PHYSICAL METHODS OF CHEMISTRY

PART IIIC OPTICAL, SPECTROSCOPIC, AND RADIOACTIVITY METHODS

WEISSBERGER AND ROSSITER: EDITORS

TECHNIQUES OF CHEMISTRY VOLUME I

TECHNIQUES OF CHEMISTRY

VOLUME I

PHYSICAL METHODS OF CHEMISTRY

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PART III
Optical, Spectroscopic, and Radioactivity Methods

PART IIIC
Polarimetry

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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 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
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Volume VIII: Investigation of Rates and Mechanisms of Reactions
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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 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. New authors of Part IIIC are Dr. Nicholas M. Bashara, Dr. Bruce Buckman, Dr. Dennis J. Caldwell, Dr. Pierre Crabbé, Dr. Henry G. Curmè, Dr. Henry Eyring, Dr. Arthur C. Hall, Dr. Petr Munk, Dr. Anton Peterlin, and Dr. James M. Thorne.

We are grateful to the many colleagues who advised us in the selection of authors and helped in the evaluation of the manuscripts. These are, for Part IIIC, Dr. Henry G. Curmè, Dr. Charles F. Farran, Dr. Richard T. Klingbiel, Mrs. Ardelle Kocher, Mr. Arthur C. Parker, Mrs. Donna S. Roets, and Dr. Melvin D. Sterman.

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

September 1971
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POLARIMETRY

Chapter I

THEORY OF OPTICAL ROTATION

Dennis J. Caldwell and Henry Eyring

Part 1 NATURAL OPTICAL ACTIVITY

1. INTRODUCTION

The interaction of light with matter is the basis of the most subtle methods for exploring molecular structure. The information obtained is classed under two broad categories, dispersion and absorption. The first measures the rate of phase propagation in the medium as a function of frequency and the second the amount of energy absorbed by the medium.

Only one independent parameter is being measured by the two experiments. The absorption is completely determined by the dispersion and vice versa; however, it must be noted that this is a purely mathematical observation that

will be tempered by the relative sensitivity of the instrumentation and the availability of the necessary regions of the spectrum.

The most precise characterization of a light wave is be means of its polarization. We may expect that the most detailed information on molecular structure is to be obtained from experiments with polarized light, while average, less sensitive properties will be determined from investigations with random polarization.

All material media exhibit the phenomena of dispersion and absorption. Over the years it has been possible to separate the absorption spectra of many compounds into regions controlled by individual groups. In the area of dispersion molar refractivities are found to be nearly additive. This phase of spectroscopy has become a means for identifying the existence of certain groups in a molecule along with any strong interactions among them.

Dissymmetric molecules, which have no improper rotations among their symmetry operations, will exhibit the phenomena of optical rotatory dispersion and circular dichroism. The properties measured are the differences between the indices of refraction and between extinction coefficients for left and right circularly polarized light. Ordinary dispersion and absorption are measured by the average values of these quantities.

It should be borne in mind that despite the traditional emphasis on configuration and asymmetric centers, dissymmetry is more a property of molecular conformation. The difference between the environment of a group in an optically active molecule and that of a group in an inactive one often involves very small energies. Normally ordinary dispersion and absorption are insensitive to conformation changes. On the other hand, rotatory dispersion and circular dichroism depend on molecular dissymmetry.

Any optically active molecule will have conformations of zero rotation. If the conformation is measured by a set of coordinates, Q_i, and $E(Q_i)$ is the associated energy, the observed parameter of optical activity is

$$\bar{A} = \int dQ_1 \cdots \int dQ_n A(Q_1 \cdots Q_n) e^{-E(Q_i)/kT}. \tag{1.1}$$

This gets us used to the idea that conformation is essentially a temperature-dependent property as is also optical activity. In some cases molecules are frozen in nearly rigid conformations with high-energy barriers. Then (Q_i) is sharply peaked at some particular set of Q_i values and the integration may be dropped. In (1.1) we must include only that set of conformations which may be continuously deformed into one another without crossing any barriers. Otherwise, a racemic mixture would always be described.

Every molecule with more than three atoms will have dissymmetric conformations or configurations. Normally only those which form stable mirror image molecules are considered optically active. For example, two

of the three staggered forms of *n*-butane (Fig. 1.1) are dissymmetric and are mirror images. The third has both a plane of symmetry and a center of inversion. The molecule is not considered optically active because the barrier separating the first two forms is too small at temperatures above the melting point. In fact this may be taken as a rough criterion for an optically active molecule: that there exists at least one conformation separated from its mirror image by a barrier with $E \gg kT_{\text{fusion}}$.

In earlier days it would have been customary to explain the fact by saying that *n*-butane does not have an asymmetric center. An asymmetric center has been considered important because it means that all so-called rotamers of the molecule would be dissymmetric. There are, of course, many optically active molecules without asymmetric centers such as the α, α' substituted biphenyls (Fig. 1.2). Here a rotational barrier exists similar to the ethane barrier except that it is sufficiently greater than the thermal energy factor kT that the criterion for optical activity is satisfied.

There is evidence for believing that in the series of optically active hydrocarbons the rotations would be an order of magnitude lower than observed if all rotamers were equally probable. It is apparent that optical activity has the potential for being a very sensitive probe into the conformation of molecules. Unfortunately, only the surface has been scratched in the art of interpreting dispersion and absorption spectra.

In any discussion of optical rotatory power it must be remembered that the optical rotation for a given molecule is the composite effect of many conformations. This tool will be most useful when one conformation is believed to predominate greatly over the others. At present there is still considerable difficulty in organizing and interpreting data on molecules with reasonably well-known conformations.

2 ELECTROMAGNETIC THEORY

The theoretical discussion will proceed along two lines: a qualitative presentation of the mechanisms, along with an outline of the quantum mechanical derivations and resulting formulas.

If precise tractable methods for calculating wave functions of complex molecules existed, spectroscopy would largely reduce to an analytical tool for identifying new compounds. As it is, many techniques are geared for deciding the positions of the nuclei. This has been the primary goal in studying optical activity, particularly from the standpoint of the biochemist.

If theoretical and empirical rules for calculating optical activity as a function of arbitrary conformation could be developed, the way would be open for using this as a universal tool in the determination of conformation. From the theoretical standpoint, spectroscopy is used as a guide in finding approximate eigenstates of the Hamiltonian.

In optical activity one is faced with the situation where most investigators are satisfied with the electronic information furnished by ordinary absorption and delve into further refinements of the wave function only as much as is necessary to construct a theory of conformations.

An electromagnetic wave is not a particularly easy phenomenon to characterize. It is, of course, a periodic disturbance with a sinusoidal dependence on space and time:

$$F = F_o \sin 2\pi(vt - x/\lambda), \tag{1.2}$$

where F is a measure of the intensity of the disturbance at x at time t. A velocity is seen to be associated with the wave, since the points of constant phase, the nodes, for example, satisfy the equation, $x/t = c = v\lambda$.

The constant c is the phase velocity of the wave. The simplest of all situations is the monochromatic wave in a vacuum. Here c is a universal constant, the so-called speed of light. In a region pervaded by matter three distinctions must be made for a monochromatic wave. The wavefront velocity is defined as the rate at which the first disturbance is propagated through the medium. It is always equal to c, the vacuum constant. The signal velocity is the rate at which the bulk of the energy is transferred to undisturbed parts of the medium. This velocity is difficult to define precisely, but it is always equal to or less than c. Once a steady state has been achieved throughout the medium, the parameter of interest is the phase velocity described above. Since all parts of the medium are under the influence of the disturbance in the steady state, the propagation of a mathematically defined quantity known as the phase, at velocities greater than c, in no way conflicts with the ideas of relativity.

In optical rotation we are concerned with the phase velocity. Two vector quantities, **E** and **B**, are associated with any electromagnetic disturbance. The constitutive equations of electromagnetic theory reduce their total of six components to four, and in an electromagnetic wave the number is reduced effectively to three. The electric vector **E** determines the accelerations of charge at rest in the observer's system, and the magnetic induction vector **B** introduces a component of force perpendicular to the instantaneous velocity for a moving charge.

The principles of electromagnetic theory are best discussed in terms of a four-dimensional space-time continuum. It is possible to construct a system of charges with arbitrary values of **B** and **E** at a given point at some time but their values over all space cannot be specified independently. This fact is implicit in the Maxwell equations:

$$\nabla \times \mathbf{E} = \frac{-1}{c}\frac{\partial \mathbf{B}}{\partial t} \tag{1.3a}$$

$$\nabla \times \mathbf{B} = \frac{1}{c}\frac{\partial \mathbf{E}}{\partial t}. \tag{1.3b}$$

If we have detailed knowledge of the charge and current distribution for a given problem, the computed values of **E** and **B** will agree entirely with (1.3*a*,*b*).

In material media it is convenient to take account of polarization effects separately. Two auxiliary vectors are defined as **M**, the magnetic moment per unit volume, and **P**, the electric dipole moment per unit volume. In cgs units these vectors have the same dimensions as **B** and **E**. The properties of the medium are manifested in the quantities, **M** and **P**. In general they will be functions of **B** and **E**.

There are several points to remember about a material medium. The force on a macroscopic charge embedded therein is equal to $q\mathbf{E}$, since **E** is defined as the space average over a region large compared with molecular dimensions. The magnetic component of the force on a moving charge is not so easy to characterize and it is preferable to define a new vector, $\mathbf{H} = \mathbf{B} - 4\pi\mathbf{M}$. In a vacuum, (1.3*a*,*b*) imply that $\nabla \cdot \mathbf{E}$ and $\nabla \cdot \mathbf{B}$ are constants, which may be set equal to zero. A simple argument shows that in the presence of a charge distribution $\nabla \cdot \mathbf{E}$ is no longer zero, but rather $\nabla \cdot \mathbf{D} = 4\pi\rho$, where $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}$ and ρ is the charge density.

A similar argument could be applied to the magnetic field if a magnetic charge existed. The difference between **B** and **H** may be resolved in the following way: If a test charge is completely free to move through all parts of a small but still macroscopic element of the medium including the electron orbits, it will experience a force derived solely from currents governed by the vector **B** according to the general equation

$$\nabla \times \mathbf{B} = \frac{4\pi}{c}\mathbf{J}_{\text{total}}, \tag{1.4}$$

where $\mathbf{J}_{\text{total}}$ is the sum of all types of currents in the medium, including migrating charge (the conventional current), the polarization current (moving bound charge), the atomic magnetization currents, and Maxwell's so-called convection current, $(1/\pi)/(\partial\mathbf{E}/\partial t)$.

It is this last current which made the early theory of radiation possible. Equation (1.4) may also be written

$$\oint \mathbf{B} \cdot d\mathbf{s} = \frac{4\pi}{c}\int_{\mathbf{S}} \mathbf{J}_{\text{total}} \cdot d\mathbf{S}, \tag{1.4a}$$

stating that the line integral of **B** over an arbitrary path in the medium is proportional to the total current flux through any surface bounded by the closed line. When the total current is resolved into its components, (1.4) becomes

$$\nabla \times \mathbf{B} = \frac{1}{c}\frac{\partial \mathbf{E}}{\partial t} + \frac{4\pi}{c}\frac{\partial \mathbf{P}}{\partial t} + \frac{4\pi}{c}(c\nabla \times \mathbf{M}) + \frac{4\pi}{c}\mathbf{J}, \tag{1.5}$$

where **J** is now the conventional macroscopic current.

It can be shown that a test charge free to move in all regions of the medium without restriction will experience an electric force **E** and a magnetic force **B**. If certain regions are to be excluded in a systematic way, other results follow. For example, it is usually assumed that the regions occupied by molecules are impenetrable. In particular, molecules may be regarded as electric and magnetic dipoles. The spatially averaged fields subject to this restriction may then be shown to be $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}$ and $\mathbf{H} = \mathbf{B} - 4\pi\mathbf{M}$ with

$$\nabla \cdot \mathbf{D} = 4\pi\rho \tag{1.6a}$$

$$\nabla \cdot \mathbf{B} = 0 \tag{1.6b}$$

These equations supplement (1.3*a*,*b*) and are assumed to hold under all conditions. The differences arise in the interpretation of the four vectors, **E**, **B**, **D**, and **H**.

The customary exposition of Maxwell's equations is

$$\nabla \times \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t} \tag{1.7a}$$

$$\nabla \times \mathbf{H} = \frac{1}{c}\frac{\partial \mathbf{D}}{\partial t} + \frac{4\pi}{c}\mathbf{J} \tag{1.7b}$$

$$\nabla \cdot \mathbf{D} = 4\pi\rho \tag{1.7c}$$

$$\nabla \cdot \mathbf{B} = 0 \tag{1.7d}$$

In order to solve these equations to determine the types of waves propagated in materials, constitutive relations connecting **B** and **H** and **E** and **D** are required. These will in turn depend on the geometry and composition of the medium.

If both **P** and **M** are zero, we are dealing in effect with a distribution of charge ρ and a current **J**. The vectors **B** and **E** may be found by a special type of integration over the charge and current densities. The solution to (1.7*a*–*d*) with $\mathbf{E} = \mathbf{D}$ and $\mathbf{H} = \mathbf{B}$ may be shown to be

$$\mathbf{B} = \nabla \times \mathbf{A} \tag{1.8a}$$

$$\mathbf{E} = -\nabla\phi - \frac{1}{c}\frac{\partial \mathbf{A}}{\partial t} \tag{1.8b}$$

$$\mathbf{A} = \int \frac{\mathbf{J}(\text{ret})}{r}\, d\tau \tag{1.8c}$$

$$\phi = \int \frac{\rho(\text{ret})}{r}\, d\tau \tag{1.8d}$$

where r is the distance from the variable volume element of integration to the field point and $\mathbf{J}(\text{ret})$ and $\rho(\text{ret})$ are the retarded potentials to be evaluated at the time $t - r/c$. It is worth noting that $\mathbf{J}$ and ρ are not entirely independent since the equation of continuity must be satisfied:

$$\nabla \cdot \mathbf{J} + \frac{\partial \rho}{\partial t} = 0. \tag{1.9}$$

If $\mathbf{J} = 0$, then ρ must be independent of time and ϕ becomes the ordinary scalar potential of electrostatics, the sum of the potentials furnished by each volume element of stationary charges. Unfortunately, (1.8*a–d*) do not provide a practical means to solve many electromagnetic problems, since the final charge and current densities are quantities to be determined in the course of the solution.

The problem is neatly reformulated in material media by absorbing the various currents involved into the vectors $\mathbf{H}$ and $\mathbf{D}$. In the problems of interest there are no macroscopic currents ($\mathbf{J} = 0$) and no time-dependent charge distributions. The electrostatic part of the field, $-\nabla\phi$, may be discarded in the treatment of the radiation problem; the equations to be solved are

$$\nabla \times \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t} \tag{1.10a}$$

$$\nabla \times \mathbf{H} = \frac{1}{c}\frac{\partial \mathbf{D}}{\partial t}. \tag{1.10b}$$

The relations $\nabla \cdot \mathbf{D} = 0$, $\nabla \cdot \mathbf{B} = 0$ are effectively implied in these equations.

Equation (1.10*a*) is satisfied by the relations

$$\mathbf{B} = \nabla \times \mathbf{A} \tag{1.11a}$$

$$\mathbf{B} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t}. \tag{1.11b}$$

In a vacuum where $\mathbf{H} = \mathbf{B}$ and $\mathbf{E} = \mathbf{D}$ the equation, $\nabla \times \mathbf{B} = (1/c)/(\partial \mathbf{E}/\partial t)$, would lead to $\nabla \times (\nabla \times \mathbf{A}) + (1/c^2)/(\partial^2 \mathbf{A}/\partial t^2) = 0$ and the result

$$\nabla^2 \mathbf{A} = \frac{1}{c^2}\frac{\partial^2 \mathbf{A}}{\partial t^2}, \tag{1.12}$$

where use has been made of the vector relation, $\nabla \times (\nabla \times \mathbf{A}) = \nabla(\nabla \cdot \mathbf{A}) - \nabla^2 \mathbf{A}$, and the fact that $\nabla \cdot \mathbf{A}$ may be set equal to zero in most radiation problems with no loss of generality.