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КАФЕДРА ОБЩЕЙ ХИМИИ

ВВЕДЕНИЕ В ТИТРИМЕТРИЧЕСКИЕ МЕТОДЫ АНАЛИЗА

INTRODUCTION TO THE TITRATION METHODS OF ANALYSIS

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А в т о р ы: доц. Т. В. Латушко; доц. С. В. Ткачѳв; ст. преп. С. Р. Казюлевич;
проф. Е. В. Барковский

Перевод с русского языка С. В. Ткачѳва

Р е ц е н з е н т ы: доц. О. Н. Ринейская, доц. Э. И. Олецкий

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Содержит теоретический и практический материал по титриметрическим методам анализа применительно к учебным программам. Рассматриваются приемы работы, приборы, методы вычислений результатов выполненных лабораторных работ. Приводятся основные вопросы каждой темы, тесты для самоконтроля, задачи с эталонами их решений. Первое издание вышло в 2011 г.

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PREFACE

Many hardworking students often fail to score good marks in the examinations. It is not because of their lack of knowledge of the subject matter but because of the basic errors in their examination problems in the titration analysis. These errors are due to their inability to write necessary and correct equations of required analytical reactions.

This guide is intended to provide useful information to students in order to prepare effectively for examination. Calculations involving equivalent concept are not as difficult as students think. Once you understand the basic principles and apply it you will have no problem.

The experimental details given have been limited.

The experimental details given have been limited, for it is hoped that users of this student's guide will be able to carry out laboratory works and there are many admirable practical text-books available.

This student's guide is written according to the official programme for medical students. Any comments, suggestions and corrections are welcome.

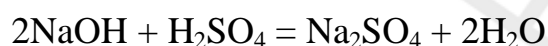
Part 1

ELEMENTS OF TITRATION ANALYSIS

MAIN CONCEPTS, TERMS AND FORMULAS

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

In chemical reactions the molar ratio of reacting substances is not always 1:1. It is determined by stoichiometric coefficients. For example, in the reaction

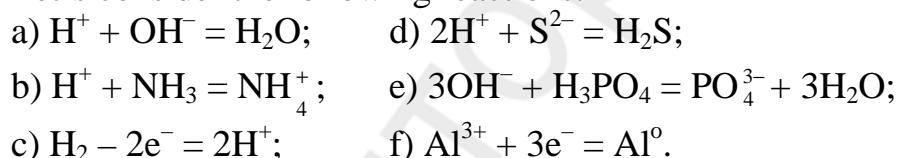


the molar ratio will be 2:1.

When considering the majority of chemical reactions it is necessary to use such notions as equivalent and equivalence factor.

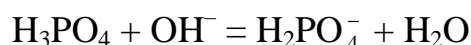
As substances behave differently in the complex formation reactions, chemists avoid using the notion of equivalent for them and use only molar masses instead. Thus, in this textbook the notion of equivalent will be used only for the substances taking part in oxidation-reduction and acid-base reactions.

Let's consider the following reactions:

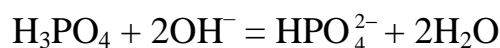


In acid-base reactions (a, b, d, e) 1 OH⁻ ion, 1/2 S²⁻ ion, 1 NH₃ molecule, 1/3 of H₃PO₄ molecule are equivalent to one H⁺ ion. In oxidation-reduction reactions (c, f) 1/2 of H₂ molecule, 1/3 of Al³⁺ ion are equivalent to one electron. The enumerated particles are considered as equivalents of substances taking part in these reactions.

From another point of view *equivalent (E(X)) is some real or conditional particle which interacts with the carrier of one elementary charge in the exchange or oxidation-reduction reactions*. For example, in the reaction:



the molecule H₃PO₄ is the same as the equivalent because it reacts with one OH⁻ ion. But in the reaction:



the molecule of H₃PO₄ reacts with two OH⁻ ions, thus the equivalent of phosphoric acid is equal to 1/2 of H₃PO₄ molecule.

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

Equivalence factor is often defined by $1/z$ ratio, where z is the overall charge of ions exchanging in a molecule for exchange reactions or the number of electrons which are accepted or lost by a molecule (an atom) of the substance for oxidation-reduction reactions; z is always a positive integer and the equivalence factor is less or equal to 1:

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

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

In acid-base reactions Na_2CO_3 can be neutralized by an acid till acid salt or till the emission of CO_2 :

- a) $\text{Na}_2\text{CO}_3 + \text{HCl} = \text{NaHCO}_3 + \text{NaCl}$, $f_{\text{eqv}}(\text{Na}_2\text{CO}_3) = 1$;
- b) $\text{Na}_2\text{CO}_3 + 2\text{HCl} = 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$, $f_{\text{eqv}}(\text{Na}_2\text{CO}_3) = 1/2$.

In oxidation-reduction reactions KMnO_4 is always an oxidizing agent:

- c) $5\text{Na}_2\text{SO}_3 + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 = 5\text{Na}_2\text{SO}_4 + 2\text{MnSO}_4 + 3\text{H}_2\text{O} + \text{K}_2\text{SO}_4$,
 $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$, $f_{\text{eqv}}(\text{KMnO}_4) = 1/5$;
- d) $3\text{Na}_2\text{SO}_3 + 2\text{KMnO}_4 + \text{H}_2\text{O} = 3\text{Na}_2\text{SO}_4 + 2\text{MnO}_2 + 2\text{KOH}$,
 $\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$, $f_{\text{eqv}}(\text{KMnO}_4) = 1/3$;
- e) $\text{Na}_2\text{SO}_3 + 2\text{KMnO}_4 + 2\text{KOH} = \text{Na}_2\text{SO}_4 + 2\text{K}_2\text{MnO}_4 + \text{H}_2\text{O}$,
 $\text{MnO}_4^- + \text{e}^- \rightarrow \text{MnO}_4^{2-}$, $f_{\text{eqv}}(\text{KMnO}_4) = 1$.

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

As we can see from these examples when using the notions of equivalent and equivalence factor it is always necessary to indicate to which definite reaction they are related to.

The unit of the amount of equivalent substance is the mole. Along with the molar mass of the substance $M(\text{X})$ in the quantitative analysis we widely use the notion of *molar mass of the equivalent of this substance* $M_{\text{eqv}}(\text{X})$.

Molar mass of the equivalent substance X is the mass of one mole of the equivalents of this substance. It is equal to the product of equivalence factor of the substance in the reaction to the molar mass of the substance X:

$$M_{\text{eqv}}(\text{X}) = f_{\text{eqv}}(\text{X}) \cdot M(\text{X}). \quad (1)$$

To illustrate the ways of writing down the calculation using formula (1) let's calculate the molar masses of Na_2CO_3 and KMnO_4 equivalents in the reactions mentioned above:

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

The amount of substance (in moles) where particles are equivalents is called *the amount of equivalent substance*. It's obvious that

$$n_e(\text{X}) = m(\text{X})/M_{\text{eqv}}(\text{X}) \cdot f_{\text{eqv}}(\text{X}). \quad (2)$$

For example, it is necessary to calculate the amount of the equivalent substance of sodium carbonate with the mass of 5.3 g when making a reaction with HCl till CO_2 (see reaction equation b). Then, according to equation (2) we have:

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

On the basis of these two equations (1) and (2) it is easy to get the equation for calculating the mass of the substance in terms of the amount of the equivalent substance and the equivalence factor of the substance:

$$m(\text{X}) = n_e(\text{X}) \cdot f_{\text{eqv}}(\text{X}) \cdot M(\text{X}).$$

In the titration analysis to express the solution composition we use *molar concentration* (C_M) and *molar concentration of the equivalent* (C_N).

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

$$C_M(\text{X}) = C(\text{X}) = n(\text{X})/V = m(\text{X})/M(\text{X}) \cdot V. \quad (3)$$

When writing down the molar concentration we can use, for example, the following forms: a solution with molar concentration of HCl equal to 0.1 mol/L or $C(\text{HCl})=0.1 \text{ mol/L}$; 0.1 M of HCl solution (decimolar solution of HCl here M denotes mol/L). All these forms mean that in one liter of the solution contains 0.1 mole of HCl. Similarly, 0.01 M is centimolar solution, 0.001 M is millimolar solution and 0.015M is fifteen-millimolar solution.

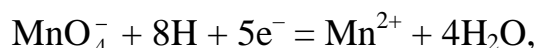
Molar equivalent concentration (or normality) is equal to the amount of the equivalent substance (in moles) which is contained in one liter of the solution. It is defined as C_N (sometimes N) and is calculated as a ratio of the amount of the equivalent of the dissolved substance X to the volume of the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

$$C_N(\text{X}) = n_e(\text{X})/V. \quad (4)$$

Having expressed in the denominator the molar mass of the equivalent through the molar mass of the substance and its equivalence factor in the reaction using equation (2) we get:

$$C_N(X) = m(X)/(f_{\text{eqv}}(X) \cdot M(X) \cdot V. \quad (5)$$

When writing down the molar concentration of the equivalent, for example, for KMnO_4 in half-reaction:



we use such forms: $C_N(\text{KMnO}_4) = 0.1 \text{ mol/L}$ or 0.1 N of KMnO_4 solution (decinormal solution of KMnO_4). To use letters M or N for denoting units of solution concentration would be incorrect. For example, you can't write:

$$C(\text{H}_2\text{SO}_4) = 0.1 \text{ M} \text{ or } C_N(\text{H}_2\text{SO}_4) = 0.1 \text{ N}.$$

If the numerical values of molar concentration and normality coincide (it can be observed in such cases when $f_{\text{eqv}}(X) = 1$) then word «molar» is used.

The quantitative connection between the molar concentration of the substance and the molar concentration of the equivalent is established on basis of equations (3) and (5). Consequently, dividing equation (3) in equation (5) we get the following:

$$C_M(X)/C_N(X) = f_{\text{eqv}}(X) \text{ or } C_N(X) = C_M(X)/f_{\text{eqv}}(X).$$

The amount of substance X and, consequently, its mass in the volume V (L) of the solution can be calculated both on the basis of molar concentration of the solution and on the basis of its normality using the equations (3)-(5).

In such cases when we speak about the ratio of the mass (or volume or the amount of substance) of the component to the mass (or volume or the amount of substance) of the whole system the term «concentration» is not used but we speak about mass, volume or molar «fraction» and we express it either by the fraction or in percent taking the system as 1 or as 100 %. Note that all kind of fractions unlike all concentration types are non-dimensional quantities.

To denote the component fraction we use the following accepted Greek letters: *mass fraction* ω (omega), *volume fraction* ϕ (phi), *mole fraction* χ (chi) and:

$$\omega(X) = m(X)/m; \quad \phi(X) = V(X)/V; \quad \chi(X) = n(X)/\Sigma n, \quad (6)$$

where $m(X)$, m — masses of the component and of the whole system respectively; $V(X)$, V — volumes of the component and of the whole system; $n(X)$, Σn — the summation of the amounts of the components substances or the amount of the whole system. Pay attention to some incorrect terminological expressions. For example, we say «20-percent concentration solution» this is not right as concentration is not expressed in percent. If we remove the word «concentration», we get the expression «20-percent solution» which in this case will be ambiguous (mass percent, volume percent, molar percent). So the correct variant will be «solution with 20-percent mass fraction of the dissolved substance».

It is clear that all kinds of ratios mentioned above are the relative values. But it's possible to express the quantitative characteristics of the component and the remaining part of the system through some other different physical magnitudes. For example, in chemistry we often make use of such magnitude as solution *molality* $C_m(\mathbf{X})$ which equals the amount of substance (in moles) dissolved in 1kg of the solvent. It is denoted as $C_m(\mathbf{X})$ and is calculated as the ratio of the amount of the substance X to the mass of the solvent in kilograms:

$$C_m(\mathbf{X}) = n(\mathbf{X})/m(\text{solvent}) = m(\mathbf{X})/M(\mathbf{X}) \cdot m(\text{solvent}). \quad (7)$$

Titer $T(\mathbf{X})$ shows the amount of grams of the dissolved substance in 1 mL of the solution:

$$T = m(\mathbf{X})/V(\text{solution, mL}).$$

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

We can use the law of equivalents for the reactions taking place in stoichiometric relations. That's why if the reaction is conducted till the end, the amount of equivalents of the determined substance is equal to the amount of reagent equivalents.

For example, at the equivalence point of titration of H_2SO_4 solution by base solution ($\text{H}_2\text{SO}_4 + 2\text{NaOH} = \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$) the equivalent amounts of H_2SO_4 and NaOH are equal:

$$n_e(\text{H}_2\text{SO}_4) = n_e(\text{NaOH}). \quad (8)$$

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

$$n_e(\text{H}_2\text{SO}_4) = C_N(\text{H}_2\text{SO}_4) \cdot V(\text{H}_2\text{SO}_4), \quad (9)$$

$$n_e(\text{NaOH}) = C_N(\text{NaOH}) \cdot V(\text{NaOH}), \quad (10)$$

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

When substituting the right parts of equations (9) and (10) in equation (8) we get a very important *expression of the equivalence principle* for the titration analysis:

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

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

$$C_N(\mathbf{X}) \cdot V(\mathbf{X}) = C_N(\mathbf{T}) \cdot V(\mathbf{T}). \quad (11)$$

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

If we know the volume of the analyzed solution, then using equation (11) it's possible to calculate its normality:

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

Having calculated the normality of the analyzed solution using the titration results we can determine the mass of the substance in any volume of the solution with the help of equations (4) and (5):

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

To conduct successfully the titration analysis you should:

1) know the exact concentration of the titrant (the notion «exact concentration» is relative as we have to deal with approximate experimental data; «exact concentration» is the one having 4 significant digits in numerical expression (e. g.: 1.523; 0.01264; 0,3000)).

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

3) choose correctly the reaction for determination and fix properly the equivalence point.

Let's consider in detail the tasks mentioned above.

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

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

The usage of special ampulas (ficksanals) produced industrially reduces greatly time loss for the preparation of standard solutions. Ficksanals contain the amount of the substance known exactly. Dissolution or dilution of the ficksanal contents in a volumetric flask allows getting the standard solution immediately.

To measure liquid volumes accurate within $0,01-0,03 \text{ cm}^3$ it is necessary to use special measuring devices: a volumetric flask, a pipette, a burette.

At the titration analysis not all chemical reactions are used but those which correspond to some definite requirements. The main of them are:

1) the reaction must be practically irreversible;

- 2) the reaction must take place in strict conformity with the equation of a chemical reaction without formation of by-products;
- 3) the reaction must occur rather quickly;
- 4) there must be a method of determination of the end of the reaction, i. e. of the equivalence point fixation.

At the titration analysis it's more common to use the reactions in which at addition of the titrant to the analyzed solution the equivalence point is easily detected. This can happen at appearance or disappearance of the coloured reaction products, ceasing of precipitation and so on. The problem of choice of the method of the equivalence point fixation is always solved with regard to every particular technique.

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

Titration techniques

Titration method is a technique which allows using this or that reaction in practice. If the chosen reaction corresponds to all requirements mentioned above we should use direct titration.

Direct titration consists in gradual addition of the titrant directly into the analyzed substance until it reaches the equivalence point.

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

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

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

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

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

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

Indirect (substitute) titration consists in adding to the analyzed substance the excess of the reagent reacting with it with further determination of the amount of the reaction product by titration.

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

Titration curves

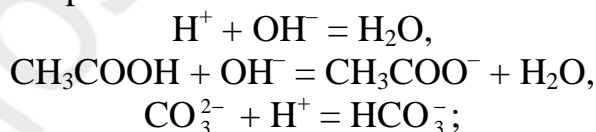
The most important characteristics of titration methods are the titration curves. The graphic show the dependence of the concentration of the participants of the reaction occurring at titration (or the concentration logarithm, or some solution property or characteristics) on the volume of the added titrant (or the titration degree). For example, for the reactions of acid-base interaction such characteristic is its pH.

The experimental titration curves result from measuring some system characteristic in the process of titration (optical density, strength of diffusion current, etc.) which changes depending on the volume of the added titrant and then we draw the corresponding diagram. We mark the amount of the added reagent on X-axis and on Y-axis (in case of liner curves) we mark the values of the quantities which change linearly with the concentration change of one of the reagents (electrical conductivity, optical density, etc.). When drawing the logarithmic curves we mark on Y-axis the values of the quantities linearly connected to the concentration logarithms of reagents (e. g. pH).

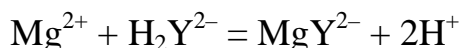
Methods of the titration analysis

In titration analysis we use the reactions of different types (acid-base interaction, complexation reactions, etc.) satisfying these demands required for titration reactions. Separate titration methods have got their names according to the type of the main reaction occurring at titration or the name of the titrant (e. g. in argentometric methods the titrant is AgNO_3 solution, in permanganatometric methods — KMnO_4 solution and so on). According to the method of equivalence point fixation we single out titration methods with colour indicators, methods of potentiometric, conductometric, photometric titration, etc. When classifying the methods on basis of the type of the main reaction occurring at titration it is possible to single out the following methods of titration analysis:

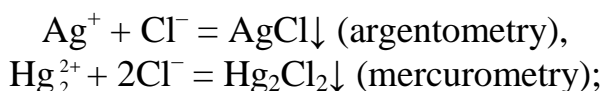
1) *methods of acid-base titration* based on the reactions which are connected to the process of proton transfer:



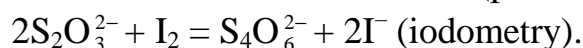
2) *complexation methods* which use the reaction of coordination compound formation (chelation):



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



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



CONTROL OF MASTERING THE TOPIC

Typical calculation tasks

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

Answer: 10 g; 238 mL.

Task 2. How many grams of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and milliliters of water should be taken to prepare 400 mL of the solution with the mass fraction of Na_2SO_4 equal to 10% (density 1,065g/mL)?

Answer: 96.6 g; 329.4 mL.

Task 3. There is a solution with the mass fraction of H_2SO_4 equal to 10 % (density 1.07 g/mL). Calculate: a) molar concentration; b) normality if $f_{\text{eqv}}(\text{H}_2\text{SO}_4) = 1/2$; c) mole fraction of H_2SO_4 in this solution.

Answer: a) 1.09 mol/L; b) 2.18 mol/L; c) 0.02.

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

Answer: a) 20 %; b), c) 6.10 mol/L; d) 6.25 mol/kg.

Task 5. 500 mL of the solution are obtained from 1.59 g of Na_2CO_3 to carry out the reaction $\text{Na}_2\text{CO}_3 + \text{HCl} = \text{NaHCO}_3 + \text{NaCl}$. Calculate the normality of the solution.

Answer: 0.03 mol/L.

Task 6. Which volume of the solution with mass fraction of H_2SO_4 equal to 80 % (density 1.75 g/mL) should be taken to prepare 500 mL 0.1 N solution? ($f_{\text{eqv}}(\text{H}_2\text{SO}_4) = 1/2$)

Answer: 1.75 mL.

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

Answer: 0.2431 mol/L.

Task 8. To titrate 0.2156g of a chemically pure sodium carbonate Na_2CO_3 we used 22.35 mL of sulphuric acid solution. Calculate the normality of the acid solution taking into account that $f_{\text{eqv}}(\text{Na}_2\text{CO}_3) = f_{\text{eqv}}(\text{H}_2\text{SO}_4) = 1/2$.

Answer: 0.1820 mol/L.

Task 9. Which mass of KMnO_4 should be taken to prepare 2L of the solution with $C_N(\text{KMnO}_4) = 0,02 \text{ mol/L}$? ($f_{\text{eqv}}(\text{KMnO}_4) = 1/5$).

Answer: 1.264 g.

QUESTIONS FOR TEST SELF-CHECK

(with only one correct answer)

- 1. Indicate the unit of quantity of a substance:**
a) kilogram; b) molar mass; c) cubic centimeter; d) mole; e) liter.
- 2. 100 mL of human blood contain 55.8 mg of iron. How many iron atoms does it contain?**
a) $6 \cdot 10^{26}$; b) 1; c) $6 \cdot 10^{17}$; d) 10^{-3} ; e) $6 \cdot 10^{20}$.
- 3. What value can the equivalence factor of HNO_3 take in acid-base ion-exchange reactions?**
a) 1/2; b) 1/5; c) 1; d) 1/3; e) 1/8.
- 4. Which amount of equivalents comprises 98 g of phosphoric acid in the reaction of neutral salt formation?**
a) 3; b) 2; c) 1/2; d) 1; e) 1/3.
- 5. In which of the reactions given below the equivalence factor of H_2SO_4 is equal to 1/8?**
a) $\text{H}_2\text{SO}_4 + 2\text{KOH} = \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O}$;
b) $\text{H}_2\text{SO}_4 + \text{KOH} = \text{KHSO}_4 + \text{H}_2\text{O}$;
c) $\text{H}_2\text{SO}_4 + \text{Cu} \rightarrow \text{CuSO}_4 + \text{SO}_2 + \text{H}_2\text{O}$;
d) $\text{H}_2\text{SO}_4 + \text{Zn} \rightarrow \text{ZnSO}_4 + \text{S} + \text{H}_2\text{O}$;
e) $\text{H}_2\text{SO}_4 + \text{HI} \rightarrow \text{I}_2 + \text{H}_2\text{S} + \text{H}_2\text{O}$.
- 6. Mass fraction of NaCl in a (physiologic) saline is 0.85 %. What mass of NaCl should be taken to prepare 1 kg of the saline?**
a) 85 g; b) 8,5 g; c) 0,85 g; d) 85 mg; e) 850 mg.
- 7. As a primary standard at titration analysis the following substance can be used:**
a) KMnO_4 ; b) $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$; c) I_2 ; d) H_2SO_4 ; e) NaOH .
- 8. How many milliliters of 0,1 M solution of AgNO_3 will be used to titrate 5 mL of 0.2M solution of NaCl ?**
a) 5 mL; b) 1 mL; c) 2.5 mL; d) 10 mL; e) 100 mL.

LABORATORY WORKS ON THE TOPIC «ELEMENTS OF TITRATION ANALYSIS»

Laboratory work 1. Measuring volumes of solutions in the titration analysis



Fig.1. Volumetric (graduated) flask

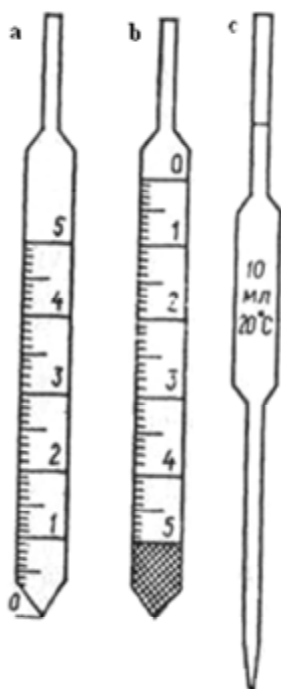


Fig.2. Pipettes
a, b - graduated pipettes
c - More's pipette

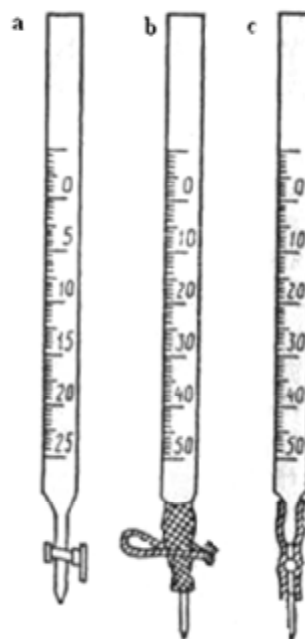


Fig.3. Burettes

Aim of the work: to get acquainted with measures used at the titration analysis and to get some skills when working with them.

- Tasks:**
- 1) to draw the samples of measures in the laboratory register;
 - 2) to fill in the graduated flask water till the mark;
 - 3) to measure 10.00 mL by More's pipette;
 - 4) to measure:
 - a) 6.2 mL; b) 3.7 mL of water by pipettes graduated 10 and 5 mL;
 - 5) to measure the volume of one drop pouring out of a burette.

Laboratory ware: graduated flasks, More's pipettes, graduated pipettes, rubber spray bulbs, burettes, funnels: at the teacher's table — a beaker, cylinders, measuring test-tubes, a microburette.

Description of apparatus for measuring volumes and main principles of working with them

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

When measuring the volume you should remember that the experimenter's eye should be at the same level with the meniscus of the measured liquid while the volume of the transparent liquids should be measured on the lower edge

of the meniscus and the volume of the intensively coloured ones, e. g. KMnO_4 solution, on the upper edge.

The labware used in a chemical analysis must be chemically pure. Before the work the pipettes and the burettes should be washed carefully with a detergent, e. g. with a chromic mixture ($\text{K}_2\text{Cr}_2\text{O}_7$ solution in concentrated H_2SO_4), with an alcoholic solution of an alkali or with an aqueous soda solution pouring it in the burette with the help of a funnel and filling the pipette with a spray bulb. Then they are carefully washed with tap and distilled water. Having persuaded in the fact that water wets inner walls with an even layer (if droplets still form on the walls, the washing should be continued) a pipette or a burette is washed 2–3 times with the same solution which we will use to fill in the burette or which we will take with the pipette.

Graduated flasks

Graduated flasks are used for the preparation of standard solutions and for the dilution of the solutions till the indicated volumes. These are the flat-bottom flasks with a long narrow neck and a circular mark applied on it; its wide part has an indication of nominal volume of the solution which can be prepared (or measured) with the help of the given flask at the definite temperature. Graduated flasks can be of different capacity ranging from 25 mL to 2 L.

Dry weights (including the content of ficksanals) are introduced into the graduated flask through a funnel and afterwards washing away the rest of the substance from the funnel (and washing up the ampoule of ficksanals) with distilled water. Bringing the solution till the mark should be done carefully and the last drops of the liquid are added with the help of an eye pipette. If the liquid appears to be poured above the mark then the primary standard solution or solution prepared from ficksanals is considered to be spoiled.

After bringing the liquid volume in the flask till the mark (the lower edge of the meniscus) the flask is closed with a cork and the solution is carefully mixed turning the flask with its bottom up.

Pipettes

Pipettes are used for measuring precise volumes of the analyzed solution or the solution of the reagent. They can be of two types: graduated (with the volume of 1, 2, 5, 10, 25 mL) and simple with one mark which are usually called More's pipettes (with the volume of 1 till 100 mL). More's pipettes are narrow tubes with a dilatation in the middle for the increase of the volume; the upper narrow part has a circular mark and an inscription about the volume of the liquid which can be measured with the help of the given pipette at a definite temperature. In biochemical research and clinical analysis we often use both graduated and ungraduated micropipettes of 0,1 and 0,2 mL. To store the pipettes a special support stand is used.

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

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

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

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

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

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

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

Burettes

Both burettes and pipettes are used for measuring volumes for pouring out. They can be of different sizes and design. Usually laboratory burettes are graduated glass tubes. In the lower end there is a glass tap or a rubber tube with a ball shutter or with a clamp. We insert a glass tube ending with a narrow capillary into the rubber tube from the other side. If a glass ball (a ball shutter) is inserted into the rubber tube, then at pulling-off the rubber tube there appears a small gap between the ball and the tube through which the liquid pours out from the burette. According to the capacity the burettes can be: macroburettes (10–100 mL) and microburettes (1–5 mL). You should titrate from the burettes very slowly at constant mixing of the solution in the titration tube in order to find out at which drop of the titrant there is the end of the titration (equivalence point). To reach high precision of the titration you should be able to make correct measurements on the burette and to know the volume of one drop pouring out of the burette. In order not to make a mistake you should begin each titra-

tion from the zero reading on the burette scale and watch carefully for the air bubbles not to be created in the burette (especially below the ball or a clamp).

To fill the burette with water you should do following:

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

2) remove the air bubbles from the lower part of the burette; in order to do it you should bind the rubber tube in such a way to get U-form communicating vessel and pulling the tube away from the ball add a jet of water which will force out the air bubbles;

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

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

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

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

QUESTIONS FOR SELF-CHECK

1. Titration analysis, its methods and tasks.
2. Classification of titration analysis methods.
3. Requirements to the methods used in titration analysis.
4. Standard solutions. Primary standards and requirements made to them. Secondary standards.
5. Calculations in titration analysis.
6. The importance of titration analysis in medical-biological research and clinical analysis.

Part 2

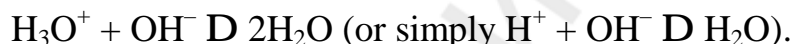
ACID-BASE TITRATION

APPLICATION OF THE METHOD

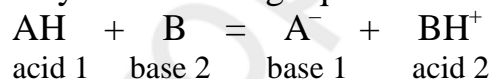
The field of practical application of acid-base titration in medical-biological research is extremely wide. In biochemical research the method of acid-base titration is used for the determination of acidity of the gastric contents, alkaline reserve of blood and plasma. In toxicology this method is used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

The essence and methods of acid-base titration

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



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



where A^- and BH^+ are the base and the acid coupled to the initial respectively.

Depending on the titrant we can differentiate the methods of *acidimetric* and *alkalimetric* titration. In acidimetry (acidum — acid) we use 0.01–0,1 N solutions of strong acids usually HCl or H_2SO_4 as titrants. In alkalimetry (alkalis — alkali) the titrants are 0.01–0,1 N solutions of alkalis such as NaOH, KOH, $\text{Ba}(\text{OH})_2$.

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

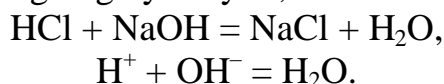
Acidimetric titration is used for determining strong and weak bases and some salts of weak acids, e. g. NaOH, NH_4OH , amines, aniline, Na_2CO_3 , NaHCO_3 and so on.

Alkalimetric titration is used for determining strong and weak acids and some salts of weak bases, e. g. HCl, H_3BO_3 , CH_3COOH , phenols, muriatic salts of very weak organic bases used as medicines and so on.

Equivalence point at acid-base titration

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

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



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

At neutralizing of a weak acid by a strong base the salt undergoing hydrolysis in an aqueous solution is formed, i. e. in this case the reaction is reversible.



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

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



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

If a polybasic acid or its salt is titrated, e. g. H_3PO_4 or Na_2CO_3 , then at titration several equivalence points can be observed:

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

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

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

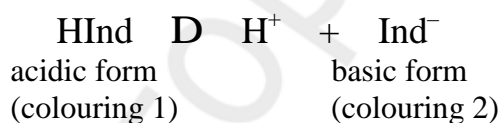
Acid-base indicators

Indicators of acid-base titration are complex organic substances capable of changing their colour depending on the pH of the solution. More than 200 acid-base indicators related to different groups of organic substances are known. The most wide-spread of them are the indicators of tritane group (phenolphthalein, thymolphthalein, phenol red, crystal violet, etc.) and azocompounds (methyl-orange, methyl red, etc.). In titration together with individual we can also use mixed indicators which are mixtures of two, three and more indicators producing clearer colouring changes at changing the pH of solutions.

Physical-chemical characteristics of acid-base indicators

At changing the solution pH all acid-base indicators change their colouring not step-wisely but gradually, i. e. in a definite interval of pH values called *the interval of colouring change indicator* ΔpH . Each indicator has its own interval of colouring change which depends on the specific features of indicator structure and its ability to ionize. Besides ΔpH indicators can be characterized by *titration indicator pT*. Titration indicator pT is the pH value in the range of colouring change indicator at which the most drastic change of the colouring indicator is observed.

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



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

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

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

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

hence,

$$\text{pH} = \text{pK} + \lg([\text{Ind}^-]/[\text{HInd}]). \quad (13)$$

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

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

Let's substitute these values in the equation (13) and get the expression determining the interval of the indicator colouring change:

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

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

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

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

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

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

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

Table 1

Some acid-base indicators

Indicator	Group of indicators	Colouring of indicator forms		ΔpH	pT
		acidic form	basic form		
crystal violet: transfer I transfer II	tritan	yellow	green	0–0,1	0,5
		green	violet	1,0–2,6	1,8
thymol blue transfer I transfer II	sulfophthalein	red	yellow	1,2–2,8	2,0
		yellow	blue	8,0–9,6	8,0
methyl yellow	azoindicator	red	yellow	2,9–4,0	3,2
methyl orange	azoindicator	red	yellow	3,1–4,4	4,0
bromocresol green	sulfophthalein	yellow	blue	3,8–5,4	4,9
methyl red	azoindicator	red	yellow	4,2–6,2	5,0
litmus	phthalein	red	blue	5,0–8,0	7,0
phenol red	sulfophthalein	yellow	red	6,4–8,0	7,0
phenolphthalein	phthalein	colourless	red	8,2–10,0	9,0
thymolphthalein	phthalein	colourless	blue	9,4–10,6	10,0

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

Indicators are used either in the form of solutions some drops of which are added to the test solution or in the form of indicator reactive paper, i. e. pieces of filter paper saturated with indicator solution and dried. At determining the pH we place several drops of the test solution on the indicator paper and we can judge (approximately) about the pH value seeing the colouring of the paper.

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

Curves of acid-base titration. Choice of the indicator

As it was shown above, the pH value in the equivalence point is determined, first of all, by the nature of the acid and the base reacting at titration. For example, the titration of a strong acid by a strong base should be finished in a neutral medium ($\text{pH}_{\text{eq.p}} = 7.0$). From the indicators listed above in Table 1 only litmus and phenol red, which drastically change their colouring in the neutral medium ($\text{pT} = 7.0$), are suitable for $\text{pH} = 7.0$ fixation. Meanwhile, the experiment doesn't prove it: not only these two indicators but all others having pT ranging from 4.0 till 10.0 give almost the same results.

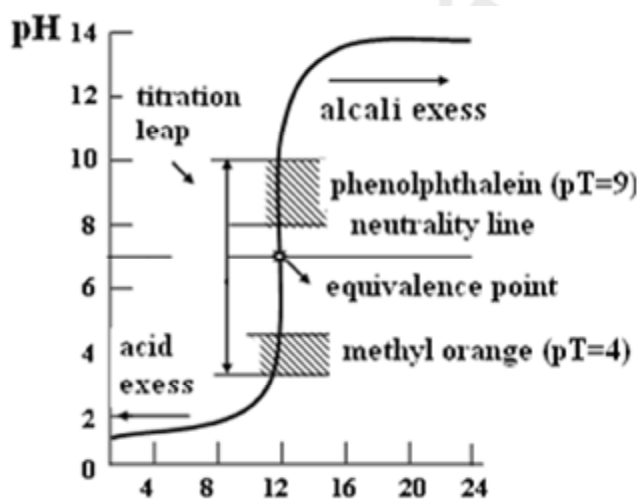


Fig. 1. Curve of titration of 10 mL 0.1 N of a strong acid solution by a solution of a strong base and the choice of the indicator

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

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

1. At titration of a strong acid by a strong base (see fig. 1) the equivalence point coincides with the neutrality point ($\text{pH} = 7.0$) and the branches of the titration curve are symmetrical relative to neutrality lines.
2. Close to the equivalence point we can observe a drastic leap of pH. Its value depends on the concentration of the titrated solution and the titrant and

the temperature. With the increase of the concentration of reagents the value of the pH leap on the titration curve increases and with its decrease the value decreases too. Really, if $C(\text{HCl}) = C(\text{NaOH}) = 1 \text{ mol/L}$, then with the help of the same calculations it's easy to demonstrate that the value of pH leap on the titration curve is 8 pH units. But if $C(\text{HCl}) = C(\text{NaOH}) = 0.01 \text{ mol/L}$, then its value is 4 pH units. With the increase of temperature the value of the pH leap on the titration curve decreases as the ion product of water increases (at 298K $K_{\text{H}_2\text{O}} = 1.0 \cdot 10^{-14}$ and at 373K $K_{\text{H}_2\text{O}} = 5.9 \cdot 10^{-14}$).

3. To fixate the equivalence point at acid-base titration we can use any indicator with the interval of colouring transfer varying in the range of the pH leap on the titration curve.

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

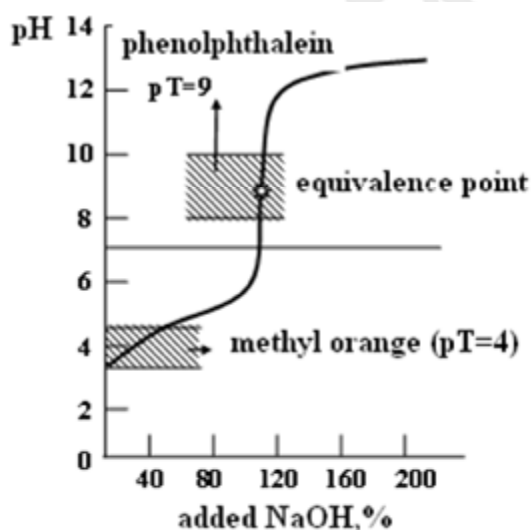


Fig. 2. Titration curve of 0.1 M of acetic acid solution by 0,1 M of alkali solution

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

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

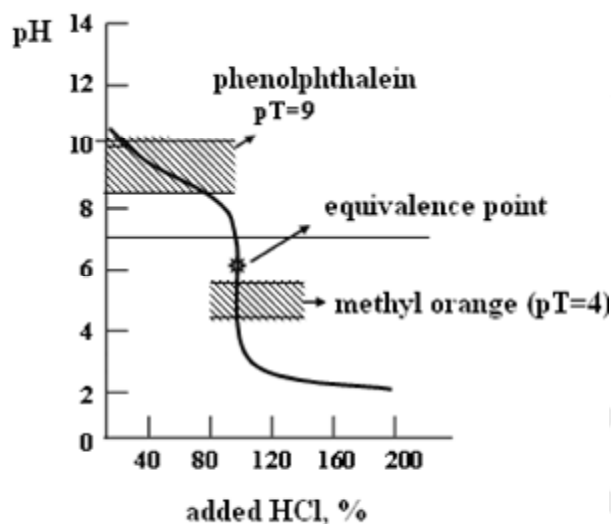


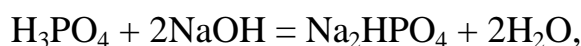
Fig. 3. Titration curve 0.1 M of ammonia solution by 0.1 M of hydrochloric acid solution

At the interaction of a weak acid and a weak base the change of the pH occurs gradually during the whole process of titration so the area of pH leap on the titration curve is absent and it's impossible to determine exactly the equivalence moment. That is why the solutions of weak acids and bases are not used as titrants at acid-base titration.

In accordance with step ionization of polybasic acids their neutralisation occurs also gradually. For example, at titration of H_3PO_4 solution by an alkali the following reactions take place:

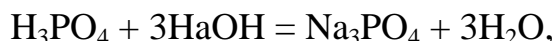
- 1) $\text{H}_3\text{PO}_4 + \text{NaOH} = \text{NaH}_2\text{PO}_4 + \text{H}_2\text{O}$ ($\text{pH}_{\text{eq.p.}} = 4.66$);
- 2) $\text{NaH}_2\text{PO}_4 + \text{NaOH} = \text{Na}_2\text{HPO}_4 + \text{H}_2\text{O}$ ($\text{pH}_{\text{eq.p.}} = 9.94$);
- 3) $\text{Na}_2\text{HPO}_4 + \text{NaOH} = \text{Na}_3\text{PO}_4 + \text{H}_2\text{O}$ ($\text{pH}_{\text{eq.p.}} \approx 12$).

In accordance with this the titration curve of H_3PO_4 by an alkali has three equivalence points instead of one and only two clear pH leaps (for the reactions 1 and 2). The first equivalence point can be determined with the help of methyl orange (or methyl red), the second — with the help of phenolphthalein (thymolphthalein to be more exact). From the given arguments it follows that in the presence of methyl orange H_3PO_4 is titrated as a monobasic acid, i. e. according to the first equation. In this case the equivalence factor is equal to 1. In contrast to this phosphoric acid is titrated with phenolphthalein according to the following equation:



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

We can't titrate H_3PO_4 directly as a tribasic acid, i. e. using the equation



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

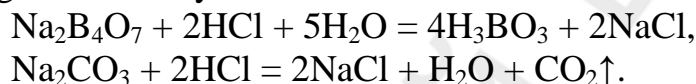
At titration of salts of weak polybasic acids (e. g. Na_2CO_3) and mixtures of acids which differ greatly on their strength (e. g. strong hydrochloric acid and weak acetic acid) we can also observe the fixation of several equivalence points on the titration curve. The right choice of the indicator in each definite case allows getting precise results of the analysis.

Standardization of titrants in methods of acid-base titration

Standard solutions of strong acids and alkali can't be prepared immediately using the exact weight or volume of a more concentrated solution. That's why at first we prepare the solutions of approximate concentration and then we standardize them.

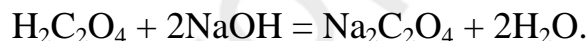
As primary standards for acid solutions we use sodium borate $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (borax), sodium carbonate Na_2CO_3 or its decahydrate $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$.

The following reactions lay the foundation of acid standardization:



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

The standardization of alkali solutions is conducted on oxalic acid dihydrate $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$; they are titrated in the presence of phenolphthalein as the medium is alkaline in the equivalence point:



Using the results of the titration we calculate the normality of the prepared process solution.

If there are any fixanals containing 0.1 mole of NaOH, HCl, H_2SO_4 then the titrants are prepared from them. There are also fixanals of the primary standards mentioned above, the use of which greatly increases the analysis fulfilment.

CONTROL OF MASTERING THE TOPIC

Typical calculation tasks

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

Answer: 1.40 g.

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

Answer: 8.3 mL.

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

Answer: 4.7675 g.

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

Answer: 0.1260 g.

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

Answer: 0.03038 mol/L; 0.05880 mol/L.

Task 6. 9.7770 g of concentrated solution of HNO_3 were diluted by water to get 1 litre of the solution in the volumetric flask. To titrate 25.0 mL of the obtained solution we used 23.40 mL of 0.1040 M of NaOH solution. Determine the mass fraction of nitric acid in its concentrated solution.

Answer: 62.73 %.

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

Answer: 0.08405 mol/L.

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

Answer: 0.08299 mol/L.

QUESTIONS FOR TEST SELF-CHECK (with multiple responses «correct-incorrect»)

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

1. In the method of acid-base titration the standard solutions are the following:

- a) NH_4OH ;
- b) H_2SO_4 ;
- c) H_3BO_3 ;
- d) NaOH.

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

- a) $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$;
- b) $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$;
- c) $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$;
- d) $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$.

LABORATORY WORKS ON THE TOPIC «ACID-BASE TITRATION»

Laboratory work 1. Preparation of titrants by the dilution of a concentrated solution

Task: to prepare a certain volume of a titrant — HCl solution of a specified concentration — by diluting the concentrated solution (the volume and the concentration of the solution are suggested by the teacher).

Aim of the work: to learn to prepare the solutions by diluting, that is to get the skills how to work with the areometers, labwares (graduated pipettes, graduated flasks) and acid solutions; to learn to make calculations of concentration when diluting solutions.

Reagents: hydrochloric acid with mass fraction of HCl in the interval of 10–20 %.

Devices and equipment: a set of areometers, the reference table «Density of aqueous solutions of some acids and alkali»; graduated flasks and pipets.

Course of work fulfilment

You should do the following:

– measure the density of the concentrated HCl solution and using the reference table «Density of aqueous solutions of some acids and alkali» determine the mass fraction of HCl in it.

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

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

As the amount of the dissolved substance is unchanged at diluting the solution with water, we can use the formula of dilution to find the volume of the concentrated HCl solution:

$$C_1V_1 = C_2V_2$$

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

For example: we need to prepare 50 mL of the HCl solution with $C = 0.14 \text{ mol/L}$.

1. The density of the concentrated HCl solution equals 1.059 g/mL.
2. We determine the mass fraction of HCl solution using the reference table «Density of aqueous solutions of some acids and alkali» — 12 %.
3. $C_1(\text{HCl}) = n/V = m/M \cdot V = m(\text{HCl}) \cdot \rho(\text{solution, g/mL}) \cdot 1000/M(\text{HCl}) \cdot m(\text{solution})$; if $\omega(\text{HCl}) = 12 \%$, then $m(\text{solution}) = 100 \text{ g}$ and $m(\text{HCl}) = 12 \text{ g}$.

$$C_1 = 12\text{g} \cdot 1.059 \text{ g/mL} \cdot 1000/36.5 \text{ g/mol} \cdot 100 \text{ g} = 3.48 \text{ mol/L.}$$

$$4. C_1V_1(\text{conc.}) = C_2V_2(\text{diluted})$$

$$V_1 = C_2 \cdot V_2/C_1 = 0.14 \cdot 0.05/3.48 = 0.00201 \text{ L} = 2.01 \text{ mL.}$$

– pour distilled water in the graduated flask till the middle of its volume.

With the help of a suction device you should fill in the graduated pipette with the concentrated HCl solution and place the previously calculated volume of the concentrated HCl solution into the graduated flask.

– mix the solution in the flask by circular motions.

– add carefully water till the mark (on the lower edge of the meniscus) adding the last drops with an eye pipette.

– close the flask with a cork and carefully mix the solution turning the flask bottom up several times.

Conclusion. In this work the conclusion can be formulated as follows: «By diluting a concentrated solution we have prepared HCl solution with the volume of ... mL and the concentration of approximately ... mol/L».

Laboratory work 2. Standardization of a titrant on the primary standard solution

Task: to standardize the titrant — HCl solution.

Aim of the work: to learn to standardize titrants on their primary standard with the usage of direct titration, that is to get the skills of working the More's pipettes and burettes and fulfilling the titration; to learn to choose the appropriate indicator for definite cases of acid-base titration; to learn to make the calculations based on the titration results.

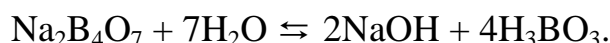
Reagents: titrant — HCl solution with the approximate concentration value in the interval 0.05–0.2 mol/L; the solution of the primary standard — 0.10 N $\text{Na}_2\text{B}_4\text{O}_7$; indicators — solutions of methyl orange and phenolphthalein.

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

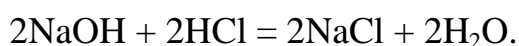
Course of work fulfilment

You should write down the equations of the reactions which lay the foundation of titrant standardization, calculate the equivalence factors and the molar masses of the equivalents of the reagents.

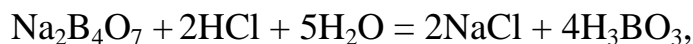
When dissolved in water borax is greatly hydrolysed on the anion with the formation of a very weak boric acid (pH = 9.24):



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



Summing up the last two equations we get the general equation of the reaction taking place at titration:



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

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

Then you should describe in words or draw a scheme explaining the following definite moments of the work:

- 1) which solution should be poured in the burette;
- 2) which solution and which volume should be measured by More's pipette into the titration flasks;
- 3) which colour change of the titrated solution should take place in the equivalence point.

Then you should titrate the solution from its yellow till the orange colouring.

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

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

The first titration has mostly tentative character. Adding small portions of the titrant from the burette it's necessary to mix constantly the contents of the flask. The titration should be finished when there will be the change of indicator colouring. The results of the titration should be immediately written down with the accuracy from 0.03–0.05 mL.

The second and the following titrations should be conducted more precisely. At first in the titration flask you should quickly add the titrant with the volume less than 0.5–1.0 mL of the volume determined during the first tentative titration. Then the titrant is added by drops observing carefully the colouring change of the solution. The titration should be stopped when obvious colouring change takes place at adding at least one drop of the titrant.

Titration should be repeated till you get three similar results (i. e. they shouldn't differ more than 0.1 mL).

All the results should be written down in the table:

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

Part 3

OXIDATION-REDUCTION TITRATION

MAIN POSTULATES OF THE ELECTRON THEORY OF OXIDATION-REDUCTION PROCESSES

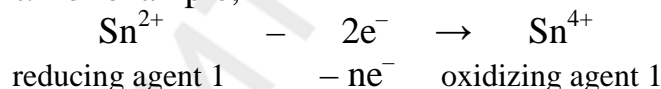
A lot of titrimetric methods used in quantitative analysis are based on the use of oxidation-reduction reactions (OR reactions). They are commonly named as oxidimetry methods.

Oxidimetry methods in clinical and biochemical research determine the catalase and peroxidase activity, the presence of ascorbic acid, sugar in blood and other biological liquids, uric acid in urine, urea in blood and urine, calcium ions in blood serum and so on.

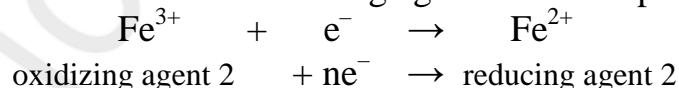
In hygiene and sanitary investigations with the help of oxidimetry it's possible to determine the oxidability of water, the content of active chlorine in drinking water, dissolved oxygen and organic admixtures in the water of natural water bodies and so on.

The reactions where there is a partial or complete electron transfer from one group of atoms or ions to other groups which is accompanied by the change of oxidation number of the elements making part of reactants are called oxidation-reduction reactions (OR-reactions).

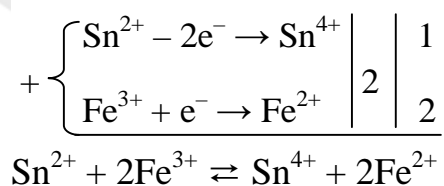
According to the electron theory of oxidation-reduction processes, oxidation is the process of losing electrons by the substance. The substance losing electrons is called a reducing agent and in the course of the reaction it transforms into its oxidized form which is the oxidizing agent coupled with the initial reducing agent. For example,

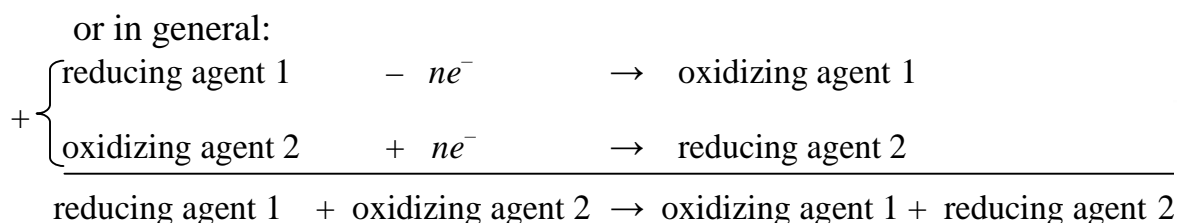


Reduction is the process of joining electrons by the substance. The substance joining the electrons in OR reactions is called the oxidizing agent and in the course of the reaction it transforms into its reduced form which is the reducing agent coupled with the initial oxidizing agent. For example,



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





So, any OR reaction is the aggregate of two coupled processes — half-reactions: oxidation of the reducing agent and the reduction of the oxidizing agent.

Writing the equations of oxidation-reduction (OR) reactions

To write an equation of an OR reactions two methods are used: the method of electron balance and electron-ion method (or the method of half-reaction).

Method of electron balance known from the school chemistry course is recommended for balancing OR reactions taking place in gaseous and solid phases.

Electron-ion method is used for writing OR reactions occurring in aqueous solutions. It is based on the writing two half-reactions for oxidation of the reducing agent and the reduction of the oxidizing agent respectively with their further summing up into a general equation.

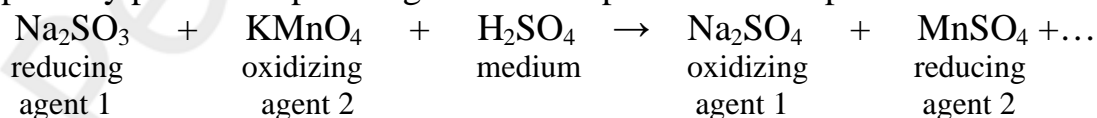
When using this method the oxidation numbers of the elements composing the reacting substances are not determined: in half-reactions we write ions or molecules of coupled oxidized and reduced forms in such a state in which they exist in the solution under the conditions of the reaction conduction.

At the same time we should make use of the general rules of ion equation writing: weak electrolytes, gases and slightly soluble substances are written down in the molecular form.

At balancing the masses of oxygen and hydrogen in the left and right parts of the half-reaction it possible to use water molecules and also H^+ and OH^- ions.

If the reaction takes place **in an acidic medium**, *only water molecules and H^+ ions can be included in the half-reaction. For each lacking oxygen atom in one of the parts of the half-reaction we should add one water molecule then in the second part of the half-reaction we should double the number of H^+ ions.*

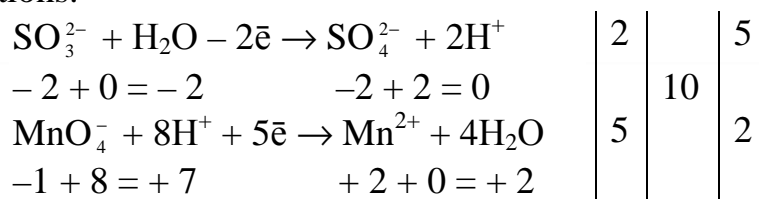
As an example let's write the equation of oxidation reaction of sodium sulphite by potassium permanganate in the presence of sulphuric acid:



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

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

Half-reactions:

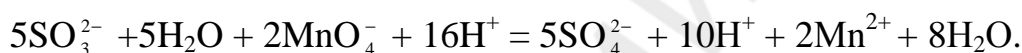


Writing of OR reaction equations is done using the following plan:

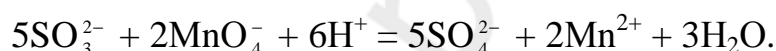
1. Let's write the half-reactions for the oxidation and reduction processes taking into account the acidity of the medium so that the mass balance and charge balance be observed in both parts.

2. Let's find the least common multiple of the number of electrons in the oxidation and reduction half-reactions (in the given case 10) and additional multipliers for the first ($10:2 = 5$) and the second ($10:2 = 5$) half-reactions.

3. Let's multiply the half-reactions by their additional multipliers and sum up the right side of the first part of the first reaction and the right side of the second reaction and the left sides of both reactions respectively. In the result we'll get on equation of OR reaction:



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

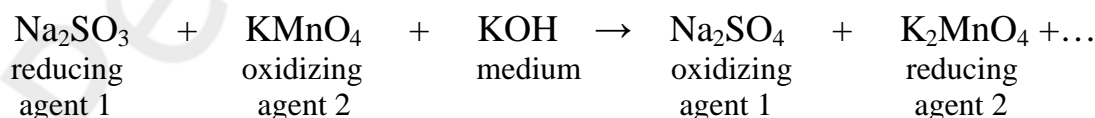


The obtained short ion equation shows the essence of the process and indicates which particular particles and in which ratio take part in the reaction and are formed in it. Using the ion equation it's easy to write a molecular one:



If the reaction occurs **in the alkaline medium**, then only water molecules and OH^- ions can be included into the half-reactions. For each lacking in one of the parts of the half-reaction oxygen atom we should add two OH^- ions, and then in the second part of the reaction the amount of water molecules will be twice smaller.

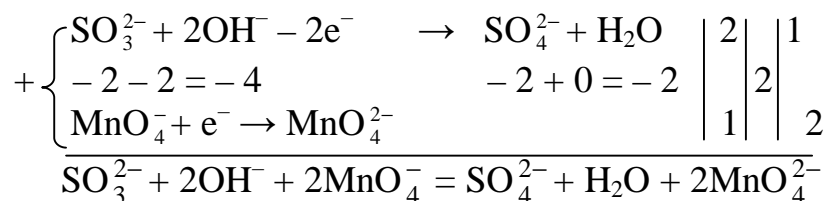
As an example let's use the plan mentioned above to write the equation for the oxidation reaction of sodium sulphite by potassium permanganate in the alkaline medium:



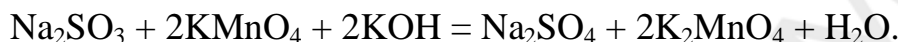
The oxidation process: $\text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-}$

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

Half-reactions:

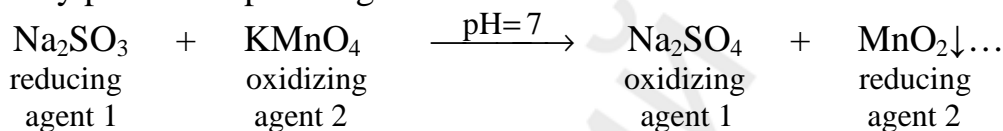


Molecular equation of the reaction:



If the reaction **occurs in a neutral medium** then we should add only water molecules to the left part. And for each lacking or extra oxygen atom in the left part of the half-reaction it's necessary to take one water molecule, and then in the right part there will be two H^+ ions or OH^- ions respectively.

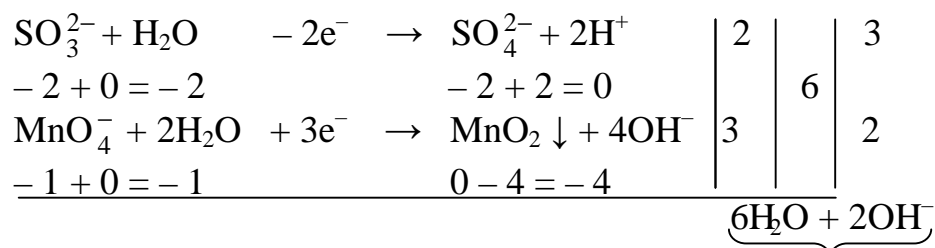
As an example let's write the equation of oxidation reaction of sodium sulphite by potassium permanganate in the neutral medium:



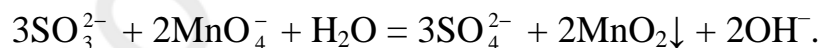
The oxidation process: $\text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-}$

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

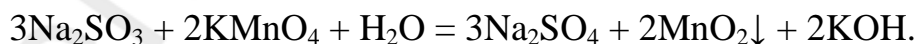
Half-reactions:



Short ion equation:



Molecular equation of the reaction:



General characteristic and classification of oxidation-reduction titration methods

Oxidation-reduction reactions are the basis of a number of methods titrimetric analysis and all bear the general name oxidimetry. As process solutions (titrants) in oxidimetry we use the solutions of oxidising and reducing agents.

Depending on the oxidizing and reducing agents used in the process solution all oxidimetry methods are classified as follows:

1) permanganatometry: the main titrant is KMnO_4 solution; solutions of iron sulphate FeSO_4 and $\text{H}_2\text{C}_2\text{O}_4$ are usually used together with it;

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

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

4) bromatometry: titrant — solution KBrO_3 ;

5) nitriometry: titrant — solution NaNO_2 and so on.

Oxidimetry methods allow quantitative determination of various reducing agents: compounds of iron (II), tin (II), sulphites, arsenites, oxalates, hydrogen peroxide and others in solutions and alloys with the help of process solutions of oxidizing agents. With the help of process solutions of reducing agents we can determine various oxidizing agents: dichromates, chlorine, hypochlorites, chlorites, bromine, bromates, iodine, iodates, hydrogen peroxide and so on.

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

The following requirements to the reactions used in oxidimetry are as follows: the reaction at titration should be quick and irreversible giving products of a very definite composition; it shouldn't be accompanied by side interactions and there should be a method to fix the end of the reaction. But a very small amount of the whole number of OR reactions can satisfy these requirements. For oxidimetric titration we choose the pairs so that the difference of their standard oxidation potentials ($E = e_{\text{oxid}}^0 - e_{\text{red}}^0$) should not be lower than 0.4–0.5 V. In the opposite case there is no a drastic potential leap close to the equivalence point at titration.

In oxidimetry there exist different methods to determine the equivalence point. For example, in permanganatometry it is fixated by the colouring change of the titrated solution which is caused by the excess of coloured process solution of KMnO_4 (so-called unindicator titration), in iodometry the equivalence point is determined with the help of starch indicator which reacts specifically with iodine. In oxidimetry we can use special redox-indicators (e. g. diphenylamine) which change the colouring due to the value of oxidation potential similar to the process when the acid-base indicators change their colouring due to the pH of the solution.

Direction of spontaneous occurring of oxidation-reduction reactions

As we can see from equation that in any OR-reaction from initial oxidizing and reducing agents (the left part of the equation) a new oxidizing and reducing agent coupled to the initial ones (the right part of the equation) are

formed. That's why there appears a question: in which direction this (forward) or that (reverse) OR-reaction can occur spontaneously?

According to the Second Law of Thermodynamics spontaneous are only the processes which are accompanied by the decrease of Gibb's free energy ($\Delta G < 0$). It can be observed in the exchange reactions if in the result of the interaction a gas, a slightly soluble substance or a weak electrolyte is formed. *For OR-reactions $\Delta G < 0$ is in such a case when weaker oxidizing and reducing agents are formed from stronger ones.*

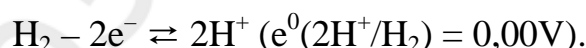
The strength of oxidizing and reducing agents depends on their ability to accept or lose electrons: the higher is the ability to accept electrons, the stronger is the oxidizing agent and vice versa a stronger reducing agent is able to give back the electrons easier. There is an inverse relation between the forces of coupled oxidizing and reducing agents: the stronger is the oxidizing agent in the couple, the weaker is the reducing agent coupled to it and vice versa a weaker oxidizing agent corresponds to a stronger reducing agent.

Oxidation-reduction potential as a measure of oxidation and reduction ability of substances

The qualitative characteristic of relative force of different OR pairs are the values of their oxidation potentials which are measured in the galvanic element.

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

A normal hydrogen electrode is a platinum plate covered by a layer of spongy platinum which is immersed in HCl or H₂SO₄ solutions with the active H⁺ ion concentration equal to 1 mol/L. Hydrogen under the pressure of 101.3 kPa (1 atm) is constantly added to the solution. The equilibrium state in this system is described by the equation of the half-reaction:



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

Let's see some examples.

1. To measure $e^0(\text{Zn}^{2+}/\text{Zn})$ a zinc plate should be immersed into ZnSO_4 solution where $[\text{Zn}^{2+}] = 1 \text{ mol/L}$.

2. To measure $e^0(\text{Fe}^{3+}/\text{Fe}^{2+})$ a platinum electrode should be immersed into the solution containing a mixture of salts FeCl_3 and FeCl_2 where $[\text{Fe}^{3+}] = [\text{Fe}^{2+}] = 1 \text{ mol/L}$.

3. When analysing the oxidation ability of KMnO_4 in the acidic medium ($\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- = \text{Mn}^{2+} + 4\text{H}_2\text{O}$) a platinum electrode should be immersed into the solution containing KMnO_4 , MnSO_4 and H_2SO_4 where $[\text{MnO}_4^-] = [\text{Mn}^{2+}] = 1 \text{ mol/L}$ and $[\text{H}^+] = 1 \text{ mol/L}$.

EMF (E) of the galvanic element is equal to the potential difference of its both component half-elements – a cathode and an anode.

$$E = e_{\text{cathode}}^0 - e_{\text{anode}}^0 \quad (14)$$

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

$$E_1 = e^0(2\text{H}^+ / \text{H}_2) - e^0(\text{Zn}^{2+} / \text{Zn}) = -0,76\text{V},$$

$$E_2 = e^0(\text{Fe}^{3+} / \text{Fe}^{2+}) - e^0(2\text{H}^+ / \text{H}_2) = +0,77\text{V},$$

$$E_3 = e^0(\text{MnO}_4^- / \text{Mn}^{2+}) - e^0(2\text{H}^+ / \text{H}_2) = +1,51\text{V}.$$

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

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

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

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

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

Table 2

Standard potentials of OR systems relative to a normal hydrogen electrode

Oxidized form	+ ne ⁻	Reduced form	e ⁰ , B
F ²	+ 2e ⁻	2F ⁻	+2.87
H ₂ O ₂ + 2H ⁺	+ 2e ⁻	2H ₂ O	+1.77
MnO ₄ ⁻ + 8H ⁺	+ 5e ⁻	Mn ²⁺ + 4H ₂ O	+1.51
Cl ₂	+ 2e ⁻	2Cl ⁻	+1.36
Cr ₂ O ₇ ²⁻ + 14H ⁺	+ 6e ⁻	2Cr ³⁺ + 7H ₂ O	+1.33
Br ₂	+ 2e ⁻	2Br	+1.06
NO ₃ ⁻ + 3H ⁺	+ 2e ⁻	HNO ₂ + H ₂ O	+0.94
O ₂ + 4H ⁺ (pH 7)	+ 4e ⁻	2H ₂ O	+0.82
Fe ³⁺	+ e ⁻	Fe ²⁺	+0.77
O ₂ + 2H ⁺	+ 2e ⁻	H ₂ O ₂	+0.69
MnO ₄ ⁻ + 2H ₂ O	+ 3e ⁻	MnO ₂ + 4OH ⁻	+0.59

Oxidized form	+ ne ⁻	Reduced form	e ⁰ , B
MnO ₄ ⁻	+ e ⁻	MnO ₄ ²⁻	+0.57
I ₂	+ 2e ⁻	2I ⁻	+0.54
H ₂ SO ₃ + 4H ⁺	+ 4e ⁻	S + 3H ₂ O	+0.45
SO ₄ ²⁻ + 8H ⁺	+ 6e ⁻	S + 4H ₂ O	+0.36
Cu ²⁺	+ 2e ⁻	Cu	+0.34
SO ₄ ²⁻ + 4H ⁺	+ 2e ⁻	H ₂ SO ₃ + H ₂ O	+0.20
S ₄ O ₆ ²⁻	+ 2e ⁻	2S ₂ O ₃ ²⁻	+0.08
2H ⁺	+ 2e ⁻	H ₂	+0.00
O ₂ + 2H ₂ O	+ 2e ⁻	H ₂ O ₂ + 2OH ⁻	-0.076
CrO ₄ ²⁻ + 4H ₂ O	+ 3e ⁻	Cr(OH) ₃ + 5OH ⁻	-0.13
Pyruvate	+ 2e ⁻	Lactate	-0.185
Cystine	-	Cysteine	-0.33
2H ⁺ (pH 7)	+ 2e ⁻	H ₂	-0.414
S	+ 2e ⁻	S ²⁻	-0.508
Zn ²⁺	+ 2e ⁻	Zn	-0.76
Al ³⁺	+ 3e ⁻	Al	-1.67

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

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

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

For example, in case of the three pairs mentioned above we can conclude that the strongest reducing agent is in the pair Zn²⁺/Zn (metallic zinc) and the strongest oxidizing agent is in the pair MnO₄⁻/Mn²⁺ (this is MnO₄⁻ ion).

Determination of OR reactions direction according to values of system oxidation potentials

In the table of standard potentials OR pairs are most often arranged in the order of decreasing of potential values corresponding to them (see table 2). At such an arrangement the substance situated in the left column of the overlying pair can be an oxidizing agent for the substance situated in the right column of the underlying pair. For example, MnO₄⁻ ions in the acidic medium (e⁰ = 1.51 V) can be an oxidizing agent for Cl⁻ ions (e⁰ = 1.36 V) converting them into Cl₂ and forming Mn²⁺ ions.

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

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

$$e = e^0 + \frac{RT}{nF} \ln \frac{[\text{oxid.}]}{[\text{red.}]}, \quad (15)$$

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

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

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

If we substitute the numerical values of the constants in equation (15) and pass from natural to common logarithms ($\ln N = 2.303 \lg N$), then for the temperature of 298 K we'll get:

$$e = e^0 + \frac{0.059}{n} \lg \frac{[\text{oxid.}]}{[\text{red.}]}. \quad (16)$$

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

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

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

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

At non-standard conditions hydrogen electrode potential on basis of equation:

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

To solve the problem of the direction of OR reaction at non-standard conditions we should at first calculate the oxidation potential according to equations (15) or (16). These calculations are especially important for the systems with close meanings of e^0 . After doing the calculations the values of oxidation potential of the pairs on basis of Nernst's equation taking into account active concentrations of all ions in the solution, the problem of reaction direction can be solved using the general rule: in a spontaneous OR reaction the role of an oxidizing agent is played by an oxidized form with a higher value of the oxidation potential from the pair and the role of a reducing agent — by a reduced form with a smaller value of the potential in the pair.

The greater is the difference of oxidation potential values of two pairs: $E = e_{\text{oxid.}} - e_{\text{red.}}$, the greater is the motive force of OR reaction. That's why if there are several reducing agents in the solution (e. g. Cl^- , Br^- , I^-), then the added oxidizing agent (e. g. acidated solution of KMnO_4) will react firstly with the strongest reducer, i.e. with I^- ions oxidizing them till free iodine ($E = 1.51 - 0.54 = 0.97 \text{ V}$, see tab. 2). After oxidizing I^- ions there begins the interaction of KMnO_4 with Br^- ions ($E = 1.51 - 1.06 = 0.45 \text{ V}$) and then with Cl^- ions ($E = 1.51 - 1.36 = 0.15 \text{ V}$).

This circumstance explains why the transfer of electron and protons in the chain of biological oxidation occurs on the following scheme:

Oxidized substrate	$e = -0.42 \text{ V}$
↓	
Dehydrogenase	$e = -0.32 \text{ V}$
↓	
Flavinic enzyme	$e = -0.06 \text{ V}$
↓	
Cytochrome	$e \text{ from } +0.04 \text{ till } +0.55 \text{ V}$
↓	
$1/2 \text{ O}_2$	$e = +0.82 \text{ V}$

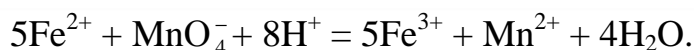
The strict enzyme sequence in the oxidation chain excludes the drastic difference between the potentials of two interacting systems and this stipulates gradual emission of oxidation energy. Such peculiarity of biological oxidation allows the organism to regulate the obtaining and usage of energy more precisely.

Curves of oxidimetric titration

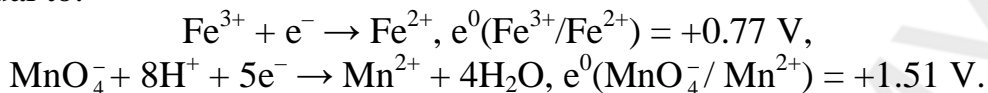
At oxidimetric titration the concentrations of the substances or ions taking part in the reaction are constantly changing which leads to the change of the solution oxidation potential (e) similar to the change of pH of the solution at the acid-base titration.

Curves of oxidimetric titration show the dependence of solution oxidation potential change on the volume of the titrant added in the titration process.

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



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



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

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

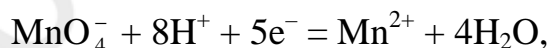
At the excess of MnO_4^- ions in the solution, i. e. after the equivalence moment it's necessary to do the calculations using the equation:

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

PERMANGANATOMETRY

The essence of the method

The method of permanganatometry is based on the oxidation reactions of different substances by potassium permanganate. The oxidation is conducted in a strongly acidic medium where permanganate-ion exhibits the strongest oxidation properties. Standard oxidation potential of $\text{MnO}_4^-/\text{Mn}^{2+}$ pair is 1.51 V, that's why potassium permanganate can react with the majority of reducing agents. The product of KMnO_4 reduction in the acidic medium is an almost colourless ion Mn^{2+} :



which is very convenient for the equivalence point fixation. At titration the rosy colouring of MnO_4^- ion becomes vivid due to one excess drop of KMnO_4 process solution that's why no special indicator is required.

To create a strongly acidic medium we use H_2SO_4 solutions. The use of hydrochloric or nitric acids is prohibited as hydrochloric acid besides its acid properties also exhibits rather evident reducing properties and is able to react with KMnO_4 with the emission of chlorine. Nitric acid besides its acid properties exhibits oxidation properties and can react with determined reducing agents.

In a pair with the main process solution of KMnO_4 oxidizing agent we use the process solutions of the following reducing agents: iron (II) sulphate or oxalic acid $\text{H}_2\text{C}_2\text{O}_4$. In the reaction with potassium permanganate in the acidic medium FeSO_4 converts into iron (III) sulphate and oxalic acid is oxidized to CO_2 .

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

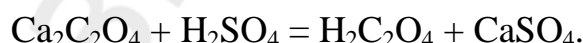
To determine reducing agents we use, as a rule, the methods of direct titration, to determine oxidizing agents — methods of back titration and to determine indifferent substances — methods of both back and substitute titration.

For example, to determine hydrogen peroxide, iron (II) ions and other reducing agents we carry out direct titration of their solutions by a standardized KMnO_4 solution.

To determine oxidizing agents such as $\text{K}_2\text{Cr}_2\text{O}_7$ and others we use the methods of back titration, the essence of which is the following: we add a deliberately excessive and precisely measured volume of the process solution of the reducing method, e. g. FeSO_4 to the solution of the oxidizing agent. Then the rest of FeSO_4 which hasn't reacted with the determined oxidizing agent is titrated by the process solution KMnO_4 . So, at permanganatometric determination of oxidizing agents we need two process solutions.

At determining indifferent substances, e. g. Ca^{2+} ions, we can use only one process solution KMnO_4 (substitute titration) or two titrants (KMnO_4 and $\text{H}_2\text{C}_2\text{O}_4$) at back (reverse) titration.

When using substitute titration the analyzed solution containing Ca^{2+} ions is treated by some soluble oxalate, e. g. $\text{Na}_2\text{C}_2\text{O}_4$, in such a way that all Ca^{2+} ions precipitate in the form of a slightly soluble CaC_2O_4 . The precipitate then is filtrated, washed and dissolved in sulphuric acid:



Oxalic acid in the obtained solution is titrated by a process solution KMnO_4 . It's obvious that

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

On basis of this we calculate the mass of Ca^{2+} ions in the analyzed sample.

When applying the method of back titration to the analysed solution containing Ca^{2+} ions we add a deliberately excessive and precisely measured volume of the standard solution $\text{H}_2\text{C}_2\text{O}_4$. The obtained precipitate CaC_2O_4 is separated and thrown away, then the rest of unreacted $\text{H}_2\text{C}_2\text{O}_4$ is titrated by the process solution KMnO_4 . In this case

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

On basis of the written equation we calculate the amount or mass of Ca^{2+} ions in the analysed sample.

Titrant standardization in permanganometry

We can't prepare a primary standard solution from the crystalline KMnO_4 which is sold in the pharmacy because even the agent of «cp» (chemically pure) type doesn't satisfy the requirements necessary for the initial substances. It usually contains traces of MnO_2 in the form of admixtures which can catalyze the reaction of water oxidation by permanganate:

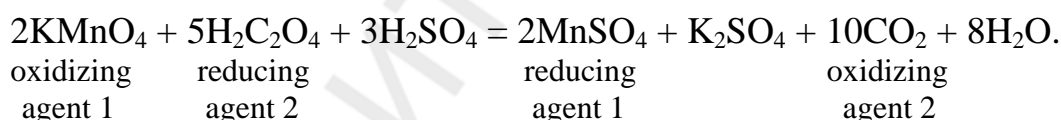


which is usually accompanied by the concentration change of KMnO_4 solution. Besides, at dissolving even the purest KMnO_4 part of it is used for the reaction with admixtures of organic substances which are always present in distilled water. Moreover, light can also influence the stability of KMnO_4 solution.

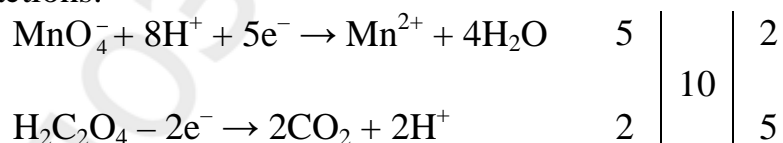
According to the principles indicated above firstly, we prepare KMnO_4 solution with the concentration approximately equal to the required one (usually 0.02 or 0.05 mol/L) and leave it for some days till the complete precipitation of MnO_2 . After that KMnO_4 solution is taken by the siphon in such a way that MnO_2 precipitate is left at the bottom.

As standard substances to determine the concentration of KMnO_4 solution we use anhydrous sodium oxalate $\text{Na}_2\text{C}_2\text{O}_4$ or oxalic acid dihydrate $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. These substances after all the preparations satisfy the requirements needed for primary substances and can be used for the preparation of standard solutions.

In a strong-acid medium KMnO_4 is quantitatively reduced by oxalic acid:



Half-reactions:



($\text{H}_2\text{C}_2\text{O}_4$ being a weak electrolyte at dissociation of the second step in a strong-acid medium exists in the form of molecules).

Although reducing properties of oxalate-ions are quite vivid ($E^0(2\text{CO}_2/\text{C}_2\text{O}_4^{2-}) = -0.49 \text{ V}$) the reaction between them and MnO_4^- ions at the beginning (the first drops of KMnO_4 solution) occurs very slowly, the following drops of KMnO_4 solution lose their colour very quickly. It is connected with the fact that the considered reaction is *autocatalytic* and is catalyzed by one of the reaction products, i. e. by Mn^{2+} ions.

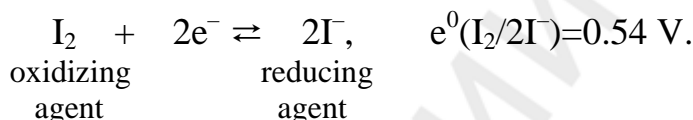
To speed up the decolouration of first portions of KMnO_4 the reacting mixture in the titration flask is heated till 80–90 °C (it mustn't be boiled to avoid the decomposition of $\text{H}_2\text{C}_2\text{O}_4$). After appearing of a catalyst — Mn^{2+} ions — in the reaction mixture the reaction becomes autocatalytic and proceeds at a very high speed so that the following portions of KMnO_4 solution during titration are decolourized immediately.

KMnO_4 solution with the established concentration in its turn can be a secondary standard solution for the standardization of the reducing agent solution of FeSO_4 method. This titration is carried out in a cold place because heating of the solution speeds up the side reaction of Fe^{2+} ion oxidation by oxygen from the air.

IODOMETRY

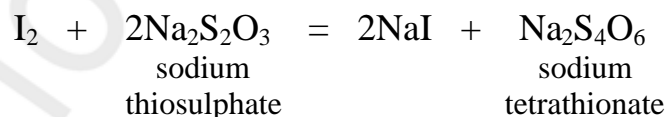
The essence of the method

The method of iodometry is based on oxidation-reduction reactions connected with the transformation of I_2 into I^- ions and vice versa:

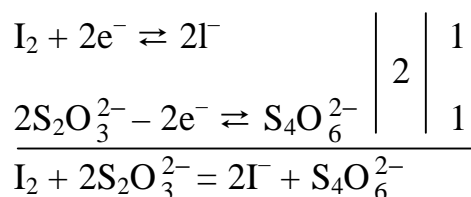


Special features of iodometry first of all are due to good reversibility of the half-reaction written above and low value of standard oxidation potential of the pair $\text{I}_2/2\text{I}^-$. The value of the oxidation potential of the pair is intermediate between the values of the potential for typical strong oxidizing and reducing agents and characterizes iodine as medium oxidizer and I^- ion as medium reducer. That's why iodometric methods are used for determination of both oxidizing and reducing agents.

The process solutions in iodometry are the standard solutions of I_2 (the oxidizer of the method) and sodium thiosulphate $\text{Na}_2\text{S}_2\text{O}_3$ (the reducer of the method). The main titrimetric reaction in this method is the interaction of iodine solution and the process solution of sodium thiosulphate:



Half-reactions and ion equation of the reaction:



As an indicator in iodometry we use aqueous solution of starch which forms iodine-starch compound of blue colour with molecular iodine. When the reducing agent is titrated by the standard solution of iodine the equivalence point is determined by the appearance of intensive-blue colouring. When iodine is titrated by the standard solution of sodium thiosulphate the end of the reaction is determined by the disappearance of the blue colouring due to adding one drop of sodium thiosulphate solution.

Starch should be added at the very end of titration when there is less iodine and the solution becomes pale yellow. The starch added to the solution with high iodine concentration becomes black and is destroyed, which causes mistake at determining the equivalence point. Very high sensitivity of starch to iodine and drastic change of solution colouring in the equivalence point allow using standard solutions of smaller concentration compared to other methods of titrimetric analysis (from 0.01 N till 0.05 N solutions).

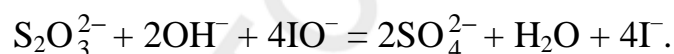
Many iodometric reactions are reversible and occur till the end only under certain conditions:

1) titration should be conducted in a cold place as, firstly, iodine is a volatile substance and, secondly, at heating starch sensitivity to iodine decreases;

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



and IO^- being a stronger oxidizer than I_2 oxidizes thiosulphate-ion up to sulphate-ion:

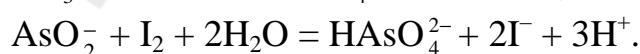
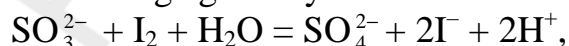


The greatest advantage of iodometric method is the availability of a very sensitive and reversible to iodine indicator. The disadvantages of the method are low stability of iodine solution and not complete reaction of iodine with many other reducing agents.

Examples of iodometric determinations

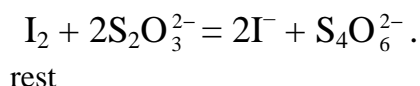
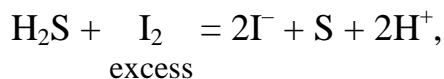
Iodometric determination of reducers is carried out using the method of direct or back titration. Oxidizing agents are determined by substitute titration.

At determining reducing agents by the method of direct titration the solution of iodine is used. This method determines arsenic (III), antimony (III), tin (II) compounds; thiosulphates, small amounts of H_2S (e. g. in mineral water), sulphides and sulphites. The examples of reactions taking place at direct titration of reducing agents by iodine are the following:



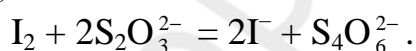
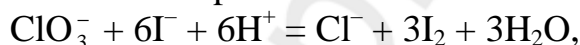
In those cases when direct titration is more complicated (e. g. the reducer is volatile or the reaction occurs very slowly) we use the method of back (reverse) titration to determine reducing agents.

To do this we need two process solutions of iodine and sodium thiosulphate. We add to the reducer an exactly measured volume of iodine solution taken in excess compared to the volume of the reducer. There occurs the reaction between iodine and the reducing agent, then the rest of unreacted iodine is titrated by thiosulphate solution. For example, to determine H_2S :



This method helps to determine high concentrations of H_2S , sulphides and sulphites, number of metals in the form of powder (e. g. zinc), some organic compounds.

To determine oxidizing agents by the method of substitute (indirect) titration we should do the following. We add an exactly measured by More's pipette volume of the solution of the determined oxidizing agent (e. g. KClO_3) to KI solution taken in excess and acidated by sulphuric acid; then the emitted iodine is titrated by sodium thiosulphate:



The number of moles of $\text{Na}_2\text{S}_2\text{O}_3$ equivalents is equal to the number of moles of iodine equivalents, the latter being equal to the number of moles of the determined oxidizing agent (KClO_3) equivalents. So, although the determined oxidizing agent and $\text{Na}_2\text{S}_2\text{O}_3$ don't react directly but their amounts are equivalent. That's why we can use an ordinary formula used at direct titration to do the calculations:

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

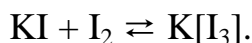
This method can help determine many oxidizing agents, e.g. Cl_2 , Br_2 , KMnO_4 , KClO_3 , CaOCl_2 , nitrites, H_2O_2 , salts of Fe(III), Cu(II), arsenic compounds (Y).

Titrant standardization in iodometry

Crystalline iodine usually contains moisture and admixtures of chlorine and bromine compounds, that's why it is purified by sublimation made up of the mixture of KI and CaO. Due to its volatility crystalline iodine can't be the initial substance and is rarely used as a primary standard. More often we usually prepare iodine solution with the concentration approximately equal to

the required one and then the exact solution concentration is established with the help of a standardized solution of sodium thiosulphate.

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

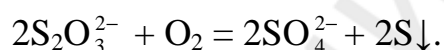


Triiodide-ion I_3^- and molecular iodine in OR reactions behave in the same way that's why in iodometric determinations the corresponding equations of the reactions are written with I_2 and not with I_3^- ion.

Sodium thiosulphate solution is prepared from $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ crystalline hydrate, the composition of which is never constant. Besides, at sodium thiosulphate dissolving there is its partial decomposition by CO_2 dissolved in water:



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

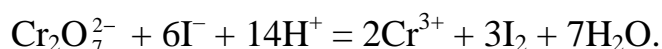


Due to sulphur precipitation the solution becomes turbid and at the bottom there is a white precipitate. To decrease the decomposition of thiosulphate-ion we should use freshly boiled and cooled water to prepare the solution. The prepared solution is left for 8–10 days and after that we should determine its concentration using the primary standard of the method.

As primary standards for the determination of $\text{Na}_2\text{S}_2\text{O}_3$ solution concentration we use potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$ or potassium iodate KIO_3 , with the help of which we can easily get by weight the solution of the known concentration.

It should be noted that sodium thiosulphate is a strong reducing agent ($e^0(\text{S}_4\text{O}_6^{2-}/2\text{S}_2\text{O}_3^{2-}) = +0.08\text{ V}$), reacts quickly and stoichiometrically with triiodide-ions with the formation of tetrathionate-ions. With many other oxidizing agents, e. g. MnO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, BrO_3^- , IO_3^- and so on, thiosulphate-ions react non-stoichiometrically. This excludes the possibility to use direct titration of oxidizing agents by $\text{Na}_2\text{S}_2\text{O}_3$ solution. That's why the determination of exact concentration of $\text{Na}_2\text{S}_2\text{O}_3$ solution using potassium dichromate or iodate as primary standard is based on the method of substitute (indirect) titration.

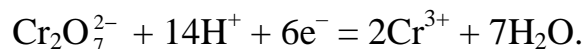
Potassium dichromate in the acidic medium reacts stoichiometrically with soluble iodates with the formation of equivalent amount of molecular iodine:



The formed molecular iodine is titrated by sodium thiosulphate solution, the exact concentration of which we have to determine. It's obvious that



as reduction reactions of dichromate-ions correspond to the half-reaction:



For dichromate-ions to react quantitatively, we use excess of KI and to increase the oxidation potential of the pair $\text{Cr}_2\text{O}_7^{2-}/2\text{Cr}^{3+}$ the reaction should take place in a strongly-acidic medium which can be created with the help of H_2SO_4 solution.

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

CONTROL OF MASTERING THE TOPIC

Writing equations of OR-reactions and determination of the direction of their passing

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

1. $\text{FeSO}_4 + \text{KMnO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \dots$
2. $\text{H}_2\text{C}_2\text{O}_4 + \text{KMnO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{CO}_2 + \dots$
3. $\text{H}_2\text{O}_2 + \text{KMnO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{O}_2 + \dots$
4. $\text{FeSO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \rightarrow \text{Cr}_2(\text{SO}_4)_3 + \dots$
5. $\text{KNO}_2 + \text{KMnO}_4 + \text{H}_2\text{O} \rightarrow \text{KNO}_3 + \dots$
6. $\text{K}_2\text{SO}_3 + \text{KMnO}_4 + \text{KOH} \rightarrow \text{K}_2\text{SO}_4 + \dots$
7. $\text{K}_2\text{SO}_3 + \text{KMnO}_4 + \text{H}_2\text{O} \rightarrow \text{K}_2\text{SO}_4 + \dots$
8. $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow \dots$
9. $\text{K}_2\text{Cr}_2\text{O}_7 + \text{FeSO}_4 + \text{H}_2\text{SO}_4 \rightarrow \dots$
10. $\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \rightarrow \dots$
11. $\text{K}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{SO}_3 + \text{H}_2\text{SO}_4 \rightarrow \dots$
12. $\text{K}_2\text{Cr}_2\text{O}_7 + \text{KI} + \text{H}_2\text{SO}_4 \rightarrow \dots$
13. $\text{H}_2\text{O}_2 + \text{KI} + \text{H}_2\text{SO}_4 \rightarrow \text{I}_2 + \dots$
14. $\text{KClO}_3 + \text{H}_2\text{O}_2 \xrightarrow{\text{pH}=7} \text{KCl} + \dots$
15. $\text{KMnO}_4 + \text{H}_2\text{O}_2 \xrightarrow{\text{pH}=7} \dots$
16. $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{S} + \text{H}_2\text{SO}_4 \rightarrow \text{S} \downarrow \dots$
17. $\text{KBrO}_3 + \text{KBr} + \text{H}_2\text{SO}_4 \rightarrow \text{Br}_2 + \dots$
18. $\text{KIO}_3 + \text{Na}_2\text{SO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{I}_2 + \dots$
19. $\text{MnSO}_4 + \text{KMnO}_4 + \text{H}_2\text{O} \rightarrow \text{MnO}_2 + \dots$

II. On basis of the values of system standard OR potentials listed below, determine which of the negatively charged ions F^- , Cl^- , Br^- , I^- can be oxidized to free halogens by manganese dioxide MnO_2 in the acidic medium (under standard conditions).

- | | |
|--|--------------------------|
| 1. $F_2 + 2e^- = 2F^-$, | $e^0 = +2.65 \text{ V.}$ |
| 2. $Cl_2 + 2e^- = 2Cl^-$, | $e^0 = +1.36 \text{ V.}$ |
| 3. $Br_2 + 2e^- = 2Br^-$, | $e^0 = +1.07 \text{ V.}$ |
| 4. $I_2 + 2e^- = 2I^-$, | $e^0 = +0.54 \text{ V.}$ |
| 5. $MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$, | $e^0 = +1.23 \text{ V.}$ |

Using method of half-reactions write the equations of possible redox processes.

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

- | | |
|---------------------------------|---|
| 1. $KMnO_4$ at $pH < 7$, | $e^0(MnO_4^- / Mn^{2+}) = +1.51 \text{ V.}$ |
| 2. $KMnO_4$ at $pH \approx 7$, | $e^0(MnO_4^- / MnO_2) = +0.59 \text{ V.}$ |
| 3. H_2O_2 at $pH > 7$, | $e^0(H_2O_2 / 2OH^-) = +1.17 \text{ V.}$ |
| 4. KIO_3 at $pH > 7$, | $e^0(IO_3^- / I^-) = +0.26 \text{ V.}$ |

TYPICAL CALCULATION TASKS

Permanganatometry

Task 1. Calculate the molar masses of the equivalents: a) Fe^{2+} ; b) $Na_2C_2O_4$; c) KI in reactions with $KMnO_4$ in the acidic medium.

Answer: a) 56 g/mol; b) 67 g/mol; c) 166 g/mol.

Task 2. To titrate 0.0244 g of $H_2C_2O_4 \cdot 2H_2O$ we used 19.5 mL of $KMnO_4$ solution. Calculate the normality of $KMnO_4$ solution.

Answer: 0.01986 mol/L.

Task 3. To titrate 25.0 mL 0.0500 N of $KMnO_4$ solution in the acidic medium we used 10.2 mL of sodium nitrite solution. How many grams of $NaNO_2$ are in 100 mL of its solution?

Answer: 0.4228 g.

Task 4. 2.50 g of hydrogen peroxide solution were diluted by water till 200 mL. To titrate 5.0 mL of the obtained solution in the acidic medium we used 20.0 mL 0.0500 N of $KMnO_4$ solution. Which is the mass fraction of H_2O_2 in the initial concentrated solution?

Answer: 27.2 %.

Task 5. We added 20.0 mL 0,1N of FeSO_4 solution to 10.0 mL of the analyzed solution of $\text{K}_2\text{Cr}_2\text{O}_7$ solution acidated by sulphuric acid. To titrate the excess of FeSO_4 we used 28.0 mL 0.0500 N of KMnO_4 solution. Calculate, how many grams of $\text{K}_2\text{Cr}_2\text{O}_7$ are in 200 mL of the analyzed solution.

Answer: 0.5884 g.

Task 6. To determine the content of calcium in blood serum it is precipitated in the form of CaC_2O_4 adding ammonium oxalate to 0.50 mL of the serum. The precipitate is filtered, washed and dissolved in sulphuric acid. The obtained solution is titrated by 0.0100 N KMnO_4 solution till the appearance of rosy colouring. Calculate the amount of calcium in milligrams per 100 mL of the serum if to titrate it we used 0.25 mL of KMnO_4 solution.

Answer: 10.02 mg.

Iodometry

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

Answer: 9.92 g.

Task 8. To titrate 20.0 mL 0,0195 N of sodium thiosulphate solution we used 20.1 mL of iodine solution. Determine the normality of iodine solution.

Answer: 0.0194 mol/L.

Task 9. To titrate the solution containing 2.5 g of technical sodium thiosulphate we used 81.5 mL 0,1 N of iodine solution. Calculate the mass fraction of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in a technical sample.

Answer: 80.85 %.

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

Answer: 0.01767 mol/L; 0.1061 mol/L.

Task 11. 0.0980 g of chemically pure $\text{K}_2\text{Cr}_2\text{O}_7$ is treated by acidated solution of potassium iodide. To titrate the emitted iodine we used 25.5 mL of sodium thiosulphate solution. Calculate the normality of $\text{Na}_2\text{S}_2\text{O}_3$ solution.

Answer: 0.07843 mol/L.

Task 12. We added 20.0 mL 0.1133 N of KMnO_4 solution to the acidated solution of potassium iodide and the emitted iodine was titrated by 25.9 mL of sodium thiosulphate solution. Calculate the normality of sodium thiosulphate solution.

Answer: 0.08749 mol/L.

Task 13. To determine the content of active chlorine we dissolved 2.5615 g of chlorinated lime in a volumetric flask of 250 mL. To titrate 5.0 mL of the solution after its treating with KI and H₂SO₄ we used 17.4 mL 0.02N of sodium thiosulphate solution. Calculate the mass fraction of active chlorine in chlorinated lime.

Answer: 24.12 %.

QUESTIONS FOR TEST SELF-CHECK
(questions with the choice of the corresponding answers
in the pair «question–answer»)

You have a list of questions (phrases) and a list of answers indicated by the letters. In each question there is only one correct answer. The letter answer can be used once, several times or not used at all. It's necessary choose the corresponding pairs «question–answer».

Questions	Answers
Which is the equivalence factor of the oxidizing agent in the following transformations: 1. $\text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+}$ 2. $\text{NO}_3^- \rightarrow \text{NO}_2^-$ 3. $\text{MnO}_4^- \rightarrow \text{MnO}_2$ 4. $\text{BrO}_3^- \rightarrow \text{Br}^-$	a) 1/2. b) 1/5. c) 1/3. d) 1/6. e) 1/4.
Which initial substances are used to standardize the following titrants: 5. KMnO_4 6. NaOH 7. $\text{Na}_2\text{S}_2\text{O}_3$ 8. H_2SO_4	a) MgSO_4 . b) $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. c) Na_2CO_3 . d) NaCl . e) $\text{K}_2\text{Cr}_2\text{O}_7$.
Which titrants are necessary for the following substances in the method of direct titration 9. $\text{Na}_2\text{C}_2\text{O}_4$ 10. NaCl 11. $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ 12. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	a) KMnO_4 . b) CH_3COOH . c) I_2 . d) HCl . e) AgNO_3 .
Which titrant pairs should be used when determining the following substances by the method of reverse titration: 13. CaCO_3 14. $\text{K}_2\text{Cr}_2\text{O}_7$ 15. Na_2SO_3 16. NH_4Cl	a) HCl and NaOH . b) I_2 and $\text{Na}_2\text{S}_2\text{O}_3$. c) CH_3COOH and NH_4OH . d) I_2 and FeSO_4 . e) KMnO_4 and FeSO_4 .

Questions	Answers
Which indicator should be used to fix the equivalence point at titration: 17. H ₂ O ₂ by KMnO ₄ solution in H ₂ SO ₄ medium 18. CH ₃ COOH by KOH solution 19. Iodine by Na ₂ S ₂ O ₃ solution 20. Ammonia solution by H ₂ SO ₄ solution	a) K ₂ CrO ₄ . b) methyl orange (pT = 4.0). c) phenolphthalein (pT= 9.0). d) starch. e) indicator is not needed.

LABORATORY WORKS ON THE TOPIC «PERMANGANOMETRY»

Laboratory work 1. Titrant standardization using a primary standard solution

Task: to standardize the titrant — KMnO₄ solution.

Aim of the work: to learn to standardize the main titrant of the method of permanganometry — KMnO₄ solution, i. e. to get the skills of making direct and nonindicator titration of reducing agents in permanganometry; to improve the skills of writing OR equations and calculation of molar masses of reducing and oxidizing equivalents; to improve the skills of making calculations of solution normality using the results of direct titration.

Reagents: titrant — KMnO₄ solution (approximate normality concentration is 0.05 mol/L); primary standard — 0,05 N Na₂C₂O₄ solution; 1 M H₂SO₄ solution — to create the medium.

Devices: one-hotplate electric cookers.

Labware: a burette with a glass tap; More's pipets, a graduated cylinder to measure H₂SO₄ solution; flasks for titration (3 pieces); funnels; a doser for pipets or a rubber spray bulb.

Course of work fulfilment

We should fill in the burette with KMnO₄ solution, the exact concentration of which is to be established, and to prepare it for operation as usual. As KMnO₄ solution has a dark colouring, zero mark on the burette and count of the volume at titration should be established and determined by the upper edge of meniscus.

We should pour 10 mL 1M of H₂SO₄ solution into the titration flask by the graduated cylinder. The content of the flask should be heated on a one-hotplate electric cooker till 80–90 °C, i. e. before the inner walls of the titration flask become misted (not to boil!) and titrate this hot reaction mixture by KMnO₄ solution. At the beginning of titration every other drop of KMnO₄ solution should be added only after the colouring of the previous drop disappears completely. Titration should be finished after appearing of pale-rosey colouring stable for 30 sec. It is necessary to repeat the titration until we get three similar (i. e. differing from each other only at 0.1 mL) results.

Using the results of titration we should calculate the normality of KMnO_4 solution as usual when using direct titration.

Report of the laboratory work should be written according to the sample given in *work 1 on the topic «Acid-base titration»*. Particular attention should be paid to writing the reaction equations with the usage of electron-ion method, the determination of equivalence factors of oxidation and reduction agents and the calculation of molar masses of their equivalents. It is also necessary to characterize the conditions of titration fulfilment.

Laboratory work 2. Determination of a substance mass in the given volume of the analyzed solution.

Task: to determine Fe^{2+} mass in the given volume of the analyzed solution of FeSO_4 (the solution volume is indicated by the teacher).

Aim of the work: to learn to use permanganatometric titration for quantitative determination of reducing agents by the method of direct titration (see Lab.work 1 for details).

Reactants: analyzed solutions of FeSO_4 (they are given by the teacher); KMnO_4 solution with the established concentration (0,05 N); 1 M of H_2SO_4 solution — to create the medium.

Laboratory ware: see Lab.work 1.

Course of work fulfilment

The burette should be filled with KMnO_4 solution as it was described in the previous work.

We should pour 10 mL 1M of H_2SO_4 solution by a graduated cylinder and 10.00 mL of the analyzed solution of FeSO_4 (by More's pipet) in the titration flask. The content of the flask should be titrated in a cold place till the appearance of pale-rosey colouring stable for 30 sec. It is necessary to repeat the titration until we get three similar (i.e. differing from each other only at 0.1 mL) results.

Using the results of titration we should calculate the normality of the analyzed solution of iron (II) salt and the mass of Fe^{2+} in the solution volume indicated by the teacher.

Report of the laboratory work should be written according to the sample given in *work 2 on the topic «Acid-base titration»*. Particular attention should be paid to writing the reaction equation with the usage of electron-ion method, the determination of equivalence factors and the calculation of molar masses of Fe^{2+} and KMnO_4 equivalents. It's necessary to characterize the conditions of carrying out the titration.

The work having been finished, KMnO_4 solution should be poured out of the burette to a container for this solution and we should rinse the burette firstly with tap and then with distilled water.

LABORATORY WORKS ON THE TOPIC «IODOMETRY»

Laboratory work 1. Titrant standardization using a primary standard solution

Task: to standardize the titrant — $\text{Na}_2\text{S}_2\text{O}_3$ solution.

Aim of the work: to learn to standardize the main titrant of the method of iodometry — $\text{Na}_2\text{S}_2\text{O}_3$ solution, i. e. to get the skills of making substitute titration of oxidizing agents in iodometry; to get the skills of calculation the normality of the solution using the results of substitution titration; to improve the skills of writing OR reaction equations using the electron-ion method and the calculation of molar masses of oxidizing and reducing agent equivalents.

Reactants: titrant — $\text{Na}_2\text{S}_2\text{O}_3$ (approximate molarity concentration 0.02 M); primary standard — 0.02 N of $\text{K}_2\text{Cr}_2\text{O}_7$ solution; KI solution with $\omega(\text{KI}) = 5\%$ — additional reducer; 1 M of H_2SO_4 solution — to create the medium; indicator — 0.5 % starch solution.

Labware: a burette; a More's pipette for $\text{K}_2\text{Cr}_2\text{O}_7$ solution; a graduated cylinder for measuring H_2SO_4 solution, graduated pipets for KI solution and starch; titration flasks (3 pieces); watch glasses; a doser for pipets or a rubber spray bulb.

Course of work fulfilment

We should fill in the burette with $\text{Na}_2\text{S}_2\text{O}_3$ solution, the exact concentration of which should be established. We should pour 10 mL 1 M of H_2SO_4 solution with the help of a graduated cylinder and 5 mL of KI solution (by a graduated pipette) into the titration flask. The solution should be colourless. Then we should pour 10.00 mL of standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution with the help of More's pipet. The flask should be closed with the watch glass and placed in the dark place for 3–5 min (for the reaction to finish). After that the emitted iodine should be quickly titrated by sodium thiosulphate solution from dark — brown till pale-yellow colouring of the solution, then we should add 1 mL of starch solution and continue slow titration vigorously shaking the content of the flask till the complete disappearance of blue colouring resulting from mixing iodine with starch (due to the presence of Cr^{3+} cations the solution will have pale blue-greyish colouring in its equivalence point).

The experiment should be continued till obtaining 3 similar (i. e. differing from each other only at 0.1 mL) results.

On basis of the titration results we can calculate the normality of $\text{Na}_2\text{S}_2\text{O}_3$ solution using the same formula of equivalence law as in the case with direct titration because:

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

Report of the laboratory work should be written according to the sample given in *work 2 on the topic «Acid-base titration»*. Particular attention should

be paid to writing the OR reaction equations which are the basis of substitution titration, to the calculation of molar masses of oxidizing and reducing agent equivalents. It's necessary to characterize the conditions of carrying out the titration.

Laboratory work 2. Determination of a substance mass in the sample

Task: to determine the mass of potassium dichromate $K_2Cr_2O_7$ weight suggested for the analysis.

Aim of the work: to learn to use iodometry for the quantitative determination of oxidizing agents, i. e. to learn to choose the titration technique for the quantitative determination of the suggested substance by the method of substitute titration in iodometry; to get the skills of calculation of the mass of the determined substance using the results of substitute titration.

Reactants: $K_2Cr_2O_7$ weight (given by the teacher to each student); titrant — $Na_2S_2O_3$ solution with the established concentration (~ 0.02 M); KI solution with $\omega(KI) = 5\%$ — auxiliary reducer; 1 M of H_2SO_4 solution — to create the medium; indicator — 0,5 % starch solution.

Labware: see Lab. work 1; additionally: graduated flask to prepare the analyzed solution from $K_2Cr_2O_7$ weight.

Course of work fulfilment

We should prepare the analyzed solution of potassium dichromate. To do this we should carry quantitatively $K_2Cr_2O_7$ weight suggested for analysis into a graduated flask (the volume of the flask is indicated by the teacher) and dissolve it in a small amount of water. Then we should add water till the mark (the last drops should be added by an eye pipet) and mix it carefully.

The burette should be filled with $Na_2S_2O_3$ solution of the known concentration.

We should pour 10 mL 1 M of H_2SO_4 solution with the help of a graduated cylinder and 5 mL of KI solution (by a graduated pipet) into the titration flask. The solution should be colourless. Then we should pour 10.00 mL of the analyzed $K_2Cr_2O_7$ solution with the help of More's pipet.

The peculiarities of titration are described in the previous work.

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

Knowing the normality of the analyzed solution the mass of $K_2Cr_2O_7$ in the suggested weight should be calculated on the following formula:

$$m(K_2Cr_2O_7) = C_N(K_2Cr_2O_7) \cdot M(K_2Cr_2O_7) \cdot f_{eqv}(K_2Cr_2O_7) \cdot V_0,$$

where V_0 — the volume of the graduated flask, i. e. the analyzed $K_2Cr_2O_7$ solution in litres.

Report of the laboratory work should be written according to the sample given in *work 2 on the topic «Acid-base titration»*. Particular attention should

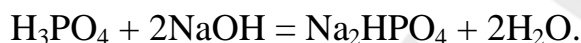
be paid to the explanation of titration method at iodometric determination of $K_2Cr_2O_7$, to writing the OR reaction equations which are the basis of the chosen method of titration and the calculation of molar masses of reducing and oxidizing agent equivalents. It's necessary to characterize the conditions of carrying out the titration and the used calculation formulas.

SOLVING OF TYPICAL TASKS

Preparation of solutions and the ways of writing their composition

Task 1. There is a solution with the mass fraction of H_3PO_4 equal to 40 % (density 1.254 g/mL). Calculate the molar concentration and normality of this solution in neutralization reactions till the formation of sodium hydrophosphate.

Solution: let's write the reaction equation:



Let's find the mass of the dissolved substance $m(H_3PO_4)$ in the definite volume of solution ($V(\text{solution})$). Mass fraction of H_3PO_4 is 40 %. This means that in 100 g of the solution there are 40 g of H_3PO_4 . Knowing the density of the solution ($\rho = 1.254 \text{ g/mL}$) we can find the volume of 100 g of the solution in litres:

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

Molar concentration and normality (or molar concentration of the equivalent) of phosphoric acid solution can be calculated using formulas (3, 5). Molar concentration:

$$C_M(H_3PO_4) = m(H_3PO_4)/M(H_3PO_4) \cdot V = 40/98 \cdot 0.08 = 5.10 \text{ (mol/L)}.$$

Normality of the solution:

$$C_N = m(H_3PO_4)/M(H_3PO_4) \cdot f_{\text{eqv}}(H_3PO_4) \cdot V = 40/98 \cdot 1/2 \cdot 0.08 = 10.20 \text{ (mol/L)}$$

or

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

Task 2. Molar mass of acetic acid in the aqueous solution is 60 %. Determine the molarity and mole fraction of the acid in the solution.

Solution: Knowing the mass fraction of CH_3COOH in the solution, we determine that in 100 g of the solution there are 60 g of CH_3COOH and 40 g of water. Let's find the amount of the dissolved acid and the solvent:

$$n(CH_3COOH) = m(CH_3COOH)/M(CH_3COOH) = 60/60 = 1 \text{ (mol)},$$

$$n(H_2O) = m(H_2O)/M(H_2O) = 40/18 = 2.22 \text{ (mol)}.$$

Let's find molality of CH_3COOH in the solution using the formula :

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

Mole fraction of CH_3COOH in the solution we'll determine using formula (6):

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

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

Solution. Let's find:

$$C(\text{K}_2\text{Cr}_2\text{O}_7) = m(\text{K}_2\text{Cr}_2\text{O}_7)/(M(\text{K}_2\text{Cr}_2\text{O}_7) \cdot V) = 0.5884/294.2 \cdot 0.2 = 0,01 \text{ (mol/L)},$$

$$C_N = N(\text{K}_2\text{Cr}_2\text{O}_7) = m(\text{K}_2\text{Cr}_2\text{O}_7)/(M(\text{K}_2\text{Cr}_2\text{O}_7) \cdot f_{\text{eqv}}(\text{K}_2\text{Cr}_2\text{O}_7) \cdot V) = 0.5884/294 \cdot 1/6 \cdot 0.2 = 0,06 \text{ (mol/L)}$$

or

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

Task 4. How many millilitres of the solution with mass fraction of H_2SO_4 equal to 40 % (density 1.30 g/mL) should be taken to prepare 500 mL 0.1 N of the H_2SO_4 solution? Equivalence factor of H_2SO_4 is $1/2$.

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

Solution: Normality of the concentrated solution of H_2SO_4 :

$$N(\text{H}_2\text{SO}_4) = n_s(\text{H}_2\text{SO}_4) / V = m(\text{H}_2\text{SO}_4)/M(\text{H}_2\text{SO}_4) \cdot f_{\text{eqv}}(\text{H}_2\text{SO}_4) \cdot V,$$

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

The volume of 100 g of H_2SO_4 solution with the mass fraction of 40 % is $V(\text{solution}) = m(\text{solution})/\rho = 100/1.30 = 76.9 \text{ (mL)}$ or 0.0769 L;

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

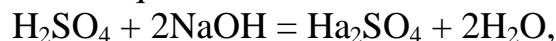
At diluting the solution the mass of the dissolved substance is unchangeable, i. e. $C_{N_1} V_1(\text{conc.}) = C_{N_2} V_2(\text{diluted})$ where C_{N_1} and C_{N_2} are the normalities (N) of two solutions and V_1 and V_2 are the volumes of the solutions. Using this formula, let's calculate the volume of the concentrated solution which should be taken to prepare 500 mL 0,1 N of H_2SO_4 solution.

$$V_1(\text{conc.}) = C_{N_2} \cdot V_2(\text{diluted})/C_{N_1}(\text{conc.}) = 0.1 \cdot 500/10.62 = 4.71 \text{ (mL)}.$$

Calculations based on the results of direct titration

Task 5. To titrate 10.0 mL 0.10 N of H_2SO_4 solution we used on the average 9.72 mL of NaOH solution. Calculate the normality of the alkaline solution.

Solution. The reaction equation at titration is the following:



where $f_{\text{eqv}}(\text{NaOH}) = 1$, $f_{\text{eqv}}(\text{H}_2\text{SO}_4) = 1/2$. According to the equivalence principle,

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

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

Let's find the normality of the alkaline solution:

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

Task 6. To titrate the solution containing 0.2490 g of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ we used 12.60 mL of hydrochloric acid. Calculate the normality of HCl solution.

Solution. The reaction equation at titration is the following:

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

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

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

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

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

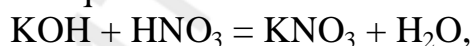
where $V(\text{HCl})$ is expressed in litres.

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

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

Task 7. How many grams of KOH are in 250 mL of the solution if to titrate 20.00 mL of this solution we use on the average 18.40 mL 0.09234 M of HNO_3 solution?

Solution: the reaction equation at titration is the following:



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

According to the equivalence principle

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

Let's find KOH mass in 250 mL (0.25L) of the solution:

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

Task 8. Calculate Na_2CO_3 mass in the solution if to titrate it in presence of methyl orange we used 22.35 mL 0.1820 N of H_2SO_4 solution.

Solution: the reaction equation at titration of Na_2CO_3 in presence of methyl orange ($pT = 4$):



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

In accordance with the equivalence principle:

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

or

$C_N(\text{H}_2\text{SO}_4) \cdot V(\text{H}_2\text{SO}_4) = m(\text{Na}_2\text{CO}_3) / M(\text{Na}_2\text{CO}_3) \cdot f_{\text{eqv}}(\text{Na}_2\text{CO}_3)$,
 where $V(\text{H}_2\text{SO}_4)$ is expressed in liters.

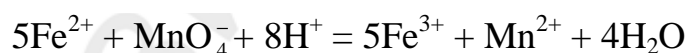
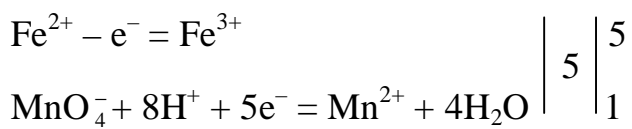
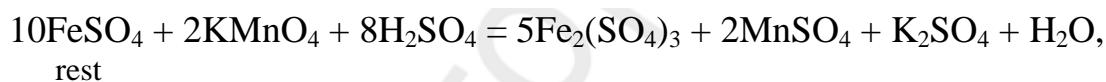
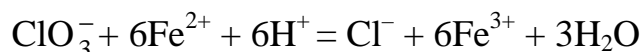
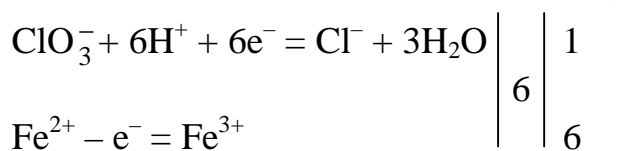
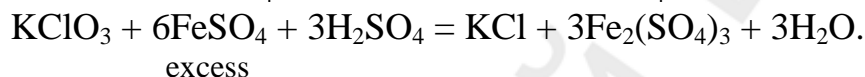
Consequently, we can find $m(\text{Na}_2\text{CO}_3)$:

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

Calculations based on the results of back titration

Task 9. We added 20.00 mL 0.1050 N of FeSO_4 solution to 10 mL of the analyzed KClO_3 solution acidated by sulphuric acid. To titrate the excess of FeSO_4 we used 12.48 mL 0.07600 N of KMnO_4 solution. How many grams of KClO_3 are in 250 mL of the analyzed solution?

Solution: in the task we used the method of back titration at quantitative determination of KClO_3 oxidizing agent in permanganometry. The process solutions: 0.1050 N of FeSO_4 and 0.07600 N of KMnO_4 . The reaction equations:



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

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

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

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

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

hence,

$$N(\text{KClO}_3) = (N(\text{FeSO}_4) \cdot V(\text{FeSO}_4) - N(\text{KMnO}_4) \cdot V(\text{KMnO}_4)) / V(\text{KClO}_3) = \\ = (0,1050 \cdot 20,00 - 0,07600 \cdot 12,48) / 10,00 = 0,1152 \text{ (mol/L)}.$$

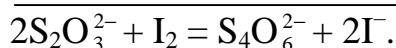
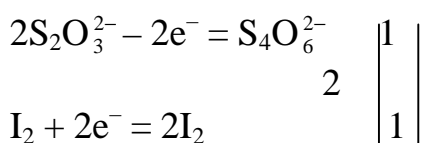
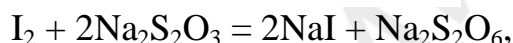
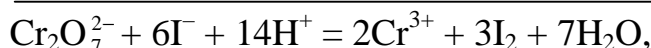
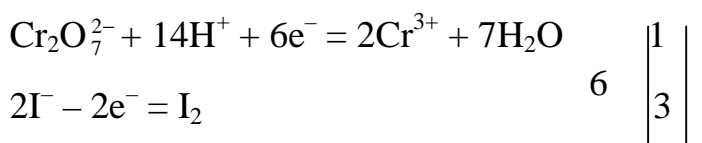
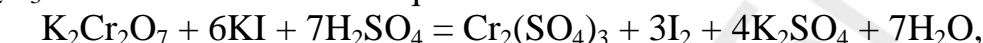
Mass of KClO_3 in 250 mL (0,25L) of the solution.

$$\begin{aligned} m(\text{KClO}_3) &= N(\text{KClO}_3) \cdot M(\text{KClO}_3) \cdot f_{\text{eqv}}(\text{KClO}_3) \cdot V(\text{KClO}_3) = \\ &= 0,1152 \cdot 122,5 \cdot 1/6 \cdot 0,25 = 0,588(\text{g}) \end{aligned}$$

Calculations based on the results of substitute titration

Task 10. In the solution containing excess of KI and acidated by sulphuric acid we added 25.00 mL 0.0500 N of $\text{K}_2\text{Cr}_2\text{O}_7$ solution. To titrate the emitted iodine we used 22.80 mL of sodium thiosulphate solution. Calculate the normality of $\text{Na}_2\text{S}_2\text{O}_3$.

Solution: in the task we used the method of substitute titration of $\text{K}_2\text{Cr}_2\text{O}_7$ oxidizing agent to standardize the main titrant of iodometric method — $\text{Na}_2\text{S}_2\text{O}_3$ solution. The reaction equation:



As we can see from the half-reactions $f_{\text{eqv}}(\text{I}_2) = 1/2$, $f_{\text{eqv}}(\text{K}_2\text{Cr}_2\text{O}_7) = 1/6$, $f_{\text{eqv}}(\text{Na}_2\text{S}_2\text{O}_3) = 1$. According to the equivalence principle, at substitution titration the amount of iodine formed in the result is equivalent to the amount of $\text{K}_2\text{Cr}_2\text{O}_7$ and to the amount of $\text{Na}_2\text{S}_2\text{O}_3$:

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

Consequently,

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

Using this expression let's find the normality concentration of $\text{Na}_2\text{S}_2\text{O}_3$ solution:

$$\begin{aligned} N(\text{Na}_2\text{S}_2\text{O}_3) &= N(\text{K}_2\text{Cr}_2\text{O}_7) \cdot V(\text{K}_2\text{Cr}_2\text{O}_7)/V(\text{Na}_2\text{S}_2\text{O}_3) = 0,0500 \cdot 25,0/22,8 = \\ &= 0.05482 \text{ (mol/L)}. \end{aligned}$$

ANSWERS FOR TESTS

Elements of titration analysis (p. 13)

1	2	3	4	5	6	7	8
d	e	c	a	e	b	b	d

Acid-base titration (p. 26)

1	2	3	4	5	6	7	8	9	10
b, d	a, b, c	a, b, c, d	b, d	a, b, c	a, c	d	a, b, c	b, d	a, c

Oxidation-reduction titration (p. 52)

1	2	3	4	5	6	7	8	9	10
d	a	c	d	b	b	e	c	a	e
11	12	13	14	15	16	17	18	19	20
d	c	a	e	b	a	e	c	d	b

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Латушко Татьяна Викторовна
Ткачѐв Сергей Викторович
Казюлевич Светлана Ричардовна
Барковский Евгений Викторович

ВВЕДЕНИЕ В ТИТРИМЕТРИЧЕСКИЕ МЕТОДЫ АНАЛИЗА

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Учебно-методическое пособие на английском языке

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