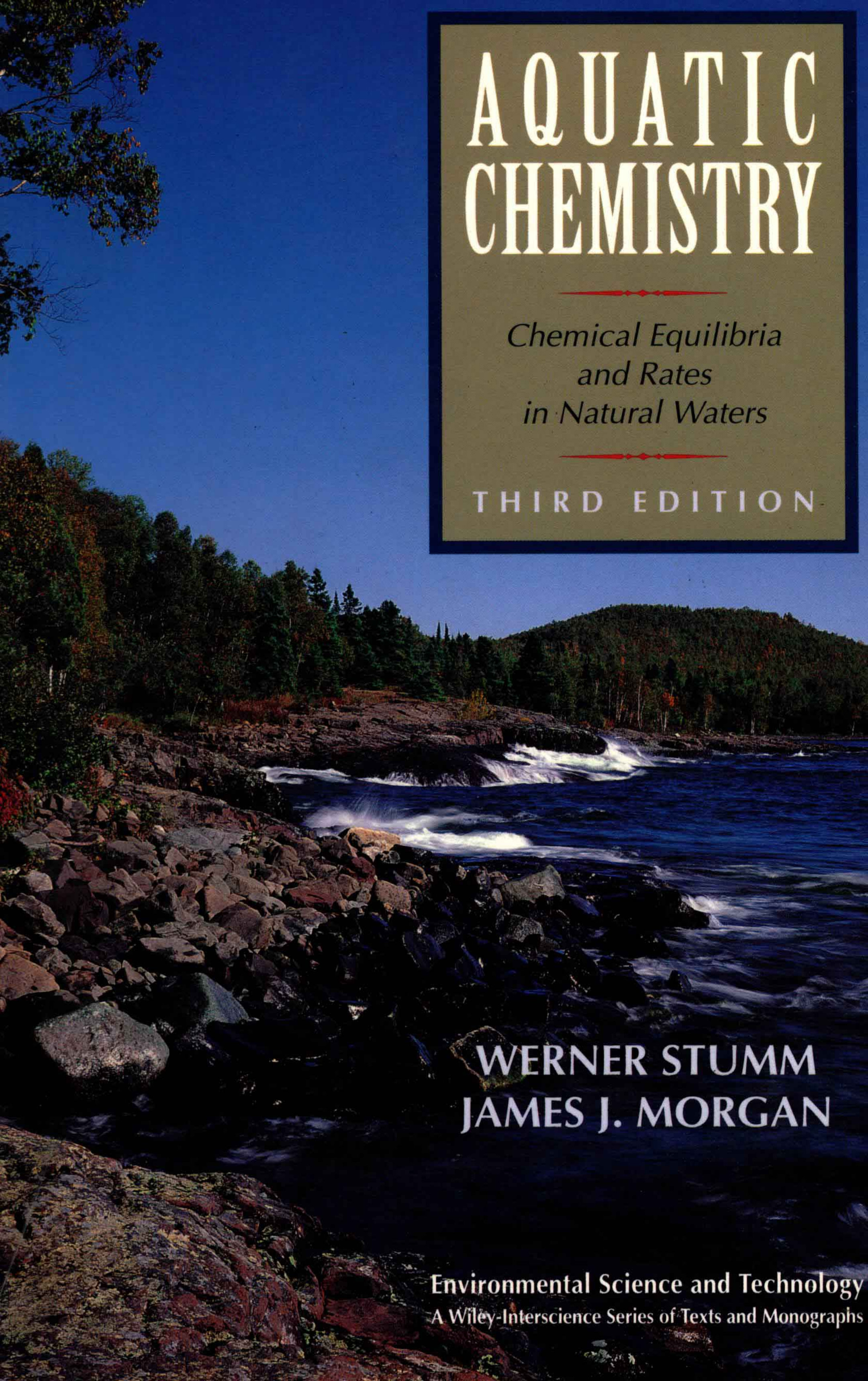

AQUATIC CHEMISTRY

Chemical Equilibria and Rates in Natural Waters

THIRD EDITION

WERNER STUMM
JAMES J. MORGAN

Environmental Science and Technology
A Wiley-Interscience Series of Texts and Monographs

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Edited by JERALD L. SCHNOOR, *University of Iowa*
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There is a new clarion for the environment. No longer are our pollution problems only local. Rather, the scale has grown to the global level. There is no such place as "upwind" any longer; we are all "downwind" from somebody else in the global environment. We must take care to preserve our resources as never before and to learn how to internalize the cost to prevent environmental degradation into the product that we make. A new "industrial ecology" is emerging that will lessen the impact our way of life has on our surroundings.

In the next 50 years, our population will come close to doubling, and if the developing countries are to improve their standard of living as is needed, we will require a gross world product several times what we currently have. This will create new pressures on the environment, both locally and globally. But there are new opportunities also. The world's people are recognizing the need for sustainable development and leaving a legacy of resources for future generations at least equal to what we had. The goal of this series is to help understand the environment, its functioning, and how problems can be over-come; the series will also provide new insights and new sustainable technologies that will allow us to preserve and hand down an intact environment to future generations.

JERALD L. SCHNOOR
ALEXANDER J. B. ZEHNDER

PREFACE

The field of natural water chemistry has continued to grow and develop over the time since the publication of the previous edition of *Aquatic Chemistry*. Our general objective in this substantially revised edition is to draw on basic chemical principles in presenting a quantitative treatment of the processes that determine the composition of natural waters. The concept of chemical equilibrium remains a major theme in our approach, but, as reflected in the new subtitle, rates of processes and chemical reactions receive greater attention than previously, reflecting increased information on these aspects of natural water chemistry acquired over the past decade. Understanding aquatic chemistry calls for both a grasp of key chemical principles and the incorporation of these principles into models that capture the essential aspects of the systems being considered. Numerical examples have been chosen to illustrate methods for attacking the most important aspects of natural water chemistry in a quantitative fashion.

There are several new features of this edition to be noted. A new chapter, Chapter 5, treats atmosphere–water interactions. This chapter illustrates that water, although a minor component of the atmosphere, plays an important role in carrying out major chemical reactions in cloud, fog, and rain—important in linking land, water, and air environments.

There are major revisions in the treatment of solid–water interfaces. Chapter 9 reflects significant progress in concepts and experimental approaches during the last decade. Interactions of solutes with solid surfaces in adsorption are characterized in terms of two basic processes: (1) formation of coordinative bonds (surface complexation) with H^+, OH^- metal ions, and ligands; and (2) hydrophobic adsorption, driven by incompatibility of nonpolar compounds with water. Both of these processes need to be understood in order to explain a variety of processes in natural systems. Surface chemistry is essential for the quantitative treatment of rate laws for geochemical processes in Chapter 13, and for a proper interpretation of the behavior of colloidal systems in particle–particle interactions in Chapter 14.

Important advances in understanding mechanisms of redox processes are treated in Chapter 8, and new interpretations of rates of electron transfer processes are considered in Chapter 11. Chapter 12, on photochemistry, analyzes important light-induced and light-catalyzed processes.

The consideration of metal ions and aqueous coordination chemistry has been updated substantially in Chapter 6. This chapter reflects recent progress made in understanding metal ion speciation and kinetics of complexation. In Chapter 10, particular attention has been directed to the cycling and the biological role of trace metals in nutrition and toxicity in aquatic systems.

Aquatic Chemistry continues to emphasize a teaching approach to the subject. The aim is to enable the reader to learn from the general concepts and methods of problem-solving so that they can then be applied to other aquatic systems of interest. The core chapters, 2 through 9, can be used as a text in an introductory course for advanced undergraduate and beginning graduate students in environmental science and engineering, earth sciences, and oceanography. The later chapters, 10 through 15, are more advanced and detailed. The combination of Chapter 9 (The Solid–Solution Interface), Chapter 13 (Kinetics at the Solid–Water Interface), and Chapter 14 (Particle–Particle Interaction) could serve for a comprehensive treatment of surface chemical principles and applications in the geochemistry of natural waters, in soil and sediment science, and in water technology.

The combination of Chapter 8 (Oxidation and Reduction), Chapter 11 (Kinetics of Redox Processes), and Chapter 12 (Photochemical Processes) introduces the reader to abiotic and biologically mediated redox processes and transformations, emphasizing, in addition to redox energetics, electron transfer mechanisms, linear free energy relationships, and photochemical processes. Chapter 6 (Metal Ions in Aqueous Solutions) and Chapter 10 (Trace Metals) provide a rather complete treatment of coordination chemistry in water and highlight new developments in chemical speciation, bioavailability, and toxicity of metals. The concluding chapter, Chapter 15 (Regulation of the Chemical Composition of Natural Waters), has the aim of acquainting the reader with major factors that regulate the chemical composition of our environment, and to emphasize the great elemental cycles moving through the rocks, water, atmosphere, and biota. We wish to illustrate the concept that pollution is no longer a local and regional problem, and that we humans are able to alter global chemical cycles.

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The authors are pleased to acknowledge the significant contribution that the book *Aquatische Chemie* (Sigg and Stumm, 1994) has made in the writing of this edition of our book.

We are grateful for permission to reproduce Table A6 from Morel and Hering (1993), and the tables on thermodynamic data by Nordstrom et al. and by Byrne et al. in Appendixes 1 and 2 of the book.

The hospitality of EAWAG extended to JJM in 1990 during preparation of the manuscript for this book is appreciated.

W.S.
J.J.M.

CONTENTS

1

INTRODUCTION

1.1 SCOPE OF AQUATIC CHEMISTRY

Aquatic chemistry is concerned with the chemical reactions and processes affecting the distribution and circulation of chemical species in natural waters. The objectives include the development of a theoretical basis for the chemical behavior of ocean waters, estuaries, rivers, lakes, groundwaters, and soil water systems, as well as the description of processes involved in water technology. Aquatic chemistry draws primarily on the fundamentals of chemistry, but it is also influenced by other sciences, especially geology and biology.

A theme of this book is that fundamental principles of physical chemistry can be used to identify the pertinent variables that determine the composition of natural water systems. The student of chemistry is perhaps not fully aware that the well known laws of physical chemistry not only apply in the chemical laboratory but also regulate the course of reactions taking place in nature. During the hydrological cycle, water interacts continuously with the earth. Thus a progressive differentiation of geological material is achieved by processes of weathering, soil erosion, and soil and sediment formation. These processes accomplished by nature on a large scale have been likened (Rankama and Sahama, 1950) to the sequence of separations carried out during the course of a chemical analysis. The basic processes—dissolution and precipitation, oxidation and reduction, acid–base and complexation interactions—are the same in nature as in the laboratory. Sillén (1965) likened the evolution of the earth's atmosphere–ocean system to a set of gigantic, coupled acid–base and oxidant–reductant titrations in which volatile acids from the interior of the earth were titrated by the bases of the rocks, and the reduced volatiles were titrated by the oxygen of the evolving atmosphere–biosphere system.

While this book treats several topics similar to those found in an analytical chemistry text, it endeavors to consider the spatial and temporal scales of the reactions in nature as distinctly different from those of the laboratory. For example, in chemical analysis, precipitates (frequently of metastable and active compounds) are formed from strongly oversaturated solutions, whereas in natural water systems, the solid phase is often formed under conditions of slight supersaturation; often crystal growth and aging may continue over geological time spans. Interfacial phenomena are particularly important because chemical processes of significance often occur only at phase discontinuities.