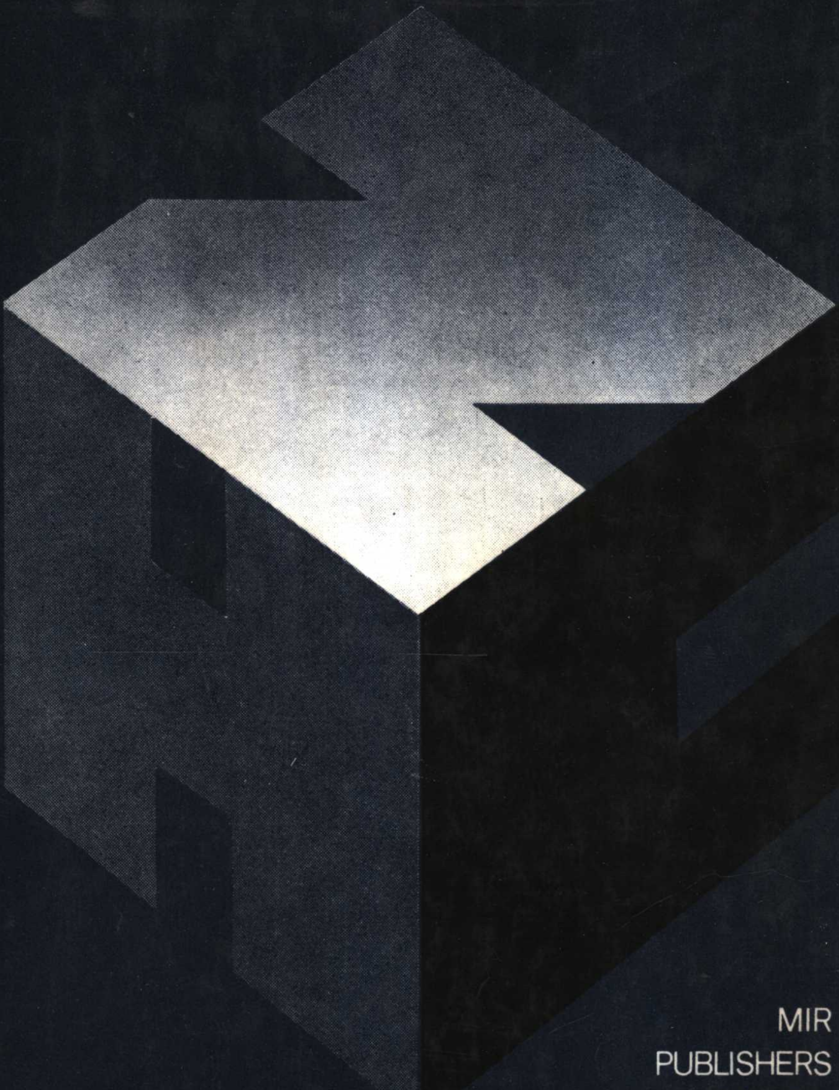
A.A. YAROSLAVTSEV

PROBLEMS AND EXERCISES IN ANALYTICAL CHEMISTRY



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THEORETICAL FOUNDATION OF MODERN CHEMICAL ANALYSIS

Yu. LYALIKOV, D.Sc.
and Yu. KLYACHKO, D.Sc.

This monograph deals with the basic principles of the unified modern theory of chemical qualitative analysis of inorganic substances. Offers analytical classifications of ions according to their solubility, ability to form colour substances, extractability, chromatographic and electrochemical characteristics, etc. Describes methods of concentrating, masking and separating the ions and molecules being determined. A separate chapter is devoted to methods of qualitative analysis of natural and industrial materials.

The book is intended for a wide circle of analytical chemists, chemistry teachers, post-graduates, and students majoring in the field of analytical chemistry.

GENERAL CHEMISTRY

N. GLINKA, D.Sc.

This book has enjoyed wide popularity for years in the Soviet Union and elsewhere. It is intended mainly for higher-school chemistry students. Offers a systematic exposition of the theoretical problems of general chemistry and extensive reference material. The present edition (translated from the 20th Russian edition published in 1978) has been considerably revised, the opportunity being taken of making many important additions to the text and bringing the contents thoroughly up-to-date. Special attention is paid to the structure of atoms and molecules, the regularities governing the occurrence of chemical reactions, and redox connection with the introduction of SI units.

LOW-TEMPERATURE PROPERTIES OF POLYMERS

I. PEREPECHKO, D.Sc.

This monograph deals systematically with the properties of polymers at low temperatures. It studies thermal, acoustic, dielectric properties of polymers and the nuclear magnetic resonance. Most sections of the book have been written from the point of view of modern solid-state physics. The book is intended for scientific workers studying physical properties of polymers at low temperatures, for engineers in plastic industry and for teachers and students of physical and chemical institutes.

A.A. YAROSLAVTSEV

PROBLEMS AND EXERCISES IN ANALYTICAL CHEMISTRY

Translated from the Russian by Alexander Rosinkin

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На английском языке

А. А. Ярославцев

Сборник задач и упражнений по аналитической химии

Москва
«Высшая школа»

ИЗДАТЕЛЬСТВО · МИР ·

FOREWORD

In collecting the problems and exercises for this book we followed the main pedagogical principle: from the simple to the complex. The problems contain examples of calculations which the future analyst will meet in his every-day work in the laboratory of a chemical plant, metallurgical enterprise and in other branches of industry. The answers to the problems were found on calculating machines. Using four-place tables of logarithms and irrational calculating techniques, the student may find his answers differ slightly from those given at the end of the book, but the difference should not exceed $\pm$ 0.0005.

In order to facilitate the use of the book both at home and in the classroom, the author presents the problems in two versions; even-numbered problems are variants of the odd-numbered ones preceding them.

The author takes this opportunity to express his deepest gratitude to V. S. Kalinina for her assistance in selecting the problems in several sections and for helping with the calculations.

Anatoly A. Yaroslavtsev

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INTRODUCTION

Mathematical calculations are the final stage in chemical analysis. However experienced and accurate in carrying out the analytical procedure the analyst may be, the final result, after much tedious and time-consuming work, can be marred down by a single error in calculation. The analyst should therefore remember that *an error in calculation is equivalent to an error in the analytical procedure.*

Calculations. For efficient mathematical calculations, the following mathematical concepts, definitions, and rules should be learned first*.

Number is an expression of quantity. Numbers are classified as accurate and approximate. An accurate number is the result of the counting of a small number of objects or the result of calculations where only accurate numbers are used. In practice accurate numbers rarely occur.

Examples of accurate numbers are the results of determinations, small weights of analytical substances and reagents, smaller units into which larger units are divided (a litre into 1000 ml, an hour into 60 minutes, etc.); the atomic and the equivalent mass of carbon ^{12}C in the atomic mass scale. An approximate number does not give an accurate expression of a quantity, but describes it only approximately, to a certain degree of accuracy. An example is measuring a mass or a volume. The result of calculations where only approximate (or approximate and accurate) numbers are used, is an approximate number as well. An approximate number is property given only when its degree of accuracy is specified.

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* For more details see the book by V. M. Bradis, *How to Calculate?*, Prosveshchenie, Moscow, 1965 (in Russian).

The accuracy of a number is determined by the number of decimal places or significant figures. *Decimal places* are figures standing on the right of the point separating the whole part of the number from its fractional part. For example, the number 25.304 has three decimal places, 10.00008 five decimal places and 734.00, two decimal places.

Significant figures of an approximate number are all figures except zeros standing on the left-hand side and those zeros on the right-hand side which represent figures which are unknown or have been deleted in rounding. All zeros standing in the middle of a number are significant figures. For example, in 230.908 all six figures are significant; in 0.00014, only two, and in 167.0000, three figures are significant. In the last case, all seven figures are significant if the number is known to be accurate. In other words, zeros can be significant only in accurate whole numbers or in the accurate part of an approximate number.

In approximate numbers a distinction is made between authentic and unauthentic figures. As we record the readings from a correct instrument, readings corresponding to the divisions of scale are considered authentic, while the readings falling between two divisions are unauthentic. As we round an accurate number we make it approximate and its last significant figure becomes unauthentic. For example, if we round the accurate number 249 to 250, the new number becomes approximate; the figure 2 remains authentic, while the figure 5 is unauthentic. In the results of calculations only those figures are authentic which are obtained by processing authentic figures. All other figures are unauthentic. The result of a calculation can be considered correct if only its last figure is unauthentic, while an instrument reading can be regarded as correct only if it contains one unauthentic figure (the 'eye' reading). The *accuracy of the result of a calculation cannot be higher than the accuracy of the least accurate number involved in the calculation....* The least accurate number is the one containing the *least* number of significant figures (multiplication and division) or decimal places (addition and subtraction).

It makes sense to attempt calculations only with numbers of equal accuracy. Before starting a calculation, it is therefore necessary to find the least accurate number and round all other numbers so, that they contain one significant figure more ('spare') than the least accurate number. The following rule should be followed in rounding: if the first figure to be deleted is 5 or greater, the preceding figure should be increased by one unit. If the first figure to be deleted is less than 5 the remaining figures are not changed. In the addition or subtraction of mixed decimals, the number given to the least number of decimal places is considered the least accurate. Calculations are continued until a 'spare' figure is obtained which is then omitted and the last remaining figure rounded. The number of significant figures (multiplication or division) or decimal places (addition and subtraction) in the final result must be equal to the number of significant figures in the least accurate number involved in the calculation.

If the data in a calculation are highly accurate, but only an approximate result is required, all initial data are rounded so that they contain one significant figure (or a decimal fraction) more than required in the result. *One should not calculate to a degree of accuracy greater than required.*

If an approximate calculation is done to a high degree of accuracy, the sign = (equals) is placed before the result. If the accuracy is low, the sign $\approx$ (equals approximately) is used. *Calculations done without observing these rules will be incorrect.*

Calculation techniques. Calculations can be performed (1) by mental arithmetic, (2) by combining mental and written arithmetic, (3) by written calculation alone, (4) using a slide rule, various tables, graphs, nomograms, etc., and (5) using a calculating machine. Mental arithmetic, mental and written calculations, and calculations with a slide rule are suitable only for approximate calculations. The multiplication and division of large numbers to a high degree of accuracy should be performed with tables of logarithms or on a calculator. Ordinary written calculations can only be used to (1) add and subtract large numbers; and (2) multiply and divide large numbers by numbers consisting of only one figure or containing one significant figure other than unity. When using a calculator, it is necessary to round all results (final and intermediate) in accordance with the above rules. *Never use your own written calculations* *to multiply or divide large numbers, especially if there are several unauthentic figures.*

When solving an analytical problem, never determine the numerical values of all the intermediate results. It is quite sufficient to devise a formula for each operation, to substitute the required values into it, and to designate the result by a letter, which is then treated as a numerical value in further operations. When it comes to the final operation, write out the general formula, cancel wherever necessary, find logarithms and use logarithm tables to determine the final result. While doing calculations, write out all operations neatly and arrange them in strict order. Write legibly. When adding or subtracting, it is especially important to write the numbers one under another so that all the figures fall into right columns. The use of squared paper facilitates this purpose.

Draw a vertical line one third of the way across the page and write down the problem, all the auxiliary data taken from tables, and perform all operations on the wider part of the page. All calculations should be done in the margin. This will prevent possible errors, the solution can be more quickly checked, and the need for rough paper is removed. Examples of such calculations are given by way of illustration.

All data in the first problem are of very low accuracy (to one significant figure) and all auxiliary data should be rounded to two significant figures. As for the result, only one significant figure should be left in it, since the accuracy of the result cannot be higher than the accuracy of the least accurate number used in the calculations. In other words, we can only say that about 10 ml of H_2SO_4 are required, and the sign $\approx$ (equals approximately) rather than the sign of equality (=) should therefore be put before the result. This example shows that the solution of the problem is much simpler if we follow the rules. The problem can be solved even faster if we use a slide rule or a calculator. True, a slide rule imposes limitations on the accuracy (to two or three significant figures only).

When performing calculations, remember that an error can be the result of inattentive rewriting. Therefore, avoid rewriting wherever possible. For example, while solving the

Wider part of the page	Margin

Problem No... . How many millilitres of 50% H_2SO_4 are required to neutralize a solution of 9 g of potassium hydroxide?

Auxiliary data:

	from table	rounded
Mol. mass of H_2SO_4	98.08	98
Mol. mass of KOH	56.11	56
Density of 50% H_2SO_4	1.395	1.4

Reaction equation

$$2KOH + H_2SO_4 = K_2SO_4 + 2H_2O$$

Solution.

1. How many grams of anhydrous H_2SO_4 are required to neutralize 9 g of KOH?

$2KOH — H_2SO_4$

$2 \times 56 — 98$ $\qquad x = \frac{9 \times 98}{2 \times 56} = a$ g

$9 — x$

Margin: $98 \times 9 = 882 \approx 880$

2. How many grams of 50% H_2SO_4 are required for the same purpose?

$50 — 100$

$a — y$ $\qquad y = \frac{a \times 100}{50} = b$ g

Margin:

$$\begin{array}{r} 56 \\ \times\ 1.4 \\ \hline 22.4 \\ +\ 56 \\ \hline 78.4 \end{array}$$

3. What is the volume of b g of a 50% solution of H_2SO_4?

1000 ml — 1400 g

z ml — b g $\qquad z = \frac{1000 \cdot b}{1400} = \frac{b}{1.4} = c$ ml;

$$c = \frac{9 \times 98 \times 100}{2 \times 56 \times 50 \times 1.4} = \frac{882}{78.4} \approx \frac{880}{78} \approx$$

$$\approx 10 \text{ ml}$$

Margin:

$$\begin{array}{r} 11 \\ 78 \overline{)\,880} \\ 78 \\ \hline 100 \\ 78 \\ \hline 22 \end{array}$$ (remainder)

Problem No... . Calculate as accurately as possible the number of millilitres of a 50% solution of H_2SO_4 required to neutralize 9.000 g of pure KOH.