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ANALYTICAL CHEMISTRY

lecture notes
for applicants for the first (bachelor's) level of higher education
of the educational and professional programme "Food Technologies"
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full-time and part-time study

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The basic theoretical concepts of the main sections of analytical chemistry are briefly presented, and methods of qualitative and quantitative analysis are described. The lecture notes will help students in completing independent work assignments and preparing for laboratory work. It is intended for students majoring in 181 Food Technologies of full-time and part-time study.

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Introduction

Analytical chemistry is the fundamental chemical science of methods for determining the chemical composition of compounds and their mixtures. It occupies a leading position in the system of theoretical and practical training of a specialist in food technology. According to its application, analytical chemistry is divided into qualitative, quantitative chemical analyses and instrumental methods of analysis. In the course of qualitative analysis, students must master the methods of detecting ions, elements and chemical compounds that are part of the substances under study and their mixtures. In the course of quantitative analysis, students must master the methods by which chemical compounds and their mixtures can be quantified.

The lecture course in the discipline "Analytical Chemistry" is designed for applicants for the first (bachelor's) level of higher education in the educational and professional programme "Food Technologies".

Lectures in analytical chemistry present the theoretical foundations of qualitative and quantitative analysis. The law of active masses and its application to processes in analytical chemistry, the role of buffer systems in analysis, and the structure and application of complex compounds in analytical practice are discussed. Quantitative analysis is represented by gravimetry and chemical titrimetric methods of analysis. Among the physicochemical methods, the theoretical foundations of optical, electrochemical, and chromatographic methods of analysis are considered

The purpose of the lecture notes is to help students learn the discipline, better prepare for laboratory work, independent work and exams.

The author hopes that the synopsis will help students to acquire basic knowledge, in particular in the field of food technology, which will become the basis for studying special disciplines; significantly improve the general education level and expand their professional outlook, which will contribute to the success of their career.

Lecture 1

INTRODUCTION. BASICS OF QUALITATIVE CHEMICAL ANALYSIS

1. Purpose and objectives of analytical chemistry;
2. Classification of qualitative analysis methods;
3. Methods and requirements for reactions in qualitative chemical analysis;
4. Chemical reagents;
5. Equipment and techniques for performing qualitative analysis.

1. Aims and objectives of analytical chemistry

Analytical chemistry is the *science of methods for determining the composition and structure of chemical systems (individual substances, their mixtures or any material).* The composition of substances and materials has qualitative and quantitative characteristics that can be determined using analytical chemistry methods - qualitative and quantitative analysis.

Analytical chemistry is of great scientific importance; it was with the help of qualitative and quantitative analysis that the basic stoichiometric laws of chemistry were formulated, the atomic masses of elements and chemical formulas of substances and chemical compounds were established.

Analytical chemistry is equally important and practical in its ability to carry out sanitary control over the condition of soils, water bodies, air, food, drinking water, and to examine goods and raw materials for compliance with quality certificates.

Qualitative analysis allows us to determine what chemical elements a substance consists of, which ions, groups of atoms, or molecules are part of it. Qualitative analysis is the first step in the study of any unknown or synthesised substance.

Quantitative analysis is a set of chemical and physical methods for determining the relative amount of elements, ions or chemical compounds in a substance under study.

Methods and techniques of qualitative and quantitative analysis are used in the production of food and non-food products:

- to detect elements (ions), functional groups, substances in the composition of raw materials in order to assess the compliance of goods with the TU and DSTU, in accordance with which they are manufactured;
- to control the flow of the technological process in order to prevent rejects, which are often caused by undesirable impurities in the raw material;
- to study the properties of raw materials and supplies, to properly organise the storage and transportation of goods, etc.

Modern laboratories are increasingly using physical and physicochemical methods of analysis, which are characterised by accuracy, sensitivity, reproducibility and speed of results. When choosing a quantitative determination method, the required accuracy of the results, the speed of the analysis, and, in the case of mass determinations, the availability and cost of the reagents used are taken into account. That is why classical chemical methods of analysis are still widely used in the practice of control and analytical and factory laboratories.

2. Classification of qualitative analysis methods

Qualitative analysis can be carried out either by chemical reactions or by using the physical properties of the constituents of a substance. Therefore, qualitative analysis methods are divided into:

- *chemical* - based on chemical reactions that are accompanied by characteristic external signs, such as the formation of sediment, colour change, and odour. Chemical analysis can be carried out both in a "wet" way (reactions are carried out in solution) and in a "dry" way - pyrochemical reactions of flame colouring (e.g, K^+ ions colour the flame purple) or "pearl" colouring (a sample of a substance is sprinkled with borax on a platinum wire in a burner flame, forming a ball, the so-called "pearl", and its colour reveals the ions contained in the sample).

- ***physical*** - based on the observation of various physical properties of the substance under study, for example, the *spectral method is* based on the study of absorption or emission spectra of the substance under analysis, the *luminescent method* - on the ability of a substance to glow in ultraviolet radiation. These methods do not require chemical reactions.

- ***physicochemical (or instrumental)*** - based on the measurement of certain physical properties of substances (optical density, sorption properties, specific electrical conductivity) in the course of a chemical reaction, for example, *spectrophotometry, conductometry, chromatography, etc.*

3. Methods and requirements for reactions in qualitative chemical analysis

For chemical analysis, larger or smaller amounts of the substances under investigation can be taken. Depending on this, a distinction is made between *macroanalysis* (macromethod) - used to analyse 0.1-1 g of a substance, such analysis is performed in test tubes, *semi-microanalysis* (semi-micro method) - 0.01-0.1 g of a substance is used, such analysis is performed in conventional or microtubes, *microanalysis* (micromethod) - no more than 0.01 g of a substance is used, such an analysis can be performed by dropwise method on strips of filter paper or watch glass (the analysis can be performed on a flask or beaker turned upside down). Since the external effect of the reaction does not depend on the amount of the substance taken for analysis, the semi-micro method is used in most cases. Sometimes it is necessary to study the qualitative and quantitative composition of a substance with a small amount of it. In such cases, *ultramicroanalysis is used,* when a very small amount of a substance is taken for analysis and the external effect of the reaction is observed under a microscope.

The chemical reactions used in qualitative chemical analysis must have characteristic external signs, i.e. have an analytical effect. Reactions that are accompanied by external signs are called *analytical* or *qualitative reactions*. Qualitative reactions that can be used to identify a particular ion or substance and distinguish it from others are called *individual* or *characteristic reactions*. However, in order to detect a particular ion using a characteristic reaction, this ion must be separated from other ions in the solution, as foreign ions can interfere with detection by forming precipitates, colouring and thus masking the characteristic external features of the individual reaction to the ion being detected.

There are reactions that do not interfere with foreign ions. Such reactions are called *specific* reactions, but there are very few of them. For example, a characteristic reaction to Fe^{3+}

-ion is a specific reaction with potassium hexacyanoferrate (II) in a slightly acidic environment. This results in the formation of a dark blue precipitate of Prussian blue:

$Fe^{3+} + K_4[Fe(CN)_6] \rightarrow KFe[Fe(CN)_6] + 3K^+$

Reactions that give the same analytical effect with several ions are called *selective* or *selective*. For example, Cl^- ions form a white precipitate with Ag^+, Hg^{2+}, Pb^{2+} ions. Selective reactions include the so-called group reactions, which are designed to detect a specific group of ions.

Other important conditions required for a characteristic reaction include:

- The acidity of the medium, e.g. precipitates that are soluble in acids and alkalis can only be obtained in a neutral medium;
- temperature of the solution;
- is the concentration of an ion sufficient for its detection in solution.

The latter condition is related to the *sensitivity of a* chemical analytical reaction, because the smaller the amount of a substance that can be detected by a particular reaction, the more sensitive it is. The smallest amount of a substance or ion that can be detected by a particular reaction under certain conditions is called the *detectable minimum.* This value is very small and is expressed in micrograms (µg) and is usually denoted by the Greek letter : $\gamma = 1µg = 10^{-6}$ g.

The sensitivity of a reaction is characterised not only by the absolute amount of a substance, but also by the concentration of the ion or substance in the solution.

The smallest concentration of a substance or ion in a solution at which it can still be detected by a given reaction is called the limiting *dilution. The limiting dilution is the* ratio of the unit mass of a substance or ion (g) to the volume of a solvent (cm^3).

4. Chemical reagents

The substances used to detect ions are called *reagents*.

The purity of the reagents is essential for the correct results of qualitative and quantitative analysis. It is costly and time-consuming to produce absolutely pure reagents that are free of impurities. Chemical reagents usually contain a certain amount of impurities, so you need to pay attention to the grade (qualification) of the reagent. Depending on the degree of purification, reagents are divided into *technical (t.), pure (p.), pure for analysis (p.a.),* and *chemically pure (c.p.)*. Technical reagents cannot be used for chemical analysis because they contain a relatively large amount of impurities. Reagents of the last three grades have a low impurity content. For educational analytical determinations, reagents are usually used as "pure", in some cases "p.a.". Chemically pure reagents are used for critical analytical determinations.

High purity chemical reagents must be handled with great care to prevent contamination of the reagent, which can cause incorrect analysis results. Solid chemicals should not be handled with hands or paper, but rather with porcelain or plastic spatulas or spoons. Beakers with concentrated acids must not be covered with a cork, as the acid vapour destroys the cork and contaminates the acids.

Jars of reagents should be well labelled with the name of the reagent, its qualification, concentration, and sometimes the maximum permissible content of impurities in the preparation.

5. Equipment and techniques for performing qualitative analysis

For chemical reactions, special chemical glassware is used: ordinary test tubes and centrifuge tubes, glass sticks, beakers and flasks, watch glasses, washers, filter funnels, etc.

When performing analytical reactions, special attention should be paid to the cleanliness of laboratory glassware. Contamination of a test tube or flask with certain chemicals can lead to an error in determining the qualitative composition of the sample under test. Chemical glassware is washed using a brush with tap water and baking soda. Heavily contaminated dishes should be washed with solutions of acids, alkalis, and a chromium mixture (5-6 g of potassium dichromate is ground and mixed with 200 cm^3 of concentrated sulfuric acid). Rinse the washed dishes several times with tap water, rinse the inner walls with distilled water and wipe the outside dry with a towel or leave to dry in an inverted position.

By the macro method, all chemical reactions are carried out in ordinary test tubes, where 1-2 cm^3 of the test solution and about the same amount of reagents are poured, and the reaction effect is observed. For filtering, use ordinary funnels.

To perform the *semi-micro* analysis, *use* conventional or centrifuge tubes. For the detection of individual ions, 2-3 drops of the test solution and the same amount of reagent are added to the test tube. The solutions are added using special 1-2 cm capillary pipettes^3 with rubber tips. In the thin capillary of the pipette, the solution evaporates quickly and dry salts clog the capillary. Therefore, after each use, the pipette should be rinsed well with water; when not in use, it is best to store the pipette in a glass of water.

When performing the semi-micro analysis, the solid precipitates are separated from the solution by centrifugation using an electric centrifuge. After the precipitation reaction has been carried out, the test tube is placed in the centrifuge slot. The level of the solution in the tube should be 6-8 mm below the edge of the tube. A second tube of water must be placed in the opposite centrifuge well for equilibrium, and the weight of both tubes must be approximately equal. If this rule is violated, the centrifuge will quickly deteriorate. The centrifugation time for crystalline precipitates is 1-2 min (at a rotational speed of 1000 rpm), for amorphous precipitates - 2-3 min at a rotational speed of up to 2000 rpm. The centrifuge speed is increased or decreased gradually, and sudden changes in rotation are not allowed to prevent damage to the centrifuge.

After centrifugation, the clear solution (centrifugate) is separated from the precipitate by **decantation** - simply pouring it into another tube. The solution can also be collected with a capillary pipette.

Solutions in test tubes are heated in special water baths. A water bath can also be used to evaporate solutions. Evaporation to dryness is carried out in a porcelain cup by heating it in a gas burner. If the dry substance is to be ground into powder, use a mortar and pestle.

To perform a droplet *microanalysis, take a drop of the* test solution, apply it to a piece of filter paper, a watch glass or a porcelain plate with a recess, and add a drop of reagent; the bottom of an upside-down beaker can be used instead of a watch glass. If you use filter paper for the colour characteristic reaction using the droplet method, a coloured spot will appear on the paper, surrounded by a wet area of colourless solution. Due to the capillary-adsorption properties of the filter paper, the least soluble compounds are located closer to the centre of the coloured spot.

When carrying out precipitation reactions, a certain excess of precipitant solution should be added. To check the completeness of the precipitation, after centrifugation, add a few more drops of the precipitant to the clear solution above the precipitate; if the precipitation is complete, the solution above the precipitate will remain clear. The precipitate must be thoroughly washed from the substances contained in the solution. To do this, pour off the bulk of the solution, then pour water or other washing liquid into the test tube and stir the precipitate with a folding stick. The solution is centrifuged again, and then the washing liquid is poured off. The described operation is repeated 2-3 more times. Often, an excess of precipitant is added to the washing liquid. For example, when washing metal sulphides, a solution of ammonium nitrate or ammonium chloride with the addition of ammonium sulphide or saturated with hydrogen sulphide is used.

Lecture 2

SYSTEMS FOR QUALITATIVE ANALYSIS OF CATIONS AND ANIONS

1. Sulfide system for cation analysis;
2. Acid-base system for cation analysis;
3. Classification of anions;
4. Systematic and fractional analysis;
5. Chemical reaction sensitivity and methods of its increase.

1. Sulphide cation analysis system

According to this system, cations are divided into five analytical groups depending on the solubility of their sulfides, carbonates and chlorides.

A reagent that can be used to separate a particular group of ions from others is called a *group reagent*.

According to the sulphide systematics of cations, the *first analytical group* includes Na^+, K^+ , NH_4^+ and Mg^{2+} . This group of cations does not *have a* group reagent. Each cation of this group is identified by its own characteristic reactions, which are carried out in a certain sequence.

The *second analytical group* includes Ba^{2+} , Sr^{2+} , Ca^{2+} cations.

They are precipitated by the group reagent ammonium carbonate $(NH\ )_{42}\ CO_3$ in an ammonia buffer solution in the form of water-insoluble carbonates $MeCO_3$. Cations of this analytical group do not precipitate $(NH_4)_2S$ and H_2S.

The *third analytical group* includes the cations Al^{3+} , Cr^{3+} , Fe^{3+} , Fe^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} , Zn^{2+} and others. They are precipitated from neutral or alkaline solutions ($pH = 7...9$) by the group reagent $(NH_4)_2S$ in the form of water-insoluble sulfides and hydroxides. Cations of this group do not precipitate in acidic solutions of H_2S.

The *fourth analytical group* includes cations Cu^{2+}, Cd^{2+}, Hg^{2+}, Bi^{3+}, As^{III}, As^{V}, Sb^{III}, Sb^{V}, Sn^{2+}, Sn^{IV} and others. All cations of the fourth group are precipitated by H_2S in an acidic environment at $pH = 0.5$ in the form of sulfides, which are practically insoluble in water and dilute mineral acids. The group reagent is H_2S in hydrochloric acid.

The fifth *analytical group of* cations includes Ag^+, Hg_2^{2+} , Pb^{2+} and others. The group reagent is a solution of hypochlorous acid with a molar concentration of the substance equivalent HCl 2 *mol/dm³* .The corresponding chlorides are poorly soluble in water and in dilute acids.

The sulphide system of cation analysis is a classic one, but it has significant drawbacks.

The solubility of sulphides of some cations of the third and fourth analytical groups is close, so the separation of cations is not complete.

The precipitation of cations of the fourth analytical group in the form of sulfides is often accompanied by co-precipitation of cations of the third group.

It takes a lot of time (up to 25-30 hours) to conduct a full analysis using this system

The analysis uses highly toxic $H_2\ S$. To work with it, a specially equipped room is required.

2. Acid-base cation analysis system

This system divides cations into six analytical groups according to their relation to chloride and sulfuric acids, alkaline and ammonia solutions.

The *first analytical group* includes Na^+ , K^+ , NH_4^+ cations.

This group of cations does not have a group reagent.

The *second analytical group* includes Ag+, Hg_2^{2+} , Pb^{2+}/

The group reagent is a solution of hydrochloric acid (c(HCl) = 2 *mol/dm* ^{3}). Under the action of a group reagent, the corresponding chlorides are formed, which are poorly soluble in water and dilute acids. *SP*(AgCl)=$1.78\cdot10^{-10}$; *SP*(Hg_2Cl_2) =$1.3\cdot10^{-1}$; *SP* ($PbCl_2$) =$1.6\cdot10^{-5}$.

The most soluble plumbum chloride dissolves well in hot water and can thus be separated from the other chlorides in this group.

The *third analytical group* includes the cations Ba^{2+} , Sr^{2+} , Ca^{2+} , and Pb^{2+} . The group reagent is a solution of sulphuric acid (c(H_2SO_4) = 2 *mol/dm*^{3}). The cations of this group precipitate as sulphates, which are poorly soluble in water and acids. *SP* ($BaSO_4$) =$1.1\cdot10^{-10}$; *SP* ($SrSO_4$) =$3.2\cdot10^{-7}$; *SP* ($CaSO_4$) =$2.5\cdot10^{-5}$; *SP* ($PbSO_4$) =$1.6\cdot10^{-8}$.

The *fourth analytical group* includes cations Al^{3+}, Cr^{3+}, Zn^{2+}, Sn^{2+}, As^{III}, As^{V}, Sb^{III}. The group reagent is an excess of NaOH or KOH solution. Hydroxides of these elements are amphoteric, dissolving in excess alkali to form anions: $[Al(OH)]_4^{-}$, $[Zn(OH)]_4^{2-}$, $[Cr(OH)]_4^{-}$, $[Sn(OH)]_4^{2-}$ and others, which are dehydrated when heated; in solution, the ions AlO_2^-, CrO_2^- , ZnO_2^{2-}, SnO_2^{2-} and others.

The fifth *analytical group* includes the cations Mg^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Bi^{3+}, Sb^{3+}, Sb^{V}. The group reagent is an excess of aqueous ammonia solution with a mass fraction of NH_3 in the solution of 25%. Under the action of the group reagent, the corresponding hydroxides are formed that are insoluble in excess alkali. $Mg(OH)_2$, $Mn(OH)_2$, $Fe(OH)_2$, $Fe(OH)_3$, $Bi(OH)_3$, $HSbO_2$, $HSbO_3$ precipitate. *SP* ($Mg(OH)_2$) =$7.1\cdot10^{-12}$; *SP* ($Fe(OH)_2$)=$7.2\cdot10^{-16}$; *SP* ($Mn(OH)_2$) = $1.9\cdot10^{-13}$; *SP* ($Fe(OH)_3$)=$3.2\cdot10^{-40}$; *SP* ($Bi(OH)_3$)=$4.3\cdot10^{-31}$.

The *sixth analytical group* includes the cations Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Hg^{2+}. The group reagent is an aqueous solution of NH_3 with a mass fraction of NH_3 in the solution of 25%. Under the action of the group reagent on a solution containing cations of this analytical group, the corresponding hydroxides are formed, which are poorly soluble in water but dissolve in excess ammonia to form complex ammoniacs: $[Cu(NH_3)_4]^{2+}$, $[Co(NH_3)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$, $[Cd(NH_3)_4]^{2+}$, $[Hg(NH_3)_4]^{2+}$.

3. Classification of anions

The most commonly used classification is that all anions are divided into three analytical groups depending on the solubility of their barium and argentium salts.

The *first analytical group* includes the anions SO_4^{2-}, SO_3^{2-}, CO_3^{2-}, PO_4^{3-} , SiO_3^{2-}, CrO_4^{2-} , $C_2O_4^{2-}$, $S_2O_3^{2-}$ and others. The group reagent for anions of this group is a solution of barium chloride in a neutral or slightly alkaline solution. Under the action of the group reagent, the corresponding barium salts are formed that are practically insoluble in water. *SP* ($BaSO_4$)=$1.1\cdot10^{-10}$; *SP* ($BaCrO_4$)=$2.3\cdot10^{-10}$; *SP* ($BaCO_3$)=$8.0\cdot10^{-9}$; *SP* ($Ba_3(PO_4)_2$)=$6.0\cdot10^{-39}$; *SP* (BaC_2O_4)=$1.7\cdot10^{-7}$; *SP* ($BaSO_3$)=$8.0\cdot10^{-7}$.

The *second analytical group of* anions includes Cl^- , Br^- , I^- , S^{2-}.

The group reagent for anions of this group is a solution of $AgNO_3$ in the presence of HNO_3. Under the action of the group reagent, the corresponding argentum salts are formed, which are practically insoluble in water and dilute nitric acid. *SP* (AgCl)=$1.78 \cdot 10^{-10}$; *SP*(AgI)=$8.3 \cdot 10^{-17}$; *SP* (AgBr)=$5.3 \cdot 10^{-13}$; *SP* (Ag_2S)=$6.3 \cdot 10^{-50}$.

The *third analytical group* includes the anions NO_2^- , NO_3^- , CH_3COO^- . There is no group reagent for the anions of this group. All salts of Barium and Argentum with these anions are soluble in water.

4. Fragmentary and systematic methods of qualitative analysis

Qualitative detection of ions in solutions can be performed by *fractional* and *systematic* methods of analysis. The *fractional method means* that each ion is detected by certain characteristic reactions in the presence of all other ions. In the fractional method of analysis, there is usually no particular sequence in the detection of individual ions. For example, you need to perform a qualitative analysis of a solution containing Cu, Fe (III) and Barium cations. The analysis can begin with the detection of Cu ions. To do this, a separate sample of the solution is exposed to an excess of ammonium hydroxide solution. In the presence of Cu cations, the solution turns blue. In this case, Iron (III) and Barium cations do not affect the analytical effect of the reaction. To detect Iron (III) cations, a second sample of the solution is exposed to an ammonium rhodanide solution. A sign of the presence of Fe^{3+} is the formation of red rhodanide. Barium ions are detected by adding a solution of sulfuric acid. The product of this reaction is a white insoluble precipitate of barium sulphate.

Fractional analyses are not always easy to perform. When complex mixtures are to be analysed, the first step is to separate out the impurities that interfere with the detection. You need to know the properties of all the ions present in the solution and how they interact with the reagent used to detect the ion. It is often not possible to find reagents that are specific for one ion and do not react with other ions to form reaction products with similar properties. In this case, a systematic method of analysis is used.

Systematic analysis means that a complex mixture of ions is first separated into several distinct groups using group reagents. Within each of these groups, the individual ions are then detected by certain characteristic reactions. The ions are separated into groups and detected in each group in a very specific sequence. The separation of ions into groups in a systematic analysis is used only for the detection of cations. The analysis of a mixture of anions is carried out according to a different scheme.

5. Sensitivity of analytical reactions

The sensitivity of an analytical reaction is determined by the smallest amount of a substance (ion) that can be detected with a given reagent. The sensitivity of a reaction can be expressed as a minimum opening, a limiting concentration, or a limiting dilution, a minimum volume of a limiting dilute solution, a limit of detection, or a sensitivity index.

The minimum opening is the smallest mass of a substance (ion) that can be opened under certain conditions with a given reagent. The minimum opening is expressed in *μg* (10^{-6} *g), ng* (10^{-9} *g), pg* (10^{-12} *g) of a* substance.

Limit concentration is the ratio of a unit mass of a substance to be detected to the largest mass of a solvent expressed in the same units. If the solvent is water, then the mass of water expressed in grams can be replaced by the number of cubic centimetres of water, since the density of water at the temperatures of such measurements is not much different from unity.

The inverse of the limiting concentration is called the limiting *dilution of the solution* or the *sensitivity of the determination*. It indicates the largest volume, expressed in cm^3 , of the aqueous solution under test that contains *1* g of the substance to be determined.

The minimum volume of the limiting dilute solution is the volume of the test solution containing the minimum opening.

The limit of detection is the smallest mass of a substance that can be detected by a particular reaction with a given probability. For confident detection, the probability must be equal to one. Therefore, in practice, the limit of detection is used at a probability of one. This is the lowest detectable amount of a substance at which the effect of the reaction is so intense that a positive result is always obtained.

Analytical reactions are known that achieve a detection limit of 10^{-7} *g of a* substance in *1* cm^3 solution. *Sensitivity is the negative* decimal logarithm of the detection limit.

The sensitivity of the reaction depends on the *pH of the* solution, temperature, ionic strength of the solution, the presence of competitive reactions, the method and method of detection, the volume of the solution to be analysed, and other factors. The sensitivity of the reaction can be used to approximate the content of the substance to be detected or its concentration in the solution.

Ways to increase the sensitivity of an analytical reaction. The sensitivity of the reaction can be increased by a number of special techniques. If the analyst has a solution of a substance whose concentration is significantly less than the limiting concentration required for the reaction, then simply *evaporating the* solution will increase the concentration of the ions to be detected.

One of the most common methods for increasing the sensitivity of the reaction is the method of *extraction with organic solvents*. For example, if the concentration of Fe^{3+} ions in an aqueous solution is very low, it is difficult to see the colour of the thiocyanate complex. If the complex is extracted with isoamyl alcohol, the complex ion is transferred to a thin layer of organic solvent and the colouration is more intense.

Adding an organic solvent can increase sensitivity for another reason. In many cases, an organic solvent that is miscible with water (e.g. acetone) reduces the dissociation of the coloured complex ion. The addition of organic solvents can increase the sensitivity of the reaction that results in precipitation, as the solubility product is reduced, e.g. by adding ethyl alcohol or acetone to the solution when precipitating calcium as calcium sulphate.

In other cases, the sensitivity of the reaction can be increased by introducing an external ion - the so-called co-precipitation with a collector. For example, the precipitation of cobalt in the form of a blue crystalline precipitate $Co[Hg(SCN)_4]$ is a very sensitive reaction. However, at a low cobalt concentration, the precipitate will not be released. If a small amount of Zn ions^{2+} is added to the solution, a blue precipitate will begin to form, consisting of a mixture of $Zn[Hg(SCN)_4]$ (collector) and $Co[Hg(SCN)_4]$.

Lecture 3

GENERAL CHARACTERISTICS AND QUALITATIVE REACTIONS OF CATIONS I - VI ANALYTICAL GROUPS

1. Characteristics of the I analytical group of cations and features of their qualitative reactions;
2. Characteristics of the II analytical group of cations and features of their qualitative reactions;
3. Characteristics of the III analytical group of cations and features of their qualitative reactions;
4. Characteristics of the IV analytical group of cations and features of their qualitative reactions;
5. Characteristics of the V analytical group of cations and features of their qualitative reactions;
6. Characteristics of the VI analytical group of cations and features of their qualitative reactions.

1. General characteristics of the first analytical group of cations and features of their qualitative reactions

The first analytical group of cations includes Na^+ , K^+ , NH_4^+ and cations of other alkali metals Rb^+ , Cs^+ , Fr^+ , which are quite rare. All these cations have high solubility of their salts and therefore there is no common group reagent for them. Li^+ has slightly different properties, as it forms poorly soluble fluorides, carbonates, and orthophosphates. It is similar to the cation of another group, Mg^{2+} , because the size of their atomic and ionic radii is very close.

Cation	Serial number	Atomic radius, nm	Ion radius, nm
Li^+	3	0,156	0,078
Na^+	11	0,192	0,098
K^+	19	0,238	0,133
NH_4^+	-	-	0,143
Mg^{2+}	12	0,160	0,078

The same factor explains the similarity of the analytical properties of K^+ and NH_4^+ . Indeed, all high-quality reagents for K^+ ions ($Na_3[Co(NO_2)_2]$, $NaHC_4H_6O_4$, H_2 [$PtCl_6$]) also interact with ammonium ions with a similar effect.

All of these cations are colourless, so their salts are coloured only when they contain a coloured anion, in particular, dyed salts: chromates are yellow; dichromates are orange; manganates - green; permanganates - crimson-red; iodides and bromides are yellow.

All cations of group I, except for NH_4^+, are resistant to both oxidants and reducing agents, so redox reactions are not used for their determination. Ammonium cations can be oxidised, for example, by chlorine, hypochlorites, and royal vodka.

In fact, all the characteristic reactions of group I cations are exchange reactions, so they are quite simple. Complex, double and acid salts are widely used in these definitions. When carrying out a reaction, certain conditions must be strictly observed. Otherwise, the result may be random. Let's take the example of the determination of Na^+ cations using potassium hexahydroxostybate (V):

$$K[Sb(OH)_6] + NaCl = Na[Sb(OH)_6]\downarrow + KCl$$

This reaction should be carried out in a neutral environment, as the reagent will decompose in an acidic environment and precipitate:

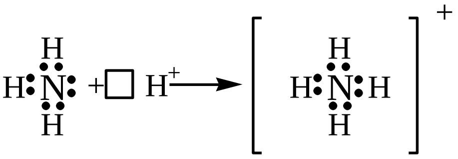
$$K[Sb(OH)_6]\downarrow + HCl = HSbO_3\downarrow + KCl + 3H_2O,$$

and in alkaline, the characteristic precipitate, on the contrary, dissolves:

$$Na[Sb(OH)_6]\downarrow + 2NaOH = Na_3SbO_4 + 4H_2O.$$

Since the precipitates formed tend to form supersaturated solutions, the determination should be carried out from concentrated solutions, rubbing the walls of the test tube with a glass rod, and cooling the solution under cold running water.

Ammonium ion is known to be formed by a donor-acceptor bond:



During crystallisation, ammonium salts are formed from the solution: NH_4Cl, NH_4NO_3, $(NH_4)_2SO_4$, $(NH_4)_3PO_4$, etc.

Ammonium salts interfere with the detection of potassium and magnesium ions, and decompose $K[Sb(OH)_6]$. In these cases, NH_4^+ cations should be removed. There are several methods for their removal.

Thermal decomposition. Some ammonium salts decompose at relatively low temperatures. For example:

$(NH_4)_2CO_3 = 2NH_3\uparrow + CO_2\uparrow + H_2O\uparrow$; $NH_4Cl = NH_3\uparrow + HCl\uparrow$.

Ammonium salts of non-volatile acids (sulphuric, orthophosphatic) decompose only at red-hot temperatures (500-600° C):

$(NH_4)_3PO_4 = NH_3\uparrow + H_3PO_4$

Ammonium nitrate and nitrite decompose in a slightly different way:

$NH_4NO_3 = N_2O + 2H_2O$; $NH_4NO_2 = N_2\uparrow + 2H_2O\uparrow$.

Boiling with caustic alkalis or sodium or potassium carbonates.

$NH_4Cl + Na_2CO_3 = 2NH_3\uparrow + CO_2\uparrow + 2NaCl + H_2O$.

Oxidation by strong oxidants:

$$2\overset{-3}{N}H_4Cl + 3\overset{0}{Cl}_2 = \overset{0}{N}_2 + 8HCl^{-1}$$

$$\begin{array}{l|l} 2N^{-3} + 6e = 2N^0 & 1 \\ 2Cl^0 + 2e = 2Cl^- & 3 \end{array}$$

Binding of nitrogen in ammonium salts with formaldehyde:

$$6CH_2O + 4NH_4^+ + 4OH^- \rightarrow (CH_2)_6N_4 + 10H_2O$$

$$\begin{array}{l|l} 6C^0 + 6\cdot 2e = 6C^{-2} & 1 \\ 4N^{-3} - 4\cdot 3e = 4N^0 & 1 \end{array}$$

2. General characteristics of the II analytical group of cations and features of their qualitative reactions

The second analytical group of cations includes Ag^+, Hg_2^{2+} (- Hg^{+1} - Hg^{+1} -), Pb^{2+}. The group reagent is HCl solution, with which these cations form white precipitates of AgCl, Hg_2Cl_2 (calomel) and $PbCl_2$.

The following circumstances should be taken into account when performing the analysis: lead and silver chlorides dissolve in excess of the precipitant to form complex compounds:

$PbCl_2\downarrow + 2HCl = H_2[PbCl_4]$; $AgCl\downarrow + HCl = H[AgCl_2]$.

Lead chloride (as well as its iodides) increases its solubility dramatically with increasing temperature. This makes it possible to separate it from silver and mercury (I) chlorides by treating the precipitate mixture with hot water.

Concentrated ammonia solution has different effects on chlorides. Silver chloride dissolves:

$AgCl\downarrow + 2NH_4OH = [Ag(NH_3)_2]Cl + 2H_2O$

Lead chloride is converted to hydroxide with a lower solubility (SP ($PbCl_2$) = $1.6\cdot10^{-6}$; SP ($Pb(OH)_2$) = $5\cdot10^{-15}$).

$PbCl_2\downarrow + 2NH_4OH = Pb(OH)_2\downarrow + 2NH_4Cl$

Due to the release of black finely dispersed metallic mercury under the influence of ammonia, the corresponding reaction is qualitative for Hg_2^{2+} cations:

$Hg_2Cl_2\downarrow + 2NH_4OH = [NH_2Hg]Cl\downarrow + Hg\downarrow + NH_4Cl + 2H_2O$

A characteristic reaction to Pb ions^{2+} is the interaction with iodide ions (golden rain):

$Pb^{2+} + 2I^- = PbI_2\downarrow$

3. General characteristics of the III analytical group of cations and features of their qualitative reactions

The third analytical group of cations includes Ca^{2+} , Sr^{2+} , Ba^{2+} . The group reagent is a 2N solution of sulfuric acid, which forms white crystalline precipitates with the ions of this group. As can be seen from the table, Ca^{2+} is incompletely precipitated due to the high solubility of $CaSO_4$.

Cations	SP $MeSO_4$	SP $MeCO_3$	SP $MeCrO_4$	SP MeC_2O_4
Ca^{2+}	$2,5\cdot10^{-5}$	$3,8\cdot10^{-9}$	$7,1\cdot10^{-4}$	$2,3\cdot10^{-9}$
Sr^{2+}	$3,2\cdot10^{-7}$	$1,1\cdot10^{-10}$	$3,6\cdot10^{-5}$	$1,6\cdot10^{-7}$
Ba^{2+}	$1,1\cdot10^{-10}$	$4,0\cdot10^{-16}$	$1,2\cdot10^{-10}$	$1,1\cdot10^{-7}$

This fact should be taken into account in the analysis process. It is preferable to use carbonates for the precipitation of group III cations, as in the hydrogen sulphide scheme for cation analysis. However, $(NH_4)_2CO_3$, which is used there as a group reagent, precipitates almost all other cations except group I.

Most compounds of cations of group III are colourless and poorly soluble in water. Their hydroxides (except $Ca(OH)_2$), halides (except fluorides), nitrates, and sulfides are well soluble. These cations are resistant to oxidising and reducing agents and are poor complexing agents. Therefore, reaction responses are rarely used in the separation and determination of cations.

Ba^{2+} cations are determined as a yellow precipitate $BaCrO_4$.

Due to the rather low solubility of its oxylate (see the table of solubility products), Ca^{2+} is determined as a precipitate of this salt:

$Ca^{2+} + C_2O_4^{2-} = CaC_2O_4\downarrow$

However, as can be seen from the table, Sr^{2+} and Ba^{2+} had to be separated beforehand.

Since the solubility product of $SrSO_4$ is two orders of magnitude lower than that of $CaSO_4$, it is possible to determine Sr^{2+} using so-called «gypsum water», which is a saturated solution of potassium sulphate:

$CaSO_4 + SrCl_2 = SrSO_4\downarrow + CaCl_2.$

4. General characteristics of the VI analytical group of cations and features of their qualitative reactions

Group IV cations according to the acid-base analytical classification include Al^{3+}, Cr^{3+}, Zn^{2+}, Sn^{2+}, Sn(IV), As(III), As(V) ions.The group precipitant is alkali, in excess of which all group ions pass into solution. As for Sn(IV), As(III), and As(V) ions, even in an acidic environment, due to coordination unsaturation, they are in the form of anionic complexes. In an alkaline environment, all the ions of the group are in the form of oxo- and hydroxo-complexes, for example

$[Al(OH)_4 (H_2O)_2]^-$, $[Zn(OH)]_4^{2+}$, AsO_3^{3-} , AsO_4^{3-} , etc.

Oxides and hydroxides of group IV ions exhibit both acidic and basic properties (amphoteric), i.e. they react with both bases and acids: for example, zinc hydroxide dissolves in excess alkali and acid:

$Zn(OH)_2 \downarrow = 2Na[Zn(OH)_4]$; $Zn(OH)_2 \downarrow + 2HCl = ZnCl_2 + 2H_2O$.

A characteristic feature of cations of analytical group IV is their ability (except for Al^{3+} and Zn^{2+}) to undergo redox interactions (see Table):

Element	Degrees of oxidation	Redox properties
Al	0, +3	
Cr	0, +2, +3, +6	Cr^{3+} reducing agent in alkaline environment $Cr_2O_7^{2-}$ - oxidising agent in acidic environment
Zn	0, +2	
Sn	0, +2, +4	Sn^{2+} is a strong reducing agent in alkaline environments
As	0, +3, +5	AsO_3^{-3} reducing agent in a slightly alkaline environment AsO_4^{3-} oxidiser in acidic environments

A characteristic reaction to Cr^{3+} cations is their oxidation in alkaline environments to yellow CrO_4^{2-} :

$Cr_2(SO_4)_3 + 3H_2O_2 + 10NaOH = 2Na_2CrO_4 + 3Na_2SO_4 + 8H_2O$

In addition to conventional, double, and complex salts, salts of isopoly- and heptopolyacids are used in the analysis. The former are formed by replacing the oxysene of an acid residue with the divalent oxygen residue of that acid, for example:

$H_3PO_4 – O^{2-} + HPO_4^{2-} \rightarrow H_4P_2O_7$

$H_3PO_4 – 3O^{2-} + 3HPO_4^{2-} \rightarrow H_6P_4O_{13}$

In the case of heteropolyacids, the oxysene is replaced by an acidic residue of another acid, e.g:

$H_2SO_4 – O^{2-} + S^{2-} \rightarrow H_2S_2O_3$

$H_2MoO_4 – 2O^{-2} + 2Mo_4^{2} = H_2Mo_3O_{10}$

$(NH_4)_3AsO_4 – 4O^{2-} + 4Mo_2O_{10}^{2-} \rightarrow (NH_4)_3[As(Mo_3O_{10})_4]$

The latter reaction is used to detect As(V) using molybdenum liquid.

The peculiarity of qualitative reactions of cations of analytical group IV is that organic reagents are also used for their determination. For example, alizarin is used to detect Al^{3+} ions, and dithizone is used for Zn^{2+} .

5. General characteristics of the V analytical group of cations and features of their qualitative reactions

The reactions of Fe^{2+} with $K_3 [Fe(CN)_6]$, Fe^{3+} with $K_4 [Fe(CN)_6]$ and KSCN, Mn^{2+} with $NaBiO_3$ (or PbO_2), Mg^{2+} with phosphate and ammonium ions are described in the Qualitative Analysis Workshop. Here, we will focus on the rather complex reactions involving thioanhydrides, thioacids and their salts, which are relevant to the analysis of stibium, as well as arsenic and tin.

Thioanhydrides, like conventional anhydrides, interact with alkalis:

$Sb_2S_5\downarrow + 2NaOH + 10H_2O \leftrightarrow 2Na[Sb(OH)_6] + 5H_2S$

$As_2S_3\downarrow + 6NaOH \leftrightarrow Na_3AsS_3 + 3H_2O$

They are also soluble in sulphides and polysulphides of alkali metals and ammonium, for example:

$Sb_2S_3\downarrow + Na_2S \leftrightarrow 2NaSbS_2$

$Sb_2S_5\downarrow + 2Na_2S \leftrightarrow 2Na_3SbS_4 + 3S\downarrow$

In some cases, salts of thioacids are formed, from which the thioacids themselves can be isolated by acid action:

$Na_3SbS_3 + 3HCl \leftrightarrow H_3SbS_3 + 3NaCl$

The latter are unstable compounds that decompose at the time of formation:

$2H_3SbS_3 \leftrightarrow 3H_2S\uparrow + Sb_2S_2\downarrow$

When ammonium sulphide interacts with thioanhydrides in which tin, arsenic and stibium are in lower oxidation states, the latter are oxidised, for example:

$As_2S_3\downarrow + 3(NH_4)_2S_2 \leftrightarrow 2(NH_4)_3SbS_4 + S\downarrow$

This is due to the oxidising properties of sulphur disulfide $-S^{-1} -S^{-1} -$. This chain is similar to the peroxide chain $-O^{-1} -O^{-1} -$.

Differences in the properties of thioanhydrides from conventional metal sulphides make it possible to separate tin, stibium and arsenic from other cations during analysis.

The analysis of a mixture of cations of the V analytical group takes into account some features of their compounds, such as

- The tendency of Bi^{3+} and Sb^{3+} cations to hydrolyse;
- Poor solubility of MnO_2 in nitric acid;
- Solubility of $Mg(OH)_2$ in $NH_4 Cl$ solution.

6. General characteristics of analytical group VI cations

Analytical group VI cations include Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+} and Hg^{2+} . These cations are united by the feature that they form soluble amino complexes (ammonia cations), which makes it possible to separate them from cations of primarily group V using a concentrated ammonia solution:

$$Fe(OH)_2\downarrow + NH_3 \cdot H_2O \neq$$

$$Cd(OH)_2\downarrow + 4NH_3\cdot H_2O \leftrightarrow [Cd(NH_3)_4](OH)_2 + 4H_2O$$

The same ions that are not part of group VI but also form amino complexes are separated earlier in the analysis, for example, Ag^{+} with group II chlorides and Zn^{2+} with group IV amphoteric hydroxides.

The peculiarity of group VI cations is their ability to undergo redox reactions. All known types of redox reactions are used in the analysis: intermolecular, intramolecular and disproportionation. For example, Mn^{2+} is oxidised to permanganate ion, which has a characteristic colour, by sodium bismuthate, ammonium persulfate or lead dioxide:

$$2Mn(NO_3)_2 + 5PbO_2 + 6HNO_3 \leftrightarrow 2HMnO_4 + 5Pb(NO_3)_2 + 2H_2O$$

$$\begin{array}{l|l} Mn^{+2} - 5e^- \rightarrow Mn^{+7} & 2 \\ Pb^{+4} - 2e^- \rightarrow Pb^{+2} & 5 \end{array}$$

$HMnO_4$ - provides a purple-red colour of the solution.

Typical reactions of this type are the reduction of mercury (I) and (II) to metallic tin (II), a similar reaction with Bi^{3+} , oxidation of Cr^{3+} to CrO^{-2}_4 , coloured yellow, hydrogen peroxide and many others.

An example of the use of the disproportionation reaction in an analysis is the decomposition of mercury (I) chloride with ammonia in the determination of the corresponding cation:

$$Hg^{+1}{}_2Cl_2 + 2NH_3 \cdot H_2O \rightarrow [NH_2Hg^{+2}]Cl\downarrow + Hg\downarrow + NH_4Cl + 2H_2O$$

$$\begin{array}{l|l} Hg^{+1} - 1e^- \rightarrow Hg^{2+} & 1 \\ Hg^{+1} + 1e^- \rightarrow Hg^0 & 1 \end{array}$$

Most pyrochemical methods of qualitative analysis related to the decomposition of oxygen-containing compounds are intramolecular reactions, for example, the identification of nitrates:

$$2Pb(NO_3)_2 \xrightarrow{t} 2PbO + 4NO_2\uparrow + O_2\uparrow$$

$$\begin{array}{l|l} 2O^{-2} - 4e^- \rightarrow 2O^0 & 1 \\ N^{+5} - 1e^- \rightarrow N^{+4} & 4 \end{array}$$

A special feature of group VI cations is the formation of numerous coloured compounds. This makes it possible to use the corresponding «colour reactions» to identify these cations.

For example, copper, nickel and cobalt form amino complexes of intense blue, blue and dirty yellow colours, respectively, when reacting with ammonia. Although Co^{2+} is usually determined using the «blue ring» reaction

$$Co^{2+} + 4SCN^- \rightarrow [Co(SCN_4)]^{2-}$$

A layer of isoamyl alcohol, which is added to increase the sensitivity of the reaction, extracts this complex from the aqueous solution, turning it blue.

Hg^{2+} ions react with iodides to form a bright red precipitate, which can then be dissolved in excess precipitant:

$$Hg^{2+} + 2I^- \rightarrow HgI_2\downarrow;\ HgI_2\downarrow + 2I^- \rightarrow [HgI_4]^{2-}.$$

Dimethylglyoxime with Ni^{2+} cations under certain conditions forms a poorly soluble compound coloured coral red (the well-known Chugaev reaction).

Cd^{2+} cations precipitate in acidic environments under the influence of hydrogen sulphide, forming a bright yellow sulphide:

$$Cd^{2+} + H_2S \rightarrow CdS\downarrow + 2H^+$$

The characteristic reactions to Cu^{2+}, Co^{2+}, Ni^{2+} and Hg^{2+} are specific enough to be determined in a fractional way. However, before this, CdS must be precipitated in a strongly acidic environment and isolated. Sulphides of other cations are not formed under these conditions. The cations Cu^{2+} , Co^{2+} , Ni^{2+} and Hg^{2+} are determined in separate solution samples using specific reactions.

Lecture 4

GENERAL CHARACTERISTICS AND QUALITATIVE REACTIONS OF ANIONS I-III ANALYTICAL GROUPS

1. Classification of anions;
2. General characteristics of the first analytical group of anions and features of their qualitative reactions;
3. General characteristics of the II analytical group of anions and features of their qualitative reactions;
4. General characteristics of the II analytical group of anions and features of their qualitative reactions.

1. Classification of anions

Although there is no generally accepted division of anions into groups, anions are generally classified into three analytical groups. This classification is based on the different solubilities of the barium and silver salts of the respective anions.

Classification of anions

Group number	Anions	Group reagent	Properties of reaction products
I	SO_4^{2-} - sulphate ion SO_3^{2-} - sulphite ion CO_3^{2-} - carbonate ion PO_4^{3-} - phosphate ion SiO_3^{2-} - silicate ion	$BaCl_2$	Barium salts are highly insoluble in water
II	Cl^- - chloride ion Br^- - bromide ion I^- - iodide ion S^{2-} -sulfide-ion	$AgNO_3$	Silver salts are highly insoluble in water and dilute with HNO_3
III	NO_3^- -nitrate ion NO_2^- -nitrite ion	no	Barium and argentium salts are soluble in water

In anion analysis, group reagents are used to determine the respective groups. To simplify the analysis of anions, so-called group tests are performed to detect the presence of the respective anion groups:

- test for oxidising anions ($Cr_2O_7^{2-}$, AsO_4^{3-} , NO_3^-) - anions are determined by the action of KJ solution in an acidic medium in the presence of chloroform, which, if present, is coloured red-violet;

- Reducing anions test ($C_2O_4^{2-}$, $S_2O_3^{2-}$, S^{2-}, SO_3^{2-}, AsO_3^{3-}, J^-, NO_2^-) - anions are determined by recording the discolouration of iodine solution in a slightly acidic environment, except for AsO_3^{3-} ions, which are determined in a slightly alkaline environment;

- the test for anions of unstable acids (H_2SO_3, $H_2S_2O_3$, H_2CO_3, etc.) is carried out by the action of HCl, which results in the formation of gaseous products (SO_2, CO_2, H_2S , etc.);

- anion test (Cl^-, Br^-, J^-,$C_2O_4^{2-}$, NO_3^-, SO_3^{2-}, $S_2O_3^{2-}$, etc.) is performed by exposing their salts to concentrated H_2SO_4, resulting in the formation of gaseous products (Cl_2, J_2, CO_2, etc.).

2. General characteristics of the first analytical group of anions and features of their qualitative reactions

The anions of the following acids belong to analytical group I: carbonate, metabolic, sulfate, sulfite, thiosulfate, orthophosphoric, silicate and others. Solutions of sodium or potassium salts are used to study the reactions of group I anions. The group reagent for anions of the first analytical group is a solution of barium salt in a neutral or slightly alkaline medium. Under these conditions, the anions form salts with Ba^{2+} ions that are insoluble in water but soluble in dilute hydrochloric acid, with the exception of $BaSO_4$.

The first group of anions, in turn, can be divided into three subgroups. The first subgroup includes anions whose barium salts are poorly soluble in mineral acids and water. Only the sulphate ion SO_4^{2-} belongs to this subgroup.

The second subgroup of group I anions is characterised by the fact that their barium salts are poorly soluble in acetic acid and water, but well soluble in mineral acids. These include SO_3^{2-} , CrO_4^{2-} , $C_2O_4^{2-}$, F^- .

The third subgroup includes the remaining anions. The barium salts of these anions are poorly soluble in water, but well soluble in acetic and mineral acids.

An important analytical property of Group 1 anions is their relation to oxidising or reducing agents, as well as their ability to decompose with the release of gases in an acidic environment. Sulfite, oxalate, and thiosulfate ions are reducing agents and can discolour potassium permanganate solution in a sulphuric acid environment (oxalate only when heated). Volatile anions are sulfite, thiosulfate (decompose in acidic environments with the release of SO_2), as well as carbonate and oxalate (release CO_2).

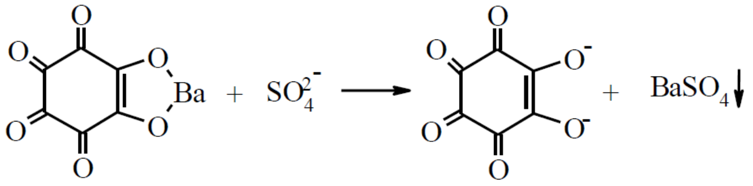
Detection of SO_4^{2-} -ions

1. Reaction with barium salts. With barium salts, sulphates form a white crystalline precipitate that is insoluble in water, acids and alkalis:

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

The sensitivity of the reaction increases with the addition of a drop of $KMnO_4$ solution, as a result of which the $BaSO_4$ precipitate turns purple.

2. Reaction with barium rhodizonate. SO_4^{2-} ions discolour the red solution of barium rhodizonate:



3. Reaction with lead (II) nitrate. Lead (II) nitrate with SO_4^{2-} - ions forms a white crystalline precipitate, practically insoluble in water and acids, well soluble in ammonium acetate due to the formation of a stable acetate complex:

$$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4\downarrow$$

$$PbSO_4 + 4CH_3COONH_4 \rightarrow (NH_4)_2[Pb(CH_3COO)_4] + (NH_4)_2SO_4$$

Detection of SO_3^{2-} ions

Most sulphites are insoluble in water. Only sulphites of alkali metals, magnesium and ammonium, are water-soluble. They have an alkaline reaction in aqueous solutions due to hydrolysis.

1. Action of oxidants. Sulfite ion is a reducing anion. It readily reduces free iodine to iodine ions J^- , permanganate ions MnO_4^- to manganese (II) ions Mn^{2+} .

$SO_3^{2-} + I_2 + H_2O = SO_4^{2-} + 2I^- + 2H^+$.

Brown iodine solution is discoloured

Permanganate can also be reduced with sulphites. The reaction can be carried out in an acidic or alkaline environment. The presence of stronger reducing agents (e.g. S^{2-} anions) interferes with the detection of SO_3^{2-} anions by these reactions.

Detection of CO_3^{2-} ions

1. Reaction with barium chloride. Barium chloride forms a white precipitate with CO_3^{2-} - ions, which is soluble in acids (except sulfuric acid):

$BaCl_2 + CO_3^{2-} \rightarrow BaCO_3\downarrow + 2Cl^-$

2. Reaction with acids. Carbonates of alkali metals are highly soluble in water, while other carbonates are poorly soluble. All carbonates dissolve in mineral and acetic acids with the release of CO_2 .

Detection of CrO_4^{2-} ions

1. Reaction with Ag^+ , Ba^{2+} and Pb^{2+}. With Ag^+ , Ba^{2+} and Pb^{2+} ions, the chromate ion CrO_4^{2-} forms insoluble compounds: Ag_2CrO_4 is brick red in colour, soluble in HNO_3 and in ammonia solution:

$Ag_2CrO_4 + 4NH_3 \rightarrow 2[Ag(NH_3)_2]^+ + CrO_4^{2-}$

$BaCrO_4$ is a yellow precipitate soluble in HNO_3, $PbCrO_4$ is a yellow precipitate soluble in HNO_3 and in caustic alkali solutions:

$PbCrO_4 + 4NaOH \rightarrow Na_2PbO_2 + Na_2CrO_4 + 2H_2O$

Detection of PO_4^{3-} ions

Of the phosphoric acid salts, only alkali metal and ammonium phosphates are soluble in water. Phosphates and hydrophosphates in aqueous solutions have an alkaline reaction due to hydrolysis.

1. Effect of the magnesium mixture (mixture of $MgCl_2$ with NH_4 OH and NH_4 Cl). With PO_4^{3-} ions, the magnesium mixture forms a white crystalline precipitate.

$Mg^{2+} + HPO_4^{2-} + NH_4OH = MgNH_4PO_4 + H_2O$.

2. Reaction with ammonium molybdate. Ammonium molybdate in nitric acid forms a yellow crystalline precipitate of ammonium phosphormolybdate with the phosphate anion.

$PO_4^{3-} + 3NH_4Cl + 12(NH_4)_2MoO_4 + 24\ HNO_3 =$

$= (NH_4)_3H_4[P(Mo_2O_7)_6] + 10H_2O + 24NH_4NO_3 + 3Cl^-$

The detection of phosphate ions is interfered with by sulfite and sulfide ions, which reduce ammonium molybdate. To remove them, the test solution is pre-boiled with concentrated nitric acid.

3. General characteristics of the II analytical group of cations and features of their qualitative reactions

Analytical group II includes anions of the following acids: chloride, bromide, iodide, hydrochloric acid (Cl^- , Br^- , I^- , CN^- , SCN^- , S^{2-}). To study the reactions of anions of this group, solutions of NaCl or KCl, NaBr or KBr, NaJ or KJ, Na_2 S or K_2 S (or hydrogen sulphide water) are used. The group reagent for anions of the second analytical group is a solution of silver nitrate in the presence of HNO_3 . The anions of this group form precipitates with Ag^+ cations that are insoluble in dilute HNO_3. Barium salts with group II anions are soluble in water.

Detection of $Cl^–$ ions

1. Reaction with silver (I) nitrate. Silver (I) nitrate forms a white, curd-like precipitate with $Cl^–$ ions, soluble in ammonia solution, insoluble in dilute acids:

$Ag^+ + Cl^– \rightarrow AgCl\downarrow$

$AgCl + 2NH_3 \rightarrow [Ag(NH_3)_2]Cl$

When exposed to HNO_3 , the complex ion decomposes:

$[Ag(NH_3)_2]Cl + 2HNO_3 \rightarrow AgCl\downarrow + 2NH_4NO_3$

AgCl is soluble in solutions of $Na_2S_2O_3$ and $(NH_4)_2CO_3$, unlike argentium bromide and iodide AgBr and Agl, which form very stable complexes: $[Ag(S_2O_3)_2]_3^–$ and $[Ag(NH_3)_2]Cl$

2. Reactions with strong oxidants. Under the influence of strong oxidising agents such as MnO_2 , $KMnO_4$, PbO_2 in an acidic environment $Cl^–$ -ions are oxidised to free chlorine:

$2KMnO_4 + 10Cl^– + 8H_2SO_4 = 2MnSO_4 + 5Cl_2 \uparrow + 6SO_4^{2–} + 8H_2O$

or

$MnO_2 + 2Cl^– + 2H_2 SO_4 = MnSO_4 + Cl_2 \uparrow + SO_4^{2–} + 2H_2O$

Cl_2 is detected by the smell or blueing of iodine-starch paper:

$Cl_2 + 2I^– = I_2 + 2Cl^–$.

References: $Br^–$, $I^–$ - ions.

Detection of $Br^–$ ions

1. Reaction with silver (I) nitrate. Argentum nitrate precipitates a yellowish precipitate AgBr, insoluble in HNO_3 , soluble in concentrated solutions of NH_3 , $Na_2S_2O_3$ and KCN to form $[Ag(NH_3)_2]Br$, $Na_3[Ag(S_2O_3)_2]$, $K[Ag(CN)_2]$, respectively.

2. Reactions with strong oxidising agents. Oxidising agents such as $KMnO_4$, MnO_2, NaClO, chlorine water in an acidic environment oxidise $Br^–$ ions to free bromine, which is well extracted by CCl_4, $CHCl_3$, CS_2 or ether (ether), turning them brown:

$2KMnO_4 + 10Br^– + 8H_2 SO_4 = 2MnSO_4 + 5Br_2\uparrow + 6SO_4^{2–} + 8H_2O$

or $Cl_2 + 2Br^– = Br_2 + 2Cl^–$.

Detection of $I^–$ -ions

1. Reaction with silver (I) nitrate. Argentum nitrate precipitates a yellow precipitate AgI, insoluble in HNO_3 and ammonia solution, soluble in $Na_2S_2O_3$ and KCN:

$Ag+ + I^– = AgI \downarrow$

$AgI + 2 Na_2S_2O_3 = Na_3 [Ag_2S_2O_3] + NaI$

$AgI + 2KCN = K[Ag(CN)_2] + KI$

2. Reaction with lead dinitrate or acetate. Pb^{2+} salts precipitate a yellow precipitate PbI_2:

$Pb^{2+} + 2I^– = PbI_2\downarrow$

The precipitate dissolves in hot water and precipitates as golden flakes when cooled.

Detection of S^{2-}-ions.

1. Reaction with silver (I) nitrate. Silver nitrate forms a black precipitate with sulfide ions, insoluble in dilute HNO_3 in cold, soluble in it when heated, and insoluble in ammonia solution:

$2Ag^{+} + S^{2-} = Ag_2S\downarrow$

2. Reaction with acids. Acids (sulphuric, chloride) when acting on sulphides decompose them to form H_2S, which is detected by the characteristic smell and blackening of lead paper containing Pb^{2+} ions:

$Na_2S + 2HCl = H_2S\uparrow + 2NaCl$

$H_2S + Pb(CH_3COO)_2 = PbS\downarrow + 2CH_3COOH$

3. Reaction with cadmium salts. Soluble salts of cadmium form a bright yellow precipitate of cadmium sulphide with sulphides:

$Cd^{2+} + S^{2-} = CdS\downarrow$

If the resulting precipitate is treated with a $CuSO_4$ solution, it will turn black due to the formation of CuS:

$CdS + CuSO_4 = CdSO_4 + CuS\downarrow$. The reaction is very typical of sulfide ions.

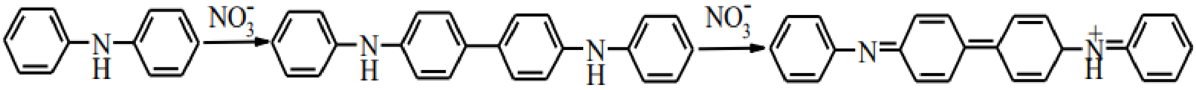
4. General characteristics of the II analytical group of cations and features of their qualitative reactions

The third analytical group includes the anions NO_3^-, NO_2^-, ClO^-, ClO_3^-, ClO_4^-, CH_3COO^-. These anions are not precipitated by barium chloride and silver nitrate, so they do not have a group reagent. Except for CH_3COO^- ions, all anions in this group are oxidising anions.

Detection of NO_3^- *-ions*

1. Reaction with biphenylamine. Diphenylamine $(C_6H_5)_2NH$ in a strongly acidic environment with NO_3^- ions forms an intense blue compound, which upon further oxidation turns into a white compound:

The reaction with diphenylamine is also used to detect MnO_4^- and NO_2^- ions.



2. Reduction reaction. The reduction of NO_3^- ions with aluminium or zinc produces ammonia, which can be detected with a wet litmus test:

$3NaNO_3 + 8Al + 5NaOH + 2H_2O \rightarrow 3NH_3\uparrow + 8NaAlO_2$

$FeSO_4$ reduces NO_3^- ions to NO (at pH = 7):

$2NaNO_3 + 6FeSO_4 + 4H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + Na_2SO_4 + 2NO\uparrow + 4H_2O$.

Nitrogen (II) oxide forms a brown complex compound with $FeSO_4$:

$FeSO_4 + NO \rightarrow [Fe(NO)]SO_4$.

Therefore, during the reaction, we observe the formation of a brown ring.

Detection of NO_2^- *ions*

1. Reaction with acids. Dilute acids, e.g. sulphuric acid, decompose all nitrites in the cold to produce nitrogen oxides:

$2NaNO_2 + H_2\ SO_4 \rightarrow Na_2SO_4 + 2HNO_2$;

$2HNO_2 \rightarrow NO_2 \uparrow + NO\uparrow + H_2O$

The release of brown gas is observed.

2. Reaction with potassium iodide. Potassium iodide reacts with nitrites to form free iodine, which can be easily identified by the action of starch:

$2KI + 2KNO_2 + 2H_2SO_4 \rightarrow I_2 + 2K_2SO_4 + 2NO\uparrow + 2H_2O$.

Detection of CH_3COO^- *-ions .*

1. Reaction with strong acids. Strong acids release acetic acid from acetates, which has a characteristic odour:

$CH_3COONa + HCl \rightarrow CH_3COOH + NaCl$.

A characteristic vinegar smell appears.

2. Reaction with iron (III) chloride. Iron (III) chloride converts acetates into a complex compound:

$FeCl_3 + 3CH_3COONa \rightarrow Fe(CH_3COO)_3\downarrow + 3NaCl$

$3Fe(CH_3COO)_3 + 2H_2O \rightarrow [Fe_3(CH_3COO)_6(OH)_2]CH_3COO + 2CH_3COOH$

Initially, a red-brown precipitate of iron (III) acetate is formed, which, when diluted with water, turns into a complex compound.

Lecture 5

QUALITATIVE ANALYSIS OF ORGANIC SUBSTANCES

1. Reactions for the detection of organic substances;
2. Qualitative elemental analysis;
3. Qualitative functional analysis.

1. Reactions for the detection of organic matter

1. Tartaric acid and its salts

Tartaric acid is a preservative, antioxidant, acidifier, acid balance regulator and emulsifier, and is used in a wide range of products: jams and ice cream, table and sparkling soda, canned food, confectionery (including sweets), jelly, and wine.

Crystals of potassium chloride (KCl) (pharmacopoeial)

When reacting with potassium chloride crystals in the presence of ethyl alcohol, a white crystalline precipitate of potassium hydrotartrate is released from concentrated solutions:

$KCl + NaHC\ H\ O_{446} = KHC\ H\ O_{446}{}^{-} + NaCl$

The precipitation is accelerated by rubbing the walls of the tube with a glass rod.

Reaction with pyrogallol (pharmacopoeial)

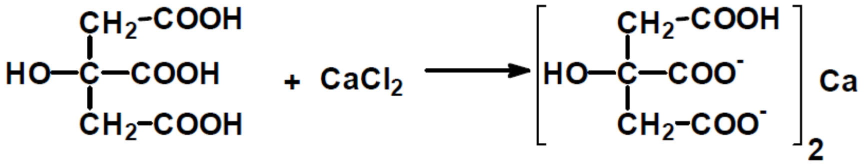
Tartaric acid salts can also be identified by reacting with pyrogallol in the presence of concentrated sulphuric acid. The reaction is carried out by heating in a water bath. In the presence of tartrates, the solution turns violet in colour.

2. Citric (citrate) acid and its salts.

Citric acid is widely used in the food industry as a flavouring agent and acidity regulator (E330). It is used in the manufacture of canned food as a preservative to increase the shelf life of meat, jellies and preserves.

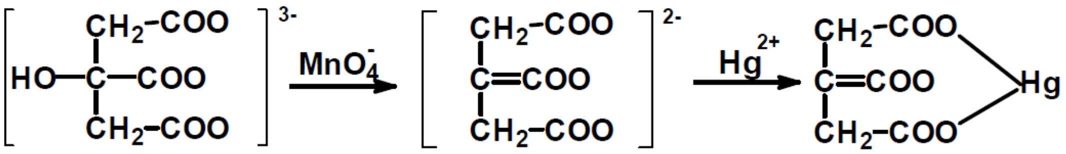
Calcium chloride ($CaCl_2$) (pharmacopoeial)

Calcium chloride with citric acid salts forms a white precipitate of calcium citrate, which is highly soluble in acids:



Mercury (II) sulphate

Citric acid and its salts can also be identified by reacting with mercury (II) sulphate in the presence of a small amount of $KMnO_4$. A white precipitate of acetone dicarboxylic acid salt is obtained:

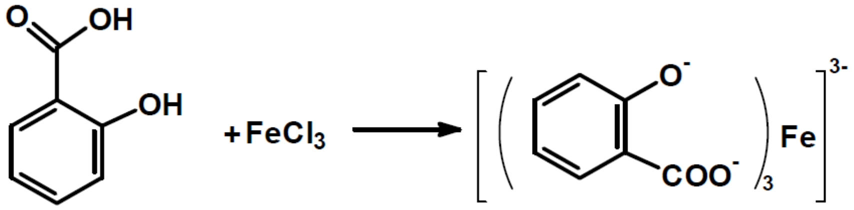


3. Salicylic acid and its salts

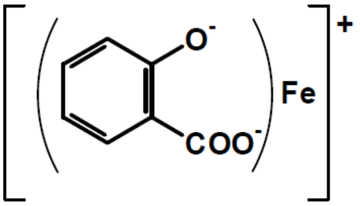
Salicylic acid compounds are widely used in medicine and the food industry.

Iron (III) chloride (pharmacopoeial)

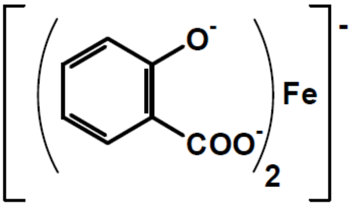
The basic reaction for the determination of salicylate ions is the reaction with iron (III) chloride:



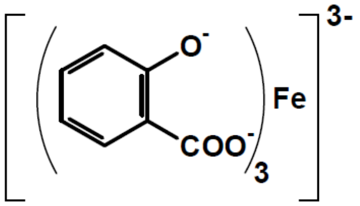
The composition and colour of the complexes formed by the interaction of salicylic acid with ferric ions depends on the pH of the medium. At pH = 1.8 - 2.5, a monosalicylate complex (I) is formed, which has a blue-violet colour. At pH = 4 - 8, disalicylate complex (II) is formed, which has a red-brown colour. The trisalicylate complex of iron (III), which has a yellow colour, is formed at pH = 8 - 11:



I



II



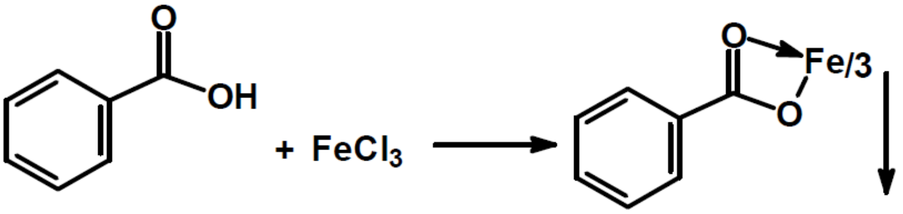
III

4. Benzoic acid and its salts

Benzoic acid (E 210) is a food additive used in the food industry as a preservative. Preservative E 210 has antimicrobial and antifungal effects, inhibits mould, yeast and certain types of bacteria. Benzoic acid is naturally found in foods such as cranberries, blueberries, and honey.

Iron (III) chloride

The main reaction for the detection of benzoic acid is the interaction with iron (III) chloride. A pinkish-yellow complex is formed in a neutral medium:



2. Qualitative elemental analysis

Organic compounds contain a limited range of elements - C, N, O, P, S, Cl, and, less frequently, As, Sb, F, and sometimes some metals. The latter are detected after ashing of the organic compound using the appropriate qualitative reactions used in inorganic analysis. As for the other components of the organic compound, they most often evaporate during ashing, so special reactions are used to detect them, primarily oxidation-reduction reactions. Below are examples of some of the detection reactions used in qualitative elemental analysis of organic compounds.

Carbon detection.

The charring test is carried out by heating a test tube with a substance in a flame of an alcohol torch or burner. In the presence of carbon, the substance is charred and blackened.

Carbon can also be detected by oxidising an organic compound with molybdenum tetrachloride MoO_3 . A small amount of the test substance is placed in a refractory tube, MoO_3 is added and heated. In the presence of carbon, MoO_3 is reduced to lower molybdenum oxides and forms molybdenum blue.

Carbon can also be detected by heating a substance with $AgAsO_3$. This oxidises carbon to CO_2 and reduces Argentum ions to metallic silver. The reaction is accompanied by the appearance of dark silver metallic silver on the walls of the test tube. The sensitivity of this reaction is 1-5 µg.

Hydrogen detection.

Hydrogen in organic compounds is identified by the reaction of pyrolysis with sulphur. This produces H_2S, which is identified by the blackening of a filter paper moistened with a solution of $Pb(CH_3 COO)_2$. The sensitivity of this reaction is 0.1-0.5 µg.

Detection of halogens.

Halogens are detected using the Beilstein reaction. Several crystals of the substance under study are placed on a copper wire and placed in a flame of an alcohol flask - observe the flame turn green.

Detection of Chlorine.

Chlorine in organic compounds is determined by reducing non-ionic chlorine to Cl^-. For this purpose, an aqueous solution of the substance is treated with sodium hydroxide and zinc dust during boiling:

$$Zn + 2NaOH \rightarrow Na_2ZnO_2 + 2H^+$$
$$R\text{-}Cl + 2H^+ \rightarrow HCl + R\text{-}H$$

After recovery, the mixture is filtered, acidified with dilute nitric acid and the chloride ions are detected by reaction with silver nitrate.

Detection of Bromine.

Bromine in organic compounds is determined by the same method as chlorine. Bromide ions are identified by reaction with an oxidising agent (chloramine) in the presence of chloroform. The organic layer will turn yellow-brown in colour.

The discovery of Iodine.

Iodine is detected after oxidation to elemental iodine by heating with concentrated sulphuric acid. The violet iodine vapour produced is identified either by its appearance, by adding chloroform to the cooled solution (violet colour of the layer) or by using iodine-starch paper (blue colour).

Detection of Fluoride.

Fluorine is detected using the same method as chlorine, reducing the substance with zinc metal in an alkaline environment:

$$Zn + 2NaOH \rightarrow Na_2ZnO_2 + 2H^+$$
$$R\text{-}F + 2H^+ \rightarrow HF + R\text{-}H.$$

Ice-cold acetic acid is added to the filtrate and the fluoride ions are detected by reacting with iron (III) thiocyanate (colour change or disappearance).

Detection of Sulphur.

Sulphur can be detected in organic compounds by the Lassen reaction. When heated with metallic sodium or potassium, organically bound sulphur is converted to sulphides, which are identified after dissolution in water.

The combustion of sulphur-containing organic compounds with calcium oxalate produces hydrogen sulphide, which is identified by the blackening of a lead test paper moistened with water:

$$CaC_2O_4 \rightarrow CaO + CO_2 + CO;$$
$$CO + S + H_2O \rightarrow CO_2 + H_2S.$$

Nitrogen detection.

Nitrogen in organic compounds can be oxidised by manganese dioxide when heated. This produces volatile oxides of nitrogen (NO, NO_2), which are identified using a piece of paper moistened with a Griess reagent (solution of sulfanilic acid and 2-naphthol). The formation of a red colour is observed.

Nitrogen can be identified by fusing the substance with sodium metal in a dry test tube. After cooling, a few drops of water and ethanol are added to the mixture. The resulting NaCN is identified by reacting with iron (II) salts.

Detection of Phosphorus.

Phosphorus in organic compounds is determined by oxidation with concentrated nitric acid under heating. The resulting phosphoric acid is identified by reaction with ammonium nitrate and molybdate.

Detection of Oxygen.

The detection of oxygen in most organic compounds is based on the formation of mixed ligand complexes of oxygen-containing compounds with iron (III) thiocyanate. These compounds are extracted with organic solvents (alcohols, ethers), and the organic layer is coloured red.

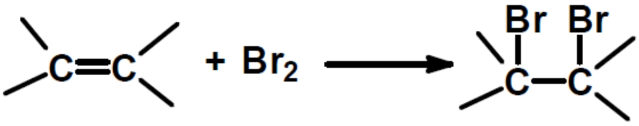
3. Qualitative functional analysis

Many organic compounds are identified by the functional groups they contain. Most reactions for identifying functional groups are based on oxidation, reduction, complexation and condensation.

1. Identifying unsaturated groups and radicals

Identification of a double bond.

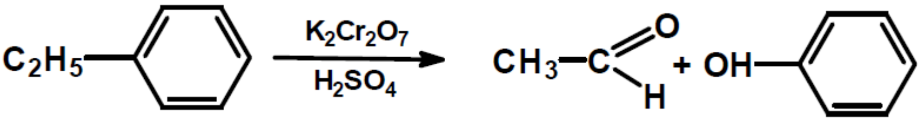
Unsaturated compounds are usually determined by the bromination reaction at the position of the double bond. The process is accompanied by discolouration of the bromine water:



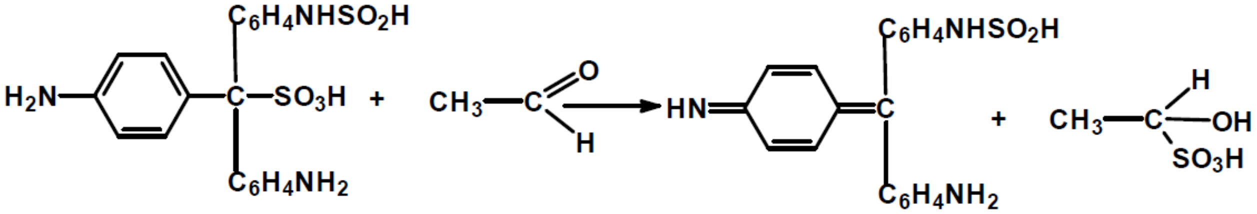
Sometimes, instead of bromine water, potassium permanganate solution is used, in which case the process of discolouration of the potassium permanganate solution and precipitation of manganese (II) dioxide is observed.

Identification of functional N-, Cl-, O-substituted, carbon-containing groups.

Functional N-, Cl-, O-substituted, carbon-containing groups - methyl, ethyl, propyl, etc. - are detected by oxidation with potassium dichromate in a sulfuric acid medium to the corresponding aldehyde:

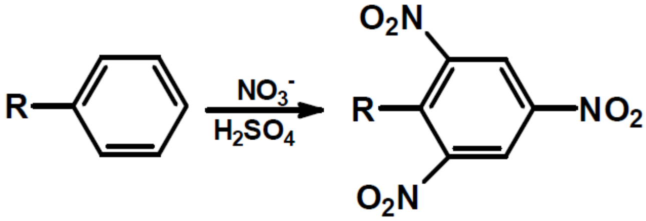


Aldehydes are usually volatile and can be identified by the red colouration of a filter paper moistened with a solution of fuchsin sulfuric acid.



Identification of a phenyl radical.

The phenyl radical can be detected by the nitration reaction. The nitration of phenyl derivatives with a mixture of sodium nitrate and sulfuric acid produces yellow nitroaromatic compounds:

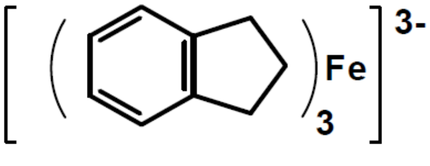


2. Identification of oxygen-containing groups

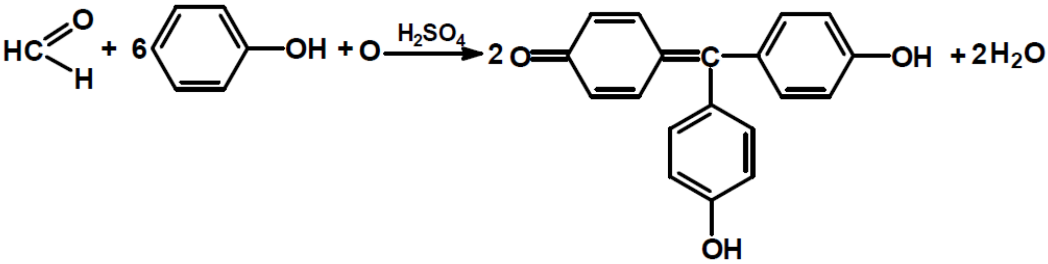
The hydroxyl groups of the ─ON differ significantly in their properties depending on whether they belong to the class of aliphatic (alcohols) or aromatic (phenols) compounds.

Identification of phenols.

Iron (III) salts. Phenols are detected by complexation with iron(III) salts. Depending on the type of phenol, complex compounds of different colours (from blue to red) are formed (in a neutral medium). For example, phenol forms a violet complex, resorcinol forms a blue complex, and pyrocatechin forms a red complex:



Mark's reaction. During condensation with formic aldehyde in concentrated sulfuric acid, phenols form coloured triphenylmethane compounds:

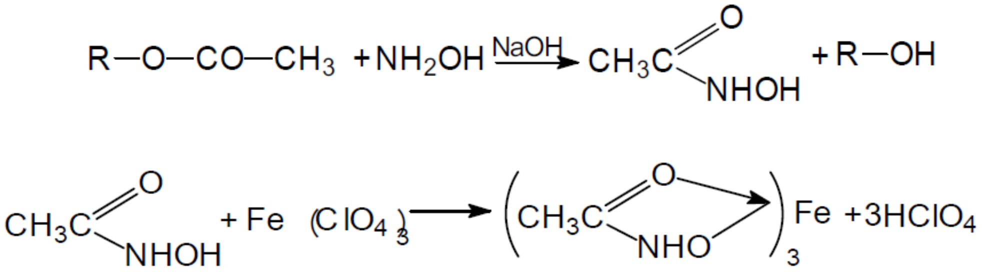


Identification of alcohols.

Esterification and oxidation reaction. Typically, esterification is carried out using an acetylating mixture (a mixture of acetate anhydride, pyridine and hydrochloric (72 %) or sulfuric acid). The product is ester:

$$R{-}OH + (CH_3COO)_2O \xrightarrow{HClO_4} R{-}O{-}CO{-}CH_3 + CH_3COOH$$

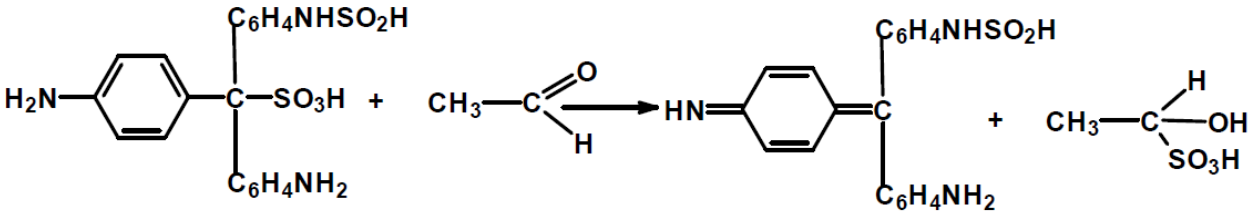
The latter is detected using hydroxylamine in an alkaline medium. This produces hydroxylamine acids, which form brown or red-brown complexes with Ferric (III) salts:



Detection of polyhydric alcohols. The detection of polyhydric alcohols (glycerol, ethylene glycol, etc.) is carried out by oxidation with periodate to formaldehyde and formic acid:

$$R(OH)nCH_2OH + (n+1)HIO_4 \rightarrow CH_2O + nHCOOH + (n+1)HIO_3 + H_2O$$

The released formaldehyde is identified using fuchsin, which causes the mixture to change colour from red to blue:



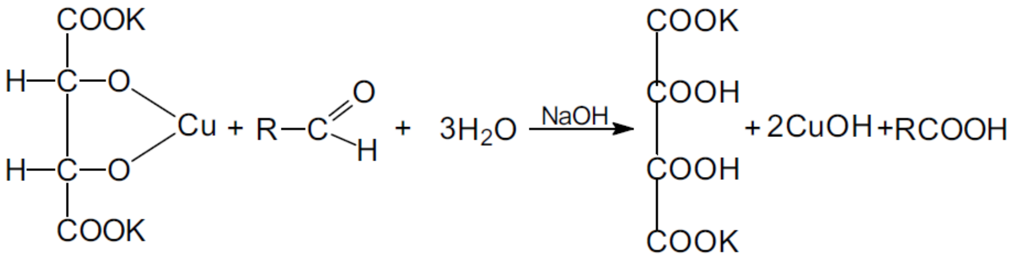
Identification of aldehyde and ketone groups

The aldehyde and ketone groups give rise to a number of characteristic reactions that can be used to identify them:

Argentum nitrate in an ammonia environment oxidises aldehydes to carboxylic acids, while argentum is reduced to metallic silver (silver mirror reaction):

$$2[Ag(NH_3)_2]Cl + 2HCHO + 2H_2O = 2Ag\downarrow + 2NH_4Cl + 2HCOONH_4$$

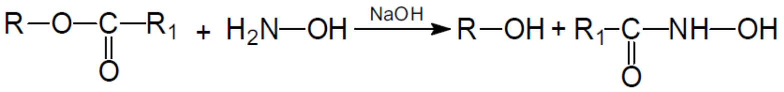
Fehling's reagent (a mixed solution of copper and potassium sodium tartrate) oxidises aldehydes to carboxylic acids. The copper is reduced to a red precipitate of copper (I) oxide:



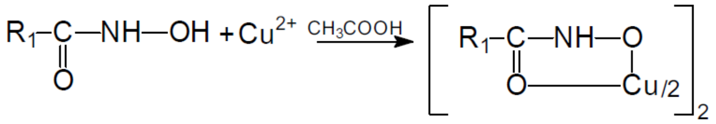
$$2CuOH \longrightarrow Cu_2O\downarrow + H_2O$$

Detection of esters

Esters are usually identified by reaction with hydroxylamine. In NaOH medium, hydroxylamine acids are formed, which upon further interaction with copper (II) salts (in acetate medium) form green copper (II) hydroxoamates:



$$R{-}O{-}\overset{\displaystyle O}{\underset{}{C}}{-}R_1 + H_2N{-}OH \xrightarrow{NaOH} R{-}OH + R_1{-}C(=O){-}NH{-}OH$$



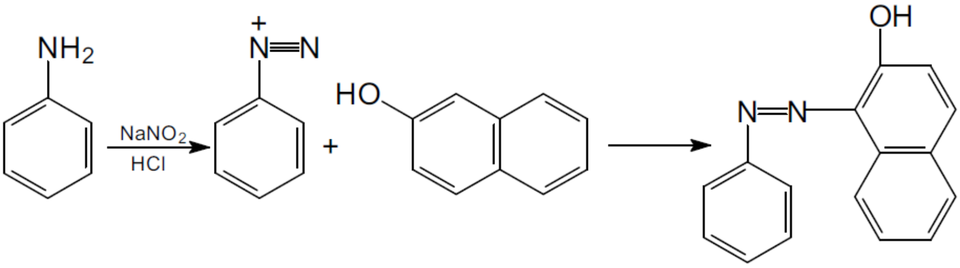
Detection of carboxylic acid carboxylic groups

The carboxyl groups of organic carboxylic acids react with coloured salts of heavy metals (d-elements) to form coloured precipitates of organic acid salts. Typically, salts of copper, ferric, and cobalt are used for identification.

3. Identification of nitrogen-containing groups.

Identification of amino groups in aromatic compounds.

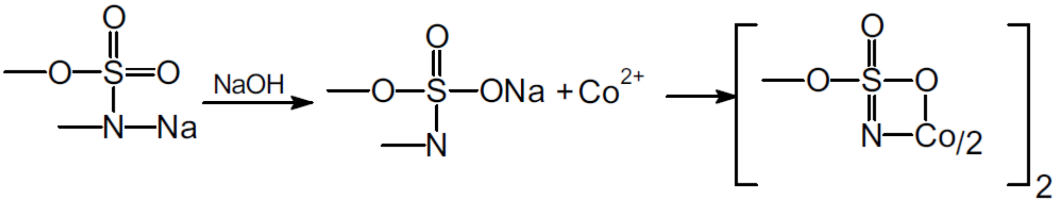
To detect the presence of an amino group in aromatic compounds, diazotation and nitrogen coupling reactions are used. Diazotation is most often carried out in an acidic environment using $NaNO_2$, and any phenol, most commonly 2-naphthol, is used as a nitrogenous component:



The resulting nitrogen compounds are red in colour.

Detection of amides.

Amides are typically detected by complexation with copper or cobalt salts in an alkaline medium. Sulphamides form pink or red complexes with cobalt, and blue or green complexes with copper:

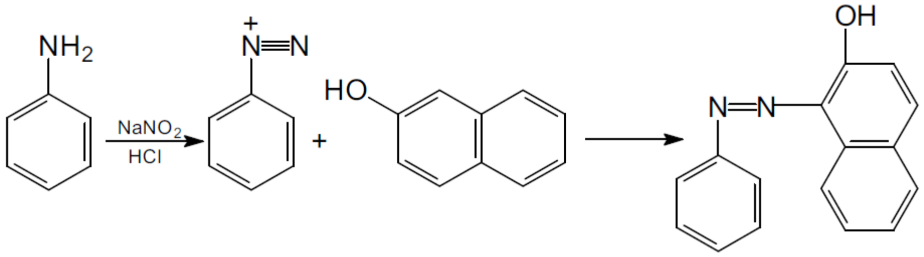


Detection of an aromatic nitro group

The aromatic nitro group is detected after reduction to an amino group by zinc in hydrochloric acid:

$$R{-}NO_2 \xrightarrow{Zn,\ H^+} R{-}NH_2$$

The latter is diazotised and a nitrogen coupling reaction is carried out:



4. Detection of sulphur and phosphorus-containing groups

Identification of the thiogroup.

The detection of thiogroups is based on the identification of hydrogen sulphide (using a filter paper moistened with plumbum salts), which is released during the thermal decomposition of sulphur-containing organic matter.

Detection of sulphur compounds.

Sulphur compounds are oxidised by heating with concentrated nitric acid or a mixture of nitric and hydrochloric acids. The resulting sulphates are determined by reaction with barium salts.

Detection of phosphorus-containing groups.

Phosphorus-containing organic compounds are detected by oxidation with nitric acid. The phosphoric acid formed is identified by the formation of magnesium-ammonium phosphate or ammonium phosphorus molybdate precipitates:

$$Na_2HPO_4 + MgCl_2 + NH_3 \cdot H_2O = MgNH_4PO_4\downarrow + 2NaCl + H_2O$$

$$(NH_4)_3PO_4 + 12(NH_4)_2MoO_4 + 24HNO_3 = (NH_4)_3H_4[P(Mo_2O_7)_6]\downarrow + 24NH_4NO_3 + 10H_2O$$

Lecture 6

EQUILIBRIA IN HOMOGENEOUS SYSTEMS

1. The theory of electrolytic dissociation;
2. The state of strong electrolytes in solutions;
3. The law of the masses;
4. Reversible and irreversible chemical reactions. The equilibrium constant;
5. Electroneutrality condition and material balance condition.

1. The theory of electrolytic dissociation

The theory of electrolytic dissociation was formulated in 1887 by Swedish scientist Svante August Arrhenius. In 1903, Arrhenius became the first Swedish scientist to receive the Nobel Prize in Chemistry «in recognition of the special significance of his theory of electrolytic dissociation for the development of chemistry». The theory is summarised in the following main points:

1. When dissolved in water, electrolytes (molecules of salts, acids and bases) dissociate into ions, i.e., they decompose into positively and negatively charged particles that behave as independent units in solution.

2. The + and - charges of the ions are equal, so the solution as a whole is electroneutral.

3. The process of dissociation is reversible, which means that undissociated molecules are present in the solution along with ions.

4. An important quantitative characteristic of electrolyte solutions is the degree of dissociation (α), which characterises the equilibrium state of the electrolyte and is determined by the ratio of the number of dissociated electrolyte molecules to the total number of molecules in the solution.

$$\alpha = \frac{N_{dissociated}}{N_{general}}.$$

The degree of dissociation α is a dimensionless quantity. The degree of dissociation is usually expressed as a fraction from 0 to 1 or as a percentage (%).

Based on the experimentally obtained values of the degree of dissociation, Arrhenius divided electrolytes into 3 groups: strong ($\alpha > 30\%$), weak ($\alpha < 5\%$), and medium strength ($30\% < \alpha < 5\%$). It is impossible to draw a sharp line between these categories.

Strong electrolytes include most salts with an ionic crystal lattice, water-soluble alkalis and strong acids (HCl, H_2SO_4, HNO_3, HI, HBr, $HMnO_4$, NaOH, KOH, $Ba(OH)_2$).

Almost all organic acids were classified as weak electrolytes: formic acid HCOOH, acetate CH_3COOH, benzoic acid C_6H_5COOH and other inorganic acids: cyanide HCN, boric H_3BO_3, sulfide H_2S, base ammonium hydroxide NH_4OH and salts with covalent bonds: mercury (II) cyanide $Hg(CN)_2$, mercury(II) chloride $HgCl_2$, cadmium chloride $CdCl_2$, cadmium iodide CdI_2 and others.

Medium-strength electrolytes include such acids phosphate H_3PO_4, arsenate (V) H_3AsO_4, chromate(VI) H_2CrO_4 , sulfite (IV) H_2SO_3 and a number of other compounds.

The Arrhenius theory was often criticised by scientists because it had a purely "physical" approach to understanding the nature of solutions, which did not take into account the chemical interactions between the solute and the solvent (hydration in the case of water, or solvation in general). Arrhenius's theory failed in the case of concentrated electrolyte solutions because it did not take into account interactions between ions (electrostatic interactions). Subsequently, I. A. Kablukov, V. A. Kistyakovsky, G. Lewis, P. Debay and E. Hückel introduced amendments to the theory of dissociation that took into account the factors of interionic interaction. The views of Mendeleev and Arrhenius were then combined in the proton theory of acids and bases.

The statement of Arrhenius' theory ***about the reversibility of the dissociation process*** is valid only for weak electrolytes.

2. State of strong electrolytes in solutions

According to the theory of Debye and Hückel (1923), strong electrolytes in aqueous solutions dissociate completely into ions regardless of concentration, i.e. their true degree of dissociation is $\alpha = 1.0$ (100%).

Since there are no molecules in solutions of strong electrolytes (only ions), the dissociation equation for strong electrolytes should be written with an equal sign, not an inverse sign, for example:

$$HCl = H^+ + Cl^- .$$

For electrolytes, there are two types of dissociation: apparent and true.

The apparent degree of dissociation of electrolytes is obtained by direct measurement of α (by measuring electrical conductivity, osmotic pressure, lowering of the freezing point and increasing of the boiling point).

The degree of dissociation of electrolytes is of great importance for analysis, as it characterises the chemical activity of the respective substances.

Direct measurement of the degree of dissociation of strong electrolytes does not always give a reliable result. This can be explained by the fact that ions are charged particles that can interact according to Coulomb's law. The action of interionic forces reduces the mobility of ions, which, accordingly, distorts the results of electrical conductivity measurements (conductivity is underestimated) and creates the effect of incomplete dissociation of the electrolyte. Interionic forces not only reduce the electrical conductivity of solutions, but also affect the osmotic pressure, freezing and boiling points of solutions, which determine the degree of dissociation.

Thus, the influence of interfacial forces in electrolyte solutions does not allow for a correct assessment of their true physical and chemical properties based on experimental data.

To evaluate the reduced ability of ions to undergo chemical reactions caused by electrostatic interaction of ions, the term "active" ion concentration is nowadays used, which means not the true concentration of an ion, but the concentration of an ion that corresponds to its effective concentration, i.e., which determines the properties of ions observed experimentally.

The effective (active) concentration of an ion for contraction is called activity and is expressed in mol/dm^3 .

The ratio between the active concentration and the true concentration:

$$a = f \cdot c,$$

where f *is a* proportionality factor that takes into account the interaction of a given ion with the environment (activity coefficient).

If the ionic content is expressed in terms of molarity (in physical chemistry), the activity coefficient is denoted by the *Greek* letter γ (*gamma).*

The activity coefficient f *is* less than 1 and only at very high dilution, when the interaction force between ions approaches 0, $f \to 1$.

The measure of the electrostatic interaction between all ions in a solution is the *ionic strength of the solution* (μ)*,* which is determined by the formula proposed by Lewis and Randall:

$$\mu = \frac{1}{2}(c_1 z_1^2 + c_2 z_2^2 + \ldots + c_n z_n^2),$$

where c_1 , c_2 , ... c_n are the molar concentrations of individual ions in solution. For dilute solutions and calculations that do not require greater accuracy, the molar concentration can be assumed to be equal to the molar concentration, i.e., "*c" is* expressed in mol/dm^3 . The molar concentration "*c"* for strong electrolytes is calculated assuming that the electrolytes dissociate completely.

The ionic strength of a solution can be calculated as follows:

$$\mu = \frac{1}{2}\sum_{i=1}^{i=n} \cdot c_i \cdot z_i^2$$

Thus, the ionic strength is equal to the half-sum of the product of the ionic concentrations and the squares of their charges.

To calculate the active concentration of ions in a solution, it is necessary to know the activity coefficients, and to determine the activity coefficients *f, it* is necessary to know the ionic strength μ.

Currently, a table of approximate values of activity coefficients is used for analytical calculations. These activity coefficients have been determined experimentally.

This table shows that the ***activity coefficients of ions of the same charge value are the same for all dilute solutions that have the same ionic strength*** **-** this is the law of ionic strength formulated by Lewis and Randall.

The activity coefficients f for intermediate values of ionic strength μ *are* found by interpolation, for example, by proportion:

$$\frac{\mu_1 - \mu_2}{f_1 - f_2} = \frac{\mu_1 - \mu_x}{f_1 - f_x}$$

However, the law of ionic strength is only fulfilled for very dilute aqueous solutions with μ not > 0.2.

In cases where more precise calculations are required, the activity coefficients can be calculated using the equation derived from the Debye-Hückel theory of strong electrolytes.

$$-\lg f = \frac{0{,}5z^2\sqrt{\mu}}{1+\sqrt{\mu}}$$

This expression is valid for concentrations in the range of 0.05-0.5 mol/dm^3 .

For more dilute solutions, the relationship between f and μ *is* simplified:

$$-\lg f = 0{,}5z^2\sqrt{\mu}\ ,$$

where z *is the* charge of the ion under study.

3. The law of the masses

Chemical reactions occur at a certain rate. Some reactions are very fast, almost instantaneous (for example, the interaction of an acid with an alkali), while others are slow (the decomposition of H_2O_2 under the influence of light). We judge the speed of a chemical reaction by the amount of substance reacted per unit of time.

The speed of a chemical reaction depends on the nature and concentration of the reacting substances, temperature, pressure, and catalysts. Concentration in the theory of analytical chemistry is usually expressed as the number of moles of a substance in 1 dm^3 of solution (molar concentration). It is conventional to place the formula of the corresponding substance in square brackets to indicate the **equilibrium** molar concentration.

The relationship between the rate of chemical reaction υ and the concentration of the interacting substances c is expressed by the law of mass action (Gouldberg and Waage's law), which is formulated as follows: the ***rate of chemical reaction is directly proportional to the molar concentrations of the reacting substances (active masses).***

For reaction

$$mA + nB \rightarrow C$$

$$\upsilon = kc(A)^m c(B)^n.$$

where *k is the* proportionality coefficient, which is called the chemical reaction rate constant.

For example, for the reaction

$$3H_2 + N_2 \rightarrow 2NH_3$$

$$\upsilon = kc(H_2)^3 c(N_2)^1$$

i.e., concentrations are taken with degree indicators equal to stoichiometric coefficients.

If the concentrations of A and B are assumed **to be** 1 mol/dm^3 , then $\upsilon = k$. Thus, the ***rate constant can be defined as the rate of reaction at which the concentration of each substance involved in the reaction is 1 mol/dm³ or the product of these concentrations is 1.***

4. Reversible and irreversible chemical reactions. Equilibrium constant

Most chemical reactions are not complete because the products react with each other to form starting materials. These reactions are called reversible reactions.

An example of a reversible analytical reaction is the reaction for the determination of potassium ions with tartaric acid, which is described by Eq:

$$KCl + H_2C_4H_4O_6 \rightleftarrows KHC_4H_4O_6 \downarrow + HCl.$$

The reaction results in a white crystalline precipitate of potassium hydrogen tartrate and hydrochloric acid. As the reaction products accumulate, the chloric acid reacts with the potassium hydrogen tartrate, and a reverse reaction begins, leading to the formation of the starting materials.

The interaction of barium ions with potassium dichromate is similarly reversible:

$$2Ba^{2+} + Cr_2O_7^{2-} + H_2O \rightleftarrows 2BaCrO_4 \downarrow + 2H^+ .$$

Each analytical reaction is reversible to a certain extent, but in many cases this reversibility is insignificant, so it can be neglected and the reaction can be considered practically irreversible.

General view of the reversible reaction equation $m\mathrm{A} + n\mathrm{B} \rightleftarrows l\mathrm{C} + d\mathrm{D}$.

A state of chemical equilibrium occurs when the rates of direct and reversible reactions are equal. Chemical equilibrium is a type of dynamic equilibrium.

Under steady-state conditions, chemical equilibrium is maintained for a long time. When an external factor (concentration, pressure, temperature) changes, the equilibrium shifts, and the rates of direct and reverse reactions become different. However, after a while, chemical equilibrium is restored.

Let's apply the law of active masses to a reversible reaction:

$$\upsilon_1 = k_1 c(\mathrm{A})^m c(\mathrm{B})^n;$$

$$\upsilon_2 = k_2 c(\mathrm{C})^l c(\mathrm{D})^d.$$

In equilibrium, we have :

$$\upsilon_1 = \upsilon_2,$$

$$\text{тоді} \quad k_1 c(\mathrm{A})^m c(\mathrm{B})^n = k_2 c(\mathrm{C})^l c(\mathrm{D})^d$$

We get

$$\frac{k_1}{k_2} = \frac{c(\mathrm{C})^l \cdot c(\mathrm{D})^d}{c(\mathrm{A})^m \cdot c(\mathrm{B})^n}.$$

Since k_1 and k_2 - the rate constants of a chemical reaction - are constant, their ratio will be a constant value, denoted by K and called the *chemical equilibrium constant.*

$$K = \frac{c(\mathrm{C})^l \cdot c(\mathrm{D})^d}{c(\mathrm{A})^m \cdot c(\mathrm{B})^n}.$$

If the constant K is expressed in terms of the equilibrium concentrations of substances (ions) involved in a chemical reaction, it is called *the concentration constant of equilibrium* and is denoted Kc.

If the equilibrium constant is expressed in terms of the activities of the substances (ions) involved in the reaction, it is called the **thermodynamic** constant and is denoted by K_0 or Ka.

The value of the equilibrium constant indicates the depth of the reaction in this direction. The higher the $K_{рівн.}$, , the more complete the reaction. Comparing the numerical values of $K_{рівн}$ for different reactions makes it possible to determine the depth of each reaction.

The relationship between the concentration and thermodynamic equilibrium constants is as follows:

$$K^0 = \frac{a(\mathrm{C})^l \cdot a(\mathrm{D})^d}{a(\mathrm{A})^m \cdot a(\mathrm{B})^n} = \frac{c(\mathrm{C})^l \cdot c(\mathrm{D})^d}{c(\mathrm{A})^m \cdot c(\mathrm{B})^n} \cdot \frac{f(\mathrm{C})^l \cdot f(\mathrm{D})^d}{f(\mathrm{A})^m \cdot f(\mathrm{B})^n} = K^c \frac{f(\mathrm{C})^l \cdot f(\mathrm{D})^d}{f(\mathrm{A})^m \cdot f(\mathrm{B})^n}.$$

The chemical equilibrium constant is a value characteristic of each reaction. It does not depend on the concentration of the reacting substances, but changes with temperature.

The law of active masses is of great importance in analytical chemistry. The law of active masses is the theoretical basis of analytical chemistry, as the entire course of general theoretical principles of analytical chemistry is based on the consistent application of the law of active masses to the reversible processes of electrolytic dissociation, hydrolysis, precipitation and dissolution, etc. Depending on the reversible chemical process in which an equilibrium constant is used, it is given a corresponding name:

1. For electrolytic dissociation of weak electrolytes

$$\mathrm{NH_4\,OH} \rightleftarrows \mathrm{NH_4^+} + \mathrm{OH^-}.$$

$$К(dis.) = \frac{[NH_4^+][OH^-])}{[NH_4OH]}$$

***is the dissociation (ionisation) constant of a weak electrolyte*.**

2. For the total dissociation process of a complex ion

$$[Ag(NH_3)_2]^+ \rightleftarrows Ag^+ + 2NH_3 .$$

Diaminargentate ion

$$K = \frac{[Ag^+][2NH_3]}{[[Ag(NH_3)_2]^+]}$$

is the total dissociation constant of the complex ion (total decay constant or total instability constant of the complex ion).

3. For reversible hydrolysis processes, it is called the ***hydrolysis constant:***

$$CH_3COONa + H_2O \rightleftarrows CH_3COOH + NaOH.$$

$$K_h = \frac{[CH_3COOH][NaOH]}{[CH_3COONa][H_2O]}, \quad K_г = K\text{eq.}\cdot [H_2O]$$

4. To describe the equilibrium between the solid phase (precipitate) and the solution above it, a new constant, ***solubility product*** (SP), is used.

$$Ag_2CrO_4 \rightleftarrows 2Ag^+ + CrO_4^{2-}$$

$$SP(Ag_2CrO_4) = [Ag]^{2+}[CrO_4].^{2-}$$

Knowing the value of the chemical equilibrium constant for any reversible process and the concentration of the starting substances, you can calculate the concentrations of all substances at the equilibrium. The equilibrium concentrations of all substances make it possible to calculate the equilibrium constant.

5. Electro-neutrality condition and material balance condition

The principle (condition) of electroneutrality and the condition of material balance are used to calculate equilibria along with the law of active masses.

The principle (condition) of electroneutrality. The essence of the electronegativity condition is that a solution containing different ions must always remain electronegative. In this case, each ion in the solution must be taken into account, including those that are not directly involved in the equilibrium under consideration. The condition of electroneutrality means that the total number of positive charges per unit volume is equal to the total number of negative charges. In general, the equation of electroneutrality is written as follows:

$$\sum_i z_i c_i = 0$$

The equation of electroneutrality for an aqueous solution of potassium nitrate will look like this

$$[K^+] + [H_3O^+] = [NO_3^-] + [OH^-].$$

An aqueous solution of potassium nitrate contains the ions K^+, NO_3^- and H_3O^+ and OH^-, which are formed during the dissociation of water.

The condition of material balance. The essence of the condition of material balance is the invariability of the number of atoms of a given type in time during the reaction in an isolated system.

Consider the material balance equation for a solution of oxalic acid $H_2C_2O_4$.

As a result of dissociation of oxalic acid, the ions $HC_2O_4^-$, $C_2O_4^{2-}$, H^+ and molecules $H_2C_2O_4$ exist in solution. The total concentration of oxalic acid consists of the sum of the equilibrium concentrations of all particles (ions, molecules) containing carbon and oxygen atoms. Therefore, the material balance equation is written as follows:

$$c(C_2O_4) = [H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{2-}]$$

$$c(H) = [H^+] + [HC_2O_4^-] + 2[H_2C_2O_4].$$

Lecture 7

ACID-BASE (PROTEOLYTIC) EQUILIBRIA

1. Application of the law of active masses to the process of dissociation (ionisation) of weak electrolytes. The ionisation constant;
2. The relationship between the degree and ionisation constant of weak electrolytes. Ostwald's dilution law;
3. Application of the law of active masses to the process of water ionisation. Ionic product of water;
4. Methods for determining the pH of solutions.
5. Calculation of the pH of solutions of strong acids, strong bases, weak acids and weak bases

1. Application of the law of active masses to the process of dissociation (ionisation) of weak electrolytes. Ionisation constant

Weak electrolytes (acids and bases) dissociate in water only partially to form hydrated cations and anions.

If the formula of a weak binary electrolyte is schematically written in the form KtAn, the ionisation equation of a weak electrolyte will be as follows:

$$\mathrm{KtAn} \rightleftarrows \mathrm{Kt}^+ + \mathrm{An}^-.$$

The Arrhenius theory of electrolytic dissociation, or rather the statement that the dissociation process is reversible, is valid only for solutions of weak electrolytes, since only the ionisation of weak electrolytes is a reversible process that leads to chemical equilibrium.

By applying the law of active masses to the reversible ionisation process of weak electrolytes, the equation for the ionisation constant of a weak electrolyte can be found:

$$K = \frac{[\mathrm{Kt}^+][\mathrm{An}^-]}{[\mathrm{KtAn}]}$$

The dissociation (ionisation) constant is the ratio of the product of the equilibrium concentrations of ions into which electrolyte molecules decompose to the equilibrium concentration of neionised electrolyte molecules.

For example, for the ionisation of acetic acid

$$\mathrm{SN_3\ SOON} \rightleftarrows \mathrm{N}^+ + \mathrm{SN_3\ SOO}^- .$$

ionisation constant can be written as follows:

$$K(\mathrm{CH_3COOH}) = \frac{\left[\mathrm{H}^+\right]\cdot\left[\mathrm{CH_3COO}^-\right]}{\mathrm{CH_3COOH}} .$$

At relatively high concentrations of a weak electrolyte, when the true degree of dissociation begins to be distorted by interionic forces, the ionisation constant expressed in terms of concentration does not take a constant value, i.e., it ceases to be a constant. In this case, the ionisation constant equation must be expressed in terms of the activity of the electrolyte ions, for example, for acetic acid:

$$K(\mathrm{CH_3COOH}) = \frac{a(\mathrm{H}^+)\cdot a(\mathrm{CH_3COO}^-)}{\mathrm{CH_3COOH}} = \frac{\left[\mathrm{H}^+\right]\cdot\left[\mathrm{CH_3COO}^-\right]\cdot f(\mathrm{H}^+)\cdot f(\mathrm{CH_3COO}^-)}{\mathrm{CH_3COOH}}.$$

Thus, the theory of strong electrolytes can also be applied to weak electrolytes.

For the dissociation of strong electrolyte solutions, the law of active masses is not applicable to reversible processes, since the true degree of dissociation is 1 (100%), i.e. there are virtually no undissociated molecules in strong electrolyte solutions.

2. The relationship between the degree and ionisation constant of weak electrolytes. Ostwald's dilution law

The degree and constant of ionisation of a weak electrolyte characterise the same process of decomposition of molecules into ions.

The degree of ionisation depends on the nature of the electrolyte and solvent, temperature, and electrolyte concentration.

The value of $K_{\text{йон.}}$ indicates the strength of the weak electrolyte. The greater the value of $K_{\text{ion.}}$, the greater the concentration of ions, the stronger the ionisation of the weak electrolyte.

The ionisation constant does not depend on the concentration of the electrolyte in the solution, but depends on the temperature, the nature of the electrolyte and the nature of the solvent.

Let us establish the relationship between the degree and the ionisation constant of a weak electrolyte.

The ionisation equation for a weak electrolyte in c will be as follows:

$$\mathrm{KtAn} \rightleftarrows \mathrm{Kt}^{+} + \mathrm{An}^{-}\ .$$

The equilibrium of this reaction is characterised by the ionisation constant of a weak electrolyte

$$K = \frac{[\mathrm{Kt}^{+}][\mathrm{An}^{-}]}{[\mathrm{KtAn}]}$$

Let us denote the initial molar concentration of the electrolyte by *c* and the degree of ionisation by α. Then the equilibrium concentration of each ion will be *cα,* and the equilibrium concentration of neionised molecules of the weak electrolyte will be (*c* - *cα)*. Substituting the obtained values into the equation for the ionisation constant of a binary electrolyte, we obtain

$$K = \frac{c^2\,\alpha^2}{c(1-\alpha)}; \quad K = \frac{c\alpha^2}{1-\alpha}$$

If the degree of ionisation is ≤ 0.1, it is possible to neglect the value of α (alpha) in the denominator for calculations that do not require high accuracy: Eq,

$$\alpha = \sqrt{\frac{K}{c}}. \qquad\qquad K \approx c \cdot \alpha^2$$

The above equations for calculating the ionisation constant and the degree of ionisation establish the relationship between them on the one hand, and on the other hand, show the dependence between the degree of ionisation of a weak electrolyte and its concentration.

The degree of ionisation increases with a decrease in the concentration of the weak electrolyte, i.e. with an increase in the dilution of the solution.

This statement reflects Ostwald's law of dilution.

The obtained expressions also show that, of two electrolytes with the same concentration, the degree of ionisation is greater for the electrolyte with the higher ionisation constant.

Ostwald's dilution law allows you to calculate the degree of ionisation if you know $K_{ion.}$ and the molar concentration of the electrolyte in solution, and vice versa, having determined the degree of ionisation experimentally, you can calculate the ionisation constant using the equation:

$$K = \frac{c\alpha^2}{1-\alpha}$$

3. Application of the law of active masses to the process of water ionisation. Ionic product of water.

Reactions that are used in analytical chemistry usually take place in aqueous solutions. In 1894, the German physicist and physical chemist F. Kohlrausch experimentally established that pure water conducts an electric current. The presence of a measurable electrical conductivity in water indicates that its molecules are dissociating, albeit not significantly:

$$H_2O \rightleftarrows H^+ + OH^-.$$

It would be more correct to say that the hydrogen ion H^+ in aqueous solutions exists in the form of the hydroxonium ion H_3O^+ . However, to simplify the writing, instead of H_3O^+, write H^+ , since this does not affect the results of the calculations.

Kohlrausch found that at room temperature, 1 dm^3 of pure water contains 10^{-7} moles of hydrogen ions and 10^{-7} moles of hydroxide ions, so it dissociates only 10^{-7} moles of H_2O molecules in 1 dm^3 of water. 1 dm^3 of water contains 1000 g/18.02 g/mol = 55.56 mol of H_2O (1000 g is the mass of 1 dm^3 of water, 18.02 g/mol is the molar mass of water), of which only 10^{-7} mol dissociate into ions. Accordingly, we can assume that the equilibrium concentration of neionised water molecules is equal to the total amount of water in 1 dm^3 , i.e. it can be considered constant.

Water ionisation is a reversible process. Applying the law of active masses to it, we derive the equation for the ionisation constant of water (concentration ionisation constant):

$$K^c(H_2O) = \frac{[H^+][OH^-]}{[H_2O]}.$$

If we express the ionisation constant in terms of activities, we obtain the so-called thermodynamic ionisation constant:

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

The activity coefficient of neionised molecules is taken to be 1. It has been experimentally found that at 25 °C, $K^a(H_2O) = 1.8\cdot10^{-16}$. Substituting the values of $K^a(H_2O)$ and $[H_2O]$ into the expression for the ionisation constant, we obtain the value for the temperature of 25 °C:

$K^a(H_2O)\cdot[H_2O] = a(H^+)\cdot a(OH^-) = 1.8\cdot10^{-16}\cdot55.56 = 1\cdot10^{-14} = \text{const}.$

$a(H^+)\cdot a(OH^-) = 1\cdot10^{-14}$.

This pattern also holds true when electrolytes are dissolved in water.

The product $a(H^+)\cdot a(OH^-)$ is called the ionic product of water (K_w). It is the most important analytical constant. At room temperature, the ionic product of water is $1\cdot10^{-14}$.

In chemically pure water and any aqueous solution at a constant temperature, the product of the activities of hydrogen and hydroxide ions is a constant value

$$a(\mathrm{H}^+) \cdot a(\mathrm{OH}^-) = \mathrm{const}$$

Since in chemically pure water and very dilute electrolyte solutions, ion concentrations are low, and ionic strengths are correspondingly low, and activity coefficients tend to 1, ionic activities can be equated to concentrations:

$$[\mathrm{H}^+]\cdot[\mathrm{OH}^-] = 1\cdot10^{-14}\ .$$

For electrolyte solutions of sufficiently high concentrations (2-3 mol/dm^3 for weak electrolytes , > 10^{-3} mol/dm for strong electrolytes^3), it is necessary to use the activities of ions and substances.

For any change in the activities of the ions H^+ and OH^- , their product in aqueous solution remains constant at a constant temperature.

A number of conclusions can be drawn from the above.

1) In chemically pure water and in neutral aqueous solutions at 25 °C

$$a(\mathrm{H}^+) = a(\mathrm{OH}^-) = \sqrt{10^{-14}} = 10^{-7}\ \text{mol/dm}^3$$

Since during the dissociation of 1 water molecule, 1 H^+ ionand 1 OH^- ion are obtained;

2) If an alkali is added to pure water or to a neutral aqueous solution, the activity of hydroxide ions becomes greater than 10^{-7} mol/dm^3 , and the activity of hydrogen ions becomes less than 10^{-7} mol/dm^3 .

$$a(\mathrm{H}^+) = \frac{K_w}{a(\mathrm{OH}^-)}$$

That is, the activities of the ions H^+ and OH^- are inversely proportional to each other. As one of them increases, the other decreases proportionally.

3) $a(\mathrm{H}^+)$ or $a(\mathrm{OH}^-)$ can never be equal to zero, since multiplication by zero gives zero. That is, *any aqueous solution, regardless of its reaction (acidic, neutral or alkaline), must contain both H^+ and OH^- ions.*

Ionisation of water is an endothermic process, i.e. it occurs with the absorption of heat. Therefore, according to the Le Chatelier principle, with increasing temperature, the ionisation equilibrium shifts towards the formation of ions, which leads to an increase in the ionisation constant of water, and, accordingly, the ionic product of water. With an increase in temperature from 0 to 100 °C, Kw increases 500 times (from $1.1\cdot10^{-15}$ to $5.5\cdot10^{-13}$).

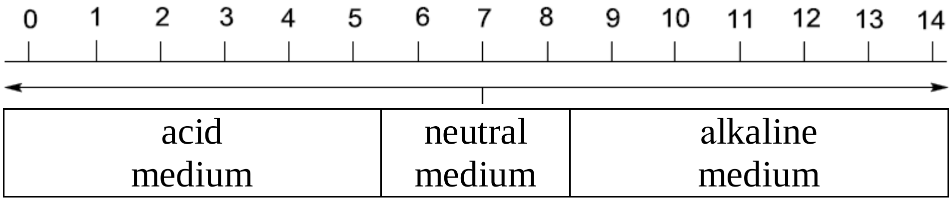
pH and pH. It turned out to be inconvenient to characterise the acidity and basicity of solutions by numbers with negative degree values. S. Serensen proposed to express the concentration of aqueous solutions by the hydrogen index, the decimal logarithm of the concentration of hydrogen ions taken with the reverse sign, and designated it as pH.

$\mathrm{pH} = -\lg[\mathrm{H}^+]$ and, accordingly, $\mathrm{pOH} = -\lg[\mathrm{OH}^-]$.

Since [H+]-[OH-] = $Kw = 10^{-14}$, logarithmising the equation of the ionic product of water, we obtain $-\lg[\mathrm{H}^+] + (-\lg[\mathrm{OH}^-]) = 14$; **pH + pH = 14**

This ratio is valid for any aqueous solution.

The relationship between the pH value and the reaction of an aqueous solution can be represented as follows:



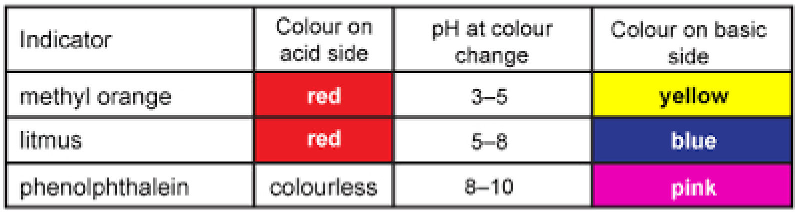
The values of **pH = 0** and **pH = 14** correspond approximately to the concentrations of hydrogen ions in 1 *M HCl* solution (pH = 0) and 1 *M* NaOH solution (pH = 14). Of course, there may be more acidic solutions of pH < 0 and more alkaline solutions of pH > 14, but the acidity and alkalinity of these solutions are usually expressed in moles of acid (alkali) in 1 dm^3 of solution.

4. Methods for determining the pH of solutions

In the course of qualitative analysis, it is often necessary to determine the pH value of the solutions under study. There are many ways to determine pH, the simplest of which is the indicator method.

In qualitative analysis laboratories, three indicators are most commonly used: methyl orange, litmus and phenolphthalein, which change colour in the pH range shown in the table.

The colours of indicators in acidic and basic solutions



Indicator	Colour on acid side	pH at colour change	Colour on basic side
methyl orange	red	3–5	yellow
litmus	red	5–8	blue
phenolphthalein	colourless	8–10	pink

To determine the pH, 1-2 drops of the indicator are added to individual samples of the test solution in sequence and the approximate pH of the solution is judged by the change in colour.

Nowadays, universal indicators, mixtures of several simple indicators, are often used to determine the pH of solutions. The universal indicator is used either in the form of a solution or in the form of an indicator paper impregnated with a universal indicator solution and dried. More precise pH values are determined using different instruments, such as a pH meter.

5. Calculation of pH of solutions of strong acids and strong bases, weak acids and weak bases

In solutions of strong acids and bases, due to their complete dissociation

$HCl = H^+ + Cl^-$; $NaOH = Na^+ + OH^-$,

the concentration of H+ or OH- ions is equal to the concentration of acid (or alkali).

In a solution of acid HCl $[H^+] = c_{acid}$.; $\mathbf{pH = -\,lg\ c_{acid}}$.

In alkali solution NaOH $[OH^-] = c_{base}$; $pH = -\,lg c_{осн.}$; $\mathbf{pH = 14 + lg\ c_{base}}$

It would be more correct to find the concentration of H^+ ions in a strong acid solution taking into account the dissociation of water molecules, but in the presence of a strong acid, water dissociation is strongly suppressed. Therefore, in solutions of strong acids (10^{-1} - 10^{-4} mol/dm^3), water dissociation can be neglected and $c(H^+) = c_{acid.}$, $pH = -\,lg\ c_{acid.}$

Similarly for aqueous solutions of strong bases.

It should be noted that the activities in solutions of strong electrolytes will not be equal to the concentrations.

For solutions of weak acids and bases, their **incomplete** dissociation must be taken into account when calculating pH and pHON. To calculate the concentration of hydrogen ions, and thus the pH, the concentration of OH^- ions (and pH), the equilibrium constant of dissociation (ionisation) of weak electrolytes is used. For example, for the ionisation of acetic acid

$$CH_3COOH \rightleftarrows H^+ + CH_3COO^-$$

ionisation constant can be written as follows:

$$K(CH_3COOH) = \frac{[H^+] \cdot [CH_3COO^-]}{CH_3COOH}.$$

Given that:

1) from the dissociation equation of a binary electrolyte $[H^+] = [CH_3COO^-]$;

2) the concentration of undissociated molecules is significantly higher than the concentration of dissociated molecules, i.e. $[CH_3COOH]_{\text{undiss.}} \approx c_{\text{general.}}$;

3) the concentration of H^+ formed during the dissociation of water can be neglected, we obtain:

$$K(CH_3COOH) = \frac{[H^+]^2}{c_{acid}} \qquad [H^+] = \sqrt{K_{acid} c_{acid}} \qquad pH = \frac{1}{2} pK_{acid} - \frac{1}{2} lg c_{acid}$$

Similarly, the equation for calculating the concentration of hydroxide ions in solutions of weak bases is derived.

$$K(NH_4OH) = \frac{[NH_4^+] \cdot [OH^-]}{NH_4OH} \qquad K(NH_4OH) = \frac{[OH^-]^2}{c_{base}}$$

From here.

$$[OH^-] = \sqrt{K_{base} c_{base}}\ ; \quad pOH = \frac{1}{2} pK_{base} - \frac{1}{2} lg c_{base}\ ; \ pH = 14 - \frac{1}{2} pK_{base} + \frac{1}{2} lg c_{base}.$$

Multi-basic acids are ionised in several steps, e.g. ionisation of carbonic acid:

$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$ I stage $\qquad$ $HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$ II stage

$$K_1 = \frac{[H^+] \cdot [HCO_3^{2-}]}{[H_2CO_3]} = 4.5 \cdot 10^{-7}; \qquad K_2 = \frac{[H^+] \cdot [CO_3^{2-}]}{[HCO_3^-]} = 4.8 \cdot 10^{-11}$$

Since the first ionisation constant is much larger than the second, the concentration of hydrogen ions will be determined mainly by the ionisation of carbonic acid in the first stage and can be calculated by the formula:

$$[H^+] = \sqrt{K_1 c_{acid}}$$

It is possible to neglect the concentration of hydrogen ions from dissociation at the second stage in cases where $K_2 < K_1$ by a factor of 1000.

Lecture 8.

BUFFER SOLUTIONS AND THEIR IMPORTANCE IN CHEMICAL ANALYSIS

1. Influence of the ions of the same name on the shift in the equilibrium of electrolytic dissociation;
2. The concept of buffer solutions;
3. Calculation of the pH of buffer solutions;
4. Buffer capacity.

1. Influence of the ions of the same name on the shift in the equilibrium of electrolytic dissociation

The equilibrium of the reverse dissociation reaction can be shifted by adding a substance containing ions of the same name to the solution. Consider the effect of adding sodium acetate CH_3COONa to a solution of acetic acid in which a weak acid is dissociating according to Eq:

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

According to the law of active masses, equilibrium in a solution of a weak acid is described by Eq:

$$K(CH_3COOH) = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}.$$

If you add its salt to a solution of acetic acid, it dissociates completely:

$$CH_3COONa = CH_3\,COO^- + Na^+ ,$$

the concentration of $CH_3\,COO^-$ ions of the same name (i.e., the same as one of the ions of a given electrolyte) will increase significantly. This will lead to a disturbance of the equilibrium

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

According to Le Chatelier's principle, the equilibrium will be shifted in the direction that opposes the increase in the concentration of CH_3COOH^- ions, i.e. in the direction of formation of undissociated CH_3COOH molecules as a result of the combination of H^+ and CH_3COOH^- ions. This means that during the establishment of a new equilibrium, the concentration of $CH_3\,COOH$ should increase and the degree of acid ionisation should decrease (the acid ionisation constant remains constant).

As a result of this process, the equilibrium concentration of hydrogen ions $[H^+]$ in an acetic acid solution is significantly reduced, causing the weak acid to behave like a stronger acid in the presence of its salt. For example, if acetic acid reacts slowly with zinc, then in the presence of sodium acetate, no hydrogen is released at all. Due to the weak dissociation (ionisation) of acetic acid and its additional inhibition, the concentration of anions CH_3COO^- will be determined by the concentration of salt CH_3COONa, and the equilibrium concentration of undissociated acetic acid molecules $[CH_3COOH]$ will be approximately equal to its initial concentration.

It is possible to add a strong acid to a solution of a weak acid, i.e. add the eponymous H^+ ion . This will also reduce the degree of dissociation of the weak acid. As a result, the concentration of hydrogen ions in a mixture of strong and weak acids will be determined almost exclusively by the concentration of the strong acid.

It is equally easy to inhibit the dissociation of NH_4OH by adding ammonium salt.

Thus, the introduction of a strong electrolyte with the same ion into a solution of a weak electrolyte reduces the degree of ionisation of the weak electrolyte, and the removal of one of the substances in chemical equilibrium from the reaction mixture leads to a reaction that produces new amounts of this substance.

2. The concept of buffer solutions

Buffer systems are systems that maintain a certain value of any parameter with a change in composition. Buffer solutions can be acid-base solutions, which maintain a constant pH value when acids or bases are added; redox solutions, which maintain a constant potential of systems with the addition of oxidants or reducing agents; and metal buffer solutions, which maintain a constant pH value.

Most chemical processes, including analytical reactions, can only take place at a certain acidity. If the reactions result in the accumulation of H^+ or OH^- ions, it is necessary to maintain a constant pH value in the solution to maintain optimal process conditions. For this purpose, buffer mixtures are used. Buffer mixtures are introduced into solutions and buffer solutions are obtained, the *pH of which hardly changes as a result of dilution with water or by adding small amounts of strong acids or alkalis.*

The following acid-base buffer mixtures can be distinguished

1) weak bases with their salts:

$NH_4OH + NH_4Cl$ is an ammonium buffer mixture.

2) weak acids with their salts:

$CH_3\,COOH + CH_3COONa$ is an acetate buffer mixture.

$HCOOH + HCOONa$ is a formate buffer mixture.

3) **medium and acidic salts:**

$Na_2HPO_4 + Na_3PO_4$ - phosphate buffer mixture.

$NaHCO_3 + Na_2CO_3$ is a carbonate buffer mixture.

4) **two acidic salts:**

$NaH_2PO_4 + Na_2HPO_4$, pH = 6.21-8.21.

The essence of the buffering action is illustrated by an acetate buffer solution (a mixture of CH_3COOH and CH_3COONa).

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

$CH_3COONa = CH_3COO^- + Na^+$.

Since the dissociation of acetic acid is negligible, the solution is dominated by undissociated molecules. Sodium acetate is a strong electrolyte that dissociates completely into ions. The presence of a large number of CH_3COO^- ions from the salt in the solution shifts the equilibrium of acetic acid dissociation towards the formation of its molecules. The dissociation of acetic acid can be so inhibited that the acid can be considered practically undissociated. As a result, the activity of H^+ ions is very low.

The addition of small amounts of strong acid leads to the binding of hydrogen ions to the acetate ions of the salt to form acetic acid:

$CH_3COONa + HCl \rightarrow NaCl + CH_3COOH$,

i.e., the hydrogen ions of the strong acid will be bound and the pH of the solution will not change.

The alkali added to the system enters into a neutralisation reaction with the acid, forming low-ionised H_2O molecules:

$CH_3COOH + NaOH = CH_3COONa + H_2O$.

The decrease in the concentration of hydrogen ions is compensated by a shift in the ionisation equilibrium of acetic acid towards the formation of H^+ and CH_3COO^- ions.

Dilution of the buffer mixture does not lead to noticeable changes in the pH of the solution. This is because two opposite processes occur simultaneously during dilution. On the one hand, dilution leads to a decrease in the concentration of the acid (base) and, consequently, a decrease in the activity of hydrogen ions. On the other hand, dilution leads to an increase in the degree of ionisation of the weak acid (base), i.e. the concentration of H^+ ions (OH^-) increases. According to the calculations, the decrease and increase in the activity of hydrogen ions during the dilution of the buffer mixture occurs approximately in the same way, so the pH of the solution does not change.

3. Calculation of the pH of buffer solutions

1. Calculate the pH of buffer solutions formed by a weak acid and its salt.

Let's consider the calculation of the pH of buffer solutions formed by a weak acid and its salt using the example of an acetate buffer mixture: $CH_3COOH + CH_3COONa$.

From the equation for the ionisation constant of acetic acid

$$CH_3COOH \leftrightarrows CH_3COO^- + H^+$$

$$K_{ion.} = \frac{[H^+]\cdot[CH_3COO^-]}{[CH_3COOH]};\ [H^+] = \frac{\cdot K_{ion.}\cdot[CH_3COOH]}{[CH_3COO^-]}$$

In the presence of sodium acetate, the dissociation of CH_3COOH will be inhibited, hence the equilibrium concentration of acetic acid $[CH_3COOH]$ can be taken to be equal to the initial concentration of acid $c_{\text{acid general}}$, the equilibrium concentration of acetate ions can be taken to be equal to the salt concentration:

$$[CH_3COO^-] = c_{solt} + c(CH_3COO^-)_{after\ acid\ dis.} \approx c_{solt}\ ,\ [H^+] = \frac{K_{acid}\cdot c_{acid}}{c_{solt}}.$$

Logarithmisation this expression and reversing the signs, we obtain an expression for calculating the pH of a buffer solution:

$-\lg[H^+] = -lgK_{acid} - lg\frac{c_{acid}}{c_{solt}}$. But $-\lg[H^+] = pH$ and $-lgK_{dis.} = pK_{dis.acid}$.

Then $pH = pK_{acid} - lg\frac{c_{acid}}{c_{solt}}$, if $c_{acid} = c_{solt} \rightarrow pH = pK_{acid}$, $[H^+] = K_{acid}$.

2. Calculate the pH of buffer solutions formed by weak bases and their salts.

Let us consider the example of an ammonia buffer mixture: $NH_4OH + NH_4Cl$.

From the equation for $K(NH_4OH)$, we find the equilibrium concentration of OH^- ions:

$$K_{ion.} = \frac{[NH_4{}^+]\cdot[OH^-]}{[NH_4OH]};\ [OH^-] = \frac{\cdot K_{ion.}\cdot[NH_4OH]}{[NH_4{}^+]} = K_{base}\cdot\frac{c_{base}}{c_{solt}}.$$

Logarithmisation this expression, we obtain the expression for calculating the pH of the buffer solution:

$$pOH = pK_{base} - lg\frac{c_{base}}{c_{solt}}.$$

Given that in any aqueous solution

$$pH = 14 - pK_{base} + lg\frac{c_{base}}{c_{solt}}.$$

4. Buffer capacity

The ability of a buffer solution to maintain a constant pH value depends on its *buffering capacity* π, which is defined as the ***amount of strong acid* or *base equivalent (mol) that must be added to 1 dm^3 of the buffer solution to change its pH by one*.** From the above definition, the following formula can be written

$$\pi = dc/d\text{pH},$$

where *ds is the* amount of substance equivalent of the introduced strong acid or base equal to the change in the molar concentration of the substance equivalent of the corresponding component of the buffer solution.

The capacity of a buffer solution is directly proportional to the concentration of the components. The greatest buffering capacity is that of a solution in which the concentrations of both components are equal. Preferably, the ratio of the concentrations of the components of the buffer solution can be in the range of 10:1 to 1:10. This ratio determines the area of effective buffering action of the buffer mixture, which extends by one unit to one side or the other of pKacid for a buffer mixture formed by a weak acid and its salt, and 14 - pK_{base} for a buffer mixture formed by a weak base and its salt.

Area of effective buffering action:

1) $NH_4OH + NH_4Cl$ $\Delta pH = 14 - pK \pm 1 = 9{,}24 \pm 1 = 8{,}24 - 10{,}24$.

2) $HCOOH + HCOONa$ $\Delta pH = pK \pm 1 = 3{,}75 \pm 1 = 2{,}75 - 4{,}75$.

3) $CH_3COOH + CH_3COONa$ $\Delta pH = pK \pm 1 = 4{,}76 \pm 1 = 3{,}76 - 5{,}76$.

4) $NaH_2PO_4 + Na_2HPO_4$ $\Delta pH = pK_2(H_3PO_4) \pm 1 = 7{,}21 \pm 1 = 6{,}21 - 8{,}21$.

When an acid or alkali is added to a buffer solution, the pH stability of the solution decreases. When using a buffer mixture in an assay, make sure that the buffer capacity is sufficiently large to ensure that the pH of the solution remains practically constant.

Buffer solutions are used in qualitative analysis for the separation of hydroxides, carbonates, sulfides (scheme of qualitative systematic analysis of cations according to the sulfide classification), precipitation of barium chromate by the action of $K_2Cr_2O_7$ and precipitation of potassium hydrogen tartrate by the action of tartaric acid $H_2C_4H_4O_6$ (carried out in the presence of an acetate buffer mixture), etc.

Buffer solutions are used in titrimetric analysis (complexometric determination of total water hardness) and gravimetric analysis, as well as in many physicochemical analysis methods.

Lecture 9

HYDROLYSIS OF SALTS. AMPHOTERICITY OF HYDROXIDES.

1. Hydrolysis of salts;
2. Equilibria in aqueous solutions of hydrolysing salts;
3. Practical methods of enhancing and weakening hydrolysis. The importance of hydrolysis in analysis;
4. Amphotericity of hydroxides.

1. Hydrolysis of salts.

The interaction of a salt with water, which results in the formation of a poorly codissociated or poorly soluble electrolyte, is called **salt hydrolysis.**

Hydrolysis reactions, of course, proceed without changing the degree of oxidation. And in general, hydrolysis is understood as an exchange decomposition reaction between water and a compound. The total effect of hydrolysis is determined by the nature of the cations and anions present in the solution.

Depending on the strength of the acid and base from which the salt is formed, there are four cases of hydrolysis:

1. Hydrolysis of salts formed by the interaction of strong bases and weak acids.

In salts formed by strong bases and weak acids, **hydrolysis** occurs **on the anion,** and solutions of these salts have **an alkaline reaction (**pH>7).

When sodium carbonate, a salt of a weak acid and a strong base, dissolves in water, the salt breaks down into ions:

$K_2CO_3 \rightarrow 2K^+ + CO_3^{2-}$.

An alkaline reaction of a solution is caused by the binding of the ion H^+, formed during the dissociation of water ($HOH \leftrightarrow H^+ + OH^-$), by a weak acid anion to form an ion or molecule of a weakly dissociated acid:

$CO_3^{2-} + HOH \leftrightarrow HCO_3^- + \mathbf{OH^-}$ abbreviated ionic equation;

$2K^+ + CO_3^{2-} + HOH \leftrightarrow 2K^+ + \mathbf{OH^-} + HCO_3^-$ full ionic equation.

2. Hydrolysis of salts formed by the interaction of a strong acid and a weak base.

Salts formed by a strong acid and a weak base undergo **cationic hydrolysis**, and solutions of such salts have an **acidic reaction (**pH < 7).

In aqueous solutions of such salts, OH^- - water ions are bound by a weak base cation and H^+ - ions accumulate in the solution. For example, hydrolysis of a solution of copper chloride formed by a weak base and a strong acid:

$CuCl_2 \rightarrow Cu^{2+} + 2Cl^-$.

$Cu^{2+} + HOH \leftrightarrow CuOH^+ + \mathbf{H^+}$ abbreviated ionic equation.

$Cu^{2+} + 2Cl^- + HOH \leftrightarrow CuOH^+ + 2Cl^- + \mathbf{H^+}$ full ionic equation.

3. Hydrolysis of salts formed by the interaction of a weak base and a weak acid.

Salts formed by a weak acid and a weak base do not exist in solutions (they are completely hydrolysed and decomposed by water).

In this case, OH^- and H^+ - water ions - are bound and the environment is close to **neutral**: $\mathbf{[H^+] \approx [OH^-]} \approx 10^{-7}$ mol/l; and **pH≈7**.

$CH_3COONH_4 \rightarrow CH_3COO^- + NH_4^+$.

$CH_3COO^- + HOH \leftrightarrow CH_3COOH + OH^-$.

$NH_4^+ + HOH \leftrightarrow NH_4OH + H^+$.

$H^+ + OH^- \leftrightarrow HOH$.

Hydrolysis occurs here to a considerable extent (due to the fact that not one, but two processes shift the ionisation equilibrium of water). You can see this by the smell of the solution CH_3 $CONH_4$, which smells like acetic acid and ammonia at the same time.

4. Salts formed by the interaction of a strong base and a strong acid.

Strong base and strong acid salts **do not hydrolyse,** since when they dissolve in water, neither H^+ nor OH^- , which arise as a result of water dissociation, bind.

Thus, the environment of salt solutions formed by strong bases and strong acids is neutral (pH 7).≈

2. Equilibria in aqueous solutions of salts that hydrolyse

Hydrolysis can be viewed as the reverse of the neutralisation reaction. Hydrolysis is quantified by two parameters: the *hydrolysis constant and the degree of hydrolysis*.

Let's apply the law of active masses to hydrolysis reactions and find the equilibrium constant:

$CH_3COONa + H_2O \rightleftarrows CH_3COOH + NaOH$

$CH_3COO^- + H_2O \rightleftarrows CH_3COOH + OH^-$

$$K_{eq.} = \frac{c(CH_3COOH)\cdot c(OH^-)}{c(CH_3COO^-)\cdot c(H_2O)}.$$

The concentration of water $c(H_2O)$ is almost constant, so $K_{eq.}\cdot c(H_2O) = K_h$ (hydrolysis constant).

$$K_h = \frac{c(CH_3COOH)\cdot c(OH^-)}{c(CH_3COO^-)}.$$

The degree of hydrolysis is the ratio of the concentration of formula units of salt that have been hydrolysed to the total concentration of the substance. The degree of hydrolysis can be described by the following equation:

$$h = \frac{c_h}{c_{general}}.$$

Formulas for calculating the hydrolysis constant $K_{h.}$ and the pH of hydrolysed salt solutions.

1. Salts formed by a weak base cation and a strong acid anion (e.g. NH_4 Cl):

$$K_h = \frac{K_{H_2O}}{K_{base}},\ h = \sqrt{\frac{K_{H_2O}}{K_{base}\cdot c_{solt}}}, \qquad pH = 7 - \frac{1}{2}pK_{base} - \frac{1}{2}lgc_{solt}.$$

$$[H^+] = \sqrt{\frac{K_{H_2O}\cdot c_{solt}}{K_{base}}} = \sqrt{K_h \cdot c_{solt}}.$$

2. Salts formed by a cation of a strong base and an anion of a weak acid (e.g. CH_3COOH):

$$K_h = \frac{K_{H_2O}}{K_{acid}},\ h = \sqrt{\frac{K_{H_2O}}{K_{acid}\cdot c_{solt}}}, \qquad pH = 7 + \frac{1}{2}pK_{acid} - \frac{1}{2}lgc_{solt}.$$

$$[H^+] = \sqrt{\frac{K_{H_2O}\cdot K_{acid}}{c_{solt}}}.$$

3. Salts formed by a weak base cation and a weak acid anion (e.g. CH_3COONH_4):

$$K_h = \frac{K_{H_2O}}{K_{acid} \cdot K_{base}},\ h = \sqrt{\frac{K_{H_2O}}{K_{acid} \cdot K_{base}}} \qquad [H^+] = \sqrt{\frac{K_{H_2O} \cdot K_{acid}}{K_{base}}},$$

$$pH = 7 + \frac{1}{2} pK_{acid} - \frac{1}{2} lg c_{base}.$$

3. Practical methods of enhancing and weakening hydrolysis. The importance of hydrolysis in analysis.

Hydrolysis phenomena occur in many processes in analytical chemistry and should therefore be taken into account in practical work.

The hydrolysis of salts can be enhanced in this way:

1) by diluting the solution for salts formed by a strong acid and a weak base and for salts formed by a weak base and a strong acid;

2) by increasing the temperature of the solution (boiling), as the *Kw* increases.

$$KCN + H_2O \rightleftharpoons KOH + HCN\uparrow.$$

Boiling the solution will also contribute to the volatility of HCN.

3) removal of hydrolysis products from the solution (hydrolysis products can be removed by binding to other substances).

$$SiO_3^{2-} + H_2O \rightleftharpoons HSiO_3^- + OH^-; \qquad HSiO_3^- + H_2O \rightleftharpoons H_2SiO_3\downarrow + OH^-.$$

The hydrolysis of silicate ion is enhanced by the addition of ammonium ions (mutual enhancement of hydrolysis):

$$SiO_3^{2-} + 2H_2O + NH_4^+ \rightleftharpoons H_2SiO_3\downarrow + 2NH_4OH\uparrow.$$

Removing both reaction products and boiling enhances hydrolysis.

Hydrolysis is often a hindrance in laboratory practice, so in some cases it is attempted to inhibit hydrolysis. Inhibiting hydrolysis by increasing the salt concentration and lowering the temperature is not very effective. The most effective method of hydrolysis inhibition is to add one of the hydrolysis products. This will increase the rate of the reaction reversible to hydrolysis - the formation of salt ions. For example:

1). When Ca^{2+} , Sr^{2+} , Ba^{2+} cations are precipitated with the group reagent ammonium carbonate $(NH_4)_2CO_3$, white precipitates of carbonates $CaCO_3$, $SrCO_3$, $BaCO_3$ are expected to form, but the salt $(NH_4)_2CO_3$ is capable of hydrolysis, which can occur both on the anion and the cation. Since carbonic acid is weaker than ammonium hydroxide, the hydrolysis of carbonate anions will occur to a greater extent than the hydrolysis of ammonium cations.

During the hydrolysis of carbonate anions, HCO_3^- ions are formed :

$CO_3^{2-} + H_2O = HCO_3^- + OH^-$.

Thus, the reaction of the salt medium $(NH_4)_2CO_3$ is weakly alkaline.

If the hydrolysis is not inhibited, then the action of $(NH_4)_2CO_3$ on Ca^{2+}, Sr^{2+}, Ba^{2+} cations will form soluble acid salts $Ca(HCO_3)_2$, $Sr(HCO_3)_2$, $Ba(HCO_3)_2$, so precipitation and separation will not occur. To prevent hydrolysis of the group reagent, ammonium hydroxide NH_4OH is added to the solution. When ammonium hydroxide is added to a solution of ammonium carbonate salt, the equilibrium of carbonate ion hydrolysis shifts to the left and the HCO_3^- anion is converted to the precipitating ion CO_3^{2-}.

2). Similarly to ammonium carbonate, the group reagent ammonium sulfide $(NH_4)_2S$ can hydrolyse by anion during the deposition of Fe^{2+}, Fe^{3+}, Zn^{2+}, Mn^{2+}:

$S^{2-} + HOH = HS^- + OH^-$.

HS^- ions formed as a result of hydrolysis will not precipitate cations. Therefore, the precipitation of ammonium sulfide cations is carried out in the presence of ammonium hydroxide to prevent the hydrolysis of the group reagent salt and to neutralise the acidic environment of the solutions of the salts of the ions of interest, which is formed as a result of the hydrolysis of these salts, for example:

$FeCl_3 + HOH = [FeOH]Cl_2 + HCl$.

3). Under the action of the reagent $(NH_4)_2S$, Al^{3+}, Cr^{3+} cations precipitate as hydroxides, not as sulfides, as other cations of the III analytical group. This is due to the fact that the concentration of OH^- ions formed during the hydrolysis of ammonium sulfide is sufficient to exceed the solubility products of $Cr(OH)_3$ and $Al(OH)_3$ and hydroxides precipitate.

This is not the case with other cations, because their hydroxides are more soluble than sulfides.

$3(NH_4)_2S + 6H_2O = 3H_2S\uparrow + 6NH_4OH$

$Cr_2(SO_4)_3 + 6NH_4OH = 2Cr(OH)_3\downarrow + 3(NH_4)_2SO_4$

or the total equation

$Cr_2(SO_4)_3 + 3(NH_4)_2S + 6H_2O = 2Cr(OH)_3\downarrow + 3(NH_4)_2SO_4 + 3H_2S\uparrow$.

Hydrolysis reactions are used as regulators of the acidity and alkalinity of the solutions to be analysed. To increase the acidity, NH_4Cl is used (for the determination of Al^{3+} cation from alkaline solutions), which hydrolyses to form hydrogen ion:

$NH_4{}^+ + H_2O \rightleftarrows NH_4OH + H^+$.

To reduce the acidity of the detection of potassium^{2+} ions by potassium dichromate, sodium acetate is used, which hydrolyses to form hydroxide ions:

$CH_3COONa + H_2O \rightleftarrows CH_3COOH + NaOH$

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

4. Amphotericity of hydroxides

Electrolytes that can behave as acids and bases depending on the environment are called *amphoteric electrolytes* or *ampholytes*.

The most typical ampholyte is water, which is capable of forming an acid - hydroxonium ion H_3O^+ and a base - hydroxide ion OH^- - upon dissociation:

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

An important class of ampholytes are hydroxides $Al(OH)_3$, $Zn(OH)_2$, $Ga(OH)_3$, $Zn(OH)_3$, $Pb(OH)_2$, $Cr(OH)_3$, $Sb(OH)_3$, $Sn(OH)_2$, $Sn(OH)_4$, $As(OH)_3$, $Be(OH)_2$.

Amphoteric hydroxides have the dual properties of an acid and a base. They are capable of dissociating both as acids and bases:

$R^+ + OH^- \leftrightarrow ROH \leftrightarrow RO^- + H^+$.

In amphoteric hydroxides, the bond between the R^+ ion and Oxygen is as unstable as the bond between Hydrogen and Oxygen. The polarity of these bonds is almost the same.

Let's consider the amphotericity of hydroxides on the example of zinc hydroxide $Zn(OH)_2$.

In a saturated aqueous solution, the following series of equilibria is established:

$ZnO_2^{2-} + H^+ \leftrightarrow Zn(OH)_2 \leftrightarrow Zn^{2+} + 2OH^-$.

With an excess of hydroxide ions, the equilibrium shifts to the left and the solution is dominated by zincate ions ZnO_2^{2-} . The introduction of an excess of hydrogen ions into the solution shifts the equilibrium to the right and leads to the accumulation of Zn^{2+} ions.

So, in acidic solutions, zinc exists as the cation Zn^{2+} , and in alkaline solutions, it is the anion ZnO_2^{2-} .

The zinc hydroxide precipitate is soluble in both acids and alkalis:

$Zn(OH)_2 + H_2SO_4 = ZnSO_4 + H_2O$,

$Zn(OH)_2 + 2KOH = K_2ZnO_2 + H_2O$ (fusion)

$Zn(OH)_2 + 2KOH = K_2[Zn(OH)_4]$ (in solution).

In the analysis, amphotericity is used to separate certain ions from others in a mixture. For example, the separation of group III cations from others in a mixture is performed by adding KOH (alkali). This results in precipitation of hydroxides of cations of the III analytical group ($Al(OH)_3$, $Zn(OH)_2$, $Cr(OH)_3$, $Ni(OH)_2$, $Fe(OH)_3$, $Fe(OH)_2$). Then, under the influence of excess alkali, hydroxides of amphoteric metals (Al, Cr, Zn) dissolve to form $[Al(OH)\ ]_6^{3-}$, $[Cr(OH)\ ]_6^{3-}$, $[Zn(OH)\ ]_4^{2-}$. Hydroxides of other cations of this group remain in the precipitate and can be easily separated from the solution.

Lecture 10

EQUILIBRIUM IN A HETEROGENEOUS SYSTEM OF PRECIPITATE - SATURATED SOLUTION

1. The mechanism of precipitation formation;
2. Equilibria in a heterogeneous system precipitate - saturated solution. The rule of solubility product;
3. Factors affecting the formation of sediments and the completeness of deposition.

1. Mechanism of precipitation formation

The processes of sediment formation and dissolution are of great importance in various fields of chemistry, geology, agrochemistry and other sciences. All previously considered equilibrium processes described equilibria in homogeneous systems. In the course of analysis, more complex heterogeneous or heterogeneous systems consisting of several phases are often encountered. Equilibria in such systems are called heterogeneous equilibria. Examples of heterogeneous equilibria include systems consisting of a gas and a liquid, two immiscible liquids, a precipitate and a saturated solution, a gas and a solid. The **separate parts of a heterogeneous system that are separated by an interface are called its *phases*.** For example, a precipitate and a saturated solution above the precipitate are different phases of a heterogeneous system.

In analytical chemistry, the most commonly used systems for the separation of substances, qualitative detection and quantification are precipitate-saturated solution. Extraction processes or systems of two immiscible liquids and a third substance distributed between them are also widely used.

The ability of substances to precipitate depends on many factors:

1) the nature and concentration of ions;
2) environment (pH);
3) temperature (T);
4) ionic strength of the solution (μ).

The process of sedimentation can be described as follows:

1. Dehydration of ions in solution $Ba(H_2O)_2^+ \rightarrow Ba^{2+} + H_2O$.

2. The formation of primary crystallisation centres (PCC) The formation of molecules does not mean that they crystallise. The formation of a PCC goes through a number of intermediate steps:

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

$BaSO_4 + Ba^{2+} \rightarrow (Ba_2SO_4)^{2+}$;

$(Ba_2SO_4)^{2+} + SO_4^{2-} \rightarrow Ba_2(SO_4)_2$;

$Ba_2(SO_4)_2 + Ba^{2+} \rightarrow (Ba_3(SO_4)_2)^{2+}$.

That is, molecules are combined into groups (10-100).

3. The growth of primary crystallisation centres due to the deposition of more and more ions on them. As a result, large aggregates are formed that have not yet precipitated. This is the colloidal stage.

4. Release of large crystals and precipitation.

2. Equilibria in a heterogeneous system precipitate - saturated solution. The rule of solubility product.

The study of equilibrium in saturated solutions of poorly soluble strong electrolytes (e.g. salts) that dissociate completely makes it possible to determine the conditions for the formation and dissolution of precipitates, as well as to determine the influence of various factors on the formation and dissolution of precipitates.

Let us consider the dissolution of a binary electrolyte, for example, a poorly soluble salt, $BaSO_4$. The ions of this poorly soluble electrolyte form a crystal lattice. The Ba^{2+} and SO_4^{2-} ions that make up the crystals of this salt will be attracted to the dipolar water molecules, gradually detach from the surface of the crystals and pass into solution as hydrated ions. Along with this process, the opposite process will occur, the hydrated ions in the solution will collide with the surface of the precipitate, dehydrate and complete the crystal lattice of the BaSO precipitate.$_4$

According to the law of active masses, the rate of dissolution of a solid is directly proportional to the size of the solid's surface (*P).*

$$\upsilon_1 = \kappa_1 P.$$

The rate of the reversible process depends on the number of Ba^{2+} and SO_4^{2-} ions. If there were no interionic interaction in the solution, the rate of this process would be equal:

$$\upsilon_2 = \kappa_2 [Ba^{2+}]\,[SO_4^{2-}].$$

Taking into account the ionic strength $\upsilon_2 = \kappa_2\, a(Ba^{2+})\; a(SO_4^{2-}).$

The passage of opposite processes leads to a state of dynamic equilibrium

$$BaSO_4\downarrow \rightleftarrows Ba^{2+} + SO_4^{2-}\text{, where } \upsilon_1 = \upsilon_2.$$

During the establishment of dynamic equilibrium, the concentration of hydrated ions in the solution will stop growing and the surface area of the precipitate will stop decreasing.

*A solution that is in equilibrium with the solid phase is called saturated***.**

Let's equalise the speeds of both processes and get

$$\kappa_1 P = \kappa_2\, a(Ba^{2+})\; a(SO_4^{2-}).$$

Taking into account that the surface area of the sediment remains unchanged, we write

$$\kappa_1 P/\kappa_2 = const = a(Ba^{2+})\; a(SO_4^{2-}).$$

The product of the concentrations (activities) of the ions of a poorly soluble electrolyte in its saturated solution at a constant temperature is a constant and is called the solubility product (SP).

$$a(Ba^{2+})\cdot a(SO_4^{2-}) = SP'(BaSO_4) = 1{,}08\cdot 10^{-10}.$$

If some poorly soluble electrolyte dissociates to form two or more identical ions, for example: $Kt_mAn_n \leftrightarrows mKt^{a+} + nAn^{\text{в}-}$,

where *m* and *n are,* respectively, the number of cations and anions formed from one electrolyte particle; *and*$^+$ and c$^-$ are the charges of the cation and anion, then

$$SP\ (Kt_mAn_n) = a^m_{Kt^{a+}}\cdot a^n_{An^{b-}}$$

In other words, when calculating the solubility product, the activity of each ion should be raised to a power equal to the number of identical ions formed during the decay of one particle.

The rule of the product of activities is formulated as follows: **in a saturated solution of a poorly soluble salt, the product of ionic activities at constant temperature and pressure is a constant value.**

It should be noted that the concentration of the solid phase in the solution-precipitate equilibrium state is taken as one.

In the case of very dilute solutions, where the activity coefficient is close to unity, the solubility product can be approximated as the product of the molar concentrations of the ions.

No matter how the concentration of the ions from which a poorly soluble electrolyte is formed changes, the product of the molar concentrations of these ions at $T = const$ is a constant value for a saturated solution of a given poorly soluble substance.

A distinction should be made between the concepts of "poorly soluble" and "poorly dissociated" substance. A substance can be poorly soluble but a strong electrolyte, i.e. the precipitate is an ionic compound. On the other hand, a highly soluble substance can be a weak electrolyte.

For the precipitation of a poorly soluble electrolyte to occur, the product of the molar concentrations of the ion to be precipitated and the precipitating ion must be greater than the solubility product of the poorly soluble electrolyte being formed, i.e., the substance begins to precipitate from a solution that is supersaturated at a given temperature; the precipitating ion must be in excess.

However, when a large excess of precipitating reagent is added, partial or complete dissolution of the precipitate may occur as a result of complexation, amphotericity, formation of colloidal systems, etc.

Thus, the general conditions for the formation and dissolution of sediment can be derived.

- if $\left[Me^{a+}\right]^m \cdot \left[A^{b-}\right]^n > ДР$, then the solution is supersaturated and the precipitate falls out;
- if $\left[Me^{a+}\right]^m \cdot \left[A^{b-}\right]^n = ДР$, then the solution is saturated, the system is in equilibrium;
- if $\left[Me^{a+}\right]^m \cdot \left[A^{b-}\right]^n < ДР$, then the solution is unsaturated, the precipitate dissolves.

Since there are no substances that are completely insoluble in water, the DR is never zero. It follows that any precipitation cannot be completely complete. Some of the ions that are precipitated always remain in solution. Sometimes this part is so small that it does not interfere with any further action. In this case, the precipitation is called **almost complete**.

Deposition is considered almost complete if the concentration of the ion to be deposited does not exceed 1.10^{-5} - 1.10^{-6} mol/dm^3 .

3. Factors affecting the formation of sediments and the completeness of deposition

The value of the solubility product is used not only in solving various issues related to ion precipitation in the form of poorly soluble compounds, but also in determining the conditions for the transfer of poorly soluble precipitates to solution. An important characteristic of poorly soluble compounds is their solubility in various solvents.

For the binary sparingly soluble compound MeA , the solubility is calculated by Eq.

$P_{MeA} = \sqrt{SP_{MeA}}$, for poorly soluble compounds such as Me_mA_n .

$$P_{Me_mA_n} = \sqrt[m+n]{\frac{ДP_{Me_mA_n}}{m^m \cdot n^n}}\ .$$

The formation and completeness of precipitation is significantly affected by temperature, salt effect, ions of the same name, etc.

Effect of temperature. As in homogeneous systems, the effect of temperature on the solubility product is related to the thermal effect of each specific reaction. For most substances, the dissolution process is endothermic, so the solubility product increases with increasing temperature. For those substances for which dissolution is an exothermic process, the dependence of the solubility product on temperature is inverse, i.e., the solubility product of such substances decreases with increasing temperature.

Influence of the ionic strength of the solution. Salt effect. Changes in the ionic strength of a solution in equilibrium with the solid phase can occur when electrolytes are introduced into such a system that are not bound by common ions with the precipitate and do not cause competing reactions in this system.

With the increase of the ionic strength of the solution due to the introduction of a strong electrolyte into the solution above the precipitate (up to a certain limit), the activity coefficients of the ions of the poorly soluble compound will decrease, the concentration of the ions of the poorly soluble compound will increase, while maintaining a constant value of the activity product. This phenomenon is called the salt effect. The salt effect is interpreted as an increase in the solubility of poorly soluble compounds in the presence of strong electrolytes that do not share ions with the precipitate and do not enter into competing reactions.

The influence of ions of the same name. In accordance with the solubility product rule, the precipitate and the solution are in equilibrium: precipitation ↔ dissolution of the precipitate, i.e. the rate of ion precipitation becomes equal to the rate of dissolution. A saturated solution is obtained in which the product of the concentrations of ions of a poorly soluble electrolyte in solution is equal to the product of the solubility of this electrolyte.

If a saturated solution of a poorly soluble electrolyte is added to a solution of another electrolyte containing a common or identical ion, the product of the ion concentrations in the solution will exceed the solubility product, the solution will become supersaturated, and then some of the ions of the poorly soluble electrolyte will pass from the solution to the precipitate. Therefore, the solubility of a poorly soluble electrolyte in a solution containing an ion of the same name as this electrolyte will be lower than in pure water. Consequently, the solubility of electrolytes decreases with the introduction of any strong electrolytes with the same ion into their saturated solution.

If several ions are present in the solution and form poorly soluble compounds with the precipitant, the sequence of their precipitation is determined by the sequence of exceeding the values of their solubility products.

The separation of ions from a mixture into a precipitate when a common precipitant is introduced in a sequence determined by the value of their solubility product is called **fractional precipitation**.

Lecture 11

COMPLEX COMPOUNDS IN THE ANALYSIS

1. Complex compounds. Basic provisions of coordination theory;
2. Classification of complex compounds;
3. Nomenclature of complex compounds;
4. The importance of complex compounds in the analysis.

1. Complex compounds. Basic provisions of coordination theory.

All inorganic compounds are conventionally divided into first-order and higher-order compounds. The first-order compounds include oxides, some acids, salts (CuO, HBr, NaCl, etc.) Higher-order compounds, *complex (coordination) compounds*, are products of the interaction of certain first-order compounds.

Complex compounds are those whose crystal lattice nodes contain complex ions capable of independent existence after the substance has passed into the dissolved or molten state.

Complexus means a combination, a conjunction; a really large number of complex compounds can be obtained during the interaction of substances as a result of a conjugation reaction: $Fe(CN)_2 + 4KCN \rightarrow K_4[Fe(CN)_6]$; $Fe + 5CO \rightarrow [Fe(CO)_5]$.

Another name for complex compounds is coordination compounds, which describes the presence of a coordination sphere in the composition of these substances.

The basic principles of the formation of complex compounds were first outlined in 1893 by the Swiss chemist Werner in the form of the so-called coordination theory. Let us consider the main provisions of the coordination theory.

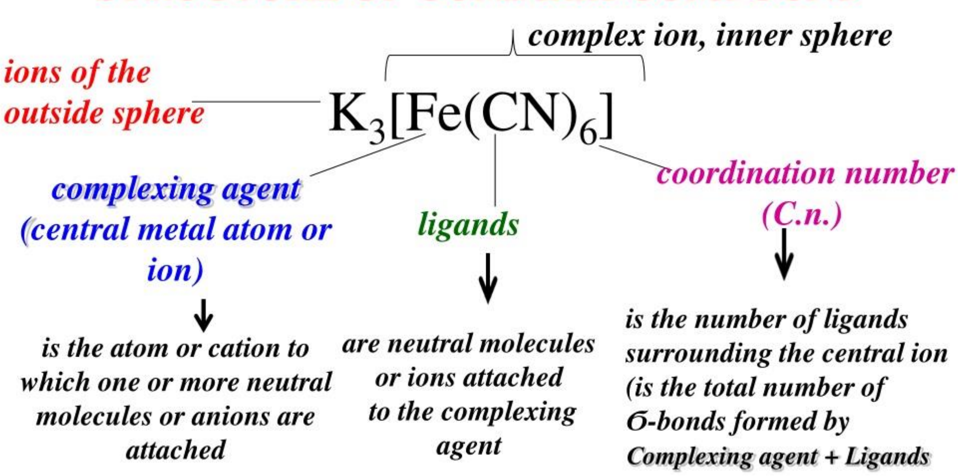
1. In the molecule of any complex compound, one of the ions occupies a central position and is called the complexing agent, or central ion.

2. A number of oppositely charged ions or neutral molecules, called ligands or adends, are arranged or concentrated around the central ion.

3. The central ion with ligands placed around it forms the so-called internal coordination sphere of the compound or complex ion.

4. The number that shows how many ligands are located around the complexing agent in the inner sphere is called the coordination number.

5. Ions located further away from the central ion make up the outer coordination sphere of the complex compound.



Let us consider in more detail the characteristics of the concepts of **complexing agent, coordination number, ligands, and coordination capacity.**

Complexing agent: almost all chemical elements of the periodic table can be represented as a complexing agent (central atom), but the most typical complexing agents are **d-elements**: platinum metals (Pt, Pd), elements of the Ferric family (Fe, Co, Ni), Cu subgroups (Cu, Ag, Au), Zinc subgroups (Zn, Cd, Hg); p-elements: metallic (Al) and non-metallic (B, Si, P), f-elements and even occasionally s-elements, which show the least tendency to complex.

The coordination number (CN) depends on the nature of the complexing agent, its degree of oxidation, the nature of the ligands, etc. The coordination number can vary in different complex compounds from 2 to 8 and higher, but is most often equal to 4 or 6 (Table). The charge of the complexing agent (or the degree of oxidation of the complexing agent) is the main factor affecting the coordination number and often the k.n. is 2 times higher than the oxidation degree of the complexing agent:

Coordination numbers of some complexing agents

Coordination number	Complexing agent	Examples of complex compounds
2	Ag^+ Cu^+ Au^+	$[Ag(NH_3)_2]NO_3$ $[Cu(NH_3)_2]Cl$ $Na[Au(CN)_2]$
4	Cu^{2+} Hg^{2+} B^{3+} Pt^{2+} Co^{2+} Zn^{2+}	$[Cu(NH_3)_4]SO_4$ $[Hg(NH_3)_4](NO_3)_2$ $H[BF_4]$ $K_2[PtCl_4]$ $(NH_4)_2[Co(SCN)_4]$ $Na_2[Zn(OH)_4]$
6	Cr^{3+} Co^{3+} AI^{3+} Pt^{4+} Si^{4+} Fe^{2+} Fe^{3+}	$[Cr(H_2O)_6]Cl_3$ $[Co(NH_3)_6]Br_3$ $Na_3[AlF_6]$ $H_2[PtCl_6]$ $Na_2[SiF_6]$ $K_4[Fe(CN)_6]$ $K_3[Fe(CN)_6]$

The value of the k.n. allows you to assess the spatial structure of the complex, for example:

The value of the k.n.	**2**	**4**	**6**
possible option spatial buildings of the complex	linear, angular	triangular, trigonal pyramid	tetrahedral, flat square

Ligands: ligands can be of ionic or molecular structure.

Coordination capacity (dentativity): according to dentativity, ligands are divided into:

monodentate (F^-, Cl^-, Br^-, I^-, OH^-, CN^-, SCN^-, $S_2O_3^{2-}$, H_2O, NH_3, CO), i.e. those containing only one donor atom and capable of forming a single chemical bond with a complexing agent;

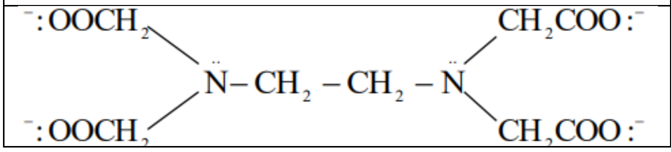
polydentate, i.e., those containing only two or more donor atoms and capable of forming two or more chemical bonds with the complexing agent (dentate 2, 3, 6) (Table).

Other ligands with denticity 2 are: hydrazine $-NH_2-NH_2$, amino acetic acid NH_2-CH_2-COOH, and SO_4^{2-}, CO_3^{2-} ions.

Thus, if the complexing agent coordinates only monodentate ligands around itself, then the k.n. = the sum of the indices near the ligands (in the compound $K_3[Fe(CN)_6]$ k.n.=6, since the ligand CN^- is monodentate; in the compound $K[Al(H_2O)_2(OH)_4]$, the k.n. also = 6, since it contains 6 different monodentate ligands of two types (H_2O and OH^-).

If a complexing agent coordinates polydentate ligands around itself, the k.n. can be defined as the product of the index at the ligand and its denticity (in the compound $K_3[Fe(C_2O_4)_3]$ the k.n. is $3 \cdot 2 = 6$, since the index at the ligand $C_2O_4^{2-}$ is 3 and its denticity is 2.

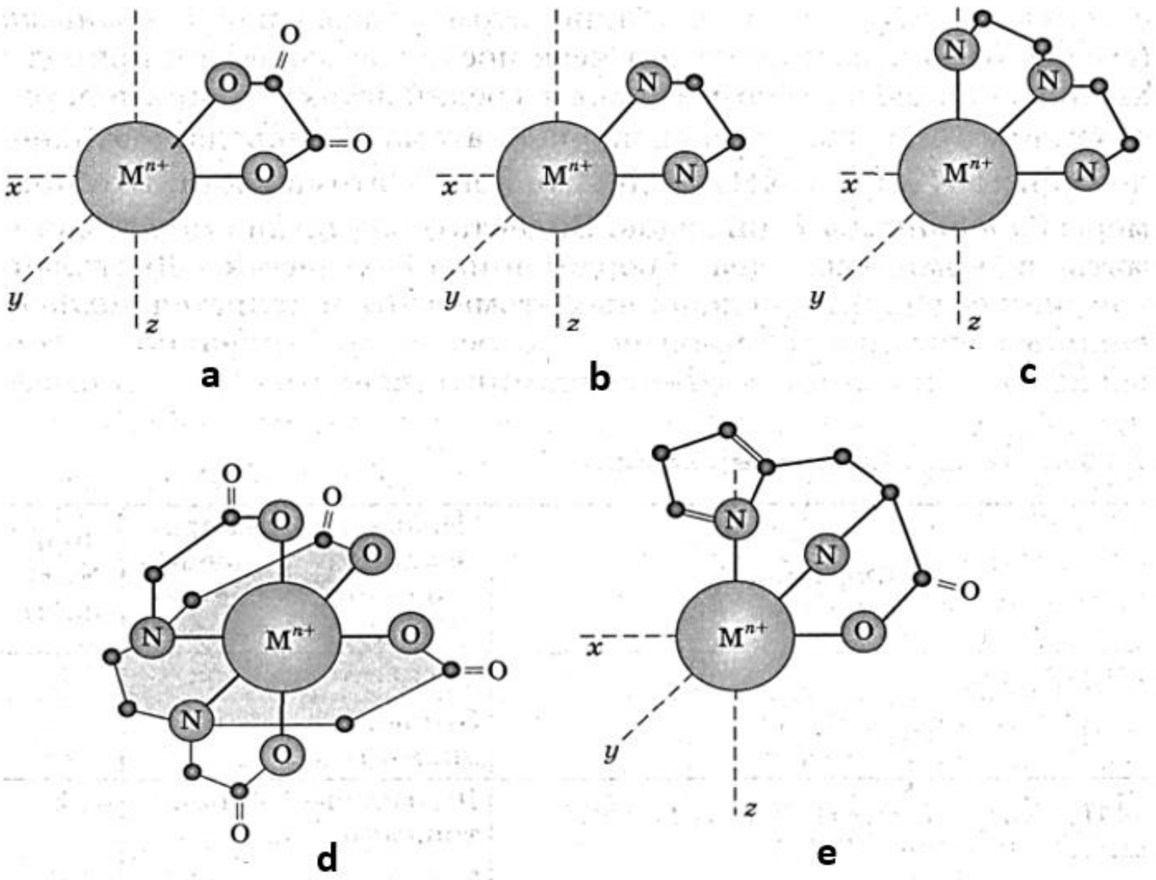
Examples of polydentate ligands

Formula.	Title	Abbreviation	Dentation
$^-:OOC-COO:^-$	oxalate-	ox	2
$\ddot{N}H_2-CH_2-CH_2-\ddot{N}H_2$	Ethylenediamino-	en	2
$\ddot{N}H_2-CH_2-CH_2-\ddot{N}H-CH_2-CH_2-\ddot{N}H_2$	Diethylenediamino -	dien	3
	Ethylenediamine tetraacetato-.	EDTA	6

A significant number of compounds containing polydentate ligands are chelates. Figure shows that bidentate ligands (dentate = 2) combine with the complexing agent in two places at once and capture it like cancer claws, which is the reason for the origin of the name chelates - claw complexes (from the Greek chele - claw).

A special feature of chelates is the formation of cyclic groupings of atoms (chelate cycles) containing a metal atom. Chelating ligands either already have or acquire a geometric shape convenient for coordination during the formation of a complex compound. When the complexing agent interacts with chelates, stronger chemical bonds are formed, which results in the chelating effect.

Chelating effect - increased stability of complex compounds with polydentate ligands.



Configurations of complex ions containing ligands as ligands:
a) oxalate ions - ox, b) ethylenediamine - en, c) diethylenediamine - dien,
d) ethylenediaminetetraacetate ion-EDTA, e) histidineaminoacid anion.

2. Classification of complex compounds

Depending on the charge of the inner sphere, all complex compounds can be divided into three categories.

1. Complex compounds of a cationic nature, in which the complex ion has a positive charge. The role of ligands in these cases is usually played by neutral molecules. For example, $[Cu(NH_3)_4]SO_4$; $[Ca(H_2O)_6]C1_2$. They can be considered as a product of the interaction of such substances:

$CuSO_4 + 4NH_4OH = [Cu(NH_3)_4]SO_4 + 4H_2O$;

$CaC1_2 + 6H_2O = [Ca(H_2O)_6]C1_2$.

In aqueous solutions, such complex compounds dissociate into complex cations and anions of acid residues:

$[Cu(NH_3)]SO_4 \leftrightarrow [Cu(NH_3)_4]^{2}+ + SO_4^{2-}$;

$[Ca(H_2O)_6]C1_2 \leftrightarrow [Ca(H_2O)_6]^{2+} + 2C1^-$.

2. Complex compounds of an anionic nature, the complex ion of which has a negative charge due to the coordination of negative ligands around a positively charged complexing agent, the total charge of which exceeds the charge of the complexing agent by absolute value. For example, $K_2[CuCl_4]$; $Na_3[Co(NO_2)_6]$. They are obtained as follows:

$2KC1 + CuCl_2 = K_2[CuCl_4]$;

$6NaNO_2 + Co(NO_3)_3 = Na_3[Co(NO_2)_6] + 3NaNO_3$.

In aqueous solutions, such complex compounds dissociate into complex anions and cations of the outer sphere:

$K_2[CuCl_4] \leftrightarrow 2K^+ + [CuCl_4]^{2-}$;

$Na_3[Co(NO_2)_6] \leftrightarrow 3Na^+ + [Co(NO_2)_6]^{3-}$.

3. Molecular complex compounds in which the absolute charges of complexing agents and ligands are equal. Such complex compounds are neutral and their aqueous solutions are not electrolytes. For example, $[Cr(H_2O)_3C1_3]$, $[Pt(NH_3)_2Cl_2]$.

Ligands are distinguished by their nature:

1. Aqua complexes: ligands are water molecules, e.g.: $[Cr(H_2O)_6]^{3+}$, $[Cu(H_2O)_4]^{2+}$, $[Be(H_2O)_4]^{2+}$, $[Al(H_2O)_6]^{3+}$.

2. Ammonia cations (amino complexes): ligands are ammonia molecules NH_3, e.g: $[Cu(NH_3)_4]^{2+}$, $[Ag(NH_3)_2]^+$;

3. Carbonyls: ligands are carbon (II) oxide molecules. Almost all carbonyl complexes belong to complex nonelectrolytes, since metal atoms in the zero degree of oxidation play the role of complexing agents, and neutral CO molecules, for example, $[Fe(CO)_5]$, play the role of ligands;

4. Hydroxocomplexes: ligands are hydroxyl ions $OH^–$, e.g: $[Zn(OH)_4]^{2–}$, $[Al(OH)_6]^{3–}$;

5. Acid complex ligands are anions of various acids, for example, oxalate ($C_2O_4^{2–}$), halide ($F^–$, $Cl^–$, $Br^–$, I -), cyanide ($CN^–$), sulfate ($SO_4^{2–}$), etc;

6. Mixed complexes A complex ion contains ligands of different nature, for example: $[Co(NH_3)_4Cl_2]$.

3. Nomenclature of complex compounds.

The main provisions of the modern nomenclature of complex compounds are as follows.

1. In the name of any type of complex compound, the cation is first named, followed by the anion in the nominative case:

a) the name of anionic complexes begins with the characteristic of the outer sphere of the complex compound;

b) for cationic complexes, the names of the ions of the outer sphere are given after the composition of the inner sphere.

2. For all types of complex compounds (cationic, anionic, molecular), a complete description of the inner sphere is given. First of all, the names of the ligand anions are given in alphabetical order, adding the ending -o (F^- - fluoro, $C1^-$ - chloro, CN^- - ciano, OH^- - hydroxo, SO_3^{2-} - sulfito, SCN^- - thiocyanato, SO_4^{2-} - sulfato, $C_2O_4^{2-}$ - oxalato, $P_2O_7^{4-}$ - diphosphato, etc.). The number of ligands is indicated by Greek numeral prefixes: 1-mono, 2-di, 3-tri, 4-tetra, 5-penta, 6-hexa, etc. (the numeral mono is usually omitted).

Ligands are further referred to as neutral molecules: NH_3 - amine, H_2O - aqua, NO - nitrosyl, CO - carbonyl. Other ligands retain their usual names.

3. The latter is called the central atom (complexing agent): a) if the central atom is part of a cation or molecule, use the Latin name of this element and indicate the degree of its oxidation in parentheses after it with Roman numerals; b) if the central atom is part of an anion,

use the Latin name of the element, adding the ending -at, and indicate the degree of its oxidation in parentheses after it with Roman numerals;

c) in the case of molecular complexes, the Latin name of the complexing agent is indicated, but its charge is not indicated.

Below are the formulas and names of complex compounds of various chemical natures.

With a complex cation:

$[Ag(NH_3)_2]NO_3$ - diaminargentum (I) nitrate;

$[Co(H_2O)_6]Br_3$ is hexaaccobalt (III) bromide.

With a complex anion:

$K_3[Fe(CN)_6]$ is potassium hexacyanoferrate (III);

$Na_2[SiF_6]$ - sodium hexafluorosilicate (IV).

A molecular complex:

$[Pt(NH_3)_2Cl_2]$ - dichlorodiamine platinum;

$[Co(H_2O)_4(NO_2)_2]$ is dinitrotetraacquacobalt.

4. The importance of complex compounds in the analysis.

Complex compounds have a wide and diverse range of applications in both qualitative and quantitative analysis.

Complex compounds are used in the practice of qualitative analysis:

1. For the detection of cations and anions. In this case, both complex compounds and complexation reactions are used. For example:

$$2K^+ + Na^+ + [Co(NO_2)_6]^{3-} \rightarrow K_2Na[Co(NO_2)_6]\downarrow$$

$$NH_4^+ + [HgI_4]^{2-} + 4OH^- \rightarrow [Hg_2ONH_2]I\downarrow + 3H_2O + 7I^-$$

$$Fe^{3+} + K^+ + [\overset{+2}{Fe}(CN)_6]^{4-} \rightarrow K\overset{+3}{Fe}[\overset{+2}{Fe}(CN)_6]\downarrow$$

$$Fe^{2+} + K^+ + [\overset{+3}{Fe}(CN)_6]^{3-} \rightarrow K\overset{+3}{Fe}[\overset{+2}{Fe}(CN)_6]\downarrow$$

2. Complexation reactions are also used to bind ions that interfere with the analysis, i.e. to mask ions.

For example, Fe^{2+} ions interfere with the detection of Ni^{2+} ions with dimethylglyoxime, Fe^{3+} ions interfere with the detection of Co^{2+} ions with SCN^-, because the identification of the blue cobalt(II) thiocyanate complex $[Co(SCN)_4]^{2-}$ in the alcohol layer is interfered with by the blood-red colour of the ferrous(III) thiocyanate complex $[Fe(SCN)_3]$.

The masking of Fe^{3+} ions can be achieved by adding orthophosphoric acid (H_3PO_4). Fe^{3+} ions are bound to a strong colourless complex $[Fe(PO_4)_2]^{3-}$. Masking of Fe^{3+} can also be achieved by adding ammonium fluoride. As a result, a strong hexafluoroferrate (III) complex $[FeF_6]^{3-}$ is obtained. Oxalates can also be used to mask Fe^{3+}.

3. The formation of complex compounds is used in the analysis to separate ions. For example, in the systematic analysis of cations according to the acid-base classification, group VI cations are separated from group V by an excess of ammonia solution $NH_3\ H_2O$. This results in the formation of soluble ammonia cations.

4. The formation of complex compounds is used to dissolve precipitates. For example, silver (I) chloride AgCl is insoluble in neither water nor acids, but dissolves well in ammonia solution $NH_3{\cdot}H_2O$ to form the complex compound diaminsilver(I) chloride $[Ag(NH_3)_2]Cl$:

$$AgCl\downarrow + 2NH_3{\cdot}H_2O \rightarrow [Ag(NH_3)_2]Cl + 2H_2O.$$

5. Complexation makes it possible to change the redox properties of a system. For example, Fe^{3+} ions can oxidise $I^–$ to free iodine under normal conditions:

$$2Fe^{3+} + 2I^– \rightarrow 2Fe^{2+} + I_2 .$$

However, in the presence of $F^–$ ions, the complex $[FeF_6]^{3–}$ is formed and the oxidation of $I^–$ to I_2 does not occur, since the oxidative properties of the pair (Fe^{3+}/Fe^{2+}), which are determined by the Nernst equation, are not affected:

$$E(Fe^{3+}/Fe^{2+}) = E^o(Fe/Fe^{3+\,2+}) + 0.059\text{-}lg([Fe^{3+}]/[Fe^{2+}]),$$

ions are sharply reduced due to a decrease in the concentration of Fe^{3+} ions as a result of the complexation reaction.

Lecture 12

SUBJECT AND OBJECTIVES OF QUANTITATIVE ANALYSIS. GRAVIMETRIC METHOD

1. Objectives and methods of quantitative analysis;
2. Processing of chemical analysis results;
3. Classification of gravimetric analysis methods;
4. The main stages of gravimetric analysis;

1. Objectives and methods of quantitative analysis

The subject of quantitative analysis is the study of methods that can be used to determine the quantitative composition of a substance or mixture of substances.

Quantitative analysis determines the quantitative content of chemical elements or their groups in compounds, the amount of a substance in solution, the content of elements in a mixture of substances, or the content of a certain component in ores, minerals, fertilisers, etc.

Quantitative analysis **methods are** divided into chemical and physical-chemical. Sometimes a group of physical methods of quantitative analysis is distinguished.

Chemical methods include gravimetric, titrimetric (volumetric) and gas analyses.

Gravimetric analysis is used to study the amount of a component in compounds or their mixtures by isolating this component in the form of a hardly soluble precipitate, the mass of which is used to calculate the amount of the component under study. Sometimes, the component to be determined is removed by heating and its amount is determined by the decrease in mass of the substance, or the volatile component is captured by a substance that absorbs it.

Titrimetric methods of analysis are based on the measurement of volumes of solutions of two substances that have reacted chemically, and the concentration of one of these solutions must be known with great accuracy. A solution whose concentration is known is called a titrated solution. The moment the reaction is complete is determined by indicators or other methods. Knowing the concentration and volume of the reagent used in the reaction with a known volume of the test solution, the content of the component under investigation is determined.

Gas analysis is based on measuring the volume of gaseous substances under investigation. The volume of the sample is measured either after absorption by solid or liquid absorbers or after combustion of the gas mixture.

Physical methods of analysis are based on the relationship between the physical properties of substances and their chemical composition. For example, if you know the density of a solution of an acid, you can determine its mass fraction in the solution. Physical methods do not involve chemical reactions.

For the quantitative determination of a substance, chemical reactions can be used that change the physical properties of a solution (electrical conductivity, change in the electrode potential of an electrode immersed in a solution, change in the colour of a solution, etc.) Analytical methods based on the observation of physical phenomena that occur during certain chemical reactions are called **physicochemical methods**.

These methods are distinguished by their high sensitivity and speed of analysis.

Physico-chemical methods of analysis are divided into spectral (optical), electrochemical, radiometric, mass spectrometric, and chromatographic.

2. Processing of chemical analysis results

When conducting experimental research, the so-called errors are an indispensable companion of any measurement.

The most common error classification options are as follows:

1) **by the method of calculation** - absolute (for example, standard deviation) and relative (for example, relative standard deviation, percentage error) errors;

2) **depending on the nature of the reasons that cause them** - random, systematic errors and omissions;

3) **by sources of origin** - instrumental, reactive, methodological, sampling errors, etc. (e.g., indicator error, co-precipitation error, etc.);

4) **depending on whether the measurement result is overstated or understated compared to the actual or average value,** they can be divided into positive and negative;

5) **according to the type of relationship between the error and the measured value, a** distinction is made between constant errors, the value of which does not depend on the measured value itself, and proportional errors, the value of which is proportional to the measured value.

During the experimental work, the analytical signal value of each (i-th) sample is measured several times under identical conditions, i.e. *n* parallel measurements. All these data are processed using mathematical statistics methods, which are used to calculate the main characteristics of the sample population using the following formulas.

Average for a sample of n results $$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n} ;$$

Dispersion characterising the scattering of results relative to the average $$V = \frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1} ;$$

Standard deviation $$s = \sqrt{V} = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}} ;$$

Relative standard deviation $$s_r = \frac{s}{\bar{x}} ;$$

The size of the confidence interval $$x - x_{icm.} = \pm \frac{t_{P,f} s}{\sqrt{n}} ,$$

where $t_{,Pf}$ - Student's distribution; *s* - standard deviation of the measured value calculated for a sample set of *n* values (*f* = *n* - 1); *P* - confidence level (usually taken as 0.95) (Table; $x_{icm.}$ - true value of the measured value.

3. Classification of gravimetric analysis methods

Gravimetric analysis *is a* method of quantitative chemical analysis based on the precise measurement of the mass of the substance under study or its constituent parts, which are released in a chemically pure state or in the form of appropriate compounds of a precisely known constant composition.

Often, the substance to be determined is precipitated as a compound of a certain composition. To do this, a suspended mass (weight) of the substance under test is transferred to a solution, and an appropriate reagent is added to the solution, which reacts with one of the components of the mixture under test to form a poorly soluble compound. As a result, a portion of the substance under test (cations or anions) is released from the solution in the form of an almost insoluble precipitate. This precipitate is separated from the solution by filtration or centrifugation, washed to remove all soluble impurities, dried or calcined to a constant weight, and weighed on an analytical balance.

The following methods of gravimetric analysis are available.

Methods of extraction. The component to be determined is quantitatively isolated in the free state from the substance under study and weighed on an analytical balance. An example of such a determination is the determination of the percentage of ash in solid fuels.

Precipitation methods. The component to be determined is quantitatively precipitated by chemical means in the form of a poorly soluble chemical compound of a strictly defined composition. The precipitate is washed, dried, or calcined.

In most cases, the precipitate is converted into a new substance of precisely known composition, which is weighed on an analytical balance. Therefore, there are two forms of the substance to be analysed: the precipitated form, i.e. the form in which the substance to be analysed is precipitated, and the gravimetric form, i.e. the form in which the substance to be analysed is weighed. Sometimes the gravimetric form is called the weighing form. Sometimes the gravimetric form may be the same as the precipitated form. For example, when determining SO_4^{2-} ions by the gravimetric method, they are precipitated with $Ba^{2+\cdot}$ ions. This produces the slightly soluble $BaSO_4$. It is separated from the solution by filtering. Thus, the precipitated form of SO_4^{2-} ions is $BaSO_4$. The $BaSO_4$ precipitate is then dried and calcined. In this case, no changes occur with $BaSO_4$. Annealed $BaSO_4$ is the gravimetric form of SO_4^{2-} ions.

In other gravimetric methods of determination, the precipitated form of a substance differs from the gravimetric form. For example, when determining Fe ions^{3+} we have:

$$2Fe^{3+} \xrightarrow{+6OH^-} 2Fe(OH)_3 \xrightarrow[3H_2O]{t^\circ} Fe_2O_3$$

The deposition and gravimetric mould must meet certain requirements.

Requirements for deposition and gravimetric moulds

№	Deposition mould	Gravimetric mould
1	The precipitate should be practically insoluble (SP $\leq 10^{-8}$)	The composition of the gravimetric mould must exactly match the chemical formula
2	The sediment must occupy a certain volume	The gravimetric mould must be chemically resistant, not reacting with oxygen, carbon dioxide and water
3	The precipitate should be quickly filtered, well washed, and not contaminated - i.e. preferably crystalline	It is convenient to keep the content of the element to be determined in the gravimetric form as small as possible, as this will reduce the error of the experimental result

Distillation methods. In this method, the component to be determined is quantitatively distilled off as a volatile compound. The part to be determined is separated by heating the substance of interest or by exposure to appropriate reagents, which is accompanied by the release of volatile products. Distillation methods are direct and indirect. In the case of direct distillation, the volatile component of interest is absorbed by a specific absorbent and the amount of the component to be determined is calculated from the increase in its mass. For example:

$$CaCO_3 + 2H^+ \rightarrow CO_2\uparrow + Ca^{2+} + H_2O;$$

$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O.$$

In indirect methods of distillation, the mass of the residual substance is determined after complete removal of the substance of interest.

The difference in mass before and after distillation of the substance under test is the amount of the component to be determined. For example, determination of crystallisation water:

$CuSO_4{\cdot}5H_2O \rightarrow CuSO_4 + 5H_2O$.

The advantage of gravimetric methods is their high accuracy. Gravimetric analysis allows determinations to be made with an accuracy of up to 0.005%, which exceeds the accuracy of titrimetric methods. However, a significant disadvantage of gravimetry is the long duration of determinations. If the gravimetric analysis is performed correctly, the determination error is determined by the weighing accuracy. Given the same absolute weighing error, a larger sample of the starting substance gives a higher relative accuracy of the analysis result, expressed as a percentage. The larger the sample weight, the higher the relative accuracy of the analysis results.

4. The main stages of gravimetric analysis

The following stages of gravimetric analysis are distinguished.

1. **Weighing**: The weight of the sample depends on the content of the component to be determined and the structure of the precipitate.

Dependence of the gravimetric shape mass on the nature of the sediment

Sediment structure	**Mass of gravimetric (weight) mould**
Amorphous lightweight	0,07...0,10
Crystal light	0,10...0,30
Crystal heavy	0,30...0,50

To calculate the weight, it is necessary to know the approximate content of the components in the sample of the substance to be analysed or the formula of the substance. The mass of the precipitate should not be too large, as working with such a precipitate is time-consuming and technically difficult. At the same time, the size of the sludge should be sufficient to make it convenient to work with. In addition, very small weights cause significant relative errors during weighing.

In gravimetric analysis, the permissible error in weighing must not exceed 0.1%. The minimum weight that can be weighed on a conventional analytical balance must not be less than 0.1 g. The lower the percentage of the test component in the sample, the greater the weight should be. The accuracy of the sample weight determines the reliability of the analysis results.

Weighing of solids is carried out on a watch glass or in bureks, and weighing of liquids in small flasks (1-2 cm^3), droppers.

Since the deposited form has a different weight from the original sample, it is necessary to calculate the weight of the material to be analysed. The calculation is based on the reaction equation:

$$Ba(NO_3)_2 \quad + \quad H_2SO_4 \quad \rightarrow \quad BaSO_4\downarrow \quad + \quad 2HNO_3$$

If the composition of the deposited form and the gravimetric form are different, the calculation is carried out according to a conversion scheme, for example:

$$2FeSO_4 \quad \rightarrow \quad Fe_2(SO_4)_3 \quad \rightarrow \quad 2Fe(OH)_3\downarrow \quad \rightarrow \quad Fe_2O_3$$

In the case of a series of analyses of the same type, the gravimetric factor (F) is used - the ratio of the molar masses of the substance to be determined and the weight form (taking into account the coefficients in the reaction equation or conversion scheme):

$$F = \frac{2 \cdot M(FeSO_4)}{M(Fe_2O_3)}.$$

From the mass of the gravimetric form $m(Fe_2O_3)$, the mass of the analysed substance can be calculated:

- For amorphous sediments, the mass of the substance to be determined $m = \frac{0{,}1 \cdot F \cdot 100}{W}$;

- for crystalline precipitates $m = \frac{0{,}5 \cdot F \cdot 100}{W}$,

where m is the weight of the substance sample, g; *F is the* gravimetric factor; *W is the* approximate composition of the substance under test, %.

First, the required mass of the substance is weighed on a technical balance with an accuracy of ±0.01 g, which is then adjusted on an analytical balance (with an accuracy of $1 \cdot 10^{-4}$ g).

2. **Dissolve the sample**.

3. **Precipitation.** The correctness and accuracy of the analysis depend on the rational choice of the precipitated form, precipitant, weight form, and precipitation conditions (solution concentration, acidity, temperature, ionic composition of the system, etc.) All of these factors affect the completeness of the precipitation and the purity of the resulting precipitate. In analytical practice, crystalline and amorphous precipitates can be obtained depending on the nature of the substances and the precipitation conditions. In gravimetry, crystalline precipitates are preferred because they are quickly filtered, are not contaminated, are well washed, and do not form colloidal solutions.

Crystalline precipitates should be separated from dilute hot solutions by stirring. As a rule, crystalline precipitates are settled in the solution from which they were precipitated for 4-24 hours, while amorphous precipitates are not settled. For some amorphous precipitates, it is recommended to separate them under conditions of high supersaturation (rapid draining of heated concentrated solutions), followed by immediate dilution of the precipitate system with water to reduce adsorption of impurities.

For the deposition of crystalline and amorphous precipitates, the amount of the precipitant solution should be approximately 1.5 times the calculated amount. An excess of precipitant is required to achieve complete deposition. However, excessive excess of the precipitant can lead to partial dissolution of the precipitate due to complexation and salt effect.

In addition, a large excess of precipitant increases the contamination of the sludge due to co-precipitation.

Further treatment of the sludge is reduced to:

4. **Filtering of the sediment**. In gravimetric analysis, ashless filters are used, which burn almost completely. The mass of ash that remains is 0.00003-0.00007g. For very precise analyses, the ash weight indicated on the filter pack wrapper is taken into account in the calculations. Sometimes, the precipitates are separated from the solution using porous glass filters or special funnels with porous glass plates. Depending on the particle size of the precipitate, paper filters of different porosity levels are used: blue tape for fine-grained precipitates; white tape for medium-grained precipitates; red tape for coarse-grained and amorphous precipitates. The size of the filter is determined by the size of the sediment, not by the volume of the liquid to be filtered. Only one third of the filter should be filled with sludge. The size of the funnel is selected so that the edges of the filter are 0.5-1 cm below the edge of the funnel. When pouring the liquid onto the filter, use a glass rod, but it should not touch the filter.

5. Flushing the **sediment**. Flushing liquids are used to rinse the filter sediments. The washing liquid is selected depending on the properties of the sludge. Most often, distilled water is used, to which a small amount of substances are added to reduce the solubility of the sediment and prevent its dissolution. However, these substances must be easily removed from the sludge when preparing it for weighing. For the determination of cations precipitated as crystalline precipitates, the washing is carried out with dilute solutions of ammonium salts that share a common anion with the precipitate. The ammonium salt remaining in the precipitate after washing is reported during the subsequent calcination of the precipitate.

6. **Converting the precipitate to the desired weight form** by drying in a drying oven ($t = 110\ °C \div 120\ °C$) or calcining in a muffle furnace ($t \geq 800\ °C$). The precipitates are calcined in porcelain, quartz and platinum crucibles. The crucible is thoroughly washed, dried and calcined in a muffle or crucible furnace. The crucible is calcined for 10-15 minutes, removed from the furnace with heated crucible tongs (to prevent the crucible from cracking due to temperature changes) and carefully placed in an exciter to cool. Close the desiccator with a polished glass lid. The dried or calcined gravimetric form of the test substance is weighed on an analytical balance.

Lecture 13

CHEMICAL TITRIMETRIC METHODS OF ANALYSIS

1. Basic concepts of titrimetric analysis;
2. Classification of titrimetric analysis methods and titration techniques;
3. Standard solutions;
4. Indicators;
5. Acid-base titration.

1. Basic concepts of titrimetric analysis

The titrimetric (volumetric) method is a quantitative analysis method based on determining the amount of reagent required to complete the reaction with a given amount of the substance to be determined.

The method consists of gradually adding a solution of a reagent of known concentration to a solution of the substance to be determined. The addition of the reagent is continued until the amount of reagent is equivalent to the amount of the substance to be determined.

A substance of interest is a chemical element, simple or complex, whose content is determined in a given product sample. Not only substances can be determined, but also atoms, ions, bound and free radicals and functional groups.

A reagent is a solid, liquid or gaseous substance that reacts with the substance to be determined.

A reagent is a chemical preparation, which can be a mixture of different substances that contains excipients and solvents along with the reagent.

Titration is the process of continuously controlling the gradual mixing of a precisely measured volume of a reagent standard solution with a solution of the substance to be tested. The amount of reagent corresponds to the content of the component to be determined, which reacts with the reagent in strictly equivalent amounts.

A standard or **titrated** solution (titrant) is a solution of a reagent of a precisely known concentration that is used for titration in titrimetric analysis. For example, if an acid solution is titrated with an alkali solution, the alkali solution is called the titrant, or working solution.

Titration is carried out until the **equivalence point is** reached, the point in the titration process when the amount of titrant added is equivalent to the amount of substance to be analysed. In practice, however, titration is terminated at the end of titration point, which corresponds to a visible change in certain properties of the solution (colour change, turbidity).

2. Classification of titrimetric analysis methods and titration techniques

Neutralisation or acid-base titration **methods are** based on the neutralisation of acids, bases, salts of weak acids or bases that are highly hydrolysed in aqueous solutions, and various inorganic and organic compounds that exhibit acidic or basic properties in non-aqueous solutions.

Oxidation-reduction methods (oxidimetry) are based on the oxidation-reduction reactions of elements that can move from lower oxidation states to higher ones and vice versa.

Precipitation titration methods use reactions that result in the formation of insoluble precipitates.

Complexometric titration is based on the formation of complex compounds, of which the most widely used are the reactions of metal ions with complexes (e.g. EDTA).

Not every chemical reaction can be used in titrimetric analysis, but only those that meet certain requirements:

- the reaction must be quantitative, i.e. its equilibrium constant must be sufficiently large and have a sufficiently high rate;
- the reaction should not be complicated by side effects;
- there must be a reliable way to determine the equivalence point.

The following titration methods can be distinguished.

Direct titration. It involves titrating an exact volume of a solution of the test substance with a working titrated solution, and the test substance reacts directly with the titrant.

For example: $HCl + NaOH \rightarrow NaCl + H_2O$.

Reverse titration (titration by residue). The idea is that an exact volume of a working titrated solution (main working solution) is added to an accurately taken solution of the test substance, which is taken in excess. This excess, which has not reacted with the test substance, is titrated with another titrated solution (auxiliary working solution). Therefore, two working solutions are required for the reverse titration method.

Example: determination of HCl in hydrochloric acid: $HCl + AgNO_3 \rightarrow AgCl\downarrow + HNO_3$.

The unreacted excess $AgNO_3$ is titrated with ammonium rhodanide.

$AgNO_3 + NH_4SCN \rightarrow AgSCN\downarrow + NH_4NO_3$.

Main working solution - $AgNO_3$ solution ; auxiliary working solution - NH_4SCN.

Titration of a substituent (indirect titration). An excess of an auxiliary reagent is added to a solution of the test substance, which reacts with the test substance to form an equivalent amount of a new substance, which is then titrated with the reagent working solution. For example:

$K_2Cr_2O_7 + 6KI + 7H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3I_2 + 4K_2SO_4 + 7H_2O$

$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$

$K_2Cr_2O_7$ - test substance; KI - auxiliary reagent; I_2 - substitute; $Na_2S_2O_3$ - titrant.

3. Standard solutions

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 a fixative and that do not change their concentration over time.

The starting materials for the preparation of primary standards shall meet the following requirements:

- compliance of the actual composition of a substance with its chemical formula;
- solutions must be stable and the concentration of such solutions must not change during storage;
- the starting material must react completely with the working solution according to the reaction equation;
- It is desirable that the starting substances have a high molar equivalent mass. In this case, a sufficiently large sample of the substance must be taken, which reduces the relative error associated with the inaccuracy of the weighing.

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

A standard titre (fixative) is a precise weighing of a dry substance (or a precisely measured volume of a substance solution) sealed in a glass ampoule. Standard titres are made in special laboratories.

Secondary standards (working solutions) are solutions that do not meet any of the above conditions. They are prepared to an approximate concentration and then adjusted to an exact concentration, i.e. standardised to the appropriate primary standard.

The part of the solution that is taken with the pipette is called the **aliquot** or **aliquot.**

Before starting work, the burette and the measuring pipette are thoroughly washed with distilled water, 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 volume of working solution used is calculated from the convergent results. The amount or mass of the substance to be determined is calculated from the volume and the 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 **point at which the** reaction is complete is called the **stoichiometric point** (p.s.). Titrate until a single drop of titrant from the burette causes a colour change in the analysed solution, i.e. the end point of the titration is reached. In this case, equality is established:

$$C_1 \cdot V_1 = C_2 \cdot V_2 ,$$

where C_1 and C_2 are the molar concentrations of the equivalent titrant and solution of the substance to be determined, respectively; V_1 and V_2 are the volumes of titrant and solution of the substance to be determined, respectively.

The titration endpoint can be set:

1) visually - with or without the introduction of an appropriate indicator into the solution;

2) instrumentally - using devices with appropriate detectors.

4. Indicators

Indicators are substances that can be used to determine the end point of a titration with a certain degree of certainty. If the indicator is selected correctly, the equivalence point coincides with the titration end point.

Internal indicators are indicators that remain in the titration solution at all times during the titration process.

External indicators are those that determine the end of a titration by taking a drop of liquid from the solution to be titrated and adding it to an indicator outside the solution of the test substance.

Reversible and irreversible indicators.

An indicator can be a reverse system that changes in one direction or another with a change in a particular physicochemical parameter (substance concentration, solution pH, redox potential, etc.). Such indicators are called **inverse** indicators. They include, for example, acid-base indicators used in the neutralisation method. These indicators are capable of changing their colour almost as many times as desired with a change in pH, depending on the acidic or alkaline reaction of the medium.

Irreversible indicators. With their help, the end point of titration can be observed only once, which is due to an irreversible change in the chemical composition and structure of the indicator. Among such indicators, one should note redox indicators, which are chemically destroyed during the oxidation-reduction process. An example is some organic dyes.

Indicators formed during the titration process. One of the substances involved in the reaction or formed during the titration process plays the role of an indicator. An example is the titration of reducing agents with permanganate, an excess of which indicates the end of the titration by changing the colour of the titration solution.

Depending on the type of reaction used for titration, indicators are divided into the following groups:

Acid-base indicators. They react to changes in the pH of a solution. They are used in neutralisation and colourimetric methods to determine the pH of the medium. Example: phenolphthalein, methyl orange, methyl red, etc.

Redox (red-ox) indicators. They respond to changes in the redox potential of the system. Examples: diphenylamine, azo dyes, etc.

Complexometric indicators. They react to changes in pKt. Examples: black T eryochrome, xylenol orange, etc.

Adsorption indicators. They respond to changes in the concentration of ions that precipitate as poorly soluble compounds. Examples: fluorescein, eosin.

Other types of indicators: radioactive, chemiluminescent, fluorescent (luminescent), etc. **Radioactive** isotopes are used to study the processes of deposition, extraction, chromatographic separation, distillation, dissolution, adsorption, etc.

The action of **chemiluminescent** indicators is based on the appearance or disappearance of visible light emission in the process of redox reactions at certain pH values of the medium. Example: luminol, siloxane, etc.

Fluorescent indicators, when illuminated with UV light during the titration process at a certain pH of the solution, cause a change in fluorescence colour that is independent of the colour or transparency of the solution being titrated. Examples: rhodamine 6G, eosin, resofurin, quinine, rivanol, etc.

5. Acid-base titration

As the name implies, the method is based on the titration of bases with acids or vice versa. In the simplest case, when strong bases interact with strong acids, the analytical reaction is as follows:

$$H^+ + OH^- = H_2O$$

However, the capabilities of the method are much broader and extend to the determination of weak acids and bases as well as salts that are hydrolysed. In the latter case, the titration is possible because the hydrolysis results in the presence of a free acid or base in the solution. By neutralising them, we shift the hydrolysis equilibrium to the right until the salt is completely decomposed. In this case, the amount of titrant used is equivalent to the amount of salt taken for analysis.

Most often, the equivalence point is determined using *indicators* - various organic substances that are acids and change colour depending on the *pH of the* solution. However, there are indicators that have amphoteric or basic properties.

The properties of acid indicators can be explained by considering the following equilibrium:

$$HInd \leftrightarrow H^+ + Ind^-.$$

In this case, the molecular (acidic) form of HInd differs in colour from the ionic (salt) form of Ind^- . By creating an acidic environment, we shift the equilibrium to the left (for phenolphthalein, HInd is colourless), and by adding alkali to the right (for phenolphthalein, Ind^- is coloured red).

Ampholyte-type indicators, as well as basic indicators, are characterised by the presence of the -NH amino group$_2$. In this case, the colour change of the indicators is due to a shift in equilibrium:

$$R–NH_2 + H^+ \leftrightarrow R–NH_3^+.$$

If the dissociation constant is known, the conditions under which the indicator changes colour can be calculated. Let's show this on the example of methyl orange (m.o.), for which the dissociation constant is approximately equal:

$$K_{інд} = \frac{[H^+]\cdot[Ind^-]}{[HInd]} = 10^{-4}$$

Since the molecular form of the m.o. is coloured red and the ionic form is coloured yellow, you can write it down:

$$\frac{[H^+]\cdot C_{ж}}{C_{чер}} = 10^{-4} \quad \text{or} \quad \frac{\cdot C_{чер}}{C_{ж}} = \frac{[H^+]}{10^{-4}}$$

It is the ratio of these colours that determines the overall colour in visual perception.

The table below shows how the colours change from one to another with the concentration of hydrogen ions.

$[H^+]$, mol/l	$\frac{C_{чер}}{C_{ж}} = \frac{[H^+]}{10^{-4}}$	Colour of the solution
10^{-1}	$\frac{10^{-1}}{10^{-4}} = 1000:1$	red
10^{-2}	$\frac{10^{-2}}{10^{-4}} = 100:1$	red
10^{-3}	$\frac{10^{-3}}{10^{-4}} = 10:1$	red with an orange tint
10^{-4}	$\frac{10^{-4}}{10^{-4}} = 1:1$	orange
10^{-5}	$\frac{10^{-5}}{10^{-4}} = 1:10$	yellow with an orange tint
10^{-6} and beyond	$\frac{10^{-6}}{10^{-4}} = 1:100$	yellow

It can be seen from the previous section that for m.o., and this also applies to other acid-base indicators, the colour of the indicator changes quite sharply with a gradual change in the *pH of the* solution. This interval is called the transition interval of the indicator. Based on the example above, we can say that it is

$pH = pK_{інд} \pm 1$; i.e., for methylorange it is 3-5.

Transition intervals for some of the most commonly used indicators in the analysis

indicator	Transition interval	pT	Colours.
Timolsinium	1-3	2	red-yellow
Methyl orange	3-5	4	red-yellow
Methyl red	4-6	5	red-yellow
Litmus	6-8	7	red-blue
Phenolphthalein	8-10	9	colourless red
Thymolphthalein	9-11	10	colourless blue

However, in volumetric analysis, the titration value *pT is more commonly* used rather than the transition interval. *pT* is the *pH* value of a solution at which the most dramatic change in colour occurs. The *pT value is* used to determine the *pH of the* end of the titration. *pT* values are close to $pK_{інд}$, and they are in the middle of the transition interval.

Titration curves are a graphical representation of the change in *pH of a* solution as working solution is gradually added to a specific volume of the solution to be analysed. They give an indication of how sharply the pH of a solution changes near the equivalence point.

Consider the construction of a titration curve in the case of titration of a strong acid with a strong base. *pH of the* solution is calculated using the following formulas: $pH = -\lg C_{HCl}$; $pH = -\lg C_{NaOH}$; $pH = 14 - pH$. For the titration, 0.1 n of HCl solution was taken. The change in *pH* due to dilution of the titration solution is neglected.

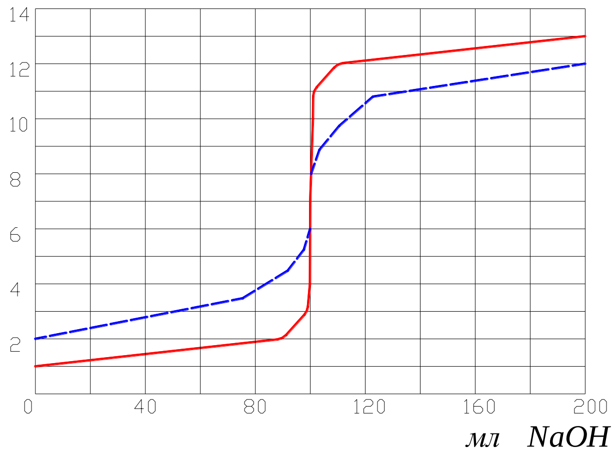
It is clear that when titrating more dilute solutions with a titrant of a lower concentration, the corresponding curve will be shorter (blue line in Fig. 1).

The titration curve of a weak acid with a strong base will look like the one shown in Fig. 2. The lower part of the curve looks like this because the reaction produces a buffer mixture CH_3 COOH- CH_3 COONa, which loses its effect only in the presence of excess alkali.

When titrating alkalis (weak bases) with strong acids, the corresponding curves are inverted.

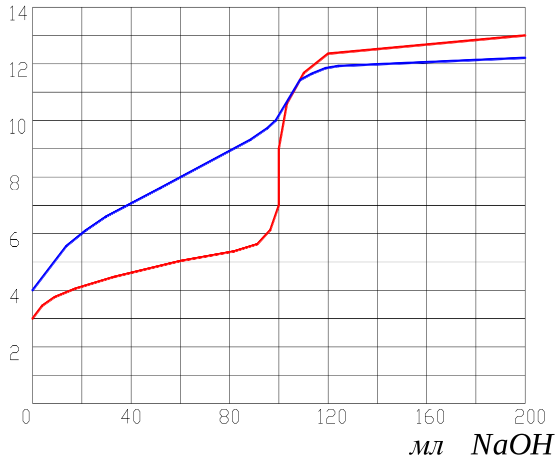
Data for plotting the titration curve of a strong acid with a strong base

Add 0.1 n NaOH solution, ml	Electrolyte that determines the *pH of a* solution	*pH*
0	0.1 n HCl	1
90,0	0.01 n HCl	2
99,0	0.001 n HCl	3
99,9	0.0001 n HCl	4
100,0	NaCl	7
100,1	0.0001 n NaCl	10
101,0	0.001 n NaCl	11
110,0	0.01 n NaCl	12
200	0.1 n NaCl	13



0.1 n HCl 0.01 n HCl

Figure 1. Titration curves of a strong acids with a strong base.



H_3 BO_4 0.01n CH_3 COOH

Figure 2. Titration curves of weak acids (CH_3 COOH and H_3 BO_3) with a strong base (NaOH)

The main rule when choosing the most suitable indicator for titration is that the *pT of the* indicator should be either as close as possible to the equivalence point (which is the inflection point on the titration curve) or at least the transition interval of the indicator should be on a steep part of the curve.

For example, in the first case (Fig. 1), the best indicator is neutral red or litmus (*pH=7)*. With a small error, however, methyl orange (*pH=4)* and phenolphthalein (*pH=9) can also be* used, but in no case should thymol blue (*pH=2)* or thymolphthalein (*pH=10) be used*, because their transition interval does not capture the steep part of the curve.

Lecture 14

REDOX TITRATION METHODS

1. General characteristics of redoxmetry;
2. Indicators of redoxmetry;
3. Methods of redox titrimetry.

1. General characteristics of redoxmetry

Redox titration or redox **methods are** based on oxidation-reduction reactions between a standard and a substance of interest.

Redox reactions are reactions that are accompanied by a change in the oxidation state of the atoms that make up the reacting substances.

Oxidation is the process of an atom, molecule or ion giving up electrons. The atoms, molecules or ions that give up electrons are called reducing agents (Red_1), and during this process they are oxidised to Ox_1 .

Reduction is the process of an atom, molecule or ion donating electrons. The atoms, molecules or ions that donate electrons are called oxidising agents (Ox_2), and as a result they are reduced to Red_2 . Each redox reaction can be described as the sum of two half-reactions - the oxidation of a reducing agent and the reduction of an oxidising agent:

$Red_1 - ne = Ox_1$ - oxidation of the reducing agent

$Ox_2 + ne = Red_2$ - reduction of the oxidant.

Thus, two redox pairs are involved in redox reactions: $Ox_2 \mid Red_1$ and $Ox_1 \mid Red_2$.

Redox titration methods include those methods whose final stages are completed by oxidation-reduction reactions.

All redox methods are classified according to the nature of the basic titrant used in a particular titration application. If the titrant is an oxidising agent, the group of redox methods is called **oxidimetry**; if the titrant is a reducing agent, the methods are called reduction.

Oxidimetry is a method for determining reducing agents by titrating them with standard oxidant solutions. Such methods include permanganate determination, iodometry, bromatometry, chromatometry and others.

Reductometry is a method for determining oxidants by titrating them with standard reductant solutions. For example, iodometry, ascorbinometry, ferrometry, etc.

Standard oxidant and reducing agent solutions can also be used to determine substances that do not have redox properties but precipitate as insoluble compounds when exposed to oxidants or reducing agents. The determination of such substances is based on their preliminary precipitation and subsequent titration of the ions bound to the precipitate or the excess oxidant or reducing agent that did not react. An example of this is the determination of calcium lactate or calcium gluconate by the permanganate method.

Redox titration processes can be represented graphically as a titration curve, which shows the change in the redox potential E of the solution to be titrated as a standard (titrated) solution of an oxidising agent or reducing agent is added to it.

The change in the concentration of the reacting components and the dependent change in potential during redox titration can be studied experimentally and, in some cases, calculated on the basis of the Nerst formula.

In the case of an experimental determination, a platinum electrode is immersed in the solution to be titrated and connected to a normal hydrogen electrode via a salt bridge. The volume of the titrant is measured using a burette, and the redox potential of the E system is measured using a potentiometer connected to the hydrogen bridge$_x$. The graphical dependence based on these data is the titration curve of this oxidimetric method.

Let's explain the calculation method of constructing titration curves using the example of titration of iron (II) with vanadate. Schematically, this process looks like this:

$$Fe^{+2} + V^{+5} = Fe^{+3} + V^{+4}$$

The values of the corresponding normal redox potentials are as follows:

$$E^{I}_{0Fe^{+3}/Fe^{+2}} = 0{,}77\ \text{B} \qquad E^{II}_{0V^{+5}/V^{+4}} = 1{,}20\ \text{B}$$

At the very beginning of the titration, the solution has a high concentration of Fe^{+2} , so the system potential will be low (Table). According to the Nernst formula,

$$E_x^{I} = 0.77 + 0.059\lg[Fe^{+3}]/[Fe]^{+2}$$

with increasing [Fe^{+2}], the potential will gradually increase (positions 2-6 of the table). Near the equivalence point (7), as in the acid-base titration, the concentration change becomes more abrupt because the addition of a small amount of V^{+5} leads to the oxidation of the Fe^{+2} residue and a sharp increase in the [Fe^{+3}]/[Fe^{+2}] ratio.

Titration of 100 mL of 0.1 n $FeSO_4$ in 10 n H_2SO_4 with NH_4VO_3

№	Add 0.1 n of NH_4VO_3, ml	Ion concentration ratios that determine the potential of the system	Potential $E_x^{II} = E_0^{II} + 0.059\lg[V^{+5}]/[V^{+4}]$, V
1*	0	$[Fe^{+3}]/[Fe^{+2}] = 0.01/100 = 10^{-4}$	$0.77 + 0.059\cdot\lg10^{-4} = 0.53$
2	1	$[Fe^{+3}]/[Fe^{+2}] = 1/100 = 10^{-2}$	$0.77 + 0.059\cdot\lg10^{-2} = 0.65$
3	9	$[Fe^{+3}]/[Fe^{+2}] = 9/91 = 10^{-1}$	$0.77 + 0.059\cdot\lg10^{-1} = 0.71$
4	50	$[Fe^{+3}]/[Fe^{+2}] = 50/50 = 1$	$0.77 + 0.059\cdot\lg1 = 0.577$
5	91	$[Fe^{+3}]/[Fe^{+2}] = 91/9 = 10$	$0.77 + 0.059\cdot\lg10 = 0.83$
6	99	$[Fe^{+3}]/[Fe^{+2}] = 99/1 = 10^{2}$	$0.77 + 0.059\cdot\lg10^{2} = 0.89$
7**	100	$[V^{+5}]/[V^{+4}] = [Fe^{+2}]/[Fe^{+3}]$	$\frac{E_0^{I} + E_0^{II}}{2} = \frac{0.77+1.20}{2} = 0.99$
8	101	$[V^{+5}]/[V^{+4}] = 1/100 = 10^{-2}$	$1.20 + 0.059\cdot\lg10^{-2} = 1.08$
9	110	$[V^{+5}]/[V^{+4}] = 10/110 = 10^{-1}$	$1.20 + 0.059\cdot\lg10^{-1} = 1.14$
10	200	$[V^{+5}]/[V^{+4}] = 100/100 = 1$	$1.20 + 0.059\cdot\lg1 = 1.20$

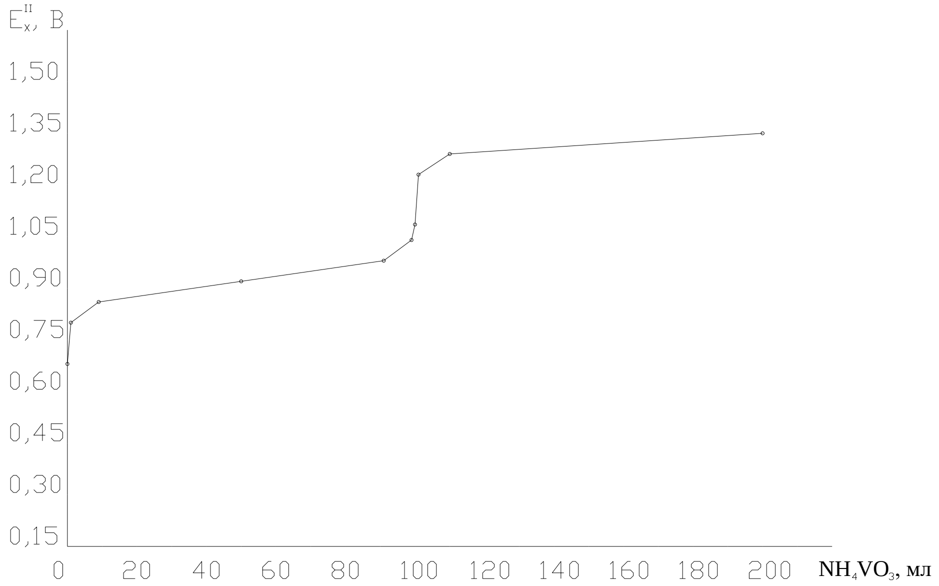
*At the beginning of the titration, it is conventionally assumed that the solution of Ferric (II) salt contains 0.01% of Iron (III). **Equivalence point.

After the equivalence point, the potential continues to change, first more sharply (position 8), then less and less (9, 10). This is due to the fact that at first there is a noticeable excess of V^{+5} , so over a small range of titrant volume increase, the ratio $[V^{+5}]/[V^{+4}]$ increases, which leads to an increase in the potential

$$E_x^{II} = E_0^{II} + 0.059\lg[V^{+5}]/[V^{+4}].$$

Further addition of excess V^{+5} solution does not lead to a rapid increase in potential.

The figure shows a redoxometry titration curve based on the data in the table. It is characterised by a noticeable jump in the redox potential of the system. This allows, firstly, to conclude that this method can be used in practice, and secondly, to select an indicator suitable for its implementation.



Titration curve of $FeSO_4$ in 10 n H_2SO_4 with NH_4VO_3 solution.

2. Redoxmetry indicators

Similarly to acid-base indicators, the best redox indicators should be substances whose redox potential and colour change near the equivalence point. Such indicators are known. However, most of these indicators have significant drawbacks. For example, the potential of the indicator changes not only depending on the potential of the system (which would be ideal), but also on the pH of the solution. Sometimes the colour change is rather slow or various intermediate compounds are formed. Therefore, many oxidimetric methods use specific reagents as indicators. In these cases, at the end of the titration, a change in colour (most often the appearance or disappearance of colour) occurs due to an excess of working solution. For example, in the case of titration of iron (III) with the reducing agent $TiCl_3$ in the presence of rhodanide, the disappearance of Fe^{+3} in the solution leads to the disappearance of the red colour of the solution:

$Fe^{3+} + 3SCN^- = Fe(SCN)_3$ red colour

$Fe^{3+} + Ti^{3+} = Fe^{2+} + Ti^{4+}$.

The group of specific indicators includes $KMnO_4$ in permanganate determination and starch in iodometry. Specific indicators are used only in this method and are not suitable for other titrations.

Indicators that change their colour depending on the redox potential of the solution are characterised by the equilibrium of the oxidised form (Ind_{ox}) and the reduced form (Ind_{red}), which have different colours

$$Ind_{ox} + n \leftrightarrow Ind_{red} .$$

Before titration, a small amount of indicator is added to the solution, while a significant amount of reagents (the substance to be measured and the products of reaction with the working solution) is present in the solution. Thus, the redox potential of the solution is determined by these substances, and depending on it, the above equilibrium state of the indicator changes. It is important that the redox potential is as close to the equivalence point as possible, or at least falls on the vertical part of the titration curve. For example, for the above-described titration of iron (II) with ammonium vanadate, phenylanthrapenic acid (a diphenylamine derivative) is most suitable, with a redox potential of +1.08 V. The reduced form of this indicator is colourless, while the oxidised form is red-purple. Other indicators of this type include diphenylamine ($E_{інд}$ = 0.76 V), variamine blue ($E_{інд}$ = 0.6 V), methyl blue ($E_{інд}$ = 0.53 V), and others.

3. Methods of redox titrimetry

Depending on the reaction used, redox titrimetry methods are divided into permanganate titrimetry, chromatometry, iodometry, cerimetry, and others.

Permanganatometry. In permanganate determination, 0.05; 0.1 n solutions of $KMnO_4$ are used as titrant (working solution). The solutions are standardised after preparation and settling (10 days) according to $Na_2C_2O_4$ or $H_2C_2O_4 \cdot 2H_2O$ (primary standard):

$2MnO_4^{-}+5C_2O_4^{2-}+16H^{+}=2Mn^{2+}+10CO_2+8H_2O$.

MnO_4^{-} ionsare a strong oxidising agent. Oxidation can be carried out in acidic, neutral or alkaline environments. In a strongly acidic solution, manganese(VII) in the composition of $KMnO_4$ is reduced to Mn^{2+} :

$MnO_4^{-} + 8H^{+} + 5e = Mn^{2+} + 4H_2O$.

The molar mass of the potassium permanganate equivalent is:

M_E (1/5 $KMnO_4$) = M($KMnO_4$)/5 = 158.03/5 = 31.61 g.

During oxidation in a neutral or alkaline environment, the manganese(VII) ion is reduced to the manganese(IV) ion, and a brown precipitate $MnO(OH)_2$ is formed :

$MnO_4^{-} + 3H_2O + 3e = MnO(OH)_2 \downarrow + 4OH^{-}$.

Thus, the molar mass of the potassium permanganate equivalent is equal to: M_E (1/3$KMnO_4$) = M($KMnO_4$)/3 = 158.03/3 = 52.68 g.

The standard vapour potential E°(MnO_4^{-} /Mn^{2+})= +1.51 V is higher than E°(MnO_4^{-} /MnO_2) = +0.59 V. This means that the oxidising ability of permanganate in an acidic environment is much higher than in an alkaline environment. In addition, during titration in an acidic environment, almost colourless Mn^{2+} ions are formed, and in an alkaline environment, a dark brown precipitate interferes with the fixation of the stoichiometric point. Therefore, in titrimetry, $KMnO_4$ is used as an oxidising agent mainly in acidic environments. Indicators are not used, as the stoichiometric point can be determined by the colour change of the potassium permanganate itself. Most determinations are carried out in the presence of 1 M H_2SO_4 . In the presence of hydrochloric acid (or chlorides), oxidation of chloride ions by permanganate is possible. To reduce the effect of conjugate oxidation of chloride ions, add salts of Mn^{2+} . Nitric acid is not suitable as it can also cause a number of side effects.

Chromatometry. In chromatometry, 0.05 and 0.1 n of $K_2Cr_2O_7$ are used as working solutions. $K_2Cr_2O_7$ is the primary standard, so its working solutions are not standardised. The standard vapour potential E°($Cr_2O_4^{2-}$ /$2Cr^{3+}$)= +1.35 V, i.e. the oxidising capacity of $Cr_2O_7^{2-}$ is slightly lower than that of MnO_4^-, but it is used to determine only reducing agents.

$Cr_2O_7^{2-} + 6e + 14H^+ = 2Cr^{3+} + 7H_2O$.

Chromatometric indicators are diphenylamine and phenylanthranilic acid.

Iodometry. Working solutions in iodometry I_2, $Na_2S_2O_3$. The solution I_2 is standardised using a titrated solution of $Na_2S_2O_3$.: $I_2 + 2\ S_2O_3.^{2-} = 2I^- + S_4O_6^{2-}$.

The $Na_2S_2O_3$ solution is standardised using the primary standard $K_2Cr_2O_7$:

$Cr_2O_7^{2-} + 6I^- + 14H^+ = Cr^{3+} + 3I_2 + 7H_2O$;

$I_2 + 2\ S_2O_3^{2-} = 2I^- + S_4O_6^{2-}$.

The standard potential of the pair E°(I_2 /$2I^-$)= +0.53 V, which indicates that the oxidative properties of I_2 are much weaker. However, I^- ions exhibit a significant reducing ability. Therefore, this system can be used to determine both oxidants and reducing agents.

In iodometry, a specific indicator is used for I_2 - starch, which is added at the end of the titration when the solution turns straw yellow, as large amounts of iodine destroy starch. The $Na_2S_2O_3$ iodine titration is performed in the cold, as heating can lead to partial loss of iodine due to evaporation, and heating also reduces the sensitivity of the iodine-starch reaction.

Iodometry can be used to determine the following substances:

- reducing agents: As (III), Sb (III), Sn (II), H_2 S, they are titrated directly with I_2 .
- oxidants are determined by substitutional titration - add KI, I_2 formed, titrate $Na_2S_2O_3$.
- organic substances are determined by reverse titration: formaldehyde, sugars, acetone, alcohols, etc.

The determination is carried out in an alkaline solution, the excess I_2 is titrated after acidification.

Lecture 15

PRECIPITATION AND COMPLEXOMETRIC METHODS OF TITRIMETRIC ANALYSIS

1. General characteristics of deposition methods;
2. Argentometry;
3. Application of complexes in analysis;
4. Indicators of complexometry;
5. Selection of conditions for titration of metal ions.

1. 1. General characteristics of deposition methods

Titrimetric methods of precipitation are based on the use of reactions in titration that are accompanied by the formation of poorly soluble compounds.

An equivalent amount of precipitant in the form of a standard solution is added to the solution of the test substance.

The reactions in a precipitation titration must meet the following requirements:

- the resulting precipitate should be practically insoluble (*SP≤10-10-10-12)*;

- the deposition reaction must be fast, quantitative, stoichiometric, and without the formation of supersaturated solutions;

- no co-precipitation reactions should occur during the deposition process.

Near the equivalence point, add the titrant slowly and stir the solution vigorously to eliminate the effects of adsorption.

Precipitation reactions are rarely used for direct titration. During precipitation, adsorption of the working solution is often observed, which interferes with the accurate determination of the equivalence point. Precipitation interferes with the observation of the colour of the indicator.

Among the titrimetric methods of deposition, the most important are argentometry, rhodanometry, and mercurometry. The most commonly used methods are titration with argentium salts (argentometry) and radonium salts (radonometry). These methods make it possible to determine the content of halide ions and some other anions. They also make it possible to determine the content of argentium in its minerals and alloys.

In precipitation titration methods, reagent indicators and adsorption indicators are used to determine the end point of titration: precipitating indicators (K_2CrO_4); adsorbed on the precipitate (fluorescein, eosin); complexing indicators (e.g: $Fe^{3+} + SCN^{-} \rightarrow [Fe(SCN)]^{2+}$ (red)).

Indicator reagents, like determinants, react with the titrant to form precipitates or soluble coloured compounds that are different in colour from the basic precipitate or solution. In addition to colour, the precipitate must have a greater solubility than the parent precipitate.

The following techniques are used in precipitation titration methods:

1. Titration without indicator (Gay-Lussac method);
2. Titration with indicators
    2.1. Titration with reagent indicators (Mohr's method, Folgard's method);
    2.2. Titration with adsorption indicators (with fluorescein and eosin).

2. Argentometry

The method is based on the use of a standard solution of argentium nitrate as a precipitant: $Ag^+ + An^- \rightarrow AgAn\downarrow$

The method is used primarily for the quantitative determination of halide ions, but also for the determination of Argentum ions. In this case, the working solution is a titrated NaCl or KCl solution. If the working solution is $AgNO_3$ solution, then this solution is used with a concentration of c = 0.1 mol/dm^3 or c = 0.05 mol/dm^3. $AgNO_3$ solution is a secondary standard solution (it is not prepared by weight, because crystalline $AgNO_3$ does not meet the requirements for primary standards). The working solution is standardised against chemically pure NaCl and KCl. $AgNO_3$ decomposes under the influence of light.

Mohr's method. The titrant of the method is a solution of $AgNO_3$, c = 0.05 mol/dm^3 or c = 0.1 mol/dm^3 . The indicator is a solution of K_2CrO_4 . Its use is based on the fact that during the titration of chloride ions in the presence of CrO_4^{2-}, Cl^- ions will be precipitated first. $SP(AgCl)=1.78\text{-}10^{-10}$, $S(AgCl)=1.2\text{-}10^{-5}$ mol/dm^3. After the complete precipitation of chloride ions, an excess drop of $AgNO_3$ solution causes the formation of a brick-red precipitate Ag_2CrO_4. $SP(Ag_2 CrO_4)=2.1\cdot10^{-12}$; $S(Ag_2 CrO_4) = 8.1\cdot10^{-5}$ mol/dm^3 .

Mohr's method has a number of significant drawbacks:

1. This method is only applicable for the determination of chlorides and bromides and is not suitable for the determination of iodides and rhodanides, as colloidal systems are formed during the titration process and adsorbed by the side I ons, making it impossible to establish the endpoint of the titration.

2. The method should not be used in acidic and strongly alkaline environments. In an acidic environment, chromate turns into dichromate, which forms a red precipitate from Ag^+ that dissolves in acid. In a strongly alkaline solution, Ag_2O and AgOH are formed. Therefore, the pH of the medium during titration should be at least 6.5 and not more than 10. In the presence of ammonium salts, the pH of the solution should be 6.5-7.2.

3. Hg^{2+} , Pb^{2+} , Ba^{2+} and other ions that form chromate precipitates with chromate ions interfere with the Mohr method.

4. The Mohr method cannot be used to titrate coloured solutions that mask the colour of argentium chromate at the equivalence point.

5. Anions (S^{2-}, PO_4^{3-} , CO_3^{2-}, $C_2O_4^{2-}$, etc.) interfere with the Mohr titration method, forming poorly soluble compounds with argentum ions.

6. This method has a significant indicator error because the solution is deliberately overtitrated.

Fayans-Khodakov method. The method is based on the direct titration of halides with a standard solution of $AgNO_3$ in the presence of adsorption indicators such as fluorescein, eosin, etc. The anions of these indicators are adsorbed on the surface of the formed Argentum halide precipitates near the equivalence point, which leads to a change in the colour of the titrated mixture and allows the end point of titration to be recorded.

Titration of chlorides in the presence of fluorescein is carried out in a neutral medium. At low pH values, fluorescein, being a HInd acid, dissociates weakly, the concentration of Ind- is insignificant, and they cause the colour. In an alkaline environment, Ag_2O is precipitated. When using the eosin indicator, it is titrated in a slightly acidic medium.

Folgard's method. Sometimes it is necessary to determine the concentration of chlorides in acidic solutions. In this case, the titration is carried out using the residue method (reverse titration). This method is called the Folgard method or rhodanometry.

A fixed excess of argentum nitrate is added to the solution to be analysed

$AgNO_3$+NaCl = AgCl + $NaNO_3$ + $AgNO_{3(excess)}$; $Ag^+_{(eq.+excess)}$ + Cl^- = AgCl + $Ag^+_{(excess)}$.

The excess amount of argentium ions is titrated with a second working solution, namely potassium rhodanide. The following reaction occurs:

$AgNO_{3(excess)}$ + NH_4SCN = AgSCN + NH_4NO_3; $Ag^+_{(excess)}$ + SCN^- = AgSCN.

As an indicator, a solution of Fe^{3+} is used, which is prepared using nitrate or iron alum. After the equivalence point, an excess of rhodanide ions appears, which form a red-coloured complex with Fe^{3+}.

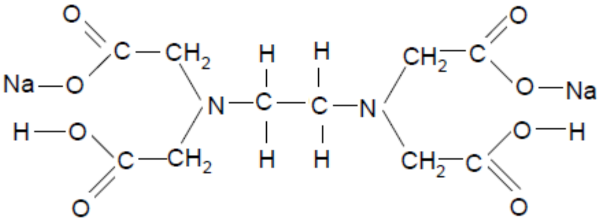
Titration of the residue of argentium nitrate with rhodanide in the presence of argentium chloride precipitate causes some difficulties. Comparison of the corresponding solubility products $SP_{AgCl} = 10^{-12}$ shows that excess rhodanide can react with AgCl precipitate, albeit slowly. Therefore, in particularly precise analyses, the precipitate is filtered off before titration.

3. Application of complexes in analysis

Since the mid-1950s, a new group of organic reagents has been widely used in chemical analysis, often referred to as complexes.

Complexes are derivatives of iminodiacetic acid: HOOC-CH_2-NH-CH_2-COOH.

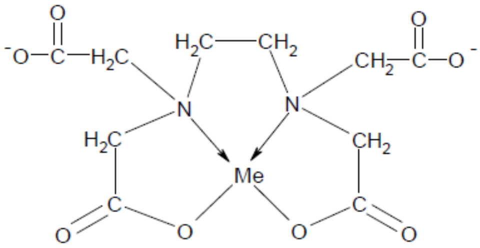
The most interesting and promising compounds of this type are organic compounds that form water-soluble complexes with ions of most metals, which are used in the method of complexometric titration. The branch of titrimetry in which complexes are used as titrants is called complexometry (chelatometry). The most widely studied is the use of ethylenediaminotetraacetic acid (abbreviated as EDTA) and its derivatives. The free acid is poorly soluble in water, so its dinitrium salt, called complexon (III) or trilon B, is usually used (hence the term trilonometry):



Schematically, the molecule of trilon B is denoted as Na_2H_2Y.

Many metal ions are capable of replacing hydrogen atoms of EDTA carboxyl groups by the acid-base mechanism, while simultaneously forming a coordination bond with the nitrogen of the amino group by the donor-acceptor mechanism. As a result, rather stable compounds containing several five-membered cycles are formed.

The structure of a complex with metal ions can be schematically represented as follows:



It is important that EDTA complexes with elements of group II A (except beryllium), aluminium, ferrum, cuprum, rare earth metals, zirconium and many other elements are very stable. It is especially important that complexes with a wide variety of metals always form under certain conditions with a melt stoichiometry, in which the ratio of metal to ligand is 1:1.

By the 1970s, methods for determining almost all metals using EDTA and other complexes had been developed.

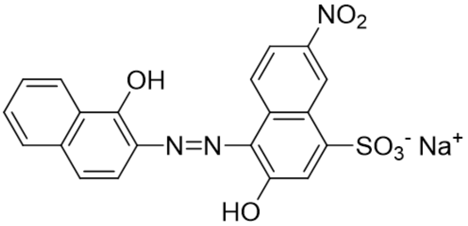
Complexon III meets the requirements for a standard substance. Therefore, its working solution can be prepared by weight. To calculate it, it is convenient to use the gross formula $C_{10}H_{14}O_8N_2Na_2 \cdot 2H_2O$, where the molar mass of the equivalent is half the molar mass of the compound.

4. Indicators of complexometry

There are two groups of complexometry indicators.

A. Specific indicators that react with a particular metal. For example, Fe^{3+} can be titrated with EDTA at pH = 2 using reagents that form coloured compounds with Fe^{3+} (salicylates, rhodanides, etc.) as an indicator.

B. Metal-chromium indicators are organic substances that have their own colour and form coloured compounds with metals. The principle of their operation will be shown by the example of the most common indicator - eryochrome black T. The formula is shown in the figure.



In the range of pH = 7-12 in aqueous solution, it has a blue colour. Complexes with metals (Me) are coloured red. The following processes occur during titration. Eryochrome black, an azo dye with two phenolic groups in the specified pH range, can be represented as HR^{2-}, reacts with a two-charged metal cation:

$$\underset{\text{blue}}{HR^{2-}} + \underset{\text{colourless}}{Me^{2+}} = \underset{\text{red}}{MeHR}.$$

When EDTA solution is added during titration, it forms a more stable complex with the metal, displacing the metal from its compound with the indicator:

$$\underset{\text{red}}{MeHR} + \underset{\text{colourless}}{\text{ЕДТА}} = \underset{\text{colourless}}{\text{MeЕДТА}} + \underset{\text{blue}}{HR^{2-}} + 2H^+.$$

Therefore, the titration should be carried out until the solution turns blue.

Other metallochromic indicators include murexide, pyrocatechin, and xelenol orange. They allow titration in all environments - from strongly acidic (xelenol orange) to strongly alkaline (murexide).

5. Selection of conditions for titration of metal ions

There are numerous methods for titrating almost all metals that form complexes with EDTA. However, for their titration, appropriate conditions must be selected. For example,

Zr^{4+}, Bi^{3+} and other highly charged ions form complexes and are titrated in an acidic environment. Zn^{2+}, Ni^{2+}, Pb^{2+} and other two-charged ions form less stable complexes and are titrated in a slightly alkaline environment. Even less stable complexes are formed by alkaline earth metals and magnesium, which titrate in an alkaline medium.

Therefore, the binding of the metal to the complex increases with increasing pH. However, do not increase the pH too much, as metal hydroxide will precipitate before the titration begins. On the other hand, it is important to keep in mind that the indicator should form a complex with the metal in question at the selected pH, but not too strong - no stronger than the metal's complex with EDTA. Otherwise, the indicator is "blocked" and will not change colour near the equivalence point.

From the above, it is possible to determine several cations in their joint presence by adjusting the acidity of the solution. For example, Zr^{4+} can be titrated in the presence of almost all elements in 2H hydrochloric acid; Fe^{3+}, Bi^{3+}, Th^{4+} - at pH = 2-3 in the presence of any divalent elements; zinc, silicon, lead, etc. - at pH = 7 in the presence of calcium and magnesium, etc.

The fact that the solubility of magnesium hydroxide is quite low is used to titrate Ca^{2+} and Mg^{2+} in a mixture. The Mg^{2+} complex with EDTA is decomposed by a caustic alkali, releasing magnesium hydroxide, while the Ca^{2+} complex with EDTA is stable under these conditions. It is therefore important to proceed, for example, as follows. At pH = 10 (in ammonia buffer), titrate the total of calcium and magnesium. Add a caustic alkali (no carbonates!) to the rest of the sample solution and titrate the calcium after the magnesium hydroxide has precipitated.

Another possibility to determine cations in their joint presence is to use masking agents. The essence of this titration method is that one or a group of metals bind to complexes that are stronger than those with EDTA. For example, Al and Ti, which interfere with the titration of rare earth metals, can be masked by binding them to a strong complex with pyrocatechin. REEs, as well as indium and lead, can be titrated in the presence of zinc, copper, cadmium, cobalt and other metals if these metals are bound into strong complexes with potassium cyanide. The titration of zinc, cadmium, etc. is interfered with by mercury (II), but it can be easily masked with iodine.

Sometimes another masking technique is used. For example, in a mixture of zinc and cadmium, the sum of the metals is first titrated. Then sodium diethyldithiocarbonate is added. It does not destroy the zinc complex with EDTA, but completely destroys the cadmium complex with EDTA, transferring Cd to a precipitate - cadmium diethyldithiocarbonate. As a result, EDTA is released in an amount equivalent to cadmium, which is titrated, for example, with a working solution of zinc salt.

Finally, in addition to adjusting the acidity of the medium and masking, the usual methods of separating ions that interfere with precipitation or extraction are of course used.

Due to the large number of masking agents, extractants, and the ability to manoeuvre the pH of the medium, the number of methods for the complexometric determination of metal cations in various combinations is very large. They have been developed for almost all metals.

Lecture 16

ELECTROCHEMICAL METHODS OF ANALYSIS

1. Characteristics of physicochemical methods of analysis;
2. Conductometry;
3. Potentiometry;
4. Voltammetry.

1. Characterisation of physical and chemical methods of analysis

Physico-chemical, or instrumental, methods of analysis are based on the measurement of certain physical properties and system parameters that occur or change during the course of an analytical reaction using instruments (tools).

The rapid development of physicochemical methods of analysis is due to the fact that classical methods of chemical analysis - gravimetry, titrimetry - are unable to meet the numerous requirements of industries such as chemical, pharmaceutical, metallurgical, semiconductor, nuclear, etc., which require an increase in the sensitivity of methods up to 10 -10^{-8-9} %, their selectivity and expressiveness. This makes it possible to control the technological process based on chemical analysis data, as well as to perform it automatically and remotely.

A number of modern physicochemical methods of analysis allow both qualitative and quantitative analysis of components in the same aqueous sample. The accuracy of modern physicochemical methods is comparable to that of classical methods, and in some cases, such as coulometry, is significantly higher.

Compared to classical methods, physicochemical or instrumental methods of analysis have a number of advantages: high sensitivity, selectivity, expressivity, objectivity, and the ability to automate and computerise the analysis process.

The disadvantages of some physicochemical methods of analysis include the high cost of the instruments used and the need to use standards. Therefore, classical methods of analysis have not lost their importance and are used where there are no restrictions on the speed of analysis, where high accuracy is required with a high content of analysis

Classification of physical and chemical methods of analysis. The classification of physico-chemical methods of analysis is based on the nature of the measured physical parameter of the analyte, the value of which is a function of the amount of the substance. Accordingly, all physicochemical methods are divided into three large groups: - electrochemical; - optical; - chromatographic.

Electrochemical methods of analysis are based on the dependence of electrical parameters: current, voltage, equilibrium electrode potentials, electrical conductivity, amount of electricity - on the concentration of the substance under study in solution.

Optical methods of analysis are based on measuring parameters that characterise the interaction of electromagnetic radiation with substances: the radiation intensity of excited atoms, the absorption of monochromatic radiation, the refractive index of light, the angle of rotation of the plane of a polarised light beam, etc. All of these parameters are a function of the concentration of the substance in the analysed object.

Chromatographic techniques are methods for separating homogeneous multicomponent mixtures into their individual components by sorption under dynamic conditions. In these conditions, the components of the mixture are distributed between two phases - mobile and stationary. The separation of components is based on the difference in their partition coefficients between the mobile and stationary phases, which leads to different rates of transfer of these components from the stationary phase to the mobile phase. Once the mixture is separated, the components are identified and determined by various analytical methods.

2. Conductometry

In accordance with IUPAC recommendations, all electrochemical methods of analysis are divided into two broad groups:

- methods without electrochemical reactions on the electrodes of the electrochemical cell: conductometry using low (50-10000 Hz) and high frequency currents (more than 1 MHz);
- methods for monitoring electrochemical reactions at the electrodes of an electrochemical cell: potentiometry (in the absence of current), coulometry and voltammetry (under the influence of current).

Conductometry (conductometric method of analysis) is based on the dependence of the electrical conductivity of electrolyte solutions on their concentration.

Under the influence of an external electric field, electrolyte ions move in a directed manner in a solution and determine the electrical conductivity of the solution. The electrical conductivity of a solution *L is caused by the* dissociation of the dissolved substance and the migration of ions as a result of an external voltage source. Both types of ions - cations and anions - participate in the electrical conductivity of solutions, moving in opposite directions in an electric field because they have opposite charges. Ions moving in a solution are inhibited by solvent molecules and oppositely charged ions surrounding them. This results in the electrical resistance of the electrolyte solution *R*.

The inverse of electrical resistance, *L, is* called electrical conductivity:

$$L = 1/R.$$

The unit of measurement for electrical conductivity is the siemens (S):

$$1\ \mathrm{S} = 1\ \mathrm{ohm}^{-1}\ .$$

The inverse of the resistivity is called the specific electrical conductivity (χ):

$$\chi = 1/\rho.$$

The unit of measurement for χ is $\mathrm{S \cdot cm^{-1}}$.

In the conductometric method of analysis, the measured value is the specific electrical conductivity, as this parameter is directly related to the concentration in the solution by the following relationship:

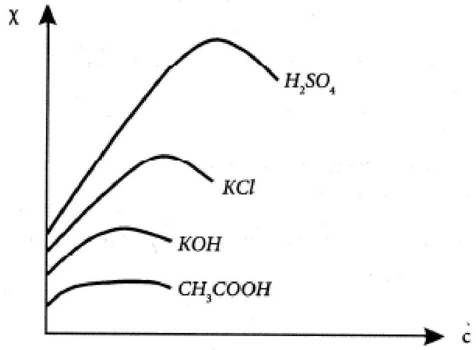
$$\chi = \sum \frac{u_i \cdot F \cdot c_i}{1000},$$

where and_i is the absolute mobility of the i-th ion, i.e. the speed of movement of the ion in an electric field at a voltage of 1 V/cm;

F is the Faraday number, *F* = 96500 Kl/mol;

c - concentration of the i-th ion, $\mathrm{mol/dm^3}$.

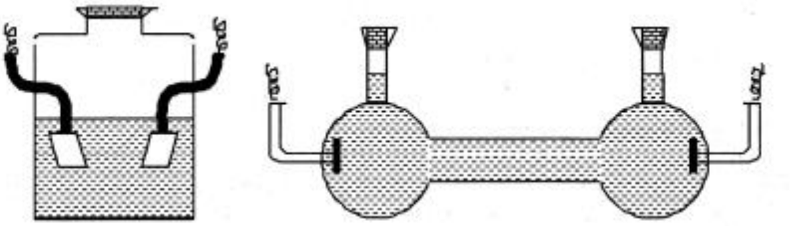
The specific electrical conductivity of electrolytes increases with the concentration of the solution up to a certain limit, passes through the maximum and begins to decrease. This is due to the fact that with increasing concentration, interionic interaction increases and the degree of ionisation of weak electrolytes decreases. The influence of these effects on the electrical conductivity becomes stronger than the overall increase in the concentration of ions in the solution, which leads to a decrease in the specific electrical conductivity of electrolyte solutions. The figure shows examples of the dependence of χ on the concentration of *c*.



Dependence of the specific electrical conductivity χ on the solution concentration *c*.

In conductometric analysis, only the concentration region where there is a linear relationship between the concentration and the electrical conductivity of the solution is used.

The electrical conductivity of electrolyte solutions is measured in conductometric cells, which are glass vessels with rigidly fixed electrodes, mostly made of platinum. The designs of the most common conductometric cells are shown in the figure.



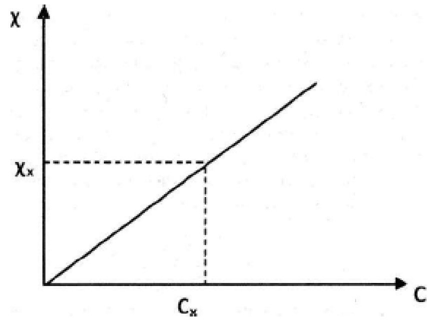
Design of conductometric cells.

Devices for measuring electrical conductivity are called conductometers. The electrical resistance measurement in conductometers is carried out using an AC electrical bridge. A number of conductometers have a digital scale that is graduated directly in units of specific electrical conductivity, while others measure the electrical resistance *R of the* solution being analysed.

There are two types of conductometric analysis methods:

- direct conductometry;
- conductometric titration.

Direct conductometry. The direct conductometry method is based on the direct determination of the concentration of an electrolyte solution from the measured value of the specific electrical conductivity χ. For this purpose, a prepared calibration graph of the dependence of the specific electrical conductivity of the analysed electrolyte solution on the concentration is used. Standard solutions of the electrolyte in question are used to construct the graph. Measurement of the specific electrical conductivity of an electrolyte with an unknown concentration is carried out under the same conditions as when the calibration curve is drawn. An example of concentration determination is shown in the figure.

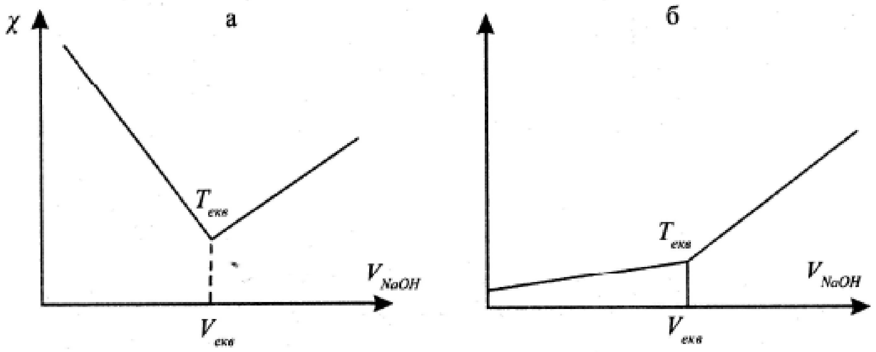


Graduation chart for conductometric determination of solution concentration.

Due to its non-selectivity, the direct conductometry method is used only for the analysis of single-component electrolyte solutions. For example, this method is used to assess the quality of distilled water, process water in pharmaceutical production, and in water purification and treatment technologies by measuring the total electrical conductivity of the analysed solution.

Conductometric titration. In the conductometric titration method, the equivalence point is determined by a sharp change in the specific electrical conductivity of the solution. This method is used only if the electrical conductivity of the solution to be titrated is significantly different from that of the titrant or reaction products.

Conductometric determination of the equivalence point is used for acid-base, precipitation, and compleximetric titrations. But it is mainly used in acid-base and precipitation titrations. In conductometric titration, the titrant is added in small portions, preferably in equal amounts, and the specific electrical conductivity χ is measured after each addition. Based on the data obtained, a titration curve is plotted in the coordinates: χ - V titrant. The equivalence point is determined at the intersection of straight lines corresponding to the change in the specific electrical conductivity of the solution before and after the equivalence point. Typical conductometric titration curves are shown in the figure.



Conductometric titration curves: a - strong acid titration; b - weak acid titration.

Conductometric titration has a number of advantages over direct conductometry: high selectivity, the ability to titrate acid or base mixtures in a differentiated manner, and the ability to titrate turbid and coloured solutions.

3. Potentiometry

Potentiometry, or the method of potentiometric analysis, is based on the use of the dependence of the electromotive force (EMF) of an electrochemical circuit on the activity (concentration) of the analysed ion.

The dependence of the electromotive force, denoted by *E, of* an electrochemical chain on the activity (concentration) of the ion under analysis is described by the Nernst equation:

$$E = E^0 + \frac{S}{n}\lg a,$$

where $E°$ is the standard emf of the circuit, V;

n is the charge of the analysed ion with the corresponding sign;

S is the steepness of the electrode function of the indicator electrode, selective to a single-charge ion;

a - activity of the analysed ion.

For potentiometric measurements, electrochemical circuits containing two electrodes are used: an indicator electrode and a reference electrode. If both electrodes are immersed in the analysed solution, the circuit is called a circuit without , transfer. If the reference electrode is connected to the analysed solution via a salt bridge, the circuit is called a transfer circuit.

In potentiometric analysis, a transfer circle is mainly used. This is represented schematically as follows:

indicator electrode | analyzed solution | salt bridge | reference electrode

An indicator electrode is an electrode whose potential determines the activity of the analysed ion according to the Nernst equation. A reference electrode is an electrode whose potential is constant and does not depend on the concentration of the ions being analysed. The salt bridge is used to prevent mixing of the test solution and the reference electrode solution. Saturated salt solutions with similar cation and anion mobility values are used as a salt bridge: KCl, KNO_3 , etc.

Two types of indicator electrodes are used in potentiometric analysis:

- electrodes on the surface of which electron exchange reactions take place, they are called electron exchange or redox electrodes. Such electrodes are made of chemically inert metals: platinum, gold, etc. In analytical practice, a commercially available platinum spot electrode, EPV-1-100, is used. Nowadays, a membrane redox electrode is made of special glass;
- electrodes on the surface of which ion exchange reactions take place. They are called ion exchange or ion selective electrodes. The main element of ion-selective electrodes is an ion-sensitive membrane, which is why they are also sometimes called membrane electrodes.

Depending on the type of membrane, ion-selective electrodes are divided into:

- electrodes with solid membranes
- electrodes with glass membranes;
- electrodes with liquid membranes.

When measuring the emf of electrochemical circuits used in potentiometry, very low currents (10^{-13} - 10^{-14} A) must be measured to avoid causing electrode polarisation. This is only possible when using the compensation method of EMF measurement. Nowadays, the industry produces special devices for this purpose: pH meters and ionometers.

Potentiometric analysis methods are divided into two types:

- direct potentiometry or ionometry
- Potentiometric titration.

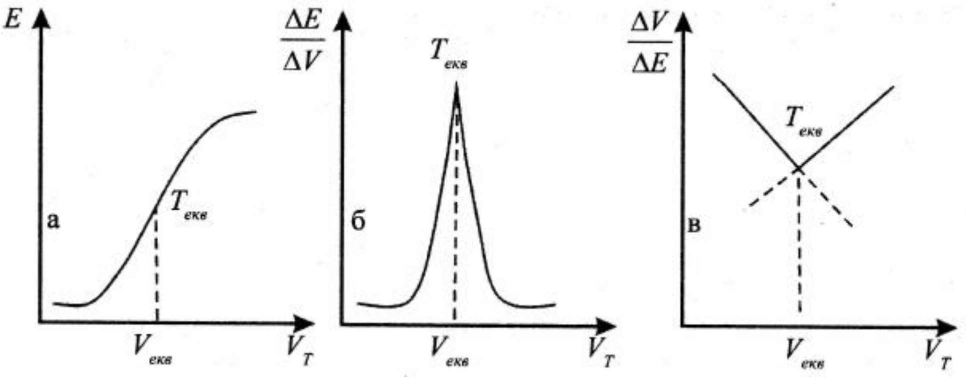
Direct potentiometry. The direct potentiometry method is based on determining the concentration of the analysed ion directly from the measured emf of the electrochemical circuit containing the corresponding ion-selective electrode. The method is used by the calibration graph method or the addition method.

The method of the graduation graph. This method is used to plot a calibration graph in coordinates in advance: EMF - lg c using standard solutions of the analysed ion having the same ionic strength. Then, at the same ionic strength, the EMF of the chain with the analysed solution is measured and the concentration of the solution is determined from the graph.

Additive method. This is a group of methods based on the introduction of an additive solution of the analysed ion with a known concentration into the analysed solution, followed by the measurement of the system's EMF. The additive can be a single additive - the single additive method; a double additive - the double additive method; a multiple additive - the multiple additive method. The concentration of the analysed ion is calculated using a specific formula.

Potentiometric titration. The potentiometric titration method is based on the determination of the equivalence point by a sharp change in the emf in an electrochemical circuit containing an indicator electrode. A sharp change in the ion concentration at the equivalence point results in a sharp change in the emf. It follows that the indicator electrode must be selective to the ions to be determined or to one of the titrant ions. For example, in acid-base titrations, an ion-selective electrode (glass electrode) can be used as an indicator electrode; in argentometric titrations, an electrode selective to argentum or to the corresponding halide ion can be used. For redox titrations, use a redox electrode capable of responding to changes in the redox potential of the system being titrated, such as a platinum electrode.

The equivalence point in potentiometric titration is determined graphically from the titration curve. Typically, one of the following types of titration curves is used: integral, differential or Gran's curve, as shown in the figure.



Potentiometric titration curves: a - integral titration curve; b - differential titration curve; c - Gran titration curve.

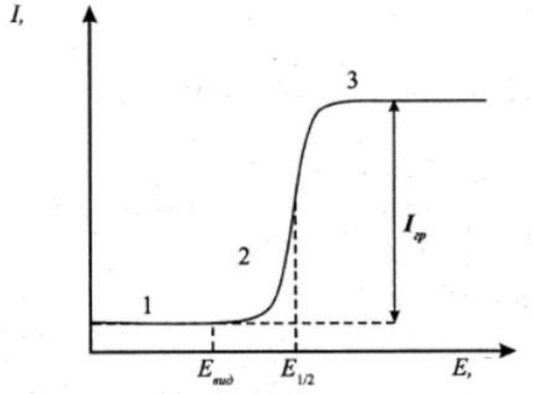
The potentiometric titration method is more accurate than ionometry. Its capabilities have been greatly expanded with the development of new ion-selective electrodes as indicator electrodes. The method is used for the analysis of turbid, contaminated and coloured solutions in mixed and non-aqueous solvents.

4. Voltammetry

Voltammetry is a group of electrochemical methods of analysis based on the electrolysis of a component of interest (electrowinning or electrooxidation) under certain conditions and the subsequent study of the resulting dependence of the current on the voltage applied to the electrodes.

An electrolyser in voltammetry contains two electrodes with very different surface sizes. The working electrode, on which the oxidation or reduction processes take place, is called a microelectrode and has a very small surface S - about 0.01-0.03 cm^2 . The second electrode has a surface hundreds of times larger and is called a macroelectrode. When the current I flows through the cell, its density on the microelectrode, i.e. the I/S ratio, is hundreds of times greater than on the macroelectrode. Therefore, the microelectrode is strongly polarised, and as a result, the processes of electrowinning or electrooxidation occur at a high rate.

The graphical relationship between voltage and current is called a voltammetric curve, or polarogram. A typical view of it is shown in the figure.



Voltammetric curve (polarogram).

Plot 1 on the polarogram is called the residual current. Its value is of the order of 10^{-7} A and is caused by the processes of restoring traces of impurities in the solution, plot 2 on the polarogram is the diffusion current plot, and plot 3 is the limiting diffusion current plot.

The potential $E_{1/2}$ is called the half-wave potential. Its value does not depend on the concentration of the analysed component, but is determined only by its nature.

Voltammetric analysis methods are divided into two types:

- polarography;
- Polarographic or amperometric titration.

An important advantage of polarography compared to other electrochemical methods of analysis is the ability to use it for both qualitative and quantitative analysis. In this case, regardless of the type of analysis, it is mandatory to obtain a polarogram of the solution to be analysed.

Qualitative analysis. One of the parameters of the polarogram, the half-wave potential ($E_{1/2}$), is only a function of the nature of the ion being reduced or oxidised on the microelectrode. Therefore, this value can be used for its identification, i.e. for the purposes of qualitative analysis by the polarographic method. The number of half-waves in the polarogram indicates the number of different ions in the solution. For most ions, the half-wave potentials in some solutions are known. Therefore, qualitative analysis can be easily performed with this method.

Quantitative analysis. The value of the limiting diffusion current I_{dif} is a function of the concentration of the ion being reduced or oxidised on the mercury droplet electrode. This dependence is described by the Ilkovich equation:

$$I_{\text{dif}} = Kc,$$

where K *is a* constant, and c *is the* concentration of the ion to be analysed. The constant K is usually determined from the polarogram of standard solutions.

The calibration graph method, the addition method and the comparison method with standard solutions are commonly used for quantitative analysis.

Lecture 17

OPTICAL METHODS OF ANALYSIS

1. Classification of optical analysis methods;
2. Refractometry;
3. Molecular adsorption analysis.

1. Classification of optical analysis methods

Optical methods of analysis are based on the interaction of substances with electromagnetic radiation.

The optical range includes electromagnetic waves with a wavelength (λ) of 100 to 10,000 nm. It is divided into three regions:

- ultraviolet (UV) - 100-380 nm;
- visible - 380-760 nm;
- infrared (IR) - 760-10,000 nm.

Optical methods of analysis, depending on the nature of the interaction of a substance with electromagnetic radiation, are divided into:

- absorption, based on measuring the absorption of light radiation by a substance. These include colourimetry, photocolourimetry, spectrophotometry and atomic absorption methods;
- emission, based on measuring the intensity of light emitted by a substance. These include fluorometry, emission spectral analysis and flame photometry.

Methods related to the interaction of light radiation with suspensions are divided into:

- turbidimetry (based on measuring the intensity of light absorbed by an uncoloured suspension);
- Nephelometry (based on measuring the intensity of light reflected or scattered by a suspension).

Methods based on the phenomenon of molecular polarisation under the influence of light radiation are divided into:

- refractometry (based on the measurement of the refractive index);
- polarimetry (based on measuring the angle of rotation of the polarisation plane of a polarised light beam passing through an optically active medium);
- interferometry (based on measuring the shift in the interference of light beams when they pass through cuvettes with a solution of a substance).

Optical methods of analysis are inextricably linked to the use of modern instruments of varying complexity, which increases the cost of analysis, but offers a number of advantages over classical chemical methods: expressivity, sample immutability, simplicity of methodology, use of small amounts of substances for analysis, the ability to analyse compounds of any nature, and rapid analysis of multi-component mixtures. In addition, they increase the sensitivity, accuracy and reproducibility of quantitative determinations.

There are visual-type instruments, in which measurements are made visually, i.e. with the help of the eye, and photoelectric-type instruments, in which the intensity of radiation is determined using photocells. In this case, the prefix "photo-" is added to the name of the respective optical method (photocolourimetry, etc.).

2. Refractometry

Refraction, or refraction (from the Latin refractus - refracted), is a change in the direction of straight-line propagation of light when it passes from one medium to another.

Refraction, as well as absorption, of light is the result of its interaction with the medium.

The term refractometry refers to the measurement of the refraction of light. The refraction of light is measured by the refractive index, which depends on the composition of individual substances and systems, the concentration and type of molecules that the light beam encounters along its path, as molecules of different substances polarise differently when exposed to light.

The ratio of the speed of light propagation in a vacuum V_v to the speed of light in a given transparent medium V_t is called the absolute refractive index of light N:

$$N = V_v / V_t .$$

The speed of light in a vacuum is 1,00027 times greater than the speed of light in air and is the limiting speed, so the refractive indices for all substances and all media are greater than one.

The relative refractive index n_{relative} . is the ratio of the speeds of light in two media:

$$n_{\text{relative}} = V_1 / V_2 .$$

where V_1 and V_2 are the speeds of light propagation in medium I and II, respectively, provided that $V_1 > V_2$.

The value of the refractive index depends on the nature of the substance, its density, the wavelength of the incident light, temperature and pressure.

The nature of a substance determines the degree of deformation of its molecules under the influence of light, i.e. the degree of polarisation. The greater the polarisation, the stronger the refraction of light. An increase in density usually leads to an increase in the refractive index, for example:

substance	**refractive index**
ethanol	1,36
glycerin	1,47
glass	1,5 – 1,9
diamond	2,42

The volume of all gaseous and liquid bodies increases when heated, the density decreases and, as a result, the refractive index decreases. For example, the refractive index of water at 15°C is 1.3395, and at 25°C it is 1.3325.

The dependence of the refractive index on the light wavelength (λ) *is* called **dispersion** (from the Latin dispersus - scattered). The smaller the λ, the greater the refraction. Therefore, light of different wavelengths is refracted differently. For visible light, the highest refractive index corresponds to violet radiation (λ = 397-424 nm), and the lowest to red (λ = 640-723 nm).

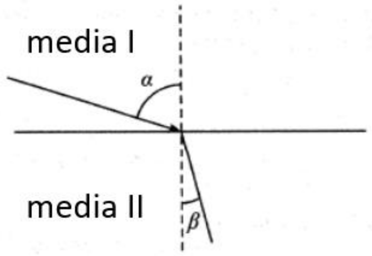
According to the laws of light refraction, when light passes from an optically less dense medium I to a medium with a higher optical density II, the angle of incidence α *is* always greater than the angle of refraction β (Fig.), and the following equations hold:

$$N = V_v / V_t = \sin\alpha / \sin\beta;$$

$$n_{\text{relative}} = \sin\alpha / \sin\beta = n / n_{21} .$$

where α *is the* angle of incidence of light, β *is the* angle of refraction of light,

n_1 and n_2 - refractive indices of media I and II.



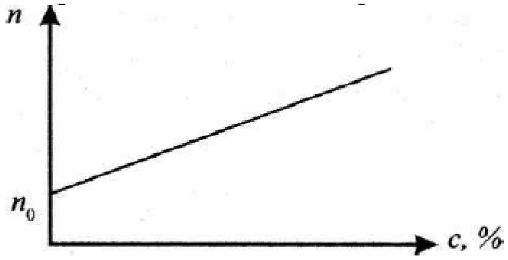
Refraction of a light beam at the boundary of an optical medium (I) with another optical medium (II).

The instruments used to measure n are called refractometers. There are two main types of refractometers: Abbe refractometers and Pulfrich refractometers. Measurements of n are based on determining the value of the refractive index.

For Abbe refractometers, the main and characteristic unit is a prismatic block consisting of measuring and illuminating prisms. The measurement accuracy of the refractive index is $\pm(1\text{-}2\cdot10^{-4})$, the measurement limits are 1.3-1.7.

Pulfrich-type refractometers have a higher measurement accuracy $\pm(1\text{-}2\cdot10^{-5})$, the measurement limit is much higher - 1.9. These instruments do not have a prismatic block, and the light sources are monochromatic (gas discharge tubes, sodium lamp).

The dependence of the refractive index *n of* a homogeneous two-component system on its composition is determined experimentally by determining the refractive index for a number of standard systems in which the content of the components is known. Based on the data obtained, a calibration graph is constructed in the coordinates: refractive index - content. For most binary solutions, this relationship is linear.



Graph of the refractive index as a function of the concentration of the dissolved substance.

Knowing the refractive index of the system under study, the graph can be used to determine its concentration.

For many aqueous solutions of acids, bases, salts, sugars, various alcohols, glycerin and other substances, the refractive indices are given in special tables.

3. Molecular adsorption analysis

Molecular absorption spectral analysis includes spectrophotometric and photocolorimetric types of analysis.

Spectrophotometric analysis is based on the determination of the absorption spectrum or measurement of light absorption at a specific wavelength that corresponds to the maximum of the absorption curve of the substance under study.

Photocolorimetric analysis is based on comparing the colour intensity of the test solution and a standard solution of a certain concentration.

Molecular absorption methods of analysis are based on two basic laws.

The first of them, the **Bouguer-Lambert** law, states that the relative amount of light absorbed by a permeable medium does not depend on the intensity of the primary radiation. Each layer of equal thickness absorbs an equal proportion of the monochromatic radiation flux.

Mathematically, this relationship is expressed in the following equation:

$$I = I_0 \cdot 10^{-kb} \quad \text{or} \quad \frac{I}{I_0} = 10^{-kb},$$

where I_0 is the intensity of radiation incident on the substance;

And - the intensity of the radiation that has passed through the substance;

b is the thickness of the layer through which monochromatic radiation passes;

k is the absorption coefficient.

The second law is **Beer's** law: the absorption of a radiation flux is directly proportional to the number of particles of the absorbing substance. Beer's law actually expresses the dependence of the absorption coefficient on the concentration of the absorbing substance in a homogeneous solution:

$$k = \varepsilon c,\ k = \kappa c,$$

where ε and k are proportionality coefficients.

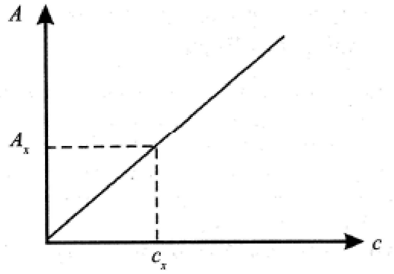
The combined **Bouguer-Lambert-Beer** law: The absorption of monochromatic light by a solution is directly proportional to the concentration of the absorbing substance and the thickness of the solution layer through which it passes.

The Bouguereau-Lambert-Beer law is the basic law of light absorption and is the basis for most photometric analysis methods. Mathematically, it is expressed as follows:

$$I = I_0 \cdot 10^{-\kappa cb} \quad \text{or in logarithmic form} \quad \lg\frac{I_0}{I} = \kappa cb.$$

The value lg I_0 /I is called the optical density of the absorbing substance and is denoted by the letter *A* or *D*.

The dependence *A* - f(*c) is* straightforward (for monochromatic radiation fluxes).



Dependence of the optical density *A* on the concentration of the solution *c*.

The value of the absorption coefficient *k* depends on the way the concentration of a substance in solution is expressed and the thickness of the absorbing layer. If the concentration is expressed in mol/dm^3 , and the thickness of the layer is in centimetres, it is called the molar absorption coefficient (index) and is denoted by ε.

It is equal to the optical density of a solution with a concentration of 1 M and a layer thickness of 1 cm. In this case, the Bouguer-Lambert-Beer law is given by

$$A = \varepsilon\text{-}c\text{-}b.$$

Causes of deviations from the Bouguer-Lambert-Behr law:

1. The law was derived and is valid only for monochromatic light, so insufficient monochromatisation can cause deviations from the law;

2. Solutions can undergo various processes that change the concentration of the absorbing substance or its nature: hydrolysis, ionisation, hydration, association, polymerisation, complexation, etc.

3. The light absorption of solutions depends significantly on the pH of the solution:

- The degree of ionisation of a weak electrolyte can change with the pH of the solution;
- The form of ionic existence can change, which leads to a change in the nature of light absorption;
- when the pH of the solution is changed, the composition of the coloured complex compounds formed may change.

Therefore, the law is valid for highly dilute solutions and its application is limited.

The colour intensity of solutions can be measured using various methods. A distinction is made between subjective (or visual) and objective (or photocolorimetric) methods of colourimetry.

Visual methods are those in which the intensity of the colour of the test solution is assessed with the naked eye.

In **objective** colourimetric methods, photocells are used to measure the colour intensity of the solution being tested. In this case, the determination is carried out using special devices - photocolorimeters, and the method is called photocolorimetric.

Visual methods include:

- standard series method;
- colourimetric titration or duplication method;
- the method of equalisation.

Photoelectrocolourimetry. It is used to measure the absorption or transmission of light by coloured solutions, using light with a narrow range of wavelengths. The instruments used are called photoelectrocolourimeters (PECs). Photoelectric methods of measuring colour intensity are associated with the use of photocells. The latter convert light energy into electrical energy. Photocells allow for colourimetric determinations not only in the visible region, but also in the ultraviolet and infrared regions of the spectrum.

The measurement of light fluxes using photoelectric photometry is quite accurate and does not depend on the characteristics of the observer's eye. The use of photocells makes it possible to automate the determination of substance concentration during chemical control of technological processes. As a result, photoelectric colourimetry is widely used in practice.

Methods of concentration determination in photoelectrocolorimetry.

Photoelectrocolourimetry is used to determine the concentration of substances to be analysed:

- a method for comparing the optical density of the standard and test solutions;
- a method of determination based on the average value of the molar or specific absorption coefficient;
- the method of a graduation chart;
- the method of additives.

The most commonly used method is the calibration graph.

To determine the concentration of a substance by this method, prepare a series of 5-8 standard solutions of different concentrations. To select the concentration interval of the standard solutions, follow these guidelines:

- It should cover the range of possible measurements of the concentration of the solution under investigation;
- The optical density of the solution to be tested should correspond to approximately the middle of the calibration curve;
- It is desirable that the basic law of light absorption is observed in this concentration range;
- the optical density should be in the range of 0.14-1.3.

Measure the optical densities of the standard solutions and plot A against c. Determine A_x of the solution under study and use the calibration graph to find c_x .

This method makes it possible to determine the concentration of a substance even in cases where the basic law of light absorption is not fulfilled. In this case, a large number of standard solutions are prepared that differ in concentration by no more than 10%. In this case, the reproducibility of the determination is lower than in the case of a linear dependence of A on c.

Lecture 18

CHROMATOGRAPHIC METHODS OF ANALYSIS

1. Classification of chromatographic methods of analysis;
2. Qualitative chromatographic analysis;
3. Quantitative chromatographic analysis.

1. Classification of optical analysis methods

Chromatography is a dynamic sorption method of separating mixtures based on the distribution of a substance between two phases, one of which is mobile and the other is stationary, and is associated with multiple repetition of sorption and desorption acts.

The stationary phase is usually a solid (sorbent) or a film of liquid deposited on a solid. The **mobile** phase is the liquid or gas flowing through the stationary phase.

The emergence of chromatography as a scientific method is associated with the name of the Russian scientist M.S. Tsvet, who in 1903 separated a mixture of plant pigments and laid the theoretical foundations of chromatography.

A distinctive feature of chromatographic methods is their versatility, i.e. the ability to be used for a wide range of applications:

- purification of substances;
- Concentration of substances from highly dilute solutions;
- separation of complex mixtures of organic and inorganic substances;
- identification of substances;
- determining the quantitative composition.

The isolation of individual chemical compounds from mixtures of various origins has always been and remains one of the main tasks of chemistry, including analytical chemistry. In the manufacture of numerous medicinal substances, natural or synthetic substances are also isolated in their pure form. A significant advantage of the chromatographic method is that, unlike other methods of separation, extraction and concentration, it allows for the simultaneous identification and quantification of the mixture being separated.

The variety of chromatographic methods, which differ in their physicochemical basis and analysis techniques, makes it impossible to classify them according to any single criterion.

Depending on the aggregate state of the mobile phase, a distinction is made:

- **gas chromatography**, which includes **gas-liquid** and **gas-solid phase chromatography**;
- **liquid chromatography**, which includes **liquid-liquid**, **liquid-solid phase** and **liquid-gel chromatography**.

The first word in the name of the method describes the aggregate state of the mobile phase, and the second - of the stationary phase.

Several types of chromatography can be distinguished by the mechanism of interaction between sorbent and sorbate:

- Separative **chromatography** - based on the difference in solubility of the substances to be separated in the stationary phase (gas-liquid chromatography) or on the difference in solubility of substances in the mobile and stationary liquid phases;

- Ion exchange chromatography - based on the different capacities of substances to ion exchange;

- adsorption chromatography - based on differences in the adsorption of substances by a solid sorbent;

- affinity chromatography - based on specific interactions characteristic of certain biological and biochemical processes.

The analysis technique is differentiated by the analysis technique:

- column chromatography - separation is carried out in special columns;

- In-plane chromatography - the separation is carried out on special paper (**paper chromatography)** or in a thin layer of sorbent (**thin-layer chromatography)**.

For the purpose of chromatography, they are separated:

- analytical chromatography - qualitative and quantitative analysis;

- Preparative chromatography - to obtain pure substances, to concentrate and isolate micro-impurities;

- industrial chromatography - chromatography for automatic process control.

2. Qualitative chromatographic analysis

In qualitative analysis, the separation and detection of cations and anions is often performed using both planar (paper and thin-layer) and ion exchange columns. The advantages of the planar chromatography variants are simplicity, expressiveness, clarity of separation, ease of detection of chromatographic zones, and the ability to analyse micro-objects.

Ion exchange in columns is used to separate cations from anions in complex mixtures.

Paper chromatography. In the paper chromatography method, substances are separated by partitioning between the aqueous phase contained in the cellulose and any other mobile phase. Organic solvents, water, or electrolyte solutions are used as mobile phases.

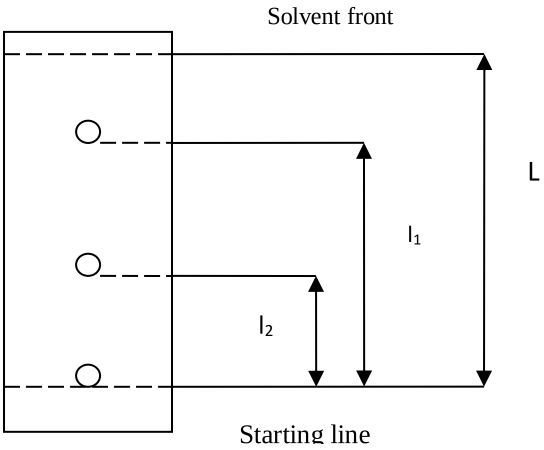
To evaluate the chromatographic behaviour of substances under certain conditions, the value R_f is used, which is equal to the ratio of the distance l travelled by the substance to the distance travelled by the solvent, L

$$R_f = l / L.$$

Usually, to calculate R_f , a point in the centre of the stain is chosen, as shown in the figure. Separation of substances is practically possible if $R_{f(1)} - R_{f(2)} \geq 0{,}1$.

The value of R_f is influenced by such factors as the nature of the substance, the composition of the mobile phase, the type of paper, temperature, and chromatography time.

Paper chromatograms can be obtained by ascending, descending, horizontal or radial movement of the solvent. In the case of upward chromatography, the mobile phase moves from bottom to top; the liquid movement is due to capillary forces.



Definition of R_f

In downward chromatography, the movement occurs in the opposite direction under the influence of gravity. In horizontal or radial chromatography, the solvent is brought to the centre of a paper disc on which a drop of the solution to be analysed has been previously applied. The rings on these chromatographs are shaped like ellipses because the speed of the solvent depends on the orientation of the paper fibres.

The method of analysis by paper chromatography will be explained on the example of separation and detection of cations by the one-dimensional ascending method.

The separation is carried out in a sealed cylinder to avoid evaporation of the solvent from the chromatographic paper strip. The solvent (HCl-acetone mixture) is added to the cylinder in advance to saturate the chamber atmosphere with its vapours.

A starting line is drawn with a pencil at a distance of 2 cm from the edge of the paper tape (2 x 20 cm). A drop of the solution to be analysed is applied from the capillary in the middle of this line. The diameter of the spot is usually 2-3 mm. The spot is traced with a pencil and dried over a sand bath.

The strip of chromatographic paper with a drop of the test solution applied is lowered into the cylinder so that its end is immersed in the solvent by no more than 0.5 cm. The process is stopped after the solvent has passed at least 10 cm from the starting line. After that, remove the paper tape, mark the position of the solvent front, and thoroughly dry the tape over a sand bath. Measure the distance between the starting line and the solvent front *L* (Fig.) and calculate the experimental value R_f for each spot.

The identification of each cation is carried out by comparing the experimental value of R_f with the table value.

Values of R_f for of some cations

Cation	R_f		Cation	R_f
Cr^{3+}	0,023		Cu^{2+}	0,7
Ni^{2+}	0,13		Zn^{2+}	0,94
Al^{3+}	0,15		Cd^{2+}	1,0
Mn^{2+}	0,25		Bi^{3+}	1,0
Co^{2+}	0,54		Fe^{3+}	1,0
Pb^{2+}	0.70			

In addition, the table allows you to determine which cations cannot be identified due to their joint presence ($R_f < 0.1$). These are, for example, mixtures of Ni^{2+} , Al^{3+}, Zn^{2+}, Cd^{2+}, Bi^{3+}, Fe^{3+} .

For greater clarity, in the presence of certain cations, the corresponding zones on the chromatogram are treated with solutions of organic and inorganic developing reagents.

Reagents for the detection of cations on a chromatogram

Cation	Reagents	Zone colour
Ni (II)	Dimethyl glyoxime, ammonia vapour	Red
Mn (II)	Benzidine, 2M NaOH	Blue
Co (II)	Saturated potassium thionate	Blue
Cu (II)	Potassium hexacyanoferrate (II)	Red-brown
Pb (II)	Potassium iodide	Yellow
Zn (II)	Dithizone in CCl_4	Red
Cd (II)	Sodium sulphide	Yellow
Fe (III)	Potassium hexacyanoferrate (II)	Blue
Bi (II)	A mixture of 8-oxyquinoline and potassium iodide	Orange
Cr (III)	2 M NaOH, 3% solution of H_20_2 ,benzidine	Blue
Al (III)	Alizarin, ammonia vapour	Pink

The capillary with the cation detection reagent is touched only to the area of the chromatogram at the height of the cation zone. The appearance of a characteristic colour confirms the presence of the cation in the test solution.

Thin-layer chromatography (TLC) differs from paper **chromatography in that a** thin layer of sorbent is firmly bonded to a glass, plastic, or aluminium foil substrate. The mobile phase and components of the mixture under study move at different speeds along a thin (0.1-0.5 mm) sorbent layer (silica gel, cellulose, aluminium oxide, polyamide, ion exchangers) in one direction under the influence of capillary forces. Since under standard conditions R_f is constant for a given substance, it is used to identify components in a mixture. TLC is most commonly used in organic chemistry to separate, determine the degree of purification and identify amino acids, lipids, peptides, carbohydrates, drugs, etc. However, it is possible to determine cations of almost all groups of elements, many anions, and some elements in multivalent states.

The technique of TLC chromatography is similar to paper chromatography.

Ion exchange chromatography. Ion exchange means that some substances absorb cations or anions from an electrolyte solution upon contact with it, releasing an equivalent number of other ions with the same charge.

Natural iodine exchangers include clays and zeolites. Synthetic iodine exchangers are high molecular weight materials. Almost all of them are based on cross-linked polystyrene matrices. Ionogenic groups are fixed in the matrix - in acidic cation exchangers ($-SO_3H$, $-COOH$, -OH, $-PO_3H_2$, $-AsO_3H_2$), in basic anion exchangers ($-N(CH_3)_3^+$, $=NH_2^+$, $\equiv NH^+$ and others). If the fixed-ion matrix is denoted by R, the reversible process of exchange of protons for ions in the solution can be written in the form of reactions:

$$R\text{-}H + Kt^+ \leftrightarrow R\text{-}Kt + H^+ ;$$

$$R\text{-}Cl + An^- \leftrightarrow R\text{-} An + Cl^- .$$

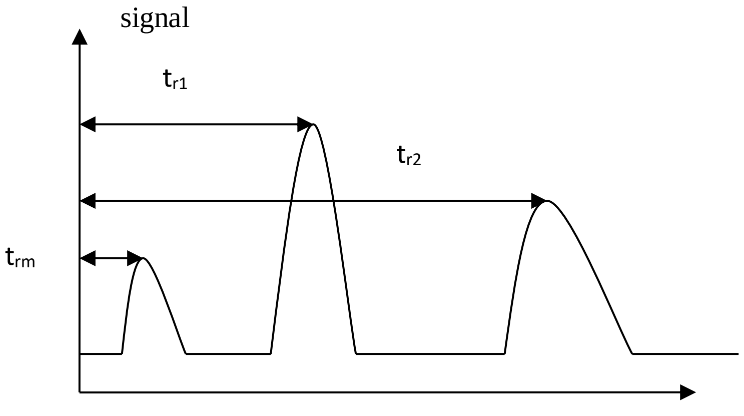
Let us illustrate the essence of ion-exchange chromatography by using the example of the analytical separation of anions and cations. The solution is passed through a column with an H-form cation exchanger (e.g. KU 2 x 8), during which the cations are sorbed and the anions remain in solution. After washing the column with water, the cations are eluted (removed from the solid carrier) with 4 M HCl.

3. Quantitative chromatographic analysis

Quantitative chromatography is a method of separation and determination of substances based on the distribution of components between two phases - mobile and stationary.

The stationary phase is a solid, porous substance (often called a sorbent) or a film of liquid deposited on a solid. The ***mobile phase is a*** liquid or gas that passes through the stationary phase, sometimes under pressure.

Quantitative chromatographic analysis is carried out using a chromatograph, an instrument that combines a chromatographic column with a flow-through device (detector).



Chromatogram of a mixture of two substances

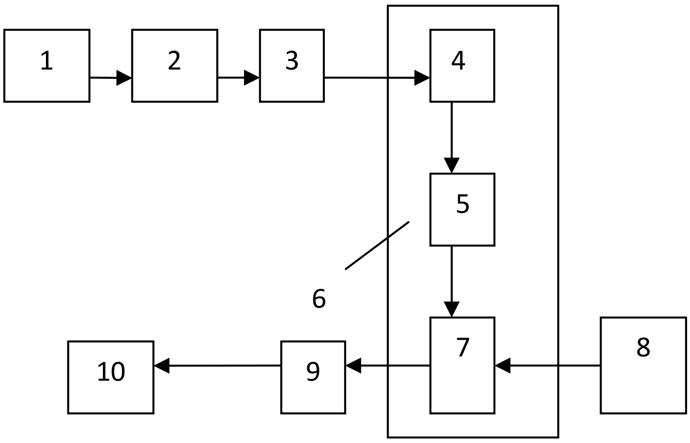
t_{rm} - residence time of substances in the mobile

To perform chromatographic analysis, the following sequence of steps is used: select the necessary mobile and stationary phases depending on the properties of the substances under study, set the desired chromatograph mode (temperature, mobile phase flow rate, detector), then perform chromatographic separation and record the signal, determine the content of each component in the mobile phase after it leaves the column. The record made on the chart paper is called a chromatogram.

A chromatogram is a graph of the instrument signal (ordinate axis) versus time (abscissa axis). A typical chromatogram is shown in the figure.

Gas-liquid chromatography. This method is used for volatile, thermostable compounds. In this case, the sample to be analysed is introduced into the chromatographic column in the form of a vapour using a carrier gas (nitrogen, argon). The separation of the sample components is achieved by repeatedly repeating the separation processes between the mobile gas and stationary liquid phases. The migration rate of components depends on their volatility and ability to dissolve in the stationary liquid phase. Components with low solubility in the liquid phase and the highest volatility at a given temperature move faster along the column, while components with low volatility and high solubility in the stationary liquid phase have low mobility. The greater the mobility, the shorter the retention time, and vice versa. For example, when polyethylene glycols are used as a stationary phase, the retention time of aliphatic alcohols increases in the following order: isopropyl < ethyl < propyl < isobutyl < butyl < isoamyl < amyl.

The principle of operation of a gas chromatograph is illustrated in the diagram below.

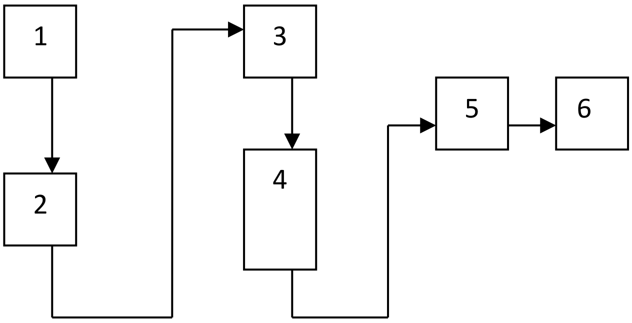


1 cylinder with carrier gas;
2 gas treatment units;
3-sample injection device;
4 evaporator;
5 chromatographic column;
6-thermostat;
7-detector;
8- power supply;
9-amplifier of the detector signal;
10-register device;

Block diagram of a gas-liquid chromatograph

Liquid chromatography. Liquid chromatography is a method for the separation and determination of a wide range of organic and inorganic substances on stationary phases (usually solid sorbents) of various nature. The mobile phase is a liquid: organic solvents, water-organic mixtures, aqueous solutions of acids, alkalis and salts. In liquid chromatography, the role of the mobile phase is much more important than in gas chromatography.

Liquid chromatography can be used for a much wider range of substances than gas chromatography, as most substances are volatile and many are unstable at elevated temperatures. In liquid chromatography, the separation usually takes place at room temperature.



Schematic diagram of a liquid chromatograph

1 eluent vessel;
2-pump;
3-dispenser;
4 columns.
5-detector;
6-recorder.

The liquid chromatograph consists of six units, each consisting of several devices of varying complexity and capabilities.

The column in a liquid chromatograph is a steel tube with an internal diameter of 4-6 mm and a length of 100-250 mm, filled with a sorbent with a small particle diameter (5-30 µm), which leads to the need to increase the pressure at the column inlet to 0.5-40 MPa.

In analytical practice, high-performance liquid chromatography is most widely used in the adsorption and ion-exchange versions. In the latter case, the chromatographic column is filled with a cationic or anionic exchanger rather than a conventional sorbent, such as silica gel.

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A-46 **Analytical chemistry** [Text]: lecture notes for applicants for the first (bachelor's) level of higher education of the educational and professional programme "Food Technologies" of the field of knowledge 18 Production and Technologies, specialty 181 Food Technologies of full-time and part-time study / compiled by. I. A. Moroz - Lutsk: Lutsk NTU, 2024. 112 p.

The basic theoretical concepts of the main sections of analytical chemistry are briefly presented, and methods of qualitative and quantitative analysis are described. The lecture notes will help students in completing independent work assignments and preparing for laboratory work.

It is intended for students majoring in 181 Food Technologies of full-time and part-time study.

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