_5COOH_2^+$-ethyloxonium), ions of the $Solv^-$ type are called lyate ions (OH^--hydroxide, $C_2H_5O^-$-ethylate, SO_4^{2-}-sulfate, NO_3^- -nitrate).

In a pure solvent and in dilute solutions as it corresponds to the thermodynamic standard state of this substance.

The balance of autoprotolysis is more or less shifted to the left, and the activities of lionium and lyate are low. Therefore, it is convenient to use negative logarithms in practice:

During the course of the autoprotolysis reaction, simultaneously with the formation of one lionium ion, one liate ion is formed.

If the activity of lionium ions exceeds the activity of the lyate ion, the medium becomes acidic, and vice versa, if the activity of lyate ions exceeds the activity of the lyium ion, the medium becomes basic (alkaline).

The degree of acidity or basicity of the environment can be quantitatively assessed using the numerical values of the activities of lionium and liate ions. In practice, it is more convenient to use not activities, but pH and pSolv indicators.

The protolithic theory does not contain the shortcomings of the classical theory. The application of this theory is not limited to aqueous solutions, it is not limited to solutions at all. Protolytic interaction can also occur in the gaseous phase. However, even when considering phenomena in aqueous solutions, the protolytic theory has significant advantages compared to the classical one:

1) common description of acid-base interactions, as a result of which there is no need to consider dissociation and hydrolysis separately;

2) made it possible to quantify the strength of acids and bases.

2. Application of the law of active masses to water ionization equilibrium. Ionic product of water.

Water is a weak electrolyte that ionizes into ions according to the equation:

$$H_2O \leftrightarrow H^+ + OH^-$$

According to the law of active masses:

$$K = \frac{[H^+] \cdot [OH^-]}{[H_2O]}$$

Since dissociation is very insignificant (for example, at a temperature of 25°C, the value of the constant is 1.8·10-16 mol/l), the denominator [H_2O] is taken as undissociated water, the constant concentration of which is:

$$[H_2O] = 1000 \text{ g/l} : 18 \text{ g/mol} = 55.56 \text{ mol/l}$$

The value of the equilibrium constant is constant at a certain temperature, therefore it is combined with the concentration of water into the value of the ion product of water Kw:

$$Kw = Kdiss \cdot [H_2O] = [H^+][OH^-]$$

Kw values are calculated based on the values of the dissociation constant. For example, at a temperature of 25 °C, it is:

$$Kw = 1.8\ 10^{-16} \cdot 55.56 = 10^{-14}\ mol^2/l^2$$

In practice, negative logarithms of values are often used:

$$-lg\ Kw = pKw$$

The value of the ion product is largely influenced by the temperature, as it increases with its growthdegree of dissociation substances S^o, at a temperature of 100 °C, the pKw indicator is already 12.265 (against 14 at a standard temperature of 25 °C).

- Dependence of pKw on pressure
- Dependence of pKw on temperature

The applied value of the ion product of water is based on the equation

$$K_w = [H^+][OH^-]$$

Based on it, it becomes possible to calculate values pH and pOH. For example, in a neutral environment, the concentrations of H+ and OH- ions are equal:

$$[H^+] = [OH^-] = \sqrt{K_w}$$

So, at a temperature of 25 °C, the value of Kw is 10-14, therefore, in a neutral environment, pH and pOH will be equal to:

$$[H^+] = [OH^-] = 10^{-7}\ mol/l;$$

$$pH = pOH = ½ \cdot 14 = 7$$

3. Розрахунок pH розчинів кислот, основ, солей, амфолітів.

Calculation of pH of solutions of acids, bases, salts, and ampholytes.

Protolytic equilibrium is an equilibrium in which a proton is involved - the Hydrogen ion H+. Reactions of acids or bases with a solvent involving protons are called protolysis reactions. Acid-base reactions (protolytic in the general sense) are one of the equilibria in a homogeneous system, so the calculation of the

equilibrium concentrations of reaction components is carried out using the law of active masses and the material balance condition.

Calculation of pH of solutions of strong acids and bases.

Write down the dissociation reaction of a strong acid

$$HA + HS \Rightarrow SH_2^+ + A^-$$

or to simplify the expression:

$$HA \Leftrightarrow H_+ + A^-.$$

Here and in further calculations, we assume that fa = 1, then in a solution of a strong acid In this case:

$$pH = -\log[H+]$$

for a solution of strong acid HA.

Example 1.. $C_m(HCl) = 0{,}01$ mol/l.

$[H^+] = C_{HCl} = 0{,}01 = 10^{-2}$ mol/l. Then $pH = -\lg C_{HCl} = -\lg 10^{-2} = 2{,}00$.

Similarly in solutionstrong base B:

$$pOH = -\log[OH^-]$$

$$pH = 14 - pOH$$

Example 2. $C_m(NaOH) = 10^{-2}$ mol/l; $[OH^-] = C_{NaOH} = 10^{-2}$ mol/l;

$$pOH = -\lg 10^{-2} = 2{,}0;\ pH = 14\text{-}2 = 12$$

Similar calculations can be performed only if there are no other sources of protons in the solution or if they can be neglected. So, for example, protons that are formed during the dissociation of water can be neglected in relatively concentrated solutions of acids ($C \geq 1 \cdot 10^{-4}$ mol/l). At concentrations of strong acids (bases) less than $1 \cdot 10^{-4}$ mol/l, dissociation of water should be taken into account. The electroneutrality equation helps to account for solvent dissociation when calculating pH.

Calculation of the pH of solutions of weak acids and bases.

In solutions of weak acids, it must be taken into account that not all acid molecules dissociate into ions. Weak acids (HA) and bases (BOH) in aqueous solutions do not completely (partially) ionize, for example:

$$HA \Leftrightarrow H^+ + A^-$$

$$BOH \Leftrightarrow B^+ + OH^-$$

Therefore, ionization in solutions of such acids and bases must obey the law of active masses:

$$К = \frac{[H^+] \cdot [A^-]}{[HA]}$$

$$К = \frac{[B^+] \cdot [OH^-]}{[BOH]}$$

Thus, the resulting equations are used to calculate pH and pOH in solutions of weak acids and bases. Formulas for calculating the equilibrium concentrations of $[H^+]$ and $[OH^-]$ can be obtained from the expression for the equilibrium constants of a weak acid or a weak base:

$$[H^+] = \sqrt{K \cdot C_{HA}}$$

$$[OH^-] = \sqrt{K \cdot C_{BOH}}$$

Values of K_a and K_b for many acids (K_a) and bases (K_b) are given in the reference literature.

Let's consider an example: Calculate $[H^+]$, pH in a 0.4% solution of hydrocyanic (hydrocyanic) acid.

Hydrocyanic acid is a weak acid and does not completely ionize in solution:

$$HCN \Leftrightarrow H^+ + CN^-$$

$$K_{HA} = 5 \cdot 10^{-10}$$

Вираз для константи іонізації:

$$K_{HA} = \frac{[H^+] \cdot [CN^-]}{[HCN]}$$

Denote $[H^+] = x$, then according to the ionization equation:

$$[H^+]=[CN^-]=x$$

Therefore, the equilibrium concentration of the non-ionized acid is equal to the initial concentration of the acid (C) minus the concentration of the ionized part (x):

$$[HCN]= C – x$$

Since hydrocyanic acid weakly ionizes into ions, assuming x<<C, we can assume Cx ≈ C, then

$$K_{HA} = \frac{x^2}{C}$$

where:

$$[H^+] = \sqrt{K \cdot C_{HCN}}$$

where C – is the molar concentration of the electrolyte.

To convert the mass percentage of HCN into molar concentration, we use the formula:

$$C_M = \frac{10 \cdot \omega \cdot \rho}{M} = 0{,}148 \text{ моль/л}$$

where: ρ – is the density of the hydrocyanic acid solution (g/cm^3), taken equal to 1 g/cm^3 due to the low concentration of the solution;

ω – concentration of hydrocyanic acid (%);

M is the molar mass of hydrocyanic acid..

Let's calculate the pH:

$$[H^+] = \sqrt{K \cdot C_{HCN}} = \sqrt{5 \cdot 10^{-10} \cdot 0{,}148} = 8{,}6 \cdot 10^{-6}$$

$$pH = -\lg 8{,}6 \cdot 10^{-6} = 5{,}06$$

4. Mechanism of buffer action.

Solutions that maintain a constant pH value when small amounts of strong acids and alkalis are added, as well as when diluted, are called protolytic buffer systems.

The ability of some solutions to maintain an unchanged concentration of hydrogen ions is called buffer action, which is the main mechanism of protolytic homeostasis

Buffer solutions are mixtures of weak bases or weak acids and their salts. In buffer solutions, according to the Brønsted-Lowry theory, the main "active" components are the proton donor and acceptor.

The reason for the emergence of a new quality in solutions - buffer action - is the combination of several protolytic equilibria.

$$B(base) + H^+ \rightleftarrows HB^+ (acid)$$

$$HA(acid) \rightleftarrows H^+ + A^- (base)$$

Combined acid-base pairs HB^+/B і HA/A^- are called buffer systems, which represent combined equilibria of ionization and hydrolysis processes.

Acetate buffer: weak acid and its salt ($CH_3COOH + CH_3COONa$).

When adding H^+ ions

$CH_3COO^- + H^+ \Leftrightarrow CH_3COOH$;

When adding OH- ions

$CH_3COOH + OH^- \Leftrightarrow CH_3COO^- + H_2O$.

When such a solution is diluted with water, the concentration of both salt and acid decreases multiple times, so the pH remains constant.

Ammonia buffer: a weak base and its salt ($NH_3 + NH_4Cl$).

When adding H^+ ions:

$NH_3 + H^+ \Leftrightarrow NH_4^+$;

When adding OH- ions:

$NH_4^+ + OH^- \Leftrightarrow NH_3 \cdot H_2O$.

Dilution of such a buffer solution with water leads to a multiple decrease in the concentration of both the base and the salt, so the pH remains constant.

The following solutions of protoliths can be used as buffer systems (solutions):

1. Concentrated solutions of strong acids and bases.

The buffer action mechanism is, of course, completely different here. It is clear that with a high concentration of acid or alkali, enough acid or alkali must be

added to noticeably change the pH of the solution. The addition of small amounts of acid or alkali practically does not change the pH.

2. Mixtures of a weak acid and its salt.

For example, acetate buffer $CH_3COOH + CH_3COONa$.

$CH_3COOH \Leftrightarrow CH_3COO^- + H^+$.

Since acetic acid is a weak acid, its dissociation is quite insignificant, and in the presence of its salt (significant concentration of the acetate ion from the salt) it is completely suppressed. Therefore $[CH_3COOH] = C_{acid}$.

The ability of buffer mixtures to maintain a practically constant pH value is based on the fact that their individual components bind H^+ or OH^- ions of acids or bases that are introduced or formed. Of course, this ability is not unlimited, its limit depends on the concentrations of the components of the buffer mixture. For example, if more than 0.1 mol of HCl or NaOH is added to 1 L of 0.1 M ammonium buffer mixture (that is, a mixture containing $NH_4OH + NH_4Cl$ in concentrations equal to 0.1 M), then in both cases a very sharp change in pH will occur solution, since the amounts of NH_4OH or NH_4Cl present in it will not be enough to bind H^+ or OH^-. At the same time, an excess of added strong acid or alkali will remain in the solution, which will cause a sharp change in pH.

Based on this, the following features of buffer solutions can be noted:

1. Any buffer mixture practically remains constant only when a certain amount of acid or alkali is added, that is, it has a buffer capacity.

Buffer capacity is the number of equivalents (or moles) of strong acid or strong base that must be added to 1 L of buffer solution to change its pH by 1.

Buffer capacity P. If a strong base is added to the solution, the pH of the solution increases due to a decrease in the concentration of the acid and an increase in the concentration of the conjugate base per dCB.

If a strong acid is added to the buffer solution, the pH of the solution decreases due to the increase in the concentration of the conjugate acid on dCHA.

To calculate the buffer capacity of a buffer solution that contained a weak acid and its salt (conjugate base), in most cases, the formula is used:

$$\Pi = 2{,}3\frac{C_A C_B}{C_A + C_B}$$

2. . The maximum buffer capacity is observed in solutions that contain equal concentrations of a weak acid and its salt or a weak base and its salt.

3. The buffer capacity of the solution is greater, the higher the concentration of the components of the buffer mixture.

4. As acid or alkali is added to the buffer solution, the resistance of the solution to pH changes gradually decreases.

Thus, when using buffer mixtures in the analysis, it is necessary to take into account their capacity.

General material and bulk-methodological support of the lecture:

- ✓ computer presentation;
- ✓ illustrative materials;
- ✓ examples of solving typical tasks or performing typical tasks;
- ✓ multimedia projector.

Questions for self-control:

1. Modern ideas about acid-base interaction.
2. Comparison of Arrhenius and Brønsted-Lowry theories.
3. Classification of solvents. Influence of the nature of the solvent on the strength of acids and bases.
4. Equilibrium in aqueous solutions of acids and bases.
5. Calculation of pH in various systems: solutions of strong and weak acids and bases, as well as hydrolyzable salts.
6. Buffer solutions. Preparation, examples

References:

General:

1. Analytical chemistry: handbook / V. V. Bolotov, O. A. Yevtifeyeva, L. Yu. Klimenko, T. A. Kostina, T. V. Zhukova, E. Yu. Ahmedov , O. A. Brizicky; edited by V. V. Bolotov.— Kharkiv: NUPh; Original, 2012.

2. Analytical chemistry (Qualitative analysis). Part I / O. A. Ievtifieieva, V. V. Bolotov, T. A. Kostina, O. M. Svechnikova, T. I. Yuschenko, N. I. Kaminska, A. E. Kosareva, L. V. Slobodyanyuk, O. P. Yashchuk ; edited by O. A. Ievtifieieva. – Kharkiv : Publishing house the CLL «Generous farmstead plus», 2014. – 168 p.
3. Analytical chemistry. Part II. Quantitative analysis: the manual for foreign students of pharmaceutical higher schools and pharmaceutical departments of medical higher schools of the III – IV accreditation levels / V. V. Bolotov, O. M. Svechnikova, T. A. Kostina et al. – Kharkiv: NUPh, 2010. – 160 p.
4. Analytical chemistry: textbook [the textbook for students of higher schools] / I.S. Grytsenko, V. V. Bolotov, L.Yu. Klimenko et al.; ed. by I.S. Grytsenko – Kharkiv: NUPh, Golden Pages, 2019. – 600 p.

Lecture No. 4

Topic: Redox balances. Redox potential and Nernst equation. Application of redox reactions in analytical chemistry.

Relevance of the topic: Analytical chemistry is a science that develops theoretical foundations and practical methods of chemical analysis. Therefore, it is relevant to solve the problems facing analytical chemistry with the help of physical, chemical and physicochemical methods used for the analysis of medicinal products.

Purpose: generalize students' knowledge of redox reactions, familiarize students with the concepts of equilibrium in redox reactions and factors affecting the course of redox reactions.

Basic concepts: analytical chemistry, oxidation-reduction reaction, oxidizer, reducing agent, oxidation, reduction

Plan and organizational structure of the lecture:

1. Redox reactions
2. Formal (real) potential E°′

3. Equilibrium constants of the redox reaction

Content of lecture material (lecture text):

1. Redox reactions

Redox reactions are reactions accompanied by the transfer of electrons from one particle (atoms, molecules, and ions) to another, which leads to a change in the degree of oxidation of elements. A redox reaction consists of two half-reactions: an oxidation half-reaction and a reduction half-reaction. Oxidation is the return of electrons, reduction is the acquisition of electrons.

The most commonly used reducing agents in analytical chemistry are: H_2O_2, $SnCl_2$, H_2S, H_2SO_3, $Na_2S_2O_3$; as oxidizing agents - Cl_2; Br_2; H_2O_2; $K_2Cr_2O_7$; $KMnO_4$; HNO_3.

The main types of redox reactions include the following:

1 – intermolecular redox reactions (elements that change the degree of oxidation are part of different molecules)

2 – intramolecular redox reactions (elements that change the degree of oxidation are part of one molecule)

3 – disproportionation reactions (self-oxidation-self-reduction) (atoms of the same element change their oxidation state differently).

2. Формальний (реальний) потенціал E°′

Formal (real) potential E°′

The value of the formal (real) potential E°′ is a characteristic of the oxidation-reduction capacity of the steam. The formal potential is equal to the equilibrium potential, in the case when the concentrations of the oxidized and reduced forms are equal to 1M, and the concentrations of all other substances participating in the redox equilibrium are known.

The formal potential takes into account the ionic strength of the solution, in the Nernst equation this is reflected by the activity coefficients of the oxidized and reduced forms.

$$E_{Ox/Red} = E°_{Ox/Red} + (0{,}059/n)\lg(\gamma_{Ox}/\gamma_{Red}) + (0{,}059/n)\lg([Ox]/[Red]);$$

$$E^{\circ\prime}_{Ox/Red} = E^{\circ}_{Ox/Red} + (0{,}059/n)\lg(\gamma_{Ox}/\gamma_{Red}).$$

The formal potential is equal to the standard potential in the case where the influence of the ionic force is neglected. In practice, the accuracy of the approximation is sufficient and equilibrium concentrations are used instead of activities for calculations.

3. Equilibrium constants of the redox reaction

A redox reaction is a combination of two half-reactions. The direction and depth of the course of the reaction are determined by the value of the equilibrium constant, which is related to the difference in the standard potentials of the oxidizer and reducer by the ratio:

$$\lg K^{\circ}_{\text{рівн}} = n\Delta E^{\circ}/0{,}059,$$

where n is the total number of electrons participating in the oxidation-reduction reaction (least common multiple).

The conditional equilibrium constant, which determines the direction and depth of the redox reaction in real conditions, is calculated for the difference in formal potentials:

$$\lg K'_{\text{рівн}} = n\Delta E^{\circ\prime}/0{,}059$$

Depending on the value of $K_{\text{рівн}}$, the following cases are possible:

– $K_{\text{рівн}} \geq 1$ (or $\Delta E > 0$), the reaction runs from left to right

– $K_{\text{рівн}} < 1$ (or $\Delta E < 0$) – in the other direction.

A redox reaction can take place in an electrochemical cell, which consists of two electrodes immersed in an electrolyte solution. A corresponding half-reaction takes place at the electrodes. The electrode at which oxidation occurs is the anode at which reduction by the cathode occurs.

The potential difference between the cathode (E_k) and the anode (E_a) determines the electromotive force (EMF) of the cell. If

$$\text{ЕДС} = E_{\text{к}} - E_{\text{а}} > 0,$$

then the redox reaction proceeds arbitrarily, and the electrochemical cell is a galvanic cell. If the EMF < 0, then the reaction takes place in the cell only when energy is supplied from an external source. Such a cell is called an electrolytic cell.

Schematically, the electrochemical cell is written from left to right: anode, phase separation boundary (vertical dash), electrolyte, salt bridge (double vertical dash), electrolyte, phase separation boundary, cathode.

Oxidation-reduction (or redox) processes play an important role in the life of living organisms and plants. Respiration and metabolism, putrefaction and fermentation, photosynthesis, human nervous activity, fuel combustion, corrosion of Purposes, electrolysis, etc. are connected with redox reactions.

Redox reactions are widely used in analytical chemistry, including for quantitative determinations in titrimetry. This is due to the effectiveness and great diversity of the action of oxidizing agents and reducing agents, differences in the conditions of the reactions, etc.

The Nernst equation is important: its analysis and calculations based on it allow predicting the possible direction of the reaction, talking about the depth of this reaction, taking into account the influence of the concentration of hydrogen ions, and choosing a suitable oxidizing agent or reducing agent.

In the lecture, such traditional methods as permanganatometry and iodometry are discussed in detail, attention is drawn to the conditions of reactions and techniques used in these methods. Such methods as dichromatometry and bromatometry are no less interesting. The conditions and features of these methods are of interest from the point of view that they use typical redox indicators as indicators, the mechanism of action of which is based on their nature. The ways of using these indicators are also important.

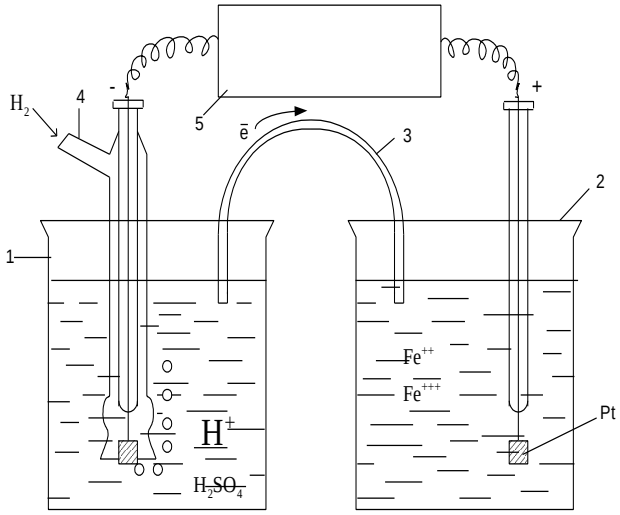

Fig. 1. Scheme of the installation for determining the standard potential of the oxidation-reduction pair Fe^{3+}/Fe^{2+}: 1, 2 glasses; 3- connecting bridge; 4- hydrogen electrode; 5 measuring device (milliammeter).

On Fig. 1 shows the setup for measuring the value of the standard potential Eo of the oxidation-reduction pair Fe^{3+}/Fe^{2+}.

In blood vessels1 and 2 undergo the following processes

$$\mathbf{H_2\uparrow - 2e \leftrightarrow 2H^+} \text{ - } \textit{oxidation}$$

$$\mathbf{2Fe^{3+} + 2e \leftrightarrow 2Fe^{2+}} \text{ - } \textit{recovery}$$

Potentialof each half-element is calculated according to the Nernst equation

$$\mathbf{E_{(2H^+/H2)} = E^o_в + (RT/nF)\ ln\ ([H^+]^2/[H_2])}$$

$$\mathbf{E_{Fe^{3+}/Fe^{2+}} = E^o_o + (RT/nF)\ ln\ ([Fe^{3+}]^2/[Fe^{2+}]^2)}$$

EMF= $E^o_o - E^o_в = 0{,}77 - O = +\ 0{,}77$ (в) = $\Delta E^o_{o/в}$ ($[H^+]$ = 1 моль/л, p = 1 atm., $[Fe^{3+}] = [Fe^{2+}]$ = 1 mol/l).

Analysis of the Nernst equation

1. The magnitude is a measure of the ability of ions to subtract electrons from hydrogen molecules or to add electrons to hydrogen ions.

2. The greater the value of Eo of a given redox pair, the stronger the oxidizing agent is its oxidized form and the weaker the reducing agent is its reduced form.

3. The stronger of the two oxidizing agents takes away electrons from the stronger reducing agent, and a weaker oxidizing agent and reducing agent are formed.

4. If hydrogen ions are consumed during the reaction, then such a reaction should be carried out in an acidic environment; if hydrogen ions are formed as a result of the reaction, then they must be bound with alkali, carbonate, bicarbonate or sodium acetate.

5. The equilibrium constant (Kravn.) of the oxidation-reduction reaction should be greater, the greater the value of ΔEo. Kravn is of great importance. indicates that the reaction proceeds almost to the end.

6. The possibility of changing the direction of the reaction should be especially taken into account when the corresponding oxidation-reduction pairs have close values of Eo.

The direction of redox reactions

Consider the interaction of the oxidizing agent Ox1 and the reducing agent Red2:

$$\text{Ox1} + \text{Red2} \overset{K_{eq.}}{\leftrightarrow} \text{Red1} + \text{Ox2}$$

Ox1 + $\mathbf{n_1 e}$ = Red1 - connected pair **1**

Red2 - $\mathbf{n_2 e}$ = Ox1 – connected pair **2**

$$K_{eq.} = a_{вос1}\, a_{ок2} / (a_{ок1}\, a_{вос2}),$$

$$E_1 = E^o_1 + (0{,}059/n_1) \lg (a_{ок1}/a_{вос1})$$

$$E_2 = E^o_2 + (0{,}059/n_2) \lg (a_{ок2}/a_{вос2})$$

At the equivalence point E1 = E2, therefore

$$E^o_1 - E^o_2 = (0{,}059/n) \lg (a_{ок2}\, a_{вос1}/a_{вос2}\, a_{ок1})$$

$$\lg K_{равн} = \frac{(E^0{}_1 - E^0{}_2) \cdot n}{0{,}059}$$

where n is the smallest multiple of n1 and n2. If Keq. >> 1 - the reaction proceeds to the end; if Keq << 1 - the reaction proceeds in the reverse direction, and if Keq.≈1 - the reaction is possible in both directions.

Example 1. Calculate the equilibrium constant of the reaction:

$$\mathbf{MnO_4^- + 5Fe^{2+} + 8H^+ \leftrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O}$$

In order to determinethe total number of electrons, we write down the half-reaction equations and the values of the standard potentials:

$$\mathbf{MnO_4^- + 8H^+ + 5e \leftrightarrow Mn^{2+} + 4H_2O \quad (E^o = +1{,}51\ B)}$$

$$\mathbf{Fe^{2+} - e \leftrightarrow Fe^{3+} \quad (E^o = +0{,}77\ B)}$$

It can be seen that n=5, therefore lgKeq.=(1.51–0.77)5/0.059=62.7 and Kravn.=$5 \cdot 10^{62}$.

Example 2.Find the direction of reactions::

а) $\mathbf{2Fe^{3+} + 2I^- \leftrightarrow 2Fe^{2+} + I_2}$ ($E^o_{Fe^{3+}/Fe^{2+}}$= +0,77 В, $E^o_{I2/2I^-}$ = +0,53 В)

б) $\mathbf{I_2 + 2Fe^{2+} \leftrightarrow 2I^- + 2Fe^{3+}}$;

Рішення:

а) $\Delta E^o_а$ = 0,77 – 0,53 = + 0,24 В; $\lg К_{равн.}$ = 8,1 или $К_{равн.} = 10^{8,1}$

б) $\Delta E^o_б$ = 0,53 – 0,77 = - 0,24 В; $\lg К_{равн.}$ =-8,1 или $К_{равн.} = 10^{-8,1}$

Calculations are givenCrown values. show that the reaction

and)flows in a straight direction because the emf the value of this reaction is positive, and the equilibrium constant is much greater than unity (Keq>> 1). And since for the reaction

b)value of EMF less than zero and Keq. << 1, then its course is impossible.

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General material and bulk-methodological support of the lecture:

- ✓ computer presentation;
- ✓ illustrative materials;
- ✓ examples of solving typical tasks or performing typical tasks;
- ✓ multimedia projector.

Questions for self-control:

1. Redox equilibria. Using the law of active masses to redox equilibria.
2. Redox potential and the Nernst equation.
3. Equilibrium constant of redox reactions.
4. Factors influencing the course of redox reactions.
5. Application of redox reactions in analytical chemistry.

References:

General:

1. Analytical chemistry: handbook / V. V. Bolotov, O. A. Yevtifeyeva, L. Yu. Klimenko, T. A. Kostina, T. V. Zhukova, E. Yu. Ahmedov , O. A. Brizicky; edited by V. V. Bolotov.— Kharkiv: NUPh; Original, 2012.
2. Analytical chemistry (Qualitative analysis). Part I / O. A. Ievtifieieva, V. V. Bolotov, T. A. Kostina, O. M. Svechnikova, T. I. Yuschenko, N. I. Kaminska, A. E. Kosareva, L. V. Slobodyanyuk, O. P. Yashchuk ; edited by O. A. Ievtifieieva. – Kharkiv : Publishing house the CLL «Generous farmstead plus», 2014. – 168 p.
3. Analytical chemistry. Part II. Quantitative analysis: the manual for foreign students of pharmaceutical higher schools and pharmaceutical departments of medical higher schools of the III – IV accreditation levels / V. V. Bolotov, O. M. Svechnikova, T. A. Kostina et al. – Kharkiv: NUPh, 2010. – 160 p.
4. Analytical chemistry: textbook [the textbook for students of higher schools] / I.S. Grytsenko, V. V. Bolotov, L.Yu. Klimenko et al.; ed. by I.S. Grytsenko – Kharkiv: NUPh, Golden Pages, 2019. – 600 p.

Lecture No. 5

Topic: Complex compounds in analytical chemistry. Factors influencing complexation. Quantitative characteristics of the stability of complex compounds. The use of complex compounds to find, separate and mask ions.

Relevance of the topic: Analytical chemistryis a science that develops theoretical foundations and practical methods of chemical analysis.Therefore, it is relevant to solve the problems facing analytical chemistry with the help of physical, chemical and physicochemical methods used for the analysis of medicinal products.

Purpose: generalize students' knowledge of complex compounds, their structure, familiarize students with the concepts of stability and instability constants.

Basic concepts:analytical chemistry, complex compounds, instability constant, chelate complexes

Plan and organizational structure of the lecture:

1. The structure of complex compounds
2. Classification of complexes
3. Equilibria in solutions of complex compounds
4. Complex instability constants
5. Chelate complexes

Content of lecture material (lecture text):

1. The structure of complex compounds

Along with compounds of the usual type, such as AgCl; $CuSO_4$; HgI_2, compounds with a more complex composition were obtained, for example $[Ag(NH_3)_2]Cl$; $[Cu(NH)_3)_4]SO_4$; $K_4[Fe(CN)_6]$.

The study of molecular compounds was delayed for a long time until new attitudes to the valence bond were introduced into chemistry, first expressed by the Swiss scientist Alfred Werner (1893). They formed the basis of the doctrine proposed by Werner aboutcomplex compounds.

To explain the structure of higher-order compounds, A. Werner introduced into chemistry the concept of main and secondary valence, the so-called

coordination bond, expanding the very concept of valence. Hence, this theory got the name coordination theory.

In most complex compounds, internal and external spheres are distinguished. For example, in the complex compound K2[HgI4], the inner sphere is a grouping of atoms (complex) [HgI4]2-, and the outer sphere is K+. The central atom or ion of the inner sphere is called a complexing agent, and molecules or ions of the opposite sign coordinated around it are called ligands (or addendums). In the formulas of complex compounds, the inner sphere (complex) is often enclosed in square brackets.

The number of addends (ions, molecules) directly connected in the inner sphere with the complexing agent is called the coordination number. It is different for different complexing agents and depends mainly on the nature of the complexing agent and addends, and on the conditions for the formation of a complex compound.

Characteristic coordination number	
Ag^{+}, Au^{+}, Cu^{+}	2
Cu^{2+}, Hg^{2+}, Pb^{2+}, Cd^{2+}	4
Cr^{3+}, Fe^{2+}, Fe^{3+}, Co^{2+}	4-6
Sn^{4+}	6
Ca^{2+}, Sr^{2+}, Ba^{2+}	8

The coordination number in the chemistry of complex compounds is of great importance and is characteristic for these compounds to the same extent as the valence of elements in the formation of simple chemical compounds.

Ligands can occupy one or more places in the coordination sphere, that is, connect to the central atom with the help of one or more atoms. Monodentate, bidentate, tridentate, and polydentate ligands are distinguished by this feature. Examples of monodentate ligands are ions Cl-, F-, CN-, OH-, molecules H_3N, H2O, CO, etc. The bidentate includes, for example, the ethylenediamine molecule H_2N-CH_2-CH_2-NH_2. Complexes with polydentate ligands are called chelate.

2. **Classification of complexes**

According to the nature of the electric charge, cationic, anionic and neutral complexes are distinguished. In the approximation of the ion model, the charge of the complex is the algebraic sum of the charges of the particles that make it up.

A cationic complex can be considered as formed as a result of coordination around a positive ion.neutralmolecules (H_2O, NH_3, etc.): $[Zn(NH_3)_4]Cl_2$.

In an anionic complex, an atom with a positive oxidation state (or a positive ion) acts as a complex former, andligandsthere are atoms of negative oxidation state (or anions): $K_2[BeF_4]$.

Neutral complexes are formed by coordination around the atom of molecules, as well as by simultaneous coordination around the positive ion-complex former of negative ions and molecules $[Pt(NH_3)_2Cl_2]$.

Electroneutral complexes are complex compounds without an outer sphere.

Any element of the periodic system can play the role of a complexing agent. According to their chemical nature, non-purpose elements usually give anionic complexes, in which the atoms of the most electronegative elements ($K[PF_6]$, $K_3[PS_4]$) play the role of ligands.

The ability to form complex compounds of typical Purpose elements is weakly expressed. The few complex ions present are cationic ($[Sr(OH_2)_6]Cl_2$).

Amphoteric elements form both cationic and anionic complexes ($[Al(OH_2)_6]Cl_3$, $K[Al(OH)_4]$).

3. **Equilibria in solutions of complex compounds**

In solutions of complex compounds, there is a system of dynamic equilibria that depends on the nature of the dissolved substance and the nature of the solvent.

Solutions of complex compounds that relate to electrolytes are characterized by dynamic ionic equilibria inherent in electrolytes, i.e. complex compounds in solutions are prone to primary electrolytic dissociation.

Complex salts that do not change in a concentrated solution, when diluted, behave in the same way as simple salts, breaking up into ions. This is confirmed by the change in electrical conductivity of solutions of complex compounds.

For example, in an aqueous solution, $K_2[PtCl_4]$ undergoes primary electrolytic dissociation according to the equation:

$$K_2[PtCl_4] \Leftrightarrow 2K^+ + [PtCl_4]^{2-}.$$

Complex ions in solutions also undergo secondary electrolytic dissociation, which is considered independently of solvation processes and depicted in the form of generally accepted simple equations of electrolytic dissociation:

$$[PtCl_4]^{2-} \leftrightarrow Pt^{2+} + 4Cl^-$$

4. **Complex instability constants**

Knowing the concentration of a complex ion, for example $[Ag(CN)_2]^-$ and determining the concentration of free ions of Purpose $[Ag^+]$ and ligands $[CN^-]$, it is possible to find the numerical value of the dynamic equilibrium constant corresponding to the secondary electrolytic dissociation of the complex.

Such constants are called instability constants, their inverse values are called stability constants. Applying the law of mass action to the equilibrium system:

$$[Ag(CN)_2]^- \leftrightarrow Ag^+ + 2CN^-$$

we will get:

$$\frac{[Ag^+][CN^-]^2}{[Ag(CN)_2^-]} = K_{[Ag(CN_2)]^-},$$

where: K[Ag(CN)2]-- The instability constant.

The smaller the value of the instability constant, the more stable the complex.

Knowing the value of the instability constant of this complex ion, it is possible to calculate the concentration of the complexing agent and the ligand.

Numerical values of the instability constants of some complex ions are given in reference books.

Example 1.Calculate the concentration of the complexing agent and the ligand in 1 M solutions of $[Ag(NH_3)_2]^+$

*Decision:*a) For $[Ag(NH_3)_2]^+$

If we denote $[Ag^+]$ by x, then according to the equation:

$[Ag(NH_3)_2]^+ \leftrightarrow Ag^+ + 2\ NH_3$,

we can write:

$[Ag(NH_3)_2]^+ = 1-x$; $[Ag^+] = x$; $[NH_3] = 2x$

Substitute the values of the concentrations of the complexing agent [Ag+] and the ligand [NH3] into the expression of the instability constant:

$$\frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = \frac{x(2x)^2}{1-x} = K_{[Ag(NH_3)_2]^+} = 5{,}89 \cdot 10^{-8}.$$

Due to the fact that [Ag+] in the weak electrolyte solution is very small compared to the concentration of the complex ion, the value of 1 can be equated to 1. Then we get:

$$4x^3 = 5.89 \cdot 10^{-8}$$

$$x = [Ag^+] = \sqrt[3]{\frac{5{,}89 \cdot 10^{-8}}{4}} = 2{,}4 \cdot 10^{-3}\ \text{моль/дм}^3$$

$$[NH_3] = 2x = 4.8 \cdot 10^{-3}\ \text{mol/dm}^3$$

From the instability constants, it can be concluded that the strength of different complexes is not the same.

Electrolytic dissociation of $[Ag(NH_3)_2]^+$and $[Ag(CN)_2]$-proceeds according to the equation:

$$[Ag(NH_3)_2]^+ \leftrightarrow Ag^+ + 2NH_3,$$

$$[Ag(CN)_2]^- \leftrightarrow Ag^+ + 2CN^-$$

Applying the law of mass action to these equilibrium systems, we get:

$$K_{[Ag(NH_3)_2]^+} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = 5{,}89 \cdot 10^{-8},$$

$$K_{[Ag(CN)_2]^-} = \frac{[Ag^+][CN^-]^2}{[Ag(CN)_2^-]} = 1 \cdot 10^{-21}.$$

A comparison of values shows that $[Ag(CN)_2]^-$ is more stable, the instability constant of which is much smaller than the instability constant of $[Ag(NH_3)_2]^+$.

The following practical conclusions can be drawn from the equations of the instability constants of the complexes:

1. Electrolytic dissociation of a complex ion decreases when an excess of a complexing agent is added, which binds this ion to a complex compound. Thus, the electrolytic dissociation of $[Ag(NH_3)_2]^+$ becomes more difficult with an increase in the concentration of ammonia in the solution.

2. Strengthening of the electrolytic dissociation of the complex can be achieved by reducing the concentration of the reagent that binds the complex compound ion.

5. Chelate complexes

An organic ligand molecule must have certain specific groups that ensure the appearance of a donor-acceptor bond, which is accompanied by an analytical effect. These groupings are called functional analytical groups (FAG). Phages are able to bind to Purposel ions, both ionic and covalent bonds. As seen in the examples above, they include heteroatoms of electronegative p-elements with lone pairs of electrons.

In complex compounds, phage binds directly to the central atom. In order to enter into a complexation reaction, an organic ligand must have phages arranged in a certain way. For example, among diatomic phenols, compounds with para- and purpose-positions of OH groups are weakly active due to the distant location of PHAG, while ortho-phenols (pyrocatechin) give strong complexes, since the OH groups are located nearby.

According to Chugaev's rule of cycles:

1. Complex formation includes organic reagents that form cycles with Purposel ions. Cycles can be 4-, 5-, 6-, 7- and 8-membered.

2. The more cycles formed around the Purposel ion, the more stable the compound.

3. If there are groups in the organic ligand that tend to form hydrogen bonds, then they increase the strength of the complex, creating additional cycles.

4. The increased strength of complex compounds with polydentate ligands is called the chelation effect.

The activity of organic ligands, in addition to phages, is influenced by other groups of atoms that change the analytical properties of the reaction product

(solubility, color intensity). These groups are called analytically active (AAG). The properties of AAG in organic ligands are played by auxochromic groups that affect the system of conjugated π-bonds and deepen the color of the complex (-Cl, -Br, -J, $-C_6H_5$, etc.), as well as groups that improve the solubility of complexes ($-SO_3H$, -COOH).

Complex compounds of the chelate type are widespread in nature, are of great importance in medicine, and are used as medicines.

General material and bulk-methodological support of the lecture:

- ✓ computer presentation;
- ✓ illustrative materials;
- ✓ examples of solving typical tasks or performing typical tasks;
- ✓ multimedia projector.

Questions for self-control:

1. The structure of complex compounds.
2. Quantitative characteristics of stability of complex compounds.
3. Complex compounds in analytical chemistry. Factors affecting complex formation.
4. The use of complex compounds for the purpose of finding, separating and masking ions.

References:

General:

1. Analytical chemistry: handbook / V. V. Bolotov, O. A. Yevtifeyeva, L. Yu. Klimenko, T. A. Kostina, T. V. Zhukova, E. Yu. Ahmedov , O. A. Brizicky; edited by V. V. Bolotov.— Kharkiv: NUPh; Original, 2012.
2. Analytical chemistry (Qualitative analysis). Part I / O. A. Ievtifieieva, V. V. Bolotov, T. A. Kostina, O. M. Svechnikova, T. I. Yuschenko, N. I. Kaminska, A. E. Kosareva, L. V. Slobodyanyuk, O. P. Yashchuk ; edited by O. A.

Ievtifieieva. – Kharkiv : Publishing house the CLL «Generous farmstead plus», 2014. – 168 p.
3. Analytical chemistry. Part II. Quantitative analysis: the manual for foreign students of pharmaceutical higher schools and pharmaceutical departments of medical higher schools of the III – IV accreditation levels / V. V. Bolotov, O. M. Svechnikova, T. A. Kostina et al. – Kharkiv: NUPh, 2010. – 160 p.
4. Analytical chemistry: textbook [the textbook for students of higher schools] / I.S. Grytsenko, V. V. Bolotov, L.Yu. Klimenko et al.; ed. by I.S. Grytsenko – Kharkiv: NUPh, Golden Pages, 2019. – 600 p.

Lecture No. 6

Topic: Quantitative analysis. Basic principles and methods. Classification. Mathematical processing of quantitative analysis results.

Relevance of the topic: Analytical chemistryis a science that develops theoretical foundations and practical methods of chemical analysis.Therefore, it is relevant to solve the problems facing analytical chemistry with the help of physical, chemical and physicochemical methods used for the analysis of medicinal products.

Purpose: to acquaint students with the general concepts of quantitative analysis, its classification, and errors that may occur during the analysis.

Basic concepts:analytical chemistry, quantitative analysis, precision, reproducibility, gravimetry, titrimetry, chemical analysis, instrumental analysis.

Plan and organizational structure of the lecture:

1. Quantitative analysis
2. Classification of errors
3. Correctness, reproducibility and accuracy of the analysis
4. Titrimetric analysis
5. Classification of titrimetric methods

Content of lecture material (lecture text):

1.Quantitative analysis

Quantitative analysis provides quantification of components that were found as a result of qualitative analysis. It makes it possible to determine the molecular and elemental composition of the analyzed substance or the content of individual components. Quantitative analysis can be complete when the content of all elements, ions and compounds is determined. Sometimes only individual elements or ions are determined, or the form in which this element is in the analyzed substance (for example, nitrogen in nitrate, nitrite, cyanide and other forms).

Depending on the task of the analysis, the content of the main substance (for example, the content of CaO in limestone) or the content of impurities can be determined. Great importance is attached to the content of micro impurities, especially when analyzing the environment. Thus, quantitative analysis can be characterized as a set of methods that allow to determine with the necessary accuracy the quantitative composition of individual components, the substance being analyzed, or the quantitative content of micro impurities.

According to the measured property of the substance, methods of quantitative analysis are classified into chemical, physical, and physicochemical.

Chemical methods of analysis are based on chemical reactions, during which an analytical signal is generated (mass of sediment - weight analysis, volume of reagent - volume analysis). Chemical methods of quantitative analysis include: weight analysis (gravimetry), volumetric analysis (volumetric, titrimetric) and volumetric gas analysis. The latter in modern practice of chemical engineeringAliza is almost not used.

Physical methods are based on the existence of a dependence between the content of the substance being analyzed and the physical properties of the sample (measurement of radiation intensity, electrical conductivity, etc.).

In physico-chemical methods, a chemical reaction is carried out, the progress of which is monitored by physical methods.

Traditionally, physical and physicochemical methods are united under the common name of instrumental methods of analysis (photometry, potentiometry,

emission spectral analysis, luminescence and others). Chemical and instrumental methods have their positive properties and disadvantages.

Chemical methods are accurate (relative error 0.5-1.0%), cheap, and do not require the use of special equipment. But they are not express (long-lasting), labor-intensive, require a lot of time to prepare the sample for analysis and are characterized by low sensitivity. Their use often requires concentration and masking. Instrumental methods have high sensitivity (low detection limit), express (sometimes 2-3 minutes), can sometimes be used without special sample preparation, but require special equipment, highly qualified personnel and have relatively low accuracy (up to 50% depending on the method and content analyzed substance).

2.Classification of errors

Metrology (from the Greek metron - measure, logos - study) is the science of measurements and methods of achieving their unity and the necessary accuracy. At the junction of applied mathematics and experimental chemistry, a new branch of science emerged - chemometrics. Chemometrics studies methods of error detection, experiment planning, and pattern recognition.

The measurement error is the deviation of the measurement result from the true value of the measured value. The true content of the component in the sample is unknown due to analysis error. In practice, the so-called valid (reliably established) content equal to the arithmetic mean of several parallel determinations is used instead of the true one.

Errors are classified as:

1. According to the method of expression: absolute is the valid content of aanalyzed component in the sample;relative

2. According to the nature of the manifestation:

2.1. Systematic errors. They remain constant during repeated measurements or change regularly. The sign of the error does not change.

2.2. Random errors. With repeated measurements, they change randomly.

2.3. Gross misses. The obtained error significantly exceeds the expected one under the given conditions. Gross errors occur as a result of gross errors of the analyst - loss of sediment during weighing, spilling of the solution with sediment during filtering, etc.

3. According to the method of processing the results of parallel determinations: – arithmetic averages; - root mean square.

Systematic errors

Their sources are quite numerous. According to the nature of the manifestation, permanent systematic errors are distinguished, they retain their value for a long time and are the most frequent. Progressive systematic errors continuously increase or decrease.

Sources of systematic errors:

-andinstrumental errors associated with the use of various devices in the analysis. The devices used in practice are characterized by a certain class of accuracy, and it is often possible to reduce the instrumental error of determination when using devices with a higher class of accuracy. The source of instrumental error can be: – untested weights; – uncalibrated measuring vessel; – displacement of the spectrophotometer prism; – dark current of photocells, etc.

These errors can be significantly reduced by introducing corrections that are found during calibration or comparing the results obtained with the readings of another device that has a higher class of accuracy and a smaller instrumental error. Inspection of measuring and other devices is carried out by the metrological service on a legal basis.

2. Methodological errors (errors of the method): - solubility of sediment during washing; - instability of photometric solutions over time; - the reaction does not proceed completely, etc.

3. Dirty reagents.

4. Operational or subjective errors, which are related to the operations performed during the analysis, and depend mainly on the analyst's qualifications. If

the analyst does not distinguish colors well, then when titrating with colored indicators, he will always overtitrate the solutions.

5. Error of bias. With repeated determinations, the analyst will choose the value that is closer to the previous result from two equally likely instrument readings.

Systematic errors should be detected and taken into account in the first place, since the estimation of random error makes sense when there is no systematic error or if it exceeds the systematic error.

Techniques for detecting a systematic error (methods of checking correctness)

1. Performing the analysis by an independent method. If the same results are obtained by two or more independent methods, it can be assumed that there is no systematic error and the results of the analysis are correct.

2. Carrying out a blank experiment. The value of the analytical signal obtained as a result of a blank test often characterizes the systematic error, and to obtain the correct result, it is usually subtracted from the analytical signal of the sample.

3. The "entered-found" method.

4. Analysis of a standard sample with certified contents of determined components. The obtained results of the analysis are compared with the passport data of the standard sample.

Standard samples are different materials, the content of the determined components in which is known with a high degree of accuracy. State standard samples (DSZ) and enterprise standard samples (SZP) are distinguished.

Requirements for standard samples:

1. The content of the reference elements should not differ from the valid content.

2. When stored for a long time, the composition of standard samples should not change.

3. The standard sample must have a high uniformity of chemical composition throughout the mass. Homogeneity is proven by special studies. Attestation of

DSZ is carried out in several highly authoritative laboratories using various methods. The analysis is performed by highly qualified analysts.

Random errors

There are no regularities in the occurrence of errors of this type. The existence of random errors is manifested, for example, in the fact that the results of parallel determinations are always slightly different from each other. These errors are processed on the basis of probability theory and mathematical statistics.

3. Correctness, reproducibility and accuracy of the analysis

Systematic error determines the most important concept - correctness, and random error - reproducibility.

The correctness of measurements is the quality of measurements, which reflects the closeness to zero of the systematic error.

Convergence of measurements is the quality of measurements, which reflects the closeness to each other of the results of measurements performed under the same conditions.

Reproducibility of measurements is the quality of measurements, which reflects the closeness to each other of the results of measurements performed under different conditions (at different times, by different methods, by different analysts, etc.).

4.Titrimetric analysis

Titrimetric analysis is a branch of quantitative analysis, which consists in measuring the volumes of solutions of two reacting substances at the moment of their stoichiometry, provided that the concentration of one of the solutions is known.

Solutions whose concentration is known to the fourth decimal place are called standard solutions. They are divided into primary and secondary.

Primary standards are solutions that are prepared from a sample (taken to the fourth decimal place) or using fixanal and that do not change their concentration for a long time.

Raw materials for the preparation of primary standards must meet the following requirements:

– correspondence of the real composition of the substance to its chemical formula;
– solutions should be stable and the concentration of such solutions should not change during storage;
– – the starting substance must react completely with the working solution in accordance with the reaction equation;
– - it is desirable that the starting substances have a high molar mass equivalent. In this case, it is necessary to take a sufficiently large weight of the substance, as a result of which the relative error associated with the inaccuracy of weighing is reduced.

There is a relatively small number of chemical compounds that fully meet all the requirements listed above. These include, for example, such substances as sodium tetraborate, oxalic acid, magnesium sulfate and some others.

Titer standard (fixanal) is an exact weight of a dry substance sealed in a glass ampoule (or an accurately measured volume of a solution of a substance). Standard titers are made in special laboratories.

Secondary standards (working solutions) are solutions that do not meet at least one of the above conditions. They are prepared for 38 approximately and then set to the exact concentration, i.e. standardized against the appropriate primary standard.

The part of the solution that is taken with a measuring pipette is called an aliquot or aliquot.

Before starting work, the burette and measuring pipette are thoroughly washed with distilled water, and then rinsed with the working solution and poured into the burette. In all cases, the titration is carried out at least three times and the average value of the spent volume of the working solution is calculated from the convergent results. The amount or mass of the substance to be determined is calculated from the volume and exact concentration of the working solution. The

process of adding a working solution (titrant) dropwise to a solution of the substance to be determined is called titration. The moment of completion of the reaction is called the stoichiometric point (t.s.). Titrate until one drop of titrant from the burette changes the color of the analyzed solution, i.e. the end point of the titration is reached.

At the same time, the equality is observed: $C_1V_1 = C_2V_2$,

where C1 and C2 are the molar concentrations of the titrant equivalent and the solution of the substance to be determined, respectively; V_1 and V_2 are the volumes of the titrant and the solution of the substance to be determined, respectively.

The end point of the titration can be set: 1) visually - with the introduction of an appropriate indicator into the solution or without an indicator; 2) instrumentally - with the help of devices with appropriate detectors. The chosen chemical reaction must meet the following requirements: - the possibility of recording the analytical effect of the reaction; - absence of adverse reactions; – quantitative interaction between reaction components; - high rate of reaction.

Depending on the type of chemical reaction that is used, the methods of titrimetric analysis are divided into appropriate groups according to the name of the titrant

When studying titrimetric methods of quantitative analysis, it is necessary to learn the Basic concepts of titrimetry. These include concepts of standard (working) solutions and methods of expressing their concentration.

Attention should be paid to the requirements for chemical reactions used in this titration method and methods of indicating the end point of the titration (k.t.p.), as well as the difference between the k.t.p. and equivalence point (TE).

It is important to be able to perform calculations for constructing theoretical titration curves, to analyze the situation of T.E. with respect to the neutrality line, the symmetry of the titration curve, the magnitude of the titration jump and the correct selection of the indicator.

It is necessary to understand the nature of the indicators used, such concepts as the titration index (pT), the interval of the transition of the color of the indicator, and the areas of their use.

The essence of titrimetric (volumetric) analysis is to establish the moment of equivalence during the interaction of solutions determined by the substance and the reagent, which is called the titrant. For this purpose, a titrant is added dropwise to a precisely measured volume of the solution, and the moment when both substances are in an equivalent amount to each other (equivalence point) is recorded.

The content of the component is calculated based on the volume of the standard solution spent on the complete course of the reaction. Therefore, titrimetry is also called a volumetric method of analysis.

Equivalence point is the moment titration, when the equivalent ratio of reacting components is reached, is determined by the substance and reagent.

The end point of the titration is the moment when the titration with the selected indicator ends. Since it is practically impossible to choose an indicator that changes its color at the equivalence point, the moment of the end of the titration does not coincide with the moment of stoichiometric chemical interaction.

Requirements for chemical reactions

1. Speed and stoichiometry of chemical interaction.

2. Absence of adverse reactions.

3. The possibility of fixing kt.t.t.

4. Practical irreversibility.

5.Classification of titrimetric methods

According to the type of chemical reaction, titrimetric methods are divided into:

1) acid-base, complexometric and precipitating (based on ion exchange or precipitation reactions);

2) oxidation-reduction (based on reactions with the transfer of electrons).

According to the method of titration, the following are distinguished:

1) direct titration - direct titration of a specified component of the analyzed object with a standard solution of the corresponding reagent. This method is used when the chemical reactions used fully satisfy the requirements proposed for them.

2) reverse titration - the measured volume of the standard solution of the reagent is titrated with a solution determined by the substance. It is used in cases where direct titration is not possible. An example can be the titration of nitrite ions in an acidic environment with a solution of potassium permanganate.

3) reverse titration (titration by residue) - titration of unreacted substance, which was added to the analyzed solution in the form of an excess of the standard solution of reagent 1; after some time required for the end of the reaction, the excess of reagent 1 is determined by direct titration using a standard solution of reagent 2.

For example, chloride ions are precipitated by adding a standard solution of silver nitrate, the excess of which is then titrated with a standard solution of sodium thiocyanate according to the scheme:

$$\mathbf{C1^- + Ag^+ (acidic) \rightarrow AgCl\downarrow}$$

stand. 1

$$\mathbf{Ag^+ (exc.) + SCN^- \longrightarrow AgSCN\downarrow}$$

stand. 2

The method is used for slow reactions between the substance to be determined and the titrant

4) substitute titration - the exact amount of an auxiliary reagent is added to the analyzed solution, with which the substance being determined forms an equivalent amount of a new substance - a substitute, which is determined by direct titration with the help of a suitable reagent. The method is used if the substance to be determined does not interact with the titrant or the reaction is not stoichiometric. For example, ammonia in ammonium salts is determined according to the scheme:

$$\mathbf{4NH_4^+ + 6CH_2O \rightarrow (CH_2)_6N_4 + 4H^+ + 6H_2O}$$

5) 5) multiplying (multiplicative) titration: during the direct titration of small amounts of substances, very small volumes of the reagent solution are consumed, and the titration error is quite high. Titrant consumption can be increased by using multiplying reactions. For example, if it is necessary to determine small amounts of iodide ions, they are pre-oxidized with chlorine water to iodate:

$$I^- + 3C1_2 + 3H_2O \leftrightarrow IO_3^- + 6C1^- + 6H^+$$

Excess chlorine is removed by boiling, cooled, potassium iodide and sulfuric acid are added:

$$IO_3^- + 5I^- + 6H^+ \leftrightarrow 3I_2 + 3H_2O$$

General material and bulk-methodological support of the lecture:

- ✓ computer presentation;
- ✓ illustrative materials;
- ✓ examples of solving typical tasks or performing typical tasks;
- ✓ multimedia projector.

Questions for self-control:

1. Quantitative analysis. Basic principles and methods. Classification
2. Mathematical processing of quantitative analysis results.
3. Classification of errors
4. Classification of titrimetric methods

References:

General:

1. Analytical chemistry: handbook / V. V. Bolotov, O. A. Yevtifeyeva, L. Yu. Klimenko, T. A. Kostina, T. V. Zhukova, E. Yu. Ahmedov , O. A. Brizicky; edited by V. V. Bolotov.— Kharkiv: NUPh; Original, 2012.
2. Analytical chemistry (Qualitative analysis). Part I / O. A. Ievtifieieva, V. V. Bolotov, T. A. Kostina, O. M. Svechnikova, T. I. Yuschenko, N. I. Kaminska,

A. E. Kosareva, L. V. Slobodyanyuk, O. P. Yashchuk ; edited by O. A. Ievtifieieva. – Kharkiv : Publishing house the CLL «Generous farmstead plus», 2014. – 168 p.

3. Analytical chemistry. Part II. Quantitative analysis: the manual for foreign students of pharmaceutical higher schools and pharmaceutical departments of medical higher schools of the III – IV accreditation levels / V. V. Bolotov, O. M. Svechnikova, T. A. Kostina et al. – Kharkiv: NUPh, 2010. – 160 p.
4. Analytical chemistry: textbook [the textbook for students of higher schools] / I.S. Grytsenko, V. V. Bolotov, L.Yu. Klimenko et al.; ed. by I.S. Grytsenko – Kharkiv: NUPh, Golden Pages, 2019. – 600 p.

Lecture No. 7

Gravimetric analysis. Application of gravimetry for the analysis of medicinal substances.

Relevance of the topic: Analytical chemistryis a science that develops theoretical foundations and practical methods of chemical analysis.Therefore, it is relevant to solve the problems facing analytical chemistry with the help of physical, chemical and physicochemical methods used for the analysis of medicinal products.

Purpose: generalize students' knowledge of gravimetric analysis, its types and the possibility of use in the analysis of medicinal products.

Basic concepts:analytical chemistry, quantitative analysis, gravimetry, solubility product

Plan and organizational structure of the lecture:

1. General characteristics of gravimetric analysis
2. Classification of gravimetric analysis methods
3. Deposition method
4. Application of gravimetric analysis

Content of lecture material (lecture text):

1.General characteristics of gravimetric analysis

General concept of gravimetric analysis

Gravimetric (weighing) analysis, or gravimetry, is one of the methods of quantitative analysis, based on determining the mass of the sought-after component of the analyzed sample by measuring - accurate weighing - the mass of a stable final substance of known composition, into which this component is completely converted.

Thus, in the gravimetric determination of sulfuric acid in an aqueous solution, an aqueous solution of a barium salt (for example, barium chloride $BaCl_2$) is added to this solution. A white precipitate of barium sulfate, sparingly soluble in water, falls out:

$$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 \downarrow + 2HCl$$

Precipitation is carried out under such conditions, in which almost all the sulfate ion passes into the $BaSO_4$ precipitate with the greatest completeness — quantitatively, with minimal losses (for example, due to the slight, but still available, solubility of barium sulfate in an aqueous solution). The precipitate of barium sulfate is separated from the mother liquor, washed to remove soluble impurities, dried, calcined to remove volatile sorbed impurities and weighed as pure anhydrous barium sulfate on an analytical balance. Knowing the mass of barium sulfate obtained, calculate the mass of sulfuric acid in the original analyzed solution.

Another example is the gravimetric determination of quinine hydrochloride in a medicinal product. Dissolve an exact amount of quinine hydrochloride (about 0.5 g) in water, add a solution of NaOH alkali. Quinine hydrochloride is converted to quinine. The resulting quinine is extracted with chloroform. The chloroform layer containing quinine is separated, the chloroform is distilled off. The residue consisting of pure quinine is dried, weighed and the quinine content of the original sample of quinine hydrochloride is calculated.

Gravimetry is a classic method of quantitative chemical analysis, one of the first thoroughly developed quantitative methods of chemistry. As mentioned earlier, gravimetric methods are easy to perform, have good reproducibility, and

high accuracy, although they are often time-consuming and time-consuming. Gravimetry is a pharmacopoeial method of analysis. Numerous methods and techniques for gravimetric determination of chemical elements and their compounds have been developed.

2. Classification of gravimetric analysis methods

According to the common classification of gravimetric methods, the following are distinguished by the method of separation of the component: precipitation, distillation, separation, thermogravimetric methods (thermogravimetry). The last group of methods is sometimes referred to as instrumental.

Deposition methods. Their essence is as follows. The determined component of the solution enters into a chemical reaction with a reagent - a precipitant, which is added, forming a poorly soluble product - a precipitate, which is separated, washed, dried (if necessary, calcined) and weighed on an analytical balance. Examples can be the determination of sulfate ions or barium cations in the form of barium sulfate $BaSO_4$, the determination of the mass fraction of iron in soluble iron salts, based on the precipitation of iron (III) in the form of $Fe(OH)_3 \cdot xH_2O$ hydroxide, followed by its separation and calcination to Fe_2O_3 oxide; determination of calcium by precipitation in the form of calcium oxalate $CaC_2O_4 \cdot H_2O$ or with subsequent weighing of $CaC_2O_4 \cdot H_2O$ or anhydrous CaC_2O_4, or conversion to $CaCO_3$ carbonate, CaO oxide, $CaSO_4$ sulfate; determination of nickel in the form of bisdimethylglyoxime nickel(II) NiL_2 where L is a single deprotonated residue of dimethylglyoxime $(CN_3CNOH)_2$, etc.

Distillation methods.The component to be determined is isolated from the analyzed sample in the form of a gaseous substance and either the mass of the expelled substance (direct method) or the mass of the residue (indirect method) is measured.

Thus, when determining the content of CO_2 in $CaCO_3$ calcium carbonate by the distillation method, the analyzed sample (weight) of calcium carbonate is dissolved in acid:

$$CaCO_3 + 2HCl \rightarrow CO_2\uparrow + CaCl_2 + H_2O$$

The released carbon dioxide is quantitatively absorbed and its mass is measured with an increase in the total mass of the absorber.

The direct distillation method is used to determine the water content in analyzed samples, for example, in medicinal preparations (pharmacopoeial method). For this, a suspension of the analyzed sample weighing 10-20 g is added to a glass flask with a capacity of 250-500 ml, connected to a reflux condenser and a graduated receiver for collecting liquid condensate, 100 ml of toluene or xylene is added and the contents of the flask are boiled. The water present in the analyzed sample slowly evaporates when the mixture is boiled and then condenses in the reflux condenser, flowing in drops into the receiver. After the end of water removal and cooling of the receiver to room temperature, measure the volume of water collected in the receiver and, taking into account its density, calculate the mass of water removed. Knowing the mass of water and the mass of the original sample, the water content in the analyzed sample is calculated.

Indirect methods of distillation are widely used to determine the content of volatile substances (including weakly bound water) in medicinal products by measuring the mass loss of the analyzed sample when it is dried in a thermostat (in a drying cabinet) at a fixed temperature. Specific conditions (temperature, duration of drying, etc.) are determined by the nature of the object being analyzed and are specified in the analysis methodology.

In a typical experiment for analysis, a portion (about 0.5-1.0 g) of the analyzed sample, weighed on an analytical balance with an accuracy of ±0.0002 g, is placed in a dry (pre-weighed) box or crucible, placed in a thermostat (drying cabinet) and kept for about two hours at a given temperature (often about 100-110 ° C), at which vapors of weakly bound water and volatile substances are removed. Then the crucible (crucible) is quickly transferred to a desiccator with a desiccant, cooled, holding for 30-50 minutes at room temperature, after which the crucible (crucible) is weighed together with the contents on analytical balances.

The described operation is repeated, placing the sample again in the thermostat (drying cabinet) for a shorter time - about an hour. Repeated operations are carried out until a constant mass of the crucible (crucible) with the sample is reached. The analysis is usually completed when the difference between the two last weighings does not exceed the weighing errors on analytical balances, i.e. ±0.0002.

In some cases, drying is carried out in a vacuum, sometimes at room temperature in a desiccator (or in a vacuum desiccator) above a dryer.

The described method of determining mass loss during drying is one of the most common methods of quality control of chemical substances. It is simple in execution, universal and systematically used (in various versions) in the analysis of many dozens and hundreds of medicinal products in control and analytical laboratories.

Listed below as examples are only some medicinal preparations (mainly substances) for which the determination of mass loss during drying by the indirect distillation method is one of the mandatory pharmacopoeial tests (in brackets the temperature (in degrees Celsius) of holding to a constant mass, in in some cases, additional conditions, as well as the permissible rate of mass loss in percent: adrenaline hydrotartrate (room temperature, in a vacuum desiccator over sulfuric acid, mass loss no more than 0.5%), acrichin (105-110°, < 8), aminazine (100-105 °, <0.5), analgin (100-105 °, <5.5), barbamil (100-105 °, <1.5), vinylin (90-95 °, 4 hours, < 15), vitamin B2 - riboflavin (100-105 °, <1.5), vitamin B6 - pyridoxine hydrochloride (100-105 °, <0.5), vitamin B12 -cyanocobalamin (in vacuum at 105 ° and 5 mm Hg 100-105 °, <0.5), dehydrocholic acid tablets of 0.2 g (in a vacuum at 110 ° and 15 mm Hg, <8.5), dibazole (70-80 °, < 1.5), diphenhydramine (100-105 °, <0.5), medical gelatin (100-110 °, <16), isoniazid (100-105 °, <0.5), calcium lactate (120 °, < 30), codeine (100-105 °, <6), codeine phosphate (100-105 °, <7.0), codeine hydrochloride (100-105 °, <0.5), caffeine (80 °, <0, 5), lanolin anhydrous (100-105 °, <1), mesatone (100-105 °, <0.5), methyltestosterone (100-105) °, <1), methionine (100-105 °, <0, 5), naphthyzine (100-105 °, <0.5),

nicotinamide (100-105 °, <0.5), nicotinic acid (100-105 °, <0.5), paracetamol (100-105 °, <0.5), pregnin (100-105 °, <0.5), prednisone (100-105 °, <0.5), rutin (135 °, 6 - 9%), sarcolysin (100-105 °, <6), sulgin (100-105 °, 5-8), tetracycline hydrochloride (60 °, in a vacuum at 5 mm Hg. st., 3 hours, <2), theobromine (100-105 °, <0.5), theophylline (100-105 °, <9.5), phenacetin (100-105 °, <0.5), phthalazole (100-105°, <1.6), ftivazide (120°, <7), furadonin (100-105°, <7.5), quinine dihydrochloride (100-105°, <3), ephedrine hydrochloride (100-105 °, < 0.5).

The impressive number of examples given above allows us to judge the scale of practical use of indirect distillation methods, the variety of variation of conditions, the exemplary content of volatile impurities in typical medicinal preparations that are subject to analysis during their quality control.

Distillation methods are sometimes used in combination with extraction. The determining component is extracted from the aqueous solution with an organic extractant (for example, chloroform) into the organic phase, which is then separated from the aqueous phase. The organic solvent (extractant) is distilled off and the resulting dry residue is weighed. This is how a number of medicines are analyzed, for example, quinine hydrochloride, quinine dihydrochloride, sodium salts of barbiturates, sodium thiopental, etc.

Calculation of the optimal weight of the initial weight in the indirect method of drive-off. In the indirect method of distillation, which, as shown above, is widely used to determine the content of volatile substances in the analyzed sample, when choosing the optimal mass of the initial weight for analysis, it is usually assumed that the relative (percentage) error of determination does not exceed ±0.2% for sample weighing conditions on analytical balances before and after mass loss. The mass t of the initial weighing is taken so that both the mass of volatile substances removed and the mass of the residue after their removal would be at least 0.1 g. Under these conditions, the minimum mass t of the initial weighing is calculated by the formula:

$$m = m(X) \cdot 100\% / W(X),$$

where t(X) is the mass of volatile substances removed by X, equal to ~ 0.1 g;

W(X) - the mass fraction (in percent) of volatile substances X in the weight of t, which does not exceed ~ 50%; W(X) < 50%.

The approximate value of W(X) must be known.

In practice, sometimes in order to determine the mass loss of volatile substances in objects containing even about 0.5% (mass fraction) of components removed during drying, a suspension of the analyzed sample with a small mass of about ~ 1 g is taken. Thus, for example, in the pharmacopoeial analysis during the quality control of medicinal products for the content of volatile impurities and moisture.

Selection methods. The component to be determined is isolated (usually from the solution), for example, during electrolysis on one of the electrodes (electrogravimetric method). Then the electrode with the released substance is washed, dried and weighed. By increasing the mass of the electrode with the substance, the mass of the substance released on the electrode is found. This is how gold and copper alloys are analyzed: the alloy is transferred into a solution and after the gold is separated, the copper(II) remaining in the solution is determined electrogravimetrically.

Thermogravimetric methods.These methods are based on measuring the mass of the analyzed substance during its continuous heating in a given temperature interval (most often from room temperature to a given one). Measurements are usually carried out on special devices — derivatographs equipped with special thermobalances for continuous weighing, an electric furnace for heating the sample, thermocouples for temperature measurement, a standard for comparison and a recorder that continuously records the change in the mass of the heated substance.

In a typical experiment, a weight of the analyte is placed in a platinum crucible (or a crucible of other material) on a continuous weighing thermobalance inside the derivatograph, and the crucible containing the contents is heated at a given rate of temperature rise. The change in mass of the analyzed sample is

automatically recorded on paper by a recorder in the form of a curve of mass change - thermogravigrams in coordinates time (most often) or temperature (abscissa axis) - mass loss (ordinate axis) - see below fig. 7.1. Heating is carried out either in air or in an inert gas atmosphere, such as nitrogen.

Most substances undergo one or another thermal transformation during heating — dehydration, melting, isomerization, decomposition, oxidation, etc. may occur. building depending on the nature of the substance, the temperature, the composition of the atmosphere where the heating is carried out. These thermal transformations, as a rule, do not occur continuously, but gradually, in a very narrow temperature range, only when a certain temperature is reached. Thermal transformations are often accompanied by a change in the mass of a substance (with the exception of melting, isomerization, etc. processes that occur without a change in mass). The change in the mass of the analyzed sample is recorded by a recorder in the form of a more or less clear degree on the thermogravigram. There can be several such steps. After the end of the experiment, the change in mass at each stage of thermal transformations is determined and the nature of thermal effects is interpreted - thermogravigrams are deciphered. Very often, the content of water and other components in the analyzed substance is determined in this way.

Usually, simultaneously with the recording of thermogravigrams (TG curves), the derivatograph recorder also records the temperature change curve (T curve); the registration curve of thermal effects (endothermic and exothermic) accompanying thermal transformations both with and without mass change (DTA curve — differential thermal analysis, or simply thermogram), differential thermogravimetric curve of mass change (DTG curve); sometimes some other curves characterizing the dynamics of thermal transformations are recorded. In general, such research is now called thermal analysis (note that in physical chemistry, thermal analysis also means obtaining thermal curves, which are used to construct melting point diagrams).

When deciphering thermogravigrams, IR absorption spectra of the original analyzed substance and the products of its thermal transformations are often

obtained. First, the IR absorption spectrum of the original substance, the thermogram and thermogravigram of this substance, as well as the IR absorption spectrum of the final product of thermal transformations - the residue in the crucible after the completion of the heating process and subsequent cooling to room temperature - are obtained. Thermograms and thermogravigrams determine the presence of thermal effects and their corresponding temperatures. Then, in separate experiments, the starting substance is heated to the temperature of one or another effect recorded on the thermogram either directly in the derivatograph or in a thermostat (in a drying cabinet) to a constant mass (at the temperature of the given thermal effect), after which the residue is cooled to room temperature and record its IR absorption spectrum. Based on the obtained spectra, it is judged which substance is formed at one or another stage of thermal transformations.

Thermogravimetric methods are most often used for the analysis of inorganic and coordination compounds, for example, to determine the water content, less often - in the analysis of organic substances.

Deposition method

The sedimentation method is one of the most common and thoroughly developed in gravimetric analysis.

The main stages of gravimetric determination

The main stages of gravimetric analysis in the sedimentation method generally include the following:

• calculation of the weight of the analyzed sample and the volume (or mass) of the precipitate;

• weighing (taking) the weight of the analyzed sample;

• dissolving the weight of the analyzed sample;

• deposition, i.e. obtaining the form of a given component;

• filtering (separation of the sediment from the mother liquor);

• sediment washing;

• drying and (if necessary) roasting the sediment to a constant mass, i.e. obtaining a gravimetric form, weighing a gravimetric form;

• calculation of analysis results, their statistical processing and presentation. Let's briefly consider each of these operations.

Calculation of the weight of the analyzed sample and the volume (mass) of the precipitator

The weight of the sample intended for analysis and, therefore, for weighing on analytical balances, is not taken arbitrarily. If the weight of the weight is taken to be very small, then the relative losses in subsequent operations can lead to a noticeable relative error of the analysis. If, on the contrary, the measurements are taken too much, then when the mold is obtained, a significant mass of sediment is formed, which complicates its filtering and washing, contributes to the coprecipitation of significant amounts of impurities from the solution, increases the duration of analyzes and the consumption of reagents. Therefore, it is necessary to estimate the optimal weight of the weight. When calculating the optimal weight of the analyzed substance, the possible mass fraction of the determined component in the analyzed sample and the gravimetric form, the mass of the gravimetric form, the systematic error of weighing on analytical balances (usually ±0.0002 g), the nature of the obtained sediment - amorphous, fine crystal large crystal are taken into account.

It is often assumed that the relative error of gravimetric analysis does not exceed ±0.2%. Such methods of analysis are used, in which the main contribution to the error of the analysis is the weighing error on the analytical balance, while the errors associated with the solubility of the sediment in the mother solution, with losses during its washing, would be less than the weighing error on the analytical balance.

Relative errorεweighing on analytical balances is determined by the ratio

$$\varepsilon=\Delta m\cdot 100\%/m,$$

whereΔm = 0.0002 g, m is the weight of the analyzed substance in grams. Since the relative error of gravimetric analysis should not exceed 0.2% in absolute value, and it is determined by the relative error of weighing, i.e. = 0.2% (no more). Then,

$$0.2\% = 0.0002 \cdot 100\%/m.$$

Therefore, the optimal weight m of the weight, at which the relative error of the gravimetric analysis is not more than ±0.2%, should be not less than

$$t = 0.0002 - 100\% / 0.2 = 0.1 \text{ g}.$$

Of course, the larger the mass m, the smaller the relative error of the analysis. However, taking too much weight is not recommended for the reasons mentioned above.

In the sedimentation method, not only the initial weight of the substance to be determined is weighed, but also the final weight of the gravimetric form, the mass of which, in accordance with the above, must also be at least 0.1 g. This condition must be kept in mind when calculating the weight of the initial weight of the analyzed substance.

In practice, when calculating the optimal mass of the initial suspension, it is assumed that the optimal mass of the final gravimetric form would be at least 0.1 g.

As a result of the generalization of numerous studies, it was recommended to set the optimal mass of the gravimetric form as follows:

for bulky amorphous sediments - about 0.1 g,

for crystalline sediments - from 0.1 to 0.5 g (for light sediments - from 0.1 to 0.2 g, for heavy sediments - from 0.4 to 0.5 g).

Knowing the required mass of the gravimetric form, its composition, as well as the exemplary content of the specified component in the original sample being analyzed, it is possible to calculate the mass of the original sample in each specific case.

Usually, the mass of the initial sample is specified in the analysis method.

In the general case, the lower limit of the optimal mass of the initial weight of the analyzed substance (in grams) is calculated according to the formula:

$$m = \frac{100m(HF)F}{}$$

$W(x)$

where m(ГФ) is the mass of the gravimetric form in grams; F - gravimetric factor (conversion factor, analytical factor), W (X) - mass fraction (in %) determined by the component in the analyzed substance.

The gravimetric factor F is numerically equal to the mass of the determined component in grams, which corresponds to one gram of gravimetric form.

The gravimetric factor is calculated as the ratio of the molar mass M/(X) determined by the component X to the molar mass of the gravimetric form M(HF), multiplied by the number of n moles is determined by the component from which one mole of the gravimetric form is obtained:

$$F = nM(X)/M(HF)$$

The amount (volume or mass) of the precipitant is calculated taking into account the possible content of the specified component in the analyzed sample. A moderate excess of precipitant is used to increase the volume of the precipitate. It is not recommended to take a large excess of precipitant to avoid contamination of the sediment with excess precipitant. If the precipitate is volatile - it is removed when the precipitate is heated (for example, the precipitate is a solution of HC1), then take two or three times its excess compared to the stoichiometric (that is, corresponding to the reaction equation for the formation of the precipitate). If the precipitate is non-volatile (for example, a solution of barium chloride $BaCl_2$), take a smaller excess of it - about one and a half times.

Basic requirements for the precipitator.

1) The precipitator must be specific, selective in relation to ion precipitation.

2) The precipitant can be as volatile as possible, i.e. should be easily removed by heating or baking the precipitated form.

So, for example, barium cations precipitate from an aqueous solution in the form of barium sulfate when adding a solution of sulfuric acid, solutions of sodium, potassium, and other soluble sulfates. Impurities of sulfuric acid sorbed by the precipitate are removed by subsequent heating and calcination of the barium sulfate precipitate, while sorbed impurities of sodium or potassium sulfates are not

removed. Therefore, for the precipitation of barium in the form of barium sulfate, a solution of sulfuric acid should be used, and not solutions of Purposel sulfates.

The most important inorganic precipitants include solutions of HC1, H_2SO_4, H_3PO_4, NaOH, NH_4OH, $AgNO_3$, $BaCl_2$, $(NH_4)_2C_2O_4$, etc.

Solutions of dimethylglyoxime, 1-nitroso-2-naphthol, 8-oxyquinoline, oxalic acid, etc. are used as organic precipitants.

The use of organic precipitants that form stable intracomplex compounds with Purposel cations has a number of advantages compared to the use of typical inorganic precipitants.

1) Internal complex compounds of Purposel, as a rule, have low solubility in water, which ensures high completeness of precipitation of the determined cation of Purposel.

2) The adsorption capacity of sediments of intracomplex compounds having a molecular crystal lattice is lower than the adsorption capacity of inorganic sediments with an ionic structure. Therefore, the precipitates of intracomplex compounds adsorb fewer impurities from the solution and come out cleaner.

3) Selective or even specific precipitation of one or another Purposel cation from solution in the presence of other cations is possible.

4) Due to the relatively large molecular weight of intracomplex compounds, the relative error of determination decreases (the value of the gravimetric factor F decreases) compared to the use of inorganic precipitants with a low molecular weight.

The volume of the precipitant solution is calculated based on the required amount of precipitant and its concentration. As mentioned above, an excess of precipitant is used. At the same time, the mass of the precipitated substance that remains in the solution due to some (albeit insignificant) solubility of it should not, as a rule, exceed 0.0002 g, i.e., the weighing error on the analytical balance. Otherwise, it is necessary to make corrections for losses of the determined component due to partial dissolution of the sediment.

Weighing (taking) weights

Weighing of the initial weight of the analyzed substance is carried out on analytical scales with a weighing error, most often equal to ±0.0002 g. Usually, the weight is placed in a clean, dry glass beaker, previously weighed on the same analytical balance. Sometimes the suspension is first weighed on technical or pharmacy scales and only after that - on analytical scales. The weight of the weight is calculated from the difference in the mass of the weight of the weighted bag and the weight of the empty weight.

Dissolving the weight

The sample is dissolved in the appropriate solvent under the conditions provided by the analysis method. Most often, distilled water or aqueous solutions of acids are used as a solvent. If distilled water is used as a solvent, then 100-150 ml of water is optimally used.

Precipitation (obtaining a precipitable form)

This operation is one of the most important in the deposition method.

The main goals in obtaining a besieged form are to

- minimize losses due to sediment dissolution in the mother liquor;

- the sediment did not contain impurities of other substances (as a result of their adsorption on the sediment, occlusion, coprecipitation);

- sediment particles would be large enough, would not pass through the pores of the filter and would not clog them.

In the deposition method, you have to deal with crystalline and amorphous sediments, although it is difficult to draw a clear line between them.

Crystalline sediments consist of larger particles than amorphous ones, absorb less impurities from the solution, and are easier to filter. Therefore, in most cases (when possible), they try to obtain not amorphous, but crystalline sediments, if possible, large-crystalline ones, carrying out deposition in conditions conducive to the formation of such sediments.

So, for example, sulfate ions precipitate from aqueous solutions in the form of CaSO4, SrSO4, BaSO4, PbSO4 precipitates. The solubility product of these sulfates at room temperature is $2.5 \cdot 10^{-5}$, $3.2 \cdot 10^{-7}$, $1.1 \cdot 10^{-10}$, $1.6 \cdot 10^{-8}$,

respectively. Barium sulfate has the lowest solubility. Therefore, barium sulfate should be selected as the precipitated form, that is, sulfate ions should be precipitated with solutions of barium salts.

2) The precipitate should not dissolve in the excess precipitant with the formation of soluble complex compounds.

3) The sediment must not contain extraneous impurities.

4) The sediment must be resistant to external influences - not oxidized, not regenerated, etc.

5) The sediment must completely transform into a gravimetric form upon drying or roasting without loss of the specified component.

6) The structure of the sediment should ensure optimal filtering and washing of the sediment from impurities. The most convenient, as already mentioned, are coarse-crystalline sediments, since they do not clog the pores of the filter, have a small surface area (that is, they do not adsorb foreign particles from the solution), and are easily washed.

In addition to the listed general requirements, some others may be specified in the analytical methods, which are determined by the specifics of the analysis of a particular object.

Conditions for the formation of crystalline and amorphous sediments. No precipitates fall out of dilute solutions. In saturated solutions, a heterogeneous equilibrium is established between the sediment and the solution, so the mass of the sediment remains unchanged. A precipitate is formed only when the concentration of the solution becomes higher than the concentration of the saturated solution, that is, the precipitate falls out of the Purposestable supersaturated solution.

Supersaturated solutions are characterized by relative supersaturation or the degree of supersaturation P according to the equation

$$P=(c\ S)/S,$$

де c - is the concentration of this supersaturated solution, S is the equilibrium concentration of the saturated solution (solubility of this substance). It is obvious that with > S. The greater the value of P, the more supersaturated this solution is.

If the P value is large, an amorphous precipitate is usually formed; if the value of P is small, then, other things being equal, a crystalline precipitate is formed.

Supersaturated solutions are thermodynamically unstable (Purposestable) and sooner or later involuntarily release precipitates of dissolved substances until the solution becomes saturated - it will pass into a thermodynamically stable state. Limits (concentration and temperature conditions) Purposestable existence of supersaturated solutions for different combinations of solutes and solvents are different.

The process of sediment formation is complex. First, small crystal nuclei appear - centers of crystallization. They arise due to the actual formation of the smallest crystal nuclei; however, the formation of nuclei is also initiated by the presence of small particles of foreign substances (for example, dust, small particles of glass formed when rubbing the wall of a glass vessel with a glass stick, etc.), which are almost always present in the solution. The resulting small crystallization centers can dissolve again; or grow, increasing in size - the growth of crystals is observed.

Speedν1 formation of crystallization centers and speed ν2 crystal growth depends differently on the degree of supersaturation of solution P according to the equations:

$\nu 1 = k1\, P''$

$\nu 2 = k2\, P$

where $n \approx 4$; k1i k2- coefficients, where k1 < k2.

According to the equations, at a small degree of supersaturationν2 >ν1, so crystal growth prevails, while the formation of new crystallization centers occurs more slowly. Under these conditions, crystalline sediments are obtained, the particles of which are relatively large in size.

On the contrary, at high values of the degree of supersaturation of the solution P already 1> 2, i.e. the formation of new centers of crystallization dominates; growth of crystals is slower. Under these conditions, either amorphous or fine-crystalline sediments are obtained, the particles of which are small in size, therefore have an increased adsorption capacity (adsorb impurities of foreign substances from the solution), can either pass through the pores of the filter, or clog them, which in general complicates the analysis and increases gravimetric determination error.

With a very low solubility of the sediment, a high level of supersaturation. solution is achieved immediately, when adding small amounts of precipitant. Under these conditions, colloidal particles (of the order of 10-7 cm in size) are formed. During their coagulation, amorphous gelatinous sediments are obtained.

Usually, they try to carry out deposition in such conditions, when the degree of supersaturation is small. This is achieved due to the slow (dropwise) addition of the precipitant solution (especially at the beginning of the precipitation process), with intensive (but careful!) mixing of the entire solution to avoid the occurrence of local areas with an increased degree of supersaturation; due to the heating of the analyzed solution and the solution of the precipitator (when the temperature increases, as a rule, the solubility of the precipitate increases, so small particles dissolve and then settle on the surface of larger centers of crystallization); due to the introduction of substances that increase the solubility of the precipitate (for example, sometimes a small amount of acid is added), which also leads to the dissolution of small crystals and the growth of larger crystals.

The formed precipitate is in dynamic equilibrium with the mother solution. It constantly exchanges ions with the mother solution. Spontaneous growth of larger crystals occurs due to the dissolution of small particles, the crystalline structure of the precipitate improves, its specific surface area decreases, as a result of which the impurities of previously absorbed substances are desorbed and pass into the solution, and the occluded (captured during precipitation) droplets of the solvent (solution) are released from the precipitate. These processes are usually accelerated

when the temperature rises. In general, nowadays, such transformation of the sediment is usually called maturation of the sediment.

In order to ripen and form crystal sediments that are well filtered, they are left for some time (from several hours to several tens of hours) together with the mother plant after falling out of the solution. The ripening time of crystalline precipitates can be shortened by heating the solution with the precipitate.

Taking into account the above, it is possible to indicate the following basic conditions for obtaining crystalline sediments in the gravimetric method of sedimentation.

1) Precipitation should be carried out from a diluted analyzed solution with a diluted precipitant solution.

2) The precipitant solution is added slowly, drop by drop (especially at the beginning of the precipitation), with continuous careful stirring of the solution.

3) Precipitation should be carried out from a hot analyzed solution with a hot precipitant solution.

4) In some cases, it is useful to carry out precipitation in the presence of substances (for example, small amounts of acid) that slightly increase the solubility of the precipitate, but do not form complex soluble compounds with it.

5) The sediment that has fallen is left for some time together with the queen for maturation of the sediment.

However, gravimetric analysis does not always deal only with crystalline sediments. Thus, when determining iron (III) or aluminum, voluminous amorphous strongly hydrated precipitates of hydroxides of iron (III) or aluminum are obtained. Having a developed surface, such sediments are able to adsorb impurities from the solution. In addition, they tend to form colloidal solutions. To prevent the formation of colloidal solutions (for coagulation of colloidal particles), an electrolyte coagulant is introduced into the analyzed solution and the temperature is increased.

When kept for a long time with the mother solution, amorphous sediments often undergo aging, changing their properties to a certain extent, as a result of

which they are poorly filtered. However, sometimes they are left for some time together with the matochnik for maturation of the sediment (which is necessarily determined by the appropriate method of analysis). When washing amorphous sediments, their peptization and partial loss together with the washing liquid is possible, so they are washed with hot water, which sometimes contains electrolytes that prevent peptization of the sediment.

If an amorphous sediment is formed as a precipitated form, then they try to get it as dense as possible in order to improve its filtering and reduce losses during its washing.

Conditions for obtaining amorphous sediments

1) A hot concentrated precipitant solution is added to the hot concentrated analyzed solution. Under these conditions, coagulation of colloidal particles occurs and sediments are denser.

2) The hot precipitant solution is added quickly, which reduces the likelihood of formation of colloidal solutions.

3) If necessary, the solution is injected with an electrolyte coagulant.

4) Long-term exposure of the precipitate with the mother liquor is avoided.

Usually, the conditions of deposition (obtaining the precipitated form) are regulated in detail by the method of analysis.

Filtration and washing of sediment

Separation of sediment from the mother liquor by filtration is carried out after its maturation (crystalline sediments) or immediately after sedimentation (amorphous sediments).

Filtering is carried out using glass or ashless paper (most often) filters.

Ashless paper filters have different densities and sizes, which is indicated by the different color of the inscriptions on the filter packages or the color of the tape (stripe) on the pack with filters. The most dense filters have a blue band, medium density filters have a white band, and the least dense have a black or red band. The most dense filters and filters of medium density are used for filtering crystalline sediments, the least dense for filtering amorphous sediments. The usual diameter

of round factory-produced ashless filters is 6, 7, 9 and 11 cm. Ashless paper filters during combustion and calcination form a residue - ash, the mass of which is less than the weighing error on analytical balances and therefore is usually not taken into account when measuring the mass of a gravimetric form.

When filtering, a transparent supernatant solution is first passed through the filter. The remaining sediment is usually washed first directly in the glass in which the sedimentation was carried out, pouring the washing liquid along with the sediment particles onto the filter, and then the entire sediment is quantitatively transferred to the filter. The sediment is washed on the filter with several portions of washing liquid. The composition of the washing liquid (hot, cold water or a solution of some substance) and washing conditions are specified in the analytical method.

If necessary, losses of sediment due to its dissolution in the mother solution and in the washing liquid are taken into account, for which it is necessary to know the volume of the mother solution, washing liquid and the solubility (concentration of the saturated solution) of the precipitated form.

Obtaining a gravimetric form

The precipitate (precipitated form) after it is transferred to the filter and washed, is dried together with the filter in a drying cabinet at a temperature of about 100°C. The dry filter with sediment is placed in a pre-fired and weighted crucible (most often porcelain) and ashed in the flame of a gas burner, making sure that the filter smolders, but does not ignite (to avoid loss of sediment when the filter burns). After deashing, the crucible with the sediment is usually roasted in a muffle furnace to a constant mass at a temperature that depends on the nature of the sediment.

For example, barium sulfate $BaSO_4$ is calcined at 700-900 ° C; at the same time, the composition of the sediment does not change, but only impurities are removed. Iron (III) hydroxide is calcined at 800-900 ° C; the precipitated form of $Fe(OH)_3$ turns into gravimetric Fe_2O_3. $CaSO_4$ precipitate is calcined at about 900 °C; its composition does not change.

A gravimetric form must meet a number of requirements, the most important of which are the following.

Requirements for gravimetric form

1) The composition of the gravimetric form must exactly correspond to its stoichiometry (for example, $CaSO_4$, $BaSO_4$, Al_2O_3, Fe_2O_3, CaO, etc.).

2) The gravimetric form must be stable in air, not decompose, not subject to oxidation-reduction processes, etc.

3) The gravimetric factor F should be as minimal as possible, because this reduces the relative error of the gravimetric determination.

Gravimetric form weighing.

Bringing the gravimetric form to a constant mass is carried out in the process of calcination of the sediment. To do this, after the first roasting for the time specified in the analysis method (often - about an hour - an hour and a half), the crucible with the sediment is quickly transferred from the muffle furnace to the desiccator, cooled to room temperature for about half an hour and weighed on an analytical balance. Then roasting, cooling and weighing are repeated until the difference of the last two weighings does not exceed the weighing error on the analytical balance (±0.0002 g). Sometimes the analytical method provides less strict requirements for the difference between the last two weighings (from 0.0003 to 0.0005 g).

Calculation of analysis results

After measuring the mass of the gravimetric form m(GF), the content of the specified component in the analyzed sample is calculated, knowing the composition of the gravimetric form. If the value of the gravimetric factor F is known, the mass determined by the component m(X) in the analyzed sample is calculated according to the formula:

$$t(X)=Ft(HF)$$

4. Application of gravimetric analysis

Gravimetry methods are used in the quantitative analysis of a wide variety of objects. Indirect distillation methods are widely used to determine the content of

volatile substances, especially in medicinal preparations (most often in substances), as well as to determine the dry residue in tinctures and extracts. Gravimetric determination of mass loss during drying of drugs is a universal pharmacopoeial method used in quality control of many drugs.

Distillation methods combined with extraction are used in the quantitative analysis of organic medicinal products.

Gravimetric methods and methods for determining most Purposel cations, anions, as well as a number of organic substances have been developed on the basis of precipitation methods.

Gravimetric methods are used in the quality control of medicinal plants and medicinal plant raw materials to determine such indicators as the content of total ash - the ash residue after burning and calcination of the analyzed sample, sulfate ash, as well as ash insoluble in hydrochloric acid.

Thermogravimetry is used in the analysis of inorganic, coordination and (rarely) organic compounds, as well as in combination with IR-spectroscopy methods to clarify the nature and quantitative characteristics of the processes of thermal transformations of various substances. Electrogravimetry is used in the analysis of alloys.

General material and bulk-methodological support of the lecture:

- ✓ computer presentation;
- ✓ illustrative materials;
- ✓ examples of solving typical tasks or performing typical tasks;
- ✓ multimedia projector.

Questions for self-control:

1. Classification of gravimetric analysis methods.
2. Methods of driving away. The technique of performing direct and indirect driving.
3. Formulate the conditions for the formation of saturated and unsaturated solutions and the formation of precipitates.

4. List the main operations of gravimetric analysis by precipitation.
5. Deposition method. Calculation of the weight of the weight.
6. How is the solvent selected in gravimetry?
7. Selection of the weight of the investigated substance by the precipitation method.
8. What are the main requirements for a precipitator in gravimetry?
9. Why is the precipitant solution taken in volume in the precipitation method?
10. What is a form? What are the requirements for it in weight analysis?
11. Conditions of deposition of crystalline sediment.
12. What processes occur with crystalline deposits during ripening? Why is this ripening beneficial for analysis?
13. Under what conditions are amorphous sediments deposited?
14. Briefly list the conditions that must be observed during the deposition of amorphous sediment?
15. What is the purpose of sediment washing? How to choose a washing liquid
16. How is sediment washing by decantation carried out?
17. Requirements for the gravimetric form of specified substances.
18. Calculation of the gravimetric factor.
19. What is the solubility product?
20. Formulate the conditions for the existence of saturated, unsaturated and supersaturated solutions. Give an example.
21. What are the basic conditions for dissolution of sediments. Give examples.
22. Based on the solubility product rules, formulate the conditions for the formation of precipitates

References:

General:

1. Analytical chemistry: handbook / V. V. Bolotov, O. A. Yevtifeyeva, L. Yu. Klimenko, T. A. Kostina, T. V. Zhukova, E. Yu. Ahmedov , O. A. Brizicky; edited by V. V. Bolotov.— Kharkiv: NUPh; Original, 2012.

2. Analytical chemistry (Qualitative analysis). Part I / O. A. Ievtifieieva, V. V. Bolotov, T. A. Kostina, O. M. Svechnikova, T. I. Yuschenko, N. I. Kaminska, A. E. Kosareva, L. V. Slobodyanyuk, O. P. Yashchuk ; edited by O. A. Ievtifieieva. – Kharkiv : Publishing house the CLL «Generous farmstead plus», 2014. – 168 p.
3. Analytical chemistry. Part II. Quantitative analysis: the manual for foreign students of pharmaceutical higher schools and pharmaceutical departments of medical higher schools of the III – IV accreditation levels / V. V. Bolotov, O. M. Svechnikova, T. A. Kostina et al. – Kharkiv: NUPh, 2010. – 160 p.
4. Analytical chemistry: textbook [the textbook for students of higher schools] / I.S. Grytsenko, V. V. Bolotov, L.Yu. Klimenko et al.; ed. by I.S. Grytsenko – Kharkiv: NUPh, Golden Pages, 2019. – 600 p.

Lecture No. 8

Topic: Titrimetric analysis. Basic concepts. Classification of methods. Titrated solutions, their preparation and standardization. Calculation in titrimetric analysis

Relevance of the topic: Analytical chemistryis a science that develops theoretical foundations and practical methods of chemical analysis.Therefore, it is relevant to solve the problems facing analytical chemistry with the help of physical, chemical and physicochemical methods used for the analysis of medicinal products.

Purpose: generalize students' knowledge of titrimetric analysis. Learn how to perform calculations. Get familiar with the concept of "standard solution" and its characteristics.

Basic concepts:analytical chemistry, quantitative analysis, titrimetry, working solution, primary standard, secondary standard, molar concentration, normal concentration, titer

Plan and organizational structure of the lecture:

1. Titrimetric method of analysis: essence, Basic concepts and classification.
2. Standard solutions
3. Classification of titrimetric methods

4. Basic methods of titration

Content of lecture material (lecture text):

1. **Titrimetric method of analysis: essence, Basic concepts and classification.**

The titrimetric method of analysis is a method of quantitative analysis, which is based on measuring the amount of reagent required to complete the reaction with a given amount of the determining substance.

In a titrimetric analysis, the volume of a solution of a reagent of known concentration is measured, which is spent on interaction with a solution of the substance to be determined, and the amount of the substance is calculated using the equation of the chemical reaction.

A chemical element, simple or complex substance, the content of which is determined in a given sample of the analyzed product, is called the substance to be determined and is denoted by A.

The method of titrimetry consists in the fact that a solution of reagent B of a known concentration is gradually added to the solution of the substance A to be determined.

A solid, liquid or gaseous substance that reacts with substance A to be determined is called a reagent and denoted by B. The concepts of "reagent" and "reactant" should be distinguished. A reagent is a substance that directly enters into a reaction, and a reagent is a chemical preparation, which can be a complex mixture of various substances, which contains, along with the reagent itself, auxiliary substances and a solvent. For example, Chugaiov's reagent is a mixture of dimethylglyoxime with alcohol and an aqueous solution of ammonia (the reagent is actually dimethylglyoxime).

Quantitative determination of substance A by the titrimetric method, in which a reagent solution of a precisely known concentration is slowly added to the solution of the product under investigation in an amount that corresponds to the content of substance A to be determined, is called titration. The word "titration" comes from the word "titre". Sometimes a reagent in a solid, liquid or gaseous state

is added to the titrated substance. Therefore, in a broad sense, titration is the process of continuous controlled gradual mixing of a measured amount of a solid, liquid or gaseous substance, or more often, an accurately measured volume of a standard solution of reagent B with the substance under study. At the same time, the amount of reagent corresponds to the content of the determined component A, which reacts with reagent A in strictly equivalent quantities.

Solutions of reagent B of precisely known concentration, which is used for titration in titrimetric analysis methods, are called standard or titrated solution or titrant.

2. Standard solutions

The main solution in titrimetric analysis is a standard (titrated) solution, during titration of which the content of the substance in the analyzed sample is determined.

Preparation of solutions of precisely known concentration requires compliance with special rules, exceptional accuracy and accuracy in work. Failure to comply with these requirements is necessarily reflected in the accuracy of all volumetric determinations performed using the prepared standard solution, and very often leads not only to the need to redo the analysis, but also to re-establish the titer of the original solution.

There are different ways of preparing titrated solutions:

1. According to the exact weight of the starting substance;
2. Using a standard substance or a standard solution;
3. With the help of "Fixanal".

1. Preparation of the titrated solution according to the exact weight of the starting substance (primary standard).

The simplest, at first glance, method of making a solution of precisely known concentration, that is, characterized by a certain titer, is to dissolve an exact weight of the original chemically pure substance in water or another solvent and dilute the resulting solution to the required volume.

Knowing the mass (a) of a chemically pure substance dissolved in water and the volume (V) of the resulting solution, it is easy to calculate the TV titer of the prepared reagent in g/ml.

This method prepares titrated solutions of substances that can be easily obtained in pure form and whose composition corresponds to a precisely defined formula and does not change during storage.

The substance is weighed in a test tube with a polished cork, on a watch glass or in a box. In view of the fact that some substances are very difficult. And sometimes it is almost impossible to obtain in pure form or difficult to weigh on analytical balances, the direct method of preparation of titrated solutions is used only in certain cases. In this way, it is not possible to prepare titrated solutions of substances that are highly hygroscopic, easily lose water of crystallization, are exposed to the action of carbon dioxide, etc.

2. Setting the titer of the solution using a standard substance (secondary standard or a solution with an established titer).

A solution of approximately the required concentration is prepared, its exact concentration is established. The titer or normality of the prepared solution is determined by titrating solutions of so-called standard substances with it.

A standard substance is a chemically pure compound of precisely known composition, which is used to determine the titer of a solution of another substance. Based on the titration data of the standard substance, the exact titer or normality of the prepared solution is calculated.

Requirements for standard substances:

1. It must have a crystalline structure and correspond to a certain chemical formula.
2. The chemical composition of the substance must correspond to the formula.
3. Do not contain extraneous impurities more than the permissible limits for substances of the "HC" brand.
4. Methods of cleaning the standard substance from accompanying impurities (crystallization, extraction, sublimation, etc.) should be available in the analytical laboratory.

5. The chemical standard substance should not be hygroscopic, but should dissolve relatively well.

6. Solutions of the standard substance should not change their titer during storage and exposure to air.

7. The standard substance should be distinguished by the largest possible equivalent mass. The greater the equivalent mass of the substance, the greater the accuracy of setting the titer of the solution, since when weighing a substance with a higher molecular weight, the weighing will be insignificant.

3. Production of titrated solutions according to "fixanal".Very often, in practice, precisely weighed quantities of solid chemically pure compounds or precisely measured volumes of their solutions, which are necessary for the manufacture of titrated solutions of a certain normality, are used for the manufacture of titrated solutions produced at chemical plants or in special laboratories.

These substances are placed in special glass ampoules and sealed. Ampoules are sold with a certain amount of substance contained in them. They are called their fixed channels.

To make the necessary titrated solution, the ampoule is broken over a special funnel that has a hammer, the ampoule is pierced from above with another hammer, the contained flask is quantitatively transferred to a measuring flask and the volume is brought up to the mark with water.

Most often, the ampoule contains 0.1 mol (eq) of the substance, that is, as much as is needed to prepare a 0.1N solution.

Rules that must be followed when preparing titrated solutions and determining their titers.

1. The starting material used for the production of the standard solution must be chemically pure.

2. The starting substance should easily and quickly react with titrated substances.

3. The solution of the starting substance must be stored for a long time without changes.

4. The reactions that take place between the original and the substance to be determined should be carried out, if possible, by direct titration methods.

5. The titration process should end quickly and clearly. The end point of the titration should be determined easily and precisely.

6. It is desirable to set the titers either by the method of individual measurements or by dissolving a measurement of the starting substance in a certain volume.

7. To prevent errors during titration, it is necessary to choose the volume of the aliquot of the primary standard or the weight of the standard substance so that the volume of the secondary standard used for titration is at least 20 ml (25 ml burette) or 40 ml (50 ml burette). With smaller volumes of used reagents and used micro burettes, the relative error will exceed the permissible error due to a decrease in measurement accuracy.

8. Do not limit yourself to one or two parallel definitions. Titration should be carried out until at least three identical results are obtained.

9. The prepared titrated solutions must be stored in conditions that exclude their absorption of moisture from the air, as well as evaporation. Titers should not change when standing in time.

10. Dishes and measuring devices used in titrimetry must be washed, calibrated, prepared for titration and stored in a clean place.

11. The accuracy with which titrations, volume measurements and subsequent calculations are performed. Must correspond to the accuracy of weighing. Therefore, it is impossible to weigh the weight of starting or standard substances on technical scales with an accuracy of 0.01-0.1 g and then measure volumes with an accuracy of 0.01 ml or, conversely, weigh with an analytical balance with an accuracy of 0.0001 g and measure the volume with tenths of a milliliter .

Equivalence point and end point of titration.

According to the equivalence rule, the titration must be continued until the amount of the added reagent B becomes equivalent to the content of the substance A to be determined. The moment of titration, when the amount of the standard solution of the reagent B (titrant) becomes theoretically strictly equivalent to the

amount of the substance to be determined A, which reacts with the added reagent B, according to the reaction equation, is called the equivalence point.

The equivalence point is set in various ways, for example, by changing the color of the indicator added to the titrated solution.

The moment at which the color of the indicator changes is called the end point of the titration. Very often, the end point of the titration does not exactly coincide with the equivalence point, which corresponds to the theoretical point of the titration.

The equivalence point occurs when the theoretically necessary amount of reagent B is added to the titrated solution. It has completely reacted with the substance A to be determined. Accordingly, theoretically there should be neither substance A nor reagent B at the equivalence point, if the reaction of their interaction proceeds quantitatively. The reactions used in titrimetry are reversible, i.e. practically do not reach the end. This is one of the reasons that the equivalence point does not always coincide with the end point of the titration.

In cases where the equivalence point completely or almost completely coincides with the end point of the titration, based on the amount of the reagent used for the reaction with the substance to be determined (TB VB), according to the law of equivalents, the amount of the substance to be determined in grams or its content in percent can be calculated. When these points do not coincide, a correction factor is introduced, which is calculated on the basis of data obtained during titration under analytical conditions of solutions with a known content of the substance to be determined.

3. Classification of titrimetric methods

Titrimetric methods are classified by the type of reaction underlying the titration. These reactions can be reactions of exchange of protons, exchange of electrons, formation of poorly dissociated (complex) particles or formation of poorly soluble electrolytes. Corresponding groups of titrimetric methods are called acid-base titration (protolithometry), oxidation-appropriate titration (redoximetry),

complexometric titration (complexometry), precipitation titration (sedimetry). Individual titrimetric methods are named after the reagents used in these methods..

Таблиця - Класифікація титриметричних методів

Groups of methods	Subgroups of methods	Separate methods	Titrants	Determined substances
Protolithometry	Acidimetry Alkalimetry		HCl, H_2SO_4 NaOH	Bases, Acids
Redoximetry	Oxidimetry	Permanganatometry Iodometry Dichromostometry Bramotometry Iodometry Cerimetry	$KMnO_4$ I_2 $K_2Cr_2O_7$ $KBrO_3$ KIO_3 $Ce(SO_4)_2$	Reductors –//– –//– –//– –//–
Compexometry	Chelatometry	Mercurimetry Compexonometry	$Hg(NO_3)_2$ Трилон Б Na_2H_2Y	Cl^-, Br^-, I^-, CN^-, SCN^- Ni(II), Co^{2x}, Al^x, Zr^{IV}, Th^{IV}
Precipitation titration		Argentometry Mercurometry	$AgNO_3$ $Hg_2(NO_3)_2$	Cl^-, Br^-, I^-, CN^-, SCN^-

Reaction requirements in titrimetry

Reactions used in titrimetric analysis must meet the following requirements:

1) The reacting substances must react in strictly defined quantitative ratios (stoichiometry of these ratios);

2) The reaction between the substance to be determined and the standard solution of the reagent must proceed quickly and practically to the end;

3) Extraneous substances that are present in the test sample, if they passed into the solution together with the substance to be determined, should not interfere with the titration of the substance to be determined;

4) i.e. must fix in one way or another sharply and precisely;

5) Reactions should take place as far as possible at room temperature;

6) Titration should not be accompanied by side reactions that distort the results of the analysis.

4. Basic methods of titration

In the practice of titrimetric determination, several methods of titration are distinguished:

1) In direct titration methods, the titrant is added directly from the burette to the solution of the substance to be determined.

2) Two standard solutions are used in reverse titration methods (residue method) - basic and auxiliary. A significant excess of the main standard solution is added to the analyzed solution, and then its excess is titrated with an auxiliary standard solution. Example,

$$KCl + AgNO_3 + KNO\downarrow \rightarrow AgCl_3;$$

$$AgNO_3 + NH_4 + NH\downarrow \rightarrow AgSCN SCN_4NO_3.$$

3) Substitute titration or substitute titration (indirect titration), when a special reagent is added to the substance to be determined, which quantitatively interacts with it, and then one of the reaction products is titrated with a standard solution. An example can be the iodometric determination of copper:

$$2Cu^{2+} + 4J^- \rightarrow J_2 + CuJ_2\downarrow;$$

$$J_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaJ. \text{ (IV)}$$

General material and bulk-methodological support of the lecture:

- ✓ computer presentation;
- ✓ illustrative materials;
- ✓ examples of solving typical tasks or performing typical tasks;
- ✓ multimedia projector.

Questions for self-control:

1. What is titration, titrant? What is the difference between the concepts of "equivalence point" and "endpoint of titration"? What methods of detection of the end point of titration do you know?
2. What solutions in titrimetric methods of analysis are called standard? Give examples of primary and secondary standard solutions
3. Give examples of primary and secondary standard substances used in titrimetry. What properties must a chemical compound have in order for it to be used as a primary standard substance?
4. Give examples of titrimetric determinations that use direct, reverse, indirect and surrogate titrations. What are the requirements for a chemical reaction used in a direct titration?

References:

General:

1. Analytical chemistry: handbook / V. V. Bolotov, O. A. Yevtifeyeva, L. Yu. Klimenko, T. A. Kostina, T. V. Zhukova, E. Yu. Ahmedov , O. A. Brizicky; edited by V. V. Bolotov.— Kharkiv: NUPh; Original, 2012.
2. Analytical chemistry (Qualitative analysis). Part I / O. A. Ievtifieieva, V. V. Bolotov, T. A. Kostina, O. M. Svechnikova, T. I. Yuschenko, N. I. Kaminska, A. E. Kosareva, L. V. Slobodyanyuk, O. P. Yashchuk ; edited by O. A. Ievtifieieva. – Kharkiv : Publishing house the CLL «Generous farmstead plus», 2014. – 168 p.
3. Analytical chemistry. Part II. Quantitative analysis: the manual for foreign students of pharmaceutical higher schools and pharmaceutical departments of medical higher schools of the III – IV accreditation levels / V. V. Bolotov, O. M. Svechnikova, T. A. Kostina et al. – Kharkiv: NUPh, 2010. – 160 p.
4. Analytical chemistry: textbook [the textbook for students of higher schools] / I.S. Grytsenko, V. V. Bolotov, L.Yu. Klimenko et al.; ed. by I.S. Grytsenko – Kharkiv: NUPh, Golden Pages, 2019. – 600 p.

Lecture No. 9

Topic: Acid-base titration. The essence of the method and its possibilities. Method indicators. Acid-base titration curves. Titration of polybasic acids, multiacid bases, mixtures of acids or bases

Relevance of the topic: Analytical chemistryis a science that develops theoretical foundations and practical methods of chemical analysis.Therefore, it is relevant to solve the problems facing analytical chemistry with the help of physical, chemical and physicochemical methods used for the analysis of medicinal products.

Purpose: generalize students' knowledge of titrimetric analysis. Familiarize yourself with the concept of acid-base titration in aqueous and non-aqueous media.

Basic concepts:analytical chemistry, quantitative analysis, titrimetry, working solution, primary standard, secondary standard, molar concentration, normal concentration, titer

Plan and organizational structure of the lecture:

1. General characteristics of the neutralization method
2. Indicators of the neutralization method
3. Titration curves
4. Practical application of the acid-base titration method.

Content of lecture material (lecture text):

1. General characteristics of the neutralization method

Neutralization method —titrimetric method of analysis, the basis of which (in an aqueous medium) is the neutralization reaction:

$$H_3O^+ + OH^- \rightleftharpoons 2H_2O.$$

Standard solutions of the method are 0.1 M...0.001 M solutions of HCl, H_2SO_4, NaOH, KOH. If acid solutions are used as titrants, the method is called acidimetry, and if bases are used, alkalimetry. Prepare secondary standard solutions; their exact molar concentration is established by standard substances or by their titration with solutions of known concentration. Standardization of acid solutions is carried out using standard substances: sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$), sodium carbonate (Na_2CO_3), tris-(oxymethyl)-aminoPurposene

or standard alkali solutions (NaOH and KOH). Standardization of alkali solutions is carried out according to standard substances: oxalic acid ($H_2C_2O_4$), succinic acid ($H_2C_4H_4O_4$), potassium hydrophthalate ($KHC_8H_4O_4$), potassium hydroiodate ($KH(IO_3)_2$), according to standard solutions of HCl, H_2SO_4.

Depending on the investigated object, different methods of ABT are used: direct, reverse, substitute. The end point of the titration in the neutralization method is determined using acid-base (pH) indicators, as well as without an indicator - by changing the pH of the environment (potentiometrically) or the electrical conductivity of the solution (conductometrically).

The choice of pH indicators is carried out in two ways: by reaction products and by titration curves. When choosing an indicator by reaction products, take into account the pH of the solution at the end point of the titration. If the pH of the medium is >7, then an indicator whose transition interval lies in the alkaline range of pH values is suitable.

E.g.: $H_2C_2O_4 + 2NaOH \rightleftharpoons Na_2C_2O_4 + 2H_2O$ (the sodium oxalate reaction product hydrolyzes and creates an alkaline environment). For this determination, phenolphthalein is used (transition interval 8.2–10.0 pH). If the reaction product at the end point of the titration creates an acidic environment (pH <7), then an indicator whose transition interval lies in the acidic range of pH values is suitable.

E.g.: $NaHCO_3+HCl \rightleftharpoons H_2CO_3+NaCl$. In this case, you can use methyl orange (transition interval 3.1–4.0 pH) to determine the end point of the titration.

The most suitable is the selection of the indicator according to the titration curves. For this purpose, a titration curve is constructed, which graphically displays the change in the pH of the solution during the titration process, for which indicators are suitable whose transition interval is completely or partially within the limits of the titration jump, i.e. indicators whose pH is within the limits of the titration jump. By the method of ABT it is possible to determine: strong acids and bases; weak acids and bases (Ka not less than $5\cdot10^{-7}$); salts formed by a weak base with Kb $\leq5\cdot10^{-7}$ or a weak acid with Ka $\leq5\cdot10^{-7}$; organic compounds with acidic or basic properties. Acids with pK_a >7 and bases with pK_b <7 are titrated using non-

aqueous solvents (see Non-aqueous titration). This method can determine not only individual substances, but also a mixture of acids (bases) of different strengths, a mixture of hydrolyzing salts, and mixtures of salts and acids (bases).

2. Indicators of the neutralization method

The neutralization reaction is not accompanied by visible changes, for example, a change in the color of the solution. Therefore, for fixing, i.e. an indicator is added to the titrated solution. In that. the solution acquires a certain pH value. Indicators in the acid-base titration method are substances whose color changes depending on the change in pH value. Therefore, these substances are called acid-base indicators. The color of each of the indicators changes within a narrow range of pH values, and this range depends only on the nature of the reacting acids and bases.

The indicators are subject to the following requirements:

1) the color of the indicator at close pH values should differ well;

2) the change in color of the indicator should occur sharply in a small range of pH values;

3) the color of the indicator should be as intense as possible;

4) the amount of alkali or acid needed to change the color of the indicator should be so small that the titration results are not distorted;

5) changing the color of the indicator should be a reversible process.

All these requirements greatly limit the choice of indicators. The number of indicators used in this way is about 20. The correct choice of indicator during titration is very important.

In 1894 Ostwald created the ion theory of indicators. Indicators in the acid-base titration method are weak acids or bases in which non-ionized molecules and ions have different colors.

$$HInd \leftrightarrow H^+ + Ind^-$$

litmus red blue

phenolphthalein colorless crimson pink

In litmus both its forms are colored. Such indicators are called two-color; in phenolphthalein - one form is colored, and the second is colorless, then such an indicator is called monochromatic.

Factors affecting indicator readings.

1) that. with an increase in t, the indicator becomes less sensitive to H+- ions in indicator-bases.

2) the presence of an organic solvent - alcohol, acetone.

protein molecules, salt changes. pK of the indicator.

The titer of the working solution should be determined under the same conditions as the determination in the sample under study.

3) It is not recommended to take a lot of indicator.

4) The order of titration is important, that is, the clarity of the color change from pink to yellow is not sharp, but from yellow to pink is sharp, so it is better to titrate with methyl orange from alkali to acid.

5) Using witnesses to catch the color transition.

6) Application of mixed indicators - indicator solution with an indifferent dye. The color of the dye should be complementary to the color of the indicator, which it will have at a pH equal to the indicator's pH. Accordingly, when this pH is reached, the solution becomes colorless.

Sometimes a mixture of two different indicators is used instead of a dye.

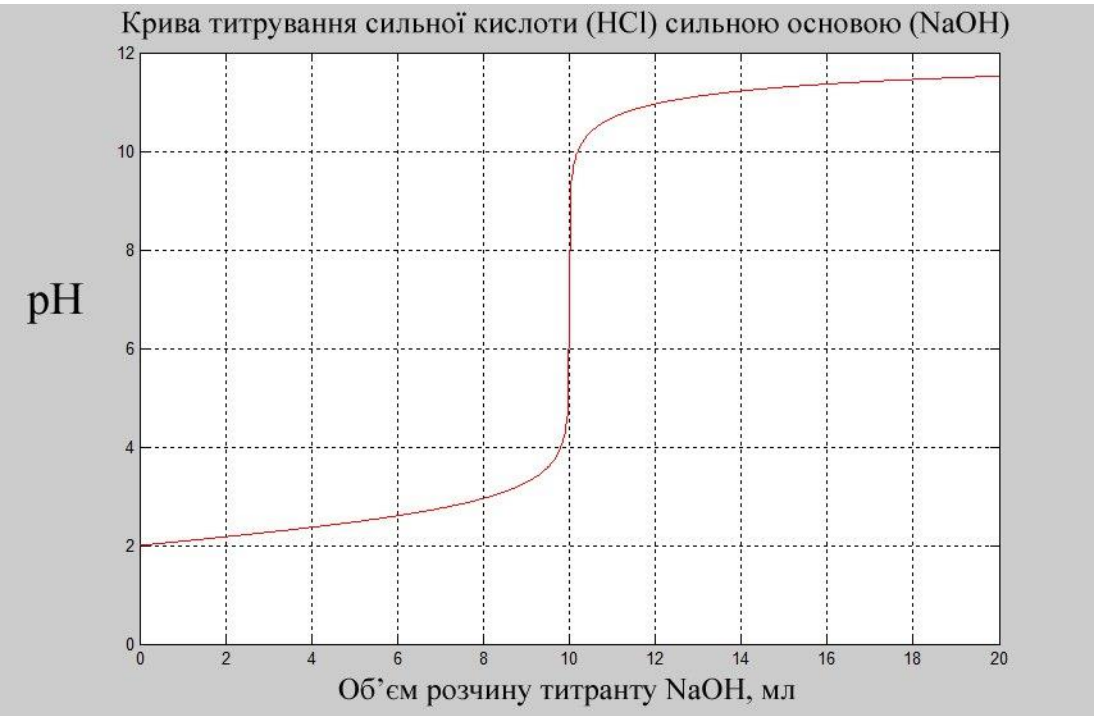
3.Titration curves

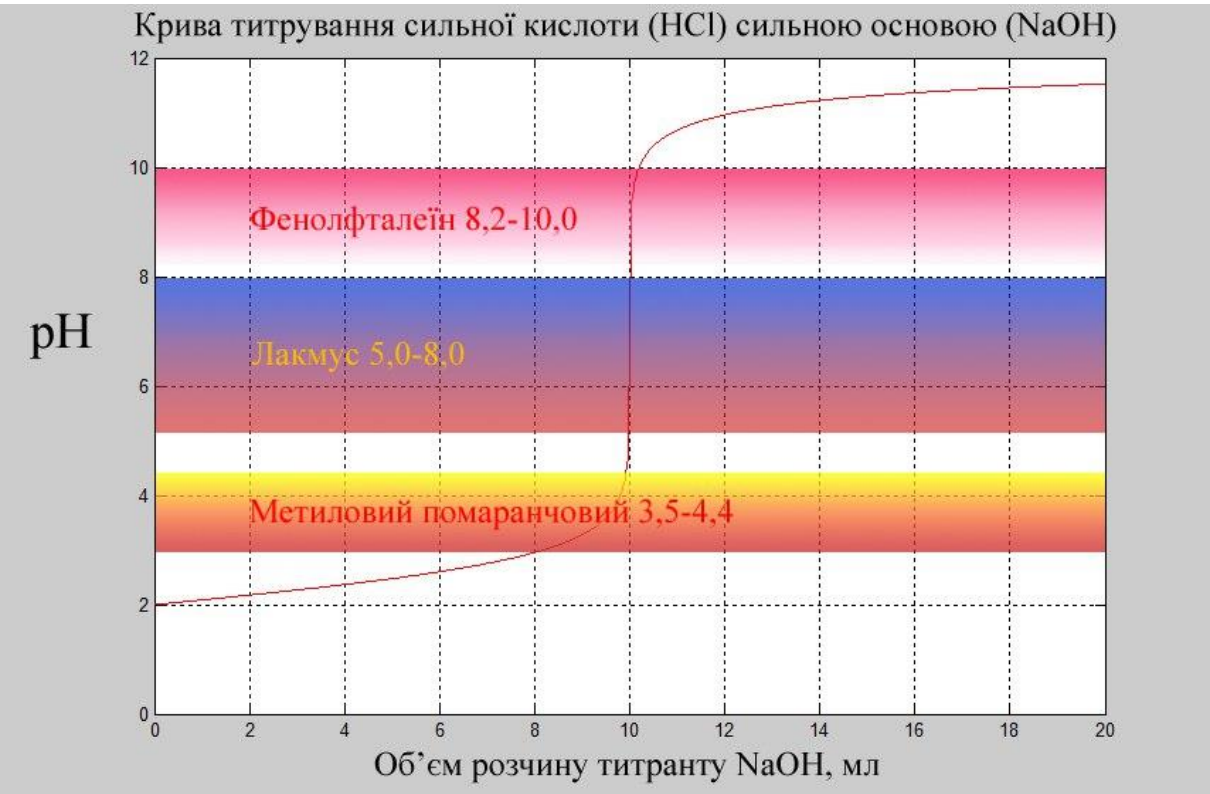
Suppose, for example, that 100 ml of a 0.1 N HCl solution is titrated with a 0.1 N NaOH solution.

An example of a titration curve and the selection of an indicator by a titration curve

Titration of polybasic acids or polyacid bases, mixtures of acids (bases), mixtures of hydrolyzing salts is carried out taking into account stepwise ionization or stepwise gradual hydrolysis of salts, polybasic acids (bases), the strength of acids Ka and the strength of bases Kb, which makes it possible to differentially titrate with fixing several equivalence points. Polybasic acids (bases) can be considered

as mixtures of acids (bases) of different strength due to their stepwise ionization. If the acids (bases) differ significantly in strength, and the ratio of ionization constants $K_1/K_2 \geq 10^4$, then each of the acids (bases) will be titrated separately. First - the strongest, then - the weakest. Thus, two titration jumps are observed on the titration curve. If $K_1/K_2 \leq 10^4$, then both acids (bases) will be titrated simultaneously and the titration curve will have one titration jump.





The acid-base titration method is used to determine inorganic, organic (including drugs) and natural compounds with acidic and basic properties, NO_3^-, NO_2^- and NH_4^+ ions, complex esters, hydroxyl- and carbonyl-containing groups in organic compounds. It is important to determine some elements in organic and biological systems (C, N, Cl, Br, F, S, P, etc.) — the element to be determined is converted into an inorganic acid or base with further determination by the neutralization method.

4. Practical application of the acid-base titration method.

Titration of a mixture of acids is practically important.

There may be several options here:

a) titration of a mixture of strong acids;

b) titration of a mixture of strong and weak acid;

c) titration of a mixture of weak acids.

In the first case, due to the complete ionization of strong acids, the titration curve of their mixture will not differ from the titration curve of only a strong acid, it is only necessary to take into account that the concentration of H+ will be the sum of the concentrations of the mixture of acids.

When a mixture of a strong acid and a weak acid is titrated, the concentration of H+ will be almost equal to the concentration of the strong acid before the start of the titration, since in its presence the dissociation of the weak acid can be neglected. For this reason, only a strong acid will be completely titrated if $K_a \leq 10^{-7}$.

The titration of a mixture of weak acids or also the titration of polybasic acids, which are a conditional mixture of acids due to their own stepwise dissociation, is interesting.

For example, orthophosphate acid:

$$H_3PO_4 \leftrightarrow H^+ + H_2PO_4^-;$$

$$H_2PO_4^- \leftrightarrow H^+ + H_2PO_4^{2-};$$

$$HPO_4^{2-} \leftrightarrow H^+ + H_2PO_4^{3-}.$$

According to the stepwise dissociation of acids, their neutralization is also stepwise:

$$H_3PO_4 + OH^- \leftrightarrow H_2O + H_2PO_4^-;$$

$$H_3PO_4^- + OH^- \leftrightarrow H_2O + H_2PO_4^{2-};$$

$$H_3PO_4^{2-} + OH^- \leftrightarrow H_2O + H_2PO_4^{3-}.$$

Accordingly, the titration curve of H_3PO_4 with NaOH has three equivalence points.

General material and bulk-methodological support of the lecture:

- ✓ computer presentation;
- ✓ illustrative materials;
- ✓ examples of solving typical tasks or performing typical tasks;
- ✓ multimedia projector.

Questions for self-control:

1. Acid-base titration. The essence of the method and its possibilities.
2. Method indicators. Curves of acid-base titration.
3. Selection of indicators.
4. Application of the acid-base titration method

References:

General:

1. Analytical chemistry: handbook / V. V. Bolotov, O. A. Yevtifeyeva, L. Yu. Klimenko, T. A. Kostina, T. V. Zhukova, E. Yu. Ahmedov , O. A. Brizicky; edited by V. V. Bolotov.— Kharkiv: NUPh; Original, 2012.
2. Analytical chemistry (Qualitative analysis). Part I / O. A. Ievtifieieva, V. V. Bolotov, T. A. Kostina, O. M. Svechnikova, T. I. Yuschenko, N. I. Kaminska, A. E. Kosareva, L. V. Slobodyanyuk, O. P. Yashchuk ; edited by O. A. Ievtifieieva. – Kharkiv : Publishing house the CLL «Generous farmstead plus», 2014. – 168 p.
3. Analytical chemistry. Part II. Quantitative analysis: the manual for foreign students of pharmaceutical higher schools and pharmaceutical departments of medical higher schools of the III – IV accreditation levels / V. V. Bolotov, O. M. Svechnikova, T. A. Kostina et al. – Kharkiv: NUPh, 2010. – 160 p.
4. Analytical chemistry: textbook [the textbook for students of higher schools] / I.S. Grytsenko, V. V. Bolotov, L.Yu. Klimenko et al.; ed. by I.S. Grytsenko – Kharkiv: NUPh, Golden Pages, 2019. – 600 p.

Lecture No. 10

Topic: Titration in non-aqueous media (protolithometry). Application of acid-base titration method for quantitative determination of chemicals and drugs

Relevance of the topic: Analytical chemistryis a science that develops theoretical foundations and practical methods of chemical analysis.Therefore, it is relevant to solve the problems facing analytical chemistry with the help of physical, chemical and physicochemical methods used for the analysis of medicinal products.

Purpose: generalize students' knowledge of titrimetric analysis. Familiarize yourself with the concept of acid-base titration in aqueous and non-aqueous media.

Basic concepts: analytical chemistry, quantitative analysis, titrimetry, working solution, primary standard, secondary standard, molar concentration, normal concentration, titer

Plan and organizational structure of the lecture:

1. Acid-base titration in a non-aqueous environment
2. Examples of application of acid-base titration methods for quantitative determination of medicinal substances
3. Titration of mixtures with fixation of two equivalence points

Content of lecture material (lecture text):

Non-aqueous acid-base titration

The method of acid-base titration in non-aqueous media significantly extends the range of analytical determinations in comparison with aqueous solvents. This method is used for the quantitative determination of compounds that are acids, bases or salts, the titration of which in water is difficult or impossible due to the weak acid-base properties of the compounds. The main advantage of this method lies, first of all, in the fact that it allows you to titrate with reliable accuracy not only strong acids and bases, but also weak and very weak acids, bases, their salts and multicomponent mixtures without their preliminary separation. With the help of this method, you can titrate both colorless and colored solutions, and it also makes it possible to determine the concentration of substances that are poorly soluble in water. The method of non-aqueous titration gives more accurate results in comparison with the accuracy of titration of aqueous solutions. Since, as a result of small, as a rule, surface tension of organic solvents, the sizes of drops of non-aqueous solutions are smaller than the sizes of drops of aqueous solutions. Under the influence of different solvents, the properties of the same substance can change dramatically. The strength of an acid or a base is determined by the degree of their interaction with the solvent. A properly selected non-aqueous solvent can enhance the basic or acidic properties of a weak base or weak acid, making their quantification possible by acid-base titration. The method is widely used in the practice of pharmaceutical analysis for the determination of drugs (barbiturates, caffeine, various hydrohalides).

Peculiarities of titration in non-aqueous solutions.

1. A rapid method of quantitative analysis of many inorganic, organic and elemental organic compounds.
2. Allows to determine substances that do not have titration jumps in aqueous solutions.
3. They allow to determine substances that are often insoluble in water, decompose in water, form stable non-salt-like substances or stable emulsions in water.
4. Can be used for titration of colored solutions.
5. The possibility of fixation, i.e. indicator and physicochemical methods.
6. There is often no need to separate and separate from accompanying impurities or fillers.
7. Due to the lower surface tension of organic solvents compared to water, the size of the drop is smaller, and the accuracy of the analysis is higher.

The previously studied properties of non-aqueous solvents allow us to formulate the following rules for their selection during acid-base titration:
- the autoprotolysis constant of the solvent should be as small as possible;
- for the titration of weak bases, the best is a solvent with pronounced protogenic properties, that is, an acidic solvent;
- for the titration of weak acids, a solvent with pronounced protophilic properties, i.e. a basic solvent, is preferable;
- the dielectric constant of the solvent should be as high as possible.

To titrate very weak bases with a solvent, of course, acetic acid is taken. For the titration of very weak acids, several amofiprotic basic solvents are used. The best of them is ethylenediamine, successfully used, also dimethylformamide, but it is weaker than ethylenediamine. Purposenol and ethanol are also widely used in acid-base titration. They are neutral solvents, like water, but with a lower autoprotolysis constant. They are used in the titration of mono- and dicarboxylic acids, amines and diamines, salts of mineral and organic acids.

Aprotic solvents have extremely low values of acidity or basicity constants. However, having low dielectric constant values, they are difficult to distinguish between acids and bases, and this, in turn, limits their scope of application.

Most of the acid-base indicators used for titration in aqueous media can also be used to determine the end point of titration in non-aqueous solvents. It is difficult to predict the behavior of such indicators in a non-aqueous environment. Therefore, the selection of indicators for non-aqueous environments is carried out empirically. The color transition of indicators in aqueous and non-aqueous environments is different. For example, when titrating bases in acetic acid, methyl violet can be used as an indicator, which changes color at the equivalence point from violet to blue or blue-green. However, the best methods of fixing the equivalence point are instrumental methods: potentiometric, conductometric.

A 0.1 M solution of HClO4 in anhydrous acetic acid is most often used as standard solutions for the titration of compounds of a basic nature in non-aqueous media. Most compounds of a basic nature are titrated in an acetic acid medium. However, sometimes a solution of perchloric acid in dioxane is used. At the same time, i.e. appears more clearly than when using perchloric acid solutions in anhydrous acetic acid. Standardization of the prepared perchloric acid solution is carried out with potassium hydrophthalate using methyl violet or crystal violet indicators. When titrating acidic compounds, inorganic bases or alkaline Purposels, organic bases are used as standards. Standard solutions are a 0.1 m solution of potassium or sodium methylate in a Purposenol-benzene mixture, a 0.1 m solution of tetrabutylammonium hydroxide in alcohol, alcoholic solutions of sodium or potassium hydroxides. Standardization of prepared base solutions is carried out using benzoic acid in the medium of the solvent in which the titration will be carried out. Thymol blue is used as an indicator because acetic acid shows a differentiating effect against strong acids, among which perchloric acid is the strongest under these conditions.

2 Examples of application of acid-base titration methods for quantitative determination of medicinal substances

1. Determination of nicotinic acid

The method is based on the following reaction:

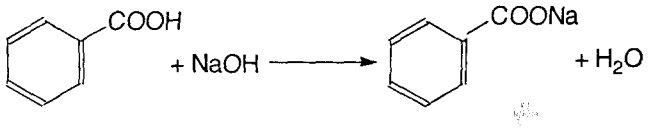
Since nicotinic acid is a weak acid, its aqueous solutions due to hydrolysis have an alkaline reaction, and therefore, phenolphthalein is used as an indicator. Direct titration.

ANALYSIS PROCESS

A portion of 0.3 g of the substance is weighed on an analytical balance, placed in a conical flask with a capacity of 100 cm 3 , dissolved in 25 ml of freshly boiled hot water, and after cooling, 2-3 drops of phenolphthalein are added and titrated with a 0.1 mol/l sodium hydroxide solution until the appearance of a pink color that does not disappear within 1-2 minutes.

2. Determination of benzoic acid

The method is based on the following reaction:



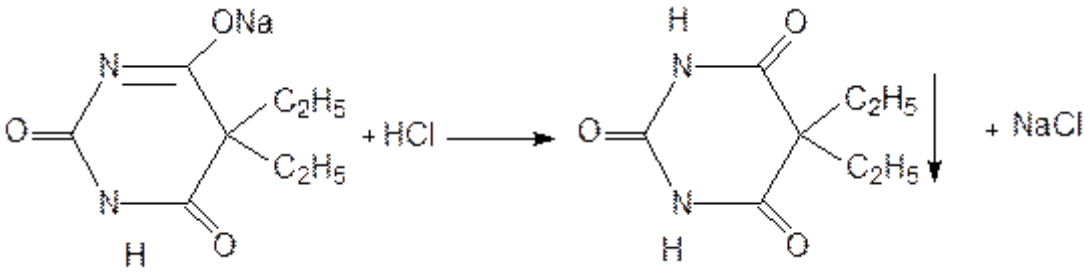
Since benzoic acid practically does not dissolve in water, the weight is dissolved in alcohol. In addition, the degree of hydrolysis of the formed salt decreases in an alcoholic environment. Full titration.

ANALYSIS PROCESS

A portion of 0.2 g of the substance is weighed on an analytical balance, placed in a conical flask with a capacity of 100 cm 3 , dissolved in 20 ml of alcohol neutralized with phenolphthalein and titrated with the same indicator with a 0.1 mol/l sodium hydroxide solution until a pink color appears, which does not disappear within 1-2 minutes.

3. Determination of sodium barbital

Since sodium barbital is both a salt formed by a strong base and a weak acid, it will hydrolyze in aqueous solutions to form sodium hydroxide, which is titrated with hydrochloric acid. The definition is based on the reaction:



Direct titration.

ANALYSIS PROCESS

A portion of 0.5 g of the substance is weighed on an analytical balance, placed in a conical flask with a capacity of 100 cm 3 , dissolved in 30 ml of freshly boiled and cooled water, 2-3 drops of methyl orange and 0.1 mol/l hydrochloric acid solution are added until a pink color appears. coloring that does not disappear within 1-2 minutes.

3. Titration of mixtures with fixation of two equivalence points

Medicinal products are often manufactured as a mixture of different ingredients that must be determined separately in the case of quantitative analysis. The method of acid-base titration makes it possible to determine not only individual substances, but also mixtures of different strengths of acids (bases), salts that hydrolyze, as well as a mixture of salts and acids (bases). Titration in suchcases are carried out taking into account stepwise ionization or stepwise stepwise hydrolysis, which enables differential titration with fixing of several equivalence points. This titration method can be used for the analysis of multicomponent medicinal mixtures that are part of modern pharmaceutical preparations, as well as to determine impurities that exhibit acid-base properties.

Analysis of a mixture of carbonate and hydroxide, carbonate and bicarbonate of alkaline Purposel using two indicators

When titrating a mixture of hydroxide and carbonate of alkaline Purposel, for example, NaOH and Na_2CO_3 and identifying the end point of the titration with the help of phenolphthalein, the following reactions occur:

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

$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl,$$

When the end point of the titration is detected using methyl orange, the reaction of the interaction of sodium hydroxide with an acid proceeds in the same way, and sodium carbonate is titrated to carbonic acid. The difference between the volumes of the titrant solution used to titrate the mixture in the presence of methyl orange and phenolphthalein will correspond to the course of the reaction:

$$NaHCO_3 + HCl \rightarrow H_2CO_3 + NaCl$$

The equivalence factor of $NaHCO_3$ in this reaction is equal to 1. If we assume that there was no $NaHCO_3$ in the initial mixture, then $n(NaHCO_3) = n_0(Na_2CO_3)$ and the mass of sodium carbonate can be calculated as follows

$$m(Na_2CO_3) = (C(HCl)\cdot(V_{MO} - V_{Ph})\cdot 10^{-3})/M(Na_2CO_3)$$

For interaction with NaOH, which is in the analyzed sample, the volume of the standard titrant solution equal to

$$V_{Ph} - (V_{MO} - V_{Ph}) = 2V_{Ph} - V_{MO},$$

therefore, the mass of NaOH is calculated according to the following formula

$$m(NaOH) = (C(HCl)\cdot(2V_{Ph} - V_{MO})\cdot 10^{-3})/M(NaOH)$$

If the titration of a mixture of alkali and carbonate with phenolphthalein and methyl orange consumes almost the same volume of the standard titrant solution, then the carbonate content in the mixture is very small. On the contrary, if the volumes of the titrant solution used for titration are significantly different, then the analyzed mixture contains a lot of carbonate.

Analysis of a mixture of bicarbonate and alkaline Purposel carbonateby titration with a solution of a strong acid in the presence of two indicators is based on the same principle as the analysis of a mixture of hydroxide and carbonate.

When titrating a mixture with phenolphthalein, only carbonate interacts with the titrant

$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$$

Both carbonate and bicarbonate are titrated with methyl orange. From the volume of HCl solution used for titration with phenolphthalein, the content of Na_2CO_3 ($f_{eq} = 1$) can be calculated, and from the difference between the volume of HCl solution used for titration with methyl orange and twice the volume used for titration with phenolphthalein, the content is determined sodium bicarbonate

$$m(Na_2CO_3) = C(HCl) \cdot V_{Ph} \cdot 10^{-3}/M(Na_2CO_3)$$

$$m(NaHCO_3) = C(HCl) \cdot (V_{MO} - 2V_{Ph}) \cdot 10\text{-}3/M(NaHCO_3)$$

The more titrant required for titration with phenolphthalein, the more carbonate is contained in the analyzed sample. If, when adding phenolphthalein to the solution being titrated, the latter turns slightly pink and only a few drops of the titrant solution are needed for its decolorization, then the carbonate content in the sample is very low.

General material and bulk-methodological support of the lecture:

- ✓ computer presentation;
- ✓ illustrative materials;
- ✓ examples of solving typical tasks or performing typical tasks;
- ✓ multimedia projector.

Questions for self-control:

1. Basic requirements for reactions used in the neutralization method.
2. What is the endpoint of a titration and the equivalence point?
3. Construction of titration curves of a strong acid with a strong base (and vice versa) and their characteristics.
4. Indicators. Ion-chromophoric theory of action of indicators.
5. Indicator transition interval. Selection of indicators.
6. Non-aqueous solvents and their use in the acid-base titration method.

References:

General:

1. Analytical chemistry: handbook / V. V. Bolotov, O. A. Yevtifeyeva, L. Yu. Klimenko, T. A. Kostina, T. V. Zhukova, E. Yu. Ahmedov , O. A. Brizicky; edited by V. V. Bolotov.— Kharkiv: NUPh; Original, 2012.
2. Analytical chemistry (Qualitative analysis). Part I / O. A. Ievtifieieva, V. V. Bolotov, T. A. Kostina, O. M. Svechnikova, T. I. Yuschenko, N. I. Kaminska, A. E. Kosareva, L. V. Slobodyanyuk, O. P. Yashchuk ; edited by O. A. Ievtifieieva. – Kharkiv : Publishing house the CLL «Generous farmstead plus», 2014. – 168 p.
3. Analytical chemistry. Part II. Quantitative analysis: the manual for foreign students of pharmaceutical higher schools and pharmaceutical departments of medical higher schools of the III – IV accreditation levels / V. V. Bolotov, O. M. Svechnikova, T. A. Kostina et al. – Kharkiv: NUPh, 2010. – 160 p.
4. Analytical chemistry: textbook [the textbook for students of higher schools] / I.S. Grytsenko, V. V. Bolotov, L.Yu. Klimenko et al.; ed. by I.S. Grytsenko – Kharkiv: NUPh, Golden Pages, 2019. – 600 p.

Lecture No. 11

Topic: Redox titration. Classification of methods. Redox titration indicators. The use of methods in the analysis of chemical compounds and drugs.

Relevance of the topic: Analytical chemistryis a science that develops theoretical foundations and practical methods of chemical analysis.Therefore, it is relevant to solve the problems facing analytical chemistry with the help of physical, chemical and physicochemical methods used for the analysis of medicinal products.

Purpose: generalize students' knowledge of titrimetric analysis. Familiarize yourself with the concept of redox titration.

Basic concepts:analytical chemistry, quantitative analysis, titrimetry, working solution, primary standard, secondary standard, molar concentration, normal concentration, titer

Plan and organizational structure of the lecture:

1. General characteristics of redox titration
2. Classification of redox methods
3. Conditions for redox titration
4.Types of redox titration
5.Classification of RedOx titration indicators
6. Characteristics of permanganatometric titration

Content of lecture material (lecture text):

1. General characteristics of redox titration

Redox titration methods, or redox methods, are based on the use of electron transfer reactions - redox reactions. In other words, redox titration, or redoxmetry, is a titration accompanied by the transfer of one or more electrons from the donor ion or molecule (reductant) Red1 to the acceptor (oxidizer) Ox2:

$$Red1 + Ox2 = Ox1 + Red2$$

The reduced form of one substance Red1, donating electrons, turns into the oxidized form Ox1 of the same substance. Both of these forms form one redox pair Oxl|Redl.

The oxidized form Ox2 of the second substance, which participates in the OB reaction, accepting electrons, turns into the reduced form Red2 of the same substance. Both of these forms also form the redox couple Ox2|Red2.

At least two redox couples are involved in any redox reaction.

The higher the RedOx potential of the redox pair Ox2|Red2, the oxidized form of which plays the role of the oxidant of this reaction, the more reducing agents Red1 can be titrated and determined using this Ox2 oxidant. Therefore, in redoxmetry, oxidants are most often used as titrants, the standard RedOx potentials of redox pairs of which have the highest possible values, for example (at room temperature):

Ce^{4+}, $E°(Ce^{4+} \mid Ce^{3+})$ = 1,44 B;

MnO_4^-, $E°(MnO_4^- \mid Mn^{2+})$ = 1,51 B,

$Cr_2O_7^{2-}$, $E°(Cr_2O_7^{2-} \mid Cr^{3+})$ = 1,33 В

Classification of redox methods

Several dozen different methods of RedOx titration are known. They are usually classified as follows.

Classification by the nature of the titrant.

In this case, RedOx titration methods are divided into two groups:

oxidimetry - methods of determining reductants using an oxidizing agent;

reductometry - methods of determining oxidants using titrant-reducing agent.

Classification by the nature of the reagent, which interacts with the conditioned substance.

Below, after the name of the corresponding method, the main active ingredient of this method is indicated in parentheses: bromatometry (potassium bromate $KBrO_3$), bromometry (bromine Br_2), dichromatometry (potassium dichromate $K_2Cr_2O_7$), iodatometry (potassium iodate KIO_3), iodometry (solution of iodine in potassium iodide KI_3, sodium thiosulfate $Na_2S_2O_3$), nitritometry (sodium nitrite $NaNO_2$), permanganatometry (potassium permanganate $KMnO_4$).

Some other methods of RedOx titration are used less often, such as: ascorbinometry (ascorbic acid), titanometry (titanium(III) salts), vanadatemetry (ammonium vanadate NH_4VO_3), etc.

3. Conditions for redox titration

Reactions used in RedOx titration methods must meet a number of requirements, the most important of which are:

*Reactions should take place almost to the end.*The more complete the RedOx reaction is, the greater the equilibrium constant K, which is determined by the ratio

$$\lg \boldsymbol{K} = n(E_1° - E_2°)/0{,}059$$

at room temperature, where E1° and E2° are, respectively, the standard RedOx potentials of redox pairs participating in the given RedOx reaction, n is the number of electrons.

So, the bigger the difference $\Delta E°$= E1° - E2°, then the higher the equilibrium constant, the more complete the reaction. For reactions of the type

A + B = Reaction products

with n = 1 and$K \geq 10^8$ (at this value of K, the reaction proceeds at least 99.99%) we get for$\Delta E°$:

$\Delta E° \geq 0.059 \lg 10^8 \geq 0.47$ V.

The reaction should proceed quite quickly, so that the equilibrium, at which the real RedOx potentials of both redox couples are equal, is established almost instantly. Usually, OV titration is carried out at room temperature. However, in the case of slow RedOx reactions, the solutions are sometimes heated to speed up the reaction. Thus, the oxidation reaction of antimony (III) by bromate ions in an acidic medium at room temperature is slow. However, at 70-80 ° C, it flows quite quickly and becomes suitable for the bromatometric determination of antimony.

To accelerate the achievement of equilibrium, homogeneous catalysts are also used. Example:

$$HAsO_2 + 2Ce^{4+} + 2H_2O = H_3AsO_4 + 2Ce^{3+} + 2H^+$$

Standard RedOx potentials of redox pairs participating in the reaction are equal at room temperature $E°(Ce^{4+} \mid Ce^{3+}) = 1.44$ V, $Eº (H_3AsO_4 \mid HAsO_2 = 0.56$ V. Hence, for the equilibrium constant of this reaction, we get (n = 2)

$$\lg K = (1{,}44 - 0{,}56) / 0{,}059 \approx 30; \quad K \approx 10^{30}$$

The equilibrium constant is large, so the reaction proceeds with a very high degree of completeness. However, under normal conditions, it flows slowly. Catalysts are introduced into the solution to speed it up.

Sometimes the catalyst is the RedOx reaction products. So, with permanganatometric titration of oxalates in an acidic environment according to the scheme

$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ = 2Mn^{2+} + 10CO_2 + 8H_2O$$

manganese(II) Mn^{2+} cations act as catalysts. Therefore, at first, when adding a titrant solution - potassium permanganate - to a titrated solution containing oxalate

ions, the reaction proceeds slowly. In this regard, the titrated solution is heated. With the formation of manganese(II) cations, reaching equilibrium is accelerated and titration is carried out easily.

*The reaction must proceed stoichiometrically,*side processes must be excluded.

*The end point of the titration must be determined precisely and unambiguously*either with indicators or without indicators.

4. Types of redox titration

In RedOx titration, as in acid-base titration, direct, reverse and substitute titrations are used. The most accurate results, other things being equal, are obtained by direct titration.

In the calculations of the results of RedOx titration, the molar mass of the equivalent of the reactant A (oxidizing agent or reducing agent) M and the molar concentration of the equivalent of Sm are calculated based on the fact that in the OB reaction, the value z is equal to the number of electrons in the reaction, i.e. the difference in oxidation states of the oxidized and reduced forms of this substance A:

$$M(^1/_2A) = M(A)/z;\ c(^1/_2A) = zc(A),$$

where M(A) и c(A) are the molar mass and molar concentration of substance A, respectively.

Direct RedOx titration is performed when the RedOx reaction meets the requirements listed above.

Consider, for example, the determination of iron (II) by direct permanganometric titration according to the scheme

$$5Fe^{2+} + MnO_4^- + 8H^+ = Mn^{2+} + 5Fe^{3+} + 4H_2O$$

An aliquot of the analyzed solution containing iron(II) is titrated with a standard solution of potassium permanganate.

Half reactions

$$Fe^{2+} - e = Fe^{3+}$$

$$MnO_4^- + 5e + 8H^+ = Mn^{2+} + 4H_2O$$

5 electrons participate in the RedOx reaction.

According to the law of equivalents $n(Fe^{2+}) = n(^1/_5\, MnO_4^-)$. The number of equivalents can, as always, be given as the product of the molar concentration of the equivalent by the volume of the corresponding solution:

$$c(Fe^{2+})V(Fe^{2+}) = c(^1/_5\, MnO_4^-)V(\, MnO_4^-),$$

$$c(Fe^{2+}) = \frac{c(^1/_5\, MnO_4^-)V(\, MnO_4^-)}{V(Fe^{2+})}$$

Knowing the volumes of the aliquots of the analyzed solution $V(Fe^{2+})$ and the titrant $V(MnO_4^-)$, as well as the concentration of the titrant solution $C(1/5MnO_4^-)$, calculate the concentration of $C(Fe^{2+})$ and determine the substance in the original analyzed solution. The mass t of iron(II) in the entire volume V (in liters) of the original analyzed solution is calculated in the usual way::

$$m = c(Fe^{2+})\, M(Fe^{2+})\, V.$$

Reverse RedOx titration is performed when the use of direct titration is impractical for one reason or another.

To an aliquot of the analyzed solution containing the specified component X, add a precisely known amount of substance A, taken in excess compared to its stoichiometric amount, and keep the solution for some time to ensure the completeness of the reaction between X and A. The unreacted excess of substance A is titrated with a standard titrant solution T.

For example, during the iodimetric determination of the sulfide ion, an excess of a precisely known amount of iodine solution is added to an aliquot of the analyzed solution containing sulfide ions. A reaction is taking place

$$S^{2-} + J_2 = S + 2J^-$$

The excess of unreacted iodine is titrated with a standard solution of sodium thiosulfate:

$$2Na_2S_2O_3 + J_2 = Na_2S_4O_6 + 2NaJ$$

Calculations:

$$n(^1/_2J_2) = n(^1/_2S^{2-}) + n(Na_2S_2O_3)$$

$$c(^1/_2S^{2-})V(S^{2-}) = c(^1/_2J_2)V(J_2) - c(Na_2S_2O_3)V(Na_2S_2O_3)$$

$$c(^1/_2S^{2-}) = \frac{c(^1/_2J_2)V(J_2) - c(Na_2S_2O_3)V(Na_2S_2O_3)}{V(S^{2-})}$$

$$m = c(^1/_2S^{2-})M(^1/_2S^{2-})V,$$

Substitute RedOx titration is used to determine substances that do not enter the RedOx reaction.

Thus, in the iodometric determination of hydrogen peroxide, an excessive amount of potassium iodide compared to the stoichiometric amount is added to an aliquot of the analyzed solution containing the specified hydrogen peroxide in a sulfuric acid medium. At the same time, a reaction occurs with the formation of iodine:

$$H_2O_2 + 2J^- + 2H^+ = J_2 + 2H_2O$$

Iodine released (substitute) in an amount equivalent to the amount of hydrogen peroxide in the aliquot. titrate with a standard solution of sodium thiosulfate:

$$2\ Na_2S_2O_3 + J_2 = Na_2S_4O_6 + 2NaJ$$

5. 5. Classification of RedOx **titration indicators.**

In titrimetric redox methods, EPT is determined by the indicator method. At the same time, the role of the indicator can be played either by the reagent itself, which participates in the RedOx reaction, or by an indicator that is specially introduced. Accordingly, the indicators used in redox measurement can be classified as follows.

Indicator - reagent, which participates in the RedOx reaction. An example can be a titrant solution - potassium permanganate $KMnO_4$ in permanganatometry. The potassium permanganate solution has an intense crimson-purple color, so the very first drop of excess titrant after TE colors the titrated solution in a pink-crimson color. The titration is finished when a stable pink-raspberry color of the solution appears.

Indicator substance, which enters into a specific interaction with the oxidizing agent or reducing agent (participating in the RedOx reaction) with the formation of colored compounds.

An example can be a freshly prepared starch solution, which turns blue in the presence of iodine.

Another example is thiocyanate ions NCS^-, which are used as an indicator in the titration of iron (III), with which they form complexes colored in an intense red color. So. when titrating iron(III) with a titrant containing titanium(III), a reaction occurs

$$Fe^{3+} + Ti^{3+} = Fe^{2+} + Ti^{4+}$$

Ammonium or potassium thiocyanate is added to the original titrated solution, so the solution has a red color due to the formation of iron(III) thiocyanate complexes. In the process of titration, iron(III) turns into iron(II). Iron(III) is already absent in TE, therefore, the red color of the solution disappears in TE.

The indicator is a substance, which at a certain potential of the solution is oxidized or reduced with a change in color. Such indicators are called redox indicators or redox indicators. In other words, redox indicators are indicators that can be oxidized or reduced with a change in color in or near the TE.

Redox indicators are reversible and irreversible. Reversible indicators change color inversely at the potential of the solution in TE or near it and do not destroy at the same time. Irreversible indicators change color upon reaching a certain value of the potential in TE or near it and are irreversibly destroyed.

Reversible redox indicators. Oxidized and reduced forms of the indicator have different colors. The color of the indicator changes at a certain value of the potential of the solution.

A large number of reversible redox indicators are known. The table describes some RedOx indicators as an example.

Indicator	E°, V	The color of the indicator shape	
		oxidized	
Diphenylamine	0.76	blue	Diphenylamine
Diphenylbenzidine	0.76	blue	Diphenylbenzidine
Ferroin	1.06	blue	Ferroin
Neutral red	-0.325 (pH 7) 0.240 (pH 0)	red	Neutral red
Indigo carmine	-0.125 (pH 7) 0.291 (pH 0)	blue	Indigo carmine

Irreversible explosive indicators. Indicators of this group include methyl orange, methyl red, and neutral red. At the potential of the solution, which is equal to the potential, and in TE, they are irreversibly oxidized, as a result of which their characteristic color of the solution disappears.

Another classification of RedOx titration indicators. In addition to the one discussed above, the following classification of RedOx titration indicators is also proposed:

1. Indicators of the group of diphenylamine and diphenylbenzidine compounds.
2. Indicators of the group of triphenylmetynew and other dyes.
3. Diiminlysis chelate complexes
4. Indicators of special (specific) action.
5. Irreversible indicators undergoing destruction.
6. Various other compounds.
7. Mixed indicators.

Characteristics of permanganatometric titration

Permanganatometric titration, or permanganatometry, is a method of quantitative determination of substances (reductants, less often - oxidants and compounds that do not have redox properties) using a titrant - a solution of potassium permanganate $KMnO_4$.

Potassium permanganate is a strong oxidizer that has an intense purple-crimson color. Depending on the acidity of the titrated solution, the oxidizing properties of the permanganate ion are manifested in different ways.

In a strongly acidic environment (pH≪7) permanganate ion is reduced to manganese(II) Mn^{2+} cations, which have a very weak pink color (practically colorless):

$$MnO_4^- + 5e + 8H^+ = Mn^{2+} + 4H_2O$$

The standard RedOx potential of the redox pair $MnO_4^-H^+ \mid Mn^{2+}$ has a fairly high value and is 1.51 V at room temperature. Therefore, a number of reducing agents can be titrated with an acidic solution of potassium permanganate, and most of such RedOx reactions proceed at a high rate. With the increase in the concentration of hydrogen ions in the solution, the real potential of the redox pair under consideration.

Since 5 electrons participate in the RedOx half-reaction, the molar mass of the equivalent of potassium permanganate as an oxidizing agent in an acidic medium is equal to

$$M(^1/_5KMnO_4) = M(KMnO_4)/5 = 31{,}608 г/моль.$$

Conditions for permanganatometric titration. When performing a permanganatometric titration, at least the following basic conditions must be observed.

1) Influence of the pH of the environment. Permanganatometric titration is carried out in a strongly acidic environment at a concentration of hydrogen ions $[H_3O^+]$ = 1-2 mol/l. An acidic environment is created by the introduction of sulfuric acid. Nitric acid cannot be used, as it is a strong oxidizer and can oxidize the substance to be determined.

Hydrochloric acid is also not used in permanganatometry, because chloride ions are oxidized by permanganate ions to chlorine according to the scheme:

$$10Cl^- + 2\ MnO_4^- + 16H^+ = 5Cl_2 + 2\ MnO^2 + 8H_2O$$

At the same time, part of the titrant is spent on the oxidation of chloride ions, which causes an overconsumption of the titrant and increases the error of the analysis. Under normal conditions, this reaction is slow, but it is accelerated in the presence of iron (II) compounds.

In a sulfuric acid environment, the mentioned side processes are absent, therefore permanganatometric titration is carried out in a sulfuric acid environment.

2) Effect of temperature. Most often, permanganatometric determination is carried out at room temperature. An exception is the reaction of the permanganate ion with oxalic acid and oxalates, which is carried out when the titrated solution is heated.

3) Fixation of the end point of the titration. In permanganatometric titration, an external indicator is not usually used, since the titrant itself - a solution of potassium permanganate - has an intense crimson-violet color. Addition of one excessive drop of titrant to the TE results in a pink coloration of the solution being titrated. So, to give a distinct color to 100 ml of water, it is enough to add only 0.2 ml of potassium permanganate solution with a molar concentration equivalent to 0.1 mol/l.

General material and bulk-methodological support of the lecture:

- ✓ computer presentation;
- ✓ illustrative materials;
- ✓ examples of solving typical tasks or performing typical tasks;
- ✓ multimedia projector.

Questions for self-control:

1. What are redox titration methods based on? Classification of methods.
2. Permanganatometry. Characteristics of the method. Methods of fixing the equivalence point.
3. Preparation of the titrant working solution and its standardization. How do divalent manganese ions affect the rate of oxidation of oxalates with potassium

permanganate?

4. Redox titration indicators. Interval of color transition of redox indicators. Selection of indicators.

References:

General:

1. Analytical chemistry: handbook / V. V. Bolotov, O. A. Yevtifeyeva, L. Yu. Klimenko, T. A. Kostina, T. V. Zhukova, E. Yu. Ahmedov , O. A. Brizicky; edited by V. V. Bolotov.— Kharkiv: NUPh; Original, 2012.
2. Analytical chemistry (Qualitative analysis). Part I / O. A. Ievtifieieva, V. V. Bolotov, T. A. Kostina, O. M. Svechnikova, T. I. Yuschenko, N. I. Kaminska, A. E. Kosareva, L. V. Slobodyanyuk, O. P. Yashchuk ; edited by O. A. Ievtifieieva. – Kharkiv : Publishing house the CLL «Generous farmstead plus», 2014. – 168 p.
3. Analytical chemistry. Part II. Quantitative analysis: the manual for foreign students of pharmaceutical higher schools and pharmaceutical departments of medical higher schools of the III – IV accreditation levels / V. V. Bolotov, O. M. Svechnikova, T. A. Kostina et al. – Kharkiv: NUPh, 2010. – 160 p.
4. Analytical chemistry: textbook [the textbook for students of higher schools] / I.S. Grytsenko, V. V. Bolotov, L.Yu. Klimenko et al.; ed. by I.S. Grytsenko – Kharkiv: NUPh, Golden Pages, 2019. – 600 p.

Lecture No. 12

Topic: Sedimentation titration. Classification of methods. Argentometric, thiocyanatometric and mercurometric titration. Indicators. Possibilities and use of methods in chemical and pharmaceutical analysis.

Relevance of the topic: Analytical chemistryis a science that develops theoretical foundations and practical methods of chemical analysis.Therefore, it is relevant to solve the problems facing analytical chemistry with the help of physical, chemical and physicochemical methods used for the analysis of medicinal products.

Purpose: generalize students' knowledge of titrimetric analysis. Familiarize yourself with the concept of redox titration.

Basic concepts:analytical chemistry, quantitative analysis, titrimetry, working solution, primary standard, secondary standard, molar concentration, normal concentration, titer, argentometry, Mohr's method, Folgard's method, thiocyanatometry, Fayans-Khodakov method, mercurometry

Plan and organizational structure of the lecture:

1. General characteristics of the method
2. Titration curves and their analysis.
3.Precipitation titration indicators
4. Characteristics of individual methods

Content of lecture material (lecture text):

1. General characteristics of the method

Precipitation titration methods are titrimetric analysis methods that use titrants that form precipitates with substances to be determined.

Requirements for reactions and substances to be determined:

1. The substance to be determined must be well soluble in water and must form an ion that would be active in the precipitation reaction.
2. The sediment obtained in the reaction should be practically insoluble ($SP<10^{-8\div-10}$, $S<10^{-5}$).
3. Titration results should not be distorted by adsorption (co-precipitation) phenomena.
4. Precipitation should occur quickly enough (that is, supersaturated solutions should not be formed).
5. It should be possible to fix the equivalence point.

Classification of precipitation titration methods:

- argentometry;
- mercurometry;
- thiocyanatometry;

2.Titration curves and their analysis.

Construction of titration curves is carried out on the basis of calculations according to the solubility product rule.

The titration curve is built in coordinates that show the change in the concentration of the determined ion depending on the volume of added titrant.

The larger the titration jump on the curve, the wider the possibilities for choosing the appropriate indicator.

Factors that affect the magnitude of the titration jump:

1. The concentration of titrant solutions and the ion to be determined (the higher the concentration, the greater the titration jump).

2. Solubility of the sediment formed in the titration process (the lower the solubility, the greater the titration jump).

Dependence of the magnitude of the titration jump on the solubility of a sparingly soluble electrolyte.

3. Temperature (the higher the temperature, the greater the solubility of the precipitate and the smaller the titration jump. Titration is carried out at room temperature).

4. The ionic strength of the solution (the effect is relatively insignificant, because the ionic strength of the solution, compared to other factors, does not change the solubility of the precipitate so much; however, the higher the ionic strength of the solution, the higher the solubility and the smaller the titration jump).

3. Індикатори осаджувального титрування

Індикатори осаджувального титрування: осаджувальні, Purposeлохромні, абсорбційні.

3.Precipitation titration indicators

Precipitation titration indicators: precipitating, Purposelochromic, absorption.

Precipitating indicators are indicators that are released from solutions in the form of a precipitate in the well-known form in T.E. or close to it. Not many precipitating indicators are known. An example can be potassium chromate in Mohr's method for argentometric titration of chloride ions with argentum nitrate. A small amount (a few drops) of an aqueous solution of potassium chromate is added

to the initial solution, which contains a certain amount of chloride ions, and titrated with a solution of $AgNO_3$.

$$Cl^- + Ag^+ = Ag\,Cl\downarrow$$

Silver chloride is less soluble than silver chromate, so a precipitate of silver chromate does not form as long as chloride ions are present in the solution. In EP all chloride ions are theoretically titrated. Addition of the first excess portion of titrant - silver nitrate solution leads to the appearance of a red precipitate of silver chromate.

$$2AgNO_3 + K_2CrO_4 = Ag_2CrO_4\downarrow + 2KNO_3.$$

When a red precipitate is obtained, the titration is finished. The determination is carried out at pH 6.5 - 10.3, because in a strongly acidic environment (pH>6.5) the silver chromate precipitate dissolves with the formation of dichromate ions:

$$Ag_2CrO_4 + 2H^+ = 4Ag^+ + Cr_2O_7^{2-} + H_2O$$

In strongly alkaline solutions, argentometric titration is not carried out, because in alkaline solutions silver salts give a brown precipitate of Ag2O.

The required acidity of the solution is maintained by the introduction of sodium bicarbonate. In the optimal case, the concentration of chromate ions in the titration solution should be approximately 0.005 mol/l. At a higher concentration of chromate ions, their own yellow color makes it difficult to distinguish the red color of the silver chromate precipitate. At low concentrations of chromate ions, some excess of titrant – silver nitrate solution – is required to form a precipitate of silver chromate, which increases the error of precipitation titration. As a rule, it is recommended to prepare a 5% aqueous solution of potassium chromate and to strictly comply with the requirements for the analysis method, which involves adding only a certain amount of the indicator solution in each specific case.

Purposelochromic indicators in precipitation titration are indicators that form colored complexes with the titrant near T.E.

One of the most well-known Purposelochromic indicators for the precipitation titration of iron (III) salts was presented by Folgard for thiocyanatometry and for argentometric determination of halogens by back titration. Iron ammonium alum $NH_4Fe(SO_4)_2 \cdot 12H_2O$ usually used as iron (III) salt.

Consider, for example, the determination of silver cations by direct titration, which contain thiocyanate ions. A small amount of indicator solution is added to the analyzed solution containing silver cations. During titration, the following reaction takes place:

$$AgNO_3 + NH_4SCN = AgSCN\downarrow + NH_4NO_3.$$

In EP all silver cations are theoretically titrated. Additions after T.E. of the first excess portion of the titrant leads to the formation of iron (III) thiocyanate complexes of red color. The solution turns red, the color is already noticeable at the concentration of iron (III) C≥6.4·10-6 mol/l, T.E. the indicator is quite sensitive to thiocyanate ions.

Iron (III) thiocyanate complexes are not formed, since thiocyanate ions are primarily bound to the poorly soluble AgSCN precipitate.

The titration is carried out in an acidic medium to neutralize the hydrolysis of iron (III), since the hydrolysis products are also colored. Solutions with an iron (III) concentration of 0.015 mol/l are used. at a higher concentration, the yellow-brown color of iron aquacomplexes is distinguished, which makes it difficult to accurately fix T.E.

The free indicator - iron ammonium alum - is pale purple transparent crystals, soluble in water, not soluble in alcohol. To prepare the indicator solution, dissolve 30 g of alum in 100 ml of water and add diluted nitric acid (so that there is no hydrolysis, until the color changes from brown to yellow-green).

Adsorption indicators are indicators whose adsorption or desorption by sediment during sedimentation titration is accompanied by a change in color in EP or near it. Indicators of this type are organic substances adsorbed by the sediment in EP and color it, and to EP are not adsorbed. They are weak protoliths of acidic or basic character.

Typical adsorption indicators are fluorescein and eosin (tetrabromofluorescein):

These indicators after EP upon adsorption on the surface have their own color:

Fluorescein: green-yellow- pink

Eosin:yellowish-red - red-violet

Free fluorescein is a yellow-red powder soluble in alkaline solutions and alcohol. In practice, a 0.1-0.2% alcohol solution is used. It is used in the argentometric determination of chlorides, bromides, iodides, and thiocyanates.

Eosin is used as an indicator in the form of sodium salt - sodium eosin, which is a red powder, easily soluble in water. In practice, a 0.5% aqueous solution of the sodium salt of eosin or a 0.1% solution of eosin in 60-70% alcohol is used. It is used in the argentometric determination of bromides, iodides, and thiocyanates. In addition to fluorescein and eosin, alizarin red, bromocresol blue, bromophenol blue, diphenylcarbazide, diphenylcarbazone, 3,3,6-dichlorofluorescein, Congo red, rhodamine Z, sulfofluorescein, Purpose yellow, tartrazine, tropeolin 00, phenosafranin are also used as adsorption indicators. fuchsin, erythrosin and some others.

4. Characteristics of individual methods

Argentometry

$$X^- + Ag^+ = AgX\downarrow,$$

where $X^- = Cl^-, Br^-, I^-, CN^-, SCN^-$

Titrant: $AgNO_3$ – second. standard solution.

Standardization for the primary standard sol. sodium chloride NaCl:

$$AgNO_3 + NaCl = AgCl\downarrow + NaNO_3.$$

Indicator there is 5% potassium chromate K_2CrO_4. Titration is carried out until a brownish-red precipitate of argentum chromate appears:

$$2AgNO_3 + K_2CrO_4 = Ag_2CrO_4\downarrow + 2KNO_3.$$

Depending on the titration method and the indicator used, argentometric methods are divided into:

Without indicators:

- Gay-Lussac method (even turbidity method)

- the method to the point of enlightenment

ANDindicative:

- Mohr's method

- Fayans-Fisher-Khodakov method

- Folgard's method

Mohr's method.

Titrant: $AgNO_3$ – second. standard solution.

Standardization for the first standard calculated sodium chloride NaCl by pipetting:

$$AgNO_3 + NaCl = AgCl\downarrow + NaNO_3.$$

*Indicator*during standardization, there is 5% potassium chromate K_2CrO_4 (before the appearance of brown-red argentum chromate):

$$2AgNO_3 + K_2CrO_4 = Ag_2CrO_4\downarrow + 2KNO_3.$$

Determined substances: Cl- chlorides, Br- bromides.

Environment: pH~ 6.5-10.3.

Application: quantitative determination of sodium chloride, potassium chloride, sodium bromide, potassium bromide, etc.

Application limitations:

1. You cannot titrate acidic solutions:

$$2CrO_4^{2-} + 2H^+ = Cr_2O_7^{2-} + H_2O.$$

2. It is not possible to titrate in the presence of ammonia and other ions, molecules that can act as ligands in relation to argentum ions in complexation reactions.

3. It is not possible to titrate in the presence of many cations (Ba^{2+}, Pb^{2+}, etc.), which form colored precipitates with chromate ions CrO_4^{2-}.

4. It is not possible to titrate in the presence of reducing agents that convert chromate - CrO_4^{2-} ions into Cr^{3+} ions.

5. It is not possible to titrate in the presence of many anions (PO_4^{3-}, AsO_4^{3-}, AsO_3^{3-}, S^{2-} etc.), which form colored precipitates of argentum with argentum ions.

Fayans-Fisher-Khodakov method

Titrant: $AgNO_3$ – second. standard solution.

Standardization for the primary standard calculated sodium chloride NaCl by pipetting:

$$AgNO_3 + NaCl = AgCl\downarrow + NaNO_3.$$

Environment: pH~ 6.5-10.3 when determining chlorides and pH~ 2.0-10.3 when determining bromides and iodides.

Indicators of the method: fluorescein when determining chlorides and eosin when determining bromides and iodides.

Mechanism of action of indicators:adsorptive Adsorption indicators are indicators whose adsorption or desorption by sediment is accompanied by a change in color, i.e. or near it.

Folgard's method (thiocyanatometry, rhodanometry) is based on the titration of a solution containing argentum ions with standard NH_4NCS or KNCS solutions (direct titration):

$$Ag^+ + NCS^- \rightleftarrows AgNCS\downarrow$$

$$f_{екв}(Ag^+) = 1;\ s = 1.$$

The indicator in this method is Fe^{3+}.

After precipitation of argentum ions in the form of a white precipitate of AgNCS, an excess drop of titrant reacts with an indicator - a solution of ferric ammonium alum $NH_4[Fe(SO_4)_2]\cdot 12H_2O$ with the formation of a soluble red complex compound:

$$Fe^{3+} + 3NCS^- \rightleftarrows [Fe(NCS)_3]$$

Йони Fe^{3+} ions form with NCS^- ions colored complexes of different composition: $[Fe(NCS)]^{2+}$, $[Fe(NCS)_2]^+$, $[Fe(NCS)_6]^{3-}$, etc., but the formation of complexes of different composition is not affects the results of the titration, since all complexes are colored.

When determining according to the Folgard method, direct and reverse titrations are used. How titrants are used:

- in the direct titration method - solutions of ammonium thiocyanate or potassium thiocyanate;
- in the reverse titration method - solutions of argentum nitrate and ammonium or potassium thiocyanate.

Titration conditions according to the Folgard method:

1) Titration must be performed in an acidic environment to prevent hydrolysis of indicator ions:

$$Fe^{3+} + H_2O \rightleftarrows FeOH^{2+} + H^+$$

1) During titration, the solution must be stirred vigorously to reduce the error due to the adsorption of ions on the sediment surface.

2) The test solution should not contain:

- mercury salts reacting with NCS– ions:

$$Hg_2^{2+} + 2NCS^- \rightleftarrows Hg_2(NCS)_2\downarrow$$

$$Hg^{2+} + 2NCS^- \rightleftarrows [Hg(NCS)_2]$$

- oxidants that oxidize NCS^- ions ($KBrO_3$, $KMnO_4$ тощо);
- anions F^-, PO_4^{3-}, $C_2O_4^{2-}$etc., which form stable complexes with the indicator:

$$Fe^{3+} + 6F^- \rightleftarrows [FeF_6]^{3-}$$

Direct titration according to the Folgard method (determination of ionsAg^+). The concentration of argentum ions is determined by direct titration with a standard solution of ammonium thiocyanate (or potassium thiocyanate) in the presence of Fe^{3+} ions.

A standard solution of ammonium thiocyanate reacts primarily with argentum ions, forming a sparingly soluble compound:

$$Ag^+ + NCS^- \rightleftarrows AgNCS\downarrow \qquad K_s(AgNCS) = 1{,}1\cdot10^{-12}$$

At the endpoint of the titration, an excess drop of titrant reacts with Fe^{3+} ions and turns the solution red:

$$Fe^{3+} + 3NCS^{-} \rightleftarrows [Fe(NCS)_3] \qquad K = 4 \cdot 1\,0^{-2}$$

Folgard's method (direct titration) is used to determine:

- content of argentum in alloys (having previously dissolved its exact weight in nitric acid);
- content of argentum cations in colloidal solutions (colargol and protargol);
- concentrations of mercury(II) salts.

Reverse titration according to the Folgard method (determination of anions).Fordetermination of anions use back titration. The essence of the determination: double the minimum precisely measured volume (40.00 cm3 or 35.00 cm3) of the standard solution of argentum nitrate (1st titrant) is added to the solution to be analyzed, which reacts with the anions under investigation, for example, chloride ions :

$$Ag^{+} + Cl^{-} \rightleftarrows AgCl\downarrow$$

The remaining unreacted argentum nitrate is titrated with a standard solution of ammonium thiocyanate (2nd titrant) in the presence of an indicator –Fe^{3+} ions:

$$Ag^{+} + NCS^{-} \rightleftarrows AgNCS\downarrow$$

At the end of the titration, an excess drop of NH4NCS solution reacts with Fe^{3+} ions:

$$Fe^{3+} + 3NCS^{-} \rightleftarrows [Fe(NCS)_3]$$

and the solution turns red.

When determining chlorides, an error occurs due to the unclear setting of the end point of the titration. This is due to the course of the exchange reaction between the argentum chloride precipitate and thiocyanate ions in the solution, since the argentum thiocyanate precipitate is less soluble than AgCl:

$$AgCl + NCS^{-} \rightleftarrows AgNCS\downarrow + Cl^{-}$$

$$K_s(AgCl) = 1{,}78 \cdot 10^{-10} \qquad K_s(AgNCS) = 1{,}1 \cdot 10^{-12}$$

This leads to significant overconsumption of NH4NCS titrant and overestimated results.

To eliminate this methodical error, the AgCl precipitate is filtered and the excess of argentum nitrate is determined in the resulting filtrate (an extra operation complicates the work).

More often, to eliminate this error, an organic solvent that does not mix with water is added to the analyzed solution (tetrachloromethane CCl_4, benzene C_6H_6, etc.). Determination of the moment of equivalence in the presence of organic solvents is quite clear. This is due to the fact that organic solvents cover the surface of the precipitate and isolate it from the solution, so the reaction between the AgCl precipitate and NCS ions practically does not proceed.

When determining bromides, an error of this kind does not occur, since the solubility constant of AgBr is less than that of argentum thiocyanate

$$K_s(AgBr)=5{,}3 \cdot 10^{-13} < K_s(AgNCS) = 1{,}1 \cdot 10^{-12}.$$

When determining iodides by the Folgard method, an error occurs due to the course of the redox reaction:

$+\bar{e} + Fe^{3+} \rightleftarrows Fe^{2+}$	2
$-\bar{e} + 2I^- \rightleftarrows I_2$	1
$2Fe^{3+} + 2I^- \rightleftarrows 2Fe^{2+} + I_2$	

This error is eliminated by adding the indicator at the end of the titration, only after an excess of $AgNO_3$ has been introduced and the iodide ions have been bound into the sparingly soluble compound AgI:

$$I^- + Ag^+ \rightleftarrows AgI \downarrow$$

According to Folgard's method, it is possible to determine:

- Ag^+ cations - by direct titration;

- anions – Cl^-, Br^-, I^-, NCS^- – by reverse titration.

Compared to Mohr's method, Folgard's method has a number of advantages:

- the determination of Ag^+, Cl^-, Br^-, I^-, NCS^- ions is performed in an acidic environment;
- cations (Ba^{2+}, Pb^{2+}, etc.), which interfere with the determination of anions by Mohr's method, do not interfere with their determination by Folgard's method.

Mercurometry

The mercurometric method of analysis is based on the formation of sparingly soluble salts of mercury(I) with chlorides, bromides and iodides

$$Hg_2^{2+} + 2Cl^- \rightleftarrows Hg_2Cl_2\downarrow \qquad K_s^0 = 1{,}3\cdot10^{-18}$$

$$Hg_2^{2+} + 2Br^- \rightleftarrows Hg_2Br_2\downarrow \qquad K_s^0 = 5{,}8\cdot10^{-23}$$

$$Hg_2^{2+} + 2I^- \rightleftarrows Hg_2I_2\downarrow \qquad K_s^0 = 4{,}5\cdot10^{-29}$$

The titrant of the mercurometry method is a 0.1 M solution of mercury(I) nitrate.

Preparation of standard solution$Hg_2(NO_3)_2$.Mercury (I) nitrate does not belong to the standard substances, since this salt is hygroscopic, unstable and contains impurities of Hg^{2+} ions. Therefore, a secondary standard solution is prepared from it. The calculated mass of $Hg_2(NO_3)_2\cdot2H_2O$ is weighed on technochemical balances, transferred to a measuring cup, a 2M solution of nitric acid is added and heated until the mass is completely dissolved. 4-5 drops of Purpose liquid mercury are added to the resulting solution. The prepared solution is kept over Purpose mercury for at least a day, which leads to the recovery of Hg^{2+} ions:

$$Hg^{2+} + Hg \rightarrow Hg_2^{2+}$$

Only after that, the obtained solution is standardized according to standard substances - NaCl or KCl, or their standard solutions. The concentration of mercury(I) nitrate solution does not change for several months.

In the mercurometry method, indicators are used:

- solution of ferrum(III) thiocyanate [$Fe(NCS)_3$];

- 1% solution of diphenylcarbazone in 95% ethanol.

When using the $[Fe(NCS)_3]$ solution, the end point of the titration is fixed by the disappearance of the red color of the indicator. The color change occurs when one excess drop of titrant interacts with the indicator solution:

$$3Hg_2^{2+} + 2[Fe(NCS)_3] \rightleftarrows 3[Hg_2(NCS)_2] + 2Fe^{3+}.$$

When titrating with the specified indicator, it is necessary to conduct a control experiment to establish the volume of titrant spent on the reaction with the indicator. To do this, all reagents are added to 20-25 cm3 of distilled water in the same quantities as when analyzing the sample under study, and titrated with a standard solution of mercury(I) nitrate. The obtained volume of titrant is subtracted from the volume spent on the titration of the test sample.

Diphenylcarbazone belongs to the group of adsorption indicators. Its use is based on the fact that after complete precipitation of halide ions, an excess drop of titrant reacts with diphenylcarbazone and forms a blue precipitate in a neutral or slightly acidic environment, and a blue solution in a strongly acidic environment, at the end point of the titration the color becomes blue-violet. When titrating with diphenylcarbazone, a “rough” titration is first carried out with an accuracy of 1.0 cm3, and then during a repeated (accurate) titration, in order to reduce the error due to adsorption, the indicator is introduced into the solution, when it remains to add 1.0-2.0 cm3 titrant In this case, correction to the indicator is not required. The diphenylcarbazone indicator has a number of advantages over iron(III) thiocyanate – it can be titrated in strongly acidic solutions, in colored and cloudy solutions (due to the fact that the color of the precipitate or solution at the end point of the titration is very bright), in the presence of peptizing substances.

Titration conditions:

1. Titration is carried out in an acidic environment to prevent hydrolysis of the titrant. For this, the solution is acidified with nitric acid.

2.Titration must be carried out with vigorous stirring of the solution to reduce the error due to adsorption.

Chloride and bromide ions can be determined by the mercurometric method.

Ammonium cations, alkaline and alkaline earth metals, Fe^{2+}, Mn^{2+}, Cr^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Al^{3+}, Pb^{2+}, Cu^{2+}.

Definition is hindered by:

- sulfate ions - they should be removed by precipitating with an excess of barium nitrate;
- ferrum(III) ions – they are bound into stable complexes by adding an excess of F^- or PO_4^{3-} ions;
- dichromate and permanganate ions - they must be reduced with hydrogen peroxide;
- sulfite and sulfide ions - they should be oxidized with hydrogen peroxide in advance.

The mercurometric method of analysis has advantages over the argentometric method:

- mercury(I) halides are less soluble than the corresponding argentum salts, so the end point of the titration in the mercurometric method is fixed more clearly;
- the method excludes the use of precious argentum salts.

The main drawback of the mercurometric method of analysis is that mercury(I) salts are poisonous, so when working with them, it is necessary to follow the rules for working with poisonous substances.

The main methodological error of all precipitation titration methods is deliberate over-titration of the solution when fixing the end point of the titration.

General material and bulk-methodological support of the lecture:

- ✓ computer presentation;
- ✓ illustrative materials;
- ✓ examples of solving typical tasks or performing typical tasks;
- ✓ multimedia projector.

Questions for self-control:

1. Deposition method. Working solutions. Basic provisions of the method.

2. Basic requirements for reactions used in the precipitation titration method.

3. How does the magnitude of the titration jump on the titration curve in the precipitation method depend on temperature, solubility product, ionic strength, and solution concentration?

4. Argentometry. Mohr's method. Fayans-Khodakov method.

5. Thiocyanatometry (rhodanometry or Folgard's method) Terms of application of the method.

6. Mercurometry. Working solutions. Basic provisions of the method and its application.

References:

General:

1. Analytical chemistry: handbook / V. V. Bolotov, O. A. Yevtifeyeva, L. Yu. Klimenko, T. A. Kostina, T. V. Zhukova, E. Yu. Ahmedov , O. A. Brizicky; edited by V. V. Bolotov.— Kharkiv: NUPh; Original, 2012.
2. Analytical chemistry (Qualitative analysis). Part I / O. A. Ievtifieieva, V. V. Bolotov, T. A. Kostina, O. M. Svechnikova, T. I. Yuschenko, N. I. Kaminska, A. E. Kosareva, L. V. Slobodyanyuk, O. P. Yashchuk ; edited by O. A. Ievtifieieva. – Kharkiv : Publishing house the CLL «Generous farmstead plus», 2014. – 168 p.
3. Analytical chemistry. Part II. Quantitative analysis: the manual for foreign students of pharmaceutical higher schools and pharmaceutical departments of medical higher schools of the III – IV accreditation levels / V. V. Bolotov, O. M. Svechnikova, T. A. Kostina et al. – Kharkiv: NUPh, 2010. – 160 p.
4. Analytical chemistry: textbook [the textbook for students of higher schools] / I.S. Grytsenko, V. V. Bolotov, L.Yu. Klimenko et al.; ed. by I.S. Grytsenko – Kharkiv: NUPh, Golden Pages, 2019. – 600 p.

Lecture No. 13

Topic: Complexometric titration. Complexometry. Titrants, their standardization. Metal-chrome indicators. Mercurimetric titration. Possibilities of methods.

Relevance of the topic: Analytical chemistryis a science that develops theoretical foundations and practical methods of chemical analysis.Therefore, it is relevant to solve the problems facing analytical chemistry with the help of physical, chemical and physicochemical methods used for the analysis of medicinal products.

Purpose: generalize students' knowledge of titrimetric analysis. Familiarize yourself with the concept of complexometric titration.

Basic concepts:analytical chemistry, quantitative analysis, titrimetry, working solution, primary standard, secondary standard, molar concentration, normal concentration, titer

Plan and organizational structure of the lecture:

1. General characteristics of the method
2. Complexonometry
3. Mercurimetry

Content of lecture material (lecture text):

1. General characteristics of the method

Complexometric methods of analysis (complexometry) are based on reactions accompanied by the formation of complex compounds with inorganic or organic ligands. Complex formation of Purposel ions with halides (Cl^-, Br^-, I^-) and pseudohalide ions (NCS^-, CH^-), as well as with a group of so-called complexons, which includes a number of aminopolycarboxylic acids, is of greatest importance in titrimetric analysis.

The method of analysis, based on the formation of complex compounds of the mercury (II) cation with inorganic ligands, is called mercurimetry and is used for the quantitative determination of inorganic and organic compounds, the composition of which includes halide ions (NaCl, KBr, KI, salts of alkaloids with hydrogen halide acids, etc.). The method based on the complexation reaction with organic ligands is more common - complexonometry. It is used to determine the

total hardness of water, many compounds containing cations of alkaline earth and heavy Purposes, including drugs (calcium lactate, calcium chloride, magnesium sulfate, etc.).

Reactions used in complexiметry must proceed quickly, quantitatively, and stoichiometrically.

The possibility of forming a complex compound with a defined stoichiometric composition depends on the following factors:

- coordination number of the complexing agent (it should be minimal);
- dentateness of the ligand (the number of bonds it can occupy in the coordination sphere of the complexing agent).

If the ligands (L) are monodentate (capable of occupying only one place in the sphere of the complexing agent), then depending on the coordination number of the complexing agent (N), a number of intermediate complexes MeL1, MeL2, MeL3,... MeLn are formed. At the same time, if their complete stability constants β1, β2, β3,... βn practically do not differ from each other, all complexes of this series will be formed, that is, the reaction will proceed non-stoichiometrically, and therefore it cannot be used for quantitative determination. Most inorganic ligands are monodentate, so complexation reactions with their participation are not widely used.

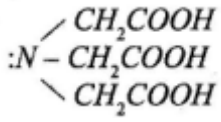
2. Complexonometry

Complexonometry is a method of analysis based on the use of the reaction of the formation of intracomplex (chelate) compounds with organic ligands - complexons.

Complexones are a group of aminopolycarboxylic acids and their derivatives.

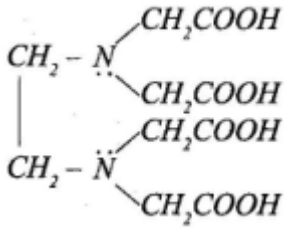
Including:

- nitrilotriacetate acid



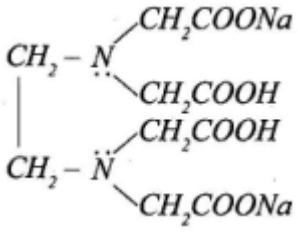
(complexon I – H_3L)

- ethylenediaminetetraacetic acid
-



(complexon II – H_4L)

The analysis uses its disodium salt, $Na_2H_2L \cdot 2H_2O$, which, unlike acid, is very soluble in water and is widely used:



(complexon III – $Na_2H_2L \cdot 2H_2O$, trilon B, EDTA, disodium edetate)

Complexons are polydentate ligands that form with many cations (Ca^{2+}, Ba^{2+}, Sr^{2+}, Mg^{2+}, Co^{2+}, Cu^{2+}, Bi^{3+}, Al^{3+}, Zn^{2+}, Fe^{3+}, Ni^{2+} etc) very stable, well soluble in water, colorless intracomplex (chelate) compounds.

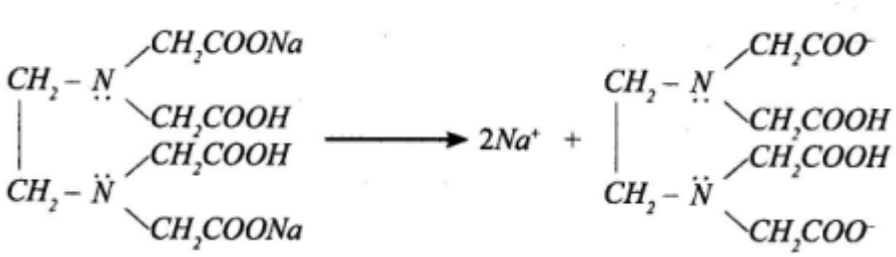
The formation of intra-complex salts is observed in cases where cations of the Purposelu-complex former replace active hydrogen atoms of functional groups of an organic compound, and also form coordination (donor-acceptor) bonds with some of its groups. Groups in which hydrogen atoms can be replaced by ions include:–COOH, $–SO_3H$, –OH, =NOH etc.

The donor-acceptor bond with the ions of the complexing agent is inherent in the groups $–NH_2$, =NH, =NOH, =S, =CO.

Complexonometry (trilonometry) is a titrimetric method of analysis based on reactions of the interaction of complexons (most often disodium edetate) with ions of alkaline earth and heavy Purposels, which leads to the formation of water-soluble, colorless stable intracomplex compounds.

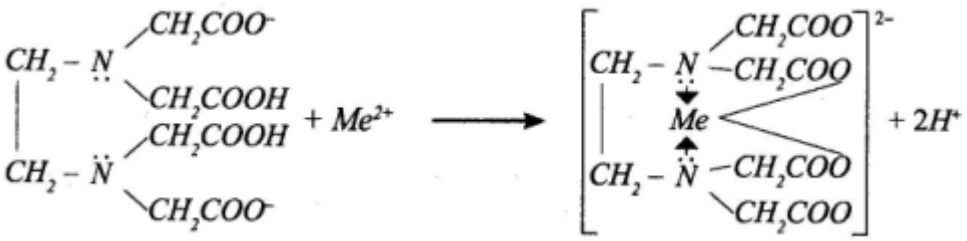
Trilon B (disodium edetate) forms intracomplex compounds with Purposel cations due to valence bonds with carboxyl groups with removal of hydrogen ions, as well as due to coordination bonds of complex-forming ions with nitrogen atoms.

In solution, trilon B dissociates into ions:



(anion is abbreviated as H_2L^{2-})

When the cation of the complexing agent interacts with trilon B, the reaction takes place:



In all cases, regardless of the cation charge, reactions with disodium edetate occur in a stoichiometric ratio of 1:1 (s = 1), so the equivalence factor for EDTA and Purposel cations is equal to one.

Schematically, complexation reactions with cations having different charges can be presented in the form:

$$H_2L^{2-} + Me^{2+} \rightleftarrows [MeL]^{2-} + 2H^+$$

$$H_2L^{2-} + Me^{3+} \rightleftarrows [MeL]^{-} + 2H^+$$

$$H_2L^{2-} + Me^{4+} \rightleftarrows [MeL] + 2H^+$$

Trilon B solutions of 0.02 M, 0.05 M or 0.1 M are used as a titrant.

In complexometric titration, Purposelochromic indicators (Purposeloindicators) are used.

Purpose indicators are organic dyes (murexide, eriochrome black T, eriochrome blue-black B, zincone, etc.) that form water-soluble, colored complex compounds with the studied ions, which are less stable than the complexes of the

Purposel cation with trilon B. At the same time, the cation complex with an indicator and a free indicator have different colors:

$$\underset{\text{(colour I)}}{H_2Ind^-} + Me^{2+} \rightleftarrows \underset{\text{(colour II)}}{[MeInd]^-} + 2H^+$$

In direct complexometric titration, the Purpose indicator is added to the test solution, which forms a complex compound with the determining ions, which has a certain color. At the end of the titration, the complex of Purposel cations with the indicator is destroyed and a colorless, very stable complex of cations with trilon B is formed, and the ions of the free indicator enter the solution:

$$\underset{\text{(colour II)}}{[MeInd]^-} + H_2L^{2-} \rightleftarrows \underset{\text{(colour I)}}{[MeL]^{2-}} + H_2Ind^-$$

The endpoint of the titration is determined by the indicator's own color (color I).

Some Purpose indicators are unstable in an aqueous solution, so they are used in the form of dry mixtures, carefully grinding the indicator with dry substances of NaCl or KSl qualification in a porcelain mortar. in a ratio of 1:100 or 1:200. For titration, use a dry glass rod to take 20-30 mg of this mixture per 100 cm3 of the solution to be titrated.

Conditionscomplexometric definitions

1. The complexation reactions should proceed quickly, quantitatively and stoichiometrically, so that near the equivalence point the studied cations are almost completely combinedtied into a complex. The instability constant of the formed complexes should be small.

2. Researchedions should form less stable complexes with the Purpose indicator than their complexes with trilon B.

3. Complexometric titration must be carried out at a certain pH value.

In the process of titration, during the interaction of cations with trilon B, hydrogen ions H^+ enter the solution, as a result of which the pH of the solution decreases, which leads to a shift of the balance of the complexation reaction to the left. To maintain a certain pH value of the medium, the titration should be carried

out in the presence of buffer solutions. Most cations are titrated with Trilon B solution in the presence of an ammonia buffer solution (NH_4OH + NH_4Cl) at pH=9.2.

Very stable complexes with trilon B form cations Fe^{3+}, Sn^{2+}, Fe^{2+}, Al^{3+}, Ca^{2+}, Mg^{2+} and many others. Some of them can be determined in an acidic environment. At the same time, cations that form less stable complexes do not interfere with the determination.

Methods of complexometric titration

Direct titration

Add a suitable buffer solution, a Purpose indicator, and titrate with a standard Trilon B solution to the test solution. The following cations are determined by the direct titration method: Cu^{2+}, Co^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, Fe^{3+}, Ba^{2+}, Cr^{3+}, Ca^{2+}, Mg^{2+} тощо.

Indirect (reverse) titration

An appropriate buffer solution is added to the solution to be analyzed, followed by an accurately measured double minimum volume (35.00-40.00 cm3) of the trilon B standard solution, which reacts with the cations to be determined. Its excess is titrated with a standard solution of magnesium sulfate or zinc sulfate in the presence of the metal indicator:

$$Me^{2+} + H_2L^{2-} \rightleftarrows [MeL]^{2-} + 2H^+$$

$$excess\ H_2L^{2-} + Zn^{2+} \rightleftarrows [ZnL]^{2-} + 2H^+$$

The reverse titration method is used:

- if the complexation reaction proceeds slowly;
- if it is not possible to choose an indicator to fix the end point of titration for direct titration;
- to determine cations whose salts are poorly soluble in water (for example, Ca^{2+} in CaC_2O_4, Mg^{2+} in $MgNH_4PO_4$, Pb^{2+} in $PbSO_4$).

Surrogate titration

The method is based on the fact that most cations form more stable complex compounds with trilon B than complexes of Mg^{2+} cations with trilon B $[MgL]^{2-}$ (lg

β = 9.72). After adding the $[MgL]^{2-}$ complex to the solution under study, an exchange reaction takes place::

$$[MgL]^{2-} + Me^{2+} \rightarrow [MeL]^{2-} + Mg^{2+}$$

This reaction is possible because Purposel ions form a more stable complex compound $[MeL]^{2-}$ (lg β > 9.7) with $H_2L_2^-$, and the equilibrium of the indicated reaction shifts to the right.

The formed Mg^{2+} ions are titrated with a standard Trilon B solution in the presence of the metalchromic indicator:

$$Mg^{2+} + H_2L^{2-} \rightarrow [MgL]^{2-} + 2H^+$$

Possibilities of complexometric titration

The trilonometric (complexonometric) method determines:

- general water hardness;
- almost all cations of alkaline earth and heavy Purposels;
- in pharmaceutical analysis – dosage forms containing cations of alkaline earth and heavy Purposels;
- in the chemical and toxicological analysis - heavy Purposel cations.

3. Mercurimetry

Mercury(II) with chloride, bromide, iodide, cyanide, thiocyanate ions, which is accompanied by the formation of complex compounds.

The complex-forming ion Hg^{2+} has a coordination number of 4, the ligands are monodentate, so the formation of complexes of different compositions is possible.

The titrant of the mercurimetry method is a 0.1 M solution of mercury(II) nitrate.

Preparation and standardization of 0.1 M solution of mercury(II) nitrate

The Hg(NO3)2 salt is hygroscopic, so a secondary standard solution is prepared from it. The calculated weight of mercury(II) nitrate (feq = 1/2) is weighed on technochemical scales, transferred to a glass or measuring flask. Salt does not dissolve well in water, therefore, to increase its solubility and to prevent

hydrolysis, nitric acid is added (for example, 20 cm^3 of 6 M nitric acid solution per 1 dm3 of solution) and the volume of the solution is adjusted to the required volume with distilled water. Standardize the solution of mercury(II) nitrate according to the standard substances sodium chloride or potassium chloride (HC) or according to the standard solution of ammonium thiocyanate.

How indicators are used:

- sodium nitroprusside $Na_2[Fe(CN)_5NO]$, which with an excess drop of titrant (Hg2+ ions) forms a white precipitate of mercury (II) nitroprusside:

$$Hg^{2+} + [Fe(CN)_5NO]^{2-} \rightleftarrows Hg[Fe(CN)_5NO]\downarrow,$$

- diphenylcarbazide or diphenylcarbazone, which at the end point of the titration with Hg2+ ions form a blue-lilac complex compound.

Determination of chlorides and bromides

When determining Cl-ions, the following reactions take place:

$Cl^- + Hg^{2+} \rightleftarrows [HgCl]^+$ $\quad\quad$ $\lg \beta_1 = 6{,}74$

$[HgCl]^+ + Cl^- \rightleftarrows [HgCl_2]$ $\quad\quad$ $\lg \beta_2 = 13{,}22$

The values of lg β1 and lg β2 are sufficiently different, so the most likely is the stoichiometric and quantitative course of the reaction of the formation of the $[HgCl_2]$ complex:

$$2NaCl + Hg(NO_3)_2 \rightleftarrows [HgCl_2]+2NaNO_3$$

$$f_{екв}\,(NaCl) = 1;\ s = 2$$

The formation of complexes of the composition $[HgCl_3]^-$ and $[HgCl_4]^{2-}$ is unlikely because the values of lg β_3 and lg β_4 are equal to 14.07 and 16.22, respectively, which is close to the value of lg β_2.

After the reaction of halide ions (Cl^- or Br^-) with Hg^{2+}, an excess drop of $Hg(NO_3)_2$ titrant reacts with the indicator.

Determination of iodides

During the titration of iodides, Hg^{2+} ions form a very stable complex:

$4I^- + Hg^{2+} \rightleftarrows [HgI_4]^{2-}$ $\quad\quad$ $\lg \beta_4 = 30.18$

The end point of the titration is determined by the indicator-free method by the formation of turbidity that does not disappear (a red precipitate of mercury(II) iodide):

$$Hg^{2+}(ex) + [HgI_4]_2 \rightleftarrows 2HgI_2\downarrow$$

The definition is based on the reaction:

$$4KI+Hg(NO_3)_2 \rightleftarrows K_2[HgI_4] +2KNO_3$$

$$feq(KI) = 2; s = 4.$$

When determining iodides, slightly underestimated results are obtained, therefore, in order to reduce this error, a certain volume (V, cm^3 $Hg(NO_3)_2$) is added to the final volume of the standard solution of mercury(II) nitrate, the amount of which depends on the volume of the solution , which is determined

Determination of thiocyanates

Thiocyanates are titrated with a standard solution of mercury(II) nitrate in the presence of an indicator - a solution of iron(III) salt. At the same time, Hg^{2+} ions bind NCS– ions into a stable colorless complex:

$$2NCS^- + Hg^{2+} \rightleftarrows [Hg(NCS)^2]$$

$$f_{eq}(NCS^-) = 1; s = 2.$$

The end point of the titration is determined by the disappearance of the red color of the $[Fe(NCS)_3]$ complex formed by the indicator ions (Fe^{3+}) with NCS^- ions, i.e., the analyzed solution becomes colorless:

$$3Hg^{2+} + 2[Fe(NCS)_3] \rightarrow 3[Hg(NCS)_2] + 2Fe^{3+}$$

At the same time, the unstable complex $[Fe(NCS)_3]$ ($\lg \beta_3$) = 4.63) is destroyed and the more stable complex $[Hg(NCS)_2]$ ($\lg \beta_2$ = 29.18) is formed.

Determination of Hg(II) salts by the method of thiocyanatometry

When determining Hg(II) salts, a standard solution of ammonium thiocyanate is used as a titrant, and Fe^{3+} ions are used as an indicator. During titration, thiocyanate ions bind Hg^{2+} ions into a stable colorless complex:

$$Hg^{2+} + 2NCS^- \rightarrow [Hg(NCS)_2]$$

$$feq\ (Hg^{2+}) = 1/2; s = 1/2.$$

At the endpoint of the titration, an excess drop of titrant reacts with Fe^{3+} ions:

$$Fe3^{+} + 3NCS^{-} \rightarrow [Fe(NCS)_3]$$

and the solution acquires a red color.

Thus, the mercurimetric method can be used to determine:

- chlorides, bromides, thiocyanates with sodium nitroprusside or diphenylcarbazone indicators, and in the case of thiocyanates - also with Fe3+;
- iodides - by an indicator-free method.

The main drawback of the method is the high toxicity of mercury(II) salts, therefore, when working with them, it is necessary to follow the general requirements for working with poisonous substances.

General material and bulk-methodological support of the lecture:

- ✓ computer presentation;
- ✓ illustrative materials;
- ✓ examples of solving typical tasks or performing typical tasks;
- ✓ multimedia projector.

Questions for self-control:

1. Methods of complex formation. Complexiметry (Mercurimetric titration).
2. Complexonometry (trilonometry). Application of the method.
3. Purposelochromic indicators, the mechanism of their action.
4. What are the requirements for reactions in the complexometric titration method?

References:

General:

1. Analytical chemistry: handbook / V. V. Bolotov, O. A. Yevtifeyeva, L. Yu. Klimenko, T. A. Kostina, T. V. Zhukova, E. Yu. Ahmedov , O. A. Brizicky; edited by V. V. Bolotov.— Kharkiv: NUPh; Original, 2012.

2. Analytical chemistry (Qualitative analysis). Part I / O. A. Ievtifieieva, V. V. Bolotov, T. A. Kostina, O. M. Svechnikova, T. I. Yuschenko, N. I. Kaminska, A. E. Kosareva, L. V. Slobodyanyuk, O. P. Yashchuk ; edited by O. A. Ievtifieieva. – Kharkiv : Publishing house the CLL «Generous farmstead plus», 2014. – 168 p.
3. Analytical chemistry. Part II. Quantitative analysis: the manual for foreign students of pharmaceutical higher schools and pharmaceutical departments of medical higher schools of the III – IV accreditation levels / V. V. Bolotov, O. M. Svechnikova, T. A. Kostina et al. – Kharkiv: NUPh, 2010. – 160 p.
4. Analytical chemistry: textbook [the textbook for students of higher schools] / I.S. Grytsenko, V. V. Bolotov, L.Yu. Klimenko et al.; ed. by I.S. Grytsenko – Kharkiv: NUPh, Golden Pages, 2019. – 600 p.

Lecture No. 14

Topic: Classification of physical methods of analysis. Optical methods of analysis, their classification. Molecular absorption spectroscopy. Refractometry. Optical methods of analysis. Luminescent analysis.

Relevance of the topic: Analytical chemistryis a science that develops theoretical foundations and practical methods of chemical analysis.Therefore, it is relevant to solve the problems facing analytical chemistry with the help of physical, chemical and physicochemical methods used for the analysis of medicinal products.

Purpose: To acquaint students with the basics of physical and chemical analysis, namely optical methods

Basic concepts:analytical chemistry, quantitative analysis, refractometry, refractometric factor, additivity, molecular refraction, absorption analysis, emission analysis

Plan and organizational structure of the lecture:

1. General characteristics of optical methods
2. Classification of spectroscopic methods
3. Refractometry

Content of lecture material (lecture text):

1. General characteristics of optical methods

Depending on the nature of the interaction of electromagnetic radiation with the analyzed substances, the following are distinguished:

1. Absorption spectral analysis, which is based on the study of the absorption of electromagnetic radiation from an external source by the substance being analyzed. It includes molecular spectral analysis (photometry) and atomic absorption spectral analysis.

2. Emission spectral analysis, which is based on the study of electromagnetic radiation emitted by the substance being analyzed under the influence of high temperatures or X-rays. This group of methods includes atomic emission spectral analysis and X-ray spectral analysis.

These methods are characterized by versatility, high sensitivity, accuracy and speed. They allow you to automate the analysis and are express. Optical methods of analysis use energy transitions of external valence electrons. A necessary condition for them is preliminary atomization (decomposition of a substance into individual atoms).

Atomic emission spectrometry – radiation by atoms excited by the kinetic energy of a plasma or arc discharge and spark.

Atomic absorption spectroscopy – absorption of radiation from an external source by atoms.

2. Classification of spectroscopic methods

Classification can be based on the nature of particles that emit or absorb light energy. Therefore, the methods of atomic and molecular spectroscopy are considered. Emission and absorption spectroscopy methods are distinguished by the type of spectra. It is possible to classify methods according to the energy of photons that are emitted or absorbed, dividing the spectral range into sections, each of which characterizes a certain process

Emission and absorption spectra are used for qualitative (substance identification) and quantitative (substance content determination) analysis.

For qualitative analysis, the most important characteristic is the position of a line, a band in the spectral range (abscissa axis, wavelength λ, frequency of oscillations ν). It is determined by the nature of the substance and does not depend on its concentration. The selectivity of the detection will depend on the width of the line and the band. As a result of the expansion of lines or bands, the overlapping of adjacent lines and bands of foreign substances is possible.

For quantitative analysis, the intensity of atomic lines (emission and absorption) or the absorption maximum of molecular bands (ordinate axis) are used, which are functions of the concentration of the substance. The value of the width of the line and stripes is also important for the correctness of the definition.

The methods of atomic spectroscopy are based on the use of spectra of atoms and electronic transitions in them - external (optical) and internal. Accordingly, the methods of optical (optical range in the UV and visible part of the spectrum) and X-ray spectroscopy (change in the energy of the internal electrons of an atom) are distinguished.

The method of atomic emission spectroscopy is based on recording the emission spectrum of thermally excited atoms. Energy of several eV is needed to change the energy of the electrons of the outer levels, which corresponds to emission in the UV, visible, and IR regions. For atoms of the same element, the set of energy levels (states) is the same, therefore the spectrum of this element is the same, specific for a given element and different from the spectra of other elements. In the unexcited state, the atom has the lowest energy. In order for an atom to radiate, it must be transferred to an excited state, when its energy (Ezb) will exceed the energy in the unexcited state E0. For example, for the K atom, its excitation corresponds to the transition of the 4s electron to the 4p, 4d, or 5s level. These energy levels are discrete, so the transition of the K atom to the unexcited level can be accompanied by radiation. The discreteness of the levels and the corresponding transitions determine the linear spectrum of the atom. The emission spectral line of an atom reflects the transition of an atom (its optical electron) between discrete energy levels, which is accompanied by radiation. Each line of an atom is

characterized by an excitation energy (potential) (Ezb). As the electron moves away from the nucleus, the energy of transferring it to a higher energy level (Ezb of a given level) decreases. The highest level of energy corresponds to the separation of an electron from the nucleus and is called the energy (potential) of ionization (Eion). The excitation energy, like the ionization energy, decreases in the series Na → Cs from 2.1 to 1.3 eV and 5.1 to 3.9 eV. For alkaline Purposels, they are the smallest. Lines with low Ezb are the most intense, because their corresponding transitions are the most probable. However, despite the low values of Ezb, some lines in the spectra of atoms are not intense or are absent at all. These lines are prohibited because they are not subject to certain selection rules.

The basics of AS are laid out in the works of the German scientists Kirchhoff and Bunsen "Chemical analysis by observing spectra" (1860). 27 chemical elements were detected with the help of atomic spectroscopy. AC has been widely used for quantitative analysis since 1927, when the internal standard method was first proposed, in which the intensity of a spectral line is compared with the line intensity of an introduced or known component of the sample. Flame photometry is a type of spectral analysis in which the source of atomization of matter is a flame. In it, atoms or molecules can be excited and radiate (emission variant of flame photometry). Unexcited atoms are able to absorb characteristic radiation, which is the basis of the atomic adsorption version of the method. Flame is the oldest source of obtaining spectra of atoms and molecules. The flame was the first source in spectral analysis, which Kirchhoff and Bunsen used in their works. It is used in various methods of spectroscopy due to the ease of obtaining and working with it, low cost and availability of starting substances - fuel and oxidants. An important advantage of flame over other sources is sufficiently high sensitivity and reproducibility of the analysis.

The most important characteristic of a flame is its temperature, which primarily affects the degree of dissociation of molecules introduced into the flame and the concentration of free atoms per unit volume. The temperature depends on the composition of the combustible mixture as well as on the stoichiometry of the

flame (C2H2-air, propane-butane-air, C2H2 – N2O, which has the highest atomizing ability. Compounds of all elements whose excitation potential does not exceed 6.5eV are completely atomized. The basis of high-quality analysis in emission flame photometry is the nature of radiation, that is, the location of a line or band in the spectrum. The intensity of radiation serves as a measure of concentration. This method is especially effective for determining elements with low excitation potentials in the range of 1.6 - 3.0 eV (alkaline and alkaline earth Purposes) . The method of flame emission photometry is a type of atomic emission spectroscopy, and the dependence between the analytical signal and the concentration of the solution can be applied to it. Atomic absorption spectroscopy (AAS) is based on measuring the absorptivity of unexcited atoms of an element of characteristic radiation. An atomic pair absorbs radiation with energy, which corresponds to the energy of the corresponding electronic transitions. These transitions, to which the absorption lines correspond, are typical transitions of atoms from the ground state to the excited state; transitions from one excited state to another are unlikely, so there are practically no corresponding lines in the spectrum. The flame absorption spectrum contains only resonant lines of atoms, which are related to transitions from the main unexcited level to the nearest excited one. It is important to note that the wavelength of the resonant absorption line is identical to the wavelength of the emission line corresponding to the same transition. For quantitative analysis, the AAS method is one of the most sensitive and effective for single-element determination of most Purposes.

Absorption spectroscopy can be classified by the type of radiation used - UV or visible, infrared, X-ray, etc. On the other hand, types of spectroscopy are distinguished by the particles that absorb: molecular, atomic, ionic.

Absorption molecular spectroscopy in the UV and visible region occupies a leading place in analytical practice and is called photometry.

The terms spectrophotometry and photocolorimetry are related to the means used to measure absorbance - spectrophotometers and photocolorimeters. The object of photometric measurements is the solution used to fill the cuvette - a

vessel with flat parallel transparent walls. Photometry is based on measuring the absorption of light flux. The regularities of radiation absorption can be applied to all sections of the spectral range - from X-ray to radio radiation. The absorption method is based on measuring the attenuation of the intensity or power of the light flux when it passes through an absorbing medium with a known layer thickness.

Analysis methods based on the absorption of electromagnetic radiation by a substance are called absorption optical methods. When light is absorbed, the atoms and molecules of the absorbing substances enter a new excited state. Depending on the type of absorbing particles and the method of transformation of the absorbed energy, the following are distinguished:

Atomic absorption analysis, which is based on the absorption of light energy by unexcited atoms of substances in the atomized gas phase.

Molecular absorption analysis, i.e. analysis of light absorption by molecules of the analyzed substance and complex ions in the UV, visible and IR regions of the spectrum (spectrophotometry, photocolorimetry, IR spectroscopy). Analysis by absorption and scattering of light energy by suspended particles of the analyzed substance (turbidimetry, nephelometry). Luminescent (fluorimetric) analysis based on the measurement of radiation resulting from the release of energy by excited molecules of the analyzed substance. All these methods are sometimes combined into one group of spectrochemical or spectroscopic methods of analysis, although they have significant differences. Photocolorimetry, colorimetry and spectrophotometry are based on the interaction of radiation with homogeneous systems and are combined into a group of photometric methods of analysis. The spectrum of electromagnetic radiation, depending on the wavelength, is divided into several areas: – ultraviolet 180 - 400 nm (nanometers; 1 nm=10-9 m); – visible 400 - 700 nm; – infrared 700 - 1100 nm. Monochromatic radiation is radiation of a certain wavelength. Polychromatic (non-monochromatic) radiation – radiation in a certain range of wavelengths. Photometric methods of analysis are based on the selectivity of absorption of UV, visible and IR light by solutions of substances. The degree of light absorption depends on the concentration of the dissolved

substance. Spectrophotometry is based on the measurement of the 4th degree of absorption of monochromatic radiation. In photocolorimetry, polychromatic radiation is used mainly in the visible region of the spectrum. In colorimetry, light absorption is judged by visual comparison of color intensity. In spectroscopy and photoelectrocolorimetry, a photocell is used as a receiver of light energy. All methods of analysis are highly sensitive and selective, and the equipment used is diverse and affordable.

3. Refractometry

Refractometry is based on the phenomenon of refraction of light when passing from one medium to another, which is called refraction. It represents a collection of methods for studying the physical and chemical properties of substances based on the measurement of their refractive indices. The index or refractive index is the ratio of the sine of the angle of incidence of light rays to the sine of its angle of refraction: n = sin a/sin b If a ray of light passes from a vacuum or air into another medium, then the angle of incidence is always greater than the angle of refraction. When the angle of incidence increases, the ratio between the amount of light energy passing into another medium and that reflected from the interface changes. At angles of incidence above the critical one, the light is completely reflected from the interface. This angle is called the angle of total internal reflection. Knowing the angle of total internal reflection a', the refractive index can be determined: n = 1/sin a' For liquids and solids, n is usually determined with respect to air, and for gases – with respect to vacuum. The refractive index depends on the internal state of the substance, its temperature, pressure, concentration, and the nature of the solvent. Therefore, to systematize the obtained results, the refractive index determined at a temperature of 20°C in the spectrum of sodium D (yellow line, 589.3 nm), denoted by n, is taken. Also, hydrogen spectral lines C (λ = 656 nm) and F (λ = 486 nm) are often used. The absolute refractive index (N) is the ratio of the speed of light propagation in a vacuum to its speed in a given medium: N 0 = CC The relative refractive index (n) is the ratio of the speed of light propagation in air to the speed of its propagation in a given medium: nïîâ

CC = N 1 The relationship between absolute and relative refractive indices is described by the formula: , = 00027 · n Limits of measuring refractive indices 1.3-1.7. In the case of gases, it is also necessary to take into account the dependence of n on pressure (indicate it or bring the data to normal pressure). For refractometry of solutions in wide ranges of concentrations, tables (for example, Roth and Eisenlor) or empirical formulas are used, the most important of which (for solutions of sucrose, ethanol, etc.) are approved by international agreements and form the basis of the construction of scales of specialized refractometers for the analysis of industrial and agricultural products .

Analytical capabilities. With the help of the refractometry method, you can carry out:

1. Qualitative analysis (identification of individual substances), since the refractive index is a constant characteristic of this substance. For example, the authenticity of liquid medicinal forms (essential oils, vitamins, sugar syrups, etc.) is controlled refractometrically.

2. Quantitative analysis, which is based on the dependence of the refractive index on the concentration of the substance. Refractometrically, it is possible to analyze 1-, 2-, and 3-component systems (medicines, alcohols, sugars, etc.). However, 2-component solutions are most often analyzed. For example, it is possible to carry out quantitative analysis of salts in aqueous solutions (NaCl, NaBr, NaI, KBr, KI, CaCl2, MgSO4, NaHCO3, Na2S2O3, etc.). For the analysis of 3-component mixtures, it is necessary to additionally determine other values - density or viscosity.

Metrological characteristics.

- Low accuracy, but the greater the difference in the refractive indices of the components of the mixture, the higher the accuracy.

- Low sensitivity, therefore the method is used for analysis in the area of igh concentrations (> 1%).

- Low selectivity, since n is a "non-specific" value (n values can be close for different substances), so the method is used only for the analysis of individual substances or the simplest mixtures (2-3 components).

- Ease of implementation and equipment.

- Expressiveness.

- Minimum number of samples.

The following factors affect the value of the refractive index:

1. Physico-chemical properties of the substance (nature of the substance): - ρ - density: the greater ρ, the greater n; - ε - dielectric constant: ε = n2; - α - polarization.

2. External conditions: - λ – wavelength: the larger λ, the smaller n. The dependence of n on λ is called variance; The decrease in n with increasing temperature is caused by a decrease in the density of the solution. In the temperature range of 15-25 ºC, with an increase in temperature by 10 ºC, the refractive index decreases by 0.0005 - to – temperature: the higher to, the lower n; - p – pressure (for gases). 3. Concentration (for solutions): under other constant conditions, the refractive index depends linearly on the concentration: np = no + Fω, where np is the refractive index of the solution; no is the refractive index of the solvent; F – analytical refractometric factor; ω is the mass fraction of the substance in the solution. 4. Type of solvent (for solutions). All refractometric measurements are carried out under constant external conditions: λ = const, to = const.

General material and bulk-methodological support of the lecture:

- ✓ computer presentation;
- ✓ illustrative materials;
- ✓ examples of solving typical tasks or performing typical tasks;
- ✓ multimedia projector.

Questions for self-control:

1. What group of methods does the spectrophotometric method belong to? What is the essence of this group of methods?

2. Types of compounds used in the spectrophotometric method of analysis.

3. The basic law of light absorption (Bouger-Lambert-Behr law). The essence of the law, its mathematical description and the characteristics of the quantities included in it.

4. What is the content of the law of additivity?

5. Name the limitations and conditions of application of the Bouguer-Lambert-Behr law.

6. Draw a block diagram of the device for the spectrophotometric method of analysis. Describe the main units of the device.

7. Errors in the measurement of light absorption. In what cases is the largest relative error observed?

8. How to determine the concentration of the substances under investigation in solutions in the spectrophotometric method of analysis?

References:

General:

1. Analytical chemistry: handbook / V. V. Bolotov, O. A. Yevtifeyeva, L. Yu. Klimenko, T. A. Kostina, T. V. Zhukova, E. Yu. Ahmedov , O. A. Brizicky; edited by V. V. Bolotov.— Kharkiv: NUPh; Original, 2012.
2. Analytical chemistry (Qualitative analysis). Part I / O. A. Ievtifieieva, V. V. Bolotov, T. A. Kostina, O. M. Svechnikova, T. I. Yuschenko, N. I. Kaminska, A. E. Kosareva, L. V. Slobodyanyuk, O. P. Yashchuk ; edited by O. A. Ievtifieieva. – Kharkiv : Publishing house the CLL «Generous farmstead plus», 2014. – 168 p.
3. Analytical chemistry. Part II. Quantitative analysis: the manual for foreign students of pharmaceutical higher schools and pharmaceutical departments of medical higher schools of the III – IV accreditation levels / V. V. Bolotov, O. M. Svechnikova, T. A. Kostina et al. – Kharkiv: NUPh, 2010. – 160 p.

4. Analytical chemistry: textbook [the textbook for students of higher schools] / I.S. Grytsenko, V. V. Bolotov, L.Yu. Klimenko et al.; ed. by I.S. Grytsenko – Kharkiv: NUPh, Golden Pages, 2019. – 600 p.

Lecture No. 15

Topic: Electrochemical methods of analysis Potentiometric analysis. Potentiometric titration of redox systems. Chromatography.

Relevance of the topic: Analytical chemistryis a science that develops theoretical foundations and practical methods of chemical analysis.Therefore, it is relevant to solve the problems facing analytical chemistry with the help of physical, chemical and physicochemical methods used for the analysis of medicinal products.

Purpose: To acquaint students with the main methods of electrochemical analysis and the possibility of their use in analytical practice

Basic concepts:analytical chemistry, quantitative analysis, potentiometry, voltage, type I electrodes, type II electrodes

Plan and organizational structure of the lecture:

1. General characteristics of electrochemical methods
2. Potentiometry
3. Classification of electrodes

Content of lecture material (lecture text):

1. General characteristics of electrochemical methods

Electrochemical methods of analysis (EMA) are based on the study of processes occurring on the surface of the electrode or in the near-electrode space. An electrical parameter (potential, current, resistance, etc.) serves as an analytical signal, a component of the solution functionally related to the concentration is determined and can be correctly measured.

concentrations) of electrolyte solutions.

Active concentration appears in the Nernst equation. Taking into account relation (3), this equation has the form:The EMA classification proposed by

IUPAC has undergone certain changes over the past decades, clarifications (explanations) and additions have been made to it.

Significant attention is paid to electrochemical cells and sensors of the analytical signal (electrode systems, various electrochemical sensors), it is these primary electrochemical converters that determine the analytical capabilities of any method. Currently, the most advanced and fast processing of the signal from the sensor, the calculation of statistical characteristics of both the output signal and the results of the entire analysis as a whole do not pose a problem. That is why it is important to obtain a reliable output signal in order to calibrate it in concentration units.

According to the general classification proposed

IUPAC, EMA are divided into methods in which the disturbed electrical signal is constant or equal to zero and methods in which the disturbed signal changes over time. These methods are classified as follows:

voltammetric - voltammetry, $I \neq 0$; $E = f(t)$;

potentiometric- potentiometer, ($I = 0$);

amperometric- amperometry ($I \neq 0$; $E = const$);

chronopotentiometric, $E = f(t)$; $I = const$;

impedance,or conductometric - measurements using the imposition of an alternating voltage of small amplitude; others, combined (for example, spectroelectrochemical).

2. Potentiometry

The potentiometric method makes it possible to determine the concentration of ions in electrolyte solutions using the Nernst equation (2), table values of normal potentials and measured values of the potentials of indicator electrodes. As a result of their interaction, the ions send signals about their existence (concentration) in a somewhat reduced form, shielded by the interaction. To describe the phenomenon of an imaginary decrease in concentration, the concept of active concentration, or simply activity, was introduced. Activity is related to concentration by the ratio:

$$I=\gamma \cdot C, \qquad (3)$$

where γ –activity coefficient; γ= 1 for ideal

$$\varphi = \varphi_0 + \frac{RT}{nF}\ln a = \varphi_0 + \frac{RT}{nF}\ln \gamma c\ .$$

Note that the concentration of ions is indicated by square brackets ([Ag^+], ([Fe^{3+}], etc.); the decimal logarithm of the concentration of hydrogen ions with a negative sign (–lg [H^+]) is usually called the hydrogen indicator, which is assigned the symbol pH. Therefore, pH =–lg [H +]. This indicator is introduced for convenience. For example, for water with [H +] = 10^{-7}, pH =–lg 10^{-7}= 7. Environments with pH < 7 – acidic, and with pH > 7 - alkaline

Indicators similar to pH are also used for other ions (the element X ion will have a pH indicator).

The Nernst equation (4) can be somewhat simplified using the pH indicator:

$$\varphi = \varphi_0 + \frac{RT}{nF}\ln c = \varphi_0 + \frac{0,058}{n}\ln c = \varphi_0 - \frac{0,058}{n}\mathrm{pX}\ , \qquad (4)$$

where the value 0.058 is formed from a combination of constants $\frac{R}{F}$ at T = 293 K, taking into account the coefficient of transition from natural to decimal logarithms (2.3026).

Equation (4) is the basis of the varieties of potentiometry. There are two options for using equation (4) for analytical definitions. The first (above) is direct potentiometry, the other (indirect potentiometry) is potentiometric titration. The difference between potentiometric titration and classical titration for analytical chemistry is that the equivalence point is determined by the characteristic change in the potential of the indicator electrode during the titration process. Under the conditions of potentiometric titration, a working solution is gradually added to the test solution, which contains a substance that reacts in a certain way with the test (precipitation, complexation, redox reactions, etc.). As a result of the reaction, the concentration of the desired substance decreases, which causes a change in the potential of the indicator electrode. The inflection point of the titration curve (Fig. 1) is the equivalence point. Its coordinates: the ordinate is the potential of the

indicator electrode at the end of the titration, the abscissa is the volume of the working solution spent during the analytical determination.

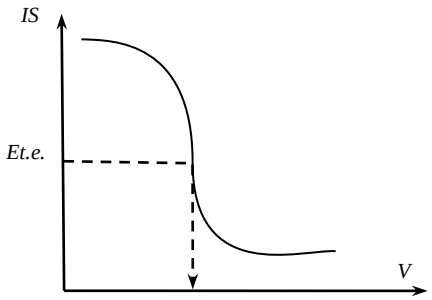


Fig. 1. Potentiometric titration curve: Et.e. is the equivalence point

The main problem when using the potentiometric method is the choice of the indicator electrode, since it must be resistant to the solution, and the electrode reaction must be reversible.

3. Classification of electrodes

An electrochemical electrode is one of the two conductors presented in an electrochemical element, on the surface of which an electrochemical reaction takes place. According to the type of electrode reaction, all electrodes can be divided into two groups: electrodes of the first and second kind.

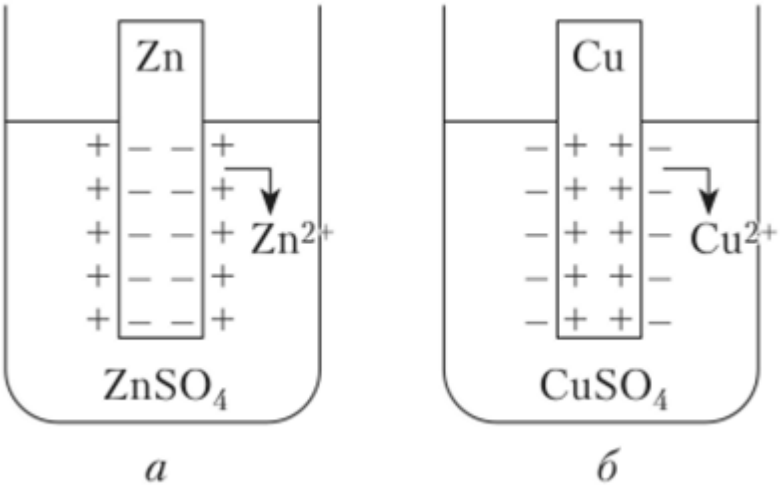
Electrodes of the first kind

Electrodes of the first type include electrodes consisting of a Purposel plate immersed in a salt solution of the same Purposel. During reversible operation of the element, which includes an electrode, the process of transition of cations from Purposel to solution or from solution to Purposel occurs on the Purposel plate. Thus, electrodes of the first kind are reversible by cation and their potential is related by the Nernst equation to the concentration of the cation. Electrodes of the first kind also include a hydrogen electrode.

a) Purpose electrode – Purpose electrode immersed in a solution of its salt $M|M^{n+}$, for example, zinc and copper electrodes:

$$Zn|Zn^{2+} \qquad Zn = Zn^{2+} + 2e^{-},$$

$$Cu|Cu^{2+} \qquad Cu = Cu^{2+} + 2e^{-}.$$



а *б*

The left electrode is selected for the cation. Its electrode potential

$$E = E^{\circ}_{M^{n+}/M} + \frac{0,059}{n} \cdot \lg a_{M^{n+}}$$

b) The gas electrode as one of the components of the electrode pair contains gas (H_2, Cl_2, etc.) adsorbed on a chemically inert conductor of the first kind (usually platinum covered with platinum black).

When the adsorbed gas comes into contact with a solution of its own ions, equilibrium is established. For chlorine and hydrogen electrodes, this equilibrium can be represented by the equations:

$$Cl_2 + 2e^- = 2Cl^-,$$

$$2H^+ + 2e^- = H_2.$$

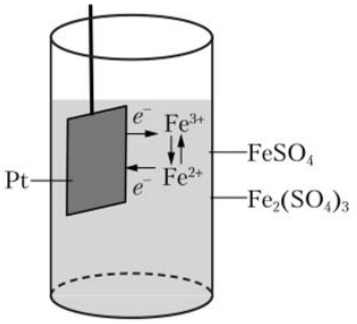
The corresponding Nernst equations have the form:

$$E_{Cl_2/2Cl^-} = E^{\circ}_{Cl_2/2Cl^-} + \frac{0,059}{2} \cdot \lg \frac{a_{Cl_2}}{a^2_{Cl^-}},$$

$$E_{2H^+/H_2} = E^{\circ}_{2H^+/H_2} + \frac{0,059}{2} \cdot \lg \frac{a^2_{H^+}}{a_{H_2}}.$$

It is obvious that their electrode potential depends on the pressure and activity (concentration) of ions in the solution.

$Fe^{2+} - e^- = Fe^{3+}$ ($Red^z - ne^- = Ox^{z+n}$);
$Fe^{3+} + e^- = Fe^{2+}$ ($Ox^{z+n} + ne^- = Red^z$).



2. Redox electrodes consist of an electrochemically inert conductor (platinum, graphite, etc.) immersed in a solution in whichthere are oxidized and reduced forms of the potential-determining substance. Such an inert conductor facilitates the transfer of electrons from the reducing agent to the oxidizing agent through the external circuit. Examples of such electrodes can be redox electrodes with ions in different oxidation states: (Pt)Sn^{4+}, Sn^{2+}, (Pt)Fe^{3+}, Fe^{2+}.

$$E_{Sn^{4+}/Sn^{2+}} = E^{\circ}_{Sn^{4+}/Sn^{2+}} + \frac{0{,}059}{2} \cdot \lg \frac{a_{Sn^{4+}}}{a_{Sn^{2+}}},$$

$$E_{Fe^{3+}/Fe^{2+}} = E^{\circ}_{Fe^{3+}/Fe^{2+}} + \frac{0{,}059}{2} \cdot \lg \frac{a^2_{Fe^{3+}}}{a^2_{Fe^{2+}}}.$$

Electrodes of the second kind

Electrodes of the second type are electrodes in which Purposel is covered with a sparingly soluble salt of this Purposel and is in a solution containing another soluble salt with the same anion. Its electrodes are reversible with respect to the anion, and the dependence of their electrode potential on temperature and anion concentration can be written in the following form:

$$\varepsilon = \varepsilon^0 - \frac{RT}{zF} \ln[A^{z-}].$$

Electrodes of the second type are Purposel electrodes covered with a layer of sparingly soluble salt of the same Purposel. When immersed in a solution of the salt of the same anion, its potential will be determined by the activity of the ion in the solution.

a) Silver chloride electrode (CSE) Ag, AgCl|Cl is a silver conductor coated with solid AgCl, which is immersed in a saturated KCl solution.

Silver interacts electrochemically with its ion:

$$Ag+ + e– = Ag.$$

The Nernst equation for this process:

$$E_{Ag^+/Ag} = E^\circ_{Ag^+/Ag} + 0{,}059 \cdot \lg a_{Ag^+}$$

However, in the presence of sparingly soluble AgCl, the activity of silver ions is very small and difficult to determine. But the activity of Ag+ ions is related to the activity of Cl- ions, which is easily set in this system, by the solubility product of silver chloride PRAgCl:

$$a_{Ag^+} = \frac{ПР_{AgCl}}{a_{Cl^-}}.$$

$$E_{Ag^+/Ag} = E^\circ_{Ag^+/Ag} + 0{,}059 \cdot \lg \frac{ПР_{AgCl}}{a_{Cl^-}} = E^\circ_{Ag^+/Ag} + 0{,}059 \cdot \lg ПР_{AgCl} - 0{,}059 \cdot \lg a_{Cl^-},$$

$$E^\circ_{Ag^+/Ag} + 0{,}059 \cdot \lg ПР_{AgCl} = E^\circ_{хсэ},$$

we get the Nernst equation for the silver chloride electrode:

$$E_{хсэ} = E^\circ_{хсэ} - 0{,}059 \cdot \lg a_{Cl^-}$$

Chlorine ions are the determining potential, and the electrode process can be represented by the equation

$$AgCl_{(т)} + e^- = Ag + Cl^-.$$

Ion-selective electrodes (ISE), sensitive to cations and anions, are electrochemical systems in which the potential is determined by the processes of ion distribution between the membrane and the solution.

The investigated solution	Membrane	Standard solution
$A^+\left(a_{A^+}\right),\ B^+\left(a_{B^+}\right)$	A^+, B^+	$A^+\left(a_{A^+}\right)$

The membrane separates two solutions (study and standard) containing ions that can penetrate the membrane and move in it. The standard solution contains

only one type of membrane-active ions A+. The composition of the standard solution is unchanged. Currently, ISEs with a clearly expressed selectivity for large cations and anions are widely used.

The most common ISEs are glass electrodes. Glass is considered as a solid electrolyte capable of ionic interaction with the solution. Glass containing Na, Li, Ca cations has an affinity for hydrogen ions, by introducing Al and B oxides into the glass, it was possible to create ISE for Na+, K+, Li+, Ag+, Tl+, etc. ions.

The glass electrode for determining the H+ concentration consists of a thin-walled glass ball soldered to a glass tube. HCl solution (internal solution, a = 0.1 mol·l–1) is poured into the ball, which has a silver chloride electrode. When a glass electrode is immersed in a solution with a measurable concentration of H+ (external solution), ion exchange processes occur between the membrane and the investigated solution (p):

$$H^+_p + Na^+_{мб} = H^+_{мб} + Na^+_p,$$

leading to a potential difference.

Electrode comparison	The investigated solution	Membrane	Standard solution
$Hg, Hg_2Cl_2 \mid Cl^-$	$H^+\left(a_{H^+}\right)$	$\left(Na^+, Li^+\right)H^+$	$H^+\left(a_{H^+}\right), Cl^-, AgCl, Ag$

The potential of the glass electrode is equal to

$$E_{ст} = E^\circ_{ст} + 0{,}059 \cdot \lg\left[H^+\right] = E^\circ_{ст} - 0{,}059 \cdot pH_{внешн}$$

Glass electrodes are commonly used for pH determination.

The hydrogen electrode chosen as the zero point when comparing electrode potentials is practically not used as a working reference electrode. This is due to many design, technological and operational difficulties: gaseous hydrogen is very critical to even the smallest impurities, its pressure must strictly correspond to 100 kPa, and the activity of hydrogen ions in the solution must strictly correspond to unity, the surface of the platinum electrode must be clean and retain catalytic properties for a long time. Therefore, electrodes of the second kind, devoid of these

inconveniences, are usually used as reference electrodes; more often than others, silver chloride (CSE) and calomel (KE), because at a constant concentration of chlorine ions, their potentials remain constant. In addition to HSE and KE, the glass electrode turned out to be very convenient to work with.

General material and bulk-methodological support of the lecture:

- ✓ computer presentation;
- ✓ illustrative materials;
- ✓ examples of solving typical tasks or performing typical tasks;
- ✓ multimedia projector.

Questions for self-control:

1. What are the electrochemical methods of analysis based on?
2. The nature of the analytical signal in potentiometric methods of analysis. Feature of potentiometry.
3. Classification and scope of use of the potentiometric method of analysis.
4. Indicator electrodes and reference electrodes in potentiometry and their properties.
5. Classification of electrodes according to their nature. Electrodes of I, II, III groups.
6. Ion-selective, membrane electrodes (IV group). The principle of action. The cause of the potential on the membrane surface of ion-selective electrodes.
7. Main characteristics of ion-selective electrodes.
8. Classification of ion-selective electrodes. Describe each group of electrodes:
   a) electrodes with a solid crystalline membrane and glass electrodes;
   b) electrodes with liquid membranes, plasticized membranes;
   c) enzyme electrode.

References:

General:

1. Analytical chemistry: handbook / V. V. Bolotov, O. A. Yevtifeyeva, L. Yu. Klimenko, T. A. Kostina, T. V. Zhukova, E. Yu. Ahmedov , O. A. Brizicky; edited by V. V. Bolotov.— Kharkiv: NUPh; Original, 2012.
2. Analytical chemistry (Qualitative analysis). Part I / O. A. Ievtifieieva, V. V. Bolotov, T. A. Kostina, O. M. Svechnikova, T. I. Yuschenko, N. I. Kaminska, A. E. Kosareva, L. V. Slobodyanyuk, O. P. Yashchuk ; edited by O. A. Ievtifieieva. – Kharkiv : Publishing house the CLL «Generous farmstead plus», 2014. – 168 p.
3. Analytical chemistry. Part II. Quantitative analysis: the manual for foreign students of pharmaceutical higher schools and pharmaceutical departments of medical higher schools of the III – IV accreditation levels / V. V. Bolotov, O. M. Svechnikova, T. A. Kostina et al. – Kharkiv: NUPh, 2010. – 160 p.
4. Analytical chemistry: textbook [the textbook for students of higher schools] / I.S. Grytsenko, V. V. Bolotov, L.Yu. Klimenko et al.; ed. by I.S. Grytsenko – Kharkiv: NUPh, Golden Pages, 2019. – 600 p.