Problems in
PHYSICOCHEMICAL
METHODS of Analysis

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ЗАДАЧНИК ПО ФИЗИКО-ХИМИЧЕСКИМ МЕТОДАМ АНАЛИЗА

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PREFACE

Courses in physicochemical methods of analysis are included in curricula of numerous educational establishments. The problems however are given little emphasis in many textbooks and manuals. The authors of the present problem book have made their aim to fill up this gap and to set up problems in the principal methods of physicochemical analysis and methods of separating substances.

Since methods of programmed instruction have recently been introduced at higher school, each chapter of the book includes assignments for programmed questioning.

Most of the chapters consist of the following sections:

1. *Examples of problem-solving.*

2. *Multivariant problems.* This section covers problems involving simple single-type calculations based on a definite formula or law.

3. *Problems.* This section contains problems of three types: A, B, and C. Problems of type A are primarily intended for college students and workers in plant laboratories. Problems of type B are more complicated and are meant for students at universities and higher schools. And, finally, problems of type C, the solution of which requires the use of literature data, are designed for students at most advanced level, who wish to major in the field of physicochemical methods of analysis. In some of the problems of types B and C, physicochemical methods are used for determination of constants such as the solubility products, complex-formation constants.

4. *Assignments for programmed questioning.* This section contains programmed assignments based on four principles. In assignments compiled according to the *multiple-choice principle*, one must choose, among a number of answers to a given question, the correct ones. In some cases, of

5 answers only one is correct, in others, among 7 to 9 answers 3 or 4 are correct, though expressed in different form. In assignments based on the *linear principle*, one group contains questions and the other gives alternately one and occasionally several answers to these questions. In assignments based on the *principle of variants*, the question placed in the first group is provided with two answers supplementing each other in two other groups. In assignments set up according to the *detailed-answer principle*, to each question there correspond two rows of answers, of which one is correct and the others (4 answers) are wrong. The second row of answers supplement or detail the answers given in the first row. This is a complex type of programmed questioning.

In certain cases assignments are included for teaching machines.

For the student to acquire the skill of using reference literature, the authors considered it expedient, in a number of problems marked with one asterisk, to leave out certain information (the densities of solutions, oxidation-reduction potentials, electrical conductances, etc.). The handbook that is recommended for use as a data source is *Handbook of Chemistry* by N. A. Lange, McGraw-Hill Book Company, 1961. The cases where other handbooks are to be resorted to are specified in the directions to a particular problem.

For more sophisticated problems marked with double asterisks, primarily those of types B and C, directions are provided at the end of the book, indicating the way a given problem is to be solved. Naturally, the student should not resort immediately to these directions.

A list of books is supplied at the end of this book, which are recommended for study and recapitulation of the theoretical foundations of physicochemical methods.

The authors wish to express their deep gratitude to the referees of the book—Professors K. N. Mochalov and Yu. A. Klyachko for valuable suggestions and advice, which contributed to the improvement of the manuscript.

This problem book is the first attempt at compiling a text of this kind, and the authors will accept with gratitude all remarks and suggestions, which, we hope, will help improve the book.

<div align="right">The authors</div>

CONTENTS

Mathematical Treatment of Analytical Results

Two techniques are used for treatment of analytical results: the statistical method and the method of approximate calculations. The former is employed in Examples 1 and 2, Multivariant Problem 1 and Problems 1-4, 13, 14, 22-25; the latter is used in the remaining problems.

Brief theoretical information on the mathematical treatment of the results of analysis may be found in *Physicochemical Methods of Analysis*, a textbook, written by Yu. S. Lyalikov (this book has been published in English by Mir Publishers, Moscow, USSR, 1968, under *Physicochemical Analysis*). More detailed information may be found in the books listed at the end of this book.

Symbols and Terms Used

Statistical Methods

The *measured value* is the observed value of the quantity being measured.

The *result* is the final value of the measured quantity, obtained after all auxiliary processes and operations.

An *individual sample value* is the measured value used for statistical treatment. It is designated by the symbol x.

A *sample array* is a certain number of individual values which are equivalent to one another from the standpoint of statistics $(x_1, x_2, x_3, \ldots)$.

The *mean value* is the sum of a set of individual values divided by their number in the sample array. The symbol is $\bar{x}$.

The *reliability* of the mean is defined as the difference between it and the true value of the magnitude measured.

The *deviation* is the difference between an individual value and the mean of the sample array to which it belongs. The symbol is *d*.

The *range* is the difference between the highest and the lowest measured value in the array. It is designated as $R = x_{max} - x_{min}$.

The *standard deviation* is found by extracting the square root of the quotient obtained by dividing the sum of the squares of the individual deviations from the mean by one less than the number of determinations made:

$$\bar{s} = \sqrt{\frac{\sum d^2}{n-1}}$$

The *standard deviation of the mean* is the standard deviation divided by the square root of the total number of determinations made. The symbol is $\sigma_{\bar{x}} = \bar{s}/\sqrt{n}$. This term is missing in the IUPAC recommendations, but it is widely used.

Dispersion or *spread* is the square of the standard deviation. It is denoted by $V = \Sigma d^2/(n-1)$.

The *relative standard deviation* is the standard deviation of the mean divided by the mean of the sample array. It is defined as follows: $s_{rel} = \sigma/\bar{x}$ or, in per cent, $s_{rel} = (\sigma/\bar{x}) \, 100$.

The *sample size* is the total number of individual values in a sample array. It is denoted by *n*.

The *error* is the difference between an actual measurement and the true value of the magnitude measured.

The *percentage error* is the error expressed in per cent of the true value.

The *confidence level* is designated by α.

The coefficient of *standardized deviations* (*Student's coefficient*) is denoted by $t_{\alpha, k}$.

The number of *degrees of freedom* is one less than the number of determinations (individual values) in a sample array. It is designated as $k = n - 1$.

The *accuracy* of a single measurement at a chosen confidence level is the product of the standard deviation by the standardized deviation coefficient divided by the

square root of the number of determinations (sample size):

$$\varepsilon_\alpha = \frac{\bar{s}t_{\alpha, k}}{\sqrt{n}} = \sigma t_{\alpha, k}$$

The *relative error* of a direct determination is the ratio of the accuracy of a measurement to the mean, expressed in per cent: $\Delta = (\varepsilon_\alpha / \bar{x})\ 100$.

The *confidence interval* (*confidence limits*) of the quantity being determined is $\bar{x} \pm \varepsilon_\alpha$.

The criterion F is equal to V_1/V_2.

The criterion Q is equal to $(x_1 - x_2)/R$ (where $x_1 - x_2$ is the difference of the neighbouring measured values, of which one is doubtful).

The Method of Approximate Calculations

The absolute error of the quantities measured is designated as f_x and f_y.

The relative error of measured values is given by

$$\delta_{x(y)} = f_{x(y)}/x\,(y) \cdot 100$$

To relieve the reader of the burden of searching for the necessary table data we give here Student's coefficients and values of the criteria F and Q (given for the most frequently used 0.95 or 95% confidence limits), which will be needed for solution of problems.

TABLE 1

Number of experiments in a series	Number of series of experiments						
	2	3	4	5	6	8	10
2	19.00	19.16	19.25	19.30	19.33	19.37	19.39
3	9.55	9.28	9.12	9.01	8.94	8.84	8.78
4	6.94	6.59	6.39	6.26	6.16	6.04	5.96
5	5.79	5.41	5.19	5.05	4.95	4.82	4.74
6	5.14	4.76	4.53	4.39	4.28	4.15	4.06
8	4.46	4.07	3.84	3.69	3.58	3.44	3.34
10	4.10	3.71	3.48	3.33	3.22	3.07	2.97

The coefficients of standardized deviations, or Student's coefficients, are as follows:

k	1	2	3	4	5
$t_{\alpha, k}$ at $\alpha = 0.95$	12.706	4.303	3.182	2.776	2.571

k	6	7	8	9	10
$t_{\alpha, k}$ at $\alpha = 0.95$	2.447	2.365	2.306	2.262	2.228

The values of the criterion F are given in Table 1.
The values of the criterion Q are as follows:

n	3	4	5	6	7	8	9	10
Q at $\alpha = 0.95$	0.94	0.77	0.64	0.56	0.51	0.48	0.44	0.42

1. EXAMPLES OF PROBLEM-SOLVING

Example 1. In determining molybdenum in ore in duplicate samples the following amounts of MoO_3 were found in weighed portions of 0.5000 g: 0.02851, 0.02856, 0.02873, 0.02852, 0.02831, 0.02856, 0.02851, 0.02853, 0.02855, 0.02850.

Treat these data according to mathematical statistics and determine the percentage content of molybdenum in the ore.

Solution. Before starting the statistical treatment of the experimental data a check is to be done to see whether there are values which differ sharply due to crude errors. If there are such values, you are to exclude them from the series to be statistically treated. To accomplish this, arrange the experimental data in increasing order: 0.02831, 0.02850, 0.02851, 0.02851, 0.02852, 0.02853, 0.02855, 0.02856, 0.02856, 0.02873.

Suppose that the values 0.02831 and 0.02873 are unreliable. Calculate the criteria Q for them:

$$Q_1 = \frac{0.02850 - 0.02831}{0.02873 - 0.02831} = 0.45$$

$$Q_{10} = \frac{0.02873 - 0.02856}{0.02873 - 0.02831} = 0.41$$

For $\alpha = 0.95$ and $n = 10$ the tabulated value of Q is equal to 0.42. Since Q_t is less or almost equal to Q_1 and Q_{10}, the two values x_1 and x_{10} are unreliable and are therefore dropped. We write down the remaining values in tabular

form (see Table 2) and find the arithmetic mean of the content of MoO_3, $\bar{g}$, the standard deviation $\bar{s}$ and the accuracy of the determination ε_α.

$$\varepsilon_{0.95} = \frac{t_{\alpha,\,k}\bar{s}}{\sqrt{n}} = \frac{2.37 \times 2.39 \times 10^{-5}}{2.82} =$$

$$= 1.98 \times 10^{-5}\ g \approx 2 \times 10^{-5}\ g$$

TABLE 2

g	$\bar{g}$	$(g-\bar{g}) \cdot 10^5$	$(g-\bar{g})^2 \cdot 10^{10}$	$\bar{s}$
0.02850		−3	9	
0.02851		−2	4	
0.02851		−2	4	$\sqrt{\dfrac{40 \times 10^{-10}}{8-1}} =$
0.02852	0.02853	−1	1	
0.02853		0	0	$= \sqrt{5.7 \times 10^{-10}} =$
0.02855		+2	4	$= 2.39 \times 10^{-5}$
0.02856		+3	9	
0.02856		+3	9	
			$\overline{40}$	

Estimating the presence of crude errors from the criteria $\varepsilon_\alpha \sqrt{2}$ and $3\bar{s}/\sqrt{n}$, we obtain:

$$\frac{\bar{s}}{\sqrt{n}} = \frac{2.39 \times 10^{-5}}{\sqrt{8}} = \frac{2.39 \times 10^{-5}}{2.82} = 8.5 \times 10^{-6}$$

$$3\frac{\bar{s}}{\sqrt{n}} = 3 \times 8.5 \times 10^{-6} = 2.55 \times 10^{-5} \approx 3 \times 10^{-5}$$

$$\varepsilon_{0.95}\sqrt{2} = 1.98 \times 10^{-5} \times 1.4 = 2.78 \times 10^{-5} \approx 3 \times 10^{-5}$$

As seen from Table 2, none of the deviations from the mean is outside the limits of the values found, which means that there are no crude errors in these measurements. The mean value of the quantity measured, which covers 95 per cent of all the measurements, is (0.02853 ± 0.00002) g of MoO_3.

Using the conversion factor for changing MoO_3 to Mo, 0.6666, we find the percentage of molybdenum in the ore:

$$\frac{(0.02853 \pm 0.00002)\,0.6666 \times 100}{0.5000} = (3.803 \pm 0.003) \text{ per cent}$$

Example 2. To determine the normality of a solution of HCl, three weighed portions of Na_2CO_3 were taken: 159.0, 174.9, and 190.8 mg (when the samples were weighed twice, the deviation did not exceed ± 0.1 mg). Each sample was dissolved in 25 ml of water. A 5-ml volume of each solution was taken for titration; therefore the volume of the acid used up was then multiplied by 5 for the volume of the whole sample to be taken into account. The following volumes of hydrochloric acid, in ml, were used for titration:

w_1 . . . . 15.10   15.15   15.07   15.05
w_2 . . . . 16.60   16.65   16.65   16.55
w_3 . . . . 18.10   18.15   18.07   18.05

Calculate the most probable value of the normality of the HCl solution and the accuracy and relative error of the determination for a confidence level of $\alpha = 0.95$.

Solution: We calculate for each series:

(1) the mean value of the volume

$$\overline{w_i} = \frac{\sum w_i}{n}$$

(2) the selective dispersion of the volumes

$$V_{w_i} = \frac{\sum (w - \overline{w_i})^2}{n-1}$$

(3) the selective dispersion of the weights of the samples, which, after double weighing, will be equal for all the series:

$$V_{p_i} = \frac{\sum (p_i - \overline{p})^2}{n-1} = \frac{2 \times 10^{-2}}{2-1} = 2 \times 10^{-2} \text{ mg}$$

(4) the dispersion of the normality values

$$V_{N_i} = \frac{\partial \left(\dfrac{p_i}{E_{Na_2CO_3} w_i} \right)^2}{\partial w_i} V_{w_i}^2 + \frac{\partial \left(\dfrac{p_i}{E_{Na_2CO_3} w_i} \right)^2}{\partial p_i} V_{p_i}^2 =$$

$$= \frac{p_i^2 V_{w_i}^2}{53^2 w_i^4} + \frac{V_{p_i}^2}{53^2 w_i^2}$$

All the calculation data can conveniently be collected in tabular form (see Table 3).

TABLE 3

Series of experiments	n_i	p_i, mg	$\bar{w}_i$, ml	$V_{w_i} = \dfrac{\sum(w-\bar{w}_i)^2}{n-1}$	$N_i = \dfrac{p_i}{E_{Na_2CO_3}\bar{w}_i}$ g-eq/litre	V_{N_i}
1	4	159.0	15.09	$\dfrac{57 \times 10^{-4}}{3} = 1.9 \times 10^{-3}$	$\dfrac{159.0}{53 \times 15.09} = 0.1988$	$\dfrac{159^2 \times 1.9 \times 10^{-3}}{53^2 \times 15.09^4} + \dfrac{2 \times 10^{-2}}{53^2 \times 15.09^2} = 32.9 \times 10^{-8} + 3.1 \times 10^{-8} = 3.60 \times 10^{-7}$
2	4	174.9	16.59	$\dfrac{69 \times 10^{-4}}{3} = 2.3 \times 10^{-3}$	$\dfrac{174.90}{53 \times 16.59} = 0.1989$	$\dfrac{174.9^2 \times 2.3 \times 10^{-3}}{53^2 \times 16.59^4} + \dfrac{2 \times 10^{-2}}{53^2 \times 16.59^2} = 33.0 \times 10^{-8} + 2.6 \times 10^{-8} = 3.56 \times 10^{-7}$
3	4	190.8	18.09	$\dfrac{57 \times 10^{-4}}{3} = 1.9 \times 10^{-3}$	$\dfrac{190.8}{53 \times 18.09} = 0.1991$	$\dfrac{190.8^2 \times 1.9 \times 10^{-3}}{53^2 \times 18.09^4} + \dfrac{2 \times 10^{-2}}{53^2 \times 18.09^2} = 23.0 \times 10^{-8} + 2.2 \times 10^{-8} = 2.52 \times 10^{-7}$

To check the magnitude of the difference between the data of the whole set of experiments the criterion F is used:

$$F_{1-2} = \frac{V_{N_1}}{V_{N_2}} = \frac{3.60 \times 10^{-7}}{3.56 \times 10^{-7}} \approx 1$$

$$F_{1-3} = \frac{V_{N_1}}{V_{N_3}} = \frac{3.60 \times 10^{-7}}{2.52 \times 10^{-7}} = 1.43$$

$$F_{2-3} = \frac{V_{N_1}}{V_{N_3}} = \frac{3.56 \times 10^{-7}}{2.52 \times 10^{-7}} = 1.42$$

Treatment of Observation Results. The criterion F at $\alpha = 0.95$ and $n - 1 = 3$ is equal to 9.28 (see Table 1). Hence, there is no statistically significant difference between the data of all the series of experiments.

The mean value $\overline{N}$, the dispersion V_N and the accuracy ε_α are therefore calculated for the data of all the three series:

$$\overline{N} = \frac{n_1 \overline{N}_1 + n_2 \overline{N}_2 + n_3 \overline{N}_3}{n_1 + n_2 + n_3} =$$

$$= \frac{4 \times 0.1988 + 4 \times 0.1989 + 4 \times 0.1991}{4 + 4 + 4} = 0.1989 \text{ g-eq/litre}$$

$$V_N = \frac{n_1 V_{N_1} + n_2 V_{N_2} + n_3 V_{N_3} + n_1 (\overline{N}_1 - \overline{N})^2 + n_2 (\overline{N}_2 - \overline{N})^2 + n_3 (\overline{N}_3 - \overline{N})^2}{n_1 + n_2 + n_3} =$$

$$= \frac{4 \times 3.60 \times 10^{-7} + 4 \times 3.56 \times 10^{-7} + 4 \times 2.52 \times 10^{-7} +}{12}$$

$$\frac{+ 4 \times 1 \times 10^{-8} + 4 \times 4 \times 10^{-8}}{12} = \frac{4 \times 101.8 \times 10^{-8}}{12} = 3.40 \times 10^{-7}$$

Having chosen the value of $t_{\alpha, k}$ at $\alpha = 0.95$ and $n_1 + n_2 + n_3 - 3$ degrees of freedom (2.26), we calculate the value of ε_α and the confidence interval for the value of N_{HCl}:

$$\varepsilon_\alpha = t_{\alpha, k} \sqrt{\frac{V_N}{n_1 + n_2 + n_3}} = 2.26 \sqrt{\frac{3.40 \times 10^{-7}}{12}} =$$

$$= 3.8 \times 10^{-4} \approx 4 \times 10^{-4} \text{ g-eq/litre}$$

$$N_{\text{HCl}} = \overline{N} \pm \varepsilon_\alpha = 0.1989 \pm 0.0004 \text{ g-eq/litre}$$

The relative error of the determination is equal to

$$\Delta = \pm \frac{\varepsilon_\alpha}{\overline{N}} 100 = \pm \frac{4 \times 10^{-4} \times 100}{0.1989} = \pm 0.20 \text{ rel. per cent}$$