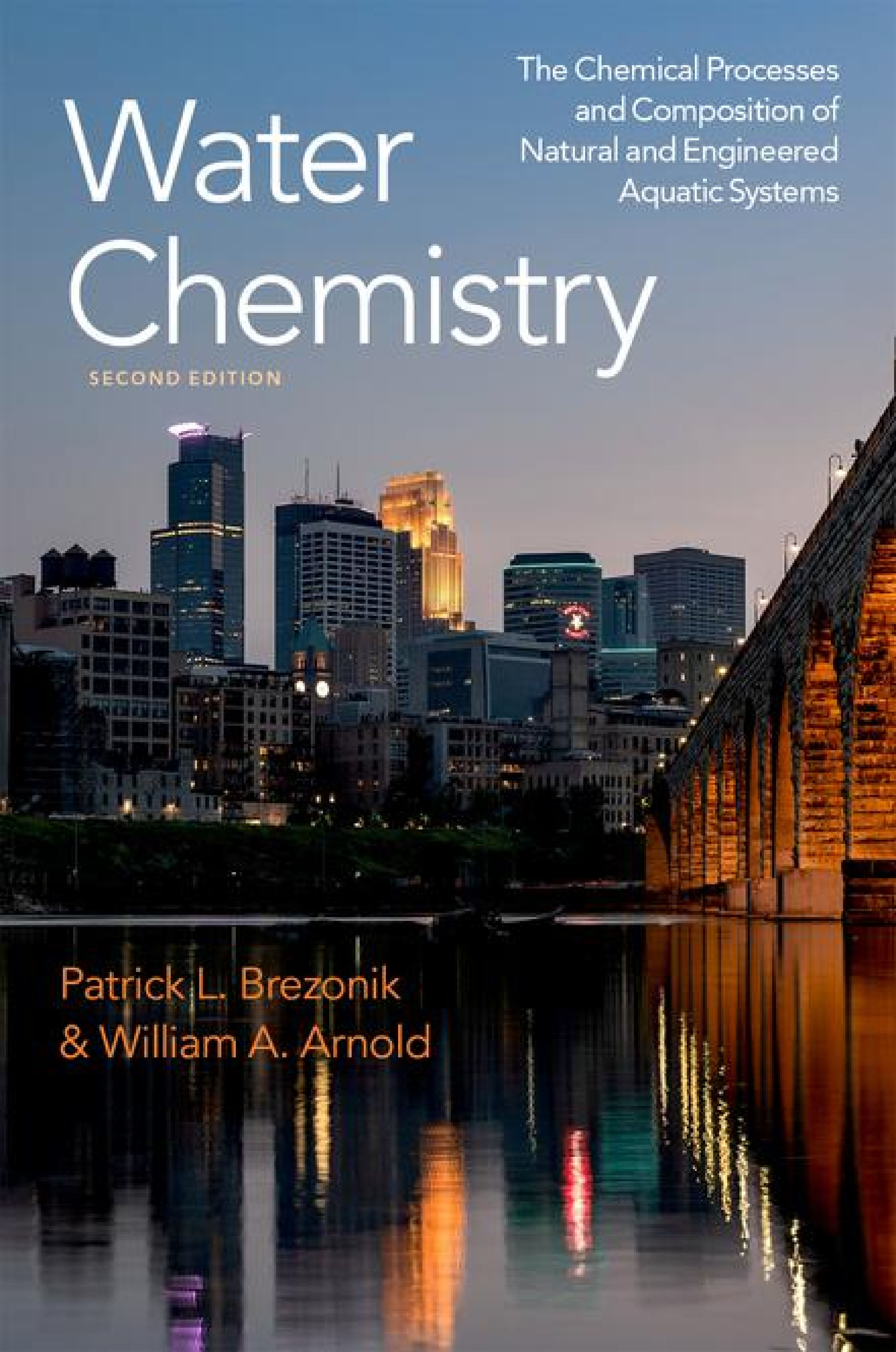

Water Chemistry

The Chemical Processes and Composition of Natural and Engineered Aquatic Systems

SECOND EDITION

Patrick L. Brezonik
& William A. Arnold

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Once again, to our extended families:

Carol Brezonik
Craig and Laura
Nicholas and Lisa
and Sarah, Joe, Billy, Niko, and Peter

Thomas and Carol Arnold
Lora Arnold
and Alex and Ben

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Preface to the Second Edition

Over the past decade, we often wondered why, after taking on the arduous task of writing a textbook, would someone want to write a second edition? After over 10 years of using the book and getting feedback from colleagues and ideas from students, we realized, however, that the book's content and structure needed to be refreshed. In some cases, we were getting frustrated with our previous decisions on topic coverage and order of presentation. The topics covered in this edition are largely the same as the first edition, but in some cases the presentation has been altered. In other cases, updated information has been added to encompass the large quantity of new knowledge in the literature of the past decade. More advanced materials were moved and additional topics were added as web-based content so as to not add too much length to the physical (or electronic) book. We also changed the software used for chemical equilibrium calculations to VMINTEQ, which is freeware, and the kinetics software to Tenua, which is open source. We hope this will make the software-text linkage available to a broader audience.

As in the first edition, Part I (Chapters 1 and 2) provides an overall introduction to the field of water chemistry. Part II provides information about the underlying concepts necessary to understand the chemistry of aquatic systems: thermodynamics (Chapter 3), activity (Chapter 4), kinetics (Chapter 5), and basic organic chemistry (Chapter 6). The primer on organic chemistry was included here because many acids/bases and ligands mentioned in Part III are organic chemicals.

Problem-solving is emphasized in Part III: Chemical equilibria and kinetics. Chapters 7 and 8 were substantially revised and reorganized, with Chapter 7 discussing the fundamentals of acids and bases and the equations needed to solve problems. Chapter 8 presents the techniques (algebraic, graphical, and computational) to solve the systems of equations that define acid-base equilibria and uses the carbonate system to bring all the pieces together. The effects of global climate change and increasing atmospheric carbon dioxide levels on the inorganic chemistry of natural waters are given increased focus. These chapters are followed by complexation (Chapter 9), solubility (Chapter 10), and redox (Chapter 11). Two more chapters now are included in this section: surface chemistry (including that of nanoparticles) and sorption (Chapter 12) and the chemistry of organic pollutants (Chapter 13). Our thought here is that the concepts flow from the previous chapters and that instructors will likely want to introduce students to these topics in a single semester class.

Part IV has similar topics, although in a different order, as the first edition. Instructors can pick and choose the chapters to be covered depending on the focus of their class. Photochemistry (Chapter 14) builds on concepts of kinetics, and concepts of acid/base equilibria, redox, and kinetics are important in chlorine and oxidant chemistry (Chapter 15). We see these chapters (or parts of them) as likely to be included in engineering-oriented classes. Chapters 16–20 provide perspectives on water chemistry in natural systems. We provide more depth on mineral weathering and the biogeochemistry of iron, manganese, and aluminum than in the first edition. We also describe the kinds of chemical inferences facilitated by stable isotope fractionation techniques and by advances in computer technology that enable analysis of large datasets encompassing broad spatial or temporal scales. The chapter on natural organic matter was completely reorganized and updated. Indeed, all the chapters in Part IV were revised to include insights gleaned from the past decade of research.

Many examples in the chapters have been updated, and additional end-of-chapter problems were created. Users of the second edition will find the substantially revised and expanded companion website to be more useful than the previous version. In addition to web boxes of supplemental information on many topics, the site has complete reference citations for each chapter; abbreviated versions of references are given in the book to save space. Spreadsheets of datasets needed to solve many end-of-chapter problems also are on the website so that students do not need to retype the data in solving problems.

We hope these changes will benefit both students and instructors. We appreciate everyone around the world who has used the book as an instructor, student, practitioner, and researcher. Your feedback has been most helpful, and we sincerely hope you find the second edition even more useful than the first one.

Finally, although this book is heavily oriented toward problem-solving, we think it also is useful to keep in mind the following:

> *Rather than a problem to be solved, the world is a joyful mystery to be contemplated with gladness and praise.*[*]

—Patrick L. Brezonik and William A. Arnold
University of Minnesota
April 2022

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[*] Francis I, *Laudato Si'. On Care for our Common Home*. Vatican, Rome, 2015.

Preface to the First Edition

In deciding whether to write a new textbook in any field, authors must answer two questions: (1) is there a need for another text in the field, and (2) how will their text be different from what is already available? It is obvious from the fact that this book exists that we answered yes to the first question. Our reasons for doing so are based on our answers to the second question, and they are related to the broad goals we set for coverage of topics in this book. Although previous introductory water chemistry textbooks provide excellent coverage on inorganic equilibrium chemistry, they do not provide much coverage on other topics that have become important aspects of the field as it has developed over the past few decades. These include non-equilibrium aspects (chemical kinetics) and organic chemistry—the behavior of organic contaminants and the characteristics and behavior of natural organic matter. In addition, most water chemistry textbooks for environmental engineering students focus their examples on engineered systems and either ignore natural waters, including nutrient chemistry and geochemical controls on chemical composition, or treat natural waters only briefly. This is in spite of the fact that environmental engineering practice and research focuses at least as much on natural systems (e.g., lakes, rivers, estuaries, and oceans) as on engineered systems (e.g., water and wastewater treatment systems and hazardous waste processing). Most existing textbooks also focus on solving inorganic ionic equilibria using graphical and manual algebraic approaches, and with a few exceptions, they do not focus on the use of computer programs to solve problems.

This book was written in an effort to address these shortcomings. Our overall goals in this textbook are to provide readers with (1) a fundamental understanding of the chemical and related processes that affect the chemistry of our water resources and (2) the ability to solve quantitative problems regarding the behavior of chemical substances in water. In our opinion, this requires knowledge of both inorganic and organic chemistry and the perspectives and tools of both chemical equilibria and kinetics. The book thus takes a broader approach to the subject than previous introductory water chemistry texts. It emphasizes the use of computer approaches to solve both equilibrium and kinetics problems. Algebraic and graphical techniques are developed sufficiently to enable students to understand the basis for equilibrium solutions, but the text emphasizes the use of computer programs to solve the typically complicated problems that water chemists must address.

An introductory chapter covers such fundamental topics as the structure of water itself, concentration units and conversion of units, and basic aspects of chemical reactions. Chapter 2 describes the chemical composition of natural waters and includes discussions on the basic chemistry and water quality significance of major and minor inorganic solutes in water, as well as natural and human sources and geochemical controls on inorganic ions. Chapters 3–7 cover important fundamentals and tools needed to solve chemical problems. The principles of thermodynamics as the foundation for chemical equilibria are covered first (Chapter 3), followed by a separate chapter on activity-concentration relationships, and a chapter on the principles of chemical kinetics. Chapter 6 provides basic information on the structure, nomenclature, and chemical behavior of organic compounds. Engineers taking their first class in water chemistry may not have had a college-level course in organic chemistry. For those who have had such a course, the chapter serves as a review focused on the parts of organic chemistry relevant to environmental water chemistry. Chapter 7 develops the basic tools—graphical techniques, algebraic methods, and computer approaches—needed to solve and display equilibria for the four main types of inorganic reactions (acid-base, solubility, complexation, and redox). The equilibrium chemistry and kinetics of these major types of inorganic reactions are presented as integrated subjects in Chapters 8–11.

Of the remaining eight chapters, six apply the principles and tools covered in the first 11 chapters to specific chemicals or groups of chemicals important in water chemistry: oxygen (12), disinfectants and oxidants (13), minor metals, silica, and silicates (15), nutrients (16), natural organic matter (18), and organic contaminants (19). The other two chapters describe two important physical-chemical processes that affect and sometimes control the behavior or inorganic and organic substances in aquatic systems: Chapter 14 describes how solutes interact with surfaces of solid particles (sorption and desorption), and Chapter 17 describes the principles of photochemistry and the role of photochemical processes in the behavior of substances in water.

The book includes more material and perhaps more topics than instructors usually cover in a single-semester course. Consequently, instructors have the opportunity to select and focus on topics of greatest interest or relevance to their course; we recognize that the "flavor" and emphasis of water chemistry courses varies depending on the program and instructor. Those wishing to emphasize natural water chemistry, for example, may wish to focus on Chapters 12, 15, 16, and 18 after covering the essential material in Chapters 1–11; others who want to focus on engineered systems and contaminant chemistry may want to focus more on Chapters 13, 14, and 19. Within several chapters, there also are *Advanced Topic* sections that an instructor may or may not use. With supplementary material from the recent literature, the book also may be suitable for a two-quarter or two-semester sequence.

A strong effort was made to write the text in a clear, didactic style without compromising technical rigor and to format the material to make the book inviting and accessible to students. We assume a fairly minimal prior knowledge of chemistry (one year of general chemistry at the college level) and provide clear definitions of technical terms. Numerous in-chapter examples are included to show the application of theory and equations and demonstrate how problems are solved, and we have made an effort to provide examples that are relevant to both natural waters and engineered systems. The problems included at the end of most of the chapters generally are ordered in terms of difficulty, with the easiest problems coming first.

—Patrick L. Brezonik and William A. Arnold
University of Minnesota
February 2010

Acknowledgments for the Second Edition

When we started down the path of a second edition, we reached out to many colleagues for their suggestions. We thank those who enthusiastically responded with ideas, input, and frustrations; we tried our best to incorporate your feedback. Once again, we greatly benefited from the knowledge of those willing to review chapters (in parentheses) when a fresh perspective was needed. We thank Paul Capel (1, 2), Erin Surdo (7, 8, 13), Teng Zeng (7, 8, 13), Chanlan Chun (9, 10), Brandy Toner (12), Kris McNeill (14), Mike Dodd (15), Bruce Monson (16), Mark Brigham (16), and Paul Bloom (20). Special thanks to Yu-Ping (Yo) Chin for doing double duty (Chapters 11 and 20) and providing many valuable insights and references.

To the hundreds of students at the University of Minnesota who noted errors, confusing explanations, and typos in the first edition, we appreciate your keen eyes. We especially thank our spouses for their patience and understanding during this two-year effort. Special thanks to Nick Brezonik for his contribution of the book cover photos for this and the first edition, Alex Arnold for his help editing the numerous equations, and Grant Goedjen for generating Figure 8.5. Last, we gratefully acknowledge our recently passed friend and colleague, Deborah Swackhamer, for her enthusiastic and dedicated efforts to ensure that water pollution was understood and taken seriously from a fundamental, scientific perspective.

Acknowledgments for the First Edition

We owe a great debt of gratitude to the individuals whose reviews of individual chapters provided many comments and suggestions that improved the content of the book, and we appreciate their efforts in finding errors. We list them here alphabetically with chapters reviewed in parentheses: Larry Baker (1, 2, 16), Paul Bloom (18), Steve Cabaniss (18), Paul Capel (4, 6, 19), Yu-Ping Chin (18, 19), Joe Delfino (1, 2), Baolin Deng (10, 11), Mike Dodd (13), Dan Giammar (7, 8), Ray Hozalski (13), Tim Kratz (12), Doug Latch (17), Alison McKay (4, 6), Kris McNeill (17), Paige Novak (6, 15), Jerry Schnoor (15), Timm Strathmann (3, 5), Brandy Toner (14), Rich Valentine (9, 11), and Tom Voice (8, 9). Any remaining errors are the authors' responsibility, but we sincerely hope that the readers will find few or no errors. We especially thank Mike Dodd for his extensive review and suggestions for Chapter 13 and Paul Bloom and Yo Chin for their detailed reviews and input to Chapter 18.

The senior author is happy to acknowledge the role that his previous book, *Chemical Kinetics and Process Dynamics in Aquatic Systems* (CRC Press, 1994), played in informing the writing of Chapters 5 and 17 and parts of Chapters 13 and 15. He also expresses his thanks to the students in his 2008 and 2009 water chemistry classes, in which drafts of various chapters were used as the textbook, for their helpful comments and for finding many errors. Special thanks go to Mike Gracz, PhD student in Geology and Geophysics, for his detailed reviews of the chapters. The junior author hopes that students in his future water chemistry classes do not find any errors.

Several individuals were helpful in supplying data used in this book. We are pleased to acknowledge Larry Baker, Joe Delfino, Paul Chadik, Charles Goldman, Patricia Arneson, and Ed Lowe for chemistry data used in Chapter 2; Tim Kratz and Jerry Schnoor for dissolved oxygen data used in Chapter 12; Rose Cory for fluorescence spectra and Abdul Khwaja for NMR spectra in Chapter 18; and Dan Giammar and Mike Dodd for some of the problems at the ends of several chapters. Thanks also to Kevin Drees and Bethany Brinkman for helping the authors collect additional data used in Chapters 2 and 18. We thank Mike Evans, graduate student in Computer Science and Engineering at the University of Minnesota, for developing a user-friendly interface to the kinetic program Acuchem, and Randal Barnes for advice on solving problems using spreadsheets.

We happily acknowledge the excellent library system of the University of Minnesota and the inventors of Internet search engines, which greatly facilitated our library research and hunts for references, enabling us to continue this work wherever we could find an Internet connection.

The senior author thanks the Department of Civil Engineering and his environmental engineering colleagues at the University of Minnesota for a light teaching load over the past few years, which enabled him to focus his time and efforts on writing the book. The junior author wishes he had the same luxury, but he still managed to squeeze in a fair bit of writing. Both authors thank their colleagues and especially their families for their understanding and patience when the writing absorbed their time.

Finally, we acknowledge with gratitude our predecessors in writing water chemistry books, starting with Werner Stumm and James J. Morgan and extending to more recent authors: Mark Benjamin, Philip Gschwend, Janet Hering, Dieter Imboden, David Jenkins, James Jensen, Francois Morel, James Pankow, Rene Schwarzenbach, Vernon Snoeyink, and others, on whose scholarly efforts our own writing has relied, and the countless researchers, only some of whom are cited in the following pages, responsible for developing the knowledge base that now enriches the field of environmental water chemistry.

Symbols and Acronyms

Symbols

[]	mass or molar concentration
{}	activity
≡M	metal center attached to a solid surface
≡S	surface site
‰	parts per thousand (per mil)
α_i	fraction of X_T present as species i
α_λ	beam attenuation coefficient of light at wavelength λ
$\alpha_{D\lambda}$	diffuse attenuation coefficient of light at wavelength λ (also K_λ)
β	buffering capacity (chapter 8)
β	cumulative stability (formation) constant (chapter 9)
β	Bunsen coefficient (chapter 18)
γ	activity coefficient
$\gamma_\pm$	mean ionic activity coefficient of a salt
γ	interfacial energy or surface tension (chapters 3, 12)
Θ	temperature coefficient in kinetics
θ_A	fraction of binding sites occupied by sorbate A (chapter 12)
ε_λ	molar absorptivity (wavelength dependent)
κ	transmission coefficient (chapter 5 only)
κ^{-1}	radius of ionic atmosphere (Debye parameter), and characteristic thickness of the electrical double layer
κ	log K_a (chapter 20)
λ	wavelength
μ	chemical potential
ν	stoichiometric coefficient
ν	kinematic viscosity ($m^2\ s^{-1}$) (chapter 18)
ν_f	fundamental frequency factor
ξ	extent of reaction
ρ	density
ρ	susceptibility factor (chapter 13)
ρ_w	flushing coefficient for water in a reactor (= Q/V)
σ	Hammett constant
τ	characteristic time
Φ	quantum yield
Ψ_0	electrostatic surface potential
Ω	saturation ratio for mineral salts (chapter 10)
ω	electrostatic interaction factor
a_λ	light absorption coefficient at wavelength λ
a_i, $\mathrm{a_i}$	activity of i
$\mathbf{a}_i$	size parameter for ion i in Debye-Hückel equation

A	pre-exponential or frequency factor in Arrhenius equation
at. wt.	atomic weight
at. no.	atomic number
b.p.	boiling point
c, C	concentration
c	correction factor (chapter 13)
C	(electrical) capacitance (Chapter 12)
C_p	heat capacity
ΔC_p	change in heat capacity for a reaction
D_λ	wavelength-dependent distribution function for scattered light (chapter 14)
D	diffusion coefficient
D	distribution coefficient (chapter 13)
$\boldsymbol{D}$	dielectric constant (relative static permittivity)
$\boldsymbol{D}_o$	permittivity in a vacuum
D_{obs}	observed distribution coefficient (chapter 4)
D	thermodynamic distribution coefficient (chapter 4)
Da	daltons (molecular weight units)
ΔE	change in internal energy
e_g	type of molecular orbital
$e_{aq}{}^-$	a hydrated electron
$E_{0\lambda,z}$	scalar irradiance at depth z (chapter 14)
$E°$	electrical (reduction) potential under standard conditions
E_H	oxidation-reduction potential measured on the hydrogen scale
E_{act}	energy of activation
E_{bg}	band gap energy
$E_{0\lambda,0}$	scalar irradiance just below the water surface (also Z_λ)
esu	electrostatic units
f	fraction of a substance in a specific phase (chapter 13)
f_i	fugacity of substance i
f_i	fragment constants for fragment i (chapter 13)
f_{oc}	fraction of organic carbon
F	Helmholtz free energy
F	Faraday, unit of capacitance (chapter 12)
F_1	Gran function (used in alkalinity titrations)
$\mathscr{F}$	Faraday's constant
G	Gibbs free energy
$\Delta_f G°$	free energy of formation under standard conditions
$\Delta_r G°$	change in free energy (or free energy of reaction under standard conditions)
$\Delta G^{\neq}$	free energy of activation
h	Planck's constant
H	enthalpy
$\Delta_f H°$	enthalpy of formation under standard conditions
$\Delta_r H°$	change in enthalpy of reaction under standard conditions
H	Henry's law constant ($= K_H{}^{-1}$)
i	current
i_0	exchange current
I	ionic strength

$\mathrm{I}_{a\lambda}$	(wavelength-dependent) number of photons absorbed per unit time
$\mathrm{I}_{0\lambda}$	total irradiance (wavelength-dependent)
$\mathrm{I}_{d\lambda}$	direct irradiance corrected for reflection (wavelength-dependent)
$\mathrm{I}_{s\lambda}$	sky irradiance corrected for reflection (wavelength-dependent)
J	joule
kPa	kilopascals (unit of pressure)
$\mathbf{k}$	Boltzmann constant (gas constant per molecule)
k_i°	molar compressibility of i
k	rate constant
$k_{a\lambda}$	specific light absorption rate constant (usually summed over wavelength range)
$k_{d\lambda}$	direct photolysis rate constant (usually summed over wavelength range)
K_{λ}	diffuse attenuation coefficient of light at wavelength λ (also $\alpha_{D\lambda}$)
K or ${}^{a}K$	thermodynamic equilibrium constant (products and reactants expressed in terms of activity)
${}^{c}K$	equilibrium constant expressed in terms of concentrations of products and reactants
K_{aw}	air-water partition coefficient
K_{d}	solid-water partition coefficient
K_{H}	Henry's law coefficient (= H^{-1})
K_{L}	gas transfer coefficient (units of length time^{-1})
K_{L}	Langmuir sorption constant
K_{oc}	organic carbon-water coefficient
K_{ow}	octanol-water partition coefficient
K_{w}	ion product of water
l_{λ}	(light path) length
L_0	ultimate (first-stage) biochemical oxygen demand
m	molal concentration
M	molar concentration
M_{T}	total mass
m/z	mass-to-charge ratio
n	number (of molecules, atoms, or molecular fragments)
n	nuclophilicity constant (chapter 13)
N	normality (equivalents/L)
N(K)	probability function for equilibrium constant K
N_{A}	Avogadro's number
pε	negative logarithm of relative electron activity; a measure of the free energy of electron transfer, pronounced "pea epsilon"
pH	negative logarithm of hydrogen ion activity
$\mathrm{pH}_{\mathrm{PZC}}$	pH of point of zero charge on surfaces
$\mathrm{pH}_{\mathrm{ZNPC}}$	pH of zero net proton charge
pX	negative logarithm of X
P	pressure
P	primary production (chapter 18)
q	heat
q	charge density in diffuse layer (chapter 12)
Q	hydraulic flow rate
r	ratio of peak areas determined via gas chromatography
R	gas constant

R	respiration (chapter 18)
R^2	coefficient of determination (statistical measure)
R	rate
s	substrate constant (chapter 13)
s_λ	wavelength-dependent light-scattering coefficient (subscripts f or b indicate forward or back scattering)
s_λ	spectral slope over wavelength range λ_1 to λ_2 (in nm) (Chapter 20)
S	entropy
S	saturation ratio
Sc	dimensionless Schmidt number (kinematic viscosity/diffusion coefficient)
$\mathrm{S_r}$	slope ratio (ratio of $s_{275\text{-}295}$ to $s_{350\text{-}400}$)
t_{2g}	type of molecular orbital
$\mathrm{t}_{\frac{1}{2}}$	half-life
$\mathrm{t_c}$	critical time (time to achieve maximum DO deficit in Streeter-Phelps model)
T	temperature
$TOT\mathrm{X}$	total concentration of X in all phases of a system
U_{10}	wind velocity 10 m above the surface
V	volume
$\mathrm{V}^\circ_{\mathrm{i}}$	standard molar volume for i
w, W	work
W_λ	sum of direct ($\mathrm{I}_{d\lambda}$) and sky ($\mathrm{I}_{s\lambda}$) irradiance corrected for reflection (wavelength-dependent)
$\mathrm{X_T}$	total concentration of all species of X in solution
$\mathrm{X_{max}}$	maximum sorption capacity
y	amount of O_2 consumed at any time in biochemical oxygen demand test
z	charge (on an ion)
z	depth (chapter 14)
$\mathrm{z_{pz}}$	depth of photic zone (chapter 14)
$\mathrm{Z_{AB}}$	collision frequency between A and B
Z_λ	scalar irradiance just below the water surface (also $\mathrm{E}_{0\lambda,0}$)

Acronyms

2,4-D	2,4-dichlorophenoxyacetic acid
AAS	atomic absorption spectrophotometry
ACD	Ahrland-Chatt-Davies classification system
ACP	actual concentration product
ACT	activated complex theory
AHM	aquatic humic matter
AIC	Akaike information criterion
ANC	acid-neutralizing capacity (= alkalinity)
AOP	advanced oxidation process
APase	alkaline phosphatase
BCF	bioconcentration factor
BET	Brunauer-Emmet-Teller sorption equation
BLM	biotic ligand model

BNC	base neutralizing capacity
BOD	biochemical oxygen demand
BSM	basic Stern model (Chapter 12)
BTEX	benzene, toluene, ethylbenzene, and xylene
CAS	Chemical Abstract Service
CB	conduction band
CCM	constant capacitance model
CD-MUSIC	charge distribution multi-site complexation (model)
CFSTR	continuous-flow stirred tank reactor
cgs	centimeter-gram-second, system of measure
CDOM	colored (or chromophoric) dissolved organic matter
CH	carbonate hardness
CLE-ACSV	competitive ligand equilibration-adsorptive cathodic stripping voltammetry
CNT	carbon nanotube
COD	chemical oxygen demand
CP-MAS NMR	cross-polarization-magic angle spinning nuclear magnetic resonance (spectroscopy)
CPU	chloroplatinate unit
CRAM	carboxyl-rich alicyclic material
CUAHSI	Consortium of Universities for the Advancement of Hydrologic Science, Inc.
DAX	resin material used to extract AHM from water
DBE	double bond equivalents
DBE/C	double bond equivalents per carbon atom
DBP	disinfection by-product
DCE	dichloroethylene
DDT	dichlorodiphenyltrichloroethane
DEAE	diethylaminoethyl (functional group)
DFAA	dissolved free amino acid
DHLL	Debye-Hückel limiting law
DIC	dissolved inorganic carbon
DLM	double-layer model
DMF	2,5-dimethylfuran
DMG	dimethylglyoxime
DO	dissolved oxygen
DOC	dissolved organic carbon
DOM	dissolved organic matter
DON	dissolved organic nitrogen
DOP	dissolved organic phosphorus
DRP	dissolved reactive phosphate
E2/E3	ratio of absorbance at 250 nm to absorbance at 365 nm
E4/E6	ratio of absorbance at 465 nm to absorbance at 665 nm
EAC	electron accepting capacity (Chapter 20)
EAWAG	German acronym for Swiss Federal Institute of Aquatic Science and Technology
EDC	electron donating capacity (Chapter 20)
EDHE	extended Debye-Hückel equation

EDTA	ethylenediaminetetraacetic acid
EEM(s)	excitation-emission matrix (matrices)
EfOM	effluent organic matter
EPC	equilibrium phosphorus concentration
EPICS	equilibrium partitioning in closed systems
EPI Suite	Estimation Programs Interface Suite
EPR	electron paramagnetic resonance (spectroscopy)
EXAFS	extended x-ray absorption fine structure spectroscopy
FA	fulvic acid
fDOM	fluorescent dissolved organic matter
FFA	furfuryl alcohol
FI	fluorescence index
FITEQL	nonlinear data fitting program
FT-ICR MS	Fourier transform ion cyclotron resonance mass spectrometry
GC-MS	gas chromatography-mass spectrometry
GCSOLAR	public domain computer program to calculate light intensity and rates of direct photolysis
HA	humic acid
HAA	haloacetic acid
HAc	acetic acid
HFO	two-layer surface complexation model for ferrihydrite
HMWDON	high-molecular-weight dissolved organic nitrogen
HOMO	highest occupied molecular orbital
HPLC	high-performance liquid chromatography
HRMS	high resolution mass spectrometry
HRT	hydraulic residence time
HSAB	(Pearson) hard-soft acid-base (system)
IAG	internal alkalinity generation
IAP	ion activity product
IC	ion chromatography
ICP	inductively coupled plasma
IEP	isoelectric point
IHSS	International Humic Substances Society
IMDA	imidodiacetic acid
IP	inositol phosphate
IR	infrared
is	inner sphere (complex)
IUPAC	International Union of Pure and Applied Chemistry
LC-MS	liquid chromatography-mass spectrometry
LED	light-emitting diode
LFER	linear free energy relationship
LMCT	ligand-to-metal charge transfer (process)
LULC	land use-land cover
LUMO	lowest unoccupied molecular orbital
MCL	maximum contaminant level
MDF	mass dependent fractionation (Chapter 16)

MEMS	microelectromechanical system
MER/MEO	mediated electrochemical reduction/oxidation (Chapter 20)
MIF	mass independent fractionation (Chapter 16)
MINEQL	computer program to calculate mineral equilibria
MINEQL+	commercially available equilibrium computer program
MW	molecular weight
NADP	National Atmospheric Deposition Program
NCH	noncarbonate hardness
NDMA	N-nitrosodimethylamine
NICA-Donnan	non-ideal competitive adsorption-Donnan (model)
NMR	nuclear magnetic resonance (spectroscopy)
NOM	natural organic matter
$^3NOM^*$	triplet excited state natural organic matter
NP	nanoparticle
NTA	nitrilotriacetic acid
NTU	nephelometric turbidity unit
os	outer sphere (complex)
PAH	polycyclic aromatic hydrocarbon
PARAFAC	parallel factor analysis; technique to evaluate DOM quality from fluorescence spectra (EEMs)
PBDE	polybrominated diphenylether
PCB	polychlorinated biphenyl
PCDD/Fs	polychlorinated dibenzodioxins/furans
PCE	perchloroethylene or tetrachloroethylene
PCU	platinum-cobalt color unit (Hazen unit)
PES	potential energy surface
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonic acid
PFR	plug-flow reactor
PON	particulate organic nitrogen
POP	persistent organic pollutant
PP	particulate phosphorus
PPC	products of proton consumption
PPCPs	pharmaceutical and personal care products
PPR	products of proton release
PPRI	photochemically produced reactive intermediate
PSU	practical salinity unit
ROS	reactive oxygen species
RPHPLC	reverse-phase high-performance liquid chromatography
S	salinity
SC	specific conductance
SCM	surface complexation model
SD	standard deviation
SEC	size-exclusion chromatography
SII	specific ion interaction
SMILES	Simplified Molecular Input Line Entry System

SMOW	standard mean ocean water
SMP	soluble microbial products
SRFA	Suwannee River fulvic acid
SRHA	Suwannee River humic acid
SRP	soluble reactive phosphate (expressed as P)
STP	standard temperature and pressure
SUVA	specific ultraviolet absorption
SWCNT	single-walled carbon nanotube
TCE	trichloroethylene
TCP	2,4,6-trichlorophenol
TDP	total dissolved phosphorus
TDS	total dissolved solids
TH	total hardness
THM	trihalomethane
ThOC	threshold odor concentration
TLM	triple-layer model
TMA	trimethylamine
TNT	trinitrotoluene
TOC	total organic carbon
TON	total organic nitrogen
TP	total phosphorus
TST	transition state theory
UF	ultrafiltration
U.S. EPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
UV	ultraviolet
VB	valence band
VMINTEQ	Visual MINTEQ (public domain equilibrium program based on MINEQL)
VOC	volatile organic compound
WHAM	Windermere humic acid model (public domain computer program) for metal binding to AHM; ver. 6 (2002) is the latest version
WWTP	wastewater treatment plant
XAD	see DAX
XANES	x-ray absorption near-edge spectroscopy

Units for physical quantities

Fundamental quantities

Quantity	**SI units**
Length	meter, m
Mass	kilogram, kg
Time	second, s
Electric current	ampere, A
Temperature	Kelvin, K
Amount of material	mole, mol

Some derived quantities

Quantity	**SI units**
Force	newton ($kg{\cdot}m{\cdot}s^{-2}$)
Volume	cubic meters (m^3)*
Electric charge	coulomb, $C = A{\cdot}s$
Power	watt, $W = J{\cdot}s^{-1}$
Electric potential	volt, $V = W{\cdot}A^{-1}$
Electric resistance	ohm, $\Omega = V{\cdot}A^{-1}$
Conductance	Siemens, $S = A{\cdot}V^{-1}$

Important constants

Atomic mass unit	1.6605×10^{-27} kg
Avogadro's constant (number)	6.022×10^{23} mol^{-1}
e (the "natural" number)	2.71828
Electron charge	1.602×10^{-19} coulombs (C) or 4.803×10^{-10} esu
Electron mass	9.109×10^{-31} kg
Fundamental frequency, ν (reciprocal of molecular vibration period)	6.2×10^{12} s^{-1}
Faraday, $\mathfrak{F}$	96,485 C mol^{-1}
Gas constant per mole, R	8.314 J mol^{-1} K^{-1} or 1.987 cal mol^{-1} K^{-1}
Gas constant per molecule, **k**, called the Boltzmann constant	1.3805×10^{-23} J K^{-1}
Gravitation constant (of the Earth)	9.806 m s^{-2}
Melting point of water	0 °C or 273.15 K
Molar volume of an ideal gas at 0 °C and 1 atm	22.414 L mol^{-1} or 22.414×10^3 cm^{-3} mol^{-1}
Molecular vibration period	1.5×10^{-13} s
Permittivity of a vacuum, ε_0, now called the electric constant	8.854×10^{-12} J^{-1} C^2 m^{-1} (or Farads per meter)
π	3.14159
Planck's constant, h	6.626×10^{-34} J s
Relative static permittivity of water, *D*, also called the dielectric constant)	80.1 (dimensionless) at 20°C
Speed of light (in a vacuum), c	2.998×10^8 m s^{-1}

---

[*] The liter (L) is not an SI unit but is widely used as the unit of volume in freshwater studies. 1 L = 10^{-3} m^3 = 1 dm^3. Some scientific journals use SI units only and use m^3 for volumetric measurements.

Conversion factors for energy-related quantities

1 newton (unit of force) = 1 N = kg m s^{-2}
1 joule (unit of energy) = 10^7 erg = 1 N m = kg m^2 s^{-2} = 1 volt coulomb (V C) = 0.239 calories (cal) = 9.9×10^{-3} L atm^{-1} = 6.242×10^{18} eV
1 cal = 4.184 J
1 watt = 1 J s^{-1} = 1 kg m^2 s^{-3} = 2.39×10^{-4} kcal s^{-1} = 0.86 kcal h^{-1}
1 entropy unit = 1 cal mol^{-1} K^{-1} = 4.184 J mol^{-1} K^{-1}

Conversion factors for pressure

1 atm = 760 mm Hg = 1.013×10^5 Pa (pascals) = 101.3 kPa = 1.013 bars
1 mm Hg = 1 torr
1 Pa = 10^{-5} bars = 1 N m^{-2}

Some useful relationships

RT ln x = 2.303RT log x = 5.709 log x (kJ mol^{-1}) = 1.364 log x (kcal mol^{-1}) at 25 °C (298.15 K)
($RT/\mathfrak{F}$) ln x = $2.303RT/\mathfrak{F}$ log x = 0.05916 log x (V at 25 °C, or 59.16 mV at 25 °C)

PART I

PROLOGUE

1

Introductory Matters

Objectives and Scope

This chapter sets the stage for the rest of the book by addressing five topics. First, a brief description of the nature and scope of water chemistry and its relationship to other environmental sciences provides context for the topics treated in this book. Second, a description of the unique properties of water and their relationship to its molecular and macroscopic structure provides an appreciation for the complexity of the medium that supports the chemistry we wish to understand. Third, the many units used to report concentrations of chemicals in water—some common, some standard chemical units, and some unique to environmental engineering and chemistry—are introduced. We show how to use them and interconvert them as a first step in analyzing the chemistry of water quantitatively. Fourth, we introduce the major types of chemical reactions that occur in natural and engineered water systems and describe the kinds of models and equations used to quantify the equilibrium conditions that they tend to approach and rates at which they occur. Finally, we provide a brief review of the origins of water chemistry and its development as a scientific discipline.

Key Concepts and Terms

- The "overlapping neighborhoods" of water chemistry, marine chemistry, aqueous geochemistry, biogeochemistry, soil chemistry, and many other environmental sciences
- The unique physical-chemical properties of water
- Liquid water as a structured fluid caused by extensive hydrogen bonding to form water "clusters"
- Common mass units of concentration: parts per million (ppm) and parts per billion (ppb); milligrams per liter (mg/L) and micrograms per liter (μg/L)
- Chemical concentration units: moles/liter (molarity, M), moles/kilogram of water (molality, m), equivalents/liter, normality (N), mole fraction
- Concentration units unique to water chemistry: mg/L as $CaCO_3$; mg/L as N, P, Cl, or other elemental components of ions and molecules
- Stoichiometric, equilibrium, and kinetic modeling approaches
- Associative reactions: acid-base, solubility (precipitation and dissolution), complex formation and dissociation
- Redox processes: oxidation as a loss of electrons; reduction as a gain in electrons

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- Sorption: a phase-transfer process
- Gas transfer and Henry's law

1.1 Introduction: Definition and scope of water chemistry

As a recognized field of science, water chemistry developed in the mid-twentieth century at the dawn of the "environmental era," but as described later in this chapter (Section 1.5), its origins go back considerably further in time. Before proceeding, it may be useful to provide a brief description of what we think the field of water chemistry comprises. Defining scientific fields in a way that is more than self-referential (i.e., "water chemistry is the chemical study of water") can be difficult because of the overlapping nature of related scientific disciplines, as illustrated in Figure 1.1. For present purposes, we propose the following description:[1]

> Water chemistry deals with the *solutes* and *suspended substances* in natural waters and aquatic systems engineered by humans, and it focuses on the reactions and phase-transfer processes that change solute concentrations in water. The theoretical rigor of fundamental chemistry supports a broader framework for water chemistry research and practice that seeks to integrate and interpret relevant biogeochemical processes across diverse natural and engineered waters using a combination of field, laboratory (experimental), and analytical (modeling) methods. Water chemistry focuses not so much on water itself but on what is *in* water. The unique characteristics of water as a solvent play important roles, however, in determining the types and rates of reactions and phase-transfer processes that occur. In addition, water chemistry generally focuses on temperatures between 0 and 40 °C, pH values between 5 and 9 (with exceptions related to volcanic activity, acid rain, and hazardous wastes), and usually on relatively dilute concentrations. Finally, the broad goals of water chemistry as a discipline include improving our *understanding* of how chemical processes affect aquatic systems and *developing techniques* to improve treatment and remediation of waters impaired by human activities.

1.2 Nature of water

1.2.1 A societal perspective

Water is by far the most common liquid on the Earth's surface, and its unique properties enable life to exist. Water is usually regarded as a public resource—a common good—because it is essential for human life and society, but too much water or water in the wrong places also is a problem: witness the extensive flooding problems caused by hurricanes and increasingly common extreme rain events. Water also is an

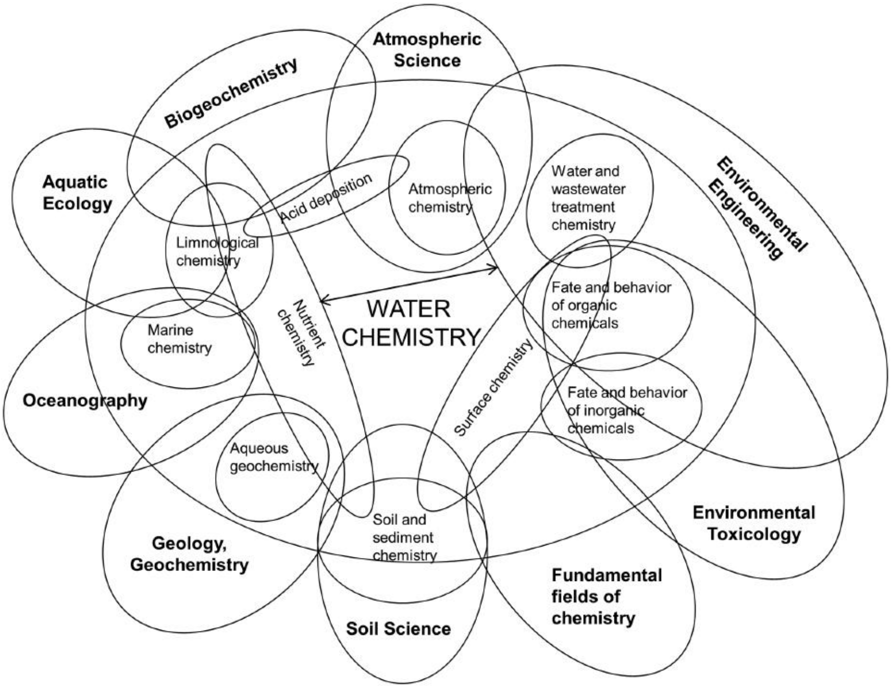

Figure 1.1 Overlapping neighborhoods of the sub-fields in water chemistry and related disciplines. The size of the ovals is not intended to indicate the importance of a given sub-field or discipline, and the extent (or lack) of overlap of ovals reflects drawing limitations more than the extent of concordance among sub-fields and disciplines. In the interest of clarity, not all active and potential interactions are illustrated; the double-headed arrow shows one obvious interaction not otherwise indicated in the diagram—that between nutrient chemistry and environmental engineering and its subfield of water/wastewater treatment.

economic resource and is sold as a commodity. Water rights in the American West are continuous source of conflict[2] and a problem of global magnitude.[3] Beyond these perspectives, water holds a special place in human society and indeed is often spoken of in terms of its mystical and transcendent properties. Water has spiritual values in many cultures and is associated with birth, spiritual cleansing, and death. The fact that about 70% of the Earth's surface is covered by water and only 30% by land makes one wonder whether "Planet Earth" more properly might be named "Planet Water."

For chemists, water is a small, simple-looking, and common molecule, H_2O, but they know it has many unusual and even unique properties, as discussed below. For civil engineers, water is a fluid to be transported via pipes and channels. When it occurs in rivers and streams, it is viewed partly as an obstacle to transportation, for which bridges need to be designed and constructed, and partly as an energy-efficient means of transportation and shipping. Scientists in many other disciplines have their own viewpoints about water that reflect how it interacts with their science.

1.2.2 Physical properties of water

Water is the medium for all the reactions and processes that comprise the foci of this book. Here we focus on the properties of water itself, describe its molecular structure, and show how that structure leads to the macroscopic structures of liquid, solid, and gaseous water and their unusual physicochemical properties. Compared with other small molecules, water has very high melting and boiling point temperatures.[4]

Compound	*Formula*	*Mol. Wt.*	*Freezing pt. (°C)*	*Boiling pt. (°C)*
Methane	CH_4	16	−182.5	−161.5
Ammonia	NH_3	17	−77.7	−33.3
Water	H_2O	18	0	100
Carbon monoxide	CO	28	−205	−191.5
Nitric oxide	NO	30	−164	−152

Moreover, as Figure 1.2a shows, water does not follow the trend of decreasing melting and boiling points with decreasing atomic weight shown by the other Group 16 (formerly called Group VI; see Periodic Table in Chapter 2) hydrides, and it also differs from typical liquids in the temperature dependence of several other physical properties (Figure 1.2b,c).

Among common liquids, water has the highest heat capacity, heat conduction, heats of vaporization and fusion, and dielectric constant (or "relative static permittivity"); see Table 1.1. The latter characteristic measures the attenuation rate of coulombic forces in a solvent compared to attenuation in a vacuum, and it is important for

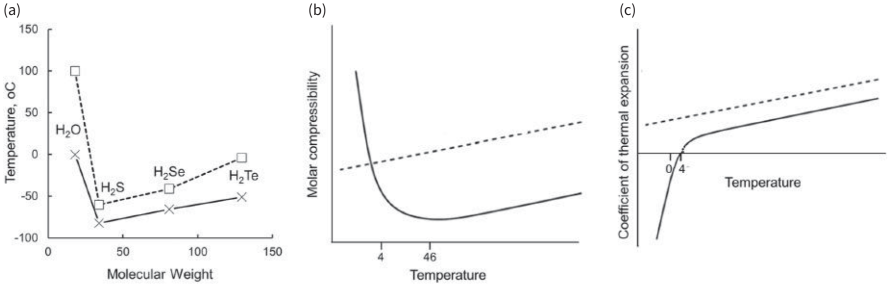

Figure 1.2 Trends in melting point (solid line) and boiling point data[4] for the Group VI hydrides (a) and temperature relationships for some physical properties of water (solid line) and typical liquids (dashed line): isothermal compressibility, k_T, a measure of how pressure affects molar volume (b), and the coefficient of thermal expansion, α_P, a measure related to density (c).

Parts (b)–(c) redrawn from Nilsson and Pettersson.[5]

Table 1.1 Physical properties of water[a]

Property	*Value*	*Comparison with other liquids*	*Environmental Importance*
State (at room temperature)	Liquid	Rather than a gas like H_2S and H_2Se	Provides medium for life
Heat capacity Specific heat	1.0 cal g^{-1} °C^{-1} 4.18 J g^{-1} °C^{-1}	Very high	Moderates climate
Latent heat of fusion	79 cal/g 330 J/g	Very high	Moderating effect; stabilizes air temperatures
Latent heat of evaporation	540 cal/g 2257 J/g	Very high	Moderating effect; important in hydrology for precipitation–evaporation balances
Density at 4 °C	1.0 g/cm^3	High; anomalous maximum at 4 °C	Causes freezing to occur from air–water surface; controls temperature distribution and water circulation in lakes and oceans
Surface tension at 20 °C	72.8 dyne/cm 72.8 mN/m	Very high	Affects adsorption, wetting, and transport across membranes
Dielectric constant[b]	80.1 at 20 °C (dimensionless)	Very high	Makes water a good solvent for ions; shields electric fields of ions
Dipole Moment	1.85 debyes	High compared with organic liquids	Cause of above characteristics and solvent properties of water
Viscosity	1.0×10^{-3} Pa·s 1 centipoise (cP) at 20 °C	2–8× higher than organic liquids	Slows movement of solutes
Transparency	High	Especially in mid-visible range	Allows thick zone for photosynthesis and photochemistry
Thermal conductivity	0.6 W m^{-1} K^{-1}	High compared with organic liquids	Critical for heat transfer in natural and engineered systems

[a] Adapted from Horne.[6]

[b] Also called relative static permittivity.

the dissolution of salts in water. Compared to solvents with low dielectric constants, the high dielectric constant of water permits like-charged ions to approach each other more closely before repulsive coulombic forces become important. Consequently, it is a key property enabling water to be such a good solvent for salts.

In general, the unusual physical properties of liquid water reflect the fact that water molecules do not behave independently but are attracted to each other and to many solutes by moderately strong "hydrogen bonds." The bond strengths of the hydrogen bonds in ice and liquid water, ~21 kJ/mol,[6] are much weaker than the O–H bond of water 464 kJ/mol but stronger than London-van der Waals forces (<4 kJ/mol). In addition, the hydrogen bonds in water are stronger than those in NH_3 (13 kJ/mol) but much weaker than those in HF (155 kJ/mol). The differences in H-bonding strengths among these molecules is explained in terms of the electronegativity of the non-H atom. The importance of hydrogen bonding in promoting structure in ice and liquid water is enhanced by the fact that H_2O has two hydrogen atoms and two pairs of electrons on the oxygen, thus allowing each water molecule to have a potential of four hydrogen bonds. In contrast, each HF can have only three bonds (because each HF has only one hydrogen atom). The importance of hydrogen bonding in NH_3 is lessened by the fact that the N atom has only one pair of electrons available to form such a bond.

1.2.3 Basic structural features of water

Hydrogen bonding is a consequence of the basic molecular structure of water. The angle between the two O–H bonds (105°) in water is greater than the 90° expected for perpendicular *p*-orbitals (Figure 1.3). This is caused by repulsion between the hydrogen atoms and indicates that there is some hybridization of the *s* and *p* orbitals in the electron shell of the O atom. Oxygen's four remaining valence electrons occupy two orbitals opposite the hydrogen atoms in a distorted cube arrangement.

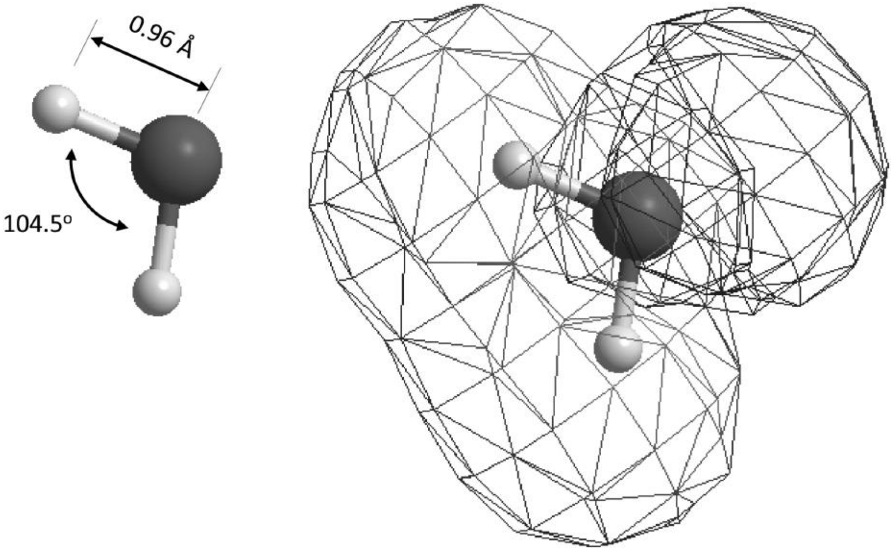

Figure 1.3 H–O bond angle and lengths in the H_2O molecule (left) lead to high polarity of the molecule with the hydrogen atoms (right: positive, red mesh) on the left side and the unshared electron pairs (right: negative, blue [darker gray] mesh) on the right side. (See color insert at end of book for a color version of this figure.)

This explains the molecule's large dipole moment. The electron pairs attract hydrogen atoms of adjacent water molecules and form hydrogen bonds with lengths of 1.74 angstroms (Å; measured in ice by X-ray diffraction), which leads to the three-dimensional structure found in ice and liquid water.

The structure of ice is known with great accuracy.[6] Ice-I_h, the form that occurs under environmental conditions, has a structure in which each water molecule is surrounded by the oxygen atoms of four adjacent water molecules in a tetrahedral arrangement (Figure 1.4). Extending this arrangement in three dimensions gives rise to a fairly open (i.e., low-density) crystalline structure of repeating hexagonal rings (hence the subscript h in I_h), each of which contains six water molecules. The density of ice calculated from measured bond lengths and the three-dimensional structure agree with the measured density of ice.

In contrast to the rigid crystalline structure of ice, gaseous water has no structure beyond that of the individual molecules themselves except for occasional, ephemeral dimers. In the gas phase, each water molecule behaves independently, and, when two water molecules collide, they do not stick together but simply bounce off each other and continue their independent existences.

The degree of structure in liquid water is intermediate between crystalline ice and unstructured gaseous water. Models of the structure of water must account for the properties in Table 1.1, which suggest that water is a structured medium. The model must also explain the variations in these properties with temperature,

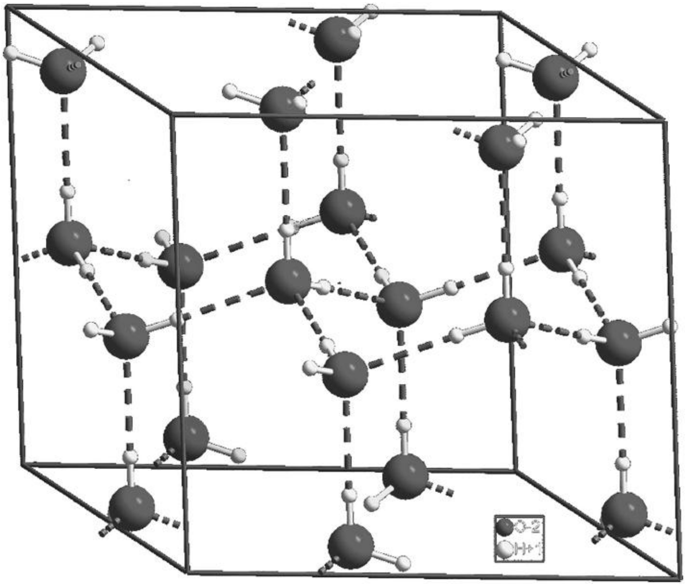

Figure 1.4 Tetrahedral arrangement of hydrogen-bonded water molecules in ice leads to an open hexagonal ring structure in crystalline ice-I_h. (See color insert at end of book for a color version of this figure.)

Source: Wikimedia Commons, file Hex ice.GIF (public domain).

the higher density of water than ice, and the density maximum at 4 °C. The heat of fusion of ice (330 J/g)—the energy required to convert ice at 0 °C to liquid water at 0 °C —suggests that only ~15% of the hydrogen bonds in ice are lost upon melting. In addition, studies using a variety of methods have reported that the average molecule in liquid water participates in 2.2–3.6 H-bonds. The structure of water has been a subject of inquiry for many decades. Proposed models include a "relic ice" model and another in which water molecules exist in a clathrate or cage-like structure.[6]

The so-called *flickering-cluster model* described by Frank and Wen[7] in 1957 was regarded for many decades as a reasonable if not exact description for the structure of liquid water. According to this model, water molecules form clusters of H-bonded molecules of indeterminate structure (Figure 1.5). The clusters have very short lives (~10^{-10} s) and are constantly forming and disintegrating with thermal fluctuations at the microscale. Although the lifetime of clusters may seem trivially short, it is about a thousand times longer than the time between molecular vibrations (~10^{-13} s), and clusters thus have a real, if very ephemeral, existence. Because of dipole effects on individual water molecules, the formation of hydrogen bonds is a cooperative phenomenon, and formation of one bond facilitates formation of the next. Consequently, rather large clusters are formed. The average cluster has 65 molecules at 0 °C but only 12 at 100 °C. Nonetheless, because the number of

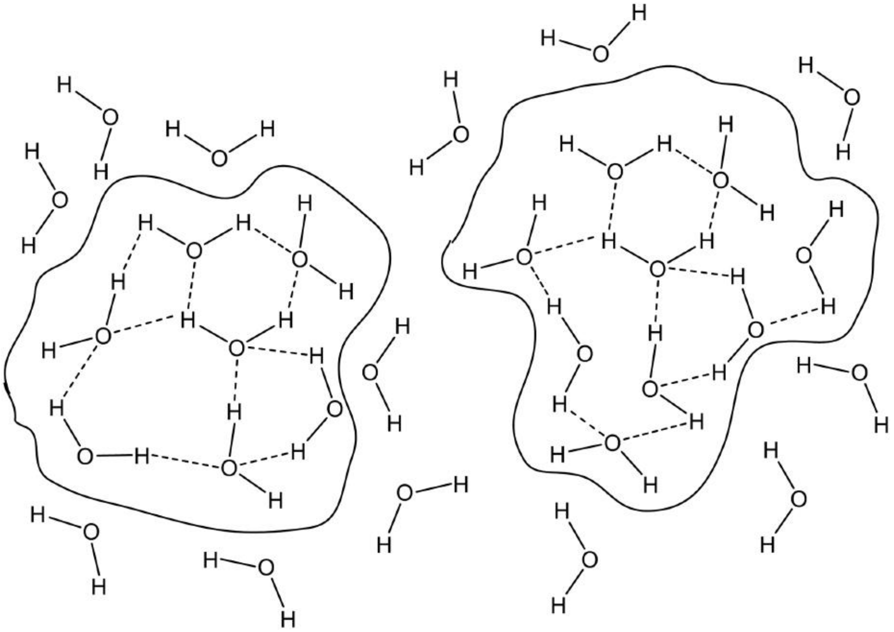

Figure 1.5 The flickering cluster model of liquid water.

clusters increases with temperature, the fraction of molecules in clusters decreases much more slowly (from ~75% at 0 °C to ~56% at 100 °C).[6] Unclustered water is considered to be "free."

1.2.4 Advanced topic: Dynamic structure of liquid water

Although the large-scale structure of water was not specified by the Frank-Wen model, the anomalous properties of water are thought to arise from a competition between the relatively bulky way of connecting molecules via the ideal tetrahedral angles arising from the molecular structure of water and more compact arrangements that have more bond strain and broken bonds. The alternatives provide a continuum of structural possibilities, but some can be ruled out by experimental evidence. For example, if the clusters were relic ice structures, the polygons formed by H-bonding would reflect the hexagonal structure of ice and contain an even number of molecules. Breaking a hydrogen bond in hexagonal ice-I_h yields a 10-membered ring; loss of a second H-bond yields a 14-membered ring. The frequency distribution of polygon sizes in water shows no evidence[8] for relic ice structures, however, and the most common polygons found in molecular dynamics simulations are five-member rings that are not possible products of ice-I_h.

Many refinements in our understanding of the complicated, dynamic structure of liquid water have been made over the past 20 years using molecular dynamics modeling[9] and sophisticated experimental methods, such as femtosecond infrared (IR) spectroscopy and X-ray emission and absorption, and Raman scattering spectroscopy.[5,10] Although the highly ephemeral nature of water's structure inherent in the Frank-Wen model still is valid, the term "flickering cluster" is no longer in vogue in chemical physics. In addition, molecular dynamics simulations indicate that the lifetime of individual water clusters is not a single value but varies over a wide range: ~10^{-13} to 10^{-9} s.[11]

Recent models suggest that at ambient temperatures most water molecules favor a closer packing than tetrahedral, with strongly distorted H-bonds and some tetrahedrally bonded water patches occurring as fluctuations. The fraction of molecules in tetrahedral structures and size of the tetrahedral patches decreases with increasing temperature. Recent studies also suggest less extensive H-bonding occurs in liquid water than previously thought. Earlier molecular dynamics simulations predicted ~3.3–3.6 H-bonds per water molecule, which agrees with estimates based on the low heat of fusion of ice. Recent studies suggest an average of 2.2 ± 0.5 H-bonds (one donating and one accepting) per water molecule at 25 °C and 2.1 ± 0.5 bonds at 90 °C. The smaller number of H-bonds was reconciled with the small heat of fusion of ice by quantum mechanical calculations, indicating that H-bonds in the proposed configuration are stronger than those in the tetrahedral ice configuration, with the net effect being only a small change in energy in spite of the larger number of broken H-bonds in liquid water. In spite of these advances, little is known about the structure of liquid water at the "nanoscale"—that is, the scale of hundreds to a few thousand water molecules. The last word has not yet been written on this topic.

1.2.5 Effects of solutes and surfaces on the structure of liquid water

Addition of solutes to pure water distorts its structure. The nature of the interactions between solutes and solvent water depends on whether the solute is a cation, anion, or nonelectrolyte. Solvation of cations results in relatively tight binding of water molecules in the "primary sphere of hydration" (Figure 1.6). Water molecules in the hydration sphere no longer act as solvent molecules, and tight binding results in a loss of volume compared to water in the bulk solvent; this phenomenon is known as ***electrostriction***. In some models, unstructured transition zones exist between hydrated ions and the clustered water in the rest of the solvent. In contrast to cations, anions are not solvated and instead occupy interstices or "holes" in the overall solvent structure. Changes in viscosity upon addition of salts to water are used to infer changes

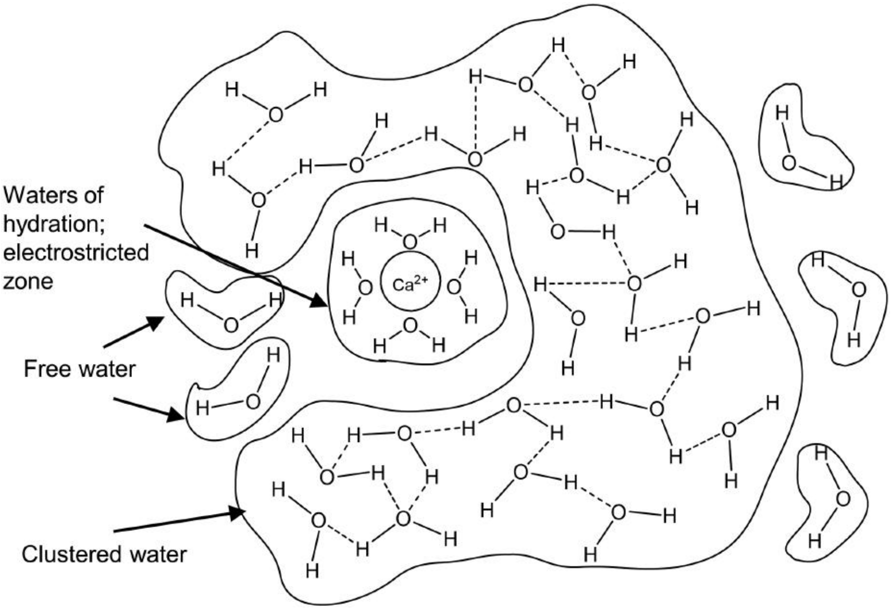

Figure 1.6 Cation hydration leads to an "electrostricted zone" surrounded by clustered and free water.

in the degree of solvent structure. Most salts are "structure-makers"—they increase viscosity—but a few salts (e.g., KCl and $CaSO_4$) are structure-breakers that decrease viscosity. The viscosity of pure water[12] (Figure 1.7) and aqueous salt solutions[13] generally decreases with increasing pressure, reaching a minimum value at pressures of ~400–800 kg/cm^2 (depending on salt content and temperature), and viscosity then increases if pressure continues to increase. Horne[6] explained this phenomenon as a result of a breakdown in the cluster structure of water as pressure increases, such that unclustered water molecules are arranged more compactly than those in the cluster state. Once the cluster structure is lost—at the viscosity minimum—further increases in pressure pack the water molecules more tightly, and viscosity increases because of increasing friction as the molecules move past each other.

Nonpolar solutes also reside in the interstices between water clusters (Figure 1.8), with water molecules surrounding the solute maintaining their H-bonds.[14] Overall, this promotes structure in liquid water and limits the freedom of the organic molecule as well.[15] Consequently, nonpolar solutes have high negative entropies of solution (see Chapter 3 for a description of the concept of entropy).

Water molecules at the air–water interface all are oriented with the oxygen atoms facing the interface with air and the hydrogen atoms facing the solution (Figure 1.9). This distorts the three-dimensional structure of clustered water in the bulk solution, and, as a result, the interfacial region has somewhat different physical properties from bulk water. The highly ordered arrangement of water molecules at the air–water interface also explains the high surface tension of water;

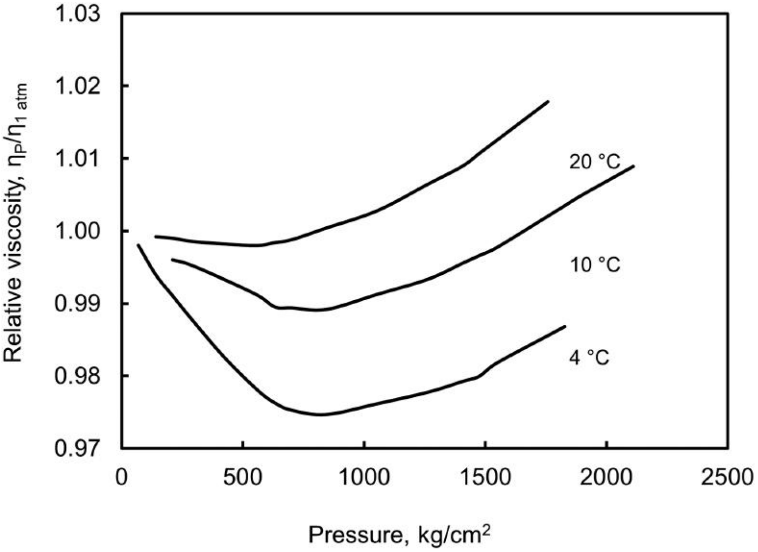

Figure 1.7 Relative viscosity of pure water versus pressure.
Drawn from data in Horne and Johnson.[12]

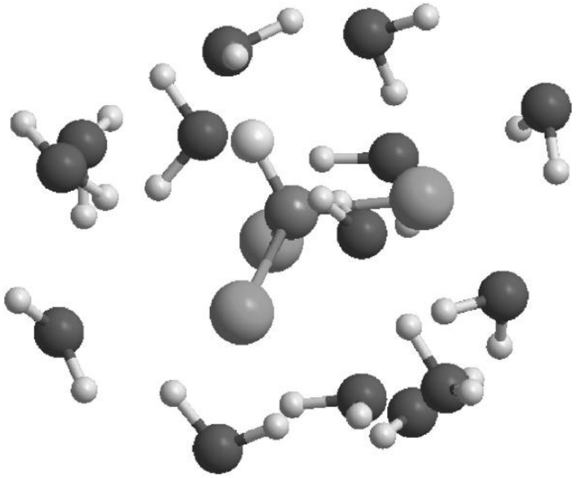

Figure 1.8 Structure of an organic (nonpolar) solute, chloroform, in liquid H_2O computed by energy minimization with MM2 force field in ChemBio3D Ultra 12.0. (See color insert at end of book for a color version of this figure.)

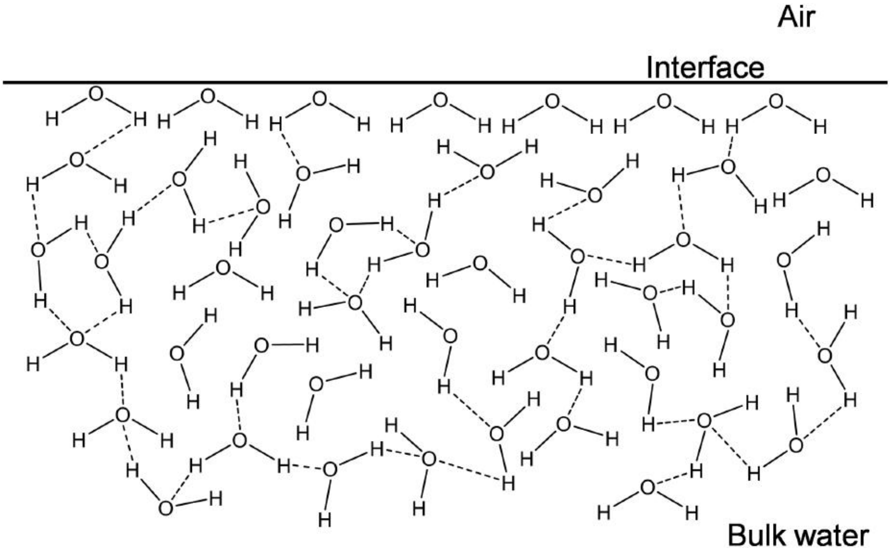

Figure 1.9 The structure of liquid water is perturbed near interfaces, as the O atoms orient toward the interface.

surface tension defines the energy needed to break the surface. An analogous situation occurs at solid–water interfaces. Water in the first few molecular layers from a solid–water interface has different physical properties (e.g., a low dielectric constant) than the bulk solution. This has important implications for solute behavior at interfaces, as discussed in Chapter 12.

1.3 Concentration units

1.3.1 Introduction

Various units are used to express concentrations of substances dissolved or suspended in natural waters. This reflects the diversity of substances in these systems, the wide range of concentrations at which they are found, and the multidisciplinary origins of water chemistry. An important first step in studying the chemistry of natural waters is to learn about the different concentration units and how they are related to each other.

In general, concentrations of substances in water are expressed in two principal ways: mass per unit volume of solution and mass per unit mass of water. Mass/volume units more accurately reflect the way we prepare and analyze solutions (i.e., based on a certain volume of solution rather than a certain weight), but they have the disadvantage of being slightly temperature dependent because the density (mass per volume) of water varies with temperature. In contrast, mass/mass concentrations are temperature invariant. For accurate work one should express mass/volume concentrations at a standard temperature, but for routine purposes, the differences caused by temperature are usually ignored. Volumetric glassware is calibrated to contain the nominal volume at 20 °C. In either mass/volume or mass/mass units, the mass of solutes and water may be expressed in common units (normally metric or SI units, although English units still are sometimes used in water and wastewater treatment chemistry) or chemical units, as described in the following sections.

1.3.2 Common units of concentration

Both mass per unit volume of solution (mass/volume) and mass per unit mass of solvent (mass/mass) are used widely, often interchangeably, to express concentrations of dissolved and suspended substances in water (Table 1.2). For major ions in freshwater, the most convenient mass/volume unit is mg/L because major ions generally occur in the range of a few to a few hundred mg/L. The corresponding mass/mass unit is parts per million (ppm; mg/kg). For practical purposes, the terms are interchangeable for freshwater because 1 mg = 10^{-3} g and 1 liter of water = 1 kg = 10^3 g (for solutions in other solvents, see Example 1.1). Thus, we can write

$$1 \text{ mg of substance in } 1 \text{ L of water} \times 1 \text{ L water}/1 \text{ kg water} = 1 \text{ mg substance}/1 \text{ kg water}$$

or

$$1 \text{ g substance}/10^6 \text{ g water} = 1 \text{ part per million.}$$

Table 1.2 Common concentration units used in water analysis

Mass/volume	*Symbol*	*Multiple of g*	*Equivalent mass/mass unit*[a]	*Substances for which units are used*
Gram/liter	g/L	1	Part per thousand, ppt (‰)	Major ions in brackish water and seawater
Milligram/L	mg/L	10^{-3}	Part per million, ppm	Major ions in freshwater
Microgram/L	µg/L	10^{-6}	Part per billion, ppb	Nutrients, minor and trace metals, many organic contaminants
Nanogram/L	ng/L	10^{-9}	Part per trillion[b]	Trace organic pollutants and some trace metals
Picogram/L	pg/L	10^{-12}	Not used	Ultratrace contaminants, e.g., methylmercury
Femtogram/L	fg/L	10^{-15}	Not used	Not commonly used

[a] This direct conversion is possible only because the density of water is 1, and so 1 L = 1 kg. This direct relationship does not hold for other solvents.

[b] To avoid ambiguity, the abbreviation "ppt" should not be used; ppt is used for parts per thousand by marine scientists.

This assumes that the dissolved substance does not affect the density of the water or contribute a significant amount to the total mass. If that were the case, the equivalency of mg/L and ppm no longer would hold. The salt content of seawater is sufficiently high (range of g/L) for there to be a slight difference between concentrations expressed in g/L of solution and concentrations expressed in parts per thousand, which are often written as the "per mil" symbol, ‰. The differences become even more pronounced in hypersaline waters (see Example 1.2). Many substances of interest in aquatic systems occur at concentrations much less than 1 mg/L, although the major ions in seawater and brines occur at much greater concentrations. Consequently, a series of concentration units are used, as shown in Table 1.2. Also, as analytical capabilities have enhanced our ability to detect and measure increasingly lower concentrations of inorganic and organic ions and compounds in water, use of mass/volume units with the prefixes micro-, nano-, and pico- have become increasingly common. Mass/mass units generally are not used for concentrations of trace and ultratrace contaminants. Because of ambiguities associated with such terms as trillion, quadrillion, and even billion, their use in expressing concentrations should be avoided.*

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* A "billion" in the United States is a thousand million (10^9), but a billion in Europe is a million million (10^{12}).

Example 1.1 Conversion between mass/volume and mass/mass units

You have 1 ppb standards of the pesticide alachlor in water and in hexane ($\rho = 0.66$ g/mL). What is concentration of each standard in μg/L?

Answer: For water, the answer is straightforward:

$$1\ \text{ppb} = \frac{1\ \mu\text{g alachor}}{\text{kg water}} \times \frac{1\ \text{kg water}}{1\ \text{L water}} = \frac{1\ \mu\text{g alachor}}{\text{L water}}.$$

For hexane, the density alters the answer:

$$1\ \text{ppb} = \frac{1\ \mu\text{g alachor}}{\text{kg hexane}} \times \frac{0.66\ \text{kg hexane}}{1\ \text{L hexane}} = \frac{0.66\ \mu\text{g alachor}}{\text{L hexane}}.$$

1.3.3 Chemical units

Use of chemical units to express solute concentrations is becoming more widespread in aquatic sciences, especially in limnology, oceanography, and geochemistry, but also in environmental engineering. The fundamental mass/volume unit is ***molarity*** (moles of solute per liter of solution), abbreviated mol/L or M (but never M/L):

$$\begin{aligned} \textit{Molarity}\ (\text{M}) &= \frac{\textit{grams of solute}}{\textit{gram formula wt.}\ (\text{g/mol}) \times \textit{vol. of solution}\ (\text{L})} \\ &= \frac{\textit{grams of solute}}{\textit{vol. of solution}\ (\text{L})} \times \frac{1}{\textit{gram formula wt.}\ (\text{g/mol})}. \end{aligned} \tag{1.1}$$

Major ions in fresh water generally are in the millimolar and submillimolar (mM) range; minor constituents and nutrients generally are in the micromolar (μM) range. Nutrients in water quality typically refer to N and P. N is usually in the range of the other major ions (mM range). P is much less (μM range).

A ***mole*** of a substance is simply a defined quantity or number of units of the substance, specifically 6.022×10^{23} units of the substance, based on the number of atoms in exactly 12 grams of carbon-12 (^{12}C). This number is given the symbol N_A and is called ***Avogadro's constant*** (see Box 1.1). The term "mole" is used mostly with reference to molecules (and ions), and a mole of a molecule is the mass, in grams, equal to the molecular weight of the substance (the sum of the ***atomic weights*** (at. wt.) of the

Box 1.1 Avogadro and his number

Avogadro's constant (or number), N_A, is arguably the most fundamental constant in chemistry. Although N_A is named for Amedeo Avogadro (1776–1856), an Italian scientist born in Turin, he actually did not measure its value or even define it precisely. Instead, Avogadro hypothesized in 1811 that equal volumes of all gases at the same temperature and pressure contain the same number of molecules. The Austrian physicist Johann Loschmidt is credited as the first person to evaluate the constant. Using the kinetic theory of gases, he computed the number of particles per unit volume of an ideal gas (the number of particles per cubic centimeter of gas at standard conditions), which is proportional to but not the same as N_A. The French Nobel Prize winner Jean Perrin was the first to propose naming the constant in honor of Avogadro, but it was not until the 1930s that use of the term became common. The precise value of N_A was uncertain until fairly recently. Values reported in the late nineteenth and early twentieth centuries ranged from Kelvin's estimate of 5×10^{23} to Perrin's estimate of $6.5–6.9 \times 10^{23}$. The currently accepted value is $6.02214179 \pm 0.00000030 \times 10^{23}$. In 1960, Avogadro's number was defined as the number of atoms in exactly 12 g of the ^{12}C isotope of carbon, and a mole was defined as one Avogadro number of atoms or molecules (or any other entity). The International System of Units (SI) adopted the mole as a fundamental unit in 1971 and reversed the above definitions: a mole was defined as the number of atoms in 12 g of ^{12}C, with a dimension of "amount of substance," and Avogadro's number became a physical constant with units of reciprocal moles (mol^{-1}).

atoms in the formula of the molecule). This quantity, the molecular or formula weight in grams, is called the ***gram-molecular weight*** or gram-formula weight of a compound. As indicated above, it contains 6.022×10^{23} molecules (or formulas) of the compound. The term "mole," however, is used to express this number of anything—atomic particles, grains of sand, stars in the sky. A mole of electrons is 6.022×10^{23} electrons, and this is known as a ***coulomb***. A mole of photons is called an ***einstein***. A gram-atomic weight of an element (its atomic weight in grams) contains 6.022×10^{23} atoms and is a mole of the element.

It is also useful to recall here that the atomic weight of any element approximately is equal to the sum of the number of protons plus the number of neutrons in the nucleus of atoms of the element. The number of protons defines the element's identity and is called the ***atomic number*** (at. no.). Fractional atomic weights for some elements result from the contributions of several ***isotopes*** (i.e., atoms having the same number of protons but different numbers of neutrons). For example, chlorine (at. no. 17) is a mixture primarily of two stable (i.e., not radioactive) isotopes: ~76% ^{35}Cl and ~24% ^{37}Cl; hence, its atomic weight is 35.45.

The standard mass/mass concentration unit in chemistry is ***molality*** (m):

$$molality\ (\mathrm{m}) = \frac{g\ of\ solute}{g\ formula\ wt. \times kg\ of\ solvent}. \tag{1.2}$$

This unit is used rarely in freshwater chemistry, but it is the unit of choice for precise measurements in marine chemistry and chemical thermodynamics. For dilute solutions, molarity and molality essentially are equivalent, but in solutions as concentrated as seawater (and higher), the equivalency breaks down (see Example 1.2). Molality is temperature invariant, but molarity is not.

Example 1.2 Molarity and molality of chloride in seawater

The salt content, or salinity (S), of "mean standard" seawater is 35.00‰ (i.e., 35.00 g/kg seawater). The chlorinity (chloride content) of seawater is related to salinity by the formula: S‰ = 1.80655 × Cl‰. What is the molality and molarity of chloride in average seawater at 25 °C?

Answer: For the mass basis, we find the $[Cl^-]$ by substitution into the relation

$$[Cl^-] = (35.00/1.80655 = 19.374‰, \text{ or } 19.374 \text{ g } Cl^-/\text{kg seawater},$$

The density of seawater at 25 °C is 1023.343 kg/m^3 or 1.023343 kg/L.[16] The volume occupied by 1 kg of seawater thus is

$$1.000 \text{ kg} \div 1.02334 \text{ kg/L} = 0.97719 \text{ L (or 977.19 mL)}.$$

For the volume basis, $[Cl^-]$ = 19.374 g/0.97719 L = 19.826 g/L, and the molar concentration is

$$[Cl^-] = \frac{19.826 \text{ g/L}}{35.45 \text{ g/mol}} = 0.5593 \text{ mol/L or } \mathbf{0.5593\ M}.$$

Because molality is moles of solute per kilogram of water, we need to find how many moles of H_2O are in 1 kg of seawater. From above, it is clear that 1 kg of seawater contains 35 g of salt. Thus, 1 kg of seawater contains 1,000 – 35 = 965 g H_2O. Because we calculated that 1 kg of seawater contains 19.374 g Cl^-, the molality of Cl^- thus is

$$[Cl^-] = \frac{19.374 \text{ g}}{0.965 \text{ kg } H_2O \ \times 35.45 \text{ g/mol}} = 0.5663 \text{ mol/kg } H_2O \text{ or } \mathbf{0.5663\ m}.$$

The difference between the molar and molal concentrations thus is 0.007, or about 1.2%.

It is simple to convert between common and chemical units of concentration: one multiplies chemical units (M, mol/L) by the gram formula weight of the substance (g/mol) to obtain common units (g/L) and divides common units by the formula weight to get chemical units (see Example 1.3). For example, sulfate ion (SO_4^{2-}) has a formula weight of 96 g/mol (or 96 mg/mmol) (S = 32; O = 16). A water containing 24 mg/L of sulfate thus has 24 mg/L divided by 96 mg/mmol = 0.25 mmol/L of sulfate. Usually, we say the sulfate concentration is 0.25 millimolar (mM).

Another mass/mass unit of concentration is the ***mole fraction***. For any substance X, the mole fraction of X in a system is simply the moles of X divided by the total moles of all substances in the system:

$$\text{mole fraction of } i = \frac{\text{moles of } i}{\sum_{i=1}^{n} \text{moles of } i}. \tag{1.3}$$

For example, for a 1.0 M solution of NaCl in water, the mole fraction of NaCl is ~1/(1 + 55.5), where 55.5 is the number of moles of water in a liter (1 L × 1,000 g/L × mol/18 g = 55.5 mol). Mole fraction units are not commonly used in inorganic solution chemistry but often are used in the solubility of organic substances in water and in thermodynamic treatment of solid phases associated with natural aquatic systems.

An additional mass/volume chemical unit of considerable importance is ***normality*** (N). This unit is similar to molarity except that the amount of the substance is based on its reactive capacity with regard to some type of chemical reaction. For acid-base reactions, the basis is the quantity of substance that can accept or donate one mole of hydrogen ions. For oxidation-reduction reactions, it is the amount that can accept or release one mole of electrons. This quantity of a substance is called an ***equivalent***, and a solution containing one equivalent (of any substance) per liter has a concentration of one normal (1 N):

$$\textit{Normality}\ (\mathrm{N}) = \frac{\textit{grams of solute}}{\textit{g eq. wt. of solute} \times \textit{volume of solution}\ (\mathrm{L})}. \tag{1.4}$$

The ***equivalent weight*** of a substance is equal to the molecular (or formula) weight divided by its reactive capacity, r_c:

$$\textit{Equivalent weight}\ (\mathrm{g}) = \frac{\textit{Molecular (formula) weight}\ (\mathrm{g})}{\textit{reactive capacity},\ \mathrm{r_c}}, \tag{1.5}$$

where r_c is the number of H^+ ions a substance can gain or lose in acid-base reactions or the number of electrons a substance can gain or lose in redox reactions. For electroneutrality (charge-balance) calculations, r_c is the absolute value of the charge on the ion. Because these quantities may differ for a given substance, equivalent weight is a potentially ambiguous term and the basis for calculation must be specified.

Normality is used in chemistry to express concentrations of titrants. For example, the concentration of an acid used to titrate a basic solution is expressed in terms of normality (N or eq/L). One special case often used in water chemistry, ***alkalinity***, defined as the sum of the "titratable bases in water," may be expressed in milliequivalents per liter (meq/L) or microequivalents per liter (μeq/L), if levels are low.

Example 1.3 Interconversion among common and chemical concentration units

The major ion concentrations of "global-average" river water[17] are reported in mg/L in the first row of numbers below, and the atomic or formula weights of the ions (in grams per mole (g/mol) or milligrams per millimole (mg/mmol)) are given in the next row. Convert the mass concentrations to molar and (charge) equivalent concentrations.

Ion	Na^+	K^+	Mg^{2+}	Ca^{2+}	HCO_3^-	SO_4^{2-}	Cl^-
Concentration (mg/L)	9.0	1.4	5.0	21	68	20	8
Atomic or formula weight	22.99	39.10	24.30	40.08	61.02	96.07	35.45

Answer: To convert from mg/L to mol/L, we divide the concentrations in mg/L by the atomic or formula weights (g/mol or mg/mmol) to get mmol/L. For example, for Mg^{2+},

1. 5.0 mg/L ÷ 24.3 mg/mmol = 0.206 mmol/L or 0.206 mM.

Results for all the major ions are shown in the first row of numbers below. Similarly, to convert the concentrations to a charge equivalent basis (meq/L), we divide the mass concentration by the equivalent weight, which for each ion is its atomic (or formula) weight divided by the absolute value of the charge on each ion. Again, for Mg^{2+}, we have

2. $5.0\ \text{mg/L} \div \dfrac{24.3\ \text{mg/mmole}}{2\ \text{meq/mmole}} = 5.0\ \text{mg/L} \div 12.15\ \text{mg/meq} = 0.412\ \text{meq/L}.$

Results for all ions are given in the second row of numbers below.

Ion	Na^+	K^+	Mg^{2+}	Ca^{2+}	HCO_3^-	SO_4^{2-}	Cl^-
mmol/L	0.391	0.0358	0.206	0.524	1.114	0.208	0.226
meq/L	0.391	0.0358	0.412	1.048	1.114	0.416	0.226

According to the ***electroneutrality constraint***, all waters are electrically neutral. That is, the sum of the concentrations of the cations must be equal to the sum of the anion concentrations when both are expressed on a charge equivalents basis. Application of this concept to the results in Example 1.3 yields the following:

Sum of cation concentrations:

$$\sum \text{Cations} = 0.391 + 0.0358 + 0.412 + 1.048 = 1.877 \text{ meq/L}$$

Sum of anion concentrations:

$$\sum \text{Anions} = 1.114 + 0.416 + 0.226 = 1.756 \text{ meq/L}$$

The cation equivalents thus exceed the anion equivalents by 1.877 – 1.756 = 0.121 meq/L, or ~6% of the total equivalent concentration of cations. This magnitude of difference usually is considered acceptable in routine water analyses and probably can be accounted for by analytical errors in the measured values of the cations and anions. Other possible explanations are that (1) the analysis did not include all the major inorganic ions, or (2) unmeasured charged moieties, such as carboxylate groups on natural organic matter, account for the anion deficit. The former explanation is unlikely; in most, but not all cases, the seven ions listed in the table account for the vast majority of the inorganic ions in natural waters.

Example 1.4 Calculations using chemical concentration units

A. Preparation of acid reagents

1. Concentrated sulfuric acid has a density of 1.83 g/mL. If the concentrated acid is 97% H_2SO_4, what is its molarity and normality?

Answer: The formula weight of H_2SO_4 is 98 (2 + 32 + 4 × 16). One liter of acid contains

$$0.97 \times 1830 \text{ g/L} = 1775 \text{ g/L}$$

and

$$\frac{1775 \text{ g/L}}{98 \text{ g/mol}} = 18.1 \text{ mol/L or } \sim \mathbf{18\ M}.$$

Because each mole of H_2SO_4 can release two moles of H^+, the normality of the acid is twice its molarity. Thus concentrated H_2SO_4 is **36 N**.

2. If 2.0 mL of concentrated H_2SO_4 is diluted with distilled water to 250 mL in a volumetric flask, what is the resulting concentration in units of molarity and normality?

Answer: The 2.0 mL of concentrated H_2SO_4 contains

$$2 \text{ mL} \times 0.97 \times 1.83 \text{ g/mL} \div 98 \text{ g/mol} = 0.0362 \text{ moles.}$$

The solution thus is 0.0362 moles/250 mL × 1,000 mL/L = **0.145 M** and **0.290 N**.

3. What is the volume of the solution in question 2 that should be diluted with distilled water to make a 0.025 N solution of sulfuric acid?

Answer: For this problem we can use the ***fundamental dilution formula***:

$V_1N_1 = V_2N_2$, where V_1 and N_1 are the volume and normality of the initial (or "stock") solution and V_2 and N_2 are the volume and normality of the diluted solution. Thus,

$$(0.29 \text{ N})V_1 = (0.025 \text{ N})(1000 \text{ mL}),$$

or

$$V_1 = 86.2 \text{ mL.}$$

Note: Reagent grade concentrated sulfuric acid is not pure acid and contains 96–98% H_2SO_4. A solution containing an exact concentration of acid thus cannot be prepared by simple dilution. It is necessary to determine the exact normality by ***titrating*** (i.e., reacting) the acid with a basic solution whose normality is known exactly. This process is called ***standardization***. Because of this, one would not bother to measure the stock solution (V_1) to three-place accuracy; instead, one would measure out ~85 mL by pipette (or graduated cylinder) and separately determine the exact normality of the diluted acid by titration (see Chapter 7).

B. Preparation of standard solutions of oxidizing agents

Potassium dichromate is a strong oxidizing agent used in the analysis of "chemical oxygen demand" (COD), a method used, primarily in the past, to estimate the total organic matter in wastewater samples.[18] In the process of oxidizing the organic matter, dichromate ion, $Cr_2O_7^{2-}$, is reduced to two chromic ions, Cr^{3+}, which involves transfer of six electrons to dichromate:

4. Exactly how many grams of reagent-grade $K_2Cr_2O_7$ must be weighed out and added to water to prepare a 1.0 L of a solution that is exactly 0.25 N $K_2Cr_2O_7$, and what is its molarity?

Answer: The formula weight of $K_2Cr_2O_7$ is $(2 \times 39.1) + (2 \times 52) + (7 \times 16) = 294.2$. Its equivalent weight thus is $294.2 \div 6 = 49.033$ g. To make a 1.0 L solution containing 0.250 eq/L of dichromate, we need to weigh out $0.250 \text{ eq} \times 49.033 \text{ g/eq} =$ **12.258 g**. The molarity of the solution is $0.25 \text{ eq/L} \div 6 \text{ eq/mol} =$ **0.04167 mol/L**.

1.3.4 Other concentration units used in environmental chemistry

The units described in the previous sections are the preferred ways to express concentrations of chemicals in water and generally are the most commonly encountered units today. A few other units, however, are used in environmental engineering and water chemistry. We describe and define these units below.

mg/L as calcium carbonate (***$CaCO_3$***). This unit was used in natural water chemistry to express concentrations of alkalinity, hardness, and ions related to these terms. Although now used only rarely in scientific literature, it still is in wide use within the water treatment industry. ***Alkalinity*** is defined as the sum of the concentration of bases titratable with strong acid and is closely related to the bicarbonate concentration in natural waters (see Chapter 8). ***Hardness*** is the sum of the divalent cations (generally Ca^{2+} and Mg^{2+}, but occasionally Fe^{2+} and Mn^{2+}), which cause problems with soap precipitation and buildup of $CaCO_3$ scale in pipes (see Chapter 10).

The unit ***mg/L as $CaCO_3$*** is based on the fact that $CaCO_3$ has a formula weight of 100 $(40 + 12 + (3 \times 16))$ and an equivalent weight of 50, in terms of its reacting capacity with H^+ and the charge equivalents of its constituent ions. Thus, 50 g of $CaCO_3$ yields 0.5 moles of carbonate and requires 1.0 moles of H^+ to be titrated to CO_2 (see Chapter 8); 50 g of $CaCO_3$ also yields one equivalent (or one mole) of cationic and anionic charges. The unit expresses concentrations of Ca^{2+}, Mg^{2+}, hardness, or alkalinity as if the constituents all have an equivalent weight of 50. As a "pseudo-equivalents per liter" or "pseudo-normal" unit, it is convenient in that concentrations expressed this way can be added in a meaningful way. For example, $[Ca^{2+}] + [Mg^{2+}]$ (each expressed in mg/L as $CaCO_3$) ≈ total hardness (in mg/L as $CaCO_3$). In contrast, $[Ca^{2+}] + [Mg^{2+}]$ (each expressed in mg/L) is not chemically meaningful.

To convert from the preferred chemical units of alkalinity (meq/L) to mg/L as $CaCO_3$, we multiply the former by the equivalent weight of $CaCO_3$:

$$\begin{aligned}\text{Alkalinity (mg / L as CaCO}_3) &= \text{Alkalinity (meq / L)} \\ &\quad \times (50 \text{ mg CaCO}_3 / \text{meq of CaCO}_3) \qquad (1.5)\end{aligned}$$

or

$$\text{Alkalinity (mg/L as CaCO}_3) = \text{Alkalinity } (\mu\text{eq/L}) \times (0.050 \text{ mg}/\mu\text{eq of CaCO}_3). \tag{1.6}$$

Conversely,

$$\text{Alkalinity}\left(\mu\text{eq/L}\right) = 20 \times \text{Alkalinity}\left(\text{mg / L as CaCO}_3\right). \tag{1.7}$$

To convert between units of mg/L for Ca^{2+} and Mg^{2+} and units of mg/L as $CaCO_3$, we divide the former by the equivalent weight of the atom (to obtain the number of equivalents of Ca or Mg) and multiply by the equivalent weight of $CaCO_3$:

$$\mathbf{Ca^{2+}}(\text{mg/L as CaCO}_3) = \frac{\text{mg/L as Ca}}{20 \text{ mg/meq of Ca}} \times 50 \text{ mg/meq of CaCO}_3 \tag{1.8}$$

$$\mathbf{Mg^{2+}}(\text{mg/L as CaCO}_3) = \frac{\text{mg/L as Mg}}{12.15 \text{ mg/meq of Mg}} \times 50 \text{ mg/meq of CaCO}_3 \tag{1.9}$$

Example 1.5 Conversion of alkalinity and hardness units

1. The sensitivity of surface waters toward acidification from atmospheric acid deposition is inversely related to the water body's alkalinity (also called acid-neutralizing capacity, ANC). Water with an alkalinity less than 200 μeq/L is considered "acid sensitive." What is this alkalinity value in mg/L as $CaCO_3$?

Answer:
200 μeq/L × 50 mg $CaCO_3$/meq × 10^{-3} meq/μeq = **10 mg/L as $CaCO_3$.**

2. Lake Okeechobee in south Florida is a large, shallow, hardwater lake with high concentrations of Ca^{2+} and Mg^{2+}, typical values of which in the lake are $[Ca^{2+}]$ = 45 mg/L and $[Mg^{2+}]$ = 18 mg/L. Convert these values to concentrations in mg/L as $CaCO_3$ and evaluate the total hardness of the lake.

Answer:
$[Ca^{2+}]$ = 45 mg/L ÷ 40 mg/mmol = 1.125 mmol/L of Ca^{2+}
1.125 mmol/L × 2 meq/mmol = 2.25 meq/L of Ca^{2+}
$[Ca^{2+}]$ = 2.25 meq/L × 50 mg/meq $CaCO_3$ = **112.5 mg/L as $CaCO_3$**.
$[Mg^{2+}]$ = 18 mg/L ÷ 24.3 mg/mmol = 0.74 mmol/L of Mg^{2+}
0.74 mmol/L × 2 meq/mmol = 1.48 meq/L of Mg^{2+}

$[\mathrm{Mg}^{2+}] = 1.48$ meq/L × 50 mg/meq $\mathrm{CaCO_3}$ = **74 mg/L as $\mathrm{CaCO_3}$**
Total hardness = $[\mathrm{Ca}^{2+}] + [\mathrm{Mg}^{2+}]$ (both in mg/L as $\mathrm{CaCO_3}$) = 112.5 + 74
= **186.5 mg/L as $\mathrm{CaCO_3}$**

mg/L as N or P (or mg N/L; mg P/L). These units are used in water quality and limnological studies and express concentrations of various chemical forms of nitrogen or phosphorus in terms of the amount of elemental N or P present. This convention is useful for several reasons. From an algal nutritional point of view, one is not interested in the concentration of nitrate or ammonium ion, for example, but in the amount of N in the nitrate or ammonium, the actual part of the ion needed by organisms. Also, because these are pseudo-molar units, we can add concentrations of various species if they are expressed in terms of N (or P), but we cannot meaningfully add concentrations of ammonium and nitrate when they are expressed in mg/L of the ions themselves.

To convert from mg/L of an N-containing species to mg/L as N, one divides the former by the formula weight of the species and multiplies the result by 14, the atomic weight of nitrogen. For nitrate,

$$\mathbf{NO_3^-}\ \text{(mg/L as N)} = \frac{\text{mg/L of } \mathrm{NO_3^-}}{62\ \text{mg/mmol}} \times (14\ \text{mg/mg-atom}) \times (1\ \text{atom N/molecule of } \mathrm{NO_3^-}). \qquad (1.10)$$

For ammonium,

$$\mathbf{NH_4^+}\ \text{(mg/L as N)} = \frac{\text{mg / L of } \mathrm{NH_4^+}}{18\ \text{mg / mmol}} \times (14\ \text{mg/mg-atom}) \times (1\ \text{atom N/molecule of } \mathrm{NH_4^+}). \qquad (1.11)$$

Similarly, for phosphate,*

$$\mathbf{PO_4^{3-}}\ \text{(mg/L as P)} = \frac{\text{mg/L of } \mathrm{PO_4^{3-}}}{95\ \text{mg/mmol}} \times (31\ \text{mg/mg-atom}) \times (1\ \text{atom P/molecule of } \mathrm{PO_4^{3-}}). \qquad (1.12)$$

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* The actual form (degree of protonation) of inorganic phosphate in water depends on pH. $\mathrm{PO_4^{3-}}$ is important only at very high pH values. Consequently, phosphate usually is reported as "dissolved inorganic P" or "dissolved reactive P" (DRP), reflecting the operational nature of the analytical results (see Chapter 19).