
HYDROGEN
PEROXIDE



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HYDROGEN PEROXIDE

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GENERAL INTRODUCTION

American Chemical Society's Series of Chemical Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical progress. The American Chemical Society named as Trustees, to make the necessary arrangements of the publication of the Monographs, Charles L. Parsons, secretary of the Society, Washington, D. C.; the late John E. Teeple, then treasurer of the Society, New York; and the late Professor Gellert Alleman of Swarthmore College. The trustees arranged for the publication of the ACS Series of (a) Scientific and (b) Technological Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successor) of New York.

The Council of the American Chemical Society, acting through its Committee on National Policy, appointed editors (the present list of whom appears at the close of this sketch) to select authors of competent authority in their respective fields and to consider critically the manuscripts submitted.

The first Monograph of the Series appeared in 1921. After twenty-three years of experience certain modifications of general policy were indicated. In the beginning there still remained from the preceding five decades a distinct though arbitrary differentiation between so-called "pure science" publications and technologic or applied science literature. By 1944 this differentiation was fast becoming nebulous. Research in private enterprise had grown apace and not a little of it was pursued on the frontiers of knowledge. Furthermore, most workers in the sciences were coming to see the artificiality of the separation. The methods of both groups of workers are the same. They employ the same instrumentalities, and frankly recognize that their objectives are common, namely, the search for new knowledge for the service of man. The officers of the Society therefore combined the two editorial Boards in a single Board of twelve representative members.

Also in the beginning of the Series, it seemed expedient to construe

rather broadly the definition of a Monograph. Needs of workers had to be recognized. Consequently among the first hundred Monographs appeared works in the form of treatises covering in some instances rather broad areas. Because such necessary works do not now want for publishers, it is considered advisable to hew more strictly to the line of the Monograph character, which means more complete and critical treatment of relatively restricted areas, and, where a broader field needs coverage, to subdivide it into logical subareas. The prodigious expansion of new knowledge makes such a change desirable.

These Monographs are intended to serve two principal purposes: first, to make available to chemists a thorough treatment of a selected area in form usable by persons working in more or less unrelated fields to the end that they may correlate their own work with a larger area of physical science discipline; second, to stimulate further research in the specific field treated. To implement this purpose the authors of Monographs are expected to give extended references to the literature. Where the literature is of such volume that a complete bibliography is impracticable, the authors are expected to append a list of references critically selected on the basis of their relative importance and significance.

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PREFACE

Since 1945 the authors have been engaged in research on hydrogen peroxide at the Massachusetts Institute of Technology. During this time more than one hundred students and staff members have been associated with us in studying a wide variety of problems concerned with hydrogen peroxide. From the beginning there was felt the lack of a critical and comprehensive source of information in the English language, and the major incentives in writing this book were to supply this need and to make available to others data and experience we have obtained. In addition we have provided background information to show the broader relationships into which hydrogen peroxide falls; for example, its structure is considered in comparison with other oxygen-hydrogen species and its reactivity with that of other peroxy compounds; in discussing its industrial uses we have tried to evaluate its position relative to competitive materials. Also discussed is the path by which the true nature of hydrogen peroxide was gradually revealed after its discovery in 1818.

The technology of hydrogen peroxide, unlike that of many inorganic chemicals, has undergone rapid development in recent years. At the beginning of the twentieth century the dilute and unstable product of the technology of the day had limited applications, primarily as a disinfectant and for bleaching articles such as hair, feathers, and wool which are easily harmed by other bleaching agents. The introduction of the electrochemical manufacturing processes in 1908 made it possible to produce a relatively pure and stable product which acquired increasing acceptance. More recently the large scale use of concentrated hydrogen peroxide as a military propellant in Germany during World War II demonstrated that this material could be handled safely in large quantities. This stimulated interest among many potential users to whom hydrogen peroxide, even in much lower concentrations, had previously appeared as an unstable and sensitive material. Moreover the introduction of new manufacturing processes in the last few years brings promise of lower costs. The increasing interest in hydrogen peroxide is measured by the five-fold increase in the U.S. production and consumption of this chemical in the last decade and the rapidly increasing numbers of published articles concerned with it, both of which attest to the need for gathering together a critical evaluation of present knowledge of this chemical.

Beyond its industrial uses, hydrogen peroxide has long been of concern

to chemists because of the unusual characteristics of the peroxide bond. Its unique position as the oxidation-reduction intermediate between oxygen and water accounts for its formation in a wide variety of reactions and its occurrence in the metabolism of living cells. This unique character and widespread occurrence make hydrogen peroxide of interest to a great variety of scientists and technologists. It is probably not generally recognized that the scope of knowledge of hydrogen peroxide is as extensive as that of most common chemicals.

The literature concerning hydrogen peroxide has become so large and diffuse that it is not practical to quote every paper dealing with it. Instead we have referred to all publications coming to our attention before mid-1954 that appeared to have some present-day usefulness. It has not been possible to incorporate more recent work, except in a few instances. In some cases reference is made to review articles rather than to all the preceding literature. Patents have been treated in the same fashion as other publications and it has not been attempted to prepare an exhaustive list of them. In some cases, particularly in the chapters on manufacture, various U.S. and British government reports of German practice give more complete information than is available elsewhere, and references are accordingly made to them instead. The so-called P.B. Reports, listed in the references, are available from the Office of Publications Board, U. S. Department of Commerce. Similar reports were issued by the Combined Intelligence Objectives Subcommittee (C.I.O.S.) and the British Intelligence Objectives Subcommittee (B.I.O.S.). Many of these are also available as P.B. Reports. Although some literature of importance may have been overlooked, we believe that substantially all the facts and ideas of current value about hydrogen peroxide have been brought to the reader's attention. We have tried to evaluate the material critically insofar as the availability to us of the original literature and our own background has permitted us to do so.

Space limitations have made it necessary to curtail the discussion of many special topics. It was decided at the outset that the related and important field of organic peroxides would not be considered except incidentally and that only an introduction could be given to the organic and biological chemistry of hydrogen peroxide. Practical techniques as such, for example, those involved in packaging and handling hydrogen peroxide, cannot be treated appropriately in a book of this kind.

The chief sources of references to work on hydrogen peroxide were Chemical Abstracts, *Chemische Zentralblatt*, two earlier monographs on hydrogen peroxide by Machu and Kausch, the indexes of early journals, the card catalogs of a number of libraries, and the bulletins of hydrogen peroxide manufacturers. Considerable material is from unpublished work and theses on hydrogen peroxide carried out at the Massachusetts Institute

of Technology. With many of the references to less available sources, a bracketed citation of the location of its abstract in Chemical Abstracts has been included. The same technique has been used to denote a number of other abstracts, notices, translations, or duplicate patents.

We would welcome reprints of papers old and new, dealing with hydrogen peroxide.

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April, 1955

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We are indebted to many individuals for their assistance; among them are the following: Donald B. Broughton, Universal Oil Products Co., originally to have been a co-author, for aid in the preparation of some preliminary manuscript and for review of the completed book; Max E. Bretschger, Becco Chemical Division, Food Machinery & Chemical Corp., and Russell E. Cushing, Pennsylvania Salt Manufacturing Co., for review of manuscript and for supplying the photographs of the German manufacturing plants; Victor W. Slater, Laporte Chemicals Ltd., for supplying a copy of the painting of the early hydrogen peroxide plant and description of its operation; Joseph S. Reichert, James H. Young, and Alfred T. Hawkinson, Electrochemicals Department, E. I. duPont de Nemours and Co., Hans O. Kauffmann and Frank P. Greenspan, Becco Chemical Division, Gerhard A. Cook, Linde Air Products Co., G. J. Minkoff, Imperial College, London University, John O. Edwards, Brown University, and Irwin W. Sizer and Robert C. Reid, M.I.T., for review of portions of the manuscript; and Paul-A. Giguère, Laval University, to whom we owe much for our very complete knowledge of the physical properties of hydrogen peroxide, for commenting on the manuscript and for supplying us on many occasions with experimental details and data in advance of publication. The staffs of several manufacturers have been most coöperative in supplying their bulletins: Becco Chemical Division, the duPont Co., LaPorte Industries, Ltd., and Pennsylvania Salt Manufacturing Co. Many of the original drawings were prepared by the M.I.T. Illustration Service.

Those who reviewed the manuscript did so with the version in report form. In many sections substantial revisions of that manuscript have been made. The responsibility for opinions and correctness of facts of course remains ours, and it will be appreciated if readers will call attention to errors.

W. C. S.
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R. L. W.

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