TECHNIQUES OF CHEMISTRY

VOLUME I

PHYSICAL METHODS OF CHEMISTRY

Edited by

ARNOLD WEISSBERGER

AND

BRYANT W. ROSSITER

PART IIA

Electrochemical Methods

TECHNIQUES OF CHEMISTRY

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 IIA
Electrochemical Methods

WILEY-INTERSCIENCE
A DIVISION OF JOHN WILEY & SONS, INC.
New York · London · Sydney · Toronto

Library of Congress Catalogue Card Number: 77-114920

ISBN 0 471 92727 9

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

TECHNIQUES OF CHEMISTRY

ARNOLD WEISSBERGER, *Editor*

VOLUME I

PHYSICAL METHODS OF CHEMISTRY

PART IIA

Electrochemical Methods

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

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

AUTHORS OF PART II

RALPH N. ADAMS,
Department of Chemistry, University of Kansas, Lawrence, Kansas

BERNARD D. BLAUSTEIN,
Pittsburgh Coal Research Center, Bureau of Mines, U.S. Department of the Interior, Pittsburgh, Pennsylvania

ERIC R. BROWN,
Research Laboratories, Eastman Kodak Company, Rochester, New York

RICHARD P. BUCK,
University of North Carolina, Chapel Hill, North Carolina

JACK CHANG,
Research Laboratories, Eastman Kodak Company, Rochester, New York

JOHN L. EISENMANN,
Ionics, Inc., Watertown, Massachusetts

YUAN C. FU,
Pittsburgh Coal Research Center, Bureau of Mines, U.S. Department of the Interior, Pittsburgh, Pennsylvania

DAVID M. HERCULES,
Department of Chemistry, University of Georgia, Athens, Georgia

SEYMOUR L. KIRSCHNER,
Food and Drug Research Laboratories, Inc., New York, New York

ROBERT F. LARGE,
Research Laboratories, Eastman Kodak Company, Rochester, New York
FRANK B. LEITZ,
Ionics, Inc., Watertown, Massachusetts
LOUIS MEITES,
Department of Chemistry, Clarkson College of Technology, Potsdam, New York
OTTO H. MÜLLER,
State University of New York, Upstate Medical Center, Syracuse, New York
ROYCE W. MURRAY,
University of North Carolina, Chapel Hill, North Carolina
RICHARD C. NELSON,
Department of Physics, The Ohio State University, Columbus, Ohio
STANLEY PIEKARSKI,
Plastics Department, E. I. du Pont de Nemours & Company, Wilmington, Delaware
GERHARD POPP,
Research Laboratory, Eastman Kodak Company, Rochester, New York
LEO SHEDLOVSKY,
Consulting Chemist, New York, New York
THEODORE SHEDLOVSKY,
The Rockefeller University, New York, New York
MICHAEL SPIRO,
Imperial College of Science and Technology, London, England
STANLEY WAWZONEK,
University of Iowa, Iowa City, Iowa

NEW BOOKS AND NEW EDITIONS OF BOOKS OF THE TECHNIQUE OF ORGANIC CHEMISTRY 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
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.

Research Laboratories
Eastman Kodak Company
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:

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 labor for the editors and the publisher. 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 II are Ralph N. Adams, Bernard D. Blaustein, Eric R. Brown, Richard P. Buck, Jack Chang, John L. Eisenmann, Yuan C. Fu, David M. Hercules, Seymour L. Kirschner, Robert F. Large, Frank B. Leitz, Royce W. Murray, Richard C. Nelson, Stanley Piekarski, and Gerhard Popp.

We are also grateful to the many colleagues who advised us in the selection of authors and helped in the evaluation of manuscripts. They are for Part II: Dr. Roger C. Baetzold, Dr. Charles J. Battaglia, Dr. Eric R. Brown, Dr. Jack Chang, Dr. Donald L. Fields, Dr. Robert L. Griffith, Dr. Arthur H. Herz, Mrs. Ardelle Kocher, Dr. Robert F. Large, Dr. Louis Meites, Dr. Louis D. Moore, Jr., Dr. Charles W. Reilley, Mrs. Donna S. Roets, Dr. Willard R. Ruby, Mr. Calvin D. Salzberg, Miss Dianne C. Smith, Dr. Donald E. Smith, Dr. Benjamin B. Snavely, Dr. R. Eliot Stauffer, and Dr. John R. Wilt.

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.

ARNOLD WEISSBERGER
BRYANT W. ROSSITER

April 1970
Research Laboratories
Eastman Kodak Company
Rochester, New York

CONTENTS

ELECTROCHEMICAL METHODS

Chapter 1

POTENTIOMETRY: OXIDATION-REDUCTION POTENTIALS

Stanley Wawzonek

I THEORETICAL INTRODUCTION

Galvanic Cells

An oxidation-reduction reaction is a reaction involving a transfer of electrons from one chemical species (atom, molecule, or ion) to another. In principle, any such reaction can form the basis of a *galvanic cell.* The only requirement is that the site of oxidation (loss of electrons) be physically separated from the site of reduction (gain of electrons) so that the reaction cannot be completed without the passage of an electric current from one site to the other except through the external circuit. The sites of oxidation and reduction are known as *electrodes.* The electrode at which oxidation occurs is called the *anode.* The site of reduction is called the *cathode.* In *potentiometry* no actual reaction is carried out, that is, no appreciable current is passed. Instead, one measures the tendency for the reaction to occur by measuring the difference in electrical potential between the anode and cathode.

The construction of a galvanic cell is conventionally represented by a line formula, beginning with the anode. If it subsequently turns out that the cell actually operates in the opposite direction, then this can be indicated without rewriting the cell formula by a negative sign for the potential, as discussed below. Thus, for example,

$$\mathrm{Zn;\ ZnCl_2}(C_1);\ \mathrm{AgCl;\ Ag} \qquad (1.\mathrm{I})$$

represents a cell with a zinc anode, a zinc chloride solution at concentration C_1, and a cathode consisting of silver chloride plated on silver. Each semicolon represents a phase boundary. The electrode reactions of this cell, writing the anode reaction first, are

$$\mathrm{Zn} \rightarrow \mathrm{Zn^{2+}} + 2e^-$$
$$2e^- + 2\mathrm{AgCl} \rightarrow 2\mathrm{Ag} + 2\mathrm{Cl^-}$$

and the overall reaction, obtained on adding these, is

$$\mathrm{Zn} + 2\mathrm{AgCl} \rightarrow 2\mathrm{Ag} + \mathrm{Zn^{2+}} + 2\mathrm{Cl^-}$$

It should be noted that the anode and cathode reactions must be written so as to involve the same number of electrons.

A second example is

$$\mathrm{Zn;\ ZnSO_4}(C_1);\ \mathrm{CuSO_4}(C_2);\ \mathrm{Cu} \qquad (1.\mathrm{II})$$

This cell consists of a zinc anode, a $\mathrm{ZnSO_4}$ solution at concentration C_1, a $\mathrm{CuSO_4}$ solution at concentration C_2, and a copper cathode. The $\mathrm{ZnSO_4}$ and $\mathrm{CuSO_4}$ solutions are in contact but are prevented from mixing with one another. This may be achieved, for example, by a porous ceramic plug.

The electrode reactions of cell (1.II) are

$$Zn \rightarrow Zn^{2+} + 2e^-$$

$$2e^- + Cu^{2+} \rightarrow Cu$$

and the overall reaction is

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

An important difference between cells (1.I) and (1.II) is that whereas cell (1.I) contains phase boundaries only at the two electrodes, cell (1.II) contains an additional boundary between the $ZnSO_4$ and $CuSO_4$ solutions. This boundary is known as a *liquid junction*, and it gives rise to a potential difference, known as a *liquid junction potential*. This potential arises from the fact that the rate of diffusion of Zn^{2+} from left to right across the boundary differs from the rate of diffusion of Cu^{2+} from right to left, so that a potential gradient is established. Unless $C_1 = C_2$, an additional contribution to this potential will arise from a difference between the rate of diffusion of sulfate across the boundary and the net rate of cationic diffusion. In any cell containing a liquid junction, therefore, the overall potential difference across the cell is not purely a measure of the tendency for the occurrence of an oxidation-reduction reaction, but also involves a contribution from the liquid junction potential.

The magnitude of the liquid junction potential may be greatly reduced by the introduction of a *salt bridge*. This is a concentrated solution, or often a saturated solution, of a salt whose cation and anion have close to the same mobility. KCl is the preferred salt, but NH_4NO_3 is often used when the adjacent solutions contain Ag^+ or some other ion that forms a precipitate with chloride ion. The salt bridge introduces two liquid junctions instead of one, that is, if a salt bridge were introduced into cell (1.II), there would be a liquid junction between the bridge and the $ZnSO_4$ solution, and another between the bridge and the $CuSO_4$ solution. The ion concentration in the salt bridge, as we have mentioned, is made very high; the concentrations C_1 and C_2 are usually relatively low. Thus the two liquid junction potentials are largely determined by the relative rates of diffusion of K^+ and Cl^- (or NH_4^+ and NO_3^-) into the adjoining solutions. Since these ions have similar mobilities, the two liquid junction potentials remain relatively small. Moreover, the two potentials have about the same value, but in opposing directions, so that the net liquid junction is kept even smaller. It should be emphasized, however, that it can never be completely eliminated.

The use of a salt bridge is indicated in the line formula for a cell by two vertical lines, for example,

$$Zn; ZnSO_4(C_1) \| CuSO_4(C_2); Cu \qquad (1.III)$$

represents the same cell as cell (1.II) with a salt bridge replacing the direct contact between the $ZnSO_4$ and $CuSO_4$ solutions. It might be noted that junction potentials also arise at all connections outside the cell between dissimilar conductors. These are taken into account by a universal agreement that the connection of the cell to the potentiometer is always by means of a copper wire. The symbol e^- in the electrode reactions thus represents an electron in a copper conductor, and all intervening potentials are automatically included in the cell potential.

Electromotive Force and the Thermodynamics of Cell Reactions

The potential difference across a galvanic cell is in general determined by the relative rates of reaction at the anode and the cathode. These rates in turn are determined by thermodynamic factors, by potential energy barriers at the electrode surface, by rates of diffusion, and so on. They may depend strongly on the current flowing and on electrode design. The results of potential measurement in general can be given no simple interpretation. If, however, the transfer of electrons can be made to occur under electrically *reversible* conditions, then the potential difference depends only on the *thermodynamics* of the cell reaction (including the changes resulting from diffusion at liquid junctions). This is a consequence of the fact that the electrical work done by the reversible transfer of electricity is the *maximum* electrical work, and this, at constant temperature and pressure, is a measure of the loss of free energy occurring in the cell reaction. The potential difference of a galvanic cell, measured under reversible conditions, is called the *electromotive force*, or *emf*, of the cell. It is the only kind of potential measurement that can be simply interpreted.

To obtain the quantitative relation between the emf, E and the free energy change a reaction can be considered which, as written, requires for completion the passage of n faradays of electricity, where $F = 1$ faraday = 1 mole of electrons = 96,493 C. The maximum electrical work that can be done is then given (in joules) by nFE, where E is measured in volts. As has been pointed out, this term represents the decrease in free energy in the overall cell reaction, that is,

$$\Delta G = -nFE. \tag{1.1}$$

It should be noted that if ΔG is desired in calories, then nFE, in joules, must be divided by 4.1840, which represents the number of joules per defined calorie.

The sign of the free energy change determines the direction in which a reaction proceeds spontaneously. A negative sign means that it proceeds spontaneously in the direction in which it is written; a positive sign means it proceeds in the opposite direction. Equation (1.1) defines the corresponding