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CHEMISTRY FOR ENVIRONMENTAL ENGINEERING

Fourth Edition

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To
the late Dr. Clair N. Sawyer
who began this venture as sole author of the first edition in 1960

AND TO OUR FAMILIES
Martha, Annette, Kyle, and Eric
who sacrificed much for this current effort.

ABOUT THE AUTHORS

The late **Clair N. Sawyer** was active in the field of sanitary chemistry for over 30 years. He received a Ph.D. from the University of Wisconsin. As Professor of Sanitary Chemistry at the Massachusetts Institute of Technology, he taught and directed research until 1958. He then was appointed Vice President and Director of Research at Metcalf and Eddy, Inc., and served as consultant on numerous water and wastewater treatment projects in the United States and many foreign countries. After retiring, he served as an environmental consultant for several years. He passed away in 1992 while this fourth edition was in preparation. He was the originator and sole author of the first edition, which was published in 1960.

Perry L. McCarty is the Silas H. Palmer Professor of environmental engineering at Stanford University, and Director of the Western Region Hazardous Substance Research Center. He received a B.S. degree in civil engineering from Wayne State University and S.M. and Sc.D. degrees in sanitary engineering from the Massachusetts Institute of Technology, where he taught for four years. In 1962 he joined the faculty at Stanford University. His research has been directed towards the application of biological processes for the solution of environmental problems. He is an honorary member of the American Water Works Association and the Water Environment Federation, and Fellow in both the American Association for the Advancement of Science and the American Academy of Microbiology. He was elected to the National Academy of Engineering in 1977. In 1992 he received the Tyler Prize for environmental achievement.

Gene F. Parkin is a Professor of Civil and Environmental Engineering at the University of Iowa, and Director of the Center for Health Effects of Environmental Contamination. He received a B.S. degree in civil engineering and an M.S. degree in sanitary engineering from the University of Iowa and a Ph.D.

degree in environmental engineering from Stanford University. He taught at Drexel University for eight years before joining the faculty at the University of Iowa in 1986. His teaching interests have been in biological treatment processes and environmental chemistry. His research has been directed toward anaerobic biological processes and bioremediation of waters contaminated with organic chemicals. He has received the J. James R. Croes Medal from the American Society of Civil Engineers and the Harrison Prescott Eddy Medal from the Water Environment Federation. In 1989 he received the Hancher-Finkbine Medallion from the University of Iowa for outstanding teaching and leadership.

PREFACE

Education in environmental engineering has historically been conducted at the graduate level, and up to the present time has drawn mainly on students with a civil engineering background. In general, education in civil engineering does not prepare a student well in chemistry and biology. Since a knowledge of these sciences is vital to the environmental engineer, the graduate program must be designed to correct this deficiency. In recent years, students from other engineering disciplines and from the natural sciences have been attracted to this field. Some have a deficiency in chemistry and biology similar to that of the civil engineer and need exposure to general concepts of importance.

A current trend in the United States is the introduction of an undergraduate environmental engineering option or degree program within civil engineering departments. These students also require an introduction to important concepts in chemistry and biology.

This book is written to serve as a textbook for a first course in chemistry for environmental engineering students with one year of college-level chemistry. Environmental engineers need a wide background in chemistry, and in recognition of this need, this book summarizes important aspects from various areas of chemistry. This treatment should help orient the students, aid them in choosing areas for advanced study, and help them develop a better "feel" for what they should expect to gain from further study.

The purpose of this book is twofold: It (1) brings into focus those aspects of chemistry that are particularly valuable to environmental engineering practice, and (2) it lays a groundwork of understanding in the area of specialized quantitative analysis, commonly referred to as water and wastewater analysis, that will serve the student as a basis in all the common phases of environmental engineering practice and research.

Substantial changes continue to occur in the emphasis of courses for environmental engineers. The trend is toward a more fundamental understanding of the chemical phenomena causing changes in the quality of surface and

groundwaters, of waters and wastewaters undergoing treatment, and of air. This fundamental understanding of chemistry will be absolutely critical as environmental engineers of the future attempt to solve complex problems such as hazardous waste pollution, air pollution from emission of toxic compounds, radioactive waste disposal, ozone depletion, and global climate change.

This book is organized into two parts. Part One is concerned solely with fundamentals of chemistry needed by environmental engineers. It includes chapters on general chemistry, physical chemistry, equilibrium chemistry, organic chemistry, biochemistry, colloid chemistry, and nuclear chemistry. Each emphasizes environmental engineering applications. In this new edition, the chapters on general and physical chemistry have been updated, and new homework problems have been added. The chapter on equilibrium chemistry has been revised, with many new example and homework problems. A new section addresses the chemistry of the solid-water interface. The revised chapter on organic chemistry now includes an added emphasis on organic compounds of environmental significance (e.g., chlorinated solvents). New sections are included on the behavior (fate) of organic compounds in the environment and in engineered systems and on the use of structure-activity relationships. The chapter on biochemistry has been revised, with new sections on biodegradation, novel biotransformations, and molecular biology and genetic engineering. New material has been added to the chapters on colloidal and nuclear chemistry. We feel that these revisions make the text even more suitable for lecture courses on environmental chemistry principles.

Part Two is concerned with analytical measurements. The first several chapters contain general information on quantitative, qualitative, and instrumental methods of analysis, useful as background material for the subsequent chapters concerned with water and wastewater analyses of particular interest to environmental engineers. These chapters are written to stress the basic chemistry of each analysis and show their significance in environmental engineering practice. They should be particularly useful when used with "Standard Methods for the Examination of Water and Wastewater," or the briefer "Selected Physical and Chemical Standard Methods for Students," published jointly by the American Public Health Association, American Water Works Association, and Water Environment Federation, and giving the details for carrying out each analytical determination. Part Two is considered to be most useful as lecture material to accompany a laboratory course on water and wastewater analysis. This new edition contains substantial revisions and additions to the chapter on instrumental methods of analysis, as well as a new chapter on trace contaminants, replacing the old chapter on trace inorganics. Significant revisions have been made in other chapters to reflect the many changes in "Standard Methods" that have occurred since the last edition of this text.

Problems are included at the end of many chapters to stress fundamentals and increase the usefulness of this book as a classroom text. Example problems throughout the text help increase the students' understanding of the principles outlined. In Part One of the book, where the emphasis is on chemical funda-

mentals, answers are included after many homework problems, allowing students to evaluate independently their understanding of the principles emphasized. In this edition, new homework problems have been included in many chapters, with substantial additions to the chapters on equilibrium chemistry, organic chemistry, and biochemistry. Many new example problems have been added to the equilibrium chemistry chapter.

To meet textbook requirements, brevity has been an important consideration throughout. For those who believe that we have been too brief, we can only beg their indulgence and recommend that they seek further information in standard references on the subject. Important references are listed at the end of each chapter in Part One of the book.

Special thanks are due Dr. Jerry Schnoor of the University of Iowa for his encouragement to become involved in teaching the Environmental Chemistry course at Iowa and for the generous use of his class notes, portions of which were used in developing materials for Part One of this text. We also wish to acknowledge Dr. Mark Benjamin of the University of Washington, Dr. Bill Batchelor of Texas A&M University, and Dr. Richard Valentine and Dr. David Gibson of the University of Iowa for their helpful suggestions for revising this book. In addition, we appreciate the suggestions made by Peter Fox, Arizona State University and M. Nazmul Karim, Colorado State University selected by the publishers.

Clair N. Sawyer
Perry L. McCarty
Gene F. Parkin

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PART I

FUNDAMENTALS OF CHEMISTRY FOR ENVIRONMENTAL ENGINEERING

CHAPTER 1

INTRODUCTION

The important role that environmental and public health engineers have played in providing us with pure and adequate water supplies, facilities for wastewater and refuse disposal, safe recreational areas, and a healthy environment within our homes and places of employment has not been generally appreciated by the public at large. Those who have experienced living in the underdeveloped areas of the world usually return home with a new sense of respect for the guardians of the public health. Among these guardians are the engineers who are in the front lines of defense, employing their knowledge of science and engineering to erect barriers against the ever-present onslaught of diseases and plagues, the most terrible of the "Four Horsemen of the Apocalypse."

For many years the attention of environmental engineering was devoted largely to the development of safe water supplies and the sanitary disposal of human wastes. Because of the success in controlling the spread of enteric diseases through the application of engineering principles, a new concept of the potentialities of preventive medicine was born. Expanding populations with resultant increased industrial operations, power production, and use of motor-driven vehicles, plus new industries based upon new technology have intensified old problems and created new ones in the fields of water supply, waste disposal, air pollution, and global environmental change. Many of these have offered a real challenge to environmental engineers, and the profession as a whole is ready to accept the challenge.

Over the years, intensification of old problems and the introduction of new ones have led to basic changes in the philosophy of environmental engineering practice. Originally the major objectives were to produce hygienically safe water supplies and to dispose of wastes in a manner that would prevent the development of nuisance conditions. Many other factors concerned with aesthetics,