A Q U A T I C 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

AQUATIC CHEMISTRY

ENVIRONMENTAL SCIENCE AND TECHNOLOGY

A Wiley-Interscience Series of Texts and Monographs

Edited by JERALD L. SCHNOOR, University of Iowa ALEXANDER ZEHNDER, Swiss Federal Institute for Water Resources and Water Pollution Control

A complete list of the titles in this series appears at the end of this volume

AQUATIC CHEMISTRY

Chemical Equilibria and Rates in Natural Waters

Third Edition

WERNER STUMM

EAWAG, Swiss Federal Institute of Technology (ETH), Zurich

JAMES J. MORGAN

Environmental Engineering Science, California Institute of Technology



A WILEY-INTERSCIENCE PUBLICATION JOHN WILEY & SONS, INC. New York • Chichester • Brisbane • Toronto • Singapore This text is printed on acid-free paper.

Copyright © 1996 by John Wiley & Sons, Inc.

All rights reserved. Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning or otherwise, except as permitted under Sections 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008.

Library of Congress Cataloging in Publication Data:

```
Stumm, Werner
Aquatic chemistry: chemical equilibria and rates in natural waters / Werner Stumm, James J. Morgan.—3rd ed.
p. cm.—(Environmental science and technology)
"A Wiley-Interscience publication."
Includes bibliographical references and index.
ISBN 0-471-51184-6 (acid-free).—ISBN 0-471-51185-4 (pbk.: acid-free)
1. Water chemistry. I. Morgan, James J. II. Title.
III. Series.
GB855.S78 1995
359.9—dc20
94-48319
```

Printed in the United States of America

20 19 18 17

SERIES PREFACE Environmental Science and Technology

We are in the third decade of the Wiley Interscience Series of texts and monographs in Environmental Science and Technology. It has a distinguished record of publishing outstanding reference texts on topics in the environmental sciences and engineering technology. Classic books have been published here, graduate students have benefited from the textbooks in this series, and the series has also provided for monographs on new developments in various environmental areas.

As new editors of this Series, we wish to continue the tradition of excellence and to emphasize the interdisciplinary nature of the field of environmental science. We publish texts and monographs in environmental science and technology as it is broadly defined from basic science (biology, chemistry, physics, toxicology) of the environment (air, water, soil) to engineering technology (water and wastewater treatment, air pollution control, solid, soil, and hazardous wastes). The series is dedicated to a scientific description of environmental processes, the prevention of environmental problems, and to preservation and remediation technology.

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 ocean-ography. 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.

> WERNER STUMM JAMES J. MORGAN

Zurich, Switzerland Pasadena, California

ACKNOWLEDGMENTS

We thank Drs. Charles O'Melia, Laura Sigg, Bruce James, Dieter Diem, and Stefan Hug, and our student colleagues, Tom Lloyd and Phil Watts, for helpful reviews of individual chapters. We are also grateful to our many colleagues who provided valuable suggestions for corrections and improvements to the third edition. Appreciation is expressed to Mrs. L. Schwarz for typing the manuscript and to Mrs. L. Scott for assistance in revision of some of the chapters.

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	1
	1.2	The Solvent Water	6
	1.3	Solute Species	9
		Suggested Readings	11
		Appendix 1.1: Some Useful Quantities, Units, Conversion	
		Factors, Constants, and Relationships	11
2.	Che	mical Thermodynamics and Kinetics	16
	2.1	Introduction	16
	2.2	Chemical Thermodynamic Principles	20
	2.3	Systems of Variable Composition: Chemical	
		Thermodynamics	29
	2.4	Gibbs Energy and Systems of Variable Chemical	
		Composition	32
	2.5	Chemical Potentials of Pure Phases and Solutions	35
	2.6	Chemical Potentials of Aqueous Electrolytes	38
	2.7	The Equilibrium Constant	41
	2.8	The Gibbs Energy of a System	44
	2.9	Driving Force for Chemical Reactions	49
	2.10	Temperature and Pressure Effects on Equilibrium	52
	2.11	Equilibrium Tools	57
	2.12	Kinetics and Thermodynamics: Time and Reaction	
		Advancement, ξ	58
	2.13	Rate and Mechanism	61
	2.14	Concentration Versus Time	64
	2.15	Theory of Elementary Processes	69
	2.16	Elementary Reactions and ACT	76
	2.17	Equilibrium Versus Steady State in Flow Systems	79
		Suggested Readings	81
		Problems	82
		Answers to Problems	85

xii Contents

3.	Acid	s and Bases	88
	3.1	Introduction	88
	3.2	The Nature of Acids and Bases	90
	3.3	The Strength of an Acid or Base	92
	3.4	Activity and pH Scales	97
	3.5	Equilibrium Calculations	105
	3.6	pH as a Master Variable; Equilibrium Calculations Using	
		a Graphical Approach	118
	3.7	Ionization Fractions of Acids, Bases, and Ampholytes	127
	3.8	Titration of Acids and Bases	130
	3.9	Buffer Intensity and Neutralizing Capacity	134
	3.10	Organic Acids	140
		Suggested Readings	144
		Problems	144
		Answers to Problems	147
4.	Disso	olved Carbon Dioxide	148
	4.1	Introduction	148
	4.2	Dissolved Carbonate Equilibria (Closed System)	150
	4.3	Aqueous Carbonate System Open to the Atmosphere	157
	4.4	Alkalinity and Acidity, Neutralizing Capacities	163
	4.5	Alkalinity Changes	172
	4.6	Analytical Considerations: Gran Plots	179
	4.7	Equilibrium with Solid Carbonates	186
	4.8	Kinetic Considerations	192
	4.9	Carbon Isotopes and Isotope Fractionation	195
		Suggested Readings	202
		Problems	202
		Answers to Problems	204
5.	Atm	osphere–Water Interactions	206
	5.1	Introduction	206
	5.2	Anthropogenic Generation of Acidity in the Atmosphere	207
	5.3	Gas-Water Partitioning: Henry's Law	212
	5.4	Gas-Water Equilibria in Closed and Open Systems	216
	5.5	Washout of Pollutants from the Atmosphere	227
	5.6	Fog	229
	5.7	Aerosols	233
	5.8	Acid Rain-Acid Lakes	235
	5.9	The Volatility of Organic Substances	238
	5.10	Gas Transfer Across Water-Gas Interface	241
		Suggested Readings	248
		Problems	249
		Answers to Problems	251

6.	6. Metal Ions in Aqueous Solution: Aspects of Coordination		
	Che	mistry	252
	61	Introduction	252
	6.2	Protons and Metal Ions	252
	63	Hydrolysis of Metal lons	263
	6.4	Solubility and Hydrolysis: Solid Hydroxides and Metal	205
	0.1	Oxides	272
	6.5	Chelates	275
	6.6	Metal Ions and Ligands: Classification of Metals	281
	6.7	Speciation in Fresh Waters	289
	6.8	Seawater Speciation	305
	6.9	Kinetics of Complex Formation	311
		Suggested Readings	319
		Problems	320
		Answers to Problems	322
		Appendix 6.1: Stability Constants	325
		Appendix 6.2: The Various Scales for Equilibrium	
		Constants, Activity Coefficients, and pH	335
_			240
7.	Prec	ripitation and Dissolution	349
	7.1	Introduction	349
	7.2	The Solubility of Oxides and Hydroxides	359
	7.3	Complex Formation and Solubility of (Hydr)oxides	368
	7.4	Carbonates	370
	7.5 The Stability of Hydroxides, Carbonates, and Hydroxide		
		Carbonates	389
	7.6	Sulfides and Phosphates	398
	7.7	The Phase Rule: Components, Phases, and Degrees of	
		Freedom	409
	7.8	Solubility of Fine Particles	413
	7.9	Solid Solutions	416
		Suggested Readings	420
		Problems	420
		Answers to Problems	424
8.	Oxie	lation and Reduction; Equilibria and Microbial	
	Mediation		425
	8.1	Introduction	425
	8.2	Redox Equilibria and the Electron Activity	426
	8.3	The Electrode Potential: The Nernst Equation and the	-
		Electrochemical Cell	441
	8.4	pe-pH, Potential-pH Diagrams	455
	8.5	Redox Conditions in Natural Waters	464
	8.6	Effect of Complex Formers on the Redox Potential	489

	8.7	Measuring the Redox Potential in Natural Waters	491
	8.8	The Potentiometric Determination of Individual Solutes	498
		Suggested Readings	506
		Problems	507
		Answers to Problems	512
		Appendix 8.1: Activity Ratio Diagrams for Redox Systems	513
9.	The	Solid-Solution Interface	516
	0.1	Introduction	510
	9.1	Introduction	510
	9.2	Adsorption	519
	9.5	Adsorption Isotherms	521
	9.4	Hydrous Oxide Surfaces; Reactions with H, OH, Metal	522
	0.5	Ions, and Ligands	535
	9.5	Surface Charge and the Electric Double Layer	549
	9.0	Surface Charge	560
	07	Sorntion of Hydronhobic Substances on Organic Carbon	308
	9.1	Bearing Darticles	575
	0.8	Jon Exchange	506
	9.0 0.0	Transport of (Ad)sorbable Constituents in Groundwater	200
	9.9	and Soil Systems	504
		Suggested Readings	500
		Problems	601
		Appendix 9.1. The Gouy-Chapman Theory	604
		Appendix 9.2: Contact Angle Adhesion and Cohesion the	004
		Oil-Water Interface	608
			000
10.	Trac	e Metals: Cycling, Regulation, and Biological Role	614
	10.1	Introduction: Global Cycling of Metals	614
	10.2	Analytical Approaches to Chemical Speciation	615
	10.3	Classification of Metal Ions and the Inorganic Chemistry	
		of Life	625
	10.4	Organometallic and Organometalloidal Compounds	628
	10.5	Bioavailability and Toxicity	632
	10.6	Metal Ions as Micronutrients	637
	10.7	The Interaction of Trace Metals with Phytoplankton at	
		the Molecular Level	641
	10.8	Regulation of Trace Elements by the Solid-Water	
		Interface in Surface Waters	648
	10.9	Regulation of Dissolved Heavy Metals in Rivers, Lakes,	
		and Oceans	654
	10.1	0 Quality Criteria in Fresh Waters: Some Aspects	666
		Suggested Readings	670

11.	Kine	tics of Redox Processes	672
	11.1	Introduction	672
	11.2	How Good an Oxidant Is O ₂ ?	672
	11.3	Can pe Be Defined for a Nonequilibrium System?	677
	11.4	Kinetics of Redox Processes: Case Studies	679
	11.5	Oxidants Used in Water and Waste Technology: A Few	
		Case Studies	691
	11.6	Linear Free Energy Relations (LFERs)	702
	11.7	The Marcus Theory of Outer-Sphere Electron Transfer:	
		An Introduction	703
	11.8	Nucleophile-Electrophile Interactions and Redox	
		Reactions Involving Organic Substances	710
	11.9	Corrosion of Metals as an Electrochemical Process	720
		Suggested Readings	725
12.	Phot	ochemical Processes	726
	12.1	Introduction	726
	12.2	Absorption of Light	729
	12.3	Photoreactants	735
	12.4	Photoredox Reactions: Photolysis of Transition Metal	
		Complexes	743
	12.5	Photochemical Reactions in Atmospheric Waters: Role of	
		Dissolved Iron Species	744
	12.6	Heterogeneous Photochemistry	748
	12.7	Semiconducting Minerals	753
		Suggested Readings	759
13.	Kine	tics at the Solid–Water Interface: Adsorption,	
	Disso	lution of Minerals, Nucleation, and Crystal Growth	760
	13.1	Introduction	760
	13.2	Kinetics of Adsorption	760
	13.3	Surface-Controlled Dissolution of Oxide Minerals: An	
		Introduction to Weathering	771
	13.4	Simple Rate Laws in Dissolution	776
	13.5	Rates of CaCO ₃ Dissolution (and of CaCO ₃ Crystal	
		Growth)	788
	13.6	Inhibition of Dissolution	795
	13.7	Nucleation and Crystal Growth	800
		Suggested Readings	816
14.	Parti	cle-Particle Interaction: Colloids, Coagulation, and	
	Filtra	ation	818
	14.1	Colloids	818
	14.2	Particle Size Distribution	826

	14.3	Surface Charge of Colloids	834
	14.4	Colloid Stability: Qualitative Considerations	837
	14.5	Effects of Surface Speciation on Colloid Stability	842
	14.6	Some Water-Technological Considerations in	
		Coagulation, Filtration, and Flotation	852
	14.7	Filtration Compared with Coagulation	857
	14.8	Transport in Aggregation and Deposition	858
		Suggested Readings	866
		Appendix 14.1: A Physical Model (DLVO) for Colloid	
		Stability	867
15.	Regu	lation of the Chemical Composition of Natural Waters	872
	15.1	Introduction	872
	15.2	Weathering and the Proton Balance	875
	15.3	Isothermal Evaporation	880
	15.4	Buffering	884
	15.5	Interactions Between Organisms and Abiotic	
		Environment: Redfield Stoichiometry	886
	15.6	The Oceans: Relative Constancy of the Composition and	
		Chemical Equilibria	895
	15.7	Constancy of Composition: Steady State	897
	15.8	Hydrothermal Vents	901
	15.9	The Sediment-Water Interface	903
	15.10	Biological Regulation of the Composition	908
	15.11	Global Cycling: The Interdependence of Biogeochemical	
		Cycles	914
	15.12	The Carbon Cycle	916
	15.13	Nitrogen Cycles: Pollution by Nitrogen Compounds	927
	15.14	The Sulfur Cycle	932
		Suggested Readings	933
Ref	erence	S	935
Ар	pendix	es: Thermodynamic Data	976
	l Re	vised Chemical Equilibrium Data for Major Water-	
	M	ineral Reactions	977
	2 Th	ermodynamic Data for Trace Metal Speciation in Seawater	984
	3 Th	ermodynamic Properties	990
Ind	ex		1005

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 oxidantreductant 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.



Figure 1.1. Natural water environments of interest in aquatic chemistry. Water links elemental cycles of the atmosphere with those of the sediments. Atmospheric chemistry, water chemistry, sediment geochemistry, soil chemistry, and groundwater chemistry of the elements are needed.

Natural water systems typically consist of numerous mineral assemblages and often include a gas phase in addition to the aqueous phase; they almost always involve a portion of the biosphere. Hence natural aquatic habitats are characterized by a complexity seldom encountered in the laboratory. In order to select the pertinent variables out of a sometimes bewildering number of possible ones, it is advantageous to compare the real systems with their idealized counterparts. Figure 1.1 shows in a very general way the kinds of natural water environments of interest to aquatic chemistry. The cycle of water links the elemental cycles of the atmosphere with those of the sediments. Thus atmospheric chemistry, water chemistry, sediment geochemistry, soil chemistry, and groundwater chemistry of the elements are all connected, on a range of time scales. Chemical models aim to capture the most important variables of complex natural water systems.

Models

To deal with the complexity of natural water systems we employ simplified and workable models to illustrate the principal regulatory factors that control the chemical composition of natural waters. In general, these models must link water composition with that of the atmosphere and the sediments. A model need not be completely realistic in order to be useful. A useful model leads to fruitful generalizations and valuable insight into the nature of aquatic chemical processes, and improves our ability to describe and measure natural water systems. Models are simplifications of a more complex reality. In simplifying, we try to be guided by sound chemical concepts. In accord with the aphorism of Albert Einstein: "Everything should be made as simple as possible, but not simpler."

Chemical equilibrium appears to be the most helpful model concept initially to facilitate identification of key variables relevant in determining water-mineral relations and water-atmosphere relations, thereby establishing the chemical boundaries of aquatic environments. Molar Gibbs free energies (chemical potentials) describe the thermodynamically stable state and characterize the direction and extent of processes approaching equilibrium. Discrepancies between predicted equilibrium composition and the data for the actual system provide valuable insight into those cases in which important chemical reactions have not been identified, in which non-equilibrium conditions prevail, or where analytical data for the system are not sufficiently accurate or specific. Such discrepancies are incentive for research and the improvement of existing models.

By comparing the actual composition of seawater (sediments + sea + air) with a model in which the pertinent components (minerals, volatiles) are allowed to reach true equilibrium, Sillén (1961) epitomized the application of equilibrium models for portraying the prominent features of the chemical composition of this system. His analysis indicated that, contrary to the traditional view. the pH of the ocean is not buffered primarily by the carbonate system; his results suggest that heterogeneous equilibria of silicate minerals comprise the principal pH buffer systems in oceanic waters. This approach has provided a more quantitative basis for Forchhammer's suggestion of 100 years ago that the quantity of the different elements in seawater is not proportional to the quantity of elements that river water pours into the sea but is inversely proportional to the facility with which the elements in seawater are made insoluble by general chemical actions in the sea. Although inland waters represent more transitory systems than the sea, equilibrium models are also useful here for interpreting observed facts. We can obtain some limits on the variational trends of chemical composition even in highly dynamic systems, and we can speculate on the type of dissolved species and solid phases one may expect.

Thermodynamic models of various systems within overall natural water systems are illustrated in Figure 1.2. Such models are employed in assessing global, partial, and local equilibrium conditions for water, air, and sediment interactions.

Natural waters indeed are open and dynamic systems with variable inputs and outputs of mass and energy for which the state of equilibrium is a construct. *Steady-state models* reflecting the time-invariant condition of a reaction system may frequently serve as an idealized counterpart of an open natural water system. The concept of free energy is not less important in dynamic systems than in equilibrium systems. The flow of energy from a higher to a lower potential or energy "drives" the hydrological and the geochemical cycles (Ma-



Figure 1.2. Models of various parts comprising overall natural water systems: (a) aqueous solution phase model; (b) aqueous solution and gas phase model; (c) aqueous solution and solid phase model; (d) three-phase aqueous, gas, and solid phase model; (e) aqueous solution plus several solid phases model; and (f) multiphase model for solids, aqueous solution, and a gas phase.

son, 1966; Morowitz, 1968). The ultimate source of the energy flow is the sun's radiation.

Ecosystems

In natural waters, organisms and their abiotic environments are interrelated and interact with each other. Because of the continuous input of solar energy (photosynthesis) necessary to maintain life, ecological systems are never in equilibrium. The ecological system, or ecosystem, may be considered a unit of the environment that contains a biological organization made up of all the organisms interacting reciprocally with the chemical and physical environment. In an ecosystem, the flow of energy and of negative entropy is reflected by the characteristic trophic structure and leads to material cycles within the system (Odum, 1969). In a balanced ecological system a steady state of production and destruction of organic material, as well as of production and consumption of O_2 , is maintained.

The distribution of chemical species in waters and sediments is strongly influenced by an interaction of mixing cycles and biological cycles (Buffle and DeVitre, 1994). Radioisotope measurements may often be used to establish the time scale of some of these processes. Similarly, evaluation of the fractionation of stable isotopes aids in the quantitative interpretation of biogeochemical and environmental processes and cycles.

Biogeochemical Cycles It is now widely recognized that the earth is one giant biogeochemical system (Schlesinger, 1991). Within this system the atmosphere, the waters of the earth, and the sedimentary reservoirs are linked to the activity of the biosphere. Global cycles of water, carbon, nitrogen, phosphorus, and sulfur are interconnected with one another and have now been affected to a noticeable degree by human activities. The minor element cycles, for example, those of mercury and lead, have been appreciably perturbed over time. Biogeochemical cycles work at local, regional, and global levels (Bidoglio and Stumm, 1994). The elucidation of the scale of these cycles is facilitated by the appropriate integration of stoichiometric (for complete reactions), equilibrium, steady-state, and kinetic (time-dependent) models.

Kinetics

Our understanding of natural water systems has, until recently, been seriously limited by a lack of kinetic information on critical reactions in water, in sediments, and at interfaces. Earlier in atmospheric chemistry (Seinfeld, 1986) and more recently in aquatic chemistry (Brezonik, 1993), a considerable growth of information on rates and mechanisms for reactions central to environmental chemistry has taken place. As a result, we are now better able to assess the characteristic time scales of chemical reactions in the environment and compare these with, for example, residence times of water in a system of interest. Schematically, as shown here, for chemical vs. fluid time scales



6 Introduction

we would like to distinguish between *slow* reactions and *rapid* reactions, judged against the time scale of fluid flow (e.g. in a lake, river, or groundwater). The fast reactions are well described by equilibrium models (reversible reactions) or stoichiometric models (irreversible reactions). Kinetic (i.e., time-dependent) descriptions are needed when τ_{ch} and τ_{fluid} are comparable.

Water as a Resource and Life Preservation System

Aquatic chemistry is of practical importance because water is an essential resource for humans. We are concerned with the quality of water and its distribution, not with the quantity, because water is an abundant substance on earth. Ecosystem resilience and buffering against change notwithstanding, human activity has become so powerful as to influence global chemical cycles (Schlesinger, 1991) as well as the local and regional chemical and hydrologic cycles. Locally and regionally, groundwater quality has been impaired by release of hazardous chemicals. The restoration of these systems will require the creative integration of chemical, biological, and hydrologic understanding. In the chemical realm, progress in water quality improvement calls for a synthesis of physical, inorganic, organic, and interfacial chemistry.

Conservation of aquatic resources cannot be accomplished by avoiding human influences on the aquatic environment. Control of water pollution and protection of the water resource demand more than waste treatment technology. We need to address questions such as these: To what extent are the oceans able to absorb wastes without harmful effects? Can we improve the fertility of the oceans? How can the ecological balance between photosynthetic and respiratory activities in nutritionally enriched but polluted waters be restored? Answers to such questions call for a greatly improved understanding of the aquatic environment.

Science needs to provide the basis for human harmony with nature, not dominance. "Man masters nature not by force but by understanding" (Bron-owski, 1965).

1.2 THE SOLVENT WATER

Water is an unusual liquid. It has a very high boiling point and high heat of vaporization; ice has a very high melting point. The maximum density of liquid water is near 4°C, not the freezing point, and water thus expands upon freezing. It has a very high surface tension. It is an excellent solvent for salts and polar molecules. It has the greatest dielectric coefficient of any liquid. These unusual properties are a consequence of the dipolar character of the H₂O molecule. Figure 1.3, from Horne (1969), depicts the electron cloud of the angular water molecule, resulting from the hybridization of s and p electrons to yield two bonding orbitals between the O and the two H atoms, and two non-bonding sp^3 orbitals on the oxygen. The molecule thus has high negative charge density



Figure 1.3. Electron cloud depiction for the H₂O molecule (Horne, 1969).

near the oxygen atom and high positive charge density near the protons. It is a dipolar molecule.

Figure 1.4 (Horne, 1969) shows the measured angle of 105° between the hydrogens and the direction of the dipole moment. The measured dipole moment of water is 1.844 debye (a debye unit is 3.336×10^{-30} C m). The dipole moment of water is responsible for its distinctive properties in the liquid state. The O-H bond length *within* the H₂O molecule is 0.96 Å (an angstrom unit, Å, is 10^{-10} m). Dipole-dipole interaction between two water molecules forms a hydrogen bond, which is electrostatic in nature. The lower part of Figure 1.4 (not to the same scale) shows the measured H-bond distance of 2.76 Å, or 0.276 nm.

The hydrogen-bonded structure of ice is shown in Figure 1.5a (Gray, 1973), and one of the several models proposed for the structure of water in the liquid state is shown in Figure 1.5b (Nemethy and Scheraga, 1962). In the open tetrahedral ice structure, each oxygen atom is bound to four nearby oxygen atoms by H bonds. The energy of each H bond is estimated to be about 20 kJ mol⁻¹. (For comparison, covalent bond energies are typically 20 times greater.) H bonds are of low energy, but they are numerous in ice and water.



Figure 1.4. Structure of the angular water molecule and the hydrogen bond (Horne, 1969).



Figure 1.5. (a) Hydrogen-bonded open tetrahedral structure of ice (Gray, 1973). (b) Frank-Wen flickering cluster model of liquid water (Nemethy and Scheraga, 1962).

Upon melting, ice loses its open structure with the "melting" of some fraction of the hydrogen bonds and so the volume of the liquid water decreases, reaching a minimum at 4° C; above this temperature thermal expansion dominates the density.

In Figure 1.5b the Frank-Wen "flickering cluster" model envisions larger clusters of H-bonded water surrounded by noncluster waters, which nonetheless interact with neighbors by dipole-dipole forces. The lifetime of the clusters is estimated at around 100 picoseconds (ps), which is long with respect to the

period of a molecular vibration, approximately 0.1 ps. The persistence (or reformation) of hydrogen bonding in liquid water is a key to understanding the physical properties of water as well as its poorer solvent properties for nonpolar, hydrophobic solutes. The highly structured water linked by H bonds must be disrupted by *any solute* (Tanford, 1980). When the solute is ionic, the attractive interactions between ion and water molecule *favor* dissolution. When the solute is a nonpolar molecule, the structural cost to the hydrogen-bonded water makes dissolution an *unfavorable* process.

1.3 SOLUTE SPECIES

Dissolution of *ionic and ionizable solutes* in water is favored by ion-dipole bonds between ions and water. Figure 1.6 illustrates a hydrated sodium ion, Na⁺(aq), for example, from dissolution of NaCl in water, surrounded by six water molecules in octahedral positions. The energy of the ion-dipole bonds depends on the size of the ion and its charge. Higher charge and smaller ionic radii favor the bonding. Further away from the central ion, the water molecules are structured through additional dipole-dipole interactions. In a similar way, the Cl⁻(aq) ion interacts with the solvent water to form ion-dipole bonds, with the hydrogen side (local positive charges) of H₂O pointing toward the central ion.

The dissolution of *polar molecules* in water is favored by dipole-dipole interactions. The solvation of the polar molecules stabilizes them in solution. *Nonpolar molecules* are difficultly soluble in water because of the already mentioned unfavorable energy cost of disrupting and re-forming the hydrogen-



Figure 1.6. Hydrated sodium ion, Na⁺, in aqueous solution. H_2O molecules form iondipole bonds to the central metal ion. The waters are in octahedral coordination to the sodium ion (Gray, 1973).

bonded water. Complicated molecules or ions with both ionic and nonpolar regions, or polar and nonpolar regions, show more complicated behavior in water (surface active species), but the stabilizing and destabilizing contributions of ion-dipole, dipole-dipole, and H-bond disrupting energies can still be recognized.

Speciation

The particular chemical form in which an element exists in water is its *speciation*. For example, an element can be present as a simple hydrated ion, as a molecule, as a complex with another ion or molecule, and so forth. From what was said previously, *bare* ions or *bare* polar molecules do not exist in water. At the least, they would be solvated species. Species of an element are distinguishable from one another stoichiometrically, structurally, and energetically. In addition to *aqueous* species, one can distinguish elements in different phases, for example, as gaseous species, as solid phases, or in adsorbed states, and on the basis of particle sizes. In the atmosphere, for example, speciation extends over liquid, gas, and aerosol phases (Seinfeld, 1986). The notion of chemical speciation is central to equilibrium and kinetic aspects of aquatic chemistry, as will be evident throughout this book.

Concentrations and Species of Important Elements in Water

Figure 1.7 illustrates, in the form of an abbreviated periodic table, the river water and marine water concentrations, oceanic residence times, and major



Figure 1.7. Some of the more important elements in natural waters: their concentrations, species, and residence times in river water and seawater (Sigg and Stumm, 1994). Elements whose distribution is significantly affected by biota are shaded.

species for several important elements. For example, consider sulfur: the predominant species present is sulfate, SO_4^{2-} , the river water concentration is given by log molarity = -3.92, or a sulfate concentration of 1.2×10^{-4} M; the total sulfate concentration in seawater is 0.028 M; and the major ion pair species of sulfate in seawater is NaSO₄⁻(aq); the oceanic residence time is 8 million years. The information presented shows that the elements exist in a variety of oxidation states, protonated versus deprotonated forms, and free (aquated) versus complexed ion forms in water. As will be discussed later, the speciation of an element is influential with respect to its residence time in natural waters.

SUGGESTED READINGS

- Berner, E. and Berner, R. A. (1987) Global Water Cycle, Geochemistry and Environment, Prentice Hall, Englewood Cliffs, NJ.
- Brezonik, P. L. (1994) Chemical Kinetics and Process Dynamics in Aquatic Systems, Lewis, Boca Raton, FL.
- Harte, J. (1988) Consider a Spherical Cow, University Science Books, Mill Valley, CA.
- Horne, R. A. (1969) Marine Chemistry, Wiley-Interscience, New York.
- Morel, F. M. M. and Hering, J. G. (1993) Principles and Applications of Aquatic Chemistry, Wiley-Interscience, New York.
- Pankow, J. F. (1991) Aquatic Chemistry Concepts, Lewis, Chelsea, MI.
- Schlesinger, W. H. (1991) Biogeochemistry: An Analysis of Global Change, Academic Press, San Diego, CA.
- Schwarzenbach, R. P., Gschwend, P. M., and Imboden, D. M. (1993) Environmental Organic Chemistry, Wiley-Interscience, New York.

Tanford, C. (1991) The Hydrophobic Effect, 2nd ed., Krieger, Melbourne, FL.

APPENDIX 1.1 SOME USEFUL QUANTITIES, UNITS, CONVERSION FACTORS, CONSTANTS, AND RELATIONSHIPS

The Earth-Hydrosphere System (Sigg and Stumm, 1994)

Earth area	5.1	×	10 ¹⁴	m^2
Ocean area	3.6	×	10 ¹⁴	m^2
Land area	1.5	×	10 ¹⁴	m ²
Atmosphere mass	52	×	10 ¹⁷	kg
Ocean mass	13,700	×	10 ¹⁷	kg
Groundwater to 750 m	42	×	10 ¹⁷	kg
Groundwater to 4000 m	95	х	10 ¹⁷	kg
Water in ice	165	×	10 ¹⁷	kg
Water in lakes and rivers	1.3	х	10 ¹⁷	kg
Water in atmosphere	0.105	×	10 ¹⁷	kg

Water in biosphere	$0.006 \times 10^{17} \text{ kg}$
Total stream discharge	$0.32 \times 10^{17} \text{ kg yr}^{-1}$
Precipitation = evaporation	$4.5 \times 10^{17} \text{ kg yr}^{-1}$

Some Properties of Water (m kg s units)

$k_B T / 10^{-21}$	Density (p)	Viscosity/ 10^{-3} (η)	Surface Tension (y)	Dielectric Coefficient (ϵ)
3.8	999.965	1.5188	0.0749	86.04
4.0	998.203	1.0050	0.07275	80.36
4.1	997.044	0.8937	0.07197	78.54
4.2	995.646	0.8007	0.07118	76.75
	$\frac{k_B T / 10^{-21}}{3.8}$ 4.0 4.1 4.2	$\begin{array}{c} \text{Density} \\ k_B T / 10^{-21} \\ \hline (\rho) \\ \hline 3.8 \\ 4.0 \\ 998.203 \\ 4.1 \\ 997.044 \\ 4.2 \\ 995.646 \\ \end{array}$	$k_BT/10^{-21}$ Density (ρ)Viscosity/10^{-3} (η)3.8999.9651.51884.0998.2031.00504.1997.0440.89374.2995.6460.8007	$\frac{k_B T/10^{-21}}{4.2} \begin{array}{c} \text{Density} \\ 0 \end{array} \begin{array}{c} \text{Viscosity}/10^{-3} \\ (\rho) \end{array} \begin{array}{c} \text{Surface} \\ \text{Tension} \\ (\eta) \end{array} \begin{array}{c} \text{Surface} \\ \text{Tension} \\ (\gamma) \end{array}$

The International Units

Physical Quantity	Unit	Symbol
Length	meter	m
Mass	kilogram	kg
Time	second	S
Electric current	ampere	А
Temperature	kelvin	K
Luminous intensity	candela	cd
Amount of material	mole	mol
The main derived units are:		
Force	newton	$N = kg m s^{-2}$
Energy, work, heat	joule	J = N m
Pressure	pascal	$1 \text{ Pa} = \text{N} \text{ m}^{-2}$
Power	watt	$\mathbf{W} = \mathbf{J} \mathbf{s}^{-1}$
Electric charge	coulomb	C = A s
Electric potential	volt	$\mathbf{V} = \mathbf{W} \mathbf{A}^{-1}$
Electric capacitance	farad	$\mathbf{F} = \mathbf{A} \mathbf{s} \mathbf{V}^{-1}$
Electric resistance	ohm	$\Omega = \mathbf{V} \mathbf{A}^{-1}$
Frequency	hertz	$Hz = s^{-1}$
Conductance	siemens	$S = A V^{-1}$
Amount of photons	einstein	einstein
Dipole moment	debye	D

Useful Conversion Factors

Energy, Work, Heat

1 joule = 1 volt coulomb = 1 newton meter = 1 watt second = 2.7778×10^{-7} kilowatt hours = 10^7 erg