MINISTRY OF HEALTH REPUBLIC OF BELARUS GOMEL STATE MEDICAL UNIVERSITY

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INTRODUCTIN IN VOLUMETRIC ANALYSES

Laboratoru manual

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«Гомельский государственный медицинский университет, 2005 And it's hard, and it's hard, ain't it hard, good Lord - Woody Guthrie

<u>CHAPTER 1</u> **INTRODUCTIN IN VOLUMETRIC ANALYSES**

1.1. The Equivalent Law

A chemical equivalent is a real or unreal particle of a substance which may interacts with one Hydrogen atom in acid-base reactions or with on electron in Redox reactions.

The Equivalent Law: chemical substances interact and are formed in quantities, which are proportional to their equivalents.

For a reaction

 $\mathbf{a} \mathbf{A} + \mathbf{b} \mathbf{B} = \mathbf{c} \mathbf{C} + \mathbf{d} \mathbf{D}$

 $v_e(A) = v_e(B) = v_e(C) = v_e(D)$

where v_e — a quantity of an equivalent, mol

 $v_{\rm e} = \frac{m}{M_{\star}},$

where m — mass of a substances, g

M_e — an equivalent molar mass, g/mol

 $M_e = f_e \times M$,

where f_e — an equivalent factor, which is equal:

for acids: $f_e = \frac{1}{a \cdot number \cdot of \cdot hydrogen \cdot atoms \cdot substituted \cdot in \cdot a \cdot molecule}$ Examples: HCl $f_e = 1$ $H_2SO_4 f_e = 1 \text{ or } \frac{1}{2}$ $H_3PO_4 f_e = 1 \text{ or } \frac{1}{2} \text{ or } \frac{1}{3}$ for bases: $f_e = \frac{1}{a \cdot number \cdot of \cdot OH - groups \cdot substituted \cdot in \cdot a \cdot molecule}$ Examples: NaOH $f_e = 1$ Ca(OH)₂ $f_e = 1 \text{ or } \frac{1}{2}$ $Al(OH)_3 f_e = 1 \text{ or } \frac{1}{2} \text{ or } \frac{1}{3}$ for salts: $f_e = \frac{1}{a \cdot number \cdot of \cdot metall \cdot atoms \times oxidation \cdot number}$ Examples: NaCl $f_e = 1$ $Na_2SO_4 f_e = \frac{1}{2}$ $Ca_3(PO_4)_2f_e = 1/6$ for elements: $f_e = \frac{1}{oxidation \cdot number}$

Examples: $f_e(N)$ in $N_2Of_e = \frac{1}{2}$

REMEMBER!!!

 $M_{e} (H) = 1 \text{ g/mol}$ $M_{e} (O) = 8 \text{ g/mol}$ $M_{e} (H_{2}O) = 9 \text{ g/mol}$

1.2. Concentration Units

Quantitative study of a solution requires that we know its concentration, that is, the amount of solute present in a given amount of a solution. Chemists use several different concentration units, each of which has advantages as well as limitations. The choice of concentration unit is generally based on the kind of measurement made of the solution. First, though, let us examine the four most common units of concentration: percent by mass, mole fraction, molarity, and molality.

Types of Concentration Units

<u>Percent by Mass (ω)</u>. The percent by mass (also called the percent by weight or the weight percent) is defined as

percent by mass of solute =
$$\frac{\text{mass of solute}}{\text{mass of solute} + \text{mass of solvent}} \times 100\%$$

percent by mass of solute = $\frac{\text{mass of solute}}{\text{mass of solute}} \times 100\%$

or

The percent by mass has no units because it is a ratio of two similar quantities.

<u>Mole Fraction (χ).</u> The mole fraction of a component of a solution, say, com-

ponent A, is written χ_A and is defined as

mole fraction of component A = χ (A) = $\frac{\text{moles of A}}{\text{sum of moles of all components}}$

The mole fraction has no units, since it too is a ratio of two similar quantities.

<u>Molality (C_m)</u>. Molality is the number of moles of a solute dissolved in 1 kg (1000 g) of solvent — that is,

 $molality = \frac{moles of solute}{mass of solvent (kg)}$

For example, to prepare a 1 mol/kg sodium sulfate (Na_2SO_4) aqueous solution, we need to dissolve 1 mole (142.0 g) of the substance in 1000 g (1 kg) of water. Depending on the nature of the solute-solvent interaction, the final volume of the solution will be either greater or less than 1000 mL. It is also possible, though very

unlikely, that the final volume could be equal to 1000 mL.

<u>Molarity (C_{M})</u>. Molarity is defined as the number of moles of solute in 1 liter of solution; that is,

molarity = <u>moles of solute</u> liters of solution

Thus, molarity has the units of mol/L or M.

<u>Normality (C_N)</u>. Normality is defined as the number of equivalent moles of a solute in 1 liter of a solution; that is,

Normality = $\frac{\text{equivalent moles of solute}}{\text{liters of solution}}$ Thus, normality has the units of mol/L or N.

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

Titer = $\frac{\text{mass of solute}}{\text{liters of solution}}$ Thus, normality has the units of g/ml. Concentration units are interconvertible. $\mathbf{C}_{\mathbf{M}} = \frac{1000 \times T}{\text{molar} \cdot \text{mass} \cdot \text{of } \cdot \text{solute}}$

 $\mathbf{C}_{\mathbf{M}} = \frac{10 \times density \cdot of \cdot so \ln \times percent \cdot by \cdot mass(\%)}{molar \cdot mass \cdot of \cdot solute}$

percent by mass of solute (%) = $\frac{molarity \times molar \cdot mass \cdot of \cdot solute}{10 \times density \cdot of \cdot so \ln}$

 $\mathbf{C}_{\mathbf{M}} = \mathbf{C}_{N} \times \mathbf{f}_{e}$ $\mathbf{C}_{\mathbf{N}} = \frac{M}{f_{e}}$ $\mathbf{C}_{\mathbf{N}} = \frac{1000 \times T}{equivalent \cdot molar \cdot mass \cdot of \cdot solute}$

1.3. Laboratory Work № 1

PREPARING OF DILUTE SOLUTIONS FROM CONCENTRATED SOLUTIONS

We frequently find it convenient to prepare a less concentrated solution from a more concentrated solution. The procedure for this preparation is called dilution. Suppose that we want to prepare 1 liter of a 0.400 M KMnO_4 solution from a solu-

tion of 1.00 M KMnO₄. This requires the use of 0.400 mole of KMnO₄ from the 1.00 M KMnO₄ solution. Since there is 1.00 mole of KMnO₄ in 1 liter, or 1000 mL, of a 1.00 M KMnO₄ solution, there is 0.400 mole of KMnO₄ in 0.400 X 1000 mL, or 400 mL, of the same solution:

1.00 mol	0.400 mol
= 1000 mL solution	400 mL solution

Therefore, we must withdraw 400 mL from the 1.00 M KMnO₄ solution and dilute it to 1000 mL by adding water (in a 1-liter volumetric flask). This method gives us 1 liter of the desired solution of 0.400 M KMnO₄. Such concentrated solutions (that is, the 1 M KMnO₄ solution) are often stored and used repeatedly over a prolonged period of time. They are stored as the "stock" of a chemical stockroom. For this reason, they are called stock solutions.

In carrying out a dilution process, it is useful to remember that adding more solvent to a given amount of the stock solution changes (decreases) the concentration of the solution without changing the number of moles of solute present in the solution; that is,

moles of solute before dilution = moles of solute after dilution

Because all the solute comes from the original stock solution, we can conclude that



Fig. 1. The dilution of a more concentrated solution in a less concentrated one does not change the total number of moles of solute

<u>*TASK*</u>: to prepare 100 mL of 6% by mass hydrochloric acid solution from a more concentrated one.

You'll fulfill this laboratory work according for the following plan:

1) determine a density of a concentrated solution using a set of densitometers;

2) find the value of a percent by mass concentration using a reference-book;

3) compute a volume of a concentrated solution necessary for a dilute solution preparing;

4) prepare a dilute solution and determine its density;

5)calculate an absolute (D) and a relative (D_o) errors of experiments:

$$D = \rho (exp) - \rho(table)$$
$$D_o = \frac{|D|}{\rho(table)} \times 100\%$$

1.4. Problems

1.The equal volumes of hydrogen gas were released from an acid at the result of it's interaction with 0.69 g of Ca and 1.13 g of Zn. Calculate M_e of Zn if M_e of Ca is 20 g/mol.

ANSWER:

Write the Equivalent Law for a given chemical reaction: $v_e(Ca) = v_e(Zn)$

$$\frac{m(Ca)}{M_e(Ca)} = \frac{m(Zn)}{M_e(Zn)}$$
$$M_e(Zn) = \frac{m(Zn) \times M_e(Ca)}{m(Ca)} = \frac{1.13 \times 20}{0.69} = 32.7g / mol$$

2. 9 g of an acid were completely neutralized by 8 g of NaOH. Calculate the equivalent molar mass of an acid.

ANSWER:

Write the Equivalent Law for a given chemical reaction: $v_e(acid) = v_e(NaOH)$ $\frac{m(acid)}{M_e(acid)} = \frac{m(NaOH)}{M_e(NaOH)}$, where M_e (NaOH) = M (NaOH) × f_e = 40 g/mol M_e (acid) = $\frac{m(acid) \times M_e(NaOH)}{m(NaOH)} = \frac{9 \times 40}{8} = 45g / mol$

3. A sample of 0.892 g of potassium chloride (KC1) is dissolved in 54.6 g of water. What is the percent by mass of KC1 in this solution?

ANSWER

percent by mass of KC1 = $\frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$

percent by mass of KC1 = $\frac{0.892 \text{ g}}{0.892 \text{ g} + 54.6 \text{ g}} \times 100\% = 1.61\%$

4. A chemist prepared a solution by adding 200.4 g of pure ethanol (C_2H_5OH) to 143.9 got water. Calculate the mole tractions of these two components. The molar masses of ethanol and water are 46.02 g and 18.02 g, respectively.

ANSWER

The number of moles of C_2H_5OH and H_2O present are

moles of C₂H₅OH = 200.4 g C₂H₅OH ×
$$\frac{1 \text{ mol } C_2H_5OH}{46.02 \text{ g } C_2H_5OH}$$
 = 4.355 mol C₂H₅OH
moles of H₂O = 143.9 g H₂O × $\frac{1 \text{ mol } H_2OH}{18.02 \text{ g } H_2O}$ = 7.986 mol H₂O

In a two-component system made up of A and B molecules, the mole fraction of A is given by

 $\chi = \frac{\text{moles of A}}{\text{sum of moles of A and}}$

Using this equation we can write the mole fractions of ethanol and water as

$$\chi(C_2H_5OH) = \frac{4.355 \text{ mol}}{(4.355 + 7.986)} = 0.3529$$

$$\chi(H_2O) = \frac{7.986 \text{ mol}}{(4.355 + 7.986)} = 0.6471$$

By definition, the sum of the mole fractions of all components in a solution must be 1.

Thus; χ (C₂H₅OH) + χ (H₂O) = 0.3529 + 0.6471 = 1.0000.

5. Calculate the molality of a sulfuric acid solution containing 24.4 g of sulfuric acid in 198 g of water. The molar mass of sulfuric acid is 98.08 g.

ANSWER

From the known molar mass of sulfuric acid, we can calculate the molality in two steps. First we need to find the number of grams of sulfuric acid dissolved in 1000 g (1 kg) of water. Next we must convert the number of grams into the number of moles. Combining these two steps we write

molality = $\frac{\text{moles of solute}}{\text{mass of solvent (kg)}}$

$$molality = \frac{24.4 \text{ g } \text{H}_2 \text{SO}_4}{198 \text{ g } \text{H}_2 0} \times \frac{1000 \text{ g } \text{H}_2 0}{1 \text{ kg } \text{H}_2 0} \times \frac{1 \text{ mol } \text{H}_2 \text{SO}_4}{98.08 \text{ g } \text{H}_2 \text{SO}_4}$$

= 1.26 mol /kg

1.5. Exercises for the self – control

1. Calculate f_e and M_e of H_3PO_4 in the following reactions: $H_3PO_4 + NaOH = NaH_2PO_4 + H_2O$ $H_3PO_4 + 2 NaOH = Na_2HPO_4 + 2 H_2O$ $H_{3}PO_{4} + 3 NaOH = Na_{3}PO_{4} + 3 H_{2}O$

2. Calculate f_e and M_e of Fe(OH)₃ in the following reactions:

 $Fe(OH)_3 + HCl = Fe(OH)_2Cl + H_2O$

 $Fe(OH)_3 + 2 HCl = FeOHCl + 2 H_2O$

 $Fe(OH)_3 + 3 HCl = FeCl_3 + 3 H_2O$

3. Calculate zink equivalent molar mass if 1.168 g of it displace 438 10^{-6} L under 17°C and 98.64 kPa.

ANSWER: 32.62 g/mol.

4. The oxygen content in a metal oxide is 28.57 % by mass. The fluorine content in its fluoride is 48.72 % by mass. Compute an equivalent molar mass of the fluorine.

ANSWER: 19 g/mol.

5. Interaction of 5.95 g of a substance and 2.75 g of hydrochloric acid gives 4.4 g of a salt. Calculate the equivalent molar mass of a given substance and an obtained salt.

ANSWER: 36.5 g/mol, 79 g/mol, 59 g/mol.

6. The reduction of 2.32 g of a tungsten oxide runs with 0.54 g of water elimination. Calculate the equivalent molar mass of a given oxide.

ANSWER: 38.7 g/mol.

7. 0.15 g of a metal displaces 0.367 g of nickel from a nickel salt or 140 mL of hydrogen gas (normal conditions) from an acid solution. Compute the equivalent molar masses of a metal and nickel.

ANSWER: 12 g/mol, 29.4 g/mol.

8. Calculate the percent by mass of the solute in each of the following aqueous solutions:

a) 5.5 g of NaBr in 78.2 g of solution;

b) 31 g of KCl in 152 g of water.

9. A solution is prepared by mixing 62.6 ml of benzene (C_6H_6) with 80.3 ml of toluene (C_7H_8). Calculate the mole fractions of these two components. The densities are: benzene, 0.879 g/cm³; and toluene, 0.867 g/cm³.

10. Calculate the molality of each of the following solutions:

a) 14.3 g of sucrose $(C_{12}H_{22}O_{11})$ in 676 g of water

b) 7.2 mole of ethylene glycol ($C_2H_6O_2$) in 3546 g of water.

11. Calculate the molalities of each of the following aqueous solutions:

c) 1.22 M NaCl solution (density of solution = 1.12 g/ml)

d) 0.87 M NaOH solution (density of solution = 1.19 g/ml)

e) 5.24 M NaHCO₃ solution (density of solution = 1.19 g/ml)

12. The concentrated sulfuric acid we use in the laboratory is 98 percent H_2SO_4 by mass. Calculate the molality and molarity of the acid solution. The density of the solution is 0.982 g/ml.

13. Calculate the mole fractions, molality and molarity of NH_3 for a solution of 30 g of NH_3 in 70 g of water. He density of the solution is 0.982 g/ml.

14. The density of an aqueous solution containing 10 percent of ethanol (C_2H_5OH) by mass is 0.984 g/ml.

a) Calculate the molality of this solution;

b) Calculate the molarity of this solution:

c) What volume of the solution would contain 0.125 mole of ethanol?

15. It is estimated that 1 ml of seawater contains about 4×10^{-12} g of gold. The total volume of ocean water is 1.5×10^{21} l. Calculate the total amount of gold present in seawater. With so much gold out there, why hasn't someone become rich by mining gold from the ocean?

1.6. Static treatment of experimental data

Introduction: Two important, though often neglected, parts of an analysis are error analysis and correct results reporting. Results should always be reported along with some estimation of the errors involved. The best way to do this is to report the most likely value along with a **confidence interval**. The confidence interval gives the range of values thought to contain the "true" value. The statistical treatment of data involves basing the error estimation on firm theoretical principles. This laboratory exercise on treatment of data should help you understand and apply these principles.

Classification of errors

Two basic classes of error occur in measurements; <u>systematic</u> and <u>random</u>. <u>Systematic errors</u> have a determinate origin. Determinate means that there is cause for the error, and that the error itself can be determined by performing an auxiliary measurement. Though possible, it is more often the case that determinate errors are not recognized until it is too late to make the auxiliary measurement. Systematic errors produce measurements that are either consistently high or low, relative to the "true" value. These errors are always in the same direction and are often of the same magnitude. An example of this is a contaminant on a balance pan that always causes measured weights to be too high. <u>Random errors</u> are indeterminate in origin and cause a measured quantity to fluctuate around a central value. Indeterminate means that one is not able to determine the error by an auxiliary measurement, just as one cannot determine the outcome of flipping a (unbiased) coin prior to the actual event. Random errors vary in direction and magnitude from measurement to measurement.

The size of the error is often independent of measurement magnitude. These types of errors are called <u>constant errors</u>. With constant errors, there is no relationship between, or correlation, measurement and error magnitude. The constant error becomes less significant as the magnitude of the measurement increases. On the other hand, the error may increase with the magnitude of the measurement. In this case, the errors are called <u>proportional errors</u>. In this case increasing the sample size does not diminish the significance of the error.

Central tendency. When reporting central tendency for a series of measurements, we often use the <u>mean</u> or <u>average value</u>. The symbol for the mean is the variable with a line over the top. The formula for the mean, for example of x, is

$$\bar{x} = \frac{1}{N} \sum_{i=1}^{N} x_i$$

For example, an average value of KOH mass is:

$$\overline{m}(KOH) = \frac{m_1 + m_2 + m_3}{3}$$

Measurement variance

The formula for <u>measurement variance</u>, s^2 , is

$$s^{2} = \frac{d_{1}^{2} + d_{2}^{2} + d_{3}^{2}}{n \times (n-1)}$$

where d is a deviation from an average value. In our experiment:

$$d_1 = m_1 - \overline{m}(KOH),$$

$$d_2 = m_2 - \overline{m}(KOH),$$

$$d_3 = m_3 - \overline{m}(KOH),$$

where n — a number of parallel experiments.

Measurement standard deviation

The <u>measurement standard deviation</u> is more often used to indicate precision or probable error. The greater the standard deviation, the less precise the data. The measurement standard deviation is simply related to the measurement variance through

 $S = \sqrt{S^2}$

where s^2 — measurement variance

Confidence intervals

Clearly, the greater the "true" standard deviation, the greater the range over which 95% of the measurements will be. For example, if the "true" mean is 25.000 g, and the "true" standard deviation is 0.5102 g, then 95% of the measurements should be between 25 ± 1 g. Put another way, one is 95% confident that a single measurement will be within the 25 ± 1 g range. For this case, ±1 g is the <u>confidence interval</u>, or range, at a 95% <u>confidence level</u>. If, on the other hand, the "true" standard deviation was 0.05102 g, then the one would state that they were 95% confident of a single measurement would be in the range or 25.0 ± 0.1 g. The smaller standard deviation results in a smaller confidence interval. In general, the fewer the measurements, the less the confidence level that can be assigned to a particular interval. Similarly, fewer measurements also means larger confidence intervals for a given confidence level.

The formula for the <u>confidence interval</u> of a determined number is:

$$\varepsilon_{\alpha} = t \times s$$
,

where t is the Student's-*t* number which indicates probabilities that the mean found from a finite number of measurements will differ from the "true" mean by a given amount. where *t* is the Student's-*t* number. One looks up *t* in a table N_{2} 4 for a given confidence and number of degrees-of-freedom (n-1).

Table 1

Degrees of Freedom	50%	90%	95%	99%
1	1.000	6.314	12.71	63.66
2	0.816	2.920	4.303	9.925
3	0.765	2.353	3.182	5.841
4	0.741	2.132	2.776	4.604
5	0.727	2.015	2.571	4.032
6	0.718	1.943	2.447	3.707
7	0.711	1.895	2.365	3.500
8	0.706	1.860	2.306	3.355
9	0.703	1.833	2.262	3.250
10	0.700	1.812	2.228	3.169
20	0.687	1.725	2.086	2.845
infinite	0.674	1.645	1.960	2.576

Student's-*t* **number** (Student's-*t* Values at Common Confidence Levels)

The result of an experimental work must be given in a following way:

$$\mathbf{x} = \overline{X} \pm \mathbf{E}_{\alpha}$$

In the experiment for KOH mass determination an answer ought to be represented as follows:

$$m (KOH) = \overline{m} (KOH) \pm \varepsilon_{\alpha}$$

1.7. The Rules of Significant figures

In one number there may be significant and insignificant figures. All figures from 1 to 9 are significant. So in a number **517** there are **3** significant figures.

Zeroes before these figures are insignificant figures.

In a number 0.00517 there are 3 significant figures.

Zeroes between and after these figures are also significant:

In a number **0.5070** there are **4** significant figures.

In multiplication and division a number of significant figures in the result is determined by the original number that has the smallest quantity of significant figures.

<u>CHAPTER 2</u> ACID — BASE TITRATION

2.1. Theoretical bases of acid-base titration

Volumetric analyses (titration method) are used for determination of a substance concentration in an analyzed solution. It is based on comparison of volumes of two solutions: an analyzed solution and a solution with a given concentration (a titrant).

Acid-base titration is one of the titration methods based on a neutralization reaction:

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

This method gives an opportunity to analyze solutions of acids, bases and salts which undergo hydrolysis. It is widely used in medicine for gastric juice and other biological liquids analyses.

Quantitative studies of acid-base neutralization reactions are most conveniently carried out using a procedure known as **titration**. Titrations are a form of quantitative volumetric analysis. In a titration, two substances in solution that react chemically with each other are combined until a given point in the reaction is reached. Usually, one of the solutions is of unknown concentration. Since the stoichiometry of the reaction is known, it is possible to determine the concentration of the unknown by performing appropriate calculations in volumetric analysis. Thus, titrations are done to accurately determine the concentration of a solution by having the solution react in a known chemical process.

In a titration experiment, a solution of accurately known concentration, called a titrant, is added gradually to another solution of unknown concentration, until the chemical reaction between the two solutions is complete. In other words, titration is fulfilled up to the equivalence or end point.

If we know the volumes of the titrant and unknown solutions used in the titration, and the concentration of the titrant, we can calculate the concentration of the unknown solution.

There two types of titrants in volumetric analyses: primary and secondary. **Primary titrants (standard solutions)** are prepared from so-called standard substances, which answer the following requirements:

they must be pure for analyses;

 \succ stable in pure state and in solutions;

> there chemical formula ought to coincide with their content.

Borax Na₂B₄O₇ · 10 H₂O, oxalic acid H₂C₂O₄ · 2 H₂O and succinic acid H₂C₄H₄O₄ are used for this purpose in acid-base titration.

Secondary titrants (working solutions) accurate concentration is measured by their titration against standard solutions. This analytical procedure is known as standardization. Solutions of hydrochloric and sulfuric acids, such hydroxides as NaOH and KOH are widely used as secondary titrants in acid-base titration.

The end point or equivalence point in an acid-base titration is signaled by a

change in the color of an acid-base indicator.

Acid-base **indicators** are usually weak organic acids or bases that have distinctly different colors in acidic and basic media. **Table 2**

Color Indicator	In acid	In base	pH rage*
Thymol blue	Red	Yellow	1.2-2.8
Bromophenol blue	Yellow	Bluish pur-	3.0-4.6
-		ple	
Methyl orange	Orange	Yellow	3.1-4.4
Methyl red	Red	Yellow	4.2-6.3
Chlorophenol blue	Yellow	Red	4.8-6.4
Bromothymol blue	Yellow	Blue	6.0–7.6
Cresol red	Yellow	Red	7.2-8.8
Phenolphthalem	Color-	Reddish pink	8.3-10.0
	less		

Some common acid-base indicators

* The pH range is defined as the range over which the indicator changes from the acid color to the base color.

One commonly used indicator is phenolphthalein, which is colorless in acidic and neutral solutions but reddish pink in basic solutions. At the equivalence point, all the acids present have been neutralized by the added NaOH and the solution is still colorless. However, if we add just one more drop of NaOH solution from the buret, the solution will immediately turn reddish pink just because the solution is now basic.

In analytical practice methyl orange and phenolphthalem are used when strong acids are titrated against strong basses; phenolphthalem – when weak acids are titrated against strong bases; methyl orange - when weak bases are titrated against strong acids.

2.2. Laboratory work № 2

ACID-BASE TITRATION

You will use the following chemical devices: burettes, pipettes, finals, volumetric flasks, flasks for titration. (Fig.2)



Fig. 2. Some common measuring devices found in a chemistry laboratory.

2.2.1. Experiment № 1

Standardization of hydrochloric solution against borax primary titrant

Reagents: borax standard solution, working solution of hydrochloric acid, potassium hydroxide solution, methyl orange and phenolphthalem solutions, distilled water.

Standardization of hydrochloric solution is fulfilled by its titration against borax standard solution. This procedure is based on the following chemical reaction:

 $Na_2B_4O_7 + 2 HCl + 5 H_2O \rightarrow 2 NaCl + 4 H_3BO_3$

Presence of H_3BO_3 gives weak acid media to a solution in the end point of a titration. Due to this **methyl orange** is the most valid acid-base indicator for an end point fixation.

Fulfill an experiment in a following order:

1) take an analytical pipette and pour 10 mL of borax solution into every flask for titration;

2) add two drops of methyl orange into each flask;

3) pour hydrochloric solution into the buret up to the zero mark;

4) titrate borax solution against hydrochloric acid up to the endpoint when yellow color of an initial solution turns red after one drop of hydrochloric acid addition;

5) repeat such a titration three times; the obtained results must not differ greatly from each other;

6) write out the obtained data in to the table N_{2} 3

Table 3

The results of borax solution titration against hydrochloric acid

N⁰	Volume of Na ₂ B ₄ O ₇ , mL	Volume of HCl, mL	C _N (HCl), mol/L	T (HCl), g/mL
1	10,0			
2	10,0			
3	10,0			

7) calculate an average volume of HCl:

$$V_{av}$$
 (HCl) = $\frac{V_1 + V_2 + V_3}{3}$

8) calculate normality (C_N) and a titer (T) of the HCl working solution:

 $C_N(HCl) \times V(HCl) = C_N(Na_2B_4O_7) \times V(Na_2B_4O_7)$

$$C_{N}(HCl) = \frac{C_{N}(Na_{2}B_{4}O_{7}) \times V(Na_{2}B_{4}O_{7})}{V_{av.}(HCl)}$$
$$T(HCl) = \frac{C_{N}(HCl) \times M_{e}(HCl)}{1000}$$

9) Write out the results of the experiment in to the table N_{2} 3.

2.2.2. Experiment № 2

Determination of KOH mass in a given solution

Calculate the mass of KOH in its solution by its titration against a working HCl solution. This procedure is based on the following chemical reaction:

$$KOH + HCl \rightarrow KCl + H_2O$$

The acid-base indicator is phenolphthalem.

Fulfill an experiment in a following order:

1) Take a volumetric flask with KOH solution of unknown concentration;

2) Take a pipet and pour 10 mL of KOH solution into every flask for titration;

3) Add two drops of phenolphthalem into each flask;

4) Pour hydrochloric acid solution into the buret up to the zero mark;

5) Titrate KOH solution against hydrochloric acid up to the endpoint when reddish pink color of an initial solution turns colorless after one drop of hydrochloric acid addition;

6) Repeat such a titration for three times; their results must not differ greatly from each other;

7) Write out the obtained data in to the table N_{2} 4

Table 4

№	Volume of KOH, mL	Volume of HCl, mL	C _N KOH, mol/L	T (KOH), g/mL	m (KOH), g
1	10,0				
2	10,0				
3	10,0				

The results of KOH solution titration against hydrochloric acid

8) Calculate C_N and T of the KOH solution:

 $C_N(HCl) \times V(HCl) = C_N(KOH) \times V(KOH)$

$$C_{N}(KOH) = \frac{C_{N}(HCl) \times V(HCl)}{V(KOH)}$$
$$T(KOH) = \frac{C_{N}(KOH) \times M_{e}(KOH)}{1000}$$

9) Calculate the mass of KOH, using the following formula:

$$m (KOH) = T (KOH) \times V (KOH),$$

where V (KOH) = 50 mL

10) Make a statistic treatment of experimental data.

2.3. Problems

1. How many milliliters (mL) of a 0.610 M NaOH solution are needed to completely neutralize 20.0 mL of a $0.245 \text{ M H}_2\text{SO}_4$ solution?

ANSWER:

 $2 \text{ NaOH } (aq) + H_2 SO_4 (aq) = Na_2 SO_4 (aq) + 2 H_2 O (L)$

Write the Equivalent Law:

 $v_e(NaOH) = v_e(H_2SO_4)$

$$C_{\rm N} = \frac{\text{equivalent moles of solute } v_{\rm e}}{\text{liters of solution V (L)}}$$

Since

 C_N (NaOH) × V (NaOH) = C_N (H₂SO₄) × V (H₂SO₄)

V (NaOH) =
$$\frac{V (H_2SO_4) \times C_N (H_2SO_4)}{C_N (NaOH)}$$

$$C_{N} (H_{2}SO_{4}) = C_{M} (H_{2}SO_{4}) / f_{e} (H_{2}SO_{4})$$
$$C_{N} (H_{2}SO_{4}) == 0.49 \text{ N.}$$
$$V (NaOH) = \frac{20.0 \times 0.49}{0.610} = 16.07 \text{ mL}$$

2. A 12.5 mL volume of 0.5000 M H_2SO_4 neutralizes 50.0 mL of KOH. What is the normality of KOH solution?

ANSWER:

2 KOH (aq) + H₂SO₄ (aq) = K₂SO₄ (aq) + 2 H₂O (L) Write the Equivalent Law: $v_e(KOH) = v_e(H_2SO_4)$ $C_N = \frac{\text{equivalent moles of solute } v_e}{\text{liters of solution } V}$ Since $C_N (KOH) \times V (KOH) = C_N (H_2SO_4) \times V (H_2SO_4)$ $C_N (KOH) = \frac{V (H_2SO_4) \times C_N (H_2SO_4)}{V (KOH)}$ $C_N (H_2SO_4) = C_M (H_2SO_4) / f_e (H_2SO_4)$ $C_N (H_2SO_4) = 1.000 \text{ N.}$ $V (NaOH) = \frac{12.5 \times 1.000}{50.0} = 0.250 \text{ N.}$

2.4. Exercises for the self control

1. Calculate the volume in mL of a 1.420 M NaOH solution required to titrate the following solution;

a) 25.00 mL of a 2.430 M HC1 solution;

b) 25.00 mL of a. 4.500 M H₂SO₄ solution;

c) 25.00 mL of a 1.500 M H₃PO₄ solution.

2. Acetic acid (CH₃COOH) is an important ingredient of vinegar. A sample of 50.0 mL of commercial vinegar is titrated against a 1.00 M NaOH solution. What is the concentration (in C_M) of acetic acid present in the vinegar if 5.75 mL of the base were required for the titration?

3. What volume of a 0.50 M KOH solution is needed to neutralize completely each of the following?

a) 10.0 mL of a 0.30 M HC1 solution;

b) 10.0 mL of a 0.20 M H₂SO₄ solution;

c) 15.0 mL of a 0.25 M H_3PO_4 solution.

4. Calculate the mass of H_3PO_4 if its solution was neutralized by 25.00 mL of 0.2 N. KOH solution.

5. Define acid-base titration, standard solution, and equivalence point.

6. Describe the basic steps involved in acid-base titration. Why is this technique of great practical value?

7. How does an acid-base indicator work?

<u>CHAPTER 3</u> REDOX TITRATIONS

3.1. General concepts of redox reactions

Oxidation-Reduction Reactions (redox reaction) — a reaction in which there is either a transfer of electrons or a change in the oxidation numbers of the atoms in substances taking part in the reaction.

Oxidation-reduction reactions are very much a part of the world around us. They range from combustion of fossil fuels to the action of household bleaching agents. Most metallic and nonmetallic elements are obtained from their ores by the process of oxidation or reduction. Most biochemical reactions are reactions of this type; they serve as the main source of energy for our bodies: for example, cells in your body derive energy through redox processes, and many essential substances such as vitamin C are biologically degraded by oxidation. This section will deal with some basic definitions, types of oxidation-reduction reactions, and a method for balancing the equations representing these reactions.

Oxidation number (also called **oxidation state**) refers to the number of charges an atom would have in a molecule (or an ionic compound) if electrons were transferred completely.

The following rules help us assign the oxidation number of elements.

1. In free elements (that is, in uncombined state), each atom has an oxidation number of zero. Thus each atom in H_2 , Br_2 , Na, Be, K, O_2 , P_4 , and S_8 has the same oxidation number: zero.

2. For ions composed of only one atom, the oxidation number is equal to the charge on the ion. Thus Li^+ has an oxidation number of +1;

 Ba^{2+} ion, +2; Fe^{3+} ion +3; and so on. All alkali metals have an oxidation number of +1, and all alkaline earth metals have an oxidation number of +2 in their compounds. Aluminum always has an oxidation number of +3 in all its compounds.

3. The oxidation number of oxygen in most compounds (for example, MgO and H_2O) is -2, but in hydrogen peroxide (H_2O_2) and peroxide ion ($O_2^{2^-}$), its oxidation number is -1.

4. The oxidation number of hydrogen is +1, except when it is bonded to metals in binary compounds (that is, compounds containing two elements). For example, in LiH, NaH, and CaH₂, its oxidation number is -1.

5. Fluorine has an oxidation number of -1 in *all* its compounds. Other halogens (Cl, Br, and I) have negative oxidation numbers when they occur as halide ions in their compounds. When combined with oxygen, for example in oxoacids and oxoanions, they have positive oxidation numbers.

6. In a neutral molecule, the sum of the oxidation numbers of all the atoms must be zero. In a polyatomic ion, the sum of oxidation numbers of all the elements in the ion must be equal to the net charge of the ion. For example, in the ammonium ion, NH_4^+ , the oxidation number of N is -3 and that of H is +1. Thus the sum of the oxidation numbers is -3 + 4 (+1) = +1, which is equal to the net charge of the ion.

3.1.1. Theory of Redox Reactions

(1914, Pisardjevsky)

1) Reducing agent loses electrons, this process is known as oxidation.

2) Oxidizing agent gains electrons, this process is known as reduction.

3) Oxidation and reduction always refer together.

The most important reducing agents are:

 \blacktriangleright metals, some nonmetals (H₂', C);

➤ some oxides (CO, NO, N₂O, SO₂);

➤ some acids (H₂S, H₂SO₃, HCL, HBr, HI);

- \triangleright salts of these acids;
- most organic compounds.

The most important oxidizing agents are: ➤ some nonmetals: O₂, O₃, F₂, CL₂, Br₂, I₂; ➤ H₂SO₄ (concentrated), HNO₃; ➤ some salts (KMnO₄, K₂Cr₂O₇, K₂CrO₄, FeCl₃, CuCl₂).

3.1.2. Types of Redox Reactions:

> Oxidizing and reducing agents are different substances For example:

$$\begin{array}{c} 2Ca(s) + O_2(g) \rightarrow 2CaO(s) \\ red \quad ox \end{array}$$

> Oxidizing and reducing agents are atoms in a molecule of a substance. For example:

$$2\mathrm{KNO}_3 \rightarrow 2\mathrm{KNO}_2 + \mathrm{O}_2$$

 \succ A disproportionation reaction, in which an element in one oxidation state is both oxidized and reduced. For example:

$$2 H_2O_2 (aq) \rightarrow 2 H_2O (L) + O_2 (g)$$

3.1.3. Balancing Oxidation-Reduction Equations

So far we have discussed several fairly simple types of redox reactions. Equations representing these reactions are relatively easy to balance. However, in the laboratory we often encounter more complex redox reactions, reactions that invariably involve oxoanions such as chromate $(CrO_4^{2^-})$, dichromate $(Cr_2O_2^{2^-})$, permanganate (MnO_4) , nitrate (NO_3^{-}) , and sulfate $(SO_4^{2^-})$. There are some special techniques for handling redox reactions. They are known as an **electron balance method** and an **ion-electron (half reaction) method**.

Electron balance method is based on comparison of atoms' oxidation numbers in reactants' and products' molecules. It may be used for balancing of any chemical reaction. For example:

$$Mn^{+4}O_{2}^{-2} + 4 H^{+1}Cl^{-1}(conc.) \rightarrow Mn^{+2}Cl^{-1}_{2} + Cl^{0}_{2} + 2 H^{+1}_{2}O^{-2}$$

$$Mn^{+4} + 2e^{-} \rightarrow Mn^{+2} \quad 1 \quad f_{e} = 1/2$$

$$2 Cl^{-1} - 2e^{-} \rightarrow Cl_{2}^{0} \quad 1 \quad f_{e} = 1/1$$

The coefficients are used to equalize the number of gained and loosed electrons.

Ion-electron (half reaction) method may be applied to balance redox reactions, which run in aqueous solutions.

In this approach, the overall reaction is divided into two half-reactions, one for oxidation and one for reduction. Each half-reaction is balanced separately and then added to produce the overall balanced equation.

In half-reactions:

Strong electrolytes, which are soluble in water, are written as ions;

> Weak electrolytes, nonelectrolytes and insoluble electrolytes are written as molecules;

> For reactions in acidic medium, add H_2O to balance the O atoms and H+ to balance the H atoms.

> For reactions in a basic medium, add OH^- ions to balance the O atoms and H_2O molecules + to balance the H atoms.

Suppose we are asked to balance the equation showing the oxidation of Fe^{2+} to Fe^{3+} ions by dichromate ions ($Cr_2O_7^{2-}$) in an acidic medium. The $Cr_2O_7^{2-}$ is reduced to Cr^{3+} ions. The following steps will help us accomplish this task.

Step 1. Write the skeletal equation for the reaction in ionic form. Separate them into two half-reactions:

$$\operatorname{Fe}^{2^+} + \operatorname{Cr}_2\operatorname{O}_7^{2^-} \longrightarrow \operatorname{Fe}^{3^+} + \operatorname{Cr}^{3^+}$$

The equations for the two half-reactions are

Oxidation: $Fe^{2+} \rightarrow Fe^{3+}$ Reduction: $Cr_2O_7^{2-} \rightarrow Cr^{3+}$

Step 2. Balance the atoms in each half-reaction separately. We begin by balancing the atoms in each half-reaction. The oxidation step is already balanced for Fe atoms. For the reduction step, we multiply the number of Cr atoms in order to balance them. Since the reaction takes place in an acidic medium, we add seven H_2O molecules to the right-hand side of the equation to balance the O ate

$$\operatorname{Cr_2O_7^{2-}} \rightarrow 2\operatorname{Cr^{3+}} + 7 \operatorname{H_2O}$$

To balance the H atoms, we add fourteen H+ ions on the left side:

$$14 \text{ H}^{+} + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2 \text{ Cr}^{3+} + 7 \text{ H}_2\text{O}$$

Step 3. Add electrons to one side of each half-reaction to balance the electrons necessary, equalize the number of electrons in the two half-reactions by appropriate coefficients. For the oxidation half-reaction we write:

$$Fe^{2+} - e^- \rightarrow Fe^{3+}$$

In the reduction half-reaction

$$14 \text{ H}^{+} + \text{Cr}_2\text{O}_7^{2-} + 6e^- \rightarrow 2 \text{ Cr}^{3+} + 7 \text{ H}_2\text{O}$$

To equalize the number of electrons in both half-reactions, we multiply the oxidation half-reaction by 6:

$$6 \operatorname{Fe}^{2+} + 6e^{-} \to 6 \operatorname{Fe}^{3+}$$

Step 4. Add the two half-reactions together and balance the final equation by inspection. The electrons on both sides must cancel. The two half-reactions are added to give

$$14 \text{ H}^{+} + \text{Cr}_2\text{O}_7^{2-} + 6 \text{ Fe}^{2+} \rightarrow 2 \text{ Cr}^{3+} + 6 \text{ Fe}^{3+} + 7 \text{ H}_2\text{O}$$

The electrons in both half-reactions cancel, and we are left with the balanced net ionic equation:

Step 5. Verify that the equation contains the same types and numbers of atoms and the same charges on both sides of the equation.

A final check shows that the resulting equation is "atomically" and "electrically" balanced.

We now apply the ion-electron method to balance the equation of a redox reaction in basic medium.

Example

Write a balanced ionic equation to represent the oxidation of iodide ion (Γ) by permanganate ion (MnO₄) in basic solution to yield molecular iodine (I₂) and manganese (IV) oxide (MnO₂).

ANSWER

Step 1: The skeletal equation is

$$MnO_4^- + I^- \rightarrow MnO_2 + I_2$$

The two half-reactions are

Oxidation: 2 I \rightarrow I₂ Reduction: MnO₄ \rightarrow MnO₂

Step 2: To balance the I atoms in the oxidation half-reaction, we write

 $2 I^{-} \rightarrow I_{2}$

In the reduction half-reaction, to balance the O atoms we add four OH^{-} ions to the right and two H_2O molecules on the left:

 $MnO_4 + 2 H_2O \rightarrow MnO_2 + 4 OH^-$

Step 3. Next, we balance the charges of the two half-reactions as follows:

 $2 \text{ I}^{-} -2e^{-} \rightarrow \text{I}_{2}$ $MnO_{4}^{-} + 2 \text{ H}_{2}\text{O} + 3e^{-} \rightarrow MnO_{2} + 4 \text{ OH}^{-}$

To equalize the number of electrons, we multiply the oxidation half-reaction by 3 and the reduction half-reaction by 2:

$$6 \text{ I}^{-} - 6e^{-} \rightarrow 3 \text{ I}_2$$

2 MnO₄⁻ + 4 H₂O + 6e⁻ \rightarrow 2 MnO₂ + 8 OH⁻

Step 4. The two half-reactions are added together to give

 $6 \text{ I}^-+2 \text{ MnO}_4^-+4 \text{ H}_2\text{O} \rightarrow 3 \text{ I}_2+2 \text{ MnO}_2+8 \text{ OH}^-$

Step 5. A final check shows that the equation is balanced in terms of both atoms and charges.

3.1.4. General Classification of Redox Titration Methods

This classification is based on the type of a titrant used for analyses. The most applied in medicine are:

> Permanganatometric titration: KMnO₄ solution is applied as a titrant;

 \blacktriangleright Iodometric titration: solutions of I₂ and Na₂S₂O₃•5 H₂O are used as titrants;

▶ Bromatometric titration: KBrO₃ solution is used as a titrant

3.2. Permanganatometric Titration

Permanganatometric titration is a method of redox titration based on potassium permanganate reduction in acidic media according to the following half-reaction:

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

The reddish violet KMnO₄solution turns colures in the endpoint of titration due to which no indicator is required for analyses.

Potassium permanganate exhibits its oxidizing properties in all media: acidic, basic and neutral as well. The reduction products depend upon a medium:

$$MnO_{4}^{-} \xrightarrow{+ 8 H^{+} + 5e^{-} \rightarrow Mn^{2+} + 4 H_{2}Oacidic mediumf_{e} = 1/5} + e^{-} \rightarrow MnO_{4}^{-2-} basic mediumf_{e} = 1/1 + 2 H_{2}O + 3e^{-} \rightarrow MnO_{2} + 4 OH^{-} neutral mediumf_{e} = 1/3$$

But in the acidic medium its oxidizing properties appeared to be the strongest.

In permanganatometric titration aqueous solutions of oxalic acid $(H_2C_2O_4 \cdot 2 H_2O)$ or its salts $(Na_2C_2O_4)$ are used as primary titrants, and KMnO₄ solution – as a secondary titrants. Dilute solutions of sulfuric acid are employed for acidic medium creation.

Permanganatometric titration is widely used for medical and biological investigations: determination of essential metals, H_2O_2 and its salts, some vitamins.

3.2.1. Laboratory work № 3

PERMANGANATOMETRIC TITRATION

You will use the following chemical devices: burettes, pipettes, finals, volumetric flasks, flasks for titration.

Experiment № 1

Standardizing of KMnO₄ solution against a primary titrant H₂C₂O₄·H₂O

Reagents: oxalic acid standard solutions, $KMnO_4$ working solutions, $1M H_2SO_4$ solutions, analyzed solutions of $FeSO_4$.

In order to standardize KMnO₄ solution it is titrated against a standard solution of oxalic acid in acidic medium:

$$\begin{array}{c|c} 2 \text{ KMnO}_4 + 5 \text{ H}_2\text{C}_2\text{O}_4 + 3 \text{ H}_2\text{SO}_4 = 2 \text{ MnSO}_4 + \text{K}_2\text{SO}_4 + 10 \text{ CO}_2 + 8 \text{ H}_2\text{O} \\ \hline \text{MnO}_4^- + 8 \text{ H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4 \text{ H}_2\text{O} \\ \hline \text{H}_2\text{C}_2\text{O}_4 - 2\text{e}^- \rightarrow 2 \text{ CO}_2 + 2 \text{ H}^+ \\ \hline 2 \text{ MnO}_4^- + 6 \text{ H}^+ + 5 \text{ H}_2\text{C}_2\text{O}_4 \rightarrow 2 \text{ Mn}^{2+} + 10 \text{ CO}_2 + 8 \text{ H}_2\text{O} \\ \hline \end{array}$$

This redox reaction is catalyzed by Mn^{2+} cations, which are formed in its process. Since cations' initial concentration is negligibly small, the rate of a process is rather low. In order to increase the rate of a reaction titration is fulfilled in hot solutions. The solutions containing a mixture of oxalic and sulfuric acids must be heated up to the boiling point but never boil in order to prevent oxalic acid decomposition. Addition of a new portion of a titrant ought to be done only after a previous one becomes colures.

Fulfill an experiment in a following order:

1) take a pipet and pour 10 mL of oxalic acid solution into every flask for titration;

2) add approximately 10 mL of sulfuric acid into them using a graduated cylinder;

3) heat a prepared mixture up to the boiling point;

4) pour KMnO₄ solution into the buret up to the zero mark;

5) titrate oxalic acid against potassium permanganate solution up to the end point when colorless acid solution turns reddish violet after one drop of a titrant addition;

6) repeat such a titration for three times; their results must not differ greatly from each other;

7) write out the results in to the table N_{2} 5

Table 5

The results of oxalic acid titration against KMnO₄ solution

N⁰	Volume of H ₂ C ₄ O ₂ , mL	Volume of KMnO4, mL	C _N KMnO ₄ , mol/L	T (KMnO ₄), g/mL
1	10,0			
2	10,0			
3	10,0			

Experiment № 2

Determination of iron of mass in an analyzed solution

Iron (Fe^{2+}) determination is based on a following redox reaction:

10 FeSO₄ + 2 KMnO₄ + 8 H₂SO₄ \rightarrow 5 Fe₂(SO₄)₃ + K₂SO₄ + 2 MnSO₄ + 8 H₂O

$$\begin{array}{c|c} MnO_4^- + 8 H^+ + 5 e^- \rightarrow Mn^{2+} + 4 H_2O & 2\\ \hline 2 Fe^{2+} - 2 e^- \rightarrow 2 Fe^{3+} & 5 \\ \hline \end{array}$$

 $2 \text{ MnO}_4^- + 10 \text{ Fe}^{2+} + 16 \text{ H}^+ \rightarrow 2 \text{ Mn}^{2+} + 10 \text{ Fe}^{3+} + 8 \text{ H}_2\text{O}$

Fulfill an experiment in a following order:

1) take a volumetric flask with FeSO₄ solution of an unknown concentration;

2) add distilled water into it up to the round mark;

3) take an analytical pipet and pour 10 mL of $FeSO_4$ solution into every t flask for titration; treat the solutions with approximately 10 mL of sulfuric acid;

4) pour potassium permanganate solution into the buret up to the zero mark;

5) titrate $FeSO_4$ solution against KMnO₄ up to the endpoint when colorless $FeSO_4$ solution turns reddish violet after one drop of a titrant addition;

6) repeat such a titration for three times; their results must not differ greatly from each other;

7) write out the obtained data in to the table N_{2} 6

Table 6

Iron (Fe²⁺) mass determination in an analyzed solution

N⁰	V (Fe ²⁺), mL	V (KMnO ₄),	$C_{\rm N} ({\rm Fe}^{2+}),$	$T (Fe^{2+}),$	$m (Fe^{2+}),$
		mL	mol /L	g/mL	g
1	10,0				
2	10,0				
3	10,0				

8) calculate normality and a titer of a given solution and a mass of iron in it;

9) fulfill the statistical treatment of experimental data.

3.3 Iodometric titration

Iodometric titration is a method of redox titration based on a reversible reaction

$$\begin{array}{ccc} \mathbf{I}_2 + 2 \ \mathbf{e}^{-} \rightarrow 2 \ \mathbf{I}^{-} \\ \mathrm{Ox} & \mathrm{Red} \end{array}$$

It can be performed to determine the concentrations of a wide variety of redoxcapable solutes, with only a few limitations. This method permits to analyze oxidizing and reducing agents' solutions, containing organic and inorganic substances as well.

The scheme of iodometric analysis of oxidizing agents' solutions

The excess of KI being added to the solution of an oxidizing agent gives rise for the following reaction:

$$Ox + 2 I \rightarrow Red + I_2$$
.

The released I₂ is titrated against $Na_2S_2O_3$ ·5H₂O up to the endpoint, which is determined with the help of a starch:

$$I_2 + 2 \operatorname{Na}_2S_2O_3 \rightarrow 2 \operatorname{NaI} + \operatorname{Na}_2S_4O_6$$

In the endpoint blue color of iodine-starch complex turns colorless after one drop of sodium tiosulfate addition from a buret. In order not to lose free iodine, starch must be added to a flask when a solution's color becomes straw yellow.

 $Na_2S_2O_3$ ·5H₂O solution is a secondary titrant, thus it ought to be standardized by titration against K₂Cr₂O₇ solution, which is a primary titrant in this method.

The scheme of iodometric analysis of reducing agents' solutions

A reducing agents' solution are titrated against standard solutions of free iodine:

$$\operatorname{Red} + \operatorname{I}_2 \to \operatorname{Ox} + 2 \operatorname{I}^-.$$

The endpoint is fixated by starch: colorless solution turns blue due to starchiodine complex formation.

3.3.1. Laboratory work № 4

IODOMETRIC TITRATION Experiment № 1

Standardizing of Na₂S₂O₃·5H₂O solution against primary titrant K₂Cr₂O₇

Standardizing of $Na_2S_2O_3$ ·5H₂O solution against primary titrant $K_2Cr_2O_7$ is based on the following reactions:

$$\frac{2 S_2 O_3^{2^-} - 2 e^- \rightarrow S_4 O_6^{2^-}}{1}$$

 $I_2 + 2 S_2 O_3^2 \rightarrow 2 I^2 + S_4 O_6^2$

Fulfill an experiment in a following order:

1) take a pipette and pour 10 mL of $K_2Cr_2O_7$ standard solution into every flask for titration; then add approximately 10 mL of sulfuric acid into them, using a graduated cylinder;

2) add an excess of potassium iodide crystals into each flask and close them with slides. Wait 3-5 minutes upon a reaction will be completed;

3) pour $Na_2S_2O_3 \cdot 5H_2O$ solution into the burette up to the zero mark;

4) titrate the released iodine against $Na_2S_2O_3 \cdot 5H_2O$ solution. In order not to lose free iodine, starch must be added to a flask when a solution's color becomes straw yellow. In the endpoint blue color of iodine-starch complex turns colorless after one drop of sodium tiosulfate addition from a burette;

5) repeat such a titration for three times; their results must not differ greatly from each other;

6) Write out the obtained data into the table N_{2} 7

Table 7

The results of iodine titration against Na₂S₂O₃·5H₂O solution

№	$V (K_2 Cr_2 O_7), \\ mL$	$V (Na_2S_2O_3), \\ mL$	V average (Na ₂ S ₂ O ₃), mL	$C_{N} (Na_{2}S_{2}O_{3}),$ mol/L	$\begin{array}{c} T(Na_2S_2O_3),\\ g/mol \end{array}$
1	10.0				
2	10,0				
3	10,0				

Experiment № 2

Determination of copper mass in an analyzed solution

Determination of copper mass in an analyzed solution is based on the following reactions:

 $2 \operatorname{CuSO}_{4} + 4 \operatorname{KI} = \operatorname{Cu}_{2}I_{2}\downarrow + I_{2} + 2 \operatorname{K}_{2}\operatorname{SO}_{4}$ $2 \operatorname{I} - 2 \operatorname{e} \rightarrow I_{2} 1$ $2 \operatorname{Cu}^{2+} + 2 \operatorname{I} + 2 \operatorname{e} \rightarrow \operatorname{Cu}_{2}I_{2} 1$

 $2 \operatorname{Cu}^{2+} + 4 \operatorname{I}^{-} = \operatorname{Cu}_2 \operatorname{I}_2 + \operatorname{I}_2$

 $I_2 + 2 Na_2S_2O_3 = 2 NaI + Na_2S_4O_6$

Fulfill an experiment in a following order:

1) take a volumetric flask with CuSO₄solution of unknown concentration;

2) add distilled water into a flask up to the round mark;

3) take a pipette and pour 10 mL of CuSO₄ solution into every flask for titration and treat them with approximately 10 mL of sulfuric acid;

4) add an excess of potassium iodide crystals into each flask and close them with slides. Wait 3-5 minutes upon a reaction will be completed;

5) Pour $Na_2S_2O_3$ ·5H₂O solution into the buret up to the zero mark;

6) titrate the released iodine against $Na_2S_2O_3 \cdot 5H_2O$ solution. In order not to lose free iodine, starch must be added to a flask when a solution's color becomes straw yellow. In the endpoint a suspension in a flask will have an ivory color;

7) repeat such a titration for three times; the results must not differ greatly from each other; 8) write out the obtained data in to the table N_{2} 8

Table 8

№	V (CuSO ₄), mL	V(Na ₂ S ₂ O ₃) mL	C _N (CuSO ₄), mol/L	T (Cu ²⁺), g/mL	$m (Cu^{2+}),$
1	10,0				
2	10,0				
3	10,0				

Copper (Cu²⁺) mass determination in an analyzed solution

9) calculate normality and a titer of a given solution and an iron mass in it;

10) Fulfill the statistical treatment of experimental data.

Experiment №3.

Determination of normality and titer in ascorbic acid solution

Ascorbic acid (vitamin C) determination is based on its oxidation by free iodine



 $C_6H_8O_6 + I_2 \rightarrow C_6H_6O_6 + 2 \text{ HI}$

Vitamin C is the organic reducing agent in an iodometric titration. Iodine is reduced while vitamin C is oxidized. Again, the endpoint is reached when all of the vitamin C has been oxidized, making this reaction suitable for determining the concentration of vitamin C in a solution

Fulfill an experiment in a following order:

1) take a pipette and pour 10 mL of ascorbic acid solution into every flask for titration; treat them with 2-3 drops of starch;

2) pour standard free iodine solution into the burette up to the zero mark;

3) titrate the ascorbic acid solution against I_2 solution up to the endpoint when colorless solution in a flask turns blue due to the iodine-starch complex formation;

4) repeat such a titration for three times; their results must not differ greatly from each other;

5) write out the obtained data in to the table N_{2} 9

Table 9

Determination of normality and titer of ascorbic acid solution

№	V(ascorbic acid), mL	V (I ₂), mL	C _N (ascorbic acid), mL	T(ascorbic acid),	m(ascorbic acid),
1	10,0	mit		B, 1112	8
2	10,0				

3	10,0		

6) calculate normality and a titer in a given solution and ascorbic acid mass in it. **3.4. Exercises for the self control**

1. Complete the following redox reactions and balance them using half-reaction method:

a) $FeSO_4 + KMnO_4 + H_2SO_4 \rightarrow$

b) $K_2SO_3 + KMnO_4 + KOH \rightarrow$

c) $KMnO_4 + KNO_2 + H_2SO_4 \rightarrow$

d) KMnO₄ + KNO₂ + H₂O \rightarrow

e) KMnO₄ + KNO₂ + KOH \rightarrow

f) $H_2O_2 + KMnO_4 + H_2SO_4 \rightarrow$

g) KMnO₄ + H₂S + H₂SO₄ \rightarrow

2. Compute KMnO4 mass, which is required to prepare 1 L of 0.1 N. solution.

Answer: 3.16 g

3. 2.5 g of H_2O_2 sample was diluted by water up to 200 mL in a volumetric flask. 5.0 mL of an obtained solution was titrated against 20 mL of 0.05 N. KMnO₄ solution in acidic medium. Compute H_2O_2 percent by mass content in its initial sample.

Answer: 27.2%

4. 10.2 mL of NaNO₂ was titrated against 25.0 mL of KMnO₄ solution (0.05 N) in acidic medium. Calculate a mass of NaNO₂ in 100 mL of a solution.

Answer: 0.423 g

5. 19.5 mL of KMnO₄ solution was titrated against a solution which contained 0.0244 g of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$). Compute normality and titer of KMnO₄ solution

Answer: 0.01986 N, 0.0627 g/mL

6. 0,098 g pure for analyses $K_2Cr_2O_7$ were treated by KI solution in acidic medium. The obtained solution was titrated against 25.5 mL Na₂S₂O₃ 5H₂O solution. Compute normality and titer of Na₂S₂O₃ 5H₂O solution.

Answer: 0.0784 N, 0.01945 g/mL

7. Analyses of $Na_2S_2O_3$ 5H₂O solution is based on the following reactions:

 $2 \operatorname{Cu}^{2+} + 4 \operatorname{I}^{-} = 2 \operatorname{CuI} + \operatorname{I}_{2}$

$$I_2 + 2 S_2 O_3^{2^-} = 2 I^- + S_4 O_6^{2^-}$$

0,153 g Cu^{2+} sample was titrated against 24.18 mL of Na₂S₂O₃·5H₂O solution. Compute normality of Na₂S₂O₃·5H₂O solution.

Answer: 0.09887 N.

8. 20.0 mL of 0.0195 N $Na_2S_2O_3$ 5H₂O solution was titrated against iodine solution. 20.1 mL of iodine solution was used. Compute normality and titer of iodine solution.

Answer: 0.0194 N, 0.00246 g/mL

9. 81.5 mL of 0.100 N iodine solution was used to titrate 2.5 g of technique sample of $Na_2S_2O_3$ 5H₂O. Compute the percent by mass content of tiosulfate in a

given sample.

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APPENDIX A

a/mI	Concentration		a/mI	Concentration	
g/mL	W, %	C _M , mol/L	g/IIIL	w, %	C _M , mol/L
		SODIUM	CHLORIDE		
1,0053	1	0.172	1.1009	14	2.639
1,0125	2	0.346	1.1162	16	3.057
1,0268	4	0.703	1.1319	18	3.489
1,0413	5	1.069	1.1478	20	3.930
1,0559	8	1.446	1.1640	22	4.384
1.0707	10	1.834	1.1804	24	4.849
1.0857	12	2.231	1.1972	26	5.329
		HYDROCH	ILORIC ACID		
1.0032	1	0,275	1.1083	22	6,684
1.0082	2	0.553	1,1187	24	7.365
1.0181	4	1.117	1.1290	26	8.051
1.0279	6	1.692	1,1392	28	8.750
1.0376	8	2.277	1,1493	30	9.454
1.0474	10	2.872	1.1593	32	10.15
1.0574	12	3,481	1.1691	34	10.93
1.0675	14	4.099	1.1789	36	11.64
1.0776	16	4.729	1.1885	38	12.39
1.0878	18	5.371	1.1980	40	13.14
1.0980	20	6.023			

DENSITY AND CONCENTRATION OF AQUEOUS SOLUTIONS (20° C)

APPENDIX B

SOME COMMON ACID-BASE INDICATORS

Color Indicator	In acid	In base	pH rage*
Thymol blue	Red	Yellow	1.2 - 2.8
Bromophenol blue	Yellow	Bluish pur- ple	3.0 - 4.6
Methyl orange	Orange	Yellow	3.1 - 4.4
Methyl red	Red	Yellow	4.2 - 6.3
Chlorophenol blue	Yellow	Red	4.8 - 6.4
Bromothymol blue	Yellow	Blue	6.0 - 7.6
Cresol red	Yellow	Red	7.2 - 8.8
Phenolphthalem	Color- less	Reddish pink	8.3 - 10.0

* The pH range is defined as the range over which the indicator changes from the acid color to the base color.

Glossary

Titration. The gradual addition of a solution of accurately known concentration to another solution of unknown concentration until the chemical reaction between the two solutions is complete.

Equivalence point (endpoint). The point at which the acid is completely reacted with or neutralized by the base.

Acid-base indicators. Substances that have distinctly different colors in acidic and basic media.

Standard solution (primary titrant). A solution of accurately known concentration.

Working solution (secondary titrant). The working solutions of accurately unknown concentration

Standardization. A working solution is titrated by a standard solution.

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Методические рекомендации к лабораторно-практическому курсу по общей химии для студентов I курса лечебного факультета, обучающихся на английском языке

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INTRODUCTIN IN VOLUMETRIC ANALYSES

Laboratory manual



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