

Study and Interpretation of the Chemical Characteristics of Natural Water

Third Edition

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PREFACE

The first and second editions of this book, published in 1959 and 1970, respectively, have had a total of some 10 printings and a worldwide circulation. If a book of this kind is to continue to be useful in a rapidly changing and developing scientific field, it must be reevaluated and updated periodically. This revision retains the basic organizational pattern of the earlier editions and is intended to serve the same general purposes.

The book is intended to serve as an introduction to the topics of low-temperature aqueous geochemistry and of applied and theoretical water chemistry, and as an aid to hydrologists and hydrogeologists who may need to evaluate water quality and incorporate water chemistry into their investigations of water resources. The needs of the latter group were uppermost in my mind when the first edition was being planned and written, but the book had an immediate broader appeal. Those who might use the book as an introduction to water geochemistry probably will continue to be the larger group. To meet their needs, I have tried to reach a compromise in the level of approach, so that the topics will be intelligible to readers who have a minimal background in chemistry and will still have some value for specialists in this or related scientific disciplines. Those who seek to study some aspect of the subject in greater depth can make a start in that direction by examining the books and journal articles that are listed as references.

The subject of water chemistry hardly qualified as a scientific discipline at the time the first edition of this book was prepared. In the ensuing years, water chemistry as it relates to geochemistry, to environmental sciences, and to water and waste treatment has developed a substantial theoretical and practical base, although it is still something of an adolescent in comparison with some other fields of applied chemistry.

The term "natural water" used in the title and elsewhere in this book is intended to mean water that occurs in a "real world" environment, as in a lake, a stream, or a ground-water body, as opposed to synthetic solutions prepared in a laboratory. Natural waters need not be pristine—unaffected by the works of man. Indeed, probably few are completely free from such influences.

Acknowledgments. This book has benefited from many comments and suggestions I received from readers of the earlier editions. I am indebted particularly to my colleagues in the U.S. Geological Survey who have reviewed, and suggested improvements in, this third edition when it was in the manuscript stage. These were W. L. Bradford, J. A. Davis, J. H. Feth, Y. K. Kharaka, D. C. Thorstenson, and A. H. Welch.

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Study and Interpretation of the Chemical Characteristics of Natural Water

By John D. Hem

Abstract

The chemical composition of natural water is derived from many different sources of solutes, including gases and aerosols from the atmosphere, weathering and erosion of rocks and soil, solution or precipitation reactions occurring below the land surface, and cultural effects resulting from human activities. Broad interrelationships among these processes and their effects can be discerned by application of principles of chemical thermodynamics. Some of the processes of solution or precipitation of minerals can be closely evaluated by means of principles of chemical equilibrium, including the law of mass action and the Nernst equation. Other processes are irreversible and require consideration of reaction mechanisms and rates. The chemical composition of the crustal rocks of the Earth and the composition of the ocean and the atmosphere are significant in evaluating sources of solutes in natural freshwater.

The ways in which solutes are taken up or precipitated and the amounts present in solution are influenced by many environmental factors, especially climate, structure and position of rock strata, and biochemical effects associated with life cycles of plants and animals, both microscopic and macroscopic. Taken together and in application with the further influence of the general circulation of all water in the hydrologic cycle, the chemical principles and environmental factors form a basis for the developing science of natural-water chemistry.

Fundamental data used in the determination of water quality are obtained by the chemical analysis of water samples in the laboratory or onsite sensing of chemical properties in the field. Sampling is complicated by changes in the composition of moving water and by the effects of particulate suspended material. Some constituents are unstable and require onsite determination or sample preservation. Most of the constituents determined are reported in gravimetric units, usually milligrams per liter or milliequivalents per liter.

More than 60 constituents and properties are included in water analyses frequently enough to provide a basis for consideration of the sources from which each is generally derived, the most probable forms of elements and ions in solution, solubility controls, expected concentration ranges, and other chemical factors. Mechanisms that control concentrations of elements commonly present in amounts less than a few tens of micrograms per liter cannot always be

easily ascertained, but present information suggests that many are controlled by solubility of their hydroxides or carbonates or by sorption on solid particles. Many dissolved organic compounds can now be specifically determined.

Chemical analyses may be grouped and statistically evaluated by means, medians, frequency distributions, or ion correlations to summarize large volumes of data. Graphing of analyses or of groups of analyses aids in showing chemical relationships among water, probable sources of solutes, areal water-quality regimen, temporal and spatial variation, and water-resources evaluation. Graphs may show water type based on chemical composition, relationships among ions, or groups of ions in individual waters or many waters considered simultaneously. The relationships of water quality to hydrogeologic characteristics, such as stream discharge rate or ground-water flow patterns, can be shown by mathematical equations, graphs, and maps.

About 80 water analyses selected from the literature are tabulated to illustrate the relationships described, and some of these, along with many others that are not tabulated, are also used in demonstrating graphing and mapping techniques.

Relationships of water composition to source rock type are illustrated by graphs of some of the tabulated analyses. Human activities may modify water composition extensively through direct effects of pollution and indirect results of water development, such as intrusion of seawater in ground-water aquifers.

Water-quality standards for domestic, agricultural, and industrial use have been published by various agencies. Irrigation project requirements for water quality are particularly intricate.

Fundamental knowledge of processes that control natural-water composition is required for rational management of water quality.

INTRODUCTION

Purpose and Scope

Definitions of the science of hydrology that were in vogue a generation or so ago tended to focus on the physical behavior of water substance, H_2O . An implication that dissolved impurities were not an appropriate

concern in hydrology was sometimes present—perhaps unintentionally. However, the study of water containing rather large amounts of dissolved matter—particularly study of the ocean, where most of the Earth's supply of water resides—was generally considered more appropriate for other disciplines.

Descriptive geochemistry has defined the hydrosphere as including all liquid water, ice, and water vapor at or near the Earth's surface and has cataloged the impurities. But most geochemists were more interested in solid rocks and their alteration products. So the topic of aqueous geochemistry, at least as applied to dilute, low-temperature conditions, for a long time was something of a scientific orphan. This situation has changed drastically, however, beginning in the 1950's and continuing in following years. There is now extensive interest and activity in this field by scientists in academic, industrial, and governmental employment.

The scope of the discussions of water chemistry in this book is not limited to any particular solute-concentration range. Most of the available information on dissolved impurities in water, however, relates to use or potential use of water as a resource. Hence, some sections of this book are concerned with relatively dilute solutions.

Although a natural water whose quality is suitable for drinking is a more dilute solution than most specialists in solution chemistry are accustomed to working with, the general principles of solution chemistry are readily applicable. These principles are the framework on which the material presented here is based. Ways in which theoretical considerations can be used in practical study of natural-water chemistry are demonstrated by citing and discussing actual examples wherever possible.

Water chemistry can be applied in various ways in planning water use and treatment. The study of natural-water chemistry also involves other disciplines, including geology, hydrology, and biological sciences. This book is intended to provide an introduction to the field of natural-water chemistry, with particular emphasis on inorganic geochemistry, that will be intelligible to scientists and engineers whose interests may lie within some part of this area and also to technically trained individuals whose interests may lie in related fields. Some knowledge of chemistry is assumed, and applications of chemical principles that are discussed require general familiarity with the subject. For the most part, however, the treatment is not as chemically demanding as would be appropriate if the book were intended for the use of chemists alone.

As the chemical composition of natural water is controlled by many interrelated processes, it follows that some understanding of these processes is needed before one can speak or act intelligently toward the aim of water-quality control and improvement. It is hoped that this book will help in providing impetus toward the needed understanding or will suggest ways by which the

present understanding of this subject may be improved. One of the principal objectives of this book, and its predecessors, is to suggest how relatively simple unifying theoretical concepts might be applied in pursuit of an understanding of the detailed observations and measurements by which the quality of water supplies and resources is evaluated.

Arrangement of Topics

The arrangement of topics in this book is similar to that used in the earlier editions. In the introduction there are some basic data from the literature on the composition of the lithosphere, the hydrosphere, and the atmosphere. The chemical principles and processes that control natural-water composition are then enumerated and described, and mathematical evaluation procedures are stated and demonstrated as appropriate.

Natural-water composition is evaluated by chemical analyses. This discussion is not concerned with analytical procedures, which are amply described elsewhere. A major part of the book, however, is concerned with the completed analysis. To this end, the subjects of sampling, units, and terminology are considered. The constituents and properties reported in the analyses are discussed individually to show what is known or can reasonably be assumed about the forms of various dissolved substances that are most likely to occur, the factors influencing solubility of various ions, and the probable sources of certain solutes. In these discussions, actual chemical analyses of natural waters are used extensively as illustrative material.

To provide examples from real systems, about 80 chemical analyses from published sources or from unpublished data on file at the U.S. Geological Survey are included in tables in this book. For the most part these are the same analyses used in the first edition of the book, which was published in 1959. Although most of these analyses were made many years ago, the accuracy standards for major constituents applied to them are equivalent to current standards. The major shortcoming of these analyses relates to pH determinations. These were mostly done in the laboratory after the water samples had been stored, and some may not represent the true pH of the water at the time the samples were collected. Samples most likely to change in pH before analysis are those from which ferric hydroxide or calcium carbonate has precipitated. Analyses showing obvious effects of this kind were screened out when selecting data to be used in the tables, except where the effects of chemical precipitation were specifically being demonstrated. Although uncertainty about some of the pH values lessens the usefulness of the tabulated analyses for chemical equilibrium modeling, it is worth noting that no analyses should be used in such models without assurance that

proper field techniques were used in sampling, regardless of the source of the data.

The treatment of chemical topics here is more extensive than in the first edition of this book, owing in part to the large amount of research in natural-water chemistry that has been done in recent years. Although the discussion of each constituent is necessarily short, references to current research papers are given wherever possible. This section of the book will require updating as additional research is done in this very active field.

The concluding sections of the book are intended to provide aids for water-analysis interpretation by hydrologists, geologists, or others who are less interested in strictly chemical aspects of the subject. Included are techniques for analysis classification, graphing, simple statistical correlations, and data extrapolation. Special attention also is given to the correlation of water composition with geology. Quantitative modeling of water quality has been an active field of study in recent years, and it is discussed more extensively in this volume than it was in earlier editions. The relationship of water quality to water use and man's influence on water quality, are briefly summarized.

The bibliography lists publications that were cited in the text as sources of information and that may be consulted for more detailed treatment of topics discussed briefly in the text. Although these cited papers should be useful as an introduction to topics of special interest, the reference list is not intended to serve as a complete review of the literature. The large and growing volume of publications that now exists would make such a review an enormous task, and the result would have a short useful life, owing to rapid obsolescence.

Publications of the U.S. Geological Survey have been cited extensively, in part because they were readily available, but also because they constitute a unique source of basic data and examples of data interpretation. Most of the other papers cited were written in the English language, or have been translated into English. This does not imply that important work in this field is limited to English-speaking countries. The general area of natural-water chemistry is being actively studied throughout the world, and important contributions have been made in many countries.

PROPERTIES AND STRUCTURE OF WATER

Water is a chemical compound of hydrogen and oxygen. In the gaseous state, at least, it has the molecular formula H_2O . Although the same formula also represents the compositions of liquid water and ice, the molecules in these two forms are associated structurally, and it is a good idea to think of the condensed phases in terms of these associations rather than as simple aggregates of

molecules. Because three isotopes of hydrogen and three of oxygen exist in nature, 18 varieties of water molecules are possible. Consideration will be given to some hydrologic applications of the isotopic composition later in this book.

The physical properties of water are unique in a number of respects, and these departures from what might be considered normal for such a compound are of great importance, with respect both to the development and continued existence of life forms and to the shape and composition of the Earth's surface. The boiling and freezing points of water are far higher than would be expected for a compound having such a low molecular weight, and the surface tension and dielectric constant of liquid water are also much greater than might be expected. When water freezes, its density decreases; in fact, the maximum density of water at 1 atmosphere pressure occurs near $4^\circ C$. Although this type of behavior is not unique in liquid-solid transitions, it is an attribute of water that is most fortunate for all life forms.

The physical properties of liquid water are best understood by considering the structure of the H_2O molecule. The two chemical bonds formed between the O^{2-} ion and the H^+ ions are at an angle of 105° to each other. As a result, the H^+ ions are on the same side of the molecule, giving it a dipolar character. Besides the simple electrostatic effect, attributable to the dipolar property, the attached hydrogen ions retain a capacity for specific interaction with electronegative ions and between water molecules. This effect, known as hydrogen bonding, is present in both liquid and solid forms of water and results in the well-defined crystal structure of ice. In liquid water there is much disorder, but the attractive forces between molecules are strongly evident. The energy required to separate the molecules is indicated by the high heat of vaporization of water, and in another way by its high surface tension. Liquid water has some of the properties of a polymer.

The presence of dissolved ions in water changes some of its physical properties, notably its ability to conduct electricity. The dipolar nature of the water molecule, however, is an important factor in the behavior of the solute ions as well as the solvent. The details of the structure of liquid water are still far from being fully understood. The present state of knowledge has been summarized in a recent review by Stillinger (1980). Earlier reviews that are still of interest were published by Drost-Hansen (1967) for pure water and by Kay (1968) for water containing dissolved ions.

The dipolar water molecules are strongly attracted to most mineral surfaces, form sheaths arranged in an orderly pattern around many forms of dissolved ions, and insulate the electrical charges on the ions from other charged species. The effectiveness of water as a solvent is related to such activities. Its effectiveness in weathering

rocks is also increased by the ability of this cohesive liquid to wet mineral surfaces and penetrate into small openings.

COMPOSITION OF THE EARTH'S CRUST

The relative abundance of elements in the crustal material of the Earth has been a subject of much interest to geochemists for many years. Although the subject of natural-water chemistry is only indirectly concerned with these averages, a knowledge of rock composition is essential to understanding the chemical composition of natural water, and it is therefore desirable to discuss the subject briefly.

The Earth is generally considered to be made up of an iron-rich core surrounded by a thick mantle made up of magnesium- and iron-rich silicates and a thin outer crust made up of rather extensively reworked silicates and other minerals. The outer crust, where it is exposed above the level of the oceans, exerts a direct influence on the composition of natural terrestrial water. Although it has been studied more extensively than less accessible parts, the composition of most of the outer crust still must be estimated by extrapolation. The bottom of the crust is considered to be at the Mohorovičić discontinuity, which occurs at a depth of 30-50 km beneath most of the continental areas. The influence of material more than a few kilometers below the surface on the composition of water circulating in the hydrologic cycle is slight.

Estimates of average composition of the Earth's crust by Clarke (1924b) and by Clarke and Washington (1924) are still extensively quoted, although more recent estimates for minor constituents have the advantage of many more analyses and better values. Among the better known more recent estimates and compilations are those of Fleischer (1953, 1954), Turekian and Wedepohl (1961), Taylor (1964), Parker (1967), and Wedepohl (1969). Data on concentrations of some of the rarer elements still are incomplete, however, and some further revisions of the abundance estimates can be expected as better analytical values become available. The amount of extrapolation and inference required to extend the analyses to large volumes of rock that cannot be sampled is obvious.

Combinations of data from earlier compilations and averages for individual elements published in current research papers commonly are used by authors of general reference works. In this vein, data assembled in table 1 were taken principally from a compilation by Horn and Adams (1966), which in turn is a synthesis, by electronic computer, of estimates published by others from Clarke's time to the date of their study. Table 1 gives values for the 65 elements covered by Horn and Adams and for two others omitted by them that are of particular interest in natural-water chemistry—nitrogen and carbon. Data on which these two values are based were taken from tabula-

tions by Parker (1967). Oxygen is the most abundant of all the elements in the crustal rocks; according to Goldschmidt (1954, p. 512), it constitutes 466,000 parts per million, or 46.6 percent of the weight of the lithosphere. Oxygen is not included in table 1. Other omissions include the elements produced in the radioactive decay of uranium and thorium, the elements produced artificially in nuclear reactions, the noble gases, hydrogen, and a few elements for which data are inadequate to make any estimates of abundance. The values of Horn and Adams were arbitrarily carried to three significant figures by the computer program from which they were produced. In preparing table 1, all concentrations reported below 100 parts per million were rounded to two significant figures. Because of the uncertainties in the estimates, they can hardly be expected to be accurate enough for many elements to justify two significant figures, and the reader should not accept the accuracy the values seem to imply; for many of the less common elements, especially when located in sedimentary rocks, the estimates may well be inaccurate by more than an order of magnitude.

Table 1 is intended simply to provide a general indication of the amounts of the various elements available in rocks for possible solution by water and, in an even more general sense, to show how some elements are typically concentrated or depleted in processes of conversion from igneous to sedimentary rocks.

According to Clarke and Washington (1924), 95 percent of the Earth's crust to a depth of 16 km (10 miles) is igneous rock. Therefore, the average composition of the 16 km crust closely approaches the average for igneous rocks. In the consideration of natural water and its relation to rock composition, however, this predominance of igneous rock is not of overriding importance. Most recoverable ground water occurs at depths of less than 2 km below the land surface, and in the part of the crust near the surface, sedimentary rocks are more prevalent than igneous rocks. As a rule, igneous rocks are poor aquifers, so they transmit little water; also, they do not present large areas of active mineral surface to be contacted by relatively small volumes of water, as do more porous rock types. In the headwater areas of many mountain streams, igneous rocks are at the surface, and they may contribute solutes to surface runoff both directly and through leaching of partly decomposed minerals in overlying soils. The areas where igneous rocks are exposed to attack by surface streams are not a predominant part of the Earth's surface. Therefore, the sedimentary rocks and the soil assume major importance as the immediate sources of soluble matter to be taken up by circulating underground and surface water. Reactions between water and the minerals of igneous rocks, however, are of fundamental importance in studies of geochemical processes, and they will be considered in some detail later in this book.

Table 1. Average composition, in parts per million, of igneous rocks and some types of sedimentary rocks

[After Horn and Adams (1966)]

Element	Igneous rocks	Sedimentary rocks		
		Resistates (sandstone)	Hydrolyzates (shale)	Precipitates (carbonates)
Si	285,000	359,000	260,000	34
Al	79,500	32,100	80,100	8,970
Fe	42,200	18,600	38,800	8,190
Ca	36,200	22,400	22,500	272,000
Na	28,100	3,870	4,850	393
K	25,700	13,200	24,900	2,390
Mg	17,600	8,100	16,400	45,300
Ti	4,830	1,950	4,440	377
P	1,100	539	733	281
Mn	937	392	575	842
F	715	220	560	112
Ba	595	193	250	30
S	410	945	1,850	4,550
Sr	368	28	290	617
C	320	13,800	15,300	113,500
Cl	305	15	170	305
Cr	198	120	423	7.1
Rb	166	197	243	46
Zr	160	204	142	18
V	149	20	101	13
Ce	130	55	45	11
Cu	97	15	45	4.4
Ni	94	2.6	29	13
Zn	80	16	130	16
Nd	56	24	18	8.0
La	48	19	28	9.4
N	46	600
Y	41	16	20	15
Li	32	15	46	5.2
Co	23	.33	8.1	.12
Nb	20	.096	20	.44
Ga	18	5.9	23	2.7
Pr	17	7.0	5.5	1.3
Pb	16	14	80	16
Sm	16	6.6	5.0	1.1
Sc	15	.73	10	.68
Th	11	3.9	13	.20
Gd	9.9	4.4	4.1	.77
Dy	9.8	3.1	4.2	.53
B	7.5	90	194	16
Yb	4.8	1.6	1.6	.20
Cs	4.3	2.2	6.2	.77
Hf	3.9	3.0	3.1	.23
Be	3.6	.26	2.1	.18
Er	3.6	.88	1.8	.45
U	2.8	1.0	4.5	2.2
Sn	2.5	.12	4.1	.17
Ho	2.4	1.1	.82	.18
Br	2.4	1.0	4.3	6.6
Eu	2.3	.94	1.1	.19

Table 1. Average composition, in parts per million, of igneous rocks and some types of sedimentary rocks—Continued

Element	Igneous rocks	Sedimentary rocks		
		Resistates (sandstone)	Hydrolyzates (shale)	Precipitates (carbonates)
Ta.....	2.0	.10	3.5	.10
Tb.....	1.8	.74	.54	.14
As.....	1.8	1.0	9.0	1.8
W.....	1.4	1.6	1.9	.56
Ge.....	1.4	.88	1.3	.036
Mo.....	1.2	.50	4.2	.75
Lu.....	1.1	.30	.28	.11
Tl.....	1.1	1.5	1.6	.065
Tm.....	.94	.30	.29	.075
Sb.....	.51	.014	.81	.20
I.....	.45	4.4	3.8	1.6
Hg.....	.33	.057	.27	.046
Cd.....	.19	.020	.18	.048
In.....	.19	.13	.22	.068
Ag.....	.15	.12	.27	.19
Se.....	.050	.52	.60	.32
Au.....	.0036	.0046	.0034	.0018

The three classes into which sedimentary rocks are divided in table 1 are adapted from Goldschmidt (1933) and from Rankama and Sahama (1950, p. 198). This classification is based on the chemical composition and the degree of alteration of the minerals making up the rocks. It is probably better suited to studies related to chemical composition than are the usual geologic classifications of sedimentary rocks by means of mineral character, texture, and stratigraphic sequence.

For the purpose of this book, the following definitions are applicable:

Resistate—A rock composed principally of residual minerals not chemically altered by the weathering of the parent rock.

Hydrolyzate—A rock composed principally of relatively insoluble minerals produced during the weathering of the parent rock.

Precipitate—A rock produced by chemical precipitation of mineral matter from aqueous solution.

A fourth rock type, evaporites, consists of soluble minerals deposited as a result of evaporation of the water in which they were dissolved. Quantitative data on composition of evaporite rocks have been given by Stewart (1963). The evaporites influence the composition of some natural water, but their average content of most of the minor elements is still not accurately known; data for this class of rocks are not included in table 1.

The severity of chemical attack in weathering ranges widely. Under severe attack, the residue from a given igneous rock might consist almost wholly of quartz sand. Under less severe attack, an arkose containing unaltered

feldspar along with the quartz might be produced from the same rock. Some types of weathering could leave less stable minerals of the original rock in the residue.

Another important factor in determining the composition of sedimentary rocks is the process of comminution and mechanical sorting accompanying weathering and transport of weathering products. Resistates, as the term is usually interpreted, are rather coarse grained. Some of the resistant mineral particles, however, may be converted to a very fine powder and deposited with the naturally fine grained hydrolyzates.

Chemical precipitation may occur in a saline environment, and the differentiation between precipitate and evaporite rock is somewhat arbitrary; thus, precipitate and evaporite components may be interbedded.

Geochemists often add other classifications such as oxidates, typified by iron ore, and redozates, for material of largely biological origin such as black shale or coal. However, the dividing lines between these and the classes already considered are inexact.

Because so many of the sedimentary rocks contain mixtures of weathering products, any division into classes must be somewhat arbitrary. Thus, although one might think of a pure quartz sand as the ideal representative of the resistates, for the purpose of this book the class also includes sandstone, conglomerate, arkose, graywacke, and even unconsolidated alluvium. Likewise, although clay is the ideal representative of the hydrolyzates, the class also includes shale, which commonly contains high percentages of quartz and other nonclay minerals. Both classes of rock commonly contain chemically precipitated

minerals as coatings, cement, or discrete particles. The precipitate rocks, such as limestone and dolomite, generally are aggregates of calcitic or dolomitic particles, with many impurities, and may be aggregates of detrital material rather than massive crystalline precipitates. More extensive discussions of classification and identification are contained in texts on sedimentary rocks.

THE HYDROSPHERE

The hydrosphere is generally defined by geochemists as the vapor, liquid, and solid water present at and near the land surface, and its dissolved constituents. Water vapor and condensed water of the atmosphere are usually included, but water that is immobilized by incorporation into mineral structures in rocks is usually not thought of as part of the hydrosphere.

The oceans constitute about 98 percent of the hydrosphere, and thus the average composition of the hydrosphere is, for all practical purposes, that of seawater. The water of the ocean basins is generally fairly well mixed with regard to major constituents, although concentrations of most minor elements are not uniform with depth or areally. The average concentrations of the major dissolved elements or ions, and of some of the minor ones, are given in table 2, which is based on a compilation by Goldberg and others (1971). These authors also suggested,

on the basis of stabilities of complex species, the predominant forms in which the dissolved constituents occur.

Substantial differences in concentration between water near the surface and water at depth, as well as areally, are characteristic of solutes that are used as nutrients by marine life. Some of the minor elements have distributions that resemble those of the nutrients. Quinby-Hunt and Turekian (1983) used this and other types of correlations to estimate mean oceanic concentrations of most of the elements. Their estimates, and results of extensive continuing research since 1971 on the behavior of minor elements in seawater, suggest that previously accepted mean values for many of these elements were too large. Average concentrations for minor constituents given in table 2 are useful in a broadly descriptive sense, but they may not be of much value in defining individual elemental behavior.

For various reasons, many geochemists have compiled estimates of the average composition of river water. Obviously, the chemical composition of surface runoff waters of the Earth is highly variable through both time and space, and this book discusses the variations and reasons for them at some length. For our purposes a global average has little significance except, perhaps, as a baseline for comparison. A widely quoted average computed by Livingstone (1963) is given in table 3. The value given in his published average for dissolved iron

Table 2. Composition of seawater

[After Goldberg and others (1971)]

Constituent	Concentration (mg/L)	Principal form(s) in which constituent occurs
Cl	19,000	Cl ⁻
Na	10,500	Na ⁺
SO ₄	2,700	SO ₄ ²⁻
Mg	1,350	Mg ²⁺
Ca	410	Ca ²⁺
K	390	K ⁺
HCO ₃	142	HCO ₃ ⁻ , H ₂ CO ₃ (aq), CO ₃ ²⁻
Br	67	Br ⁻
Sr	8	Sr ²⁺
SiO ₂	6.4	H ₄ SiO ₄ (aq), H ₃ SiO ₄ ⁻
B	4.5	H ₃ BO ₃ (aq), H ₂ BO ₃ ⁻
F	1.3	F ⁻
N67	^a NO ₃ ⁻
Li17	Li ⁺
Rb12	Rb ⁺
C (organic)10
P09	HPO ₄ ²⁻ , H ₂ PO ₄ ⁻ , PO ₄ ³⁻
I06	IO ₃ ⁻ , I ⁻
Ba02	Ba ²⁺
Mo01	MoO ₄ ²⁻
Zn01	Zn ²⁺
Ni007	Ni ²⁺

Table 2. Composition of seawater—Continued

Constituent	Concentration (mg/L)	Principal form(s) in which constituent occurs
As	.003	HAsO_4^{2-} , H_2AsO_4^-
Cu	.003	Cu^{2+}
Fe	.003	
U	.003	$\text{UO}_2(\text{CO}_3)_3^{4-}$
Mn	.002	Mn^{2+}
V	.002	$\text{VO}_2(\text{OH})_3^{2-}$
Al	.001	
Ti	.001	
Sn	.0008	
Co	.0004	Co^{2+}
Cs	.0003	Cs^+
Sb	.0003	
Ag	.0003	AgCl_2^-
Hg	.0002	$\text{HgCl}_2(\text{aq})$
Cd	.00011	Cd^{2+}
W	.0001	WO_4^{2-}
Se	.00009	SeO_4^{2-}
Ge	.00007	$\text{Ge}(\text{OH})_4(\text{aq})$
Cr	.00005	
Ga	.00003	
Pb	.00003	Pb^{2+} , PbCl_3^- , PbCl^+
Bi	.00002	
Au	.00001	AuCl_4^-
Nb	.00001	
Ce	.000001	
Sc	<.000004	
La	.000003	$\text{La}(\text{OH})_3(\text{aq})$
Y	.000003	$\text{Y}(\text{OH})_3(\text{aq})$
Be	.0000006	
Th	<.0000005	
Pa	2×10^{-9}	
Ra	1×10^{-10}	Ra^{2+}

^a Does not include dissolved N_2 .

appears to be much too high and is omitted here. Meybeck (1979) has compiled more recent data on river water composition and has computed an average total concentration slightly lower than that of Livingstone. This average is also given in table 3. With coworkers (for example, Martin and Meybeck, 1979), Meybeck has also studied composition of particulate matter carried to the ocean by rivers and many of the factors that influence river-water quality.

Averages like those of Livingstone and Meybeck are strongly influenced by the composition of the world's large rivers. An average analysis for the Mississippi is given in table 3, along with a single analysis for the Amazon, the world's largest river. The major-ion composition of the Mississippi is well known, through many years of intensive sampling. That of the Amazon, however, was poorly known until studies by Brazilian and other

scientific agencies were intensified in the 1960's and 1970's. The average discharge for the Mississippi into the Gulf of Mexico is given by Iseri and Langbein (1974) as 18,100 m^3/sec (640,000 ft^3/sec). For the Amazon, a total mean discharge to the ocean of 175,000 m^3/sec (6,100,000 ft^3/sec) was estimated by Oltman (1968). The analysis for the Amazon is of a sample taken at a time of high discharge, and the water has a lower than average concentration of dissolved ions. The period represented by the Mississippi River analysis had an average discharge nearly equal to the long-term mean and is probably more nearly representative of average conditions than the analysis given in the second edition of this book.

THE ATMOSPHERE

The composition of the atmosphere in terms of volume percentage and partial pressures of the gaseous

Table 3. Composition of river water

[Date under sample number is date of collection. Sources of data: 1, Oltman (1968, p. 13); 2, U.S. Geological Survey Water-Supply Paper 1964; 3, Livingstone (1963, p. G41); 4, Maybeck (1979)]

Constituent	1		2		3		4	
	July 16, 1963		Oct. 1, 1964 - Sept. 30, 1965					
	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
Silica (SiO ₂)	7.0		7.9		13		10.4	
Aluminum (Al)	.07							
Iron (Fe)	.06		.02					
Calcium (Ca)	4.3	.215	38	1.896	15	.749	13.4	.669
Magnesium (Mg)	1.1	.091	10	.823	4.1	.337	3.35	.276
Sodium (Na)	1.8	.078	20	.870	6.3	.274	5.15	.224
Potassium (K)			2.9	.074	2.3	.059	1.3	.033
Bicarbonate (HCO ₃)	19	.311	113	1.852	58	.951	52	.852
Sulfate (SO ₄)	3.0	.062	51	1.062	11	.239	8.25	.172
Chloride (Cl)	1.9	.054	24	.677	7.8	.220	5.75	.162
Fluoride (F)	.2	.011	.3	.016				
Nitrate (NO ₃)	.1	.002	2.4	.039	1	.017		
Dissolved solids	28.		232		89		73.2	
Hardness as CaCO ₃	15		138		54		47	
Noncarbonate	0		45		7		5	
Specific conductance (micromhos at 25°C)	40		371					
pH	6.5		7.4					
Color			10					
Dissolved oxygen	5.8							
Temperature (°C)	28.4							

1. Amazon at Obidos, Brazil. Discharge, 216,000 m³/s (7,640,000 cfs) (high stage).
2. Mississippi at Luling Ferry, La. (17 mi west of New Orleans). Time-weighted mean of daily samples.
- 3, 4. Mean composition of river water of the world (estimated). Dissolved-solids computed as sum of solute concentrations, with HCO₃ converted to equivalent amount of CO₃.

components is given in table 4. Local variations in atmospheric composition are produced by the activities of humans, plant and animal metabolism and decay, and gases from volcanoes and other geothermal areas. Particulate matter carried into the air by wind, discharged from smokestacks, or entering the atmosphere from outer space provides a number of atmospheric components that may influence the composition of water but that cannot be readily evaluated in terms of average contents. Minor constituents such as CO, SO₂, O₃, and NO₂ or other nitrogen-containing gases may play important roles in air pollution and may influence the composition of rainwater; they may be present locally in concentrations greater than those given in table 4.

Among the minor constituents of air are certain nuclides produced in the outer reaches of the atmosphere by cosmic-ray bombardment and by other processes. Some of these nuclides are radioactive, notably tritium and carbon-14. Naturally produced radioactive materials are present in the atmosphere in very small concentrations, however, and can be detected only by highly sensitive techniques.

Ultraviolet radiation from the Sun is depleted by photochemical reactions with atmospheric gases, and most of the radiation with wavelengths less than 300 nanometers (nm) does not reach the Earth's surface. These reactions produce traces of highly reactive intermediates such as peroxy and hydroxyl radicals that oxidize

Table 4. Mean composition of the atmosphere

[After Mirtov (1961)]

Gas	Percentage by volume	Partial pressure (atm)
N ₂	78.1	0.781
O ₂	20.9	.209
Ar93	.0093
H ₂ O1-2.8	.001-0.028
CO ₂03	.0003
Ne	1.8×10 ⁻³	1.8×10 ⁻⁵
He	5.2×10 ⁻⁴	5.2×10 ⁻⁶
CH ₄	1.5×10 ⁻⁴	1.5×10 ⁻⁶
Kr	1.1×10 ⁻⁴	1.1×10 ⁻⁶
CO	(0.06-1)×10 ⁻⁴	(0.06-1)×10 ⁻⁶
SO ₂	1×10 ⁻⁴	1×10 ⁻⁶
N ₂ O	5×10 ⁻⁵	5×10 ⁻⁷
H ₂	~5×10 ⁻⁵	~5×10 ⁻⁷
O ₃	(0.1-1.0)×10 ⁻⁵	(0.1-1.0)×10 ⁻⁷
Xe	8.7×10 ⁻⁶	8.7×10 ⁻⁸
NO ₂	(0.05-2)×10 ⁻⁶	(0.05-2)×10 ⁻⁸
Rn	6×10 ⁻¹⁸	6×10 ⁻²⁰

other atmospheric constituents. Some of the chemical processes in the atmosphere and the research being done on them were described by Chameides and Davis (1982).

PRINCIPLES AND PROCESSES CONTROLLING COMPOSITION OF NATURAL WATER

Solutes contained in natural water represent the net effect of a series of antecedent chemical reactions that have dissolved material from another phase, have altered previously dissolved components, or have eliminated them from solution by precipitation or other processes. The chemical processes are influenced strongly by biologic activity in some environments and by a great many processes of a physical nature.

Achieving the goal of understanding these processes, and being able to make quantitative statements about them, requires the application of theoretical analysis to develop tentative models. These hypotheses are sometimes referred to as "conceptual models." The models can be quantified and tested using data and techniques that will be briefly described here.

The fundamental concepts relating to chemical processes that are most useful in developing a unified approach to the chemistry of natural water are mainly related to chemical thermodynamics and to reaction mechanisms and rates. These are summarized here briefly, and their use is later demonstrated by applications to real-world conditions, or in other ways.

Thermodynamic principles may also be useful in correlating chemical processes with biological or physical processes. However, for many environmental effects it is

not usually possible to use this approach very rigorously. The statements here about nonchemical factors are generalized and somewhat qualitative. Nevertheless, the interrelationships of water chemistry and water environment constitute the principal theme of this book, and an improved understanding of them is the goal of workers in this field.

Theoretical concepts and mathematical derivations have been held to a minimum in this discussion of chemical thermodynamics. Readers who require a more comprehensive treatment should refer to texts on physical chemistry such as that of Glasstone and Lewis (1960) (and many others) or, at a more sophisticated level, to specialized texts on chemical thermodynamics such as those of Wall (1958) or Lewis and Randall (1961). The text of Stumm and Morgan (1981, p. 8-120) discusses thermodynamics and kinetics as they relate to water chemistry.

Thermodynamics of Aqueous Systems

Energy occurs in various forms in the natural universe. It may, for example, have the form of radiation, heat, electricity, motion, or chemical interaction. The principle of conservation of energy states, however, that although its form may change, the total amount of energy in the universe remains constant. This principle is also known as the first law of thermodynamics. A second broad principle, based on experience and observation, states that energy transfers occur only along favorable potential gradients. For example, water flows down slopes, heat passes from hot objects to cooler ones, and electrical currents flow from points of high potential to points of lower potential. This general principle also implies that energy in any closed system tends to become evenly distributed. It is known as the second law of thermodynamics.

Thermodynamic principles, applied to chemical-energy transfers, form a basis for evaluating quantitatively the feasibility of various possible chemical processes in natural water systems, for predicting the direction in which chemical reactions may go, and in many instances for predicting the actual dissolved concentrations of reaction products that should be present in the water.

Thermodynamics also offers a unified way of viewing chemical and physical processes occurring in natural systems, but it has not been applied this way in hydrology to any significant degree. The total energy in a groundwater system, for example, includes components of gravitational, thermal, and chemical energy, but generalized thermodynamic treatments of hydrologic systems including all three parameters are rare.

The term "system" as used here refers to a body of water, its dissolved material, and the potentially interacting solids and gases that are in contact with the water.