AQUATIC CHEMISTRY

*Chemical Equilibria
and Rates
in Natural Waters*

THIRD EDITION

WERNER STUMM
JAMES J. MORGAN

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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*

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Chemical Equilibria and Rates in Natural Waters

Third Edition

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SERIES PREFACE
Environmental Science and Technology

We are in the third decade of the Wiley Interscience Series of texts and mono-graphs 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 some-body else in the global environment. We must take care to preserve our re-sources 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 gen-erations 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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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.

1

ATMOSPHERE

gas species $\rightleftharpoons$ cloud
                                solutes

gas species

SURFACE
WATER   solutes

reactions of aqueous solutions

solutes $\rightleftharpoons$ particulate
                              phases

solutes

solid phases   **GROUND**
               WATER
SEDIMENTS solutes $\rightleftharpoons$ solid phases
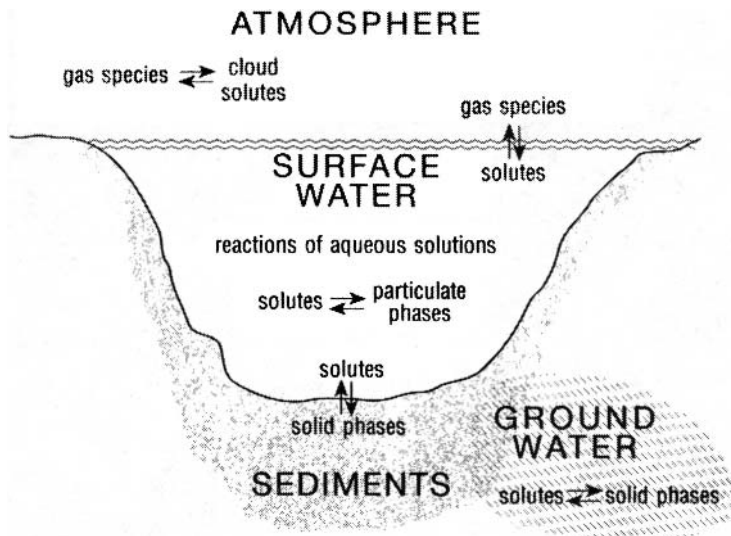
Figure 1.1. Natural water environments of interest in aquatic chemistry. Water links elemental cycles of the atmosphere with those of the sediments. Atmospheric chemistry, water chemistry, sediment geochemistry, soil chemistry, and groundwater chemistry of the elements are needed.

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 ideal-ized 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 chemis-try, 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-
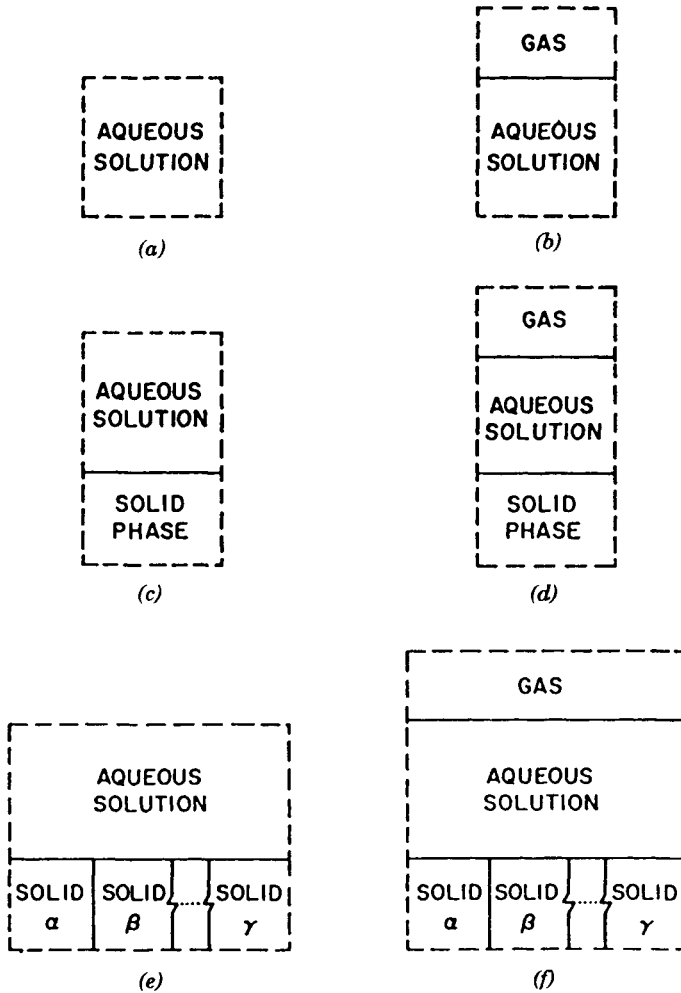
Figure 1.2. Models of various parts comprising overall natural water systems: (a) aqueous solution phase model; (b) aqueous solution and gas phase model; (c) aqueous solution and solid phase model; (d) three-phase aqueous, gas, and solid phase model; (e) aqueous solution plus several solid phases model; 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 (pho-

tosynthesis) 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
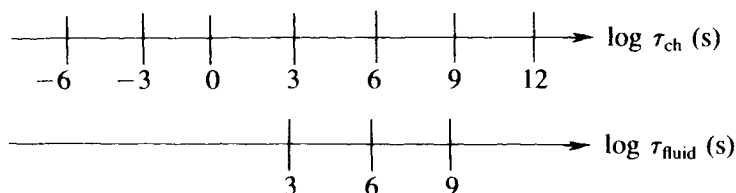
we would like to distinguish between *slow* reactions and *rapid* reactions, judged against the time scale of fluid flow (e.g. in a lake, river, or groundwater). The fast reactions are well described by equilibrium models (reversible reactions) or stoichiometric models (irreversible reactions). Kinetic (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" (Bronowski, 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 H_2O 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
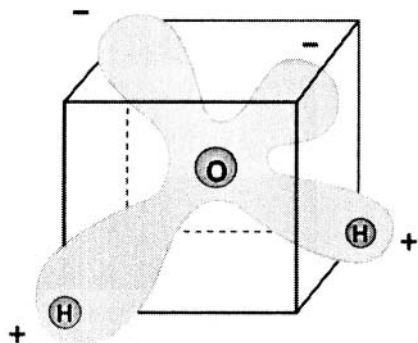
Figure 1.3. Electron cloud depiction for the H_2O molecule (Horne, 1969).

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 H_2O 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.
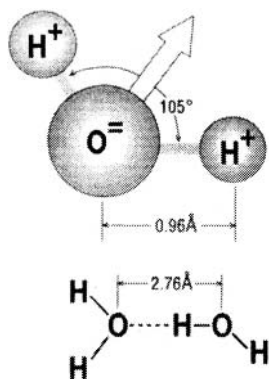
Figure 1.4. Structure of the angular water molecule and the hydrogen bond (Horne, 1969).

(a)

Clusters

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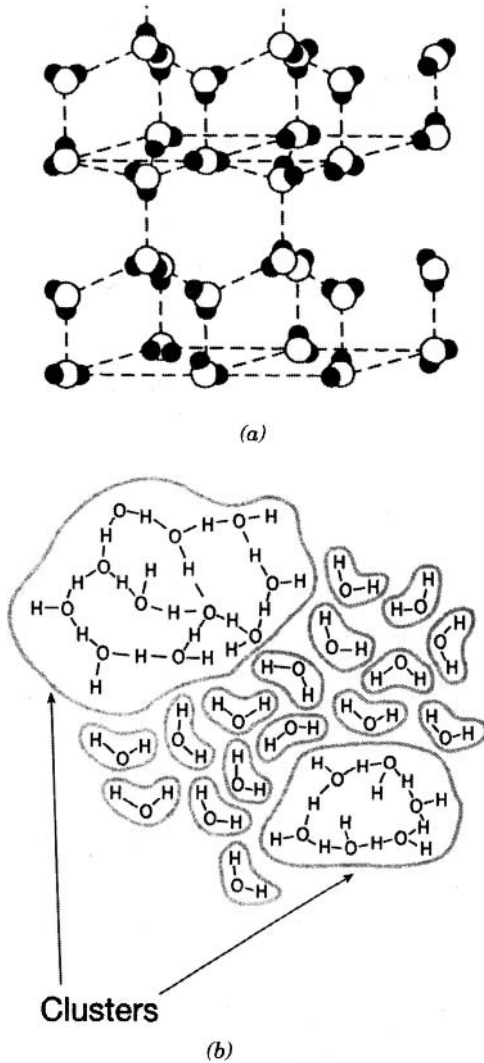
Figure 1.5. (a) Hydrogen-bonded open tetrahedral structure of ice (Gray, 1973). (b) Frank–Wen flickering cluster model of liquid water (Nemethy and Scheraga, 1962).

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 re-formation) 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 H_2O 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-
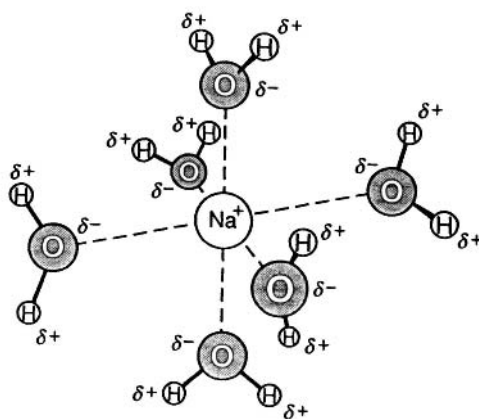

Figure 1.6. Hydrated sodium ion, Na^+, in aqueous solution. H_2O molecules form ion-dipole bonds to the central metal ion. The waters are in octahedral coordination to the sodium ion (Gray, 1973).

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
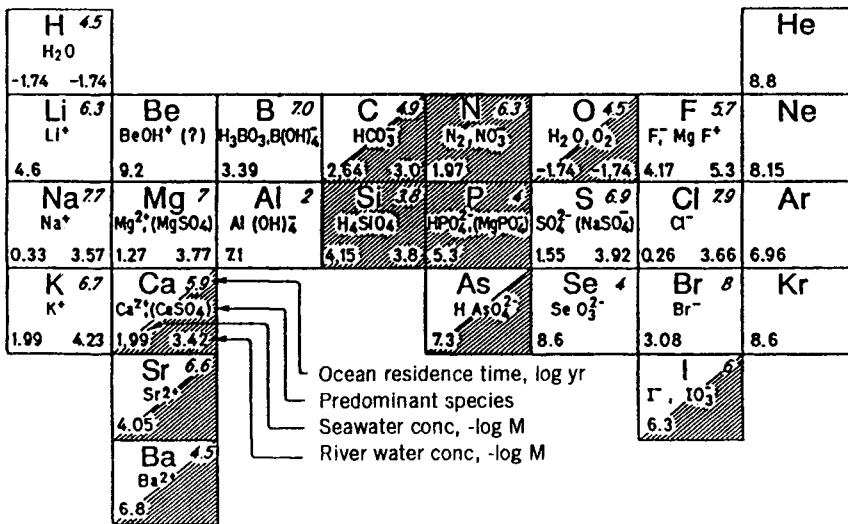

Figure 1.7. Some of the more important elements in natural waters: their concentrations, species, and residence times in river water and seawater (Sigg and Stumm, 1994). Elements whose distribution is significantly affected by biota are shaded.

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 $NaSO_4^-(aq)$; 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.

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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	$13,700 \times 10^{17}$ kg
Groundwater to 750 m	42×10^{17} kg
Groundwater to 4000 m	95×10^{17} kg
Water in ice	165×10^{17} kg
Water in lakes and rivers	1.3×10^{17} kg
Water in atmosphere	0.105×10^{17} kg

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

Some Properties of Water (m kg s units)

Temperature (°C)	$k_B T/10^{-21}$	Density (ρ)	Viscosity/10^{-3} (η)	Surface Tension (γ)	Dielectric Coefficient (ϵ)
5	3.8	999.965	1.5188	0.0749	86.04
20	4.0	998.203	1.0050	0.07275	80.36
25	4.1	997.044	0.8937	0.07197	78.54
30	4.2	995.646	0.8007	0.07118	76.75

The International Units

Physical Quantity	Unit	Symbol
Length	meter	m
Mass	kilogram	kg
Time	second	s
Electric current	ampere	A
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	$1 \, Pa = N \, m^{-2}$
Power	watt	$W = J \, s^{-1}$
Electric charge	coulomb	$C = A \, s$
Electric potential	volt	$V = W \, A^{-1}$
Electric capacitance	farad	$F = A \, s \, V^{-1}$
Electric resistance	ohm	$\Omega = V \, A^{-1}$
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

$$1 \text{ joule} = 1 \text{ volt coulomb} = 1 \text{ newton meter}$$
$$= 1 \text{ watt second} = 2.7778 \times 10^{-7} \text{ kilowatt hours}$$
$$= 10^7 \text{ erg}$$