TECHNIQUES OF CHEMISTRY

VOLUME I

PHYSICAL METHODS OE CHEMISTRY

Edited by

ARNOLD WEISSBERGER

AND

BRYANT W. ROSSITER

PART III

Optical, Spectroscopic, and Radioactivity Methods

PART IIID

X-Ray, Nuclear, Molecular Beam, and Radioactivity 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

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Research Laboratories
Eastman Kodak Company
Rochester, New York

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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*
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 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 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 new authors to the series. New authors of Part III-D are Dr. R. G. Albridge, Dr. I. Amdur, Dr. L. S. Bartell, Dr. H. M. Clark, Dr. J. H. Green, Dr. V. C. Guinn, Dr. W. C. Hamilton, Dr. Y. Hazony, Dr. R. H. Herber, Dr. R. A. Jacobson, Dr. J. E. Jordan, Dr. E. A. Mason, Dr. J. A. Merrigan, Dr. J. M. Nielsen, and Dr. S. Tao.

The Chapter on "Mass Spectrometry" by Dr. Guy P. Arsenault was not received by the publication deadline. This chapter will appear in a supplemental volume, since it would have been unfair to the authors of the other chapters to delay 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 are, for Part III-D, Dr. Thomas Carlson, Mr. John A. Hamilton, Mrs. Ardelle Kocher, Dr. Edwin P. Przybylowicz, and Dr. Douglas L. Smith. Also, the help of Mrs. Donna S. Roets is gratefully acknowledged.

The editors express their deep sorrow upon learning of the untimely death of Professor Isador Amdur.

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
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CONTENTS

X-RAY, NUCLEAR, MOLECULAR BEAM, AND RADIOACTIVITY METHODS

Chapter I

X-RAY CRYSTAL STRUCTURE ANALYSIS

William N. Lipscomb and Robert A. Jacobson

In Section 1 the reader is introduced to the general principles of a complete structure determination, and two specific methods of structure determination, symbolic addition and Patterson superposition, are chosen to illustrate in a

simple way some of the methods that practicing crystallographers now use to solve complex structures. Many other methods are available, and a few of these are also described briefly here. Equations for the computation of amplitudes of scattering, the electron density, and the vector map are derived in Section 2. No mathematics beyond elementary calculus is assumed, and all the necessary properties of vectors, complex numbers, and Fourier series are presented in detail. Section 3 is a geometrical description of symmetry in crystals with emphasis on the symmetries most frequently encountered in complex crystals. This section owes very much to Professor J. H. Sturdivant, who kindly gave his permission for the use of his notes on symmetry which formed the basis from which Section 3 was written. In Section 4 the relation between the experimental methods and the preceding sections are outlined, and one complete structure determination is described in detail.

These sections are independent of one another and can be read separately. Section 1 is designed primarily for the reader who wishes to obtain a general idea of how complex structures are determined. The later sections elucidate different aspects of these methods of structure investigation, and they have been used during the past several years for notes in a course on X-ray crystallography.

1 INTRODUCTION AND ILLUSTRATION OF SOME TYPICAL METHODS FOR THE DETERMINATION OF COMPLEX STRUCTURES*

Introduction

Some of the finest recent achievements of X-ray crystallography are undoubtedly the determinations of the structures of myoglobin [1], hemoglobin [2, 3], lysozyme [4], carboxypeptidase A [5], ribonuclease [6, 7], and other large biological molecules [8]. These structures are among the most complex elucidated at present and represent, of course, many man-years of effort. However, the routine determination of almost any complex structure containing say 40 or more atoms can be expected from any one of many crystallographic laboratories at the present time. The purpose of this chapter is to introduce the general principles of X-ray crystallography and to illustrate a few of the frequently used methods for the solution of such structures.

The complexity of structures solved by X-ray diffraction techniques has increased greatly since about 1950. New developments in the methods by

* For more detailed discussion of the topics in this section, the reader should consult C. W. Bunn, *Chemical Crystallography*, 2d ed., Oxford University Press, New York, 1961; K. Lonsdale, *Crystals and X-rays*, Van Nostrand, New York, 1949; J. M. Robertson, *Organic Crystals and Molecules*, Cornell University Press, Ithaca, N.Y., 1953; G. H. Stout and L. H. Jenson, *X-ray Structure Determination*, Macmillan, New York, 1968.

which the first approximately correct atomic arrangement (trial structure) in the unit cell of a previously unsolved structure is obtained have greatly increased the power of this technique. At present it is reasonable to expect a complete structure determination of nearly any molecule containing up to forty atoms (excluding hydrogens) with the expenditure of a week to 6 months of effort.

A structure that has been established by careful X-ray diffraction techniques is unlikely to be incorrect [9]. The crystallographer is in a very favorable position with respect to the ratio of observations to unknowns, which usually ranges from 6 up to 10 to 1 when complete data are obtained. For example, in the structure determination of di-μ-diphenylphosphinatoacetylacetonatochromium(III) [10] some 4,400 independent X-ray diffraction maxima were observed. The unknowns in this case are the x, y, z coordinates of the chromium, oxygen, phosphorus, and carbon atoms of which there are a total of 60 atoms, a scale parameter, six anisotropic temperature parameters for each of the chromium, oxygen, and phosphorus atoms, and single isotropic temperature parameters for each of the carbon atoms, giving 140 temperature parameters in all. The total number of parameters is thus 321.

Unfortunately the equations relating these 321 unknowns to the 4400 observations are not simple. For example, the 180 distance parameters are related to the observations by complicated trigonometric expressions. Hence it is usually necessary to combine mathematical methods with methods into which chemical reasonableness can be introduced. We describe in this introduction a few of the common methods of structure determination based either on the direct use of the intensities or on the analysis of the Patterson function, a three-dimensional map of all the vectors that can be drawn between pairs of atoms in the structure and then plotted on a common origin. This map can be computed directly from the observed data with no chemical assumptions. These methods are not the only ones available but in general have proved to be the ones of most generality, hence most widely used.

The final test of correctness of a structure is the agreement between the observed and the calculated intensities. How good this agreement is varies according to the structure, the methods used to acquire the data, and other things, but it should be comparable with that obtained in similar structural studies, which are in general readily available. The trial structure may be obtained by mathematical techniques involving few or no chemical assumptions or by other techniques involving intuition, guesses, and the background available in the "scientific method," but the test of obtaining good agreement with large numbers of observations with relatively few parameters is so severe that the results can usually be considered equally as good whatever the method.

The beginning stages of a structure determination are similar in all methods

of attack; hence we start with a brief description of what the chemist can learn from the preliminary stages. Briefly, these stages are the identification from powder photographs or from a determination of the unit cell and molecular weight, the unit cell symmetry, and the complete structure determination.

Identification by Powder Photography

X-rays are very short wavelength electromagnetic radiations produced when L electrons fall into the K shell of elements of moderately high or high atomic number, when M electrons fall into the L shell of the elements of high atomic number, or when electrons are decelerated rapidly. These three types of radiation are called characteristic K, characteristic L, or white radiation, respectively. The vacancies necessary for these transitions to occur are produced when electrons are accelerated through a potential of about 50,000 V toward a water-cooled target of a heavy metal such as copper (1.54-Å radiation) or molybdenum (0.711-Å radiation). X-rays are not appreciably deviated by an ordinary lens system; hence pinholes are used to produce a collimated beam, or a self-focusing arrangement is used in which the source, a large area of sample, and the film or counter detector all lie on the circumference of a circle. If a flat sample is used in this way, absorption problems are usually negligible. However, if a cylindrical specimen of powder or a single crystal is used, the X-rays must pass through part of the sample, and excessive absorption of X-rays can occur if the sample is too large. For a sample of a given size the amount of reduction of intensity is proportional to the intensity and to the thickness of the sample, that is, $dI = -\mu I\,dx$, where μ is called the linear absorption coefficient. It may be calculated from $\mu = \rho[f_A\mu_A^{(m)} + f_B\mu_B^{(m)} + f_C\mu_C^{(m)} + \cdots]$, where ρ is the density of the sample and f_A is the weight fraction of element A having mass absorption coefficient $\mu_A^{(m)}$. Tables of $\mu_A^{(m)}$ can be found in *International Tables for X-ray Crystallography* (The Kynoch Press, Birmingham, England, 1952). Integration of this expression gives $I = I_0e^{-\mu x}$, where I is the resultant intensity for a sample of thickness x on which an initial intensity of I_0 falls. The intensity of diffracted radiation depends on I and on the total size of the specimen, which is proportional to x^3 for a cylindrical specimen. Hence $I_{diff} = KIx^3$. The maximum value of I_{diff} is obtained by setting $dI_{diff}/dx = KI_0\,d(x^3e^{-\mu x})/dx = 0$, from which the optimum size of sample is found to be $x = 2/\mu$. Typical values of $1/\mu$ are 0.5 mm for Cu$K\alpha$ radiation and 4 mm for Mo$K\alpha$ radiation for diamond, and 0.006 mm for Cu$K\alpha$ and 0.05 mm for Mo$K\alpha$ radiation for I_2. In order to avoid appreciable corrections for absorption it is necessary to keep the sample thickness to about $\frac{1}{4}$ or less of $1/\mu$. More often, however, one does not wish to sacrifice intensities of weak reflections; hence absorption corrections are made.

When K radiation is produced from a target, the $K\alpha$ doublet (resolved only at high diffraction angles) is the desired line. However an additional line ($K\beta$) is produced which can effectively be reduced by the use of special absorption filters. For example, a 10-μ ($1\ \mu = 10^{-4}$ cm) nickel filter will reduce the Cu$K\alpha$ line to about $\frac{1}{2}$ of its original intensity, while at the same time reducing the Cu$K\beta$ line to 1/85 of its original intensity or about 1/300 of the intensity of the reduced Cu$K\alpha$ intensity. For molybdenum radiation a zirconium filter of 80 to 100 μ is employed to obtain similar results.

A given diffraction maximum from a small crystal is quite sharply defined. It is intrinsically small because of the large number of unit cells, for reasons discussed below, but for practical purposes most of its width comes from divergence of the X-ray beam and from crystal imperfections. Its angle of deviation (2θ) from the direct beam of X-rays is given by the Bragg law, which arises from the condition that the path difference for a set of equivalent planes into which the structure is resolved shall be some integral number of wavelengths. If the spacing of these planes is called d'_{hkl} and if the integer is n (the order of the reflection), the relation is

$$n\lambda = 2d'_{hkl} \sin \theta.$$

The derivation of this equation and the definition of hkl, the three numbers describing the reflecting plane, are discussed in detail below. In a finely powdered sample all orientations of crystals can occur; thus a given plane diffracting in a given order, say $n = 1$, would give a diffraction maximum whenever it is oriented so that the Bragg law is satisfied for specular reflection. Thus all reflections from a given plane in a powdered sample would lie on a cone making an angle of 2θ with respect to its axis (Fig. 1.1). Because 2θ can have values from 0 to 180°, a cylindrical strip of film is ordinarily used instead of a flat plate (Fig. 1.2).

A powder sample that is not sufficiently randomly oriented or that is too coarse will give discrete spots instead of continuous powder lines. Hence it is usual to grind the sample until it passes through about a 300-mesh screen, which will give a crystallite size of about 40 μ or less. In addition, the sample

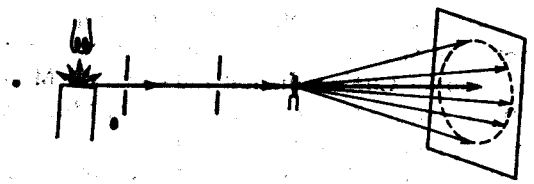

Fig. 1.1 Experimental arrangement showing a single powder line at an angle of deviation 2θ from the X-ray beam.