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TECHNIQUES OF CHEMISTRY

VOLUME I

PHYSICAL METHODS OF CHEMISTRY



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VOLUME I

PHYSICAL METHODS OF CHEMISTRY

INCORPORATING FOURTH COMPLETELY REVISED AND AUGMENTED
EDITION OF TECHNIQUE OF ORGANIC CHEMISTRY,
VOLUME I, PHYSICAL METHODS OF ORGANIC CHEMISTRY

Edited by

ARNOLD WEISSBERGER

AND

BRYANT W. ROSSITER

Research Laboratories
Eastman Kodak Company
Rochester, New York

PART IV

*Determination of Mass, Transport, and Electrical-Magnetic
Properties*

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ARNOLD WEISSBERGER, *Editor*

VOLUME I

PHYSICAL METHODS OF CHEMISTRY

PART IV

Determination of Mass, Transport, and Electrical-Magnetic Properties

TECHNIQUES OF CHEMISTRY

ARNOLD WEISSBERGER, *Editor*

VOLUME I

PHYSICAL METHODS OF CHEMISTRY, in Five Parts
(INCORPORATING FOURTH COMPLETELY REVISED AND AUGMENTED
EDITION OF PHYSICAL METHODS OF ORGANIC CHEMISTRY,
Edited by Arnold Weissberger and Bryant W. Rossiter

VOLUME II

ORGANIC SOLVENTS, Third Edition
John A. Riddick and William S. Bunger

VOLUME III

PHOTOCHROMISM
Edited by Glenn H. Brown

PLAN FOR

PHYSICAL METHODS OF CHEMISTRY

PART I

Components of Scientific Instruments, Automatic Recording and Control, Computers in Chemical Research

PART II

Electrochemical Methods

PART III

Optical, Spectroscopic, and Radioactivity Methods

PART IV

Determination of Mass, Transport, and Electrical-Magnetic Properties

PART V

Determination of Thermodynamic and Surface Properties

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NEW BOOKS AND NEW EDITIONS OF BOOKS OF THE TECHNIQUE OF ORGANIC CHEMISTRY SERIES WILL NOW APPEAR IN TECHNIQUES OF CHEMISTRY. A LIST OF PRESENTLY PUBLISHED VOLUMES IS GIVEN BELOW.

TECHNIQUE OF ORGANIC CHEMISTRY

ARNOLD WEISSBERGER, *Editor*

- Volume I:* Physical Methods of Organic Chemistry
Third Edition—in Four Parts
- Volume II:* Catalytic, Photochemical, and Electrolytic Reactions
Second Edition
- Volume III:* Part I. Separation and Purification
Part II. Laboratory Engineering
Second Edition
- Volume IV:* Distillation
Second Edition
- Volume V:* Adsorption and Chromatography
- Volume VI:* Micro and Semimicro Methods
- Volume VII:* Organic Solvents
Second Edition
- Volume VIII:* Investigation of Rates and Mechanisms of Reactions
Second Edition—in Two Parts
- Volume IX:* Chemical Applications of Spectroscopy
Second Edition—in Two Parts
- Volume X:* Fundamentals of Chromatography
- Volume XI:* Elucidation of Structures by Physical and Chemical Methods
In Two Parts
- Volume XII:* Thin-Layer Chromatography
- Volume XIII:* Gas Chromatography
- Volume XIV:* Energy Transfer and Organic Photochemistry

INTRODUCTION TO THE SERIES

Techniques of Chemistry is the successor to the Technique of Organic Chemistry Series and its companion—Technique of Inorganic Chemistry. Because many of the methods are employed in all branches of chemical science, the division into techniques for organic and inorganic chemistry has become increasingly artificial. Accordingly, the new series reflects the wider application of techniques, and the component volumes for the most part provide complete treatments of the methods covered. Volumes in which limited areas of application are discussed can be easily recognized by their titles.

Like its predecessors, the series is devoted to a comprehensive presentation of the respective techniques. The authors give the theoretical background for an understanding of the various methods and operations and describe the techniques and tools, their modifications, their merits and limitations, and their handling. It is hoped that the series will contribute to a better understanding and a more rational and effective application of the respective techniques.

Authors and editors hope that readers will find the volumes in his series useful and will communicate to them any criticisms and suggestions for improvements.

*Research Laboratories
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Rochester, New York*

ARNOLD WEISSBERGER

PREFACE

Physical Methods of Chemistry succeeds, and incorporates the material of, three editions of *Physical Methods of Organic Chemistry* (1945, 1949, and 1959). It has been broadened in scope to include physical methods important in the study of all varieties of chemical compounds. Accordingly, it is published as Volume I of the new *Techniques of Chemistry* series.

Some of the methods described in *Physical Methods of Chemistry* are relatively simple laboratory procedures, such as weighing and the measurement of temperature or refractive index, and determination of melting and boiling points. Other techniques require very sophisticated apparatus and specialists to make the measurements and to interpret the data; x-ray diffraction, mass spectrometry, and nuclear magnetic resonance are examples of this class. Authors of chapters describing the first class of methods aim to provide all information that is necessary for the successful handling of the respective techniques. Alternatively, the aim of authors treating the more sophisticated methods is to provide the reader with a clear understanding of the basic theory and apparatus involved, together with an appreciation for the value, potential, and limitations of the respective techniques. Representative applications are included to illustrate these points, and liberal references to monographs and other scientific literature providing greater detail are given for readers who want to apply the techniques. Still other methods that are successfully used to solve chemical problems range between these examples in complexity and sophistication and are treated accordingly. All chapters are written by specialists. In many cases authors have acquired a profound knowledge of the respective methods by their own pioneering work in the use of these techniques.

In the earlier editions of *Physical Methods* an attempt was made to arrange the chapters in a logical sequence. In order to make the organization of the treatise lucid and helpful to the reader, a further step has been taken in the new edition—the treatise has been subdivided into technical families and parts.

- Part I Components of Scientific Instruments, Automatic Recording and Control, Computers in Chemical Research
- Part II Electrochemical Methods

- Part III Optical, Spectroscopic, and Radioactivity Methods
- Part IV Determination of Mass, Transport, and Electrical-Magnetic Properties
- Part V Determination of Thermodynamic and Surface Properties

This organization into technical families provides more consistent volumes and should make it easier for the reader to obtain from a library or purchase at minimum cost those parts of the treatise in which he is most interested.

The more systematic organization has caused additional labors for the editors and the publishers. We hope that it is worth the effort. We thank the many authors who made it possible by adhering closely to the agreed dates of delivery of their manuscripts and who promptly returned their proofs. To those authors who were meticulous in meeting deadlines we offer our apologies for delays caused by late arrival of other manuscripts, in some cases necessitating rewriting and additions.

The changes in subject matter from the Third Edition are too numerous to list in detail. We thank previous authors for their continuing cooperation and welcome new authors to the Series. The new authors for Part IV are Dr. P. J. Dunlop, Dr. J. E. Lane, Dr. L. N. Mulay, Dr. J. G. Powles, Dr. B. J. Steel, Dr. W. E. Vaughan.

Chapters on "Determination of Viscosity" and "Determinations with the Ultracentrifuge" were not received until long after the deadline. Chapters dealing with these subjects will appear in a supplemental volume, since it would have been unfair to the authors of other chapters to delay the publication of their work any longer.

We are grateful to the many colleagues who advised us in the selection of authors and helped in the evaluation of the manuscripts. These, for Part IV, are: Dr. Ronald J. Gledhill, Dr. Walter K. Grimwood, Mrs. Ardelle Kocher, Mr. Donald F. Ketchum, Dr. James C. Owens, Dr. Rex B. Pontius, and Mrs. Donna S. Roets.

The senior editor expresses his gratitude to Bryant W. Rossiter for joining him in the work and taking on the very heavy burden with exceptional devotion and ability.

September 1971
Research Laboratories
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Rochester, New York

ARNOLD WEISSBERGER
 BRYANT W. ROSSITER

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ELECTRICAL-MAGNETIC PROPERTIES**

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WEIGHING

Alsoph H. Corwin

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1 INTRODUCTION

In commercial analytical operations, time is of the essence. Even in university research laboratories, where the financial pressure for speed is not urgent, natural human impatience generates the desire for faster weighings. Manufacturers respond with quick weighing balances which may sacrifice precision unduly to obtain rapidity.

A second factor that creates pressure on the reliability of weighings is the increasing interest of chemists in materials that are difficult to obtain and therefore costly. This causes the use of smaller and smaller samples, which require balances of increased sensitivity.

As a consequence of the requirements for greater speed and greater sensitivity, the classical acceptance of weighing as a process adequate to take care of the routine requirements of the chemical laboratory now is called into question. In the past, operators have not had to be more than superficially aware of the theory and details of construction of the chemical balance. This situation has changed to the point that the purchaser of an instrument should understand its operation and be prepared to submit it to critical performance tests.

Weighings in organic chemical laboratories may be performed with different objectives in view. High precision is not required for organic preparations, and difficulties are not usually encountered in securing satisfactory results. Rough analytical weighings are sometimes made for exploratory purposes, but these should also present few problems. Finer weighings must frequently be made in the course of the determination of the kinetics of organic reactions. These may sometimes present problems with respect to speed or reliability. Decigram and centigram analyses are also performed, presenting increasing difficulties as the sample size is diminished. The greatest relative errors in weighing occur, however, in analyses on milligram and submilligram quantities in the so-called microchemical procedures. In spite of this, the organic chemist is not justified in assuming that weighings performed on larger quantities with quick-weighing balances are of the necessary degree of reliability. For these reasons, major attention is given here to possible sources of error in quick-weighing balances and in weighings for milligram, centigram, and decigram analyses.

Recent improvements in weighing procedures and instrumentation have been largely centered on the vacuum microbalance field [1] because of the use of these instruments in studies concerned with electronic instrumentation. Physicists working in this field have largely continued the custom of the past century of ignoring the possibilities of knife-edge balances in the mistaken notion that their sensitivity limit is easily exceeded in the submicrogram range. Although the organic chemist seldom has need for the techniques of

vacuum microbalance work, the persistent neglect of systematic study of the characteristics of fine knife-edge balances has deprived him of the basic design work necessary to secure reliable weighings for his fast work and for his precise analyses. It is for this reason that the chemist who wants to secure reliable analytical results still needs to concern himself with balance design and to understand the sources of error in weighing.

Errors that may prove intolerable can occur in fast-weighing balances [2], and the precision commonly accepted as being attainable with microchemical balances has proved illusory [3]. Instead of the expected tolerance of ± 1 to $2 \mu\text{g}$, Schwarz-Bergkamp [4] found errors in a microchemical balance ranging as high as $24 \mu\text{g}$, and Loscalzo and Benedetti-Pichler [5] found a standard deviation of $13.1 \mu\text{g}$ on a Kuhlmann balance at 2 to 3 g load. Holtz [6] states that the reproducibility of the Kuhlmann balance is $5 \mu\text{g}$ but that errors of $10 \mu\text{g}$ are sometimes encountered. The sources of error in the Kuhlmann balance were investigated by Corwin [7], and reviews on weighing errors due to instrumental design and other causes have appeared at intervals in the literature [8-10]. The most useful treatise on the subject of weighing is that by Felgentraeger [11].

Choice of a Balance

For rapid weighing of moderately heavy loads with relatively low precision, a range of top-loading balances is available. The factors that limit the precision of these balances are not discussed here, since they are seldom used to secure results that are beyond their capabilities.

For the routine weighing of small samples, specially designed balances have found some favor. These balances have high sensitivity but limited load capacity and consequently do not fall into the category of high-precision instruments. Some of these, like the quartz fiber balances are of the torsion type. Others, like the electromagnetic balances [12] may be either of the torsion type or of the pivot type.

For industrial operations where many weighings are to be performed on similar objects, special-purpose balances have been designed to achieve no more than the required accuracy in the shortest possible time. Thus Smith and Stevens [13] have described an electro-servo balance that is quick acting for repetitive weighing. In these cases a greater investment in the instrument can be paid for in the saving of the operator's time.

To achieve maximum economy of time, as many operations as possible should be carried out automatically (see Section 2, p. 42). Partial automation through the use of digital readouts has become quite common, and most manufacturers now supply balances with this feature.

In the research laboratory, where a wide variety of operations is to be performed, a more flexible instrument is desirable. In particular, a balance

that is required to weigh chemical glassware in addition to samples must have precision of a different order of magnitude from that which is required to weigh only samples. Features of design that are acceptable for sample-weighing balances will prove to be entirely unacceptable when applied to utensil-weighing balances.

The choice of a research balance usually involves a choice between speed and precision. It is poor economy to save time in weighing and obtain inaccurate results that may cause otherwise acceptable factory or laboratory experiments to be discarded because of unacceptable analyses. In the case of an analyst who sits as a "court of last resort," with no operational check on the reliability of his results, it is imperative that all sources of significant error be examined and eliminated.

To aid in making decisions between instruments, one of the major topics of discussion in this chapter is the sources of error in weighing and their elimination by means of balance design or weighing technique.

Errors

Error in weighing is defined as the difference between the observed value and the true value of the weight. The true value, however, is unknown, and thus the error must be calculated on the basis of some assumption. It is usually assumed that the best value of a number of observations is the arithmetic mean. In averaging, accidental errors are reduced by multiple observations. The *accidental error* is that portion of the observational error which may be reduced by increasing sufficiently the number of similar observations. This method ultimately meets with diminishing returns because the reliability of the result so obtained increases only as the square root of the number of observations. It is also limited because not all errors belong to this category. The *constant error* or *systematic error* is that part of the error of observation which cannot be reduced by increasing the number of similar observations. The word "constant" in this context does not imply that the error always has the same value; rather, it implies that it is constantly present during the series of observations. The *precision* of an instrument measure the degree to which it can reproduce its indications.

To test the precision of a balance, the operator may use repetitive weighings or he may have recourse to the device of *redundancy*, that is, the use of more operations than the minimum required to secure a desired result. Thus he may record the values and corrections for each of the fractional weights making up one gram. This will give him an estimate of the summed error in the series. If he now compares the sum of the weights with a standard gram weight, the observation will be redundant and will serve as a check upon the reliability of the summed errors. Most weight-calibration procedures secure

their checks by redundancy of observations, and the careful analyst includes either repetitive or redundant observations routinely at some point to make sure that some significant error has not crept into his work.

2 THE KNIFE-EDGE BALANCE

Although other types of weighing instruments are sometimes used for special purposes in chemical laboratories, main reliance in weighing is placed on knife-edge balances. For this reason, our emphasis is on the factors in these instruments that may contribute to faulty weighing, and since fast-weighing balances have now become so popular, first attention is devoted to the special sources of error in these instruments.

Fast-Weighing Balances

Mechanical Weight Changers

The major single factor in securing rapid weighing is the use of a mechanical weight changer, preferably with a digital readout. Such a device may be used either to add weights on a two-pan balance or to subtract weights on a single-pan balance. Accuracy need not be sacrificed if necessary precautions are observed. Indeed, the use of mechanical weight changers may lead to an increase in accuracy in two ways: through the avoidance of error in the choice of combinations of weights used to secure a given sum, and through the avoidance of abrasion due to improper handling. In weighing chemical utensils such as porcelain crucibles, absorption tubes, and similar apparatus, the use of tares is essential to the attainment of precision, and in such cases the user of the balance must not allow himself the convenience of balance-included weights for tares.

The prospective user of a balance must insist on one specification with respect to mechanical weight changers: That is, that the design shall be such that standardization of the weights may be readily accomplished [2]. Unless calibration corrections are applied, the precision of a weighing can be no greater than the precision of the weights used in the process. The user can now purchase balances with weights within specified tolerances, but the actual magnitude of the errors must be subject to observation. Because weights on mechanical weight changers may corrode or pick up dirt, a regular schedule of restandardization must be adopted if errors are to be avoided.

To take full advantage of the convenience inherent in mechanical weight changers, it would be necessary for balance manufacturers to prepare weights for use in them that were adjusted to the tolerable error of the intended weighings. Lacking weights adjusted to weighing tolerances, either the manufacturer or the user of the balance must standardize each individual weight and determine how its correction should be applied in all the combinations