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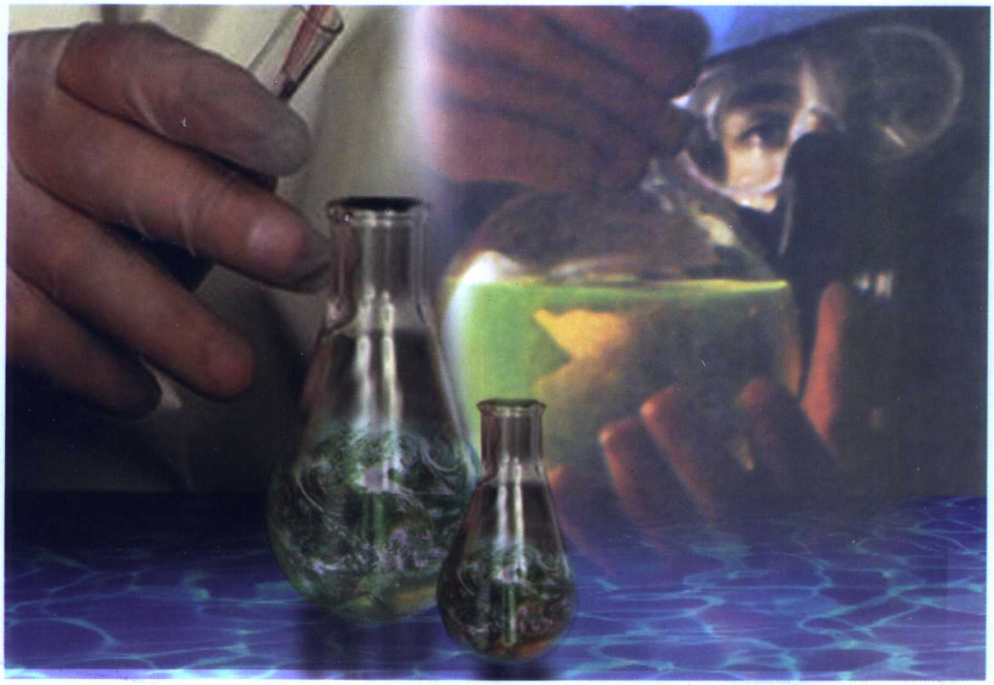
Clair N. Sawyer
Perry L. McCarty
Gene F. Parkin

# Chemistry for Environmental Engineering

## (fourth edition)

# 环境工程化学

## （第 4 版）



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CHEMISTRY FOR ENVIRONMENTAL ENGINEERING, fourth edition

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# 出版前言

在跨入21世纪之际,面临不断恶化的生存环境,人类清醒地认识到要走可持续发展之路。而发展环境教育是解决环境问题和实施可持续发展战略的根本。高等学校的环境教育,是提高新世纪建设者的环境意识,并向社会输送环境保护专门人才的重要途径。为了反映国外环境类教材的最新内容和编写风格,同时也为了提高学生阅读专业文献和获取信息的能力,我们精选了一些国外优秀的环境类教材,组成大学环境教育丛书(影印版),本书即为其中的一册。所选教材均在国外被广泛采用,多数已再版,书中不仅介绍了有关概念、原理及技术方法,给出了丰富的数据,还反映了作者不同的学术观点。

我们希望这套丛书能对高等院校师生和广大科技人员有所帮助,同时对我国环境教育的发展作出贡献。

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2000年1月

# 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 fundamentals, 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, economics, recreation, and other elements of better living are important considerations and have become part of the responsibilities of the modern environmental engineer. If one were to develop a list of the most important problems facing the environmental engineer of today, it would include, but not be limited to, water and wastewater treatment, groundwater contamination, hazardous waste management, radioactive waste management, acid rain, air toxics emission, ozone depletion, and global climate change. Understanding these problems and development of processes to minimize or eliminate them requires a fundamental understanding of chemistry.

## 1-1 WATER

Water is one of the materials required to sustain life and has long been suspected of being the source of much human illness. It was not until approximately 150 years ago that definite proof of disease transmission through water was established. For many years following, the major consideration was to produce adequate supplies that were hygienically safe. However, source waters (surface water and groundwater) have become increasingly contaminated due to increased industrial and agricultural activity. The public has been more exacting in its demands as time has passed, and today water engineers are expected to produce finished waters that are free of color, turbidity, taste, odor, nitrate, harmful metal ions, and a wide variety of organic chemicals such as pesticides and chlorinated solvents. Health problems associated with some of these chemicals include cancer, birth defects, central nervous system disorders, and heart disease. At the present time, more than 75 specific chemicals are listed in the U.S. Environmental Protection Agency's drinking water standards. In addition, the public desires water that is low in hardness and total solids, noncorrosive, and non-scale-forming. To provide such water, chemists, biologists, and engineers must combine their efforts and talents. Chemists, through their knowledge of colloidal, physical, and organic chemistry, are especially helpful in solving problems related to the removal of color, turbidity, hardness, harmful metal ions, and organic compounds, and to the control of corrosion and scaling. The biologist is often of great help in taste and odor problems that derive from aquatic growths. In a true sense, therefore, all who cooperate in the effort regardless of discipline are environmental engineers.

As populations increase, the demand for water grows accordingly and at a much more rapid rate if the population growth is to be accompanied by improved living standards. The combination of these two factors is placing greater and greater stress upon water engineers to find adequate supplies. In many cases inferior-quality, and often polluted, water supplies must be utilized to meet the demand. It is to be expected that this condition will continue and grow more complicated as long as population and industrial growth occurs. In many situations in water-short areas, purposeful recycling of treated wastewaters will be required in some degree to avoid serious curtailing of per-capita usage and industrial development. The ingenuity of scientists and engineers will be taxed to the limit to meet this need.

The problems faced by water-supply engineers in the developed countries are significantly different from those in the underdeveloped countries. For example, in the United States many of the drinking water standards for organic chemicals are based on the desire to minimize the risk of developing cancer from drinking water containing suspected carcinogens. The level of acceptable risk is currently considered to be one-in-ten-thousand to one-in-a-million. That is, if one drinks water containing the chemical of interest at the level of the drinking water standard over a 70-year lifetime, the risk of developing cancer is increased by $10^{-4}$ to $10^{-6}$. Removing these compounds to these levels is a significant engineering challenge. In the underdeveloped world, however, millions of children under the age of 5 die each year due to waterborne diseases. Thus, the goal of the water-supply engineer is this situation is significantly different.

## 1-2 WASTEWATER AND WATER POLLUTION CONTROL

The disposal of human wastes has always constituted a serious problem. With the development of urban areas, it became necessary, from public health and aesthetic considerations, to provide drainage or sewer systems to carry such wastes away from the area. The normal repository was usually the nearest watercourse. It soon became apparent that rivers and other receiving bodies of water have a limited ability to handle waste materials without creating nuisance conditions. This led to the development of purification or treatment facilities in which chemists, biologists, and engineers have played important roles. The chemist in particular has been responsible for the development of test methods for evaluating the effectiveness of treatment processes and providing a knowledge of the biochemical and physicochemical changes involved. Great strides have been made in the art and science of waste treatment in the past few decades. These have been made possible by the fundamental knowledge of wastewater treatment established by scientists with a wide variety of training. It has been the responsibility of the engineers to synthesize this basic knowledge into practical systems of wastewater treatment that are effective and economical.

It has long been known that all natural bodies of water have the ability to oxidize organic matter without the development of nuisance conditions, provided that the organic and nitrogen (primarily ammonia) loading is kept within the limits of the oxygen resources of the water. It is also known that certain levels of dissolved oxygen must be maintained at all times if certain forms of aquatic life are to be preserved. A great deal of research has been conducted to establish these limits. Such surveys require the combined efforts of biologists, chemists, and engineers if their full value is to be realized. In the past, streams have been classified into the following four broad categories: (1) those to be used for the transportation of wastes without regard to aquatic growths but maintained to avoid the development of nuisance conditions, (2) those in which the pollutional load will be restricted to allow fish to flourish, (3) those to be used for recreational purposes, and (4) those that are used for water supplies.

The consensus at the present time in the United States is to require the highest practical degree of treatment of all wastewaters, regardless of stream purification capability. Thus, effluent quality or effluent standards have for the most part superseded stream standards.

Historically, the major concern with regard to pollution of surface waters was with their oxygen resources as described above. However, in the past two decades, an increasing concern is the pollution of surface waters and groundwaters with other pollutants of primarily industrial or agricultural origin. During the past three decades, many new chemicals have been produced for agricultural purposes. Some of them are used for weed control, others for pest control. There has also been a dramatic increase in the application of nitrogen fertilizers, although this trend appears to be changing recently. Residues of these materials are often carried to watercourses during periods of heavy rainfall and have had serious effects upon the biota of streams. A great deal of research by chemists and biologists has demonstrated which of the materials have been most damaging to the environment, and many products have been outlawed. Continuing studies will be needed, but hopefully new products will be more environmentally friendly and will be kept from general use until proven equal or even less harmful than those in current use. The wide variety of organic chemicals and heavy metals produced and used by industry has also been shown to contaminate surface waters and groundwaters. These compounds are of public health concern, and they also may have an adverse impact on desirable aquatic life. Many municipal wastewater treatment plants are required to remove these types of chemicals prior to discharge to receiving waters. A sound knowledge of chemistry is required to understand the environmental fate of these chemicals and to develop methods for their removal.

## 1-3 INDUSTRIAL AND HAZARDOUS WASTES

Perhaps the most challenging field in environmental engineering practice at the present time is the treatment and disposal of industrial and hazardous wastes. Because of the great variety of wastes produced from established industries and the introduction of wastes from new processes, a knowledge of chemistry is essential to a solution of most of the problems. Some may be solved with a knowledge of inorganic chemistry; others may require a knowledge of organic, physical, or colloidal chemistry, biochemistry, or even radiochemistry. It is to be expected that, as further technological advances are made and industrial wastes of even greater variety appear, chemistry will serve as the basis for the development and selection of treatment methods.