PHYSICAL METHODS OF CHEMISTRY

PART V DETERMINATION OF THERMODYNAMIC AND SURFACE PROPERTIES

WEISSBERGER AND ROSSITER: EDITORS

TECHNIQUES OF CHEMISTRY VOLUME I

TECHNIQUES OF CHEMISTRY

VOLUME I

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PART V

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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

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

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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*
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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 this series useful and will communicate to them any criticisms and suggestions for improvements.

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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, 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:

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 the new authors to the series. New authors of Part V are D. R. Douslin, Lee T. Grady, J. R. Overton, Bernhard Wunderlich, John B. Hayter, and G. E. Hibberd.

The editors sincerely regret the death of Professor A. E. Alexander just prior to the completion of his manuscripts. We are indebted to Professor Alexander's co-authors, Mr. John B. Hayter and Dr. G. E. Hibberd for contributing to and completing the work.

We are grateful to the many colleagues who advised us in the selection of authors and helped in the evaluation of manuscripts. They are for Part V: Dr. George F. Beyer, Dr. James J. Christensen, Dr. J. Robert Dann, Dr. Reed M. Izatt, Dr. Louis D. Moore, Jr., Dr. Michael W. Orem, Dr. S. Elaine B. Petrie, Mrs. Donna S. Roets, Dr. Willard R. Ruby, and Dr. Don W. Vanas.

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.

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BRYANT W. ROSSITER

January 1970
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DETERMINATION OF THERMODYNAMIC AND SURFACE PROPERTIES

Chapter I

TEMPERATURE MEASUREMENT

Julian M. Sturtevant

1 INTRODUCTION

Temperature measurement and, to a lesser extent, temperature control are fundamental to nearly all experimental work in the natural sciences. Very few of the important attributes of material substances are even approximately independent of temperature. Scientists in general, and chemists in particular, must therefore be familiar with modern developments in temperature measurement and control.

In this chapter we discuss the principles and methods of temperature measurement, with attention limited for the most part to the temperature range from 90 to 1000°K within which the great bulk of chemical work is carried out. Chapter VIII, Part IB, includes a discussion of temperature control.

2 DEFINITION OF A TEMPERATURE SCALE [1, 2]

International Practical Temperature Scale

Temperatures in scientific work are expressed in terms of the International Temperature Scale, adopted in 1927 by the Seventh General Conference on

Weights and Measures and revised in 1948 by the Ninth General Conference. At the Eleventh General Conference in 1960, the title of the scale was changed to the International Practical Temperature Scale, and the text of the 1948 definition was clarified by an extensive revision. Further major revisions were incorporated in 1968. A comprehensive discussion of the current International Practical Temperature Scale of 1968 (IPTS-68) is given in Chapter IV, p. 233.

Fixed Defining Points

The fixed defining points of the IPTS-68 are the temperatures in degrees Celsius, °C, of eleven equilibria. For the temperature range −180 to 1000°C the pertinent equilibria, all except (*b*) at a pressure of one standard atmosphere are (*a*) liquid and gaseous oxygen, −182.962°C; (*b*) the triple point of water, 0.01°C; (*c*) liquid water and stream, 100°C; (*d*) solid and liquid zinc, 419.58°C; (*e*) solid and liquid silver, 961.93°C; and (*f*) solid and liquid gold, 1064.43°C.

The temperature of equilibrium between ice and water saturated with air at one atmosphere, the "ice point," is very closely 0.00°C on the International Scale. The thermodynamic scale of temperature agrees within present experimental uncertainties with the Kelvin scale defined by the relation $TK = t°C + 273.15$ over the range of validity of IPTS-68. (According to IPTS-68, temperatures may be expressed in degrees Celsius, as above, or in kelvins, abbreviated K, *not* °K.) The term degree Centigrade commonly used in this country carries, for all practical purposes, the same meaning as the degree Celsius.

Interpolation

From 0 to 630°C the temperature, t, is deduced from the resistance, R_t, of a platinum resistance thermometer by means of a three-constant equation (p. 237), the constants being determined by calibration at the triple point of water and at the steam and zinc points. From −183 to 0°C a four-constant interpolation equation (p. 237) is employed, with the constants determined by measurements at the boiling point of oxygen and at the three fixed points used for the range 0 to 630°C. The purity and physical condition of the thermometer should be such that $R_{100}/R_0 > 1.3925$.

From 630° to the gold point, interpolation is accomplished by means of a standard platinum versus platinum-rhodium thermocouple, one junction of which is at 0°. Above the gold point, temperatures are defined in terms of Planck's radiation formula.

The chief value of the International Practical Temperature Scale lies in the fact that its practically universal acceptance has removed the ambiguities formerly present in the specification of temperatures.

Secondary Temperature Standards

For many applications it is convenient to have reference temperatures more closely spaced than those provided by the International Practical Temperature Scale. Temperatures defined by the equilibria between the liquid and solid forms of pure substances are usually preferable to those defined by the equilibria between the liquid and gaseous forms because of the difficulty of avoiding errors due to superheating and pressure effects in boiling-point determinations. (See, however, Chapter IV.)

One of the best-defined and most reproducible secondary standard temperatures is the freezing point of benzoic acid. Schwab and Wichers [3] have shown that pure benzoic acid (supplied by the National Bureau of Standards) sealed in a partially evacuated tube containing a thermometer well gives a thermometric standard reproducible to 0.002° and is considerably easier to apply than the steampoint. The freezing point is 122.37°.

Pure samples of tin (freezing point 231.90°) and lead (freezing point 327.4°) may also be obtained from the National Bureau of Standards, and furnish convenient thermometric standards.

Lower reference temperatures are supplied by the equilibrium between anhydrous sodium sulfate and its decahydrate (32.37°) [4], and by the equilibrium between solid and gaseous carbon dioxide (−78.48°) [5]. In the latter case, pressure corrections are important, and care must be taken to establish equilibrium between the solid and its pure vapor rather than between the solid and its vapor diluted with air. Commercial dry ice appears to be sufficiently pure for this purpose. Numerous additional secondary standards are listed by Coxon [6].

3 LIQUID-IN-GLASS THERMOMETERS [7]

Mercury-in-Glass Thermometers

The vast majority of temperature measurements in chemical work has been done in the past, and undoubtedly will be done in the future, with mercury-in-glass thermometers. It is therefore important to understand the limitations of this type of thermometer and the errors likely to arise in its use.

Mercury thermometers allow the measurement of temperatures in the range from −25 to 360°, or up to 600° in the case of thermometers constructed of Supremax glass and containing mercury under nitrogen pressure. Gallium in fused silica has been used for thermometry up to 1100°. For measurements of the greatest precision mercury thermometers have been largely replaced by resistance thermometers or thermocouples. However, short-interval mercury thermometers still find some application in calorimetric [8,9] and other types