Ministry of Health of Ukraine
Zaporizhzhia State Medical and Pharmaceutical University
Department of Physical, Colloid and Analytical Chemistry

ANALYTICAL CHEMISTRY

ACID-BASE TITRATION

Study and methodological guide
for 2-nd year students of
Speciality «Pharmacy, Industrial Pharmacy»

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and recommended for use in the educational process

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PREFACE

Analytical Chemistry is studied according to the model curriculum approved by the Ministry of Health of Ukraine on April 19, 2017, and on the basis of the working academic plan approved by the Academic Council of ZDMPhU (Protocol No. 11 of May 28, 2024), and the working program of the academic discipline «Analytical Chemistry» from 2024.

The relevance and expediency of this guidel are due to the change in the structure of the KROK 1 licensure examination, Pharmacy.

This manual contains material that ensures the acquisition of general and professional competencies and program learning outcomes.

According to the curriculum, analytical chemistry is studied in the III and IV semesters.

The discipline's program is structured into 2 sections: Section 1 – «Qualitative Analysis. Acid-base titration», Section 2 – «Quantitative analysis. Instrumental methods of analysis».

Section 1 consists of 4 basic topics:

1. Analytical chemistry and chemical analysis. Theory of solutions of strong and weak electrolytes. Law of mass action and its application to various types of ionic equilibria in analytical chemistry. Use of the law of mass action for equilibria in heterogeneous systems and its significance in analytical chemistry. Theory and practice of analysis of cations of I-III analytical groups.
2. Application of the law of mass action to acid-base equilibrium and to complexation equilibrium, and their role in analytical chemistry. Theory and practice of analysis of cations of IV-VI analytical groups.
3. Application of the law of mass action to redox equilibrium. Separation and preconcentration methods. Theory and practice of analysis of anions and an unknown sample.
4. Acid-base titration and its application in chemical and pharmaceutical analysis.

QUANTITATIVE ANALYSIS

Analytical chemistry, or analytics, is a branch of chemistry that develops principal methods and procedures for qualitative and quantitative analysis of the atomic, molecular, and phase composition of substances based on laws of fundamental chemistry and physics.

Modern analytical chemistry (analytics) includes three subdisciplines: qualitative chemical analysis, quantitative chemical analysis, and instrumental (physical and physicochemical) methods of analysis. Separation of instrumental methods of analysis into an autonomous subdiscipline of analytical chemistry is relative to some degree because both qualitative and quantitative analyses are performed by these methods.

Quantitative analysis of a substance is empirical determination (measurement) of concentration (quantity) of chemical elements (compounds) or their forms in analyte, expressed as *confidence limits* or value with an indication of *standard deviation.*

Quantitative analysis is widely used in pharmaceutical analysis and is an essential part of the pharmacopoeial analysis of *any* drug product. Quantitative analysis methods are usually classified as follows: *chemical, physico-chemical, physical, biological ones.*

Chemical methods of analysis include *gravimetric (weight)* and *titrimetric (volumetric) methods.*

Gravimetric methods are based on precise mass measurement of the analyzed component of a sample, separated from other components of the system, in elemental form (i.e., in the stable form of a given chemical element) or in the form of a compound with a precisely known composition. Gravimetric methods are simple to perform, highly accurate and reproducible, but quite laborious and time-consuming.

Titrimetric methods are based on measuring the volume or mass of reagent (titrant) required for reaction with the analyzed substance (analysis is based on titration). Methods are simple, highly accurate and reproducible, but in most cases *indicators* are required to determine the endpoint of the titration.

Physico-chemical and physical (instrumental) methods of analysis include *optical, chromatographic, electrochemical,* and some other methods (for example, radiometric, thermal, mass spectrometric, pycnometric, ultrasonic, etc.).

TITRIMETRIC (VOLUMETRIC) ANALYSIS BASIC

Titrimetric or *volumetric analysis is* a method of quantitative analysis based on measuring the volume (or mass) of reagent consumed for reaction with determined substance X. In other words, titrimetric analysis is an analysis based on *titration.*

Titration is the process of determining substance by the gradual addition of small amounts of substance, during which a point (moment) when all substance has reacted is determined in some way. Titration allows to determine the amount of substance by the known amount of substance added up to this point (moment), taking into account that the ratio in which and react is known from stoichiometry or otherwise.

A *titrant* is a solution containing the active reagent, which is used to perform titration.

Reactions used in the titrimetric analysis should meet the following main requirements.

1. The reaction must proceed according to a strictly defined stoichiometric equation. Side reactions must be eliminated.
2. The reaction must proceed quantitatively, i.e., almost to the end. Equilibrium in the system must be completely shifted to the side of reaction products. The degree of conversion of an initial substance into reaction products at EP must be at least 99.90-99.99%. The equilibrium constant must be sufficiently large. For the reaction of type A + B = C, in which two initial reagents A and B are involved, the equilibrium constant K must be $K > 10^8$; under these conditions, the reaction proceeds by at least 99.99%.
3. The reaction must proceed quickly so that equilibrium is established almost immediately at any moment of titration. Sometimes, in order to accelerate the achievement of equilibrium, the solutions are heated, or catalysts are added to them.
4. The reaction must allow determining EPT near EP precisely and conveniently.

Classification of titrimetric analysis methods

The most common classification of titrimetric analysis methods is based on different typed of used reactions.

1. ***Acid-base titration (neutralization method)*** is titration based on the reaction of proton transfer from one reacting particle to another in solution. It includes acidimetry and alkalimetry.

$$HA + B \leftrightarrow BH^+ + A^-$$

Acidimetry (acidimetric titration) is the determination of substances by titration with a standard solution of an acid.

Alkalimetry (alkalimetric titration) is the determination of substances by titration with a standard solution of a strong base.

2. ***Oxidation-reduction (redox) titration (redoxometry)*** is titration accompanied by a transition of one or more electrons from donor ion or molecule (reducing agent) to an acceptor (oxidizing agent).

$$Ox_1 + Red_2 \leftrightarrow Red_1 + Ox_2$$

3. ***Precipitation titration*** *is* a type of titration, during which the titrated substance is precipitated from solution due to interaction with the titrant.

$$Kt^{n+} + An^{m-} \leftrightarrow Kt_mAn_n$$

4. ***Complexometric titration*** is titration of a substance with a compound solution that interacts with the titrated substance forming a weakly dissociating soluble complex.

$$M + nL \leftrightarrow M(L)_n$$

Law of equivalence

he interaction between substances must take place in strictly defined ratios, ie according to the law of equivalents, according to which substances react with each other in equivalent quantities $n_1 = n_2$. Whereas

$$n = C_{Me} \cdot V, \text{ where}$$

C_{Me} – molar concentration of equivalent;

V – volume;

then for two stoichiometrically reactive substances, a fair ratio:

$$C_{Me1} \cdot V_1 = C_{Me2} \cdot V_2$$

Thus, it is possible to find an unnecessary concentration in one part (for example, C_{Me2}), if you know the volume of its conversation and the volume concentration that reacted with it, as a result of which they react with each other in equivalent quantities.

***The equivalent** of a compound is a real or conditional particle that can attach, release or otherwise be equivalent to one hydrogen ion in acid-base reactions or one electron in redox reactions.*

*A number indicating what proportion of a real particle of a substance is equivalent to one hydrogen cation in a given acid-base reaction or one electron in a redox reaction is called the **equivalence factor fe**.*

This is a dimensionless quantity that is calculated on the basis of stoichiometric coefficients of a particular reaction.

For example, in the reaction:

$$2NaOH + H_2SO_4 \leftrightarrow Na_2SO_4 + 2H_2O$$

at the equivalence point, each reacting particle H_2SO_4 will be equivalent to two particles NaOH. The same reaction equation can be written as:

$$NaOH + ½\ H_2SO_4 \leftrightarrow ½\ Na_2SO_4 + H_2O$$

It is clear that $f_e(H_2SO_4) = ½$, that is, the amounts of reactants will be equivalent when $n(NaOH) = n(½\ H_2SO_4)$.

In the redox reaction

$$MnO_4^- + 8H^+ + 5\bar{e} \leftrightarrow Mn^{2+} + 4H_2O$$

molecule $KMnO_4$ takes 5 electrons, ie one electron is equivalent to a conditional particle 1/5 of the molecule $KMnO_4$, $f_e = 1/5$.

The equivalence factor and the equivalent of a given substance are not constants, but depend on the stoichiometry of the reaction in which they participate.

The equivalence factor is a dimensionless quantity equal to or less than one.

Important in titrimetric analysis is the concept of molar mass equivalent.

The molar mass of the equivalent of a substance is the mass of one mole of the equivalent of this substance, which is equal to the product of the equivalence factor and the molar mass of the substance.

$$M_e = f_e \cdot M$$

In the examples:

$M_e(H_2SO_4) = f_e(H_2SO_4) \cdot M(H_2SO_4) = 1/2 \cdot 98{,}08 = 49.04$ g/mol;

$M_e(KMnO_4) = f_e(KMnO_4) \cdot M(KMnO_4) = 1/5 \cdot 158 = 31.6$ g/mol.

To determine the titrimetric method requires the presence of: analytical balances; measuring utensils; titrated solutions (standard solutions); indicators or devices that allow you to record CTT.

Measuring glassware

Measuring glassware, used in titrimetric analysis are divided into vessels for accurate measurement of volumes (measuring flasks, measuring pipettes, burettes), approximate measurement of volumes (measuring cylinders, measuring cups, measuring tubes) and just containers (titration flasks).

Table of permissible deviations from nominal volumes
measuring glassware (20ºС, ДГСТ 1771-74)

Nominal capacity, ml	Tolerances, ml			
	Measuring flasks		Measuring pipettes	
	1st grade	2nd grade	1st grade	2nd grade
5	–	–	0,01	0,02
10	0,025	0,05	0,02	0,04
20	–	–	0,03	0,06
25	0,03	0,06	0,04	0,08
50	0,05	0,10	0,05	0,10
100	0,10	0,20	0,08	0,16
200	0,15	0,30	–	–

Titrated (standard) solutions

Titrated (standard) solutions *are solutions with a known concentration (titer), intended for titration purposes in volumetric analysis.*

Titrated solutions are prepared in three ways: by the method of the prepared titer (according to the sample weight of the standard substance), by the method of the established titer and from the fixanals.

1. The method of the prepared titer

Weigh the exact weight of the substance on the analytical balance, transfer it to a volumetric flask and make up to volume with distilled water. Calculate the titer and molar concentration of the equivalent by the formulas:

$$T = \frac{a}{V_к}, \qquad C_{M_e} = \frac{T}{M_e'}, \text{ where}$$

T – the titer of the solution, g / ml;

a – mass of the sample weight, g;

$V_к$ – capacity of a measuring flask, ml;

C_{Me} – molar concentration of the equivalent solution;

M_e' – millimolar mass of equivalent substance.

Thus prepare solutions of titrants from the starting materials (primary standards), which meet the following requirements:

1. Exact correspondence to the chemical formula.
2. High degree of chemical purity or possibility of easy cleaning.
3. Stability in solid state and in solution during storage.
4. Availability, good solubility in water.
5. The presence of a large value of the molar mass of the equivalent, when taking a sample, the relative error of weighing decreases.

2. The method of the set titer.

Prepare a solution of the substance of approximate concentration, and then set its exact concentration by titrating the solution of the starting material (primary standard). The titer and molar concentration of the equivalent of such a solution are determined by primary or secondary standards.

Calculations are based on formulas:

$$C_{M_e} = \frac{C_{M_{e1}} \cdot V_1}{V}, \qquad T = C_{M_e} \cdot M_{e'}, \text{ where}$$

C_{Me} and C_{Me1} – molar concentration of the equivalent of the test solution and a solution with a known concentration;

V and V_1 – volume of test solution and volume of solution with known concentration.

A portion of the starting material for the preparation of a certain volume of V solution with a molar concentration of C_M or molar concentration of equivalent C_{Me} calculated by formulas:

For solids: $a = \frac{C_{M_e} \cdot f \cdot M_e}{1000}$;

For solutions: $a = \frac{C_{M_e} \cdot f \cdot M_e \cdot 100}{C\% \cdot 1000}$, where

V_f – the capacity of the volumetric flask, ml;

C% - the percentage concentration of the substance in the initial solution.

3. Preparation of titrants from «fixanals». «Fixanals» are often used for preparation of titrated solutions. *»*. «Fixanals», or the standard-titre, is a sealed glass ampoule, which contains the amount of the substance exactly known in a dry form or in solution. More often there is 0.1 mole of the substance in the ampoule. To prepare the titrated solution the ampoule is broken, its content is quantitatively transferred into a measuring flask of the required volume, diluted by fresh boiled and cooled distilled water, dilute to the volume and mixed thoroughly.

Methods for expressing concentrations in titrimetric analysis

The concentration of titrated solutions is expressed by molar concentration C_M, molar concentration of equivalent C_{Me}, titer T_x and titer of the solution for determined substance, or titrimetric conversion factor $T_{a/x}$.

Molar concentration C_M – is the amount of dissolved substance in moles contained in one liter of solution

$$C_M = \frac{n_x}{V} = \frac{a_x}{M_x \cdot V}, \text{ where}$$

a_x – is a mass of the dissolved substance , g

n_x – *is* the amount of dissolved substance, mol;

M_x – is molar mass of dissolved substance A, g/mol;

V – *is* the volume of solution, L.

Molar equivalent concentration, or *normality* (previous name) is the amount of dissolved substance in moles corresponding to the equivalent of A contained in one liter of solution.

$$C_{M_e} = \frac{n_x}{V} = \frac{a_x}{M_{ex} \cdot V}, \text{ where}$$

n_x – is the amount of substance equal to equivalent of A in the solution, mol;

V – volume of solution, l;

a_x – mass of solute, g;

Me_x – is molar the equivalent mass of dissolved substance A, g/mol.

Molar equivalent concentration is measured in mol/L.

Titer T of dissolved substance is a mass of dissolved substance contained in one milliliter of a solution. A titer is measured in g/ml.

$$T_x = \frac{a_x}{V}, \text{ where}$$

a_x – the mass of the substance contained in the volume V.

A titer of the solution for determined substance or *titrimetric conversion factor* $T_{(a/x)}$, is mass of titrated substance interacting with one milliliter of titrant.

Measured, as the titer of a solution, in g/ml.

The titrimetric conversion factor is related to the molar concentration of the equivalent solution by the formula:

$$T_{a/x} = \frac{C_{M_e} \cdot M_{e_x}}{1000}, \text{ where}$$

C_{Me} – molar concentration of solution equivalent, mol/L;

Me_x – molar mass equivalent of solute, g/mol.

Expression of measurement and calculation results in quantitative analysis. Significant figures

The data obtained as a result of the analysis must be correctly recorded and taken into account in the calculations. Each result cannot be more accurate than the measuring instruments allow, and the accuracy of the analysis cannot be increased by mathematical calculations. All numerical values of measurement and calculation results must contain so many significant digits that only the last digit is questionable.

Significant digits are all digits of a given number, except for the zeros to the left of the digit and the zeros to the right of the digit if they do not indicate the accuracy of the measurement.

Example:

0,0035 – the number has two significant digits «3» and «5»;

7,2500 – the number has significant digits «7», «2», «5»; zeros will be insignificant if the mass is obtained on technical scales; zeros will be significant if the mass is obtained on analytical balances (accuracy ± 0.0001 – 0.0002).

The zeros in the middle of the number are significant, for example, in the number 20.0604 six significant digits.

Decimal characters should be distinguished from significant numbers. For example, the number 0.0035 has four decimal places, but two significant digits.

Transfer from one dimension to another: 23.4 g transfer to 23400 mg - incorrect! Right $2.34 \cdot 10^4$ mg or $23.4 \cdot 10^3$ mg or $0{,}234 \cdot 10^5$ mg.

The accuracy of the calculation result cannot be greater than the least accurate of the numbers included in the calculation. Therefore, determine the least accurate of the numbers and accordingly determine how many decimal places or significant digits should contain the result of calculations.

The result of the quantitative analysis is expressed by a number that contains several significant digits. *If the accuracy of the analysis is not warned in advance, the concentration is calculated to the fourth significant digit, the mass - to the fourth decimal place, the percentage - to hundredths.*

Tutorial 10

1. THEME: Introduction to quantitative analysis. Weighing technique. Titrometric methods of analysis. Acid-base titration.

2. PURPOSE: Get acquainted with the basics of quantitative analysis, learn the general provisions of titrimetric methods and master the skills of working with analytical measuring instruments, measuring vessels and preparation of titrated solutions

3. OBJECTIVIES:

3.1. Understand the tasks, principles and methods of quantitative analysis, its role and significance in pharmacy and cosmetology.

3.2. Learn to weigh on analytical scales.

3.3. Learn the basics of titrimetric methods of analysis, learn to use analytical measuring instruments - measuring flasks and measuring pipettes and calibrate them.

3.4. To study the methods of preparation of titrated solutions and to master the method of preparation of titrants by the method of the established titer.

3.5. Learn to record the results of measurements in accordance with the accuracy of measurements and design a laboratory journal.

4. PLAN AND ORGANIZATIONAL STRUCTURE OF THE TUTORIAL:

4.1. An organizational issue ……………………………………………….3 min

4.2. Setting of the goal of the tutorial and motivation for studying the topic (introductory speech by the teacher)..7 min

4.3. The assessment of the initial level of knowledge and skills (assignments in paper cards)………...…..10 min

4.4. Correction of the initial level of knowledge and skills…………….…..40 min

4.5. Organization of students' independent work (target instructions by the teacher, safety precautions)...5 min

4.6. Laboratory work……………………….…………………………....140 min

4.7. Summative assessment: checking the results of the laboratory work and protocols……...…...……..15 min

4.8. Concluding speech by the teacher, instructions for the next lesson...........5 min

5. REFERENCE FOR SELF STUDY:

5.1. To repeat the theoretical material from the course of inorganic chemistry and qualitative analysis: ways of expressing the concentration of solutions, the law of equivalents. Repeat the structure of analytical scales from the physics course.

5.2. Study the program material on this topic, using the recommended literature and lectures.

Questions for self-study

1. The essence and objectives of quantitative analysis. Areas of application of quantitative analysis.

2. Classification of methods of quantitative analysis.

3. The essence of titrimetric methods of analysis. Basic concepts.
4. Classification of methods of titrimetric analysis by type of chemical reaction.
5. Requirements for reactions in titrimetry.
6. Conditions for titrimetric determinations.
7. Volume measurement. Measuring utensils. Checking the capacity of measuring utensils.
8. Titrated solutions. Methods of their preparation. Primary and secondary standards. Requirements for primary standards. Methods of expressing the concentration of titrated solutions.
9. Calculations in titrimetric analysis. Expression of measurement results.

Solve the tasks:

Task 1. Calculate the sample weight of sodium tetraborate decahydrate ($M(Na_2B_4O_7 \cdot 10H_2O) = 381.4$ g/mol) for the preparation of 200.0 mL of 0.05000 n. solution.

Answer: 1.907 g.

Task 2. How many ml of 60% solution of sulfuric acid (density 1.50 g / ml) must be taken to prepare 10 liters of 0.1 N. its solution?

Answer: 54.49 ml.

Task 3. A sample weight of sodium carbonate 1.083 g is dissolved in a volumetric flask with a capacity of 200.0 ml. Calculate the titer and molar concentration of the resulting solution.

Answer: 0.005415 g/ml; 0.05110 mol/L.

Task 4. The density of 15% (by weight) solution of sulfuric acid is equal to 1.105 g / ml. Calculate: a) the molar concentration, b) the molar concentration of the equivalent.

Answer: 1.691 mol/L; 3.383 mol/L.
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Examples of the solved tasks:

Task 1. Calculate the volume of 20% hydrochloric acid solution (p = 1.10 g/ml) required to prepare 2 L of 0.1 N. solution.

Solution. Calculate the mass of a sample of hydrochloric acid according to the formula for solutions:

$$a = \frac{C_{M_e} \cdot f \cdot M_{e'} \cdot 100}{C\%};$$

$M(HCl) = 36.46$ g/mol;
$f_e(HCl) = 1$;
$M_{e'}(HCl) = M(HCl) \cdot f_e(HCl) : 1000 = 0.03646$.

$$a = \frac{0{,}1 \cdot 2000 \cdot 0{,}03646 \cdot 100}{20} = 36.46.$$

Знаючи густину розчину, знайдемо об’єм вихідного розчину:

$V = \frac{m}{\rho} = \frac{36,46}{1,100} = 33.15$ ml.

Answer: 33.15 ml.

Task 2. For titration 20.00 ml 0.09218 N. sodium tetraborate solution consumes 19.42 ml of hydrochloric acid solution. Calculate the titer and molar concentration of the equivalent HCl solution.

Solution. According to the law of equivalence:

$$C_{Me}(Na_2B_4O_7) \cdot V(Na_2B_4O_7) = C_{Me}(HCl) \cdot V(HCl),$$

where the molar concentration of the equivalent solution of HCl is equal to:

$C_{M_e}(\mathrm{HCl}) = \frac{C_{M_e}(\mathrm{Na_2}B_4O_7) \cdot V(\mathrm{Na_2}B_4O_7)}{V(\mathrm{HCl})} = \frac{0.09218 \cdot 20.00}{19.42} = 0.09493$ mol/L.

Calculate the titer of HCl solution according to the formula:

$$T = C_{Me}(HCl) \cdot Me'(HCl);$$

$M(HCl) = 36.46$ g/mol;
$f_e(HCl) = 1$;
$M_{e'}(HCl) = M(HCl) \cdot f_e(HCl):1000 = 0.03646$.

$T = 0.09493 \cdot 0.03646 = 0.003461$.

Answer: 0.003461 g/ml; 0.09493 mol/L.

LABORATORY WORK

1. Weighing on analytical balances. Checking the capacity of measuring pipettes

Assay procedure. A weighing bottle is weighed on an analytical balance. Distilled water is collected in a measuring pipette up to the mark (water level reading along the lower edge of the meniscus). Pour water into a weighed weighing bottle and weigh it with water. Again, distilled water is collected in a measuring pipette up to the mark and poured into the same weighing bottle, weighed. The experiment is repeated once more (differences in weighing results should not differ by more than 0.005 g). Record the weighing results.Calculate the error ΔV, compare it with the allowable and determine the accuracy class of the pipette calibration. Tolerances in volume for 5.00 ml pipettes: Grade 1 - 0.01 ml, Grade 2 - 0.02 ml.

2. Preparation of standard solutions of the method acid-base titration

2.1. Preparation of 250 ml of 0.1 M NaOH solution

Method of preparation - set titer

Assay procedure. Measure 25 ml of 1 M NaOH solution with a measuring cylinder and place in a 250 ml measuring cylinder, bring to the mark with distilled water, mix, pour into a glass, close with a stopper, stick a label indicating the concentration and volume of the prepared solution, date of preparation, name and group number. The prepared solution is left to work on in the next lessons.

2.2. Preparation of 250 ml of 0.1 M HCl solution

Method of preparation - set titer
$M(HCl) = 36.46$ g/mol;
$f_e(HCl) = 1$;
$M_e(HCl) = 36.46$ g/mol.

$$a_{(HCl)} = \frac{C_{M_e} \cdot M_e \cdot V \cdot 100}{C\% \cdot 1000}, \text{ where}$$

a – sample weight, ml;
C_{Me} – given concentration;
M_e – molar mass equivalent of hydrochloric acid;
V – provided volume;
C% – the percentage concentration of the hydrochloric acid solution from which the solution of a given concentration is prepared.

Assay procedure. The hydrochloric acid solution available in the laboratory is poured into the measuring cylinder, the density is measured with the help of a hydrometer. According to the table find the concentration corresponding to the density of hydrochloric acid. The calculated volume of hydrochloric acid is measured with a small-capacity measuring cylinder, transferred to a 250 ml measuring cylinder and made up to the mark with distilled water. The prepared solution is poured into a glass, closed with a stopper, a label indicating the concentration and volume of the prepared solution, date of preparation, name and group number. The prepared solution is left to work on the next lessons.

Visual materials, learning and control tools

1. Tabular resources on the topic of the lesson.
2. Textbooks, handbook on analytical chemistry.
3. Learning and control tools: cards for assessing the initial level of knowledge; test questions.

ACID-BASE TITRATION

An acid-base titration is a method for determination of acids, bases, salts, based on the reaction between protoliths (acid HA and base B):

$$\underset{a_1}{HA} + \underset{b_2}{B} \leftrightarrow \underset{a_2}{HB^+} + \underset{b_1}{A^-}$$

therefore, the method of acid-base titration is also called neutralization method.

Titrants of the method are solutions of strong acids and bases: HC1, H_2SO_4, NaOH, KOH. These substances do not meet the requirements for standard substances; therefore, the concentration of titrants is determined by standardization of their solutions. Borax $Na_2B_4O_7 \cdot 10H_2O$, anhydrous sodium carbonate Na_2CO_3, oxalic acid dihydrate $H_2C_2O_4 \cdot 2H_2O$, and some others are commonly used as primary standards.

Types of acid-base titration

As mentioned above, in the classification of titrimetric methods, there exist two types of acid-base titration.

Alkalimetric titration (alkalimetry') is a method for determining:

– strong acids: $H_3O^+ + OH^- \leftrightarrow 2H_2O$

– molecular acids: $HA + OH^- \leftrightarrow A^- + H_2O$
$CH_3COOH + OH^- \leftrightarrow CH_3COO^- + H_2O$

– cationic acids: $HB^+ + OH^- \leftrightarrow B + H_2O$
$C_5H_5NH^+ + OH^- \leftrightarrow C_5H_5N + H_2O$

– anionic acids: $HA^- + OH^- \leftrightarrow A^{2-} + H_2O$
$H_2PO_4^- + OH^- \leftrightarrow HPO_4^{2-} + H_2O$

Acidimetric titration (acidimetry) is a method for determination:

– strong bases: $OH^- + H_3O^+ \leftrightarrow 2H_2O$

– molecular bases: $B + H_3O^+ \leftrightarrow HB^+ + H_2O$
$NH_3 + H_3O^+ \leftrightarrow NH_4^+ + H_2O$

– anionic bases: $A^- + H_3O^+ \leftrightarrow HA + H_2O$
$C_6H_5COO^- + H_3O^+ \leftrightarrow C_6H_5COOH + H_2O$

– cationic bases: $B^+ + H_3O^+ \leftrightarrow HB^{2+} + H_2O$
$H_2N{-}NH_3^+ + H_3O^+ \leftrightarrow [H_3N{-}NH_3]^{2+} + H_2O$

The possibility of using acid-base titration is determined by the total equilibrium constant of the acid-base reaction, which should be greater than $1 \cdot 10^8$, if the completeness of the binding of the titrating substance is 99.99% and its residue is 0.01%.

Because acid-base reactions are associated with hydrogen ion transfer and are accompanied by changes in the concentration of hydrogen ions $[H^+]$, this is important for determining the moment of equivalence in acid-base titration.

The moment of equivalence is determined by the pH of the solution.

The pH of the solution (hydrogen index) is the negative decimal logarithm of the concentration of hydrogen ions, expressed in mol/L:

$$pH = -\lg[H^+]$$

In the process of titration, the pH value of the solution changes and reaches the calculated value, which corresponds to the point of equivalence of TE. Indicators are used to determine the endpoint of CTT titration in practice.

An indicator is a substance which exhibits a visible change at an equivalent point, or close to it.

An acid-base indicator is an acid or a base itself, and during acid-base titration it changes its color at or near EP.

In case of indicator visual method of determining EPT in an acid-base titration, the addition of titrant to a titrated solution is stopped when solution color changes sharply due to color change of indicator added to the titrated solution.

There are two ways to select pH indicators:

1. **Qualitative method** - by reaction products. At the point of equivalence, determine the reaction of the medium and select indicators that change color in this medium.

For example, when titrating a strong acid HCl with a strong base of NaOH in TE in the solution is sodium chloride and water:

$$HCl + NaOH \leftrightarrow NaCl + H_2O$$

As a salt of a strong base and a strong acid, it has no pronounced acidic or basic properties, and therefore this solution has a neutral reaction medium, pH = 7. Therefore, you need to choose indicators that change their color in a neutral environment - litmus, phenolic red.

When titrating a weak acid *CH_3COOH strong base NaOH* in TE in the solution is sodium acetate and water:

$$CH_3COOH + NaOH \leftrightarrow CH_3COONa + H_2O$$
$$CH_3COOH + OH^- \leftrightarrow CH_3COO^- + H_2O$$

From the point of view of the protolytic theory, the acetate ion is an anionic base, and from the standpoint of the theory of electrolytic dissociation, it is a salt that hydrolyzes after the anion, as a result of which hydroxide ions accumulate in the solution. The solution has an alkaline reaction medium, $pH > 7$. Suitable indicators are phenolphthalein, thymolphthalein.

When titrating a weak base *$NH_3 \cdot H_2O$ strong acid HCl* in EP in the solution is ammonium chloride and water:

$$NH_3 \cdot H_2O + HCl \leftrightarrow NH_4Cl + H_2O$$
$$NH_3 \cdot H_2O + H^+ \leftrightarrow NH_4^+ + H_2O$$

According to the protolytic theory, the ammonium cation is a cationic acid, and from the standpoint of the theory of electrolytic dissociation, it is a salt that is hydrolyzed by the cation, as a result of which hydrogen ions accumulate. Therefore, the solution has an acidic reaction medium, $pH < 7$. Suitable indicators are methyl orange or methyl red.

2. Quantitative method A *titration curve* is a plot of concentration change of determined substance or any associated feature of the system (solution) against the volume of titrant added.

To construct the titration curve, calculate the pH at different points of titration, at least 5 points:

- pH of the initial solution,
- pH at the time of semi-neutralization,
- pH at the beginning of the titration jump (the analyzed solution is untitled by 0.1%),
- pH at the point of equivalence,
- pH at the end of the titration jump (analyzed solution is titrated by 0.1%).

Tutorial 11

1. THEME: Acid-base titration. Titration of the strong acids with strong bases and vice versa

2. PURPOSE: To study the theoretical bases of the method of acid-base titration and to acquire skills of titrimetric quantitative determination of strong acids and strong bases

3. OBJECTIVIES:

3.1. To study the theoretical foundations of the method of acid-base titration.

3.2. To study the properties of acid-base indicators and to learn to select indicators for fixing the end point of titration by reaction products and by the titration curve.

3.3. Master the technique of acidimetric and alkalimetric titration.

3.4. Acquire skills in the preparation of titrated solutions and standardization of solutions of acids and alkalis according to primary and secondary standards.

4. PLAN AND ORGANIZATIONAL STRUCTURE OF THE TUTORIAL:

4.1. An organizational issue ……………………………………………….3 min

4.2. Setting of the goal of the tutorial and motivation for studying the topic (introductory speech by the teacher)...7 min

4.3. The assessment of the initial level of knowledge and skills (assignments in paper cards)………...…..10 min

4.4. Correction of the initial level of knowledge and skills………………...40 min

4.5. Organization of students’ independent work (target instructions by the teacher, safety precautions)..5 min

4.6. Laboratory work…………………….……………………….……….....140 min

4.7. Summative assessment: checking the results of the laboratory work and protocols……...…...……..15 min

4.8. Concluding speech by the teacher, instructions for the next lesson...........5 min

5. REFERENCE FOR SELF STUDY:

5.1. Repeat the theoretical material from the course of inorganic chemistry and qualitative analysis: acid-base properties of substances; the proto-political theory of Bransted and Lowry; acidity and basicity constants; hydrogen pH; equilibria in aqueous solutions of strong acids and bases.

5.2. Study the program material on this topic, using the recommended literature and lectures.

Questions for self-study

1. What reactions underlie the method of acid-base titration? What is the essence of acid and alkalimetry?
2. What substances can be determined by acid-base titration?

3. In what direction are the reactions of acid-base interaction. At what value of the equilibrium constant do the reactions pass to the end?
4. What is the basis of fixing the end point of the titration?
5. Theory of acid-base indicators. Ionic, chromophore and ion-chromophore theories of explaining the nature of color change of indicators. What is the transition interval of the acid-base indicator, the titration index of pT?
6. What are the ways to select indicators to capture the end point of the titration?
7. Titration curves. How to calculate the pH value for the construction of the titration curve of a strong acid with a strong base and vice versa. What do such titration curves look like?
8. What is a titration jump? How do pH indicators pick up after the titration jump?
9. How to prepare titrated solutions of acids and alkalis? What substances are used as primary standards?

Solve the tasks:

Task 1. Calculate the pH of solutions containing 1 l of: a) 0.01 mol of HCl; b) 0.056 g of KOH.

Answer: a) 2; b) 11.

Task 2. the pH of the solutions is equal to: a) 2.63; b) 12.45. Why are the concentrations of H^+ and OH^- equal in these solutions?

Answer: a) $[H^+] = 2.34 \cdot 10^{-3}$; $[OH^-] = 4.27 \cdot 10^{-12}$;
b) $[H^+] = 3.54 \cdot 10^{-13}$; $[OH^-] = 2.82 \cdot 10^{-2}$.

Task 3. To 20 ml of 0.1 M NaOH solution was added 10 ml of 0.1 M HCl solution. Calculate the pH of the solution.

Answer: 12.5.

Task 4. Calculate the molar equivalent concentration, titre and correction factor for sodium hydroxide solution if 19.50 ml of this solution is used to titrate 20.00 ml of 0.05075 M oxalic acid solution.

Answer: 0.1041 mol/L; 0.004164 g/ml; 1,041.

Examples of the solved tasks:

In solutions of monoprotonic strong acids of the HA type, which completely dissociate into ions, the concentration of hydrogen ions is equal to the acid concentration (mol/L): $[H^+] = [HA]$.

pH calculated by the formula:

$$pH = -\lg [H^+]$$

In solutions of strong single-proton bases of the MeOH type, the concentration of OH ions is equal to the concentration of the base (mol/L): $[OH^-] = [MeOH]$. pOH is found by the formula:

$$pOH = –lg[OH^-],$$

and the pH is calculated by the formula:

$$pH = 14 – pOH$$

and the pH is calculated by the formula: $[H^+]$ or $[OH^-]$ 2 times more the concentration of acid or base, etc.

Task 1. Titrate 20.00 ml of 0.1 M HCl with 0.1 M KOH solution. Determine the pH and pOH of the solution when 18 ml of alkali was added.

Solution. $KOH + HCl \leftrightarrow KCl + H_2O$

Before the reaction in the initial solution was: $20 \cdot 0.1 = 2.0$ mmol HCl.
When titrated, added: $18 \cdot 0.1 = 1.8$ mmol KOH.
After the reaction in the solution remained: $2.0 – 1.8 = 0.2$ mmol HCl.
The volume of the solution became equal: $V_s = 20.0 + 18.0 = 38.0$ ml.

After the reaction, the HCl concentration became equal:

0,2 mmol HCl contained in 38 ml
x mmol – in 1 ml

$$C_M(HCl) = 0,005\ M$$

Find the pH of the solution: $pH = –lg[H^+] = –lg\ 0.005 = 2.3$.
Find the pOH of the solution: $pOH = 14 – pH = 14 – 2.3 = 11.7$.

Answer: pH = 2.3; pOH = 11.7.

Task 2. The pH value of the solution H_2SO_4 is equal to 5.46. Calculate how many grams H_2SO_4 contained in 1 liter of this solution.

Solution. Find the molar concentration of hydrogen ions in solution:

$$pH = –lg[H^+], \text{ where}$$

$$[H^+] = 10^{-pH} = 10^{-5,46} = 3.47 \cdot 10^{-6} \text{ mol/L}.$$

Because ionization H_2SO_4 passes according to the scheme:

$$H_2SO_4 \leftrightarrow 2H^+ + SO_4^{2-},$$

then the molar concentration H_2SO_4 is equal to:
$C_M = [H_2SO_4] = ½\ [H^+] = 3.47 \cdot 10^{-6} : 2 = 1.74 \cdot 10^{-6}$ mol/L.
Calculate how many grams H_2SO_4 contained in 1 liter of this solution:
$M(H_2SO_4) = 98.07$ g/mol;
$m(H_2SO_4) = C_M \cdot M(H_2SO_4) = 1.74 \cdot 10^{-6} \cdot 98.07 = 1.71 \cdot 10^{-4}$ mol/L.

Answer: $1.71 \cdot 10^{-4}$ mol/L.

Work on test tasks:

1. Titrants (standard solutions, working solutions) are solutions of reagents:
A. With a known concentration used in the titration. *
B. A certain concentration.
C. With a known title.
D. With a known concentration.
E. Used in the titration of the analyte.

2. The titration constant is:
A. The ratio of the constant of the ionic product of the solvent to the acidity constant of the analyte (for substances with acidic properties). *
B. The ratio of the next acidity constant (or basicity) of the analyte to the previous one (for polyprotic acids and bases). *
C. The ratio of the constant of the ionic product of the solvent to the basicity constant of the analyte (for substances with basic properties). *
E. The ratio of the acidity constant (or basicity) of the analyte to the solvent ionic product constant (for substances with acid-base properties).

3. The main characteristics of pH indicators are:
A. Transition interval. *
B. Titration rate. *
C. Acidity constant. *
E. Molar mass.
E. The concentration of the applied solution.

4. In the methods of acid-base titration titrated solutions (titrants) are prepared:
A. For the method of preparation titer. *
B. For the method of setting the titer. *
C. From standard titles. *
D. For the method of pipetting.
E. For the method of individual samples.

5. To analyze the titrimetric method, which is required:
A. Microvessels for accurate measurement of objects.
B. Micro ware for approximate washing of objects.
C. Indicators and devices for fixing equivalence points.
D. Titrated solutions.
E. First of all, the above. *

6. Specify the methods of selection of pH indicators:
A. Qualitative and quantitative. *
B. Pipetting and individual samples.
C. Direct and indirect.
D. Prepared and set titer.
E. Indicator and instrumental.

7. Select the primary standard for standardization of sulfuric acid solution:
A. Diphenylguanidine. *
B. Hydrochloric acid.
C. Benzoic acid.
D. Sodium bicarbonate.
E. Potassium hydroxide.

8. Select the primary standard for standardization of sodium hydroxide solution:
A. Benzoic Acid. *
B. Hydrochloric acid.
C. Diphenylguanidine.
D. Sodium bicarbonate.
E. Potassium hydroxide.

9. Select the primary standard for standardization of potassium hydroxide solution:
A. Benzoic Acid. *
B. Hydrochloric acid.
C. Diphenylguanidine.
D. Sodium bicarbonate.
E. Potassium hydroxide.

10. Select the primary standard for standardization of nitric acid solution:
A. Diphenylguanidine. *
B. Hydrochloric acid.
C. Benzoic acid.
D. Sodium bicarbonate.
E. Potassium hydroxide.

11. Select the primary standard for standardization of barium hydroxide solution:
A. Benzoic Acid. *
B. Hydrochloric acid.
C. Diphenylguanidine.
D. Sodium bicarbonate.
E. Potassium hydroxide.

12. Choose the method of acid-base titration in the determination of sulfuric acid:
A. Alkalimetry. *
B. Acidimetry
C. Both.
D. Neither one nor the other.

13. Choose the method of acid-base titration in the determination of potassium hydrophthalate:
A. Both. *
B. Acidimetry.
C. Alkalimetry.
D. Neither one nor the other.

14. Reactions in titrimetric methods of analysis include the following requirements:
A. Sufficient reaction rate. *
B. Stoichiometric ratio of components. *
C. Ability to fix an equivalence point. *
E. The reaction products must be soluble.
E. The reaction products must be colorless.

15. On the basis of which data, judge the amount of the analyte in titrimetric methods of analysis:
A. The volume of titrant that has reacted with the test substance.
B. Concentrations of reagent that have reacted with the analyte.
C. Mass of the reagent that reacted with the analyte.
D. Volumes of titrant and test solution reacted. *

16. The end point of titration in the method of acid-base titration is determined using pH indicators. When selecting pH indicators take into account:
A. pH of the medium at the point of equivalence. *

B. The nature of the titrant.
C. Properties of reaction products.
D. Change in pH during titration.
E. The nature of the analyte.

17. Specify the main way of expressing the concentration of titrants:
A. The molar concentration of the equivalent. *
B. Title.
C. Titer for the determined substance.
E. Percentage.
E. Molar.

18. Specify the methods of preparation of titrated solvents:
A. Prepared and set titer. *
B. Qualitative and quantitative.
C. Direct and indirect.
D. Pipetting and individual samples.
E. Indicator and instrumental.

19. Specify ways to fix the end points of the titration:
A. Indicator and instrumental. *
B. Qualitative and quantitative.
C. Direct and indirect.
D. Prepared and set titer.
E. Pipetting and individual samples.

20. What solutions can be standardized using the primary standard of potassium hydrophthalate in aqueous solutions:
A. Both. *
B. Alkali solution.
C. Acid solution.
D. Neither one nor the other.

21. What solutions can be standardized using the primary standard of sodium tetraborate in aqueous solutions:
A. Acid solution. *
B. Alkali solution.
C. Both.
D. Neither one nor the other.

22. What solutions can be standardized using the primary standard of oxalic acid in aqueous solutions:
A. Alkali solution. *
B. Acid solution.
C. Both.
D. Neither one nor the other.

23. What solutions can be standardized using the primary standard of succinic acid in aqueous solutions:
A. Alkali solution. *
B. Acid solution.
C. Both.
D. Neither one nor the other.

24. What solutions can be standardized using the primary standard of sodium sulfate in aqueous solutions:
A. Neither. *

B. Alkali solution.
C. Both.
D. Acid solution.

25. What indicators are used in the titration of NaOH solution HCl solution:
A. Both. *
B. Phenolphthalein.
C. Methyl orange.
D. Neither one nor the other.

26. Choose formulas for calculating the titer by sample weight:
A. $\frac{a}{V_f}$ *
B. $\frac{C_{M_E} \cdot M_{e\,(s.)}}{1000}$
C. $\frac{a \cdot 1000}{V \cdot M_e}$
D. $\frac{C_{M_E} \cdot V_f \cdot M_e}{1000}$
E. $\frac{T \cdot 1000}{M_e}$

27. Choose formulas for calculating the titer of the substance to be determined:
A. $\frac{C_{M_E} \cdot M_{e\,(s.)}}{1000}$ *
B. $\frac{a \cdot 1000}{V \cdot M_e}$
C. $\frac{C_{M_E} \cdot V_f \cdot M_e}{1000}$
D. $\frac{T \cdot 1000}{M_e}$
E. $\frac{a}{V_f}$

28. Choose formulas to calculate the molar concentration of the equivalent of the sample weight:
A. $\frac{a \cdot 1000}{V \cdot M_e}$ *
B. $\frac{C_{M_E} \cdot V_f \cdot M_e}{1000}$
C. $\frac{T \cdot 1000}{M_e}$
D. $\frac{C_{M_E} \cdot M_{e\,(s.)}}{1000}$

E. $\frac{a}{V_f}$

29. Choose formulas to calculate the molar concentration of the equivalent by titer:

A. $\frac{T \cdot 1000}{M_e}$ *

B. $\frac{C_{M_E} \cdot V_f \cdot M_e}{1000}$

C. $\frac{C_{M_E} \cdot M_{e\,(s.)}}{1000}$

D. $\frac{a \cdot 1000}{V \cdot M_e}$

E. $\frac{a}{V_f}$

30. Choose formulas to calculate sample weight of solids:

A. $\frac{C_{M_E} \cdot V_f \cdot M_e}{1000}$ *

B. $\frac{T \cdot 1000}{M_e}$

C. $\frac{C_{M_E} \cdot M_{e\,(s.)}}{1000}$

D. $\frac{a \cdot 1000}{V \cdot M_e}$

E. $\frac{a}{V_f}$

31. What methods of acid-base titration can determine the content of sulfuric acid in the solution:
A. Alkalimetry. *
B. Acidimetry.
C. Both.
D. Neither one nor the other.

32. What methods of acid-base titration can determine the content in sodium bicarbonate solution:
A. Acidimetry. *
B. Alkalimetry.
C. Both.
D. Neither one nor the other.

33. What methods of acid-base titration can determine the content of sodium hydrogen phosphate in the solution:
A. Acidimetry. *
B. Alkalimetry.
C. Both.
D. Neither one nor the other.

34. What methods of acid-base titration can determine the content of potassium sulfate in the solution:
A. Neither. *
B. Acidimetry.
C. Both.
D. Alkalimetry.

35. What methods of acid-base titration can determine the content of potassium hydrophthalate in the solution:
A. Both. *
B. Acidimetry.
C. Alkalimetry.
D. Neither one nor the other.

36. Primary standards must meet the requirements of:
A. Be chemically pure and comply with the chemical formula.
B. To be stable when stored in solid form and in solution.
C. Have a large molar mass equivalent.
D. Easy to clean by recrystallization or otherwise.
D. All of the above. *

37. Primary standards are substances:
A. Possessing all these properties. *
B. Well soluble in water.
C. Stable during storage.
D. Having a large molar mass equivalent.
E. Corresponding to the chemical formula.

38. The titration curve is:
A. Graphical representation of pH change during titration. *
B. A sharp change in pH near the equivalence point.
C. Untitred 0.1% of the substance.
D. Strictly equivalent amount of titrant was added.
E. The substance is exaggerated by 0.1%.

39. The titration jump is:
A. A sharp change in pH near the equivalence point. *
B. Graphic representation of pH change during titration.
C. Non-titrated 0.1% of the substance.
D. Strictly equivalent amount of titrant was added.
E. The substance is over-titration by 0.1%.

40. The beginning of the titration jump is:
A. Non-titrated 0.1% of materials. *
B. The graphic image changes the pH during the titration process.
C. A sharp change in pH near the equivalence point.
D. Strictly equivalent amount of titrant was added.
E. The substance is over-titration by 0.1%.

41. The end of the titration jump is:
A. The substance is over-titration d by 0.1% .. *
B. Graphic representation of pH change during titration.
C. Non-titrated 0.1% of the substance.
D. Strictly equivalent amount of titrant was added.
E. A sharp change in pH near the equivalence point.

42. Choose a formula to calculate the sample weight of solids:

A. $\frac{C_{M_E} \cdot V_f \cdot M_e}{1000}$ *

B. $\frac{C_{M_E} \cdot M_e}{1000}$

C. $\frac{C_{M_E} \cdot V_f \cdot M_e \cdot 100}{C\% \cdot 1000}$

D. $\frac{C_{M_E\text{pract.}}}{C_{M_E\text{theor.}}}$

E. $\frac{C_{M_E 1} \cdot V_1}{V}$

43. Choose a formula to calculate the titer of the solution:

A. $\frac{C_{M_E} \cdot M_e}{1000}$ *

B. $\frac{C_{M_E} \cdot V_f \cdot M_e}{1000}$

C. $\frac{C_{M_E} \cdot V_f \cdot M_e \cdot 100}{C\% \cdot 1000}$

D. $\frac{C_{M_E\text{pract.}}}{C_{M_E\text{theor.}}}$

E. $\frac{C_{M_E 1} \cdot V_1}{V}$

44. Choose a formula for calculating a sample weight of the solution:

A. $\frac{C_{M_E} \cdot V_f \cdot M_e \cdot 100}{C\% \cdot 1000}$ *

B. $\frac{C_{M_E} \cdot M_e}{1000}$

C. $\frac{C_{M_E} \cdot V_f \cdot M_e}{1000}$

D. $\frac{C_{M_E\text{pract.}}}{C_{M_E\text{theor.}}}$

E. $\frac{C_{M_E 1} \cdot V_1}{V}$

45. Choose a formula for calculating the correction factor to the molar concentration of the equivalent:

A. $\frac{C_{M_E\text{pract.}}}{C_{M_E\text{theor.}}}$ *

B. $\frac{C_{M_E} \cdot V_f \cdot M_e}{1000}$

C. $\frac{C_{M_E} \cdot V_f \cdot M_e \cdot 100}{C\% \cdot 1000}$

D. $\frac{C_{M_E} \cdot M_e}{1000}$

E. $\frac{C_{M_{E1}} \cdot V_1}{V}$

46. Choose a formula to calculate the molar concentration of titrant equivalence:

A. $\frac{C_{M_{E1}} \cdot V_1}{V}$ *

B. $\frac{C_{M_E} \cdot V_f \cdot M_e}{1000}$

C. $\frac{C_{M_E} \cdot V_f \cdot M_e \cdot 100}{C\% \cdot 1000}$

D. $\frac{C_{M_E \text{pract.}}}{C_{M_E \text{theor.}}}$

E. $\frac{C_{M_E} \cdot M_e}{1000}$

47. Specify the standard of sodium hydroxide:
A. Secondary standard. *
B. Primary standard.
C. Both.
D. Neither one nor the other.

48. Indicate which standard is oxalic acid:
A. Primary Standard. *
B. Secondary standard.
C. Both.
D. Neither one nor the other.

49. Indicate the standard of sodium tetraborate:
A. Primary Standard. *
B. Secondary standard.
C. Both.
D. Neither one nor the other.

50. Indicate which standard is 0.1000 M hydrochloric acid solution:
A. Secondary standard. *
B. Primary standard.
C. Both.
D. Neither one nor the other.

51. Reactions used in titrimetric methods of analysis must meet the requirements of:
A. Carried out in stoichiometric ratios. *

B. Carried out at a sufficient speed. *
C. It must be possible to fix an equivalence point. *
E. Adverse reactions should not occur. *
E. The reaction must be quantitative. *

52. Which of the following laws is the theoretical basis of titrimetric methods of analysis:
A. The law of equivalents. *
B. The law of conservation of body weight.
C. The law of multiple recovery.
D. The law of volumetric relations.

53. Choose the definition of "equivalence point":
A. The amount of titrant is strictly equivalent to the amount of the detected substance. *
B. The pH value at which there is a visible change in the color of the indicator.
C. The pH value at which the titration ends with this indicator.
D. The moment of titration, when pH = 7.
E. The end of titration.

54. Choose the definition of "end point of titration":
A. The end of the titration. *
B. The pH value at which there is a visible change in the color of the indicator.
C. The amount of titrant is strictly equivalent to the amount of the detected substance.
D. The moment of titration, when pH = 7.
E. The pH value at which the titration ends with this indicator.

55. Choose the definition of "indicator titration index":
A. The pH value at which the titration ends with this indicator. *
B. The pH value at which there is a visible change in the color of the indicator.
C. The amount of titrant is strictly equivalent to the amount of the detected substance.
D. The moment of titration, when pH = 7.
E. The end of titration.

56. Choose the definition of "point of neutrality":
A. The moment of titration, when pH = 7. *
B. The pH value at which there is a visible change in the color of the indicator.
C. The amount of titrant is strictly equivalent to the amount of the detected substance.
D. The pH value at which the titration with this indicator ends.
E. The end of titration.

57. Choose the definition of "indicator transition interval":
A. The pH value at which there is a visible change in the color of the indicator. *
B. The pH value at which the titration ends with this indicator.
C. The amount of titrant is strictly equivalent to the amount of the detected substance.
D. The moment of titration, when pH = 7.
E. The end of titration.

58. Select the primary standard for standardization of approximately 0.05 M sulfuric acid solution:
A. Sodium carbonate. *
B. Sodium chloride.
C. Oxalic acid.
D. Arsenic oxide.
E. Sodium nitrate.

59. Select the primary standard for standardization of approximately 0.1 M potassium hydroxide solution:
A. Oxalic acid. *

B. Sodium chloride.
C. Sodium carbonate.
D. Arsenic oxide.
E. Sodium nitrate.

60. Select the primary standard for standardization of approximately 0.1 M hydrochloric acid solution:
A. Sodium carbonate. *
B. Sodium chloride.
C. Oxalic acid.
D. Arsenic oxide.
E. Sodium nitrate.

61. Select the primary standard for standardization of approximately 0.05 M barium hydroxide solution:
A. Oxalic acid. *
B. Sodium chloride.
C. Sodium carbonate.
D. Arsenic oxide.
E. Sodium nitrate.

62. Select the primary standard for standardization of approximately 0.1 M nitric acid solution:
A. Sodium carbonate. *
B. Sodium chloride.
C. Oxalic acid.
D. Arsenic oxide.
E. Sodium nitrate.

63. To construct a titration curve, it is necessary to calculate the pH at different points of titration:
A. Before titration. *
B. At the time of semi-neutralization. *
C. At the beginning of the titration jump. *
D. At the point of equivalence. *
E. At the end of the titration jump. *

64. When selecting pH indicators, the most important is:
A. pH of the medium at the point of equivalence. *
B. The nature of the titrant.
C. Properties of reaction products.
D. The nature of the determined substances.
E. Changing the pH of the medium during the titration.

65. Specify the substance in the titration of which 0.1 M hydrochloric acid solution has the largest titration jump:
A. Sodium hydroxide. *
B. Barium hydroxide ($K_{b2} = 2,3 \cdot 10^{-1}$).
C. Lithium hydroxide ($K_b = 6,8 \cdot 10^{-1}$).
D. Triethylamine ($K_b = 1 \cdot 10^{-3}$).
E. Calcium hydroxide ($K_{b2} = 4,0 \cdot 10^{-2}$).

66. Choose the appropriate nature of the titration curve when titrating a strong base with a strong acid:
A. pH during titration changes dramatically. *
B. There is no jump on the titration curve.
S. pH during titration changes smoothly.
D. Two jumps on the titration curve.
E. Two jumps on the curve, the second jump is small.

67. For the standardization of alkali solutions as primary standards use oxalic acid, benzoic, sulfamic, etc., BECAUSE these acids meet the requirements for primary standards and react with alkalis quickly, stoichiometrically, with a sharp change in pH near equivalence:

A. 1-Right. 2-Right. Link – Right.*
B. 1-Right. 2-Right. Link – Wrong.
C. 1-Right. 2-Wrong. Link – Wrong.
D. 1-Wrong. 2-Right. Link – Wrong.
E. 1-Wrong. 2-Wrong. Link – Wrong.

68. The use of pH indicators in the form of mixed indicators makes the change in color of the indicators at the end of the titration sharper, BECAUSE the color of the pH indicator on the background of indifferent dye is fixed by our eyes more clearly:

A. 1-Right. 2-Right. Link – Right.*
B. 1-Right. 2-Right. Link – Wrong.
C. 1-Right. 2-Wrong. Link – Wrong.
D. 1-Wrong. 2-Right. Link – Wrong.
E. 1-Wrong. 2-Wrong. Link – Wrong.

69. Titrated hydrochloric acid solution is prepared by the method of the established titer, BECAUSE hydrochloric acid does not meet the requirements for primary standards:

A. 1-Right. 2-Right. Link – Right.*
B. 1-Right. 2-Right. Link – Wrong.
C. 1-Right. 2-Wrong. Link – Wrong.
D. 1-Wrong. 2-Right. Link – Wrong.
E. 1-Wrong. 2-Wrong. Link – Wrong.

70. The method of acid-base titration can determine all acids and bases, BECAUSE all acids interact with alkalis, and all bases interact with acids:

A. 1-Right. 2-Right. Link – Right.
B. 1-Right. 2-Right. Link – Wrong.
C. 1-Right. 2-Wrong. Link – Wrong.
D. 1-Wrong. 2-Right. Link – Wrong.*
E. 1-Wrong. 2-Wrong. Link – Wrong.

LABORATORY WORK

Preparation and standardization of titrated solutions of acid-base titration method

1. Preparation of a solution of the primary standard of sodium tetraborate - 0.1 N. 200.0 ml

$M(Na_2B_4O_7 \cdot 10H_2O) = 381.4$ g/mol;
$f_e(Na_2B_4O_7 \cdot 10H_2O) = ½$;
$M_e(Na_2B_4O_7 \cdot 10H_2O) = f_e(Na_2B_4O_7 \cdot 10H_2O) \cdot M(Na_2B_4O_7 \cdot 10H_2O)$;
$M_e(Na_2B_4O_7 \cdot 10H_2O) = ½ \cdot 381,4 = 190.7$ g/mol;
$M_{e'}(Na_2B_4O_7 \cdot 10H_2O) = M_e(Na_2B_4O_7 \cdot 10H_2O):1000 = 0.1907$;
$a(Na_2B_4O_7 \cdot 10H_2O) = C_{Me}(Na_2B_4O_7 \cdot 10H_2O) \cdot V_f \cdot M_{e'}(Na_2B_4O_7 \cdot 10H_2O)$.

Assay procedure. The sample weight of sodium tetraborate, taken on analytical balances by difference, is transferred to a volumetric flask with a capacity of 200.0

ml, dissolved in a small amount of hot distilled water, cooled, adjusted to the mark with water and mixed thoroughly.

Calculate the titer and molar concentration of the equivalent of the prepared solution to the nearest four significant digits.

$$T_{(Na_2B_4O_7 \cdot 10H_2O)} = \frac{a_{(Na_2B_4O_7 \cdot 10H_2O)}}{V_к}$$

$$C_{M\,e\,(Na_2B_4O_7 \cdot 10H_2O)} = \frac{T_{(Na_2B_4O_7 \cdot 10H_2O)}}{M_{e'(Na_2B_4O_7 \cdot 10H_2O)}}$$

2. Standardization of titrated hydrochloric acid solution according to the primary standard - sodium tetraborate

The titration method is direct

Titration method – pipetting

$$2HCl + Na_2B_4O_7 + 5H_2O \leftrightarrow 2NaCl + 4H_3BO_3$$
$$2H^+ + B_4O_7^{2-} + 5H_2O \leftrightarrow 4H_3BO_3$$

M(HCl) = 36.46 g/mol;
f_e(HCl) = 1;
M_e(HCl) = f_e(HCl)·M(HCl) = 1·36.46 = 36.46 g/mol;
$M_{e'}$(HCl) = M_e(HCl):1000 = 0.03646.

Assay procedure. Transfer 20.00 ml of the prepared sodium tetraborate solution to a conical flask for titration with a measuring pipette, add 1-2 drops of methyl orange indicator and titrate with hydrochloric acid solution until the transition from yellow to orange. Titration is performed until three reproducible results are obtained (the difference between the results of repeated titrations should not exceed 0.10 ml).

The titer, the molar concentration of the hydrochloric acid solution and the correction factor are calculated from the average volume of HCl.

$$C_{M(HCl)} = \frac{C_{M_e(Na_2B_4O_7 \cdot 10H_2O)} \cdot V_{(Na_2B_4O_7 \cdot 10H_2O)}}{V_{(HCl)}}$$

$$T_{(HCl)} = C_{M(HCl)} \cdot M_{e'(HCl)}$$

$$C_f = \frac{C_{M(\mathrm{HCl})\mathrm{pract.}}}{C_{M(\mathrm{HCl})\mathrm{theor.}}}$$

2. Standardization of titrated sodium hydroxide solution according to secondary standards - hydrochloric acid solution

The titration method is direct

Titration method – pipetting

$$NaOH + HCl \leftrightarrow NaCl + H_2O$$
$$OH^- + H^+ \leftrightarrow H_2O$$

$M(NaOH) = 40.00$ g/mol;

$f_e(NaOH) = 1$;

$M_e(NaOH) = f_e(NaOH) \cdot M(NaOH) = 1 \cdot 40.00 = 40.00$ g/mol;

$M_{e'}(NaOH) = M_e(NaOH):1000 = 0.04000$.

A. Titration with methyl orange indicator

Assay procedure. To the titration flask measure 20.00 ml of sodium hydroxide solution with a measuring pipette, add 1-2 drops of methyl orange indicator and titrate with hydrochloric acid solution until the transition from yellow to orange. The titration is repeated until three reproducible results are obtained.

The titer, molar concentration of sodium hydroxide solution and correction factor are calculated from the average volume of hydrochloric acid solution..

$$C_{M(NaOH)} = \frac{C_{M(HCl)} \cdot V_{(HCl)}}{V_{(NaOH)}}$$

$$T_{(NaOH)} = C_{M\,(NaOH)} \cdot M_{e'\,(NaOH)}$$

$$C_f = \frac{C_{M(\mathrm{NaOH})\mathrm{pract.}}}{C_{M(\mathrm{NaOH})\mathrm{theor.}}}$$

B. Titration with phenolphthalein indicator

Assay procedure. Measure 20.00 ml of hydrochloric acid solution into the titration flask with a pipette, add 1-2 drops of phenolphthalein indicator and titrate with sodium hydroxide solution to a stable (not disappearing for 30 s) pale pink color of the solution. The titration is repeated until three reproducible results are obtained.

The titer, molar concentration of sodium hydroxide, and correction factor are calculated from the mean volume of sodium hydroxide solution.

$$C_{M(NaOH)} = \frac{C_{M(HCl)} \cdot V_{(HCl)}}{V_{(NaOH)}}$$

$$T_{(NaOH)} = C_{M\,(NaOH)} \cdot M_{e'\,(NaOH)}$$

$$C_f = \frac{C_{M(\mathrm{NaOH})\mathrm{pract.}}}{C_{M(\mathrm{NaOH})\mathrm{theor.}}}$$

Visual materials, learning and control tools

1. Tabular resources on the topic of the lesson.
2. Textbooks, handbook on analytical chemistry.
3. Learning and control tools: cards for assessing the initial level of knowledge; test questions.

TYPES OF TITRATION USED IN TITRIMETRIC ANALYSIS

Direct titration, back titration, and *indirect titration,* or *titration with substituent (substitution titration) are used in the titrimetric analysis.*

Direct titration is a type of titration during which the determined substance is directly titrated with standard titrant solution or vice versa.

$$HA + OH^- \leftrightarrow A^- + H_2O$$
$$\text{or} \quad B + H_3O^+ \leftrightarrow HB^+ + H_2O$$

Back titration (titration by residue) is titration of unreacted substance, which has been added as a standard solution in excess to the analyzed solution.

$$A^- + H_3O^+_{ex.} \leftrightarrow HA + H_2O$$
$$H_3O^+_{rem.} + OH^- \leftrightarrow 2H_2O$$

Indirect titration (substitution titration) is titration, during which a determined substance does not react directly with a titrant, and is determined indirectly by using a stoichiometrically proceeding reaction leading to the formation of another substance that reacts with the titrant.

$$HA + OH^- \leftrightarrow A^- + H_2O$$
$$\text{or } B + H_3O^+ \leftrightarrow HB^+ + H_2O$$

During titration, either a predetermined mass of the analyzed substance or precisely measured volume of the analyzed solution can be taken. According to this, two methods are distinguished: *the method of individual weights* and *method of pipetting.*

In the method of ***individual weights***, an exact sample weight of substance is weighted using an analytical balance, quantitatively transferred to a titration flask, dissolved by adding a certain amount of solvent to the flask, and the resulting solution is titrated. In this case, it is not necessary to measure the volume of the titrated solution.

In ***the pipetting method***, an aliquot is sampled using a calibrated pipette, which corresponds to the precisely measured volume of the analyzed substance solution with an unknown molar equivalent concentration, and the aliquot is titrated with standard titrant solution with molar equivalent concentration.

Direct and substitution titration

The method of separate samples

$$m = \frac{C_{(\mathrm{t})} \cdot V_{(\mathrm{t})} \cdot \mathrm{M}_{\mathrm{e\ (s)}}}{1000}$$

$$\omega = \frac{C_{(t)} \cdot V_{(t)} \cdot M_{e\,(s)}}{a_{(s)} \cdot 1000} \cdot 100\%$$

The pipetting method $m = \frac{C_{(t)} \cdot V_{(t)} \cdot M_{e(s)} \cdot V_f}{1000 \cdot V_p}$

$$\omega = \frac{C_{(t)} \cdot V_{(t)} \cdot M_{e\,(s)} \cdot V_f}{a_{(s)} \cdot 1000 \cdot V_p} \cdot 100\%$$

Back titration

The method of separate samples

$$m = \frac{(V_{(t1)} \cdot C_{(t\,1)} - V_{(t\,2)} \cdot C_{(t\,2)}) \cdot M_{e\,(s)}}{1000}$$

$$\omega = \frac{(V_{(t\,1)} \cdot C_{(t\,1)} - V_{(t\,2)} \cdot C_{(t\,2)}) \cdot M_{e\,(s)}}{a_{(s)} \cdot 1000} \cdot 100\%$$

The pipetting method $m = \frac{(V_{(t1)} \cdot C_{(t\,1)} - V_{(t\,2)} \cdot C_{(t\,2)}) \cdot M_{e(s)} \cdot V_f}{1000 \cdot V_p}$

$$\omega = \frac{(V_{(t\,1)} \cdot C_{(t\,1)} - V_{(t\,2)} \cdot C_{(t\;2)}) \cdot M_{e\,(s)} \cdot V_f}{a_{(s)} \cdot 1000 \cdot V_p} \cdot 100\%$$

* In the given formulas cognition is accepted:
$a_{(s)}$ – separate sample of analyzed substance, g;
$C_{(t)}$ – titrant concentration, mol/L;
$V_{(t)}$ – titrant volume, ml;
$M_{e(s)}$ - molar mass equivalent of the analyzed substance, g/mol;
V_f – volume of volumetric flask, ml;
V_p – volume of the pipette, ie the volume of solution taken for titration, ml.

ACID-BASIC TITRATION OF WEAK ELECTROLYTES

Weak acids and bases are weak electrolytes and in aqueous solutions decompose into ions in part. In their solutions, an equilibrium is established between ions and undissociated molecules. The proportion of dissociated molecules is called the degree of ionization or the degree of dissociation.

The dissociation of the weak acid HA can be represented by the following equation:

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

The equilibrium constant of ionization of this acid, based on the law of active masses (LAM), has the form:

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

The equilibrium constant of ionization of weak acids or bases is called the ionization constant and is denoted:

K_a – acid ionization constant (acidity constant);

K_b – base ionization constant (basicity constant).

The values of Ka and Kb are a quantitative characteristic of the strength of the acid and the base and allow you to calculate the pH of solutions of weak electrolytes.

The reference literature often gives the values of pK constants for acids and bases, which are defined as:

$$pK_a = -lgK_a\,; \qquad pK_b = -lgK_b$$

A larger value of Ka (or Kb) corresponds to a smaller value of pKa (or pKb) and a greater strength of acid (or base).

When titrating acids and bases, it is necessary to take into account the value of their ionization constants.

It is practically established that at titration of 0,1 M of solutions of acids and bases with indicator fixing of EPT the ionization constant of acid or basis has to be not less 10^{-7}.

If the ionization constant and the concentration of the weak acid or base and the concentration of the titrant are known, the pH can be calculated at any time during the titration.

The calculation of pH in solutions of weak acids, weak bases and buffer systems is carried out according to the following formulas:

for weak acids: $pH = \frac{1}{2}\,pK_a - \frac{1}{2}\,lgC_a$

for weak basic: $pH = 7 + \frac{1}{2}\,pK_a + \frac{1}{2}\,lgC_b$

for buffer systems: $pH = pK_a + lg\frac{C_b}{C_a}$

where C_a –concentration of acid, mol/L; C_b –concentration of salt, mol/L.

Buffer solutions are a mixture of a weak acid and a salt of this acid, or a mixture of a weak base and a salt of this base. The buffer is formed during the titration of weak electrolytes. For example, when titrating acetic acid with alkali, an acetate ion appears in solution, which in a mixture with untitled acetic acid forms an acetate buffer solution. (CH_3COOH, CH_3COO^-).

Buffer systems prevent a sharp change in pH in the area of buffer action when adding acid or base.

Tutorial 12

1. THEME: Acid-base titration. Titration of the weak acids with alkalis and weak bases with strong acids

2. PURPOSE: To study the theory of titration of weak acids with alkalis and weak bases by strong acids and to acquire skills of quantitative determination of weak acids and weak bases

3. OBJECTIVIES:

3.1. To study the theoretical bases of titration of weak acids with alkalis and weak bases with strong acids.

3.2. Learn to evaluate the possibility of titrimetric determination of weak acids and weak bases in aqueous media with visual fixation of the end of titration.

3.3. Learn to calculate pH at different points of titration of weak electrolytes, analyze titration curves.

3.4. Learn the essence of methods and techniques of titration and learn to choose them for a particular method of titrimetric determination. Study the formulas for calculating the result of titrimetric analysis.

4. PLAN AND ORGANIZATIONAL STRUCTURE OF THE TUTORIAL:

4.1. An organizational issue ……………………………………………….3 min

4.2. Setting of the goal of the tutorial and motivation for studying the topic (introductory speech by the teacher)...7 min

4.3. The assessment of the initial level of knowledge and skills (assignments in paper cards)………...…...10 min

4.4. Correction of the initial level of knowledge and skills………………...40 min

4.5. Organization of students' independent work (target instructions by the teacher, safety precautions)...5 min

4.6. Laboratory work…………………….……………….…………....140 min

4.7. Summative assessment: checking the results of the laboratory work and protocols……..…..…...15 min

4.8. Concluding speech by the teacher, instructions for the next lesson...........5 min

5. REFERENCE FOR SELF STUDY:

5.1. Repeat the theoretical foundations of acid-base titration, the theory of weak electrolytes.

5.2. Study the program material on this topic, using the recommended literature and lectures.

Questions for self-study

1. What substances are weak electrolytes? How do weak electrolytes dissociate in solutions? What is the degree of dissociation (ionization), dissociation constant, acidity or basicity?
2. On the basis of what it is possible to draw a conclusion about possibility of titration in water environments with indicator fixing of the end of titration of weak electrolytes?
3. How to calculate the pH at different times of titration (before titration, at the time of semi-neutralization, at the beginning of the titration jump, at the equivalence point, at the end of the titration jump) when titrating weak acids and weak bases?
4. What are the titration curves of weak acids and weak bases? Compare them with the titration curves of strong acids and alkalis.
5. Why does the pH change slowly to the equivalence point when titrating weak acids and weak bases?
6. Does the pH at the point of equivalence in the titration of weak acids and weak bases coincide with the line of neutrality?
7. What is the relationshipLink between the magnitude of the titration jump and the constants of acidity or basicity of the determined substances?
8. What is the essence and when it is possible to use direct titration, back titration, substitution titration?
9. What is the essence, advantages and disadvantages of pipetting methods and individual samples? What formulas are used to calculate the result of titrimetric analysis?

Solve the tasks:

Task 1. A 0.1 M acetic acid solution was titrated with a 0.1 M sodium hydroxide solution at 80%. Calculate the pH of the solution.

Answer: 5.35.

Task 2. Calculate the pH of the solution obtained by adding to 18 ml of 0.11 M formic acid solution 10 ml of 0.16 M sodium hydroxide solution.

Answer: 4.37.

Task 3. A separate samples of the ammonium salt weighing 1,000 g was treated with an excess of concentrated NaOH solution. The released ammonia was absorbed in 50.00 ml of 1.072 M HCl solution and the excess acid was titrated with 25.40 ml of NaOH (T (NaOH) = 0.004120 g/ml). Calculate the mass fraction (in%) of NH_3 in the sample.

Answer: 86.67%.

Examples of the solved tasks:

Task 1. Calculate the pH of a solution containing 4.6 g of formate acid in 1 liter of solution.

Solution. Find the molar concentration of formic acid:

$M_{(HCOOH)} = 46.03$ g/mol;

$C_{M(HCOOH)} = \frac{m_{(HCOOH)}}{M_{(HCOOH)}} = \frac{4.6}{46.03} = 0.09993 \text{ M} \approx 0.1 \text{ M}.$

Find the value in the directory $pK_a(HCOOH)$ and calculate the pH of the solution according to the formula for weak acids:

$pK_a\,(HCOOH) = 3.75$;

$pH = ½\, pK_a – ½ \lg C_a = ½ \cdot 3.75 – ½ \cdot \lg 0.1 = 2.36$.

Answer: 2.36.

Task 2. Titrate 25 ml of 0.1 M CH_3COOH solution with NaOH solution of the same concentration. Calculate the pH of the solution by adding a) 5 ml, b) 25 ml and c) 30 ml of baced.

Solution. To calculate the pH of an aqueous solution, it is necessary to take into account which substances having acidic or basic properties are in the solution and to know their molar concentration at the time of pH calculation.

Titration of the acetic acid solution with a solution of sodium hydroxide is carried out according to the equation:

$$CH_3COOH + NaOH \leftrightarrow CH_3COONa + H_2O$$

a). From the beginning of the titration to the point of equivalence in the solution there is a buffer mixture, so the pH value is calculated by the formula:

$$pH = pK_a + \lg \frac{C_b}{C_a}$$

$pK_a(CH_3COOH) = 4.76$.

The initial solution was: 25 · 0.1 = 2.5 mmol CH_3COOH. Added 5 · 0.1 = 0.5 mmol NaOH. The substances reacted in equivalent quantities, which means that 0.5 mmol of CH_3COONa was formed and 2.5 - 0.5 = 2.0 mmol of CH3COOH remained. Since CH_3COONa and CH_3COOH are in the same volume of solution (25 + 5 = 30 ml), it is possible to substitute in the formula their quantities, but not the concentration:

$$pH = 4{,}76 + \lg\frac{0{,}5}{2{,}0} = 4{,}15$$

b). After adding 25 ml of NaOH, the reaction was complete, ie all acetic acid (2.5 mmol) was converted into sodium acetate - anionic base (2.5 mmol). The pH value is calculated by the formula for weak bases:

$$pH = 7 + ½\, pK_a + ½\, \lg C_b$$

Calculate the molar concentration CH_3COONa:

2,5 mmol CH_3COONa are in (25 + 25) ml of solution

x mmol CH_3COONa are in 1 ml of solution

$C_M(CH_3COONa) = 0.05$ M

pH = 7 + ½ · 4.76 + ½ · lg 0.05 = 8.73

c). After adding 30 ml of NaOH, the solution will be titrated with a strong base, and the pH of the medium will be determined by hydroxyl ions, the concentration of which is equal to: $[OH^-] = \frac{0.1 \cdot 10}{(25+30)} = 0.018$

pOH = = –lg[OH^-] = –lg 0.018 = 1.74

pH = 14 – pOH = 14 – 1.74 = 12.3.

Answer: 4.15; 8.73; 12.3.

Work on test tasks

1. Specify the titration methods:
A. Direct and indirect. *
B. Qualitative and quantitative.
C. Pipetting and separate samples.
D. Prepared and set titer.
E. Indicator and instrumental.

2. Specify the titration methods:
A. Pipetting and separate samples. *
B. Qualitative and quantitative.
C. Direct and indirect.
D. Prepared and set titer.
E. Indicator and instrumental.

3. Select the appropriate method if the substance reacts with the titrant stoichiometrically with sufficient speed:
A. Method of direct titration. *
B. The method of back titration.
C. Substitution titration.
D. Titration with instrumental fixation of the equivalence point.
E. The method of taking individual samples.

4. Choose the appropriate method, if it really reacts with the titrant stoichiometrically, but slowly:
A. Method of back titration *
B. The method of direct titration.
C. Substitution titration.
D. Titration with instrumental fixation of equivalence points.
E. The method of taking ызэфкфеу samples.

5. What indicators are used in cases of titration of NH_3 solution with HCl solution:
A. Phenolphthalein.
B. Methyl orange. *
C. Both.
D. Neither one nor the other.

6. What indicators are used in cases of titration of CH_3COOH solution with NaOH solution:
A. Phenolphthalein. *

B. Methyl orange.
C. Both.
D. Neither one nor the other.

7. When titrating substances by the method of direct titration, the result of the analysis can be calculated by the formulas:

A. $\frac{C_{(t)} \cdot V_{(t)} \cdot M_{e\,(s.)}}{1000}$ *

B. $\frac{C_{(t)} \cdot V_{(t)} \cdot M_{e\,(s.)}}{a_{(s.)} \cdot 1000} \cdot 100\%$ *

C. $\frac{T_{(t\,/s.)} \cdot V_{(t)} \cdot C_{f}}{a_{(s.)}} \cdot 100\%$ *

D. $\frac{T_{(t\,/s.)} \cdot V_{(t)} \cdot V_{f} \cdot C_{f}}{a_{(s.)} \cdot V_{p}} \cdot 100\%$ *

E. $\frac{T_{(t/s.)} \cdot V_{(t)} \cdot V_{f} \cdot C_{f}}{V_{p}}$ *

8. Choose the appropriate method if the substance reacts with the titrant stoichiometrically and quickly, but it is impossible to choose the indicator:
A. Titration with instrumental fixation of the equivalence point. *
B. The method of direct titration.
C. Substitution titration.
D. Pipetting method.
E. The method of taking separate samples.

9. Choose the appropriate method if the substance reacts with the titrant quickly, but not stoichiometrically:
A. Titration by substitution. *
B. The method of direct titration.
C. The method of back titration
D. Titration with instrumental fixation of the equivalence point.
E. The method of taking separate samples.

10. Select the appropriate method, if the substance does not directly interact with the titrant:
A. Titration by substitution. *
B. The method of direct titration.
C. The method of back titration.
D. Titration with instrumental fixation of the equivalence point.
E. The method of taking separate samples.

11. Select the appropriate methods, taking into account the following conditions of determination, if the analyte is sufficient:
A. Pipetting method. *
B. The method of direct titration.
C. Fixing the equivalence point by instrumental methods.
D. The method of separate samples.
E. The method of back titration.

12. The content of ammonium salts can be determined:
A. By way of back titration (in excess). *

B. By way of substitution. *
C. Formal titration. *
D. By direct titration.
E. By the method of separate samples.

13. Select the appropriate methods, taking into account the following conditions of determination, if the analyzed substance was not enough:
A. The method of separate samples. *
B. The method of direct titration.
C. Fixing the equivalence point by instrumental methods.
D. The method of back titration.
E. Pipetting method.

14. Select the appropriate methods, taking into account the following conditions of determination, if you want high accuracy of determination:
A. The method of separate samples. *.
B. The method of direct titration.
C. Fixing the equivalence point by instrumental methods.
D. Pipetting method.
E. The method of back titration.

15. Select the appropriate methods, taking into account the following conditions of determination, if the analysis must be carried out quickly:
A. Pipetting method. *
B. The method of direct titration.
C. Fixing the equivalence point by instrumental methods.
D. The method of separate samples.
E. The method of back titration.

16. Select the appropriate methods, taking into account the following conditions of determination, if the analyzed solution is colored:
A. Fixing the equivalence point by instrumental methods. *
B. The method of direct titration.
C. The method of back titration.
D. The method of separate samples.
E. Pipetting method.

17. The calculation of the pH of a solution of a strong acid is carried out according to the formula:
A. $pH = –lg[H^+]$*
B. $pH = pK_a + lg\frac{C_b}{C_a}$
C. $pH = 7 + ½\ pK_a + ½\ lgC_b$
D. $pH = ½\ pK_a – ½\ lgC_a$
E. $pH = \frac{pK_{a_1} + pK_{a_2}}{2}$

18. The calculation of the pH of a solution of a weak acid is carried out according to the formula:
A. $pH = ½\ pK_a – ½\ lgC_a$ *
B. $pH = –lg[H^+]$
C. $pH = pK_a + lg\frac{C_b}{C_a}$
D. $pH = 7 + ½\ pK_a + ½\ lgC_b$
E. $pH = \frac{pK_{a_1} + pK_{a_2}}{2}$

19. The calculation of the pH of a solution of a strong base is carried out according to the formula:
A. $pH = 14 – pOH$*
B. $pH = –lg[H^+]$
C. $pH = pK_a + \lg\frac{C_b}{C_a}$
D. $pH = 7 + ½\,pK_a + ½\,lgC_b$
E. $pH = ½\,pK_a – ½\,lgC_a$

20. The calculation of the pH of a solution of a weak base is carried out according to the formula:
A. $pH = 7 + ½\,pK_a + ½\,lgC_b$*
B. $pH = 14 – pOH$
C. $pH = –lg[H^+]$
D. $pH = pK_a + \lg\frac{C_b}{C_a}$
E. $pH = ½\,pK_a – ½\,lgC_a$

21. The calculation of the pH of a solution containing a weak acid and a salt of this acid is carried out according to the formula:
A. $pH = pK_a + \lg\frac{C_b}{C_a}$ *
B. $pH = –lg[H^+]$
C. $pH = 7 + ½\,pK_a + ½\,lgC_b$
D. $pH = ½\,pK_a – ½\,lgC_a$
E. $pH = \frac{pK_{a_1} + pK_{a_2}}{2}$

22. Choose the formula for calculating the mass fraction (in%) of the analyzed substance, taking into account the direct method of titration and the method of separate samples:
A. $\frac{T_{(t/s.)} \cdot V_{(t)} \cdot C_f}{a_{(s.)}} \cdot 100\%$ *
B. $\frac{T_{(t/s.)} \cdot V_{(t)} \cdot V_f \cdot C_f}{a_{(c.)} \cdot V_p} \cdot 100\%$
C. $\frac{(V_{(t1)} \cdot C_{(t1)} - V_{(t2)} \cdot C_{(t2)}) \cdot M_{e(s.)}}{a_{(s.)} \cdot 1000} \cdot 100\%$
D. $\frac{(V_{(t1)} \cdot C_{(t1)} - V_{(t2)} \cdot C_{(t2)}) \cdot M_{e(s.)} \cdot V_f}{1000 \cdot V_p}$
E. $\frac{C_{(t)} \cdot V_{(t)} \cdot M_{e(s.)}}{1000}$

23. Choose a formula to calculate the mass fraction (in%) of the analyzed substance according to the direct method of titration and the pipetting method:
A. $\frac{T_{(t/s.)} \cdot V_{(t)} \cdot V_f \cdot C_f}{a_{(s.)} \cdot V_p} \cdot 100\%$ *
B. $\frac{T_{(t/s.)} \cdot V_{(t)} \cdot C_f}{a_{(s.)}} \cdot 100\%$

C. $\dfrac{(V_{(t1)}\cdot C_{(t1)} - V_{(t2)}\cdot C_{(t2)})\cdot M_{e(s.)}}{a_{(s.)}\cdot 1000}\cdot 100\%$

D. $\dfrac{(V_{(t1)}\cdot C_{(t1)} - V_{(t2)}\cdot C_{(t2)})\cdot M_{e(s.)}\cdot V_f}{1000\cdot V_p}$

E. $\dfrac{C_{(t)}\cdot V_{(t)}\cdot M_{e(s.)}}{1000}$

24. Choose a formula to calculate the mass fraction (in%) of the analyzed substance according to back titration and the method of separate samples:

A. $\dfrac{(V_{(t1)}\cdot C_{(t1)} - V_{(t2)}\cdot C_{(t2)})\cdot M_{e(s.)}}{a_{(s.)}\cdot 1000}\cdot 100\%^{*}$

B. $\dfrac{T_{(t/s.)}\cdot V_{(t)}\cdot V_f\cdot C_f}{a_{(s.)}\cdot V_p}\cdot 100\%$

C. $\dfrac{T_{(t/s.)}\cdot V_{(t)}\cdot C_f}{a_{(s.)}}\cdot 100\%$

D. $\dfrac{(V_{(t1)}\cdot C_{(t1)} - V_{(t2)}\cdot C_{(t2)})\cdot M_{e(s.)}\cdot V_f}{1000\cdot V_p}$

E. $\dfrac{C_{(t)}\cdot V_{(t)}\cdot M_{e(s.)}}{1000}$

25. Choose a formula to calculate the mass fraction (in%) of the analyzed substance according to back titration and the pipetting method:

A. $\dfrac{(V_{(t1)}\cdot C_{(t1)} - V_{(t2)}\cdot C_{(t2)})\cdot M_{e(s.)}\cdot V_f}{a_{(s.)}\cdot 1000\cdot V_p}\cdot 100\%^{*}$

B. $\dfrac{T_{(t/s.)}\cdot V_{(t)}\cdot V_f\cdot C_f}{a_{(s.)}\cdot V_p}\cdot 100\%$

C. $\dfrac{T_{(t/s.)}\cdot V_{(t)}\cdot C_f}{a_{(s.)}}\cdot 100\%$

D. $\dfrac{C_{(t)}\cdot V_{(t)}\cdot M_{e(s.)}}{1000}$

E. $\dfrac{(V_{(t1)}\cdot C_{(t1)} - V_{(t2)}\cdot C_{(t2)})\cdot M_{e(s.)}\cdot V_f}{1000\cdot V_p}$

26. Choose a formula to calculate the mass fraction (in %) of the analyzed substance according to displacement titration and the method of separate samples:

A. $\dfrac{T_{(t/s.)}\cdot V_{(t)}\cdot C_f}{a_{(s.)}}\cdot 100\%^{*}$

B. $\dfrac{T_{(t/s.)}\cdot V_{(t)}\cdot V_f\cdot C_f}{a_{(s.)}\cdot V_p}\cdot 100\%$

C. $\dfrac{(V_{(t1)}\cdot C_{(t1)} - V_{(t2)}\cdot C_{(t2)})\cdot M_{e(s.)}}{a_{(s.)}\cdot 1000}\cdot 100\%$

D. $\frac{(V_{(t\,1)} \cdot C_{(t\,1)} - V_{(t\,2)} \cdot C_{(t\,2)}) \cdot M_{e\,(s.)} \cdot V_f}{1000 \cdot V_p}$

E. $\frac{C_{(t)} \cdot V_{(t)} \cdot M_{e\,(s.)}}{1000}$

27. To construct a titration curve of a weak acid with a strong base, the pH before the titration is calculated by the formula:

A. $pH = ½\ pK_a – ½\ lgC_a$ *
B. $pH = pK_a + \lg\frac{C_b}{C_a}$
C. $pH = 7 + ½\ pK_a + ½\ lgC_b$
D. $pH = \frac{pK_{a_1} + pK_{a_2}}{2}$
E. pH = 14 – pOH

28. To construct a titration curve of a weak acid with a strong base, the pH from the beginning of the titration to the equivalence point is calculated by the formula:

A. $pH = pK_a + \lg\frac{C_b}{C_a}$ *
B. $pH = ½\ pK_a – ½\ lgC_a$
C. $pH = 7 + ½\ pK_a + ½\ lgC_b$
D. $pH = \frac{pK_{a_1} + pK_{a_2}}{2}$
E. pH = 14 – pOH

29. To build a titration curve of a weak acid with a strong base pH at the beginning of the titration jump is calculated by the formula:

A. $pH = pK_a + \lg\frac{C_b}{C_a}$ *
B. $pH = ½\ pK_a – ½\ lgC_a$
C. $pH = 7 + ½\ pK_a + ½\ lgC_b$
D. $pH = \frac{pK_{a_1} + pK_{a_2}}{2}$
E. pH = 14 – pOH

30. To construct a titration curve of a weak acid with a strong base pH at the equivalence point is calculated by the formula:

A. $pH = 7 + ½\ pK_a + ½\ lgC_b$*
B. $pH = ½\ pK_a – ½\ lgC_a$
C. $pH = pK_a + \lg\frac{C_b}{C_a}$
D. $pH = \frac{pK_{a_1} + pK_{a_2}}{2}$
E. pH = 14 – pOH

31. To construct a titration curve of a weak acid with a strong base pH at the end of the jump titration is calculated by the formula:

A. pH = 14 – pOH *

B. $pH = \frac{pK_{a_1} + pK_{a_2}}{2}$
C. $pH = ½\ pK_a – ½\ lgC_a$
D. $pH = 7 + ½\ pK_a + ½\ \ lgC_b$
E. $pH = pK_a + lg\frac{C_b}{C_a}$

32. The possibility of titration of the substance by the method of acid-base titration is determined by:
A. The value of the acid or basic ionization constant of the analyzed substance. *
B. The titration index of the applied indicator.
C. The value of the titration constant. *
D. Properties of the applied titrant.
E. The reaction rate between the analyte and the titrant.

33. To construct a titration curve of a weak base with a strong acid, the pH before the titration is calculated by the formula:
A. $pH = 7 + ½\ pK_a + ½\ \ lgC_b$*
B. $pH = pK_a + lg\frac{C_b}{C_a}$
C. $pH = ½\ pK_a – ½\ lgC_a$
D. $pH = \frac{pK_{a_1} + pK_{a_2}}{2}$
E. $pH = –lg[H^+]$

34. To construct a titration curve of a weak base with a strong acid, the pH at the time of semi-neutralization is calculated by the formula:
A. $pH = pK_a + lg\frac{C_b}{C_a}$ *
B. $pH = 7 + ½\ pK_a + ½\ \ lgC_b$
C. $pH = ½\ pK_a – ½\ lgC_a$
D. $pH = \frac{pK_{a_1} + pK_{a_2}}{2}$
E. $pH = –lg[H^+]$

35. To construct a titration curve of a weak base with a strong acid, the pH at the beginning of the titration jump is calculated by the formula:
A. $pH = pK_a + lg\frac{C_b}{C_a}$ *
B. $pH = 7 + ½\ pK_a + ½\ \ lgC_b$
C. $pH = ½\ pK_a – ½\ lgC_a$
D. $pH = \frac{pK_{a_1} + pK_{a_2}}{2}$
E. $pH = –lg[H^+]$

36. To construct a titration curve of a weak base with a strong acid, the pH at the equivalence point is calculated by the formula:
A. $pH = ½\ pK_a – ½\ lgC_a$*
B. $pH = pK_a + lg\frac{C_b}{C_a}$
C. $pH = 7 + ½\ pK_a + ½\ \ lgC_b$

D. $pH = \frac{pK_{a_1} + pK_{a_2}}{2}$

E. $pH = -\lg[H^+]$

37. To construct a titration curve of a weak base with a strong acid, the pH at the end of the titration jump is calculated by the formula:

A. $pH = -\lg[H^+]$*

B. $pH = pK_a + \lg\frac{C_b}{C_a}$

C. $pH = 7 + ½\,pK_a + ½\,\lg C_b$

D. $pH = ½\,pK_a - ½\,\lg C_a$

E. $pH = \frac{pK_{a_1} + pK_{a_2}}{2}$

38. The mass fraction (in%) of sulfuric acid in the analyzed sample by direct titration by the pipetting method with an alkali solution can be calculated by the formula:

A. $\frac{C_{(NaOH)} \cdot V_{(NaOH)} \cdot M_{e\,(H_2SO_4)} \cdot V_{\text{к}}}{a_{(H_2SO_4)} \cdot 1000 \cdot V_p} \cdot 100\%$ *

B. $\frac{C_{(NaOH)} \cdot V_{(NaOH)} \cdot M_{e\,(H_2SO_4)}}{1000}$

C. $\frac{C_{(NaOH)} \cdot V_{(NaOH)} \cdot M_{e\,(H_2SO_4)}}{a_{(H_2SO_4)} \cdot 1000} \cdot 100\%$

D. $\frac{C_{(NaOH)} \cdot V_{(NaOH)} \cdot M_{e\,(H_2SO_4)} \cdot V_f}{1000 \cdot V_p}$

E. $V_{(NaOH)} \cdot T_{(NaOH)} \cdot C_f$

39. The mass fraction (in%) of sulfuric acid in the analyzed sample by direct titration by the method of separate samples of alkali solution can be calculated by the formula:

A. $\frac{C_{(NaOH)} \cdot V_{(NaOH)} \cdot M_{e\,(H_2SO_4)}}{a_{(H_2SO_4)} \cdot 1000} \cdot 100\%$ *

B. $\frac{C_{(NaOH)} \cdot V_{(NaOH)} \cdot M_{e\,(H_2SO_4)}}{1000}$

C. $\frac{C_{(NaOH)} \cdot V_{(NaOH)} \cdot M_{e\,(H_2SO_4)} \cdot V_f}{a_{(H_2SO_4)} \cdot 1000 \cdot V_p} \cdot 100\%$

D. $\frac{C_{(NaOH)} \cdot V_{(NaOH)} \cdot M_{e\,(H_2SO_4)} \cdot V_f}{1000 \cdot V_p}$

E. $V_{(NaOH)} \cdot T_{(NaOH/H_2SO_4)} \cdot C_f$

40. The gram content of sulfuric acid in the analyzed sample by direct titration with an alkali solution by the method of separate samples can be calculated by the formula:

A. $\frac{C_{(NaOH)} \cdot V_{(NaOH)} \cdot M_{e\,(H_2SO_4)}}{1000}$ *

B. $$\frac{C_{(NaOH)} \cdot V_{(NaOH)} \cdot M_{e\,(H_2SO_4)}}{a_{(H_2SO_4)} \cdot 1000} \cdot 100\%$$

C. $$\frac{C_{(NaOH)} \cdot V_{(NaOH)} \cdot M_{e\,(H_2SO_4)} \cdot V_f}{a_{(H_2SO_4)} \cdot 1000 \cdot V_p} \cdot 100\%$$

D. $$\frac{C_{(NaOH)} \cdot V_{(NaOH)} \cdot M_{e\,(H_2SO_4)} \cdot V_f}{1000 \cdot V_p}$$

E. $$V_{(NaOH)} \cdot T_{(NaOH\ /H_2SO_4)} \cdot C_f$$

41. The gram content of sulfuric acid in the analyzed sample by direct titration with an alkali solution by the method of pipetting can be calculated by the formula:

A. $$\frac{C_{(NaOH)} \cdot V_{(NaOH)} \cdot M_{e\,(H_2SO_4)} \cdot V_f}{1000 \cdot V_p} \ *$$

B. $$\frac{C_{(NaOH)} \cdot V_{(NaOH)} \cdot M_{e\,(H_2SO_4)}}{1000}$$

C. $$\frac{C_{(NaOH)} \cdot V_{(NaOH)} \cdot M_{e\,(H_2SO_4)}}{a_{(H_2SO_4)} \cdot 1000} \cdot 100\%$$

Д. $$\frac{C_{(NaOH)} \cdot V_{(NaOH)} \cdot M_{e\,(H_2SO_4)} \cdot V_f}{a_{(H_2SO_4)} \cdot 1000 \cdot V_p} \cdot 100\%$$

E. $$V_{(NaOH)} \cdot T_{(NaOH\ /H_2SO_4)} \cdot C_f$$

42. The gram content of sulfuric acid in the analyzed sample by direct titration with an alkali solution by the method of separate samples through the titer for the determined substance can be calculated by the formula:

A. $$V_{(NaOH)} \cdot T_{(NaOH\ /H_2SO_4)} \cdot C_f \ *$$

B. $$\frac{C_{(NaOH)} \cdot V_{(NaOH)} \cdot M_{e\,(H_2SO_4)} \cdot V_f}{1000 \cdot V_p}$$

C. $$\frac{C_{(NaOH)} \cdot V_{(NaOH)} \cdot M_{e\,(H_2SO_4)}}{1000}$$

D. $$\frac{C_{(NaOH)} \cdot V_{(NaOH)} \cdot M_{e\,(H_2SO_4)}}{a_{(H_2SO_4)} \cdot 1000} \cdot 100\%$$

E. $$\frac{C_{(NaOH)} \cdot V_{(NaOH)} \cdot M_{e\,(H_2SO_4)} \cdot V_f}{a_{(H_2SO_4)} \cdot 1000 \cdot V_p} \cdot 100\%$$

43. What indicators can be used to titrate orthophosphoric acid:
A. Both. *
B. Phenolphthalein.
C. Methyl orange.
D. Neither one nor the other.

44. Weak acids with an acidity constant equal to or greater than $5 \cdot 10^{-7}$ can be titrated with an alkali solution, BECAUSE on the titration curve of acids with an acidity constant equal to or greater than $5 \cdot 10^{-7}$, the titration jump is much narrower than when titrating strong acids:

A. 1-Right. 2-Right. Link – Right.
B. 1-Right. 2-Right. Link – Wrong.
C. 1-Right. 2-Wrong. Link – Wrong.
Д. 1-Wrong. 2-Right. Link – Wrong.*
E. 1-Wrong. 2-Wrong. Link – Wrong.

45. What indicators can be used to titrate sodium oxalate:

A. Neither. *
B. Phenolphthalein.
C. Both.
D. Methyl orange.

46. What indicators can be used to titrate sodium carbonate:

A. Both. *
B. Phenolphthalein.
C. Methyl orange.
D. Neither one nor the other.

47. What indicators can be used to titrate sodium bicarbonate:

A. Methyl orange. *
B. Phenolphthalein.
C. Both.
D. Neither one nor the other.

48. What indicators can be used to titrate sodium dihydrogen phosphate:

A. Phenolphthalein. *
B. Methyl orange.
C. Both.
D. Neither one nor the other.

49. Depending on the pH at the equivalence point, different acid-base parameters are used in the titration of different substances. What indicators can be used for titration with sufficient accuracy of sodium hydroxide:

A. Both. *
B. Phenolphthalein.
C. Methyl orange.
D. Neither one nor the other.

50. Select the appropriate character of the titration curve when titrating a strong acid with a strong base:

A. pH during titration changes dramatically. *
B. There is no jump on the titration curve.
S. pH during titration changes smoothly.
D. Two jumps on the titration curve.
E. Two jumps on the curve, the second jump is small.

51. Select the appropriate character of the titration curve when titrating a weak acid with a strong base:

A. pH during titration changes smoothly. *
V. pH during titration changes dramatically.
C. There is no jump on the titration curve.
D. Two jumps on the titration curve.
E. Two jumps on the curve, the second jump is small.

52. Select the appropriate character of the titration curve when titrating a weak base of strong acidity:
A. pH during titration changes smoothly. *
V. pH during titration changes dramatically.
C. Jump on the titration curve available.
D. Two jumps on the titration curve.
E. Two jumps on the curve, the second jump is small.

53. Select the appropriate character of the titration curve when titrating a weak acid with a weak base:
A. There is no jump on the titration curve. *
V. pH during titration changes dramatically.
S. pH during titration changes smoothly.
D. Two jumps on the titration curve.
E. Two jumps on the curve, the second jump is small.

54. Choose the formula for calculating the gram content of the analyzed substance by direct titration, by the method of separate samples:

A. $\frac{C_{(t)} \cdot V_{(t)} \cdot M_{e(s.)}}{1000}$ *

B. $\frac{C_{(t)} \cdot V_{(t)} \cdot M_{e(s.)}}{a_{(s.)} \cdot 1000} \cdot 100\%$

C. $\frac{(V_{(t1)} \cdot C_{(t1)} - V_{(t2)} \cdot C_{(t2)}) \cdot M_{e(s.)}}{a_{(s.)} \cdot 1000} \cdot 100\%$

D. $V_{(t)} \cdot T_{(t/s.)} \cdot C_f$

E. $\frac{(V_{(t1)} \cdot C_{(t1)} - V_{(t2)} \cdot C_{(t2)}) \cdot M_{e(s.)} \cdot V_f}{a_{(s.)} \cdot 1000 \cdot V_p} \cdot 100\%$

55. Choose the formula for calculating the mass fraction (in%) of the analyzed substance by back titration, by the method of separate samples:

A. $\frac{(V_{(t1)} \cdot C_{(t1)} - V_{(t2)} \cdot C_{(t2)}) \cdot M_{e(s.)}}{a_{(s.)} \cdot 1000} \cdot 100\%$ *

B. $\frac{C_{(t)} \cdot V_{(t)} \cdot M_{e(s.)}}{1000}$

C. $\frac{C_{(t)} \cdot V_{(t)} \cdot M_{e(s.)}}{a_{(s.)} \cdot 1000} \cdot 100\%$

D. $V_{(t)} \cdot T_{(t/s.)} \cdot C_f$

E. $\frac{(V_{(t1)} \cdot C_{(t1)} - V_{(t2)} \cdot C_{(t2)}) \cdot M_{e(s.)} \cdot V_f}{a_{(s.)} \cdot 1000 \cdot V_p} \cdot 100\%$

56. Choose the formula for calculating the mass fraction (in%) of the analyzed substance by direct titration, by the method of separate samples:

A. $\frac{C_{(t)} \cdot V_{(t)} \cdot M_{e(s.)}}{a_{(s.)} \cdot 1000} \cdot 100\%$ *

B. $\frac{(V_{(t1)} \cdot C_{(t1)} - V_{(t2)} \cdot C_{(t2)}) \cdot M_{e(s.)}}{a_{(s.)} \cdot 1000} \cdot 100\%$

C. $V_{(t)} \cdot T_{(t/s.)} \cdot C_f$

D. $\dfrac{C_{(t)} \cdot V_{(t)} \cdot M_{e(s.)}}{1000}$

E. $\dfrac{(V_{(t\,1)} \cdot C_{(t\,1)} - V_{(t\,2)} \cdot C_{(t\,2)}) \cdot M_{e(s.)} \cdot V_{f}}{a_{(s.)} \cdot 1000 \cdot V_p} \cdot 100\%$

57. Choose the formula for calculating the mass fraction (in%) of the analyzed substance by back titration, by the pipetting method:

A. $\dfrac{(V_{(t\,1)} \cdot C_{(t\,1)} - V_{(t\,2)} \cdot C_{(t\,2)}) \cdot M_{e(s.)} \cdot V_{f}}{a_{(s.)} \cdot 1000 \cdot V_p} \cdot 100\%$ *

B. $\dfrac{(V_{(t\,1)} \cdot C_{(t\,1)} - V_{(t\,2)} \cdot C_{(t\,2)}) \cdot M_{e(s.)}}{a_{(s.)} \cdot 1000} \cdot 100\%$

C. $\dfrac{C_{(t)} \cdot V_{(t)} \cdot M_{e(s.)}}{1000}$

D. $\dfrac{C_{(t)} \cdot V_{(t)} \cdot M_{e(s.)}}{a_{(s.)} \cdot 1000} \cdot 100\%$

E. $V_{(t)} \cdot T_{(t/s.)} \cdot C_f$

58. Choose the formula for calculating the gram content of the analyzed substance by direct titration, by the method of separate samples, through the titer of the determined substance:

A. $V_{(t)} \cdot T_{(t/s.)} \cdot C_f$ *

B. $\dfrac{C_{(t)} \cdot V_{(t)} \cdot M_{e(s.)}}{a_{(s.)} \cdot 1000} \cdot 100\%$

C. $\dfrac{(V_{(t\,1)} \cdot C_{(t\,1)} - V_{(t\,2)} \cdot C_{(t\,2)}) \cdot M_{e(s.)}}{a_{(s.)} \cdot 1000} \cdot 100\%$

D. $\dfrac{C_{(t)} \cdot V_{(t)} \cdot M_{e(s.)}}{1000}$

E. $\dfrac{(V_{(t\,1)} \cdot C_{(t\,1)} - V_{(t\,2)} \cdot C_{(t\,2)}) \cdot M_{e(s.)} \cdot V_{f}}{a_{(s.)} \cdot 1000 \cdot V_p} \cdot 100\%$

59. Select the appropriate formula for calculating the sample weight of the analyzed substance when titrating by the method of separate samples:

A. $\dfrac{C_{M_E} \cdot V_{(t)} \cdot M_e}{1000}$ ($V_t = 10 – 20$ ml)*

B. $\dfrac{C_{(t)} \cdot V_{(t)} \cdot M_{e(s.)} \cdot V_{f}}{1000 \cdot V_p}$

C. $\dfrac{C_{M_E} \cdot V_{f} \cdot M_e}{1000}$

D. $\dfrac{C_{(t)} \cdot V_{(t)} \cdot M_{e(s.)}}{1000}$

E. $\frac{(V_{(t\,1)} \cdot C_{(t\,1)} - V_{(t\,2)} \cdot C_{(t\,2)}) \cdot M_{e\,(s.)}}{1000}$

60. Select the appropriate formula to calculate the sample weight of the analyzed substance when titrated by the pipetting method:

A. $\frac{C_{M_E} \cdot V_f \cdot M_e}{1000}$ *

B. $\frac{C_{M_E} \cdot V_{(t)} \cdot M_e}{1000}$ (V_t = 10 – 20 ml)

C. $\frac{C_{(t)} \cdot V_{(t)} \cdot M_{e\,(s.)} \cdot V_f}{1000 \cdot V_p}$

D. $\frac{C_{(t)} \cdot V_{(t)} \cdot M_{e\,(s.)}}{1000}$

E. $\frac{(V_{(t\,1)} \cdot C_{(t\,1)} - V_{(t\,2)} \cdot C_{(t\,2)}) \cdot M_{e\,(s.)}}{1000}$

61. Select the appropriate formula for calculating the mass of the analyzed substance, direct titration, pipetting method:

A. $\frac{C_{(t)} \cdot V_{(t)} \cdot M_{e\,(s.)} \cdot V_f}{1000 \cdot V_p}$ *

B. $\frac{C_{M_E} \cdot V_{(t)} \cdot M_e}{1000}$ (V_t = 10 – 20 ml)

C. $\frac{C_{M_E} \cdot V_f \cdot M_e}{1000}$

D. $\frac{C_{(t)} \cdot V_{(t)} \cdot M_{e\,(s.)}}{1000}$

E. $\frac{(V_{(t\,1)} \cdot C_{(t\,1)} - V_{(t\,2)} \cdot C_{(t\,2)}) \cdot M_{e\,(s.)}}{1000}$

62. Select the appropriate formula for calculating the mass of the analyzed substance, direct titration, the method of separate samples:

A. $\frac{C_{(t)} \cdot V_{(t)} \cdot M_{e\,(s.)}}{1000}$ *

B. $\frac{C_{(t)} \cdot V_{(t)} \cdot M_{e\,(s.)} \cdot V_f}{1000 \cdot V_p}$

C. $\frac{C_{M_E} \cdot V_{(t)} \cdot M_e}{1000}$ (V_t = 10 – 20 ml)

D. $\frac{C_{M_E} \cdot V_f \cdot M_e}{1000}$

E. $\frac{(V_{(t\,1)} \cdot C_{(t\,1)} - V_{(t\,2)} \cdot C_{(t\,2)}) \cdot M_{e\,(s.)}}{1000}$

63. Select the appropriate formula for calculating the mass of the analyzed substance, back titration, the method of separate samples:

A. $\frac{(V_{(t\,1)} \cdot C_{(t\,1)} - V_{(t\,2)} \cdot C_{(t\,2)}) \cdot M_{e\,(s.)}}{1000}$ *

B. $\frac{C_{(t)} \cdot V_{(t)} \cdot M_{e(s.)}}{1000}$
C. $\frac{C_{(t)} \cdot V_{(t)} \cdot M_{e(s.)} \cdot V_f}{1000 \cdot V_p}$
D. $\frac{C_{M_E} \cdot V_{(t)} \cdot M_e}{1000}$ ($V_t = 10 - 20$ ml)
E. $\frac{C_{M_E} \cdot V_к \cdot M_e}{1000}$

64. Weak acids with an acidity constant greater than or equal to $5 \cdot 10^{-7}$ can be titrated with an alkali solution with visual fixation of the equivalence point, BECAUSE on the titration curve of acids with an acidity constant equal to or greater than $5 \cdot 10^{-7}$ jump still allows you to choose the indicator:
A. 1-Right. 2-Right. Link – Right.*
B. 1-Right. 2-Right. Link – Wrong.
C. 1-Right. 2-Wrong. Link – Wrong.
D. 1-Wrong. 2-Right. Link – Wrong.
E. 1-Wrong. 2-Wrong. Link – Wrong.

65. In titrimetric methods of analysis in direct and substitution titration add an equivalent amount of titrant, BECAUSE the basis of titrimetric methods is the law of equivalents:
A. 1-Right. 2-Right. Link – Right.*
B. 1-Right. 2-Right. Link – Wrong.
C. 1-Right. 2-Wrong. Link – Wrong.
D. 1-Wrong. 2-Right. Link – Wrong.
E. 1-Wrong. 2-Wrong. Link – Wrong.

LABORATORY WORK

1. Determination of mass fraction (in%) of acetic acid in solution

The titration method is direct
Titration method – pipetting

$$CH_3COOH + NaOH \leftrightarrow CH_3COONa + H_2O$$
$$CH_3COOH + OH^- \leftrightarrow CH_3COO^- + H_2O$$

$M(CH_3COOH) = 60.06$ g/mol;
$f_e(CH_3COOH) = 1$;
$M_e(CH_3COOH) = f_e(CH_3COOH) \cdot M(CH_3COOH)$;
$M_e(CH_3COOH) = 1 \cdot 60.06 = 60.06$ g/mol.

Assay procedure. In a volumetric flask with a capacity of 50.00 ml, transfer 5.00 ml of the analyzed substance with a pipette, bring to the mark with distilled water and mix thoroughly. From the resulting dilution, measure 10.00 ml with a pipette, transfer to a titration flask, add 1-2 drops of phenolphthalein indicator and titrate with 0.1000 M sodium hydroxide solution until a slightly pink color appears, which does not disappear within 30 s. The titration is repeated until three reproducible results are obtained. The mass fraction (in%) of acetic acid is calculated from the average value of the titrant volume.

$$\omega_{(CH_3COOH)} = \frac{V_{(NaOH)} \cdot C_{M(NaOH)} \cdot M_{e(CH_3COOH)} \cdot V_f \cdot 100\%}{a_{(CH_3COOH)} \cdot V_p \cdot 1000}$$

2. Determination of gram content of ammonia in aqueous ammonia solution

Titration method - reverse (in excess)
Titration method – pipetting

$$NH_3 \cdot H_2O + HCl_{(ex.)} \leftrightarrow NH_4Cl + H_2O$$
$$NH_3 \cdot H_2O + H^+_{(ex.)} \leftrightarrow NH_4^+ + H_2O$$
$$HCl_{(зал.)} + NaOH \leftrightarrow NaCl + H_2O$$
$$H^+_{(res.)} + OH^- \leftrightarrow H_2O$$

$M(NH_3) = 17.03$ g/mol;
$f_e(NH_3) = 1$;
$M_e(NH_3) = f_e(NH_3) \cdot M(NH_3) = 17.03$ g/mol.

<u>Assay procedure.</u> The obtained task is quantitatively transferred to a volumetric flask with a capacity of 50.00 ml, brought to the mark with distilled water and mixed thoroughly. From the dilution, 10.00 ml is taken with a pipette, transferred to a titration flask, where 20.00 ml of 0.1000 M hydrochloric acid solution is preliminarily measured with a pipette. Add 1-2 drops of methyl orange indicator. Titrate with 0.1000 M sodium hydroxide solution until the pink color of the solution turns orange. The titration is repeated until three reproducible results are obtained.

According to the average value of the titrant volume, the gram content of ammonia in an aqueous solution of ammonia is calculated by the formula:

$$m_{(NH_3)} = \frac{(C_{M(HCl)} \cdot V_{(HCl)} - C_{M(NaOH)} \cdot V_{(NaOH)}) \cdot M_{e(NH_3)} \cdot V_f}{V_p \cdot 1000}$$

Visual materials, learning and control tools

1. Tabular resources on the topic of the lesson.
2. Textbooks, handbook on analytical chemistry.
3. Learning and control tools: cards for assessing the initial level of knowledge; test questions.

TITRATION OF POLYBASIC ACIDS, POLYACIDIC BASES, MIXTURES OF ACIDS OR BASES

Polybasic acids dissociate sequentially, in a stepwise manner. The first dissociation constant is larger than the second one, and so on. The first-stage dissociation suppresses the dissociation by the following stages. During the titration of a solution of polybasic acid with a standard solution of alkali, hydrogen ions corresponding to the first stage of acid dissociation are primarily titrated, then occurs the dissociation of hydrogen ions corresponding to the second stage, and so on. According to it, breaks for each step may appear in the titration curve. The separation and clear manifestation of these breaks in the titration curve depend on the values of *the constants of sequential step ionization of the acid Ka.*

If the value of Ka is very small (pKa > 5-6), then the break in the titration curve is indistinct, in the form of inflection or not at all. Therefore, it is difficult to choose an appropriate indicator and is impossible to perform separate titration in such cases.

If the pKa values of the sequential ionization stage of an acid differ by at least 4 units, viz. the Ka constants differ by at least 10,000 times, then the breaks in the titration curve can be separated.

To determine the possibility of titration, use the concept of the *titration constant* - Kt, which is the ratio of neighboring dissociation constants, or *titration exponent*, which is the difference between adjacent dissociation constants. For example, there are such constants and exponents for quadruple citric acid:

$K_{a1} = 7.40 \cdot 10^{-4}$, $pK_1 = 3.13$;
$K_{a2} = 2.20 \cdot 10^{-5}$, $pK_2 = 4.66$;
$K_{a3} = 4.00 \cdot 10^{-7}$, $pK_3 = 6.40$;
$K_{a4} = 1.00 \cdot 10^{-16}$, $pK_4 = 16.00$.

$$K_{T_1} = \frac{K_{a_2}}{K_{a_1}} = \frac{2.20 \cdot 10^{-5}}{7.40 \cdot 10^{-4}} = 3.00 \cdot 10^{-2};$$
$$pK_{T_1} = pK_{a2} - pK_{a1} = 4.66 - 3.13 = 1.53;$$

$$K_{T_2} = \frac{K_{a_3}}{K_{a_2}} = \frac{4.00 \cdot 10^{-7}}{2.20 \cdot 10^{-5}} = 1.80 \cdot 10^{-2};$$
$$pK_{T_2} = pK_{a3} - pK_{a2} = 6.40 - 4.66 = 1.74;$$

$$K_{T_3} = \frac{K_{a_4}}{K_{a_3}} = \frac{1.00 \cdot 10^{-16}}{4.00 \cdot 10^{-7}} = 2.50 \cdot 10^{-10};$$
$$pK_{T_3} = pK_{a4} - pK_{a3} = 16.00 - 6.40 = 9.60.$$

The dissociation constants of citric acid by the first, second and third stages differ less than 10,000 times (exponents of acid dissociation constants differ by less than 4 units), so there is only one (third) break in the titration curve of citric acid. The ionization constant by the fourth stage K_4 is very small (less than 10^{-7}), so the fourth break does not appear either. Therefore, citric acid can only be titrated as a tribasic acid.

The possibility of titration of ***polyacidic bases*** by stages is determined according to the values of the sequential ionization stage constants of the bases Kb and the values of pKb. Breaks in the titration curve are separated if the difference of pKb values of sequential stages of bases dissociation is not less than 4 units, as in the case of titration of solutions of polybasic acids with a standard solution of a strong base.

Mixtures of strong acids, each of which dissociates completely in an aqueous solution, give one total break in the titration curve and are titrated together as the sum of strong acids with a standard solution of an alkali.

The mixture of strong and weak acids is titrated with alkali sequentially. The strong acid suppresses the dissociation of a weak acid and is therefore titrated first. When the strong acid is completely titrated, then following titration of a weak acid.

Mixtures of weak or medium strength acids or bases can be titrated separately (differentiative) if the difference in pKa or pKb is at least 4 units (as for polybasic acids and polyacidic bases).

Tutorial 13

1. THEME: Acid-base titration. Titration of polybasic acids, polyacidic bases, mixtures of acids or bases

2. PURPOSE: Get acquainted with the basics of titration of complex acid-base systems, acquire the ability to apply the method of acid-base titration in the analysis of polybasic acids, polyacidic bases, mixtures of acids or bases

3. OBJECTIVIES:

3.1. To study the theoretical bases of titration of polybasic acids, polyacidic bases, mixtures of acids or bases.

3.2. Study to evaluate the possibility of differentiated titration of polybasic acids, polyacidic bases; study the conditions of titration of mixtures of acids or bases in aqueous media with visual fixation of the end point of titration.

3.3. Master the method of quantitative determination of sodium bicarbonate and sodium carbonate in the mixture.

3.4. Study to calculate the concentration of individual components in mixtures.

3.5. Study to record the results of measurements in a laboratory journal.

4. PLAN AND ORGANIZATIONAL STRUCTURE OF THE TUTORIAL:

4.1. Organizational moment.....……………………………….......................2 min

4.2. Description of the purpose of the lesson (introductory speech of the teacher)……………...3 min

4.3. Assessment of the initial level of knowledge (card control)…………...10 min

4.4. Correction of the initial level of knowledge and skills……….................40 min

4.5. Organization of independent work of students (teacher's instructions, safety instruction)…………………...3 min

4.6. Laboratory work………........…….…………………………………..110 min

4.7. Final control: check of laboratory results and protocols………………10 min

4.8. Concluding speech of the teacher, instructions for the next lesson……..2 min

5. REFERENCE FOR SELF STUDY:

5.1. Repeat the following topics from the course of inorganic chemistry and qualitative analysis: protolytic equilibria in aqueous solutions of polybasic acids and bases, constants of sequential stepwise ionization of acids and bases.

5.2. Study the program materials on this topic, using the recommended literature and lectures.

Questions for self-study

1. Features of titration of polybasic acids and bases. Titration of phosphoric and carbonic acids; sodium bicarbonate and sodium carbonate in the mixture. Is it possible to titrate phosphoric acid as a tribasic acid?

2. Calculation of pH at equivalence points for each stage in the titration of solutions of polybasic acids and polyacidic bases. Calculation of pH of solutions of mixtures of acids or bases.

3. Analysis of titration curves. In which cases are several breaks differentiated in the titration curve?

4. Titration constant, exponent of titration constant. The possibility of titration of polybasic acids and bases by stages, and differentiated titration of mixtures of acids or bases.

5. Differentiated quantitative determination of the components of the mixture:
– *sodium carbonate and sodium hydroxide;*
– *phosphoric and hydrochloric acids;*
– *phosphoric acid and monosodium phosphate.*

5.3. Solve the tasks:

Task 1. Calculate the pH values at the first and second equivalence points in case of the titration of 0.1 M maleic acid solution with 0.1 M sodium hydroxide solution.

Answer: $pH_1 = 4.07$; $pH_2 = 9.61$.

Task 2. Calculate the titer of 0.1011 M sodium hydroxide solution for phosphoric acid if the titration was conducted in the presence of phenolphthalein.

Answer: 0.004954 g/ml.

Task 3. A weighed portion of the mixture of NaOH and Na_2CO_3 (1.8017 g) is dissolved in a 500.0 ml volumetric flask. To titrate 25.00 ml of the prepared solution in the presence of phenolphthalein, 20.50 ml of 0.1035 M HCl solution was consumed. When the same portion of analyzed solution was titrated in the presence of methyl orange, 21.53 ml of 0.1035 M HCl solution was taken. Calculate the concentration of Na_2CO_3 (in %) in the sample.

Answer: 12.5%.

Task 4. Several solutions, which may contain hydrochloric acid, phosphoric acid, and monosodium phosphate (one or two components), were titrated with 0.1200 M sodium hydroxide solution. To titrate 25.00 ml of each solution, V_1 (NaOH) in the presence of methyl orange and V_2 (NaOH) in the presence of phenolphthalein were consumed. The results of quantitative determination are shown below. Based on these results, determine the composition of solutions, and calculate the concentration of each substance in mg/ml.

№ of the solution	V_1 with m.o	V_2 with p.p.
1	18.70	23.60
2	7.95	7.95
3	0.00	16.77
4	13.12	35.19
5	13.35	26.65

Answer: a) 2.422 mg/ml HCl и 2.30 mg/ml H_3PO_4;
b) 1.39 mg/ml HCl;
c) 9.651 mg/ml NaH_2PO_4;
d) 6.046 mg/ml H_3PO_4 и 5.11 mg/ml NaH_2PO_4;
e) 6.270 mg/ml H_3PO_4.

Examples of the solved tasks:

Task 1. 5.00 ml of the mixture of hydrochloric and phosphoric acids were diluted to 200.0 ml. To titrate 20.00 ml of the obtained solution in the presence of methyl orange, 18.20 ml of 0.1012 M sodium hydroxide solution was consumed; when titration was conducted in the presence of phenolphthalein, 34.70 ml of NaOH solution was taken. What is the mass of HCl and H_3PO_4 contained in 100.0 ml of the mixture?

Solution.

$$HCl + NaOH \leftrightarrow NaCl + H_2O$$

HCl is titrated completely with both indicators, such as m.o. and p.p. (f = 1).

$$H_3PO_4 + NaOH \leftrightarrow NaH_2PO_4 + H_2O$$

$K_{a1} = 7.10 \cdot 10^{-3}$; $pK_{a1} = 2.15$;

$$NaH_2PO_4 + NaOH \leftrightarrow Na_2HPO_4 + H_2O$$

$K_{a2} = 6.20 \cdot 10^{-8}$; $pK_{a2} = 7.21$;

$$Na_2HPO_4 + NaOH \leftrightarrow Na_3PO_4 + H_2O$$

$K_{a3} = 5.00 \cdot 10^{-13}$; $pK_{a3} = 12.30$.

Phosphoric acid can be titrated by only two stages, because $K_{a3} < 10^{-8}$.

By the first stage H_3PO_4 is titrated in the presence of m.o. (f = 1);

$pH_{EP1} = (pK_{a1} + pK_{a2}): 2 = 2.15 + 7.21 = 4.68$.

By the second stage H_3PO_4 is titrated in the presence of p.p. (f = ½);

$pH_{EP2} = (pK_{a2} + pK_{a3}): 2 = 7.21 + 12.30 = 9.76$.

Thus, according to the conditions of the task, in the presence of m.o. HCl is titrated completely and H_3PO_4 is titrated only by the first stage. In the presence of p.p., HCl is also titrated completely and H_3PO_4 is titrated in this case by two (I and II) stages.

Find the volumes of NaOH standard solution that were consumed for the titration of each component of the mixture:

V for H_3PO_4 by the one stage = Vp.p. – Vm.o. = 34.70 – 18.20 = 16.50 ml
($f_e(H_3PO_4) = 1$).
V for HCl = Vm.o. – V for H_3PO_4 by the one stage = 18.20 – 16.50 = 1.70 ml
($f_e(H_3PO_4) = 1$).
$M(H_3PO_4) = 98.00$ g/mol;
$f_e(H_3PO_4) = 1$;
$M_e(H_3PO_4) = M(H_3PO_4) \cdot f_e(H_3PO_4) = 98.00$ g/mol;
$M(HCl) = 36.46$ g/mol;
$f_e(HCl) = 1$;
$M_e(HCl) = M(HCl) \cdot fe(HCl) = 36.46$ g/mol.

Calculate the mass of HCl and H_3PO_4 contained in 100.0 ml of the mixture by the formula written below:

$$m = \frac{V_{(\text{NaOH})} \cdot C_{(\text{NaOH})} \cdot \text{M}_\text{e} \cdot V_\text{к} \cdot 100{,}0}{1000 \cdot V_\text{п} \cdot \text{a}};$$

$$m_{(H_3\text{PO}_4)} = \frac{16.50 \cdot 0.1012 \cdot 98.00 \cdot 200.0 \cdot 100.0}{1000 \cdot 20.00 \cdot 5.00} = 32.73 \text{ g};$$

$$m_{(\text{HCl})} = \frac{1.70 \cdot 0.1012 \cdot 36.46 \cdot 200.0 \cdot 100.0}{1000 \cdot 20.00 \cdot 5.00} = 1.26 \text{ g}.$$

Answer: 1.26 g HCl and 32.73 g H_3PO_4.

Task 2. Several solutions, which may contain sodium hydroxide, sodium carbonate and sodium bicarbonate (one or more components), were titrated with 0.1200 M HCl solution. The table below shows the volumes of standard hydrochloric acid required to titrate 25.00 ml of each analyzed solution till the end point (V_1 – in the presence of phenolphthalein; V_2 – in the presence of methyl orange). Based on the received data, determine the composition of the analyzed solutions, and calculate the concentration of each component of the mixture in mg/ml.

№ of the solution	V_1 with p.p.	V_2 with m.o.
1	22.42	22.44
2	15.67	42.13
3	29.64	36.42
4	16.12	32.23
5	0.00	33.33

Solution. Solving the task, it is necessary to determine how sodium hydroxide, sodium carbonate and sodium bicarbonate are titrated with a solution of hydrochloric acid in the presence of methyl orange and phenolphthalein.

a). $NaOH + HCl \leftrightarrow NaCl + H_2O$

In this case, the end point in titration can be reached with both methyl orange and phenolphthalein. Because near the equivalence point, pH changes sharply, and at that moment, both indicators change their colors. The volumes of acid are used for the titration of sodium hydroxide with methyl orange and phenolphthalein are almost the same. Therefore, only sodium hydroxide may be present in solution № 1.

M(NaOH) = 40.00 g/mol;
f_e(NaOH) = 1;
M_e(NaOH) = M(NaOH) · f_e(NaOH) = 40.00 g/mol.

$$C_{(NaOH)} = \frac{V_{1(HCl)} \cdot C_{(HCl)} \cdot M_{e\ (NaOH)} \cdot 1000}{1000 \cdot V_{п}};$$

$$C_{(NaOH)} = \frac{22.42 \cdot 0.1200 \cdot 40.00 \cdot 1000}{1000 \cdot 25.00} = 4.309 \text{ mg/ml}.$$

b). $Na_2CO_3 + HCl \leftrightarrow NaHCO_3 + NaCl$
$NaHCO_3 + HCl \leftrightarrow H_2CO_3 + NaCl$

The titration of sodium carbonate with hydrochloric acid proceeds by two stages. When this substance is titrated using a solution of phenolphthalein as an indicator, it reacts as a monoacidic base, and the reaction goes until all the sodium carbonate is converted into sodium hydrogen carbonate ($f_e = 1$).

M(Na_2CO_3) = 106.0 g/mol;
f_e(Na_2CO_3) = 1;
M_e(Na_2CO_3) = M(Na_2CO_3) · f_e(Na_2CO_3) = 106.0 g/mol.

When the titration is carried out with methyl orange, the indicator turns orange only after all the salt has been converted into carbonic acid. It means that sodium carbonate is titrated with this pH indicator as a diacidic base. The reaction goes by two stages ($f_e = ½$).

M(Na_2CO_3) = 106.0 g/mol;
f_e(Na_2CO_3) = ½;
M_e(Na_2CO_3) = M(Na_2CO_3) · f_e(Na_2CO_3) = 53.00 g/mol.

Thus, the volume of acid consumed for the titration of sodium carbonate in the presence of methyl orange V_1 is twice as great as the volume of acid consumed in the titration in the presence of phenolphthalein V_2. Hence, solution № 4 contains only sodium carbonate.

$$C_{(Na_2CO_3)} = \frac{V_{1(HCl)} \cdot C_{(HCl)} \cdot M_{e\ (Na_2CO_3)} \cdot 1000}{1000 \cdot V_{п}};$$

$$C_{(Na_2CO_3)} = \frac{16.12 \cdot 0.1200 \cdot 106.0 \cdot 1000}{1000 \cdot 25.00} = 8.202 \text{ mg/ml.}$$

c). $NaHCO_3 + HCl \leftrightarrow H_2CO_3 + NaCl$

Sodium bicarbonate is titrated with hydrochloric acid in the presence of a methyl orange indicator as a monoacidic base (fe = 1). Sodium bicarbonate cannot be titrated with phenolphthalein (V_1 = 0.00). Therefore, solution № 5 contains only sodium bicarbonate.

$M(NaHCO_3)$ = 84.01 g/mol;
$f_e(NaHCO_3) = 1$;
$M_e(NaHCO_3) = M(NaHCO_3) \cdot f_e(NaHCO_3)$ = 84.01 g/mol.

$$C_{(NaHCO_3)} = \frac{V_{2(HCl)} \cdot C_{(HCl)} \cdot M_{e(NaHCO_3)} \cdot 1000}{1000 \cdot V_{п}};$$

$$C_{(NaHCO_3)} = \frac{33.33 \cdot 0.1200 \cdot 84.01 \cdot 1000}{1000 \cdot 25.00} = 13.44 \text{ mg/ml.}$$

d). During the titration of solution № 2, V_2 is greater than V_1 more than twice. This means that the solution contains two components, one of which is titrated with phenolphthalein and methyl orange, $V_2 = 2V_1$; the second component is titrated only with methyl orange. This corresponds to a solution containing a mixture of sodium carbonate and sodium bicarbonate.

The volume of acid used to titrate sodium carbonate by the first stage is V_1. The volume difference ($V_2 - 2V_1$) is the volume of acid used to titrate sodium bicarbonate.

Calculate the concentration of sodium carbonate:

$M(Na_2CO_3)$ = 106.0 g/mol;
$f_e(Na_2CO_3) = 1$;
$M_e(Na_2CO_3) = M(Na_2CO_3) \cdot f_e(Na_2CO_3)$ = 106.0 g/mol.

$$C_{(Na_2CO_3)} = \frac{V_{1(HCl)} \cdot C_{(HCl)} \cdot M_{e\,(Na_2CO_3)} \cdot 1000}{1000 \cdot V_{п}};$$

$$C_{(Na_2CO_3)} = \frac{15.67 \cdot 0.1200 \cdot 106.0 \cdot 1000}{1000 \cdot 25.00} = 7.973 \text{ mg/ml.}$$

Calculate the concentration of sodium hydrogen carbonate:

$M(NaHCO_3)$ = 84.01 g/mol;
$f_e(NaHCO_3) = 1$;
$M_e(NaHCO_3) = M(NaHCO_3) \cdot f_e(NaHCO_3)$ = 84.01 g/mol.

$$C_{(\mathrm{NaHCO_3})} = \frac{\left(V_{2(\mathrm{HCl})} - 2V_{1(\mathrm{HCl})}\right) \cdot C_{(\mathrm{HCl})} \cdot \mathrm{M}_{\mathrm{e}\ (\mathrm{NaHCO_3})} \cdot 1000}{1000 \cdot V_{\text{п}}};$$

$$C_{(\mathrm{NaHCO_3})} = \frac{(42.13 - 2 \cdot 15.67) \cdot 0.1200 \cdot 84.01 \cdot 1000}{1000 \cdot 25.00} = 4.351 \text{ mg/ml.}$$

e). During the titration of solution № 3, V_2 is greater than V_1 less than twice. Therefore, the solution contains two components, one of which is titrated with phenolphthalein and methyl orange, $V_2 = 2V_1$; the second component is also titrated with two indicators, but for it – $V_2 = V_1$. This corresponds to a solution containing a mixture of sodium carbonate and sodium hydroxide.

The volume difference (V_2 - $2V_1$) is the volume of acid consumed for the titration of sodium carbonate by the second stage. Hence, $2(V_2 - V_1)$ is taken for the complete titration of sodium carbonate. Both sodium hydroxide and sodium carbonate are completely titrated in the presence of methyl orange. That's why the volume of the hydrochloric acid solution used for titration of sodium hydroxide is equal to the difference ($V_2 - 2(V_2 - V_1)$).

M(NaOH) = 40.00 g/mol;
f_e(NaOH) = 1;
M_e(NaOH) = M(NaOH) · f_e(NaOH) = 40.00 g/mol.

$$C_{(\mathrm{NaOH})} = \frac{\left(V_{2(\mathrm{HCl})} - 2 \cdot \left(V_{2(\mathrm{HCl})} - \mathrm{V}_{1(\mathrm{HCl})}\right)\right) \cdot C_{(\mathrm{HCl})} \cdot \mathrm{M}_{\mathrm{e}\ (\mathrm{NaOH})} \cdot 1000}{1000 \cdot V_{\text{п}}};$$

$$C_{(\mathrm{NaOH})} = \frac{\left(36.42 - 2 \cdot (36.42 - 29.64)\right) \cdot 0.1200 \cdot 40.00 \cdot 1000}{1000 \cdot 25.00} = 4.389 \text{ mg/ml.}$$

M(Na_2CO_3) = 106.0 g/mol;
f_e(Na_2CO_3) = ½;
M_e(Na_2CO_3) = M(Na_2CO_3) · f_e(Na_2CO_3) = 53.00 g/mol.

$$C_{(\mathrm{Na_2CO_3})} = \frac{2 \cdot \left(V_{2(\mathrm{HCl})} - \mathrm{V}_{1(\mathrm{HCl})}\right) \cdot C_{(\mathrm{HCl})} \mathrm{M}_{\mathrm{e}\ (\mathrm{Na_2CO_3})} 1000}{1000 \cdot V_{\text{п}}};$$

$$C_{(\mathrm{Na_2CO_3})} = \frac{2 \cdot (36.42 - 29.64) \cdot 0.1200 \cdot 106.0 \cdot 1000}{1000 \cdot 25.00} = 3.450 \text{ mg/ml.}$$

Answer: 1. 4.309 mg/ml NaOH.
2. 7.973 mg/ml Na_2CO_3; 4.350 mg/ml $NaHCO_3$.
3. 4.389 mg/ml NaOH; 3.451 mg/ml Na_2CO_3.
4. 8.202 mg/ml Na_2CO_3.
5. 13.44 mg/ml $NaHCO_3$.

Work on test tasks

1. A solution may contain hydrochloric acid, phosphoric acid or sodium dihydrogen phosphate (one component or two in a combination). To titrate 25.00 ml of this solution, 0.1 M sodium hydroxide solution was used. 18.72 ml of the titrant was consumed for the titration in the presence of methyl orange, and 23.60 ml – in the presence of phenolphthalein. Use this information to determine the composition of the solution and choose the most appropriate answer:

A. The solution contains hydrochloric and phosphoric acids.*
B. The solution contains phosphoric acid.
C. The solution contains hydrochloric acid.
D. The solution contains sodium dihydrogen phosphate.
E. The solution contains phosphoric acid and sodium dihydrogen phosphate.

2. The concentration of sodium carbonate and sodium bicarbonate in a mixture by direct titration (the titrant is a solution of hydrochloric acid) in the presence of two indicators (phenolphthalein and methyl orange) can be calculated by the formulas:

A. $\frac{2\mathrm{V}_{1(\mathrm{HCl})} \cdot T_{(\mathrm{HCl/Na_2CO_3})} \cdot C_f \cdot 100}{a}$*

B. $\frac{2\mathrm{V}_{1(\mathrm{HCl})} \cdot C_{M(\mathrm{HCl})} \cdot M_{\mathrm{e}\,(\mathrm{Na_2CO_3})} \cdot C_f \cdot 100}{a \cdot 1000}$*

C. $\frac{V_{1(\mathrm{HCl})} \cdot C_{M(\mathrm{HCl})} \cdot M_{\mathrm{e}\,(\mathrm{Na_2CO_3})} \cdot C_f \cdot 100}{a \cdot 1000}$*

D. $\frac{\left(V_{2(\mathrm{HCl})} - 2\mathrm{V}_{1(\mathrm{HCl})}\right) \cdot C_{M(\mathrm{HCl})} \cdot M_{\mathrm{e}\,(\mathrm{NaHCO_3})} \cdot C_f \cdot 100}{a \cdot 1000}$*

E. $\frac{\left(V_{2(\mathrm{HCl})} - 2\mathrm{V}_{1(\mathrm{HCl})}\right) \cdot T_{(\mathrm{HCl/NaHCO_3})} \cdot C_f \cdot 100}{a}$*

3. A solution may contain hydrochloric acid, phosphoric acid or sodium dihydrogen phosphate (one component or two in a combination). To titrate 25.00 ml of this solution, 0.1 M sodium hydroxide solution was used. 7.93 ml of the titrant was consumed for the titration in the presence of methyl orange, and 7.95 ml – in the presence of phenolphthalein. Use this information to determine the composition of the solution and choose the most appropriate answer:

A. The solution contains hydrochloric and phosphoric acids.
B. The solution contains phosphoric acid.
C. The solution contains hydrochloric acid.*
D. The solution contains sodium dihydrogen phosphate.
E. The solution contains phosphoric acid and sodium dihydrogen phosphate.

4. A solution may contain hydrochloric acid, phosphoric acid or sodium dihydrogen phosphate (one component or two in a combination). To titrate 25.00 ml of this solution, 0.1 M sodium hydroxide solution was used. 0.00 ml of the titrant was consumed for the titration in the presence of methyl orange, and 16.77 ml – in the presence of phenolphthalein. Use this information to determine the composition of the solution and choose the most appropriate answer:

A. The solution contains hydrochloric and phosphoric acids.
B. The solution contains phosphoric acid.
C. The solution contains hydrochloric acid.
D. The solution contains sodium dihydrogen phosphate.*
E. The solution contains phosphoric acid and sodium dihydrogen phosphate.

5. How is oxalic acid $H_2C_2O_4$ ($K_{a1} = 5.60 \cdot 10^{-2}$, $K_{a2} = 5.40 \cdot 10^{-5}$) titrated in the presence of indicators:

A. As a dibasic acid.*
B. As a monobasic acid.
C. Both.

D. Neither one thing nor the other.

6. How is boric acid H_3BO_3 ($K_{a1} = 7.10 \cdot 10^{-10}$, $K_{a2} = 1.80 \cdot 10^{-13}$, $K_{a3} = 1.60 \cdot 10^{-14}$) titrated in the presence of indicators:
A. As a dibasic acid.
B. As a monobasic acid.
C. Both.
D. Neither one thing nor the other.*

7. How is malonic acid $HOOCCH_2COOH$ ($K_{a1} = 4.20 \cdot 10^{-2}$, $K_{a2} = 2.10 \cdot 10^{-6}$) titrated in the presence of indicators:
A. As a dibasic acid.
B. As a monobasic acid.
C. Both.*
Д. Neither one thing nor the other.

8. How is glutaric acid $HOOC(CH_2)_3COOH$ ($K_{a1} = 4.60 \cdot 10^{-5}$, $K_{a2} = 5.40 \cdot 10^{-6}$) titrated in the presence of indicators:
A. As a dibasic acid.*
B. As a monobasic acid.
C. Both.
D. Neither one thing nor the other.

9. How is carbonic acid H_2CO_3 ($K_{a1} = 4.50 \cdot 10^{-7}$, $K_{a2} = 4.80 \cdot 10^{-11}$) titrated in the presence of indicators:
A. As a dibasic acid.
B. As a monobasic acid.*
C. Both.
D. Neither one thing nor the other.

10. A solution may contain hydrochloric acid, phosphoric acid or sodium dihydrogen phosphate (one component or two in a combination). To titrate 25.00 ml of this solution, 0.1 M sodium hydroxide solution was used. 13.12 ml of the titrant was consumed for the titration in the presence of methyl orange, and 35.19 ml – in the presence of phenolphthalein. Use this information to determine the composition of the solution and choose the most appropriate answer:
A. The solution contains hydrochloric and phosphoric acids.
B. The solution contains phosphoric acid.
C. The solution contains hydrochloric acid.
D. The solution contains sodium dihydrogen phosphate.*
E. The solution contains phosphoric acid and sodium dihydrogen phosphate.

11. A solution may contain hydrochloric acid, phosphoric acid or sodium dihydrogen phosphate (one component or two in a combination). To titrate 25.00 ml of this solution, 0.1 M sodium hydroxide solution was used. 13.12 ml of the titrant was consumed for the titration in the presence of methyl orange, and 26.24 ml – in the presence of phenolphthalein. Use this information to determine the composition of the solution and choose the most appropriate answer:
A. The solution contains hydrochloric and phosphoric acids.
B. The solution contains phosphoric acid.*
C. The solution contains hydrochloric acid.
D. The solution contains sodium dihydrogen phosphate.
E. The solution contains phosphoric acid and sodium dihydrogen phosphate.

12. Depending on the pH at the equivalence point, different acid-base indicators are used for the titration of different substances. What indicator is used in the precise titration of sodium carbonate $K_{a1} = 4.50 \cdot 10^{-7}$, $K_{a2} = 4.80 \cdot 10^{-11}$:
A. Both.*

B. Phenolphthalein.
C. Methyl orange.
D. Neither one thing nor the other.

13. The substance can be titrated by acid-base titration if the dissociation constant:
A. K_T is greater than 10^{-4}.
B. K_T is less than $10^{-4} – 10^{-5}$.*
C. K_T is greater than 10^{-3}.
D. K_T is equal to 10^{-3}.
E. K_T is equal to 10^{-2}.

14. What is the equivalent weight of sodium carbonate in its titration with 0.1 M hydrochloric acid solution? As an indicator, a solution of methyl orange is used:
A. It is equal to half of its molar mass.*
B. It is equal to its molar mass.
C. Both.
D. Neither one thing nor the other.

15. What is the equivalent weight of sodium carbonate in its titration with 0.1 M hydrochloric acid solution? As an indicator, a solution of phenolphthalein is used:
A. It is equal to half of its molar mass.
B. It is the same as a molar mass.*
C. Both.
D. Neither one thing nor the other.

16. What is the equivalent weight of phosphoric acid in its titration with 0.1 M sodium hydroxide solution in the presence of methyl orange and phenolphthalein:
A. It is equal to half of its molar mass.
B. It is the same as a molar mass.
C. Both.*
D. Neither one thing nor the other.

17. What is the equivalent weight of phosphoric acid, if for its solution calcium chloride was added, and, then, the released hydrochloric acid was neutralized by titrating it with a solution of alkali in the presence of methyl orange:
A. It is equal to half of its molar mass.
B. It is the same as a molar mass.
C. Both.
D. Neither one thing nor the other.*

18. What is the equivalent weight of oxalic acid in its titration with 0.1 M sodium hydroxide solution in the presence of phenolphthalein:
A. It is equal to half of its molar mass.*
B. It is the same as a molar mass.
C. Both.
D. Neither one thing nor the other.

19. Specify the shape of the titration curve in the titration of boric acid H_3BO_3 ($K_{a1} = 7.10 \cdot 10^{-10}$, $K_{a2} = 1.80 \cdot 10^{-13}$, $K_{a3} = 1.60 \cdot 10^{-14}$) with 0,1 M solution of alkali:
A. There is no abrupt change on the titration curve.*
B. The break in the titration curve is large.
C. Two breaks in the titration curve are clearly observed.
D. There are two breaks in the titration curve, but the second break is small.
E. There are two breaks in the titration curve, but the first break is small.

20. Specify the shape of the titration curve in the titration of dichloroacetic acid solution ($Cl_2CHCOOH$, $K_a = 5 \cdot 10^{-2}$) with 0.1 M solution of alkali:

A. There is no abrupt change on the titration curve.
B. The break in the titration curve is large.*
C. Two breaks in the titration curve are clearly observed.
D. There are two breaks in the titration curve, but the second break is small.
E. There are two breaks in the titration curve, but the first break is small.

21. Specify the shape of the titration curve in the titration of oxalic acid solution $H_2C_2O_4$ ($K_{a1} = 5.60 \cdot 10^{-2}$, $K_{a2} = 5.40 \cdot 10^{-5}$) with 0,1 M solution of alkali:

A. There is no abrupt change on the titration curve.
B. The break in the titration curve is large.
C. Two breaks in the titration curve are clearly observed.
D. There are two breaks in the titration curve, but the second break is small.
E. There are two breaks in the titration curve, but the first break is small.*

22. Specify the shape of the titration curve in the titration of sulfurous acid solution H_2SO_3 ($K_{a1} = 1.40 \cdot 10^{-2}$, $K_{a2} = 6.20 \cdot 10^{-8}$) with 0.1 M solution of alkali:

A. There is no abrupt change on the titration curve.
B. The break in the titration curve is large.
C. Two breaks in the titration curve are clearly observed.
D. There are two breaks in the titration curve, but the second break is small.*
E. There are two breaks in the titration curve, but the first break is small.

23. Specify the shape of the titration curve in the titration of maleic acid solution HOOC–CH=CH–COOH ($K_{a1} = 1.20 \cdot 10^{-2}$, $K_{a2} = 6.00 \cdot 10^{-7}$) with 0.1 M solution of alkali:

A. There is no abrupt change on the titration curve.
B. The break in the titration curve is large.
C. Two breaks in the titration curve are clearly observed.*
D. There are two breaks in the titration curve, but the second break is small.
E. There are two breaks in the titration curve, but the first break is small.

24. Choose the method of acid-base titration for the determination of sodium carbonate:

A. Acidimetry.*
B. Alkalimetry.
C. Both.
D. Neither one thing nor the other.

25. Choose the method of acid-base titration for the determination of sodium hydrogen carbonate:

A. Acidimetry.*
B. Alkalimetry.
C. Both.
D. Neither one thing nor the other.

26. What indicators are used in the case of titration of Na_2CO_3 solution with HCl solution:

A. Methyl orange.
B. Phenolphthalein.
C. Both.*
D. Neither one thing nor the other.

27. How is tartaric acid $H_2C_4H_4O_6$ ($K_{a1} = 1.30 \cdot 10^{-3}$, $K_{a2} = 3.00 \cdot 10^{-5}$) titrated in the presence of indicators:

A. As a dibasic acid.*
B. As a monobasic acid.
C. Both.
D. Neither one thing nor the other.

28. How is glycolic acid HO–CH$_2$–COOH ($K_a = 1.50 \cdot 10^{-4}$) titrated in the presence of indicators:
A. As a dibasic acid.
B. As a monobasic acid.*
C. Both.
D. Neither one thing nor the other.

29. How is glutamic acid HOOC–(CH$_2$)$_2$–CH(NH$_2$)–COOH ($K_{a1} = 4.70 \cdot 10^{-5}$, $K_{a2} = 8.70 \cdot 10^{-11}$) titrated in the presence of indicators:
A. As a dibasic acid.
B. As a monobasic acid.*
C. Both.
D. Neither one thing nor the other.

30. How is maleic acid HOOC–CH=CH–COOH ($K_{a1} = 1.20 \cdot 10^{-2}$, $K_{a2} = 6.00 \cdot 10^{-7}$) titrated in the presence of indicators:
A. As a dibasic acid.
B. As a monobasic acid.
C. Both.*
D. Neither one thing nor the other.

31. How is arsenous acid H_3AsO_3 ($K_{a1} = 5.90 \cdot 10^{-10}$) titrated in the presence of indicators:
A. As a dibasic acid.
B. As a monobasic acid.
C. Both.
D. Neither one thing nor the other.*

32. A solution may contain one of the substances: sodium hydroxide, sodium bicarbonate, sodium carbonate, or one of the mixtures: sodium carbonate and sodium hydroxide, sodium carbonate and sodium bicarbonate. This solution was titrated with a solution of hydrochloric acid sequentially in the presence of phenolphthalein ($V_{1(HCl)}$ = 10.00 ml) and methyl orange ($V_{2(HCl)}$ = 20.00 ml). Based on the results of titration, indicate which substance or mixture is in the solution:
A. Sodium carbonate.*
B. Sodium hydroxide and sodium carbonate.
C. Sodium carbonate and sodium bicarbonate.
D. Sodium hydroxide.
E. Sodium bicarbonate.

33. A solution may contain one of the substances: sodium hydroxide, sodium bicarbonate, sodium carbonate, or one of the mixtures: sodium carbonate and sodium hydroxide, sodium carbonate and sodium bicarbonate. This solution was titrated with a solution of hydrochloric acid sequentially in the presence of phenolphthalein ($V_{1(HCl)}$ = 7.50 ml) and methyl orange ($V_{2(HCl)}$ = 25.00 ml). Based on the results of titration, indicate which substance or mixture is in the solution:
A. Sodium carbonate.
B. Sodium hydroxide and sodium carbonate.
C. Sodium carbonate and sodium bicarbonate.*
D. Sodium hydroxide.
E. Sodium bicarbonate.

34. A solution may contain one of the substances: sodium hydroxide, sodium bicarbonate, sodium carbonate, or one of the mixtures: sodium carbonate and sodium hydroxide, sodium carbonate and sodium bicarbonate. This solution was titrated with a solution of hydrochloric acid sequentially in the presence of phenolphthalein ($V_{1(HCl)}$ = 18.00 ml) and methyl orange ($V_{2(HCl)}$ = 26.00 ml). Based on the results of titration, indicate which substance or mixture is in the solution:
A. Sodium carbonate.
B. Sodium hydroxide and sodium carbonate.*

C. Sodium carbonate and sodium bicarbonate.
D. Sodium hydroxide.
E. Sodium bicarbonate.

35. A solution may contain one of the substances: sodium hydroxide, sodium bicarbonate, sodium carbonate, or one of the mixtures: sodium carbonate and sodium hydroxide, sodium carbonate and sodium bicarbonate. This solution was titrated with a solution of hydrochloric acid sequentially in the presence of phenolphthalein ($V_{1(HCl)}$ = 0.00 ml) and methyl orange ($V_{2(HCl)}$ = 16.00 ml). Based on the results of titration, indicate which substance or mixture is in the solution:
A. Sodium carbonate.
B. Sodium hydroxide and sodium carbonate.
C. Sodium carbonate and sodium bicarbonate.
D. Sodium hydroxide.
E. Sodium bicarbonate.*

36. A solution may contain one of the substances: sodium hydroxide, sodium bicarbonate, sodium carbonate, or one of the mixtures: sodium carbonate and sodium hydroxide, sodium carbonate and sodium bicarbonate. This solution was titrated with a solution of hydrochloric acid sequentially in the presence of phenolphthalein ($V_{1(HCl)}$ = 20.00 ml) and methyl orange ($V_{2(HCl)}$ = 20.00 ml). Based on the results of titration, indicate which substance or mixture is in the solution:
A. Sodium carbonate.
B. Sodium hydroxide and sodium carbonate.
C. Sodium carbonate and sodium bicarbonate.
D. Sodium hydroxide.*
E. Sodium bicarbonate.

37. Indicate how polybasic ascorbic acid is titrated in aqueous media with visual fixation of the equivalence point ($K_{a1} = 9.10 \cdot 10^{-5}$, $K_{a2} = 4.60 \cdot 10^{-12}$):
A. As a dibasic acid.
B. As a monobasic acid.*
C. Both.
D. Neither one thing nor the other.

38. Indicate how polybasic glutamic acid is titrated in aqueous media with visual fixation of the equivalence point ($K_{a1} = 4.70 \cdot 10^{-5}$, $K_{a2} = 8.70 \cdot 10^{-11}$):
A. As a dibasic acid.
B. As a monobasic acid.*
C. Both.
D. Neither one thing nor the other.

39. Indicate how polybasic maleic acid is titrated in aqueous media with visual fixation of the equivalence point ($K_{a1} = 1.20 \cdot 10^{-2}$, $K_{a2} = 6.00 \cdot 10^{-7}$):
A. As a dibasic acid.
B. As a monobasic acid.
C. Both.*
D. Neither one thing nor the other.

40. Indicate how polybasic orthosilicic acid is titrated in aqueous media with visual fixation of the equivalence point ($K_{a1} = 1.30 \cdot 10^{-10}$, $K_{a2} = 1.60 \cdot 10^{-12}$, $K_{a3} = 2.00 \cdot 10^{-14}$):
A. As a dibasic acid.
B. As a monobasic acid.
C. Both.
D. Neither one thing nor the other.*

41. Sodium carbonate and sodium bicarbonate in a mixture cannot be determined separately, BECAUSE in the titration of this mixture with a solution of acid, sodium bicarbonate will be obtained from sodium carbonate.

A. 1- Right. 2- Right. Link – Right.
B. 1- Right. 2- Right. Link – Wrong.
C. 1- Right. 2-Wrong. Link – Wrong.
D. 1-Wrong. 2- Right. Link – Wrong.*
E. 1-Wrong. 2-Wrong. Link– Wrong.

LABORATORY WORK

Determination of concentration (in %) of sodium bicarbonate and sodium carbonate in a mixture

Direct titration.
Method of separate samples.

$$Na_2CO_3 + HCl \leftrightarrow NaHCO_3 + NaCl$$
$$CO_3^{2-} + H^+ \leftrightarrow HCO_3^-$$
$$NaHCO_3 + HCl \leftrightarrow H_2CO_3 + NaCl$$
$$HCO_3^- + H^+ \leftrightarrow H_2CO_3$$

$M(Na_2CO_3) = 105.9$ g/mol;
$f_e(Na_2CO_3) = ½$;
$M_e(Na_2CO_3) = f_e(Na_2CO_3) \cdot M(Na_2CO_3)$;
$M_e(Na_2CO_3) = 105{,}9 \cdot ½ = 52.99$ g/mol;
$M_{e'}(Na_2CO_3) = M_e(Na_2CO_3):1000 = 0.05299$;
$T(HCl/Na_2CO_3) = C_M(HCl) \cdot M_{e'}(Na_2CO_3)$;
$T(HCl/Na_2CO_3) = 0.1000 \cdot 0.05299 = 0.005299$ g/ml;

$M(NaHCO_3) = 84.01$ g/mol;
$f_e(NaHCO_3) = 1$;
$M_e(NaHCO_3) = f_e(NaHCO_3) \cdot M(NaHCO_3)$;
$M_e(NaHCO_3) = 84.01 \cdot 1 = 84.,01$ g/mol;
$M_{e'}(NaHCO_3) = M_e(NaHCO_3) : 1000 = 0.08401$;
$T(HCl/NaHCO_3) = C_M(HCl) \cdot M_{e'}(NaHCO_3)$;
$T(HCl/NaHCO_3) = 0.1000 \cdot 0.08401 = 0.008401$ g/ml;
$a(NaHCO_3)= C_M(HCl) \cdot M_{e'}(NaHCO_3) \cdot V$.

Assay procedure. Take on a weighed sample of a mixture calculated for 20.00 ml of the titrant (the basic component – sodium hydrogen carbonate) and dissolve in a conical flask in 20.00 ml of distilled fresh water. Add to the solution 1-2 drops of 0.1% phenolphthalein solution and titrate with standard 0.1000 M HCl solution until the color disappears after the addition of a single drop. Write down the burette reading $V_1(HCl)$.

Then, add 1-2 drops of methyl orange to the titrated solution. The solution turns yellow. Continue the titration (don’t add the titrant in the burette!!!) until the solution becomes a permanent orange. Take the burette reading again. Repeat the precise titration at least twice more and take the average of the concordant results for the following calculations of percentage concentration of sodium carbonate and sodium hydrogen carbonate.

$$\omega_{(\mathrm{Na_2CO_3})} = \frac{2\mathrm{V}_{1_{(\mathrm{HCl})}} \cdot T_{(\mathrm{HCl/Na_2CO_3})} \cdot C_f \cdot 100}{a}$$

$$\omega_{(\mathrm{NaHCO_3})} = \frac{\left(V_{2_{(\mathrm{HCl})}} - 2\mathrm{V}_{1(\mathrm{HCl})}\right) \cdot T_{(\mathrm{HCl/NaHCO_3})} \cdot C_f \cdot 100}{a}$$

Visual materials, learning and control tools

1. Tabular resources on the topic of the lesson.
2. Textbooks, handbook on analytical chemistry.
3. Learning and control tools: cards for assessing the initial level of knowledge; test questions.

TITRATION OF AMPHOLYTES

Some substances can behave in solutions both as an acid and as a base depending on the conditions.

Compounds with such properties are called ampholytes. These include water, ethanol, hydroxides of some metals, anions of acid salts (HCO_3^-, $H_2PO_4^-$, HPO_4^{2-} etc.).

If a stronger proton donor (strong acid) is present in the solution of an amphoteric compound, it exhibits basic properties, being their acceptor; in the presence of a strong acceptor of protons (base), the ampholyte donates its protons, exhibiting acidic properties.

Amphoteric substances have *weak acidic* and *weak basic* properties. To choose the method of acid-base titration of ampholyte (acidimetry or alkalimetry), compare its constants of acidity and basicity.

Consider how sodium hydrogen phosphate Na_2HPO_4 and sodium dihydrogen phosphate NaH_2PO_4 can be titrated.

Determination of sodium hydrogen phosphate Na_2HPO_4

In aqueous solutions, sodium hydrogen phosphate exhibits both acidic and basic properties.

The *acidity constant* of sodium hydrogen phosphate $К_{а\left(\mathrm{HPO_4^{2-}}\right)}$ is equal to the third dissociation constant of phosphoric acid:

$$\underset{a_1}{HPO_4^{2-}} + \underset{b_2}{H_2O} \leftrightarrow \underset{b_1}{PO_4^{3-}} + \underset{a_2}{H_3O^+}$$

$$К_{а\left(\mathrm{HPO_4^{2-}}\right)} = К_{a_3(H_3\mathrm{PO_4})} = 5.00 \cdot 10^{-13}$$

The *basicity constant* of sodium hydrogen phosphate $К_{в\left(\mathrm{HPO_4^{2-}}\right)}$ is calculated as the ratio of the water constant to the second acidity constant of phosphoric acid:

$$\underset{b_1}{HPO_4^{2-}} + \underset{a_2}{H_2O} \leftrightarrow \underset{a_1}{H_2PO_4^-} + \underset{b_2}{OH^-}$$

$$К_{в\left(\mathrm{HPO_4^{2-}}\right)} = \frac{К_w}{К_{a_2(H_3\mathrm{PO_4})}} = \frac{10^{-14}}{6.20 \cdot 10^{-8}} = 1.61 \cdot 10^{-7}$$

$К_{в\left(\mathrm{HPO_4^{2-}}\right)} >> К_{а\left(\mathrm{HPO_4^{2-}}\right)}$, hence, sodium hydrogen phosphate, to a greater extent, will exhibit basic properties.

Therefore, the titrimetric determination of sodium hydrogen phosphate is carried out by acidimetry (HCl – titrant) in the presence of methyl orange, because the pH value at the equivalence point is equal to:

$$\text{pH} = \frac{\text{pК}_{\text{a}_1(H_3\text{PO}_4)} + \text{pК}_{\text{a}_2(H_3\text{PO}_4)}}{2} = \frac{2.15 + 7.21}{2} = 4.68$$

Chemism of titration:

$$HPO_4^{2-} + H_3O^+ \leftrightarrow H_2PO_4^- + H_2O$$

Determination of sodium dihydrogen phosphate NaH_2PO_4

Sodium dihydrogen phosphate in aqueous solutions also exhibits both acidic as well as basic properties.

The *acidity constant* of sodium dihydrogen phosphate К_a is equal to the second acidity constant of phosphoric acid:

$$\underset{a_1}{H_2PO_4^-} + \underset{b_2}{H_2O} \leftrightarrow \underset{b_1}{HPO_4^{2-}} + \underset{a_2}{H_3O^+}$$

$$\text{К}_{\text{a}\,(H_2\text{PO}_4^-)} = \text{К}_{\text{a}_2(H_3\text{PO}_4)} = 6.20 \cdot 10^{-8}$$

The *basicity constant* of sodium dihydrogen phosphate $\text{К}_\text{в}$ is calculated as the ratio of the water constant to the first acidity constant of phosphoric acid:

$$\underset{b_1}{H_2PO_4^-} + \underset{a_2}{H_2O} \leftrightarrow \underset{a_1}{H_3PO_4} + \underset{b_2}{OH^-}$$

$$\text{К}_{\text{в}\,(H_2\text{PO}_4^-)} = \frac{\text{К}_w}{\text{К}_{a_1(H_3\text{PO}_4)}} = \frac{10^{-14}}{7.10 \cdot 10^{-3}} = 1.41 \cdot 10^{-12}$$

$\text{К}_\text{b} >> \text{К}_\text{a}$, therefore, sodium dihydrogen phosphate will exhibit, to a greater extent, acidic properties.

Therefore, the titrimetric determination of sodium dihydrogen phosphate is carried out by alkalimetry (NaOH – titrant) in the presence of phenolphthalein, because the pH value at the equivalence point is equal to:

$$\text{pH} = \frac{\text{pК}_{\text{a}_2(H_3\text{PO}_4)} + \text{pК}_{\text{a}_3(H_3\text{PO}_4)}}{2} = \frac{7.21 + 12.0}{2} = 9.60$$

Chemism of titration:

$$H_2PO_4^- + OH^- \leftrightarrow HPO_4^{2-} + H_2O$$

INDICATOR ERRORS IN TITRATION

The indicator error is the error caused by the difference between the titration exponent of a given indicator and the pH at the equivalence point (EP). It is almost impossible to choose such an indicator of acid-base titration, the pH value of which would exactly coincide with the pH value at the EP. Therefore, the indicator changes its color at the end point of titration (EPT), before or after it. If the color change of an indicator occurs before the EP, a solution is undertitrated, there is a certain amount of undertitrated analyzed substance in the solution. If the color of an indicator changes after the EP, a solution is overtitrated, there is some excess amount of the titrant in the solution. Therefore, the volume of the titrant consumed in the titration may be either less or more than the stoichiometric volume at the EP. The greater the difference between the pH value of the indicator and the pH of the titrating solution at the EP, the more noticeable the value of the indicator error.

Usually, try to minimize indicator errors so that they, in any case, would not exceed 0.2%. It is achieved mainly by selecting the appropriate indicator. In an acid-base titration, there are several types of indicator errors:

– *proton or hydrogen error* ($H^+_{er.}$) - due to the presence of excess hydrogen ions H^+ in a solution; occurs when a strong acid is undertitrated or when the base is overtitrated with a standard solution of a strong acid. The hydrogen error is calculated by the formula:

$$\mathrm{H}^+_{er.} = \frac{(V_{H^+} + V_{OH^-}) \cdot 10^{-pT}}{C_{H^+} \cdot V_{H^+}} \cdot 100\%$$

– *hydroxyl error* ($OH^-_{er.}$) – due to the presence of excess hydroxide ions of alkali in a solution or it can be a result of undertitration of a solution of alkali with acid (negative error), or overtitration of a solution of acid with a strong base (positive error). Hydroxyl error is calculated by the formula:

$$\mathrm{OH}^-_{\mathrm{er.}} = \frac{(V_{H^+} + V_{OH^-}) \cdot 10^{pT-14}}{C_{OH^-} \cdot V_{OH^-}} \cdot 100\%$$

– *acid error* ($HA_{er.}$) – due to the presence of undissociated molecules of a weak acid in a solution at the end of the titration. The acid error is calculated by the formula:

$$\mathrm{HA}_{\mathrm{er.}} = \frac{10^{-\mathrm{pT}}}{10^{-\mathrm{pK_a}}} \cdot 100\% = 10^{\mathrm{pK_a} - \mathrm{pT}} 100\%$$

– *alkali error* ($MeOH_{er..}$) – due to the presence of undissociated molecules of a weak base in a solution at the end of the titration. The alkali error is calculated by the formula:

$$MeOH_{\mathrm{er.}} = \frac{10^{\mathrm{pT}-14}}{10^{-\mathrm{pK_в}}} \cdot 100\% = 10^{\mathrm{pK_в} + \mathrm{pT} - 14} 100\%$$

Tutorial 14

1. THEME: Acid-base titration. Titration of ampholytes

2. PURPOSE: To study the basic features of titrimetric determination of ampholytes. To study indicator errors in acid-base titration

3. OBJECTIVIES:

3.1. Get acquainted with the theoretical foundations of titration of ampholytes and study to choose the method (acidimetry or alkalimetry) for the determination of ampholytes.

3.2. Prove the choice of methods for the titrimetric determination of sodium hydrogen phosphate and sodium dihydrogen phosphate.

3.3. Conduct the quantitative determination of sodium hydrogen phosphate and sodium dihydrogen phosphate in analyzed samples.

3.4. Study to make conclusions about the conformity of the composition of a studied sample with the formula, to identify the composition of an analyzed sample.

3.5. Study indicator errors in an acid-base titration, study to calculate them and select the indicator according to the calculations.

4. PLAN AND ORGANIZATIONAL STRUCTURE OF THE TUTORIAL:

4.1. Organizational moment.....…………………….……………..................2 min

4.2. Description of the purpose of the lesson (introductory speech of the teacher)……………...3 min

4.3. Assessment of the initial level of knowledge (card control)…….……..10 min

4.4. Correction of the initial level of knowledge and skills………...............40 min

4.5. Organization of independent work of students (teacher's instructions, safety instruction)…………………..…...........3 min

4.6. Laboratory work……….......…….………………………………….. ..110 min

4.7. Final control: check of laboratory results and protocols……………. …10 min

4.8. Concluding speech of the teacher, instructions for the next lesson…… ..2 min

5. REFERENCE FOR SELF STUDY:

5.1. Repeat the following topics from the course of inorganic chemistry and qualitative analysis: ampholytes, equilibria in aqueous solutions of ampholytes.

5.2. Study the program materials on this topic, using the recommended literature and lectures.

Questions for self-study

1. Equilibria in aqueous solutions of ampholytes. Which properties show ampholytes during the interaction with acids and bases? Show by the example of hydrocarbonate, hydro- and dihydrogen phosphate, hydro- and dihydroarsenate.

2. The choice of method of acid-base titration for the quantitative determination of ampholyte.

3. How to calculate the acidity or basicity constant of ampholyte, if one of these values is known?

4. How to calculate the pH at the equivalence point in the titration of ampholyte?

5. Indicator errors in an acid-base titration: proton (hydrogen), hydroxide, acid and alkali. What are the sources of these errors?

6. Calculation of indicator errors.

Solve the tasks:

Task 1. Calculate the pH of 0.01 M sodium hydrocarbonate solution.

Answer: 8.34.

Task 2. Determine the type and calculate the indicator error in the titration of 0.1 M ammonia solution with 0.1 M hydrochloric acid solution in the presence of methyl red (pT = 5.0).

Answer: 0.02%.

Task 3. Which indicator can be used for the titration of ammonia solution so that the alkali error does not exceed 0.1%?

Examples of the solved tasks:

Task 1. Calculate the pH of 0.05 M disodium phosphate solution.

Solution. Monohydrogen phosphate ion is an ampholyte, which in aqueous solution can both give a hydrogen ion, turning into a phosphate ion, and receive the hydrogen ion, turning into dihydrogen phosphate ion:

$$HPO_4^{2-} + H_2O \leftrightarrow PO_4^{3-} + H_3O^+$$
$$HPO_4^{2-} + H_2O \leftrightarrow H_2PO_4^- + OH^-$$

Therefore, the pH will be determined by the presence of phosphate and dihydrogen phosphate ions in the solution, which corresponds to the second and third ionization of phosphoric acid.

$pK_{a2}\ H_3PO_4 = 7{,}21$
$pK_{a3}\ H_3PO_4 = 12{,}30$

$$pH = \frac{pK_{a_2 H_3PO_4} + pK_{a_3 H_3PO_4}}{2} = \frac{7.21+12.30}{2} = 9.76$$

Answer: 9.76.

Task 2. Determine the type and calculate the indicator error in the titration of 0.1 M NaOH with 0.1 M HCl in the presence of thymolphthalein (pT = 10.0).

Solution. In the titration of 0.1 M NaOH with 0.1 M HCl, the pH at the equivalence point is equal to 7.

$$\mathrm{NaOH + HCl \leftrightarrow NaCl + H_2O}$$

This titration will be finished in the presence of thymolphthalein at pH = 10.0. The presence of an excess of hydroxide ions of alkali in the solution will cause a hydroxyl error marked with the "-" because the solution is undertitrated. Solutions with the same concentration were used in the titration, therefore

$V_{OH^-} = V_{H^+} = V$:

$$\mathrm{OH}^-_{\mathrm{er}} - \frac{(V_{\mathrm{OH}^-} + V_{H^+}) \cdot 10^{\mathrm{pT}-14}}{V_{\mathrm{OH}^-} \cdot C_{\mathrm{OH}^-}} \cdot 100\% = -\frac{2\mathrm{V} \cdot 10^{10-14}}{V \cdot 0{,}1} \cdot 100\% = -0{,}2\%$$

Answer: - 0.2%.

Task 3. Which indicator should be used in the titration of acetic acid solution if the acetic error should not exceed 0.1%?

Solution. The acid error is due to the presence in a solution of undissociated molecules of a weak acid and is calculated by the formula:

$$\mathrm{HA_{er.}} = 10^{\ \mathrm{pK_a - pT}}$$

In the task, $\mathrm{HA_{er.}}$ is restricted to 0.1%. Therefore, the portion of undertitrated acid is 0.001 of the total amount of acid. Then the equation for $\mathrm{HA_{er.}}$ is:

$$10^{-3} \geq 10^{\ \mathrm{pK_a - pT}}$$

After logarithm we get:

$$\mathrm{pT} \geq \mathrm{pK} + 3.$$

Thus, indicators with pT ≥ 4.76 + 3 = 7.76 can be used for the titration of acetic acid. For example, phenolphthalein, m-cresol purple, tropeolin 00, and so on.

Work on test tasks

1. The calculation of indicator errors is one of the methods of quantitative selection of pH indicators. They are caused by the difference between the pH at the equivalence point and the pH at the end point in a titration (the pT of a given indicator). Choose the name of indicator error and formula for its calculation if the indicator error is concerned either with the undertitration of strong acids or with the overtitration of weak bases.

A. Hydrogen error: $H^{+=}_{er.}$*
B. Hydroxyl error: $OH^{-=}_{er.}$
C. Acid error: $HA_{er.} = 10^{pK_a - pT} \cdot 100\%$
D. Error in the indicator concentration: $pT - pT_1$
E. Alkali error: $B_{er.} = 10^{pK_\text{в} + pT - 14} \cdot 100\%$

2. The calculation of indicator errors is one of the methods of quantitative selection of pH indicators. They are caused by the difference between the pH at the equivalence point and the pH at the end point in a titration (the pT of a given indicator). What is the indicator error and its formula when alkali is either undertitrated or a weak acid is somewhat overtitrated?
A. Hydrogen error: $H^{+=}_{er.}$
B. Hydroxyl error: $OH^{-=}_{er.}$*
C. Acid error: $HA_{er.} = 10^{pK_a - pT} \cdot 100\%$
D. Error in the indicator concentration: $pT - pT_1$
E. Alkali error: $B_{er.} = 10^{pK_\text{в} + pT - 14} \cdot 100\%$

3. The calculation of indicator errors is one of the methods of quantitative selection of pH indicators. They are caused by the difference between the pH at the equivalence point and the pH at the end point in a titration (the pT of a given indicator). Choose the name of indicator error and formula for its calculation if the indicator error is concerned with the undertitration of weak acids:
A. Hydrogen error: $H^{+=}_{er.}$
B. Hydroxyl error: $OH^{-=}_{er.}$
C. Acid error: $HA_{er.} = 10^{pK_a - pT} \cdot 100\%$*
D. Error in the indicator concentration: $pT - pT_1$
E. Alkali error: $B_{er.} = 10^{pK_\text{в} + pT - 14} \cdot 100\%$

4. The calculation of indicator errors is one of the methods of quantitative selection of pH indicators. They are caused by the difference between the pH at the equivalence point and the pH at the end point in a titration (the pT of a given indicator). Choose the name of indicator error and formula for its calculation if the indicator error is concerned with the undertitration of weak bases:
A. Hydrogen error: $H^{+=}_{er.}$
B. Hydroxyl error: $OH^{-=}_{er.}$
C. Acid error: $HA_{er.} = 10^{pK_a - pT} \cdot 100\%$
D. Error in the indicator concentration: $pT - pT_1$
E. Alkali error: $B_{er.} = 10^{pK_\text{в} + pT - 14} \cdot 100\%$*

5. The calculation of indicator errors is one of the methods of quantitative selection of pH indicators. They are caused by the difference between the pH at the equivalence point and the pH at the end point in a titration (the pT of a given indicator). Choose the name of indicator error and formula for its calculation if it is concerned with the shift of end point of titration due to increasing the concentration of an indicator:
A. Hydrogen error: $H^{+=}_{er.}$
B. Hydroxyl error: $OH^{-=}_{er.}$
C. Acid error: $HA_{er.} = 10^{pK_a - pT} \cdot 100\%$
D. Error in the indicator concentration: $pT - pT_1$*
E. Alkali error: $B_{er.} = 10^{pK_\text{в} + pT - 14} \cdot 100\%$

LABORATORY WORK

1. Determination of concentration (in %) of sodium hydrogen phosphate in a sample

Direct titration.
Method of separate samples.

$$Na_2HPO_4 + HCl \leftrightarrow NaH_2PO_4 + NaCl$$
$$HPO_4^{2-} + H^+ \leftrightarrow H_2PO_4^-$$

$M(Na_2HPO_4 \cdot 12H_2O) = 358.1$ g/mol;
$M(Na_2HPO_4) = 142.0$ g/mol;
$f_e(Na_2HPO_4 \cdot 12H_2O) = f_e(Na_2HPO_4) = 1$;
$M_{e'} = f_e \cdot M : 1000$;
$M_{e'}(Na_2HPO_4 \cdot 12H_2O) = 358.0 \cdot 1 : 1000 = 0.3581$ g/mol;
$M_{e'}(Na_2HPO_4) = 142.0 \cdot 1 : 1000 = 0.1420$ g/mol;
$T(HCl/Na_2HPO_4 \cdot 12H_2O) = C_M(HCl) \cdot M_{e'}(Na_2HPO_4 \cdot 12H_2O)$;
$T(HCl/Na_2HPO_4 \cdot 12H_2O) = 0.1000 \cdot 0.3581 = 0.03581$ g/ml;
$T(HCl/Na_2HPO_4) = C_M(HCl) \cdot M_{e'}(Na_2HPO_4)$;
$T(HCl/Na_2HPO_4) = 0.1000 \cdot 0{,}1420 = 0.01420$ g/ml;
$a(Na_2HPO_4 \cdot 12H_2O) = T(HCl/Na_2HPO_4 \cdot 12H_2O) \cdot V$.

Assay procedure. Take on a weighed sample of sodium hydrogen phosphate calculated for 10.00 ml of the titrant on the analytical balance by difference, transfer it to a conical flask and dissolve in 5 ml of distilled water. Add to the solution 2.7 g of sodium chloride for a more drastic change in color of the indicator at the end point of titration. Then, add 1-2 drops of methyl orange solution, the solution turns yellow. Titrate the solution with 0,1000 M hydrochloric acid solution until the solution becomes a permanent orange. Write down the burette reading.

The titration of sodium hydrogen phosphate is performed until three concordant results are obtained. For each determination, calculate percentage concentrations of anhydrous sodium hydrogen phosphate and crystal hydrate.

$$\omega_{(\mathrm{Na_2HPO_4})} = \frac{V_{(\mathrm{HCl})} T_{(\mathrm{HCl/Na_2HPO_4})} C_f 100}{a}$$

$$\omega_{(\mathrm{Na_2HPO_4 \cdot 12H_2}O)} = \frac{V_{(\mathrm{HCl})} T_{(\mathrm{HCl/Na_2HPO_4 \cdot 12H_20})} C_f 100}{a}$$

According to the obtained data, calculate average values of the percentage concentration for anhydrous sodium hydrogen phosphate and crystal hydrate and find the actual content of water of crystallization in $Na_2HPO_4 \cdot 12H_2O$.

2. Determination of concentration (in %) of sodium dihydrogen phosphate in a sample

Direct titration.

Method of separate samples.

$$NaH_2PO_4 + NaOH \leftrightarrow Na_2HPO_4 + H_2O$$
$$H_2PO_4^- + OH^- \leftrightarrow HPO_4^{2-} + H_2O$$

$M(NaH_2PO_4 \cdot 2H_2O) = 156.0$ g/mol;
$M(NaH_2PO_4) = 120.0$ g/mol;
$f_e(NaH_2PO_4 \cdot 2H_2O) = f_e(NaH_2PO_4) = 1$;
$M_{e'} = f_e \cdot M : 1000$;
$M_{e'}(NaH_2PO_4 \cdot 2H_2O) = 156.0 \cdot 1 : 1000 = 0.1560$ g/mol;
$M_{e'}(NaH_2PO_4) = 120.0 \cdot 1 : 1000 = 0.1200$ g/mol;
$T(NaOH/NaH_2PO_4 \cdot 2H_2O) = C_M(NaOH) \cdot M_{e'}(NaH_2PO_4 \cdot 2H_2O)$;
$T(NaOH/NaH_2PO_4 \cdot 2H_2O) = 0.1000 \cdot 0.1560 = 0.01560$ g/ml;
$T(NaOH/NaH_2PO_4) = C_M(NaOH) \cdot M_{e'}(NaH_2PO_4)$;
$T(NaOH/NaH_2PO_4) = 0.1000 \cdot 0.1200 = 0.01200$ g/ml;
$a(NaH_2PO_4 \cdot 2H_2O)= T(NaOH/NaH_2PO_4 \cdot 2H_2O) \cdot V$.

Assay procedure. Take on the sample of sodium dihydrogen phosphate calculated for 10.00 ml of the titrant on the analytical balance by difference, transfer it to a conical flask and dissolve in 5 ml of distilled water. Add to the solution 2.7 g of sodium chloride for a more drastic change in color of the indicator at the end point of titration. Then, add 1-2 drops of phenolphthalein solution. Titrate the mixture with 0.1000 M sodium hydroxide solution. The solution should be faint pink Write down the burette reading.

The titration of sodium dihydrogen phosphate is performed until three concordant results are obtained. For each determination, calculate the concentration (in%) of anhydrous sodium dihydrogen phosphate and crystal hydrate.

$$\omega_{(\mathrm{NaH_2PO_4})} = \frac{V_{(\mathrm{NaOH})} \cdot T_{(\mathrm{NaOH/NaH_2PO_4})} \cdot C_f \cdot 100}{a}$$

$$\omega_{(\mathrm{NaH_2PO_4 \cdot 2H_2}O)} = \frac{V_{(\mathrm{NaOH})} \cdot T_{(\mathrm{NaOH/NaH_2PO_4 \cdot 2H_2O})} \cdot C_f \cdot 100}{a}$$

According to the obtained data, calculate average values of the concentration for anhydrous sodium dihydrogen phosphate and crystal hydrate and find the actual content of water of crystallization in $NaH_2PO_4 \cdot 2H_2O$.

Visual materials, learning and control tools

1. Tabular resources on the topic of the lesson.
2. Textbooks, handbook on analytical chemistry.
3. Learning and control tools: cards for assessing the initial level of knowledge; test questions.

APPLICATION OF ACID-BASE TITRATION IN QUANTITATIVE ANALYSIS OF CHEMICAL SUBSTANCES AND MEDICINES

An acid-base titration in aqueous media is widely used for the quantitative analysis of inorganic, organic and biological substances which have acid-base properties (strong and weak acids and bases, acid and basic salts, as well as salts containing anions of weak acids and cations of weak basics). It is also possible to identify substances that do not have acid-base properties but react with acids or bases. Acid-base titration has been used for many years for the elemental analysis of organic compounds. Typically, these methods are used to determine non-metals: carbon, nitrogen, chlorine, bromine, sulfur, phosphorus etc.

ERRORS IN QUANTITATIVE ANALYSIS. STATISTICAL PROCESSING AND EVALUATION OF ANALYSIS RESULTS

There are systematic (definite) and random (indefinite) errors. The reasons for systematic errors may be faults in the method of analysis, instrument failure or errors of the analyst. Random errors, in contrast to the systematic, cannot be eliminated. They can be estimated by methods of mathematical statistics. Mistakes are rude errors that greatly distort analytical results and are usually easily detected. They are usually caused by the negligence or incompetence of the analyst. They include errors caused by incorrect counting of weights or wrong readings on the scale in weighing, wrong burette readings in titration, errors caused by spilling of the solution or precipitate during the determination, etc.

The results of the analysis must be accurate, precise and reproducible. The accuracy expresses the closeness of the result to the “Link value”. Reproducibility is determined by the agreement of results with each other and is usually expressed by the ratio of experimental data and their arithmetic mean.

After obtaining some results, statistical processing is performed to assess the correctness of analysis.

The term “sample” refers to a set of statistically equivalent results (variants).

In most cases, the average of the sample is the best estimation of the Link value of the measured value μ, it is calculated as the arithmetic mean of all variants:

$$\bar{x} = \frac{\sum_1^n x_i}{n}$$

The scatter of variants x_i around the mean is characterized by the value of the standard deviation S. In quantitative analysis, the value of S is often considered as an estimation of the random error inherent in this method of analysis. The square deviation S^2 is called dispersion. The value of dispersion can be considered as a measure of reproducibility of the results presented in this selected data:

$$S^2 = \frac{\sum_1^n x_i^2 - n\bar{x}^2}{n-1}$$

$$S = \sqrt{S^2}$$

The standard deviation of a mean result $S_{\bar{x}}$ is calculated by the equation:

$$S_{\overline{x}} = \frac{S}{\sqrt{n}}$$

The results obtained from the statistical processing of a sample will be reliable only if this sample is homogeneous, i.e. if variants included in it are not burdened with gross errors. The check of homogeneity of small samples ($n < 10$) is carried out without first calculating statistical characteristics. For this purpose, after presenting the sample in ascending order of data values, the value of *control criterion* Q is calculated (based on the magnitude of variation R):

$$R = |\mathrm{x}_1 - x_n|$$

$$Q_1 = \frac{|\mathrm{x}_1 - x_2|}{R}$$

$$Q_n = \frac{|\mathrm{x}_n - x_{n-1}|}{R}$$

A sample is considered inhomogeneous if at least one of the calculated Q values exceeds the tabular value $Q(\mathrm{P}, \mathrm{n})$ found for the confidence interval $\overline{\mathrm{P}}$.Variants x_1 or x_n for which $Q > Q(P, n)$ are discarded, and for the obtained sample with a reduced size a new cycle of calculations is performed. It is necessary for the verifying of its homogeneity.

For a large sample ($n \geq 10$), the homogeneity check is performed after preliminary calculations of statistical characteristics $\overline{x}$, S^2, S, $S_{\overline{x}}$. The sample is considered homogeneous if the following condition is fulfilled for all variants:

$$|x_i - \overline{x}| \leq 3S$$

If the sample is considered inhomogeneous, then the variants for which $|x_i - \overline{x}| > 3S$ are rejected. They are considered burdened with a gross error. In this case, the calculation of statistical characteristics for the obtained sample with a reduced volume is repeated. It is considered complete when the sample with a reduced volume is homogeneous.

For a more reliable assessment of reproducibility, the calculation of limit values of the confidence interval according to Student:

$$\overline{x} \pm \Delta\overline{x} = \overline{x} \pm \frac{t(\mathrm{P,f}) \cdot S}{\sqrt{n}},$$

where t(P,f) – is a tabular value in a Student’s T-Distribution (Student’s coefficient).

A confidence level P is a probability of finding the actual value of the determined value within the confidence interval. It varies from 0 to 1 (from 0% to 100%). In pharmaceutical analysis, the confidence level is often equal to P = 0.95 = 95% and denoted as $P_{0.95}$.

If results do not exceed the confidence interval, it means that all sampling variants that are within the confidence interval are reliable. The value $\Delta\overline{x}$ is used for the calculation of a relative error of the mean result ($\overline{\varepsilon}$) (in %):

$$\overline{\varepsilon} = \frac{\Delta\overline{\mathrm{x}}}{\overline{\mathrm{x}}} \cdot 100\%$$

If the value $|\mu - \overline{x}| > 0$ for the sample with a volume m is Link, the question about the presence or absence of systematic error should be resolved. To do this, calculate the Student's T-test:

$$t = \frac{|\mu - \overline{x}| \cdot \sqrt{m}}{S}$$

For example, when P = 95% and f = m - 1, the inequality t> t (P, f) is realized, the results obtained by this method are burdened with a systematic error, the relative value of which δ is calculated by the formula:

$$\delta = \frac{\overline{x} - \mu}{\eta} \cdot 100\%$$

For comparing two methods by reproducibility at the same method of analysis, calculate the value of the Fisher test (F-test):

$$F = \frac{S_1^2}{S_2^2}$$

In that case, the F-test value characterizes the significance of the difference between S_1^2 and S_2^2 at $S_1^2 > S_2^2$. The calculated value is compared with a tabular value of F (P, f_1, f_2) found for the required confidence level (P). If the calculated F-test value is greater than the tabular, then the difference of dispersions is recognized as statistically significant. This allows us to conclude about the higher reproducibility of one of the methods.

If it is necessary to estimate statistically average means of two completely independent samples, calculate the value of the Student's criterion:

$$t_{\mathrm{st}} = \frac{(\overline{x}_1 - \overline{x}_2)}{S}\sqrt{\frac{n_1 n_2}{n_1 + n_2}},$$

the number of degrees of freedom is equal to $f = n_1 + n_2 - 2$.

Using the Student's T-test, arithmetic means of the control and controlled methods are considered. Because these values are not correlated with each other, Student's criterion allows proving whether the compared data are the result of an erroneous series of analyzes or not. In this case, the test is performed by comparing the calculated t_{st}-criterion with those in the table.

Tutorial № 15

1. THEME: Acid-base titration. Application of acid-base titration

2. PURPOSE: Study to evaluate the possibilities of methods of acid-base titration and apply them in the analysis of chemical compounds and medicines

3. OBJECTIVIES:

3.1. Study the possibility of usage of acid-base titration to determine substances that exhibit acidic or basic properties.

3.2. Study to choose the method of titration and select an indicator correctly, calculate the concentration of identified substances.

3.3. Develop the ability to apply the method of acid-base titration for the quantitative determination of chemical compounds and pharmaceutical drugs.

4. PLAN AND ORGANIZATIONAL STRUCTURE OF THE LESSON:

4.1. Organizational moment.....………………………………........................2 min

4.2. Description of the purpose of the lesson (introductory speech of the teacher)……………...3 min

4.3. Assessment of the initial level of knowledge (card control)……………10 min

4.4. Correction of the initial level of knowledge and skills……….................40 min

4.5. Organization of independent work of students (teacher's instructions, safety instruction)…………………...3 min

4.6. Laboratory work…………........…….……………………………...110 min

4.7. Final control: check of laboratory results and protocols……………..…10 min

4.8. Concluding speech of the teacher, instructions for the next lesson……...2 min

5. REFERENCE FOR SELF STUDY:

5.1. Repeat the theoretical material, solving tasks in topics 1-5.

5.2. Study the program materials on this topic using recommended literature and lectures.

Questions for self-study

1. Determination of ammonium salts by the method of acid-base titration (method and type of titration, chemical reaction, conditions for the determination).
2. Application of acid-base titration to determine functional groups of organic compounds. How can you identify substances containing the following groups: a carboxyl, a sulfo and an ester? Write down chemical reactions, indicate the method, type, and conditions of titration.
3. Application of acid-base titration for the analysis of organic compounds by functional groups. How are substances containing alcohol hydroxyl, carbonyl and amino groups determined?
4. Field of application of acid-base titration. Which acids can be determined by this method? Describe the determination of boric acid in concentrated and dilute

solutions (method and type of titration, chemical reaction, indicator selection, calculation of the result).

5. Application of acid-base titration for elemental analysis. What is the basis for the determination of sulfur, chlorine, bromine in organic compounds? Write down chemical reactions.

6. Alkalimetry, direct and back titration. Write down chemical reactions of the determination of hydrazine salts, hydroxy acids and esters of salicylic acid.

7. Is it possible to determine salicylic acid, esters of salicylic acid by acid-base titration? Write down the chemical reaction and explain the choice of an indicator.

8. Nitrogen determination by the Kjeldahl method. The essence of the method, chemical reaction.

Solve the tasks:

Task 1. To determine a mixture of amino acids containing 0.1046 g of glycine (M = 75.07 g/mol) and 0.0848 g of alanine (M = 89.10 g/mol), the excess of formalin, previously neutralized with phenolphthalein, was added. The obtained compounds were titrated with 0.1016 M NaOH solution. Calculate the volume of the titrant.

Answer: 23,08 ml.

Task 2. A sample of formaldehyde solution with a volume of 5.00 ml was diluted to 100.0 ml. To 5.00 ml of the aliquot, sodium sulfite was added:

$$HCOH + SO_3^{2-} + H_2O \leftrightarrow CH_2(OH)SO_3^- + OH^-$$

The formed hydroxyl ions were titrated with 22.45 ml of 0.1000 N (f_e = 1/2) sulphuric acid solution. Calculate the concentration (g/l) of CH_2O in the stock solution.

Answer: 269,7 g/l.

Task 3. Calcium was determined by gravimetry, and the following CaO results were obtained (in %): 12.86; 12.90; 12.93; 12.84. Calculate the standard deviation in the determination of calcium concentration.

Answer: 0,04.

Task 4. To titrate 0.1285 M standard hydrochloric acid solution, the following results of the molar concentration (mol/l) of sodium hydroxide were received: 0.1274; 0.1278; 0.1280; 0.1275. Determine whether there is a systematic error in determining the molar concentration of hydrochloric acid.

Answer: presents.

Examples of the solved tasks:

Task 1. To determine the formaldehyde content in a sample, a sample of 3.0170 g of the medicine was weighed and treated with 50.00 ml of 1.000 M NaOH solution (C_f = 0.9022) in the presence of hydrogen peroxide. During heating, the written below reaction proceeded:

$$HCOH + OH^- + H_2O_2 \leftrightarrow HCOO^- + 2H_2O$$

After cooling, the excess alkali was titrated with 20.12 ml of HCl solution (T (HCl) = 0.03798). Calculate the concentration (in %) of formaldehyde in the sample.

Solution.

The determination was performed by back titration, by the method of separate samples. The calculation of the result is carried out according to the formula:

$$\omega_{(\mathrm{HCOH})} = \frac{\left(C_{M(\mathrm{NaOH})} \cdot V_{(\mathrm{NaOH})} \cdot C_f \text{-} \mathrm{C}_{M(\mathrm{HCl})} \cdot V_{(\mathrm{HCl})}\right) \cdot M_{\mathrm{E}'(\mathrm{HCOH})} \cdot 100}{a_{(\mathrm{HCOH})}}.$$

M(HCOH) = 30.03 g/mol;

f_e(HCOH) = 1;

$M_{e'}$(HCOH) = M(HCOH) · f_e(HCOH):1000 = 0.03003.

Since the titer of HCl is given in the conditions of the task, first, we calculate the molar concentration of HCl:

C_M(HCl) = T : $M_{e'}$(HCl) = 0.03798 : 0.03646 = 1.042 M

Put the values into the formula:

$$\omega_{(\mathrm{HCOH})} = \frac{\left(1{,}000 \cdot 50{,}00 \cdot 0{,}9022 \text{-} 1{,}042 \cdot 20{,}12\right) \cdot 0{,}03003 \cdot 100}{3{,}0170} = 24.04\%.$$

Answer: 24.04%.

Task 2. To determine benzaldehyde, a sample with a mass of 0.4728 g was treated with a hydroxylamine hydrochloride solution:

$$C_6H_5CHO + NH_2OH \cdot HCl \leftrightarrow C_6H_5CHNOH + HCl + H_2O,$$

A hydrochloric acid released due to the reaction was titrated with 19.45 ml of 0.2500 M NaOH (C_f = 0.9845). During the determination of hydroxylamine hydrochloride, 1.75 ml of the same NaOH solution was taken for a blank experiment. Calculate the concentration (in %) of benzaldehyde in the stock product.

Solution. The calculation formula is written below:

$$\omega_{(C_6H_5\mathrm{CHO})} = \frac{c_{M(\mathrm{NaOH})} \cdot (V_{(\mathrm{NaOH})} - V_{\mathrm{bl.exp.}}) \cdot C_f \cdot \mathrm{M}_{\mathrm{E}'(C_6H_5\mathrm{CHO})} \cdot 100}{a_{(C_6H_5\mathrm{CHO})}}.$$

$M(C_6H_5CHO) = 106.1$ g/mol;
$f_e(C_6H_5CHO) = 1$;
$M_{e'}(C_6H_5CHO) = M(C_6H_5CHO) \cdot f_e(C_6H_5CHO):1000 = 0.1061$.

Put the values in the formula:

$$\omega_{(C_6H_5\mathrm{CHO})} = \frac{0.2500 \cdot (19.45 - 1.75) \cdot 0.9845 \cdot 0.1061 \cdot 100}{0.4728} = 97.8\%.$$

Answer: 97.8%.

Task 3. A standard sample containing 1.47% Ag was analyzed, and the following results were obtained (in %): 1.31; 1.45; 1.42; 1.32; 1.30. Determine S and $\Delta\overline{x}$, conclude about the possible existence of systematic error in the method used to determine silver in the sample.

Solution. Find the arithmetic mean:

$$\overline{x} = \frac{\sum_1^n x_i}{n} = \frac{1.31+1.45+1.42+1.32+1.30}{5} = 1.36.$$

Calculate the standard deviation by the formula:

$$S = \sqrt{\frac{\sum (x_i - \overline{x})^2}{n - 1}}$$

$$S = \sqrt{\frac{0.05^2+0.09^2+0.06^2+0.04^2+0.06^2}{5-1}} = 6.96 \cdot 10^{-2}.$$

Calculate the confidence interval of the value $\overline{x}$:

$$\overline{x} \pm \Delta\overline{x} = \overline{x} \pm \frac{t(\mathrm{P,f}) \cdot S}{\sqrt{n}} = \frac{1.36 \pm 2.78 \cdot 6.96 \cdot 10^{-2}}{\sqrt{5}} = 1.36 \pm 0.09.$$

t = 2.78 (P = 0.95, f = 4) – a tabular value.

The “Link value” of the silver content doesn’t in the confidence interval. Therefore, this method of silver determining has a systematic error.

Work on test tasks

1. Depending on the pH at the equivalence point, different acid-base indicators are used in the titration of substances. Which indicators are suitable for the titration with sufficient precision of benzoic acid ($K_a = 6.3 \cdot 10^{-5}$):

A. Methyl orange.

B. Phenolphthalein.*
C. Both.
D. Neither one thing nor the other.

2. Depending on the pH at the equivalence point, different acid-base indicators are used in the titration of substances. Which indicators are suitable for the titration with sufficient precision of methylamine ($K_{в} = 4.6 \cdot 10^{-3}$):

A. Methyl orange.*
B. Phenolphthalein.
C. Both.
D. Neither one thing nor the other.

3. Depending on the pH at the equivalence point, different acid-base indicators are used in the titration of substances. Which indicators are suitable for the titration with sufficient precision of aniline ($K_{в} = 4.3 \cdot 10^{-10}$):

A. Methyl orange.
B. Phenolphthalein.
C. Both.
D. Neither one thing nor the other.*

4. Which substances can be determined by direct acidimetry?

A. Strong and weak bases ($K_b \geq 10^{-7}$).*
B. Aliphatic amines ($K_b \geq 10^{-7}$).*
C. Some soluble salts (carbonates, bicarbonates, dihydrogen phosphates).*
D. Some sparingly soluble salts (Ca^{2+}, Mg^{2+}, etc.).
E. Organic nitrogen-containing bases ($K_b < 10^{-7}$).

5. In which of the following mixtures differentiate titration of components can be carried out?

A. Picric acid ($K_a = 4.2 \cdot 10^{-1}$) and anthranilic acid ($K_a = 1.1 \cdot 10^{-5}$).*
B. Dichloroacetic acid ($K_a = 5 \cdot 10^{-2}$) and acetic acid ($K_a = 1.7 \cdot 10^{-5}$).
C. Formic acid ($K_a = 1.8 \cdot 10^{-4}$) and hydrocyanic acid ($K_a = 5 \cdot 10^{-10}$).
D. Benzoic acid ($K_a = 6.3 \cdot 10^{-5}$) and aminobenzoic acid ($K_a = 1.1 \cdot 10^{-5}$).

6. Quantitative Nitrogen determination by the Kjeldahl method includes the following steps:

A. Preliminary reduction in the analysis of inorganic nitrates and nitrites, organic nitro- and azo compounds.
B. Digestion procedure (oxidation with concentrated sulfuric acid).
C. Distillation of ammonia.
D. Acid-base titration of excess hydrochloric acid or metaborate ion.
E. All the above mentioned.*

7. Phosphoric acid can be titrated as a tribasic acid BECAUSE phosphoric acid can be replaced by the equivalent amount of hydrochloric acid by adding calcium chloride:

A. 1- Right. 2- Right. Link – Right.*
B. 1- Right. 2- Right. Link – Wrong.
C. 1- Right. 2-Wrong. Link – Wrong.
D. 1-Wrong. 2- Right. Link – Wrong.
E. 1-Wrong. 2-Wrong. Link– Wrong.

8. Propionic and acetic acids can be titrated in a solution differentially BECAUSE these acids have similar values of acidity (for propionic acid pKa = 4.87, for acetic acid pKa = 4.76):

A. 1- Right. 2- Right. Link – Right.
B. 1- Right. 2- Right. Link – Wrong.
C. 1- Right. 2-Wrong. Link – Wrong.
D. 1-Wrong. 2- Right. Link – Wrong.*
E. 1-Wrong. 2-Wrong. Link– Wrong.

9. Formic acid ($K_a = 1.8 \cdot 10^{-4}$) and acetic acid ($K_a = 1.7 \cdot 10^{-5}$) cannot be titrated in a mixture separately BECAUSE they have similar values of acidity constants:

A. 1- Right. 2- Right. Link – Right.*
B. 1- Right. 2- Right. Link – Wrong.
C. 1- Right. 2-Wrong. Link – Wrong.
D. 1-Wrong. 2- Right. Link – Wrong.
E. 1-Wrong. 2-Wrong. Link– Wrong.

10. Which substances can be determined in aqueous solutions by acid-base titration with the visual fixation of the equivalence point:

A. Strong acids.*
B. Strong bases.*
C. Weak bases with $K_b \geq 10^{-7}$.*
D. Very weak bases.
E. Salts of strong acids and strong bases.

11. Which substances can be determined by direct acid-base titration?

A. Strong acids.
B. Weak acids with a certain value of K_a.
C. Weak bases with a certain value of $K_{b.}$
D. Strong bases.
E. Substances with acid-base properties, if $K_{a(b)} \geq 5 \cdot 10^{-7}$.*

12. Choose the method of acid-base titration for the determination of carbolic acid ($K_a = 1 \cdot 10^{-10}$):

A. Acidimetry.
B. Alkalimetry.
C. Both.
D. Neither one thing nor the other.*

13. Which indicators are used in the case of titration of $Na_2B_4O_7$ solution with HCl solution?

A. Methyl orange.*
B. Phenolphthalein.
C. Both.
D. Neither one thing nor the other.

14. Which substances can be quantitatively estimated by back alkalimetry?

A. Esters of carbonic acids.*
B. Mixtures of sodium carbonate and sodium bicarbonate.
C. Ammonium salts, chloral hydrate, etc.*
D. Formaldehyde in formalin.

15. Amino acids cannot be titrated by direct titration BECAUSE amino acids in aqueous solutions form internal salts (zwitterions):

A. 1- Right. 2- Right. Link – Right.*
B. 1- Right. 2- Right. Link – Wrong.
C. 1- Right. 2-Wrong. Link – Wrong.
D. 1-Wrong. 2- Right. Link – Wrong.
E. 1-Wrong. 2-Wrong. Link– Wrong.

16. Mercury (II) amidochloride is determined acidimetrically by back titration BECAUSE when mercury (II) amidochloride is dissolved in excess of 0.1 M HCl solution in the presence of KI, one part of hydrochloric acid reacts, and the unreacted part of HCl is titrated with a solution of alkali:

A. 1- Right. 2- Right. Link – Right.*
B. 1- Right. 2- Right. Link – Wrong.
C. 1- Right. 2-Wrong. Link – Wrong.

D. 1-Wrong. 2- Right. Link – Wrong.
E. 1-Wrong. 2-Wrong. Link– Wrong.

17. Standard solutions of strong acids are prepared according to the method of the established titer BECAUSE strong acids do not satisfy the requirements for primary standards:

A. 1- Right. 2- Right. Link – Right.*
B. 1- Right. 2- Right. Link – Wrong.
C. 1- Right. 2-Wrong. Link – Wrong.
D. 1-Wrong. 2-Right Link – Wrong.
E. 1-Wrong. 2-Wrong. Link– Wrong.

18. By acid-base titration, you can determine all the salts BECAUSE the cations and anions of all salts are either acids conjugated to bases or bases conjugated to acids:

A. 1- Right. 2- Right. Link – Right.
B. 1- Right. 2- Right. Link – Wrong.
C. 1- Right. 2-Wrong. Link – Wrong.
D. 1-Wrong. 2- Right. Link – Wrong.*
E. 1-Wrong. 2-Wrong. Link– Wrong.

19. Salicylic acid $C_6H_4(OH)COOH$ ($K_{a1} = 1.1 \cdot 10^{3}$, $K_{a2} = 2.6 \cdot 10^{-14}$) can be titrated either as a dibasic or monobasic acid BECAUSE salicylic acid dissociates sequentially; by the first stage – as a monobasic acid, by the second – as a dibasic acid.

A. 1- Right. 2- Right. Link – Right.
B. 1- Right. 2- Right. Link – Wrong.
C. 1- Right. 2-Wrong. Link – Wrong.
D. 1-Wrong. 2- Right. Link – Wrong.*
E. 1-Wrong. 2-Wrong. Link– Wrong.

20. Diphenylamine $(C_6H_5)_2NH$ can be titrated with an acid solution with an indicator fixation of the equivalence point, BECAUSE diphenylamine is a strong base ($pK_b = 13.21$):

A. 1- Right. 2- Right. Link – Right.
B. 1- Right. 2- Right. Link – Wrong.
C. 1- Right. 2-Wrong. Link – Wrong.
D. 1-Wrong. 2- Right. Link – Wrong.
E. 1-Wrong. 2-Wrong. Link– Wrong.*

21. Hydrazine ($N_2H_4 \cdot H_2O$ ($K_b = 9.3 \cdot 10^{-7}$)) cannot be titrated with a strong acid solution, BECAUSE the hydrazine molecule does not contain hydroxide ions:

A. 1- Right. 2- Right. Link – Right.
B. 1- Right. 2- Right. Link – Wrong.
C. 1- Right. 2-Wrong. Link – Wrong.
D. 1-Wrong. 2- Right. Link – Wrong.*
E. 1-Wrong. 2-Wrong. Link– Wrong.

22. An acid-base titration is applied for the determination of:

A. Inorganic and organic substances with acid-base properties.*
B. Elemental composition of organic substances (determination of Nitrogen, Sulfur, Carbon, Phosphorus, etc.). *
C. Functional groups of organic compounds: carboxyl, sulfo-, amino-, hydroxyl, carbonyl groups. *
D. Some substances that do not have acid-base properties (nitrates, nitrites). *
E. Pharmaceutical drugs with acid-base properties. *

LABORATORY WORK

Determination of ammonium chloride concentration (in %) in a sample

Displacement titration.

Method of separate samples.

$$4NH_4Cl + 6CH_2O \leftrightarrow (CH_2)_6N_4 + 4HCl + 6H_2O$$
$$4NH_4^+ + 6CH_2O \leftrightarrow (CH_2)_6N_4 + 4H^+ + 6H_2O$$
$$HCl + NaOH \leftrightarrow NaCl + H_2O$$
$$H^+ + OH^- \leftrightarrow H_2O$$

$M(NH_4Cl) = 53.49$ g/mol;
$f_e(NH_4Cl) = 1$;
$M_e(NH_4Cl) = M(NH_4Cl) \cdot f_e(NH_4Cl) = 53.49$ g/mol;
$M_{e'}(NH_4Cl) = 0.05349$;
$T(NaOH/NH_4Cl) = C_M(NaOH) \cdot M_{e'}(NH_4Cl)$;
$T(NaOH/NH_4Cl) = 0.1000 \cdot 0.05349 = 0.005349$ g/mol;
$a\ (NH_4Cl) = C_M(NaOH) \cdot M_{e'}(NH_4Cl) \cdot V$.

Assay procedure. Weigh the sample of ammonium chloride calculated for 20 ml of the titrant on an analytical balance by difference. Transfer it to a conical flask, dissolve in 15 ml of distilled water. Add 5 ml of formalin (40 % formaldehyde solution), previously neutralized by phenolphthalein, and 1-2 drops of phenolphthalein solution. Leave the mixture for 2 min, and titrate it with 0.1000 M sodium hydroxide solution to turn the color into faint pink, which does not disappear for 30 s.

For each determination, calculate the concentration (in %) of ammonium chloride. Conduct the titration until three concordant results are obtained.

$$\omega_{(\mathrm{NH_4Cl})} = \frac{V_{(\mathrm{NaOH})} T_{(\mathrm{NaOH/NH_4Cl})} C_f\, 100}{a_{(\mathrm{NH_4Cl})}}$$

According to the obtained results, the average value of the percentage concentration of ammonium chloride is calculated.

Visual materials, learning and control tools

1. Tabular resources on the topic of the lesson.
2. Textbooks, handbook on analytical chemistry.
3. Learning and control tools: cards for assessing the initial level of knowledge; test questions.

Tutorial № 16

1. **THEME: Final lesson of the section «Titrimetric methods of analysis. Acid-base titration»**

2. **PURPOSE: Summarize the material, check students' knowledge in the section and the ability to apply acid-base titration in the analysis of chemical compounds, pharmaceutical drugs and cosmetics**

3. OBJECTIVIES:

3.1. To carry out the concluding control of knowledge and skills in the section: a card control, individual interviews with students on the written work and computer testing.

3.2. To pay attention to issues and tasks that cause difficulties for students.

3.3. To check the protocols of laboratory works.

4. PLAN AND ORGANIZATIONAL STRUCTURE OF THE TUTORIAL:

4.1. Organizational moment.....……………………………..................2 min

4.2. Description of the purpose of the lesson (a teacher’s introductory speech to students)…………………………………………………………………..3 min

4.3. Assessment of the initial level of knowledge (a card control)……...40 min

4.4. Computer-test control……………………………..……….........40 min

4.5. Individual interview………..95 min

4.6. Check of protocols………..........…….…………………………...8 min

4.7. Concluding speech of the teacher, instructions for the next lesson…..2 min

5. REFERENCE FOR SELF STUDY:

5.1. Repeat the theoretical material on topics 1-7, solving tasks from the section.

5.2. Study the questions on topics, which are not included in topics 1-6 (for instance, titration in non-aqueous media) using the recommended literature and lectures.

Questions from the studied section of quantitative analysis

1. Titrimetric methods of analysis

1. The essence and classification of titrimetric methods of analysis.
2. Requirements for reactions used in titrimetric methods of analysis.
3. Titrants (standard solutions). Methods for their preparation.
4. Ways of expressing the concentration of the titrant: molar concentration (molarity), normal concentration (normality, equivalent concentration), titer, titer for the substance determined, correction factor.
5. Types (direct, back and substitution) and methods (method of separate samples; pipetting method) of titration. The essence, advantages, and disadvantages.
6. The equivalence point, the end point of a titration. Methods to determine the equivalence point.

7. Volume measurement devices in the laboratory, their classification. Precision of volume measurements. Calibration of measuring devices.

8. Calculations in titrimetric methods of analysis.

8.1. Formulas for the calculation of the weight of a substance, normality of the titrant, titer, titer of the titrant for the substance determined, mass and percentage of a substance according to titration results for different types and methods of titration, taking into account different ways of expressing the titrant concentration.

8.2. Precision of the record of measurements obtained and expression of results of the analysis taking into account significant figures.

8.3. Accuracy and reproducibility of results. Errors in the quantitative analysis. Statistical processing of analysis results.

It is necessary to be able to:

9. Choose the method of titration depending on the chemical and analytical properties of substances.

10. Choose and explain the method of the preparation of a titrant.

11. Explain the choice of type and method of titration.

12. Carry out calculations in titrimetric methods: preliminary, the concentration of a titrant, results of the analysis, metrological characteristics (statistical processing of results).

2. Acid-base titration

1. The essence of acid-base titration. Acidimetry. Alkalimetry.

2. Acid-base properties of substances. Representation about acids and bases. Cationic, anionic and molecular acids and bases. Ampholytes. Acidity and basicity constants.

3. The influence of the nature of a solvent on acid-base properties of substances. Classification of non-aqueous solvents: protogenic (acidic), protophilic (basic), amphiprotic and aprotic.

4. The reaction of acid-base interaction in the titration of strong and weak acids (cationic, anionic, molecular); conjugate acid-base pairs.

5. Titrants of acid-base titration. Preparation and standardization of solutions of acids and bases. Primary and secondary standards in alkali- and acidimetry.

6. Types of detection of the end point of titration. pH indicators.

7. Main characteristics of pH indicators: the indicator exponent, the titration exponent and the useful (working) range of an indicator. Structure and color of methyl orange and phenolphthalein in different media.

8. Selection of indicators: qualitative and quantitative methods.

9. The principle of plotting titration curves. Calculation of pH to plot titration curves. The shape of titration curves in titration of different acids and bases (strong, weak, poly-). Selection of an indicator according to titration curves.

10. Indicator errors in titration. The calculation of hydrogen, hydroxyl, acid and alkali errors.

11. Possibilities and application areas of acid-base titration. Substantiation of the possibility of determining substances with acid-base properties based on acidity or basicity constants, and titration constants: titration of strong acids with strong bases (and vice versa); titration of weak acids with strong bases and weak bases with strong acids; titration of polybasic acids and polyacidic bases.

12. Non-aqueous titration (protolithometry). Titrants and indicators of the method. Areas of application. Advantages and disadvantages.

It is necessary to be able to:

13. Write reactions of acid-base interaction for different types of acids and bases.

14. Explain the influence of the nature of a solvent on acid-base properties of substances.

15. Plot and analyze titration curves for different acid-base systems.

16. Choose acid-base indicators to fix the end point of titration of substances with acidic or basic properties.

17. Apply the neutralization method and substantiate conditions for determinations described below.

17.1. Elemental analysis: determination of nitrogen, sulfur, chlorine, bromine.

17.2. Functional analysis: determination of compounds containing carboxyl, sulfo-, amino-, aldehyde and alcohol hydroxyl groups.

17.3. Alkalimetric determinations:

– by direct titration: free acids (inorganic and organic) - hydrochloric, sulfamic, acetic, medium-chain, long-chain and very long-chain fatty acids; tartaric, citric, glutamic, nicotinic, ascorbic acids, etc.; salts (cationic and anionic acids) - potassium iodate, potassium hydrogen phthalate, hydrazine sulfate, pyridinium perchlorate, sodium dihydrogen phosphate, etc.

– by back titration: ammonium salts, esters;

– by displacement titration: boric acid in the presence of glycerol or mannitol; ammonium salts (formol titration); amino acids in the presence of formaldehyde; formaldehyde in formalin, etc.

17.4. Acidimetric determinations:

– by direct titration: strong and weak bases – sodium hydroxide, ammonia solution, diphenylguanidine, tris(oxymethyl)aminomethane, etc.; salts (anionic bases and ampholytes) - soluble carbonates, bicarbonates, hydrogen phosphates, tetraborates, salicylates, benzoates; mixtures of sodium carbonate and sodium bicarbonate, sodium hydroxide and sodium carbonate;

– by back titration: solutions of ammonia, nitrogenous bases and alkaloids, insoluble salts of calcium, magnesium, etc.; hexamethylenetetramine (urotropine); mercury (II) amidochloride;

– by displacement titration: chlorides and nitrates according to Tananaev; mercury (II) oxide.

18. Determination of substances in non-aqueous media.

18.1. Titration of sulfanilamides and phenols in the media of protophilic solvents.

18.2. Titration of sulfanilamides in the media of protogenic solvents.

18.3. Titration of amines and acids in the media of amphiprotic solvents.

Work on test tasks

1. Along with acid-base titration in aqueous media, titration in non-aqueous media is often used in the analysis. Select the appropriate solvents to quantify pyridine ($K_b = 1.5 \cdot 10^{-9}$):

A. Protogenic solvents (glacial acetic acid, formic acid, acetic anhydride, etc.). *
B. Protophilic solvents (DMF, formamide, pyridine, ethylenediamine).
C. Amphiprotic (neutral) solvents (methanol, ethanol).
D. Aprotic solvents (benzene, chloroform).
E. Differentiating solvents (ketones, nitriles).

2. Along with acid-base titration in aqueous media, titration in non-aqueous media is often used in the analysis. Select the appropriate solvents to quantify the mixture of weak acids:

A. Differentiating solvents (ketones, nitriles). *
B. Protophilic solvents (DMF, formamide, pyridine, ethylenediamine).
C. Protogenic solvents (glacial acetic acid, formic acid, acetic anhydride, etc.).
D. Aprotic solvents (benzene, chloroform).
E. Amphiprotic (neutral) solvents (methanol, ethanol).

3. Along with acid-base titration in aqueous media, titration in non-aqueous media is often used in the analysis. Select the appropriate solvents to quantify very weak acids ($K_a < 5 \cdot 10^{-7}$):

A. Protophilic solvents (DMF, formamide, pyridine, ethylenediamine). *
B. Amphiprotic (neutral) solvents (methanol, ethanol).
C. Protogenic solvents (glacial acetic acid, formic acid, acetic anhydride, etc.).
D. Aprotic solvents (benzene, chloroform)).
E. Differentiating solvents (ketones, nitriles).

4. Along with acid-base titration in aqueous media, titration in non-aqueous media is often used in the analysis. Select the appropriate solvents to quantify nitrogen-containing bases ($K_b = 5 \cdot 10^{-7}$):

A. Protogenic solvents (glacial acetic acid, formic acid, acetic anhydride, etc.). *
B. Protophilic solvents (DMF, formamide, pyridine, ethylenediamine).
C. Amphiprotic (neutral) solvents (methanol, ethanol).
D. Aprotic solvents (benzene, chloroform).
E. Differentiating solvents (ketones, nitriles).

5. Along with acid-base titration in aqueous media, titration in non-aqueous media is often used in the analysis. Select the appropriate solvents to quantify benzoic acid ($K_a = 6.3 \cdot 10^{-5}$):

A. Amphiprotic (neutral) solvents (methanol, ethanol). *
B. Protophilic solvents (DMF, formamide, pyridine, ethylenediamine).
C. Protogenic solvents (glacial acetic acid, formic acid, acetic anhydride, etc.).
D. Aprotic solvents (benzene, chloroform).
E. Differentiating solvents (ketones, nitriles).

Visual materials, learning and control tools

1. Tabular resources on the topic of the lesson.
2. Textbooks, handbook on analytical chemistry.
3. Learning and control tools: cards for assessing the initial level of knowledge; test questions.

Recommended literature

General literature

1. Priti Malhotra. Analytical chemistry. Basic Techniques and Methods. Springer International Publishing, 2023. 339 p.
2. Alana Wood. Chemical Analysis. Modern Methods and Techniques. Willford Press, 2023. 247 p.
3. Christian Gary D., Purnendu K. Dasgupta, Kevin A. Schug. Analytical chemistry. 7 E. Wiley, 2020. 960 p.
4. Fondamentals of analytical chemistry / Scoog D., West D., Holler F. J., Crouch S. P. 10 E. Cengage, 2022. 1072 p.
5. Qualitative analysis. Acid-basic titration. Section 1. Theory and analysis of cations of I-III analytical groups. Basic topic 1. Theory and analysis of cations of IV-VI analytical groups. Basic topic 2. Theory and analysis of anions and compounds of unknown composition. Basic topic 3. Manual for students of the 2-nd course of the Pharmaceutical Faculty speciality 226 «Pharmacy, Industrial Pharmacy». – S. O. Vasyuk, A. S. Korzhova, A. O. Donchenko. – Zaporizhzhia, 2021 – 131 p.
6. Qualitative analysis. Acid-basic titration. Section 1. Acid-base titration and its application in chemical and pharmaceutical analysis. Basic topic 4. Manual for students of the 2-nd course of the Pharmaceutical Faculty speciality 226 «Pharmacy, Industrial Pharmacy». – S. O. Vasyuk, A. S. Korzhova, N. O. Nagorna, K. P. Miedviedieva. – Zaporizhzhia, 2021 – 110 p.
7. Quantitative analysis. Instrumental methods of analysis. Section 2. Oxidation-reduction titration and its application in the analysis of chemical compounds and medicines. Basic topic 1. Manual for students of the 2-st course of the Pharmaceutical Faculty specialty 226 «Pharmacy, Industrial Pharmacy». – S. O. Vasyuk, A. S. Korzhova, K. P. Miedviedieva. – Zaporizhzhia, 2021 – 66 p.

Additional literature

1. Modern analytical laboratory practice: manual for students of the 2-nd course speciality 226 «Pharmacy, Industrial pharmacy», qualifications of the professional «Pharmacist» / S.O. Vasyuk, A.S. Korzhova, N. O. Nagorna, K.P.Medvedeva, Y.M. Zhuk, A.O. Donchenko. - Zaporizhzhia: ZSMPU, 2023. - 97 p.
2. Fundamentals of chemical metrology: study guide for students of the 2nd year of the specialty « Pharmacy, industrial pharmacy» / Vasyuk S. A., Korzhova A. S., Nagorna N. O., Miedviedieva K.P., Zhuk Y. M., Donchenko A.O. Zaporizhzhia: ZDMU, 2023. 94 p.
3. Державна Фармакопея України : в 3 т. / ДП «Український науковий фармакопейний центр якості лікарських засобів». 2-е вид. Х. : ДП «Український науковий фармакопейний центр якості лікарських засобів», 2015. Т. 1. 1128 с.
4. Державна Фармакопея України: в 3 т. / ДП «Український науковий фармакопейний центр якості лікарських засобів». 2-е вид. Х. : ДП «Український науковий фармакопейний центр якості лікарських засобів», 2014. Т. 2. 724 с.
5. Державна Фармакопея України: в 3 т. / ДП «Український науковий фармакопейний центр якості лікарських засобів». 2-е вид. Х. : ДП «Український науковий фармакопейний центр якості лікарських засобів», 2014. Т. 3. 732 с.