Study and Interpretation of the Chemical Characteristics of Natural Water

Third Edition

United States
Geological
Survey
Water-Supply
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By JOHN D. HEM

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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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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°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 tabulations 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 differentation 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 reduzates, 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^-, $H_2CO_3(aq)$, CO_3^{2-}
Br	67	Br^-
Sr	8	Sr^{2+}
SiO_2	6.4	$H_4SiO_4(aq)$, $H_3SiO_4^-$
B	4.5	$H_3BO_3(aq)$, $H_2BO_3^-$
F	1.3	F^-
N	.67	[a]NO_3^-
Li	.17	Li^+
Rb	.12	Rb^+
C (organic)	.10	....
P	.09	HPO_4^{2-}, $H_2PO_4^-$, PO_4^{3-}
I	.06	IO_3^-, I^-
Ba	.02	Ba^{2+}
Mo	.01	MoO_4^{2-}
Zn	.01	Zn^{2+}
Ni	.007	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	$UO_2(CO_3)_3^{4-}$
Mn	.002	Mn^{2+}
V	.002	$VO_2(OH)_3^{2-}$
Al	.001	
Ti	.001	
Sn	.0008	
Co	.0004	Co^{2+}
Cs	.0003	Cs^+
Sb	.0003	
Ag	.0003	$AgCl_2^-$
Hg	.0002	$HgCl_2(aq)$
Cd	.00011	Cd^{2+}
W	.0001	WO_4^{2-}
Se	.00009	SeO_4^{2-}
Ge	.00007	$Ge(OH)_4(aq)$
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	$La(OH)_3(aq)$
Y	.000003	$Y(OH)_3(aq)$
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 m^3/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 HCO_3 converted to equivalent amount of CO_3.

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, SO_2, O_3, and NO_2 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
Ar	.93	.0093
H_2O	.1–2.8	.001–0.028
CO_2	.03	.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	$(0.06–1)\times10^{-4}$	$(0.06–1)\times10^{-6}$
SO_2	1×10^{-4}	1×10^{-6}
N_2O	5×10^{-5}	5×10^{-7}
H_2	$\sim5\times10^{-5}$	$\sim5\times10^{-7}$
O_3	$(0.1–1.0)\times10^{-5}$	$(0.1–1.0)\times10^{-7}$
Xe	8.7×10^{-6}	8.7×10^{-8}
NO_2	$(0.05–2)\times10^{-6}$	$(0.05–2)\times10^{-8}$
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.

Systems may be open, with fairly free access for exchange of matter and energy with their surroundings, or they may be closed, with confining boundaries that prevent such exchanges. Besides the chemical energy input and stored chemical energy in natural aqueous systems, direct or indirect energy input may occur from sources such as the Sun's radiation, geothermal heat, or radioactivity.

A brief review of certain fundamental relationships and principles relating to chemical energy is helpful in understanding how thermodynamic data may be used. The chemical energy stored in a substance at constant temperature and pressure is termed "enthalpy" and is represented by the symbol ΔH. The delta attached to this quantity indicates that it represents a departure from an arbitrary standard state or zero point. For the chemical elements this standard reference state is that of 1 mole (an amount equal to the atomic weight, in grams) at 25.0°C and 1 atmosphere pressure. Standard enthalpies of formation for aqueous ions and compounds as tabulated in thermodynamic data compilations are designated "ΔH°_f" and represent enthalpies of 1 mole of the substance at that temperature and pressure, synthesized from its elemental components at their standard states.

Enthalpy may be thought of as having two components, an internal component which is termed "entropy," ΔS, and a component that is or can become available externally which is termed "free energy," ΔG. The concept of entropy is fundamentally implied by the second law of thermodynamics, which can be stated: A spontaneously occurring process in an isolated system will tend to convert less probable to more probable states. Probability is such systems tends to favor a generally random or disordered condition, or, finally, a state of relative chaos. Entropy may thus be considered a measure of organization, or order, within a system.

The tendency of systems to become disordered is readily observable in many contexts and needs no further amplification. However, entropy is more difficult to evaluate and observe quantitatively than its corollary, free energy, which is always released in a spontaneous process. The relationship governing these chemical energy manifestations is

$$\Delta H = \Delta G + T \Delta S,$$

where T is temperature on the Kelvin scale. This is a general statement of the third law of thermodynamics, which also may be paraphrased "the entropy of a substance at absolute zero (T=0) is zero." The relationship holds under all conditions, including those involving standard states. As noted above, standard thermodynamic values are designated by a superscript degree sign. The standard thermodynamic values for free energy (ΔG°) are of direct interest in the study of chemical processes and are the principal form in which thermodynamic data are used in this book.

Enthalpy, entropy, and free energy values are expressed in terms of heat units. In this book the unit used is the calorie, and ΔG values are given in kilocalories, in accord with most chemical thermodynamic literature. In the International System of Units (SI) the recommended unit for heat energy is the joule. One calorie, as used in chemical thermodynamics, is defined as being equal to 4.184 joules.

Standard free energy values for minerals, gases, dissolved ions, and other substances that may participate in chemical reactions are available in the literature. One may therefore write chemical reactions that involve such substances in terms of free energies of participating material. The algebraic sum of the standard free energies of products minus the sum of the standard free energies of reactants is mathematically related to the equilibrium constant for the reaction, as will be shown later. This quantity is the standard free energy of reaction, ΔG°_R. An equivalent expression used by some authors is "standard reaction potential."

Generally, not all substances participating in chemical reactions occurring in real systems are at standard states. However, if concentrations of the reacting substances in the system are determined, and if ΔG°_R is known, the extent of departure from a state of thermodynamic equilibrium can be evaluated. Expressed in energy units, this disequilibrium index represents the thermodynamic driving force available to promote the chemical reaction. This quantity has been given several different names in nomenclature systems used in thermodynamic literature. It will be referred to here as affinity of reaction, **A**. A positive value of **A** indicates that the reaction is thermodynamically feasible.

The second law of thermodynamics predicts that in a closed system the reaction affinities will tend to reach minimum values. At equilibrium for a specific reaction, the value of **A** will be zero. One may apply this principle to design theoretical models of natural chemical systems.

To apply such a model rigorously requires assumptions that cannot be completely verified. Real-world systems are, in fact, likely to be open to exchange of energy and reactants with their surroundings; a large number of reactions may be occurring, reactions that may not be in the model; and some of the processes may be effectively irreversible. Some reactions that are thermodynamically feasible require catalysis to proceed at a significant rate. Also, practical application of thermodynamic calculations may require adjustment of standard free energy or other thermodynamic quantities to allow for deviations from standard temperature and pressure. Methods for making such adjustments are given in standard textbooks on thermodynamics and physical chemistry and will be considered later as appropriate.

In spite of these limitations, the second law of thermodynamics remains a fundamental concept of great value in studying natural-water chemistry. Applications that will be made in this book range from predicting equilibrium solute concentrations and solubility limits to more general conceptual models. In such models it may be thought of as a guidepost to reaction pathways most likely to be followed or, as some authors call it, the "arrow of time," in the sense that it points the way a process is going with the passage of time.

Life forms require energy released in spontaneous processes, but they also are dependent on processes that entail some net energy input—processes that might not otherwise occur. Plants, for example, are able to use radiant energy from the Sun to synthesize carbohydrates from carbon dioxide and water. Animals may use the product as a source of food energy. On a higher scale, humans use solar energy stored in petroleum or coal in many ways—for transportation, electric-power generation, or conversion of ferric oxide to metallic iron, to cite a few examples.

The distinction of changes in free energy and entropy may be less clear-cut in life processes than in simple inorganic systems, but the broad thermodynamic principles still fundamentally govern such processes as well.

Chemical Reactions

The chemical reactions in which elements participate involve changes in the arrangement and association of atoms and molecules and interactions among electrons that surround the atomic nuclei. The field of natural-water chemistry is concerned principally with reactions that occur in relatively dilute aqueous solution, although some natural waters have rather high solute concentrations. The reacting systems of interest are generally heterogeneous—that is, they involve both a liquid phase and a solid or a gaseous phase, or all three.

Reversible and Irreversible Reactions in Water Chemistry

Many kinds of chemical reactions can be important in establishing and maintaining the composition of natural water. Concepts that are appropriate for evaluating these processes differ somewhat depending on the nature of the reactions involved. Therefore, some attention needs to be given to reaction types here, although this cannot be a rigorous classification scheme.

Chemical literature refers extensively to the concepts of reversibility and irreversibility in a chemical reaction. In a strict sense an irreversible process is one in which reactants are totally converted to products, and a zero value for the reaction affinity cannot be attained so long as any reactant remains. In this sense a reversible process would be one in which reactants and products can be present when the reaction affinity is zero, or nearly zero, for the reaction as written, or for its reverse. It is inferred that to reach and sustain this condition, both the forward and reverse reactions are occurring simultaneously, at least on a micro scale, and at comparable rates when reaction affinities are small.

These definitions are not entirely satisfactory for our purposes. It has already been pointed out that some reactions do not take place to a significant extent, even though they may be favored thermodynamically, owing to energy barriers in some of the reaction pathways. If such a condition applies to one of the reactions in a reversible process as defined above, the process will seem to behave irreversibly. Also, in reversible reactions in open systems in which reactants and (or) products may enter and leave, irreversible behavior is to be expected.

Whether a given chemical reaction in a natural-water system is reversible or irreversible is therefore dependent on kinetic factors and on some of the physical features of the system of interest, as well as on thermodynamic considerations.

The ease with which a particular reaction can be reversed is important because readily reversible processes can be expected generally to approach chemical equilibrium closely. Irreversible processes can reach a steady state, but thermodynamic principles apply to them in a different way. Easily reversed processes in natural-water systems are those that require only small positive reaction affinities to bring about compensating chemical changes.

The chemical reactions of interest in natural-water systems can be considered as being of three general types: (1) readily reversible processes, (2) processes whose reversibility is hindered, and (3) processes that are irreversible in a fundamental (thermodynamic) sense. Specific processes in natural-water systems represent a continuum from types 1 to 3. Some examples can be cited to aid in understanding this.

An example of an easily reversed process is the formation of complex ions or similar homogeneous (single-phase) reactions. Dissolved carbon dioxide, represented as H_2CO_3, dissociates reversibly:

$$H_2CO_3(aq) \rightleftharpoons HCO_3^- + H^+ \rightleftharpoons CO_3^{2-} + H^+,$$

and aluminum ions form a hydroxide complex which may be reconverted to the free ion:

$$Al^{3+} + H_2O \rightleftharpoons AlOH^{2+} + H^+.$$

Some heterogeneous reactions, such as the solution of unreactive gases, are readily reversible, for example,

$$N_2(g) \rightleftharpoons N_2(aq).$$

The association of N_2 molecules with water molecules that occurs in this reaction is implied in the notation N_2 (aq) but is not specifically indicated by the equation. Other symbols used here to indicate the phase of reactants or products are: (c)=solid, (l)=liquid, and (g)=gas. Dissolved ions and their electronic charges are designated by superscript + and − signs. Unless otherwise indicated H_2O is assumed to be in the liquid state.

Many sorption-desorption or ion-exchange reactions are readily reversed—for example,

$$Na_2X+Ca^{2+} \rightleftharpoons CaX+2Na^+.$$

Some solution-dissolution processes can be considered readily reversible, for example, the solution of carbon dioxide gas,

$$CO_2(g)+H_2O \rightleftharpoons H_2CO_3(aq),$$

and reactions involving calcite and some other carbonates apparently can be reversed rather easily in many natural systems:

$$CaCO_3(c)+H^+ \rightleftharpoons HCO_3^-+Ca^{2+}.$$

Some oxidation-reduction reactions (reactions involving electron transfers) can be viewed as readily reversible. These commonly are written as half-reactions or redox couples, with electrons involved being represented by the symbol e^-. Homogeneous processes include oxidation of ferrous ions:

$$Fe^{2+} \rightleftharpoons Fe^{3+}+e^-.$$

The reduction of aqueous oxygen is less readily reversible:

$$O_2(aq)+4H^++4e^-=2H_2O(l).$$

(This reaction takes place in steps and is more complicated than this statement indicates.)

A heterogeneous redox process is the production of ferric hydroxide from aqueous ferrous ions:

$$Fe^{2+}+3H_2O \rightleftharpoons Fe(OH)_3(c)+e^-+3H^+.$$

Redox couples are not complete reactions, as the electrons shown are not available reactants unless a corollary couple is present that can supply or consume the necessary electrons.

Examples of reactions in which reversibility is more severely hindered are numerous. This effect can be seen in the weathering of albite, a common feldspar mineral, in which a solid product, kaolinite, is formed:

$$2NaAlSi_3O_8(c)+2H^++9H_2O \rightarrow 2Na^++4H_4SiO_4(aq)+Al_2Si_2O_5(OH)_4(c).$$

The kaolinite may dissolve reversibly:

$$Al_2Si_2O_5(OH)_4(c)+7H_2O \rightleftharpoons 2Al(OH)_4^-+2Si(OH)_4(aq)+2H^+.$$

Here the dissolution of albite is essentially irreversible because it cannot be reconstituted to a significant extent without imposing temperatures and pressures that differ greatly from those of normal weathering regimes.

Energy barriers of various kinds may inhibit reversibility. Precipitation reactions may be slowed or stopped by the energy demand imposed by the formation of the nucleus of a crystal. Oxidation-reduction reactions, especially those involving sulfur or nitrogen, may be very slow unless biota are present to mediate the critical steps in the process.

A process that is thermodynamically irreversible is that of altering the crystal structure of a solid to a more stable form during aging. For example, when a ferric hydroxide amorphous precipitate ages to goethite,

$$Fe(OH)_3(c) \rightarrow FeOOH(c)+H_2O,$$

the reaction affinity will be greater than zero as long as any $Fe(OH)_3$ remains.

Processes whose reversibility is hindered may occur in steps. It has been suggested (Hem and others, 1982) that an irreversible process for alteration of manganese oxide to a more stable form can give a nonequilibrium steady state Mn^{2+} concentration if it occurs in an open system. The two steps in the process are

$$2Mn^{2+}+½O_2(aq)+3H_2O \rightarrow 2MnOOH(c)+4H^+$$

and

$$2MnOOH(c)+2H^+ \rightarrow MnO_2(c)+Mn^{2+}+2H_2O.$$

These add up to

$$Mn^{2+}+½O_2(aq) \rightarrow MnO_2(c)+2H^+$$

and could be viewed as forward and reverse versions of the summary reaction. Both processes can have positive A values at the same time.

The most important single factor that makes many of the reactions in natural aqueous systems irreversible is the openness of many systems to fluxes of reactants that may totally control the thermodynamics and may drive the reactions in one direction only.

Methods of using thermodynamic principles in irreversible systems are of great potential usefulness in natural-water chemical models. Such methods can be expected to be more widely applied in the future but are in a primitive state of development at this time.

Chemical Equilibrium—The Law of Mass Action

The study of chemical equilibria is based on the law of mass action, which states that the rate of a chemical reaction is proportional to the active masses of the participating substances. This principle was proposed by Guldberg and Waage in the mid-19th century.

A hypothetical reaction between substances A and B to produce products C and D, in a *closed system*, can be written

$$aA+bB \rightleftharpoons cC+dD,$$

where lower case letters represent multiples required to balance the equation. The rates of forward and reverse reaction, according to the mass law, will be, respectively,

$$\mathbf{R}_1=k_1'\,[A]^a[B]^b$$

and

$$\mathbf{R}_2=k_2'\,[C]^c[D]^d,$$

where bracketed terms represent active masses. The quantities k_1' and k_2' are proportionality constants for the forward and reverse reactions. When $\mathbf{R}_1=\mathbf{R}_2$, the system will be in a state of dynamic equilibrium and no change in active concentrations (represented by the bracketed quantities) will occur. This leads to the expression

$$\frac{[C]^c[D]^d}{[A]^a[B]^b}=\frac{k_1'}{k_2'}=K.$$

The quantity K is referred to as the equilibrium constant. It has a characteristic value for any given set of reactants and products, and many experimentally determined values are available in published chemical literature.

The value of the equilibrium constant is influenced by temperature and pressure. Standard thermodynamic conditions (25°C and 1 atmosphere of pressure) are usually specified, but K values for many reactions have been determined at other temperatures, or over a temperature range.

It should be noted that this form of the mass law is a statement of final conditions in a system at equilibrium and really says little specifically about the mechanism by which final equilibrium was reached. The derivation given above does imply a mechanism, but the meaning of the exponents *a*, *b*, etc., is not necessarily related to kinetic order of the forward and reverse processes. The subject of reaction kinetics will be considered later.

A further flaw in the derivation is that it implies reactions proceeding in opposition to each other, when values for **A** for both processes must be near zero. However, this difficulty can be avoided by deriving the mass law from fundamental thermodynamic concepts. This derivation is based on the convention that the bracketed terms given above represent "activities" of reactants and products. The activity, "α," is related to thermodynamic quantities by the relationship

$$\mu=\mu^\circ+RT\ln\alpha.$$

Here the quantities μ and μ° are termed "chemical potentials." The chemical potential of a reaction participant is further defined as its partial molal free energy. If present at standard state ($\alpha=1.0$), the chemical potential of the participant is equal to the standard free energy of the substance:

$$\Delta G^\circ=\mu^\circ.$$

The quantities R and T are the gas constant and the temperature on the Kelvin scale, and α is activity of the species in question.

For the reaction

$$aA+bB=cC+dD,$$

one may express the net potential of the reaction $\Delta\mu_R$ as the difference between chemical potentials of reactants and products:

$$c\mu_C+d\mu_D-a\mu_A-b\mu_B=\Delta\mu_R.$$

At standard states,

$$c\Delta G^\circ_C+d\Delta G^\circ_D-a\Delta G^\circ_A-b\Delta G^\circ_B=\Delta G^\circ_R.$$

As shown above,

$$\mu_A=\Delta G^\circ_A+RT\ \ln\alpha_A,$$

and a similar relationship holds for the other chemical potentials. Substituting these in the expression for $\Delta\mu_R$ gives

$$c(\Delta G^\circ_C+RT\ln\alpha_C)+d(\Delta G^\circ_D+RT\ln\alpha_D)$$
$$-a(\Delta G^\circ_A+RT\ln\alpha_A)-b(\Delta G^\circ_B+RT\ln\alpha_B)=\Delta\mu_R.$$

This rearranges to

$$\Delta\mu_R=\Delta G^\circ_R+RT\ln\ \frac{\alpha^c_C\times\alpha^d_D}{\mu^a_A\times\alpha^b_B}\ .$$

At equilibrium, $\Delta\mu_R=0$. Hence,

$$-\Delta G^{\circ}_{R}=RT\ln\frac{\alpha^{c}{}_{C}\times\alpha^{d}{}_{D}}{\alpha^{a}{}_{A}\times\alpha^{b}{}_{B}}\ .$$

The quantity $\Delta\mu_R$ represents the departure of the system from thermodynamic equilibrium and is equal to the reaction affinity **A** but is opposite in sign.

When brackets are used to denote activities, the logarithmic term describing the standard equilibrium state can be written

$$K=\frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}\text{, and }\Delta G^{\circ}_{R}=-RT\ln K.$$

It follows that one may also write, for systems not at standard states,

$$\Delta\mu_R=RT\ln Q-RT\ln K$$

and

$$\mathbf{A}=-RT\ln(Q/K).$$

where Q is an "activity quotient" based on observed activities of participating substances in an actual system and K is the equilibrium constant, attained when all participants are at standard states.

For practical use, when the temperature is 25°C, pressure is 1 atmosphere and base 10 rather than base e logs are employed, the relationship for reaction affinity becomes

$$\mathbf{A}=-1.364\log(Q/K).$$

for ΔG° and **A** values in kilocalories/mole.

Ionic Activity

Using these relationships to test real systems for adherence to or departure from equilibrium requires a means for calculating or determining activities. The activities of solid species participating in a reaction are, by definition, unity. They are present in their standard states, and their chemical potentials therefore must equal their standard free energies. Hence, for solids,

$$RT\ln\alpha=0.$$

The solvent, H_2O, is usually also present in its standard state and can depart significantly from it only when solute concentrations are very high. Therefore, it also generally has unit activity.

The solutes in aqueous systems do not display thermodynamically ideal behavior—that is, concentrations observed do not correspond to activities except in very dilute solutions, where ideal behavior is approached. These deviations from ideality are the result of electrostatic effects among the charged ions and other types of interactions among solute ions and solvent.

A few techniques for direct measurement of solute ion activities exist. Specific ion electrodes are capable of such measurements. The most widely used of these electrodes is the glass electrode for measuring hydrogen ion activity, or pH.

For solute species it is convenient to define activity as the product of the measured concentration and a correction factor called the "activity coefficient":

$$\alpha_i=C_i\gamma_i=[i],$$

where α_i is activity of ionic species i, C_i is its concentration on the molal (moles of $i/\mathrm{kgH_2O}$) or molar (moles of i/L) scale, and γ_i is the activity coefficient. The use of brackets to denote activity is the convention followed in this book. Molar activities will be used throughout. In dilute solutions, molal and molar scales are nearly the same.

Although in a strict sense the activities of solute species are dimensionless, it is necessary to attach a dimension to the quantity $C_i\gamma_i$. For practical purposes, the activities of dissolved species will be considered to represent moles per liter. This convention is commonly used in aqueous geochemistry and seems a reasonable, practical expedient.

For dilute solutions, activity coefficients of single ions can be computed by means of the Debye-Hückel equation. Various forms of this equation exist. The equation is based on an assumption that ions behave as charged particles of finite sizes in an electrostatic field of uniform intensity. Several of the parameters in the equation have been empirically determined, but it seems generally agreed that the equation works satisfactorily for solutions whose total concentration is not much over 0.10 mol/L of univalent salts. This would be equivalent to a concentration of about 5,800 mg/L (milligrams per liter) of dissolved ions in a sodium chloride solution. Ions having charges greater than 1 give a more intense effect, and their maximum permissible concentration is somewhat lower.

The form of the Debye-Hückel equation used here is

$$-\log\gamma_i=\frac{Az_i^2\sqrt{I}}{1+Ba_i\sqrt{I}},$$

where

γ_i is the activity coefficient of the ion,

A is a constant relating to the solvent (for water at 25°C it is 0.5085),
z_i is the ionic charge,
B is a constant relating to the solvent (for water at 25°C it is 0.3281),
a_i is a constant related to the effective diameter of the ion in solution, and
I is the ionic strength of the solution.

The values of a_i for various ions of interest are given in table 5 and were adapted from Kielland (1937) and Butler (1964).

Table 5. Values for the parameter a_i in the Debye-Hückel equation

[After Kielland (1937) and Butler (1964, p. 435)]

a_i	Ions
11	Th^{4+}, Sn^{4+}.
9	Al^{3+}, Fe^{3+}, Cr^{3+}, H^+.
8	Mg^{2+}, Be^{2+}.
6	Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Li^+.
5	$Fe(CN)_6^{4-}$, Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}, Pb^{2+}, CO_3^{2-}, SO_3^{2-}, MoO_4^{2-}.
4	PO_4^{3-}, $Fe(CN)_6^{3-}$, Hg_2^{2+}, SO_4^{2-}, SeO_4^{2-}, CrO_4^{2-}, HPO_4^{2-}, Na^+, HCO_3^-, $H_2PO_4^-$.
3	OH^-, F^-, CNS^-, CNO^-, HS^-, ClO_4^-, K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-, Rb^+, Cs^+, NH_4^+, Ag^+.

The ionic strength of a solution is a measure of the strength of the electrostatic field caused by the ions and is computed from the expression

$$I = \Sigma(m_i z_i^2/2),$$

where m is the concentration of a given ion in moles per liter and z is the charge on that ion. The terms in the summation include one for each ionic species present. A nomograph, which simplifies calculation of ionic strength from analytical data in milligrams per liter, published earlier by the writer (Hem, 1961), is reproduced in modified form here as plate 1.

To use the nomograph, a transparent straightedge or a drafting triangle is laid horizontally on the "milligrams per liter concentration" value for one of the major ions reported in the chemical analysis, and the increment of I is read on the scale in either the right-hand or left-hand margin. The value on both sides should be the same. This value is recorded and the process repeated for each of the other ions for which values are given in the analysis. The sum of the incremental I values represents the ionic strength of the water.

An approximate value of I can be computed from the specific conductance of the solution if this has been measured (Lind, 1970). This calculation should not be made, however, unless one has some knowledge of what the principal dissolved species in the solution are. If the composition is unknown for a water with a specific conductance of 1,000 μmhos, the calculated value of I could range from 0.0085 to 0.027.

In solutions containing less than 50 mg/L of dissolved ions, the ionic strength normally is less than 10^{-4}, and activity coefficients for most ions are 0.95 or more. In solutions that dilute, activity values are equal to measured concentrations within ordinary analytical error. If concentrations are near 500 mg/L of dissolved solids, the value of γ may be as low as 0.70 for divalent ions. At the maximum ionic strength at which the Debye-Hückel equation can be accurately used, the activity coefficients of some divalent ions may be less than 0.40.

Figure 1 is a graph for determining γ when I is known for the various major ions, and some minor ions, of natural water. The graph was prepared using the Debye-Hückel equation and assumes a temperature of 25°C. Ions listed in table 5 that have the same ionic charge and a_i value plot on the same line (Al^{3+} and Fe^{3+}, for example). Figure 1 can therefore be used for many species besides those specifically identified on the graph.

Calculation of Activity Coefficients at Higher Ionic Strength

Ion activity coefficients in solutions whose ionic strength exceeds 0.10 can be estimated by various methods. Butler (1964, p. 438) discussed some of these and, on the basis of the equation of Davies (given later in this book in the discussion of calcium), gave a nomograph that can be used to estimate activity in solutions having ionic strengths up to 0.5.

An extended form of the Debye-Hückel equation that includes a final term, $+bI$, was used by Truesdell and Jones (1974) to compute activity coefficients in solutions having ionic strengths as high as 4.0. Values for the parameters a_i and b for major ions that they used in the extended Debye-Hückel equation were given by these authors. Their a_i values differ somewhat from those given in table 5.

Some chemists have preferred to conduct solubility experiments in the presence of constant and rather high concentrations of inert ions. The operational equilibrum constants resulting are strictly applicable only to solutions having the same ionic strength and solute composition as the system that was investigated. For the concentration ranges of principal interest in natural-water chemistry, conversion of concentrations to activities by means of an appropriate equation and use of equilibrium constants

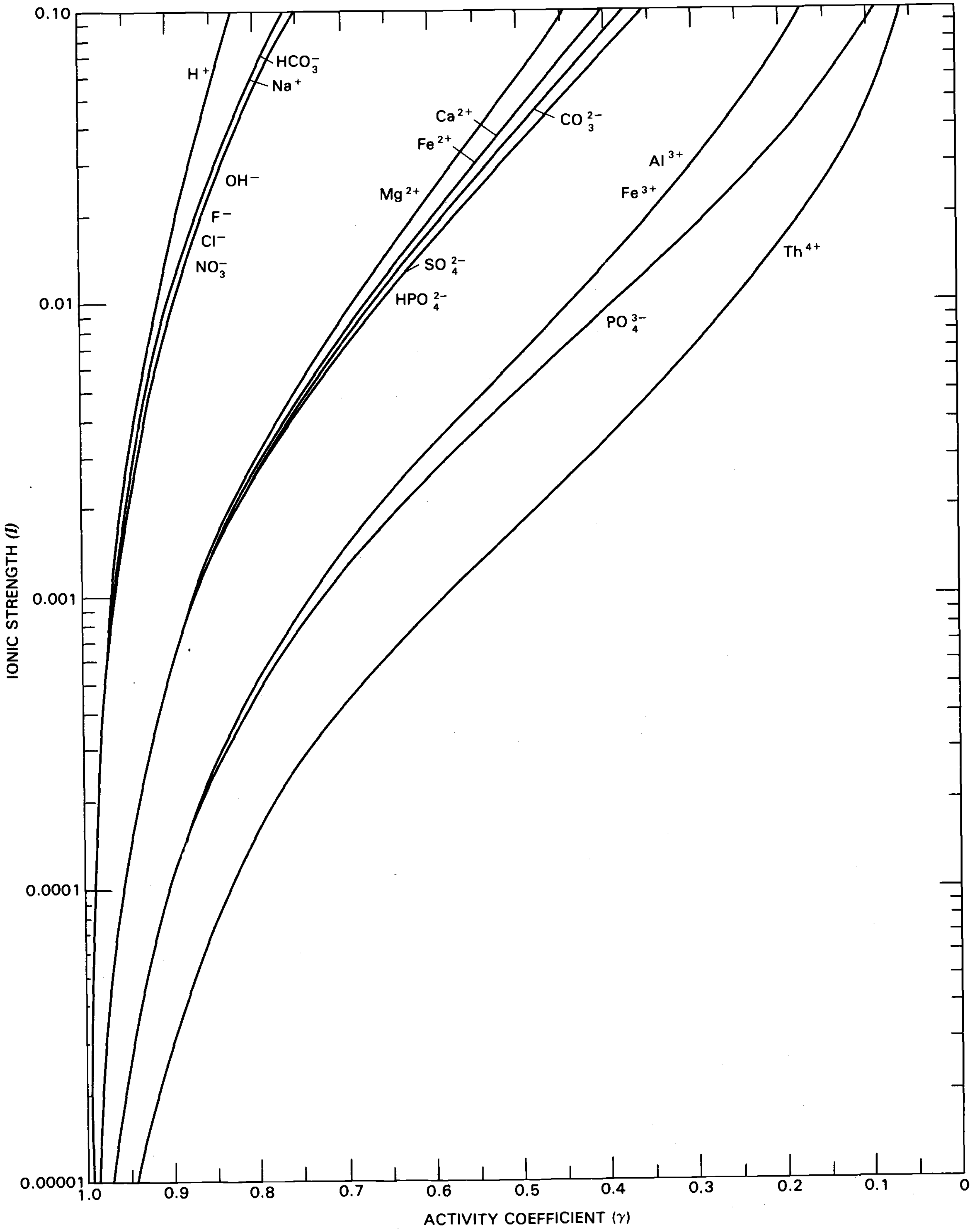

Figure 1. Relation of activity coefficients for dissolved ions to ionic strength of solution (25°C).

applicable at zero ionic strength provides the most versatile approach. Chemists working with more highly concentrated solutions such as seawater may prefer to use operational constants directly applicable to those solutions.

Effects of Temperature and Pressure on Chemical Equilibria

Many of the calculations and examples given in this book were made by assuming standard conditions (25°C and 1 atmosphere pressure). The effects of moderate departures from standard conditions (a few atmospheres pressure and ±10° or 15°C) can be ignored for many practical applications. Unavoidable errors of sampling and analysis generally can be expected to affect equilibrium calculations for many systems at least as much as these small departures from standard temperature and pressure. However, some systems are highly sensitive to temperature, and for some purposes the approximate treatment that results from ignoring temperature effects is not adequate. Unfortunately, carbonate systems are among the more sensitive ones in this respect.

Temperature affects the parameters A and B in the Debye-Hückel equation, and values are in the literature (Garrels and Christ, 1964, p. 61) for temperatures other than 25°C. The value of A ranges from 0.4883 at 0°C to 0.5425 at 60°C, but the value of B changes only from 0.3241 to 0.3338. The effect of temperature on activity coefficients is therefore relatively minor, and often it can be ignored. The relationship between temperature and the equilibrium constant has been determined experimentally for some of the more important reactions of interest in natural-water systems or can be derived from data compilations such as that of Sillen and Martell (1964). Methods of developing mathematical relationships between log K and temperature from data compilations are briefly described by Truesdell and Jones (1974).

If standard enthalpy ($\Delta H°$) values are available for the reacting species, and if pressure remains constant (near 1 atmosphere), those values may be used to compute a value for $\Delta H°_R$ by a summation like that used to compute $\Delta G°_R$. From a thermodynamically derived relationship known as the van't Hoff equation, one may relate equilibrium constants K_1 (at temperature 1) to K_2 (at temperature 2) as follows:

$$\log K_2 - \log K_1 = \frac{\Delta H°_R}{2.303R} \cdot \frac{T_2 - T_1}{T_1 T_2},$$

where the temperature values T_1 and T_2 are in Kelvins and $\Delta H°_R$ is in calories/mole. R has a value of 1.987 calories per degree per mole. This form of the van't Hoff equation assumes that $\Delta H°$ is essentially constant between T_1 and T_2. This approximation is applicable over temperature ranges to be expected in most natural water. A more complex form of the equation that can be used over wider temperature ranges is given in standard textbooks on physical chemistry (for example, Glasstone and Lewis, 1960, p. 318).

In systems that include a gas phase, the activity of gaseous components is represented by their partial pressures:

$$\frac{\text{Volume percent} \times \text{total pressure (atmospheres)}}{100}$$

In such systems the total pressure has obvious influences. The definition of standard state, however, also implies that equilibrium constants may be different at pressures differing from 1 atmosphere in all chemical systems. The effect of pressure of a few atmospheres on equilibrium constants in condensed systems is not large enough to require consideration for most purposes. Methods for applying corrections to basic thermodynamic data to incorporate nonstandard pressures were summarized by Garrels and Christ (1964, p. 331–351).

In applications of chemical equilibrium calculations that will be described later in this book, temperature effects will be taken into account where essential and appropriate. Pressure effects are generally not considered unless gases are involved.

Solution of Calcite

The use of mass-law calculations in natural-water chemistry can be conveniently illustrated for a system containing no gas phase, where solid calcite and water are present. The solution of calcite follows the chemical equation

$$CaCO_3(c) + H^+ = Ca^{2+} + HCO_3^-.$$

An equilibrium will be attained, with the H^+ derived from the water or other source attacking the solid to give calcium and bicarbonate ions. In mass-law form, the equation for the equilibrium constant will be

$$K = \frac{[Ca^{2+}][HCO_3^-]}{[CaCO_3(c)][H^+]}.$$

The quantities in square brackets represent activities in moles per liter. The activity of the solid is taken as unity. It is essential that some solid calcite be present to have equilibrium, but the total quantity need not be specified because the equilibrium condition is independent of the amounts of the phases present in the system.

The requirement that specified solids actually must be present is easily overlooked, and information on solids is obviously not given in the usual water analysis. Without reasonable assurance that solids specified are present, the application of equilibrium calculations may be misleading.

The equilibrium constants that have been published for a great many reactions have been compiled by Sillen and Martell (1964, 1967). Critical compilations by Smith and Martell (1976) and by Baes and Mesmer (1976) give values believed by the compilers to be the most reliable. A large number of equilibrium constants as functions of temperature, and of pressure in some instances, are available in equilibrium computer programs such as WATEQF (Plummer and others, 1976) and SOLMNEQ (Kharaka and Barnes, 1973). The value for a particular reaction, however, may not always be available. Sometimes a simple series of additions or subtractions of equilibria for which constants are known will yield the desired value, for example,

$$CaCO_3(c)=Ca^{2+}+CO_3^{2-} \qquad K_1=3.80\times10^{-9}$$

$$HCO_3^-=CO_3^{2-}+H^+ \qquad K_2=4.68\times10^{-11}$$

If the second equilibrium is subtracted from the first, we obtain

$$CaCO_3(c)+H^+=Ca^{2+}+HCO_3^-.$$

The equilibrium constant for the combined reaction is obtained by dividing the equation for K_1 by the equation for K_2:

$$\frac{[Ca^{2+}][CO_3^{2-}]}{[CaCO_3(c)]}\div\frac{[CO_3^{2-}][H^+]}{[HCO_3^-]}=\frac{3.80\times10^{-9}}{4.68\times10^{-11}}=0.81\times10^2.$$

At equilibrium in the calcite + water system then, the activities of solutes are related by the equation

$$\frac{[Ca^{2+}][HCO_3^-]}{0.81\times10^2}=[H^+].$$

This type of relationship can be used to test whether a given water is unsaturated and can dissolve more calcite (at the temperature at which K_1 and K_2 were determined, here 25°C), is supersaturated and can precipitate calcite, or is at equilibrium. A measurement of pH, calcium and bicarbonate concentrations, and temperature and ionic strength will give this information. From the product of activity of calcium and bicarbonate and the value of K, the equilibrium value for $[H^+]$ or pH can be computed. The difference between this computed pH and the actual measured value is equal to the saturation index, S.I., which also can be defined as $\log Q-\log K$.

The conventions followed in this derivation result in positive values for the saturation index, indicating that the reaction as written is thermodynamically favored to proceed to the left (supersaturation).

In water treatment processes, a finished product with a slight degree of calcite supersaturation is usually desired. This is indicated by a positive value for S.I. computed from

$$pH(meas)-pH(equil)=S.I.$$

The quantity S.I. computed this way is sometimes referred to as the "Langelier index" (Langelier, 1936) in the technology of water-supply treatment. This method of calculating S.I. obviously is not valid for equilibria in which $[H^+]$ does not appear. Methods for computing saturation indices and related quantities will be considered further in a later section of this book.

The value used for K_1 above was determined by Jacobson and Langmuir (1974), who also gave values for the constant of 4.47×10^{-9} at 0°C and 2.32×10^{-9} at 50°C. Values for K_2 for temperatures other than 25°C are readily available (Sillen and Martell, 1964, p. 133–135). Selected data are given in table 33.

In the section of this book dealing with calcium chemistry, a more detailed development of calcite solubility equilibria is given, and a simple graphical procedure is derived that can be used to estimate calcite saturation status for any temperature between 0°C and 50°C corrected for effects of ionic strength up to 0.5.

Free Energy and the Equilibrium Constant

The quantity $\Delta G°_R$ has previously been defined as a measure of the thermodynamic driving force available for a given reaction going from left to right when all the reacting species are present in standard states. It has been shown mathematically that $\Delta G°_R$ has the following relation to the equilibrium constant:

$$-\Delta G°_R=RT\ln K,$$

where R is the gas constant, a conversion factor for the units in which the other quantities are expressed, T is temperature in kelvins, and $\ln K$ is the natural logarithm of the equilibrium constant. When a temperature of 25°C is specified (298.15°K) and base-10 logs are used, the expression becomes

$$-\Delta G°_R=1.364\log K,$$

when $\Delta G°_R$ is in kilocalories per mole. For data given in kilojoules per mole, the expression becomes

$$-\Delta G°_R=5.707\log K.$$

These are important and useful relationships because they can be used to calculate equilibrium constants for a wide variety of possible chemical reactions. Compilations of ΔG° values for elements, compounds, and aqueous ions that can be used for this purpose are available. The better known and more useful ones include Robie and others (1978), Naumov and others (1974), and chapters 3-6 of NBS Technical Note 270 (Wagman and others, 1968, 1969, 1971; Parker and others, 1971).

Data of this kind are not available for all chemical substances, and some of the existing thermodynamic values are rather inaccurate. Several authors have suggested methods for estimating some of the missing numbers. Latimer (1952) made a considerable number of estimates of ΔG° and S°, and more recently Tardy and Garrels (1974, 1976, 1977), Chen (1975), and Nriagu (1975) have proposed new methods for estimating thermodynamic data for silicates and other species of geochemical interest.

As an illustration of the application of free energy data, it may be of interest to review the calcite dissolution reaction,

$$CaCO_3(c)+H^+=Ca^{2+}+HCO_3^-.$$

Standard free energy of formation values for the participating species (Wagman and others, 1968; Parker and others, 1971) are as follows:

Species	ΔG°_f
$CaCO_3$(c) (calcite)	-269.80 kcal/mol
H^+	0 (reference state)
Ca^{2+}	-132.30
HCO_3	-140.26

$$\Delta G^\circ_R=-132.30-140.26-(-269.80)=-2.76$$

$$\log K=\frac{-(-2.76)}{1.364}=2.02$$

$$K=1.05\times10^2$$

This value for the equilibrium constant compares with 0.81×10^2 for 25°C computed from solubility studies by Jacobson and Langmuir (1974). Differences of this sort are large enough to be of concern for many purposes. However, the compilations of free energy data can be used to make many useful theoretical evaluations of chemical processes that might control natural-water composition. Where appropriate, extensive arrays of equilibria may be set up and solved simultaneously, or a given water composition can be tested for possible equilibrium with a long list of mineral species. Computations of this type are routine tasks for modern computer technology, and a large number of programs have been set up to perform them (Nordstrom, Plummer, and others, 1979). Most such computations, however, postulate the widespread existence of equilibrium in the natural systems being modeled. The extent to which such assumptions may be valid remains uncertain and controversial. Ways of treating various kinds of systems with respect to equilibrium thermodynamics will be considered more closely later in this book.

The attractiveness of thermodynamic models and calculations is evident in current literature. but it must be remembered that actual measurements and observations are preferable to computed numbers when it is possible to make them. Some properties of natural systems are difficult to measure, but there is little justification for failure to measure important variables that are readily accessible in field and laboratory experiments.

Obviously, calculations made with standard Gibbs free energies are fully valid only for systems at 25°C and 1 atmosphere. Performing calculations that are valid for other temperatures requires thermodynamic data that are applicable at those temperatures. Methods for calculating ΔG values from experimental data over a range of temperatures above 25°C were summarized by Robie and others (1978), and the other compilations referred to give some consideration to this. Naumov and others (1974) gave ΔG estimates for many solutes at temperatures other than 25°C.

An important caveat should be noted here. Thermodynamic data compilations like the ones referred to above are produced for the most part from calorimetric measurements and data, beginning with simple systems and using the results to develop values for the more complex ions or compounds. The computation of ΔG°'s from equilibrium solubility data, like those based on calorimetry, must use the same fundamental thermodynamic data throughout this chain of calculations. Although all compilers make efforts to avoid such internal inconsistencies, it seems nearly impossible to eliminate them completely. Before using ΔG° values from different sources in the same computation, one must be sure they are compatible in this sense.

Electrochemical Equilibrium

Chemical reactions in which a participating element changes valence number, losing or gaining orbital electrons, are referred to as oxidations or reductions. In oxidation an element loses electrons, and in reduction it gains them. The reduction process can be represented by an expression such as

$$Fe^{3+}+e^-=Fe^{2+},$$

where ferric iron is reduced to the ferrous state. A further reduction,

$$\mathrm{Fe}^{2+}+2e^{-}=\mathrm{Fe}^{0},$$

would carry the ferrous ion to metallic iron. The symbol "e^{-}" represents the electron, or unit negative charge.

These representations are "half-reactions," or redox couples. To take place, a reduction requires a source of electrons. This source may be another element that is simultaneously oxidized, or it could be an actual source of electric current.

Under standard conditions, 25°C and 1 atmosphere, and with unit activity of reactants, it follows that at equilibrium a certain electrical potential would be present in a couple such as

$$\mathrm{Fe}^{2+}+2e^{-}=\mathrm{Fe}^{0},$$

and this standard potential is conventionally represented by the symbol $E°$. The potential is given in volts, with the potential of the hydrogen electrode, representing the reduction of H^{+} ions to H_2 gas,

$$2\mathrm{H}^{+}+2e^{-}=\mathrm{H}_2(\mathrm{g})$$

taken as zero.

The sign of the potential associated with a half-reaction written as a reduction is negative if the system is reducing and positive if the system is oxidizing. The magnitude of the positive or negative value is a measure of the oxidizing or reducing tendency of the system. Tables of standard potentials are available in reference books such as Latimer (1952) and Sillen and Martell (1964). The sign convention used by Latimer results in his data having signs opposite the ones given in most other standard references.

When the activities of participating species in a system differ from unity, the potential observed at equilibrium is termed the "redox potential." The redox potential, represented by the symbol Eh, is related to the standard potential and to the activities of participating substances at thermodynamic equilibrium by the Nernst equation.

The general thermodynamic relationship on which the Nernst equation is based is similar to that used in the thermodynamic derivation of the mass law. It can be stated

$$\Delta\mu_R=\Delta G°_R+RT\ln\frac{\alpha_{\text{reduced species}}}{\alpha_{\text{oxidized species}}\times\alpha_{e^-}}.$$

The activity terms include all the species given in the particular half-reaction of interest. The above statement is intended to indicate that activities of all species on the reduced side of the reaction are in the numerator and all those on the oxidized side are in the denominator.

The electron activity drops out of this expression. When all species are at standard states,

$$\Delta G°_R=\Sigma\Delta G°_{\text{red}}-\Delta G°_{e^-}-\Sigma\Delta G°_{\text{ox}}$$

and

$$\Delta G°_{e^-}=0.$$

The thermodynamic equilibrium condition for the couple requires that $\alpha°_{e^-}=1$ so that the redox status of the couple can be expressed in terms of the solute species.

To convert the energy units from thermal to electrical ones, the relationship

$$-\Delta G_R=nFE$$

is substituted for ΔG_R and $\Delta\mu_R$ terms in the thermodynamic expression to give

$$-nFE=-nFE°+RT\ln\frac{\alpha_{\text{red}}}{\alpha_{\text{ox}}}.$$

F in these expressions is the faraday constant, n is the number of electrons appearing in the balanced half-reaction, and E is the electrical potential. Dividing by $-nF$ and inverting the logarithmic term gives the Nernst equation,

$$E=\mathrm{Eh}=E°+\frac{RT}{nF}\ln\frac{[\text{oxidized}]}{[\text{reduced}]}.$$

The same form of the Nernst equation would be obtained if the half-reaction were written as an oxidation if the conversion of the units were made by specifying that

$$+\Delta G°_R=nFE°.$$

The convention of writing half-reactions as reductions is used by the writer in this book and in other papers involving redox computations. The designation "Eh" is used for redox potential, also by convention.

The bracketed quantities are the activities of participating solutes. At the standard temperature of 25°C, with base-10 logarithms instead of natural logarithms, this expression becomes

$$\mathrm{Eh}=E°+\frac{0.0592}{n}\log\frac{[\text{oxidized}]}{[\text{reduced}]}.$$

The Nernst equation is derived from thermodynamic principles and is applicable only to solutions and associated species when chemical equilibrium has been established. It should be noted, however, that the electron does not appear as a reactant in the log term of the Nernst equation.

As noted, for a reduction actually to occur, a source of electrons must be available. For example, ferric iron might be reduced to the ferrous state in a reaction in which organic carbon is being oxidized. The complete reaction can be evaluated by means of the mass law.

Standard potentials are not always available for half-reactions of interest, but usually they can be computed from the relationship

$$-\Delta G^\circ_R = nFE^\circ,$$

where E° is the standard potential. If E° is to be in volts, when ΔG°_R is in kcal/mole

$$E^\circ = \frac{-\Delta G^\circ_R}{23.06n}.$$

For this to give the correct sign, the half-reaction must be written as a reduction.

With these equations and free-energy data from the literature, one can estimate equilibrium ion activities and redox potentials for a great many systems of geochemical interest. As in similar calculations based on the law of mass action, the application of such estimates to natural systems may furnish useful guidelines as to what to expect. Calculations based on the Nernst equation have been particularly useful, for example, in studying the chemistry of iron in ground water.

Practical measurement of a redox potential poses some important problems. Direct measurement of Eh in the ground-water environment (actually, in the aquifer) is generally not feasible with presently available instrumentation. Measurement of Eh of pumped ground water requires special equipment and exercise of great care to prevent contact with air. Such measurements and their limitations are discussed in the section titled "Redox Potential."

Another form of expressing redox potential was favored by Sillen (1967b), and through his advocacy it has been used widely in recent geochemical literature. Basically, this nomenclature writes electrochemical potentials in terms of the negative base-10 logs of "activities of electrons" per liter, represented by the symbol pE. Under standard conditions, when Eh is in volts,

$$\mathrm{pE} = \mathrm{Eh}/0.0592.$$

The use of pE in this way avoids some mathematical steps in calculations that use redox equilibria along with other types of reactions. It does not appear to have been used much outside the general field of aqueous environmental chemistry, however. The thermodynamic implications of the concept of activity of aqueous electrons seem not to have been fully explored by proponents of this nomenclature. Electrons may be transferred from one aqueous ion to another or to a solid surface component during chemical reactions, but they do not exist independently in the solution and can have no activity there in the sense that the participating solutes do. These complications can perhaps best be avoided by using the standard Nernst equation approach, and applications of electrochemical calculations in this book do not use the pE convention. Hostettler (1984) has reviewed the theoretical background of these conventions.

Disequilibrium Indices

The extent and direction of departure from equilibrium for a given chemical system can be represented in several ways. Some of these have been derived and demonstrated in foregoing sections of this book. A brief review of this topic and of some other nomenclature that has been used elsewhere is appropriate.

A strictly chemical procedure for evaluating departure from equilibrium is the saturation index, S.I. This is the difference between the logs of the activity quotient, Q, and the equilibrium constant, K:

$$\mathrm{S.I.} = \log Q - \log K = \log (Q/K)$$

A positive value for S.I. indicates that the solution is supersaturated and the reaction should go in the direction that will precipitate more solid. For the calcite dissolution process given as an example, the reaction is written

$$\mathrm{CaCO_3(c)} + \mathrm{H^+} \rightleftharpoons \mathrm{Ca^{2+}} + \mathrm{HCO_3^-},$$

and a positive S.I. would favor the reaction going to the left. The S.I. is a dimensionless number. It should probably be reserved for evaluating solubility equilibrium systems.

The reaction affinity **A** which was defined earlier as

$$\mathbf{A} = -RT \ln (Q/K)$$

or, at 25°C for base-10 logs and kcal/mole,

$$\mathbf{A} = -1.364 (\log Q - \log K).$$

This is essentially a statement of S.I. in terms of energy units. The sign convention used, however, is different in that a positive value for **A** denotes favorable energy conditions for the reaction to proceed to the right, as written.

Some writers have used systems of notation that do not clearly distinguish between ΔG's as free energies of individual reactants and the free energy difference for the reaction, ΔG_R, or have defined ΔG_R as an index of disequilibrium equivalent to $\Delta \mu_R$ as defined here. Earlier we defined chemical potential (μ) as the partial molal free energy of individual reactants and products. A summation of these values for products in the reaction minus the values for reactants is equivalent to $\Delta \mu_R$. When all participants are at standard states, this summation gives a value equivalent to ΔG°_R.

Disequilibrium indices expressed in energy units can be used to compare the relative feasibility of chemical reactions in complicated systems and provide a useful tool for developing mathematical models of such systems.

Thermodynamics of Nonequilibrium Systems

The chemical derivation of the mass law and much of the literature on equilibrium chemistry stress a dynamic hypothesis for the equilibrium condition. This hypothesis requires that a reaction proceed reversibly at equilibrium. The thermodynamic view of the equilibrium condition does not imply a chemical mechanism. From this point of view, a reaction can continue in one direction as long as **A** remains positive. This can form the basis of application of the second law of thermodynamics to irreversible processes. As has been mentioned before, natural-water chemistry probably is influenced by many irreversible processes, and techniques for studying them more effectively are needed. A final value of zero for **A** is probably rather seldom attained. In some kinds of irreversible processes, one reactant would have to be totally removed to attain this level of reaction affinity.

For many natural chemical systems, the effects of energy and material inputs and the feedbacks from various thermodynamically feasible processes will tend to maintain a more or less continuous steady state that can be observed, while many reaction affinities for specific processes maintain values greater than zero. Some theoretical concepts applicable to such systems have been summarized by Prigogine (1978).

Many possibilities obviously exist for the application of nonequilibrium models in natural-water chemistry, but very few examples can be found in published literature. The writer has applied a nonequilibrium model to explain the oxidation behavior of manganese (Hem, 1980), and some general observations related to clay mineral–water interactions were made by Pačes (1978). Earlier, more general treatments of the topic were published by Helgeson (1968) and by Helgeson and others (1969) and, more recently, by Lasaga and Kirkpatrick (1981).

Rates of Chemical Reactions

As noted earlier, a chemical reaction can occur spontaneously in a closed system when the total free energy of reactants exceeds that of the reaction products. The chemical equation representing such a process and standard free energy data for participating species can be used to determine whether the reaction can be spontaneous. However, finding that a given reaction is thermodynamically favorable gives only a limited amount of information that can be used to predict how fast the process will occur. In fact, many feasible reactions do not occur at significant rates, and some consideration of reaction rate theory and application is necessary in a study of natural-water chemistry.

Most chemical reactions occur in a series of steps, some of which are likely to require an energy input. The stepwise mechanisms involved in going from initial reactants to final products are somewhat analogous to a roadway leading across a series of hills and valleys. The final destination can be lower in elevation than the starting point, but energy must be expended in climbing the hills. A high energy barrier in the early steps of a process may prevent the reaction from proceeding. However, energy released in later steps may feed back to greatly increase the rate once such a reaction has begun.

A mechanical analogy to this kind of feedback effect is evident in a long freight train traversing a mountain pass. As the locomotive reaches the summit and starts downgrade, the kinetic energy of that part of the train moving downhill becomes available to help move the remaining part of the train still on the uphill portion of the track.

Thermodynamic principles have many uses in studies of reaction rates. However, quantitative evaluation of rate processes requires careful attention to details of reaction mechanisms so that the actual rate controls can be determined and understood. Many natural processes occur in open systems, and the potential for energy input, or alteration of reaction paths by biota, also must be taken into account. For these and other reasons, the development and application of kinetic models in natural-water chemistry has not progressed very far.

Rate Constants: Order of Reaction

The rate at which a chemical reaction occurs can be observed in a controlled system by noting the rate at which a reactant disappears or the rate at which a product is formed. In an irreversible chemical process (one in which products are removed from the reaction site or back-reaction effects, for whatever reason, do not influence the system significantly)

$$aA \rightarrow \text{products}$$

the rate of reaction of A can be represented as

$$-\frac{d[A]}{dt}=k[A]^a.$$

The rate constant, k, and the exponent, a, are proportionality factors that must be determined experimentally. When the value of the exponent, a, is unity, the process is termed "first order" in A. This implies that the rate of the process as written, at constant temperature and pressure, is a function only of the concentration of A and that the ions or molecules of A do not interact with each other during the process.[1] It is possible for a process to be second order in A (when a=2), implying that two ions of A must interact to create a product. Another type of second-order process is one involving two reactants:

$$aA+bB \rightarrow \text{products}.$$

The rate of such a reaction, where a and b are both unity, would be

$$\frac{-d[A]}{dt}=\frac{-d[B]}{dt}=k[A][B].$$

Higher reaction orders could occur, in the event that a and (or) b in the above schematic reaction are greater than 1. Usually such processes are better described by simplification, to consider the process as occurring in steps having first- or second-order properties.

Zero-order reactions also can occur and are of substantial interest in some kinds of natural-water systems. In a zero-order reaction, the rate is independent of concentration of the reactant considered. For the decomposition of A,

$$-\frac{d[A]}{dt}=k.$$

Such a process might occur when the concentration of A is always very small compared with that of another reacting substance. There are some processes whose rate is controlled by availability of reaction sites at a solid surface. These could display zero-order kinetics if the number of sites is always large compared to the concentration of A.

Fractional reaction orders also can be observed for some processes. Generally these involve combinations of several reaction steps or effects that are not entirely chemical in nature, such as diffusion or mixing rate. In evaluating the kinetic properties of any chemical process it is most important to consider the effects of complications like these. Commonly, one step in the process can control the rate and order of the whole reaction. This is known as the rate-determining step.

Integration of the first-order rate expression leads to

$$kt=2.303\log\frac{[A]_0}{[A]_t},$$

where $[A]_0$ is concentration of reactant A at t=0 and $[A]_t$ is its concentration at time=t. From this expression it is evident that the rate constant will be in units of reciprocal time and that the fraction of reactant A disappearing is a function of the time interval, t. A useful measure of the rate of a first-order process, therefore, is the time required for a specific fraction of the reactant to disappear. For instance, the time required for half the amount of A present at any moment to disappear is

$$t_{1/2}=\frac{2.303\log 2}{k}=\frac{0.693}{k}.$$

The process of radioactive decay is a good example of first-order kinetics, and the rate is generally given in terms of half-life. A first-order process can be identified by this behavior. Plotting the log of the unreacted concentration of A versus time should give a straight line.

For the second-order reaction of the type

$$2A \rightarrow \text{products},$$

the expression for the rate of loss of A is

$$\frac{-d[A]}{dt}=k[A]^2.$$

Integration of this equation leads to

$$kt=\frac{1}{[A]_t}-\frac{1}{[A]_0}=\frac{[A]_0-[A]_t}{[A]_0[A]_t}.$$

For this kind of process, a plot of $[A]_t^{-1}$ versus time should give a straight line, but the intercept will depend on $[A]_0$. Hence, the time for a specific fraction of A to disappear will be different for different starting concentrations of A. The behavior of reactants in second-order

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[1] For this discussion of kinetics in aqueous solution, ideal thermodynamic behavior, concentration≡activity, is implied. Fundamentally, however, kinetic models are based on measured concentrations of reacting species. The effects of ionic strength on reaction rates are discussed by Benson (1960, p. 525) and in other texts on chemical kinetics. The topic is beyond the scope of this brief treatment.

processes can thus be expected to differ substantially from that observed in first-order processes.

For a second-order process of the type

$$aA+bB \rightarrow \text{products},$$

the rate expression after integration gives

$$kt=\frac{2.303}{[A]_0-[B]_0}\log\frac{[B]_0[A]_t}{[A]_0[B]_t}.$$

Rate constants and reaction order and mechanisms are generally determined in laboratory experiments in which as many of the variable quantities as possible are controlled. Rate data of a qualitative nature, and sometimes useful quantitative information, can be derived from careful field observations. A field study of sulfide oxidation rates in an inactive mining area in Shasta County, Calif., by Nordstrom (1977) is an example.

The application of laboratory values to natural systems is not always practicable, but knowledge of the relative importance of kinetic factors and plausible reaction mechanisms is essential to understanding "real-world" conditions.

A summary of studies of kinetics of a specific process is sometimes expressed in terms of a rate law, in which the behavior of a component is equated to a series of rate constants multiplied by reactant and product activities.

Effect of Temperature on Reaction Rate

The rates of most chemical reactions are rather highly sensitive to temperature. Commonly, an increase of 10°C can double the rate of a reaction. Some insight into the thermodynamics of reaction steps can be gained by determining rate constants at different temperatures and applying the Arrhenius equation to the results. This relationship is

$$k=Ae^{-E/RT},$$

where A is the "frequency factor" related to the probability of conditions favorable for a reaction to occur, e is the base of natural logarithms, R and T have their usual meanings, and E is an energy term, called the activation energy. By rearrangement of the equation, it can be shown that a plot of log k versus T^{-1} should be a straight line, and its slope and intercept can be used to compute E and A, respectively.

The potential for thermodynamic interpretation of numbers derived from the Arrhenius equation is somewhat obscure, but a large value for activation energy, derived from a strong dependence of rate constants on temperature, does have useful implications. Such a relationship suggests the existence of a high energy barrier at some step in the reaction path.

Chemical Kinetics and the Law of Mass Action

In deriving the law of mass action it was noted that the equilibrium constant is conceptually the ratio of rate constants for the forward and reverse reactions. Kinetic equations developed here, however, represent irreversible processes and can be applied in systems in which the back reaction does not have a major effect.

The chemical process summarized in a mass-law equilibrium can be adequately treated by thermodynamic methods that have been described. The resulting ΔG°_R, or equilibrium constant, is a summary of what might, under more careful study, turn out to be a complicated series of stepwise reactions. A kinetic model applied to a summarizing equilibrium reaction is not likely to be meaningful or useful. Instead, the reaction mechanism must be looked at in detail, and kinetic data must be derived for the significant parts of it.

For these reasons, models using concepts of kinetics have great potential for determining how natural processes that control water composition operate. Some further aspects of the application of theoretical models to natural-water systems will be discussed in other parts of this volume.

Solubility Concepts

The chemist generally defines solubility in terms of equilibrium. Solubility represents the total amount of solute species that can be retained permanently in solution under a given set of conditions (fixed temperature and pressure) and in the presence of an excess of undissolved material of definitely known composition and crystal structure from which the solute is derived. A full elaboration of the concept and its application to mixed solutions, such as natural water, is beyond the scope of this book. However, the factors that control the amounts of the major and minor inorganic constituents of natural water are a subject of fundamental concern in this discussion, and the term "solubility" will be used frequently in discussing the behavior of individual constituents.

Water analyses are expressed in terms of concentration of elements or of ions, sometimes implying a single species or form of constituent and sometimes indicating only the totality of an element present without regard to the species. Actually, however, the common analytical procedures are designed to determine total concentrations and do not necessarily provide indications of species. For example, chloride concentrations reported in a chemical analysis include the amount of chloride present as free Cl^- ions as well as any that might be present as ion pairs or as complexes with metals. When the term is used in this discussion, solubility will include all forms of a particular element or ion that can be considered to be present as solutes but will not include amounts present as suspended solid particles.

Solubility Product

A solubility product is an equilibrium constant for the solution of a compound that dissociates into ions. For example, the chemical equation representing the dissolution of gypsum is

$$CaSO_4\ 2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O,$$

and the corresponding solubility product expression is (with water having unit activity)

$$[Ca^{2+}][SO_4^{2-}] = K_{s0}.$$

Solubility products have been determined for a great many inorganic compounds of interest in natural-water chemistry. Certain precautions must be observed when applying them, however. By definition, the solubility product represents a reversible equilibrium. The solid is pure and has a known crystal structure. The ions involved have specific forms, and, as indicated by the brackets, they participate in proportion to their thermodynamic concentrations (activities).

Some of the adjustments required to reconcile solubility-product calculations with actual determined concentrations can be illustrated with the gypsum solubility product. Suppose one wishes to test a particular water analysis for saturation with respect to gypsum and that thermodynamic data applicable at the temperature of the water are available. The analysis should provide enough information to compute an ionic strength, and values for activity coefficients if the reported ionic concentrations accurately represent the species actually present. Analytical data cannot be directly used for computing activities of the species Ca^{2+} and SO_4^{2-}, however, because interaction between the ions gives rise to an ion pair,

$$Ca^{2+} + SO_4^{2-} = CaSO_4^0.$$

An equilibrium expression for the stability of the ion pair, representing the reverse of the above reaction, may be written

$$K = \frac{[Ca^{2+}][SO_4^{2-}]}{[CaSO_4^0]}.$$

Conversion of total analytical concentrations of calcium and sulfate to activities is mathematically represented as

$$C_{Ca}(\text{total}) = \frac{[Ca^{2+}]}{\gamma_{Ca^{2+}}} + \frac{[CaSO_4^0]}{\gamma_{CaSO_4^0}}$$

and

$$C_{SO_4}(\text{total}) = \frac{[SO_4^{2-}]}{\gamma_{SO_4^{2-}}} + \frac{[CaSO_4^0]}{\gamma_{CaSO_4^0}}.$$

If no other ions are present to form complexes with calcium or sulfate, the three equations containing activity (bracketed) terms above should describe the aqueous chemical species adequately. The equilibrium constants needed can be found in data compilations such as that of Smith and Martell (1976), $C_{Ca^{2+}}$ and $C_{SO_4^{2-}}$ are known, and $\gamma_{CaSO_4^0}$, the activity coefficient for the uncharged ion pair, can be assumed to be unity. There remain five unknown terms, including two activity coefficients, for which initial estimates can be made by ignoring $CaSO_4$ ion pairing. Thus, there are three unknowns to be determined and three equations that may be solved simultaneously. The activity of $CaSO_4^0$ thus obtained can be used to correct the initial estimate of ionic strength, and the whole computation repeated until further recycling does not change the calculated activities of calcium and sulfate. These can then be used to compute an activity product for comparison with the solubility product for gypsum.

When other cations and anions are present in large amounts, more ion pairs must be taken into account by adding them as terms to the equations for $C_{Ca^{2+}}$ and $C_{SO_4^{2-}}$ and by including stability equilibria for them in the calculations. In principle, the method is applicable to highly complicated systems, and it becomes desirable in practice to program the equations for an electronic computer.

Reactions at Interfaces

The surfaces at which water is in contact with solid phases or gases represent sites of critical importance in both physical and chemical processes.

Gas-Liquid Interfaces

The surface of a body of water in contact with the atmosphere at standard pressure and temperature is rather rigidly maintained by intermolecular forces, as shown by the surface tension of water, which is 72.2 dynes per centimeter at 20°C, a value higher than that of most liquids. Water molecules, however, are able to pass through this surface into the air, and gas molecules from the air can diffuse into the water. Both processes tend to produce mutual saturation near the interface. Rates of absorption of gases by water or rates of evaporation of water are functions of the characteristics of the system. Important factors in both kinds of rates are the total area of interface, the degree of departure from saturation just beyond the interface, and the rate at which the molecules of the dissolved or vaporized phase are transported away from the interface. The transport rate could be slow if it depended solely on molecular diffusion. In most natural systems, however, motion of the gas or liquid phase helps to move the evaporated or dissolved material away from the interface.

The processes by which gases from the atmosphere dissolve in water are of direct concern in water quality. The solution of oxygen in stream or lake water is dependent on such physical and chemical characteristics as area of interface, mechanisms of transport away from interface, temperature, and pressure. Because dissolved oxygen is essential to the clean-water organisms that thrive only under oxidizing conditions, the occurrence, solution, and transport of oxygen are important to the study of biochemical processes relating to water pollution. The process of photosynthesis is a major source of oxygen in some water bodies, and oxygen concentration is not a function simply of assimilation of atmospheric gases at a liquid-gas interface. However, nonbiological exchange across the interface is of fundamental importance. Langbein and Durum (1967) reviewed some properties of stream-channel geometry and streamflow rates as they apply to the effectiveness of rivers in absorbing oxygen from the air. Understanding systems of this kind entails consideration of rates and the way in which the rate of one process may limit the rate of another.

Some gases, notably carbon dioxide, react with water, and their rate of assimilation is affected by subsequent changes in form. Carbon dioxide is an important participant in many geochemical processes.

In general, the solubility of a gas in water at constant temperature is proportional to the pressure, in atmospheres, of the gas phase in contact with the water (Henry's law). For a mixture of gases, the effective pressure of each component is proportional to its fraction, by volume, in the mixture. The partial pressure (*P*) of a gaseous component is its volume percentage × total pressure, in atmospheres, × .01.

For carbon dioxide, the solubility relationship may be written

$$CO_2(g)+H_2O=H_2CO_3(aq)$$

$$K_h=\frac{[H_2CO_3]}{P_{CO_2}}.$$

The further reaction of $H_2CO_3(aq)$ produces other dissolved species, but the amount of dissolved carbon dioxide in undissociated form is accurately predicted by the value of K_h, which is known for a wide range of temperatures. Values for K_h in table 33 entail the conventional assignment of all undissociated aqueous CO_2 to the H_2CO_3 form.

Liquid-Solid Interfaces

Interactions that occur at interfaces between solid and solution phases obviously are important. Any reaction involving dissolution or precipitation of a solid ultimately occurs at such an interface. Also of interest here, however, are reactions of a different type, reactions that do not destroy old or build up new surface. The solid surface exposed to the solution is covered with a tightly bound layer of water molecules, and also near or within this layer are solute ions or molecules held by electrostatic attractive forces of various types. The solute species at the interface may be removed or exchanged for other solutes without greatly affecting the properties of the solid surface. These processes are generally called adsorption, implying that they occur at the water-solid interface, or sometimes, more vaguely, "sorption", which is a more noncommittal term that could include other processes.

The most abundant rock and soil minerals are silicates, aluminosilicates, and oxides or hydroxides. Structures of all these minerals are dominated by symmetrically arranged oxygen and hydroxide ions, with cations occupying interstices in the packed structure, their positive charges balancing the negative charges of the oxygens. Because of broken chemical bonds at crystal edges, lattice imperfections, or local charge imbalance caused by substitution of cations having lower valence numbers than needed to equal the oxygen charges, certain sites on the surface normally have rather strong negative electrical charges. In general, these oxygen-dominated surfaces will thus have a negative rather than a positive electrical charge.

Protons (H^+ ions) will be attracted to the more strongly charged sites, and the surface will thus have an apparent capacity for reversible participation in acid-base reactions. This property can be evaluated by titration experiments.

If the surface is immersed in an aqueous solution, a layer of immobilized water molecules will be accumulated on the surface, their positively charged sides turned toward the solid. The sites having a strong negative charge will attract cations from solution to attain a charge balance.

Properties that can be used to characterize surfaces include their area per unit weight of solid, the sign, intensity, and spatial distribution of charge sites, the specific interactions of various types of charge sites with the solute ions, and the free energy or other energy characteristics per unit area of interfacial surface.

Purely thermodynamic theoretical models of adsorption at mineral surfaces are beyond the scope of this discussion. This transition from the solution phase to the solid phase, however, can be represented in terms of energy, and this has useful implications in solution or deposition processes. A very finely divided precipitate, for example, may have a greater solubility than a precipitate that is identical in composition and structure but is present in larger crystals. This difference can be assigned to the surface free energy of the solid. The magnitude of this quantity (generally a few tens or hundreds of ergs per square centimeter) is too small to be noticed until the area per unit weight of solid becomes very large, as it would be, for example, if the mean diameter of solid particles were 0.1 μm or less. Some observations of this effect have been reported by Schindler (1967), Hostetler (1963), and many other investigators.

The area of solid surface per unit weight of solid is an essential characteristic in the study of solute-solid systems. Areas can be estimated by geometric assumptions about particle shape, if the mean diameter of particles is known. More useful estimates, however, can usually be made through measurements. The tendency for a gas or liquid phase to form a layer 1 atom or molecule thick over a solid surface is one basis for measurement. Adsorption of nitrogen gas on a surface after purging other material from the surface in a high vacuum is the basis of the so-called BET procedure for area measurement. The amount of nitrogen adsorbed is calculated from the change in weight of the solid sample, and the area covered by a monomolecular layer of this quantity of N_2 can then be computed. Methods in which monomolecular layers of organic dyes are adsorbed by solids suspended in aqueous solution are also used (Lawrie, 1961).

The assumed "monolayer" adsorption mechanism is sometimes called physical adsorption and is assumed not to be limited to specific sites. Theoretical assumptions obviously influence surface area measurements, and their physical meaning is thus somewhat qualitative. The term "van der Waals adsorption" is sometimes used to characterize these adsorption processes.

The surface charge on a solid particle may be positive or negative. The sign and intensity of the charge can be determined by studying the behavior of particles in an electrostatic field. Another property of interest is the behavior of charge sites toward solution species. This can be measured by various titration techniques applied to solid suspensions. One of the stronger effects is that due to solution pH. Characteristically, a solid will take up H^+ ions to neutralize negatively charged sites, and the pH at which the surface charge becomes neutral is called the "zpc," or zero point of charge. Specific interactions between other solute ions and binding sites at the solid surface occur. These are influenced by site characteristics, ionic charge and radius, degree of ion hydration, bond configuration, and other properties. A complicated interrelationship results, one that is difficult to model theoretically.

A general review of literature on adsorption processes and their significance in natural-water systems was prepared by Jenne (1975). An earlier paper by Parks (1967) reviewed the concepts of isoelectric point and zero point of charge as means of characterizing mineral surfaces. The broader topic of colloidal systems in relation to aqueous geochemistry was explored in a book by Yariv and Cross (1979). The general subject of surface chemistry is covered in the well-known text by Adamson (1976).

Adsorption Equations

Adsorption of a single solute species by a solid can be evaluated mathematically by several different types of equations. An adsorption isotherm is a mathematical equation for relating concentrations of adsorbed and free adsorbate at a surface at a constant temperature.

For the adsorption of solute A from solution by a mass of solid, m, one such relationship can be stated

$$\frac{\overline{A_x}}{m}=D[A],$$

where $\overline{A_x}$ is mass of solute adsorbed, D is the distribution coefficient, and $[A]$ is the active concentration of A in the solution. For most systems, D is constant only over a limited concentration range, especially if the quantity $\overline{A_x}/m$ is a simple mass ratio. The Freundlich isotherm is more generally applicable. It may be written

$$\frac{\overline{A_x}}{m}=k[A]^n,$$

where both k and n are constants. It is obvious that a more realistic representation of the adsorbed fraction would be to use units for m that express the adsorption capacity of the active solid surface. This could be done by using surface area or better, the number of available adsorption or charge sites per unit area on the active surface. This concept of finite adsorption capacity enters into the Langmuir isotherm

$$\theta=\frac{k[A]}{1+k[A]},$$

where θ is the fraction of adsorption capacity that is occupied by $\overline{A_x}$. This isotherm can be applied over a considerable range of concentrations.

Cation Exchange Capacity, Selectivity

The quantity CEC, or cation-exchange capacity, represents the total number of negative charge sites in a given amount of solid at which reversible cation adsorption and desorption can occur. This quantity is an important property of soils, and standard soil chemistry procedures exist for determining it (Chapman, 1965, p. 891–900). Soil CEC values are normally expressed in terms of milliequivalents of cations per unit weight (usually 100 g) of solid. A more useful form for water chemistry would be in terms of number of charge sites per unit surface area.

In any event, the reversibility of the process suggests that a mass law model might be used, and a substantial number of water-chemistry studies have used this approach. For solutions containing sodium and potassium, the equation would be

$$\mathrm{Na}^{+} + \overline{\mathrm{K}_x} = \mathrm{K}^{+} + \overline{\mathrm{Na}_x}$$

or

$$K_s = \frac{[\mathrm{K}^{+}]\ [\overline{\mathrm{Na}_x^{+}}]}{[\overline{\mathrm{K}_x^{+}}]\ [\mathrm{Na}^{+}]}\,.$$

This K_s is called the selectivity coefficient. Reasonably consistent K_s values can be obtained in systems in which both cations have the same charge. Assignment of an activity coefficient to the adsorbed material K_x and Na_x poses some difficulty. For systems in which the two ions of interest have different ionic charges, as for Na^+ and Ca^{2+}, for example, using a standard mass law format with the term $[Na_x]^2$ seems to compound this problem.

A general survey of the literature then existing on ion-exchange phenomena of particular interest in water chemistry was prepared by Robinson (1962). The ion-exchange process and mathematical means of evaluating it were described in greater detail by Helfferich (1962).

Electrical Double-Layer Models

A theoretical model of the cation adsorption process can be developed from electrostatic considerations. As noted earlier, the surface of a mineral solid immersed in a solution normally has a net negative electrostatic charge that attracts cations from the solution to maintain electroneutrality. The charge tends to immobilize a "fixed layer" of cations at the solid surface. At greater distances from the surface the charge intensity is lower, but ions of charge opposite to that of the surface will be present in larger concentrations than in the bulk solution. This "diffuse layer" of ions extends outward until the distance from the surface is great enough that the surface potential no longer affects the solution properties. The concept of layers of charge near the interface is broadly termed the "electrical double-layer" (EDL) theory.

By evaluating both the electrostatic and the chemical properties of solid surfaces, a substantial improvement in understanding specific adsorption effects should be possible. Rigorous application of EDL theories has thus far been limited to rather simple oxide surfaces, but application to more complex mineral systems should be feasible. An EDL model for computing properties of oxide surfaces and predicting behavior of solutes was described by Davis and others (1978). An application to lead adsorption on a stream-sediment fraction has been described by Brown (1979). A review by James and Parks (1980) described EDL concepts and their applicability to various liquid–solid systems.

Membrane Effects

If two aqueous solutions that have different concentrations of solutes are separated by a selectively permeable membrane, there will be a tendency for water molecules to migrate through the membrane from the more dilute into the more concentrated solution. This effect, called osmosis, is particularly important in biological and biochemical processes because cell walls and many forms of biological membranes are selectively permeable (or semipermeable). In the process of osmosis, a pressure differential can be generated if the system is closed. This osmotic pressure, π, is given by the relationship

$$\pi = \frac{RT}{V} \ln \frac{\alpha_{1\mathrm{H_2O}}}{\alpha_{2\mathrm{H_2O}}}\,,$$

where

R = gas constant (for conversion of units),
T = temperature, in Kelvins,
V = molar volume of water,
$\alpha_{1\mathrm{H_2O}}$ = activity of water in more dilute solution, and
$\alpha_{2\mathrm{H_2O}}$ = activity of water in more concentrated solution.

The approximation used earlier, that water activity in chemical reactions in dilute solution can be considered constant, obviously is not applicable here. The effect of solute concentrations on solvent activities is expressed by Raoult's law, which can be written

$$N = \frac{P_0 - P}{P_0} = \text{mole fraction of solute,}$$

where, on the molar scale,

$$N = \frac{\text{mol/L of solute}}{\text{mol/L of solute} + \text{mol/L of solvent}}\,,$$

P_0 = vapor pressure of solvent,
and P = vapor pressure of solution.

Vapor-pressure measurements, therefore, permit calculation of solvent activities and, in turn, computation of osmotic pressure for systems exhibiting ideal behavior. Membranes of various types may show differing osmotic behavior. The departure from ideality can be represented by an efficiency factor, E, a number less than 1.0, which is entered as a factor on the right-hand side of the equation for π above.

Semipermeable or selectively permeable membranes are used in industrial water purification; in such processes, the osmotic effect is used in reverse, with pressure being applied to the solution from which one wishes to extract water, leaving solutes behind.

For evaluating the effect of saline water on irrigated plants, the ion content of a water can be expressed in terms of its effect on osmotic pressure. According to U.S. Department of Agriculture Handbook 60 (U.S. Salinity Laboratory Staff, 1954), a solution having a specific conductance of 3,000 μmho/cm will give rise to a pressure differential of 1.0 atmosphere; if the conductance is 30,000, the pressure becomes 12.5 atmospheres. Thus, as the salinity of the water in the root zone of the soil increases, it becomes more difficult for plants to obtain moisture from the soil, because the plants must overcome this pressure.

Besides the osmotic effect, some membranes also show different permeabilities for different ions. An electrical charge imposed on a membrane increases this effect. The reverse is also to be expected—that is, there may be a difference in electrical potential across a semipermeable membrane that separates two solutions. This effect is the principle of operation of certain types of specific ion electrodes.

Clays as Semipermeable Membranes

In many ground-water circulation systems, strata of high permeability may be separated by clay or shale layers of much lower permeability. These layers can act as semipermeable membranes and thus give rise to anomalous effects on the pressure head of the water and the concentrations of dissolved ions. There also may be electrical-potential differences from layer to layer. Several other kinds of electrochemical influences in the subsurface may also bring about measurable potentials. The spontaneous potential measured by well-logging equipment is an indicator of such effects.

The behavior of clay and shale membranes in water-bearing sedimentary rocks has been studied extensively following early work on this topic by DeSitter (1947) and by Berry (1959) that helped focus attention on its importance. Some findings of substantial significance in aqueous geochemistry were reported from laboratory experiments by Coplen and Hanshaw (1973), Hanshaw and Coplen (1973), and by Kharaka and Berry (1973). These investigators found that clay membranes could filter out sodium, and fractionate hydrogen and oxygen isotopes, and that the efficiency of clay membranes for exclusion of solutes was increased by using clays having high ion-exchange capacity and by increasing the pressure. The efficiency was decreased by increasing ion concentration in the solutions filtered and was lower at elevated temperature. This work also showed an ionic selectivity sequence; for example, small monovalent ions such as Li^+ were able to pass through the membranes more readily than were larger monovalent ions such as Cs^+ or Rb^+. There also was some selectivity for anions, but it was less well defined. The possible importance of clay membrane filtration in concentrating solutes in subsurface brines was pointed out by Bredehoeft and others (1962). Field studies of such effects in the Kettleman North Dome oil field in California were reported by Kharaka and Berry (1974).

Relationships Among Environmental Factors and Natural-Water Composition

The chemical processes and the relevant thermodynamic principles that have been summarized briefly represent mechanisms for transfer of solid or gaseous components of the Earth and atmosphere into the liquid water of the hydrosphere. For these processes to operate, there must be a means of supplying water and the other reaction components, and the effectiveness of the chemical processes is influenced by numerous environmental factors.

The supply of liquid water is replenished by precipitation. Obviously, amount and rate of rainfall, runoff, and evaporation are important factors in the control of natural-water composition. The temperature of the systems also is of obvious importance. These are all components of regional climate.

The supply of naturally occurring solid reactants is ultimately controlled by geologic processes. Elements not available in the rock minerals contacted by the water cannot be expected to be present in the final solution. Nonavailability can be related to the structure of the rocks as well as to their composition.

Besides factors influencing reactant supplies, the ways in which the chemical reactions occur and their results are influenced by and may be controlled by biologic and biochemical processes.

Climate

The processes of rock weathering are strongly influenced by temperature and by amount and distribution of precipitation. The influence of climate on water quality goes beyond these direct effects, however. Climatic patterns tend to produce characteristic plant communities and soil types, and the composition of water of streams draining such areas could be thought of as a product of the ecologic balance. A somewhat similar concept seems to have been used in the study and classification of water composition in some areas of the U.S.S.R., but has not been widely applied in water-quality studies by investigators in the United States.

Certain of the major ionic constituents of natural water are influenced more strongly than others by climatic effects. Bicarbonate, for example, tends to predominate in water in areas where vegetation grows profusely. Some metals are accumulated by vegetation and may reach peak concentrations when plant-decay cycles cause extra amounts of these metals to enter the circulating water. These effects are most readily observed in river water, because most of the runoff that enters the streams has spent some time within soils of the drainage basin and also may contact fallen leaves and other plant debris.

Humid temperate climates and warm, wet climates generally are the most favorable for growth of vegetation. Runoff from tropical rain forest areas commonly is low in dissolved-solids concentration. An example is the water of the Amazon, for which an analysis is given in table 3. An arid climate is unfavorable for rapid rates of solvent erosion, but concentration of dissolved weathering products in the soil by evaporation can give rise to water high in dissolved-solids content. On the other hand, the occasional flood runoff in such regions can be very low in dissolved material if soluble weathering products are not available in major quantity.

Climates characterized by alternating wet and dry seasons may favor weathering reactions that produce considerably larger amounts of soluble inorganic matter at some seasons of the year than at other seasons. Streams in regions having this kind of climate may fluctuate greatly in volume of flow, and the water may have a wide range of chemical composition. The influence of climate on water quality may thus be displayed not only in amounts and kinds of solute ions, but also in the annual regime of water-quality fluctuation. Kennedy (1971) made an intensive study of some of these effects in a stream in north-coastal California.

Effects of very cold climates on water composition are at least twofold: the low temperature inhibits weathering reaction rates, including any processes mediated by biota, and most of the precipitation in cold regions generally is in the form of snow, so that water is in the solid state much of the time. Thus, most surface runoff in cold regions is likely to be low in solute concentration. The Greenland and Antarctic icecaps are, in fact, mostly fossil snow, and they offer a record going back thousands of years of the chemical composition of precipitation in those regions. Studies of trace metal compositions in ancient ice have been made by various investigators, including Murozumi and others (1969) and Herron and others (1977).

Analyses of water from Arctic rivers in the U.S.S.R. have been published by Alekin and Brazhnikova (1964). Analyses of rivers and lakes in the Mackenzie River basin in northwestern Canada were published by Reeder and others (1972). The Mackenzie data show effects of different rock types on water composition.

Rates of solvent erosion by streams that are fed by glaciers in the temperate climate of the northern Cascade Range of Washington are among the highest reported in the literature (Reynolds and Johnson, 1972). The mechanical action of the moving ice presumably aids the breakdown of rock minerals in such environments.

Geologic Effects

The ultimate source of most dissolved ions is the mineral assemblage in rocks near the land surface. This topic will be discussed in more detail later in this book, with the aim of developing some indications of the rock type that might have been associated with a given water. The importance of rock composition, however, is only part of the story. The purity and crystal size of minerals, the rock texture and porosity, the regional structure, the degree of fissuring, the length of previous exposure time, and a good number of other factors might influence the composition of water passing over and through the rock.

Rock temperatures increase with depth below the land surface. Where water circulates to a considerable depth, it attains a substantially higher temperature than water near the land surface. Increased temperature raises both the solubility and the rate of dissolution of most rock minerals. With the recent interest in geothermal energy sources, renewed attention has been given to these effects. The chemical composition of water of thermal springs may give indications of the temperature of the rocks at depth.

Most thermal ground waters (hot springs) are found in areas where the temperature gradient with depth is abnormally steep. The solute content of such water is commonly higher than that of nonthermal water. Some thermal water may be notably high in dissolved-solids concentration and may contain unusual amounts of metal ions. The brines from deep wells in Imperial Valley, Calif. (White, 1968), and from deep basins at the bottom of the Red Sea (Miller and others, 1966) are interesting examples. The Imperial Valley brine contained 155,000 mg/kg (milligrams per kilogram) of chloride, and also contained about 2,000 mg/kg of iron, 1,400 mg/kg of manganese, 500 mg/kg of zinc, 90 mg/kg of lead, and 1.4 mg/kg of silver, as well as considerable concentrations of other unusual constituents. The compositions of some of these waters may be the result of metamorphic alteration of associated rocks. More recently, oceanographers have discovered water discharging at high temperatures on the ocean bottom near the Galapagos Islands in the eastern Pacific Ocean. This water appears to be high in sulfur and metal ion concentrations (East Pacific Rise Study Group, 1981).

The term "metamorphic water" was first defined by White (1957a). In recent years, many examples of metamorphic water having unusual composition have been cited by other workers and have been correlated with rock alteration processes occurring below the surface (Barnes, 1970; Barnes and others, 1972; Barnes and O'Neil, 1976).

White (1957b) also defined "magmatic water" as water released when rocks deep within the crust or mantle are converted to a molten state. An older term used by some geochemists is "juvenile water," meaning water that has not previously been involved in the circulating system of the hydrologic cycle. The water that is, or has recently been, in circulation is termed "meteoric." The difficulty in ascertaining whether any fraction of a natural water is juvenile makes this classification virtually useless. Some water of meteoric origin may remain in storage in aquifers for very long periods of time.

Magmatic water may perhaps be associated with volcanism. The amount of water that might be released by fusion of rocks has been thought by some geochemists to be substantial. For example, Clarke and Washington (1924) estimated that a little over 1 percent of the weight of average igneous rock is water. Others have doubted the validity of this estimate (Goldschmidt, 1954, p. 126).

The data reported by White and Waring (1963) on the composition of volcanic gases show that water vapor is generally predominant. However, the degree to which the water associated with volcanic activity is of magmatic origin rather than meteoric origin is difficult to determine. White (1957a, b) studied the composition of water from many thermal-spring areas and concluded that in such areas there are few, if any, conclusive indications that any of the water is juvenile.

Another classification term sometimes applied to water having high solute concentrations is "connate," which implies that the solute source is fossil seawater trapped in sedimentary formations when they were laid down. The high dissolved-solids concentrations of oilfield waters commonly are thought to be of connate origin. Collins (1975) discussed many aspects of the geochemistry of water associated with petroleum. Analyses for many oilfield waters are tabulated in White and others (1963).

Biochemical Factors

Life forms and the chemical processes associated with them are intimately related to water and to the solutes contained in water. Extensive discussions of this relationship can be found in the literature of various branches of the life sciences. Although the principal concern of this book is inorganic aspects of water chemistry, the biological aspects cannot be avoided. In fact, the water chemist will find that biological factors are important in almost all aspects of natural-water composition. Much of the support for a water chemist's work derives from the importance of water to humans and the standards required for safe drinking water. Water pollution control programs commonly aim to benefit desirable forms of aquatic life as well as to provide water safe for domestic use. The following brief discussion points out some biochemical processes and shows how they fit into and complement other factors that control natural-water composition.

Ecology Applied to Natural Water

Ecology is the study of relationships between organisms and their environment. It thus implies what might be considered a study of biological systems and the way in which the various parts of such systems influence each other. For example, the development of a particular set of plant and animal species, soil type, and general land form can be thought of as the end result of a particular set of climatic and geologic factors that have reached an optimal, steady-state condition. Input of energy from outside the system must equal output plus storage changes. Living species in the system can be considered as locally decreasing the net entropy of the system, a process that requires a continuing energy input—from the Sun and from incoming reactants. Or the entropy decreases in one part of the system may be balanced by increases in another part.

Obviously, this kind of system is not readily treated by a thermodynamic equilibrium model, because, on the scale implied, the processes that go on are irreversible. Attainment of a steady state in such a system, at least as viewed in a broad sense, is possible if the inputs remain relatively constant. But biological systems in any regional sense are subject to such an enormous number of feedbacks and variations, some cyclic and some random or one-time-only, that conditions are in a continual state of dynamic flux. Studies in ecology, therefore, probably should be directed toward understanding and evaluating mechanisms and rates.

In a sense, the study of natural-water composition involves concepts of ecology, because a large number of factors and processes are interrelated in bringing about the composition of the water. As in ecologic systems, changes in one factor may bring about a considerable number of other changes that can influence the particular variable being observed. Also as in ecologic systems, the separation of cause from effect can become difficult.

Whether biochemical processes like the ones described here are best viewed as independent factors or as integral parts of the chemical thermodynamic system governing water composition is partly a matter of opinion, but their importance is unquestionable. The life processes of principal interest in water chemistry can be classified in a general way on the basis of energy relationships, to include the following:

1. Processes that use energy captured from the Sun or some other source for promotion of chemical reactions that require a net energy input.
2. Processes that redistribute chemically stored energy.
3. Processes that convert chemically stored energy to other forms of energy.
4. Processes without significant energy transfer.

The first type of process is represented by photosynthesis, in which carbon dioxide, water, and radiant energy are used to manufacture carbohydrates and gaseous oxygen is liberated. This process in turn provides the fuel for most of the processes of the second and third type.

Processes of metabolism and decay are included in types 2 and 3. These chemical reactions may involve a net release of energy from the original materials, but not all the reactions can be made to proceed at observable rates in the absence of life forms. For such reactions, the biological processes seem to offer pathways for reactions that do not have the high stepwise energy barriers that prevent the reaction from occurring spontaneously or that cause it to be slow in the absence of biota.

Reactions that promote chemical reduction or oxidation might be thought of as type 3, although no actual electrical energy may be produced. It is possible, however, to make a cell that is capable of producing a current as a result of biochemical processes. The production of heat, chemiluminescence, and motion are biological manifestations of the third type of reaction.

Effects that come within type 4 can be represented by indirect influences such as stabilization of inorganic colloids in water by soluble organic matter or the release of various waste products to water.

The processes that sustain life are particularly strongly developed in water bodies exposed to air and sunlight. In environments in which neither is present, as in ground-water aquifers, biological activity normally is much less important. At some stage in its movement through the hydrologic cycle, however, all water is influenced by biochemical processes, and the residual effects of these processes are widely discernible, even in ground water.

Influence of Soil and Soil-Forming Processes

The systems of classification of soils in common use emphasize strongly the effect of climate and vegetation and do not place as much emphasis on the nature of the original rock from which the soil came. Soils of high productivity generally contain a considerable amount of organic debris, and in most the mineral-species distribution inherited from the parent rock has been altered extensively. The minerals themselves also commonly have been changed. Discussions of rock-weathering processes that lead to soil formation are plentiful. Examples are papers by Keller (1957) and Reiche (1950), who discussed the processes with some attention to soluble products and from a geologically oriented viewpoint. Drever (1982, p. 162–199) discussed these relationships for several areas having differing climatic and geologic conditions.

The major features of the chemical composition of many natural waters are the result of soil-forming processes or reactions that occur within the soil zone. Consequently, a considerable area of common interest exists between water chemistry and soil chemistry. This fact, however, has not been recognized very extensively by workers in the two fields. A large part of the atmospheric precipitation that reaches the land surface falls on soil surfaces; generally, the fraction that ultimately appears as runoff or ground water has had some contact with the soil, and much of it has spent a considerable period of time as soil moisture. The chemical composition of soil moisture and the processes that go on in soil to dissolve or precipitate minerals or otherwise to alter the composition of soil moisture probably have not received adequate attention from workers in the field of natural-water chemistry.

Among the factors influencing the chemical composition of soil moisture are dissolution or alteration of silicate and other minerals, precipitation of sparingly soluble salts (notable calcium carbonate), selective removal and circulation of nutrient elements by plants, biochemical reactions producing carbon dioxide, sorption and desorption of ions by mineral and organic surfaces, concentration of solutes by evapotranspiration, and conversion of gaseous nitrogen to forms available for plant nutrition. Of these, one of the most important is the production of carbon dioxide. The air in soil interstices is commonly 10–100 times richer in CO_2 than ordinary air (Bolt and Bruggenwert, 1978, p. 11). Water moving through soil dissolves some of this CO_2, and the H^+, HCO_3^-, and CO_3^{2-} ions are potent forces in controlling the pH of the water and in attacking rock minerals.

Aquatic Biota

Those life forms that occur in water bodies or in close association with them form an ecologic system that has been studied widely. The science of limnology is concerned to a high degree with freshwater ecology. Hutchinson's (1957) well-known text covers this subject in considerable detail. The ecology of river systems has been discussed in detail by Hynes (1970).

Many of the chemical processes occurring in soil also occur in freshwater bodies. Photosynthesis by plant species rooted in the pond or stream bottom, as well as by floating species, produces oxygen and consumes carbon dioxide, and respiration and decay consume oxygen and produce carbon dioxide. A well-defined diurnal cyclic fluctuation of pH often can be observed in near-surface water of lakes and streams (Livingstone, 1963, p. 9). Aquatic plants also require nutrient elements, especially nitrogen and phosphorus, which they may take up through roots in the bottom sediment or may assimilate directly from the water. The photosynthesizing biota help provide food and oxygen for other life forms in the water where they grow. Cycles of growth and decay produce organic debris that is partly precipitated to the bottom of the water body, where it may serve as food for other kinds of organisms. Diatoms extract silica from water in which they grow. Other solutes, including some trace constituents, are essential nutrients for certain species of biota. As a result, the concentrations of some trace elements may be controlled by biological processes. Biological effects on iron concentrations were noted by Oborn and Hem (1962).

Respiration, in which oxygen is consumed and carbon dioxide is formed, is a basic process of all aerobic life forms. Oxygen is supplied to surface water bodies by direct assimilation from the atmosphere as well as from photosynthesis. Under normal conditions, an ecologic balance is (or should be) attained in most rivers and lakes, with the various species of biota living together in harmony. A measure of the amount of biologic activity in a water body is its productivity. This is generally expressed in terms of the amount of organic carbon that is produced within a specified area or a volume of water per unit time.

Water bodies in environments in which water is plentiful and soluble nutrients are scarce will support very little living material. Such waters are sometimes called "oligotrophic." This term was coined from Greek words equivalent to "nutrient-poor." Its opposite, "eutrophic," strictly means "nutrient-rich" but is often used as the equivalent of "polluted." During warm weather, nutrient-enriched lakes may exhibit surges of algal growth that can interfere with the ecologic balance.

Lakes in environments in which growing conditions are favorable and nonaquatic vegetation is abundant generally are highly productive and may have short careers in the geologic sense. Such water bodies tend to evolve into marshland or peat bog, owing to accumulation of organic debris. Lakes in environments less favorable to vegetative growth may fill with inorganic sediment or may be drained by stream erosion at their outlets. Obviously, the career of a lake involves factors in addition to organic productivity, but pollution by organic wastes can bring about extensive changes in properties of the water and in a rather short time may convert a clear, oligotrophic lake to a turbid, eutrophic one. The rates at which such changes might occur and the feasibility of reversing them are areas that are being studied by limnologists.

The Hydrologic Cycle

A characteristic property of the free water of the Earth is its continual motion, imparted primarily by the input of radiant energy from the Sun. This energy input causes some liquid water, wherever a water surface is exposed to the atmosphere, to be converted to the vapor state and carried off by wind. When atmospheric conditions become favorable, the vapor returns to the liquid state with a release of energy, first forming the very small droplets of clouds and then, if temperatures are low enough, tiny ice crystals. Rain or snow may be produced if the condensation proceeds under favorable conditions. The amounts of energy involved in water circulation in the atmosphere are very large in total and when concentrated, as in tropical storms, may have spectacular consequences. The water reaching the land surface by precipitation moves downgradient in the general direction of the ocean or a point of minimum gravitational energy.

A wide variety of representations of the hydrologic cycle exist in the literature (for example, U.S. Department of Agriculture, 1955, p. 42), and the hydrologist interested in detail can find many different paths through which continuous circulation can occur or places where water can be stored for very long periods. The cycle itself, however, deals only with pure H_2O. In those parts of the cycle when water is in the liquid state, solutes are always present, and amounts and rates of solute transport are of substantial interest in many ways in hydrology and geochemistry. Livingstone (1963, p. 38) calculated that rivers of North America carry an average load of 85 metric tons (tonnes) per year in solution from each square mile of drainage basins. This is equivalent to 32.8 tonnes per square kilometer.

Sources of Solutes in the Atmosphere

Table 4 shows the principal gaseous constituents of the atmosphere. Any liquid water in the atmosphere naturally would be expected to be saturated with respect to these gases, the amount in solution being proportional to the solubility and the partial pressure of each and to the temperature. Gases that enter into reactions with water in general are more soluble than those that do not. For this reason, the effect of carbon dioxide is relatively great, even though it makes up only 0.03 precent by volume of normal air.

The composition data in table 4 are supposed to represent clean air that is not affected significantly by local environmental factors. Gases such as H_2O, SO_2, NH_3, N_2O, NO_2, HCl, CO, and CO_2 are produced in substantial amounts by burning of fuels, by metallurgical processes, and by other anthropogenic activities, and also by biochemical processes in soil and water and by volcanic or geothermal activity. This can result in local enrichment of these gases. The chemical properties of rainwater can be substantially affected by these substances.

Some elements form solids or liquids with a significant vapor pressure at ordinary temperatures. Certain boron compounds, for example (Gast and Thompson, 1959), tend to evaporate from the ocean to a significant extent for this reason. The elements iodine and mercury have appreciable vapor pressures at low temperature, but those elements are comparatively rare and do not influence air or rainfall composition appreciably.

Radionuclides such as tritium and carbon-14 are produced in the atmosphere by cosmic-ray bombardment. The atmosphere also contains particles of extraterrestrial material introduced from outer space. On the basis of the nickel content of snow in Antarctica, Brocas and Picciotto (1967) estimated that 3 to 10 million tons of such material fall on the Earth's surface each year.

Naturally occurring atmospheric particulate matter consists of terrestrial dust carried aloft by wind or propelled upward by volcanic eruptions and of sodium chloride or other salts picked up as a result of wind agitation of the ocean surface. This material is augmented by manmade discharges from industrial plants, vehicle exhausts, and many other sources. The particulate matter is important in forming nuclei for condensation of water and as a source of solutes in precipitation; it also influences surface-mediated chemical processes.

The subject of atmospheric chemistry has a large literature of its own. Well-known textbooks are those of Junge (1963) and Holland (1978). Chameides and Davis (1982) summarized more recent developments. Efforts to understand and control air pollution have increased greatly in recent years, especially in areas affected by "acid rain."

Composition of Atmospheric Precipitation

Studies of the composition of rainfall have been carried on for many years. In summarizing this subject, Clarke (1924b) quoted some 30 early investigators who published data between 1880 and 1920. In more recent times, interest in this field has increased, especially in northern Europe and the U.S.S.R. and in the United States and Canada. Continuing studies in Scandinavian countries have produced many data, beginning about 1950 (Egner and Eriksson, 1955). A major emphasis in much of this early work was determining quantities of plant nutrients and of sea salts that were transported to the land in rainfall. Ericksson (1955, 1960) was particularly interested in evaluating the influence of airborne salts on river-water composition. He estimated that, on the average, rainfall deposits 10 kg of chloride per hectare per year on the land surface, and about the same amount of sulfur computed as S. In terms of SO_4^{2-} ions, the weight would be about three times as great. Not all this sulfur can be attributed to marine sources.

Gorham (1955) made extensive observations of rainfall composition in the English Lake District, an area about 50 km east of the Irish Sea. These data showed a resemblance to seawater in the ratios of sodium to chloride and magnesium to chloride. Gorham (1961) discussed the general influence of atmospheric factors on water quality in a later paper. Some of the rather voluminous data from work done in the U.S.S.R. were summarized by Drozdova and Makhon'ko (1970). The occurrence of minor constituents, for example fluoride (Mikey, 1963), in rainfall was studied in some of this work.

The first nationwide study of rainfall composition in the United States was conducted by Junge and his associates. These investigators operated about 60 rainfall-sampling stations distributed over the entire country (except Alaska and Hawaii) for a year, from July 1955 to July 1956. The results, described by Junge and Gustafson (1957) and by Junge and Werby (1958), showed that the average chloride concentration in rainfall decreases rapidly from several milligrams per liter near the oceans to a few tenths of a milligram per liter inland, whereas sulfate increases inland to values between 1 and 3 mg/L on the average. Nitrate and ammonia concentrations also were determined.

Feth, Rogers, and Roberson (1964) reported data for snow in the Western United States, especially in the northern part of the Sierra Nevada, and Gambell and Fisher (1966) reported on composition of rain in North Carolina and Virginia. A study of rainfall composition in New England and New York was made by Pearson and Fisher (1971). In other studies of rainfall chemistry, the content of minor and trace constituents was emphasized (Chow and Earl, 1970; Lazrus and others, 1970; Dethier, 1979). A compilation of rainfall-composition data for North America for the period 1971 to 1981 was prepared by Munger and Eisenreich (1983).

Concern about evident trends toward lower pH of rainfall and surface water in Scandinavian countries and England began to be expressed in the 1950's and 1960's, and this aspect of the chemistry of precipitation has been studied extensively in the United States and Canada in subsequent years. Likens and Bormann (1974) stated that annual average pH's of rainfall in parts of the northeastern United States were near 4.0 in 1970–71. "Acid rain" has become a matter of substantial national and international concern. Cowling (1982) has reviewed the history of scientific efforts in this field and has assembled an extensive bibliography. Reliable measurements of pH and concentrations of other ions in rainfall do not extend far enough back in time to permit a close estimate of the date of the onset of acidification. Peters and others (1982) observed no general downward trend in pH of rain in New York State during the period 1965–78; some sites showed increases, and others showed decreases. A review of chemical models and evaluation techniques that might be used for comparing historical and recent data for poorly buffered waters has been published by Kramer and Tessier (1982).

The reported composition of rainfall is influenced by the methods used to obtain samples for analysis. The samples collected for some investigations represent only material present in rain or in snow; particulate matter was filtered out before analysis and the sampling container was kept closed when rain was not falling. Other investigators wanted to obtain total fallout and kept their sampling containers open at all times; generally, however, the insoluble material was filtered out of these samples also. For meteorologic purposes, the composition of rainfally without any influence from antecedent or subsequent dry fallout is perhaps of primary interest. The geochemist, however, and most other users of such data may well need total values, including dry fallout; this is the "bulk precipitation" defined by Whitehead and Feth (1964). The extent to which data of the two kinds may differ is uncertain. Whitehead and Feth ascribed considerable importance to the dry fallout factor, but Gambell and Fisher (1966) did not. It has also been pointed out by some investigators that aerosols may deposit particulate matter on vertical surfaces on which the wind impinges. Thus, the foliage of trees near the seacoast may pick up salt particles from landward-blowing winds. The importance of this effect is not known.

The values given in table 6 show that rainfall composition is highly variable, not only from place to place, but also from storm to storm in a single area—and within individual storm systems as well. A very large volume of air passes through a storm system. The very nature of the conditions that often produce rain, a mingling of air masses of different properties and origins, ensures a high degree of vertical and horizontal nonhomogeneity. Analyses 3 and 4 in table 6 represent samples of rain collected successively during a rainy period at Menlo Park, Calif. The later sample shows a considerably higher concentration of solutes than the earlier. Analyses 2 and 6 in table 6 represent bulk precipitation, and analysis 1 probably can be assumed to have been influenced by dry fallout. The other data in the table represent composition of rainfall unaffected by dry fallout. The variability of solute concentrations in rain at Menlo Park and at a site about 550 km further north was studied intensively by Kennedy and others (1979) during parts of 1971 and 1972.

Table 6. Composition, in milligrams per liter, of rain and snow

Constituent	1	2	3	4	5	6
SiO_2	0.0		1.2	0.3		0.1
Al	.01					
Fe	.00					.015
Ca	.0	.65	1.2	.8	1.41	.075
Mg	.2	.14	.7	1.2		.027
Na	.6	.56	.0	9.4	.42	.220
K	.6	.11	.0	.0		.072
NH_4	.0					
HCO_3	3		7	4		
SO_4	1.6	2.18	.7	7.6	2.14	1.1
Cl	.2	.57	.8	17	.22	
NO_2	.02		.00	.02		
NO_3	.1	.62	.2	.0		
Total dissolved solids	4.8		8.2	38		
pH	5.6		6.4	5.5		4.9

1. Snow, Spooner Summit, U.S. Highway 50, Nevada (east of Lake Tahoe) (Feth, Rogers, and Roberson, 1964).
2. Average composition of rain, August 1962 to July 1963, at 27 points in North Carolina and Virginia (Gambell and Fisher, 1966).
3. Rain, Menlo Park, Calif., 7:00 p.m. Jan. 9 to 8:00 a.m. Jan. 10, 1958 (Whitehead and Feth, 1964).
4. Rain, Menlo Park, Calif., 8:00 a.m. to 2:00 p.m. Jan. 10, 1958 (Whitehead and Feth, 1964).
5. Average for inland sampling stations in the United States for 1 year. Data from Junge and Werby (1958), as reported by Whitehead and Feth (1964).
6. Average composition of precipitation, Williamson Creek, Snohomish County, Wash., 1973–75. Also reported: As, 0.00045 mg/L; Cu, 0.0025 mg/L; Pb, 0.0033 mg/L; Zn, 0.0036 mg/L (Deithier, D.P., 1977, Ph.D. thesis, University of Washington, Seattle).

Reactions of sulfur and nitrogen species in the atmosphere tend to generate H^+ and are commonly thought to be the main causes of decreased pH of rainfall.

Influence of Humans

A major impact on the environmental factors influencing the composition of water results from the activities of humans. The power of humans to alter the environment is great and is widely evident in the changes they can bring about in water composition. Solutes may be directly added to water by disposal of wastes, or may be directly removed in water treatment or recovery of minerals. The ecology of whole drainage basins may be profoundly altered by bringing forested land into cultivated agriculture. Water-movement rates and solute-circulation rates may be altered by water diversions and by structures and paved surfaces that replace open land as cities expand in population and area. After the addition of nutrients, especially phosphorus and nitrogen, to lakes and rivers as a result of the increasing density of human population and intensified agriculture in much of the United States, many water bodies have undergone substantial changes in ecologic balance. Increased crops of algae that result from nutrient enrichment are plainly visible to any observer, and changes of this type may take place in rather short periods of time. Most inorganic composition changes are more subtle and attract less attention, but they may be more difficult to reverse.

Chemical Thermodynamic Models Applied to Natural Water

The foregoing discussion of environmental factors that influence natural-water composition indicates clearly that many complications exist. Nevertheless, the theoretical concepts and application techniques briefly described in earlier sections hold much promise for evaluating and understanding these processes and their effects. At this point it is worthwhile to review some recent efforts to apply equilibrium thermodynamics to develop models of natural-water chemistry, and the ways in which the models have been used in different kinds of systems.

Early efforts to develop mathematical models for aqueous geochemical systems generally consisted of assembling an array of homogeneous chemical equilibria relating solute species, including complexes but not involving solid phases, and combining this array with what might be thought appropriate or probable heterogenous equilibria governing solubilities.

Thermodynamic data in the form of equilibrium constants or standard Gibbs free energies were then used to make a set of mass-law equations. Temperature and pressure were specified (usually 25°C and 1 atmosphere). The set of equations relating the concentrations that are limited by solubility equilibria was then solved simultaneously. The inclusion of activity coefficient calculations and temperature effects in these calculations complicates the mathematics, but the electronic computer readily overcomes such difficulties. Simple examples of this type of model applied to carbonate systems were given by Garrels and Christ (1964, p. 74–92), and the solubility calculation for gypsum given earlier in this book is a very simple application of this approach. Much more complicated multicomponent models have evolved in more recent years. The model described by Morel and Morgan (1972) was elaborated on by others and has produced MINEQL (Westall and others, 1976), GEOCHEM (Mattigod and Sposito (1979), and other variations. Some of these variations include ion exchange and surface chemical factors and many organic complexes. Related models developed by U.S. Geological Survey research programs include SOLMNEQ (Kharaka and Barnes, 1973) and WATEQ (Truesdell and Jones, 1974).

In practice, one may use models of this kind either to predict equilibrium solute concentrations or, in an inverse fashion, to test for the degree of departure from equilibrium displayed by available water-analysis data from a system in which various mineral solids are present (or are presumed to be present).

A procedure for improving the accuracy of solubility computations at high ionic strength ($I > 1.0$) was used in a model developed by Harvie and Weare (1980). This procedure uses ion activity concepts proposed by Pitzer (1973).

These models may be broadened by introducing stoichiometric or mass-balance considerations. The program PHREEQE (Parkhurst and others, 1980) is capable of evaluating mixing and other processes that occur along flow paths between water sampling points.

A description of many chemical models and a discussion of their applicability to various situations was published by Nordstrom, Plummer, and others (1979). A description of the approaches used in the U.S. Geological Survey model development process was published by Plummer and others (1983). Coupling of water quality to water-transport models is considered elsewhere in this book.

The Phase Rule

Systems in which natural waters occur are heterogeneous—that is, they include more than one phase (solids, liquid water, and gases). In evaluating the degree to which the solute concentrations of water in such systems can vary independently, it is sometimes helpful to apply the phase rule formulated in the 19th century by J.W. Gibbs. This principle is applicable to closed systems at chemical equilibrium and is stated:

$$\text{number of components} - \text{number of phases} + 2 = \text{degrees of freedom.}$$

Phases in this context represent the parts of the system that are homogeneous within themselves and have definable boundary surfaces. Components are the minimum number of independent chemical constituents derived from or constituting the phases that must be present to reproduce the system. The degrees of freedom are the number of factors, such as temperature, pressure, or solute concentration, that must be given fixed values to make the whole system invariant at equilibrium.

The application of these concepts can be illustrated by evaluating a simple system: crystalline calcite in liquid water, with no gas phase present. By this definition, the system has two phases, liquid and solid. Chemical reactions that might occur in this system include

1. Dissociation of water:

$$H_2O(l) = H^+ + OH^-.$$

2. Reaction of calcite with aqueous H^+:

$$CaCO_3(c) + H^+ = Ca^{2+} + HCO_3^-.$$

3. Interactions among dissolved carbonate species:

$$HCO_3^- = CO_3^{2-} + H^+$$

or

$$HCO_3^- + H^+ = H_2CO_3(aq).$$

Although all the chemical constituents shown in the equations can be present, they originate from the two substances $CaCO_3$ and H_2O. It would not be possible to generate all the solutes unless at least these two things are present. The minimum number of components as defined for use in the phase rule therefore is 2, and one may write

$$\text{degrees of freedom} = 2 + 2 - 2 = 2.$$

If temperature and pressure are specified, the solute activities will all have single fixed values at equilibrium.

The result of applying the phase rule to this simple system also would be reached intuitively, but in more complicated systems it may sometimes be a useful approach to systematic evaluation (Sillen, 1967a). As components are added, however, it becomes more difficult to ascertain which are independent and essential as specified by the phase rule, and the implied simplicity of the concept is not fulfilled.

Phase diagrams in which pressure and temperature are variables and other similar applications of phase-rule principles have been widely used in geochemistry in connection with rock melts and hydrothermal systems, and in the solution of many chemical and engineering problems. Isothermal and isobaric conditions can reasonably be specified for many natural-water systems of interest to hydrologists.

Difficulties in assigning the number of components in chemical systems of the type we are concerned with can be avoided by using an algebraic approach, as described for carbonate systems by Garrels and Christ (1964, p. 74–92) and applied later in this book. This approach assembles pertinent equilibrium, ion-balance, and stoichiometric equations and determines the degrees of freedom by subtracting from the total number of variables the total number of equations. Temperature and pressure are, of necessity, specified or at least implied in values used for equilibrium constants.

A system having zero degrees of freedom is invariant—each of the terms has a single, unique numerical value. When the system has one degree of freedom, it can be conveniently illustrated by means of a line on a two-coordinate graph. A system having two degrees of freedom can be reduced to a series of contours on a two-dimensional plot, or can be shown in more detail on a three-dimensional graph. Numerous graphical representations of equilibrium among dissolved and solid species in aqueous systems have been published. A few examples are given in this book, and many discussions and applications are available in the literature (Butler, 1964, p. 267, 321–363; Hem, 1972b; Stumm and Morgan, 1981, p. 230–322).

The mathematical analysis of natural-water systems suggests that, in general, the variability is largest when only a few phases are at equilibrium. Increasing the number of phases that are at equilibrium with a given group of components decreases the possibilities of variation. This conclusion would be reached intuitively from simple chemical reasoning: the more equilibria there are in a system, the fewer things will be left that can vary independently.

Some of the hydrologic properties of different kinds of natural-water systems are pertinent in evaluating the applicability of theoretical models of water chemistry to them.

Some Characteristics of Ground-Water Systems

The application of equilibrium models to ground-water chemistry has had considerable appeal to theoretically minded investigators. Although the mineral composition of the solids in such heterogeneous systems commonly is poorly known, the activities of solute species can be determined completely, and because movement of water is slow, there is a considerable time span available for completion of slow reactions. Presumably, any reaction that reasonably could be expected to reach equilibrium would do so in the usual aquifer system.

Models that postulate the existence of reversible chemical equilibrium have been found to fit the behavior of solutes in carbonate-dominated systems, especially where the controlling phase is calcite (Back, 1963; Back and Hanshaw, 1970). In some systems, as in Florida, the ground water may not attain saturation until it has moved through the aquifer for long distances (Back and Hanshaw, 1971). In other systems, equilibrium is attained more rapidly (Langmuir, 1971) and perhaps is approached while potential recharge is still moving through the soil zone. Equilibrium behavior with respect to gypsum (Cherry, 1968), dolomite (Barnes and Back, 1964a), fluorite (Nordstrom and Jenne, 1977), with some other simple mineral species has been documented, although dolomite does not precipitate readily. Redox equilibria appear to control behavior of iron in ground water (Barnes and Back, 1964b) and also may be extended to other oxidizable or reducible elements that can be coupled to the iron system (Hem, 1978). Some other kinds of equilibria, for example, those of ion exchange and adsorption, also may prove to be applicable in these systems.

Some of the solute activities may be unstable, requiring extra care in sampling and analysis. However, such problems, if they are recognized, usually can be overcome. A more difficult problem to evaluate can result from the pattern of movement of water through the system to be sampled. In ground-water systems in which strata of high and low permeability are interbedded, a flow pattern can occur in which water movement is largely confined to the more permeable layers. Differences between mineral composition in the layers may result in considerable variation in water composition with depth at any given site. Wells that penetrate several of these layers may yield water that is a mixture, enriched in the types of solutions present in the more permeable beds but also influenced by the efficiency of well construction and development, rate of pumping, and related factors. A well influenced by factors such as these is unlikely to give usable geochemical information. Unfortunately, there is no good way of evaluating the importance of these effects or, sometimes, of knowing for certain whether they are present or absent.

Systematic changes in composition of ground water along its flow path can be observed in many systems.

Examples that are given later in this book show how these patterns can be interpreted. Mathematical models that define such changes on the basis of equilibria and irreversible processes were described by Plummer and Back (1980) for the Floridan and Madison limestone aquifers. In these systems, calcite is first dissolved and then precipitated further along the flow path, while dolomite and gypsum dissolve irreversibly. A smaller scale model for the Aquia aquifer in Maryland explained observed changes in relation to calcite dissolution, reprecipitation, and cation exchange (Chapelle, 1983).

Surface Water Systems—Rivers

The water carried in streams is often considered to consist of a base-flow fraction made up of ground water that infiltrates into the channel and a direct-runoff fraction that enters the drainage system during and soon after precipitation. The direct runoff presumably has had no residence time in the ground-water reservoir and only short contact with soil or vegetation. Reactions in the soil zone, however, are commonly extensive enough that the direct runoff has a considerably higher dissolved-solids concentration than the original rain or snow. The base flow has a still greater dissolved-solids concentration. The solute concentration of river water thus tends to be inversely related to flow rate. At very high flow rates, the water may be nearly as dilute as rainwater.

It is usually not feasible to evaluate the composition of base flow exactly or, for most medium-sized and large streams, to separate the chemical effects of base flow completely from those of direct runoff. The quantity of base flow changes with time and the relative importance of different contributing sources changes, and the result is a complex fluctuation of solute concentration. Steele (1968b, p. 21) was able to develop a chemical means of distinguishing base flow from direct runoff for a small stream in northern California.

In addition to mixing of ground water and runoff, the natural factors that influence stream composition include reactions of water with mineral solids in the steambed and in suspension, reactions among solutes, losses of water by evaporation and by transpiration from plants growing in and near the stream, and effects of organic matter and water-dwelling biota. This latter set of natural factors results in fluctuations of composition that bear little relation to discharge rate.

Superimposed on all these factors are the influences of humans—stream pollution and waste disposal by all kinds of activities within the river basin, and flow diversions and augmentation.

Chemical equilibria probably control a few properties of water in flowing streams. For example, the ion-exchange reactions of solutes with suspended sediment probably are rapid enough that they usually are at equilibrium. Kennedy and Brown (1966) found that sodium-saturated natural sediments from Brandywine Creek, Del., exchanged 90 percent of their adsorbed sodium for calcium in 3–7 minutes in laboratory experiments. Certain oxidations, ferrous to ferric iron, for example, also normally may reach equilibrium quickly. The equilibrium approach, however, seems inadequate for studies of most biologically mediated processes such as use and production of carbon dioxide and oxygen. A river is by nature a dynamic system, and kinetic principles would seem much better suited to stream chemistry than the steady-state equilibrium approach. For example, the processes whereby biota consume organic-pollution loads of streams often can be most effective studied by application of kinetics and nonequilibrium models.

Lakes and Reservoirs

A lake that has a surface outlet represents a holding and mixing basin for the streamflow that emerges. The detention time of water in a lake provides an opportunity for slow reactions to come closer to completion than they can in the rapidly moving water of a river. Mixing, however, may not be complete, so at any given time the water in one part of the lake may be greatly different in composition and properties from that in other parts of the lake. Closed-basin lakes become saline owing to evaporation of water and continued influx of solutes.

An important influence on lake composition is thermal stratification. During warm weather, an upper, heated layer of water of relatively low density may form at the surface, floating on the deeper, cooler water below and insulating the deeper layers from direct contact with atmospheric oxygen. In deep lakes, during the summer season, this stratification may persist for long periods, and in time the deeper water becomes depleted in oxygen, owing to biochemical processes. In cooler seasons, the stratification disappears, surface and deeper water physically overturn, and oxygen again becomes dispersed throughout the lake.

Hutchison (1957) described the physical and chemical aspects of lakes in detail, and there is an extensive literature on stratification effects. More recent publications that relate to this subject include books by Wetzel (1975) and Lerman (1978).

Estuaries

The mixing zones at the mouths of rivers where they enter the ocean are highly complex chemically and biologically. Where the mixing zone lies within an estuary, the zone also has a complex water-flow pattern. Estuaries are the result of tectonic or sea-level changes that caused the lower reaches of a river valley to become submerged. Notable examples are Chesapeake Bay on the U.S. Atlantic coast and San Francisco Bay on the Pacific coast.

The zone in which freshwater mixes with seawater in an estuary commonly extends upstream, as well as seaward from the river mouth, and fluctuates in position depending on river flow, winds, and ocean tides. The actual boundary between freshwater and salty water is, therefore, dynamic and shifting. The zone of mixing effects extends farthest upstream in regions where the coastal plain is nearly flat and the bottoms of submerged valleys are below sea level for some distance inland.

The energy of freshwater flowing down the river tends to push a freshwater front out into the estuary. This force is continuous but fluctuates in response to the volume of flow. The cyclic rise and fall of the ocean in response to tides periodically opposes the flushing action of the stream, and, as a result, saltwater periodically is pushed back upstream as far as the tidal force can move it in opposition to the freshwater movement.

Because it is denser, seawater tends to move along the bottom of the channel, whereas the freshwater is pushed upward nearer the surface. There is considerable turbulence along the freshwater–saltwater boundary, and this turbulence results in mixing. The effects of turbulence and other physical factors promoting mixing, such as channel obstructions, are more important than ionic diffusion in bringing about mixing in tidal streams.

As a result of these effects, the water of a tidal stream varies in composition vertically and horizontally in the cross section at any point, and the water changes in quality with passage of time in response to changes in streamflow and to tidal fluctutions, winds, and storm waves. The general conditions that can be expected in the tidal zone can be predicted when the effects of the various factors in the area of interest have been evaluated satisfactorily. Study of tidal streams requires extensive sampling along horizontal and vertical cross sections and integration of the results with data on streamflow and tides. A number of such studies have been made. The subject was discussed by Keighton (1966) with respect to the special problems of the Delaware River estuary. The behavior of the salt wedge in the Duwamish estuary at Seattle, Wash., was described by Dawson and Tilley (1972). Other papers resulting from studies of that estuary were written by Welch (1969) and by Santos and Stoner (1972).

In subsequent years, the Geological Survey conducted extensive studies in several other estuaries, notably in San Francisco Bay, Calif. and in the Potomac River estuary, and many data compilations and research reports have been produced. Examples of individual estuarine reseach studies are given in the annual volumes of "Geological Survey Research" (U.S. Geological Survey, 1980a, p. 159–162; 1980b, p. 167–174). An overview of water-quality aspects of an intensive study of the Potomac Estuary and the section of the Potomac River affected by tides is given by Callender and others (1984). Much of the information obtained in estuarine studies is unique to the system where it was collected, but some broad understanding of processes is gained from such studies.

The changing of the river from freshwater to saltwater conditions has substantial effects on suspended material in the river within the estuary. Destabilization of colloids and alteration of adsorption equilibria are among the commonly observed changes. There is a general tendency for trace metals to be trapped in estuarine sediments as a result of these and other processes. The subject of trace-metal partitioning among various kinds of particulates in estuaries was reviewed by Luoma and Davis (1983). They concluded that principles of surface chemistry should be useful in studying these complicated processes.

Water Chemistry and Movement in the Unsaturated Zone

Hydrologists for many years considered themselves members of ground-water or surface-water "disciplines." This division left out an important sector of water flow paths. Most streams or lakes are in rather direct communication with ground water that saturates the available pores or flow channels. However, between those land surfaces that are not continually covered with water and the underlying ground-water body there is an intermediate zone where openings and pore spaces are filled mainly with air. Periodically, water is added to this zone, by rainfall or by irrigation of crops, for example, and the portion that is not returned by evapotranspiration to the atmosphere can move downward toward the ground-water table. Where water is plentiful and the openings are large, the water may percolate through this unsaturated zone fairly quickly, and if the ground water is under unconfined conditions this percolation may be a major means of recharge. Movement of water through unsaturated granular material, however, is very slow. Where the water table lies tens or hundreds of meters below the surface and amounts of water in the soil that manage to escape the demands of evapotranspiration are small, a long time will be required for water to move from the land surface to the water table. Movement of solutes can be even slower, owing to interaction of the ions in the water films on mineral surfaces and surface charge sites. Precipitation or dissolution reactions, as well as sorption and ion exchange, may occur at these surfaces.

The movement of water and solutes through the unsatuated zone has been studied rather extensively in recent years but remains incompletely understood. Because it is through this route that many pollutants enter ground-water systems, a better understanding of processes in the unsaturated zone is much needed. Pollutants of many types enter this zone in all urbanized areas and many rural areas. Some of these substances can be expected to appear, eventually, in shallow ground water in such areas.

One of the difficulties in studying the unsaturated zone is obtaining samples of water from it. One method of extracting water involves placing a porous ceramic cup below the ground surface. A vacuum is then applied, and water that collects is later withdrawn by applying compressed gas (Wood, 1976). Samples of soil moisture and water in the unsaturated zone in bottom land adjacent to the Gila River in the upper part of the San Carlos reservoir area, Arizona, were obtained by a somewhat similar procedure (Laney, 1977). Methods of obtaining soil extracts are in common use in soil chemistry work (U.S. Salinity Laboratory Staff, 1954), and such procedures were used in the San Carlos reservoir area by McQueen and Miller (1972).

Results reported by Laney (1977) and by McQueen and Miller (1972) showed that water in the unsaturated zone may have relatively high solute concentrations compared with the underlying ground water. In studies of movement of nitrate through the unsaturated zone in southern and central California, Pratt and Adriano (1973) and Pratt and others (1972) measured the moisture content of soil cores taken at various depths and determined nitrate by extracting the solutes with water. Besides showing that nitrate concentrations of hundreds of milligrams per liter existed in some of these unsaturated zone waters, this work also suggested that movement of this solute from land surface to the water table was slow—less than a meter a year in some places (Pratt and others, 1972).

Geochemical Cycles

Before proceeding to more specialized discussion of water chemistry, there are certain geochemical concepts relating to large-scale behavior of the elements that should be considered. Geochemists sometimes speak of the cycle through which an element moves—from its initial incorporation in crystalline material deep within the Earth, through processes by which it may be transported into other environments or incorporated into other materials, and, finally, to its restoration to its original state by geologic processes. Those elements that are readily extracted from crystalline minerals and brought into solution are easily transported and have sometimes been referred to as "mobile."

For many years, geochemists have been interested in these circulation patterns, and some have tried to deduce the Earth's erosional history from differences in distribution of elements between igneous rocks on one hand and the sedimentary rocks and the ocean on the other. If the premise is accepted that the sediments were derived from erosion of igneous rocks having an average composition similar to the igneous rocks now available for sampling, and that the surplus of eroded elements not accounted for in the observable present volume of sediments was left in the ocean, it is possible to estimate how much erosion of the outer crust has taken place. Goldschmidt (1933, 1937, 1954) made a series of such estimates on the basis of the distribution of sodium among igneous and sedimentary rocks and the water of the oceans. His figure, which is widely known and quoted, is that the equivalent of 160 kg of igneous rock has been eroded from each square centimeter of the Earth's surface.

If one calculates the balance of elements as the amount not accounted for in the total volume of sediments, using Goldschmidt's figure for the volume of eroded rock and the generally accepted abundance data for the elements, a figure in reasonable agreement with observed seawater composition is obtained. Some of the elements, however, especially chlorine, are far too abundant in the ocean to fit this concept, and sources other than igneous rock (or at least sources other than igneous rock like that which can now be sampled) must be found for them.

Barth (1952) proposed a somewhat different view of the behavior of the elements in weathering. He suggested that one might assume that a general balance has been attained between the rates of accretion of elements to the ocean (in solution in river water for the most part) and the rates at which these elements are returned to sediments. The average time in years for an atom of any element to remain in solution in the ocean (T) can be computed from the formula

$$T = \frac{A}{dA/dt} ,$$

where A is the total amount of the element dissolved in the ocean and dA/dt is the rate at which the element is added to the ocean. This rate can be estimated from observations of the annual solute discharge by rivers. Clarke (1924b, p. 119) estimated average river composition and discharge, and his data were later reviewed by Conway (1943) in the context of elemental fluxes to the ocean. As better values for composition and discharge become available for large rivers in less developed regions, the accuracy of flux estimates has improved. Well-known data compilations are those of Livingstone (1963) and Durum and others (1960). Martin and Meybeck (1979) prepared a summary of the present state of knowledge of this subject, with estimates of particulate as well as dissolved river loads.

Amounts of some of the elements that are contributed annually to the ocean by rivers are still imperfectly known. Goldberg and Arhennius (1958), however, prepared estimates of removal rates and residence times of a large number of elements by determining the composition and rate of accumulation of sediment in the ocean. This approach uses the same fundamental concept as Barth's, and residence times agreed reasonably well where they could be computed for some of the elements by both methods. The residence times of the elements determined by Goldberg (1963a) are given in table 7. These range from 2.6×10^8 years for sodium to only 100 years for aluminum. Similar results were reported by MacKenzie and Garrels (1966).

In most respects, the concept of residence time in the ocean is more satisfying to the chemist interested in aqueous behavior of the elements than is the Goldschmidt model with its dependence on average igneous and sedimentary rock composition. As Barth (1961) has pointed out, the igneous rocks that lie near the surface of the continents, which are the ones available for collection of rock samples for analysis, represent material that has in all probability been reworked many times and may, therefore, have a composition very different from its original composition. The present compositions of rocks and the oceans represent the result of a long-continued process of fractionation, and the residence time of elements in the ocean is, therefore, useful as an index of their geochemical behavior. The elements whose chemistry definitely favors retention in aqueous species have long residence times, and those preferentially bound into solids have short residence times.

Processes of sea-floor spreading and plate tectonics can be viewed as the way in which the cycle of weathering is closed and the oceanic sediments are returned to the continental crust. However, the quantitative evaluation of such processes does not appear feasible at this time.

Cycles of some elements are interrelated. Lasaga (1980) evaluated some aspects of coupling between the cycles of carbon and oxygen, using concepts of thermodynamics of irreversible processes. This approach has interesting possibilities for future theoretical studies, because one can predict stable states that are not at thermodynamic equilibrium.

EVALUATION OF WATER COMPOSITION

The composition of natural water must be determined by physical and chemical means, usually by collection and examination of samples. The standard practice of collection of samples and later analysis in the laboratory is changing somewhat in response to the growing trend to use automatic sampling and continuous-sensing devices. It is with the study and interpretation of water composition, however the water is obtained, that we are principally concerned.

Collection of Water Samples

Sampling is a vital part of studies of natural-water composition and is perhaps the major source of error in the whole process of obtaining water-quality information. This fact is not well enough recognized, and some emphasis on it seems desirable.

In any type of study in which only small samples of the whole substance under consideration may be examined, there is inherent uncertainty because of possible sampling error. The extent to which a small sample may be considered to be reliably representative of a large volume of material depends on several factors. These include, first, the homogeneity of the material being sampled and, second, the number of samples, the manner of collection, and the size of the individual samples.

The sampling of a completely homogeneous body is a simple matter, and the sample may be very small. Because most materials are not homogeneous, obtaining

Table 7. Average residence time of elements in the ocean

[After Goldberg (1963a)]

Element	Residence time (yr)	Element	Residence time (yr)	Element	Residence time (yr)
Na	2.6×10^8	Rb	2.7×10^5	Sc	5.6×10^3
Mg	4.5×10^7	Zn	1.8×10^5	Pb	2.0×10^3
Li	2.0×10^7	Ba	8.4×10^4	Ga	1.4×10^3
Sr	1.9×10^7	Cu	5.0×10^4	Mn	1.4×10^3
K	1.1×10^7	Hg	4.2×10^4	W	1.0×10^3
Ca	8.0×10^6	Cs	4.0×10^4	Th	3.5×10^2
Ag	2.1×10^6	Co	1.8×10^4	Cr	3.5×10^2
Au	5.6×10^5	Ni	1.8×10^4	Nb	3.0×10^2
Cd	5.0×10^5	La	1.1×10^4	Ti	1.6×10^2
Mo	5.0×10^5	V	1.0×10^4	Be	1.5×10^2
Sn	5.0×10^5	Si	8.0×10^3	Fe	1.4×10^2
U	5.0×10^5	Y	7.5×10^3	Al	1.0×10^2
Bi	4.5×10^5	Ge	7.0×10^3		
Sb	3.5×10^5	Ce	6.1×10^3		

truly representative samples depends to a great degree on the sampling technique. A sample integrated by taking small portions of the material at systematically distributed points over the whole body represents the material better than a sample collected from a single point. The more portions taken, the more nearly the sample represents the whole. The sample error would reach zero when the size of the sample became equal to the original volume of material being sampled, but for obvious reasons this method of decreasing sampling error has practical limits.

One of the primary goals of a water-quality investigation may be to provide information that can be used to determine the composition of the whole volume of water within or available to a region. The object of study may be a slowly circulating mass in a lake or reservoir, the water in an aquifer, or the water carried by a river during some finite time period. Also, information may be required on the variations in composition at a point, or over the whole water body, with passage of time. For other types of studies, a synoptic evaluation of water composition in a river drainage system may be desired, with the goal of emphasizing spatial rather than temporal variations. The design of sampling programs that will accomplish all these objectives encounters different kinds of problems in surface- and ground-water systems, and rather careful attention to sample collection is required.

The purpose underlying a water-quality study largely governs the sampling procedures that should be followed. Commonly, the investigator wishes to know the composition of a cross section of a river at a specific time. For some purposes, however, only the composition that would occur at a fixed water-intake point is of interest, and in this case the procedure would be somewhat simpler to design.

Sampling of River Water

To determine adequately the instantaneous composition of a flowing stream, the sample, or set of samples taken simultaneously, must be representative of the entire flow at the sampling point at that instant. Furthermore, the sampling process must be repeated if the results of analysis are to be extrapolated in time, and the sampling interval chosen must represent adequately any changes that might occur. Changes occurring along the length of the stream can be evaluated by adding more sampling points.

The homogeneity of a stream at a cross section is determined by such physical factors as proximity of inflows and turbulence in the channel. Locally, poor lateral or vertical mixing can be observed in most stream systems. Immediately below the confluence of a stream and a tributary there may be a distinct physical separation between the water of the tributary and that of the main stream, and, particularly in large rivers, this separation may persist for many kilometers downstream. The effect is more pronounced if the water of the tributary differs markedly from the water of the main stream in concentration of dissolved or suspended solids or in temperature. Where a river enters the ocean there is, of course, also a possiblity of seawater mixing incompletely with the flow. These effects may be of special interest in some studies, but if the average composition of the whole flow of a stream or its changes in composition over a period of time are the factors of principal significance, sampling locations where mixing is incomplete should be avoided.

An outstanding example of incomplete mixing across the stream is afforded by the Susquehanna River at Harrisburg, Pa. The stream at the highway bridge where samples were collected is about half a mile wide and is split into two channels by an island. The composition of the water is indicated by six samples spaced across the stream and is given in figure 2. More than 20 years of observations by the U.S. Geological Survey (Anderson, 1963) show that this pattern is always present in some degree, except at very high stages. The anthracite-mining region northeast of Harrisburg produces large volumes of drainage containing high sulfate concentrations and having a low pH. Tributaries entering the river from the west above Harrisburg, especially the Juniata River, are less influenced by mine drainage and usually carry alkaline water having much lower sulfate contents. Obviously, it is difficult to characterize the whole flow of the stream at Harrisburg, although samples at one point would indicate what an intake located there would obtain.

A composite sample that will represent accurately the water in a vertical cross section of a stream can be obtained by combining appropriate volumes of samples taken at a series of points along the cross section. At each point, samples should be obtained at enough different depths to compensate for vertical inhomogeneity. Obviously, it is physically impossible to obtain all these samples at one instant. The water in the stream is in motion at different rates in different parts of the cross section, and this further complicates the problem.

In practice, the collection of river-water samples is somewhat simplified by use of portable integrating sampling devices which allow water to enter the sample container at a rate proportional to water flow rate at the intake nozzle. The sampling device is raised or lowered from a selected position on a bridge or cableway to obtain a sample that will represent all the river flow at the particular point along the cross section. This process is repeated at other points along the cross section (commonly five or more) and the individual depth-integrated (or flow-rate-integrated) samples are combined.

Integrating samplers were developed beginning in the 1940's to obtain representative samples for calculating suspended sediment loads of streams. This sampling equipment and techniques for its use were described by

Guy and Norman (1970). The equipment may require modification to avoid contaminating samples collected for determining minor dissolved constituents.

If it is known or can be determined by field study that a stream at a proposed sampling site is uniform in composition at all flow stages, a single grab sample will satisfactorily represent the flow at the time it is collected. In earlier U.S. Geological Survey studies, efforts were made to establish river-sampling sites where homogeneity of solute concentrations across the stream was reasonably assured. For major solute constituents, some degree of homogeneity is common. For minor constituents that may be associated with suspended material, single grab samples may be very poor representations of the whole stream.

Some of the uncertainty in representativeness of individual samples was compensated for when samples were obtained at daily or shorter intervals. Most recent policy has been to obtain less frequent samples but to make a greater effort to be sure each represents the flow accurately. Sampling techniques used in studies made up to the mid-1970's were described by Brown and others (1970). Modifications of these procedures are required for unstable or trace constituents, and care must be taken to avoid contamination of samples by containers, preservatives, or sampling equipment. Some properties of water must be determined in the field. Detailed guidelines for sampling of river water have been set for U.S. Geological Survey studies by the technical memoranda circulated through the Water Resources Division. The major features of these guidelines are indicated above. Continuous sensing of specific conductance or other properties of the water supplements the periodic samples for detailed analysis.

Separate consideration of solution and solid phase portions of the sample is necessary, because free solutes and those associated with the solids will have very different physical and chemical behavior in the stream. Sampling and analytical procedures that do not make this separation adequately yield misleading and scientifically worthless results. At least a part of the sample generally must be filtered at the time of collection. Guidelines for filtration and preservation of samples were given by Brown and others (1970). Some aspects of sample treatment will be discussed later, as appropriate, in relation to specific solutes.

When a sampling point has been found and a procedure adopted that ensures that each sample adequately represents the water flowing at that instant, a decision generally is needed as to how frequently samples or measurements must be obtained. The composition of all surface streams is subject to change with time. Long-term changes may result from long rainfall or runoff cycles or from changes in land or in water use. Seasonal changes are to be expected from varying rates of runoff, evaporation, and transpiration typical of the seasons. Daily or even hourly changes of considerable magnitude may occur in some streams owing to flash floods, regulation of flow by humans, dumping of wastes, or biochemical changes.

Stream discharge commonly is computed in terms of mean daily rates. A strictly comparable water-quality observation would be the daily mean of a continuously determined property. A single grab sample, however, ought to be considered only to represent the instantaneous discharge at the time of sampling.

To determine the water-quality regimen of a river at a fixed sampling point, samples should be collected or measurements made at such intervals that no important cycle of change in concentration could pass unnoticed between sampling times. For some streams, where flow is completely controlled by large storage reservoirs or is

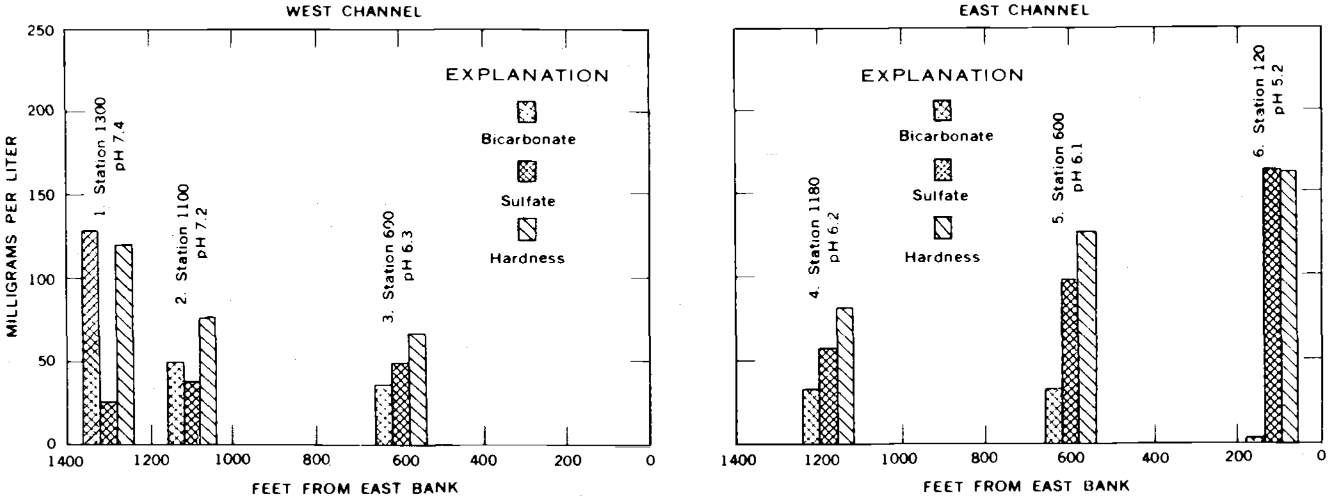


Figure 2. Bicarbonate, sulfate, hardness (as $CaCO_3$), and pH of samples collected in cross section of Susquehanna River at Harrisburg, Pa., July 8, 1947.

maintained at a nearly steady rate by large, constant, ground-water inflows, a single sample or observation may represent the composition accurately for many days or weeks. For many streams, however, one sample cannot be safely assumed to represent the water composition closely for more than a day or two, and for some streams not for more than a few hours.

The U.S. Geological Survey began extensive investigations of the chemical quality of river water shortly after 1900 (Dole, 1909; Stabler, 1911), as a part of the agency's program for appraisal of water resources of the country. In these studies, samples were collected by a local observer once a day for a period of a year or more at each sampling site, which also was the site of a gaging station for measuring the flow of water. Once-daily sampling schedules were standard practice for many years in later work of this kind by the Geological Survey. Although this frequency of sampling might miss a few significant changes, it generally was thought to provide a reasonably complete record for most large rivers. After some records of this kind have been obtained, however, it is often possible to decrease sampling frequency and still maintain a useful, although less detailed, record.

A single daily sample usually was assumed to represent all the water passing the sampling point on the day it was collected and also to represent a discharge rate equal to the daily mean. The descriptive text accompanying the published river-water analyses for the early years of this century does not tell much about sampling methods and gives no reasons for the decision to obtain one sample each day. Continuous water-stage recorders were not in wide use at that time (Corbett and others, 1945, p. 191). It may be that investigators who were conditioned to accept once- or twice-daily gage readings as a basis for calculating mean daily water discharge felt that a once-daily sampling schedule was so obviously indicated that no alternative needed to be considered.

In recent years, equipment has been developed that can be installed on a streambank or a bridge to obtain various measurements of water quality every few minutes and to record or transmit the information to a central point. Developments in this field have been rapid, and such equipment obviously can provide much more detailed information than could be obtained by the old sampling methods. Some limitations of sampling remain, however, because the water on which measurements are made has to be brought to the instrument through a fixed intake. The site of the intake represents a fixed sampling point.

In the early studies mentioned above, the daily samples were combined into composite samples before the analysis was begun. The composites usually included 10 daily samples, and 3 composites were prepared for each month. In later investigations, a single determination, usually of specific conductance, was made for each daily sample before making the composite with the remaining water. One of the principal reasons for combining individual daily samples into composites was the need for a large volume of water for the analytical procedures that were then in use. Another reason, of course, was economic, as the analytical work was expensive. The composite samples usually included 10 to 30 daily samples, but shorter periods were used at times to avoid obscuring day-to-day changes and to study the composition of water at times of unusually high or unusually low discharge rate. Samples of water that differed widely in conductance usually were not included in the same composite, nor were samples representing widely different discharge rates; such samples were analyzed separately. In studies of streams in the Missouri River basin beginning in 1946, composites were prepared by using amounts of each daily sample proportional to the discharge rate observed at the time of sampling. That procedure yields discharge-weighted analytical results. Similar procedures were followed for some other streams, but for many streams, composites continuted to be made by equal volumes of each daily sample. The publications in the U.S. Geological Survey Water-Supply Paper series "Quality of Surface Waters of the United States," in which the results up to 1970 were released, describe compositing methods used. For various reasons there has been a trend in recent years away from daily sampling and compositing of samples for analysis. Depending on the requirements for information that the sampling program is expected to satisfy, the frequency of sampling may range from a few collections a week to once every 3 to 6 months. When comprehensive data on fluctuations are needed, these samples are supplemented by continuous automated records of conductivity and other properties.

In a statistical study, Sanders and Adrian (1978) developed a method for determining optimum sampling frequency for river-monitoring stations on the basis of water-discharge fluctuations. Stations in the Geological Survey's NASQAN network follow an operating schedule that includes once-a-day or continuous conductivity measurements and once-a-month or less frequent sampling for determination of major dissolved constituents. A similar schedule has been adopted for many other stream sampling stations operated by the Geological Survey.

The range between high and low extremes of dissolved-solids concentration at a sampling point on a stream is rarely as wide as that between high and low flow rates. Maximum dissolved-solids concentrations 20–40 times as great as the minimum have been observed over long periods of record in some nontidal streams in the United States, but for most of the larger rivers the range is much narrower. Usually the changes in dissolved-solids concentration are somewhat related to the rate of water discharge and the rate of change of discharge, but this relationship is complicated by other factors related to both the hydrology and the geochemistry of the system. For some streams, past records can be used directly to estimate water quality from discharge. For other streams, such estimates are too inaccurate to be of any value.

Automated or continous-recording equipment for conductivity and other solution variables, supplemented by properly designed sampling and chemical analyses, provides many details on water-quality regimens that are not attainable by sampling alone. This approach is particularly useful in streams having tributaries that supply water that varies extensively in composition, in streams having large actual or potential inflows of waste, and in streams influenced by oceanic tidal inflow.

From compilations of water-quality records obtained at properly chosen sites on a stream system, a hydrologist can put together a basin-wide or statewide summary of stream chemistry. For example, Wood (1970) summarized the composition of Michigan stream water using maps and selected analyses. Anderson and Faust (1973) made a much more detailed summary of water-quality and hydrologic factors that control it in a 762-square-mile area drained by the Passaic River in New Jersey.

Water-quality data for U.S. streams obtained after 1970 have been published in annual reports for each State in a series entitled "Water Resources Data for (State) ________ , Water Year ________ ," available from the National Technical Information Service, Springfield, Va. The data also are stored in computer data banks (WATSTORE and STORET) and can be located by the National Water Data Exchange (NAWDEX), U.S. Geological Survey, Reston, Va. These records provide an enormous volume of factual information and have many practical applications.

A basin-wide summary of water-quality characteristics can also be obtained by making simultaneous observations and measurements at many sites along the main stream and important tributaries. The synoptic overview thus obtained can be repeated at different times of the year to give an indication of the effects of discharge changes and seasonal variations. A broad-scale application of this approach to the Willamette River Basin in Oregon was described by Rickert and others (1976).

The way water composition changes at a specific sampling and measuring point can best be determined by continuous sensing of specific conductance or related variables. There may be gaps in such records owing to instrument malfunction, and the feasibility of extrapolating or interpolating such records depends on the hydrologist's knowledge of water-chemistry variation at that site.

The Rio Grande at the San Acacia gaging station in central New Mexico is an example of a stream exhibiting considerable fluctuations of discharge and quality. Figures 3 and 4 show the way in which discharge fluctuates and specific conductance of the water changes at different time of the year. Figure 3 covers the spring-runoff period when melting snow in the river's headwater region caused the flow to increase from a few hundred cubic feet per second in April to nearly 10,000 cubic feet per second in May. The flow decreased to low stages again in June. During this period, the conductance of the water declined and then rose, but the day-to-day change was minor; the maximum for the 3 months was only about double the minimum. Daily, or less frequent, sampling will define such a period adequately. During the summer much of the runoff passing San Acacia results from flash floods in ephemeral tributaries in which both the quantity and the quality of the water vary widely. In figure 4 the results of samples collected from one to five times a day during part of the month of August were plotted with discharge rates observed at sampling times. On August 17, two samples collected a few hours apart showed a nearly threefold difference in concentration.

During the snowmelt period, a relatively small uncertainty is introduced by extrapolation of specific conductance over several days. During the summer-runoff period, however, the water composition is obviously difficult to predict without frequent measurements.

The implication here that discharge or flow measurements should be available for sampling sites is intentional. Chemical analyses of river water generally require some sort of extrapolation, if only because the water sampled has long since passed on downstream by the time a laboratory analysis is completed. The discharge record provides a means of extrapolating the chemical record if the two are closely enough related. The discharge data also serve as a means of averaging the water analyses, give an idea of total solute discharges, and permit evaluation of the composition of water that might be obtained from storage reservoirs.

Comparability of Records

The U.S. Geological Survey has now compiled detailed but discontinuous records of water quality for a great number of river-sampling sites over a time span exceeding three-quarters of a century. These records have a potential for indicating trends in water composition. Comments regarding methods of detecting such trends will be made later. However, as the preceding discussion has noted, the protocols for sampling and analysis have changed significantly during the period of record, and the direct comparison of published data obtained at different times may give misleading results unless the effect of these changes is considered.

For a few sampling stations, records of daily determinations of specific conductance exist that span more than 40 years. Specific conductance was not determined routinely in Geological Survey analyses before about

1935. The daily conductivity records prior to about 1970 mostly were not published, but were stored in Geological Survey district office files. Prior to 1935, chemical analyses of composites of about 10 daily samples constitute most of the published records. Virtually no determinations were made on the daily samples before compositing. The composites generally were made by combining equal volumes of the daily samples. If flow rate and solute concentration in the stream vary substantially, this method of compositing introduces a bias and can cause errors in attempts to correlate water composition with stream discharge. Composites weighted by discharge were used for some stations beginning about 1946. This practice became more common later but was never used for all sampling points.

During the 1970's the practice of compositing daily samples before analysis was almost completely abandoned in favor of making complete analyses of single samples collected less frequently. Rigorous comparison of newer and older records entails going back to daily measurement records and extending or coordinating data from the differing types of analytical records. Although some studies of this kind have been made, it appears likely that the uncertainty in computed data will result in an exces-

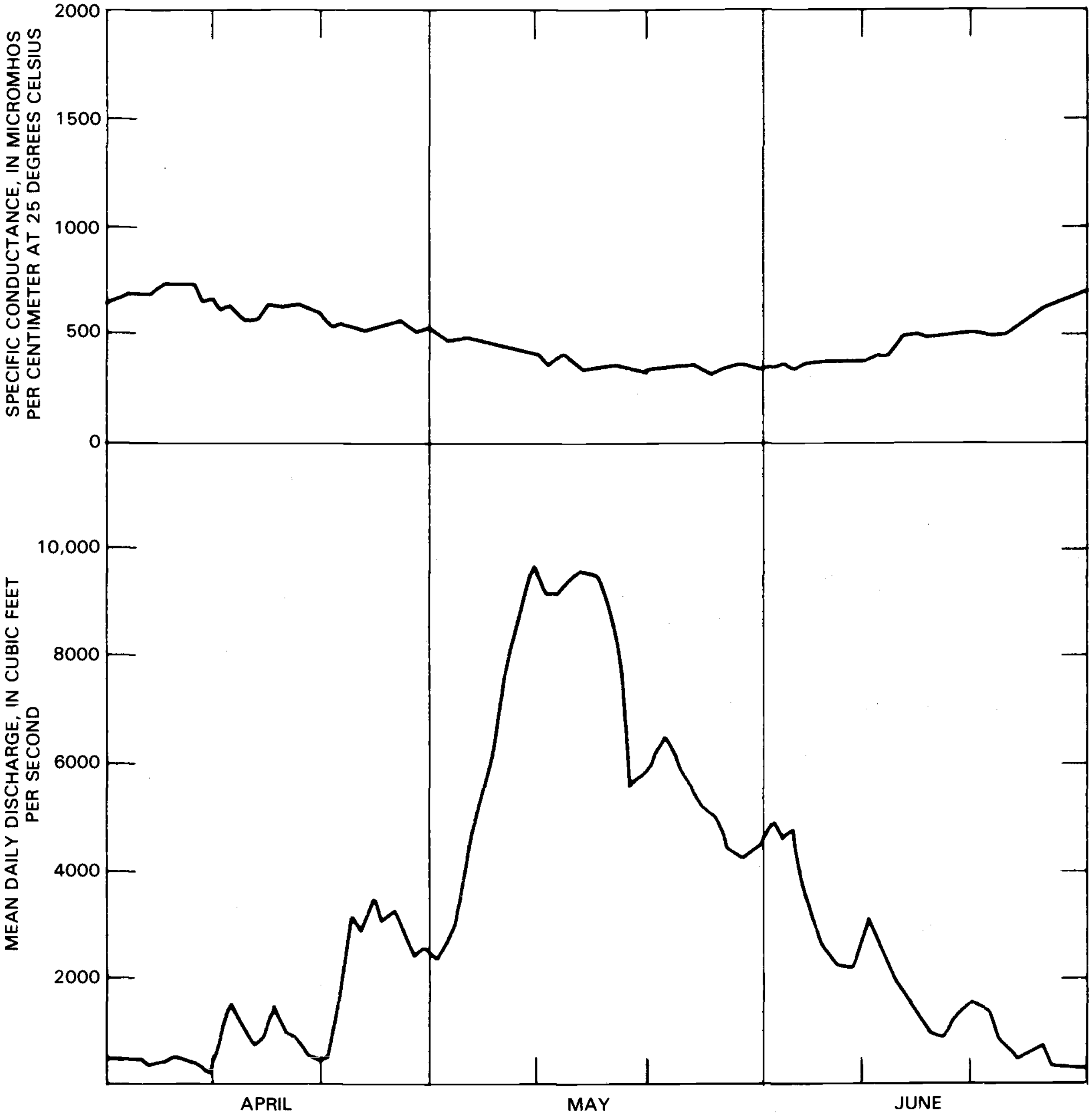


Figure 3. Conductance of daily samples and mean daily discharge of Rio Grande at San Acacia, N.Mex., 1945.

sively large noise-to-signal ratio that may mask the more subtle long-term changes in water composition.

Lake and Reservoir Sampling

Water stored in lakes and reservoirs commonly is not uniformly mixed. Thermal stratification and associated changes in water composition are among the most frequently observed effects. Single samples from lakes or reservoirs can be assumed to represent only the spot within the water body from which they come.

The effect of stratification on water composition is noticeable in concentrations of ions whose behavior is influenced by oxidation and reduction, the reduced species commonly increasing in concentration with depth below the surface and assuming particulate form in oxidizing shallower water. The components that are used by life forms in the water also are often considerably affected.

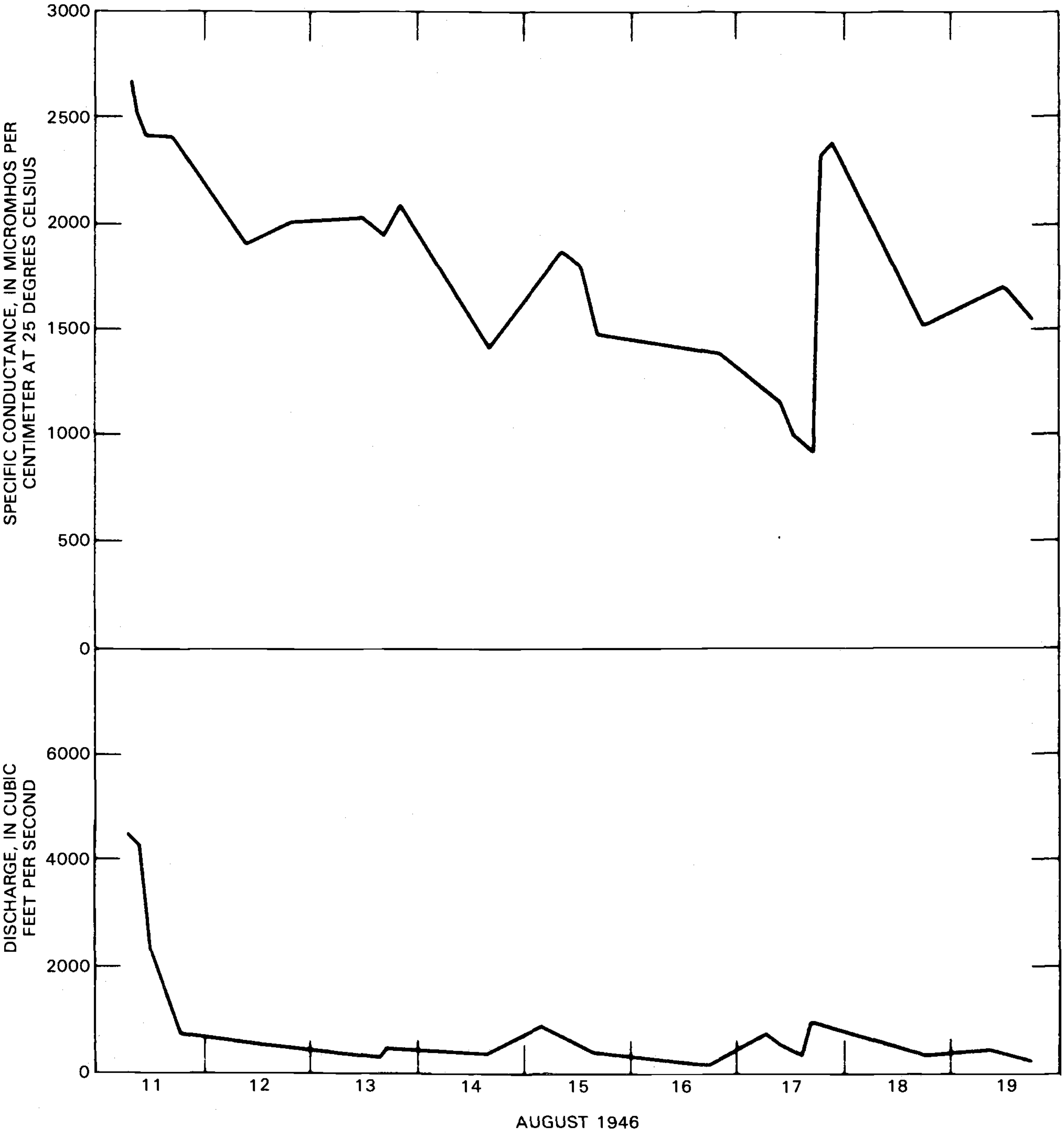


Figure 4. Conductance and discharge at times of sampling of Rio Grande at San Acacia, N.Mex., under typical summer-flow conditions.

A detailed study of these effects in water of a lake in the English Lake District was made by Sholkovitz and Copland (1982). The mechanics of stratification in lakes have been studied by many limnologists and will not be reviewed further here.

Many reservoir outlets are located in positions where they may intercept water that is depleted in dissolved oxygen. From a practical point of view, the water user is interested only in the composition of water available at the outlet, and most samples from storage reservoirs for which analyses are available come from released water.

Ground-Water Sampling

Most of the physical factors that promote mixing in surface waters are absent or are much less effective in ground-water systems. Even in thick sand of uniform permeability, the movement of water in the zone of saturation is slow and mixing is poor. In most sediments, the horizontal permeability is greater than the vertical permeability. This inhibits vertical movement of water, and water in a particular stratum may develop chemical characteristics that are substantially different from water in strata above or below.

Means of studying differing composition of water in different parts of the saturated zone are not entirely adequate. Wells commonly obtain water from a considerable thickness of saturated material and from several different strata. These components are mixed by the turbulent flow of water in the well before they reach the surface of the land and become available for sampling. Springs may obtain water from a lesser thickness of saturated material, but often the exact source is difficult to ascertain. Most techniques for detailed well sampling and exploration are usable only in unfinished or nonoperating wells. Usually, the only means of evaluating the quality of water tapped by a well is an analysis of a pumped sample. The limitations of a preexisting well as a sampling device are obvious but unavoidable. Observation wells specifically designed and installed for obtaining water-quality information may be necessary to avoid some of these problems.

Mixing of water from different strata in a well, and in some instances exposure of the water to the atmosphere, may bring about chemical instability, even though the original water in place was in equilibrium with its surroundings. This chemical instability may cause changes in certain constituents and requires sample preservation or onsite determination. This subject has been discussed by Wood (1976).

The differences in water quality with depth below the surface, and associated differences in lithology, are shown for three wells in the western part of Pinal County, Ariz., in figure 5. Water samples were obtained at several depths in each well during periods when the pumps were not operating; the specific conductance of each sample is indicated on the diagram opposite the depth at which the sample was obtained. Kister and Hardt (1966), in whose publication the illustration first appeared, reported a range in specific conductance in one well from 1,480 μmho/cm at a depth of 300 ft. below land surface to 29,400 μmho/cm at 550 ft. Water pumped from the well had a specific conductance of 5,960 μmho/cm. As Kister and Hardt pointed out (p. 10), "Chemical analyses of water samples collected from the discharge pipe of a pumping well are not necessarily indicative of the quality of water throughout the sequence of sediments penetrated by the well."

Although the range of conductance is unusually great, the data show how water yielded by a well could change in quality in response to changes in pumping rate or regional drawdown of the water table. Many wells are influenced to some degree by water-quality stratification, and the interpretation of ground-water analyses must always consider the possibility of such effects. Electric logs may provide useful indications of the location of water of poor quality in the saturated material penetrated by wells.

Although one rarely can be certain that a sample from a well represents exactly the composition of all the water in the vertical section at that point, it is usually a useful indication of the average composition of available water at that point. Where a considerable number of wells reaching the same aquifer are available for sampling and show similar composition, the investigator usually is justified in assuming homogeneity in drawing some conclusions about the chemistry of the ground water in the aquifer. If a well penetrates a large, relatively homogeneous aquifer, the composition of the pumped water generally will not change much over long periods of time. Areal variations in ground-water quality are evaluated by sampling wells distributed over the study area as appropriate to the amount of detail that is desired.

Because rates of movement and mixing in ground-water systems are generally very slow, changes in composition of the water yielded by a well or spring with respect to time can usually be monitored by annual or seasonal sampling. Exceptions may occur in aquifers having large open channels (as in cavernous limestone) or where there is recharge or contamination near the well. Some fluctuations in composition may be artifacts related to well-construction defects, casing failure or leakage, that permit entry of small amounts of water of poor quality.

Some examples of month-to-month changes in very shallow ground water in the alluvium of the Gila River in Safford Valley, Ariz. (Hem, 1950, p. 15), are shown in figure 6. These fluctuations are more rapid than those usually observed in wells of greater depth, and because many factors such as changes in river discharge, rainfall, irrigation pumping, and return flow may influence the water composition, no well-defined pattern of quality fluctuation can be discerned.

A long-term trend in ground-water composition is shown in figure 7. The two wells indicated in the graph were used for irrigation in the Welton-Mohawk area along the Gila River in southwestern Arizona (Babcock and others, 1947) before Colorado River water was brought into this area in the 1950's. The dissolved solids increased greatly over the period of record.

Completeness of Sample Coverage

In areas where hydrologic studies are being made, a decision is needed as to how many samples or other water-quality observations are required. Aside from administrative limitations in funds and personnel, this decision should be based on the conditions in the area to be studied. Factors to be weighed include the amount of information of this type already available, the hydrologic complexity of the area, the extent to which water of inferior quality is known or thought likely to be present, and other similar considerations. The aim of many water-quality investigations is to evaluate the resource as thoroughly as possible, and this usually requires many samples and field observations. The amount of laboratory work per sample often can be decreased if, by means of field determinations and laboratory determinations of certain key constituents, it can be shown that many of the samples have similar composition. The experienced water chemist thus can determine the water quality of an area by the most efficient combination of complete and partial chemical analyses. The water chemist's place on the team of any hydrologic investigation is important beyond the actual performance of analytical determinations.

Analysis of Water Samples

The analysis of water for its dissolved components is a part of the work done by a large number of chemical laboratories, including many supported by State, Federal, and local governments, academic and research institutions, and private enterprise. The methods used in water analysis are fairly well standardized and will not be discussed here. There are certain procedures for field testing and exploration, however, that should be commented on.

Field Testing of Water

Examination of water in the field is an important part of hydrologic studies. Certain properties of water, especially its pH, are so closely related to the environment of the water that they are likely to be altered by sampling and storage, and a meaningful value can be obtained only in the field. Other properties of water, its specific conductance, for example, are easily determined in the field with simple equipment, and the results are useful in

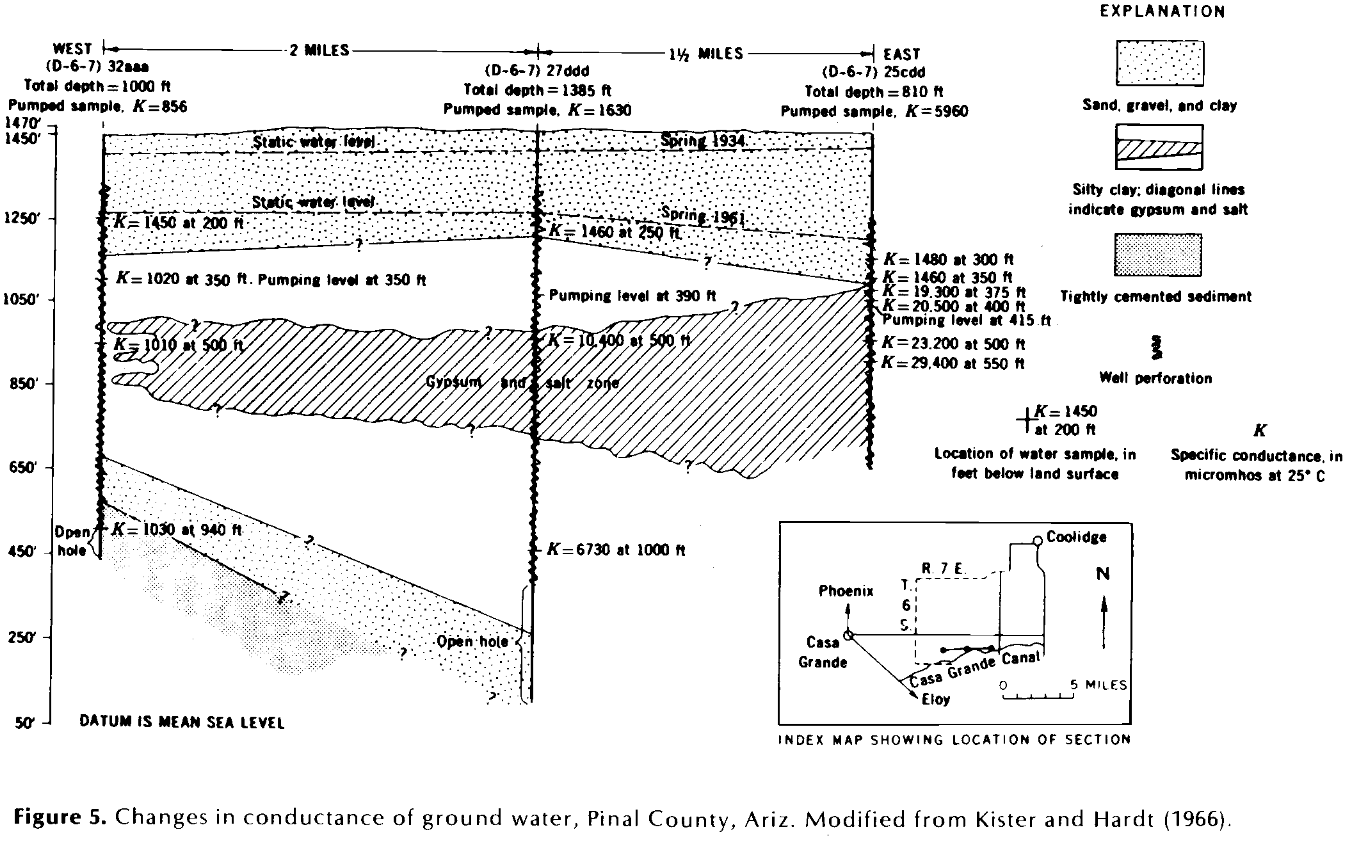


Figure 5. Changes in conductance of ground water, Pinal County, Ariz. Modified from Kister and Hardt (1966).

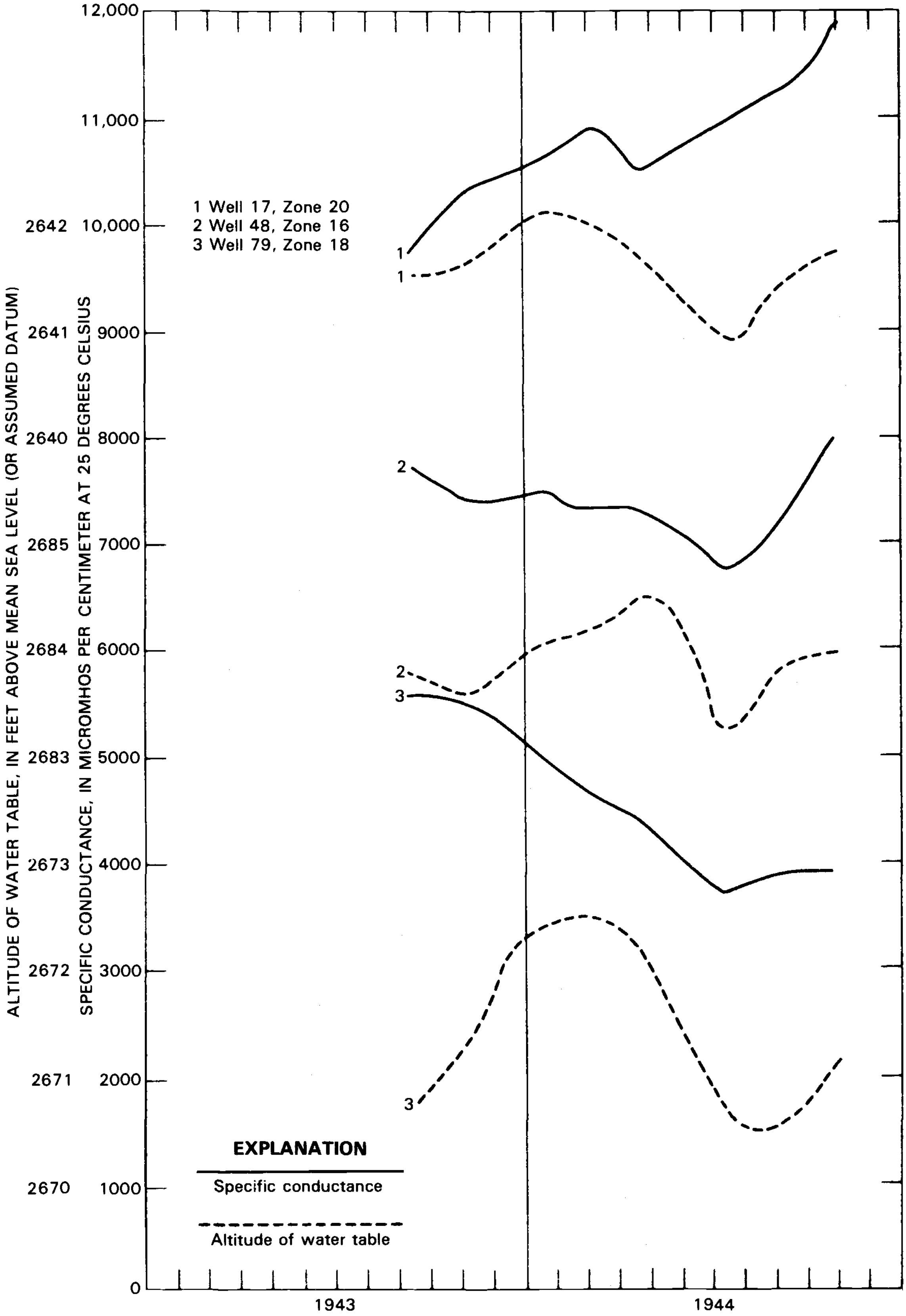


Figure 6. Specific conductance and altitude of water table for three typical observation wells, Safford Valley, Ariz. (Hem, 1950, p. 15).

supplementing information obtained from analyses of samples and as a guide to which sources should be sampled for more intensive study. Commercial equipment is available or can be adapted to field use, ranging from pocket-sized testing kits to trailer- or bus-mounted mobile laboratories. In the more elaborate units, almost any kind of standard analysis can be made.

The early history of field testing shows that its importance was recognized as long ago as the early 1900's, but equipment available then generally was rather crude. As early as 1896, a portable Wheatstone bridge for measuring the conductivity of water and saturated soil was being used by the U.S. Department of Agriculture (Scofield, 1932). The equipment for measuring water conductivity in the field has evolved into fairly sophisticated models that yield digital readings of temperature and specific conductance of samples. The units are battery powered, light, and easy to carry and give results nearly as accurate as those obtained in the usual laboratory installation. Sensing cells also can be incorporated in well-exploration equipment. Specific-conductance measurements and their meaning are discussed under that heading in a later section of this book.

A rapidly expanding application has been the continuous measurement of conductivity or other characteristics of river water with equipment installed at the sampling site. These units can be made to record results in a form that can be fed directly into an electronic computer. Power for operating the installation usually is best obtained from a 115-volt alternating-current line.

Any determination that can be made by potentiometric methods can easily be accomplished in the field or can be built into an onsite sensor. The pH of a water, for example, generally is determined by means of a sensitive electrometer and suitable reference and glass electrodes. For most ground water, the pH needs to be determined immediately after the water issues from the well or spring, if the value is to represent conditions within the system in which the water occurs (Barnes, 1964). Electrode systems for determining dissolved oxygen and many individual ions also are available.

Although almost any property or component of natural water can now be determined at a streambank location and probably could be automated if necessary, the cost of the most elaborate installations is high, and a real need must exist as justification.

Geophysical Indicators of Ground-Water Quality

One of the most widely used means of geophysical exploration of subsurface conditions is electric logging of boreholes. One of the principal determinations made as part of the logging procedure is the resistance to passage of an electric current through the formations penetrated by the borehole. One form of resistivity logging uses a pair of electrodes which are spaced a specific distance apart and held against the side of the uncased hole. As the electrodes are moved up or down the hole, the electrical resistance observed between them changes in response to environmental changes. A recording device traces the resistance on a chart as the probe moves in or out of the hole. The result is a curve showing resistance plotted against depth below the surface.

The resistance of water-bearing material in place is a function of the resistance of the rock itself, the resistance of the interstitial water, and the length of the path through which current passes in the water contained in the interconnected openings in the rock. Resistance of most dry rocks is high, and, in effect, the resistance measured by electric loggers is controlled by the water conductivity

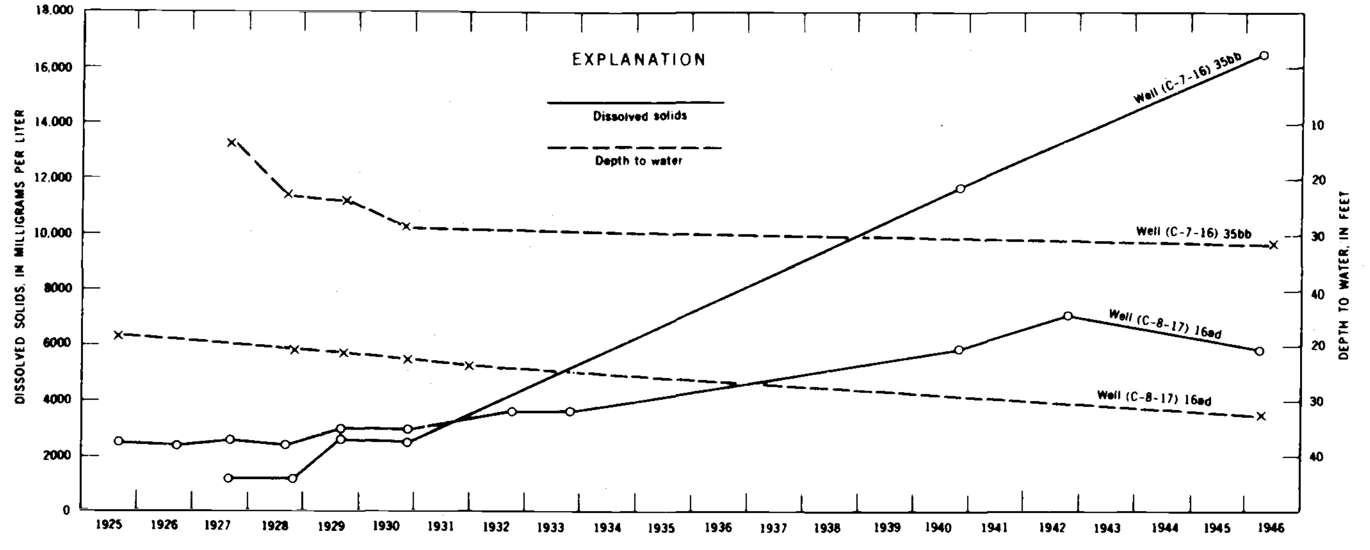


Figure 7. Dissolved solids and depth to water in two irrigation wells, Welton-Mohawk area, Yuma County, Ariz.

and the length of the current path. The resistance is expressed as resistivity (the reciprocal of conductivity), usually in ohms per meter per square meter. Values for resistivity of aquifers obtained through electric logging thus are closely related to conductivity of the water and porosity of the rocks. The principal use of electric logs in the water-well industry has been as an aid in determining the physical properties of water-bearing formations and in correlating formations from well to well. Applications of logging equipment in hydrology were described by Patten and Bennett (1963) and by Keys and MacCary (1971).

If the conductivity of the water is considered the unknown, and if the other features of the aquifer that influence the observed resistivity can be evaluated on the basis of laboratory tests of drill cuttings from the formation or on the basis of previous experience with the same aquifer, the resistivity log provides an indication of water quality in place underground.

To determine water conductivity reliably from a resistivity log, the aquifer properties must be well known. Some investigators have used resistivity logs to compute approximate chemical analyses for water; however, this may be done satisfactorily only when water from the formation in question is known to display a well-defined relationship between conductivity and each of the constituents for which the computation is made. Jones and Buford (1951) described such computations for ground waters in Louisiana.

Another property generally determined in electric logging is the spontaneous potential that can be observed between an electrode and the land surface when no current is introduced. This potential is partly related to electrochemical effects such as selective movement of ions and water through clays acting as semipermeable membranes, and to electrical potentials that occur at interfaces between solutions of dissimilar composition.

Some work has been done in relating the observed potentials more specifically to the water-bearing materials and the composition of the water, but more would seem to be justified, because this technique, when carefully refined, might give considerable insight into electrochemical relationships in ground-water systems that may influence both water quality and movement. Resistivity measurements can also be made at the land surface and may indicate something about the composition of ground water near the surface. Techniques of surface geophysical exploration for water resources studies were described by Zohdy and others (1974).

Laboratory Procedures

The procedures considered to be sufficiently accurate and most acceptable for general use in water analysis in the United States have been described in several publications. The most widely known of these is "Standard Methods for the Examination of Water and Wastewater" (American Public Health Association and others, 1980, 1985). It is revised every few years by the American Public Health Association, the American Water Works Association, and the Water Pollution Control Federation; and the 1980 volume is the 15th edition. A 16th edition was published in 1985. Other compilations widely used are those of the American Society for Testing and Materials (1978), the Association of Official Analytical Chemists (1980), and the U.S. Salinity Laboratory staff (1954). The U.S. Geological Survey compilation by Skougstad and others (1979) is also well known. A review of perodical literature on water analysis is published every 2 years in the journal *Analytical Chemistry.* The large volume of current literature in this field is indicated by the 665 articles referenced for the 2-year period October 1980 through September 1982 (Fishman and others, 1983). Automation and new instrumental methods have strongly influenced laboratory practice in the analysis of natural water in recent years.

Expression of Water Analyses

Various terms and units are commonly employed in the expression of data obtained in the chemical analysis of water. An understanding of those more frequently used is required for the interpretation of analyses.

Hypothetical Combinations

Water analyses published before 1900 generally were expressed in terms of concentrations of combined salts, such as sodium chloride or calcium sulfate. This kind of terminology probably was used in part as an attempt to describe the residue obtained when the water was evaporated, but it also predated the concept of dissociated ions in solution introduced in the late 19th century by Arrhenius.

Although water chemists often use terms such as "calcium bicarbonate water" to describe a solution in which Ca^{2+} and HCO_3^- are the principal ionic species, they recognize this as a form of shorthand or abbreviation for the much more clumsy expression "a water in which calcium and bicarbonate are the predominant cation and anion, respectively."

Ionic Statement

Many organic compounds and some inorganic compounds exist in solution in water as uncharged molecules, but most inorganic solids dissociate when they go into solution in water. The closely knit structure of the solid is broken into positively charged cations and negatively charged anions that are separated by solvent molecules. On a macro scale, the positive and negative charges must be in balance.

Because the water analysis is intended to reflect the true composition of the solution, most of the reported concentrations are in terms of actual cations and anions that are present. There are some important exceptions, however. Elements such as nitrogen or boron that may occur in several different forms, or whose actual form in solution is unknown, may be reported in terms of the total concentration of the element. The very abundant element silicon is generally present in water as undissociated silicic acid but is conventionally reported in terms of the oxide, SiO_2. For some purposes, a considerably more detailed breakdown of constituents than is usually furnished is necessary to show which solute species are actually present.

Determinations Included in Analyses

With the sophisticated equipment and analytical methods now available, the analysis of a water sample could include most of the elements in the periodic table, as well as a considerable suite of naturally or artificially produced isotopes of these elements and a great many specific organic compounds. The principal interest of the analyst and the great preponderance of data, however, traditionally have been directed at major constituents that make up nearly all the dissolved inorganic material. Concern with minor constituents has increased greatly in recent times owing to their possible effects on human health and on animal and plant nutrition and toxicity, or effects related to other kinds of water use.

For the purposes of this discussion, major constituents are defined as those commonly present in concentrations exceeding 1.0 mg/L. The dissolved cations that constitute a major part of the dissolved-solids content generally are calcium, magnesium, sodium, and potassium; the major anions are sulfate, chloride, fluoride, nitrate, and those contributing to alkalinity, most generally assumed to be bicarbonate and carbonate. The silicon present usually is nonionic and is reported in terms of an equivalent concentration of the oxide, silica (SiO_2).

Some other dissolved constituents are included in many chemical analyses because they may be particularly significant in considering suitability of water for certain purposes. Sometimes these constituents attain concentrations comparable to those of major components. They include aluminum, boron, hydrogen ion or acidity, iron, manganese, phosphate, organic carbon, forms of nitrogen other than nitrate, and dissolved gases, especially carbon dioxide, oxygen, and hydrogen sulfide.

Minor constituents in addition to the ones listed above, whose occurrence in fresh natural water has been investigated to a significant extent, include the alkali metals lithium, rubidium, and cesium, the alkaline-earth metals beryllium, strontium, and barium, the metallic elements titanium, vanadium, chromium, molybdenum, cobalt, nickel, copper, silver, zinc, cadmium, mercury, and lead, the nonmetals arsenic, antimony, selenium, bromine, and iodine, and the naturally radioactive elements uranium, radium, radon, and thorium. Each of these is separately discussed in a later section of this book.

Increasing concern over the presence of undesirable wastes or waste-alteration products and residues has produced a growing body of data on specific organic compounds, both natural and manmade, in water and on manmade radioactive elements and nuclides.

Certain properties of water solutions besides the contents of specific ions have commonly been included in water analyses. Hardness in water is commonly expressed in terms of an equivalent quantity of calcium carbonate. Other properties often included in a water analysis are color, specific conductance, dissolved solids, specific gravity, suspended matter, turbidity, biochemical or chemical oxygen demand, sodium-adsorption ratio, and various forms of radioactivity. These constituents and properties will be discussed in more detail as appropriate in following sections of this book

Units Used in Reporting Analyses

Over the years, a wide variety of units have been used in reporting water analyses. Considerable progress has been made toward standardization of these units, but using the data available in published literature often requires a general understanding of the units and systems used in the past and how they compare with more modern units. The two most common types of concentration units are those that report weights of solute per weight of solution and those that report weights of solute per unit volume of solution.

Weight-Per-Weight Units

A concentration reported in weight-per-weight is a dimensionless ratio and is independent of the system of weights and measures used in determining it. For many years, the water analyses made by U.S. Geological Survey and many other laboratories in the United States were reported in "parts per million." One part per million is equivalent to one milligram of solute per kilogram of solution. One percent, of course, is one part per hundred, or ten thousand parts per million.

"Parts per thousand" sometimes is used in reporting the composition of seawater. In this connection, "chlorinity" and "salinity" have been defined in terms of parts per thousand (grams per kilogram) for use in studies of seawater composition (Rankama and Sahama, 1950, p. 287).

At one time the unit "parts per hundred thousand" was in common use. "Parts per billion" or "parts per trillion" is sometimes used in reporting trace constituents.

Weight-Per-Volume Units

Because water is a liquid, definite quantities for analysis are ordinarily measured in the laboratory by means of volumetric glassware. The laboratory results, therefore, are in terms of weights of solute per unit volume of water. These results must be converted to a weight basis to obtain parts-per-million values. The conversion usually is done by assuming that a liter of water weighs exactly 1 kilogram and, hence, that milligrams per liter and parts per million are equivalent. This assumption is strictly true only for pure water at 3.89°C. The presence of dissolved mineral matter tends to increase the density, and at higher temperatures the density decreases. For practical purposes, however, the error introduced by assuming unit density does not reach a magnitude comparable to other anticipated analytical errors until the concentration of dissolved solids exceeds about 7,000 milligrams per liter. For highly mineralized waters, a density correction should be used when computing parts per million from milligrams per liter. Volumetric glassware is calibrated for use at 20°C, and ordinary laboratory temperatures are usually close to this value. Concentrations expressed in milligrams per liter are strictly applicable only at the temperatures at which the determination was made, but for most purposes for which the concentration values might be used, the effect of volume change caused by temperature changes of the solution is not important.

The reporting of dissolved constituents in milligrams (or micrograms) per liter has become standard practice in water analysis throughout the world. This avoids calculated density corrections.

Where the English or U.S. customary system of units is used, analyses are sometimes expressed in grains per gallon. The particular gallon that is meant must be specified, as the U.S. gallon and the Imperial, or British, gallon are not the same. The unit is still seen fairly frequently in connection with hardness in water. Reports dealing with irrigation water commonly express concentrations in tons per acrefoot. The ton is 2,000 pounds, and an acre-foot is the amount of water needed to cover 1 acre to a depth of 1 foot.

Streamflow or discharge represents a rate quantity. Rate concepts may be significant in some studies of river-water composition, and the dissolved-solids load, a rate quantity, is generally expressed in tons per day.

Conversion factors that indicate the relationships of the various units to each other are given in table 8. Factors changing grains per gallon or tons per acre-foot to parts per million, or the reverse, would be the same as those shown for conversions to or from milligrams per liter, if it is valid to assume unit density of the water. For highly mineralized water, these factors must take into account the density of the water. Hardness values are sometimes expressed in degrees. Conversion factors for these units, which differ in different countries, are given in the discussion of hardness in water elsewhere in this book.

Equivalent-Weight Units

For manipulations that involve the chemical behavior of dissolved material, the chemist must express analytical results in units that recognize that ions of different species have different weights and different electrical

Table 8. Conversion factors for quality-of-water data

[U.S. gallon is used for all units involving gallons]

To convert—	To—	Multiply by—
Calories	Joules	4.184
Grains per gallon	Milligrams per liter	17.12
Milligrams per liter	Grains per gallon	.05841
Milligrams per liter	Tons per acre-foot	.001360
Milligrams per liter	Tons per day	second-feet× 0.002697
Tons (U.S. short)	Tons (metric)	.9072
Acres	Hectares	.4047
Miles	Kilometers	1.609
Tons per acre	Metric tons per hectare	2.2417
Parts per hundred thousand	Parts per million	10
Grams	Ounces (avoirdupois)	.03527
Ounces (avoirdupois)	Grams	28.35
Gallons (Imperial)	Gallons (U.S.)	1.2009
Liters	Quarts (U.S.)	1.057
Quarts (U.S.)	Liters	.9463
Second-foot days[a]	Acre-feet	1.983471
Second-feet[b]	Gallons per minute	448.8
Second-foot days	Gallons per day	646,317
Gallons per minute	Liters per second	.06309
Acre-feet[c]	Gallons	325,851
Acre-feet	Cubic feet	43,560
Acre-feet	Cubic meters	1,233.5
Cubic feet	Cubic meters	.028317
Cubic feet	Gallons	7.481
Ca^{2+}	$CaCO_3$	2.497
$CaCl_2$	$CaCO_3$	.9018
HCO_3^-	$CaCO_3$	.8202
[d]HCO_3^-	CO_3^{2-}	.4917
Mg^{2+}	$CaCO_3$	4.116
Na_2CO_3	$CaCO_3$	.9442
NO_3^-	N	.2259
N	NO_3^-	4.4266

[a] 1 s-ft/d=1 cfs for 24 h.

[b] 1 s-ft=1 cfs.

[c] 1 acre-ft=an area of 1 acre 1 ft deep.

[d] In the reaction $2HCO_3^- = CO_3^{2-} + H_2O + CO_2(g)$ (for computing total dissolved solids).

charges. For example, in the mass-law calculations discussed earlier, concentrations of ions and other dissolved species are given in moles per liter. A mole of a substance is its atomic or molecular weight in grams. A solution having a concentration of 1 mole per liter is a molar solution; thus, the molarity of a solution is its concentration in a weight per volume unit. A molal solution is one that contains 1 mole of solute per 1,000 grams of solvent. For dilute solutions up to about 0.01 molar, these two units are equal, within ordinary experimental error.

Concentrations in milligrams per liter are readily converted to moles per liter by dividing by the atomic or formula weight of the constituent, in milligrams. When parts-per-million values are treated in this way, the concentration unit obtained is usually called "formality," the number of formula weights per 1,000 grams of solution.

The concept of chemical equivalence can be introduced by taking into account the ionic charge. If the formula weight of the ion is divided by the charge, the result is termed the "combining weight" or "equivalent weight." When a concentration value in milligrams per liter is divided by the combining weight of that species, the result is an equivalent concentration that is useful for many purposes. Table 9 contains reciprocals of combining weights of cations and anions generally reported in water analyses. Milligrams-per-liter values may be converted to milliequivalents per liter by multiplying the milligrams per liter by the reciprocals of the combining weights of the appropriate ions.

The term "equivalents per million," which is used for the value obtained when parts per million is used instead of milligrams per liter as a starting point, is a contraction that has been generally adopted for the sake of convenience. In more exact language, the unit is "milligram-equivalents per kilogram" if derived from parts per million and "milligram-equivalents per liter" if derived from milligrams per liter. The term "milligram equivalents" is shortened by chemists to "milliequivalents," abbreviated "meq."

In an analysis expressed in milliequivalents per liter, unit concentrations of all ions are chemically equivalent. This means that if all ions have been correctly determined, the total milliequivalents per liter of cations is equal to the total milliequivalents per liter of anions. The relation of water composition to solid-mineral composition is made more clearly evident when the analysis is expressed in milliequivalents per liter. There are disadvantages to using these units, however, in that they require knowledge or assumptions about the exact form and charge of dissolved species. Laboratory determinations do not always provide this kind of information. For a species whose charge is zero, as for silica, an equivalent weight cannot be computed. A concentration of such species in moles or millimoles per liter is generally equally useful, however.

Table 9. Conversion factors: milligrams per liter×F_1=milliequivalents per liter; milligrams per liter×F_2=millimoles per liter (based on 1975 atomic weights, referred to carbon-12)

Element and reported species	F_1	F_2
Aluminum (Al^{3+})	0.11119	0.03715
Ammonium (NH_4^+)	.05544	.05544
Antimony (Sb)		.00821
Arsenic (As)		.01334
Barium (Ba^{2+})	.01456	.00728
Beryllium (Be^{2+})	.22192	.11096
Bicarbonate (HCO_3^-)	.01639	.01639
Boron (B)		.09250
Bromide (Br^-)	.01252	.01252
Cadmium (Cd^{2+})	.01779	.00890
Calcium (Ca^{2+})	.04990	.02495
Carbonate (CO_3^{2-})	.03333	.01666
Cesium (Cs^+)	.00752	.00752
Chloride (Cl^-)	.02821	.02821
Chromium (Cr)		.01923
Cobalt (Co^{2+})	.03394	.01697
Copper (Cu^{2+})	.03147	.01574
Fluoride (F^-)	.05264	.05264
Hydrogen (H^+)	.99216	.99216
Hydroxide (OH^-)	.05880	.05880
Iodide (I^-)	.00788	.00788
Iron (Fe^{2+})	.03581	.01791
Iron (Fe^{3+})	.05372	.01791
Lead (Pb^{2+})	.00965	.00483
Lithium (Li^+)	.14407	.14407
Magnesium (Mg^{2+})	.08229	.04114
Manganese (Mn^{2+})	.03640	.01820
Mercury (Hg)		.00499
Molybdenum (Mo)		.01042
Nickel (Ni)		.01704
Nitrate (NO_3^-)	.01613	.01613
Nitrite (NO_2^-)	.02174	.02174
Phosphate (PO_4^{3-})	.03159	.01053
Phosphate (HPO_4^{2-})	.02084	.01042
Phosphate ($H_2PO_4^-$)	.01031	.01031
Potassium (K^+)	.02558	.02558
Rubidium (Rb^+)	.01170	.01170
Selenium (Se)		.01266
Silica (SiO_2)		.01664
Silver (Ag^+)	.00927	.00927
Sodium (Na^+)	.04350	.04350
Strontium (Sr^{2+})	.02283	.01141
Sulfate (SO_4^{2-})	.02082	.01041
Sulfide (S^{2-})	.06238	.03119
Thorium (Th)		.00431
Titanium (Ti)		.02088
Uranium (U)		.00420
Vanadium (V)		.01963
Zinc (Zn^{2+})	.03059	.01530

Composition of Anhydrous Residue

The means of expressing analytical results discussed to this point all use concentrations of solutes. These concentration values are generally the deciding factors in the evaluation of water quality. Some geochemists, however, have preferred to express analytical data for water in terms they believed were more directly comparable to rock-composition data. To this end, they expressed analyses in terms of the percentage of each element or ion in the anhydrous residue remaining after evaporating the water. Clarke (1924a, b) used this reporting procedure, usually with a value for dissolved-solids concentration and percentages of the components which he termed "percentage composition of anhydrous residue."

The supposed advantage of this method of expressing analyses is that it may demonstrate similarities among waters that have similar geochemical origins but whose analyses might appear dissimilar because of dilution effects. For example, the composition of water from a river usually will appear to change a great deal as a result of increases or decreases in flow rate when one examines water analyses expressed in concentrations. When the data are recalculated to percentage composition of dry residue, at least part of the fluctuation in composition disappears.

Although for some geochemical considerations the calculation of percentage composition of residue is useful, this is not a good way of expressing the chemical composition of a solution, and since Clarke's time it has gradually disappeared from the literature.

Instead of computing percentage composition from actual weights of constituents, some investigators have computed percentages based on total anions or cations, in equivalents per million. The first extensive use of this kind of computation was by Chase Palmer (1911), and a related procedure has been adapted extensively in more recent times in certain graphical methods of study of water quality. These methods will be considered later in this book.

Concentration in Terms of Calcium Carbonate

The hardness of water is conventionally expressed in water analyses made in the United States in terms of an equivalent quantity of calcium carbonate. Some such convention is needed for hardness because it is a property imparted by several different cations, which may be present in varying proportions. However, the actual presence of the indicated number of milligrams per liter of calcium and carbonate ions certainly should not be assumed.

Another convention that is followed by many water-analysis laboratories is to express the results of the alkalinity titration in terms of an equivalent amount of calcium carbonate. Although the titrated alkalinity is sometimes not exactly assignable to one or more specific ionic species, the latter assignment gives a much clearer indication of the composition of the solution. In any event, alkalinity (to methyl-orange end point) expressed as milligrams per liter of $CaCO_3$ can be converted to an equivalent concentration of HCO_3^- in milligrams per liter by dividing the former by 0.8202. (See table 8.)

The formula weight of $CaCO_3$ is very near 100. Thus, hardness or alkalinity values in terms of milligrams per liter of $CaCO_3$ can be converted to milliequivalents per liter of cations or anions by dividing by 50. Analyses are occasionally seen in which other constituents are reported in terms of calcium carbonate. This form of expression is a way of expressing concentrations in terms of equivalent weights. The use of milliequivalents per liter for each specific ion gives at least equally useful results.

Comparison of Units of Expression

Table 10 shows a single water analysis expressed in milligrams per liter, milliequivalents per liter, millimoles per liter, percentage composition of dry residue, percentage of total cation and anion equivalents, and grains per U.S. gallon. It is assumed that the milligrams-per-liter values are equal to parts per million and that milliequivalents per liter are equal to equivalents per million for a water of this dissolved-solids concentration.

All the numbers in table 10 were derived from the same original analytical data. It is assumed that dissolved bicarbonate would be converted to carbonate in the dry residue, with loss of an equivalent amount of carbon dioxide and water. Computations of the type used in preparing the table use conversion factors given in table 8.

Forms of Dissolved Material—Complexes, Ion Pairs, and Polymers

Organic compounds and some inorganic substances occur in aqueous solution as uncharged molecules. Most inorganic compounds, however, dissociate into charged ions when they dissolve in water. Positively charged units are cations and negatively charged units are anions. There must be an overall balance between cations and anions in solution to maintain electrical neutrality. However, there are some interactions among ionic species that result in association of oppositely charged ions to form complex ions. Some examples have already been cited, and many more will be considered later in this book.

Chemical analyses of water generally report the total quantity of a particular element or ion without indicating its actual form in solution. For use in chemical thermodynamic calculations, the concentrations of participating reactants or products must be identified as specific solute species.

Complex ions are solute species made up from two or more single ions of opposite charge. For example, ferric iron in solution may hydrolyze to form a hydroxide complex:

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+.$$

The Fe^{3+} and OH^- in this unit are chemically bound to each other. If the concentration of ferric iron is high enough, the formation of complex species may also involve association of monomeric units to give dimers

$$2FeOH^{2+} \rightarrow [Fe(OH)_2Fe]^{4+},$$

and hydrolysis and polymerization may continue, giving a final product approaching the composition $Fe(OH)_3^0$ that contains many individual Fe^{3+} and OH^- ions linked together.

A special type of complex, here called an ion-pair, is an association of equally charged units to form a neutral species:

$$Ca^{2+} + SO_4^{2-} \rightleftharpoons CaSO_4(aq).$$

In this complex, the Ca^{2+} and SO_4^{2-} components are believed to be separated by one or more layers of intervening water molecules. Some authors have used the term "ion pair" in a less rigorous context.

"Polynuclear" complexes are defined by Baes and Mesmer (1976, p. 2) as complexes containing more than one cation. This is a broader definition than the one implied above for polymeric species. The term "polynuclear" will not be used in this book.

SIGNIFICANCE OF PROPERTIES AND CONSTITUENTS REPORTED IN WATER ANALYSES

The properties and constituents that are determined in water analyses are discussed individually in the following sections. For most constituents, the subjects considered are the form of dissolved species, solubility and

Table 10. Chemical analysis of a water sample expressed in six ways

[Sample from flowing well, 488 ft deep. Water from the Lance Formation. NW1/4 sec. 30, T. 57 N., R. 85 W., Sheridan County, Wyo. Collected August 3, 1946]

Constituent	mg/L or ppm	meq/L or epm	mM/L	Gravimetric percent	Percentage of epm	Grains per U.S. gallon
Silica (SiO_2)	7.9		0.131	0.40		0.46
Iron (Fe)	.17		.003	.01		.01
Calcium (Ca)	37	1.85	.925	1.87	6.1	2.16
Magnesium (Mg)	24	1.97	.985	1.21	6.5	1.40
Sodium (Na) Potassium (K)	611	26.58	26.58	30.80	87.4	35.69
Bicarbonate (HCO_3)	429	7.03	7.03	[1]10.63	23.1	25.06
Sulfate (SO_4)	1,010	21.03	10.52	50.90	69.2	59.00
Chloride (Cl)	82	2.31	2.31	4.14	7.6	4.79
Fluoride (F)	.6	.03	.032	.03	.1	.04
Nitrate (NO_3)	.0	.00	.000	.00	.0	.00
Boron (B)	.2		.019	.01		.01
Dissolved solids:						
Calculated	1,980	60.80	48.535	100.00	200.00	115.65
Hardness as $CaCO_3$:						
Total	191		1.91			11.16
Noncarbonate	0		.00			0
Specific conductance (micromhos at 25°C).	2,880	2,880	2,880	2,880	2,880	2,880
pH	7.3	7.3	7.3	7.3	7.3	7.3

[1] As carbonate (CO_3).

other concentration controls in relation to other dissolved substances, the source of the material, the range of concentration that may be expected, and factors that may influence the accuracy or precision of analytical determinations. Appropriate environmental influences are considered, and chemical analyses are used to illustrate the discussions. Literature references are given to aid readers who may be interested in learning more about the topic.

The chemistry of some solutes in natural water is reasonably well understood. For others, much remains to be learned. New research results will tend to make many statements made here subject to rather rapid obsolescence. This is one reason for keeping the discussions of individual constituents generalized and rather brief.

Nature of the Dissolved State

The discussions so far have presupposed that the dissolved state was well enough understood that it did not need to be defined. An exact definition of the term, however, does pose some difficulties. An aqueous solution can be defined as a uniformly homogeneous mixture of water and solute units that constitutes a single phase. Each of the dissolved solute units is surrounded by solvent molecules and has no direct contact with other like particles except as permitted by migration through the solution. The particles may carry an electrical charge, or they may be electrically neutral. There can be no doubt that individual ions, or pairs of ions, or even complexes made up of several ions, are in the dissolved state. If the particles are large aggregates that will settle out of the solvent by gravity, they certainly can no longer be said to be in the dissolved state.

Between these extremes lie particles of widely varying sizes that may, under favorable conditions, be retained in suspension indefinitely. These particles generally are considered colloidal, and the smaller colloidal particles merge into the dissolved state. Some textbooks suggest size ranges; for example, Glasstone and Lewis (1960, p. 571) stated that colloidal particles range in diameter from about 5 nanometers (nm) up to about 0.2 micrometer (μm). A micrometer is 10^3 nanometers, or 10^4 angstrom units (A). Therefore by this definition, the lower limit of diameter of colloidal particles is 50 A. A considerable number of organic compounds that may occur in natural water, such as those that impart a brown color, have molecules that are more than 50 A in diameter; hence, by this definition, they can occur only in the colloidal state, even though all particles may be single molecules. Inorganic polymeric ions may also attain collodial size. For example, aluminum hydroxide polymers form charged units containing hundreds of aluminum ions linked together by hydroxide ions (Smith and Hem, 1972, p. D38) that would have diameters between 50 and 100 A. Data presented by Smith and Hem (1972, p. D38) indicate that there is a change in chemical behavior of these polymers when they attain this size, which suggests that a transition between dissolved and particulate states occurs at that point.

Natural surface waters and ground waters carry both dissolved and suspended particles. The amounts of the latter present in ground water before it is brought to the land surface generally are small. But in river water, the concentration of suspended material may be large, and at a high stage of flow in many streams it greatly exceeds the concentration of dissolved solids. This suspended material poses something of a dilemma for the water chemist. In the usual water-chemistry study, the suspended solids are removed before analysis either by filtration or by settling. Both procedures remove particles more than a few tenths of a micrometer in diameter, that is, particles large enough to produce substantial light scattering. The suspended solids are then discarded, and the clear solution is analyzed. Some kinds of suspended material, however, may have an important bearing on the sanitary condition of the water. For example, analyses for the biochemical oxygen demand or for bacterial counts must be made using unfiltered samples. For many of the river-sampling sites used by the U.S. Geological Survey, the quantity of suspended load of streams is determined, but, except for separation into size ranges, very little has been done to determine the chemical composition and related properties of suspended loads of streams. Water users can justifiably say they are not interested in the composition of material they would filter out of the water before they used it in any event; hence, for many practical water-use applications the practice of filtering a sample and analyzing only the filtrate is entirely correct.

Characterization of Suspended Particulate Material

Particle-size distributions of suspended sediment are determined by various procedures, including wet sieving and analyzing differences in settling rate (Guy, 1969). Instrumental procedures also have become available (Ritker and Helley, 1969). Another physical property that has considerable significance is the effective surface area of sediment per unit weight. Surface area measurements of sediment fractions would have a more direct bearing on the physical-chemical behavior of the material than would the particle-size measurements.

A generalized terminology used in many U.S. Geological Survey reports calls sediment having particle diameters ranging from 0.24 μm to 4 μm "clay." Material in the range from 4 to 62 μm is termed "silt," and that in the range from 62 μm to 2.0 mm is termed "sand." In this context, "clay" does not have mineralogic significance.

Chemical composition of sediment can be determined by methods of rock analysis in which all constituents are rendered soluble by strong acid treatment or fusion. The composition may be expressed in mineralogic terms, generally by identifying species present by optical methods or by X-ray diffraction. Besides the various aluminosilicate minerals, metal oxide, hydroxide, and organic materials commonly are present, especially in the finer size classes. The oxide, hydroxide, and organic material also may be present on surfaces of clay particles or other silicate mineral particles in all size ranges. Solute cations are adsorbed on the particle surfaces as well, in proportions related to their relative dissolved concentrations and physicochemical properties of the ions and surfaces.

Physicochemical properties of sediment material that are important in evaluating their behavior toward solutes include the distribution, sign, and intensity of surface electrical charge and the way such charges interact with solute ions. The determinations that can be made to evaluate these properties include charge-site distribution (usually in equivalents or moles of positive or negative charge per unit area), zero point of charge (zpc), cation-exchange capacity (in equivalents per unit weight), and distribution or selectivity coefficients.

The zpc is defined as the pH at which the surface charge is neutral or effectively zero. At lower pH's the charge would be positive, and at higher ones, negative. The other measurements were described earlier in the section titled "Reactions at Interfaces."

Solute-sediment interactions obviously are fraught with complexity. Many attempts to devise methods and techniques for practical evaluation of the effects have been made, but much more work will be required before a good understanding of processes at particle surfaces can be reached.

Gibbs (1973) presented some preliminary data evaluating the relative importance of some solute-sediment interactions in the Amazon and Yukon Rivers. Kennedy (1965) studied the mineralogy and exchange capacity of sediments from 21 U.S. streams and estimated that in many streams, when flow and sediment concentrations were high, the ratio of total adsorbed to total dissolved cations exceeded 0.1 and in some streams was greater than 1.0. The streams studied represented a wide range of geologic and hydrologic condtions. A more recent study of the Amazon by Sayles and Mangelsdorf (1979) also showed that at flood stages the ratio exceeded 0.1, but these writers believed the adsorbed fraction was insignificant on an average annual basis because the Amazon usually carries low sediment concentrations. On reaching the ocean, many of the adsorbed ions are probably exchanged for sodium. The adsorbed ions also may be exchanged for solute ions in the stream water if the composition of the water changes owing to inflows of fresh or saline water.

Technologies for evaluating the adsorbed or readily available fractions of solutes held by stream sediment have been suggested by Gibbs (1973), Malo (1977), and many others. However, methods that will produce reliable, complete, and reproducible results at what would generally be considered acceptable cost, for routine data-collection purposes, do not presently exist.

In the first place, separation of the solution phase from the solids is required. It should be evident to the most uninitiated student of water chemistry that the chemical and physical behavior of the adsorbed material will differ from that of the dissolved material both in the steam itself and during any treatment process. Determinations of inorganic constituents on unfiltered samples, which is practiced by some laboratories that analyze river water routinely, give results that can be interpreted only in a gross, qualitative way. Unfortunately, also, some of the data obtained by this procedure have been stored in data banks or have been published without any clear indication that they represent unfiltered samples.

Separation of the phases is routinely done by filtration in the field through membrane filters having pores 0.45 μm in diameter. This size opening has come to be generally adopted as defining "dissolved," as opposed to "particulate," material. Most of the time, however, samples having significant sediment contents tend to plug many of the filter pores and effectively decrease the pore diameters to some value less than 0.45 μm. Observations of the effectiveness of filtration in removing fine particles of aluminum, iron, manganese, and titanium oxides and hydroxides from river water were reported by Kennedy and others (1974). These investigators found that filter membranes having pores 0.10 μm in diameter were considerably more effective for removing these materials than were membranes having larger pore diameters.

After filtration, the preferable procedure is to analyze both phases. Part of the filtrate is usually stabilized by acidification, which generally dissolves any colloidal material that might be present and minimizes adsorption of cations on container walls. Major constituents are determined using an unacidified fraction of the filtrate, because some constituents would be altered or destroyed by acid treatment. Analysis of the filtrate is straightforward. Characterization of the residue on the filter is much more difficult. The amount of original sample filtered needs to be known so that results may be properly assigned to a specific volume of water. The total weight of residue must be determined. Various types of treatment may then be used, either serially or on separate aliquots, to recover potentially soluble material. The treatments that have been used to recover the material range from simple to very complex, from extractions with neutral solutions of ammonium salts to displace adsorbed ions, through mild reducing agents, dilute acids or bases, oxidizing acids, and, finally, dissolution in hydrofluoric acid mixtures or through alkali fusion procedures used in rock analysis.

Owing to the complexity of some of these analysis schemes and the difficulty in carrying them out or in interpreting the results, simpler analytical procedures have been used in the U.S. Geological Survey water laboratories. A determination of "total recoverable" inorganic constituents is made using a specific volume of unfiltered sample that is acidified with hydrochloric acid to a molarity near 0.3 in H^+ and is held at a temperature near the boiling point for 30 minutes. The sample is then filtered and the required analytical determinations are made on the filtrate (Skougstad and others, 1979).

Data obtained in this way must be supplemented by comparable analyses of filtered fractions of the same sample. The amount of total solute that was associated with the solid phase can then be estimated.

The bulk composition of sediments carried to the ocean by many large rivers was determined by Martin and Meybeck (1979). They also estimated proportions of the various elements transported in suspended as opposed to dissolved forms. According to these authors, the ratio of dissolved to total quantity transported exceeds 0.5 only for bromine, iodine, sulfur, chlorine, calcium, sodium, and strontium.

Hydrogen-Ion Activity (pH)

The effective concentration (activity) of hydrogen ions could be expressed in the same kinds of units as other dissolved species, but H^+ concentrations in milligrams per liter or moles per liter are very low for water solutions that are not strongly acid. The activity of hydrogen ions can be expressed most conveniently in logarithmic units, and the abbreviation "pH" represents the negative base-10 log of the hydrogen-ion activity in moles per liter.

Theoretical concepts and various practical aspects of pH determination have been discussed at length in the literature. Bates (1973) has prepared an excellent and authoritative summary of these topics. The notation "pH" is now generally taken to mean hydrogen-ion activity rather than concentration, although the distinction between these concepts was not understood at the time Sorensen proposed the use of the pH notation in 1909. Throughout this discussion the term "hydrogen ion" is used with the reservation that such species exist only in hydrated form in aqueous solution.

Even when no other solutes are present, a few of the H_2O molecules in liquid water will be broken up into H^+ and OH^- ions. This process of dissociation is a chemical equilibrium that may be written

$$H_2O(l)=H^++OH^-.$$

In mass-law form, the equilibrium can be expressed as the equation

$$\frac{[H^+][OH^-]}{[H_2O]}=K_w.$$

By convention, the activity of the liquid water is taken to be unity in this very dilute solution, and the constant K_w is then equal to the product of the activities of H^+ and OH^-. This ion-activity product for water at 25°C is, in exponential terms, $10^{-14.000}$ (Covington and others, 1966). The two-place log of K_w is -14.00. At neutrality, by definition $[H^+]=[OH^-]$ and therefore pH=7.00.

At higher temperatures, K_w increases and the neutral value of pH becomes smaller; the value for 30°C given by Covington and others (1966) is $10^{-13.837}$. Neutral pH at 30°C therefore would be 6.92. The value of K_w at 0°C was given by Ackerman (1958) as $10^{-14.955}$, which means that neutral pH at that temperature is 7.48. The strong effect of temperature on hydrogen-ion behavior has considerable geochemical significance and must be taken into account in measurements of pH and in calculations using pH data.

The hydrogen-ion content of a natural water computed in moles per liter (milligrams per liter for H^+ is nearly the same as millimoles per liter) is usually in the "trace constituent" range. At pH 7, only 1×10^{-7} moles per liter of hydrogen ion is present, for example. The major constituents of most waters are in the concentration range of 10^{-4} moles per liter and up. Thus the hydrogen-ion content does not begin to approach the status of a major component of the solution until the pH goes below 4.0. A pH of less than 0 or greater than 14 can be attained in concentrated acid or base solutions.

The hydrogen-ion activity in an aqueous solution is controlled by interrelated chemical reactions that produce or consume hydrogen ions. The dissociation equilibrium for water is always applicable to any aqueous solution, but many other equilibria and many nonequilibrium reactions that occur in natural water among solute, solid and gaseous, or other liquid species also involve hydrogen ions. The pH of a natural water is a useful index of the status of equilibrium reactions in which the water participates.

The reaction of dissolved carbon dioxide with water, which is one of the most important in establishing pH in natural-water systems, is represented by the three steps

$$CO_2(g)+H_2O(l)=H_2CO_3(aq),$$

$$H_2CO_3(aq)=H^++HCO_3^-,$$

and

$$HCO_3^-=H^++CO_3^{2-}.$$

Both the second and third steps produce H^+ and influence the pH of the solution. Other reactions involving dissociations of acidic solutes include

$$H_2PO_4^-=HPO_4^{2-}+H^+,$$

$$H_2S(aq)=HS^-+H^+,$$

and

$$HSO_4^-=SO_4^{2-}+H^+.$$

Many of the reactions between water and solid species consume H^+; for example,

$$CaCO_3(c)+H^+=Ca^{2+}+HCO_3^-$$

and

$$2NaAlSi_3O_8(c)+2H^++9H_2O(l)$$
$$=Al_2Si_2O_5(OH)_4(c)+4H_4SiO_4(aq)+2Na^+.$$

The second of these involves alteration of water, and the first could also be written as

$$CaCO_3(c)+H_2O(l)=Ca^{2+}+HCO_3^-+OH^-.$$

These are commonly called hydrolysis reactions, and all such reactions influence or are influenced by pH.

Certain reactions in which precipitates are formed, such as

$$Fe^{3+}+3H_2O=Fe(OH)_3(c)+3H^+,$$

influence pH, and most oxidation reactions are pH related,

$$FeS_2(c)+8H_2O=Fe^{2+}+2SO_4^{2-}+16H^++14e^-$$

This reaction requires something to take up the electrons it produces—that is, something must be reduced as the sulfur is oxidized. The usual oxidizing agent probably is atmospheric oxygen. The rest of the complete equation, then, would be

$$^7/_2O_2+14e^-+14H^+=7H_2O.$$

Adding these together gives

$$FeS_2+^7/_2O_2+H_2O=Fe^{2+}+2SO_4^{2-}+2H^+.$$

If a particular reaction or set of reactions involving water, hydrogen ions, other solutes, and solids or gases has attained equilibrium, the pH that should be attained can be computed by the mass law and a set of simultaneous equations. General procedures for making such computations have already been outlined.

Under nonequilibrium conditions, the pH of the natural water can reach a steady value effectively controlled by a single dominant chemical process or a set of interrelated reactions. The controlling species are generally those present in the system or available to it in the largest quantity or those whose reaction rates are fastest.

The control of pH by chemical equilibria can be illustrated by a simplified example. When pure water is in contact with a constant supply of gas containing CO_2 such as the atmosphere, carbon dioxide will be dissolved up to a specific solubility limit depending on temperature and pressure. At 25°C and 1 atmosphere of pressure, the chemical equilibria involved are those already given for the solution and dissociation of dissolved carbon dioxide and of water. Mass-law equations for these equilibria at 25°C and 1 atmosphere are

$$\frac{[H_2CO_3]}{P_{CO_2}}=K_h=10^{-1.43},$$

$$\frac{[HCO_3^-][H^+]}{[H_2CO_3]}=K_1=10^{-6.35},$$

$$\frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}=K_2=10^{-10.33},$$

and

$$[H^+][OH^-]=K_w=10^{-14.00}.$$

Also, the constraint of electrical neutrality requires that there must be a cation-anion balance in the solution, represented by $C_{H^+}=C_{HCO_3^-}+2C_{CO_3^{2-}}+C_{OH^-}$. The quantity P_{CO_2} is the partial pressure of carbon dioxide in the gas phase—that is, the volume percent of CO_2 multiplied by the total pressure, in atmospheres, and divided by 100. The bracketed quantities are activities of solute species, in moles per liter, and **C** terms represent ion concentrations in the same units. Because this will be a very dilute solution, ion activities and actual concentrations are virtually the same.

There are five equations governing this system and a total of six variables—the P_{CO_2} and five solute activities.

Therefore, if one variable is specified, all the others will be fixed. The average value of P_{CO_2} for the atmosphere is $10^{-3.53}$ and is nearly constant; therefore, pure water in contact with air having the average CO_2 content will have a fixed pH and compatible concentrations of the related ions. The pH calculated for these conditions is 5.65. At 0°C the pH would be 5.60.

Although natural water can be expected to contain other ions, rainwater, in the absence of atmospheric pollution, might be expected to approach the conditions specified in this example, and a pH in the vicinity of 5.6 is frequently observed. The pH of ordinary laboratory distilled water often is near this value also.

If it is further specified that the system contains an excess of solid calcite, $CaCO_3(c)$, the four mass-law equations for equilibria still apply, along with a fifth representing the solution of calcite:

$$\frac{[Ca^{2+}][HCO_3^-]}{[H^+]}=K_{eq}.$$

One more solute species is added to the ion balance equation, giving

$$2C_{Ca^{2+}}+C_{H^+}=C_{HCO_3^-}+2C_{CO_3^{2-}}+C_{OH^-}.$$

The system now has seven variables related by six equations, and, again, if one is specified all the others will be fixed. For example, at equilibrium in this system, according to Garrels and Christ (1964, p. 83), if the gas phase is ordinary air, the pH at 25°C will be 8.4.

Garrels and Christ (1964, p. 83–91) gave calculations for other conditions involving carbonates. It should be evident from the examples how the pH enters into the equilibrium calculations. Furthermore, it should be apparent that this way of studying natural-water composition has many interesting possibilities. It is unsafe, however, to assume that pH in natural water is always at a value fixed by carbonate equilibria.

Buffered Solutions

A solution is said to be buffered if its pH is not greatly altered by the addition of moderate quantities of acid or base. Buffering effects occur in systems in which pH is controlled by reversible equilibria involving hydrogen and other ions, and the range of pH over which buffering is effective depends on the nature of the other solute species. Most natural waters are buffered to some extent by reactions that involve dissolved carbon dioxide species. The most effective buffering action by these species is within the pH range of most natural waters.

Some insight into the mechanisms can be obtained by briefly reviewing the carbon dioxide–water equilibria just discussed. If the principal solutes are H_2CO_3 and HCO_3^- the first dissociation of carbonic acid,

$$H_2CO_3=HCO_3^-+H^+,$$

will be the dominant control over pH. In mass-law form at 25°C and 1 atmosphere,

$$\frac{[HCO_3^-]}{[H_2CO_3]}=\frac{10^{-6.35}}{[H^+]}.$$

If strong acid is added to this system, the reaction will be driven to the left, but a considerable number of hydrogen ions may be used up before the ratio changes enough to alter the pH noticeably. This buffering effect is strong in solutions that contain considerable amounts of two dissolved CO_2 species. In this example, if the total activity of the two species is 2×10^{-2} moles/L, when their ratio is unity, each will be present in an activity of 1×10^{-2} moles/L (610 mg/L HCO_3), and the pH will be 6.35. To produce enough change in the ratio to cause a noticeable decrease in pH (about 0.01 pH unit), one would have to add at least 10^{-4} moles/L of hydrogen ions to convert HCO_3^- ions to H_2CO_3 species. The free hydrogen ions in the system, as indicated by pH, would remain less than 10^{-6} moles/L. Thus the quantity of reacted H^+ would be some 100 times as great as the activity of free H^+.

Other equilibria within the system also are affected when H^+ is added or removed, and redistribution of the H^+ among all these other reactions adds to buffering effects. The observed pH of a natural water is, in this sense, a convenient indicator of the status of these equilibria, but H^+ ions themselves normally are minor constituents of the solution. The pH of some waters is held at levels considerably below the buffering range of dissolved carbon dioxide species by redox reactions, such as the oxidation of pyrite or sulfur in other forms.

Although the concept of control of pH by buffering is related to the capacity of a system to participate in a chemical reaction, the property of buffer "intensity" is also a useful concept. For any given solution, this property is defined as the reciprocal of the slope of the titration curve at any given point in the titration (Stumm and Morgan, 1981, p. 159).

The concept of buffering action can be extended to heterogeneous systems, in which interactions between solutes and solids may effectively maintain relatively constant concentrations of H^+ and other solute species (Stumm and Morgan, 1981, p. 558).

Range of pH of Natural Water

As stated previously, the pH of pure water at 25°C is 7.00. Most ground waters found in the United States have pH values ranging from about 6.0 to about 8.5, but water having lower pH is not uncommon in thermal springs. Water having a pH much greater than 9.0 is unusual but by no means unknown. Values as high as 11.6 (Feth and others, 1961) and 12.0 (Barnes and O'Neil, 1969) have been observed in springs. The high pH values of waters studied by Barnes and O'Neil were ascribed to reactions of meteoric water with ultramafic rock in which serpentinite was produced. These reactions evidently consume H^+ more rapidly than it can be supplied in this system by any influx of carbon dioxide species. In contrast, some thermal springs (for example, analysis 3, table 18) may yield water whose pH is below 2.0.

River water in areas not influenced by pollution generally has a pH in the range 6.5 to 8.5. Where photosynthesis by aquatic organisms takes up dissolved carbon dioxide during daylight and the organisms release CO_2 by respiration at night, pH fluctuation may occur and the maximum pH value may sometimes reach as high as 9.0. Livingstone (1963, p. G9) gave an example of diurnal pH fluctuations in what was evidently a poorly buffered lake water in which the maximum pH exceeded 12.

In carbonate-dominated systems the arrays of equilibrium equations cited earlier may provide a basis for calculating the relative intensity of carbon dioxide sources. This calculation requires assuming that measured alkalinity and pH values can be used to calculate a partial pressure of carbon dioxide in an initial source, such as the air present in soil.

Table 11 gives three analyses of waters whose pH is controlled by equilibria involving carbon dioxide species and solid calcium carbonate. Analysis 1 is for a spring whose water was rather highly charged with carbon dioxide. The pH measured in the field at the time of sampling was 7.54. The water precipitated calcium carbonate in the sample bottle, and a second analysis of the sample made 6 months after the first shows a major change in both calcium and bicarbonate concentrations, accompanied by an increase in pH of almost a full unit. Analysis 3 is for a spring issuing from limestone near the mouth of the Little Colorado River in Arizona. This water deposits travertine in the riverbed, and it is likely that a pH value considerably higher than the 6.5 reported in analysis 3 would be observed in the water where precipitation was nearing completion. The pH of 9.4 reported for analysis 1, table 18, may be associated with hydrolysis reactions involving silicates in a system containing little carbon dioxide. The pH of the sodium carbonate brine from Wyoming (analysis 2, table 18) probably was near 11, but it was not reported in the published analysis. The low pH value (1.9) for analysis 3, table 18, results from the oxidation of sulfur species. Fumaroles in the vicinity yield sulfur dioxide.

The pH of a water sample can also be affected by oxidation of dissolved ferrous iron. The data in the following table represent successive determinations of ferrous iron and pH on a sample of water collected from the overflow of the Seneca anthracite mine at Duryea, Pa., on July 16, 1963 (unpub. analyses by U.S. Geological Survey):

Date (1963)	*Time after sampling (days)*	Fe^{+2} (mg/L)	*pH*
July 16	0	....	4.98
July 30	14	135	3.98
Aug. 20	35	87	3.05
Sept. 24	70	41	2.81
Oct. 29	105	2.2	2.69

The sample contained a high concentration of iron, and its pH decreased by more than 2 units as the ferrous iron was oxidized and precipitated as ferric hydroxide.

Measurement and Interpretation of pH

Electrochemical measurement of hydrogen-ion activity and the logarithmic pH scale for expressing the results originated in the first decade of the 20th century. During the 1920's and 1930's, the glass electrode was developed into a reliable and convenient sensing device (Dole, 1941) and the determination of pH was widely practiced in industrial and water treatment process control laboratories. Baylis (1927), for example, described the use of pH data in treating water to decrease its corrosiveness toward iron pipe. A paper by Atkins (1930) pointed out some possible applications in geochemistry, and measured pH values appear in many water analyses published during the 1930's.

A compilation of analyses of water from the Rio Grande at various points in Colorado, New Mexico and Texas (Scofield, 1938) indicates that the U.S. Department of Agriculture laboratory at Riverside, Calif., began publishing pH values as part of their water analyses in late 1933. U.S. Geological Survey laboratories did not begin to publish such data for river water until about a decade later. All these early measurements were made in the laboratory, and instrumental field measurements did not become common practice until the 1950's.

The design and construction of pH meters and electrodes were greatly improved during the 1950's and 1960's, and modern instruments are capable of measuring pH either in the laboratory or in the field with an experimental reproducibility of ±0.01 or 0.02 unit. This degree of precision requires careful work and special attention to electrode maintenance, buffer solutions, and temperature corrections. Barnes (1964) described procedures for precise field measurements.

A more primitive method formerly used for measuring pH in the field employed colored pH indicators. This technique is capable of measuring pH with an experimental reproducibility of only ±0.10 unit under the most favorable conditions and is not suitable for water that is naturally colored or poorly buffered. For the indicator compound to develop its color, it must participate in a reaction using or generating H^+, and this, in a nearly unbuffered solution, can overwhelm the buffering system and give a false pH value.

The measured pH is a very important piece of information in many types of geochemical equilibrium or solubility calculations, and values that are inaccurate or unrepresentative are a substantial source of error in such work. Measurements of pH that date back to the early 1950's or before may have rather large experimental uncertainties owing to equipment or methods. In addition, another serious type of uncertainty affects many pH values that are reported in older water analysis literature. Many of these values were determined in the laboratory after the samples had been stored for a considerable period of time. Field determinations of pH did not become common practice in U.S. Geological Survey investigations until the late 1960's. Obviously, field determinations are much more likely to represent conditions in the water that was sampled than are laboratory pH determinations. Effects of temperature and mixing of water from different aquifer sections in pumping wells may make interpreta-

Table 11. Analyses of waters with unstable pH

[Analyses by U.S. Geological Survey. Date under sample number is date of collection. Sources of data: 1, 2, U.S. Geological Survey, unpublished data; 3, Cooley (1976, p. F10)]

Constituent	1 Jan. 5, 1967		2 Jan. 5, 1967		3 June 14, 1950	
	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
Silica (SiO_2)	22		22		19	
Iron (Fe)	.02		.00		.01	
Manganese (Mn)	.01					
Zinc (Zn)	.02					
Calcium (Ca)	93	4.64	22	1.10	264	13.17
Magnesium (Mg)	58	4.77	54	4.44	79	6.50
Sodium (Na)	15	.65	15	.65	513	22.31
Potassium (K)	1.2	.03	1.1	.03	23	.59
Strontium (Sr)	.50	.01				
Carbonate (CO_3)					0	
Bicarbonate (HCO_3)	556	9.02	297	4.87	964	15.80
Sulfate (SO_4)	50	1.04	55	1.15	147	3.06
Chloride (Cl)	16	.45	17	.48	815	22.99
Fluoride (F)	.3	.02			.2	.01
Nitrate (NO_3)	.1	.00			3.2	.05
Boron (B)	.02					
Dissolved solids:						
Calculated	530		332		2,340	
Residue at 180°C						
Hardness as $CaCO_3$	470		277		984	
Noncarbonate	19		34		194	
Specific conductance (micromhos at 25°C).					3,940	
pH	7.54		8.40		6.5	

1. Spring on headwaters of Blackbird Creek, SE1/4 sec. 6, T. 6 S., R. 5 E., San Mateo County, Calif. Temperature, 7°C. pH measured at time of collection. Calcium determined on acidified sample.
2. Reanalysis of unacidified fraction of sample 1 after 6 months of storage in laboratory.
3. Spring discharging into Little Colorado River, 13 mi from mouth, Coconino County, Ariz. One of a group known as Blue Springs. Water-bearing formation: Redwall Limestone. Water contains CO_2 and deposits travertine. Discharge of group, about 200 cfs; temperature, 20.6°C. pH measured in laboratory.

tion of the most carefully determined pH values a very uncertain and difficult task.

As implied in the examples in this section, H^+ ions are produced within natural-water systems by various types of chemical reactions and are largely consumed by participating in subsequent chemical reactions in the system. Graphical summaries of solute and solid phase chemistry commonly use pH as one of the plotted variables, and some examples will be given in later sections of this book.

Specific Electrical Conductance

Electrical conductance, or conductivity, is the ability of a substance to conduct an electric current. Specific electrical conductance is the conductance of a body of unit length and unit cross section at a specified temperature. This term is synonymous with "volume conductivity" and is the reciprocal of "volume resistivity" (Weast, 1968, p. F-71). The American Society for Testing and Materials (1964, p. 383) defined electrical conductivity of water as "the reciprocal of the resistance in ohms measured between opposite faces of a centimeter cube of an aqueous solution at a specified temperature." This definition further specifies that units for reporting conductivity shall be "micromhos per centimeter at t°C." Because the definition already specifies the dimensions of the cube to which the measurement applies, the added precaution of including the length in the unit may not be essential and is often omitted in practice. Geophysical measurements of resistivity, however, commonly are expressed in ohm-meters, referring to a cube 1 m on a side, so it may be a good idea to emphasize that conductances of water refer to a centimeter cube. The standard temperature for laboratory measurements is 25°C, but because other standard temperatures were used in the past it is important that the temperature of measurement be specified.

Units for Reporting Conductance

Because conductance is the reciprocal of resistance, the units in which specific conductance is reported are reciprocal ohms, or mhos. Natural waters have specific conductances much less than 1 mho, and to avoid inconvenient decimals, data are reported in micromhos—that is, the observed value of mhos is multiplied by 10^6. Before October 1, 1947, the specific conductance values reported by the U.S. Geological Survey were mhos$\times 10^5$. To convert these older values to micromhos, they should be multiplied by 10.

Under the International System of Units (SI) it has been proposed that the unit of conductivity by renamed the "siemens." The microsiemens (μS) is numerically the same as the micromho. The change in terminology has not yet been fully adopted in the U.S. literature.

Physical Basis of Conductance

Pure liquid water has a very low electrical conductance: a few hundredths of a micromho per centimeter at 25°C. This value has only theoretical significance, because water this pure is very difficult to produce. The presence of charged ionic species in solution makes the solution conductive. As ion concentrations increase, conductance of the solution increases; therefore, the conductance measurement provides an indication of ion concentration.

The relationship between ionic concentration and specific conductance is fairly simple and direct in dilute solutions of single salts. Figure 8 is a graph of the specific conductance at 25°C of potassium chloride solutions with concentrations up to 0.01 molar (746 mg/L). The relationship over this range of concentration is a straight line. As the concentration is increased, however, the slope decreases slightly; for a concentration of 7,460 mg/L, the conductance is 12,880 μmho/cm rather than near 14,000, as an extrapolation of the slope in figure 8 would predict. This general behavior is typical of all salts, but the slope of the straight part of the curve and the degree to which it flattens with increasing concentration are different for different salts.

Figure 9 shows the change in conductance of a solution containing 746 mg/L of potassium chloride between 0° and 35°C. Over this temperature range the conductance of the solution more than doubles. This demonstrates the need for referring specific-conductance measurements to a definite temperature. The response of the conductance value to temperature change is somewhat different for different salts and different concentrations, but in dilute solutions for most ions an increase of 1°C

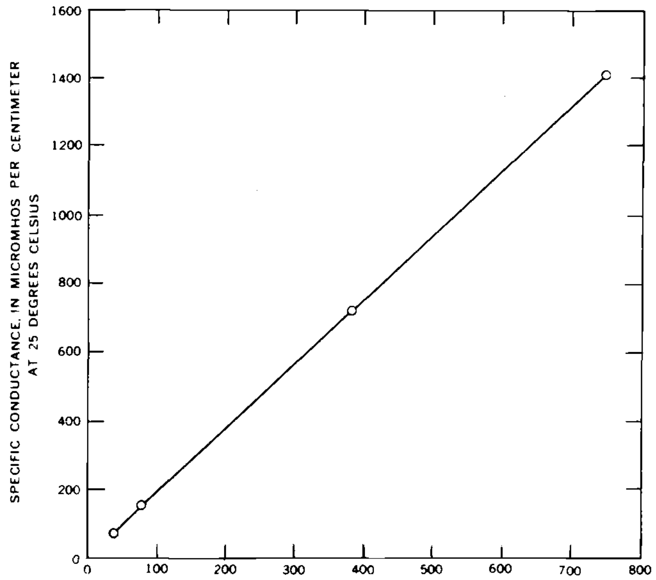


Figure 8. Specific conductance of potassium chloride solutions.

increases conductance by about 2 percent over the range of temperature likely to be applicable to laboratory conditions.

To conduct a current, solute ions actually must move through the solution to transfer charges, and the effectiveness of a particular ion in this process depends on its charge, its size, the way it interacts with the solvent, and other factors. The property called "ionic mobility" represents the velocity of an ion in a potential gradient of 1 V/cm. (It should be noted that this is not the same property as the geochemical mobility of an element, a concept relating to the ease of transport of elements in geochemical cycles). Ionic mobility is decreased by increasing concentration owing to interferences and interactions among the ions. Limiting values attained in solutions of very low concentration for the major ions in natural water are in the vicinity of 6×10^{-4} cm/s at 25°C (Glasstone and Lewis, 1960, p. 445).

It is apparent that even in rather simple solutions the relationships that affect conductance may be complicated. More complete discussions of theory and application of conductance such as those in textbooks of physical chemistry (Glasstone and Lewis, 1960, p. 415–451) further emphasize this fact. Natural waters are not simple solutions. They contain a variety of both ionic and undissociated species, and the amounts and proportions of each may range widely. When applied to natural water, therefore, the conductance determination cannot be expected to be simply related to ion concentrations or to dissolved solids. Some water sources, however, can display well-defined relationships.

Figure 10 is a plot of the dissolved-solids concentration in composite samples of water from the Gila River at Bylas, Ariz., for a year (U.S. Geological Survey, 1947) against the specific conductance of the samples. A reasonably well defined relationship is indicated for the range; thus, for any given conductance value a dissolved-solids value can be estimated with an uncertainty of only about ±100 mg/L, using the curve, which was fitted by eye to the points in figure 10. The whole set of data fit a straight line regression closely (r=.98) with a value for A in the formula

$$KA=S$$

of 0.59. (K in this formula is specific conductance in μmhos/cm and S is dissolved solids in mg/L.) However, the data points show that the slope of the regression is steeper for the lower conductance values. This is in accord with the earlier discussion of the relationship of conductivity to dissolved-solids concentration, which indicated that A would not be constant over a wide concentration range in solutions of a single anion and cation species. This kind of formula is often used, however, in calculating approximate dissolved-solids values from conductance determinations. For the analyses of natural waters given in this report, the range of A is about 0.54 to 0.96, which represents nearly the full range to be expected. A is mostly between 0.55 and 0.75, the higher values generally being associated with water high in sulfate concentration.

Figure 11 shows the relationship of specific conductance to hardness and ion concentrations for the same set of chemical analyses used in preparing figure 10. Rather well defined relationships again exist for chloride and sulfate, and almost as good a relationship for hardness (calcium+magnesium) is indicated. The bicarbonate concentration of these solutions (not shown in fig. 11) is less closely related to conductance, however. Lines drawn by

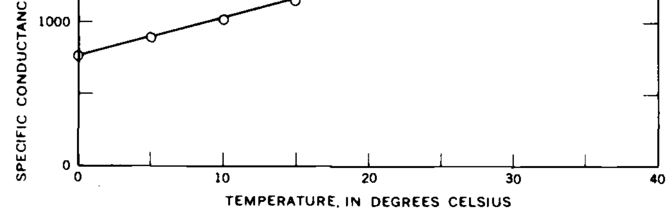


Figure 9. Specific conductance of 0.01-molar solution of potassium chloride at various temperatures.

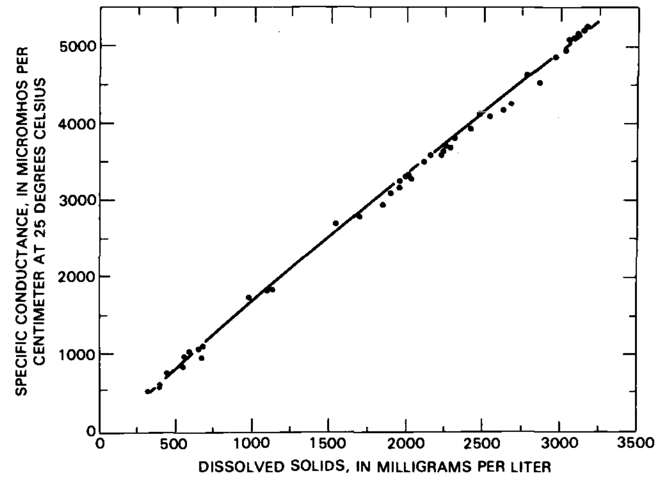


Figure 10. Dissolved solids and specific conductance of composites of daily samples, Gila River at Bylas, Ariz., October 1, 1943, to September 30, 1944.

eye through the points for chloride and sulfate show slight curvature, but the departure from linearity is insignificant.

The data used in figures 10 and 11 were obtained from a river that has a rather saline base flow maintained by irrigation drainage and ground-water inflows. The chemical characteristics of the base flow are rather constant and are subject to dilution by runoff. It seems evident that a record of conductivity at this station could be used to compute the other chemical characteristics of the water with a good level of accuracy for major ions, except at high flow when the relationships would not be as well defined.

When a satisfactory set of relationships between conductance and ion concentrations can be developed from a few years of intensive sampling, a record of major-ion concentrations, suitable for most uses, could be obtained by measuring conductivity continuously and feeding the output into a computer set up to convert the data to concentrations averaged for whatever periods might be desired. The sampling and analysis could be directed toward determination of constituents that did not correlate with conductance. The extent to which such uses of conductance data can be made depends, of course, on ascertaining relationships like those in figures 10 and 11; however, this cannot be done for all streams or all dissolved species of possible interest.

Conductance determinations are also useful in areal extrapolation of ground-water analyses in areas where comprehensive analyses are available for part of the sampled points. Conductivity probes are of value in exploring wells to determine differences in water quality with depth.

Range of Conductance Values

The specific conductance of the purest water that can be made would approach 0.05 μmho/cm, but ordinary single-distilled water or water passed through a deionizing exchange unit normally has a conductance of at least 1.0 μmho/cm. Carbon dioxide from the air in the laboratory dissolves in distilled water that is open to the air, and the resulting bicarbonate and hydrogen ions impart most of the observed conductivity.

Rainwater has ample opportunity before touching the Earth to dissolve gases from the air and also may

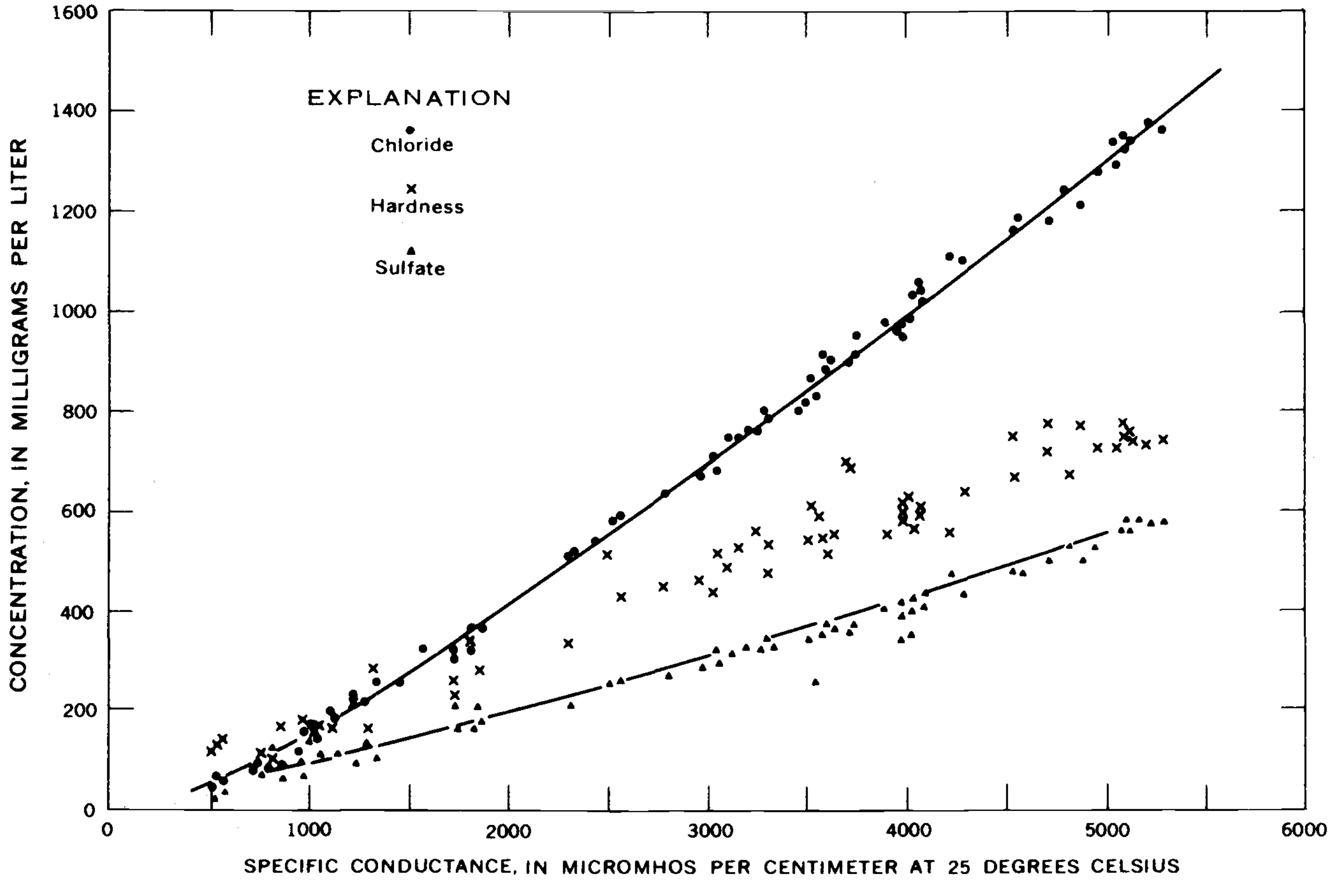


Figure 11. Relation of conductance to chloride, hardness, and sulfate concentrations, Gila River at Bylas, Ariz., October 1, 1943, to September 30, 1944.

dissolve particles of dust or other airborne material. As a result, rain may have a conductance much higher than distilled water, especially near the ocean or near sources of atmospheric pollution. Feth and others (1964) reported conductivities of melted snow in the Western United States ranging from about 2 to 42 μmho/cm. Whitehead and Feth (1964) observed conductivity values of greater than 100 in several rainstorms in Menlo Park, Calif.

The conductance of surface and ground waters has a wide range, of course, and in some areas may be as low as 50 μmho/cm where precipitation is low in solutes and rocks are resistant to attack. In other areas, conductances of 50,000 μmho/cm or more may be reached; this is the approximate conductance of seawater. Brine associated with halite may contain as much as ten times the dissolved-solids concentration of seawater. Analysis 8 in table 17 represents such a water; its specific conductance, however, is 225,000 μmho/cm, about five times that of seawater. At these high concentrations the correlation between dissolved solids and conductivity is not well defined.

Accuracy and Reproducibility

The equipment usually used to obtain conductance values of water, if carefully operated, may produce accuracy and precision of from ±2 to ±5 percent. Instruments that have a built-in capacity for compensating for temperature effects are available. The response of specific conductance to temperature is different for different ions, however, and therefore completely accurate temperature compensation applicable to all types of water is not feasible. The best accuracy will be obtained by making all measurements at temperatures near 25°C.

The accuracy of field measurements of conductivity made with good portable equipment and proper attention to temperature effects should be about the same as the accuracy of laboratory measurements if the temperature is near 25°C. Conductivity devices that have been permanently installed in the field require periodic maintenance to prevent electrode fouling and (or) other interferences that may cause erroneous readings and loss of record.

A more comprehensive discussion of conductance theory and practice in water analysis has been published elsewhere by the writer (Hem, 1982).

Silica

The element silicon, as noted earlier, is second only to oxygen in abundance in the Earth's crust. The chemical bond between silicon and oxygen is very strong, and the Si^{4+} ion is the right size to fit closely within the space at the center of a group of four closely packed oxygen ions. Silicon thus located is said to be tetrahedrally coordinated with respect to oxygen. The same structure occurs also with hydroxide ions, which are nearly the same size as the O^{2-} ion. The $SiO_4{}^{4-}$ tetrahedron is a fundamental building unit of most of the minerals making up igneous and metamorphic rocks and is present in some form in most other rocks and soils, as well as in natural water. The term "silica," meaning the oxide SiO_2, is widely used in referring to silicon in natural water, but it should be understood that the actual form is hydrated and is more accurately represented as H_4SiO_4 or $Si(OH)_4$.

The structure and composition of silicate minerals cannot be considered in detail here, but some knowledge of the subject is useful in understanding the behavior of silicon in natural water. There are six principal patterns in which the SiO_4 tetrahedra are joined to build up the framework of silicate minerals. The kind of pattern that occurs is a function of the relative abundance of oxygen in the rock compared with the abundance of silicon. In systems in which oxygen is abundant relative to silicon, the predominant pattern is one in which adjacent tetrahedra are linked through chemical bonding of oxygen with a divalent cation such as magnesium, for example, in the magnesian olivine, forsterite (Mg_2SiO_4). This pattern extends in three dimensions, and silicates of this type are called nesosilicates. A second structural pattern is made up of pairs of tetrahedra sharing one oxygen ion between them, the sorosilicates. Few natural minerals have this structural pattern. A third pattern consists of rings in which three or more tetrahedra each share two oxygen ions. A six-member ring structure occurs in the mineral beryl ($Be_3Al_2Si_6O_{18}$). The silicates having isolated rings in their structure are called cyclosilicates. This structure also is rather uncommon.

A structural pattern in which each tetrahedron shares two oxygen ions with neighbors can produce a long single chain as in the pyroxenes ($R_2(SiO_3)_2$). If two adjacent chains are cross-linked by sharing some additional oxygen, the structure of the amphiboles is formed. For those amphiboles in which no aluminum is substituted for silicon and no univalent cations are present, the composition may be expressed as $R_7(OH)_2Si_8O_{22}$. The symbol R in these formulas represents various divalent cations; most commonly these are Ca^{2+}, Mg^{2+}, and Fe^{2+}. The chain silicates are called inosilicates.

The tetrahedra also may form planar structures in which three oxygen ions of each tetrahedron are shared with adjacent tetrahedra, all lying in a plane. The resulting sheet structure appears in such mineral species as micas and clays, for example kaolinite ($Al_2Si_2O_5(OH)_4$). The sheet structures are called phyllosilicates. The tectosilicates are made up of tetrahedra in which all oxygen ions are shared among adjacent tetrahedra in three dimensions. The structure of quartz $(SiO_2)_n$ follows this pattern. Feldspars also partially display it but contain some aluminum and other cations in place of silicon, as in potassium feldspar ($KAlSi_3O_8$).

The structural features of silicate minerals are described in greater detail by Hückel (1950, p. 740_755) and in many more recent texts on inorganic chemistry and mineralogy. The structural pattern is rather closely related to the stability of the various mineral species when they are attacked by water. The silicon-oxygen bond is stronger than the metal-oxygen bonds that occur in the silicate minerals. Thus, the resistance to chemical attack, which involves breaking the bonds holding the structure together, is greatest in mineral structures in which a larger proportion of the bonds are between silicon and oxygen.

The nesosilicates and inosilicates represent structures in which a relatively high proportion of the bonding is the linking of divalent metal cations to oxygen. These bonds represent zones of weakness that can be disrupted relatively easily compared with silicon-oxygen or aluminum-oxygen bonds. The ferromagnesian minerals, which belong largely to these two classes of silicate structures, are less resistant to weathering attack than are structures like the tectosilicates in which silicon-oxygen bonding predominates to a greater degree.

Crystalline SiO_2 as quartz is a major constituent of many igneous rocks and also constitutes the bulk of the grains in most sandstones. Of the common rock minerals, quartz is one of the more resistant to attack by water. The cryptocrystalline and amorphous forms of silica such as chert and opal are more soluble. It seems probable, however, that most of the dissolved silica observed in natural water results originally from the chemical breakdown of silicate minerals in processes of weathering. These processes are irreversible, and the silica retained in

Table 12. Analyses of waters

[Analyses by U.S. Geological Survey. Date below sample number is date of collection. Sources of data: 1, Scott and Barker (1962, p. 39); 2, 4, 5, and 9, U.S. (1954b, p. 286); 8, U.S. Geological Survey Water-Supply Paper 1102 (p. 400)]

Constituent	1 Nov. 23, 1953		2 Aug. 1, 1947		3 Oct. 16, 1957		4 June 13, 1952	
	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
Silica (SiO_2)	99		103		363		49	
Aluminum (Al)					.2			
Iron (Fe)	.04		.0		.06		.01	
Manganese (Mn)					.0		.00	
Calcium (Ca)	2.4	.120	6.5	.324	.8	.04	32	1.597
Magnesium (Mg)	1.4	.115	1.1	.090	.0	.00	12	.987
Sodium (Na)	100	4.348	40	1.729	352	15.30	30	1.305
Potassium (K)	2.9	.074			24	.61	5.2	.133
Carbonate (CO_3)	24	[1].800	0	0	([2])	3.86	0	.0
Bicarbonate (HCO_3)	111	1.819	77	1.262			220	3.605
Sulfate (SO_4)	30	.625	15	.312	23	.48	11	.299
Chloride (Cl)	10	.282	17	.479	405	11.42	7.9	.223
Fluoride (F)	22	1.158	1.6	.084	25	1.32	.2	.011
Nitrate (NO_3)	.5	.008	.4	.006	1.8	.03	2.9	.047
Boron (B)	.19		.0		4.4		.08	
Dissolved solids:								
Calculated	348		222		1,310		225	
Residue on evaporation							257	
Hardness as $CaCO_3$	12		20		2		129	
Noncarbonate	0		0		0		0	
Specific conductance (micromhos at 25°C).	449		167		1,790		358	
pH	9.2		6.7		9.6		7.8	
Color							10	

[1] Includes some silicate ion, probably $H_3SiO_4^-$, calculated at 0.389 meq/L.

[2] Original analysis reports carbonate and hydroxide alkalinity of 3.86 meq/L total, probably mostly attributable to silicate.

1. Flowing well 7S 6E-9ba2, Owyhee County, Idaho. Depth, 960 ft; temperature, 50.0°C.
2. Spring on the Rio San Antonio, SW1/4 sec. 7, T. 20 N., R. 4 E. (unsurveyed), Sandoval County, N. Mex. Flow, about 25 gpm; temperature, 38°C. Water from rhyolite.
3. Spring, 650 ft south of Three Sisters Springs in Upper Geyser Basin, Yellowstone National Park, Wyo. Temperature, 94°C. Also reported: 1.5 mg/L As, 5.2 mg/L Li, 1.5 mg/L Br, 0.3 mg/L I, 1.3 mg/L PO_4^{-3}, and 2.6 mg/L H_2S.

solution is probably controlled either by kinetic factors in the dissolution process, adsorption on mineral or other surfaces, or by precipitation of a secondary mineral species such as one of the less organized forms of silica. This could be a clay mineral precursor that includes other cations as well as the silicon. The direct precipitation of quartz is unlikely to control solubility of silica in most natural waters at Earth surface temperatures.

Studies relating to weathering mechanisms and silica concentration controls made in recent years have suggested and applied nonequilibrium models to good effect (Helgeson, 1968, 1971; Busenberg and Clemency, 1976; Paces, 1978).

Forms of Dissolved Silica

The convention of representing dissolved silica as the oxide SiO_2 has been followed by all water analysts. Some of the older literature implied that the material was present in colloidal form, but occasionally a charged ionic species, SiO_3^{2-}, was specified. In most waters, it is fully evident that the dissolved silicon does not behave like a charged ion. Nor does it exhibit behavior typical of a colloid in most waters.

The dissociation of silicic acid, which for this discussion may be assumed to have the formula $Si(OH)_4$ or H_4SiO_4, begins with the reaction

containing high proportions of silica

Geological Survey, unpublished data; 3, White, Hem, and Waring (1963, p. F40); 6, U.S. Geological Survey Water-Supply Paper 1022 (p. 266); 7, Lohr and Love

5 Apr. 18, 1952		6 Apr. 11 -19, 1944		7 Oct. 12, 1951		8 May 6, 1947		9 Mar. 22, 1952	
mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
38		48		71		62		29	
.24		.03		.0		.01		.33	
.00								.00	
12	.559	43	2.15	32	1.597	22	1.098	17	.848
6.6	.543	20	1.64	8.8	.724	4.4	.362	1.7	.140
7.2	.313	28	1.22	42	1.826	20	.870	7.4	.323
3.1	.079	4.6	.12						
0	.0	.0	.0	0	.0	.0	.0	0	.0
85	1.393	254	4.15	161	2.639	104	1.704	69	1.131
4.4	.092	8.3	.17	54	1.124	29	.604	6.9	.144
1.2	.034	28	.79	12	.338	0	.000	1.1	.031
.3	.016	.5	.03	.7	.037	.3	.016	.1	.005
.2	.003	.1	.00	.6	.010	1.4	.023		.0
		0							
115		306		310		190		98	
114						158		98	
57		190		116		73		49	
0		0		0		0		0	
136		463		404		198		130	
7.9				7.9		8.1		7.1	
8				2				5	

4. Drilled well, NW1/4 sec. 10, T. 2 N., R. 32 E., Umatilla County, Oreg. Depth, 761 ft. Water from basalt of the Columbia River Group.
5. Flowing well, SE1/4 sec. 16, T. 12 N., R. 17 E., Yakima County, Wash. Depth, 1,078 ft; temperature, 17.2 °C. Water from basalt.
6. Eagle Creek at P-D pumping plant near Morenci, Greenlee County, Ariz. Mean discharge for composite period, 9.9 cfs. Drainage basin of about 600-mi^2 area in which virtually all rocks exposed are extrusive volcanic rocks.
7. Main pump station, Albuquerque, N. Mex. Public supply. Seven wells, 250 to 716 ft deep. Water from the Santa Fe Formation (valley fill).
8. Middle Loup River at Dunning, Nebr. Discharge, 394 cfs. Drainage from Nebraska sand hills; flow maintained by ground water.
9. Well at Valdese General Hospital, Rutherford College, Burke County, N.C. Depth, 400 ft; temperature, 15.0°C. Water from mica schist.

$$H_4SiO_4(aq)=H^+ + H_3SiO_4^-.$$

Values collected by Sillen and Martell (1964, p. 145) for the equilibrium constant for this reaction at 25°C range from $10^{-9.41}$ to $10^{-9.91}$. These values indicate that the first dissociation step is half completed at a pH value somewhere between 9.41 and 9.91, and silicate ions ($H_3SiO_4^-$) might constitute no more than 10 percent of the total dissolved silica species at a pH between 8.41 and 8.91. Any silicate ions that might be present are converted to silicic acid in the alkalinity titration and appear in the analysis as an equivalent amount of carbonate or bicarbonate. As a result, the ionic balance is maintained in the analysis, and there is no obvious indication that the ionic species are incorrectly identified. In any detailed interpretation of the chemistry of high-pH waters, the contribution of $H_3SiO_4^-$ to the alkalinity must be taken into account.

Analysis 1, table 12, is for a water that had a pH of 9.2. By using the dissociation constant for silicic acid determined by Greenberg and Price (1957) of $10^{-9.71}$, it can be calculated that about 0.389 meq/L of dissociated silicate ions are present. The analysis reports 0.800 meq/L of carbonate alkalinity, of which almost half actually must have been caused by silicate.

The method generally used for determining silica concentrations in water requires that the silica form a colored molybdate complex in solution. The response of dissolved silica to this procedure is normally rapid and apparently complete, which suggests that silica must be present in units of very small size, probably approaching, if not actually having, the dimensions of single molecules. Some hot-spring waters are known, however, in which the total silica is several hundred milligrams per liter and in which the silica tends to polymerize on standing at 25°C to form colloidal particles. White and others (1956) observed that the polymerized silica thus formed reacted very slowly with complexing reagents. Analysis 3, table 12, represents hot-spring water that precipitates silica on cooling.

In reviewing the available literature on the dissolution of silica, Krauskopf (1956) concluded that silica in natural water was mostly in the form of monomolecular silicic acid, $H_4SiO_4(aq)$. This is equivalent to a silicon ion tetrahedrally coordinated with four hydroxide ions, and by analogy with mineral structures it seemed the most likely form. Some investigators quoted by Sillen and Martell (1964, p. 145) suggest polynuclear species such as $Si_4O_4(OH)_{12}^{4-}$, and Iler (1955, p. 19) proposed that in solution silica might be coordinated with six OH^- ions to form ions of the same type as the fluosilicate ion, SiF_6^{2-}. In the absence of more definite evidence of the existence of more complicated species, the simplest form, $Si(OH)_4$, is probably the best postulate. This may also be considered equivalent to SiO_2 combined with two water molecules.

The possible existence of fluosilicate complex ions in natural water was investigated by Roberson and Barnes (1978), who found that substantial proportions of the silica was present as SiF_6^{2-} in samples of condensed gaseous material from fumaroles and drill holes near Kilauea Iki volcano, Hawaii. The amount of this species in water associated with vulcanism elsewhere seemed small, however, judging from applications of the same model to data given by White and others (1963).

Solubility Controls

The solubility of quartz has been determined by Morey and others (1962) as 6.0 mg/L at 25°C and 26 mg/L at 84°C (as SiO_2). Fournier and Rowe (1962) reported the solubility of cristobalite to be 27 mg/L at 25°C and 94 mg/L at 84°C. Morey and others (1964) reported the solubility of amorphous silica to be 115 mg/L at 25°C, and Akabane and Kurosawa (1958) reported the solubility of this material at 100°C to be 370 mg/L. Fournier and Rowe (1966) suggested that the silica content of water from hot springs could be used to calculate the temperature of reservoir rocks, assuming an equilibrium with quartz at depth. This method has been widely used in evaluating geothermal resources. The solubility of quartz over the temperature range 25°C to 900°C and at pressures up to 10,000 bars was later determined by Fournier and Potter (1982), and the effects of sodium chloride in solution on these relationships were evaluated by Fournier and others (1982).

The first precipitate formed on cooling a silica-rich solution to 25°C is amorphous silica, and this material is not readily converted at this temperature to the better crystallized forms of lower solubility. Morey and others (1962) reported one experiment in which quartz grains were rotated in water for 386 days at 25°C, during which time the SiO_2 concentration in the water was 80 mg/L. The concentration dropped suddenly to 6 mg/L and held that value for about 5 months. It was concluded this was the reversible solubility for quartz.

Natural water normally has more dissolved silica than the quartz equilibrium value but less than the amorphous silica value, which is the likely upper equilibrium limit. The general tendency for silica concentrations in natural water to fall within a rather narrow range suggests that some other type of solubility control may exist. Hem and others (1973) suggested that an amorphous clay mineral having the composition of halloysite could be produced by weathering igneous rock minerals and that an equilibrium with such a species may control aluminum and silica concentrations in some natural water. A somewhat similar mechanism was proposed by Paces (1978).

The dissolution of the sodium feldspar, albite, can be summarized

$$2NaAlSi_3O_8(c)+2H^++9H_2O(l) = Al_2Si_2O_5(OH)_4(c)+4H_4SiO_4(aq)+2Na^+.$$

If the clay mineral produced dissolves reversibly,

$$Al_2Si_2O_5(OH)_4+6H^+=2H_4SiO_4(aq)+2Al^{3+}+H_2O.$$

An upper limit for silica concentration might be fixed by

$$H_4SiO_4(aq)=SiO_2(c)\ (amorph)+2H_2O.$$

These reactions are oversimplified. A higher Si:Al ratio in the clay mineral, admixtures of other cations, and many other complications can occur. Adsorption of silica on other mineral surfaces can also be a factor, as noted by Siever and Woodford (1973, 1979).

The kinetics of dissolution of igneous rock minerals have been studied extensively in recent years. Among papers on feldspar are those of Busenberg and Clemency (1976), Petrovic (1976), and Holdren and Berner (1979). Studies of inosilicate minerals were made by Luce and others (1972), Siever and Woodford (1979), and other groups. Rate-controlling mechanisms of various types have been proposed to explain the experimental data. Kinetics of dissolution and precipitation of quartz and three other forms of solid SiO_2 from 0° to 300°C were determined by Rimstidt and Barnes (1980).

Occurrence in Natural Water

Analyses in table 12 were selected to show several types of water that have rather high concentrations of dissolved silica. Some of these show the increased solubility attained as water temperatures rise. The highest concentration in natural water encountered by the writer was reported by Feth and others (1961) for Aqua de Ney, a mineralized cold spring near the town of Mount Shasta, Calif. This water has a pH of 11.6 and more than 3,400 mg/L SiO_2, presumably mostly as dissociated silicate.

Seawater near the surface is very low in silica (commonly less than 1 mg/L), apparently because marine organisms (primarily diatoms) extract and use silica in their shells and skeletons. Similar depletion effects are noticeable in the surface layers of some lakes and reservoirs.

The range of concentrations of silica most commonly observed in natural water is from 1 to about 30 mg/L. Concentrations up to 100 mg/L, however, are not infrequent in ground water in some areas. Davis (1964) quoted a median value of silica for surface waters of 14 mg/L and for ground water of 17 mg/L. The higher concentrations found in ground waters are related to rock type and to temperature of the water. A general review of silica occurrence in natural water has been published by Ginzburg and Kabanova (1960). Some geologic factors related to silica concentrations in water are considered elsewhere in this volume.

Inspection of analyses of surface waters of the world assembled by Livingstone (1963) indicates that most streams in the Northeastern United States carry water containing less than 10 mg/L of silica, but water from drainage basins in the West and from some in the South seem generally to be higher.

The silica concentration of water samples collected and stored in some types of glass bottles may increase if stored for a long time owing to solution of the glass. Bottles made of Pyrex and other resistant formulations of glass probably are not a serious source of contamination for most natural waters, however. Polyethylene and polypropylene bottles are superior to glass in this respect.

Aluminum

Although aluminum is the third most abundant element in the Earth's outer crust, it rarely occurs in solution in natural water in concentrations greater than a few tenths or hundredths of a milligram per liter. The exceptions are mostly waters of very low pH. Because aluminum is so abundant and so widely distributed, most natural waters have ample opportunity to dissolve it. The low concentrations common to water at near-neutral pH must, therefore, be a result of the chemistry of the element. These chemical properties are also indicated by aluminum's short oceanic residence time (table 7).

Sources of Aluminum in Water

Aluminum occurs in substantial amounts in many silicate igneous rock minerals such as the feldspars, the feldspathoids, the micas, and many amphiboles. The aluminum ion is small enough to fit approximately into fourfold coordination with oxygen and therefore can substitute, in a sense, for silicon in tetrahedral structural sites. It also is commonly six-coordinated, and occupies octahedral crystal sites similar to those occupied by magnesium and iron. Aluminum is trivalent, and substitutions of these kinds may require adding or removing cations or protons to maintain a net charge balance in the structure.

On weathering of igneous rocks, the aluminum is mostly retained in new solid species, some of which may be greatly enriched in aluminum. Nearly pure aluminum hydroxide in the form of gibbsite is a fairly common mineral, and less common hydroxides include nordstrandite and bayerite, whose composition and structure are similar to that of gibbsite. In low-pH environments aluminum may be precipitated as an aluminum hydroxysulfate. The most common of the sedimentary aluminum-enriched minerals are clays. The clay minerals have a layered structure in which aluminum octahedrally coordinated with six oxide or hydroxide ions (gibbsite structure) forms one type of layer, and silicon tetrahedrally coordinated with oxygen forms a second type of layer. These layers alternate in various ways, forming the various clay structures. The layers are bound together by Si–O–Al bonds. Diagrams of the structures of the common clay minerals have been given by many investigators, including Grim (1968, p. 51–125) and Robinson (1962, p. 31–58). Clays are present in most natural-water environments and are abundant in most soils and in hydrolyzate sedimentary rocks.

Species in Solution

The cation Al^{3+} predominates in many solutions in which pH is less than 4.0. The actual ion is probably an octahedron of six water molecules with a aluminum ion at the center (fig. 12). One of these water molecules may become an OH^- ion if the pH is raised slightly, and at pH 4.5–6.5 a process of polymerization occurs that results in units of various sizes with the structural pattern of gibbsite (Hsu and Bates, 1964; Hem and Roberson, 1967). This structure is characterized by hexagonal rings of aluminum ions bound together by sharing pairs of hydroxide ions. Under some conditions the polymerization may stop when the units are still small, but in studies described by Smith and Hem (1972) the polymers continued growing until they became crystalline gibbsite particles a few hundredths to a few tenths of a micrometer in diameter. Above neutral pH, the predominant dissolved form of aluminum is the anion $Al(OH)_4^-$.

In some of the published research on aqueous chemistry of aluminum, certain specific aluminum hydroxide polymeric ions are suggested as the predominant forms to be expected in solution in natural water. The work on aluminum hydrolysis species was summarized by Baes and Mesmer (1976, 112–123). As noted above, there are some conditions under which the polymeric ions may stop growing. However, they should be viewed as precursors of a crystalline solid of well-defined structure with which the form of the ions must be compatible. This requirement is not met by some of the proposed species. Further, if the polymeric ions increase in size with time they are inappropriate for consideration as chemical-equilibrium species.

The polymerization of aluminum hydroxide species proceeds in a different way in the presence of dissolved silica than when silica is absent. When sufficient silica is present, the aluminum appears to be precipitated rapidly as rather poorly crystallized clay-mineral species (Hem and others, 1973). In the presence of an organic solute capable of complexing aluminum, these mixed silica and aluminum solutions produced well-crystallized kaolinite on aging at 25°C (Hem and Lind, 1974).

In the presence of fluoride, strong complexes of aluminum and fluoride are formed. The ions AlF^{2+} and AlF_2^+ appear to be most likely in natural water containing from a few tenths of a milligram per liter to a few milligrams per liter of fluoride (Hem, 1968b). Soluble phosphate complexes of aluminum have been reported (Sillen and Martell, 1964, p. 186) and the sulfate complex $AlSO_4^+$ may predominate in acid solutions in which much sulfate is present (Hem, 1968b).

Organic complexing of aluminum apparently occurs in some natural waters that are colored owing to solution of "humic" material. Lind and Hem (1975) quoted analyses of 28 such solutions taken from published records for U.S. streams, in which aluminum concentrations ranged between 100 and 1,300 μg/L. One sample contained 38 mg/L and had a pH of 9.4, owing, however, to direct pollution from bauxite mines and alumina processing plants (Halbert and others, 1968). All these samples were filtered through 0.45-μm porosity filters and some may have contained colloidal forms of aluminum that passed through the filters, as Kennedy and others (1974) observed to occur in their studies of the effectivenes of filtration techniques.

Solubility Controls

Application of equilibrium models to aluminum behavior requires special attention to identifying the form of dissolved species and special sampling techniques. This may entail adding some analytical reagents and performing part of the determination in the field (Barnes, 1975). In solutions that contain fluoride, sulfate, or other complexing agents, the form of dissolved species can be determined from the ionic equilibria (Hem, 1968b), and

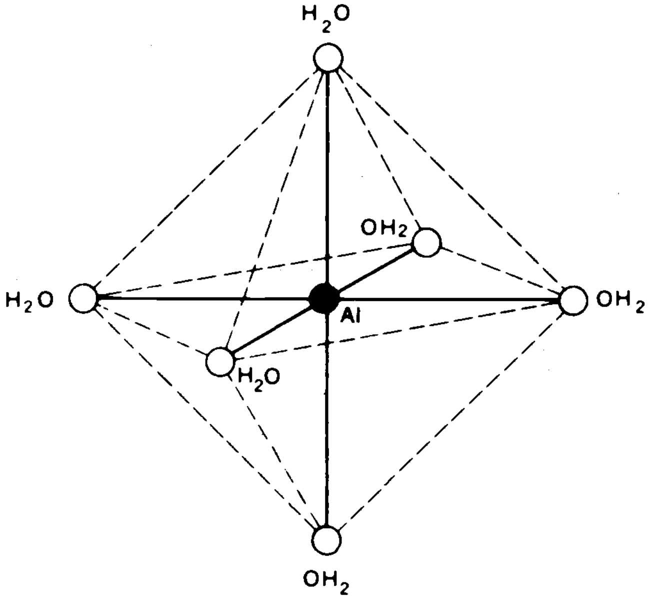


Figure 12. Schematic diagram of hydrated aluminum ion, $Al(H_2O)_6^{3+}$. (From Hem, 1968b, *in* "Trace Inorganics in Water," Advances in Chemistry Series, 73, copyright American Chemical Society, 1968, used by permission.)

if silica concentrations are very low, the solubility product for aluminum hydroxide as bayerite gives a reasonable basis for calculating solubility of aluminum in alkaline solutions (Hem and Roberson, 1967). In solutions whose pH is below 4.0, the solubility usually can be calculated from the solubility product for gibbsite. Nordstrom (1982) has suggested that aluminum sulfate and hydroxysulfate minerals may control the solubility of the element in acidic waters that contain sulfate. Between the high and low pH regions, aluminum solubility reaches a minimum. The minimum solubility calculated by Roberson and Hem (1969) is a little less than 10 μg/L, near a pH of 6.0. May and others (1979) determined a minimum solubility of 6.7 μg/L for synthetic gibbsite at pH 6.0 and about 27 μg/L for natural gibbsite at the same pH. These data would be applicable at 25°C to a solution with a low dissolved-solids concentration containing less than 0.10 mg/L of fluoride. Higher fluoride concentrations increase the solubility of aluminum. Figure 13 is a graph of solubility of aluminum as a function of pH in a system that has no complexing species other than OH. The polymeric forms of aluminum and hydroxide cannot be represented in a solubility diagram, because they are unstable and are converted to solid particulate matter on aging (Hem and Roberson, 1967). The dashed line labeled "microcrystalline gibbsite" represents the equilibrium activity of uncomplexed aluminum, and the other two dashed lines represent the equilibrium activity of $Al(OH)_4^-$. The solid line shows the effect of including the monomeric complex $AlOH^{2+}$ in the solubility calculation.

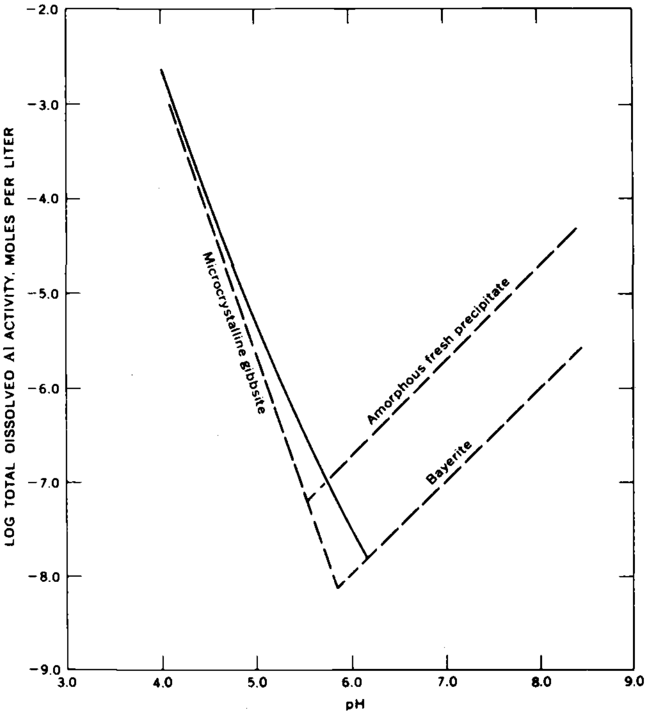


Figure 13. Equilibrium activities of free aluminum for three forms of aluminum hydroxide (dashed lines) and calculated activity of $Al^{3+}+AlOH^{2+}$ (solid line).

Although the influence of silica cannot be fully evaluated by equilibrium calculations, aluminum solubility generally is considerably decreased when silica is present owing to formation of clay-mineral species. The equilibrium activity of aluminum in uncomplexed form in the presence of kaolinite or halloysite can be calculated for various silica concentrations and pH values by using equations given by Polzer and Hem (1965) and by Hem and others (1973) and may be less than 1.0 μg/L in some natural waters. This concentration, however, is not equivalent to the total possible dissolved aluminum, which could be much greater if complexing anions were present.

Occurrence of Aluminum in Water

Commonly, aluminum determinations are not included in general-purpose water analyses, and the reliability of the limited amount of information that is available is questionable. Occasional reported concentrations of 1.0 mg/L or more in water having near-neutral pH and no unusual concentrations of complexing ions probably represent particulate material. Whether this particulate material is aluminum hydroxide or an aluminosilicate is not presently known. The writer's work (Hem and Roberson, 1967) has shown, however, that gibbsite crystals near 0.10 μm in diameter have considerable physical and chemical stability. Particles of this size will pass through most filter media and may need to be considered in water-quality evaluations. Carefully detemined aluminum values for runoff from granitic terrane were only a few hundredths of a milligram per liter at most (Feth and others, 1964). These determinations probably did not include particulate material.

The addition of aluminum sulfate (alum) in water-treatment processes to flocculate suspended particles may leave a residue of aluminum in the finished water, probably as small, suspended hydroxide particles. For a study of quality of water supplies of major U.S. cities (Durfor and Becker, 1964), spectrographic analyses were made of various minor constituents including aluminum. The aluminum concentrations commonly were higher in finished water after alum had been used as a flocculating agent than they were in the original untreated water. More recently, Miller and others (1984) observed a similar effect in a study of water samples from 186 water utility systems in the United States.

Water having a pH below 4.0 may contain several hundred or even several thousand milligrams of aluminum per liter. Such water occurs in some springs and in drainage from mines. Table 13 contains analyses of some waters that are high in aluminum. Some of the commonly used analytical procedures are not sensitive to all polymeric aluminum species, and this further decreases the usefulness of analytical data when methodology is unknown.

Analyses 1 and 4 in table 13 represent water of low pH, and the thermal spring represented by analysis 3 had a rather high fluoride concentration. The explanation for the aluminum concentrations in the other two samples may be related to the presence of particulates or polymers, but neither analysis 2 nor 5 exhibits high concentrations.

Elevated aluminum concentrations have been observed in runoff and lake waters in areas affected by precipitation having a low pH ("acid rain"). An occurrence in New England was described by Johnson and others (1981). The dissolved aluminum in waters having low pH has a deleterious effect on fish and some other forms of aquatic life (Driscoll and others, 1980).

The aluminum concentrations in analyses 2, 3, and 9 in table 14 and 1, 8, and 10 in table 16, which range from 0.6 to 1.4 mg/L, probably can be ascribed to polymeric colloidal material.

Iron

Although iron is the second most abundant metallic element in the Earth's outer crust, concentrations present

Table 13. Analyses of waters high in dissolved aluminum or manganese

[Analyses by U.S. Geological Survey. Date under sample number is date of collection. Sources of data: 1 and 2, Scott and Barker (1962, p. 23, 111); 3, U.S. Geological Survey, unpublished data; 4, U.S. Geological Survey Water-Supply Paper 1948 (p. 38); 5, White, Hem, and Waring (1963, p. F26)]

Constituent	1 Dec. 13, 1955		2 Dec. 3, 1955		3 Aug. 31, 1958		4 Mar. 1-6, 8-10, 1963		5 Mar. 25, 1953	
	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
Silica (SiO_2)	98		10		92		9.7		31	
Aluminum (Al)	28		.1		.35		3.5		.2	
Iron (Fe)	.88		.04		.02		.10		2.7	
Manganese (Mn)	9.6		1.3		.31		2.5		.22	
Calcium (Ca)	424	21.16	58	2.89	67	3.34	32	1.60	28	1.40
Magnesium (Mg)	194	15.96	13	1.07	.0	.00	11	.90	1.9	.16
Sodium (Na)	416	18.10	23	1.00	477	20.75	12	.52	6.8	.30
Potassium (K)	11	.28	2.8	.07	40	1.02	3.7	.09	4.2	.11
Hydrogen (H)		.10						.16		
Carbonate (CO_3)	0		0		0	.00	0			
Bicarbonate (HCO_3)	0		101	1.66	1,020	16.72	0		121	1.98
Sulfate (SO_4)	2,420	50.38	116	2.42	169	3.52	171	3.56	1.4	.03
Chloride (Cl)	380	10.72	39	1.10	206	5.81	5.0	.14	1.0	.03
Fluoride (F)	1.8	.09	.0		6.8	.36	.1	.01	.1	.01
Nitrate (NO_3)	3.1	.05	.6	.01	1.8	.03	5.3	.09	.2	.00
Orthophosphate (PO_4)	.0		.1		.11				.0	
Boron (B)					2.8					
Dissolved solids:										
Calculated	3,990		314		1,570		256		137	
Residue at 180°C	4,190		338		1,560		260			
Hardness as $CaCO_3$	1,860		198		168		125		78	
Noncarbonate	1,860		115		0		125		0	
Specific conductance (micromhos at 25°C).	4,570		517		2,430		507		192	
pH	4.0		7.0		6.7		3.8		6.9	

1. Well, 7 mi northeast of Monticello, Drew County, Ark. Depth, 22 ft. Water-bearing formation, shale, sand, and marl of the Jackson Group. Also contained radium (Ra), 1.7 pCi/L, and uranium (U), 17 μg/L.
2. Composite from two radial collector wells at Parkersburg, Kanawha County, W. Va. Depth, 52 ft. Water from sand and gravel. Also contained copper (Cu), 0.01 mg/L, and zinc (Zn), 0.01 mg/L.
3. Wagon Wheel Gap hot spring, Mineral County, Colo. Discharge, 20 gpm; temperature, 62.2°C. Associated with vein of the Wagon Wheel Gap fluorite mine. Also contained 2.3 mg/L Li, 0.9 mg/L NH_4, 0.3 mg/L Br, and 0.3 mg/L I.
4. Kiskiminitas River at Leechburg (Vandergrift), Pa. Composite of nine daily samples. Mean discharge for period, 10,880 cfs.
5. Well, 167 ft deep, Baltimore County, Md. Water-bearing formation, Port Deposit granitic gneiss. Also contained 0.01 mg/L copper (Cu).

in water generally are small. The chemical behavior of iron and its solubility in water depend strongly on the oxidation intensity in the system in which it occurs; pH is a strong influence as well. The chemistry of iron in aqueous systems has been studied extensively, and its general outline can be readily discerned by applications of equilibrium chemical principles.

Iron is an essential element in the metabolism of animals and plants. If present in water in excessive amounts, however, it forms red oxyhydroxide precipitates that stain laundry and plumbing fixtures and, therefore, is an objectionable impurity in domestic and industrial water supplies. For this reason, iron determinations are commonly included in chemical analyses of water. A recommended upper limit for iron in public water supplies is 0.3 mg/L (NAS-NAE, 1972).

Sources of Iron

Igneous rock minerals whose iron content is relatively high include the pyroxenes, the amphiboles, biotite, magnetite, and, especially, the nesosilicate olivine. The latter is essentially a solid solution whose end members are forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4). For the most part, iron in these minerals is in the ferrous, Fe^{2+}, oxidation state, but ferric (Fe^{3+}) may also be present, as in magnetite, Fe_3O_4.

When these minerals are attacked by water, the iron that may be released is generally reprecipitated nearby as sedimentary species. Under reducing conditions when sulfur is available, the ferrous polysulfides such as pyrite, marcasite, and the less stable species mackinawite and griegite may occur. Where sulfur is less abundant, siderite ($FeCO_3$) may form. In oxidizing environments the sedimentary species will be ferric oxides or oxyhydroxides such as hematite, Fe_2O_3, goethite, FeOOH, or other minerals having these compositions. Freshly precipitated material may have poorly developed crystal structure and is commonly designated ferric hydroxide, $Fe(OH)_3$.

Magnetite tends to resist attack by water and is commonly present as a residue in resistate sediments. Iron is a common constituent of sulfide ores of other metals, and ferrous sulfide is generally associated with coal seams.

Availability of iron for aqueous solution is strikingly affected by environmental conditions, especially changes in degree or intensity of oxidation or reduction. High concentrations of dissolved ferrous iron can occur in solution at the sites of either reduction of ferric oxyhydroxides or oxidation of ferrous sulfides. In the latter process the sulfur is attacked first and altered to sulfate, releasing the ferrous iron. Iron is present in organic wastes and in plant debris in soils, and the activities in the biosphere may have a strong influence on the occurrence of iron in water. Micro-organisms are commonly involved in processes of oxidation and reduction of iron, and some species may use these reactions as energy sources.

Species of Iron in Natural Water

The most common form of iron in solution in ground water is the ferrous ion Fe^{2+}. Like aluminum and many other metal ions, this ion has an octahedral hydration shell of six water molecules. Except where hydration may have special significance, water of hydration shells will not be shown in the formula of this or other ions that follow. The monohydroxide complex $FeOH^+$ can be predominant above a pH of about 9.5 (Baes and Mesmer, 1976, p. 100) and may be significant at somewhat lower pH's. Above a pH of 11, the anion $Fe(OH_3)^-$ or $HFeO_2^-$ can exist in water in appreciable concentrations, but such a high pH is rarely attained in natural systems. An ion pair $FeSO_4(aq)$ reported in Sillen and Martell (1964, p. 240) could be important in solutions that have more than a few hundred milligrams of sulfate per liter. Ferrous complexes are formed by many organic molecules, and some of the complexes may be considerably more resistant to oxidation than free ferrous ions would be. Organic compounds containing iron are particularly important in life processes, such as photosynthesis, and in the functions of hemoglobin in the blood of animals.

Ferric iron can occur in acid solutions as Fe^{3+}, $FeOH^{2+}$, and $Fe(OH)_2^+$ and in polymeric hydroxide forms, the predominant form and concentration depending on the pH. Above a pH of 4.8, however, the total activity of these species in equilibrium with ferric hydroxide will be less than 10 μg/L. Dimeric or polymeric ferric hydroxy cations ($Fe_2(OH)_2^{4+}$, etc.) can become important in solutions in which total dissolved ferric iron exceeds 1,000 mg/L. Such iron concentrations are rare in natural water. However, a process of polymerization somewhat like the one described for aluminum precedes the formation of solid ferric oxyhydroxide, and macroions or microcrystalline forms approaching the composition $Fe(OH)_3$ may often be present in natural water at very low concentrations. The species $Fe(OH)_3(aq)$ that is sometimes reported to be among the forms of dissolved ferric iron may actually represent such polymers. The stability of this material as reported by Lamb and Jacques (1938) limits the equilibrium concentration to less than 1.0 μg/L in the presence of ferric hydroxide.

A $\Delta G_f°$ value for the species FeO_4^{2-} in which iron is in the 6+ oxidation state was given by Garrels and Christ (1964, p. 413). This form of iron is not likely to be important in natural water because it could dominate only in very strongly oxidizing systems at high pH, and it is not included in the pH-Eh diagrams in this book.

The only anionic ferric species for which data are available is $Fe(OH)_4^-$. Langmuir (1969b) indicated that his value for its $\Delta G_f°$ was a rough estimate. The value used here was calculated from a stability constant estimated by Baes and Mesmer (1976, p. 104). The effect of $Fe(OH)_4^-$ on iron solubility is not significant, in any event, unless the pH is 10 or greater.

Ferric iron forms inorganic solution complexes with many anions besides OH^-. The chloride, fluoride, sulfate, and phosphate complexes may be important in some natural systems. Organic complexes containing iron are present in important amounts in some waters. Complexes can occur either with ferrous iron (Theis and Singer, 1974) or ferric iron (Stumm and Morgan, 1970, p. 531). The latter form may be associated with organic colloids or humic-type material that gives some waters a yellow or brown color. Such associations may be important in trapping iron in estuaries by a process of coagulation (Sholkovitz, 1976).

Ferric oxyhydroxide surfaces have a substantial adsorption capacity which may affect the concentration of minor constituents of water associated with such material. Redox coprecipitation processes may occur that can control solubilities of other metal ions under some conditions (Hem, 1977a).

Solubility Calculations: pH-Eh Diagrams

The chemical behavior of iron can be predicted theoretically as a function of solution pH, oxidation (or redox) potential, and activity of other ions. A convenient summarizing technique that has been used extensively in publications on iron chemistry is the pH-Eh (or pH-redox potential) diagram. This is a two-dimensional graph in which pH is plotted on the abscissa and redox potential on the ordinate. From tables of chemical thermodynamic data applied to the Nernst equation and pertinent mass-law expressions, an array of equations can be developed. If enough of the variables are specified, the equations can be solved simultaneously, leading to relationships expressed as points or lines on the pH-Eh grid.

The pH-Eh diagram wes extensively developed by Marcel Pourbaix in Belgium in the years prior to World War II. The diagrams began to be used in geochemistry after a compilation (Pourbaix, 1949) and applications by R.M. Garrels (1960) in the United States made Pourbaix's work more widely known. Details of preparation of the diagrams are given in various publications (Hem and Cropper, 1959; Garrels and Christ, 1964; Hem, 1965). Application of these diagrams to iron systems has been used as a textbook example, and a general agreement between theoretical calculations and field behavior of iron has been demonstrated by Barnes and Back (1964b) and many other investigators. Experience, therefore, suggests that reactions represented in the theoretical model for iron commonly approach chemical equilibrium in the real world closely enough that the most important processes are reasonably well represented in such a model. This is perhaps less likely for most other elements that are subject to redox reactions owing either to unfavorable kinetics or to lack of, or failure to include, some of the fundamental thermodynamic data and reactions in the model. Nevertheless, the pH-Eh diagram is a very useful method of clarifying complicated chemical relationships and illustrating boundary conditions and thermodynamically permissible reactions and products.

Two general types of information are furnished by these diagrams. If the total solute activities are specified, the diagram can show pH-Eh domains in which various solid species will be thermodynamically stable. Diagrams stressing this kind of information have sometimes been called "stability field" diagrams. Conversely, if a a certain assemblage of solids is specified, the diagram can be used to show metal solubilities under a range of pH and Eh conditions. Figures 14 and 15 illustrate these two applications for the iron + water + oxygen + sulfur + carbon dioxide system.

Because of the broad usefulness of the diagrams, the steps in their preparation are given in some detail so that the reader may apply the technique and understand its implications.

For the calculations used in constructing these diagrams, standard conditions (25°C and 1 atmosphere) were assumed, and the calculations are in terms of thermodynamic activities rather than concentrations.

The water-stability region obviously defines the range of conditions to be expected at equilibrium in aqueous systems. Upper and lower limits for water stability in terms of Eh and pH are computed from the relationship (all half-reactions are written as reductions):

$$O_2(g)+4H^++4e^-=2H_2O(l)$$

$$2H^++2e^-=H_2(g).$$

Chemical thermodynamic data needed for construction of figures 14 and 15 and references to sources of data are given in tables 30 and 31 (appendix). From the standard free energies, ΔG°_R is computed for the first equation (as stated in the discussion of electrochemical equilibrium, the standard free energy of the electron must be taken as zero):

$$2\Delta G^\circ_{H_2O(l)}-\Delta G^\circ_{O_2(g)}-4\Delta G^\circ_{H^+}=\Delta G^\circ_R$$

$$-113.38-0-0=-113.38 \text{ kcal.}$$

The kilocalorie units are converted to a standard potential by the relationship

$$E^\circ=\frac{-\Delta G^\circ_R}{nF}$$

in which n is the number of electrons shown in the half-reaction and F is the faraday constant, equal to 23.06 to give potentials in volts:

$$E^\circ=\frac{+113.38}{4\times 23.06}=1.229\ \text{V}.$$

The Nernst equation (discussed in the section "Electrochemical Equilibrium") applied to this reaction is

$$\text{Eh}=E^\circ+\frac{2.303\,RT}{nF}\log\left(P_{O_2}\times[\text{H}^+]^4\right).$$

The value of $2.303\,RT/F$ for standard conditions is 0.0592. The maximum partial pressure of oxygen permissible in the system as defined (1 atmosphere total pressure) is 1 atmosphere and n=4. The relationship thus reduces to

$$\text{Eh}=1.229-0.0592\ \text{pH},$$

which defines the upper stability boundary for water. The lower boundary similarly calculated is

$$\text{Eh}=0.000-0.0592\ \text{pH}.$$

Boundaries between ferric and ferrous solute species domains are fixed by calculations typified by that for FeOH^{2+} and Fe^{2+}:

$$\text{FeOH}^{2+}+\text{H}^++e^-=\text{Fe}^{2+}+\text{H}_2\text{O}.$$

The value of ΔG_R° is determined for this half-reaction as indicated above and is used to derive the standard potential E°, which in this case is equal to 0.898 V. The Nernst equation gives the value for Eh as follows:

$$\text{Eh}=0.898+0.0592\log\frac{[\text{FeOH}^{2+}][\text{H}^+]}{[\text{Fe}^{2+}]}.$$

At the boundary between the species domains, $[\text{FeOH}^{2+}]=[\text{Fe}^{2+}]$; hence the relationship becomes

$$\text{Eh}=0.898-0.0592\ \text{pH}.$$

Boundaries between species in which iron is at the same oxidation state are fixed by mass-law equilibria. For example,

$$\text{Fe}^{3+}+\text{H}_2\text{O}=\text{FeOH}^{2+}+\text{H}^+.$$

The equilibrium constant is obtained from

$$\frac{-\Delta G^\circ_R}{2.303\,RT}=\log K_{\text{eq.}}$$

The value of 2.303 RT under the specified conditions is 1.364. The value obtained for K eq is $10^{-2.17}$. Hence,

$$\frac{[\text{FeOH}^{2+}][\text{H}^+]}{[\text{Fe}^{3+}]}=10^{-2.17}.$$

Again specifying that

$$[\text{FeOH}^{2+}]=[\text{Fe}^{3+}]$$

leads to

$$[\text{H}]=10^{-2.17},$$

which is the vertical boundary between the two domains. These boundaries obviously terminate when they intersect. If the mathematics are done correctly, changes in slope of the horizontal or sloping boundaries should occur only where they intersect or are intersected by a vertical boundary.

Lines designating stability domains of solids are located by similar reasoning. For a boundary between $\text{Fe(OH)}_3\text{(c)}$ and Fe^{2+},

$$\text{Fe(OH)}_3\text{(c)}+3\text{H}^++e^-=\text{Fe}^{2+}+3\text{H}_2\text{O}.$$

The standard potential for this half-reaction is 0.994 V and

$$\text{Eh}=0.994+0.0592\log\frac{[\text{H}^+]^3}{[\text{Fe}^{2+}]}$$

A value for $[\text{Fe}^{2+}]$ must be specified to fix this boundary. For $[\text{Fe}^{2+}]=10^{-6.00}$ moles/L (56 μg/L),

$$\text{Eh}=1.349-0.178\ \text{pH}.$$

Activities of solids and of $\text{H}_2\text{O(l)}$ are assigned values of 1.0 throughout and do not appear in the Nernst equation. The boundaries for some solids may involve activities of dissolved sulfur species, for example,

$$\text{Fe}^{2+}+2\text{SO}_4^{2-}+16\text{H}^++14e^-=\text{FeS}_2\text{(c)}+8\text{H}_2\text{O},$$

or dissolved carbon dioxide species,

$$\text{Fe}^{2+}+\text{HCO}_3^-=\text{FeCO}_3\text{(c)}+\text{H}^+.$$

A specified total concentration for sulfate was used in drawing figure 14. The mass-law statement for siderite precipitation must be supplemented with equilibrium equations for carbon dioxide species to derive from the total amount specified the fraction that is present as HCO_3^- at the pH of the boundary.

Thermodynamic data used in drawing figures 14 and 15 were mostly taken from Wagman and others (1968) or from Robie and others (1978), and some differ slightly from values used in the earlier edition of this book. As noted earlier in this book, some writers have preferred to use a notation "pE" (Sillen, 1967b, p. 52) or "pϵ" (Stumm and Morgan, 1981, p. 422–436) in place of Eh. The rationale for this notation is primarily that it simplifies calculations in which redox and other types of chemical equilibria must be considered simultaneously. In this writer's opinion, the concept of pE as a measure of molar activity of electrons tends to obscure the electrochemical factors involved in redox processes and the greater mathematical simplicity is not very important in an age of electronic computers. However, the value of the diagrams for summarizing chemical relationships is not affected by the choice of notation.

Figure 14 represents a system containing a constant total amount of dissolved sulfur and carbon dioxide species equivalent to 96 mg/L as SO_4^{2-} and 61 mg/L as HCO_3^-. Boundaries are drawn for a dissolved iron activity of $10^{-6.00}$ molar (56 μg/L). Solids indicated by the shaded areas would be thermodynamically stable in their designated domains. Boundaries between solute species are not sensitive to specified dissolved iron activity, but the domains of solid species will increase in area if more dissolved iron is present.

The boundaries for sulfides and elemental iron shown in figure 14 extend below the water stability boundary and were extended to that area only to show what conditions are required for thermodynamic stability of elemental iron. These conditions include the absence of liquid water.

Under the conditions specified for figure 14, siderite ($FeCO_3$) saturation is not reached. Therefore, $FeCO_3$ is not a stable phase and it does not have a stability domain in the diagram. The more stable ferric or mixed valence oxyhydroxides (magnetite, goethite, hematite, etc.) were not considered as likely equilibrium species in aqueous systems at low temperatures.

Figure 15 is an iron solubility diagram for which most conditions are the same as those for figure 14. The lower solubility of $10^{-7.00}$ molar is equivalent to 5.6 μg/L and the upper limit shown is $10^{-3.00}$ molar, equivalent to 56 mg/L. The contours are plotted as the stability boundaries for solids when the indicated activities of dissolved iron are present. Calculations can be extended to show higher and lower iron solubilities, but there is little practical significance in doing so. As iron content becomes greater, the solubility of ferrous iron is controlled by siderite precipitation rather than by FeO. The boundary between FeO and $FeCO_3$ in the presence of the specified bicarbonate activity would be at pH 8.55. This corresponds to an Fe^{2+} activity of about 100 μg/L. The solubility of iron in the siderite-controlled area is also a function of the bicarbonate species activity specified.

Figure 15 demonstrates that there are two general Eh-pH conditions under which iron solubility is very low. One of these is a condition of strong reduction in the presence of sulfur and covers a wide pH range, within the field of stability for pyrite. The second is a condition of moderate oxidation above a pH of 5 and is in the ferric hydroxide stability region. Between these regions, and especially at low pH, iron is relatively soluble. The high-solubility regions at high pH are outside the range that is common in natural systems.

It is evident from the solubility diagram that exposing an equilibrated system to relatively small shifts in Eh or pH can cause great changes in iron solubility. Thus,

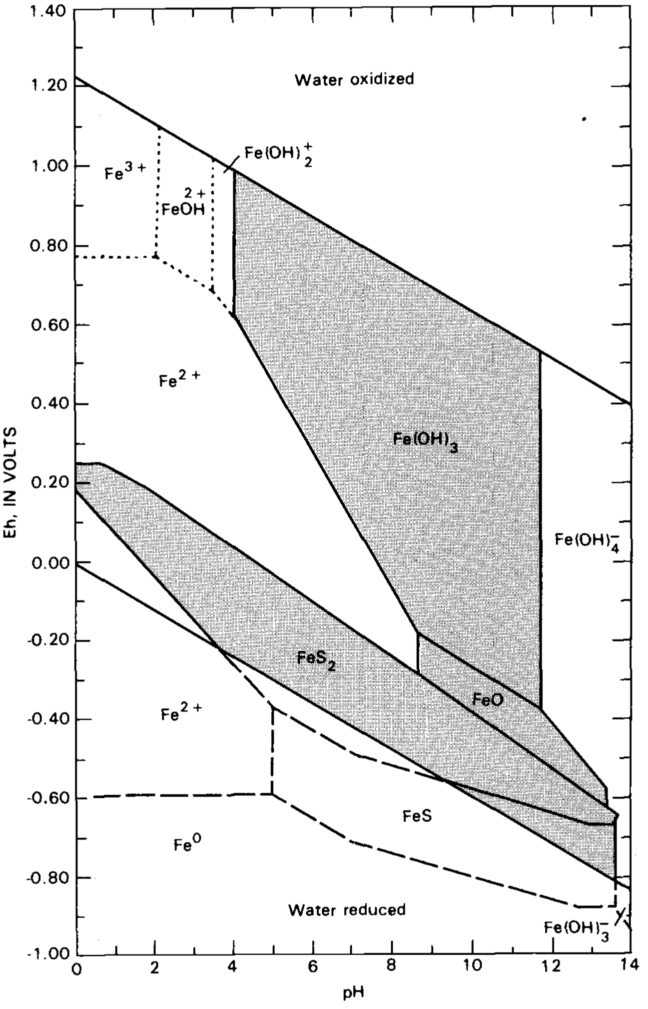


Figure 14. Fields of stability for solid and dissolved forms of iron as a function of Eh and pH at 25°C and 1 atmosphere pressure. Activity of sulfur species 96 mg/L as SO_4^{2-}, carbon dioxide species 61 mg/L as HCO_3^-, and dissolved iron 56 μg/L.

when pyrite is exposed to oxygenated water or ferric hydroxide is in contact with reducing substances, iron will tend to go into solution. It also is evident that if pH and dissolved iron activity and the nature of the solid are known, an equilibrium Eh of the system can be calculated, or at least a range of possible values can be given.

Within the usual pH range of natural water (pH 5–9), the maintenance of an Eh below 0.20 and above -0.10 V (or lower if sulfide is absent) can permit a considerable ferrous iron concentration in equilibrium. This goes a long way toward explaining the behavior of iron in underground water, where a relatively low Eh can be attained owing to chemical reactions that may deplete dissolved oxygen. The reaction of oxygen with pyrite is itself such a process, and the reaction products SO_4^{2-} and Fe^{2+} may be transported stably in the moving solution after the oxygen that might react with Fe^{2+} to convert it to Fe^{3+} has been used up. It is notable also that in a considerable part of this range of Eh, the solubility of iron may be controlled by precipitation of ferrous carbonate. In this part of the system, iron solubility is a function of pH and dissolved bicarbonate species but is independent of Eh. Thermodynamics of siderite control of ferrous iron solubility were discussed by the writer in earlier papers (Hem, 1960, 1965). If an iron-bearing ground water of this type dissolves oxygen from the air, however, iron is oxidized to the ferric form, which may precipitate as ferric hydroxide.

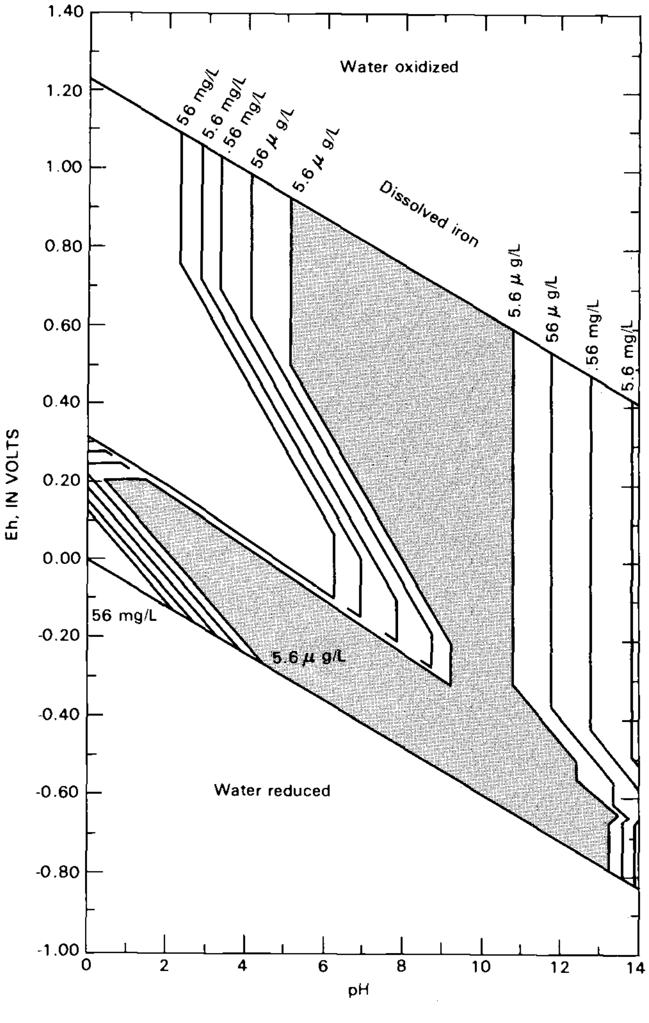


Figure 15. Equilibrium activity of dissolved iron as a function of Eh and pH at 25°C and 1 atmosphere pressure. Activity of sulfur species 96 mg/L as SO_4^{2-}, and carbon dioxide species 61 mg/L as HCO_3^-.

The positions of solubility contours like those in figure 15 are strongly influenced by the thermodynamic properties of the postulated solids. The free energy value used for $Fe(OH)_3(c)$ in figure 15 is -166.0 kcal/mole, which represents a poorly crystallized precipitate that has undergone some aging. According to Langmuir and Whittemore (1971), natural fresh precipitates may have ΔG° values as high as -164.5 kcal/mole, but more stable material is produced on aging. Attainment of significant crystallinity may be very slow and, according to these authors, could take thousands of years if dissolved iron activity is below 50 μg/L. More stable oxyhydroxides such as hematite and goethite have very low solubilities, but their roles in equilibrium control of iron solubility in freshwater natural systems probably are seldom major.

Redox equilibrium calculations are useful in some other aspects of the aqueous chemistry of iron. Barnes and Clarke (1969), for example applied such calculations in studies of the tendency of waters to corrode or encrust steel well casings and screens, and much of the impetus for the development of pH-Eh diagrams by Pourbaix was the need for a better theoretical understanding of metal-corrosion processes.

Nevertheless, the field application of redox principles and of pH-Eh diagrams is fraught with many uncertainties and complexities, which can lead to erroneous interpretations. Some errors stem from uncertainties about what is producing the potential one might measure in a natural water using a reference and inert metal electrode pair. Such potentials will not be rigorously related to specific dissolved metal ion activities if reversible equlibrium is not attained. But nonequilibrium conditions are widely prevalent in natural aqueous systems. Some of the problems in interpreting such potentials were discussed by Stumm and Morgan (1981, p. 490). Interpretations based on measured potentials are likely to be very uncertain unless the system can be well characterized by other information.

Although the pH-potential diagram is an effective means of summarizing redox equilibria, the simplifications that are required to prepare the diagram should be kept in mind. Some of the limitations of the diagrams merit attention.

Standard temperature and pressure (25°C and 1 atmosphere) are generally specified. However, diagrams could be prepared for other conditions if thermodynamic data used are appropriate for those conditions. As a rule, the departures from 25°C that are observed in natural water systems, other than geothermal systems, do not introduce enough deviation from standard conditions to justify correcting for them. The effect of ionic strength cannot be readily incorporated in the diagrams and thermodynamic activities rather than concentrations must be used.

A diagram such as figure 14 or 15 is an imperfect representation of a real-world system in other important ways. The prescribed constant total dissolved carbon and sulfur species, for example, implies, incorrectly, that one can evaluate the effect of changing some other variable, such as pH, independently without concern about its probable influence on total carbonate availability. The mingling of open- and closed-system concepts that is required for preparation of these diagrams limits their applicability to natural conditions. The numerical value of Eh, or pE, is an indicator of redox intensity, but it has little value as an indicator of redox capacity. This constraint also applies in some degree to pH values.

Reaction Rates

The requirement that rates of the reactions modeled in pH-Eh diagrams be relatively fast has been noted. Kinetics of relevant processes in the iron system have been evaluated by many investigators.

Precipitation of ferric oxyhydroxide by oxygenation of ferrous solutions is rapid at near-neutral pH. Data compiled by Sung and Morgan (1980) and determined from their own investigations suggest that the process has a half-time of about 18 minutes in aerated solutions with ionic strengths of 0.02 or less at 25°C and pH 6.84 in the presence of about 550 mg/L HCO_3^-. The rate is very sensitive to temperature and to OH^- activity and above about pH 5 (Stumm and Morgan, 1970, p. 538) is second-order in $[OH^-]$. That is, the rate increases by a factor of 100 for each unit increase in log $[OH^-]$. Below pH 3, the uncatalyzed rate of conversion of Fe^{2+} to Fe^{3+} is very slow. The rate also is slowed by complexing of Fe^{2+}, especially by organic material (Theis and Singer, 1974).

Oxidation rates of pyrite and other sulfides are slow in sterile systems but are greatly speeded by bacteria. Biological mediation is generally necessary to reach equilibrium in sulfide systems. Measurements of rates and evaluation of mechanisms, especially the oxidation of pyrite by Fe^{3+}, were reported by Nordstrom, Jenne, and Ball (1979).

Kinetic studies of ferric oxyhydroxide aging in relation to iron solubility were made by Langmuir and Whittemore (1971).

Roles of Bacteria in Solution and Precipitation of Iron

The ways in which microbiota may influence the occurrence of iron in water appear to be widely misunderstood. One result is a semi-"folklore" interpretation that blames all high concentrations of iron in water on activities of bacteria and leads to laborious and expensive efforts to eliminate bacteria, and thus the troublesome iron problem, by disinfecting wells, pipelines, and well-drilling equipment. These activities may have temporary effects but do not eliminate all iron problems.

From a thermodynamic point of view, the ways in which bacteria may be involved in the behavior of iron in water include the following:

1. Processes in which bacteria exert a catalytic effect to speed reactions that are thermodynamically favorable but occur rather slowly in the absence of bacteria. The biota may derive energy from them but may not use the iron otherwise.
2. Processes that require a contribution of energy from another source to alter the iron status and can be promoted by bacteria that consume some other substance as a source of energy.

Processes of the first type are involved in the oxidation of dissolved ferrous iron by *Gallionella, Crenothrix,* and *Leptothrix.* These genera require oxygen; hence, they live in environments in which ferrous iron is unstable. The bacteria may become established in wells and remove some iron by precipitation of ferric hydroxide before the water gets to the surface of the ground. Sulfur-oxidizing bacteria may exert an indirect effect on iron behavior by catalyzing reactions that bring iron into solution, the oxidation of pyrite, for example. Bacterial catalysis may increase the rate of conversion of Fe^{2+} to Fe^{3+} in acid solutions in the presence of pyrite by as much as six orders of magnitude and can be a major factor in generation of acid mine drainage (Nordstrom, Jenne, and Ball, 1979).

Processes of the second type typically involve iron- and sulfur-reducing species which require an oxidizable substance, usually organic, as a source of food and energy. Reduction or oxidation of iron may occur incidentally, and iron may play no essential role in the life processes of the bacteria. Some species of bacteria that have been shown to influence the precipitation of iron were discussed by Clark and others (1967). There have been many studies in microbiology concerning the roles of iron in the lives of these microorganisms (Neilands, 1974).

The net effect of bacteria may be either to increase or to decrease dissolved-iron concentrations in water after it is intercepted by a well. Bacterial colonies in wells and pipelines may be partly dislodged by moving water from time to time and thus give rise to occasional releases of accumulated ferric hydroxide. The occurrence of iron in ground water, however, is primarily a chemical phenomenon and cannot be ascribed solely to the bacteria. The biota associated with iron solution and deposition may aggravate some types of problems related to iron-bearing water. These biota are abundant and will inevitably become established in favorable situations.

Different types of bacteria may live together in a symbiotic relationship, with one species providing food for another. Sulfur reducing and oxidizing species may establish such relationships and greatly aggravate problems with well performance and corrosion of iron pipe or well casing and other exposed metallic iron in water-supply systems.

Occurrence of Iron in Water

Water in a flowing surface stream that is fully aerated should not contain more than a few micrograms per liter of uncomplexed dissolved iron at equilibrium in the pH range of about 6.5 to 8.5. The higher concentrations sometimes reported in such waters are generally particulates (Kennedy and others, 1974) small enough to pass through 0.45 μm porosity filter membranes. A typical river-water concentration of 10 μg/L is given in analysis 8, table 12. The effect of organic complexing is indicated by analysis 4, table 14, which is for a stream in northeastern Minnesota. The reported color for this water is 140 units, indicating a large amount of dissolved organic material. The iron in solution, 1.4 mg/L, is presumably complexed or stabilized by this material.

Another condition is shown in analysis 7, table 14, which is for a Pennsylvania stream carrying drainage from coal mines. The water has a pH of 3.0 and 15 mg/L of iron. Lower pH and higher iron concentration can occur in coal-mine drainage water. The water represented by analysis 6 in table 14, which is from a Michigan iron mine, has a pH of 7.5 and an iron content of only 0.31 mg/L. Iron ores in the Lake Superior region are primarily ferric oxides and silicates not readily soluble in water. Analysis 3, table 18, represents water having a pH of 1.9 and 33 mg/L of iron.

In lakes and reservoirs in which a stratified condition becomes established, water at and near the bottom may become enriched in organic matter and depleted in oxygen and may attain a low Eh. Ferrous iron can be retained in solution in water of this type to the extent of many milligrams per liter (Livingstone, 1963, p. G11). The iron content of lake water also can be influenced by aquatic vegetation, both rooted and free-floating forms (Oborn and Hem, 1962).

Occurrence of iron in ground waters of near-neutral pH can generally be at least qualitatively explained by chemical reactions that have been described and summarized in the pH-Eh diagrams. Deviations from these simple models generally can be ascribed to water circulation and mixing mechanisms.

When it reaches the ground-water body, recharge can be expected to contain oxygen acquired from exposure to air. Dissolved-oxygen activity of $10^{-3.5}$ moles/L represents approximate atmospheric saturation at ordinary air temperatures. If this amount of oxygen is depleted by reacting with pyrite, the final solution could contain about 5 mg/L of ferrous iron and about 17 mg/L of sulfate. A once-through continuous-flow system in which oxygen is not replenished after this reaction has occurred should have a final iron concentration in the water approaching 5 mg/L. Higher iron concentrations in such systems are common, however—perhaps owing to faster transport of oxygen than water in the unsaturated zone or to occasional flow reversals accompanied by reactions between ferric iron and pyrite.

Higher iron concentrations in simple hydraulic systems could result from interactions between oxidized iron minerals and organic matter or by dissolution of $FeCO_3$. Such waters should be relatively low in sulfate. The latter effect may not be diagnostic, however, because sulfate produced by pyrite oxidation may be reduced again in some systems and lost from solution.

Analyses 1, 2, and 3 in table 14 probably typify iron-containing ground water where a pyrite-oxidation mechanism is plausible. Regional development of a zone of oxidation near the surface overlying a zone of reduction at depth was described for interbedded sands of the Mississippi Embayment in northeastern Texas by Broom (1966). The ground water in this region is characterized by low iron concentrations in the upper oxidized and lower reduced strata, but iron concentrations are high near the contact between zones at intermediate depth where oxidation is currently active (Hem, 1965). Chemical zonations of iron in a lateral pattern in confined or semiconfined aquifers in parts of New Jersey were described by Langmuir (1969a).

Ground water having a pH of between 6 and 8 can be sufficiently reducing to retain as much as 50 mg/L of ferrous iron at equilibrium, when bicarbonate activity does not exceed 61 mg/L. In many areas, the occurrence of 1.0–10 mg/L of iron in ground water is common. This type of water is clear when first drawn from the well but soon becomes cloudy and then brown from precipitating ferric hydroxide. Wells that yield water of this type may appear to be erratically distributed around an area, and some exhibit changes in composition of their water with time that are difficult for hydrologists to explain. For example, in eastern Maryland and at other localities of the Atlantic Coastal Plain, the permeability of some coastal sedimentary beds is much greater than others, and a well may encounter solutions with different oxidation-reduction potentials at different depths. Mingling of these waters at contacts between strata and particularly where the strata are locally short-circuited, either naturally or by a well that penetrates them, can cause deposition or solution of iron minerals. In many wells, corrosion of the iron casing adds iron to the water pumped out, and iron may be precipitated in various forms within the well under some conditions.

Brines such as that represented by analysis 5, table 14, can retain iron that is stabilized by complex ion formation.

Because of the unstable nature of ferrous iron in samples of alkaline ground water, the iron orignially present may have been oxidized and precipitated by the time the analysis is made. To ensure that concentrations of iron reported in analyses represent the amounts in solution at the time of sampling, waters suspected of containing iron should be filtered at the time of sampling, and an aliquot of the filtrate acidified to prevent precipitation. The iron in untreated portions of samples represented by analyses 1–3, 8, and 9, table 14, had largely been lost from solution before analysis. Concentrations of iron reported are the totals originally present in a filtered, acidified fraction of the sample. The oxidation and precipitation reactions decreased the pH and altered the alkalinity originally present in the unacidified solutions used for the rest of the analysis. Although it might be possible to reconstruct these data to give the original composition of the water at the time of sampling, it is not common practice to do so. The effect of precipitation of iron may be readily noticeable in dilute solutions such as the one represented by analysis 9, table 14.

Manganese

Although manganese is one of the more abundant metallic elements, there is only about one-fiftieth as

Table 14. Analyses of

[Analyses by U.S. Geological Survey. Date below sample number is date of collection. Sources of data: 1, 5, and 6, U.S. Geological Survey, unpublished data; 2, 3, 21); 8, Simpson (1929, p. 298)]

Constituent	1 May 28, 1952		2 Mar. 8, 1952		3 Feb. 27, 1952		4 Oct. 1-31, 1962	
	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
Silica (SiO_2)	20		12		26		11	
Aluminum (Al)			1.2		1.2			
Iron (Fe)	2.3		2.9		10		1.4	
Manganese (Mn)	.00							
Calcium (Ca)	126	6.29	2.7	.135	8.8	.439	18	.898
Magnesium (Mg)	43	3.54	2.0	.164	8.4	.691	8.0	.658
Sodium (Na)	13	.56	35	1.522	34	1.478	9.3	.40
Potassium (K)	2.1	.05	1.7	.044	2.9	.074		
Bicarbonate (HCO_3)	440	7.21	100	1.639	65	1.065	69	1.131
Sulfate (SO_4)	139	2.89	5.6	.117	71	1.478	29	.604
Chloride (Cl)	8.0	.23	2.0	.056	2.0	.056	6.4	.181
Fluoride (F)	.7	.04	.1	.005	.3	.016		
Nitrate (NO_3)	.2	.00	.6	.010	.0	.000	2.9	.046
Dissolved solids:								
Calculated	594		113		187			
Residue on evaporation	571		101		180		156	
Hardness as $CaCO_3$	490		15		56		78	
Noncarbonate	131		0		3		21	
Specific conductance (micromhos at 25°C).	885		162		264		188	
pH	7.6		7.4		6.4		6.9	
Color	1		23		7		140	
Acidity as H_2SO_4 (total)								

1. Well 3, Nelson Rd., Water Works, Columbus, Ohio. Depth, 117 ft; temperature, 13.3°C. Water from glacial outwash.
2. Well 79:8–50, public supply, Memphis, Tenn. Depth, 1,310 ft; temperature, 22.2°C. Water from sand of the Wilcox Formation.
3. Well 5:290–1, 6 mi southeast of Maryville, Blount County, Tenn. Depth, 66 ft; temperature, 14.4°C. Water from the Chattanooga Shale.
4. Partridge River near Aurora, Minn. Composite sample. Mean discharge, 30.8 cfs.
5. Brine produced with oil from well in NW1/4 sec. 3, T. 11 N., R. 12 E., Okmulgee County, Okla. Depth, 2,394 ft. Water from the Gilcrease sand of drillers, Atoka Formation.

much manganese in the Earth's crust as there is iron. Manganese is not an essential constituent of any of the more common silicate rock minerals, but it can substitute for iron, magnesium, or calcium in silicate structures.

The chemistry of manganese is somewhat like that of iron in that both metals participate in redox processes in weathering environments. Manganese, however, has three possible valence states in such environments rather than two (2+, 3+, and 4+) and can form a wide variety of mixed-valence oxides. The 3+ species are unstable in that they may disproportionate. That is, two Mn^{3+} ions may interact spontaneously to produce one Mn^{2+} and one Mn^{4+} ion, and these products are more stable thermodynamically than the original Mn^{3+} species. This ability has a number of interesting ramifications in the chemistry of the element in natural water.

Manganese is an undesirable impurity in water supplies, mainly owing to a tendency to deposit black oxide stains. The recommended upper limit for manganese in public water supplies in the United States is 0.05 mg/L (50 μg/L) (NAS-NAE, 1972). No mandatory limit is specified for this element by the U.S. Environmental Protection Agency. It is an essential element for both plant and animal life forms.

Sources of Manganese

Many igneous and metamorphic minerals contain divalent manganese as a minor constituent. It is a significant constituent of basalt and many olivines and of pyroxene and amphibole. Small amounts commonly are present in dolomite and limestone, substituting for calcium. The silicate, rhodonite ($MnSiO_3$), and the carbonate, rhodochrosite ($MnCO_3$), are pink to red minerals sometimes used as gemstones.

When divalent manganese is released to aqueous solution during weathering, it is somewhat more stable

waters containing iron

and 9, Scott and Barker (1962, p. 63, 101); 4, U.S. Geological Survey Water-Supply Paper 1948 (p. 297); 7, U.S. Geological Survey Water-Supply Paper 1022 (p.

5 Mar. 11, 1952		6 Jan. 30, 1952		7 Aug. 8, 1944		8 June 24, 1921		9 Oct. 26, 1954	
ppm	epm	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
9.1		8.1		21		23		7.9	
				29	3.23			.6	
32		.31		15	.81	4.8		11	
		.34		10	.36			.32	
7,470	372.75	264	13.17	119	5.94	136	6.79	8.4	.419
1,330	109.37	17	1.40	68	5.59	35	2.88	1.5	.123
43,800	1,940.59	52	2.26	17	.74	960	41.74	1.5	.065
129	3.30	31	.80					3.6	.092
76	1.25	61	1.00	0	.00	249	4.08	30	.492
47	.98	757	15.76	817	17.01	1,260	26.23	5.9	.123
83,800	2,363.43	24	.68	22	.62	734	20.70	1.8	.051
0		.8	.04	.1	.01			.1	.005
		.0	.00	.4	.01	7.5	.12	.4	.006
137,000		1,280		1,260		3,280		47	
140,000		1,180				3,450		44	
24,200		730		845		484		27	
24,100		679		845		280		2	
146,000		1,460		1,780				68.8	
7.4		7.5		3.0				6.3	
15		2		8				3	
				342					

6. Drainage at collar, drill hole 89, 7th level, Mather A iron mine, Ishpeming, Mich. Temperature, 15.1°C.
7. Shamokin Creek at Weighscale, Pa. Discharge, 64.2 cfs; affected by drainage from coal mines.
8. Flowing well, Minneapolis, St. Paul, and Sault Ste. Marie R.R., Enderlin, Ramsom County, N. Dak. Depth, 613 ft. Water from the Dakota Sandstone.
9. City well 4, Fulton, Miss. Depth, 210 ft; temperature, 17.2°C. Water from the Tuscaloosa Formation.

toward oxidation than is ferrous iron. Generally, however, if it is in contact with the atmosphere, it will be precipitated, at sites where pH is high enough, as a crust of manganese 4+ oxide. These encrustations generally contain a substantial quantity of coprecipitated iron and, under some conditions, significant amounts of other metal ions as well, especially cobalt, lead, zinc, copper, nickel and barium. A particularly favorable substrate for manganese oxide precipitation is a previously existing manganese oxide surface. Thus the deposit may become thicker with time and form nodules around some central nucleus, as on the bottoms of certain lakes and at many localities on the ocean bottom. Small, discrete particles of oxide or coatings on other particles are widely distributed in stream sediments and soils. Coatings of manganese oxides in streambeds occur in many places. These coatings generally do not become very thick, owing to mechanical erosion and changes in water properties. In some areas manganese oxide may accumulate with other material in the form of a bog. The deposits in streams and bogs in New Brunswick, Canada, were described by Brown (1964). Other descriptions of streambed deposits concern streams in Sweden (Ljunggren, 1952, 1953, 1955), Colorado (Theobald and others, 1963), and Maine (Canney and Post, 1964; Nowlan, 1976). The mechanisms that produce these deposits are different. The deposits studied by Ljunggren seemed to be associated with an aquatic moss. In the other areas, however, the deposition seemed to occur without any organic intervention. Moran and Wentz (1974) and Wentz (1974) studied Colorado mountain streams affected by drainage from mines. There, as in the area described by Theobald and others, a low-pH, metal-enriched water is neutralized by mixing with normal stream water, and much of the dissolved-metal load is precipitated.

Manganese nodules in Oneida Lake, N.Y., were described by Dean and Greeson (1979). Literature on all aspects of marine manganese oxide nodules is voluminous and growing.

In lakes and reservoirs where thermal stratification develops, the bottom sediments may become anoxic and manganese oxide previously deposited may be reduced and dissolved. Water drawn from the deeper part of the supply reservoir may at times contain significant concentrations of dissolved Mn^{2+}. Reduction of manganese oxides at depth in buried sediment may be a factor in accumulations of manganese nodules in many environments. Diffusing Mn^{2+} can be redeposited as oxide when it reaches the surface of the sediment layer and encounters oxygenated water (Callender and Bowser, 1980).

Manganese is an essential element in plant metabolism, and it is to be expected that organic circulation of manganese can influence its occurrence in natural water. Specific mention of manganese accumulation in tree leaves appears in published literature. Some species of trees are much more effective accumulators than others. Bloss and Steiner (1960) found considerable quantities in the leaves of the chestnut oak, and Ljunggren (1951) reported similar findings for the needles of spruce trees in southern Sweden. Aquatic plants were noted by Oborn (1964) to be accumulators of manganese. Manganese in plant parts that die back or are shed becomes available for solution in runoff and soil moisture. The importance of this source of manganese in river water is not completely known, although some preliminary studies by Slack and Feltz (1968) of the effects of fallen leaves on the water quality of a small stream in Virginia showed it could be important at times.

Lateritic weathering processes have produced manganese oxide accumulations of economic importance in many locations, and manganese oxides are a constituent of the dark stain ("desert varnish") present on rocks in arid regions (Hem, 1964, p. 10).

Form of Dissolved Manganese

Under conditions to be expected in natural-water systems, any dissolved manganese will be in the 2+ oxidation state. The ion Mn^{2+} will predominate in most situations. The hydroxide complex $MnOH^+$ becomes the principal form above pH 10.5, and anionic forms will be significant at pH 12.0 or higher. The complex ion $MnHCO_3^+$ can be important in solutions having bicarbonate concentrations near 1,000 mg/L as HCO_3 (Hem, 1963a, b). The $MnSO_4(aq)$ ion pair could be important in solutions in which sulfate activity is greater than a few hundred milligrams per liter, judging from stability data reported by Nair and Nancollas (1959). Organic complexes of manganese may play a significant role in its transport in some situations. In general, however, the Mn^{2+} ion is considerably more stable than Fe^{2+} in aerated water, and it can be transported at higher concentrations without the protection of complexation.

Some Mn^{3+} species may be stable in strongly acid solutions, and stable organic complexes of Mn^{3+} are known to exist under some conditions. However, the role of Mn^{3+} in natural systems probably is related more closely to the instability of this form of the element with respect to disproportionation.

Manganese at higher oxidation states than Mn^{4+} is not likely to occur to a significant extent in natural aqueous systems. Very small amounts of such species could theoretically occur at very high pH. Permanganate (MnO_4^-) is used extensively in water treatment as an oxidant for removal of iron, manganese, and organic material. The MnO_2 produced in such interactions is removed by filtration.

Quantification of Manganese Redox Processes

Equilibria among dissoved and solid forms of manganese in the 2+, 3+, and 4+ oxidation states can be conveniently summarized in an pH-Eh diagram (fig. 16). Use of the diagram to explain natural aqueous systems, however, is not as simple and straightforward as in the case of iron. The two pH-Eh diagrams for iron specify oxyhydroxides that are not the most stable species known. However, natural systems appear to be well enough controlled by equilibria involving these metastable species to justify their use in the model.

For manganese, the situation is less clear cut. The common, naturally occurring oxides are generally forms of MnO_2, when the manganese is at the Mn^{4+} oxidation state, or mixed-valence oxides in which the oxidation state of manganese is less than +4.0 but substantially above +3.0. Species where the oxidation state is +3.0 as in MnOOH or below 3.0 as in Mn_3O_4 are readily produced when Mn^{2+} solutes are oxidized by air in laboratory experiments. Although these oxides do occur naturally, they are relatively uncommon.

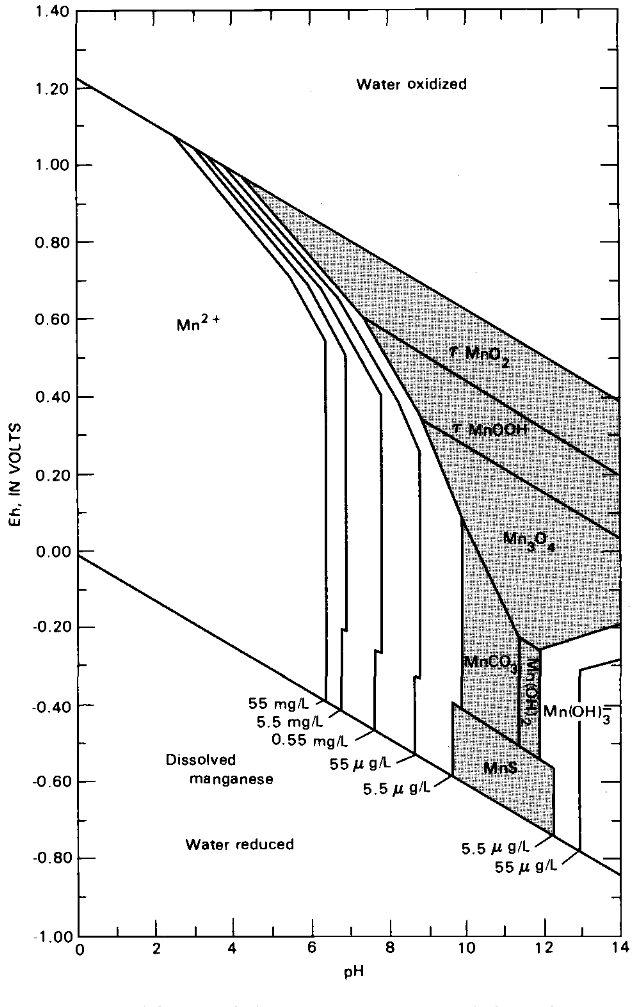


Figure 16. Fields of stability of manganese solids and equilibrium dissolved manganese activity as a function of Eh and pH at 25°C and 1 atmosphere pressure. Activity of sulfur species 96 mg/L as SO_4^{2-}, and carbon dioxide species 61 mg/L as HCO_3^-.

Thermodynamic data used for preparing figure 16 are given in tables 30 and 32. If certain other forms of oxyhydroxides or other published stability data are used, the boundaries in the figure would be shifted somewhat, but the general features would remain about the same. The total activities of sulfur and carbon dioxide species are $10^{-3.00}$ molar throughout, as in figure 14 and 15. The manganous sulfide, alabandite, does not have as important an effect as the iron sulfides, but the manganese carbonate, rhodochrosite, appears to have more influence than the corresponding ferrous carbonate, siderite. Figure 16 shows solid stability domains and equilibrium manganese activities from $10^{-3.00}$ to $10^{-7.00}$ moles/L (55 mg/L to 5.5 μg/L).

Natural oxygenated water commonly contains manganese concentrations near those predicted by figure 16 for equilibria involving γMnOOH but does not usually have the extremely small concentrations that are permitted in much of the MnO_2 stability field. For example, the chemical reaction

$$Mn^{2+}+\tfrac{1}{2}O_2(aq)+H_2O=MnO_2(c)+2H^+$$

gives an equilibrium activity of dissolved Mn^{2+} of less than 1 nanogram/L (ng/L) at pH 7.00 in aerated water. Apparently this simple equilibrium mechanism does not control manganese activity in such systems.

A chemical mechanism for manganese oxidation in aerated water that may help explain the generally observed behavior of this element has been proposed (Hem, 1978). In this model, precipitation of the oxide occurs in an open system and manganese will ultimately attain a steady-state concentation that is a function of kinetics of oxidation and of disproportionation of an Mn^{3+} intermediate. Essentially, this mechanism proposes a first step in which an oxide containing Mn^{3+} is produced and a second step immediately following in which two of the Mn^{3+} ions still at the solid-solution interface disproportionate. The Mn^{4+} ion that is formed enters the oxide crystal structure and the Mn^{2+} ion again becomes available for interaction with $O_2(aq)$.

The coupled oxidation-disproportionation mechanism can be summarized graphically by plotting equilibrium lines for the reactions, for example,

$$1.\ 3Mn^{2+}+\tfrac{1}{2}O_2(aq)+3H_2O=Mn_3O_4(c)+6H^+$$

and

$$2.\ Mn_3O_4(c)+4H^+=MnO_2(c)+2H_2O+2Mn^{2+}$$

on a pH versus log $[Mn^{2+}]$ grid (fig. 17).

In the region between lines 1 and 2 in figure 17, both reactions are thermodynamically favored to go to the right as written. If the process occurs in an open system, that is, a system in which dissolved oxygen is brought in by flowing water, and if there are continuing supplies of Mn^{2+} and continuing removal of surplus H^+, a steady-state control of Mn^{2+} concentration can be maintained. Figure 17 shows that for the solid species specified, activity of Mn^{2+} could range from about $10^{-6.2}$ to $10^{-8.3}$ molar at pH 7.5 (about 34 to about 0.3 μg/L).

If a less stable Mn^{3+} oxide is the initial form, the positions of the lines would be shifted somewhat to the right and solubilities would be greater, but the general range of concentrations observed in oxygenated natural waters are in reasonable accord with values this precipitation mechanism forecasts.

Information available on the sources of samples whose analyses are in tables 12–20 is not adequate to evaluate the applicability of this model closely. However, 7 of the 13 analyses that include specific manganese concentrations and pH values are plotted in figure 17. Of these, 6 plot between lines 1 and 2 and the other is just outside line 2. Four of the remaining 6 analyses not shown in figure 17 represent water having a pH of 4.0 or less that clearly should not be expected to precipitate manganese oxide. The other 2 are substantially higher in manganese than the oxidation model would predict. One of these (analysis 2, table 13) probably represents a reduced system, and both it and the other (analysis 2, table 18) have about the manganese activity one would predict for equilibrium with rhodochrosite. These evaluations take into account effects of ionic strength and complex-ion formation but are inexact because of uncertainties in the applicability of the laboratory pH determinations.

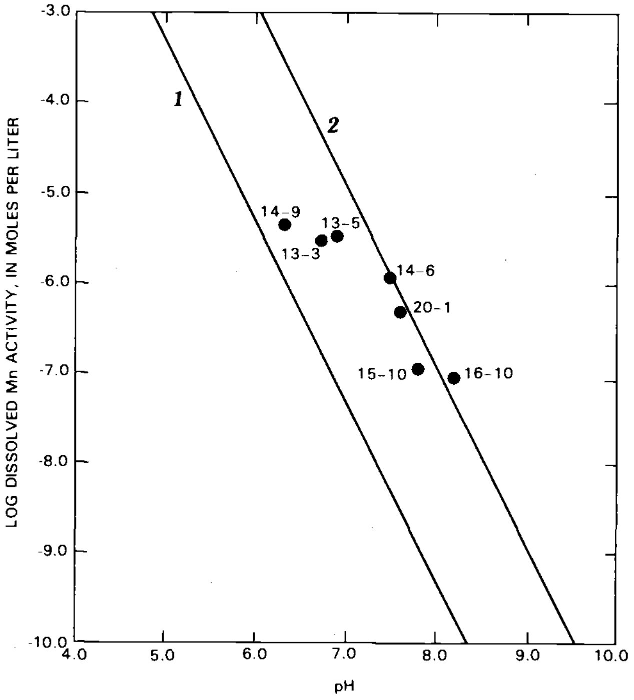


Figure 17. Activity of dissolved manganese at equilibrium at 25°C and 1 atmosphere pressure as a function of pH in aerated water. Line 1, oxidation of Mn^{2+} to form Mn_3O_4. Line 2, disproportionation of Mn_3O_4 to form γMnO_2 and Mn^{2+}. Plotted points represent analytical data from tables 13-16 and 20 (e.g., "14-9"=table 14, analysis 9).

Research by Morgan (1967), Wilson (1980), and Sung and Morgan (1981) on kinetics of manganese oxidation has demonstrated the importance of solid surfaces as sites for oxidation and precipitation. Manganese oxide surfaces are especially favorable for catalysis of the oxidation process. These surfaces have a high density of negative charge sites and are capable of adsorbing large numbers of cations per unit area, when conditions favor this process (Murray, 1974).

Whether the processes of adsorption or of coprecipitation are the more important depends on the composition of water in contact with the manganese oxides. The oxides, in any event, are effective scavengers (Jenne, 1968, 1975) and may be useful as indicators in geochemical prospecting for ore deposits (Chao and Anderson, 1974; Nowlan, 1976).

The rate of manganese oxidation in aerated solutions displays a second-order dependence on OH^- activity and is relatively slow in laboratory systems below pH 9.0. In river waters in which favorable surfaces are plentiful, the kinetic behavior may be pseudo-first-order; half-times of the order of a few days were observed in the Susquehanna River in Pennsylvania (Lewis, 1976) at near-neutral pH and temperatures of 5° to 20°C.

The rate of oxidation also is strongly temperature dependent, and lower temperatures (near 0°C) seem to favor the formation of more fully oxidized species (Hem, 1981; Hem and others, 1982) as initial precipitates ($\beta MnOOH$ rather than Mn_3O_4).

Bacteria may influence the rates of manganese oxidation, probably in a manner similar to the effects of bacteria in oxidation of ferrous iron. Tyler and Marshall (1967) found *Hyphomicrobium* in deposits of manganese oxide in pipelines. Schweisfurth has conducted extensive research on manganese oxidizing bacteria and has published many papers in Germany (for example, Schweisfurth, 1973; Jung and Schweisfurth, 1976).

Occurence of Manganese in Water

Manganese is often present to the extent of more than 1 mg/L in streams that have received acid drainage from coal mines. Manganese usually persists in the water for greater distances downstream from the pollution source than the iron contained in the drainage inflows.

As the acidity is gradually neutralized, ferric hydroxide precipitates first. Manganese, however, also disappears from solution after a longer time. These effects can be noted for streams in the Ohio River basin (U.S. Geological Survey Water-Supply Paper 1948). Analysis 4, table 13, presents water from a river influenced by acid mine drainage from which most of the iron has been precipitated. Analysis 7, table 14, is for water affected by mine drainage in which much iron was still present. Manganese concentrations exceeding 1 mg/L have been measured in water from small streams in the Northern United States during winter low-flow conditions (U.S. Geological Survey, 1969, p. 240, for example). During long periods of ice cover the dissolved-oxygen concentration in the water is depleted and manganese may be extracted from organic-rich sediment. Records of composition of many U.S. streams collected since about 1970 include manganese concentrations. These data indicate that concentrations up to a few hundred micrograms per liter occur in many streams at times. Some of the manganese reported in these analyses may be particulate material that can pass through 0.45 μm filter pores. Data obtained by Kennedy and others (1974), however, suggest that this is a much less important effect for manganese than it is for iron or aluminum.

Ground waters may contain more than 1.0 mg/L of manganese under some circumstances. High iron concentrations may accompany the manganese, but this is not invariably true. Analysis 1, table 13, is for a low-pH water that is very high in manganese, but some of the iron that might originally have been in solution in the water could have been lost by precipitation of ferric hydroxide in the sample after collection.

Analysis 2, table 13, represents water pumped from two radial collector wells located along the Ohio River at Parkersburg, W. Va. The manganese concentration of this water is 1.3 mg/L, compared with only 40 μg/L of iron. Excessive manganese concentrations also have been reported in other localities where wells were located with the aim of withdrawing water from gravel deposits adjacent to or within stream channels. Streambed materials may include sand grains and pebbles having manganese oxide coatings. The coatings may be reduced and dissolved by water of different composition that reaches them. Dissolved organic solutes, for example, may reduce the oxide and liberate Mn^{2+}. Anaysis 5 in table 13 and analysis 9 in table 14 represent ground waters high in iron that also contain several hundred micrograms per liter of manganese. The manganese may well have come from the same initial source as the iron.

Many of the ground waters reported to carry large manganese concentrations are from thermal springs. White and others (1963, p. F50) reported some examples of these. In many places these springs seem to be closely associated with manganese oxide deposits. Analysis 3, table 13, represents water from a thermal spring that contains 0.31 mg/L of manganese.

Calcium

Calcium is the most abundant of the alkaline-earth metals and is a major constituent of many common rock minerals. It is an essential element for plant and animal life forms and is a major component of the solutes in most natural water. Calcium has only one oxidation state, Ca^{2+}. Its behavior in natural aqueous systems is generally governed by the availability of the more soluble calcium-containing solids and by solution- and gas-phase equilibria that involve carbon dioxide species, or by the availability of sulfur in the form of sulfate. Calcium also participates in cation-exchange equilibria at aluminosilicate and other mineral surfaces. Solubility equilibrium models have been used widely in studying the chemical behavior of calcium.

Sources of Calcium

Calcium is an essential constituent of many igneous-rock minerals, especially of the chain silicates pyroxene and amphibole, and the feldspars. The plagioclase feldspar group of minerals represents mixtures in various proportions of the end members albite, $NaAlSi_3O_8$, and anorthite, $CaAl_2Si_2O_8$. Calcium also occurs in other silicate minerals that are produced in metamorphism. Some calcium is, therefore, to be expected in water that has been in contact with igneous and metamorphic rock. The concentration generally is low, however, mainly because the rate of decomposition of most igneous-rock minerals is slow. The decomposition of anorthite can be represented as

$$CaAl_2Si_2O_8+H_2O+2H^+=Al_2Si_2O_5(OH)_4+Ca^{2+}$$

The normal composition of plagioclase feldspar lies between the pure sodium and pure calcium forms, and decomposition will, therefore, generally yield both calcium and sodium and some soluble silica. Under some conditions the solution may attain saturation with respect to calcium carbonate.

The most common forms of calcium in sedimentary rock are carbonates. The two crystalline forms, calcite and aragonite, both have the formula $CaCO_3$, and the mineral dolomite can be represented as $CaMg(CO_3)_2$. Limestone consists mostly of calcite with admixtures of magnesium carbonate and other impurities. A carbonate rock is commonly termed "dolomite" if the magnesium is present in amounts approaching the theoretical 1 : 1 mole ratio with calcium. Other calcium minerals common in sediments include the sulfates gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$), and, more rarely, the fluoride, fluorite (CaF_2). Calcium is also a component of some types of zeolites and montmorillonite.

In sandstone and other detrital rocks, calcium carbonate commonly is present as a cement between particles or a partial filling of interstices. Calcium also is present in the form of adsorbed ions on negatively charged mineral surfaces in soils and rocks. Because divalent ions are held more strongly than monovalent ions at surface charge sites, and because calcium is generally the dominant divalent ion in solution, most such sites are occupied by calcium ions in the usual river or ground-water system.

Solute Species

Calcium ions are rather large, having an ionic radius near 1 angstrom. The charged field around the ion is therefore not as intense as the fields of smaller divalent ions. Calcium ions have a less strongly retained shell of oriented water molecules surrounding them in solution. The usual dissolved form can be simply represented as the ion Ca^{2+}. Calcium does form complexes with some organic anions, but the influence of such species on the concentrations of calcium in natural water is probably not important. In some solutions, complexes such as $CaHCO_3^+$ can exist. Data published by Greenwald (1941) show that about 10 percent of the calcium might be in this form if the bicarbonate concentration were near 1,000 mg/L. The ion pair $CaSO_4(aq)$ is more important. In solutions in which sulfate concentrations exceed 1,000 mg/L, more than half the calcium could be present in the form of the $CaSO_4$ ion pair. Both of these generalizations assume that the calcium concentration is small compared with the bicarbonate or sulfate concentrations.

Garrels and Christ (1964, p. 96) also mentioned hydroxide and carbonate ion pairs with calcium. These species could be present in appreciable concentrations in strongly alkaline solutions. Other calcium ion pairs, such as those with phosphate, are known but are not likely to influence the behavior of calcium in natural water to a significant extent. However, small amounts of phosphate are sometimes added in water treatment to inhibit $CaCO_3$ precipitation and phosphate is a constituent of many types of wastewater.

Chemical Controls of Calcium Concentration

Equilibria involving carbonates are the major factor in limiting the solubility of calcium in most natural water. The calcite dissolution-precipitation and dissolved carbon dioxide species equilibria were introduced earlier to demonstrate chemical equilibrium calculations, and the discussion of pH. Calculations required to determine whether a particular solution may be in thermodynamic equilibrium with calcite require values for activities of Ca^{2+}, HCO_3^- and H^+ and solution temperature. Analytical concentrations must be corrected for ionic strength effects and complexing, and equilibrium constants used must be appropriate for the temperature of the system.

Computer programs such as WATEQ (Truesdell and Jones, 1974) can perform all the necessary computations. For many interim or preliminary studies of water chemistry data, however, it may be convenient to evaluate the calcite equilibrium by a graphical procedure. Two forms of the calcite-solubility relationship are given here, as plate 2a and 2b and in figure 18. Both entail some simplifying assumptions that limit their applicability range to some extent.

Plate 2 is for a system lacking a gas phase and is based on the calcite-solubility equilibrium equation already extensively discussed:

$$\frac{[Ca^{2+}][HCO_3^-]}{[H^+]} = K_s{}^1.$$

The illustration consists of two parts, a log-log grid of calcium concentration versus bicarbonate concentration (both in mg/L) and a pH-grid overlay. When in use, the overlay is alined on the log-log plot so that the x-axes match.

Equilibrium constants at various temperatures, based on data in published literature, are given in table 33. The equilibrium solubility of calcite has a strong temperature dependence in this range. The solubility at 0° is more than five times as great as at 50°. To determine equilibrium conditions for a single temperature in this range when the effect of ion activity corrections can be ignored (ionic strength $\simeq 0.0$), the overlay may be moved right or left until the extension of the pH 8.0 line intersects the appropriate point on the temperature scale of the log-log base sheet. A saturation index for a water sample having this temperature can be obtained by plotting the point of intersection of the calcium and bicarbonate concentrations given in the analysis and reading the equilibrium pH from the pH grid. This pH is subtracted from the measured pH given in the analysis to give the S.I. value. A positive value for S.I. indicates supersaturation.

To permit the use of the graph for ionic strengths >0.0, conversion of stoichiometric concentrations to thermodynamic activities was incorporated in plate 2 by including activity coefficients in the equilibrium constant. The mass-law expression in terms of concentrations, C_{i+}, may be written

---

[1] The symbol K_s represents the solubility equilibrium constant for calcite in the reaction $CaCO_3 + H^+ = HCO_3^- + Ca^{2+}$

$$\frac{C_{Ca^{2+}}\gamma_{Ca^{2+}} \times C_{HCO_3^-}\gamma_{HCO_3^-}}{[H]} = K_s$$

or

$$\frac{C_{Ca^{2+}} \times C_{HCO_3^-}}{[H]} = \frac{K_s}{\gamma_{Ca^{2+}}\gamma_{HCO_3^-}} .$$

The activity coefficients (gamma terms) were evaluated by means of the Davies equation for values of I from 0.0 to 0.5. This relationship is

$$-\log \gamma_i = 0.509 Z_i^2 \frac{\sqrt{I}}{1+\sqrt{I}} - 0.2I ,$$

where Z_i is the ionic charge and I is ionic strength (Butler, 1964, p. 473).

The ionic-strength scale on the pH-grid overlay represents the positions to which the pH 8.0 line would be shifted by increased ionic strength. Simultaneous calibration of the graph for temperature and ionic-strength effects is accomplished by positioning the pH grid at the point where the temperature of the solution matches its ionic strength, using the scales on the match line in the lower parts of the two sheets.

Plate 2 provides a simple means of checking chemical analyses for possible conformance to calcite equilibrium. The only computation required is for ionic strength, and this can be obtained by using plate 1; as noted earlier, it also may be possible to estimate a usable number from the specific conductance. The graph does have some practical and theoretical limitations, however, and it is not applicable to all natural waters. Chemical analyses report calcium as a total Ca^{2+}, which includes any calcium complexes or ion pairs that are present. Any equilibrium calculation, however, must be based on the actual species of the solutes involved. Calcium forms complexes with bicarbonate and sulfate. The calcium bicarbonate complexes do not affect the usefulness of plate 2 because the basic data of Jacobson and Langmuir (1974) that were used compensate for these complexes. However, the effect of the calcium sulfate ion pair can be substantial, and waters that contain more than a few hundred milligrams of sulfate per liter require a more comprehensive mathematical treatment. Determinations of HCO_3^- by titration are subject to uncertainties noted in the discussion of alkalinity in a later section of this book. The bicarbonate concentration required when using plate 2 is that fraction of the alkalinity present as HCO_3^- (not total alkalinity as HCO_3^-).

The Davies equation does not include a temperature effect on the ion activity. Such a effect is indicated in the extended Debye-Hückel expression used elsewhere in this book. The design of plate 2 of necessity requires that temperature does not affect the activity coefficient calculation. This simplification probably does not introduce important errors compared with those resulting from other factors that are inherent in applying simple equilibrium models, however.

The system postulated does not contain a gas phase, and an equilibrium among dissolved CO_2 species is assumed. Measurements of pH and bicarbonate concentration must be as closely representative of the actual system as possible. This generally requires measurement of both properties in the field at the sampling site, at the temperature of the water source (Barnes, 1964). The calcium concentration in a sample can be stabilized by acidifying the sample at the time of collection so that this property can be measured later in the laboratory. Enough additional determinations must be made to permit calculation of ionic strength.

A less readily controllable requirement for applying calcite equilibrium calculations is that the solid involved is pure calcite and the reaction is directly reversible. The calcium carbonate in most limestones has significant amounts of other divalent cations substitued for Ca^{2+} in the lattice. A congruent reversible equilibrium may not be attainable in such a system, especially if the attacking solution has a Ca:Mg ratio substantially different from the solution in which the initial limestone was produced. However, in many if not most practical systems, a relatively pure secondary calcite precipitate can exist, and its behavior may indeed approximate reversibility well enough to make the model useful. In some environments films of organic matter may form on calcium carbonate surfaces and inhibit precipitation or dissolution.

Plummer and Busenberg (1982) have provided additional solubility data for calcium carbonates that can be used over the temperature range 0°–90°C. A saturation index (S.I.) for a water can be derived using plate 2 as noted above. Most investigators seem to have thought that experimental and other uncertainties in S.I. values are unlikely to be less than ±0.10 (Langmuir, 1971) and any system in which the graphically estimated S.I. value is in the range ±0.3 is probably close to equilibrium.

The determination of S.I. is useful as an indicator of chemical stability and of probable behavior of ground water encountered in wells, where there may be concern over possible deposition of carbonate precipitates on well screens, gravel packs, and water-yielding rock faces. Some aspects of this were discussed by Barnes and Clarke (1969). Such precipitates may be mixtures of various solids and can be expected if waters of differing chemical composition enter the well during operation of the pump.

The occurrence of siderite ($FeCO_3$) in carbonate precipitates that form in pipelines where some iron is available either from the water itself or the distribution system was noted by Sontheimer and others (1981). These authors suggested that siderite formation was an essential step in the development of a protective calcium carbonate coating, which prevents corrosion of water-distribution pipes.

In the presence of a gas phase containing CO_2, computations of calcite solubility can be made in terms of the partial pressure of CO_2 and pH. This requires consideration of carbon dioxide solubility, from Henry's Law

$$\frac{[H_2CO_3]}{P_{CO_2}}=K_h$$

and the first dissociation of carbonic acid

$$\frac{[HCO_3^-][H^+]}{[H_2CO_3]}=K_1.$$

The activity of H_2CO_3 is assumed to include any uncombined dissolved CO_2 as well, in accord with conventional practice. Combining these equations with the one for calcite solubility gives, when all three are at equilibrium:

$$\frac{[Ca^{2+}]K_1K_hP_{CO_2}}{[H^+]^-}=K_S.$$

Values of the equilibrium constants from 0° to 50°C are given in table 33.

This expression gives an indication of the CO_2 content of the gas phase that provided a water with its capacity for dissolving calcite. It might be interpreted for ground water as indicative of the partial pressure of CO_2 in the unsaturated zone through which recharge passed as it moved toward the water table. Subsequent reaction between CO_2 species and calcite would presumably have occurred in the absence of a gas phase, and no replenishment of CO_2 could occur. Depending on the nature of water circulation and water table fluctuations, this may or may not be a valid assumption. Some replenishment of the dissolved CO_2 in the zone of saturation might occur in some systems, owing to SO_4^{2-} reduction.

Observations and calculations were made by Deines and others (1974), on the basis of ^{13}C contents and the foregoing equilibria, on ground-water systems in limestone in the Nittany Valley of Pennsylvania. The P_{CO_2} values for these waters ranged from $10^{-1.3}$ to $10^{-1.8}$ atmospheres. It appeared that after equilibrating with the gas phase the water generally reacted with calcite under closed-system conditions like those postulated for plate 2.

In the discussions of pH and of the phase rule it was shown that a closed system containing water, carbon dioxide gas, and calcite would have 1 degree of freedom. The activity of dissolved calcium in such a system is therefore specified if a value for P_{CO_2} is specified. The equations required for computing the activity of Ca^{2+} include five chemical equilibria and a cation-anion balance equation, and enough information to permit calculating activity coefficients. Temperature effects can be included by using appropriate equilibrium constants from table 33. The final product could be a graph of calcium concentration versus P_{CO_2} for specified temperature and ionic strength. Calculations of this type were described by Garrels and Christ (1964, p. 81–83).

Natural systems contain other solutes and solids, and this kind of calculation has a somewhat limited practical applicability. Figure 18 is a graph of calcite solubility in terms of calcium concentration and CO_2 partial pressure based on laboratory experimental data at 25°C that were published by Frear and Johnston (1929).

The CO_2 content of normal air is 0.03 percent (by volume), or 0.0003 atmosphere. At this P_{CO_2}, the solubility indicated by the Frear and Johnston data in figure 18 for calcium in water in contact with air is about 20 mg/L. Garrels and Christ (1964, p. 83), using other

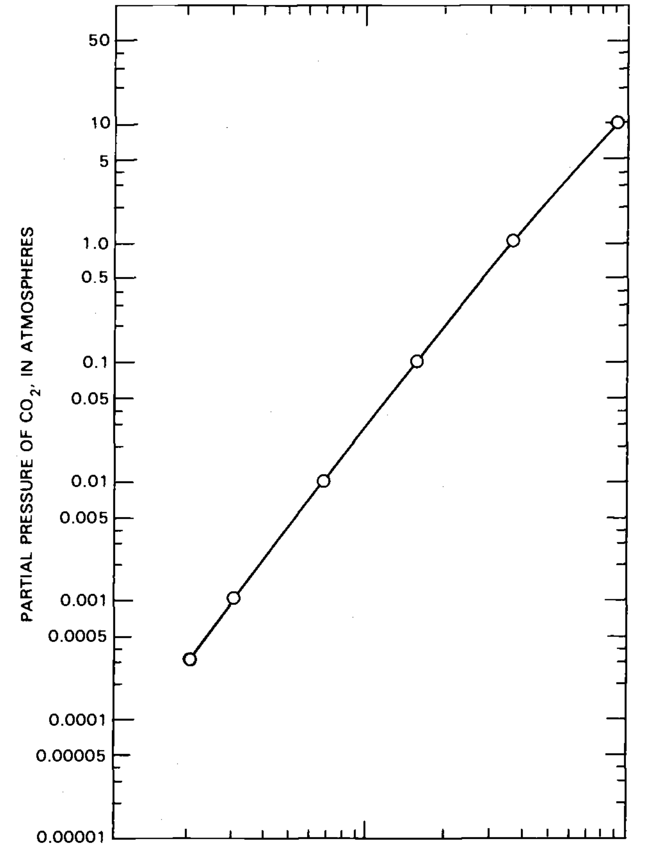


Figure 18. Solubility of calcium carbonate (calcite) in water at 25°C as a function of partial pressure of CO_2.

published thermodynamic data, calculated a solubility of 16 mg/L under these conditions.

If the input of H^+ is solely from the water itself and carbon dioxide is absent, the solubility of calcite is 5.4 mg/L of calcium (Askew, 1923). It is of interest to note that this solution would have a pH between 9.0 and 10.0. Garrels and Christ (1964, p. 81) observed this experimentally. They further calculated (p. 88) that rainwater that had dissolved all the carbon dioxide possible through equilibrium with air and then was equilibrated with calcite in the absence of a gas phase could dissolve hardly any more calcium than pure water and would also reach a high pH. Such a solution is not a very effective solvent for calcite in a stoichiometric sense. However, other solutes that may be present in rainwater ("acid rain") may substantially increase its solvent power.

From figure 18 it is evident that the concentrations of calcium that are common in waters in regions where carbonate rocks occur generally are well above the level specified for the partial pressure of carbon dioxide in the atmosphere. Water percolating through the soil and the unsaturated zone above the water table, however, is exposed to air in pore spaces in the soil, which is greatly enriched in carbon dioxide. Partial pressures of carbon dioxide in soil air are commonly 10–100 times the levels reached in the atmosphere (Bolt and Bruggenwert, 1978, p. 11). The carbon dioxide content of soil air for the most part results from plant respiration and from decay of dead plant material and can be expected to be greatest in environments that support dense stands of vegetation.

Observations and calculations of P_{CO_2} for groundwater systems commonly give values between $10^{-1.0}$ and $10^{-2.5}$ for P_{CO_2} in the gas phase. Values reported by Deines and others (1974) already cited are typical of systems in temperate regions where vegetation is abundant. Other souces of CO_2 such as sulfate reduction and oxidation of lignite fragments may be significant in some systems.

For dolomitic terranes, a reversible equilibrium is more difficult to attain, but a model postulating equilibrium has been shown by some workers to predict composition of ground water reasonably well (Barnes and Back, 1964a; Langmuir, 1971). This equilibrium will be considered more fully in discussing magnesium in the next section.

In environments in which hydrogen ions are supplied for rock weathering by processes other than dissociation of dissolved carbon dioxide species, for example, by oxidation of sulfur or sulfides, calcium may be brought into solution in amounts greater than the stoichiometric equivalent of bicarbonate. In such a system, or where water is in contact with solid gypsum or anhydrite, the maximum calcium concentration that could be reached would generally be determined by equilibria in which gypsum is a stable solid. Systems in which calcium solubility might be controlled by fluoride, phosphate, or other anions likely to occur only at low concentrations can be postulated but are likely to be rare in the real world.

The effect of cation-exchange processes on calcium concentrations in water differs from mineral dissolutions or precipitations in that only cations are directly involved. The requirement of anion-cation balance in the reacting solution thus prevents simple cation exchange or desorption from increasing or decreasing the total ionic load. Cation-exchange processes can bring about changes in the ratio of calcium to other cations in solution. Also, this effect in systems in which each liter of the water is in contact with an extensive area of solid surface tends to maintain a relatively constant Ca:Na ratio.

Reaction rates for calcium carbonate precipitation have been studied rather extensively. The presence of a favorable solid surface is a substantial aid in starting precipitation from a solution that is supersaturated. The rate of attainment of calcite saturation in ground water moving through a limestone aquifer depends on the nature of the flow system and the intimacy of contact of the water with calcite surfaces as well as on chemical factors. Studies in Pennsylvania showed that water of "conduit type" springs where residence time of the water was short (days or weeks) commonly is unsaturated. Water from "diffuse type" springs where residence time is measured in months is generally near saturation (Deines and others, 1974).

Studies by Plummer and Back (1980) showed that a continuing irreversible dissolution of dolomite and gypsum with some precipitation of calcite occurred along flow paths in the Floridan aquifer in Florida, and in the Madison limestone in South Dakota.

Occurrence of Calcium in Water

Applicability of the chemical models for calcium to natural waters can be illustrated with some of the tabulated analyses in this paper.

Generally calcium is the predominant cation in river water. Analysis 7 in table 15 is for the Cumberland River at Smithland, Ky., near the point where it joins the Ohio River. The pH of river water is influenced by many factors, especially by photosynthesizing organisms. These organisms commonly cause diurnal and seasonal fluctuations, with higher pH values on summer days and lower values at night and during other periods of low photosynthetic activity. The measured pH in river water is generally not well correlated with calcium and bicarbonate activities. However, the calcium concentration of the Cumberland River water, 25 mg/L, is not greatly above that which could occur in water in equilibrium with calcite in contact with air (20 mg/L, as shown in fig. 18). It is interesting to note that the average concentration of calcium in river water, shown as 13.4 to 15 mg/L in table 3, is also not far from an equilibrium value for a system containing calcite in contact with air. At equilibrium, however, a pH much greater than is usually observed in river water would be predicted.

Rivers in more arid regions, especially where some of the more soluble rock types are exposed, tend to have much higher dissolved-calcium concentrations. Analysis 8, table 15, is a discharge-weighted average of the composition observed for a year in the Pecos River at Artesia in southeastern New Mexico. It shows clearly the influence of gypsum, which is abundant in the Pecos drainage basin.

When river water is impounded in a storage reservoir, changes may occur in calcium content as a result of calcium carbonate precipitation. The increased pH near the water surface, caused by algae and plankton, may bring about supersaturation, and precipitation can occur on solid surfaces around the edges of the water body. A conspicuous white deposit developed around the edges of Lake Mead on the Colorado River between Arizona and Nevada as a result of this process. In part, the deposition in that reservoir also was related to inflows that are high in calcium and to the solution of gypsum beds exposed in the reservoir in the first few decades after the beginning of the storage of water (Howard, 1960, p. 119–124). A quantitative study of the changes that occurred in stored water composition, owing to gypsum solution and calcium carbonate deposition, was made by Bolke (1979) on the Flaming Gorge reservoir on the Green River in Wyoming and Utah. During the period 1963–75, there was a net gain of 1,947,000 metric tons in dissolved-solids load of the river attributable to effects of this kind within the reservoir. The freshwater deposit called marl, which is formed in many lakes, is made up partly of calcium carbonate.

Table 15. Analyses of waters in which

[Analyses by U.S. Geological Survey. Date below sample number is date of collection. Sources of data: 1, 4, and 9, Scott and Barker (1962, p. 19, 47, 59); 2,

Constituent	1 Mar. 28, 1952		2 May 20, 1950		3 Nov. 25, 1949		4 Mar. 26, 1952	
	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
Silica (SiO_2)	8.6		22		29		130	
Iron (Fe)	.05						41	
Manganese (Mn)								
Calcium (Ca)	48	2.395	144	7.19	636	31.74	93,500	4,665.65
Magnesium (Mg)	3.6	.296	55	4.52	43	3.54	12,100	995.35
Sodium (Na)	2.1	.091	29	1.24	17	.74	28,100	1,222.35
Potassium (K)							11,700	299.17
Bicarbonate (HCO_3)	152	2.491	622	10.19	143	2.34	0	.00
Sulfate (SO_4)	3.2	.067	60	1.25	1,570	32.69	17	.35
Chloride (Cl)	8.0	.226	53	1.49	24	.68	255,000	7,193.55
Fluoride (F)	.0		.4	.02				
Nitrate (NO_3)			.3	.00	18	.29		
Dissolved solids:								
Calculated	148		670		2,410		[1]408,000	
Residue on evaporation							415,000	
Hardness as $CaCO_3$	135		586		1,760			
Noncarbonate	10		76		1,650			
Specific conductance (micromhos at 25°C).	269		1,120		2,510		([3])	
pH	7.5						5.29	
Color								

[1] Includes strontium (Sr) 3,480 mg/L, 79.43 meq/L; bromide (Br) 3,720 mg/L, 46.56 meq/L; iodide (I) 48 mg/L, 0.38 meq/L.

[2] Includes 0.70 mg/L lithium (Li) and 0.03 mg/L zinc (Zn).

[3] Density at 46°C, 1.275 g/mL.

1. Big Spring, Huntsville, Ala. Temperature, 16.1°C. Water-bearing formation, Tuscumbia Limestone.
2. Spring on Havasu Creek near Grand Canyon, Ariz. Flow, 100 gpm; temperature, 19.4°C. Water-bearing formation, limestone in the Supai Formation. Water deposits travertine.
3. Jumping Springs, SE1/4 sec. 17, T. 26 S., R. 26 E., Eddy County, N. Mex. Flow, 5 gpm. Water-bearing formation, gypsum in the Castile Formation.
4. Brine well 3 Monroe, SE1/4 sec. 27, T. 14 N., R. 2 E., Midland, Mich. Depth, 5,150 ft; temperature, 46.1°C. Water-bearing formation, Sylvania Sandstone.

In closed basins, water can escape only by evaporation, and the residual water can be expected to change in composition after a fairly well defined evolutionary pattern. The less soluble substances, including calcium carbonate, are lost first, followed by calcium sulfate (Swenson and Colby, 1955, p. 24–27). The Salton Sea in Imperial Valley, Calif., is fed by irrigation drainage, and since its origin, during flooding by the Colorado River in 1907, it has become rather highly mineralized. Hely and others (1966) concluded that the water of the Salton Sea in 1965 was at saturation with respect to gypsum because the water seemed incapable of dissolving powdered gypsum in a laboratory experiment.

Equilibrium solubilities can be expected to control calcium concentrations in many ground-water systems. Unfortunately, many published chemical analyses of such waters are unsuitable for rigorous testing of calcite-solubility models owing to lack of accurate onsite measurements for pH and alkalinity. Most of the analyses in the tables in this book also have this shortcoming. However, if the acceptable uncertainty in saturation index calculations is broadened, the application of calcite equilibria to some of the ground-water analyses may be useful here. Approximations of this kind often are of value in water-analysis interpretation.

Analysis 1 in table 15 represents a large limestone spring, and as might be expected the water evidently is not far from calcite equilibrium. The calculated S.I. value for this solution is –0.21. The water represented by analysis 9 in table 16 also came from a limestone. Although this solution is less dominated by calcium and bicarbonate, it also is near calcite equilibrium, with an S.I. of +0.20.

Springs that form deposits of travertine are common in many areas of the United States (Feth and Barnes, 1979). Analysis 3, table 11, represents the water from such a spring which issues from Redwall Limestone in the Grand Canyon region of Arizona. Such waters are

calcium is a major constituent

6, and 10, U.S. Geological Survey, unpublished data; 3 and 5, Hendrickson and Jones (1952); 8, U.S. Geological Survey Water-Supply Paper 1163 (p. 360)]

5 Jan. 26, 1948		6 June 23, 1949		7 May 19, 1952		8 1948 and 1949		9 June 6, 1954		10 Dec. 8, 1954	
mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
...	...	74	...	4.9	...	17	...	24	...	15	...
...	...	...	...	.04	...	...	...	.02	...	1.0	...
...	...	...	...	...	...	...	...	.00	...	.01	...
99	4.94	277	13.82	25	1.248	394	19.66	88	4.39	96	4.790
28	2.30	64	5.26	3.9	.321	93	7.65	7.3	.60	19	1.562
4.1	.18	53	2.29	4.5	.196	333	14.48	19	.83	18	.783
				1.4	.036			2.8	.07	1.5	.038
287	4.70	85	1.39	90	1.475	157	2.57	320	5.24	133	2.180
120	2.50	113	2.35	12	.250	1,150	23.94	6.7	.14	208	4.330
6	.17	605	17.06	2.2	.062	538	15.17	13	.37	25	.705
...	...	.2	.01	.1	.005	...	...	.3	.02	.4	.021
2.8	.05	35	.56	1.9	.031	5.0	.08	4.6	.07	.4	.006
401	...	1,260	...	100	...	2,610	...	323	...	[2]449	...
...	...	...	...	99	...	...	...	322	...	468	...
362	...	954	...	78	...	1,370	...	250	...	318	...
127	...	884	...	5	...	1,240	...	0	...	209	...
651	...	2,340	...	172	...	3,540	...	543	...	690	...
...	...	...	...	6.7	...	...	...	7.5	...	7.8	...
...	...	...	...	5	...	...	...	2	...	3	...

5. Rattlesnake Spring, sec. 25, T. 24 S., R. 23 E., Eddy County, N. Mex. Flow, 2,500 gpm. Water-bearing formation, alluvium, probably fed by the Capitan Limestone.
6. Irrigation well, NE1/4 sec. 35, T. 1 S., R. 6 E., Maricopa County, Ariz. Temperature, 25.6°C. Water-bearing formation, alluvium.
7. Cumberland River at Smithland, Ky. Discharge, 17,100 cfs.
8. Pecos River near Artesia, N. Mex. Discharge-weighted average, 1949 water year; mean discharge, 298 cfs.
9. City well at Bushton, Rice County, Kans. Depth, 99 ft. Water-bearing formation, Dakota Sandstone.
10. Industrial well, Willimansett, Mass. Depth, 120 ft; temperature, 12.2°C. Water-bearing formation, Portland Arkose.

substantially supersaturated at normal atmospheric pressure. Reaching the calcium activity in this analysis by solution of calcite would require a partial pressure of CO_2 near 0.4 atmosphere (fig. 18). The S.I. calculated for this analysis is +0.13. Other travertine-depositing springs are represented by analyses given by White and others (1963, p. F54).

Analysis 9 in table 15 represents water from sandstone with calcareous cement that has given the solution a character typical of saturation with calcite. The S.I. for this solution is +0.28.

Analysis 3 in table 15 is for a spring that issues from gypsum. From the expressions

$$[Ca^{2+}][SO_4^{2-+}]=10^{-4.625}$$

and

$$\frac{[CaSO_4]}{[Ca^{2+}][SO_4^{2-}]}=10^{2.31}$$

(equilibrium constants for 25°C from Sillen and Martell, 1964) the saturation index for this water can be calculated, by the procedure outlined under the heading "Solubility Product." The S.I. value obtained is –0.025, indicating a close approach to equilibrium. The effect of temperature departure from 25°C was not considered in this calculation but is less important for gypsum that it would be for calcite equilibria. Evaluations for gypsum saturation pose few measurement or sample-stability problems, but calculations are tedious if done by hand.

Equilibrium with respect to gypsum is obviously to be expected in ground water from a gypsiferous aquifer. The water represented by analysis 3, table 15, is predominantly a solution of calcium and sulfate. As the amount of other solutes increases, the solubility of gypsum will tend to increase owing to greater ionic strength and smaller activity coefficients. In a solution containing 2,500 mg/L of chloride and about 1,500 mg/L of sodium, the equilibrium concentration of calcium would be near 700 mg/L. These calculations presuppose nearly equivalent concentrations of calcium and sulfate. Frequently, this does not occur in natural water. When the solution is in equilibrium with gypsum, however, any increase in sulfate activity would be matched by a decrease in calcium as $CaSO_4$ precipitates (see also fig. 21).

Natural brines in which the predominant dissolved ions are calcium and chloride are fairly common. An example is represented by analysis 4 in table 15. There is no general agreement as to how such a composition is reached. Water that has been trapped underground for a long time could be altered from its original composition by selective permeability of strata for different solutes, by the bacterial reduction of sulfate and other dissolved ions, and by adsorption or desorption of dissolved ions, as well as by chemical solution or precipitation of minerals. The formation of calcium chloride brine was ascribed by Valyashko and Vlasova (1965) to a combination of concentration and ion-exchange processes.

The process of cation exchange in ground-water bodies has been observed extensively since early studies by Renick (1924) called attention to natural softening of ground water by cation exchange in sediments underlying the northern Great Plains area of the United States. Ground water that has exchanged calcium for sodium is common in many areas (see analyses 1 and 2, table 17). The reverse effect, exchange of sodium for calcium, also can be expected but is less well documented. In localities near the ocean where seawater has entered freshwater aquifers, the advancing saltwater front commonly carries higher proportions of calcium to sodium than are characteristic of seawater (Poland and others, 1959, p. 193), owing to release of calcium from exchange positions by the sodium brought in by the advancing saltwater.

In irrigated areas, the exchange of calcium for sodium in soil moisture may proceed forward or in reverse at different times and in any specific spot may fluctuate extensively. The residual solutes from the irrigation water that was used by the crop or evaporated from the soil, however, will partly reappear in drainage water. The water of the Salt River, which is extensively used for irrigation in the Phoenix, Ariz., area, is shown by analysis 5, table 17, to contain nearly twice as many milliequivalents per liter of Na^+ as of $Ca^{2+}+Mg^{2+}$. The ion ratio in the effluent, principally drainage of residual irrigation water, is represented by analysis 6, table 17; it has a slightly higher proportion of the divalent ions, and this suggests that the exchange reactions are occurring, even though a good deal of the calcium present in the initial water probably is precipitated as carbonate or, possibly, sulfate in the irrigated area. The effect is more strongly shown by analysis 6, table 15, which represents water from a well in the area irrigated with Salt River water, where recharge is composed of irrigation drainage water. The milliequivalents per liter concentration of sodium in the water is far lower than that of calcium.

Water that is strongly influenced by irrigation return flow may approach simultaneous equilibrium with both calcite and gypsum. Water of the Gila River at Gillespie Dam near Gila Bend, Ariz., and the Rio Grande at Fort Quitman, Tex., shows these properties at times (Hem, 1966). Whether analysis 3, table 15, depicts equilibrium with both solids cannot be determined because the pH is not known.

Magnesium

Magnesium is an alkaline-earth metal and has only one oxidation state of significance in water chemistry, Mg^{2+}. It is a common element and is essential in plant and animal nutrition.

In some aspects of water chemistry, calcium and magnesium may be considered as having similar effects, as in their contributions to the property of hardness. The geochemical behavior of magnesium, however, is substantially different from that of calcium. Magnesium ions are smaller than sodium or calcium ions and can be accommodated in the space at the center of six octahedrally coordinated water molecules, an arrangement similar to that described for aluminum. The hydration shell of the magnesium ion is not as strongly held as that of aluminum ions, but the effect of hydration is much greater for magnesium than for the larger ions of calcium and sodium. The tendency for precipitated crystalline magnesium compounds to contain water or hydroxide is probably related to this hydration tendency.

Sources of Magnesium

In igneous rock, magnesium is typically a major constituent of the dark-colored ferromagnesian minerals. Specifically, these include olivine, the pyroxenes, the amphiboles, and the dark-colored micas, along with various less common species. In altered rocks, magnesian mineral species such as chlorite and serpentine occur. Sedimentary forms of magnesium include carbonates such as magnesite and hydromagnesite, the hydroxide brucite, and mixtures of magnesium with calcium carbonate. Dolomite has a definite crystal structure in which calcium and magnesium ions are present in equal amounts.

The alteration of magnesian olivine (forsterite) to serpentinite can be written

$$5Mg_2SiO_4+8H^++2H_2O$$
$$=Mg_6(OH)_8Si_4O_{10}+4Mg^{2+}+H_4SiO_4.$$

This is somewhat analogous to the reactions shown previously for weathering of feldspar and produces a solid alteration product, serpentinite. The reaction, like that for the alteration of other silicates, is not reversible and cannot be treated as a chemical equilibrium. Released products, however, can be expected to participate in additional reactions.

Form of Dissolved Magnesium

The magnesium ion, Mg^{2+}, will normally be the predominant form of magnesium in solution in natural water. Data given by Sillen and Martell (1964, p. 41–42) show that the complex $MgOH^+$ will not be significant below about pH 10. The ion pair $MgSO_4(aq)$ has about the same stability as the species $CaSO_4(aq)$, and magnesium complexes with carbonate or bicarbonate have approximately the same stability as the similar species of calcium. The sulfate ion pair and the bicarbonate complex will be significant if the solution contains more than 1,000 mg/L of sulfate or bicarbonate.

Chemical Controls of Magnesium Concentration

Carbonate equilibria involving magnesium are more complicated that those governing calcium activities. There are several different forms of magnesium carbonates and hydroxycarbonates and they may not dissolve reversibly. Magnesite, $MgCO_3$, from solubility products given by Sillen and Martell (1964, p. 136, 137), seems to be about twice as soluble as calcite. However, the hydrated species nesquehonite, $MgCO_3\cdot 3H_2O$, and lansfordite, $MgCO_3\cdot 5H_2O$, are considerably more soluble than magnesite. The basic carbonate hydromagnesite, $Mg_4(CO_3)_3(OH)_2\cdot 3H_2O$, may be the least soluble species under some conditions. Magnesite apparently is not usually precipitated directly from solution, and, as noted by Hostetler (1964), a considerable degree of supersaturation with respect to all magnesium carbonate species may be required before precipitation can occur. In any event, such species are rarely significant factors in limiting magnesium content of water.

Magnesium occurs in significant amounts in most limestones. The dissolution of this material obviously brings magnesium into solution, but the process is not readily reversible—that is, the precipitate that forms from a solution that has attacked a magnesian limestone may be nearly pure calcite. Magnesium concentration would tend to increase along the flow path of a ground water undergoing such processes, until a rather high [Mg]:[Ca] ratio is reached.

Conditions under which direct precipitation of dolomite from solution occurs are not commonly found in natural-water (nonmarine) environments. Dolomite precipitates have been found in saline lakes in various places. Hostetler (1964) cited reports of its occurrence from South Australia, Austria, Utah, and the U.S.S.R. but noted that the concentrations of magnesium, calcium, and carbonate ions in water associated with the dolomite seemed to be above theoretical saturation limits in many instances.

Recent workers seem to be in fairly general agreement that the solubility product for dolomite is near $10^{-17.0}$ at 25 °C. Langmuir (1971) accepted this value and calculated values of $10^{-16.56}$ at 0°, $10^{-16.71}$ at 10°, and $10^{-16.89}$ at 20°C. Earlier, several investigators (Hsu, 1963; Barnes and Back, 1964a; Holland and others, 1964) used analyses of ground water in association with dolomite to calculate an ion-activity product near $10^{-16.5}$. The general characteristics of ground water from dolomitic terrane suggest that saturation with respect to calcite also occurs in many such waters. Yanat'eva (1954) reported that dolomite was somewhat more soluble than calcite under a partial pressure of CO_2 approaching that of ordinary air.

The attainment of a relatively stable value for the activity product is possible in a system in which calcite is precipitated while dolomite dissolves. Long residence times of water in such systems would produce [Mg]:[Ca] ratios above 1.0 and a high pH, with both tending to increase along the flow path. This mechanism is treated quantitatively in the mass-balance model that Plummer and Back (1980) applied to the Floridan and the Madison Limestone aquifers. Carbon dioxide could be replenished within these systems through sulfate reduction and, theoretically at least, very high magnesium concentrations might ultimately be reached. Magnesium hydroxide (brucite) occurs naturally, and the solubility product at 25°C is between 10^{-10} and 10^{-11} (Sillen and Martell, 1964, p. 41–42). Precipitation of this solid implies a high pH and a solution impoverished in dissolved carbon dioxide species.

The cation-exchange behavior of magnesium is similar to that of calcium. Both ions are strongly adsorbed by clay minerals and other surfaces having exchange sites.

Some magnesium silicate minerals can be synthesized readily in the laboratory at 25°C. Siffert (1962), for example, prepared sepiolite ($Mg_3Si_4O_{11}\cdot4H_2O$) by precipitation from solutions of $Si(OH)_4$ and $MgCl_2$ at a pH of 8.73 or higher. This mineral or a related species may have a significant effect on magnesium concentration in weathering solutions acting on magnesium-rich igneous rock.

Eaton and others (1968) proposed that the solubility of magnesium in irrigation drainage water might be limited by precipitation of a magnesium silicate of unspecified composition in the soil. A magnesium sink is needed to explain the loss of magnesium that is commonly observed in such waters.

Table 7, which shows residence times of the elements in the ocean, points up another factor of some importance: Magnesium has a very long residence time compared

Table 16. Analyses of waters in which

[Analyses by U.S. Geological Survey except as indicated. Date under sample number is date of collection. Sources of data: 1, 3–7, and 9, U.S. Geological Survey,

Constituent	1 Feb. 27, 1952		2 April 11, 1952		3 Sept. 29, 1948		4 Oct. 18, 1957	
	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
Silica (SiO_2)	8.4		18		31		175	
Aluminum (Al)	1.4							
Iron (Fe)	.24		1.4					
Calcium (Ca)	40	1.996	94	4.69	20	1.00	34	1.70
Magnesium (Mg)	22	1.809	40	3.29	42	3.45	242	19.90
Sodium (Na)	.4	.017	17	.74	19	.83	184	8.00
Potassium (K)	1.2	.031	2.2	.06			18	.46
Carbonate (CO_3)	0		0		0		0	
Bicarbonate (HCO_3)	213	3.491	471	7.72	279	4.57	1,300	21.31
Sulfate (SO_4)	4.9	.102	49	1.02	22	.46	6.6	.14
Chloride (Cl)	2.0	.056	9.0	.25	7	.20	265	7.47
Fluoride (F)	.0	.000	.8	.04	.2	.01	1.0	.05
Nitrate (NO_3)	4.8	.077	2.4	.04	2.5	.04	.2	.00
Dissolved solids:								
Calculated	190		466		281		[1]1,580	
Residue on evaporation	180		527					
Hardness as $CaCO_3$	190		400		222		1,080	
Noncarbonate	16		13		0		14	
Specific conductance (micromhos at 25°C).	326		764		458		2,500	
pH	7.4		6.7		8.2		6.5	
Color	5		5					

[1] Includes 18 mg/L of boron (B).

[2] Contains 0.01 mg/L of manganese (Mn) and 0.9 mg/L of lithium (Li).

[3] Density, 1,345 g/mL.

1. Spring 2½ mi northwest of Jefferson City, Tenn. Flow, 5,000 gpm; temperature, 14.4°C. From the Knox Dolomite.
2. Well number 5, City of Sidney, Ohio. Depth, 231 ft; temperature, 11.7°C. Water-bearing formation, Niagara Group.
3. Spring in Buell Park, Navajo Indian Reservation, Ariz. Flow, 18 gpm; temperature 12.2°C. Water-bearing formation, olivine tuff-breccia.
4. Main spring at Siegler Hot Springs, NE1/4 sec. 24, T. 12 N., R. 8 W., Lake County, Calif. Water issues from contact with serpentine and sedimentary rocks. Temperature, 52.5°C.

with calcium. Organisms that require calcium for shell or skeletal parts represent an important factor in calcium precipitation. Such demands on magnesium are much smaller.

Occurrence of Magnesium in Water

Analyses in table 16 can be used to demonstrate some of the effects of dolomite dissolution on magnesium content and other properties of natural water. As noted earlier, the calculation of S.I. values from these data is subject to an unknown but probably substantial uncertainty because the reported pH values are laboratory determinations. Analyses 1, 2, and 10 represent ground waters from dolomitic terranes and analysis 9 is for ground water from limestone containing dolomite.

Before it reaches saturation with respect to either dolomite or calcite, a water passing through dolomite should dissolve equal molar amounts of calcium and magnesium. Analyses 1 and 2 in table 16 have negative values for S.I. for calcite and for dolomite. Analysis 1 has nearly equal meq/L values for calcium and magnesium. The greater proportion of calcium in analysis 2 may reflect the fact that the rocks of the Niagara Group, from which the water comes, include limestone as well as dolomite.

Water represented by analysis 10, table 16, has substantial supersaturation with respect to calcite (S.I.=+0.40) and a calculated S.I. for dolomite of +0.99. Dissolved magnesium exceeds calcium in this water, and this can be explained by calcite precipitation after reaching supersaturation. As noted earlier, dolomite does not precipitate readily under these conditions. Analysis 5 in table 16 illustrates this behavior even more strongly. This water is from a pool in Carlsbad Caverns, N. Mex., in which calcite is precipitating. The dolomite S.I. in this solution is +1.58.

magnesium is a major constituent

unpublished data; 2, 8, and 10, Scott and Barker (1962, p. 19, 87, 113)]

5		6		7		8		9		10	
Apr. 20, 1945		Feb. 7, 1939		May 21, 1952		May 27, 1952		Mar. 11, 1952		Oct. 29, 1954	
mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
11				4.2		12		13		18	
						1.0				.2	
.04				.13		.03		.01		.39	
16	.80	130	6.49	18	.898	23	1.148	140	6.99	35	1.747
71	5.84	51,500	4,236.39	8.5	.699	12	.987	43	3.54	33	2.714
7.8	.34	59,000	2,566.60	2.5	.109	1.7	.074	21	.91	28	1.218
		2,810	71.85	2.4	.061	1.6	.041			1.3	.033
21	.70			0		0		0		0	.000
320	5.25	1,860	30.49	90	1.475	127	2.081	241	3.95	241	3.950
21	.44	299,000	6,225.18	9.5	.198	1.6	.033	303	6.31	88	1.832
8	.23	22,600	637.55	1.5	.042	2.0	.056	38	1.07	1.0	.028
1.0	.05			.0	.000	.0	.000	.8	.04	.9	.047
19	.31			.8	.013	.9	.014	4.1	.07	1.2	.019
333		436,000		92		119		682		[2]326	
321		510,000		106		108		701		329	
332				80		107		526		224	
34				6		3		329		27	
570		(3)		165		197		997		511	
8.3				7.0		7.6		7.4		8.2	
				35		5					

5. Green Lake in Carlsbad Caverns, N. Mex. Pool of ground-water seepage.
6. Test well one, SW1/4 sec. 24, T. 25 S., R. 26 E., Eddy County, N. Mex. Water from 142–195 ft.
7. Wisconsin River at Muscoda, Grant County, Wis. Flows through area of magnesian limestone.
8. Spring, SW1/4 sec. 26, T. 16 S., R. 7 E., Calhoun County, Ala. Supplies city of Anniston. Flow, 46 cfs; temperature, 17.8°C. Water-bearing formation, quartzite.
9. Oasis flowing well, SW1/4 sec. 15, T. 11 S., R. 25 E., Chaves County, N. Mex. Depth, 843 ft; flow, more than 9,000 gpm when drilled. Water-bearing formation, San Andreas Limestone (limestone and dolomitic limestone, with minor amounts of sandstone, gypsum, and anhydrite). Temperature, 20.6°C.
10. Drilled well, NW1/4 sec. 6, T. 6 N., R. 21 E., Milwaukee County, Wis. Depth, 500 ft; temperature, 10.0°C. Water-bearing formation, Niagara Dolomite.

A similar effect may be noted by comparing analyses 1 and 2 in table 11. These represent "before and after" composition of a water that lost calcium from solution by formation of a calcium carbonate precipitate inside the sample bottle during storage.

Analysis 9 in table 16 represents water from the Roswell artesian system in southeastern New Mexico. This water is in contact with limestone and dolomite and appears to be near saturation with respect to both calcite and dolomite; computed values for S.I. are +0.20 and +0.18, respectively.

Analysis 7 in table 16 represents water from the Wisconsin River. The rather high proportion of magnesium to calcium in streams of that region was pointed out many years ago by Clarke (1924a).

The chemical reaction written earlier in this discussion for the conversion of olivine to serpentinite indicates that the process consumes much H^+. This could also be considered equivalent to production of OH^-. Barnes and others (1967) called attention to ground waters of unusual composition that they observed in association with fresh or partly serpentinized peridotite or dunite. An example is given as analysis 5, table 18. This water had a pH of 11.78 and carbonate species were below detection. The magnesium concentration is very small owing to precipitation of brucite ($Mg(OH)_2$). At the calcium concentration reported in the analysis, only a few tenths of a milligram of CO_3^{2-} per liter could be present at equilibrium with $CaCO_3$. Barnes, O'Neil, and Trescases (1978) have cited other examples of these "ultrabasic" waters, from Oman, New Caledonia, and Yugoslavia. The hydroxide concentration in analysis 5, table 18, was calculated from the pH value, which was measured in the field at the time of sample collection. Some of the calcium is probably present as the $CaOH^+$ complex, and the silica and aluminum would be present in anionic form at this pH. With these factors taken into account, the cation-anion balance is satisfactory.

Sodium

Sodium is the most abundant member of the alkali-metal group of the periodic table. The other naturally occurring members of this group are lithium, potassium, rubidium, and cesium. In igneous rocks, sodium is slightly more abundant than potassium, but in sediments, sodium is much less abundant. The amounts of sodium held in evaporite sediments and in solution in the ocean are an important part of the total. All the alkali metals occur in the 1+ oxidation state and do not participate in redox processes. Sodium ions have a radius somewhat greater than 1 angstrom and are not strongly hydrated.

When sodium has been brought into solution, it tends to remain in that status. There are no important precipitation reactions that can maintain low sodium concentrations in water, in the way that carbonate precipitation controls calcium concentrations. Sodium is retained by adsorption on mineral surfaces, especially by minerals having high cation-exchange capacities such as clays. However, the interaction between surface sites and sodium, and with monovalent ions generally, is much weaker than the interactions with divalent ions. Cation-exchange processes in freshwater systems tend to extract divalent ions from solution and to replace them with monovalent ions.

Sources of Sodium

According to Clarke's (1924a, p. 6) estimate, about 60 percent of the body of igneous rock in the Earth's outer crust consists of feldspar minerals. The feldspars are tectosilicates, with some aluminum substituted for silica and with other cations making up for the positive-charge deficiency that results. The common feldspars are orthoclase and microcline, which have the formula $KAlSi_3O_8$, and the plagioclase series ranging in composition from albite, $NaAlSi_3O_8$, to anorthite, $CaAl_2Si_2O_8$. Some sodium may be present, substituting for potassium in orthoclase and microcline.

Potassium feldspar is resistant to chemical attack. However, species containing sodium and calcium are somewhat more susceptible to weathering; they yield the metal cation and silica to solution and commonly form a clay mineral with the aluminum and part of the original silica. Besides the kaolinite shown as a product in earlier discussions of this reaction in this book, other clays such as illite or montmorillonite may be formed. Feth and others (1964), in studies of water in the feldspar-rich granitic terrane of the Sierra Nevada of California and Nevada, found that, in general, calcium and sodium ions were the most important cations in stream and spring water and that these tended to reflect abundance of the ions in the type of rock and the rate at which the minerals were attacked.

In resistate sediments, sodium may be present in unaltered mineral grains, as an impurity in the cementing material, or as crystals of readily soluble sodium salts deposited with the sediments or left in them by saline water that entered them at some later time. The soluble salts go into solution readily and are rather quickly removed from coarse-grained sediments after environmental changes, such as an uplift of land surface or a decline of sea level, impose a freshwater leaching regimen. During the early stages of the leaching process, the water leaving the formation may have high concentrations of sodium in solution. The last traces of marine salt or connate water may persist for long periods where circulation of water is impaired.

In hydrolyzate sediments, the particles normally are very small, and the circulation of water through the material is impaired. Thus, the water trapped in the sediment when it was laid down may be retained with its solute load for long periods. The hydrolyzates include a large proportion of clay minerals having large cation-exchange capacities. Where sands and clays are interbedded, water and sodium may be retained longer in the less permeable strata during leaching and flushing by freshwater circulation. When such interbedded sections are penetrated by wells, water will be drawn mainly from more permeable sections at first. Long-continued withdrawals and water-table declines can be expected to alter water-circulation patterns, and saline solutions can be induced to move from the clay and shale layers. When this occurs on a large scale, a substantial increase in sodium concentration of the pumped water will occur. Kister and Hardt (1966) observed this effect in irrigation wells of the Santa Cruz basin in Arizona, where extensive declines in water levels had occurred.

Human activities can have a significant influence on the concentrations of sodium in surface water and ground water. The use of salt for deicing highways in winter and the disposal of brine pumped or flowing from oil wells, for example, have had direct, noticeable regional effects. Somewhat less directly, the reuse of water for irrigation commonly leaves a residual that is much higher in sodium concentration than was the original water. Pumping of ground water, which alters hydraulic gradients, can induce lateral movement of seawater into freshwater coastal aquifers.

Ion-exchange and membrane effects associated with clays were described under the topic "Membrane Effects." Some of these factors may influence sodium concentrations. Hanshaw (1964), for example, showed that when compacted, clays may preferentially adsorb sodium, but when dispersed in water, they may preferentially adsorb calcium.

Dissolved Species

The sodium of dilute waters in which dissolved-solids concentrations are below 1,000 mg/L is generally in the form of the Na^+ ion. In more concentrated solutions, however, a variety of complex ions and ion pairs is possible. Species for which stability constants are given in Sillen and Martell (1964, p. 136, 235) include $NaCO_3^-$, $NaHCO_3(aq)$, and $NaSO_4^-$. These and other ion pairs or complexes involving sodium are substantially less stable than the ones involving divalent cations such as calcium or magnesium.

Solubility Controls

Because of the high sodium concentrations that can be reached before any precipitate is formed, the sodium concentrations in natural water can have a very wide range, from less than 1 mg/L in rainwater and dilute stream runoff in areas of high rainfall to very high levels in brines associated with evaporite deposits and in brines of closed basins, where more than 100,000 mg/L may be present.

Sodium bicarbonate is one of the less soluble of the common sodium salts. At ordinary room temperature, however, a pure solution of this salt could contain as much as about 15,000 mg/L of sodium. In natural water, the conditions required for precipitation of pure sodium bicarbonate are unlikely to be attained, although water in some closed basins may attain high concentrations of carbonate and bicarbonate and leave a residue of solid forms of sodium carbonate. These are somewhat more soluble than the bicarbonate.

Sodium carbonate residual brines occur in some closed basins in California, Oregon, and Washington and elsewhere. Garrels and MacKenzie (1967) described a sequence of concentration and precipitation of solids from water that originally obtained its solute contents from weathering of silicate minerals in igneous rock. These processes may lead to solutions having a pH of more than 10.

A higher solubility limit on sodium concentration is exerted by the separation of solid sodium chloride, or halite. When saturated with respect to halite, a solution could have as much as 150,000 mg/L of sodium and about 230,000 mg/L of chloride, but concentrations this high are seldom reached in natural environments. Inclusions of brine are present in some halite formations. It can be shown, theoretically at least, that such inclusions may be able to migrate through the salt if a temperature gradient exists, by dissolving salt at the warmer end of the inclusion and precipitating it at the cooler end.

Sodium sulfate solubility is strongly influenced by temperature. The solid precipitated may contain various amounts of water, ranging from mirabilite or Glauber's salt with the formula $Na_2SO_4 \cdot 10H_2O$, through the heptahydate with seven molecules of water and the anhydrous form. Closed-basin lakes in cool climates may precipitate mirabilite during cool weather, which may be redissolved at higher temperatures. Mitten and others (1968) discribed such effects in eastern Stump Lake, N. Dak. Sodium concentrations in the lake during a 5-year period of intermittent sampling generally were between 20,000 and 30,000 ppm. An apparent decrease of about 25 percent in sodium concentration and a corresponding loss of sulfate was reported over a 1-week period when the water temperature decreased from 11° to 3°C (Mitten and others, 1968, p. 26). Somewhat similar deposition of mirabilite has been observed in Great Salt Lake, Utah (Eardley, 1938).

Occurrence of Sodium in Water

In table 17 and some other places in this book are analyses that illustrate the various features of sodium behavior in natural aqueous systems.

Analysis 2 in table 12 represents water from rhyolitic volcanic rock and indicates the predominance of sodium over other cations that ought to be observed in water that has attacked albite. Waters that are low in dissolved solids, and in which calcium and magnesium have been depleted and sodium increased through cation exchange, are common in sediments of the Atlantic Coastal Plain and the Mississippi embayment. Analysis 2 in table 14 is for a dilute water from the Wilcox Formation showing this effect. A more strongly influenced example is analysis 1 in table 17, which represents a well in Atlantic Coastal Plain sediments. Analysis 2 in table 17 also shows the influence of cation exchange.

Some effects on surface-stream chemistry of solutes retained in fine-grained sediment are demonstrated by analysis 4, table 17. This analysis represents a stream in western South Dakota where the country rock is fine grained and contains soluble material. In the process of weathering, the exposed surfaces of these rocks may develop noticeable efflorescences of salts by evaporation of water between rainy periods. Aqueous precipitation heavy enough to wash away these deposits occurs occasionally, and at the same time the layer of leached sediment at the surface also may be stripped away. Colby and others (1953) have discussed these effects in greater detail.

Wells that penetrate clay and shale to reach lower, more permeable beds may at times obtain water high in dissolved solids directly from the shale layers, as seems indicated in analysis 9, table 17. Analysis 8, table 14,

Table 17. Analyses of water in which

[Analyses by U.S. Geological Survey. Date below sample number is date of collection. Sources of data: 1, 3, 7, and 8, U.S. Geological Survey, unpublished data; 2, 214); 9, Griggs and Hendrickson (1951, p. 111)]

Constituent	1 June 3, 1952		2 Oct. 3, 1949		3 May 13, 1952		4 July 2-3, 1949	
	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
Silica (SiO_2)	22		16		22		8.2	
Iron (Fe)	.20		.15		.00		.04	
Calcium (Ca)	2.5	.12	3.0	.15	49	2.45	40	2.00
Magnesium (Mg)	2.1	.17	7.4	.61	18	1.48	50	4.11
Sodium (Na)	1,182	7.90	857	37.28	168	7.29	699	30.40
Potassium (K)			2.4	.06			16	.41
Carbonate (CO_3)	30	1.00	57	1.90	0		26	.87
Bicarbonate (HCO_3)	412	6.75	2,080	34.09	202	3.31	456	7.47
Sulfate (SO_4)	3.5	.07	1.6	.03	44	.92	1,320	27.48
Chloride (Cl)	9.5	.27	71	2.00	246	6.94	17	.48
Fluoride (F)	1.7	.09	2.0	.11	.1	.01	1.0	.05
Nitrate (NO_3)	.6	.01	.2	.00	2.2	.04	1.9	.03
Boron (B)			.40				.60	
Dissolved solids:								
Calculated	457		2,060		649		2,400	
Residue on evaporation	452				651		2,410	
Hardness as $CaCO_3$	15		38		196		306	
Noncarbonate	0		0		31		0	
Specific conductance (micromhos at 25°C).	718		2,960		1,200		3,140	
pH	8.7		8.3		7.7		8.2	
Color	1				2			

[1] Density, 1.019 g/mL at 20°C.

[2] Density, 1.21 g/mL.

1. Well at the Raleigh-Durham Airport, Wake County, N.C. Depth, 184 ft. Water-bearing formation, Coastal Plain sedimentary rocks.
2. Well, SE1/4 NE1/4 sec. 2, T. 22 N., R. 59 E., Richland County, Mont. Depth, 500 ft. Water-bearing formation, Fort Union Formation (sandstone and shale).
3. Irrigation well, SE1/4 sec. 3, T. 1 N., R. 5 E., Maricopa County, Ariz. Depth, 500 ft.; temperature, 20.5°C. Water-bearing formation, valley fill.

shows the composition of water obtained from the Dakota Sandstone in southeastern North Dakota. The water is high in sodium and in sulfate. Solute contents of water in the formation in this region may be derived from overlying and underlying finer grained materials (Swenson, 1968).

Water associated with evaporite formations generally has a very high sodium concentration. Analysis 2 in table 18 represents a sodium carbonate brine from Wyoming. Sodium carbonate evaporite deposits occuring in southern Wyoming are mined as a source of soda ash.

Water affected by solution of halite is represented by analyses 7 and 8 in table 17. Analysis 8 displays near-saturation with respect to sodium chloride. The source of the salinity in the Salt Banks spring is not evident at the surface. Inflows of this type have a significant influence on the water of the Salt River, which is impounded for use in irrigation of the area near Phoenix, Ariz. The composition of this supply is represented by analysis 5 in table 17.

Anthropogenic effects on sodium concentrations are demonstrated by high sodium concentration of residual drainage from the Salt River Valley irrigated area (analysis 6, table 17). Somewhat higher average concentrations occurred at this sampling point during the 10 years following 1952. Most of the increase was in sodium, chloride, and sulfate. The water at low flow is near saturation with respect to calcite and gypsum (Hem, 1966). Analysis 3, table 17, represents a well in the irrigated area upstream where recharge is virtually all brought about by applied irrigation water. The analysis

sodium is a major constituent

Torrey and Kohout (1956, p. 44); 4, U.S. Geological Survey Water-Supply Paper 1162 (p. 457); 5 and 6, U.S. Geological Survey Water-Supply Paper 1253 (p. 205,

5 1951 -52		6 1951 -52		7 Dec. 8, 1951		8 Jan. 31, 1938		9 Oct. 15, 1946	
mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
18		31		46				13	
.01		.01							
48	2.40	353	17.61	505	25.20	722	36.03	30	1.50
14	1.15	149	12.25	291	23.94	2,490	204.83	31	2.55
150	6.52	1,220	53.05	10,100	439.35	121,000	5,263.50	279	12.13
5.8	.15	9.8	.25	170	4.35	3,700	94.61		
0		0		0		63	2.10	0	
153	2.51	355	5.82	1,520	24.91	40	.66	445	7.29
50	1.04	1,000	20.82	899	18.72	11,700	243.59	303	6.31
233	6.57	1,980	55.84	16,200	457.00	189,000	5,331.69	80	2.26
.4	.02	1.9	.10					1.2	.06
2.4	.04	24	.39					17	.27
.15		2.4		17					
597		4,940		[1]29,000		[2]329,000		973	
611									
178		1,490		2,460				202	
52		1,200		1,210				0	
1,090		7,620		41,500		225,000		1,510	
				7.1					

4. Moreau River at Bixby, S. Dak.; composite of two daily samples. Mean discharge, 1.7 cfs. Drains the Pierre Shale, the Fox Hills Sandstone, and the Hell Creek Formation.
5. Salt River below the Stewart Mountain Dam, Ariz. Discharge-weighted average, 1952 water year; mean discharge, 362 cfs.
6. Gila River at the Gillespie Dam, Ariz. Discharge-weighted average, 1952 water year; mean discharge, 71.1 cfs.
7. Spring entering the Salt River at Salt Banks near Chrysotile, Ariz. Temperature, 21.1°C. Water-bearing formation, quartzite and diabase.
8. Test well 3, sec. 8, T. 24 S., R. 29, E., Eddy County N. Mex. Depth, 292 ft. Brine from the Salalado Formation and the Rustler Formation.
9. Well in SW1/4 sec. 7, T. 17 N., R. 26 E., San Miguel County, N. Mex. Depth, 50 ft. Water-bearing formation, shale of the Chinle Formation.

is nearly the same as that for the river water (analysis 5, table 17). The effect of seawater encroachment in a coastal aquifer near Los Angeles, Calif. is shown by analyses in table 22.

Many water analyses in the earlier literature report a computed value for sodium rather than an actually determined one. The computed value represents the difference between the sum of the determined anions, in milliequivalents per liter, and the determined cations, expressed in the same units. Obviously, the computation cannot be made unless all the other major ions have been determined. Potassium is commonly lumped with sodium in the computation, and the value reported as "sodium and potassium, as sodium." The principal reason for omitting sodium from the analysis in former years was that the determination was difficult, tedious, and expensive by the procedures then available. After about 1955, the flame photometer and related flame spectrochemical methods made the sodium determination one of the quickest and easiest in the analytical chemists' repertoire, and, thus, analyses with computed sodium values are no longer common. The principal objection to the computation of sodium is that it prevents any really effective check of the accuracy of the determinations of the major dissolved components; therefore, analyses reporting computed sodium values are more likely to contain major errors.

Potassium

As shown in table 1, potassium is slightly less common than sodium in igneous rock but more abundant in all the sedimentary rocks. In the ocean the concentration of potassium, though substantial, is far less than that of sodium. The figures point up the very different behavior of these two alkali metals in natural systems. Sodium tends to remain in solution rather persistently once it has been liberated from silicate-mineral structures. Potassium is liberated with greater difficulty from silicate minerals and exhibits a strong tendency to be reincorporated into solid weathering products, especially certain clay minerals. In most natural water, the concentration of potassium is much lower than the concentration of sodium.

Another important factor in the hydrochemical behavior of potassium is its involvement in the biosphere, especially in vegetation and soil. Potassium is an essential element for both plants and animals. Maintenance of optimum soil fertility entails providing a supply of available potassium. The element is present in plant material and is lost from agricultural soil by crop harvesting and removal as well as by leaching and runoff acting on organic residues.

Sources of Potassium

The principal potassium minerals of silicate rocks are the feldspars orthoclase and microcline ($KAlSi_3O_8$), the micas, and the feldspathoid leucite ($KAlSi_2O_6$). The potassium feldspars are resistant to attack by water. Presumably they are altered to silica, clay, and potassium ions by the same process as other feldspars, only more slowly.

In sediments, the potassium commonly is present in unaltered feldspar or mica particles or in illite or other clay minerals. Evaporite rocks may locally include beds of potassium salts and constitute a source for high potassium concentration in brines.

Average content of potassium in living plants, according to data given by Mason (1952, p. 199), is near 0.3 percent. Concentrations in dry plant material and in ash are substantially greater. Wood ashes have been used by humans as a potash source for many centuries.

Control Mechanisms for Potassium Concentration

Although potassium is an abundant element and its common salts are highly soluble, it seldom occurs in high concentrations in natural water. Chemical mechanisms that might be expected to bring about such a result, however, are not of a type that is readily quantified. The broad generalizations already stated suggest that potassium concentrations in water are low partly because of the high degree of stability of potassium-bearing aluminosilicate minerals. Unaltered potassium feldspar grains occur in many sandstones.

The potassium ion is substantially larger than the sodium ion, and it would normally be expected to be adsorbed less strongly than sodium in ion-exchange reactions. Actually, however, potassium is incorporated in a special way into some clay-mineral structures. In illite, potassium ions are incorporated in spaces between crystal layers, and they cannot be removed by further ion-exchange reactions.

Potassium ions assimilated by plants become available for re-solution when the plants mature and die, or when leaves and other parts are shed at the end of the growing season. In the natural recycling that occurs in forests and grasslands, this potassium is leached into the soil by rains during the dormant season or made available by the gradual decay of the organic material. Some leakage of potassium to ground water and runoff during these processes would be expected.

There are indications that biological factors may be important in controlling the availability of potassium for solution in river water and ground water. Records of quality of surface waters of the United States show that at times of relatively high water discharge many streams in the central part of the country carry potassium concentrations nearly as high as (or higher than) they do at times of low discharge. This may be the result of soil leaching by runoff. Similar effects were noted by Steele (1968b), in Pescadero Creek, Calif., and by Kennedy and Malcolm (1977), who made very detailed studies of discharge and solute contents of the Mattole River in northern California. Slack (1964) observed increased potassium in water of pools in the Cacapon River of West Virginia during autumn, when the water was affected by the leaching of recently fallen tree leaves.

Some closed-basin lakes in the Sand Hills region of northern Nebraska contain water having notable concentrations of potassium (Clarke, 1924a) and were considered possible domestic commercial sources of potash (Hicks, 1921) before the discovery of potassium-rich evaporite deposits in New Mexico. The reasons for potassium accumulation in these lake waters have not been fully established. Hicks (1921) hypothesized that the leaching of potassium from the ashes of grass destroyed in prairie fires was a possible source. Such an exotic mechanism is perhaps unnecessary. The concentration of potassium in at least some of the near-surface strata in the entire High Plains region of western Nebraska and Kansas is greater than the sodium concentration, as indicated by rock analyses tabulated by Hill and others (1967). Ground water in the Ogallala and some other formations in the region may also have relatively high proportions of potassium to sodium (Johnson, 1960). These waters are uniformly low in dissolved solids, as the rock formations do not contain readily soluble minerals. However, where water circulation is impaired and the water table intersects the surface, evaporation could eventually build up potassium concentrations in the water to levels observed in the Nebraska lakes. Mobilization of potassium by grasses growing on the highly permeable soil may also play a significant role.

Occurrence of Potassium in Water

In dilute natural waters in which the sum of sodium and potassium is less than 10 mg/L, it is not unusual for the potassium concentration to equal or even exceed the sodium concentration. This can be seen in analysis 9, table 14, which represents water from sandstone, and analyses 1 and 8, table 16, representing water from dolomite and quartzite, respectively. Analysis 7, table 16, for the Wisconsin River, also shows this property.

Water containing 10 to 20 mg/L of sodium and nearly equal concentrations of potassium appears to be fairly common in the Ogalala Formation in southwestern Nebraska (Johnson, 1960). However, in most other freshwater aquifers, if the sodium concentration substantially exceeds 10 mg/L the potassium concentration commonly is half or a tenth that of sodium. Concentrations of potassium more than a few tens of milligrams per liter are decidedly unusual except in water having high dissolved-solids concentration or in water from hot springs. The concentrations of potassium in the two most saline waters represented in table 17 (analyses 7 and 8) are high, but potassium:sodium molar ratios are less than 0.02.

Seawater contains 390 mg/L of potassium (table 2). Analysis 6, table 14, representing mine water, and analysis 3, table 18, representing an acidic thermal spring, both have rather high potassium to sodium ratios.

There are deficiencies in the basic information about the chemistry of potassium in water. Many of the available chemical analyses of water and some of the analyses included in this book do not include potassium determinations. Some of the old wet-chemical methods for potassium required considerable analytical skill, and the accuracy of some of the earlier published values for potassium concentrations obtained using these methods appears to be questionable. In more recent years, better methods have become available, but potassium has remained one of the more difficult ions to analyze accurately. Research aimed at attaining a better understanding of the chemical behavior of potassium in natural aqueous systems is needed.

Alkalinity and Acidity

The properties of alkalinity and acidity are important characteristics of natural and polluted waters and are almost always included in the chemical determinations. However, these properties differ in important ways from most of the other determinations reported in the analysis. Both are defined as "capacity" functions—that is, the capacity of the solution to neutralize acid or base. Both properties may be imparted by several different solute species, and both are evaluated by acid-base titration, to appropriate end points. Systems having these properties are commonly referred to by chemists as "buffered systems."

Most quantities determined in chemical analyses are "intensity" functions—that is, they are actual concentrations of a particular dissolved species at the time of analysis. The measurement of pH provides values of concentrations of H^+ and OH^- in solution. These species contribute, of course, to acidity or alkalinity, but within the pH range commonly seen in natural water they are minor constituents, at concentrations of $10^{-5.00}$ molar or lower. The principal solutes that constitute alkalinity are imparted to natural water during its passage in liquid form through the hydrologic cycle. They reflect the history of the water, as an imprint left by these encounters. The properties of alkalinity or acidity also evaluate the potential of the solution for some kinds of water-rock interaction or interaction with other material the water may contact.

Most natural waters contain substantial amounts of dissolved carbon dioxide species, which are the principal source of alkalinity and can conveniently be evaluated by acid titrations. Undissociated dissolved carbon dioxide contributes to acidity rather than to titratable alkalinity and can also be determined by titration using a basic solution.

Alkalinity

The alkalinity of a solution may be defined as the capacity for solutes it contains to react with and neutralize acid. The property of alkalinity must be determined by titration with a strong acid, and the end point of the titration is the pH at which virtually all solutes contributing to alkalinity have reacted. The end-point pH that should be used in this titration is a function of the kinds of solute species responsible for the alkalinity and their concentrations. However, the correct titration end point for a particular solution can be identified from the experimental data when the species involved are unknown. It is the point at which the rate of change of pH per added volume of titrant (dpH/dV_{acid}) is at a maximum. As dissociation constants in table 33 show, the ratio $[HCO_3]$:$[H_2CO_3]$ will be near 100:1 at pH 4.4, and the ratio $[HCO_3^-]$:$[CO_3^{2-}]$ will have a similar value at pH 8.3 at temperatures near 20°C. The best values for the end points for a particular sample depend on ionic strength and temperature. Analytical procedures may specify a pH value between 5.1 and 4.5, or that of the methyl-orange end point (about pH 4.0-4.6). Sometimes, however, an alkalinity above the phenolphthalein end point (about pH 8.3) is also specified. Thus one may find terms such as "methyl-orange alkalinity," or its equivalent, "total alkalinity," and "phenolphthalein alkalinity." Dilute solutions such as rainwater require special procedures for this determination (Stumm and Morgan, 1981, p. 226–229).

Several different solute species contribute to the alkalinity of water as defined above, and titration with acid does not specifically identify them. The property of alkalinity can be expressed in quantitative terms in various ways. The most common practice is to report it in terms of an equivalent amount of calcium carbonate. It could also be expressed in milliequivalents per liter, where meq/L is 1/50 times mg/L $CaCO_3$.

In almost all natural waters the alkalinity is produced by the dissolved carbon dioxide species, bicarbonate and carbonate, and the end points mentioned above were selected with this in mind. Analyses in this book, and most others in current geochemical literature, follow the convention of reporting titrated alkalinity in terms of the equivalent amount of bicarbonate and carbonate.

The more important noncarbonate contributors to alkalinity include hydroxide, silicate, borate, and organic ligands, especially acetate and propionate. Rarely, other species such as NH_4OH or HS^- may contribute significantly to alkalinity. If alkalinity is expressed in milliequivalents per liter, or as $CaCO_3$, the contributions from these species will affect the cation-anion balance of the analysis only if some of them are determined by other methods and are thus included in the balance computation in two places.

Except for waters having high pH (greater than about 9.50) and some others having unusual chemical composition, especially water associated with petroleum and natural gas or water having much dissolved organic carbon, the alkalinity of natural waters can be assigned entirely to dissolved bicarbonate and carbonate without serious error. The important contribution of short-chain aliphatic acid anions to titratable alkalinity in water from certain oil fields was pointed out by Willey and others (1975).

Sources of Alkalinity

The principal source of carbon dioxide species that produce alkalinity in surface or ground water is the CO_2 gas fraction of the atmosphere, or the atmospheric gases present in the soil or in the unsaturated zone lying between the surface of the land and the water table. The CO_2 content of the atmosphere is near 0.03 percent by volume. Soil-zone and unsaturated-zone air can be substantially enriched in carbon dioxide, usually owing to respiration by plants and the oxidation of organic matter.

In some natural systems there may be sources of carbon dioxide other than dissolution of atmospheric or soil-zone CO_2. Possible major local sources include biologically mediated sulfate reduction and metamorphism of carbonate rocks. In some areas, outgassing from rocks in the mantle 15 km or more below the surface has been suggested (Irwin and Barnes, 1980). Indications of source can sometimes be obtained from stable isotope ($\delta^{13}C$) data.

From studies of $\delta^{13}C$ values in dissolved HCO_3^- in 15 oil and gas fields, Carothers and Kharaka (1980) concluded that the decarboxylation of acetate and other short-chain aliphatic acids was an important CO_2 source in these waters. This process also produces methane and other hydrocarbon gases.

Carbon dioxide species are important participants in reactions tht control the pH of natural waters. Various aspects of this fact were discussed in the section on pH. Reactions among the alkalinity-related species, aqueous CO_2, $H_2CO_3(aq)$, HCO_3^-, and CO_3^{2-}, and directly pH-related species, OH^- and H^+, are relatively fast and can be evaluated with chemical equilibrium models. Rates of equilibration between solute species and gaseous CO_2 across a phase boundary are slower, and water bodies exposed to the atmosphere may not be in equilibrium with it at all times. The oceans are a major factor in maintaining atmospheric CO_2 contents. It may be of interest to note that carbonic acid, H_2CO_3, is conventionally used to represent all the dissolved undissociated carbon dioxide. In actuality, only about 0.01 percent of the dissolved carbon dioxide is present in this form. We will use the H_2CO_3 convention in discussing these systems, however, as the choice of terminology has no practical effect on final results.

Relationships among the dissolved carbon dioxide species and pH are summarized in figure 19, which is a CO_2 species distribution diagram. The lines on this graph were computed from the first and second dissociation equilibrium expressions,

$$\frac{[H_2CO_3^-]}{[H_2CO_3]}=K_1[H^+]^{-1}$$

and

$$\frac{[CO_3^{2-}]}{[HCO_3^-]}=K_2[H^+]^{-1},$$

and an assumption that the total alkalinity is the sum of the carbonate and bicarbonate activities. Values for K_1 and K_2 at various temperatures are given in table 33 (appendix). The contribution of hydroxide to alkalinity can become significant above about pH 10, where the activity of OH^- is about 1.7 mg/L.

The ratio of molar activities in the dissociation equations is a function of pH, and it is not necessary to know the total amounts of the dissolved species. However, in practice it is easier to use the percentage composition, and the calculations for the graph were made using an arbitrary total of 100 for activities of the dissolved carbon dioxide species. The graph shows the effect of temperature from 0°C to 50°C at 1 atmosphere pressure; no gas phase was considered, and activity coefficients were assumed to be unity. These and other simplifications limit the practical usefulness of the diagram to some extent, but modified forms can be prepared using equilibrium constants for other temperatures and including calculated or assumed ionic strengths. Diagrams of this type are useful for summarizing species' pH dependence and for other purposes (Butler, 1964, p. 120).

Figure 19 indicates that carbon dioxide species can contribute small amounts to alkalinity down to pH 4.0. The value of the $HCO_3^-:H_2CO_3$ ratio changes with temperature and ionic strength. Barnes (1964) showed that the correct titration end point pH may range between 4.4 and 5.4 and recommended that the titration be done at the sample collection site. Similar variation can occur in the carbonate:bicarbonate end point. The diagram shows why small concentrations of carbonate cannot be determined very accurately by titration. The pH at which carbonate constitutes 1 percent of the total dissolved carbon dioxide species, about 8.3, is where the titration end point for carbonate would generally be placed. This is a low enough pH that about 1 percent of the total now also is in the form of H_2CO_3. If a water contains much bicarbonate and only a little carbonate, the overlapping of the two steps in the vicinity of pH 8.3 may make it impossible to determine the carbonate even to the nearest milligram per liter. Because of the overlap, the change in pH as acid is added may be gradual rather than abrupt at this end point. Usually, if the carbonate concentration is

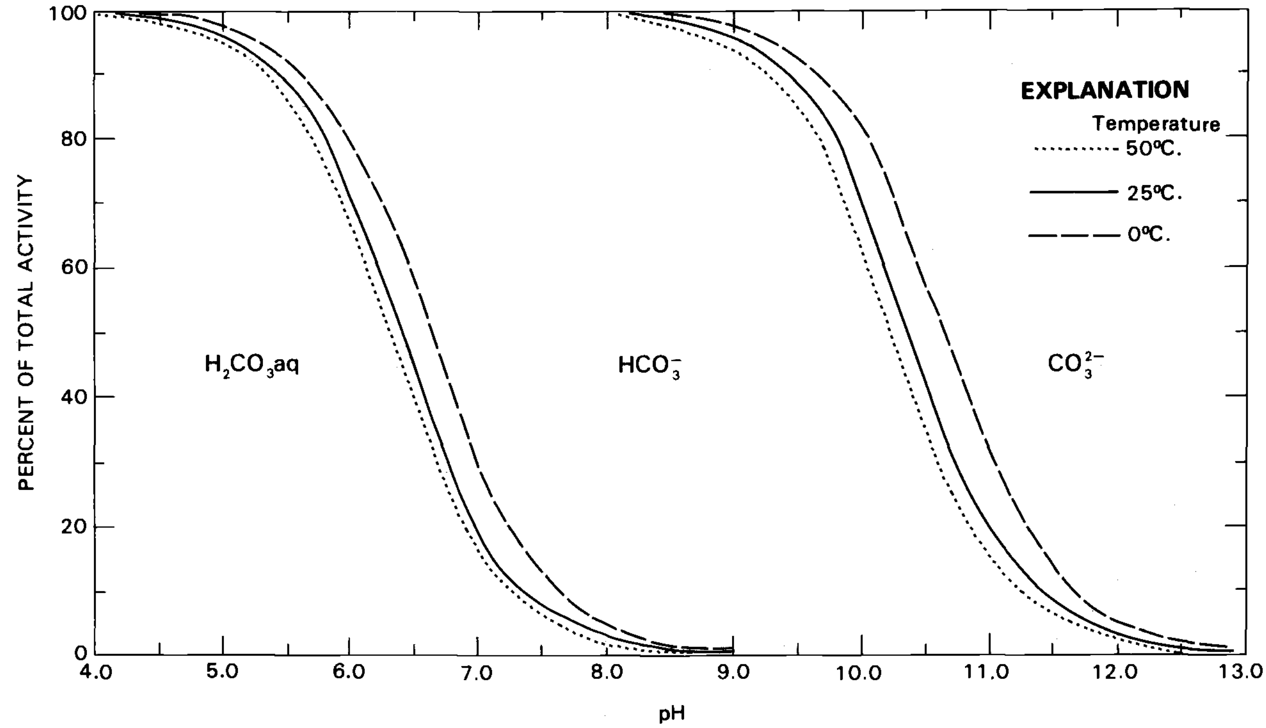


Figure 19. Percentages of dissolved carbon dioxide species activities at 1 atmosphere pressure and various temperatures as a function of pH.

small compared with the bicarbonate concentration, a value for carbonate can be calculated from the equilibrium equations more accurately than it can be measured by titration.

As noted in the earlier discussions of pH and calcium carbonate equilibria, a measurement of pH and of total alkalinity provides enough data to calculate activities of both the dissociated and undissociated carbon dioxide species. A rigorous discussion of the chemical principles involved in evaluating alkalinity and acidity was given by Kramer (1982).

The Carbon Cycle

The general circulation pattern of carbon through the various natural reservoirs of the element is termed the "carbon cycle." Estimates are available in the literature for the amounts stored in these reservoirs, and for at least some of the exchange rates. The latter are of direct concern in natural-water chemistry.

Data given by Wehmiller (1972) show that by far the largest reservoirs are the carbonate sedimentary rocks and the carbon present in other forms in rock. Together these constitute about 25×10^{15} metric tons of carbon. The amount of carbon in solution in the ocean, in contrast, is about 0.035×10^{15} tons. Quantities of carbon that are in forms more readily available for circulation are much smaller. The atmosphere contains about one-fifth as much carbon as the ocean, and the biosphere, living and dead organic matter, contains about one-tenth as much as the ocean. Amounts present in freshwater are very much smaller.

Rates of exchange of carbon dioxide between atmosphere and biosphere have been estimated by many investigators, but many factors remain poorly known. The rate of CO_2 exchange between the atmosphere and the ocean depends in part on mixing rates, and the oceans' role in controlling atmospheric CO_2 concentration has not been closely quantified.

The impact of humans on the carbon cycle has been substantial. Mainly as a result of fossil fuel consumption, the CO_2 concentration in the atmosphere increased by 12 ± 1 ppm (by volume) during the decade of the 1970's (Hileman, 1982) and had reached a level of 335 ppm in 1980. The concentration of CO_2 that was present during the 19th century is less accurately known, but most scientists agree that the concentration has increased by about 10 percent during the past century or so. A continued increase in CO_2 concentration probably can be expected. Although there is no consensus as to the ultimate CO_2 concentration that will be attained, a value double the present concentration is often predicted for the 21st century. The consequences of such an increase cannot be predicted with certainty on the basis of present knowledge, but it is important to try to achieve a better understanding of the processes involved. One of the effects that is commonly predicted is a rise in average surface temperature of the Earth owing to the so-called greenhouse effect. Carbon dioxide absorbs infrared radiation from the Earth's surface and prevents the escape of some of the Sun's energy that would otherwise be lost (Hileman, 1982).

In a summary article Lieth (1963) gave some figures on productivity, defined as the amount of carbon dioxide converted into organic matter per unit land or water area per year. In a middle-latitude forest, the estimated rate was 15 metric tons of CO_2 per hectare per year. A tropical forest was estimated to have a rate 2½ times as high. Rates for swamps and highly eutrophic lakes are reported to approach or even exceed 100 metric tons per hectare per year. For grassland and most common agricultural crops, however, the rates are much lower. Lieth (1963) estimated that the rate of biological assimilation of CO_2 balanced by an equal rate of release, over the whole land area of the Earth, averages about 3.7 tons per hectare per year. This number includes CO_2 released in respiration by plants. The uncertainty in this estimate obviously is large.

These numbers for the carbon cycle are relevant in some aspects of the aqueous chemistry of bicarbonate and carbonate ions. For example, in a eutrophic lake the rate of assimilation of dissolved CO_2 by algae and plankton on sunny days can exceed the rate at which CO_2 from the air can be brought into solution. As a result, the pH of the water near the surface may increase as the ratio of HCO_3^- to H_2CO_3 becomes greater. At night or on cloudy days the rate of respiration by aquatic vegetation exceeds the assimilation rate and the pH declines. Limnologic literature contains many examples of this type of diurnal pH fluctuation, which may cover a range of 1 pH unit or more. The H_2CO_3-HCO_3^- boundary in figure 19 shows how this effect can occur.

The sensitivity toward pH change through this effect obviously is related to the total concentration of dissolved carbon dioxide species. An extreme example cited by Livingstone (1963, p. 9) shows maximum pH values exceeding 12.0 in what must have been a poorly buffered system low in total CO_2. Biological activity in water tends to decrease greatly at the maximum or minimum pH levels included in figure 19.

Biological activity can be an aid in the precipitation of calcium carbonate. Through photosynthetic depletion of dissolved carbon dioxide, a substantial increase in the calcite saturation index can occur. Barnes (1965) described the association of photosynthetic biota with calcite deposition in a small stream in the White Mountains of eastern California.

In soils supporting vegetation, the respired CO_2 and part of the CO_2 that may be released by decay of dead plant material can be mobilized in soil moisture and ground-water recharge and can take part in chemical reactions. The biological productivity gives an indication of extreme upper limits for carbonate rock erosion rates, if it is assumed that each CO_2 molecule could react with solid CO_3 to give two HCO_3^- ions. Reactions with noncarbonate minerals would yield one HCO_3^- ion for each participating CO_2 molecule.

Available data suggest that only a small part of the potentially available CO_2 species appears in runoff. Data on average river-water composition published by Livingstone (1963) suggest that the annual bicarbonate removal rate for North America averages about 0.15 t/ha and for the entire land area of the Earth draining to the oceans about 0.19 t/ha. The estimated average rate of CO_2 circulation given earlier (3.7 t/ha/year) would give a potential maximum HCO_3^- tonnage ranging from 5.13 to 10.26 t/ha/yr, depending on how much solid carbonate rock was dissolved by the CO_2. Thus, the average global rate of conversion of carbon cycle CO_2 to bicarbonate runoff appears to be between 2 and 4 percent of the total amount available from terrestrial biological sources.

For water analyses and related information for rivers of the United States published in reports of the U.S. Geological Survey it is apparent that some rivers draining limestone areas may remove as much as 0.75 t/ha/yr of bicarbonate. This is about five times the average rate estimated by Livingstone (1963) for North America, but these drainage basins probably have higher than average biological CO_2 production rates.

Occurrence of Bicarbonate and Carbonate

Soils of humid, temperate regions may become depleted in calcium carbonate by leaching, and the pH of ground water at shallow depths may be rather low. Analysis 4, table 18, shows this effect in ground water in northeastern Texas. The soil minerals in such areas may adsorb H^+, which could be released from time to time by addition of soil amendments or by other changes in chemical environment, to reinforce the hydrogen-ion content of ground-water recharge. If it is assumed the pH of this water is controlled by carbon dioxide equilibria, it can be estimated that the water contains about 160 mg/L of H_2CO_3, and this would be the principal dissolved species in the water.

In more calcareous environments, the circulation of water rich in carbon dioxide may produce solutions that are highly supersaturated with respect to $CaCO_3$ when exposed to air. Such solutions may deposit large quantities of calcium carbonate as travertine near their points of discharge. Blue Springs, represented by analysis 3, table 11, deposit travertine in the bottom of the lower section of the Little Colorado River canyon in Arizona. The springs issue from deeply buried cavernous limestone.

Analysis 1, table 18, represents water of high pH in which about half the titrated alkalinity is assignable to silicate anions. Analyses 1 and 3, table 12, also have alkalinity attributable to silicate. The sodium carbonate brine represented by analysis 2, table 18, has been discussed in the section on sodium.

The bicarbonate concentration of natural water generally is held within a moderate range by the effects of carbonate equilibria. The concentration in rainwater commonly is below 10 mg/L and sometimes is much less than 1.0 mg/L, depending on pH. Most surface streams contain less than 200 mg/L, but in ground waters somewhat higher concentrations are not uncommon. Concentrations over 1,000 mg/L occur in some waters that are low in calcium and magnesium, especially where processes releasing carbon dioxide (such as sulfate reduction) are occurring in the ground-water reservoir. The results of the latter effect are evident in analysis 2, table 17.

Acidity

The term "acidity," as applied to water, is defined by the American Society for Testing and Materials (1964, p. 364) as "the quantitative capacity of aqueous media to react with hydroxyl ions." The definition of alkalinity, or "basicity," given by that reference is the same except for the substitution of the word "hydrogen" for "hydroxyl." As noted in the discussion of alkalinity, a statement of the end-point pH or the indicator used is required to interpret the results of an alkalinity titration. The same requirement applies to determinations of acidity. The acidity titration, however, measures a property that is somewhat more difficult to quantify. Metals such as iron that form hydroxides of low solubility react with hydroxide solutions used for acidity titration, but precipitation and hydrolysis reactions may be slow and the end point may be obscure. The usual acidity titration cannot be interpreted in terms of any single ion, and in any event, the solutes contributing to acidity are normally separately determined by other procedures. Therefore, the determined acidity expressed as hydrogen-ion concentration cannot easily be used in calculating a cation-anion balance. In contrast, the alkalinity determination can be defined for almost all waters as a determination of the carbonate- and bicarbonate-ion concentrations and used directly in the cation-anion-balance calculation.

The determination of acidity may provide an index of the severity of pollution or may indicate the probable behavior of a water in treatment processes. A water that is appreciably acidic will be highly aggressive; that is, it will have a high reaction affinity toward dissolution of many of the solids that it is likely to encounter in natural or manmade systems.

Acidity determined by titration in water analyses can be expressed in terms of milliequivalents per liter without specifying its form. It may also be reported in meq/L of H^+, which is nearly equal numerically to mg/L

H^+. In some analyses it may be reported in equivalent mg/L of $CaCO_3$ or H_2SO_4. The titration end point is usually arbitrarily specified. "Total acidity" generally represents a titration with sodium hydroxide to the phenolphthalein end point (pH 8.3). This end point includes H_2CO_3 that may be present as part of the acidity. A titration to the methyl-orange end point (near pH 4) is sometimes made, with results reported as "free mineral acidity." These forms of acidity—total acidity and free mineral acidity—may also be designated "phenolphthalein acidity" and "methyl-orange acidity," respectively.

Sources of Acidity

Acid waters may occur naturally as a result of solution of volcanic gases or gaseous emanations in geothermal areas. Similar gases in lower concentrations occur in combustion products vented to the atmosphere

Table 18. Analyses of waters with various alkalinity-acidity-pH relations

[Analyses by U.S. Geological Survey. Date under sample number is date of collection. Sources of data: 1 and 4, U.S. Geological Survey, unpublished data; 2, Lindeman (1954); 3, White, Hem, and Waring (1963, p. F46); 5, Barnes and others (1967)]

Constituent	1 Sept. 9, 1954		2 December 1935		3 Aug. 31, 1949		4 Aug. 23, 1963		5 1967	
	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
Silica (SiO_2)	75				213		14		5.2	
Aluminum (Al)					56	6.23			.4	
Iron (Fe)	.05				33	1.18	.03		.03	
Manganese (Mn)	.08				3.3	.12			.02	
Calcium (Ca)	1.3	.065	0	0	185	9.23	12	.599	48	2.395
Magnesium (Mg)	.3	.025	20	1.65	52	4.28	2.9	.239	.4	.033
Sodium (Na)	72	3.131	22,700	987.45	6.7	.29	8.3	.361	40	1.740
Potassium (K)	2.4	.061	160	4.09	24	.61	5.2	.133	1.1	.028
Hydrogen (H)					13	12.6				
Carbonate (CO_3)	38	[1]1.266	17,800	593.27	0				0	
Bicarbonate (HCO_3)	20	.328	5,090	83.43	0		10	.164	0	
Sulfate (SO_4)	32	.666	780	16.24	1,570	32.69	13	.271	1.4	.029
Chloride (Cl)	6.5	.183	10,600	299.03	3.5	.10	12	.339	32	.903
Fluoride (F)	16	.842			1.1	.06	.1	.005	.00	
Nitrate (NO_3)	0	.0			.0	.00	36	.581	.01	
Dissolved solids:										
Calculated	254		57,100				109		176	
Residue on evaporation	239									
Hardness as $CaCO_3$	4		82				42		121	
Noncarbonate	0		0				34		121	
Specific conductance (micromhos at 25°C).	328		([2])		4,570		164			
pH	9.4				1.9		5.2		11.78	
Acidity as H_2SO_4 (total)					913					

[1] Probably about 0.6 meq/L of the total alkalinity is actually present in the form $H_3SiO_4^-$.

[2] Density, 1.046 g/mL.

1. Spring NW1/4 sec. 36, T. 11 N., R. 13 E., Custer County, Idaho. Temperature, 57.2°C. Water-bearing formation, quartz monzonite.
2. Brine well MFS 1, NW1/4 sec. 26, T. 18 N., R. 107 W., Sweetwater County, Wyo. Depth, 439 ft. Water-bearing formation, evaporites.
3. Lemonade Spring, Sulfur Springs, Sandoval County, N. Mex. Temperature, 65.6°C. Water-bearing formation, volcanic rocks. Fumaroles emit H_2S and SO_2 in vicinity.
4. Spring at Winnsboro city well field, Winnsboro, Franklin County, Tex. Flow, 25 gpm; temperature, 18.3°C.
5. Spring at Red Mountain, Stanislaus County, Calif. SE1/4 sec. 15, T. 6 S., R. 5 E. Temperature, 15.6°C. Also contained hydroxide (OH), 53 mg/L, 3.099 meq/L; Sr, 0.03 mg/L; Li, 0.03 mg/L; B, 0.1 mg/L; and NH_4^+, 0.2 mg/L. From ultrabasic rock.

by humans, and their presence is generally believed to be responsible for lowering the pH of rainfall in many industrialized regions.

Another major factor in producing strongly acid water in many areas is the oxidation of sulfide minerals exposed to the air by mining operations. There are some areas in which natural sediments at or near the surface contain enough reduced minerals to lower the pH of natural runoff significantly. As noted earlier, oxidation processes, in general, produce H^+.

Weak acids and solutes derived from them can be considered as contributing to either acidity or alkalinity or to both, depending on the pH at which dissociation occurs. Thus, carbonic acid, H_2CO_3, is converted to HCO_3^- in the titration to pH 8.3 and is part of the acidity

$$H_2CO_3+OH^-=HCO_3^-+H_2O$$

but silicic acid $Si(OH)_4$ (or, as it is commonly represented, SiO_2) does not dissociate significantly below pH 8.3. Organic acids and dissociation products tend to behave somewhat like carbonic acid in this titration. Rarely, less common weak inorganic acids may contribute significantly to acidity. Hydrogen sulfide, $H_2S(aq)$, for example, is converted to HS^- near pH 7.0.

Hydrolysis reactions of metal ions, such as ferrous and ferric iron, may consume titrating base as the ions are precipitated at pH 8.3 or below. The oxidation of ferrous iron to the ferric form by dissolved oxygen also produces H^+ and contributes to acidity. These reactions tend to be slow and may interfere significantly in the titration if much dissolved metal is present. Iron and aluminum are the most significant metallic contributors to this effect in most acid waters.

Water having a pH of 3.0 or less may contain significant amounts of partially dissociated sulfuric acid in the form HSO_4^-. More rarely, undissociated HF^0 may be present at low pH.

Occurrence of Acidity in Water

Examples of waters that owe their acidity to factors cited above are represented in the tabulated analyses. Lemonade Spring, represented by analysis 3, table 18, has a pH of 1.9 and issues from a geothermal area where sulfur and both oxidized and reduced sulfur gases are abundant. A substantial part of the acidity in this solution can be assigned to the ion HSO_4^-, which is not reported separately in the analysis.

The widespread occurrence in recent years of rain and snow with pH's near or below 4.0 has been well documented, especially in Europe and North America (Likens and Bormann, 1974). In regions where surficial rock and soil have been well leached and little capacity for reaction with H^+ remains, this "acid rain" may cause lake and stream waters to attain low pH's, and their biological productivity can be severely impaired.

Oxidation of sulfide minerals causes low pH in water draining or pumped from many coal and metal mines. The volume of acid drainage produced in a major mining district can be large and may continue long after mining has ceased. Analysis 4, table 13, represents water from a stream in the bituminous coal mining region of western Pennsylvania which has a pH of 3.8. The streamflow represented by this analysis, 308,000 L/s, was probably near the maximum runoff rate for that year of record. The amount of acid required to maintain this pH in such a large volume of water is certainly substantial.

Analyses 2 and 3, table 20, are of waters from metal mines. The pH was not determined, but substantial titrated acidities are shown. Nordstrom, Jenne, and Ball (1979) observed pH's near 1.0 in water draining from abandoned copper workings in California. A general discussion of acid mine drainage was published by Barton (1978), with special emphasis on the Appalachian coal mining region of the Eastern United States. Analysis 7, table 14, represents a stream in the anthracite coal mining region of Pennsylvania. Analysis 1, table 13, represents water from a shallow well which has a pH of 4.0. The sulfate content of the water indicates that pyrite oxidation is a likely explanation of the low pH.

Acidity attributable to dissolved undissociated carbon dioxide is present in water represented by analysis 4, table 18. As already noted, the calculated H_2CO_3 in this solution is near 160 mg/L. This water has a pH of 5.2 and therefore also has some alkalinity. An even greater dissolved carbon dioxide content is indicated by the analysis for Blue Springs, analysis 3 in table 11. At a pH of 6.5, the activity of H_2CO_3 should be nearly as great as that of HCO_3^-.

As noted by Willey and others (1975), some oilfield waters owe their apparent alkalinity to dissolved acetate, propionate, and other short-chain aliphatic acid anions. Examples quoted by them for water from the Kettleman North Dome oil field of California include waters that contained alkalinities as high as 50 meq/L, entirely attributable to these organic species. The pH of these solutions generally was between 6.0 and 7.0, and the organic acids were mostly dissociated. Water containing significant amounts of organic acid anions is apparently not uncommon in association with petroleum, although this fact seems not to have been widely recognized.

Large organic molecules with active carboxyl or phenolic sites may be present in water from vegetation-rich areas. Colored waters that occur in some streams, lakes, and swamps pose substantial problems in analysis because of the difficulty in evaluating the acidity or alkalinity assignable to these materials. Some of these organic-rich waters have pH's below 4.5.

Sulfur

Because this element occurs in oxidation states ranging all the way from S^{2-} to S^{6+}, the chemical behavior of sulfur is related strongly to redox properties of aqueous systems. In the most highly oxidized form, the effective radius of the sulfur ion is only 0.20 angstrom and it forms a stable, four-coordinated structure with oxygen, the SO_4^{2-} anion. The reduced ion, S^{2-}, forms sulfides of low solubility with most metals. Because iron is common and widely distributed, the iron sulfides have a substantial influence on sulfur geochemistry. The element is essential in the life processes of plants and animals. The environmental aspects of sulfur have been reviewed by Nriagu (1978).

Redox Properties of Sulfur

Oxidation and reduction processes that involve sulfur species are inclined to be slow unless mediated by microorganisms. A simple equilibrium treatment of sulfur chemistry may therefore lead to unrealistic results. However, some major features can be defined using the Eh-pH diagram (fig. 20). The technique used in preparing this diagram is similar to that employed for the iron systems described earlier.

Figure 20 shows fields of dominance for two oxidized (HSO_4^- and SO_4^{2-}) and three reduced (H_2S(aq), HS^-, and S^{2-}) sulfur ions and a stability region for elemental sulfur. The sulfur stability field would be larger if a higher total sulfur concentration had been assumed. The total sulfur species activity used in figure 20 is 10^{-3} moles/L, the same value used earlier in preparing the Eh-pH diagram for iron. The system is closed to outside sources of sulfur.

The dashed line traversing the reduced sulfur region in figure 20 is the boundary between CH_4(aq) and dissolved H_2CO_3(aq), HCO_3^-, and CO_3^{2-}, where the latter species are present at a total constant concentration of $10^{-3.00}$ moles/L. The position of this line suggests that sulfate is not thermodynamically stable in the presence of methane. The bacteria involved in sulfate reduction can use the process as an energy source in anaerobic systems. Other organic compounds would behave similarly. Thorstenson (1970) calculated equilibrium solute concentrations for several systems of this kind.

Boulegue (1976) showed that where sulfur is abundant, and especially at a pH above about 9.0, polysulfide species may become important. In these forms the sulfur oxidation state ranges between 0 and 2–. In other work Boulegue (1978) and Boulegue and others (1982) demonstrated that redox-potential measurements could be used to determine the amounts of metastable polysulfide in these systems, and that the behavior of copper and iron in systems in which hydrogen sulfide oxidation occurred was in accord with theoretical predictions. Sulfur-rich systems may also contain other metastable solute species not shown in figure 20. Chemistries of these and other sulfur species were described by Nriagu and Hem (1978).

Sources of Sulfur

Sulfur is widely distributed in reduced form in both igneous and sedimentary rocks as metallic sulfides. Concentrations of these sulfides commonly constitute ores of economic importance. When sulfide minerals undergo weathering in contact with aerated water, the sulfur is oxidized to yield sulfate ions that go into solution in the water. Hydrogen ions are produced in considerable quantity in this oxidation process. Pyrite crystals occur in many sedimentary rocks and constitute a source of both ferrous iron and sulfate in ground water. Pyrite, particularly, is commonly associated with biogenic deposits such as coal, which were formed under strongly reducing conditions.

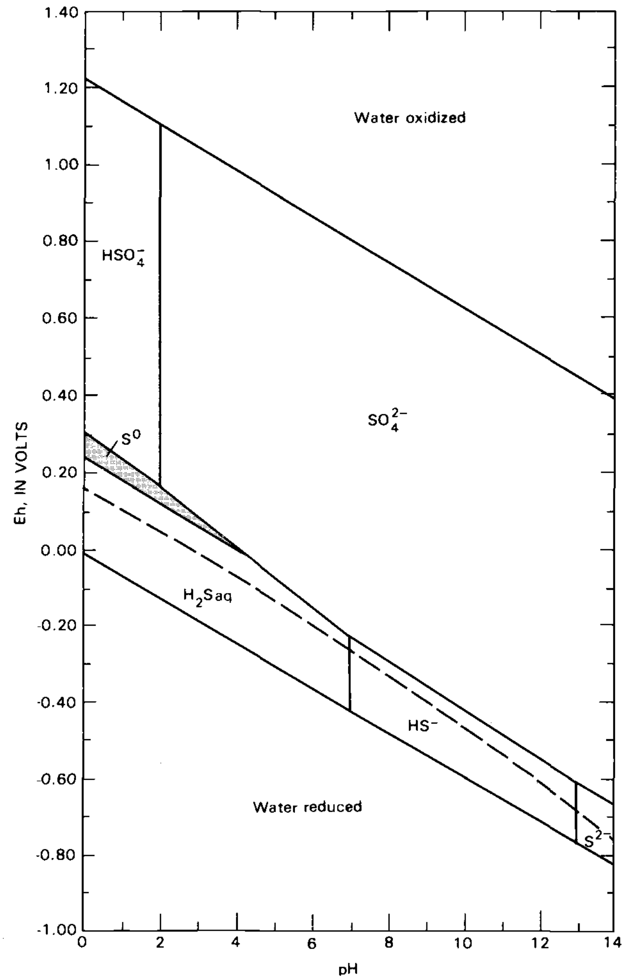


Figure 20. Fields of dominance of sulfur species at equilibrium at 25°C and 1 atmosphere pressure. Total dissolved sulfur activity 96 mg/L as SO_4^{2-}. Dashed line represents redox equilibrium between dissolved CO_2 species and methane ($CH_{4(aq)}$).

Oxidation of pyrite and other forms of sulfur also is promoted by humans: the combustion of fuels and the smelting of ores are major sources of sulfate for natural water. Organic sulfides also may undergo oxidation in natural soil processes or in organic waste treatment.

Sulfur in reduced or oxidized form may be volatilized and released in large amounts in volcanic regions and can be present in geothermal water, generally in oxidized form. The importance of bacteria in converting H_2S to SO_2 in geothermal systems was pointed out by Ehrlich and Schoen (1967).

Sulfate occurs in certain igneous-rock minerals of the feldspathoid group, but the most extensive and important occurrences are in evaporite sediments. Calcium sulfate as gypsum, $CaSO_4 \cdot 2H_2O$, or as anhydrite, which contains no water of crystallization, makes up a considerable part of many evaporite-rock sequences. Barium and strontium sulfates are less soluble than calcium sulfate but are relatively rare. Sodium sulfate is formed in some closed-basin lakes, as noted in the discussion of sodium occurrence.

The Sulfur Cycle

The geochemical cycle of sulfur is characterized by a rather rapid recycling of solute forms in water and of gases and aerosols in the atmosphere. Sulfur that occurs in reduced form in the sulfide minerals is relatively immobile. A much more soluble pool of solid sulfate species exists, incorporated in sediments for the most part or dissolved in the ocean.

A quantitative understanding of the sulfur cycle entails knowing something about the quantities available in the various reservoirs and the rates and mechanisms that govern fluxes of the element from one reservoir to another. Obtaining this understanding is important because modern industrial civilization is making a substantial contribution to the cycling rate. The ecological consequences of this effect are incompletely known.

From available data the amounts of sulfur in the various reservoirs can be approximated. Data for calculating the fluxes are much more difficult to interpret. An estimate by Kaplan (1972) indicates that about half the total sulfur in the Earth's crust is in igneous and metamorphic rocks and that about 7 percent of the total is in solution in seawater. The remainder is virtually all in sediments. The fractions in freshwater and in the atmosphere and biosphere are insignificant on this scale (less than 0.1 percent).

Quantities for some of the sulfur fluxes can be estimated with reasonable accuracy. From data given by Livingstone (1963) the rate of sulfate discharge to the ocean by world rivers can be estimated as about 120 million metric tons (as S) a year. A more recent study (Meybeck, 1979) gives a value of 116 million metric tons for this flux. The principal natural sources of dissolved sulfur in river water include rock weathering, input from volcanoes, and input from biological or biochemical processes. An additional major source is anthropogenic—attributable to human activities. Some of these sources contribute sulfur directly to runoff, and others circulate sulfur to the atmosphere, from which it may be returned to the Earth's surface by rainfall or dry fallout. The relative importance of these sources is difficult to assess closely.

Sulfate concentrations in river and lake waters before the Industrial Revolution are not known with certainty. Substantial increases in sulfate concentration have been documented for the Great Lakes (except for Lake Superior) during the past century (Beeton, 1965). Nriagu and Hem (1978, p. 255) quoted a study that indicated the sulfate concentration of the lower Rhine had increased by a factor of six over the period 1837–1971.

Substantial increases in sulfate concentrations in the Mississippi River seem to have occurred since the early years of the 20th century. Analyses for that river at New Orleans for 1905–06 (Dole, 1909, p. 77) give a mean value of 24 mg/L for SO_4. The average given for 1964–65 in table 3 is 51 mg/L—about double the 1905–6 value. Some of the difference may be related to differences in water discharge, but sulfate concentrations as low as 30 mg/L at this site have occurred only a few times during the period of recent records (1952 to date) published by the U.S. Geological Survey.

Holser and Kaplan (1966) estimated that from 54 million to 61 million tons of sulfur annually might be contributed to runoff by rock weathering and volcanism. This leaves about half of the river sulfate load to be accounted for by biochemical and anthropogenic sources. A major factor in the sulfur cycle is the combustion of coal and petroleum and other industrial processes such as smelting of sulfide ores which produce sulfur oxides that are at least partly released into the atmosphere. Data from the U.S. Bureau of Mines (1980a) show a worldwide production of 3.364×10^9 tons of coal in 1976 and 21.19×10^9 barrels of petroleum. At an average sulfur content of 1.0 percent, this production has a potential annual atmospheric sulfur loading of about 60 million metric tons. Bertine and Goldberg (1971) estimated that about 75 million tons of sulfur were emitted annually by burning coal and other fuels, and Almer and others (1978) estimated an emission rate nearly half this great for Europe alone in 1973.

It is commonly believed that anthropogenic sulfur emissions are a major factor in producing rain of low pH that has had many undesirable ecologic effects in northern Europe and in parts of the United States and Canada (Almer and others, 1978). However, the amount of sulfate brought to the land surface in rain and snow and in dry fallout is not known precisely. The amount of sulfur (probably in the form of H_2S) that may enter the atmosphere from natural biogenic sources also is poorly known but is probably much smaller. A substantial interchange of sulfur does occur between the Earth's surface and the atmosphere. Kaplan (1972) estimated that more than 40 million tons per year of sulfur was being cycled through the atmosphere.

Concentrations of sulfate in rainfall over the land surface (table 4) generally exceed 1 mg/L and are mostly considerably greater than chloride concentrations except in rain falling on or near the ocean. Concentrations of sulfate in excess of 10 mg/L in rainfall have been reported frequently.

The sulfate in rainfall has been attributed by different writers to a number of factors. Conway (1943) thought sulfate reached the atmosphere through emission of H_2S from shallow ocean water near the continental margins. The additional knowledge of rainfall composition gained since 1943, however, seems conclusively to indicate that other factors are more important. The H_2S that reaches the atmosphere is ultimately oxidized to sulfur dioxide and thence to sulfate.

The effect of air pollution, especially the contribution from the combustion of fuel, is noticeable in many places; Junge (1960) attribued about 30 percent of the sulfate in rainfall to this source. Rain falling through unpolluted inland rural air contains considerably larger concentrations of sulfate than unpolluted rain near the ocean. Junge (1960) suggested that this might be explained by assuming a more rapid rate of sulfur oxidation in the atmosphere over land, owing to catalytic effects of dust particles in cloud droplets. Terrestrial sources of sulfur oxides, however, would seem to offer a simpler explanation.

Analyses of cores from the Greenland icecap (Herron and others, 1977) suggest that sulfur in precipitation currently is being deposited at a rate two or three times as great as the rate before 1900. Sulfate concentrations in recent precipitation in Greenland are reported by these investigators to be near 0.2 mg/L. Increasing levels of sulfate concentration in water of the Great Lakes (except Lake Superior) during the past century were documented by Beeton (1965). The concentration in Lake Ontario increased from about 15 to near 30 mg/L between 1860 and 1960.

The effectiveness of runoff in removing sulfate produced by weathering or other processes is variable. In regions where the country rock was initially well supplied with sulfides, as most shales and fine-grained sediments are when freshly raised above sea level, the natural processes of weathering bring about oxidation from the surface down to or below the water table, and the sulfate produced is available for transport away from the area. The rate at which the sulfate is removed is a function of the runoff rate, however, and may lag behind the rate at which sulfate is produced. In humid regions, the upper layers of soil and rock are kept thoroughly leached, and as fast as the soluble products are formed they are removed from the area in a solution diluted because the amount of water available is large in proportion to the supply of solutes.

In semiarid and arid regions having these kinds of bedrock, on the other hand, the soils are generally not fully leached, and surplus solutes may accumulate near the surface. The amount of drainage water that leaves such an area is a small fraction of the total received in precipitation. Because of these factors, the supply of solutes is large in proportion to the water volume in which it can be carried away. As a result, surface and underground waters in semiarid regions tend to be comparatively high in dissolved solids. Sulfate is a predominant anion in many places.

From the time of the earliest explorations in the western half of the United States, aridity has been cited as a cause of the high dissolved-solids content of many of the streams, and comments about "alkali" occur in all the early reports on such explorations. (In this context alkali meant any white efflorescence; it is commonly mostly sodium sulfate.) However, attributing high solute concentrations to aridity alone is an oversimplification. Where rocks do not contain unstable minerals or other major sources of readily soluble matter, the solutes may not accumulate in soil or ground water. Except for basins having interior drainage, from which the solutes cannot escape, the water occurring in regions where the rocks are of igneous or metamorphic origin can be of very good quality even though annual precipitation may be no more than 5 in. In some desert regions of southern Arizona, the ground water has less than 300 mg/L of dissolved solids where the rock has low solubility, the water is poorly supplied with carbon dioxide species, and human activities have not had a significant impact.

Forms of Dissolved Sulfate

The dissociation of sulfuric acid is not complete in the lower pH range of natural water, and in some acid waters the bisulfate (HSO_4^-) ion constitutes a considerable part of the total sulfate concentration. As shown in figure 20, the HSO_4^- ion predominates below about pH 1.99. At a pH one unit higher (2.99), about 10 percent of the total sulfate would be in that form, and at a pH of 3.99 only 1 percent. Thus, above a pH of 3.99, the contribution of HSO_4^- is insignificant. Calculation of HSO_4^- activity can be made if pH, total sulfate, and ionic strength of the solution are known.

The usual analytical procedures for sulfate do not discriminate between the SO_4^{2-} and HSO_4^- forms, but the amount present as HSO_4^- may need to be computed to attain a satisfactory anion-cation balance in the analysis of an acid water. If no other sulfate complexes of importance are present, the two equations required are

$$[H^+][SO_4^{2-}]=[HSO_4^-]\times10^{-1.99}$$

and

$$C_{SO_4}=\frac{[SO_4^{2-}]}{\gamma_{SO_4^{2-}}}+\frac{[HSO_4^-]}{\gamma_{HSO_4^-}}.$$

Square brackets indicate molar activities, or thermodynamic concentrations, and C_{SO_4} is the analytical concentration of sulfate reported. The value of $[H^+]$ can be obtained directly from pH, and the ion-activity coefficients, the γ terms, can be calculated from the ionic strength of the solution by using the Debye-Hückel equation.

Sulfate is itself a complex ion, but it displays a strong tendency to form further complex species. The most important of these in natural-water chemistry are associations of the type $NaSO_4^-$ and $CaSO_4^0$. These generally are referred to as "ion pairs." As sulfate concentrations increase, an increasing proportion of the sulfate in solution becomes tied up in this way. Where the term "ion pair" is used in this book, it denotes a special type of interionic association involving two ions of opposite charge. In an ion pair there is at least one molecule of water from the original hydration sheaths that remains between the cation and the anion. A complex ion, accordingly, is an association of oppositely charged ions that are bound to each other directly. These are sometimes referred to as "inner-sphere" complexes (Stumm and Morgan, 1981, p. 346).

Thermodynamic data on sulfate ion pairs given by Sillen and Martell (1964, p. 232–251) show that the strongest ones are formed with divalent or trivalent cations. For calcium, the relationship

$$\frac{[CaSO_4^0]}{[Ca^{2-}][SO_4^{2-}]}=10^{2.31}$$

implies that solutions containing 10^{-2}–10^{-3} moles/L of sulfate (~1,000–100 mg/L) will contain significant amounts of the ion pair. The ionic balance of the analysis is not affected if species of this type are present, and they are not separately reported in chemical analyses. The ion pairs do influence solubility of calcium- or sulfate-containing solids such as gypsum, however, and because the ion pairs have lower charges than the free ions (actually, zero charge for the $CaSO_4^0$ form), their presence complicates calculation of dissolved solids from conductivity determinations and influences the behavior of ions in the chemical analysis of the solution.

Sulfate Solubility

Figure 21 shows the calulated solubility of gypsum in solutions of sodium chloride, based on a report by Tanji and Doneen (1966). The calculations used a solubility product for gypsum of 2.4×10^{-5} and the ion-pair stability given above and considered the effects of ionic strength from the four ionic species Na^+, Ca^{2+}, Cl^-, and SO_4^{-2}. The data apply at 25°C. Natural waters are likely to contain other ions that may influence gypsum solubility.

The concentrations of calcium and sulfate are equivalent in the simple system represented by figure 21; under this condition, the sulfate concentration would be about 1,480 mg/L in the absence of sodium and chloride, and 1,800 mg/L in the presence of 2,500 mg/L of sodium plus chloride.

The procedure for calculating gypsum equilibrium solubility has been given previously, in the discussion of solubility product, and illustrates the effects of ion pairing on such calculations. In many, if not most, natural waters that attain equilibrium with gypsum, saturation with respect to calcite also will occur. The combination of solubility equilibria for this condition leads to the expression

$$\frac{[SO_4^{2-}][H^+]}{[HCO_3^-]}=10^{-6.534},$$

applicable at 25°C and 1 atmosphere. It should be noted that the activity of sulfate required is that of the free ion and will differ from the total analytical value. The relationship has potential usefulness in representing real-world conditions, where multiphase equilibria are likely to occur.

Plummer and Back (1980) described an irreversible process that can occur in dolomitic rock, where gypsum is present. There, water moving through the formation dissolves dolomite and gypsum and precipitates calcite. This process is thermodynamically favored as long as the gypsum solubility limit is not reached.

Strontium sulfate is sparingly soluble, and barium sulfate is nearly insoluble in water. The solubility products for these solids listed by Sillen and Martell (1964, p. 236) generally are near $10^{-6.5}$ for $SrSO_4$ and $10^{-10.0}$ for $BaSO_4$. Thus, a water containing ~10 mg/L of Sr^{2+} should have no more than a few hundred milligrams per liter of sulfate, and a water containing 1 mg/L of barium should have only a few milligrams per liter of SO_4^{2-}. These are rough approximations given only to indicate the general effects of barium and strontium on sulfate solubility. More exact solubilities can be calculated from thermodynamic data in the literature. The influence of barium and strontium on the sulfate concentration of natural waters is seldom important. More commonly, low sulfate concentrations result from bacterial reduction of sulfate. The greater natural abundance of sulfate in aqueous systems tends to make sulfate concentrations a suppressing influence on barium and strontium solubility.

Occurrence of Sulfate in Water

Moderately low sulfate concentrations typical of rainfall in relatively unpolluted areas are displayed in analyses 1 and 3 in table 6. Junge (1960) determined average sulfate content in rainfall at about 60 sampling points over the United States during 1955 and 1956. The values obtained ranged from about 0.7 up to more than 10 mg/L, but over most of the country were between 1.0 and 3.0 mg/L. Local effects of air pollution cited by Pearson and Fisher (1971) gave rise to sulfate concentrations many times greater than this in an area downwind from Buffalo, N.Y. Although sulfur oxides are probably a major factor in producing rainfall having a low pH, the correlation between acidity and sulfate concentration is not always close. In some areas nitrogen oxides may be more important contributors (McColl, 1981).

Sulfate concentrations below the level expected in present-day rainfall occur in ground waters that have undergone sulfate reduction. Analysis 2, and probably analysis 1, in table 17, show this effect. Water from other wells in the Fort Union Formation and from wells in sediments of the Atlantic Coastal Plain and the Mississippi Embayment of the United States may contain less than 0.10 mg/L of sulfate, owing to this effect. Sometimes such waters contain noticeable concentrations of dissolved hydrogen sulfide, but in many places they do not.

Waters showing the effects of sulfur gases are common in some geothermal areas. Analysis 3, table 18, is an example. Oxidation of pyrite or other metal sulfides is primarily responsible for mine drainage acidity and the associated properties displayed by analyses 4 in table 13, 7 in table 14, and 2 and 3 in table 20. Effects of pyrite oxidation on ground waters is sometimes more subtle, as the iron so released may be precipitated or lost by cation exchange and the sulfate may be lost by reduction as the water moves through the aquifer. Characteristics of the water represented by analysis 1, table 13, appear likely to have resulted from sulfide oxidation.

Extensively eroded terranes of fine-grained sediments, such as the badlands of certain areas in the Western United States, provide a source of soluble matter that is constantly renewed as the insoluble detritus is mechanically removed by water running off the exposed rock surfaces and fresh surfaces containing soluble material mixed with the insoluble components are exposed for future solution. Such a source is at least partly responsible for the sulfate in the water of the Moreau River repre-

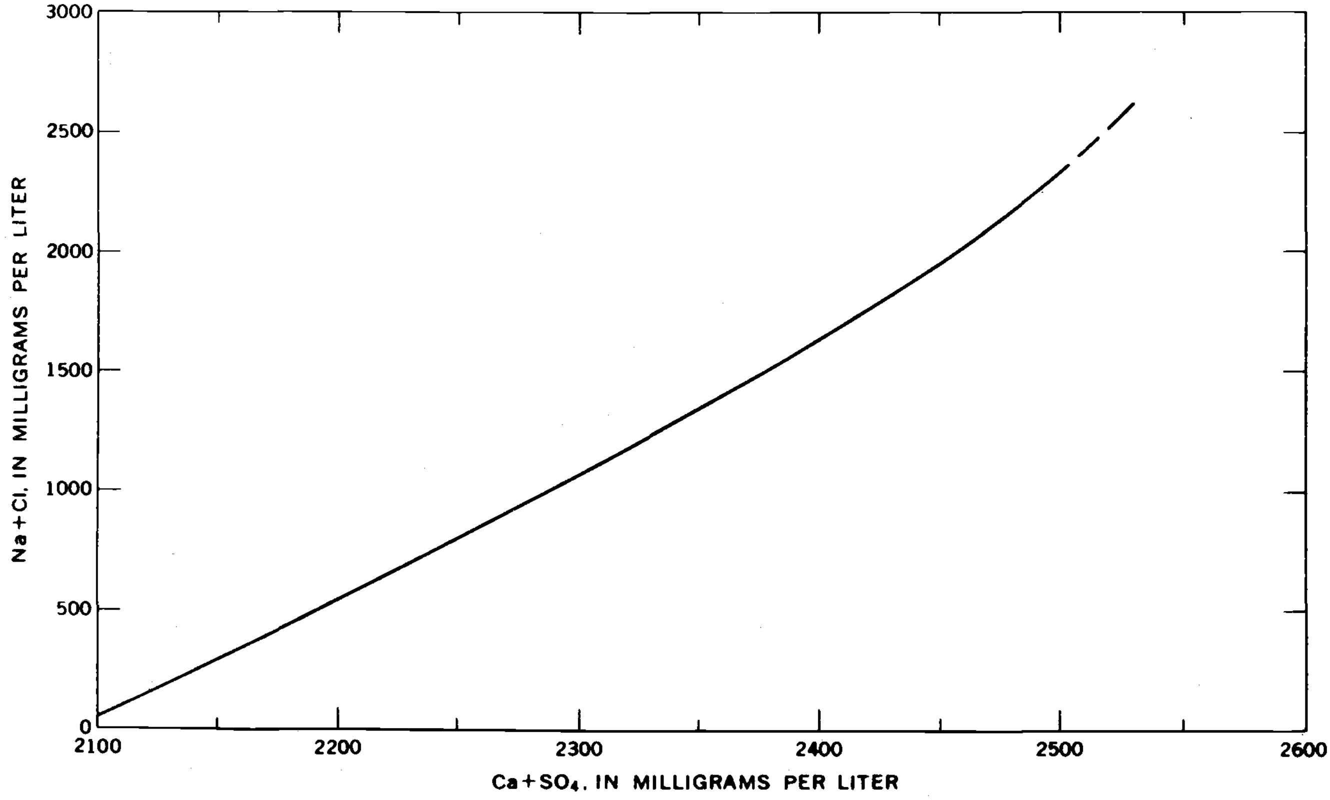


Figure 21. Solubility of gypsum in sodium chloride solutions at 25°C and 1 atmosphere pressure.

sented by analysis 4, table 17, and for water in the Rio Grande during summer flow periods (fig. 4). Salts also are brought to the surface of such rocks through capillary action and surface evaporation (Colby and others, 1953, p. 12). As noted earlier, the original source of sulfur in some of these kinds of sediments was probably pyrite or some other form of ferrous sulfide.

Analysis 3, table 18, represents a water in which a considerable part of the sulfate probably is present as HSO_4^-. The exact amounts of the various sulfate species present, however, may also depend on the concentrations of other sulfate-metal complexes.

When an area of low rainfall and accumulated solutes is reclaimed by irrigation, the increased water supply tends to leach away the solutes, and they appear in drainage water or return flow. The process is an acceleration of natural leaching and will increase the dissolved-solids concentrations and loads in the residual water of the affected area for a considerable period. Even where the soil is fairly free from soluble salts, the sulfate concentrations and chloride concentrations of the residual water draining from an irrigated area are generally much higher than they were in the original water supply, owing to water lost by evapotranspiration. Waters showing effects of irrigation return flow include analysis 6 in table 17, and to some extent analysis 8 in table 15. The latter represents water from the Pecos River, which has been affected strongly by dissolution of gypsiferous rocks exposed in the drainage basin.

As noted earlier, the water represented by analysis 3, table 15, is saturated with respect to gypsum. The observed concentrations of calcium and sulfate total 2,206 mg/L, which is near the amount predicted by figure 21 for a solution containing a moderate amount of other solutes.

Where calcium is not available in sufficient concentration to maintain a gypsum solubility control, the sulfate content of brines may become very high. The brine represented by analysis 6, table 16, is an extreme example, with a sulfate concentration of 299,000 mg/L.

Occurrence of Sulfide in Water

The rotten-egg odor of hydrogen sulfide can be detected by most people in waters that have only a few tenths of a milligram per liter of this material in solution. Natural waters subjected to unusual conditions may attain high concentrations of hydrogen sulfide. Such waters are fairly common in association with petroleum. Concentrations of H_2S in some examples cited by White and others (1963, p. F56) exceeded 100 mg/L. The water of Aqua de Ney, Calif., was reported by Feth and others (1961) to contain 400 mg/L of H_2S. This spring was mentioned previously in connection with the exceptionally high silica concentration in its water. A still higher concentration (3,190 mg/L) of H_2S was determined (U.S. Geological Survey, unpub. data) in a sample of water taken at a depth of 24 m in Soap Lake in eastern Washington, September 28, 1978. In this lake the deep water is a dense brine having a dissolved-solids concentration near 140,000 mg/L which is overlain by more dilute water. This stratification prevents air from reaching the bottom layer, and the deep water evidently has been subject to intense sulfate reduction activity, although the sulfate concentration in the bottom water still exceeded 25,000 mg/L. Systems exhibiting biochemical activity this intense appear to be rare at present. However, they may have had considerable geologic importance in the past. Sodium carbonate brines like the one represented by analysis 2, table 18, and associated deposits of trona (Na_2CO_3) are thought by some (Postgate, 1972) to have been formed through sulfate reduction, and more direct effects could include the formation of deposits of metal sulfides and native sulfur.

Chloride

The element chlorine is the most abundant of the halogens. Others in this group of elements are fluorine, bromine, and iodine. The geochemical behavior of chlorine reflects the volatility of the element and the fact that compounds of chlorine with common metallic elements, alkali metals, and alkaline earth metals are readily soluble in water.

Although chlorine can occur in various oxidation states ranging from Cl^{1-} to Cl^{7+}, the chloride form is the only one of major significance in water exposed to the atmosphere.

A significant fact illustrating the geochemical behavior of this element is that more than three-fourths of the total amount present in the Earth's outer crust, atmosphere, and hydrosphere is in solution in the ocean as Cl^- ions. Chloride forms ion pairs or complex ions with some of the cations present in natural waters, but these complexes are not strong enough to be of significance in the chemistry of freshwaters. They may be of more significance in seawater and brine.

Chlorine gas dissolves readily in water and has a somewhat stronger and more rapid oxidizing effect than does dissolved oxygen. The element has long been used as a disinfectant or biocide in purification of water supplies. Organic solutes are attacked also, as are other easily oxidized species, and the biological sterility of the solution after the reactions have been completed is readily ascertainable by testing for the presence of free chlorine. It is common practice in water-supply technology to maintain a few hundred micrograms per liter "residual" of free chlorine in solution throughout the distribution system.

Although some of the oxidized chlorine species, once formed, are fairly stable, they are not found in significant concentrations in any natural water. The presence of chlorine residuals in treated water may influence laboratory tests for some other ions, however.

Sources of Chloride

According to data in table 1, chloride is present in the various rock types in concentrations lower than any of the other major constituents of natural water. Among the chloride-bearing minerals occurring in igneous rock are the feldspathoid sodalite, $Na_8[Cl_2(AlSiO_4)_6]$, and the phosphate mineral apatite. Johns and Huang (1967) summarized the available data on chlorine content of rocks. Minerals in which chloride is an essential component are not very common, and chloride is more likely to be present as an impurity. For example, Kuroda and Sandell (1953) suggested that chloride may replace hydroxide in biotite and hornblende and may be in solid solution in glassy rocks such as obsidian. Noble, Smith, and Peck (1967) showed that most of the halogens present in glassy rocks were lost on crystallization.

On the whole, it must be concluded that igneous rocks, at least those available to the geochemist for sampling and analysis, cannot yield very high concentrations of chloride to normally circulating natural water. Considerably more important souces are associated with sedimentary rocks, particularly the evaporites. Chloride may be present in resistates as the result of inclusion of connate brine and in cementing material and is to be expected in any incompletely leached deposit laid down in the sea or in a closed drainage basin. When porous rocks are submerged by the sea at any time after their formation, they become impregnated with soluble salts, in which chloride plays a major role. Fine-grained marine shale might retain some of this chloride for very long periods. In all these rock types, the chloride is mostly present either as sodium chloride crystals or as a solution of sodium and chloride ions.

Billings and Williams (1967), from analyses of deeply buried rock, computed an average chloride content of 1,466 parts per million for shale. This contrasts with the figure of 170 parts per million given in table 1 and similar values in other compilations of this type. Billings and Williams believed that most analyses of shale represent specimens that have lost chloride by leaching as a result of near-surface exposure and that their higher value for chloride is more realistic for the bulk of this type of rock.

There is no general agreement as to the nature of the Earth's atmosphere and hydrosphere during the very early stages of their development. One hypothesis is that chloride, because of its volatility, was separated from the developing crust at an early stage and that the oceans have held a relatively constant chloride content over most of their existence. There may still be some chloride reaching the Earth's surface through out-gassing of the mantle. This would be evidenced in the composition of volcanic gases. Data presented by White and Waring (1963) show HCl to be a common constituent of fumarole gases, but it is still uncertain how important this effect may be.

The behavior of chloride in the hydrosphere can be represented by a cycle, one considerably simpler than the cycles of carbon and sulfur. Chloride is present in rain and snow owing primarily to physical processes that entrain marine solutes in air at the surface of the sea. Some of the entrained chloride also reaches the land and its freshwater by dry fallout. Leaching of evaporites and return of connate water to circulating ground water are important routes by which marine chloride is returned to the sea. Humans use salt in many ways, and the return of this material to the sea by various routes can have important local effects on natural-water composition.

Occurrence and Chemistry of Chloride in Water

The chemical behavior of chloride in natural water is tame and subdued compared with the other major ions. Chloride ions do not significantly enter into oxidation or reduction reactions, form no important solute complexes with other ions unless the chloride concentation is extremely high, do not form salts of low solubility, are not significantly adsorbed on mineral surfaces, and play few vital biochemical roles. The circulation of chloride ions in the hydrologic cycle is largely through physical processes. The lack of complications is illustrated by experiments with tracers in ground water described by Kaufman and Orlob (1956). These investigators found that chloride ions moved with the water through most soils tested with less retardation or loss than any of the other tracers tested—including tritium that had actually been incorporated into the water molecules. This conservative behavior should not be expected where movement is through compacted clay or shale, however.

Chloride is present in all natural waters, but mostly the concentrations are low. In most surface streams, chloride concentrations are lower than those of sulfate or bicarbonate. Exceptions occur where streams receive inflows of high-chloride ground water or industrial waste or are affected by oceanic tides. It would seem, from lack of complications in chemical behavior, that chloride circulation in natural water could be rather fully and simply explained, and some literature suggests that there are no difficulties in making this kind of explanation. Unfortunately, serious problems lie in wait for the investigator who makes this assumption. An excellent review of available information on the behavior of chloride in natural water has been prepared by Feth (1981).

Rainwater close to the ocean commonly contains from one to several tens of milligrams per liter of chloride, but the concentrations observed generally decrease rapidly in a landward direction; the average over the United States, as indicated by Junge and Werby (1958), is only a few tenths of a milligram per liter. Whether these figures give a completely reliable basis for computing the total landward flux of chloride during a given year could be questioned. Air masses containing sodium chloride particles may move inland and drop out salt by mechanisms other than by washing out in rainfall. Eriksson (1960) and other investigators have mentioned the effects of direct fallout and interception of airborne sodium chloride by vegetation. Most geochemists who have discussed this topic in recent years have assumed that the chloride in river water reaching the ocean comes from rainfall or other forms of precipitation and is therefore cyclic—that is, it represents recycled chloride from the ocean. Relatively few investigations, however, have included enough actual measurements of quantities of chloride brought into a drainage basin in rainfall as well as quantities carried out in streamflow to ascertain how closely this assumption can be verified. In all studies to date in the United States, where enough data have been obtained to permit reliable computations to be made, the amount of chloride brought in by rainfall seems inadequate to explain the amounts appearing in runoff.

Gambell and Fisher (1966) compared the loads of ions brought in by precipitation to the drainage basins of four North Carolina streams and the loads carried out of the basins in streamflow by the four streams. These results covered a period of 1 year. During this period the chloride outflow was more than four times the influx from precipitation. Gambel and Fisher suggested that this indicates a substantial contribution of chloride from erosion of the crytalline rock that underlies most of the area studied. The degree to which the chloride loads into and out of the basins studied varied from year to year was not known, however, and final conclusions cannot be drawn from this study alone. It seems obvious that the chloride discharge in any one year would include contributions from precipitation that occurred before that year. Fisher (1968), in reporting on a continuation of this investigation for a second year, however, found again that the chloride outflow was about four times as great as the amount brought in by rainfall. Fisher pointed out that the total sales of salt in the area studied accounted for a considerable part of the discrepancy and suggested that human activities might be a major factor in chloride circulation. An important source of chloride in water in some areas is the use of salt for deicing highways. The chloride dispersed in this way can be expected to appear eventually in ground water or runoff.

Van Denburgh and Feth (1965) used the data of Junge and Werby (1958) on composition of rainfall, along with water-quality records for 5 years for river basins covering 545,000 mi^2 in the Western United States, to determine solute loads removed from the area and the percentage of the chloride load that could be attributed to rainfall and snowfall. They concluded that most of the chloride load in all basins came from sources other than rain and snow. The percentage of the chloride load derived from precipitation ranged from 17 percent for the Rogue River basin in Oregon to 1.6 percent for the Pecos River basin in New Mexico.

Chloride that is not accounted for by rain and snowfall is most logically assignable to leaching of sediments; especially this would be true for the Pecos River, which is strongly influenced by evaporites. Pollution caused by humans is a major factor in some basins. A continuing source of uncertainty is the possible addition of airborne chloride that is not effectively captured by existing techniques for sampling fallout.

The influence of chloride from hot springs is clearly evident in the chloride loads of some streams. For example, the Gila River system in Arizona receives inflows from deep-seated springs, especially those along the Salt River in the central highlands of the State. Feth and Hem (1963) pointed out that several hundred tons per day of sodium chloride enter the stream from such springs and strongly influence the composition of the river water.

The widely published assumption that chloride loads of rivers represent recycled oceanic chloride is not entirely vitiated by individual examples such as those mentioned, but these examples certainly imply that not all oceanic chloride reaches streams by way of rainfall. The chloride of marine evaporite sediments and connate water also is of marine origin and is recycled when it goes into solution in streamflow. Even some of the chloride emitted by volcanoes may be from the ocean. Opportunity for penetration of seawater at the bases of volcanic islands might well exist. The assumption, however, that the bulk of the chloride now in the ocean was driven out of near-surface rocks in past geologic time by some natural process is certainly open to the interpretation that the process may not have entirely stopped, and careful studies might reveal places where, on a small scale, the process is still active. The quantity of new chloride gained by the ocean each year could now be so small in comparison with the total already stored there that its effect is not measurable and could be overshadowed by processes in oceanic sediments that convey oceanic chloride to rock minerals, from which their re-solution will be very long delayed.

Some investigators have ascribed the chloride accumulations of well-known hydrologically closed basins, such as the Dead Sea, to oceanic chloride transported inland in the atmosphere. Geologists have not agreed on the importance of this effect in most areas, however. Most inland closed basins have short lives in a geologic sense, and those with important salt lakes or saline accumulations contain exposures of evaporite sediments and saline springs that contribute solutes to runoff. Airborne sea salt seems to be agreed upon as the most likely source of salinity in parts of the arid interior of Australia. Anderson (1945) noted that surface waters in the arid parts of Australia bore a resemblance to diluted seawater, and most Australian literature accepts the atmospheric circulation mechanism as the most likely one. Yaalon (1961) attributed the salinity of soil in arid regions of Israel to accumulations of airborne oceanic salt.

Chloride ions may be concluded characteristically to be retained in solution through most of the processes that tend to separate out other ions. Residual brines, therefore, would be high in chloride concentration for this reason alone. Because the chloride ion is physically large compared with many of the other major ions in water, it could be expected to be held back in interstitial or pore water in clay and shale while water itself was transmitted.

The differential permeability of clay and shale may be a major factor in the behavior and composition of saline ground water associated with fine-grained sediments. For example, chloride held back while water molecules passed through a clay layer might accumulate until high concentrations were reached. The selective behavior of such a layer also influences the residual concentration of cations. The more strongly retained ions in such a solution would be the ones most strongly attracted to cation-exchange sites. Calcium is commonly the ion preferentially held. Thus, a mechanism is suggested for the origin of calcium chloride brines, an example of which is represented by analysis 4, table 15. Brines of this type have been discussed by many geochemists. Valyashko and Vlasova (1965) described calcium chloride brines occurring in the U.S.S.R. and cited mechanisms for their formation.

A less extreme instance of an altered water in which calcium and chloride are the principal components is represented by analysis 6, table 15. This water is from an irrigation and drainage well in the Salt River Valley of Arizona. The water applied in irrigating this area came originally from the Salt River and had a composition like that represented by analysis 5, table 17. The river water, with its ions concentrated by evapotranspiration, is the source of recharge for the ground water. However, ion-exchange reactions in the soil and subsoil zones, and probably other processes, have changed the relative concentrations of cations in solution.

The most common type of water in which chloride is the dominant anion is one in which sodium is the predominant cation. Waters of this type range from dilute solutions influenced by rainfall near the ocean (analysis 4, table 6) to brines near saturation with respect to sodium chloride. Analysis 8, table 17, is a brine of this type which has 189,000 mg/L of chloride and 121,000 mg/L of sodium. Seawater normally has a chloride concentration near 19,000 mg/L, but where mixing is impaired, higher or lower values may be observed.

Although a few acid waters in which chloride is the dominant anion are known, none of the analyses in this book have such characteristics. White and others (1963, p. F44) gave analyses for some waters of this type.

Accuracy of Determination

The determination of chloride is commonly assumed to be one of the simplest and most dependable procedures in water analysis. However, a commonly used procedure, the Mohr titration, which uses a standard silver nitrate solution with chromate to indicate the end point, has fundamental limitations that have not always been adequately recognized. The optimum range of concentration for this procedure is from about 20 to about 5,000 mg/L. Accuracy and precision of the Mohr procedure are inadequate for determining concentrations of chloride below about 10 mg/L unless the sample is concentrated by evaporation of a large aliquot, and this entails a risk of contamination. Methods more satisfactory for very low concentrations (mercuric nitrate titration, Skougstad and others, 1979, p. 585) or for very high concentrations (gravimetric as silver chloride; Rainwater and Thatcher, 1960, p. 143) are readily available, however.

Fluoride

The inclusion of fluoride among the major solutes in natural water is arbitrary. Concentrations of fluoride are determined as a part of most water analyses, but concentrations present in most natural waters are small, generally less than 1.0 mg/L.

Fluorine is the lightest member of the halogen group of elements. In a number of respects, its chemical behavior is different from that of other halogens, and some of these differences are evident in its behavior in natural water. Fluorine is the most electronegative of all the elements. "Electronegativity" is the relative tendency of an atom to acquire negative charge. In solutions, it forms F^- ions. Other oxidation states are not found in natural aqueous systems, although uncharged complexes may be. Fluoride ions have the same charge and nearly the same radius as hydroxide ions; thus the ions may replace each other in mineral structures. Fluoride forms strong solute complexes with many cations, and some fairly common mineral species of low solubility contain fluoride.

A significant fact noted earlier in summarizing the geochemistry of chlorine is that more than 75 percent of the total amount of that element known to be present in the outer part of the Earth is contained as chloride in solution in the ocean. Fluorine, on the other hand, is almost all tied up in rock minerals, and only a small percentage of the total is contained in seawater. Table 1 shows that the amount of fluorine in rocks exceeds the amount of chlorine. When all forms of the two elements are considered, however, chlorine is by far the more abundant.

The element fluorine is used by higher life forms in the structure of bones and teeth. The importance of fluoride in forming human teeth and the role of fluoride intake from drinking water in controlling the characteristics of tooth structure was recognized during the 1930's. Since that time the fluoride content of natural water has been studied extensively.

Sources of Fluoride in Water

Fluorite (CaF_2) is a common fluoride mineral. This mineral has a rather low solubility and occurs in both igneous and sedimentary rock. Apatite, $Ca_5(Cl,F,OH)(PO_4)_3$, commonly contains fluoride. Amphiboles, such as hornblende and some of the micas, may contain fluoride which has replaced part of the hydroxide. According to Rankama and Sahama (1950, p. 758), rocks rich in alkali metals, and also obsidian, are as a class higher in fluoride content than most other igneous rocks. Fluoride is commonly associated with volcanic or fumarolic gases, and in some areas these may be important sources of fluoride for natural water. Reference already has been made to the occurrence of fluoride species in volcanic condensates from Hawaii (Roberson and Barnes, 1978). Because of similarity of charge and radius, substitution of fluoride for hydroxide ions at mineral surfaces is an obvious possibility. These fluoride ions could be replaced by hydroxide ions in a pH-dependent fashion. Fresh volcanic ash may be rather rich in fluoride, and ash that is interbedded with other sediments could contribute later to fluoride concentrations in ground water in such areas.

Aluminum fluoride and hydroxy-fluoride species occurring in rocks include cryolite (Na_3AlF_6) and ralstonite. The latter mineral ranges in composition from $NaMgAl(F,OH)_6 \cdot H_2O$ to $Al_2(F,OH)_6 \cdot H_2O$, the end members of a solid-solution series. These minerals are rare but could become fluoride sources during weathering.

Mineral particles that contain fluoride are widespread constituents of resistate sediments. Ground water containing fluoride concentrations exceeding 1.0 mg/L has been found in many places in the United States, in a wide variety of geologic terranes.

Chemistry of Fluoride in Water

The analyst reports fluoride concentrations in terms of the free F^- ion. This form probably is the predominant one in most water, but other varieties of dissolved fluorine are certainly possible. At low pH the form HF^0 could occur. From dissociation constants given by Sillen and Martell (1964, p. 256–257) it would appear that below a pH of 3.5 the HF^0 form probably would be predominant. Data in the same reference suggest that strong fluoride complexes would be formed with aluminum, beryllium, and ferric iron and that a series of mixed fluoride-hydroxide complexes is possible with boron. In acid solutions, the fluoride could well be associated with silica in six-coordinated or four-coordinated structures such as SiF_6^{2-} or SiF_4^0; however, the conditions required for stability of these two species probably are seldom reached in natural water. Calculations by the writer (Hem, 1968b) show that aluminum fluoride complexes are likely to be found in waters whose pH is somewhat below neutrality. Although most of the dissolved aluminum in such solutions would be complexed, the concentration of fluoride commonly would exceed that of aluminum, and the proportion of the total fluoride present as complexes might not be great.

There are several potential solubility controls that can limit the dissolved-fluoride concentration in water. In solutions that contain sufficient amounts of calcium there may be an equilibrium with respect to fluorite. Solubility products in the literature for fluorite at 25°C and 1 atmosphere have a rather wide range. A laboratory study of two natural fluorites reported by Brown and Roberson (1977) gave a value of $10^{-10.58 \pm 0.17}$. Nordstrom and Jenne (1977) computed a value of $10^{-10.96}$ from a review of published data and showed that many thermal spring waters approached equilibrium with respect to CaF_2.

If the Brown and Roberson value is applied to a water having an activity of $10^{-3.00}$ moles/L of Ca^{2+}, at equilibrium

$$[F^-]^2 = 10^{-10.58} \times 10^{3.00}$$

and

$$[F^-] = 10^{-3.79} = 3.1 \text{ mg/L.}$$

The total concentration of fluoride in such a solution generally will be somewhat greater owing to ionic strength and complexing effects, but it appears evident that high fluoride concentrations are more likely to occur in water that has a low calcium concentration.

Ion-exchange effects on fluoride concentrations brought about by various minerals and soils were studied by Bower and Hatcher (1967). The amount of adsorption was shown to be large for gibbsite, kaolinite, and halloysite, and especially for a fresh $Al(OH)_3$ precipitate. Although Bower and Hatcher implied that F^- adsorption was favored at lower pH, the pH dependence of the effect was not quantitatively determined.

The solubility equilibria for cryolite given by Roberson and Hem (1969) indicate that in a solution containing 2,300 mg/L Na^+ and 2.7 mg/L Al^{3+} the concentration of fluoride would be limited to about 30 mg/L. These represent total concentrations, including all complex ions, but it seems evident that water with this much aluminum would also require a pH at least as low as 4.0. Cryolite solubility does not appear to be a common limiting factor for fluoride concentrations.

Range of Concentration

The concentration of fluoride in most natural water, which has a dissolved-solids concentration of less than 1,000 mg/L, is less than 1 mg/L. Concentrations as high as 50 mg/L have been reported, however, in solutions that might otherwise be considered potable. The highest concentration reported in the analyses in this book is 32 mg/L in the water represented by analysis 1, table 19. The sample was obtained from an abandoned flowing well near San Simon in southeastern Arizona. The pH of this water was not determined, but judging from the ratio of carbonate to bicarbonate reported it probably exceeded 9.5. Analysis 1, table 18, is for a thermal water that contains 16 mg/L of F^- and has a pH of 9.4. Two other notably high fluoride concentrations are reported in analyses 1 and 3 in table 12. Both are for thermal waters with high pH and low calcium concentrations.

Table 19. Analyses of waters containing fluoride,

[Analyses by U.S. Geological Survey. Date below sample number is date of collection. Sources of data: 1, Hem (1950, p. 87); 2, 4, 5, 8, and 9, U.S. Geological 591)]

Constituent	1 Apr. 29, 1941		2 Aug. 14, 1952		3 Sept. 16, 1947		4 Jan. 31, 1946	
	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
Silica (SiO_2)			23		27			
Aluminum (Al)								
Boron (B)								
Iron (Fe)					.28			
Manganese (Mn)								
Arsenic (As)								
Strontium (Sr)								
Calcium (Ca)	5.5	.27	92	4.59	64	3.19	36	1.80
Magnesium (Mg)	4.4	.36	38	3.12	19	1.56	18	1.48
Sodium (Na)	157	6.81	110	4.80	114	4.96	102	4.44
Potassium (K)					9.5	.24		
Lithium (Li)								
Carbonate (CO_3)	58	1.93	0		0		0	
Bicarbonate (HCO_3)	163	2.67	153	2.51	402	6.59	303	4.97
Sulfate (SO_4)	42	.87	137	2.85	74	1.54	34	.71
Chloride (Cl)	10	.28	205	5.78	30	.85	32	.90
Fluoride (F)	32	1.68	.6	.03	.1	.01	.4	.02
Nitrate (NO_3)			83	1.34	60	.97	68	1.10
Phosphate (PO_4)								
Ammonium (NH_4^+)								
Dissolved solids:								
Calculated	389		764		596			
Residue on evaporation					578		440	
Hardness as $CaCO_3$	32		386		238		164	
Noncarbonate	0		260		0		0	
Specific conductance (micromhos at 25°C).	660		1,320		875		724	
pH					7.4			
Color								

1. Flowing well NE1/4 sec. 24, T. 13 S., R. 30 E., Cochise County, Ariz. Depth, 850 ft; temperature, 18.3°C. Water-bearing formation, valley fill.
2. Irrigation well, SE1/4 sec. 25, T. 2 N., R. 2 W. Maricopa County, Ariz. Depth, 275 ft; temperature, 29.4°C. Water-bearing formation, valley fill.
3. Well, SE1/4 sec. 21, T. 12 S., R. 10 W., Lincoln County, Kans. Depth, 32 ft; temperature, 14.4°C. Water-bearing formation, alluvium.
4. Well, NW1/4 sec. 2, T. 8 S., R. 5 W., Maricopa County, Ariz. Depth, 495 ft. Water-bearing formation, valley fill.
5. Peace Creek at State Highway 17 bridge, Salfa Springs, Fla. Flow, 140 cfs.

With one notable exception the saturation indices for these waters with respect to fluorite are in the range of ±0.50, which suggests that they are near equilibrium with that mineral. Thermal waters from springs in Idaho were found by Roberson and Schoen to be near equilibrium with fluorite. Water represented by analysis 1, table 19, is supersaturated by nearly 1.0 log unit. Possibly this water represents a mixture of solutions derived from different parts of the saturated zone tapped by the well from which the sample was taken.

Some other occurrences of relatively high fluoride concentrations are reported. Bond (1946, p. 43) found 67 mg/L in a ground water from the Union of South Africa. High values were reported by White and others (1963, p. F44) in water affected by volcanism. Fluoride concentrations in river water seldom are greater than a few tenths of a milligram per liter, but there are some exceptions. The Gila River above the Safford Valley in southeastern Arizona is characteristically high in fluoride and carried an average concentration greater than 1 mg/L for the whole 5-year period of daily sampling record from 1943 to 1948. Zack (1980) ascribed 2- to 3-mg/L concentrations of fluoride in ground water from a coastal plain aquifer in South Carolina to dissolution of fluorapatite in fossil sharks' teeth in the aquifer material.

nitrogen, phosphorus, or boron in unusual amounts

Survey, unpublished data; 3, Berry (1952); 6, U.S. Geological Survey Water-Supply Paper 1198 (p. 24); 7, U.S. Geological Survey Water-Supply Paper 1945 (p.

5 May 19, 1952		6 Oct. 1950-Sept. 1951		7 Oct. 3, 1961		8 Sept. 26, 1960		9 Mar. 26, 1957	
mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
18		15		17		314		72	
						.22			
						48		660	
		.05				.52			
.00						.00			
						4.0		.02	
						.67			
42	2.10	49	2.45	24	1.20	3.6	.18	7.0	.35
19	1.56	14	1.15	11	.90	.0	.00	22	1.81
29	1.26	5.4	.23	34	1.48	660	28.69	1,100	47.85
.7	.02	3.1	.08	6.2	.16	65	1.66	33	.84
.3	.04					7.0	1.01	4.8	.69
0									
65	1.07	168	2.75	129	2.11	312	5.11	2,960	48.51
114	2.37	40	.83	32	.67	108	2.25	454	9.45
13	.37	4.3	.12	18	.51	874	24.65	690	19.46
5.0	.26	.2	.01	.4	.02	2.6	.14	1.0	.05
.3	.00	14	.23	13	.21	2.7	.04	0	.00
30	.95			14		.24			
				.1		.0		476	26.38
303				236		2,240		4,990	
318		251				2,360			
183		180		106		9.0		108	
130		42		0		0		0	
413		365		361		3,430		7,060	
7.2				7.5		8.9		7.5	
20				20					

6. Iowa River at Iowa City, Iowa. Discharge-weighted average of composites of daily samples, Oct. 1, 1950, to Sept. 30, 1951; Mean discharge, 2,543 cfs.
7. Powder River, 4.5 mi north of Baker, Baker County, Oreg.
8. Nevada Thermal well 4, Steamboat Springs, Washoe County, Nev. Depth, 746 ft; bottom temperature, 186°C. Also contained bromide (Br), 1.5 mg/L, and iodide (I), 0.6 mg/L.
9. Spring at Sulphur Bank, sec. 5, T. 13 N., R. 7 W., Lake County, Calif. Temperature, 77°C. Also contained H_2S, 3.6 mg/L; Br, 1.4 mg/L; and I, 3.6 mg/L.

Nitrogen

Aqueous geochemical behavior of nitrogen is strongly influenced by the vital importance of the element in plant and animal nutrition. It is present in the atmosphere, hydrosphere, and biosphere at oxidation states covering the full range from N^{3-} to N^{5+}. Most of the Earth's atmosphere is nitrogen gas.

Sources and Chemistry of Nitrogen

Data given by Horn and Adams (1966) and by Stevenson (1972) indicate that the crustal rocks of the Earth contain about one-fourth of the total nitrogen present in the crust, atmosphere, hydrosphere, and biosphere and that nearly three-fourths is in the atmosphere. Amounts in the hydrosphere and biosphere are much smaller. A much larger quantity may be present in the mantle at depths below 16 km. Amounts there are not known with certainty, nor are they significant in the biochemical cycle of the element.

Chemical and biological processes that transfer nitrogen to and from the lithosphere, atmosphere, hydrosphere, and biosphere represent the nitrogen cycle. A very large amount of scientific investigation of the nitrogen cycle has been done, and the related literature is voluminous. The importance of these processes in governing concentrations, form, and behavior of nitrogen in water is obvious, and they merit brief consideration.

Processes by which N_2 gas is changed in oxidation state and converted to chemical compounds containing nitrogen are referred to in general as "nitrogen fixation." A substantial energy input is required because the two atoms in molecular N_2 are very strongly bound to each other. Biological fixation is accomplished by blue-green algae and certain related organisms that have the capacity of photosynthesis, and by certain species of bacteria that use other organic material as energy sources. The latter may grow symbiotically on roots of some species of higher plants, notably legumes. Inorganic fixation occurs naturally in the atmosphere, but amounts produced in this way are small. Lightning discharges produce nitric oxides and were thought at one time to be a major factor in producing nitrate nitrogen in rainwater.

Man's influence on the nitrogen cycle includes production and use of synthetic fertilizers such as ammonia and other nitrogen compounds. Some of this fixed nitrogen escapes to the hydrosphere. According to Wlotzka (1972), production of fixed nitrogen by the fertilizer industry was about 30 percent of the amount naturally fixed in 1969–70. This industry continued expanding during the 1970's.

Nitrogen in reduced or organic forms is converted by soil bacteria into nitrite and nitrate. This process is commonly termed "nitrification." The nitrogen used by plants is largely in the oxidized form. Nitrate in anaerobic systems can be reduced by other strains of bacteria to nitrous oxide or nitrogen gas. Biochemists refer to this process as denitrification.

Nitrogen oxides are present in the atmosphere, in part, from combustion of fossil fuel. Coal and petroleum generally contain about 1 percent nitrogen. A part of this is converted to nitrogen oxides on burning and escapes to the atmosphere. Gasoline and diesel engines and most other combustion devices also emit nitrogen oxides that are synthesized by high-temperature fixation of atmospheric nitrogen.

Nitrogen oxides in the atmosphere undergo various chemical alterations that produce H^+ and finally leave the nitrogen as nitrate. These processes can lower the pH of precipitation in the same way sulfur oxides do. Ammonia nitrogen is generally present in rainfall also.

Nitrogen occurs in water as nitrite or nitrate anions (NO_2^- and NO_3^-), in cationic form as ammonium (NH_4^+), and at intermediate oxidation states as a part of organic solutes. Some other forms such as cyanide (CN^-) may occur in water affected by waste disposal. The differences in chemical properties among these species obviously is substantial. Ammonium cations are strongly adsorbed on mineral surfaces. Anionic species such as nitrate are readily transported in water and are stable over a considerable range of conditions. Above a pH of 9.20 the form of most dissolved ammonium ions will be $NH_4OH(aq)$, an uncharged species. The nitrite and organic species are unstable in aerated water and are generally considered to be indicators of pollution through disposal of sewage or organic waste. The presence of nitrate or ammonium might be indicative of such pollution also, but generally the pollution would have occurred at a site or time substantially removed from the sampling point. Ammonium and cyanide ions form rather strong soluble complexes with some metal ions, and certain types of industrial waste effluents may contain such species.

Nitrogen concentrations are determined and reported in different ways in published analyses. Most laboratories engaged in studies of organic pollution report ammonia, amino and organic nitrogen, and nitrite either separately or as a combined figure and in terms of equivalent concentration of elemental nitrogen. Other laboratories that have been more interested in the inorganic contents of water have determined and reported only nitrate, usually in terms of concentration of the nitrate ion, NO_3^-. The result of this selectivity has been that the total nitrogen content of many natural waters is not determined. Analyses in this book give nitrate or ammonium concentrations in terms of milligrams per liter of the ionic species indicated. None of the analyses report total dissolved nitrogen, and none report nitrite concentrations. Nitrite is seldom present in concentrations large enough to influence ionic balance to a noticeable degree.

The literature on sources of nitrogen has been reviewed by Feth (1966), whose paper summarizes the subject in more detail than is possible here. The relationships of nitrogen to water pollution are considered by Ingram and others (1966).

Occurrence of Nitrogen in Water

Excessive concentrations of nitrate in drinking water may cause methemoglobinemia in small children. Concentrations in excess of 10 mg/L as N, equivalent to 44 mg/L of NO_3^- evidently present this hazard (NAS-NAE, 1972, p. 73). Occurrence of nitrate and nitrite in water has been studied rather extensively because of the public health relationship.

Concentrations of nitrate that approach or exceed 44 mg/L NO_3^- are present in many rural water-supply wells. Most investigators have attributed this nitrate to drainage from nearby barnyards or septic tanks and cesspools. Farm animals produce considerable amounts of nitrogenous organic waste that tends to concentrate in places where large number of animals are confined. The occurrence of high nitrate concentrations in shallow ground water in certain areas in Kansas has been attributed to leaching from livestock corrals by rainfall (Durum, *in* Berry, 1952). The recent general trend toward confining many animals to small areas, such as to feeding pens for beef cattle, probably will bring about more occurrences of this type. In past years, most investigators, however, seem to have thought this effect had only local significance and have stated that the high nitrate concentration in ground water in extensive areas cannot be explained by barnyard pollution. Stewart and others (1967), in quantitative studies of soil moisture and shallow ground water in the South Platte valley of Colorado, found that substantial contributions of both nitrogen and phosphorus had reached the ground water beneath irrigated fields and that particularly large contributions were associated with animal feedlots.

The amount of nitrogen fertilizers used on U.S. agricultural land has increased greatly in recent decades, and this has prompted considerable concern as to possible resulting increases in nitrate in rivers and ground waters. The full impact of leached fertilizer nitrogen on ground water is slow to develop in many areas because transport of solutes through the unsaturated zone between the land surface and the water table is slow. Pratt and others (1972) estimated that nitrate moved to a vertical distance of 30 m in the unsaturated zone in a period ranging from 1 to 49 years. These estimates were for irrigated citrus orchards in southern California. In some soil profiles a substantial fraction of the transported nitrate was lost by denitrification.

Concentrations of nitrate in water moving through the unsaturated zone under irrigated fields in California (25 sites) measured by Pratt and Adriano (1973) ranged from 53 to 540 mg/L NO_3^-. When this solution reaches the water table, some dilution can generally be expected, but the potential for high nitrate concentrations in the ground water obviously is present in the area studied.

Analysis 2, table 19, is for water containing 83 mg/L of NO_3^- from a well in the Salt River Valley of Arizona, an area that is intensively irrigated and fertilized. It seems probable that the occurrence of high nitrate concentrations in many wells in that area is caused by leaching of irrigated soil. Analysis 4, table 19, is for water from a well about 12 miles south of Gila Bend, Ariz., in a desert basin that was undeveloped at the time of sampling. The high nitrate concentration of this water (68 mg/L) is much more difficult to explain. Some species of desert vegetation are legumes, and it is possible that nitrate could accumulate in successive soil zones as a basin is filled with rock debris if precipitation were not sufficient to keep the soils leached of soluble salts. The extensive nitrate deposits of northern Chile occur in an arid environment, but the manner in which the deposits were formed is not fully known.

Water from many small and medium-sized rivers in agricultural areas has nitrate concentrations exceeding 10 mg/L NO_3^- at times. Harmeson and others (1971) reported a trend toward increasing concentrations at a number of sampling sites in Illinois between 1951 and 1966. McCarty and others (1967) cited data showing increases in NO_3^- in many streams in the Western United States between the early 1900's and 1966 but did not find consistent upward trends in the lower Mississippi or in most Eastern U.S. streams for that period. Water-quality records published by the U.S. Geological Survey for the Ohio River at Lock and Dam 53 near Grand Chain, Ill., for the period 1954–79, show an increasing trend of nitrate concentration for the years between 1961 and 1974. The maximum time-weighted average NO_3^- concentration reached 7.7 mg/L in 1971. Average NO_3^- was between 3.2 and 3.9 mg/L for the years preceding 1962. From 1975 to 1979, however, the annual average was less than 5.0 mg/L. This sampling point is near the confluence of the Ohio and Mississippi Rivers.

Biesecker and Leifeste (1975) observed that nitrate concentrations in stream samples collected at "hydrologic benchmark stations" had median nitrate concentrations substantially below those observed in samples from selected major streams in the same general region. The benchmark stations were selected to represent as nearly as possible conditions not influenced by human activity.

Additional evidence of the importance of soil leaching in producing the nitrate concentrations observed in river water can be gathered from records of river-water quality for streams in the more highly productive agricultural regions. The Iowa River at Iowa City, Iowa, for example, had average concentrations of nitrate near or above 10 mg/L during most years of a 7-year period from 1944 to 1951, and highest concentrations commonly occurred during periods of above-average runoff, when much of the flow must have been drainage from the surfaces of cultivated fields. Analysis 6, table 19, represents the discharge-weighted average for the 1951 water year. Analysis 6, table 17, gives an annual average of 24 mg/L for the Gila River at Gillespie Dam, Ariz., where nitrate is attributable to irrigation return flows.

Nitrate from certain other sources has been observed and is worth mentioning. Limestone caves that are used for shelter by large numbers of bats may accumulate guano that serves as a nitrogen source to ground water in the vicinity. Analysis 5, table 16, represents water from a pool in Carlsbad Caverns, N. Mex., containing 19 mg/L of NO_3^-. Pools nearer the section of the Caverns frequented by bats have been known to contain water with more than 1,000 mg/L of NO_3^- (U.S. Geological Survey, unpub. data). An instance of industrial pollution that greatly increased the nitrate content of a stream was cited by McCarty and others (1967). The Dolores River near Cisco, Utah, had average nitrate concentrations near 25 mg/L for the entire year of 1963, owing to release of the nitrate by a uranium ore processing plant upstream.

The sources of reduced forms of nitrogen in natural water presumably are similar to the sources of nitrate, and the state of oxidation of nitrogen probably is controlled by biochemical processes. Although the reduced forms normally would be transformed to nitrate in most surface-water environments, there is considerable evidence that a significant amount of reduced nitrogen is present in many ground waters.

The pH at which the transformation of aqueous ammonia to ammonium ion is half completed is about 9.24 (Sillen and Martell, 1964, p. 150). This is above the pH of most natural water and suggests that in most environments any ammonia nitrogen in solution would have the form NH_4^+. Analysis 9, table 19, represents water from a thermal spring in California that is high in ammonium. Some oilfield brines also display this property.

As noted by Feth (1966), most of the nitrogen dissolved in rainwater appears to occur in the form of ammonium ions. The escape of nitrogen from the land surface into the atmosphere is facilitated by the volatility of NH_3.

More studies are needed to evaluate the rates at which species such as ammonium and amino or nitrite nitrogen are converted to nitrate in surface water. Organic forms may be partly removed from water by filtration. Available data suggest that the total nitrogen content of polluted streams may include a significant proportion of reduced species. Nitrogen may be associated with the organic coloring material present in some unpolluted natural water.

A study of the stability of ammonia nitrogen in water from a spring at Sulphur Bank, Calif. (analysis 9, table 19), and from another spring area where high ammonia contents were observed was made by Roberson and Whitehead (1961). Oxidation of ammonia to nitrite and nitrate occurred both in spring flow as it moved out of the discharge area and in stored water samples exposed to air.

Phosphorus

Phosphorus is a rather common element in igneous rock, as indicated by data in table 1. It is also fairly abundant in sediments, but concentrations present in solution in natural water are normally no more than a few tenths of a milligram per liter. Major features of phosphorus chemistry that govern its behavior include the low solubility of most of its inorganic compounds and its use by biota as a nutrient.

Phosphorus is in the same group in the periodic table as nitrogen. It can occur at oxidation states ranging from P^{3-} to P^{5+}, but the fully oxidized (phosphate) form is the only one of significance in most natural-water systems. The aqueous chemistry of phosphorus was reviewed by McCarty and others (1970). The most common mineral form is apatite, which is a calcium phosphate with variable amounts of OH^-, Cl^-, and F^- (hydroxy-, chloro-, or fluoro-apatite) and various impurities. Some other phosphate minerals contain aluminum or iron. Phosphorus that is released into seawater by marine biota can be precipitated as phosphorite, an impure calcium phosphate.

Marine phosphorites occurring at various localities in the United States, notably in Florida and Idaho, are mined and processed into calcium phosphate fertilizer and phosphorus in other forms for industrial uses. Phosphate mining, concentrating, and processing are sources of phosphate in river water in some areas. The use of phosphate fertilizers has a potential for increasing the phosphorus content of drainage, but this seems generally to be a rather minor factor as phosphates are not very mobile in soils or sediments. Soil erosion, however, may add considerable amounts of suspended phosphate to streams.

Phosphorus is a component of sewage, as the element is essential in metabolism, and it is always present in animal metabolic waste. During the 1950's and 1960's, the increased use of sodium phosphate as a "builder" to increase the cleaning power of household detergents tended to increase the output of phosphate by sewage-disposal plants. During the decade of the 1960's, the public became increasingly aware of the role of phosphorus as a nutrient for aquatic biota and the implication of phosphorus as a major cause of eutrophication problems in lakes. Various actions were taken by political units, detergent manufacturers, and consumers to limit the use of phosphate in detergents. However, domestic and industrial sewage effluents probably remain important sources of phosphorus in surface water.

Reduced forms of phosphorus are present in certain synthetic organic chemicals, including some that are used in insecticides. These compounds are unstable in aerated water but may persist in reducing environments long enough to be of some significance. Organic phosphate species synthesized by plants and animals constitute a significant fraction of the dissolved and particulate phosphorus in many natural waters.

Chemistry of Phosphate in Water

The orthophosphate ion (PO_4^{3-}) is the final dissociation product of phosphoric acid, H_3PO_4. The dissociation of the acid occurs in steps, and four solute species are possible: $H_3PO_4(aq)$, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}. Figure 22 is a species-distribution diagram showing the proportions of total activity of phosphorus present in each form from pH=0 to pH=14 at 25°C.

Like the similar diagram for carbon dioxide (fig. 19), the positions of the boundaries were calculated for conditions where activity coefficients are unity. Activity coefficient calculations are required to apply the graph accurately to actual water analyses, and temperatures should not depart substantially from 25.0°C.

Within these limitations the diagram can be used to give a reasonable estimate of the proportions of dissolved phosphate to assign to the three species when pH is known. In water whose pH is 7.21, the phosphate activities would be evenly divided between $H_2PO_4^-$ and HPO_4^{2-}. In the process of titrating alkalinity in such a water, all the HPO_4^{2-} will be converted to $H_2PO_4^-$ and that fraction would appear in the alkalinity value as an equivalent quantity of bicarbonate. There is no significant area of the graph in which more than two species could be present at once in concentrations worth considering, and the trivalent and neutral ions occur only outside the common pH range of natural fresh water.

The orthophosphate species are the most thermodynamically stable of the P^{5+} forms likely to occur in natural water, and the most commonly used analytical

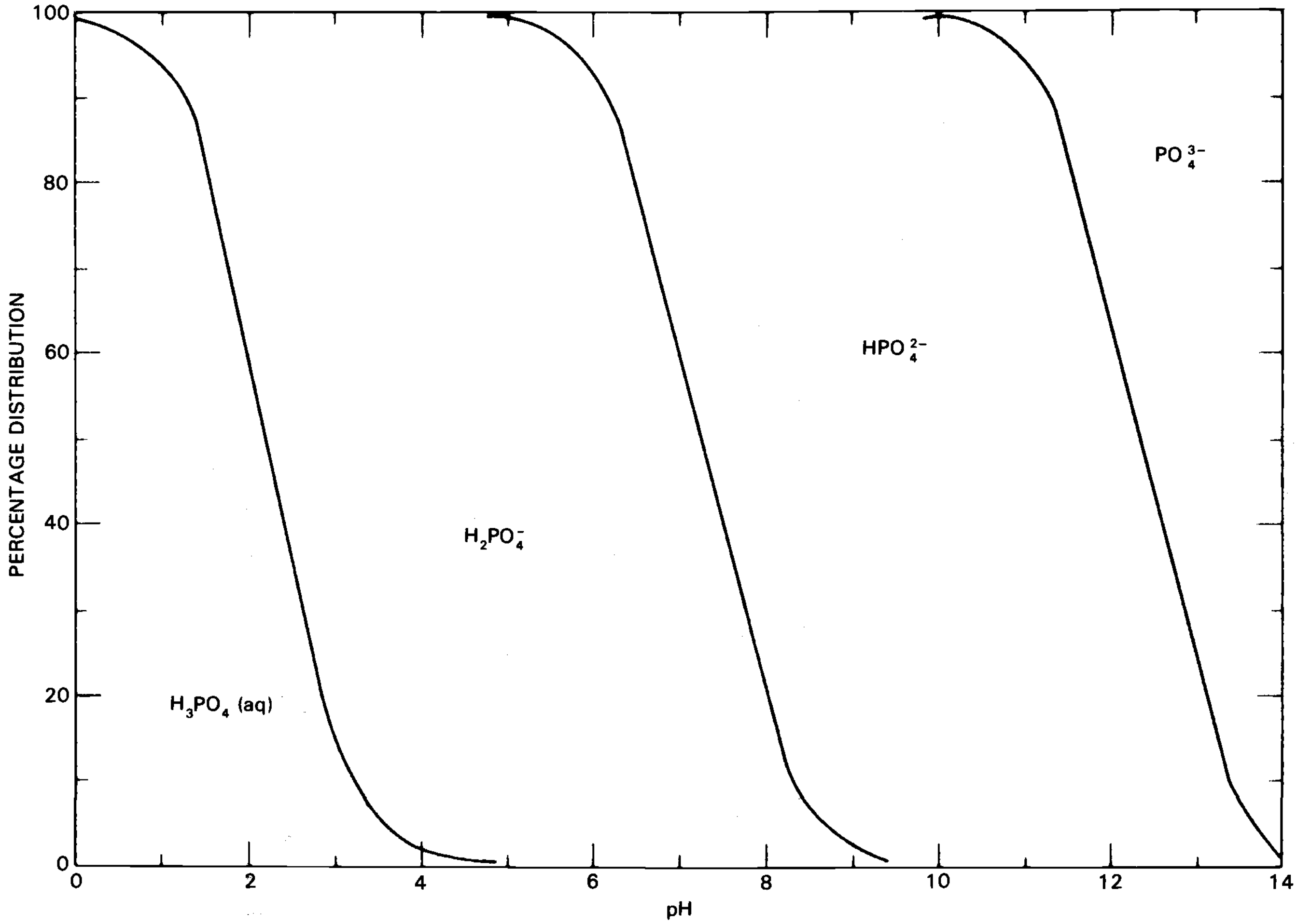


Figure 22. Percentages of dissolved phosphate species activity as a function of pH at 25°C and 1 atmosphere pressure.

procedures aim to convert all the phosphorus present to that form. Final results are reported as total phosphorus, without indicating species.

Condensed forms of phosphate, including pyrophosphate and various polyphosphate species, are strong complexing agents for some metal ions. Small amounts of sodium polyphosphate may be added to water during treatment processes with the aim of inhibiting precipitation of iron oxides or calcium carbonate. The condensed phosphates are unstable in water, however, and in time they revert to orthophosphate.

Major solubility controls of phosphorus are related to coprecipitation and adsorption, as well as to uptake by biota. Use of phosphorus by aquatic vegetation and perhaps the adsorption of phosphate ions by metal oxides, especially ferric and manganese oxy-hydroxides, can prevent concentrations greater than a few tenths or hundredths of a milligram per liter from being present in solution in most waters. Nriagu and Dell (1974) observed vivianite and other iron phosphates in sediment cores from Lake Erie and expressed the opinion that these precipitates can control the rate of release of phosphorus to lake water.

Occurrence of Phosphate in Water

Phosphate determinations are included in only a few of the analyses tabulated in this book. Analysis 2, table 13, represents water from radial collector wells on the bank of the Ohio River and the 0.1 mg/L is a characteristic level for dissolved phosphate for the river. More recent records obtained by the U.S. Geological Survey indicate that the Ohio near its mouth had a mean concentration of 0.58 mg/L of "total" phosphorus during the 1970's. This included all forms of phosphorus, some of which was particulate (Smith and others, 1982). The 30 mg/L present in water from Peace Creek in Florida (analysis 5, table 19) is not an unusual concentration for surface water in that vicinity, and it is related to the mining of phosphate ore nearby.

Analysis 7, table 19, represents water from the Powder River, a tributary of the Snake River in northeastern Oregon. The high phosphate concentration (14 mg/L PO_4) as well as the nitrate content may be related to waste disposal (Laird, 1964). The concentration of phosphate present in other samples obtained at this sampling point in 1962 was much less. Phosphate has been reported to occur in rather high concentrations in geothermal water in certain localities. Stauffer and Thompson (1978) found, however, that high concentrations reported for Yellowstone Park waters actually represented mostly arsenic, which can interfere with the orthophosphate determination.

Phosphorus associated with particulate material in a surface water is of interest in evaluating potential effects on aquatic biota, and a "total" or "total extractable" value for phosphorus is commonly reported. Such numbers have little or no relationship to solution composition. Data in the literature or stored in data banks may not distinguish clearly between dissolved and dissolved-plus-particulate status for phosphorus. Abadian and Lippmann (1976) identified the mineral brushite ($CaHPO_4 \cdot 2H_2O$) in particulate form in the Neckar River in Germany.

Meybeck (1982) estimated that naturally occurring dissolved inorganic phosphate in river water should average about 10 μg/L as P and total dissolved phosphorus about 25 μg/L. He also noted that particulate forms constituted about 95 percent of the total phosphorus carried in river water. The impact of waste disposal by humans apparently is substantial. Maybeck's estimates indicate that dissolved inorganic phosporus concentrations in some European and North American rivers ten-to a hundredfold higher than normal background are assignable to human activities. He also estimated that human contributions were about equal to the natural sources of dissolved phosphorus on a global scale.

A statistical evaluation of recent trends in "total" phosphorus concentrations at more than 300 NASQAN stream-sampling stations during the period 1972–79 was prepared by Smith and others (1982). At most stations, no significant trend could be discerned. Where there were apparent trends, more were in a downward direction than upward.

Nitrogen and Phosphorus as Nutrients

As noted in the preceding sections, nitrogen and phosphorus are essential nutrients for plant growth. Aquatic vegetation of the free-floating types, such as algae, depends on dissolved nitrogen and phosphorus compounds for its nutrient supply. Growth of these species may also be influenced by the availability of other required elements. Dense, rapidly multiplying algal growths or blooms sometimes occur in water bodies that periodically receive increased concentrations of nitrogen or phosphorus. These dense growths are generally undesirable to water users and may interfere with other forms of aquatic life, especially if the water body becomes overloaded with oxidizable debris as a result of the sudden dieback of an algal bloom.

The enrichment of a water body with nutrients is accompanied by a high rate of production of plant material in the water. Troublesome production rates of vegetation presumably occur when optimum supplies of all nutrients are present and available. Phosphorus availability is generally believed to be a critical factor in eutrophication of water bodies, as the nutrient in shortest supply will tend to be the control on production rates.

As noted earlier, the chemistry of the element favors its precipitation, and dissolved phosphorus added through disposal of waste or leaching of fertilized fields may not remain available for long periods. Thus, a decrease in phosphate inflows may decrease productivity more quickly than would be possible by altering the influx of readily available nitrogen. Examples of rapid change in lake water quality were cited by the Committee on Water Quality Criteria (NAS-NAE, 1972, p. 20).

Boron

Although it is a minor constituent of most water, a considerable amount of information exists on the concentration of boron in natural water. Many of the determinations of this element were made because boron is important in agriculture. Small amounts are essential to plant growth. Greater concentrations of boron in soil and in irrigation water, are harmful, however, and for some plants such as lemon or orange trees the toxic concentration is as low as 1 mg/L.

Sources of Boron

The most widely distributed mineral of igneous rocks in which boron is an essential constituent is tourmaline. This mineral is highly resistant to chemical attack and may appear in resistate sediments as well as in original igneous rock. The mineral is typically a constituent of granitic rocks and pegmatites. Boron, however, also may be present as an accessory constituent of biotite and the amphiboles.

Boron is a light element, and its ionic and solute species tend to be somewhat volatile. Boron may be liberated in volcanic gases in the form of orthoboric acid, H_3BO_3, or as halogenides such as BF_3. Water in volcanic areas and the water of many thermal springs, therefore, may contain considerable concentrations of boron. Ocean water has 4.6 mg/L of boron, probably mostly in the form of undissociated boric acid. This compound has an appreciable vapor pressure at ordinary surface temperatures of the Earth, and some is vaporized into the air over the ocean as a result (Gast and Thompson, 1959). Boron is a contributor to the buffer capacity of the ocean and some other natural waters.

Evaporite deposits of certain closed basins, especially in southeastern California, contain considerable amounts of boron and constitute ores from which boron salts are extracted. The common boron minerals are colemanite, $Ca_2B_6O_{11}\cdot 5H_2O$, and kernite, $Na_2B_4O_7\cdot 4H_2O$. Sodium tetraborate (borax) is widely used as a cleaning aid and, hence, boron may be present in sewage and industrial wastes. The element has numerous industrial uses.

Chemistry and Occurrence of Boron in Water

Water analyses normally report boron concentrations in terms of elemental B, without attempting to define the actual species that are present. Boron forms an extensive series of complexes and polymeric ions. Hydroxide monomeric species include boric acid, H_3BO_3, which may also be written $B(OH)_3(aq)$, and its dissociation products. However, it is a weak acid and does not dissociate readily. The preferred value for the first dissociation constant is $10^{-9.24}$ (Bassett, 1980). This means that the uncharged ion predominates up to pH 9.24 and is the most likely form in most natural water. Polymeric hydroxide species of boron are not sufficiently stable to be significant in solutions containing less than 500 mg/L boron (as B) (Bassett, 1980). A series of fluoroborate complexes occurs in which all or part of the hydroxide in $B(OH)_4^-$ is replaced by F^-. Because the more important boron solute species are anionic or uncharged, they are probably not extensively adsorbed on other mineral surfaces. Available data on stabilities of cationic complexes of borate and metal ions are sparse.

The high boron content of water from thermal springs has been noted. Schofield (1960) attributed the high boron concentration in water in the Waikato district of New Zealand to thermal effects. Koga (1957) observed high boron concentrations in the hot springs of Beppu, Japan. Because of their volatility, boron species may accompany geothermal steam and can be of environmental significance in development of geothermal power.

Analyses 8 and 9, table 19, represent water from thermal springs that are relatively high in boron. Analyses in other tables in this book suggest that boron in concentrations up to a few tenths of a milligram per liter can be expected in a good many types of surface and ground water.

Minor and Trace Constituents

The terms "minor" and "trace" used in reference to solutes in natural water cannot be precisely defined. Commonly, the terms are used for substances tht always or nearly always occur in concentrations less than 1.0 mg/L. Although it is reasonable to suppose that all the naturally occurring elements are present in most natural waters, the sensitivity of most analytical procedures is not adequate to detect those present at concentrations much below 1.0 or 0.1 μg/L.

The crustal abundances of elements listed in table 1 have a range of some eight orders of magnitude. The concentrations of solutes in water analyses given in this book cover a similar range—from hundreds of thousands of milligrams per liter to less than 0.01 mg/L (10 μg/L). However, the element with lowest reported concentration in water in many of the analyses is iron—the third most abundant in igneous rock. This emphasizes the fact that chemical properties can be more important in controlling concentrations of an element in water than its availability, suggested by average abundance in rocks. Elements that are rare to begin with, and that tend to form compounds of low aqueous solubility, may thus be expected to occur in the nanogram- or picogram-per-liter concentration ranges. For some elements, detection at these levels is possible by mass spectrometry or by radiochemical techniques; for most inorganic constituents, however, the analytical detection limit is above 0.10 μg/L when conventional instrumental and wet chemical procedures are used. Hydrogen ion activity (pH) is measurable over a range of some 14 orders of magnitude. It represents a special type of solute that is not considered in this section.

Specific organic compounds, mostly manmade, related to waste disposal, water treatment, and environmental pollution have received considerable recent attention, and techniques exist and are being developed for detecting these at extremely low levels in water.

The history of research on minor constituents of natural water is punctuated by discoveries that some supposedly insignificant trace constituent was actually or potentially of vital importance to human health, plant nutrition, or other areas of general interest. Some of these discoveries have already been cited—for example, the relation of fluoride concentration in drinking water to the occurrence of tooth decay was discovered in the 1930's, and prior to that time fluoride concentrations in water were rarely determined. Other discoveries relating to minor constituents can be expected in the future, as more is learned about their occurrence and importance. Elements that have recently received special attention include mercury, lead, and selenium.

Availability of Analytical Data

Much of the improvement in sensitivity of determinations of minor metals and metaloid elements in water has stemmed from improved spectroscopic instruments. The emission spectrograph measures the intensity of light emitted at the specific wavelengths characteristic of each element when it is heated to a very high temperature. This information is interpretable in terms of concentration in the sample when the instrument is calibrated with a standard of known composition. Many of the trace-element data for water obtained prior to about 1960 were obtained with a type of spectrograph in which the residue from a dehydrated sample was vaporized in an electric arc. This technique was not altogether convenient, nor highly accurate for water samples and was partly supplanted by flame photometry in which a portion of the water sample was atomized directly into a high-temperature gas flame and the intensity of emitted light measured at the desired wavelength. Instruments available before about 1970 were of limited value because the temperature of the flame was not high enough to give good sensitivity for more than a few elements.

During the 1960's the atomic-absorption flame photometer became the most widely used instrument for determination of dissolved metals. In this device the absorption of light energy at certain wavelengths by the sample vaporized in the gas flame was measured. This principle gives a greatly enhanced sensitivity for most elements and a much better freedom from interferences. The atomic-absorption procedure also was adaptable to samples vaporized by heating in other ways, which permits a longer optical path and further enhancement in sensitivity. In the later 1970's improved emission spectrographs lowered detection limits for some elements even more. These instruments vaporize the sample in a high temperature plasma. Optical methods of these kinds have provided much of the information on minor element composition of natural water that has become available in the past two decades.

The high sensitivity of radiochemical techniques has been mentioned. Induced radioactivity can be imparted by exposing the sample to a neutron flux. The neutron-activation technique has some unique capabilities, and the literature contains many papers on the subject. However, there are some problems in applying this procedure to the determination of trace constituents in water, and it has not been used widely for this purpose.

The principal tool used for low-level organic analysis has been the gas chromatograph, which has been refined to a very high degree by the use of a mass spectrograph as the readout device to determine the composition of the chromatographic fractions. The mass spectrograph determines relative amounts of atoms of the same mass present in the sample. This instrument, of course, can also be used in inorganic analysis.

Other methods used in trace-element analysis include wet chemical and instrumental methods, such as ultraviolet fluorescence and other forms of spectrophotometry, and various forms of polarography. Regardless of the methodology used, the accuracy of data obtained also depends critically on the care used in sample collection, pretreatment, and preservation.

Sample Collection and Treatment

If proper care is not taken to avoid sample contamination or loss of the minor constituents during manipulation, misleading results will be obtained. Any analyst familiar with minor-element analysis is aware of these problems. Water samples for minor-element analysis are usually acidified after collection to minimize loss of metals by adsorption on container walls. If the container is not carefully cleaned or the acid used is impure, contamination results.

Surface water poses special sampling problems. Minor constituents of river water were rarely determined prior to the early 1950's. The usual practice in U.S. Geological Survey sampling programs was to allow the water samples to stand undisturbed in the laboratory storage area until they appear to be clear (usually for several weeks) and then to open the samples and draw off the clear water without disturbing the sediment. If obvious deterioration had occurred, as a result of biologic activity in the sediment layer, for example, that sample was discarded. This procedure for separating solid and liquid phases was assumed to be satisfactory for major constituents, but obviously it was questionable for minor ones. Hence, when studies of such constituents in river water became of more interest, a different approach was required.

The procedure that seems most logical is to filter a sample immediately after collecting it and then to acidify it; the filter used most widely is a membrane type having pores 0.45 μm in average diameter (Skougstad and Scarboro, 1968). There is good evidence that particulate metal hydroxides, and probably aluminosilicates, exist in most surface streams in the form of particles smaller than 0.45 μm. Solid organic matter may also be present in particles in this size range. Minor metallic constituents commonly are associated with particulate matter, adsorbed at the surface of the solid or dispersed through the particle as a coprecipitate or an original component. Particles commonly have coatings or partial coatings of metal oxides and organic material of low solubility. In one way or another solid particulates may carry a substantial part of the minor element load in surface water.

Most investigators have agreed that it is important to known how much readily available solute material is present in the suspended or bed sediment of a river, and various analytical schemes aimed at providing this information have been proposed. Ideally, several different types of sample treatment might be used to ascertain how a potential solute is bound to the solid and thus to indicate how easily it might be displaced. Treatments that have been used range in rigor from exposing the solid to an ammonium chloride solution at neutral pH to release only ions adsorbed or present on exchange sites, through leaching with strongly alkaline solutions or with weak or strong acid, reducing with oxalate, hydroxylamine, or other reductants, and attacking by strong oxidizing acid or hydrogen fluoride, to finally, fusing the solid with carbonate or other fluxes (as in silicate rock analysis) to provide a complete determination of all constituents of the sediment. Organic matter can be extracted by means of organic solvents. A study of the effectiveness of 10 such techniques for extracting metals from estuarine sediments was made by Luoma and Bryan (1981). There is no agreement among workers in this field as to the meaning of results obtained by using the various extraction techniques.

The brief paper by Gibbs (1973) cited earlier described modes of transport of metals by sediment in the Amazon and Yukon rivers. Some detailed studies of a more site-specific nature are papers by Förstner and Patchineelam (1980) describing forms of six different metals on polluted sediment from the Rhine River and a paper by Eisenreich and others (1980) concerning mode of transport of six metals in the upper Mississippi River in Minnesota. Because of the complicated nature of the solute-sediment relationship, it seems safe to state that no selective extraction technique will give readily interpretible results for all sediments.

Strong acid treatment dissolves most metal oxides and other precipitates, and also attacks the matrix of clay minerals and other sedimentary mineral structures. The complete dissolution of the solid phase gives complete and straightforward analytical data, but the results have little value for predicting how sediment-associated metal ions or other trace constituents might behave in real-world situations.

A compromise approach to the problem has been used by U.S. Geological Survey laboratories whereby an unfiltered representative sample of water and sediment is brought to about 0.3 molar in HCl by adding purified acid and the mixture is held just below the boiling point for 30 minutes. After this, the mixture is filtered and the filtrate analyzed for metals. Concentrations determined in this way are termed "total recoverable" or "total" as opposed to "dissolved" concentrations determined on filtered aliquots. Comparisons among different sediments analyzed by this and some other techniques were published by Malo (1977).

An important point must be specified here. An analysis of a suspended sediment-water mixture which reports only total metal concentrations is entirely useless in studies of trace-metal geochemistry because it does not differentiate between the fractions held in dissolved form and those in adsorbed or precipitated form. If a "total" metal determination is made by a technique like the one described above, it must at least be supplemented by a determination of the dissolved fraction on a separate aliquot filtered at the time of collection. An alternative but rarely used procedure is to filter a known volume of the sample at the time of collection and make separate determinations on the filtrate and the solid particulate material held on the filter.

Unfortunately, the literature contains examples of rather detailed chemical analyses that were performed on so called "whole water" samples. This term implies that the sample was a solution-sediment mixture of unknown proportions. It is not always clearly stated that the data actually were obtained on such mixtures. Although there are certain properties of natural waters that may require evaluation in this way, most of the inorganic solutes discussed in this book require a more exacting analytical approach.

Sources of Information

Analyses for minor constituents are scattered through the literature of aqueous geochemistry. However, prior to the mid-1950's such determinations were usually included in water analyses only when the water being studied appeared to have unusual properties. Much of the earlier information, therefore, referred only to unusual conditions. Minor-element concentrations of major rivers or of ground water of low to moderate dissolved-solids concentration were for the most part unknown.

As methods of determining minor constituents were improved, the amount of information on concentrations in all kinds of natural water began to increase dramatically. An international program for determining the minor- and major-element composition of water of large rivers of the world was launched in 1957, and analyses made for that program included 24 minor elements, determined spectrographically. Reports summarizing the data included a progress report by Durum and others (1960), a tabulation of data by Durum and Haffty (1961), and some interpretation of the results by Durum and Haffty (1963). Somewhat similar information for major rivers of the U.S.S.R. was being obtained at that time, and some of those results were published by Konovalov (1959). Kroner and Kopp (1965) and Kopp and Kroner (1968) reported concentrations of 17 minor elements in major U.S. streams determined spectrographically on composite samples. These two reports are compilations of material from annual summaries of the data from a stream-sampling network operated by the U.S. Federal Water Pollution Control Adminstration and its successor, the Environmental Protection Agency.

Federal stream-sampling networks established and operated by the U.S. Geological Survey have greatly expanded the data base for minor constituents in U.S. rivers. Organized collection of minor element and related trace constituent data was begun at a group of 57 "hydrologic benchmark stations" in 1967 (Biesecker and Leifeste, 1975). These sites were chosen to represent conditions as they were prior to human-caused pollution.

A more comprehensive network planned to cover the entire United States, the National Stream Quality Accounting Network (NASQAN), was established in 1973 and was in full operation by the end of the decade, with more than 500 sampling sites. At most of these locations a suite of 10 minor elements was to be determined four or more times a year for 5 years or more (Ficke and Hawkinson, 1975). This schedule was not maintained at all sites, but a large body of data has been obtained in the NASQAN program.

A reconnaissance of concentrations of seven minor elements in streams and lakes of the United States was made in October 1970, when samples were collected at more than 720 sites (Durum and others, 1971).

In the earlier trace-element studies mentioned here, the techniques for filtration of samples in the field had not been standardized, and some of the analyses reported by Durum and others (1960) showed effects that Kennedy and others (1974) believed indicated the presence of particulates at the time the samples were acidified for preservation.

Plastic membrane filters having rather closely controlled effective pore diameters were used widely in industry and elsewhere by the mid-1960's and filters of this type having effective mean pore diameters of 0.45 μm were in common use for clarifying beverages and other uses. General adoption of this filter for separating suspended matter from water samples came about before 1970 but is difficult to date precisely. The filtration technique prescribed by Rainwater and Thatcher (1960, p. 41) used a 0.5-μm-porosity filter through which water was to be passed "by gravity." This slow procedure often required great patience, and filtrations were not commonly done in the field.

Ten years later, Brown and others (1970) prescribed a 0.45-μm membrane filter and described a mounting device in which nitrogen gas under pressure was used to speed the filtration. The size of filter pores is recognized as a compromise to attain a satisfactory filtration rate with reasonably effective removal of particulate material. The 0.45-μm-porosity membrane filter is mentioned in an ASTM analysis procedure dated 1966 (American Society for Testing and Materials, 1966).

Minor-element concentrations of river-water samples determined by U.S. Geological Survey laboratories are published in annual reports of water resources data for the various States. The U.S. Geological Survey Water Supply Paper series titled "Quality of Surface Water of the United States" was discontinued after September 30, 1970, and subsequent records have been published in an annual series, "U.S. Geological Survey Water-Data Reports," with one or more volumes for each State for each year.

The National Water Data Exchange (NAWDEX) operated by the Geological Survey maintains comprehensive computer-stored records that include many unpublished and recently collected data on quality and quantity of water in the United States. The computerized water-quality data files WATSTORE and STORET contain many values for minor constituents of water. Water-quality data including minor-element concentrations of public water supplies in 100 U.S. cities were compiled by Durfor and Becker (1964). Their report contains data for 26 minor constituents detected in these waters by means of the emission spectrograph. Silvey (1967) studied the occurrence of 17 minor elements in surface- and ground-water sources in California.

Studies undertaken to evaluate relationships between trace elements and human health have added substantially to the stock of basic data on minor elements in ground water. Some of these studies concern particular geographic areas, as the geochemical survey of the State of Missouri by Feder (1979). Emphasis in much of the more recent work related to health has been on the possibility of dietary deficiencies in humans in many areas due to underconsumption of minor elements.

Unfortunately, the accuracy of much of the information on minor elements that is stored in general purpose, computerized, water-quality data banks is not uniformly good. Anyone wishing to investigate chemical thermodynamics and solubilities of minor elements with any substantial degree of rigor undoubtedly will need to obtain much or all of the basic data by sampling and analysis techniques whose reliability are under his or her own control.

Information on occurrence of radioactive substances in water is widely scattered in the literature. A large number of analyses for the purpose of determining natural radioactivity in ground water were compiled by Scott and Barker (1962). A monitoring network for determining radioactivity in surface water in the United States has been operated since the early 1960's, and results are published in annual water-resources data reports for each State mentioned above. A general summary of data obtained in a 1961 reconnaissance of 36 U.S. rivers was published by Mallory and others (1969). Data on tritium concentration in rainfall in the United States have been collected since the early 1960's. Some of the results were summarized by Stewart and Wyerman (1970).

A substantial and rapidly growing amount of data for certain organic compounds in water also has been obtained. This field of activity has developed rapidly in recent years, and methods now available can identify and determine very small concentrations of many specific compounds.

Minor Elements in Seawater

A large amount of work has been done on minor-element occurrence and chemistry in seawater. Table 2 gives concentration values for many elements about whose occurrence in freshwater almost no information is available. Chemical oceanographers have examined mechanisms and processes that control the occurrence of these elements. As for minor elements in freshwater, there seem to be few whose occurrence can be explained by simple chemical-solubility mechanisms.

Anthropogenic Factors

Human activities have had a particularly strong influence on the occurrence of many of the minor constituents of water. Industrial societies use large quantities of many elements that would otherwise not be readily available for solution in natural water. The ways in which these elements are used may tend to disperse them in the environment. A particularly significant example is lead, which has been used in various forms since pre-Roman times but has been most extensively dispersed during the mid 20th century by the burning of leaded motor fuel (Chow and Earl, 1970). The amounts of lead used in this way have decreased since the mid-1970's but remain large.

An index of potential pollution suggested by Bowen (1966, p. 159-172) compares the annual rate of production of various industrially important elements with the estimated rate of transport of such elements to the ocean in river water. Bowen's calculations for some elements show that man's manipulations could be a far greater influence than natural circulation processes, even on a worldwide scale.

A more recent paper by Lantzy and MacKenzie (1979) estimated fluxes of elements into the Earth's atmosphere by natural processes and compared these quantities with anthropogenic releases to the atmosphere. These authors indicated that the elements copper, cadmium, zinc, arsenic, antimony, molybdenum, selenium, mercury, and lead are transported through the atmosphere in significant amounts compared with transport in water. Human activities have greatly increased the amounts of these elements that reach the atmosphere.

Occurrence of Minor Constituents

The minor constituents considered here will be taken up by groups, as follows:

Alkali metals
Alkaline earth metals
Transition metals
Other metallic elements
Nonmetallic elements
Radioactive elements and nuclides
Organic constituents

Alkali Metals

Compared with sodium and potassium, the other alkali metals—lithium, rubidium, and cesium—are rare. They form no weathering products of low solubility. A sixth alkali metal, francium, has the atomic number 87. Its nucleus is inherently unstable and the element does not exist naturally.

Lithium-bearing minerals occur in pegmatites. The most important include spodumene, $LiAl(Si_2O_6)$, amblygonite $(Li,Na)Al(PO_4)(F,OH)$, and lepidolite, a lithium mica whose composition is $K_2Li_3Al_3(OH,F)_4(AlSi_3O_{10})_2$. Lithium is recovered commercially from these minerals and also is found in evaporites and natural brines, notably at Searles Lake, Calif. Lithium ions substitute for magnesium in some minerals (Heier and Billings, 1970). The common ion-exchange minerals in soil apparently adsorb lithium less strongly than they do other common elements (Kelly, 1948, p. 61). Therefore, when lithium is brought into solution by weathering reactions, it should tend to remain in the dissolved state. Rubidium is much more abundant than lithium. Its geochemical behavior probably is somewhat like that of potassium, according to Rankama and Sahama (1950, p. 439–440), who also stated that rubidium is generally more strongly held at cation-exchange sites than potassium. This characteristic might tend to prevent the appearance of much rubidium in solution in natural water. Cesium is a rarer element and is more strongly adsorbed by clays than either rubidium or lithium.

Lithium can be toxic to plants. According to Bradford (1963), citrus trees may be damaged by irrigation water containing 60 to 100 μg/L of lithium. His studies of the occurrence of the element in California ground water and surface water suggest that concentrations in this range are not uncommon in some areas.

Lithium can be determined fairly easily down to concentrations of about 1 μg/L, and a considerable number of water analyses including lithium values exist. The determination is included in some of the analyses in tables 12, 13, 16, and 19. Concentrations of a few milligrams per liter occur in some waters having high dissolved-solids concentrations. Data on rubidium concentrations are much less plentiful.

The data for major rivers of North America (Durum and Haffty, 1963) show a slightly higher median concentration of rubidium than lithium (1.5 μg/L versus 1.1 μg/L). Durfor and Becker (1964), however, reported a median value of 2.0 μg/L for lithium and 1.05 μg/L for rubidium. On the basis of these and other available data it seems probable that lithium and rubidium occur in about the same general concentration range in dilute natural water. Fewer data are available for cesium, and the detection limit is somewhat higher than that for rubidium. Cesium was not detected in any of the analyses of Durfor and Becker. Probably it is logical to conclude that cesium is normally present in natural water at lower concentrations than lithium or rubidium. Turekian (1969) estimated an average concentration of 0.02 μg/L of cesium in river water.

Keith and others (1983) reported lithium, rubidium, and cesium concentrations for 40 water samples from wells and springs in the Upper and Lower Geyser Basins in Yellowstone National Park. The lithium concentrations in these waters are mostly from 2.0 to 5.0 mg/L. Cesium generally was present at higher concentrations than rubidium in these waters. Concentrations reported for cesium generally ranged from about 300 to 700 μg/L, but only a few rubidium concentrations exceeded 200 μg/L. These geothermal waters obviously differ from the usual river and ground waters in their concentrations of the rare alkali metals.

Alkaline-Earth Metals

Besides the common elements magnesium and calcium, this group includes the less common elements beryllium, strontium, and barium, and the unstable radioactive element radium. Supplies of radium are renewed by radioactive decay of uranium and thorium, and this element will be considered under the topic "Radioactive Elements."

All the alkaline-earth metals are divalent and do not exist at other oxidation states in natural water or crustal rock minerals.

Beryllium

Although nominally included in the alkaline-earth group, the element beryllium has little in its chemistry that is in common with the typical alkaline-earth metals. Beryllium ions are small enough to replace silicon in igneous-rock minerals. One of the more important of the minerals in which beryllium is an essential constituent is beryl, a silicate of aluminum and berryllium that is found most commonly in pegmatites. Other silicates or hydroxy-silicates may also be important sources of beryllium. The element has some important technologic applications. The amount consumed (as BeO) in the United States in 1979 was about 9,500 tons (U.S. Bureau of Mines, 1980b, p. 111).

Berylium is a rather rare element; its abundance in crustal rocks is similar to that of cesium (table 1). Beryllium sulfate and carbonate compounds appear to be too soluble to be important controls, but the oxide and hydroxides have very low solubilities. Beryllium may form anionic fluoride complexes that could increase its aqueous mobility (Hormann, 1969, p. 4H 1).

The solubility of beryllium hydroxide, according to data compiled by Baes and Mesmer (1976), reaches a minimum of about $10^{-7.0}$ moles/L of Be^{2+} near pH 8.5. This is equivalent to 0.9 μg/L. In systems in which the dissolved species Be^{2+}, $BeOH^{+}$, $Be(OH)_2(aq)$, and $Be(OH)_3^{-}$ are the only significant forms, the equilibrium solubility at pH 6.0 would be near 100 μg/L in dilute solutions and would be higher in highly mineralized waters and brines. A potential for concentrations exceeding 1.0 mg/L evidently exists in acid waters such as might occur in mine drainage or industrial-waste streams.

Beryllium dust has been implicated in occupational diseases of individuals who have breathed air containing 1 to 100 $\mu g/m^3$ of Be (McKee and Wolf, 1963). However, there seems to be no evidence that beryllium is absorbed in significant amounts when present in drinking water in concentrations substantially greater than the hydroxide solubility limits mentioned above. U.S. drinking water standards contain no limits for beryllium, but an irrigation-water limit of 100 μg/L for continuous use on all soils and of 500 μg/L for use on "neutral to alkaline fine textured soils for a 20 year period" has been suggested (NAS-NAE, 1972). Very few data on beryllium concentrations in natural freshwater exist. Durum and Haffty (1963) found no beryllium in the water they examined. Durfor and Becker (1964) reported finding only one sample with a detectable concentration (0.75 μg/L). Beryllium concentrations were below the detection limit (0.3 μg/L) in all samples analyzed by Silvey (1967). From these results and some others reported by Hormann (1969) it appears that river waters normally can be expected to carry no more than a few tenths of a microgram per liter of Be in solution. Whether prevailing low levels are brought about by adsorption and coprecipitation or are more a result of the element's scarcity is uncertain.

Strontium

The chemistry of strontium is similar to that of calcium. Strontium is a fairly common element, replacing calcium or potassium in igneous-rock minerals in minor amounts, although apparently favoring those species that are typical of granitic and syenitic rocks rather than ultrabasic rocks (Rankama and Sahama, 1950, p. 476). The carbonate (strontianite) and the sulfate (celesite) are common in sediments. According to Kulp and others (1952), the strontium-to-calcium ratio in most limestone is less than 1:1,000, although fossils in the limestone tend to be enriched in strontium.

The usual wet-chemical analysis methods for calcium also are sensitive to strontium but register any strontium present as an equivalent amount of calcium. As a result, the presence of small to moderate amounts of strontium does not cause analytical problems when these methods are used, but the strontium would go unreported unless special attention were given to determining strontium separately.

Spectrographic procedures are convenient for determining strontium in the concentration range normally seen in natural water. Radioactive isotopes of strontium, especially ^{90}Sr, are among the more common products of ^{235}U fission, and concern about the escape of such material into the environment was partly responsible for an increased interest in the levels of nonradioactive strontium that can be expected in natural water. A substantial amount of data has been obtained on this subject since 1950.

From free-energy data given by Parker and others (1971) for strontianite, the value of *K* in the relationship

$$\frac{[HCO_3^-][Sr^{2+}]}{[H^+]}=K$$

is calculated to be $10^{1.08}$. Thus, at a pH of 8.0, when the activity of bicarbonate is 10^{-3} molal (about 61 mg/L), strontium activity would be about 10 mg/L. The activity of calcium at equilibrium with calcite under these conditions would be about 32 mg/L. Thus, strontianite is considerably less soluble than calcite.

Solubility products for strontium sulfate quoted by Sillen and Martell (1964, p. 236) are mostly near $10^{-6.50}$ at 25°C. This value is nearly two log units more negative than the corresponding solubility product for gypsum and suggests that celestite solubility might be an important control on strontium concentrations. For example, a sulfate activity of 100 mg/L would permit only 28 mg/L for strontium activity. The analytical value for sulfate concentration in such a solution could be considerably greater owing to the effects of ionic strength and formation of sulfate ion-pairs.

The strontium concentration in most natural waters does not approach the solubility limit of either strontianite or celestite. Ground water in certain areas of the United States, however, contains rather large concentrations of strontium. Analysis 1, table 20, represents water from a well in Waukesha, Wis. The strontium in this water (52 mg/L) is one of the highest reported for potable water, although some brines (analysis 4, footnote table 15) contain much more. Nichols and McNall (1957) found that many wells in the eastern part of Wisconsin yielded water containing more than 1 mg/L of strontium. Rather high concentrations also are known to be present in ground water at certain localities in Ohio (Feulner and Hubble, 1960) and in Florida (Odum, 1951). Feulner and Hubble attributed the strontium in the Ohio waters to dissolution of celestite, which they stated occurred in evaporite rock formations of Silurian age in that region.

Calculations taking into account the effects of ionic strength and ion pairing show that the water from the Waukesha well (analysis 1, table 20) is close to saturation with respect to strontium sulfate. Equilibrium with respect to strontianite cannot be verified closely because the pH reported in the analysis is a laboratory value. The data given in the analysis indicated moderate supersaturation. Durum and Haffty (1963) found the median value for strontium in major North American rivers to be 0.06 mg/L. Skougstad and Horr (1963) published an intensive study of the occurrence of strontium in natural water, both surface and underground, in the United States. Their paper contains more than 200 analyses. The median content of strontium for the larger U.S. public water supplies is 0.11 mg/L.

Barium

Table 1 indicates that barium is somewhat more abundant in igneous rocks than strontium, but that the carbonate rocks contain considerably less barium than

Table 20. Analyses of waters containing unusual concentrations of metals and other constituents

[Analyses by U.S. Geological Survey. Date below sample number is date of collection. Sources of data: 1, Lohr and Love (1954a); 2 and 3, Emmons (1917); 4, Goldblatt and others (1963); 5, U.S. Geological Survey, unpublished data]

Constituent	1 May 2, 1952		2 About 1911		3 About 1917		4 Mar. 29, 1963.		5 Dec. 8, 1934	
	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
Silica (SiO_2)	8.7		56		23		10		21	
Aluminum (Al)			433	48.65	12	1.32				
Iron (Fe)	.37		2,178	77.99	143		.10		.04	
Manganese (Mn)	.05		.2	.01						
Copper (Cu)			312	9.82						
Zinc (Zn)			200	6.12	345	10.55				
Calcium (Ca)	60	2.99	68	3.39	260	12.97	5.0	0.25	452	22.55
Magnesium (Mg)	31	2.55	41	3.37	49	4.03	1.0	.08	555	45.64
Strontium (Sr)	52	1.19								
Sodium (Na)	12	.52	23	1.00	13	.57	136	5.92	1,900	82.65
Potassium (K)	4.0	.10	20	.51	3.2	.08	1.2	.03	17	.43
Carbonate (CO_3)							10	.33		
Bicarbonate (HCO_3)	285	4.67	0		0		296	4.85	476	7.80
Sulfate (SO_4)	111	2.31	6,600	138.65	1,650	34.35	10	.21	6,330	131.79
Chloride (Cl)	12	.34	.1	.00	3.7	.10	34	.96	288	8.12
Fluoride (F)	.5	.03					.8	.04		
Nitrate (NO_3)	.8	.01					.7	.01	244	3.94
Orthophosphate (PO_4)							2.6			
Arsenic (As)							1.3			
Selenium (Se)									1.98	
Boron (B)							4.6			
Dissolved solids:										
Calculated	440		9,990		2,500		363		10,900	
Residue on evaporation										
Hardness as $CaCO_3$	337						17		3,410	
Noncarbonate	104						0			
Specific conductance (micromhos at 25°C).	658						594			
pH	7.6						8.5			
Acidity as H_2SO_4			130		252					

1. North Street well, Waukesha, Wis. Public supply. Depth, 1,907 ft. Water-bearing formation, sandstone of Cambrian and Ordovician age.
2. Water from first level below black copper workings, Burra-Burra mine, Ducktown, Tenn.
3. Water from Victor mine, Joplin district, Mo.
4. Well, NW1/4 SW1/4 sec. 11, T. 19 S., R. 3 W., Lane County, Oreg. Depth, 150 ft. Water-bearing formation, Fisher Formation.
5. New drainage ditch about 4 mi north of Mack, Mesa County, Colo.

strontium. Barium ions have a larger radius than strontium ions and probably cannot as readily enter the crystal lattices of the carbonates of lighter alkaline-earth metals. The solubility of barium carbonate is about the same as that of calcite (Sillen and Martell, 1964, p. 138).

A likely control over the concentration of barium in natural water is the solubility of barite ($BaSO_4$), which is a fairly common mineral. The solubility product for this material is near 10^{-10} (Sillen and Martell, 1964, p. 236), and at sulfate molar activities near 10^{-4} (~10 mg/L) or 10^{-3} (~100 mg/L) the corresponding equilibrium molar activities of Ba^{2+} would be 10^{-6} or 10^{-7} (~ 0.14 mg/L) or (~ 0.014 mg/L), respectively.

Another factor that seems likely to influence the concentration of barium in natural water is adsorption by metal oxides or hydroxides. Barium seems commonly to be found in deep-sea manganese nodules and also in freshwater manganese oxide deposits (Ljunggren, 1955).

The median concentration of barium in public water supplies reported by Durfor and Becker (1964, p. 78) was 0.043 mg/L, a value which is in the range that would be expected were the concentration under the control of barium sulfate solubility equilibria. Durum and Haffty (1963) reported a median concentration of 0.045 mg/L in the larger rivers of North America.

If the concentration of barium in natural water actually tends to be controlled by $BaSO_4$ solubility, one would expect a narrower range between the upper and lower extreme values than for elements whose concentration is more likely to be a function of the availability of the element in the environment. Strontium is more likely to fit in the latter category. It is interesting to note that in the two compilations cited, barium did indeed have a narrower range of concentration from maximum to minimum than did the other elements whose concentrations were determined.

High barium concentrations in certain oilfield waters and other brines were reported by White and others (1963, p. F-32). In every instance the sulfate concentration reported was very low. It seems likely that sulfate concentrations in these waters are kept low by sulfate reduction, enabling the barium to increase, at least up to the point where the carbonate solubility limit is reached.

Barium is considered an undesirable impurity in drinking water; the U.S. mandatory limit is 1.0 mg/L (U.S. Environmental Protection Agency, 1976b).

Transition Metals

For the purpose of this discussion, the transition metals are considered to be elements 21-28, 39-46, and 72-78 in the periodic table. Two of these have been considered previously (Mn and Fe), and only 6 of the remaining 21 merit individual mention here. The others are rare, and their occurrence in natural water has not been studied extensively.

The transition metals commonly have more than one oxidation state that is thermodynamically stable in the presence of water. Several of these elements are likely to be present in water in the form of anionic complexes at neutral pH.

Titanium

Although titanium is an abundant element in crustal rocks, as indicated by data in table 1, it is present in natural water in very low concentrations. The Ti^{4+} oxides include rutile and anatase, and the element is commonly associated with iron in ilmenite, $FeTiO_3$, and related minerals with other Fe-Ti proportions. These minerals are highly resistant to weathering and tend to persist in detrital sediments.

Chemical thermodynamic data in the literature on titanium are inadequate for any theoretical evaluation of the aqueous behavior of the element beyond a few very broad generalizations. Latimer (1952, p. 267) estimated stabilities for aqueous ionic species, and a few data are given by Sillen and Martell (1964, p. 45) and by Baes and Mesmer (1976, p. 153–157). It seems likely that the principal aqueous form at low pH is TiO^{2+} or $Ti(OH)_2^{2+}$. The solubility of the less stable forms of the oxide TiO_2 may exceed 1 mg/L below pH 2.0. Above about pH 3 an uncharged species, $Ti(OH)_4(aq)$, has been proposed. Its solubility between pH 4 and pH 8, according to data accepted by Baes and Mesmer, is about 150 μg/L. As noted earlier, some uncharged hydroxide solute species of this type that have been postulated for other metals are more probably polymeric macro ions, which evolve into solid crystals in the colloidal size range; some of the titanium in natural waters may be in such a form. The solubility of titanium may be influenced by complexes with fluoride or with organic ligands, but no data are available to evalute this possibility or to predict the behavior of the element above pH 8.

The Ti^{3+} ion may occur in strongly acid-reducing systems. It seems likely, however, that only the Ti^{4+} species should be expected in natural water.

Data compilations and estimates of titanium concentrations in natural water indicate that the element is generally present in amounts ranging up to a few tens of micrograms per liter. Turekian (1969, p. 314) estimated an average of 3 μg/L for river water.

The median concentration of titanium in major rivers of North America reported by Durum and Haffty (1963) was 8.6 μg/L. The median for public water supplies of the United States was reported by Durfor and Becker (1964, p. 78) to be "less than 1.5 μg/L." Somewhat similar concentrations were reported by Silvey (1967). The higher values reported may represent colloidal material not separated from the samples by the filtration techniques used. A few of the acidic waters and brines for which analyses were given by White and others (1963) contain more than 1,000 μg/L of titanium.

Metallic titanium is used extensively in the aircraft and space industries. The oxide is used principally as a white pigment in paint. This constitutes a potentially important anthropogenic source of titanium, but, as noted earlier, the element is common and widely distributed in rocks and soil and would be readily available without man's intervention.

Vanadium

The aqueous geochemistry of vanadium is rather complicated. Three oxidation states—V^{3+}, V^{4+}, and V^{5+}—

can be stable in aqueous systems, but the dominant forms probably are V^{5+} anionic complexes with oxygen and hydroxide. A pH-Eh diagram published by Hem (1977a) shows regions of stability for 10 solute species in a system containing 5 μg/L total V and the equivalent of approximately 10 mg/L SO_4^{2-} and 61 mg/L HCO_3^- . Because of vanadium's tendency to form anions, a fairly high solubility is possible in oxidizing alkaline environments. However, the solubility of metal vanadates may control V activity in many such systems. Hem (1977a) suggested a mechanism involving ferrous vanadate that could control vanadium contents of ground water. The association of vanadium with uranium in certain types of ore deposits has been studied rather extensively. Some of the important papers are mentioned by Garrels and Christ (1964, p. 388–393). The less highly oxidized forms of vanadium have relatively low solubilities unless the pH is below about 4.0. Evidently both uranium and vanadium have low solubilities in reducing environments.

Vanadium is involved in biochemical processes in living matter. It is present in plants and in coal and petroleum. Combustion of the later substances may release the element to the environment.

Vanadium concentrations as high as 70 μg/L were found in the study of U.S. public water supplies by Durfor and Becker (1964). However, the mediam value was reported as <4.3 μg/L. Turekian (1969, p. 314) estimated an average concentration of 0.9 μg/L for river water. Data on vanadium concentrations quoted by Landergren (1974) suggest that acid water from thermal springs may contain a few hundred micrograms per liter, but ordinary ground and surface waters rarely carry more than 10 μg/L.

Chromium

The crustal abundance of chromium is similar to that of vanadium. In rock minerals the predominant oxidation state is Cr^{3+}. Dissolved chromium, however, may be present as trivalent cations or as anions in which the oxidation state is Cr^{6+}. In alkaline oxidizing solutions, chromate anions may be stable, but some cations form chromates having low solubilities. The ultramafic igneous rocks are higher in chromium content than other rock species. Chromite, $FeCr_2O_4$, may be concentrated in lateritic residue overlying ultramafic rocks. Chromite is highly resistant to weathering.

pH-Eh diagrams showing the aqueous chemical properties of chromium were published by Hem (1977a). Six different ionic forms of chromium were considered to be stable in aqueous systems. The reduced forms are Cr^{3+}, $CrOH^{2+}$, $Cr(OH)_2^+$, and $Cr(OH)_4^-$. Anionic forms, present under oxidizing conditions, include dichromate $Cr_2O_7^{2-}$ and chromate CrO_4^{2-}. The dissolved forms that predominate in reduced systems between pH 5 and pH 9 probably are $CrOH^{2+}$ and $Cr(OH)_2^+$.

A metastable hydroxide, $Cr(OH)_3$, has a minimum solubility near 5 μg/L at about pH 9.0. This material might precipitate from solutions containing chromate anions if there are reducing agents present. The solubility of chromic oxide is much below 1 μg/L between pH 5 and 13, but it is unlikely to be directly precipitated from solution. Chromate anions are the dominant species in solutions that are alkaline and mildly oxidizing.

Industrial applications of chromium may produce waste solutions containing chromate anions. A maximum permissible concentration of 50 μg/L total chromium has been included in U.S. mandatory drinking water standards (U.S. Environmental Protection Agency, 1976b). Incidents of ground-water pollution with chromate have occurred in many localities. In such an occurrence on Long Island, N.Y., the chromate moved from an industrial waste disposal pit to contaminate shallow ground water and persisted in concentrations as great as 14 mg/L of Cr^{6+} more than 3,000 ft away from the original source some 20 years after the contamination was first noticed in water nearer the source (Perlmutter and others, 1963).

Concentrations of chromium in natural waters that have not been affected by waste disposal are commonly less than 10 μg/L. The median value for the public water supplies studied by Durfor and Becker (1964, p. 78) was 0.43 μg/L as Cr, and for North American rivers reported by Durum and Haffty (1963), 5.8 μg/L. In more recent studies Kharkar and others (1968) estimated an average for river waters of 1.4 μg/L. Durum and others (1971) found concentrations exceeding 5 μg/L in only 11 of the more than 720 samples from surface waters in the United States. Many of the samples in this study probably were affected by waste disposal. In view of the more recent data the Durum and Haffty (1963) median appears to be high.

A study by Robertson (1975) indicated that chromium in hexavalent form was present in uncontaminated ground water in Paradise Valley north of Phoenix, Ariz. Concentrations between 100 and 200 μg/L were observed in samples from some wells. These high concentrations were attributed to dissolution and oxidation of Cr^{3+} species by oxygen-bearing recharge from the rock debris that constitutes the valley fill in this region. The pH of waters highest in chromium was near 9.0.

Cobalt

The concentration of cobalt in the Earth's outer crust is similar to that of lithium. The element is essential in plant and animal nutrition, especially for ruminant animals. Cobalt ions can substitute for part of the iron in ferromagnesian rock minerals and, like iron, cobalt may occur in 2+ or 3+ oxidation states. Coprecipitation or adsorption of cobalt by oxides of manganese and iron appears to be an important factor in controlling the amounts that can occur in solution in natural water (Hem, 1978, 1980). When associated with manganese oxide, as in marine manganese nodules, the oxidation state of cobalt seems generally to be Co^{3+} (Murray and Dillard, 1979). A theoretical model coupling cobalt oxidation to a two-step manganese oxidation process appears to be capable of predicting cobalt activity in aqueous systems in which manganese oxide precipitates are being formed (Hem, 1978). With the possible exception of certain complex ions, aqueous species of Co^{3+} are not thermodynamically stable under Eh and pH conditions that commonly occur in natural water.

The coupled oxidation model mentioned above predicts that cobalt activities will generally be from one-tenth to one-hundredth of the activity of dissolved manganese in oxygenated water between pH 5 and pH 8.

The solubility of $Co(OH)_2$ is similar to that of ferrous hydroxide and probably is not a control of cobalt concentrations in natural water. The solubility of $CoCO_3$, however, is much lower than that of siderite and could be an important factor. Thus, at a pH of 8.0 in the presence of about 100 mg/L of HCO_3^-, the solubility of cobalt would be 10^{-7} molal, or about 6 μg/L. Cobalt forms many complex ions that tend to increase the solubility above calculated values that do not allow for complexing effects.

Although cobalt carbonate has a very low solubility, data in table 1 and a compilation by Graf (1962) show that cobalt is only a minor constituent of carbonate rocks.

Concentrations of cobalt commonly present in river water are vanishingly small, and most compilations of data include many notations of "below detection limit" for this element. Recent determinations of cobalt in seawater (Turekian, 1978) cluster near 0.03 μg/L. This is only about one-tenth as great as the concentration given in table 2 of this volume. An estimated mean value for river water of 0.2 μg/L was given by Kharkar and others (1968). The reconnaissance of U.S. surface waters in 1970 mentioned earlier (Durum and others, 1971) found that nearly two-thirds of the 720 samples contained less than 1.0 μg/L (which was the detection limit for the analytical procedure used). Maliuga (1950) reported average concentrations of 20 μg/L in water of mineralized zones in the southern Ural area of the U.S.S.R.

It appears reasonable to conclude that uncontaminated natural water should generally contain no more than a few micrograms per liter of cobalt.

Nickel

Data in table 1 show that nickel is somewhat more abundant in crustal rocks than cobalt. The two elements have some similar characteristics in that they may substitute for iron in ferromagnesian igneous-rock minerals and tend to be coprecipitated with iron oxides and especially with manganese oxides.

According to Latimer (1952, p. 198), the aqueous chemistry of nickel is primarily concerned with the Ni^{2+} oxidation state. Solid species for which thermodynamic data are given by Latimer include the Ni^{4+} oxide NiO_2 and the hydroxide species $Ni(OH)_3$.

Nickel is an important industrial metal. It is used extensively in stainless steel and other corrosion-resistant alloys, and to a lesser extent for other purposes. The commercially exploited ores include ferrous sulfides in which nickel is substituted for part of the iron, and nickel-bearing laterites deveoped on ultramafic bedrock terranes. Because of its extensive cultural use, nickel can be contributed to the environment in significant amounts by waste disposal.

Some nickel compounds for which thermodynamic data are available are more soluble than corresponding cobalt species. Coupled oxidation processes for coprecipitating nickel with manganese may also be less effective. However, the mechanisms of oxide coprecipitation have not been studied closely. The rather high nickel content of marine manganese nodules present in parts of the Pacific Ocean suggests that coprecipitation processes may be involved in controlling amounts of the element present in seawater, as coprecipitation with manganese oxides probably can maintain lower dissolved nickel activities than any of the simple direct-precipitation mechanisms for Ni^{2+}. Stability data accepted by Baes and Mesmer (1976, p. 252) indicate that $Ni(OH)_2$ is more stable than the corresponding cobalt species and might maintain activities of Ni^{2+} below 100 μg/L at pH 8.5. This is not likely to be a significant factor in controlling nickel solubility in natural water.

From data that are available, the median concentration of nickel in river water and probably in most other natural freshwater is somewhat greater than the median concentration of cobalt. Besides the possible influences of chemical processes, this greater concentration may be a reflection of the greater natural abundance of nickel and the much greater amount of nickel potentially available from anthropogenic sources.

The median concentration of nickel in North American rivers reported by Durum and Haffty (1963) was 10 μg/L. A value of "less than 2.7 μg/L" for the larger public water supplies was reported by Durfor and Becker (1964). Both studies gave higher values for nickel than for cobalt. Other compilations show a similar tendency for nickel to occur in water in higher concentrations that cobalt. Maliuga (1950) found an average of 40 μg/L of nickel in water from a mineralized region in the southern Urals of the U.S.S.R., a value twice as great as the average concentration for cobalt. Turekian (1969) estimated a median Ni concentration in river water of 0.3 μg/L, slightly greater than his estimate of 0.2 μg/L for cobalt.

Molybdenum

As data in table 1 indicate, molybdenum is a rather rare element. It occurs in oxidation states ranging from Mo^{3+} to Mo^{6+}, but the most common solid and aqueous species contain Mo^{4+} or Mo^{6+}. The sulfide molybdenite, MoS_2, is an ore mineral in several districts in the Rocky Mountain region of the United States. In oxidizing conditions the predominant oxidation state is Mo^{6+}, which forms molybdate anions in water. Below pH 2 the predominant molybdate species is the undissociated form, $H_2MoO_4(aq)$. The $HMoO_4^-$ ion is predominant between about pH 2 and pH 5. Above pH 5 the dominant species is the molybdate ion MoO_4^{2-}. Many of the metallic elements have molybdates of low solubility. Molybdate ions tend to polymerize, and an extensive series of such species can exist, depending on pH and total molybdenum concentration. The polymers do not occur as major components, however, unless the total molybdenum in solution exceeds about 10 mg/L (Baes and Mesmer, 1976, p. 261; Mannheim, 1978).

These generalizations about molybdenum geochemistry indicate that it has a relatively high geochemical mobility—a tendency to enter into solution in water under normal Earth-surface conditions (Pentcheva, 1967; Kaback, 1976).

Solubility controls of molybdenum concentrations could include precipitation with common metals as metal molybdates. For example, ferrous molybdate solubility can limit molybdenum activity to less than 100 μg/L in relatively iron-rich waters below about pH 5 (Hem, 1977a). This solubility control is less effective in oxidizing waters of higher pH, in which iron solubility is lower.

In studies of molybdenum geochemistry in the stream system draining the Climax area of Colorado, Kaback and Runnels (1980) attributed the downstream attenuation of molybdenum in water and sediment to adsorption by amorphous ferric oxyhydroxide. The solubility product for calcium molybdate quoted by Mannheim (1978) is $10^{-8.7}$, which suggests that waters containing substantial concentrations of dissolved Ca^{2+} should not contain large concentrations of dissolved molybdenum.

Molybdenum is an accessory element in many metal ores. Soluble molybdates may be produced in oxidized sectors of these deposits and may appear in detectable concentrations in stream water, sediments, ground water, and vegetation at considerable distances from their source. This characteristic has been taken into account in designing techniques for geochemical prospecting, as noted by Kaback and Runnells (1980).

Molybdenum is an essential element in animal and plant nutrition, especially for legumes. The element tends to accumulate in vegetation and may be present in excessive amounts that cause problems for grazing animals (Dye and O'Hara, 1959). Its role in human nutrition is not well known, but it is not one of the elements for which upper limits for drinking water have been set. An upper limit for irrigation water of 10 μg/L for continuous use and 50 μg/L for short-term use has been proposed (NAS-NAE, 1972).

Molybdenum is used extensively as an alloy in steel and in welding rods and is also used as a lubricant additive and in ceramics. The quantity used in the United States in 1979 was about 24×10^6 kg (U.S. Bureau of Mines, 1980b, p. 577).

Molybdenum is generally present in fossil fuels and can be spread through the environment by burning of these materials. Major local sources include wastes from molybdenum mines and ore-treatment facilities. One such location near Climax, Colo. has already been mentioned.

Rather extensive compilations of data cited by Mannheim (1978) suggest that river and lake waters from areas not extensively affected by pollution sources generally have less than 1 μg/L Mo. It is rather easy, however, to find higher concentrations. Voegeli and King (1969) found more than 1 μg/L in most samples obtained from streams in the State of Colorado, and in those streams affected by molybdenum mining, concentrations as great as 3,800 μg/L were present. The median value for public water supplies reported by Durfor and Becker (1964) was 1.4 μg/L. A study by Barnett and others (1969) showed molydenum concentrations exceeding 100 μg/L in water from Dillon Reservoir, one of the sources of the Denver, Colo., public supply.

Vinogradov (1957) described an area in the U.S.S.R. where background, or normal, concentrations of molybdenum in ground water were near 3 μg/L and where anomalous concentrations useful for geochemical prospecting ranged from 10 μg/L to 10 mg/L.

Kopp and Kroner (1968) reported molybdenum concentrations above their detection limit in about one-third of 1,500 samples of stream water from 130 locations in the United States. The detection limit in their study varied from sample to sample but generally was around 3 to 5 μg/L. The maximum value reported was 1.1 mg/L, and concentrations of more than 100 μg/L were observed rather frequently. The mean concentration for the samples that contained measurable amounts was 68 μg/L.

Other Metallic Elements

Elements included here are those at the end of the transition series in the periodic table and the heavy metals mercury and lead. Aqueous geochemistries of some of these elements have been studied rather extensively.

Copper

Modern industrial civilization uses copper extensively, and many of these uses result in its dispersal in the environment. Copper is an essential element in plant and animal metabolism. It may occur in the Earth's crust as the free native metal, Cu^0, or in Cu^+ or Cu^{2+} minerals. Copper forms rather stable sulfide minerals; some of the common species that are important as ore minerals also contain iron.

Copper may occur in solution in either Cu^{2+} or Cu^{1+} oxidation states, but the redox conditions in oxygenated water and the tendency of Cu^+ ions to disproportionate ($2Cu^+ \rightarrow Cu^0 + Cu^{2+}$) favor the more oxidized form. Cupric ions form complexes with many different ligands. In solutions above neutral pH the form $Cu(OH)_3^-$ may predominate. A strong $CuCO_3(aq)$ ion pair appears likely to be the major form in aerated natural water containing dissolved CO_2 species (Hem, 1977a). Copper hydroxycarbonates are slightly soluble and may maintain copper concentrations below 10 μg/L, but adsorption or coprecipitation with ferric oxyhydroxides can bring about even lower solubility limits (Hem, 1977a).

Copper may be dissolved from water pipes and plumbing fixtures, especially by water whose pH is below 7. Copper salts are sometimes purposely added in small amounts to water-supply reservoirs to suppress the growth of algae. Organic and inorganic compounds of copper have been used extensively in agricultural pesticide sprays. The element is therefore likely to be more readily available for solution in surface and ground water than its low average abundance in rocks might imply.

The U.S. Environmental Protection Agency (1976b) mandatory drinking water standards do not include a value for copper. An upper limit of 1 mg/L of copper in pubic water supplies was suggested in "Water Quality Criteria, 1972" (NAS-NAE, 1972), which also stated that this limit was based on the taste threshold for this element. The same report suggested an upper limit of 0.5 mg/L in water to be used by livestock, and 0.20 mg/L for continuous use in irrigation of crops. Toxicity for fish varies with species and major-ion concentrations of the water, but the NAS-NAE report implies that concentrations greater than a few hundredths of a milligram per liter are potentially harmful for many species.

Copper may be present in concentrations as great as a few hundred mg/L in acid drainage from metal mines (analysis 2, table 20). When the acidity of such solutions is neutralized, the copper is mostly precipitated. Data quoted by Turekian (1969, p. 314) suggest that levels of copper near 10 μg/L can be commonly expected in river water. Data published by Duror and Becker (1964) gave a median value of 8.3 μg/L for treated water from the 100 largest public supply systems in the United States. River water containing higher concentrations is not uncommon. Concentrations in the Allegheny and Monongahela Rivers above Pittsburgh in western Pennsylvania, for example, may exceed 100 μg/L when flow stages are low and the effects of coal-mine drainage on water chemistry are most strongly evident (U.S. Geological Survey, 1970).

In general, the concentrations of copper in river and ground waters are near or below predictions based on pH-Eh diagrams (Hem, 1977a). The lower concentrations are readily explainable as results of coprecipitation by oxides or adsorption on mineral surfaces.

Silver

Although it is a rare element in crustal rocks, silver is extensively used by humans, especially in photography. It is a common minor constituent of industrial wastes but is sufficiently valuable to justify intensive efforts to reclaim it. The pH-Eh diagram for silver (Hem, 1977a) suggests that metallic silver and silver chloride or sulfide solids are likely to limit the solubility of the element to much less than 10 μg/L in most natural water. Kharkar and others (1968) suggested an average of 0.3 μg/L in river water.

Silver has been proposed as a disinfectant for water, and Woodward (1963) quoted data showing that as little as 10 μg/L in alkaline water was effective in removing *Escherichia coli*, although at this low concentration the reaction was slow. The possibility of residual silver in water from biocidal treatment, therefore, exists, although the element is unlikely ever to be used widely for this purpose.

Silver iodide has been used in seeding of clouds with condensation nuclei to induce or intensify rain- or snowfall. Amounts that appear in rain or runoff that might result are too small to have any significant environmental effects but are of considerable interest in studying the effectiveness of the seeding techniques. According to Sheaffer and others (1978), the concentration of silver in unseeded precipitation is from .001 to .01 μg/L (1 to 10 nanograms/L (ng/L)). In seeded precipitation the silver concentration may be as high as 1 μg/L. Analytical procedures, generally using flameless atomic absorption spectrophotometry, have been developed that can meet the challenge of determining these extremely low concentrations (Woodriff and others, 1973; Sheaffer and others, 1978).

"Water Quality Criteria, 1972" (NAS—NAE, 1972) did not recommend limits for silver concentrations in drinking water, but did indicate that values above 5 μg/L pose a hazard in marine environments. The 1976 interim drinking-water standards (U.S. Environmental

Protection Agency, 1976b), however, give an upper limit of 50 μg/L.

Zinc

Major aspects of the aqueous geochemistry of zinc were described by the writer in an earlier publication (Hem, 1972b). Zinc has about the same abundance in crustal rocks as copper or nickel and is thus fairly common. However, zinc has only one significant oxidation state, Zn^{2+}, and tends to be substantially more soluble in most types of natural water than are the other two metals. Zinc is essential in plant and animal metabolism, but water is not a significant source of the element in a dietary sense.

Zinc is widely used in metallurgy, principally as a constituent of brass and bronze, or for galvanizing, in which it is deposited as a coating to inhibit corrosion of steel. Zinc also is used extensively as a white pigment (zinc oxide) in paint and rubber. These applications tend to disperse the element widely in the environment, and its availability for solution in water has been greatly enhanced by modern industrial civilization.

Solubility data for zinc carbonate and hydroxide summarized by Hem (1972b) suggest that water containing 610 mg/L HCO_3^- should contain less than 100 μg/L of zinc over the pH range from 8.0 to 11. At equilibrium with the zinc silicate willemite, the solubility of zinc might be less than 10 μg/L at this pH range, but whether this mineral could be precipitated from low-temperature water solutions is unknown. Another factor that may inhibit zinc concentrations in natural water is the probability of interaction with preexisting mineral surfaces, through simple adsorption, ion exchange, or coprecipitation processes.

Values quoted by Turkeian (1969, p. 314) for zinc concentrations in river water range from 5 to 45 μg/L. More extensive results for the U.S. streams studied by Durum and others (1971) gave a median value of 20 μg/L for samples from 726 sites. Bowen (1966 p. 164) estimated an average concentration of 10 μg/L in all surface water. Streams affected by mine drainage commonly contain 100 μg/L or more. For example, the dissolved zinc concentration in monthly composites of daily samples from the Allegheny River at Oakmont, Pa., exceeded 100 μg/L for 5 of the 12 months in the water year ending September 30, 1970 (U.S. Geological Survey, 1970).

Water quality standards suggested by "Water Quality Criteria, 1972" (NAS–NAE, 1972) gave an upper limit of 5 mg/L for zinc, because above that limit a significant number of people can detect zinc by taste. No health effects were considered likely. Zinc is an undesirable contaminant for some species of aquatic life at much lower concentrations (NAS–NAE, 1972, p. 182), but the amount that can be tolerated is also a function of other properties of the solution.

Cadmium

Zinc and cadmium have some chemical similarities, but cadmium is much less abundant. Generally, cadmium is present in zinc ore minerals such as sphalerite and is recovered from some copper ores during smelting and refining.

Cadmium is used for electroplating and for pigments used in paint, printing ink, and plastics. It also is used extensively as a stabilizer for PVC plastic and in electrical batteries and fluorescent and video tubes. Many of these uses will tend to make the element available to water that comes in contact with buried wastes. Another factor of importance is the tendency for cadmium to enter the atmosphere through vaporization at high temperatures. Cadmium may therefore be liberated to the environment in metallurgical processes and in the combustion of fossil fuel.

The equilibrium solubility of cadmium carbonate was suggested by Hem (1972a) as a possible limit for concentrations in natural water, but values observed are generally well below saturation. Cadmium may be coprecipitated with manganese oxide or adsorbed on mineral surfaces.

A median concentration near 1 μg/L was observed by Durum and others (1971) in their reconnaissance of metal contents of U.S. surface waters. Of 726 samples, about 4 percent contained more than 10 μg/L, the mandatory upper limit for public water supplies given in the 1976 drinking water regulations (U.S. Environmental Protection Agency, 1976b). Cadmium in mining waste entering a stream in Japan was stated by Kobayashi (1969) to have caused deterioration of the bones of farmers and their families who had eaten rice grown in fields irrigated with that stream water. The recommended upper limit for irrigation water also is 10 μg/L (NAS-NAE, 1972, p. 342), owing to the toxicity of the element and its known tendency to accumulate in plants.

Mercury

During the late 1960's and early 1970's, the potential significance of mercury as an environmental pollutant came to be recognized and steps were taken to curtail uses that had allowed it to enter natural water and sediments.

Elemental mercury is a liquid at normal Earth-surface temperatures, but it is also somewhat volatile at these temperatures. The stable form in most natural-water systems is the free metal, Hg(aq) (Hem, 1970), which has an equilibrium solubility of 25 μg/L in a closed system without a gas phase over a considerable pH-Eh range. The amount that would be present in water open to the atmosphere is likely to be much lower owing to its tendency to escape as vapor. Mercury may form chloride or hydroxide complexes depending on pH and total chloride concentration. Organic complexes such as methyl mercury, $HgCH_3^+$, and other similar forms can be produced by methane-generating bacteria in contact with metallic mercury in lake or stream sediment (Wood and others, 1968). In this form the element appears to be concentrated in successive biological species along aquatic food chains so that fish that live in mildly contaminated environments may contain too much mercury to be used safely for food. A well-studied occurrence of mercury poisoning occurred in the 1950's at Minimata, Japan, where shellfish that had accumulated mercury from industrial waste released into Minimata Bay were eaten by the local population (Doi and Ui, 1974).

Organomercuric compounds were widely used as biocides for treatment of seed grain and in various other applications until these uses were banned in the 1960's. A major source of mercury pollution in surface water prior to 1970 was its escape during the electrolysis of molten sodium chloride to produce chlorine and sodium hydroxide (mercury was used in the electrolysis cells (Wershaw, 1970)). As noted above, the amounts escaping to the environment through this source have decreased greatly since 1970. Various cultural uses of mercury and its release to the atmosphere in smelting and fossil-fuel combustion have probably raised the general background level of this element in the environment substantially above its preindustrial status. It should be noted, however, that even though the element is rare, its natural tendency to volatilize tends to disperse it widely.

Many determinations of mercury concentrations in water that appear in data banks and publications represent unfiltered samples. An association of mercury with the generally unidentified solids present in such samples is evident in the higher concentrations that are characteristic of many unfiltered samples.

Concentrations of mercury in filtered natural river water generally are very small, rarely exceeding a few tenths of a microgram per liter. Concentrations of a few micrograms per liter occur in some thermal ground waters and in water associated with mercury ores or with mining areas (Wershaw, 1970; White and others, 1970). The amount of dissolved mercury that may occur in the form of organic complexes is uncertain, although it appears from available thermodynamic data that the concentrations of mercury occurring in solution even in water that is known to be polluted are below the solubility limits for the common inorganic forms (Hem, 1970).

Equilibrium constants for methyl mercury complexes and other mercury solute species were given by Stumm and Morgan (1981, p. 387), who also noted that methyl mercury complexes tend to decompose slowly and that concentrations greater than equilibrium values may persist for long periods of time in some kinds of systems.

Lead

The Latin word for lead, "plumbum," is preserved in the English terms relating to water conveyance ("plumbing," etc.) and suggest the long history of the use of lead for water pipes. As the data in table 1 indicate, lead is comparable in abundance to cobalt and is rather widely dispersed in sedimentary rocks. Its natural mobility is low, however, owing to the low solubility of lead hydroxy carbonates (Hem and Durum, 1973; Hem, 1976b; Bilinski and Schindler, 1982) and phosphate (Nriagu, 1974). The adsorption of lead on organic and inorganic sediment surfaces (Hem, 1976a) and the coprecipitation of lead with manganese oxide (Hem, 1980) also tend to maintain low concentration levels in surface and ground water.

Certain of the uses of lead by humans have tended to disperse the element widely through the environment. In the 1920's, addition of tetraethyl lead was found to promote more efficient combustion of gasoline used in automobile engines. "Leaded" gasoline permitted a higher compression of the fuel-air mixture, which in turn increased the power output. The lead content of the fuel is emitted as an aerosol in exhaust gases, and the quantities so dispersed increased greatly as the number of automobiles in use grew.

Regulation of exhaust emissions of automobiles in the United States substantially decreased this source of lead aerosols during the 1970's and 1980's. The amount of lead used annually in gasoline additives, as reported by the U.S. Bureau of Mines (1972, p. 656; 1982, p. 520) declined from a peak of about 253,000 metric tons in 1970 to about 101,000 metric tons in 1981. Large amounts also are released in the smelting of ores and burning of coal.

Lead pipe once was commonly used to convey drinking water and is still present in many old buildings in the United States and elsewhere. Water that has a pH below neutrality or is poorly buffered may dissolve considerable amounts of lead from such pipe, and may also obtain lead from solder used to join copper pipe and fittings. The extent of these effects is not well known, because few chemical analyses are available for water taken from consumer taps. The mandatory upper limit for lead in drinking water in the United States is 50 $\mu g/L$ (U.S. Environmental Protection Agency, 1976b). A study by Schock (1980) of the factors that might affect the corrosiveness of water toward lead pipe indicated that maintaining a tap-water lead concentration below 50 $\mu g/L$ might be possible by careful control of pH and alkalinity in water supplies. However, the range of conditions that appeared to maintain proper control is narrow and would be a difficult target for any treatment technique to hit consistently.

The principal dissolved inorganic forms of lead are the free ion Pb^{2+}, hydroxide complexes, and, probably, the carbonate and sulfate ion pairs. The importance of organic complexes is uncertain, but they may constitute a significant part of the dissolved lead in some waters.

Solubility calculations (Hem and Durum, 1973) show that equilibria involving basic lead carbonates can maintain the dissolved-lead concentration below about 50 μg/L in water having 61 mg/L HCO_3 and a pH between 7.5 and 8.5. Water having lower alkalinity and pH can retain larger concentrations.

Concentrations of lead in rain and snow range from 100 μg/L or more in areas subject to substantial air pollution down to 1.0 μg/L or less in more remote areas. Lazrus and others (1970) reported an average of 34 μg/L for 32 sampling points in the United States during 6 months in 1966 and 1967. Measurements of lead in rain in Menlo Park, Calif., during the period 1971–74 (unpub. data, U.S. Geological Survey files) showed a wide concentration range, from 200 μg/L to less than 1.0 μg/L. Part of the lead could generally be removed by filtration through 0.10-μm-porosity filter membranes. Lead concentrations of Greenland snow in that general time period (1966–74) were between about 0.1 and 0.2 μg/kg (Herron and others, 1977). These authors found concentrations of a few hundredths μg/L in most of an ice core that covered a time period extending back about 800 years.

Dry fallout and rainout of particulate lead is probably a factor of major importance in the circulation of the element, especially in areas of heavy automobile traffic (Chow and Earl, 1970). Washing of this material into streams during runoff events is a potential source of dissolved lead in river water.

Dissolved lead concentrations of surface water of the United States determined in the 1970 study of Durum and others (1971) were 1.0 μg/L or greater in most of the sources sampled in the northeastern and southeastern sections of the United States, and in about half those sampled in the central part of the country. Concentrations below 1 μg/L were more common in the western part of the United States. However, concentrations above 10 μg/L were observed in a substantial number of the samples from all regions except the northwest.

Occasional concentrations of dissolved lead in excess of 10 μg/L have been reported at many river-sampling stations in the NASQAN network, but the records indicate that most of the lead that was present was in particulate form. A summary of data available through 1971 was published by Fishman and Hem (1976).

The radioactive beta-emitting isotope ^{210}Pb is produced in the decay series of ^{238}U. It has a 21.4-year half-life and has been used as a tracer in various kinds of hydrologic studies. A precursor in this decay series is radon-222, which is widely disseminated in the atmosphere (Goldberg, 1963b; Koide and others, 1973; Turekian and others, 1977).

Nonmetallic Elements

The elements considered in this group are arsenic, antimony, selenium, and the heavy halogens bromine and iodine.

Arsenic

Because small amounts of arsenic can be toxic to humans, it is considered a highly undesirable impurity in water supplies and an upper concentration limit of 50 μg/L was given in the 1976 drinking water standards (U.S. Environmental Protection Agency, 1976b).

Arsenic may form metal arsenides in which its oxidation state is negative. Arsenic may also form sulfides and can be present as an accessory element in sulfide ore deposits. In solution in water the stable forms are arsenate (As^{5+}) or arsenite (As^{3+}) oxyanions. A pH-Eh diagram showing fields of dominance of aqueous arsenates (Hem, 1977a) indicates that the monovalent arsenate anion $H_2AsO_4^-$ would be expected to predominate between pH 3 and pH 7, and the divalent species $HAsO_4^{2-}$ would take over from pH 7 to pH 11. Mildly reducing conditions would favor the arsenite uncharged ion $HAsO_2(aq)$. Although ferric arsenate and some other metal arsenates have rather low solubilities, the importance of solubility controls of this type in the aqueous chemistry of arsenic cannot be closely evaluated. Data on arsenite solubilities are sparse.

Adsorption by hydrous iron oxide (Pierce and Moore, 1980) or coprecipitation, or combination with sulfide in reduced bottom mud (Kobayashi and Lee, 1978), appear to be major inorganic factors that can maintain concentrations of arsenic at very low levels in water.

The organic and biochemical aspects of arsenic chemistry are potentially of considerable significance. The element is extensively involved in biochemical processes. As a result of biologically mediated methylation, derivatives of arsenic such as dimethyl arsenic and methyl arsonic acids ($(CH_3)_2AsOOH$ and $CH_3AsO(OH)_2$, respectively) can be synthesized. Braman and Foreback (1973) reported that dimethyl arsenic acid is difficult to oxidize and may be a major part of the dissolved arsenic in surface water. The importance of biochemical processes in arsenic aqueous chemistry is still being studied.

Arsenic has been used as a component of pesticides and thus may enter streams or ground water through waste disposal or agricultural drainage. An important factor in the natural circulation of arsenic, however, is the volatility of the element and some of its compounds. Arsenic is present in volcanic gases and is a common constituent of geothermal water. Analysis 8, table 19, for example, reported a concentration of 40 mg/L in water from Steamboat Springs, Nev. Arsenic also may be released in the burning of coal and the smelting of ores, and it is a minor impurity in phosphate rock.

An incident of arsenic pollution of ground water in Nova Scotia, Canada, was reported by Grantham and Jones (1977). Arsenopyrite was present in rock associated with gold in that area, and oxidation of this material in mining wastes exposed to the air evidently released arsenic, which appeared in excessive quantities in some water wells. The highest concentration reported was 5 mg/L (as As). An arsenic concentration of 1.3 mg/L has been documented in a private well in Lane County, Oreg. (analysis 4, table 20). Concentrations of up to 1.0 mg/L have reportedly been present in water used for drinking and, at least for short periods of time, have produced no apparent ill effects (McKee and Wolf, 1963, p. 140), but long-term use of a concentration of 0.21 mg/L was reported to be poisonous. Toxicities of the various forms of arsenic can be expected to be different, but commonly used analytical procedures report only the total amount present, as As.

Deaths among cattle as a result of drinking natural water containing arsenic were said by McKee and Wolf (1963) to have been reported from New Zealand. Toxicity studies quoted by NAS–NAE (1972, p. 310) suggested that 5.5 mg/L of arsenic in drinking water for cattle would have no harmful effect. However, NAS–NAE (1972) recommended an upper limit for livestock water of 0.2 mg/L.

Concentrations in stream waters studied by Durum and others (1971) were below their detection limit (10 μg/L) in 79 percent of the samples analyzed. However, concentrations greater than 50 μg/L were found in 2 percent of the samples, presumably the result of waste disposal. Waslenchuk (1979) found concentrations ranging from 0.15 to 0.45 μg/L in streams in the Southeastern United States.

Cherry and others (1979) proposed the use of the $As^{5+}:As^{3+}$ ratio in dissolved arsenic as a means of estimating the insitu redox potential of ground water. Highly sensitive procedures for determining these species separately are available and can detect arsenic in concentrations well below 10 μg/L (Braman and others, 1977; Shaikh and Tallman, 1978).

Antimony

Although some of its chemical traits are similar to those of arsenic, antimony appears to be only about one-tenth as abundant in rocks. The concentrations of antimony that occur in natural waters can be expected to be very small, but few actual determinations exist. Analyses of hot spring waters from Yellowstone Park and elsewhere given by White and others (1963) indicate that thermal waters may commonly contain a few hundred micrograms of antimony per liter. This implies a tendency for volatilization, similar to arsenic.

Data on concentrations of antimony in river water and ground water are sparse. An estimate by Kharkar and others (1968) of 1.1 μg/L for average river water appears to have been strongly influenced by a sample from the Amazon that was reported to contain about 5 μg/L, about 10 times as much as was present in the seven U.S. streams that were sampled. A paper by Shvartsev and others (1974) gave data on antimony in ground waters of an area in central Asia indicating that concentrations may reach 3 to 6 mg/L in mine drainage water in that area.

Selenium

The chemistry of selenium is similar in some respects to that of sulfur, but selenium is a much less common element. In the 1930's it was discovered that a disease of livestock in certain areas of the Western United States was caused by an excessive intake of selenium, and an extensive research program was carried out by the U.S. Department of Agriculture during the ensuing decade. Results of this work were summarized by Anderson and others (1961). Ongoing studies later established that selenium is essential in the nutrition of grazing animals. This aspect of the subject was summarized by Oldfield (1972).

The intake of selenium by animals is mainly from vegetation. Some species of the genus *Astragalus* are particularly notable for taking up and accumulating selenium from the soil, and some plants have been found to contain several thousand milligrams of selenium per kilogram of dry plant parts. Drainage water from seleniferous irrigated soil has been reported to contain as much as 1 mg/L of dissolved selenium. This type of water (analysis 5, table 20) is so high in dissolved solids, however, that it is not likely to be used by humans as drinking water. A case of selenium toxicity was, however, described by Beath (1962), who gave the cause as use of drinking water containing 9 mg/L of selenium over a 3-month period.

The low-temperature geochemistry of selenium, with particular reference to associations with iron and uranium, has been studied and summarized by Howard (1977). The element occurs in oxidizing solutions as selenite (SeO_3^{2-}) or selenate (SeO_4^{2-}) ionic species, but it is readily reduced to elemental and relatively insoluble Se^0. In the presence of iron it may be coprecipitated with pyrite or may form the mineral ferroselite, $FeSe_2$. The more oxidized forms may be adsorbed on, or otherwise interact with, ferric oxyhydroxides. These minerals are associated with some of the uranium ore deposits in sandstones of the Western United States. The compound H_2Se is a gas at ordinary Earth-surface temperatures.

As shown by the data in table 1, selenium is a relatively rare element. In view of that fact and the geochemical controls that tend to limit its aqueous mobility, one would expect concentrations in natural water to be low. Many analyses of surface and ground water from widely distributed sources in the United States include selenium determinations, but concentrations rarely exceed 1 μg/L. The average concentration in stream water estimated by Goldberg and others (1971) is 0.2 μg/L. Dall'Aglio and others (1978) reported values below 0.1 μg/L for most Italian rivers sampled. Anderson and others (1961) reported 80 μg/L in one sample from the Gunnison River in the vicinity of Grand Junction, Colo. In most samples from the Colorado River and its tributaries, however, the concentrations were much lower. The maximum concentration of selenium for drinking water set by the Environmental Protection Agency (1976b) is 0.01 mg/L, the same level as the 1962 standard.

A study of selenium behavior in water in an irrigated area of central Wyoming made by Crist (1974) who found concentrations as great as 1 to 3 mg/L in some of the shallow ground water affected by irrigation drainage. All the higher selenium concentrations were in water that had high dissolved-solids concentrations.

Bromine

Bromine is similar in chemical behavior to chlorine but is much less abundant. Bromine in natural water is always present as the bromide ion Br^-. The concentration present in seawater is 65 mg/L, an amount sufficient to make bromide an important constituent. The total quantity in the ocean probably is a major fraction of the quantity present in the outer 16 km of the Earth's crust, but the available data do not form a satisfactory basis for deciding whether the quantity of bromine in the ocean is as high a percentage of the total Br in the Earth's crust as it is for chlorine. The literature on the geochemistry of bromine was reviewed by Correns (1956), and a more recent summary of bromine geochemistry in relation to the atmosphere and natural waters was written by Fuge (1973).

Bromide is present in major concentrations in some brines. Analysis 4, table 15, represents such a brine which contains 3,720 mg/L of bromide. The concentration of bromide in a chloride brine can increase as a result of evaporation, even after the solution reaches saturation with respect to sodium chloride. Bromide may be selectively concentrated by the clay-membrane effects noted previously for enrichment of brines in other ions, as the Br^- ion is larger than the Cl^- ion.

Bromide concentrations in rainwater and snow range from about 5 to more than 150 μg/L, and a wider range is given for river water by Fuge (1973). Geothermal water may contain more than 20 mg/L. The oxidation of bromide to elemental bromine, which is volatile, would increase the mobility of the element. Such an effect may occur in marine aerosols (Duce and others, 1965).

Anthropogenic effects are probably significant in urban areas. Bromine is extracted commercially from seawater and from brines, and in 1973 the amount consumed in the United States was about 170,000 metric tons (Klingman, 1976). The largest use of this element was as ethylene dibromide, a gasoline additive. Other uses, such as in fumigants and fire-retardant agents, will also release bromine compounds to the environment. The presence of small amounts of the element in freshwater is not known to have any ecologic significance.

Iodine

Although iodine is not a particularly abundant element, it is widely distributed. It is essential in the nutrition of higher animals, including humans, and concentrations in natural water have received considerable attention. The circulation of the element appears to be strongly influenced by biochemical processes. Nearshore marine vegetation, especially kelp, concentrates iodine from seawater, which itself has only 0.06 mg/L of iodine. The volatility of the element and some of its solid salts probably adds to the general tendency for iodine to be circulated in the atmosphere. Concentrations of iodide in rainwater reported by Rankama and Sahama (1950, p.767) were 1–3 μg/L. Konovalov (1959) reported concentrations ranging from 42.4 to 3.3 μg/L for principal rivers of the U.S.S.R. Many data on iodide in natural freshwater have been obtained by Soviet investigators. The element is rather easily oxidized, and although the form in solution is usually indicated as the anion I^-, thermodynamic considerations (Sillén, 1961) suggest that the more stable form in seawater is the iodate anion IO_3^-. The iodine in Chilean nitrate deposits also is mostly in this form (Goldschmidt, 1954, p. 612). Goldberg and others (1971) noted, however, that both iodide and iodate are present in seawater. Iodide can be converted to elemental iodine by photochemical oxidation; as noted by Duce and others (1965), this may influence its behavior in the atmosphere. Also, elemental iodine can participate in disproportionations, which might explain the presence of both iodide and iodate in seawater. Liss and others (1973) suggested that the proportion of IO_3^- to I^- could be an index of redox potential in seawater.

Iodide is concentrated in some brines; analysis 4, table 15, reports 48 mg/L as I.

Radioactive Elements

Discussion of the subject of radioactivity in any detail is beyond the scope of this book. The treatment here is necessarily brief and emphasizes naturally occurring radioactive nuclides. A large number of radioactive nuclides produced in the process of nuclear fission of certain elements. The fission process is used extensively for the production of energy, and fission products pose problems of containment, storage, use, and disposal that have received much scientific study. For more comprehensive discussions of the broad topic of radioactivity, the reader is referred to standard texts such as Friedlander and others (1964).

Radioactivity is the release of energy and energetic particles by changes occurring within atomic or nuclear structures. Certain arrangements within these structures are inherently unstable and spontaneously break down to form more stable arrangements. The most unstable configurations disintegrate rapidly and do not now exist in measurable amounts in the Earth's crust. For example, chemical elements 85 and 87, astatine and francium, do not now exist naturally. Other unstable nuclides, however, ^{40}K and ^{87}Rb, for example, have a slow rate of decay and still exist in significant quantity.

The decay of a radioactive nuclide is a first-order kinetic process and can be expressed in terms of a rate constant, as described in the discussion of reaction rates elsewhere in this book. Usually, for radioactive elements the decay rate is expressed as a half-life, that is, the length of time required for half the quantity present at time zero to disintegrate.

Radioactive energy is released in various ways. The three types of radiation of principal interest in natural-water chemistry are (1) alpha radiation, consisting of positively charged helium nuclei, (2) beta radiation, consisting of electrons or positrons, and (3) gamma radiation, consisting of electromagnetic wave-type energy similar to X-rays.

Radioactivity in water is produced principally by dissolved constituents. However, the radioactive hydrogen isotope tritium (^{3}H) may replace normal hydrogen in water molecules.

Three nuclides of high atomic weight, uranium-238, thorium-232, and uranium-235, which exist naturally, are spontaneously radioactive and give rise to most of the naturally occurring radioactivity in water. They disintegrate in steps, forming a series of radioactive nuclide "daughter" products, mostly short lived, until a stable lead isotope is produced. The uranium-238 series produces the greatest part of the radioactivity observed in natural water, although the thorium-232 series also may be significant in some places. The uranium-235 or actinium series is less important than the others because only a very small fraction of natural uranium is composed of this isotope.

Alpha-emitting substances in natural water are mainly isotopes of radium and radon, which are members of the uranium and thorium series. Beta and gamma activity is evidenced by some members of these series and also is characteristic of potassium-40 and rubidium-87. Many of the fission products are strong beta and gamma emitters. Among the ones of special interest in water chemistry are strontium-89, strontium-90, iodine-131, phosphorus-32, and cobalt-60.

It has been known since the early years of the 20th century that some natural waters are radioactive, especially those of certain thermal springs. Internal and external use of such water was once commonly believed to be beneficial for certain human ailments. An investigation of radioactive springs by George and others (1920) is noteworthy. It entailed visits to and analyses of water from hundreds of springs in the State of Colorado. For many of the springs, radioactivity measurements were made in the field during the summer of 1914 using equipment carried about in an automobile—a rather heroic undertaking.

These and other early measurements of radioactivity in natural water were made using an electroscope, which is sensitive to small ionizing effects. The Geiger-Müller tube and various scintillation devices, with counters and scalers, and other more sensitive ionization measuring techniques are now employed extensively for such purposes.

Where possible, radioactivity data are expressed in terms of concentration of specific nuclides. General measurements of total or gross alpha or beta and gamma activity also are often reported. The element uranium is here considered a radioactive constituent, but it is most conveniently measured by chemical means. For some elements, radiochemical techniques permit detection of concentrations far smaller than any chemical method can attain.

Various terms and units are used in reporting radioactivity in water. Some studies have merely reported observed counts per minute or disintegrations per minute for specific volumes of sample. These data cannot be considered quantitative unless amounts of sample used, counter efficiency, and various details of the conditions of measurement are given. To standardize results and make comparisons possible, the radioactivity of water is usually expressed in terms of an equivalent quantity of radium, or in terms of the rate of radioactive disintegration (curies) per liter of water. One curie (Ci) is defined as 3.7×10^{10} disintegrations per second, the approximate specific activity of 1 gram of radium in equilibrium with its disintegration products. This unit is very large for the purpose of expressing natural radioactivity levels, and for this reason such data are often expressed in picocuries (curies$\times 10^{-12}$, or pCi). Other units, such as the Rutherford (2.7×10^{-5} Ci) and the Mache unit (3.6×10^{-10} Ci), occasionally are seen in the older literature.

Interpreting measurements of radioactivity expressed in picocuries or concentrations of specific nuclides determined by radiochemical procedures requires consideration of detection limits for the procedures used. Counting procedures are limited in sensitivity by natural radiation background and by the manner in which the counting is done. Many samples do not give a reading that is significantly above the background, and tabulated data usually contain many entries of "less than" some specific activity level that represented the background. The user of such data should remember that the number so quoted is not indicative of a specific activity in the sample; rather, it is essentially a statement that the activity present was below the detection limit for the determination in that particular sample.

A program to study the occurrence of radioactivity in natural water was begun by the U.S. Geological Survey in 1953. During this study, ground waters from a wide variety of aquifers in the conterminous United States were sampled and analyzed. Some results of the ground-water study were published by Scott and Barker (1962). A continuing program of monitoring stream water at selected locations was developed, and results were published in the annual Water Resources Data publication series already mentioned.

Analytical techniques used in radioactivity studies were described by Thatcher and others (1977). A general assay of alpha and beta activity and specific determinations of radium-226 and uranium are included in determinations made periodically at the stations in the surveillance network. The methods used for tritium were described by Hoffman and Stewart (1966), and methods for strontium-90, by Johnson and Edwards (1967).

Uranium

Natural uranium is composed of several isotopes, of which uranium-238 is predominant. This nuclide is the starting point in a radioactive-decay series that ends with the stable lead isotope lead-206. The half-life of uranium-238 is 4.5×10^9 years, which indicates that the nuclide is only weakly radioactive. Chemical methods of detection are sufficiently sensitive to determine uranium in the concentrations at which it is commonly present in water.

The geochemistry of uranium has been studied extensively. pH-Eh and solubility diagrams published by Garrels and Christ (1964, p. 254–256) show that reduced species, where the oxidation state is U^{4+}, are only slightly soluble, but that more highly oxidized forms such as the uranyl ion, UO_2^{2+}, or the anionic species present at high pH are more soluble. Uranyl complexes with carbonate and sulfate (Sillén and Martell, 1964, p. 139, 239) may influence the behavior of dissolved uranium. The chemical properties of the U^{6+} state favor the wide dispersion of uranium in the oxidized portion of the Earth's crust.

Uranium is present in concentrations between 0.1 and 10 µg/L in most natural water. Concentrations greater than 1 mg/L can occur in water associated with uranium-ore deposits. A concentration near 15 mg/L was determined in water from a 90-m-deep well in Helsinki, Finland. High uranium concentrations in ground water of this area were attributed by Asikainen and Kahlos (1979) to uranium-bearing minerals present in igneous bedrock.

Possible uses for uranium isotopic ratios in hydrologic studies were reviewed by Osmond and Cowart (1976).

Radium

Four isotopes of radium occur naturally: radium-223, radium-224, radium-226, and radium-228. Two of these, radium-228 and radium-224, are disintegration products of thorium-232. Radium-223 is a disintegration product of uranium-235, and radium-226 is a disintegration product of uranium-238. The half-life of radium-226 is 1,620 years, much longer than any of the other naturally occurring radium isotopes, and it has been widely assumed that radium-226 is normally the dominant form in natural water. This assumption has been challenged by King and others (1982), who found a relatively high proportion of radium-228 in ground water of South Carolina. All radium isotopes are strongly radioactive and can be detected in small concentrations. The data obtained by the various analytical procedures that are available may not be entirely comparable because of differing efficiencies toward the various isotopes, but most published data probably represent principally radium-226. The procedures commonly use alpha-particle counting, which is effective for the three lighter isotopes but does not determine radium-228, a beta-emitter.

Radium is an alkaline-earth metal and behaves chemically somewhat like barium. The solubility of $RaSO_4$ at 25°C appears, from data quoted by Sillen and Martell (1964, p. 237), to be somewhat less than the solubility of barium sulfate under comparable conditions.

In theory, if uranium or thorium undergoes disintegration in a closed system in which the products do not escape, a state of radioactive equilibrium will ultimately be reached. Under these conditions the rates of disintegration of daughter elements become equal to the rates at which they are produced by disintegration of parent elements. This in turn fixes the abundance ratios between any two members of the radioactive series. Equilibrium between parent and daughter is reached rapidly or slowly, depending on relative and absolute disintegration rates.

When disintegration rates of parent and daughter nuclides are known, a determination of the isotopic ratio can sometimes be used to determine how long the system has been closed to the escape of the daughter product. Isotopic ratios in such systems as $^{40}K-^{40}Ar$ are used for dating geologic formations. It seems likely, however, that few aqueous sytems could be capable of reaching an equilibrium between uranium-238 and radium-226 because of the long time period required. Because the chemistries of the two elements are so different, the likelihood of separation is further increased. The degree of disequilibrium among some of the products of the U and Th decay series has potential usefulness in evaluating the efficiency of transport or retention of solute ions in aquifers (Krishnaswami and others, 1982).

The concentration of radium in most natural waters is far less than that of uranium and is mostly below 1.0 pCi/L. The highest concentration reported by Scott and Barker (1962) was 720 pCi/L in water from the brine well represented by analysis 4, table 15. Values for radium of several thousand picocuries per liter have been reported in the literature, but it seems likely that some of these data were obtained by methods that did not distinguish between radium and radon; they should be interpreted accordingly (Stehney, 1955).

Radium concentrations amounting to more than 3.3 pCi/L have been found in potable water from deep aquifers in a considerable area of Iowa, Illinois, and Wisconsin (Scott and Barker, 1961). The upper limit recommended for drinking water is 5 pCi/L (U.S. Environmental Protection Agency, 1976a). Literature on the occurrence of radium in water supplies in the United States was reviewed by Sorg and Logsdon (1980), who concluded that relatively high concentrations of radium are most likely to occur in water from deep aquifers like those mentioned above, or in areas affected by mining for uranium or phosphate. Water from certain deep wells in the Helsinki, Finland area was reported by Asikainen and Kahlos (1979) to contain ^{226}Ra at levels of more than 100 pCi/L.

Radon

Radium isotopes 223, 224, and 226 decay to produce isotopes of radon, an alpha-emitting noble gas. Early investigators of radioactivity called these "emanations." Radon-222 produced in the decay of radium-226 has a half-life of 3.8 days and is the only radon isotope of importance in the environment, as the other radon isotopes have half-lives of less than a minute. Radon is soluble in water and also can be transported in the gas phase. Small amounts are present in the atmosphere, and large quantities occur in gases below the land surface. Many ground waters contain readily detectable quantities of radon, which appear substantial in comparison with the accompanying dissolved-radium concentration. The radon in these waters is derived mostly from radium in the solids in the aquifer. Rogers (1958) calculated that a ground water in a porous aquifer that contained 1 mg/kg of uranium in the solid phase could have a radon activity greater than 800pCi/L. Such concentrations of uranium in rocks and soils are by no means unusual. Rogers and Adams (1969b) assembled data that indicate that a median concentration below 1 ppm is attained only in basaltic and ultramafic rocks.

Radon is lost from solution by release to the atmosphere and by radioactive decay, and analyses generally must be performed in the field. Various techniques for doing this have been used (George and others, 1920; Kuroda and Yokoyama, 1954; Rogers, 1958). Interest in radon contents of ground water, especially thermal springs, motivated the earlier work. It was later suggested that radon concentrations in stream water might aid interpretations of geologic structures traversed by the stream (Rogers, 1958), but this idea has not been pursued extensively. The problems of sampling and analysis of the element and the fluctuation of radon concentration in response to many different factors are serious obstacles to obtaining and interpreting data. More recently, the fluctuation of radon concentrations of ground water and subterranean gases in the vicinity of active faults has been investigated as a possible aid in earthquake prediction (Shapiro, 1980).

The possible public health significance of radon-222 in drinking water has not received much attention. Brutsaert and others (1981) reported on its occurrence in ground waters of Maine and expressed concern about possible hazards. Where the water does not have opportunity to lose radon to the atmosphere, the concentration can substantially exceed 1,000 pCi/L. Radon-222 decays through a series of short-lived daughters to lead-210, which has a half-life of 21.8 years.

Thorium

Thorium is element 90 in the periodic table. Its principal isotope, ^{232}Th, has a half-life of 1.39×10^{10} years. Data in table 1 indicate that thorium is more abundant than uranium in most types of rock. However, the thorium concentration in most natural water is probably small. Not much is known about actual concentrations, because few analyses have included determinations for this element. Rogers and Adams (1969a) and Turekian (1969, p. 316) reported analyses suggesting that concentrations are unlikely to be more than a few tenths or hundredths of micrograms per liter. Baes and Mesmer (1976, p. 172) computed a solubility for the element that is near these values at neutral pH.

Thorium may occur in association with uranium in some types of rock, but the two elements differ greatly in their behavior in solution. Thorium occurs only in the tetravalent Th^{4+} state, and the low solubility of the oxide tends to keep thorium in resistate minerals. Uranium, on the other hand, is rather soluble in oxidizing alkaline systems.

Thorium-232 decay products include isotopes of radium, radon, and lead, as indicated elsewhere. The aqueous geochemistry of the element remains rather poorly known. A review by Langmuir and Herman (1980) gives thermodynamic data and equilibrium constants for many solid and aqueous species of thorium. These authors believe that complexation with organic and inorganic ligands tends to enhance thorium mobility, but that the concentration range to be expected in freshwater probably is only from 0.01 to 1 $\mu g/L$.

Thorium-230, which has a half-life of 80,000 years, is the immediate precursor of radium-226 in the uranium-238 decay series. Hence, thorium chemistry may have some significance in controlling the behavior of the disintegrations products of uranium in aqueous systems.

Other Radioactive Nuclides

When the nucleus of an atom is bombarded by sufficiently energetic subatomic particles, various changes in its structure can occur. Research in this field made rapid strides during the 1930's as new types of charged-particle generators were developed.

In 1939 it was discovered that when atoms of certain of the heavier elements are bombarded by sufficiently energetic neutrons the nucleus of the heavy element can be split into smaller units, which then become the nuclei of newly formed atoms of lighter weight elements. These "fission products" may have unstable configurations, and these unstable configurations are radioactive while they are spontaneously altering to stable nuclides. The fission process itself releases neutrons, and some of the heavy nuclides were found to be capable of a sustained chain reaction in which neutrons are produced more rapidly than they are consumed. Conversion of nuclear mass to energy occurs in these processes. The nuclides capable of sustained fission that are of particular interest include the natural isotope uranium-235 and the man-made isotope plutonium-239. Use of the fission process by humans has provided many radioactive byproducts, and these have entered the hydrosphere through many different routes.

As noted earlier, many measurements of gross radioactivity in water have been made. The determination of gross alpha or beta activity is a general indicator of radioactive contamination. The principal beta-emitting nuclides that can be expected in surface and ground water are artificially produced. The presence of excessive gross activity requires identification of sources by more specific methods.

Some of the fisson products that have been released into the atmosphere and other parts of the environment have appeared in water in significant amounts. Presumably, fallout of fission products from bomb tests in the atmosphere was responsible for some of the otherwise-unexplained high values of beta activity that were reported in rivers and public water supplies during the 1950's and early 1960's (Setter and others, 1959). Amounts of radioactive fallout decreased after most of the atmospheric testing of nuclear devices was stopped in the early 1960's.

A policy of containment of radioactive material has been followed for higher level types of waste, including byproducts of nuclear-power generation and weapons production. The growing volume of such material increases the containment problem, however, and its ultimate disposal continues to be controversial.

Besides the nuclides produced by humans, several naturally produced species are of interest in hydrologic studies.

LEAD-210

The natural decay of radon-222 produces a series of radioactive daughter nuclides ending with the stable isotope lead-206. One of these radionuclides is lead-210, which has a half-life of 21.8 years. This beta-emitting isotope is used as a dating tool for water and sediment systems, as noted in the discussion of lead in water. Dating techniques for near-shore marine sediments, for example, were described by Smith and Walton (1980). Carpenter and others (1981) studied mechanisms of lead-210 deposition offshore from the State of Washington.

TRITIUM

Tritium, ^3H, emits low-energy beta particles and has a half-life of about 12.3 years. It is produced naturally in small amounts in the outer atmosphere and in larger amounts in nuclear reactors. Tritium in water is incorporated in water molecules. Methods for determination were described by Hoffman and Stewart (1966).

If the initial concentration of tritium in rainfall is known, a determination of the amount present in water in other parts of the hydrologic cycle permits determining the time elapsed since the water entered the system as rain. The U.S. Geological Survey has gathered data on tritium in rainfall over the United States since the 1960's (Stewart and Farnsworth, 1968; Stewart and Wyerman, 1970). The amounts present are highly variable but have tended to decrease as nuclear-weapons testing in the atmosphere decreased. Prior to weapons testing, the natural tritium content of rainwater was only about 10 tritium atoms per 10^{18} normal H atoms. The use of tritium for timing processes and(or) for other purposes in hydrology has been extensive after introductory papers appeared during the 1950's describing work done by W. F. Libby and coworkers (Begemann and Libby, 1957).

A bibliography and brief summary of tritium use in hydrology through 1966 was prepared by Rodehamel and others (1971). The bibliography contains more than 1,200 references.

CARBON-14

Another radioactive nuclide formed by cosmic-ray bombardment in the atmosphere is carbon-14. This carbon isotope occurs naturally in small amounts in atmospheric carbon dioxide and is incorporated in organic material synthesized by growing plants. Carbon-14 has a half-life of 5,730 years, and if a constant production rate is assumed it can be used as a means of determining the age of plant material such as wood or of other substances containing carbon that originated from the atmosphere at a specific time and then was cut off from further carbon-14 supplies. Ground-water movement rates were estimated by Hanshaw, Back, and Rubin (1965) using carbon-14 measurements. They calculated that the movement rate in the principal artesian aquifer of central Florida was 23 feet a year on the average over a distance of 85 miles. Pearson and White (1967) found that movement rates in the Carrizo Sand aquifer in Atascosa County, Tex., were 8 feet a year 10 miles downdip from the outcrop of the formation and 5.3 feet a year at a distance of 31 miles. The rates obtained in both studies by the carbon-14 technique agree with values calculated from hydrologic measurements. Further applications of carbon-isotope measurements in the Floridan aquifer were described by Plummer (1977).

Other possible uses of radioactive nuclides in hydrology have been the subject of many papers, but descriptions of actual applications are less common. Besides the dating studies mentioned above, some experiments have been made by adding radioactive material to water and measuring recovery at other points. An indication of the nature of pilot-type studies can be gained from the work of Kaufman and Orlob (1956). Several papers describing work on tritium as a hydrologic tool (Carlston and Thatcher, 1962; Carlston, 1964) were issued as a result of U.S. Geological Survey research. Gloyna and others (1971) used radiotracers in experimental flumes. Adding radioactive material to natural hydrologic systems obviously may be objectionable.

STRONTIUM-90

Strontium-90 has been considered one of the more undesirable of the fission products and the 1972 water quality criteria (NAS–NAE, 1972) recommend an upper limit of 2.5 pCi/L in drinking water. Later standards proposed by U.S. Environmental Protection Agency (1976a) suggest maximum concentrations of 8 pCi/L for strontium-90 and 20,000 pCi/L for tritium.

PLUTONIUM AND OTHER TRANSURANIUM ELEMENTS

Elements with atomic numbers 89–103 constitute a series analogous to the rare-earth group in the periodic table. These elements constitute the "actinide series." Like the rare-earth elements, the actinides tend to resemble each other in chemical behavior. The transuranium elements—those with atomic numbers of 93 or greater—are a subset of the actinide series. All transuranium elements are artificially produced, and all are radioactive.

Plutonium occupies position 94 in the periodic table. Besides the intentional dispersion of the element into the environment that occurred during weapons testing and nuclear blasts, plutonium is generated in nuclear reactors. Because of its 24,000-year half-life and its high toxicity, extraordinary efforts at management and control of the principal plutonium isotope, ^{239}Pu, are required. The state of knowledge of the chemistry of the element was summarized by Cleveland (1970).

Small amounts of plutonium can be detected in rainfall worldwide. For example, data collected by Thein and others (1980) in Monaco showed that ^{239}Pu commonly reached 10 or more femto (10^{-15}) curies per liter (but was widely variable). Total rainout of $^{239+240}$Pu was estimated to be 8.1 ± 0.1 pCi/m^2/year. Lesser concentrations of ^{238}Pu and ^{241}Am also were found.

Neptunium-237, an isotope of element 93, has a long half-life (2.2×10^6 years) and is a member of a radioactive decay series that begins with plutonium-241. Americium-241 (element 95), with a half-life of 500 years, is also a member of this series. Little is known about the environmental occurrence and behavior of these elements. They may require consideration in studies of radioactive-waste containment.

Organic Constituents

The intimate relationship between water in the hydrologic cycle and living matter and its waste products ensures that all natural water contains organic material. The amounts present in most waters are small compared with dissolved inorganic solute concentrations, but even small amounts can have significant effects on the chemical properties of aqueous systems. For example, various organic solutes form complexes that affect metal solubilities, participate in redox reactions, serve as nutrients for microbiota that mediate chemical processes, and influence both physical and chemical properties of solid–liquid or liquid–gas interfaces. When present in large enough concentrations, organic solutes may need to be considered in the analytical cation-anion balance, and even small concentrations of certain organic solutes can render a water unsuitable for use by humans or toxic to aquatic or other life forms.

Naturally occurring organic solutes are generally assumed to be somewhat similar to the organic material present in soils—however, their chemical properties remain incompletely understood.

Approximate determinations of the total concentration of organic material in a water sample include measurements such as "dissolved organic carbon" (DOC) and "total organic carbon" (TOC). Less specific information also may be obtained by measuring color intensity or total oxidizable material.

The properties of dissolved organic material may be evaluated in a general way by ancillary measurements such as acid-base titration and capacity for complex formation with metal ions. Techniques involving chromatographic separation and selective uptake by ion-exchange resins can be used for segregating portions of the organic solutes and concentrating them for further study. Solvent-extraction techniques also have been used for such purposes. Finally, the fractionated material can be analyzed by means of a mass spectrograph to identify specific compounds.

Dissolved and Total Organic Carbon

The determination of organic carbon is done by converting all carbon species present to carbon dioxide and correcting the subsequent determination of CO_2 for any dissolved CO_2 species that were initially present. The DOC concentration in river water has been reviewed by Meybeck (1981, 1982). He calculated an average DOC for all rivers of 5.75 mg/L, noting that the rivers of the subarctic zone have a relatively high average (19 mg/L) compared with those of tropical regions (6 mg/L) and those of temperate and arid or semiarid zones (3 mg/L). The total organic carbon transported to the ocean by rivers is from 1 to 2 percent of the primary production (through photosynthesis) of organic carbon. There is, of course, a substantial range in DOC in any given stream as well as wide differences from one drainage basin to another.

Organic-carbon concentrations in ground water normally are smaller than those in surface water, but information on actual concentrations is still scarce, and what is available refers generally to systems that have been affected by pollution. Ground water is characteristically exposed to a very large area of rock surface per unit water volume as it moves from points of recharge to points of discharge. Organics that may be present in recharge can be lost by adsorption. Evidence of adsorption of organics by stream sediment and bed material is plentiful, but available surface areas per unit volume of water in river systems are much smaller than in ground water systems.

Some ground waters may contact organic debris along the flow path to add DOC, and both dissolved and solid-phase material may serve as reactants in such processes as sulfate reduction. Thorstenson and others (1979) reported TOC values for water from the Fox Hills–basal Hell Creek aquifer of the western Dakotas ranging from 1.9 to 20 mg/L. In this area the sulfate content of the water is greatly depleted by reduction as the water moves through the system. It is evident, however, that the TOC data do not correlate with apparent loss of sulfate, suggesting that organic material from the aquifer is the principal reductant source.

Indirect Evaluation of DOC Effects

Participation of dissolved organic matter in ground water in metal oxide reduction can help explain increases in manganese and(or) iron in water withdrawn from wells near organic-carbon sources. A high DOC concentration is likely to be characteristic of leachate from landfill waste dumps (Baedecker and Back, 1979).

A substantial effect on minor metal concentration can be expected through formation of metal-organic complexes. The nature of organic compounds in solution generally is not well enough known to permit using the type of rigorous mathematical model that is being used to predict inorganic complexing and speciation, although a start in this direction was made by Mattigod and Sposito (1979). Two general approaches have been used to avoid this difficulty. One may use the actual water of interest and evaluate its interaction with added metal ions, using ion specific electrodes, or polarography to identify complexing (Sunda and Hanson, 1979). This may be appropriate for natural waters of constant composition. The second approach has been to use a model compound which is available as a pure substance and bears enough resemblance to the natural organics that it may give results similar to those observable in the field. Tannic acid has been used, for example, as a means of evaluating some features of iron chemistry in the presence of organic solutes (Theis and Singer, 1974).

In some waters organic solutes are major constituents. For example, short-chain aliphatic acid anions such as acetate, propionate, and butyrate in some places occur in water associated with petroleum (Willey and others, 1975). In such waters these ions will be partly titrated by strong acid added during the determination of alkalinity and may be erroneously reported as an equivalent amount of bicarbonate.

Color

The determination of color that is sometimes included in water analyses represents an evaluation of a physical property and has no direct chemical significance. The color of natural water usually results from leaching of organic debris. The color ranges from a pale yellow to a dark brown, and it can generally be matched fairly well by dilutions of a mixture of cobalt chloride and potassium chloroplatinate solutions. An arbitrary standard solution containing 1 g of cobalt chloride, 1.245 g of potassium chloroplatinate, and 100 mL of concentrated hydrochloric acid in a total volume of 1 L has a color rating of 500. Permanently colored glass discs are commonly used as standards with which tubes of a specific depth, containing samples of water, are compared in a color-matching device. The intensity of color is rated numerically, a color of 5 being equivalent to one-hundredth that of the standard. The color number has no direct connection with the actual amount of organic material causing the color.

Intensely colored waters occur in many different environments where vegetation is plentiful, as in swamps and bogs, from the tropical Amazon to Alaskan tundra. The materials causing the color can hardly be chemically identical in all those places. It is also rather unlikely that such materials are identical to the organic material extracted by standard soil-analysis techniques. However, the nomenclature used in soil chemistry has been carried into this aspect of water chemistry and requires consideration here. The organic fraction of soils can be partly brought into solution by treating the soil with a sodium hydroxide solution. The colored extract is further treated by acidification, which causes part of the organic material to precipitate. This acid-insoluble fraction is termed "humic acid." The acid-soluble organic matter is termed "fulvic acid" (Black and others, 1965, p. 1414–1416). These terms do not denote definite chemical compounds but are operational definitions that might imply that the materials obtained from different soils by one kind of treatment have some chemical similarity. Other names are applied by soil chemists to certain other fractions of the organic extract that can be separated using organic solvents. These are not of concern in water chemistry.

The terms "humic" and "fulvic" are widely used to refer to colored organic material in water. Without more specific identification of chemical composition and structure, such terminology conveys little useful information. Studies to characterize the materials more specifically have been made by several investigators.

Black and Christman (1963b, p. 897) reported the colored materials in water they studied were mostly of the fulvic-acid type, and they described them as polyhydroxy aromatic methoxy carboxylic acids. They found most of the colored material was particulate (Black and Christman, 1963a, p. 766) having diameters between 4.8 and 10 nm, as determined by membrane filtration and dialysis. This size range indicates that some or all the material could represent single or polymerized molecules. The equivalent weight of the material, defined as the molecular weight per mole of carboxylic plus phenolic hydrogen, was found to range from 89 to 138 (Black and Christman, 1963b). This value is in approximate agreement with some others for probably similar material. Pommer and Breger (1960), for example, reported a value of 144 for humic acid. However, the literature contains a wide range of values for molecular weights for these materials.

Continuing research on the chemistry and structure of these organics has shown that fractionation of the material by adsorption on synthetic resin may aid in characterization (Thurman and Malcolm, 1981). Lamar and Goerlitz (1966) identified 13 organic acids in colored water by gas chromatography. Most of the colored material, however, was not sufficiently volatile to be identifiable by this technique.

Complexing and adsorptive behavior of dissolved organic coloring matter toward metal ions has been of considerable interest, but it is difficult to evaluate because of the ill-defined nature of the organics. An empirical approach was used by Schnitzer (1968), who determined stability constants for a suite of metals complexed with fulvic acid extracted from a podzolic soil. It should be noted, however, that the stability constants reported by Schnitzer are applicable only to solutions having certain specified pH values. Also, the composition and behavior of fulvic or humic acid extracted from different soils may be different. Consequently, the reporting of stability constants for combinations of metal ions with these rather ill-defined organic solutes does not provide a complete understanding of the behavior of organic solutes in natural water toward metal cations. More information on the chemical composition and structure of the organic material as well as the complexes must eventually be obtained to achieve an understanding comparable to that which has been attained for many inorganic complexes. Jenne (1975) reviewed the literature on trace-element interactions with these materials.

The color of some streams in the Southeastern United States that drain swamps exceeds 200 units at times. Color below 10 units is barely noticeable to the casual observer.

Synthetic Organics

The chemical industries of the United States and other developed nations have produced and continue to produce enormous amounts of synthetic organic materials. Many of these substances do not occur naturally. Besides the various intermediate and end products of industry, substantial volumes of exotic organic wastes are generated.

End uses of many of these products tend to disperse them in the environment. The production and waste-disposal sites also can be expected to release synthetic organic chemicals and their decomposition products into the atmosphere and hydrosphere. Presence of these materials in water and the hazards thus produced have been of increasing concern in the United States during the 1980's. Programs to rectify effects of unwise waste-disposal practices have received much public attention.

Obviously, the first line of defense here should be minimizing the escape of these materials into surface and, especially, underground waters. Coping with existing and inevitable future problems relating to these materials will require a reasoned approach. The total number of potential organic chemical compounds that might escape is enormous. However, the number that pose any significant threat to potable water supplies is much smaller.

Factors that should be considered in connection with these compounds, in addition to their toxicity, include quantities produced and released, stability of the compound in aqueous systems, especially those in which organisms that might attack and consume or alter them are present, the degree to which the material might dissolve in water or be adsorbed on sediment, and such chemical properties as complexing behavior toward other solutes, especially metal ions, and interaction with hydrogen and hydroxide ions.

Over the years, attention has been directed toward various organic compounds that tend to be stable in natural aqueous systems. Phenol and cyanide (the latter is not usually considered an organic substance) were recognized as toxic pollutants and limits were fixed for them in drinking water standards established early in the 20th century.

Halogenated organics are among the more stable species in water. This was thought an advantageous feature of the persistent pesticides such as DDT and chlordane. Other substances such as the polychlorinated biphenyls (PCB's) once widely used in electrical equipment and elsewhere were purposely designed to be chemically inert. Low-boiling materials in refrigeration systems (freon, for example) or related compounds used as propellants for aerosol sprays and as dry-cleaning solvents have been widely disseminated in air and water and have even been suggested as possible hydrologic tracers or dating tools (Russell and Thompson, 1981). Specific methods have been developed for identifying compounds of these types. Most of them are hydrophobic; they have low aqueous solubilities and tend to associate with particulate surfaces. In the later 1970's, it was discovered that undesirable chlorinated hydrocarbons could be formed when waters containing natural organic solutes were treated with chlorine in the process of disinfection and sterilization.

Techniques for fractionation of organic constituents in water using ion-exchange resins followed by various elution procedures (Leenheer and Huffman, 1979) can be used to segregate organic compounds that have similar chemical properties. These procedures are useful in developing methods for analysis and in improving our understanding of both natural and synthetic organics.

In the late 1970's the U.S. Environmental Protection Agency, under the terms of a Federal court settlement, proposed a list of toxic materials termed "priority pollutants" for which it was to provide effluent limitations and guidelines. This list includes 113 specific organic compounds, 13 inorganic elements (antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc) and 3 general categories including fibrous asbestos, total cyanides, and total phenols. Some aspects of the development of the list of materials and possible means of analyses were described by Keith and Telliard (1979). The priority pollutant list is an initial effort to cope with the very difficult problems posed by synthetic organic materials in the environment.

Dissolved Gases

Several of the dissolved constituents already discussed are gases at ordinary Earth-surface conditions or are produced by reactions between gas and water. Dissolved carbon dioxide, for example, is important in relation to bicarbonate and carbonate alkalinity. Dissolved gases discussed here are principally species derived from the atmosphere or gases present in soil or at depth. Dissolved gaseous forms of nitrogen, sulfur, and carbon that are reactive have been discussed elsewhere and are not considered here.

The general thermodynamic relationship for solubility of a gas in a liquid at constant temperature is Henry's law, which was used in the discussion of carbon dioxide species earlier in this book. The concentration of a particular gas in a mixed-gas phase is represented in this relationship by its partial pressure in atmospheres. Departures from thermodynamically ideal behavior of solutes require that concentration terms in the law of mass action be expressed as activities to make them useful in thermodynamic calculations. Departure from ideal behavior by gas phase constituents requires a similar correction in Henry's law calculations. The parallel term for activity of gas phase constituents is "fugacity." For the purpose of this discussion, ideal behavior of gases is assumed—that is, the partial pressures of gases are taken as equal to their fugacities. For the range of temperature and pressure of interest in natural-water chemistry, this assumption generally is sufficiently accurate.

Inert Gases

Unreactive gases of interest or potential concern in natural water include species derived from the atmosphere including nitrogen and noble gases such as argon. Nitrogen is also produced in denitrification reactions and may be enriched in some ground waters as a result of such reactions in the soil and in unsaturated zones. Concentrations of nitrogen gas in solution have not been considered significant, and analyses rarely report such data.

Concentrations of noble gases in solution in a ground water should reflect their concentrations in the atmosphere and effects of processes that might generate or fractionate such gases at depth. Argon, for example, is produced by radioactive decay of potassium-40. Radon, also produced by radioactive decay, in this case by decay of nuclides in the uranium and thorium series, has been discussed in the section dealing with radioactive constituents. Mazor (1972) determined proportions of noble gases in some thermal ground waters from the Jordan Rift Valley, Israel, using a mass spectrometer, and used the data to estimate the origin and initial temperature of recharge.

Oxygen

The equilibrium concentration of dissolved oxygen (DO) in water in contact with air is a function of temperature and pressure, and to a lesser degree, of the concentration of other solutes. Tabulated values for DO in water in equilibrium with water-saturated air at 101.3 kilopascals (1 atmosphere) at temperatures from 0° to 50°C, and having 0 to 20,000 mg/L dissolved Cl^-, are given in "Standard Methods for the Examination of Water and Waste Water" (American Public Health Association and others, 1980, p. 392). At 5°C in freshwater the equilibrium DO value is 12.75 mg/L. At 30°C the concentration is 7.54 mg/L. Values for DO in water analyses may be given in milligrams per liter or as a percentage of saturation at the temperature of measurement.

The higher forms of aquatic life require oxygen for survival, and the DO determination is used widely in evaluations of the biochemistry of streams and lakes. The DO concentration may be depleted by processes that consume dissolved, suspended, or precipitated organic matter, and values above equilibrium can be produced in systems containing actively photosynthesizing biota. These aspects of water chemistry are not a primary object of concern in this book, important though they may be in many ways. The extent to which a supply of oxygen can be maintained in a polluted stream or lake depends in part on the hydraulic properties that influence rates at which atmospheric oxygen can be supplied in the water column; the stream can assimilate more organic or other oxidizable material without significant degradation when the rate is rapid than when it is slow (Langbein and Durum, 1967). Various mathematical models of these kinds of systems have been constructed (for example, Bauer and Bennett, 1976).

Electrodes for determining DO can be used for obtaining continuous records at field sites. The oxygen concentration in a surface water body is a dynamic indicator of the balance between oxygen-consuming and oxygen-producing processes at the moment of sampling.

Abiotic chemical reactions involving dissolved oxygen are also important, and some have already been discussed. Atmospheric oxygen is the principal electron sink for redox processes in the hydrosphere. A statement of the dissolved oxygen redox process may be written

$$O_2(aq)+2H^++4e^-=2\ OH^-.$$

In aerated water under standard conditions, this relationship predicts an Eh only a short distance below the upper water-stability line in the pH-Eh diagram. The equation, however, implies a multielectron transfer which is likely to proceed in a step-wise fashion. The mechanisms by which aqueous oxygen participates in redox processes seem not to be fully understood, but a rather complicated route involving peroxide intermediate species is commonly postulated (Latimer, 1952, p. 39–44). The oxidation intensity in aerated systems, as indicated by the apparent equilibrium distributions of oxidizable species such as iron, is much below the value predicted by the summarizing equation but is in more reasonable agreement with values predicted by the peroxide mechanism.

According to Cooper and Zika (1983), hydrogen peroxide (H_2O_2) is present in aerated natural waters exposed to sunlight, and these investigators believed its presence is related to photochemical processes mediated by organic solutes (humic material). Concentrations greater than 100 μg/L of H_2O_2 were observed in surface-water samples exposed to sunlight (1.0 watt-hour/m^2). The samples contained from 12 to 18 mg/L TOC. Similar results were obtained using ground-water samples.

Thermodynamic data of Wagman and others (1968, p. 11–13) indicate that the equilibrium concentration of H_2O_2 in aerated water is about 12 orders of magnitude smaller than the concentrations reported by Cooper and Zika (1983). However, other investigators referenced in Cooper and Zika's paper have found H_2O_2 in rainwater and seawater. Implications of these results for natural-water chemistry need further exploration. A review of the photochemical processes occurring in natural water was published by Zafiriou and others (1984).

Oxygen is supplied to ground water through recharge and by movement of air through unsaturated material above the water table. This oxygen reacts with oxidizable material encountered along the flow path of the water. Water containing measurable amounts of dissolved oxygen may penetrate long distances into the system if little reactive material is available. The principal reacting species are organic materials and reduced inorganic minerals such as pyrite and siderite. As time passes the oxidizable material in the aquifer will be removed or altered for long distances from the point of recharge.

For various reasons, determining dissolved oxygen in ground water has not been a standard practice. The dissolved-oxygen concentration of a ground water could not be used as an indicator of organic pollution. Nor would it be significant in evaluating the usability of the water for ordinary purposes. The determination would require special sampling equipment and care and would normally need to be completed immediately after sampling.

In part because few analyses have included this constituent, there is a general impression among hydrologists that most ground waters contain little or no dissolved oxygen. Actually, the water that enters ground-water systems as recharge can be expected to contain oxygen at concentrations similar to those of surface water in contact with the atmosphere, unless the recharge has encountered oxidizable material below the land surface. Buried organic matter or oxidizable minerals are plentiful enough in some systems to deplete oxygen quickly. However, in systems in which oxygen-depleting processes are less intense, ground water containing readily measurable dissolved-oxygen concentrations probably is not uncommon. Winograd and Robertson (1982), for example, reported dissolved-oxygen concentrations of 2–5 mg/L in many ground waters sampled in southern and western Arizona. It seems likely that significant concentrations of dissolved oxygen occur in ground water in many other areas.

In a study of hydrogeochemistry of a sandstone aquifer in the East Midlands of England, Edmunds and others (1982) found dissolved oxygen in significant concentrations in water that had entered the aquifer as recharge relatively recently. From the down-dip depletion of dissolved oxygen, these authors estimated a maximum time of about 5,000 years for the dissolved oxygen in recharge entering this system to be depleted to 0.1 mg/L or less under natural conditions. Such slow rates require a system that contains little oxidizable material.

Hydrocarbon Gases

Certain anaerobic bacterial processes involved in the breakdown of organic compounds produce methane, and light hydrocarbon gases from deep reservoirs can diffuse into shallower ground water. Methane is commonly present in ground water in reduced geochemical systems. Aside from being an indicator of a reducing environment, the methane has some geochemical significance as a possible mobile reductant. In wells and water-distribution facilities, methane accumulation can be a significant safety hazard because it may lead to fires or explosions.

Chemically Related Properties

The kinds of data discussed here are included in many water analyses but are not readily definable in terms of single, specific, chemical components. They may be properties resulting from the combined effects of several constituents, or they may be general evaluations of water quality that have been developed as empirical indices for certain purposes.

Residue on Evaporation

The total concentration of dissolved material in water is ordinarily determined from the weight of the dry residue remaining after evaporation of the volatile portion of an aliquot of the water sample. Total solids, total dissolved solids, and dissolved solids are terms used more or less synonymously for this value. The dissolved solids also may be calculated if the concentrations of major ions are known, and it is not always clearly indicated whether the value given in tabulated data was determined or calculated.

SIGNIFICANCE OF DETERMINATION

Although evaporating the water from an aliquot and weighing the residue seems about as simple and direct a way of measuring the solute content as could be devised, the results of such a determination can be difficult to interpret. Water is strongly retained by some types of residue. Some solutes are volatile or partly volatile at the drying temperature. Furthermore, comparison among analyses from different sources may be troublesome because different drying temperatures have been used. The American Society for Testing and Materials' (1964) procedure specifies that final drying should be for 1 hour at 103°C or 180°C (temperature to be reported in the analysis). "Standard Methods for the Examination of Water and Waste Water" (American Public Health Association and others, 1980) and the U.S. Geological Survey (Skougstad and others, 1979) also specify the 180°C temperature, but these sources do not agree on the lower temperature: The temperature specified in "Standard Methods" is 103°C–105°C, and in Skougstad and others (1979) it is 105°C–110°C. Earlier procedure manuals commonly specified only one temperature—but not always the same one.

The higher drying temperature is intended mainly to remove a higher proportion of the water of crystallization that some residues contain. The different drying temperatures, however, do not produce significantly different results for most of the more dilute natural waters compared with the other factors that may influence this determination.

At 100°C bicarbonate ions are unstable. Half are converted to water and carbon dioxide, and the other half to carbonate ions:

$$2HCO_3^- = CO_3^{-2} + H_2O(g) + CO_2(g).$$

The bicarbonate-ion content of a solution, therefore, is partly volatile, and that part does not appear in the dissolved-solids residue.

Organic matter, if present, may be partly volatile, but it is not completely removed unless the residue is strongly ignited. Some inorganic constituents such as nitrate and boron are partly volatile, and water that has a low pH generally will lose a considerable amount of its anion content when evaporated to dryness owing to volatilization of acids. On the other hand, waters high in sulfate, especially those from which crystals of gypsum are deposited, give residues containing water of crystallization that will not be removed even at 180°C.

Dissolved-solids values often are used to compute rates at which rivers transport weathering products to the ocean and to compute the rate at which rock weathering is lowering the land surface. It is an interesting fact, however, that a considerable part of the dissolved-solids load of a stream draining an igneous terrane represents bicarbonate ions that were derived from the atmosphere rather than from rocks.

Dissolved-solids values, in spite of the handicaps noted above, are widely used in evaluating water quality and are a convenient means of comparing waters with one another. The residue left after evaporation can be used as an approximate check on the general accuracy of an analysis when compared with the computed dissolved-solids value.

In regions of high rainfall and relatively insoluble rocks, dissolved-solids concentrations in runoff may be as low as 25 mg/L. A saturated sodium chloride brine, on the other hand, may contain more than 300,000 mg/L. Robinove and others (1958) assigned terms for water of high dissolved solids as follows:

	Dissolved solids (mg/L)
Slightly saline	1,000-3,000.
Moderately saline	3,000-10,000.
Very saline	10,000-35,000.
Briny	More than 35,000.

Dissolved Solids–Computed

Measurement of the dissolved mineral matter in water by evaporating an aliquot to dryness and weighing the residue has been discussed. The specific conductance of the water provides another general indication of the content of dissolved matter for water that is not too saline or too dilute. An approximate measure for water very high in dissolved solids can be obtained from its specific gravity. A fourth procedure for measuring dissolved solutes is to sum the concentrations reported for the various dissolved constituents. For certain types of water, this computed value may give a more useful indication of total dissolved-ion concentration than the residue left by evaporation. A rather complete analysis is required, however, to obtain an accurate total.

CHEMICAL FACTORS IN DISSOLVED-SOLIDS COMPUTATIONS

In developing standard procedures for computing the dissolved constituents, the assumption has generally been made that the result will be used either as a substitute for the determined residue left by evaporation or as a means of checking the analysis by comparing the computed value with the corresponding determined value. In the determination of dissolved solids, the bicarbonate ions present in solution are converted to carbonate in the solid phase. Therefore, in calculating dissolved solids, the bicarbonate is generally converted by a gravimetric factor (mg/L $HCO_3 \times 0.4917$=mg/L CO_3) that assumes that half the bicarbonate is volatilized as CO_2 and H_2O, and the computed carbonate value is used in the summation. The value obtained is thus supposed to correspond to the conditions that would exist in dry residue. The assumption that titrated alkalinity represents only OH^-, CO_3^{2-}, and HCO_3^- ions is inherent in this computation. As pointed out elsewhere, this assumption is not always correct, but it is generally a good approximation.

Even though dehydration of gypsum is supposed to be complete at 180°C, it is not uncommon for water high in calcium and sulfate concentrations to yield a residue after drying for an hour at 180°C that exceeds the computed dissolved solids by several hundred milligrams per liter. On the other hand, some waters give residues that are partly decomposed or volatilized at the drying temperature. Such effects can be observed in some waters high in magnesium, chloride, and nitrate. Other waters may yield residues that are hygroscopic and difficult to weigh, and if the water is acid ($pH<4.5$), some of the solutes may form liquids such as H_2SO_4; thus a meaningful dissolved-solids determination is perhaps impossible to obtain. In many instances, especially if the concentration is greater than 1,000 mg/L, the calculated dissolved-solids value may be preferable to the determined residue-on-evaporation value.

The computed dissolved solids value may differ from the residue-on-evaporation value by 10–20 mg/L in either a positive or negative direction when the solids concentration is on the order of 100–500 mg/L. It is evident that only major analytical or computation errors can be detected by comparing these values.

In the sixth edition of "Data of Geochemistry" (White and others, 1963) water-analysis tables include a value for "total, as reported" applicable to dissolved components in which no adjustment of bicarbonate to carbonate ions was made. These are not comparable with usual dissolved-solids values but were believed to represent a more useful total-ion content for most geochemical purposes. In comparing dissolved loads of rivers and rates of erosion by solution processes, as estimated by different authors, it is necessary to know how this kind of computation was handled.

Oxygen Demand and Other Evaluations of Organic Pollution Load

The dissolved-oxygen concentration of a water body represents the status of the system at the point and moment of sampling. The processes by which organic debris, or other kinds of material in the water, react with oxygen are relatively slow. The processes generally are biological, which means a suitable incubation and growth period is required for the organism involved. As the organisms multiply, the rate at which they use oxygen may exceed the rate at which the dissolved oxygen in the water can be replenished from the atmosphere, and the dissolved-oxygen concentration may decrease—perhaps drastically. After the processes have attained virtual completion, the normal oxygen level of the water can be reestablished. If the oxidizable load is light, the oxygen level may not be depleted much at any time. If considerable oxidizable material is present, however, the oxygen may be substantially depleted while the digestive processes are going on. A system may be so overloaded by pollutants that oxygen levels fall practically to zero and aerobic organisms are destroyed. Because considerable time may be required for the natural purification processes to become effective again, the polluted water may move through many miles of river channel with very low oxygen concentrations.

Various methods have been used to estimate the requirement of a given water for oxygen or to evaluate the organic pollution load in a quantitative way. These include measurement of biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon. The latter has already been discussed.

Biochemical Oxygen Demand (BOD)

The BOD determination is commonly made by diluting portions of a sample with oxygenated water and measuring the residual dissolved oxygen after a period of incubation (usually 5 days at 20°C). The results are commonly expressed in terms of weight of oxygen required per unit volume of the initial sample. Sometimes the pollution load of a given waste stream is expressed in terms of the human population level whose normal domestic sewage production would equal the BOD of the stream. The determination is slow to make and has no particularly direct geochemical significance, but it is extensively applied in pollution studies. It is generally considered to be a useful way of expressing stream-pollution loads and of comparing one set of conditions with another.

Chemical Oxygen Demand (COD)

To determine pollution or oxidizable material loads more quickly, wet oxidations with strong oxidizing agents have been used extensively. The results can be expressed in terms of oxygen equivalent. Heating the sample with an aliquot of standard permanganate or dichromate is one such procedure. The results of COD determinations obviously do not correspond to values obtained by BOD determinations, but they may be helpful in comparing conditions in a stream at one time with those at another time.

Hardness

The concept of hardness as an evaluation of certain chemical properties of water has become deeply imbedded in the literature of water analysis and in the habits of thought of almost everyone concerned with water quality. In spite of wide usage, however, the property of hardness is difficult to define exactly, and several definitions are in common use.

The terms "hard" and "soft" are contained in a discourse on water quality by Hippocrates (460–377 B.C.), quoted as follows by Baker (1949): "Consider the waters which the inhabitants use, whether they be marshy and soft, or hard and running from elevated and rocky situations***." The use of the terms there could have some of the modern meaning; at least limestone was probably present in many of the upland regions familiar to Hippocrates. Over the years, the property of hardness has been associated with effects observed in the use of soap or with the encrustations left by some types of water when they are heated. If the reactions with soap are the only ones considered, one might say that hardness represents the soap-consuming capacity of a water. The effect results from cations that form insoluble compounds with soap. In the mid-19th century, a procedure was developed for titration of hardness with standard soap solution.

Because most of the effect observed with soap results from the presence of calcium and magnesium, hardness is now generally defined in terms of these constituents alone, with some rather indefinite reservations about interferences (American Society for Testing and Materials, 1964, p. 391). The other ions that might precipitate soap include H^+ and all polyvalent metal cations, but they are present mostly in insignificant amounts in waters of the type that are usable domestically and for which hardness data might be obtained.

Because hardness is a property not attributable to a single constituent, some convention has to be used for expressing concentrations in quantitative terms. Usually, this consists of reporting hardness in terms of an equivalent concentration of calcium carbonate. In practical water analysis, the hardness is computed by multiplying the sum of milliequivalents per liter of calcium and magnesium by 50. The hardness value resulting is generally called "hardness as $CaCO_3$" in tabulated data. The same quantity is sometimes referred to as "calcium+magnesium hardness" or "total hardness." The usual wet-chemical procedures for determining calcium and magnesium include an amount of these metals approximately equivalent to any other alkaline-earth metals; hence, a reasonable, practical definition of hardness is "the effect of alkaline-earth cations."

Carbonate hardness, when reported, includes that part of the hardness equivalent to the bicarbonate+carbonate (or alkalinity). If the hardness exceeds the alkalinity (in milligrams per liter of $CaCO_3$ or other equivalent units), the excess is termed "noncarbonate hardness" and frequently is reported in water analyses. In some older reports the terms "temporary" and "permanent" are used instead of "carbonate" and "noncarbonate" in speaking of these subdivisions of hardness. All hardness concentrations given in this book are in terms of equivalent quantities of $CaCO_3$ in milligrams per liter.

Hardness values are reported in some European countries in terms of "degrees." One French degree is equivalent to 10 mg/L, one German degree to 17.8 mg/L, and one English or Clark degree to 14.3 mg/L, all in terms of calcium carbonate.

The soap procedure for titration of hardness has been supplanted by chelation methods for titration of the alkaline-earth metal and by spectrophotometric procedures for the individual elements. Analyses made since the late 1940's can generally be assumed not to have used the soap procedure. Modern methods give results that are far more reliable than the old procedure.

Hardness determinations have a limited value in geochemical studies. Modern analytical procedures can provide separate calcium and magnesium values practically as easily as combined ones, and the increase in usefulness of the results is well worth the trouble. In most water analyses in current literature hardness values, if reported, are probably calculated from calcium and magnesium concentrations.

RANGE OF HARDNESS CONCENTRATION

The adjectives "hard" and "soft" as applied to water are inexact, and some writers have tried to improve on this situation by adding qualifying adverbs. Durfor and Becker (1964, p.27) used the following classification.

Hardness range (mg/L of $CaCO_3$)	*Description*
0–60	Soft.
61–120	Moderately hard.
121–180	Hard.
More than 180	Very hard.

In some areas of the United States, however, where most water has a low dissolved-solids content, a water containing 50 mg/L of hardness would be considered hard by most residents.

The standards by which water hardness is judged have tended to become more rigorous over the years. Many public water supplies now are softened to less than 100 mg/L of hardness. The U.S. Public Health Service (1962) and later U.S. drinking water standards do not specify any value for hardness. The World Health Organization (1971) suggested an upper limit of 500 mg/L. According to the American Water Works Association (Bean, 1962), however, "ideal" water should not contain more than 80 mg/L of hardness.

Hardness in water used for ordinary domestic purposes does not become particularly objectionable until it reaches a level of 100 mg/L or so. Hardness can greatly exceed this level, and in many places—especially where waters have been in contact wihth limestone or gypsum—200 or 300 mg/L or more of hardness is common. Hardness becomes noticeable in all uses at these levels, and becomes increasingly troublesome as the concentration rises. In water from gypsiferous formation, 1,000 mg/L or more of hardness may be present.

In recent years, some authors have reported apparent statistical correlations between the hardness or other properties of drinking-water supplies and the death rates from cardiovascular diseases. Muss (1962) reviewed literature on this subject and expressed the belief that in a very general way the lower death rates from heart and circulatory diseases occurred in States where the public water supplies are highest in hardness. Kobayashi (1957) reported that the geographical distribution of high death rates for apoplexy in Japan seemed to suggest the high rates occurred in areas where the river waters had low alkalinity and relatively high sulfate content. All these Japanese waters, however, were relatively soft. Because many other factors affect these apparent correlations, their significance is uncertain.

A paper by Neri and others (1975) presented data from Canada supporting the hypothesis that hard water provided some protection from heart disease because of its increased magnesium content. Hopps (1979) reviewed the general subject of health in relation to the geochemical environment.

Redox Potential

In the section "Electrochemical Equilibrium" the concept of the redox potential, or Eh, of an aqueous system was introduced. It was shown that when the oxidation and reduction processes within the system are at a state of equilibrium, the Eh of the system is a function of the standard potential of the reduction half-reaction and the activities of participating species. This relationship, the Nernst equation, was used in the discussion of iron chemistry to develop pH-Eh diagrams that summarize the redox chemistry of the element.

The redox potential is a numerical index of the intensity of oxidizing or reducing conditions within a system, with the hydrogen-electrode potential serving as a reference point of zero volts. Positive potentials indicate that the system is relatively oxidizing, and negative potentials indicate that it is relatively reducing. In the notation used in this book, Eh values are given in volts. As noted earlier, the calculated pH-Eh relationships are useful for predicting and defining equilibrium behavior of multivalent elements.

If an inert metal electrode is immersed in a solution containing oxidized and reduced species, it should attain an electrical potential matching that of the redox couples in the system—assuming that a reversible equilibrium among electron-donating and electron-accepting species and the electrode surface exists. The size and sign of the potential can be evaluated if a standard electrode, having a known potential, is also immersed in the solution and both electrodes are connected to a sensitive electrometer. Most pH meters are capable of these measurements. Potentiometric measurements have been used for a long time in analytical chemistry, to determine the end point in redox titrations, for example. The inert metal electrode generally is one made of platinum.

If all the necessary requirements are fulfilled, it should be possible to measure redox potentials in natural-water systems. Such measured values would then represent the redox intensity in a manner completely analogous to the calculated or theoretical values based on ratios of solute activities and the Nernst equation. Many investigators have made measurements of this type and have interpreted them, or attempted to interpret them, with various degrees of success. ZoBell (1946) was one of the first investigators to make measurements in materials of geologic interest. A large number of published measurements on various kinds of water and sediment-water mixtures were compiled by Baas-Becking and others (1960). Measurements have been made in connection with studies of ground-water composition, especially with respect to iron chemistry (Back and Barnes, 1961, 1965; Barnes and Back, 1964b) in connection with water-treatment plant operations (Weart and Margrave, 1957), as an indication of the conditions in sewage digestors, and in numerous studies of soils, biochemical systems, and lake and ocean sediments. Redox data also were used by Clarke (1966) and by Barnes and Clarke (1969) in describing and studying causes of corrosion and encrustation of well casings. Measurements in ground water in the U.S.S.R. were described by Germanov and others (1959). A theoretical evaluation of measured redox potentials in aqueous iron systems by Doyle (1968) suggested that ferric oxyhydroxide is deposited on the platinum electrode during the measurement, giving a stable potential that is in accord with the one predicted by the Nernst equation.

The measurement of electrode potentials in natural aqueous systems that correspond to theoretical Eh values encounters many difficulties. Many redox couples do not behave in a reversible fashion at the platinum-electrode surface. Some systems may be perturbed by the presence of the electrodes, and others give mixed potentials that are influenced by several different couples. Some of these limitations were described by Stumm and Morgan (1981, p. 490–495) and by Bricker (1982, p. 59–65).

Factors that stabilize the redox potential in an aqueous system are similar to those involved in stabilizing other properties of solutions in these systems. A system whose Eh is stabilized toward the effects of minor environmental changes is said to be "poised." The poising effect can be exerted by large reserves of reactants, in the same way pH may be stabilized by buffering through reserves of reactants that interact with H^+ ions.

In its natural environment, a ground water may be poised by reactive solids or adsorbed species on solid surfaces. When brought to the land surface and into contact with air, the unpoised redox system in the water may be quickly overwhelmed by reactions involving oxygen. Solutions in contact with air give a measurable redox potential, but one that is far from the thermodynamically predicted value for the $H_2O-O_2(aq)$ couple. The mechanism establishing this potential has been ascribed to several different effects, but the effect of oxygen tends to be the dominant control on measurements of redox potential in natural water in contact with air.

Difficulty of measurement of redox potential in ground-water systems has led to suggestions by some investigators that a calculated value would be more dependable. Such calculated values can be obtained by applying the Nernst equation to determined data on activities of species participating in redox couples, with the further assumption that these activities were equilibrium values. Cherry and others (1979) suggested, for example, the use of determined values for arsenic solute species to compute Eh. Dissolved-iron concentrations can be used for this purpose in some waters (Hem and Cropper, 1959, p.17–20).

Measured redox potentials have been shown to be useful in studies of systems that can be well characterized, or that are controlled in the laboratory and in which the reactants behave reversibly. Studies related to iron chemistry have already been cited. Bricker (1965) used Eh measurements in studies of manganese chemistry. Berner (1963) and Boulegue and Michard (1979) used such measurements in evaluating reduced sulfur species.

Whether Eh values are measured or calculated, they relate to ratios of solute activities and give little or no indication of the quantitative capacity of the system to oxidize or reduce material that might be introduced from outside. Other characteristics of the system must be evaluated to apply predictive redox models.

Whatever the experimental difficulties in measuring Eh values, the usefulness of the Nernst equation and the pH-Eh diagram in generalized theoretical studies of redox equilibria in natural water is well established. The diagram is an indication of limiting conditions and is a clear, simple, and convenient means of evaluating the chemical-equilibrium status of multivalent elements in a specified environment. Techniques for preparing such diagrams are given in the discussion of iron chemistry in an earlier section of this book.

RANGE OF REDOX POTENTIAL IN NATURAL WATER

Although the data collected by Baas-Becking and others (1960) include many measurements of doubtful significance, the observed values are well clustered within the stability limits for water. At a pH of 7.0 this is a maximum range of +0.82 to -0.42 V. Values reported for ground water in Maryland (Back and Barnes, 1965) ranged from 0.471 to -0.020 V, and a value of -0.103 V was measured by Barnes and others (1964) in a flooded coal mine in Pennsylvania. The latter water had a pH of 3.92. Very low values are commonly observed in the pore water of anoxic sediments.

Sodium-Adsorption Ratio (SAR)

The U.S. Salinity Laboratory (1954) defined the sodium-adsorption ratio (SAR) of a water as

$$\mathrm{SAR} = \frac{(\mathrm{Na}^{+})}{\sqrt{\tfrac{1}{2}[(\mathrm{Ca}^{2+}) + (\mathrm{Mg}^{2+})]}},$$

where ion concentrations (in parentheses) are expressed in milliequivalents per liter. The experiments cited by the Salinity Laboratory show that the SAR predicts reasonably well the degree to which irrigation water tends to enter into cation-exchange reactions in soil. High values for SAR imply a hazard of sodium replacing adsorbed calcium and magnesium, a situation ultimately damaging to soil structure.

Values for SAR are included in chemical analyses of irrigation water and water that might be considered for that use. The value is empirical and of otherwise limited geochemical significance.

In older reports, the tendency for a water to enter into cation-exchange reactions was commonly evaluated in terms of the "sodium percentage." The sodium percentage is the percentage of total cations made up by sodium (concentrations expressed in milliequivalents per liter). Because divalent cations usually are preferentially held in exchange positions on clay minerals, the extensive displacement of Ca^{2+} and Mg^{2+} by Na^{+} is unlikely unless the sodium percentage is considerably higher than 50 or the total concentration of solutes is large.

The correlation of SAR with observable ion-exchange effects is superior to that obtained by using sodium percentage. This is probably related to the fact that the equation used for calculating SAR has the form of a mass-law equilibrium relationship, whereas the equation for sodium percentage does not.

Density

The density of a water solution is a function of temperature and the amounts and kinds of dissolved solutes. It also is influenced by pressure, but to a lesser degree. The determination of density is often included in analyses of waters of high solute content. In routine analyses made by the U.S. Geological Survey the density generally has not been determined unless the dissolved-solids concentration exceeded 7,000 mg/L. The density is usually determined to three decimal places, and the temperature at which the determination was made (usually 20°C) is given. The density of a water is a significant physical property that affects its behavior in natural systems and may influence its chemical composition in an indirect way. The density value is required to convert concentrations in weight per weight units to weight per volume units (ppm to mg/L) or the reverse. It is a useful indicator of salinity in brines in which sodium and chloride are predominant. Density effects related to temperature, solute concentrations, or suspended sediment concentration can be observed in water movements within reservoirs and lakes, and sometimes density effects may also be observed in ground-water circulation patterns.

Stable Isotopes

The hydrologic significance and use of radioactive nuclides has already been noted. Most of the elements occur naturally as mixtures of two or more stable isotopes. All the isotopes of an element exhibit the same chemical properties; however, their behavior in some kinds of physical, chemical, or biochemical processes may be influenced by their relative weights. As a result, the observed isotopic makeup of an element within a water body may be useful as an index of its history.

These differences in isotopic composition are small enough that a standard atomic weight can be specified to at least four significant figures for almost all the elements. However, with the mass spectrograph it is possible to separate and determine the quantities of isotopic components in a sample with a high degree of accuracy. This permits determinations of isotopic ratios that can be compared to an average or standard value. From the difference between observed and standard ratios the relative enrichment or impoverishment of the isotope of interest can be evaluated. An extensive literature has developed dealing with the use of stable-isotope compositions to deduce the hydrologic and geochemical factors that acted to produce these compositions.

Isotopic enrichment or impoverishment factors are reported as ±δ values computed from the formula

$$\delta_x = \frac{R_x - R_{\mathrm{STD}}}{R_{\mathrm{STD}}} \times 1{,}000$$

where R_x is the ratio of isotopes measured in the sample and R_{STD} is the ratio of the same isotopes in the reference standard. The δ_x value is in parts per thousand, commonly abbreviated "permil."

The isotopes most extensively used in hydrology are deuterium (D or hydrogen-2) and oxygen-18. These are present in average proportions of 0.01 percent and 0.2 percent of hydrogen and oxygen, respectively. For hydrologic purposes, the reference standard composition is that of average seawater (SMOW, standard mean ocean water), and relative enrichment or impoverishment of the isotope in water samples is expressed as a δ^2H or $\delta^{18}O$ departure above or below SMOW=0, in parts per thousand. Compared with deuterium, the radioactive isotope ^3H (tritium) is extremely rare. Even in the higher concentrations observed in rainfall in the United States from 1963 to 1965 (Stewart and Farnsworth, 1968), the abundance of tritium seldom reached as much as 1 tritium atom for each 10^{14} atoms of hydrogen. This is some 10 orders of magnitude below the abundance of deuterium. Deuterium and ^{18}O are of particular hydrologic significance because they produce a significant proportion of molecules of H_2O that are heavier than normal water. In the process of evaporation, the heavier molecules tend to become enriched in residual water, and the lighter species are more abundant in water vapor, rain and snow, and most freshwater of the hydrologic cycle; the heavier forms are more abundant in the ocean.

Some of the early studies of deuterium and oxygen-18 contents of water from various sources were made by Friedman (1953) and by Epstein and Mayeda (1953), and the usefulness of isotopic-abundance data in studies of water circulation has been amply demonstrated by subsequent applications. The abundance of the hydrogen isotopic species has been considered a useful key to deciding whether a water from a thermal spring contains a significant fraction of water of magmatic or juvenile origin that has not been in the hydrologic cycle previously (Craig, 1963).

Biological processes tend to produce some fractionation of isotopes. Among the studies of these effects is the paper by Kaplan and others (1960) relating to enrichment of sulfur-32 over sulfur-34 in bacterially reduced forms of the element, and the papers on fractionation of carbon-12 and carbon-13, as in fermentation and other biologically mediated processes (Nakai, 1960) or in processes related to calcite deposition (Cheney and Jensen, 1965). Nitrogen isotopes ^{14}N and ^{15}N also can be fractionated biologically. Carbon-13 has been used in developing mass-balance models of ground-water systems (Wigley and others, 1978).

Summaries of this extensive field of research have been assembled by Fritz and Fontes (1980). The fractionation factors of stable isotopes that are of geochemical interest were compiled by Friedman and O'Neil (1977). Fractionation effects are likely to be most noticeable in the lighter weight elements, as the relative differences in mass of isotopes is larger for such elements.

ORGANIZATION AND STUDY OF WATER-ANALYSIS DATA

Hydrologists and others who use water analyses must interpret individual analyses or large numbers of analyses at the same time. From these interpretations final decisions regarding water use and development are made. Although the details of water chemistry often must play an important part in water-analysis interpretation, a fundamental need is for means of correlating analyses with each other and with hydrologic or other kinds of information that are relatively simple as well as scientifically reasonable and correct. It may be necessary, for example, in the process of making an organized evaluation in a summary report of the water resources of a region, to correlate water quality with environmental influences and to develop plans for management of water quality, control of pollution, setting of water-quality standards, or selecting and treating public or industrial water supplies.

The objective of this section is to present some techniques by which chemical analyses of waters can be used as a part of hydrologic investigations. One may reasonably suppose that geologic, hydrologic, cultural, and perhaps other factors have left their mark on the water of any region. Finding and deciphering these effects is the task that must be addressed. The procedures range from simple comparisons and inspection of analytical data to more extensive statistical analyses and the preparation of graphs and maps that show significant relationships and allow for extrapolation of available data to an extent sufficient to be most practical and useful.

The use of water-quality data as a tool in hydrologic investigations of surface- and ground-water systems often has been neglected. In appropriate circumstances, chemical data may rank with geologic, engineering, and geophysical data in usefulness in the solution of hydrologic problems. Arraying and manipulating the data, as suggested in the following pages, may lead the hydrologist to insight into a problem that appears from other available information to be insoluble.

Perhaps the most significant development in the field of water-quality hydrology during the 1970's was the increasing use of mathematical modeling techniques. Some consideration of this topic is essential here, although the discussion cannot cover the subject in detail (nor would it be useful to do so in view of probable future improvements in modeling techniques). The subject of mathematical modeling will be considered further in the section of this book entitled "Mathematical Simulations—Flow Models."

Evaluation of the Water Analysis

The chemical analysis, with its columns of concentration values reported to two or three significant figures accompanied by descriptive material related to the source and the sampling and preservation techniques, has an authoritative appearance which, unfortunately, can be misleading. Although mention has already been made of some of the effects of sampling techniques, preservation methods, and length of storage before analysis on the accuracy of results, it should be noted again that many completed analyses include values for constituents and properties that may be different from the values in the original water body. Many analyses, for example, report a pH determined in the laboratory; almost certainly, such pH values deviate from the pH at time of sampling. Roberson and others (1963) published some data on the extent of such deviations. The user of the analysis also should be concerned with the general reliability of all the analytical values, including those for constituents generally assumed to be stable.

Accuracy and Reproducibility

Under optimum conditions, the analytical results for major constituents of water have an accuracy of ±2–±10 percent. That is, the difference between the reported result and the actual concentration in the sample at the time of analysis should be between 2 and 10 percent of the actual value. Solutes present in concentrations above 100 mg/L generally can be determined with an accuracy of better than ±5 percent. Limits of precision (reproducibility) are similar. For solutes present in concentrations below 1 mg/L, the accuracy is generally not better than ±10 percent and can be poorer. Specific statements about accuracy and reproducibility have not been made for most of the analytical determinations discussed in this book because such statements are meaningful only in the context of a specific method and individual analyst. When concentrations are near the detection limit of the method used, and in all determinations of constituents that are near or below the microgram-per-liter level, both accuracy and precision are even more strongly affected by the experience and skill of the analyst.

Analytical errors are at least partly within the control of the chemist, and for many years efforts have been made to improve the reliability of analytical methods and instruments and to bring about uniformity in procedures. The majority of laboratories active in the water-analysis field in the United States use procedures described in "Standard Methods for Analysis of Water and Waste Water" (American Public Health Association and others, 1980), which is kept up to date by frequent revisions. Other manuals such as those of the U.S. Geological Survey (Skougstad and others, 1979) specify much the same set of procedures.

Increasing reliance on instrumental methods and automation has been necessary in most institutional laboratories to cope with increased workloads and to control costs. These developments have both positive and negative effects on accuracy of the product. Quality control must be emphasized continually. This is usually done by submitting samples of known composition along with the samples of unknown composition. The Analytical Reference Service operated by the U.S. Environmental Protection Agency at its Taft Center laboratory in Cincinnati, Ohio, circulated many standard samples among cooperating testing laboratories that use these methods and observed many interesting and, at times, somewhat disconcerting results. The results that have been published show that when the same sample is analyzed by different laboratories, a spread of analytical values is obtained that considerably exceeds the degree of precision most analytical chemists hope to attain. The need for quality control in the production of analytical data and in methods of evaluating and improving accuracy were summarized by Kirchmer (1983).

Lishka and others (1963) summarized results of several Analytical Reference Service studies in which the spread in analytical values reported by different laboratories for the same sample were pointed out. For example, of 182 reported results for a standard water sample, 50 percent were within ±6 mg/L of the correct value for chloride (241 mg/L). The standard deviation reported for this set of determinations was 9.632 mg/L. If these results are evaluated in terms of confidence limits, or probability, assuming a normal distribution, the conclusions may be drawn that a single determination for chloride in a sample having about 250 mg/L has an even chance of being within ±6 mg/L of the correct value and that probability is 68 percent that the result will be within ±9.6 mg/L of the correct value. The probability of the result being within ±20 mg/L of the correct value is 95 percent. The results for other determinations reported by Lishka and others were in the same general range of accuracy. Before the statistical analysis was made, however, Lishka and others rejected values that were grossly in error. The rejected determinations amounted to about 8 percent of the total number of reported values. The probable accuracy would have been poorer had the rejected data been included, but it may not be too unrealistic to reject the grossly erroneous results. In practice, the analytical laboratory and the user of the results will often be able to detect major errors in concentration values and will reject such results if there is some prior knowledge of the composition of the water or if the analysis is reasonably complete. Methods of detecting major errors will be described later.

The results of a single analyst or of one laboratory should have somewhat lower deviations than the data cited above. It would appear, however, that the third significant figure reported in water analysis determinations is usually not really meaningful and that the second figure may in some instances have a fairly low confidence limit. In the data cited by Lishka and others, there is only a 5-percent chance that a chloride determination in this range of concentration would be as much as 10 percent in error. The effects of sampling and other nonanalytical uncertainty are excluded from this consideration.

Quality-control programs for U.S. Geological Survey water-analysis laboratories and laboratories of its contractors and cooperators use standard reference samples that are analyzed by all participants. Results of these analyses are released to all the laboratories taking part. Quality-assurance practices in U.S. Geological Survey investigations were described by Friedman and Erdmann (1983).

Results of an international study in which 7 water samples were analyzed by 48 different laboratories in 18 countries were reported by Ellis (1976). These results led Ellis to conclude (p. 1370): "While progress has been made in recent years in improving the standard of trace element analysis, in many laboratories the standard of water analysis for many common constituents still leaves much to be desired." The 95-percent confidence range for major constituents in Ellis' study was generally similar to that of Lishka and others (1963).

It should also be noted that in the interlaboratory studies described by Lishka and others (1963) and by Ellis (1976) the laboratories participating were aware of the special nature of the samples involved and may have given them somewhat better than routine treatment. Internal quality control practices for analytical laboratories (Friedman and Erdmann, 1983) generally utilize "blind" samples of known composition, submitted without being identified in any special way.

Organizations in Federal and State governments and other laboratories that publish analyses intended for general purposes use accuracy standards that are generally adequate for the types of interpretation to be discussed in this section of this book. The personnel at all such organizations, however, share human tendencies toward occasional error. A first consideration in acceptance of an analysis is the data-user's opinion of the originating laboratory's reputation for accuracy of results, and perhaps its motivation for obtaining maximum accuracy. Data obtained for some special purposes may not be satisfactory for other uses. For example, some laboratories are concerned with evaluating water for conformity to certain standards and may not determine concentrations closely if they are far above or far below some limiting value.

Accuracy Checks

The accuracy of major dissolved-constituent values in a reasonably complete chemical analysis of a water sample can be checked by calculating the cation-anion balance. When all the major anions and cations have been determined, the sum of the cations in milliequivalents per liter should equal the sum of the anions expressed in the same units. If the analytical work has been done carefully, the difference between the two sums will generally not exceed 1 or 2 percent of the total of cations and anions in waters of moderate concentration (250–1,000 mg/L). If the total of anions and cations is less than about 5.00 meq/L, a somewhat larger percentage difference can be tolerated. If an analysis is found acceptable on the basis of this check, it can be assumed there are no important errors in concentrations reported for major constituents.

Water having dissolved-solids concentrations much greater than 1,000 mg/L tends to have large concentrations of a few constituents. In such water, the test of anion-cation balance does not adequately evaluate the accuracy of the values of the lesser constituents.

The concept of equivalence of cations to anions is chemically sound, but in some waters it may be difficult to ascertain the forms of some of the ions reported in the analysis. To check the ionic balance, it must be assumed that the water does not contain undetermined species participating in the balance and that the formula and charge of all the anions or cations reported in the analysis are known. Solutions that are strongly colored, for example, commonly have organic anions that form complexes with metals, and the usual analytical procedures will not give results that can be balanced satisfactorily.

The determination of alkalinity or acidity by titration entails assumptions about the ionic species that may lead to errors. The end point of such a tritration is best identified from a titration curve or a derivative curve (Barnes, 1964). The use of fixed pH as the end point can lead to errors. Some ions that contribute to alkalinity or acidity may be determined specifically by other procedures and can thus appear in the ionic balance twice. For most common types of natural water this effect will not be significant. Water having a pH below 4.50 presents analytical problems because, as noted in the discussion of acidity earlier in this book, the titration is affected by several kinds of reactions and may not provide a value that can be used in reaching an ionic balance.

Many analyses that were made before about 1960 reported computed values for sodium or for sodium plus potassium. These values were obtained by assigning the difference between milliequivalents per liter of total anions determined and the sum of milliequivalents per liter of calcium and magnesium. Obviously, such an analysis cannot be readily checked for accuracy by cation–anion balance. Although calculated sodium concentrations are not always identified specifically, exact or nearly exact agreement between cation and anion totals for a series of analyses is a good indication that sodium concentrations were calculated. Modern instruments have greatly simplified the determination of alkali metals, and analyses with calculated values are no longer common.

Another procedure for checking analytical accuracy that is sometimes useful is to compare determined and calculated values for dissolved solids. The two values should agree within a few milligrams or tens of milligrams per liter unless the water is of exceptional composition, as noted in the discussion of these determinations earlier in this book. The comparison is often helpful in identifying major analytical or transcribing errors.

An approximate accuracy check is possible using the conductivity and dissolved-solids determinations. The dissolved-solids value in milligrams per liter should generally be from 0.55 to 0.75 times the specific conductance in micromhos per centimeter for waters of ordinary composition, up to dissolved-solids concentrations as high as a few thousand milligrams per liter. Water in which anions are mostly bicarbonate and chloride will have a factor near the lower end of this range, and waters high in sulfate may reach or even exceed the upper end. Waters saturated with respect to gypsum (analysis 3, table 15, for example) or containing large concentrations of silica may have factors as high as 1.0. For repeated samples from the same source, a well-defined relationship of conductivity to dissolved solids often can be established, and this can afford a good general accuracy check for analyses of these samples. The total of milliequivalents per liter for either anions or cations multiplied by 100 usually agrees approximately with the conductivity in micromhos per centimeter. This relationship is not exact, but it is somewhat less variable than the relationship between conductivity and dissolved solids in milligrams per liter. The relationship of dissolved solids to conductance becomes more poorly defined for waters high in dissolved solids (those exceeding about 50,000 mg/L) and also for very dilute solutions, such as rainwater, if the nature of the principal solutes is unknown. For solutions of well-defined composition such as seawater, however, conductivity is a useful indicator of ionic concentration.

A simple screening procedure for evaluating analyses for the same or similar sources is to compare the results with one another. Errors in transcribing or analytical error in minor constituents containing factors of 2 or 10 sometimes become evident when this is done. It is common practice, however, to make this type of scrutiny before data are released from the laboratory, and it is most useful to do it before the sample is discarded so that any suspect values can be redetermined.

Analyses reporting calculated zero values for sodium or indicating sodium concentration as less than some round number commonly result from analytical errors causing milliequivalents per liter for calcium and magnesium to equal or exceed the total milliequivalents per liter reported for anions; thus, there is nothing to assign to sodium for calculation purposes. A zero concentration for sodium is rarely found if the element is determined.

Certain unusual concentration relationships among major cations can be considered as grounds for suspicion of the analysis' validity. A zero value for calcium when more than a few milligrams per liter are reported for magnesium, or a potassium concentration substantially exceeding that of sodium unless both are below about 5 mg/L, are examples. This is not to say that waters having these properties do not exist. They are rare, however, and should be found only in systems having unusual geochemical features.

Groups of analyses from the same or similar sources in which all magnesium concentrations are similar but calcium concentrations have a rather wide range may indicate that calcium and bicarbonate were lost by precipitations of calcium carbonate. This can occur in water-sample bottles during storage and also in the water-circulation system before sampling.

Significant Figures

Water analyses in which concentrations in milligrams per liter are reported to four or five significant figures are commonly seen. The notion of high accuracy and precision conveyed by such figures is misleading, because ordinary chemical analytical procedures rarely give better than two-place accuracy. Usually, the third significant figure is in doubt, and more than three is entirely superfluous. Analytical data in terms of milliequivalents per liter in the tables in this book were calculated from the original analytical data in mg/L. They are routinely carried to two or three decimal places but are not accurate to more significant figures than the mg/L values.

A concentration of 0 mg/L reported in chemical analyses in this book should be interpreted as meaning that the amount present was less than 0.5 mg/L and that the procedure used could not detect concentrations less than 0.5 mg/L. Concentrations of 0.0 or 0.00 mg/L imply lower detection limits. Some analysts report such findings in terms such as "<0.05 mg/L" when the figure given is the detection limit. These values should not be interpreted as indicating that any specific concentrations of the element was present. Other authors may use different conventions.

General Evaluations of Areal Water Quality

The type of water-analysis interpretation most commonly required of hydrologists is preparation of a report summarizing the water quality in a river, a drainage basin, or some other areal unit that is under study. The writer of such a report is confronted with many difficulties. The chemical analyses with which the writer must work usually represent only a few of the water sources in the area and must be extrapolated. The finished report must convey water-quality information in ways that will be understandable both to technically trained specialists and to interested individuals less familiar with the field. Conclusions or recommendations relating to existing conditions or to conditions expected in the future are usually required.

As an aid in interpreting groups of chemical analyses, several approaches will be cited that can serve to relate analyses to each other and to provide means of extrapolating data areally and temporally. Different types of visual aids that are useful in reports will be described. The basic methods considered are inspection and simple mathematical or statistical treatment to bring out resemblances among chemical analyses, procedures for extrapolation of data in space and time, and preparation of graphs, maps, and diagrams to show the relationships developed.

The final product of many hydrologic studies is now expected to be a mathematical model that can relate observable effects to specific causes and can provide a basis for predicting quantitatively the future behavior of the system studied.

Mathematical modeling of water quality is commonly thought of as representing the application of the modern electronic computer in the field of chemical hydrology. It is clear, however, that the principles on which such models are designed and the application of these principles through relationships of physics and chemistry for quantitative prediction of solute behavior are not new. The computer has made such applications simpler and more practicable. Its ability to solve complex problems holds bright promise for future applications.

Inspection and Comparison

The first step in examining water analyses, after accepting their reliability, is generally to group them by hydrologic or geologic categories, as appropriate. After this has been done, simple inspection of a group of chemical analyses generally will make possible a separation into obviously interrelated subgroups. For example, it is easy to group together the waters that have dissolved-solids concentrations falling within certain ranges. The consideration of dissolved solids, however, should be accompanied by consideration of the kinds of ions present as well.

A common practice in literature on water quality is to refer to or classify waters by such terms as "calcium bicarbonate water" or "sodium chloride water." These classifications are derived from inspection of the analysis and represent the predominant cation and anion, expressed in milliequivalents per liter. These classifications are meant only to convey general information and cannot be expected to be precise. They may, however, be somewhat misleading if carelessly applied. For example, a water ought not be classed as a sodium chloride water if the sodium and chloride concentrations constitute less than half the total of cations and anions, respectively, even though no other ions exceed them. Water in which no one cation or anion constitutes as much as 50 percent of the totals should be recognized as a mixed type and should be identified by the names of all the important cations and anions.

Ion Ratios and Water Types

Classifications of the type just described are only rough approximations, and for most purposes in the study of chemical analyses a more exact and quantitative procedure is required. Expression of the relationships among ions, or of one constituent to the total concentration in terms of mathematical ratios, is often helpful in making resemblances and differences among waters stand out clearly. An example of the use of ratios is given in table 21, in which three hypothetical chemical analyses are compared. All three analyses could be considered to represent sodium bicarbonate waters, and they do not differ greatly in total concentration. The high proportion of silica in waters B and C, their similiar Ca:Mg and Na:Cl ratios, and their similiar proportions of SO_4 to total anions establish the close similarity of B and C and the dissimilarity of both to A. For most comparisons of this type, concentration values expressed in terms of milliequivalents per liter or moles per liter are the more useful, although both gravimetric and chemically equivalent units have been used. Data in the latter form show more directly the sort of 1:1 ionic relationship that would result if solid NaCl were being dissolved.

The data in table 21 are synthetic, and actual analyses often do not show such well-defined relationships. Ratios are obviously useful, however, in establishing chemical similarities among waters, for example, in grouping analyses representing a single geologic terrane, or a single aquifer, or a water-bearing zone. Fixed rules regarding selection of the most significant values to compare by ratios cannot be given, but some thought as to the sources of ions and the chemical behavior that might be expected can aid in this selection. The ratio of silica to dissolved solids may aid in identifying water influenced by the solution of silicate minerals, and the type of mineral itself may be indicated in some instances by ratios among major cations (Garrels and MacKenzie, 1967). The ratio of calcium to magnesium may be useful in studying water from limestone and dolomite (Meisler and Becker,

1967) and may help in tracing seawater contamination. The ratio of sodium to total cations is useful in areas of natural cation exchange. The ratio of chloride to other ions also may be useful in studies of water contaminated with common salt (sodium chloride).

The study of analyses using ratios has many undeveloped possibilities. Schoeller (1955) made some suggestions for the use of ratios in connection with water associated with petroleum, and White (1960) published a set of median ratios of ion concentrations in parts per million which he believed to be characteristic of water of different origins (ratios are included for all the analyses of ground waters given by White and others (1963)). An ion-ratio calculation technique using molar concentrations of Na, K, and Ca proposed by Fournier and Truesdell (1973) has been widely used for estimating temperatures of geothermal reservoirs.

Extensions of the concept of ion ratios to develop comprehensive water-classification schemes have appeared in the literature from time to time. Most of these schemes are not simple two-ion ratios, but are attempts to express proportions of all the major ions within the total concentration of solutes.

The principal classification schemes that have been proposed in the literature have been reviewed well by Konzewitsch (1967), who also described the principal

Table 21. Hypothetical chemical analyses compared by means of ratios

[Date below sample letter is date of collection]

Constituent	A Jan. 11, 1950		B Feb. 20, 1950		C Mar. 5, 1950	
	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
Silica (SiO_2)	12	...	33	...	30	...
Iron (Fe)	...	...	...	...	...	...
Calcium (Ca)	26	1.30	12	.60	11	.55
Magnesium (Mg)	8.8	.72	10	.82	9.2	.76
Sodium (Na) Potassium (K)	73	3.16	89	3.85	80	3.50
Bicarbonate (HCO_3)	156	2.56	275	4.51	250	4.10
Sulfate (SO_4)	92	1.92	16	.33	15	.31
Chloride (Cl)	24	.68	12	.34	12	.34
Fluoride (F)	.2	.01	1.5	.08	1.2	.06
Nitrate (NO_3)	.4	.01	.5	.01	.2	.00
Dissolved solids:						
Calculated (mg/L)	313	...	309	...	282	...
Calculated (tons per acre-ft)	.42	...	.42	...	.38	...
Hardness as $CaCO_3$:						
Ca and Mg	101	...	71	...	66	...
Noncarbonate	0	...	0	...	0	...
Specific conductance (micromhos at 25°C).	475	...	468	...	427	...
pH	7.7	...	8.0	...	8.1	...

Comparison of analyses of the samples

Sample	SiO_2 (mg/L) / Dissolved solids (mg/L)	Ca (mg/L) / Mg (mg/L)	Na (mg/L) / Cl (mg/L)	SO_4 (mg/L) / Total anions (mg/L)
A	0.038	1.8	4.6	0.37
B	.11	.73	11.3	.063
C	.11	.72	10.3	.064

graphical methods that have been used. Some classification methods and graphs also were described by Schoeller (1962). Some of the schemes are elaborate, recognizing more than 40 types of water.

Although some practical and theoretical usefulness can be claimed for chemical classification schemes, a higher level of sophistication is generally needed to identify useful chemical hydrologic relationships. Interest in developing new kinds of chemical classifications of water apparently has declined, as few papers on this topic have been published in recent years.

Statistical Treatment of Water-Quality Data

Various simple procedures such as averaging, determining frequency distributions, and making simple or multiple correlations are widely used in water-analysis interpretation. More sophisticated applications of statistical methods using digital computers have come into wide use. The labor inherent in examining a large volume of data is thus greatly decreased. Before applying statistical techniques, however, one must develop some conception of the systems being treated and of the kinds of inferences that could be derived. The literature of all fields of science abounds with questionable applications of statistical procedures. In general, demonstrating statistical correlations does not establish cause and effect. Rather, the factors that may be controlling water composition should be recognized in advance and the statistical methods then used to select and help verify the more likely ones.

Averages

The average of a group of related numerical values is useful in water-quality studies in various ways, but the principal application has been in the analysis of records of river-water composition. The composition of water passing a fixed sampling point is characteristically observed to vary with time. A series of measurements over a given time period can, if means and extremes of concentration are correctly represented, provide an average that summarizes the record for that time period. Continuous records of conductivity are commonly reduced to daily average values for publication. Longer term averages may be computed to summarize a month or a year of record if the data are complete enough, as is common practice for water-discharge data. Other kinds of analytical data can sometimes be conveniently summarized by averaging. The analyses of composites of daily samples that constitute much of the U.S. Geological Survey stream-quality record before about 1970 were published in annual reports with an average computed for the year for most sampling points.

One of the potential uses of averages of analytical data is in computing loads of solutes transported by a stream. The concentrations of solutes generally are decreased by increases in stream discharge, and if this effect is substantial a time-based average of concentrations should not be used for load computations. A discharge-based, or discharge-weighted, average is more appropriate for solute-load computations. Such an average is obtained by multiplying each concentration value by the stream discharge applicable to that sample, summing these products, and dividing by the sum of the discharges. If the solution analyzed is a composite made up from several field samples, the volumes used from each sample to prepare the composite should be proportional to the discharge rate at the time that sample was collected.

Average compositions computed in different ways for a sampling station on the Rio Grande in New Mexico were given in earlier editions of this book. They showed that for some constituents the time-weighted annual average gave concentrations 40 percent greater than those given by the discharge-weighted average for the same year. For most constituents the effect was smaller.

As new modes of operation of river-quality data programs have evolved, the computation of average analyses has been deemphasized. For example, at stations in the NASQAN network, daily or continuous conductivity measurements are supplemented with a single monthly or quarterly sample for complete chemical and other determinations. Averages of the monthly data are not published. Many other sampling stations now follow a similar protocol.Trends and correlations that can be developed from a long-term record of this type can be considerably more useful than simple annual averages. As will be shown later in this book, the annual discharge-weighted average is not a very sensitive indicator of hydrologic conditions or trends.

A discharge-weighted average tends to emphasize strongly the composition of water during periods of high flow rate. A reliable record of flow must be available for such periods, with sufficient frequency of sampling to cover the possible changes of water composition. Many discharge-weighted averages have been estimated for chemical analyses of the composites of equal volumes of daily samples. The composition of a composite made in this way is not directly related to the water discharge during the composite period. However, if either discharge or concentration does not change greatly during the period of the composite, the analysis can be used to compute a weighted average without serious distortion of the final result.

The discharge-weighted average may be thought of as representing the composition the water passing the sampling point during the period of the average would have had if it had been collected and mixed in a large reservoir. Actually, reservoir storage could bring about changes in the composition of the water owing to evaporation and other complications such as precipitation of some components; however, the discharge-weighted average does give a reasonably good indication of the composition of water likely to be available from a proposed storage reservoir and is useful in preconstruction investigations for water-development projects.

Averages weighted by time are useful to water users or potential users who do not have storage facilities and must use the water available in the river. The discharge-weighted average is strongly affected by comparatively short periods of very high discharge, but the influence of high flow rate on the chemistry of the river flow observable at a point is quickly dissipated when discharge returns to normal.

Important facts relating the composition of river water to environmental influences may be brought out by means of averages of several kinds, by using time periods that have been judiciously selected and with some knowledge of the important factors involved.

In the early literature of stream-water quality, the influence of discharge rate was sometimes considered a simple dilution effect. If this premise is accepted, the composition of the water could be represented for all time by a single analysis in which the results are expressed in terms of percentages of the dry residue. Clarke (1924a, b) gave many analyses for river water expressed in this way. Although the assumption that the water at any other time could be duplicated by either dilution or concentration is obviously a gross oversimplification, this way of expressing analyses makes it possible to compare the composition of streams and to make broad generalizations from sketchy data. In Clarke's time, this approach was about the only one possible. It should not be necessary to belabor the point that the composition of the water of only a few rivers can be characterized satisfactorily solely on the basis of dilution effects.

Frequency Distribution

A useful generalization about an array of data, such as a series of chemical analyses of a stream, often may be obtained by grouping them by frequency of occurrence. Figure 23 is a duration diagram showing the dissolved-solids concentration of water in the Colorado River at Grand Canyon, Ariz., from 1926 to 1955 (essentially uncontrolled at that time) compared with the dissolved solids in the outflow at Hoover Dam, the next downstream sampling point from 1937 to 1955. Although the periods of record do not completely coincide, the curves show that the water is much less variable in composition as a result of storage in Lake Mead above Hoover Dam. The median point (represented by 50 percent on the abscissa) for dissolved solids is also higher for the water at Grand Canyon than for virtually the same water after storage, mixing, and release at Hoover Dam. Daily conductivity values for a period of record may be summarized conveniently by a graph of this type. Figure 24 shows this kind of information for the Ohio River and its two source streams, the Allegheny and Monongahela Rivers in the vicinity of Pittsburgh, Pa. Figures 23 and 24 are time distributions.

A frequency distribution for percent sodium in ground waters from wells in the San Simon artesian basin of Arizona is shown in figure 25. The clustering pattern shown by these data indicates that the waters were of two types, which were identified as occurring in separate areas of the basin. This distribution is not related to time. Other applications of frequency distributions obviously are possible. This type of graphic presentation may be considered most useful as a means of summarizing a volume of data and often gives more information than a simple mean or median value alone would give.

Solute Correlations

The examination of an array of water analyses frequently involves a search for relationships among constituents. Determining the existence of correlations that are sufficiently well defined to be of possible hydrologic or geochemical significance has sometimes been attempted in a random fashion, for example, by preparing many scatter diagrams with concentrations of one component as abscissa and another as ordinate. Commonly, one or more of the diagrams give a pattern of points to which a regression line can be fitted. The statistical procedures for fitting the line, and the evaluation of goodness of fit by a correlation coefficient, provide a means of determining the apparent correlation rather closely in a numerical way. The significance of the correlation in a broader sense, for example, as the indicator of a particular geochemical relationship, is, however, likely to be a very different matter.

Random correlation procedures of the type suggested above are too laborious to do by hand if many analyses are used, but the electronic computer has made this type of correlation a simple process. Accordingly, a wide variety of calculations of this kind could be made, and their significance evaluated later should this procedure offer any reasonable promise of improving the investigator's understanding of hydrochemical systems.

The difficulties of interpreting random correlations are substantial. The chemical analyses of a series of more or less related samples of water have certain internal constraints that may result in correlations that have slight hydrologic or geochemical significance. For example, the total concentration of cations in milliequivalents per liter in each analysis must equal the total concentration of anions expressed in the same units. If many of the waters in the group being studied have one predominant anion and one predominant cation, these two constituents may have a good mutual correlation. Some of this effect may also be noticeable among less abundant constituents because their concentrations also represent a part of the ionic balance of each analysis. A correlation between calcium and bicarbonate concentrations exists in many waters. Calcium, however, can be derived from many different sources and bicarbonate is produced in most weathering processes involving dissolved carbon dioxide. A test for departure from calcite solubility equilibrium is more meaningful.

Before attempting to make correlations among ions in solution, the investigator should set up hypothetical relationships that might reasonably be expected to hold and then proceed to test them with the data. Two kinds of relationships that might be anticipated will be described here. The first represents the simple solution of a rock mineral with no other chemical processes that could alter the proportions of dissolved ions. This relationship is based on simple stoichiometry, requires no chemical equilibria, and generally postulates a molar ratio between dissolved ions equal to the mole ratio of these ions in the source mineral. The second type of relationship, one that is common, is more complex. In it, concentrations of ions may rise freely until saturation with respect to one or more species is reached. From this point on, the concentrations are controlled by chemical equilibria.

Suppose it is desired to check the validity of assuming that the sodium and chloride concentrations shown by a series of analyses of a river water or of samples from various locations in a ground-water body have been derived from solution of common salt, NaCl. These two ions will be brought into solution in equal quantity and retained in solution over a wide concentration range because of the rather high solubility of both ions. Over this range one might expect

$$C_{\mathrm{Na}}=nC_{\mathrm{Cl}},$$

where the C terms are ion concentrations and n is the conversion factor required to make the units in which C terms are reported chemically equivalent. If the values of

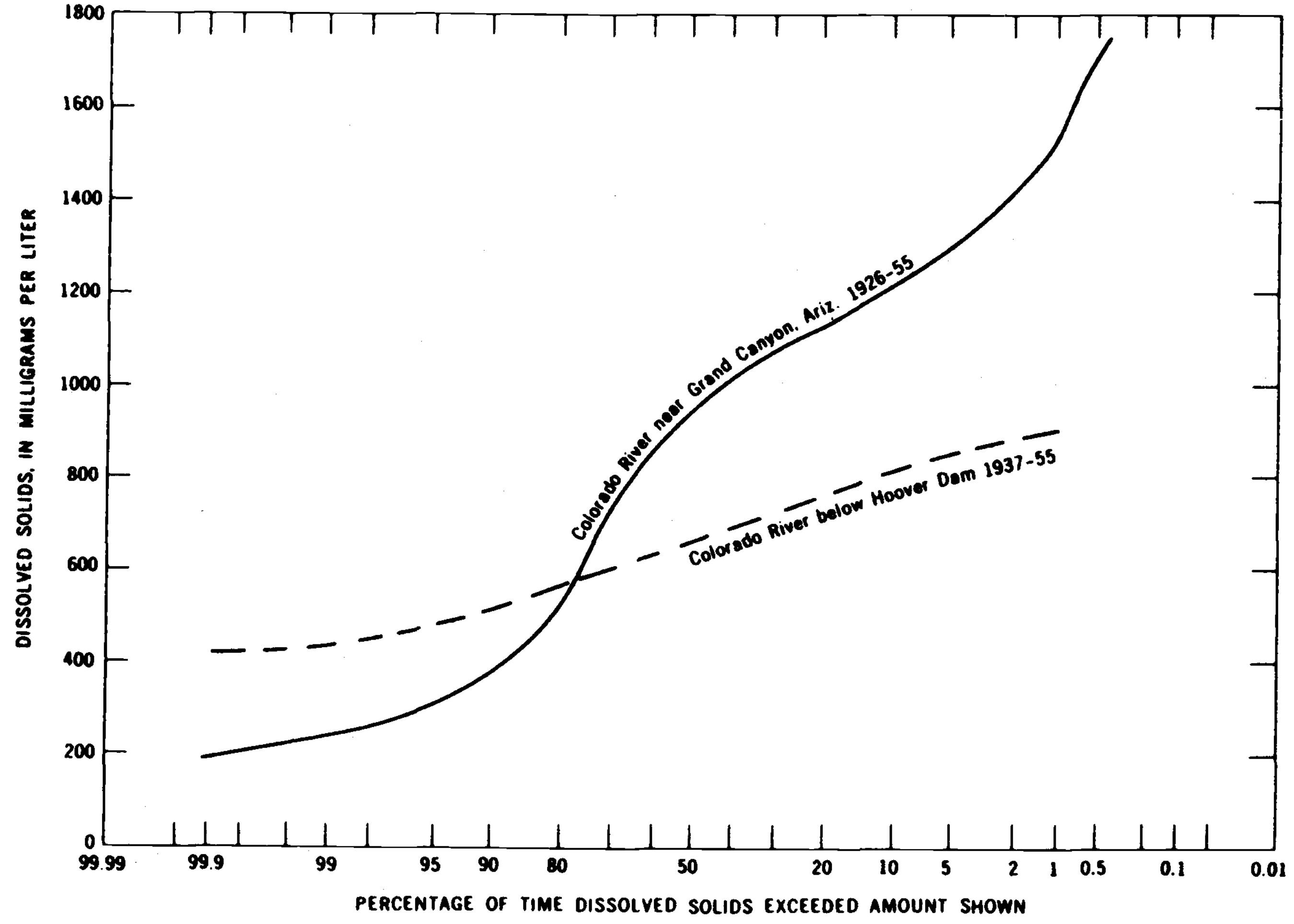


Figure 23. Cumulative frequency of dissolved solids concentrations for Colorado River above and below Hoover Dam, Ariz. and Nev., for time periods indicated.

C are in milliequivalents per liter, $n=1$. If data are in milligrams per liter, n is the ratio of the combining weight of sodium to the combining weight of chloride, or 0.65.

If the data fit the assumption, a plot of the concentration of sodium versus the concentration of chloride should give a straight line of slope 1.0 or 0.65, depending on units used. Curvature of the line or deviation from the two permissible slopes indicates that the hypothesis is incorrect. If one plots log C_{Na} versus log C_{Cl}, a straight line also should be obtained, but it will have a slope of 1.0 and an intercept of log n.

Figure 26 is a plot of sodium concentrations versus chloride concentrations, in meq/L, for samples from the Gila River at Bylas, Ariz. The curved part of the regression line shows that sources of the ions other than common salt are involved, although at the higher concentrations the theoretical slope of 1.0 is closely approached.

The correlation cited above does not involve much chemistry and is too simplified to have much practical value. If considerations of solubility are involved, the constituents may be correlated in a different way. For example, the solution of calcium and sulfate can continue only up to the solubility limit of gypsum. When this level is reached, at equilibrium the solubility-product relationship would hold. The two conditions would be (1) for dilute solutions,

$$C_{\mathrm{Ca}}{}^{2+}=nC_{\mathrm{SO}_4}{}^{2-},$$

and (2) at saturation,

$$[\mathrm{Ca}^{2+}]\,[\mathrm{SO}_4{}^{2+}]=K_{\mathrm{sp}},$$

where K_{sp} is the solubility product.

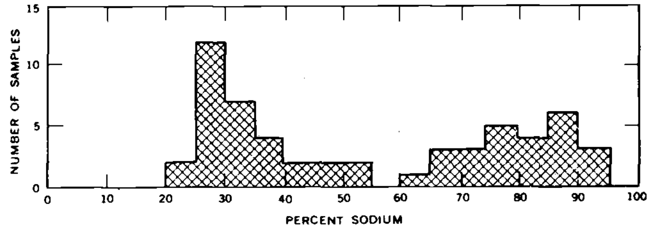
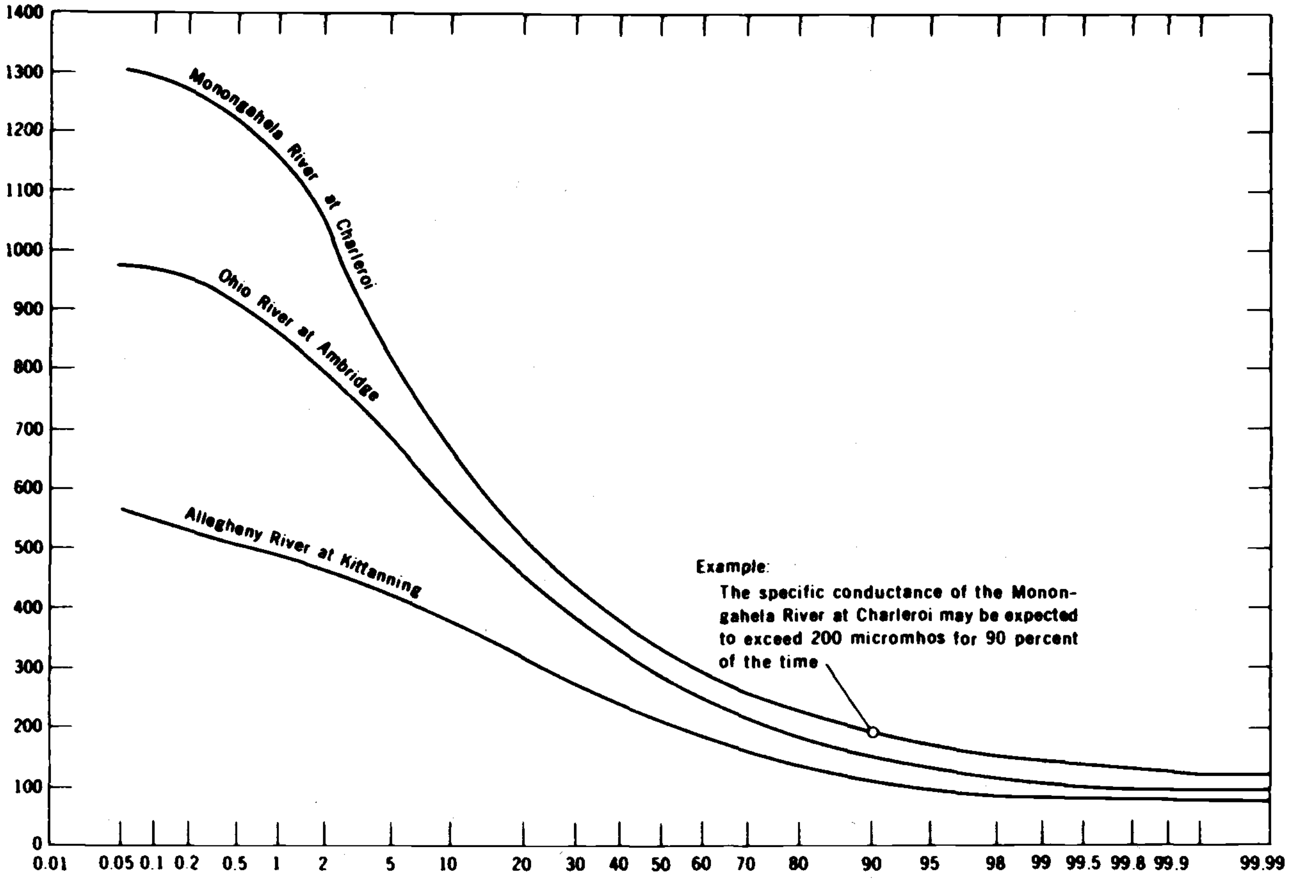


Figure 25. Number of water samples having percent-sodium values within ranges indicated, San Simon artesian basin, Arizona.



Example:
The specific conductance of the Monongahela River at Charleroi may be expected to exceed 200 micromhos for 90 percent of the time

Figure 24. Cumulative frequency of conductance, Allegheny, Monongahela, and Ohio River waters, Pittsburgh area, Pennsylvania, 1944-50.

If the influence of ionic strength and ion-pair formation are ignored for the moment, one could represent the second equation in terms of concentrations rather than activities so that the same variables would be present in both expressions. All concentrations are expressed in moles per liter.

The first equation would give a straight line if calcium concentrations were plotted against sulfate. The second equation, however, is for a hyperbola, and therefore an attempt to make a linear correlation of a group of analyses, including concentrations affected by both relationships, is likely to give ambiguous results. If both expressions are placed in logarithmic form, as follows, however, both give straight lines:

$$\log C_{\mathrm{Ca}} = \log C_{\mathrm{SO_4}}$$

and

$$\log C_{\mathrm{Ca}} = \log K' - \log C_{\mathrm{SO_4}}.$$

The first relationship should hold up to the point where precipitation of gypsum begins, and the second, thereafter. A break in slope of the regression line would occur at that point. It should be noted that in this example K' is a conditional equilibrium constant that includes the effects of ionic strength and ion-pairing. Therefore, the value of K' increases as concentrations increase, and the nature of the correlation under conditions of saturation is more complex than this treatment implies.

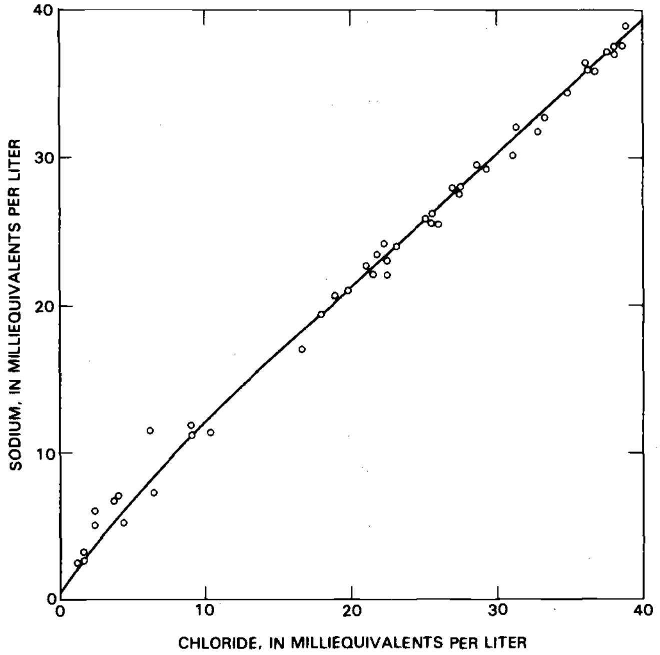


Figure 26. Relationship of chloride to sodium, Gila River at Bylas, Ariz., October 1, 1943, to September 30, 1944.

This is a very simple form of a reaction-path simulation. A model of this type uses a series of equilibria or stoichiometric processes to explain changes in composition observed along the flow path of water in an aquifer or other system of interest. Geochemical models using this approach were described by Plummer and others (1983). A similar progression of controls can be observed during the process of evaporation.

A more complicated equilibrium is that for calcite solubility; it involves three variables, as noted earlier:

$$\frac{[\mathrm{Ca}^{2+}]\,[\mathrm{HCO_3^-}]}{[\mathrm{H}^+]} = K_s.$$

This could still be converted to a two-variable relationship by combining the bicarbonate and hydrogen ion into a single term, as follows:

$$[\mathrm{Ca}^{2+}] \cdot \frac{[\mathrm{HCO_3^-}]}{[\mathrm{H}^+]} = K_s$$

$$\log\,[\mathrm{Ca}^{2+}] + \log \frac{[\mathrm{HCO_3^-}]}{[\mathrm{H}^+]} = \log K_s.$$

However, a more useful graphical technique for representing this equilibrium by itself is to use a pH overlay on a plot of log $[\mathrm{Ca}^{2+}]$ versus log $[\mathrm{HCO_3^-}]$ as in plate 2. The applicability and potential modifications of this diagram were discussed in the section of this book dealing with calcium chemistry.

The degree to which correlations of the types mentioned above can be obtained is of geochemical significance in many systems. Analyses may be checked for conformance to equilibrium with several solids at once. For example, one might want to examine data for equilibrium with gypsum and calcite. Figure 27 is one approach to this type of correlation. Several analyses from tables 11 and 15 are plotted in the diagram. This relationship also could be represented as

$$\mathrm{CaCO_3(c)} + \mathrm{H}^+ + \mathrm{SO_4^{2-}} = \mathrm{CaSO_4(c)} + \mathrm{HCO_3^-},$$

$$\frac{[\mathrm{HCO_3^-}]}{[\mathrm{H}^+]} \cdot [\mathrm{SO_4^{2-}}] = K,$$

or

$$\log \frac{[\mathrm{HCO_3^-}]}{[\mathrm{H}^+]} + \log\,[\mathrm{SO_4^{2-}}] = \log K,$$

where K is a combination of the two constants for the solubility equilibria for gypsum and calcite.

There are other combinations of equilibria that might be significant in ground-water systems and at low flow in some streams. For example, the relationship of cation-exchange equilibria in soil to the solubility of calcite could be studied in this way.

The abscissa and ordinate in figure 27 represent ion-activity products for the calcite-solubility equilibrium and the solubility-product equation for gypsum. Values greater than the equilibrium constant indicate supersaturation with respect to these two solids. The activities of the ions must be calculated from analytical concentrations with due attention to the effects of ionic strength and complex or ion-pair formation. Irrigation drainage water in some areas evolves to a composition that is near saturation with respect to both solids (Hem, 1966).

A study by Feth and others (1964) of water composition associated with granitic rocks uses diagrams on which areas of stability for different rock minerals are shown in terms of activity of silica as abscissa and ratios of sodium or potassium to hydrogen activity as ordinate. These diagrams follow models used by Garrels and Christ (1964, p. 352–378) and have been used widely in evaluating the effects of the weathering of silicate rocks. However, some of the reactions involved in silicate dissolution and clay-mineral synthesis are incongruent, and these stability diagrams, which are based on assumed thermodynamic equilibrium, have only a limited usefulness in predicting solute concentrations to be expected in natural systems.

The development of computerized chemical models makes it possible to handle systems that are more complex than these simple examples. The characteristics of various models were summarized by Nordstrom, Plummer, and others (1979). The models can test water analyses for possible equilibrium with a large number of minerals, over a range of temperatures and ionic strengths.

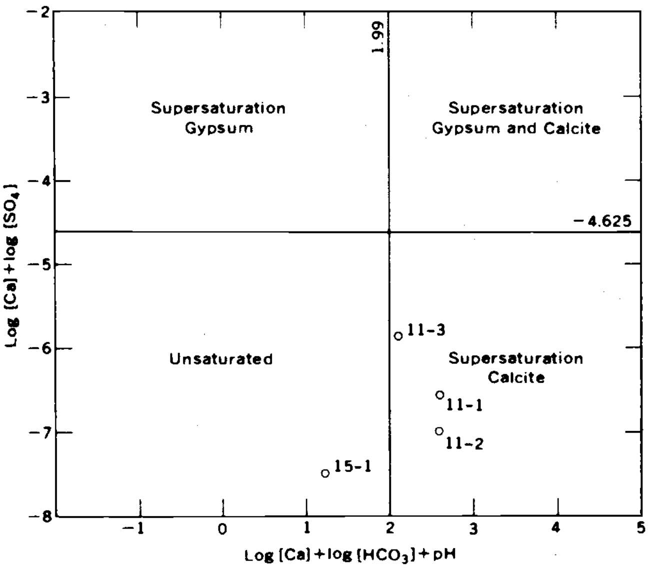


Figure 27. Calcite and gypsum equilibrium solubility relationships, 25°C and 1 atmosphere pressure. Plotted points represent analytical data from tables 11 and 15 (e.g., "11-1"=table 11, analysis 1).

The statistical technique, factor analysis, has been used by some investigators to develop or refine correlations among solutes and environmental factors. Dawdy and Feth (1967) used this approach to study controls of ground-water composition in the Mojave River valley near Victorville, Calif. The first of a series of four papers (Reeder and others, 1972) on chemistry of water and sediments in the Mackenzie River system in Canada used this technique to aid in the assignment of sources to the solute load of this large northern river.

Graphical Methods of Representing Analyses

Over the years, a considerable number of techniques for graphical representation of analyses have been proposed. Some of these are useful principally for display purposes—that is, to illustrate oral or written reports on water quality, to provide means for comparing the analyses with each other, or to emphasize differences and similarities. Graphical procedures do this much more effectively than numbers presented in tables.

In addition to the types of graphs suitable for displays and comparison of analyses, graphical procedures have been devised to help detect and identify mixing of waters of different composition and to identify some of the chemical processes that may take place as natural waters circulate. Graphing techniques of the latter type may be useful in the study of data prior to preparing reports or arriving at conclusions. Some of the graphical techniques that appear to be useful are described here, but this discussion is not intended to include all the methods that have been suggested in the literature. Graphing of water analyses is a study technique and not an end in itself.

Ion-Concentration Diagrams

Most methods of graphing analyses are designed to represent simultaneously the total solute concentration and the proportions assigned to each ionic species for one analysis or a group of analyses. The units in which concentrations are expressed in these diagrams generally are milliequivalents per liter.

In the ion-concentration graphing procedure originated by the late W. D. Collins (1923), each analysis is represented by a vertical bar graph whose total height is proportional to the concentration of determined anions or cations, in milliequivalents per liter. The bar is divided by a vertical line, with the left half representing cations and the right half anions. These segments are then divided by horizontal lines to show the concentrations of the major ions, and these ions are identified by distinctive colors or patterns. Usually six divisions are used, but more can be used if necessary. The concentrations of closely related ions are often added together and represented by a single pattern.

An example of Collins' ion-concentration graphing procedure representing four analyses from tables in this book is given in figure 28. (The other graphing procedures discussed here are for the most part illustrated with the same four analyses.) The Collins' system as described does not consider nonionic constituents, but they may be represented, if desired, by adding an extra bar or other indicating device with a supplementary scale. In figure 29, the hardness of two waters is shown. The hardness in milligrams per liter as $CaCO_3$ is equivalent to the height of the calcium plus the magnesium segments, in milliequivalents per liter, multiplied by 50. In figure 30, the concentration of silica is represented in millimoles per liter, because milliequivalents cannot be used for uncharged solute species or species whose form in solution

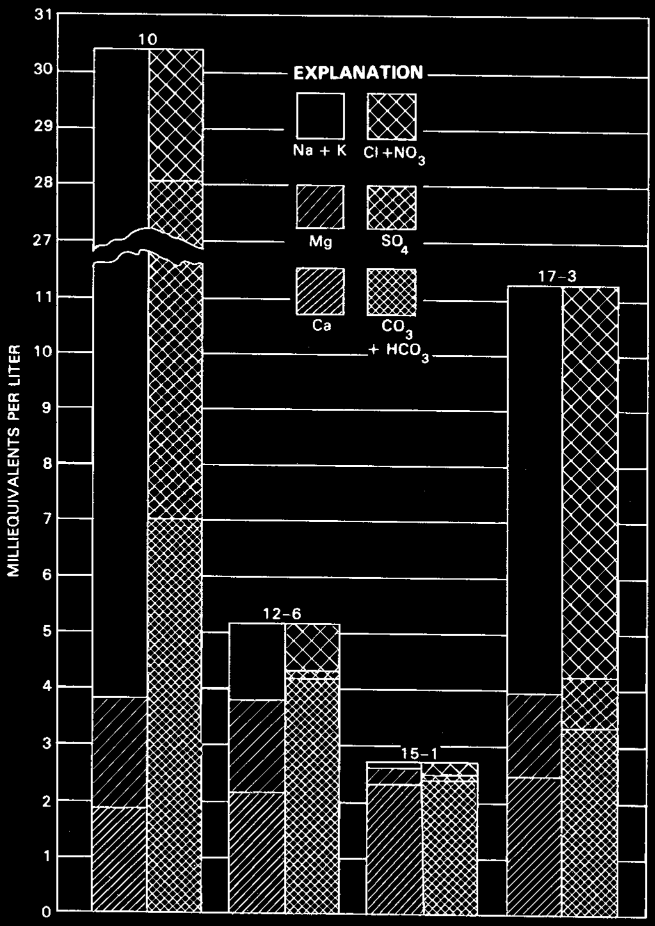


Figure 28. Analyses represented by bar lengths in milliequivalents per liter. Numbers above bars indicate source of data in tables 10, 12, 15, and 17 (e.g., "12-6"=table 12, analysis 6).

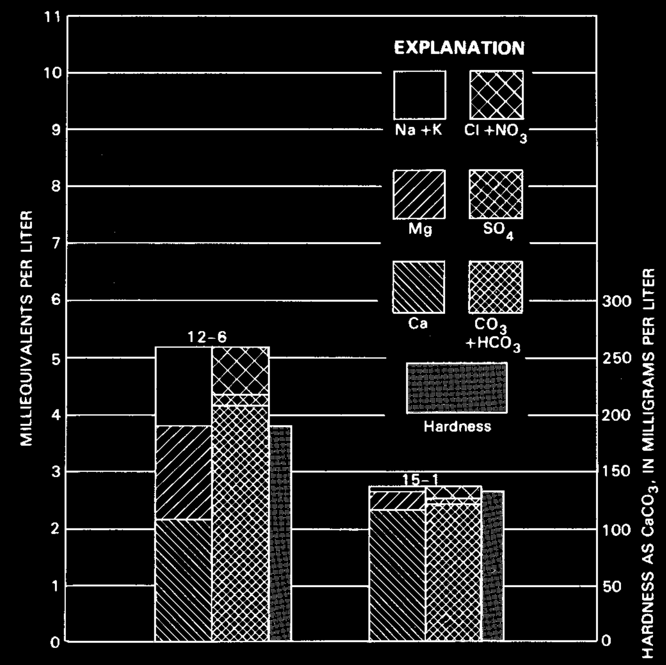


Figure 29. Analyses represented by bar lengths in milliequivalents per liter, with hardness values in milligrams per liter. Numbers above bars indicate source of data in tables 12 and 15 (e.g., "12-6"=table 12, analysis 6).

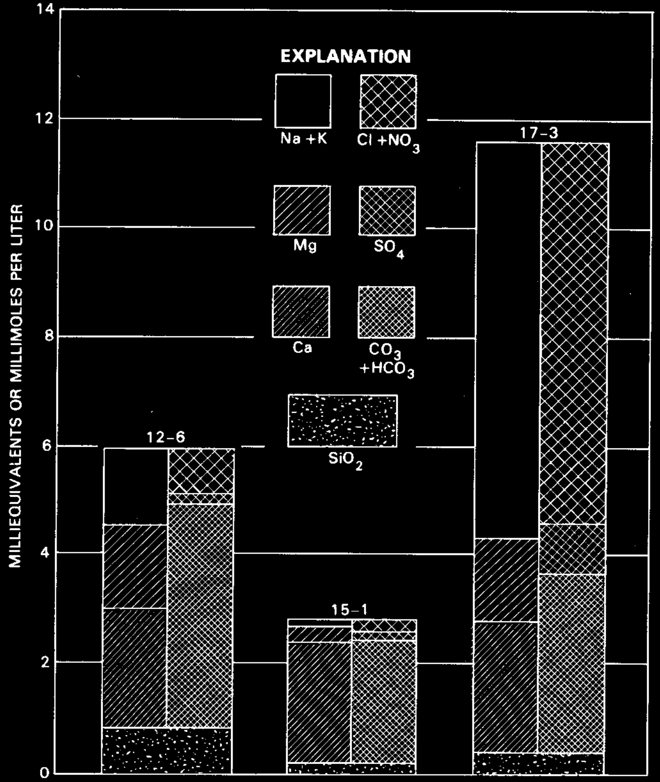


Figure 30. Analyses represented by bar lengths in milliequivalents per liter, with dissolved silica in millimoles per liter. Numbers above bars indicate source of data in tables 12, 15, and 17 (e.g., "12-6"=table 12, analysis 6).

is not specifically known. The units are closely related to milliequivalents per liter, and this type of graph will be used in depicting analyses of water associated with different rock types later in this book. The pattern representing silica occupies the full width of the bar graph because the solute species H_4SiO_4 consists of a silicate anion whose charge is balanced by H^+. This modification is sometimes useful in showing results of geochemical processes. The concentration of silica in millimoles per liter is readily computed from gravimetric data in water-analysis tabulations.

A system of plotting analyses by radiating vectors proposed by Maucha (1949) of Hungary is illustrated in figure 31. The distance each of the six vectors extends from the center represents the concentration of one or more ions in milliequivalents per liter. This plotting system has not been used widely, but it may have some potential as a means of showing analytical values in a small space, for example, as a symbol on a map. A system suggested by Stiff (1951) seems to give a more distinctive pattern and has been used in many papers, especially those dealing with oilfield waters. The Stiff plotting technique uses four parallel horizontal axes extending on each side of a vertical zero axis. Concentrations of four cations can be plotted, one on each axis to the left of zero, and likewise four anions concentrations can be plotted, one on each axis to the right of zero; the ions should always be plotted in the same sequence. The concentrations are in milliequivalents per liter. The resulting points are connected to give an irregular polygonal shape or pattern, as in figure 32. The Stiff patterns can be a relatively distinctive method of showing water-composition differences and similarities. The width of the pattern is an approximate indication of total ionic content. Stiff patterns were used as map symbols by Halberg and others (1968).

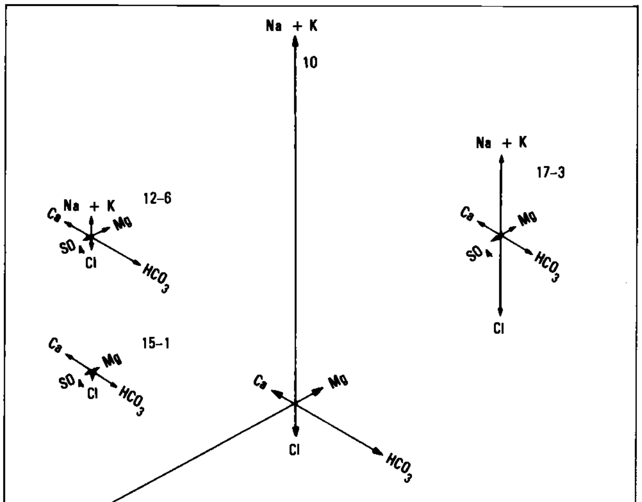


Figure 31. Analyses represented by vectors based on milliequivalents per liter. Numbers near symbols indicate source of data in tables 10, 12, 15, and 17 (e.g., "12-6"=table 12, analysis 6).

Two other procedures that have been used to prepare pattern diagrams are worthy of mention. The "pie" diagram can be drawn with a scale for the radii which makes the area of the circle represent the total ionic concentration (fig. 33) and subdivisions of the area represent proportions of the different ions. Colby and others (1956) used a pattern diagram in which four components, Ca+Mg, CO_3+HCO_3, Na+K, and Cl+SO_4+NO_3, were represented on rectangular coordinates. The kitelike figure resulting from connecting the four points made a convenient map symbol (fig. 34).

A nomograph proposed by Schoeller (1935) and modified by R. C. Vorhis of the U.S. Geological Survey is shown in figure 35. This diagram is a means of depicting

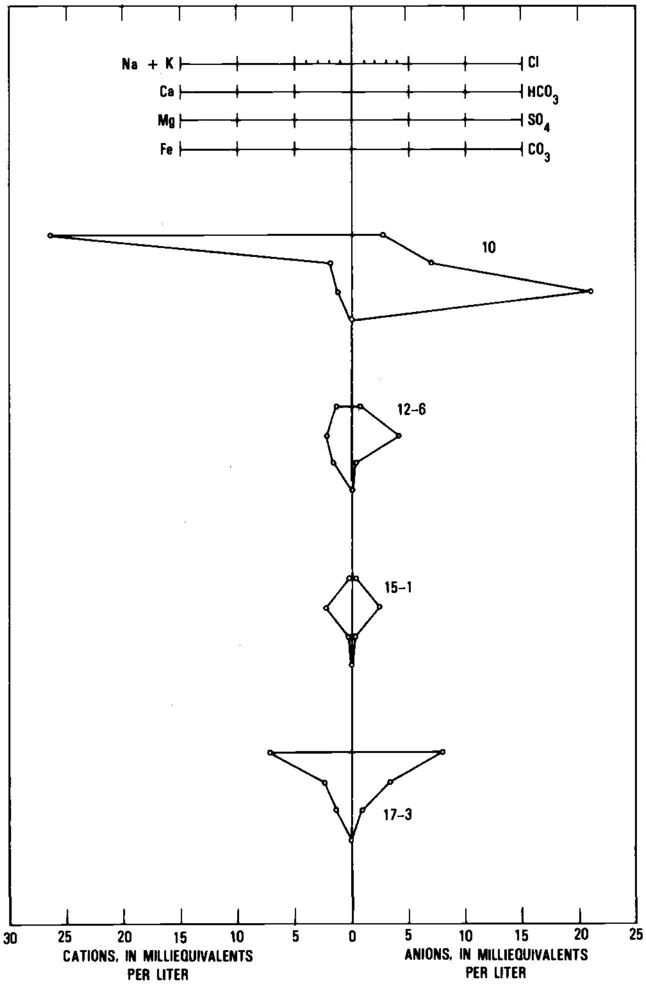


Figure 32. Analyses represented by patterns based on milliequivalents per liter. Numbers near patterns indicate source of data in tables 10, 12, 15, and 17 (e.g., "12-6"=table 12, analysis 6).

a group of analyses that has the advantage of also showing relationships among milligrams per liter and milliequivalents per liter for the different ions. Waters of similar composition plot as near-parallel lines. This diagram, however, uses logarithmic scales, and this may complicate the interpretation for waters that differ greatly in concentration.

Figure 36 is a cumulative percentage plot of analyses in milligrams per liter. This method of graphing permits differentiating between types of water on the basis of the shape of the profile formed by joining the successive points.

Some other graphical display techniques used in study of oil-field brines were described by Collins (1975, p. 128–132).

Ion-concentration diagrams are useful for several purposes. They aid in correlating and studying analyses and are especially helpful to the novice in this field. They also aid in presenting summaries and conclusions about water quality in areal-evaluation reports. The Collins' diagram can serve as an effective visual aid in oral presentations on water composition for semitechnical and nontechnical groups. For this purpose, the bar symbols can be made at a scale of about 10 cm = 1 meq/L, by using cards fastened together end to end with hinges of flexible tape to give a length sufficient to represent the total concentration of ions. Segments representing the ions are then drawn on the graph, and they can be colored distinctively to show the six species. While discussing the analyses, the lecturer can take out the appropriate set of cards and hang them up in view of the audience. The contrast between water of low concentration shown by only one or two cards and more concentrated solutions, occurring naturally or as a result of pollution, shown perhaps by a thick stack of cards that might reach a length of 20 ft when unfolded, is a potent attention-getter.

Trilinear Plotting Systems

If one considers only the major dissolved ionic constituents in milliequivalents per liter and lumps potassium and sodium together and fluoride and nitrate with

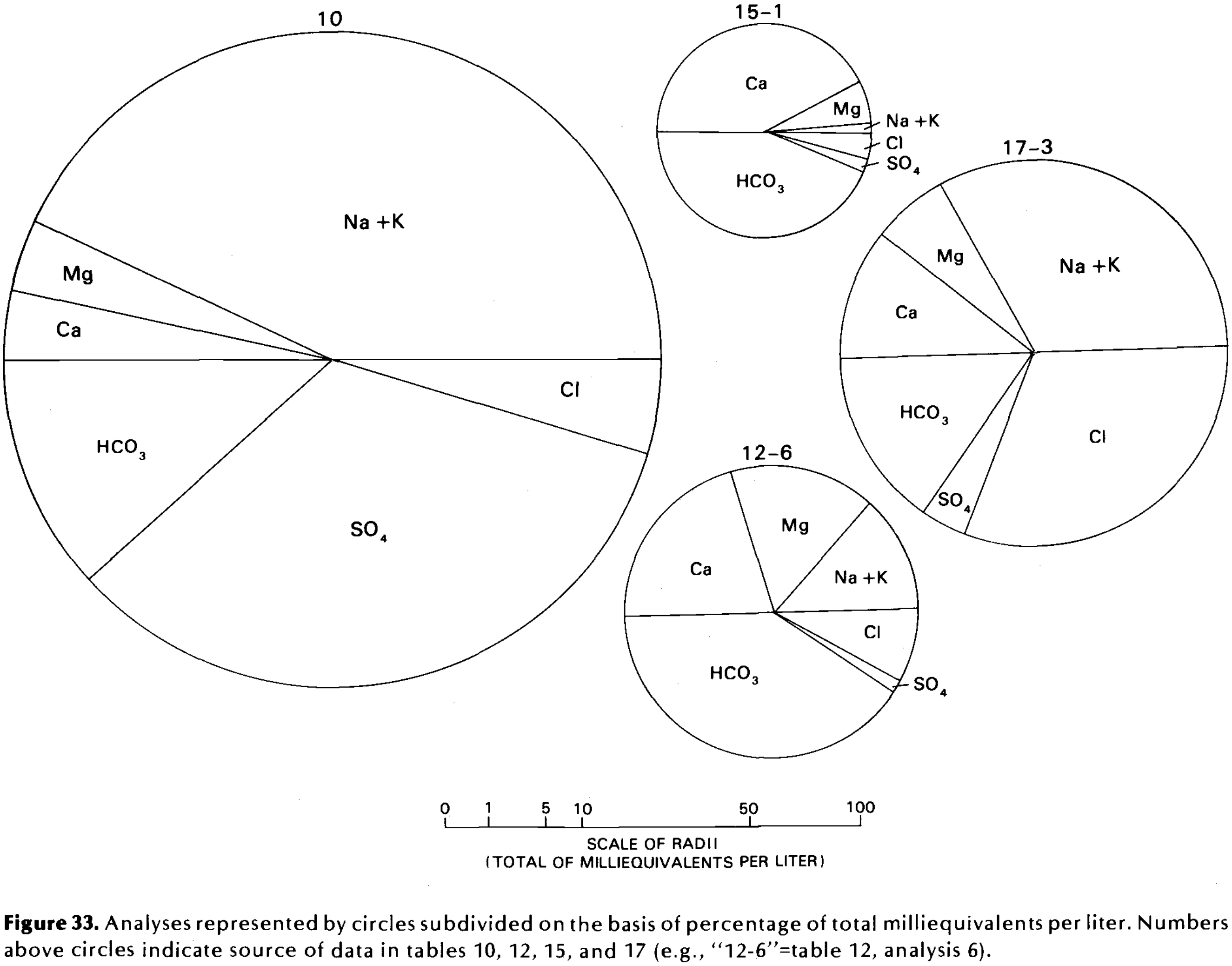


Figure 33. Analyses represented by circles subdivided on the basis of percentage of total milliequivalents per liter. Numbers above circles indicate source of data in tables 10, 12, 15, and 17 (e.g., "12-6"=table 12, analysis 6).

chloride, the composition of most natural waters can be closely approximated in terms of three cationic and three anionic species. If the values are expressed as percentages of the total milliequivalents per liter of cations, and of anions, the composition of the water can be represented conveniently by a trilinear plotting technique.

The simplest trilinear plots use two equilateral triangles, one for anions and one for cations. Each vertex represents 100 percent of a particular ion or group of ions. The composition of the water with respect to cations is indicated by a point plotted in the cation triangle, and the composition with respect to anions by a point plotted in the anion triangle. The coordinates at each point add to 100 percent.

Emmons and Harrington (1913) used trilinear plots in studies of mine-water composition. This application was the earliest found by the writer in surveying published literature on water composition, even though Emmons and Harrington do not claim originality for the idea of using trilinear plots for this purpose. In the form used by Emmons and Harrington, the cation triangle lumps calcium with magnesium at one vertex and sodium with potassium at another. This leaves the third vertex for "other metals" that might be present in the mine waters that were of principal interest to these investigators. For most natural water, the concentration of these other metals is not a significant percentage of the total.

Dela O. Careño (1951, p. 87–88) described a method of trilinear plotting, which he attributed to Hermion Larios, that combines the plotting with a classification and reference system. The three principal cations are plotted conventionally in one triangle and the three anions in another. Each triangle is divided into 10 approximately equal areas numbered from zero to nine. A two-digit number is then used to characterize the water. The first digit is the number of the area within the cation triangle in which the water plots. The second digit is the number of the area in the anion triangle in which the

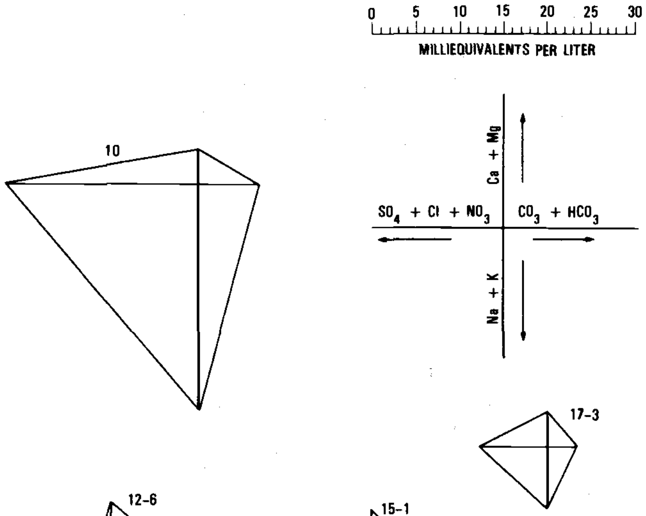


Figure 34. Analyses represented by patterns based on combined anion and cation concentrations. Numbers above patterns indicate source of data in tables 10, 12, 15, and 17 (e.g., "12-6"=table 12, analysis 6).

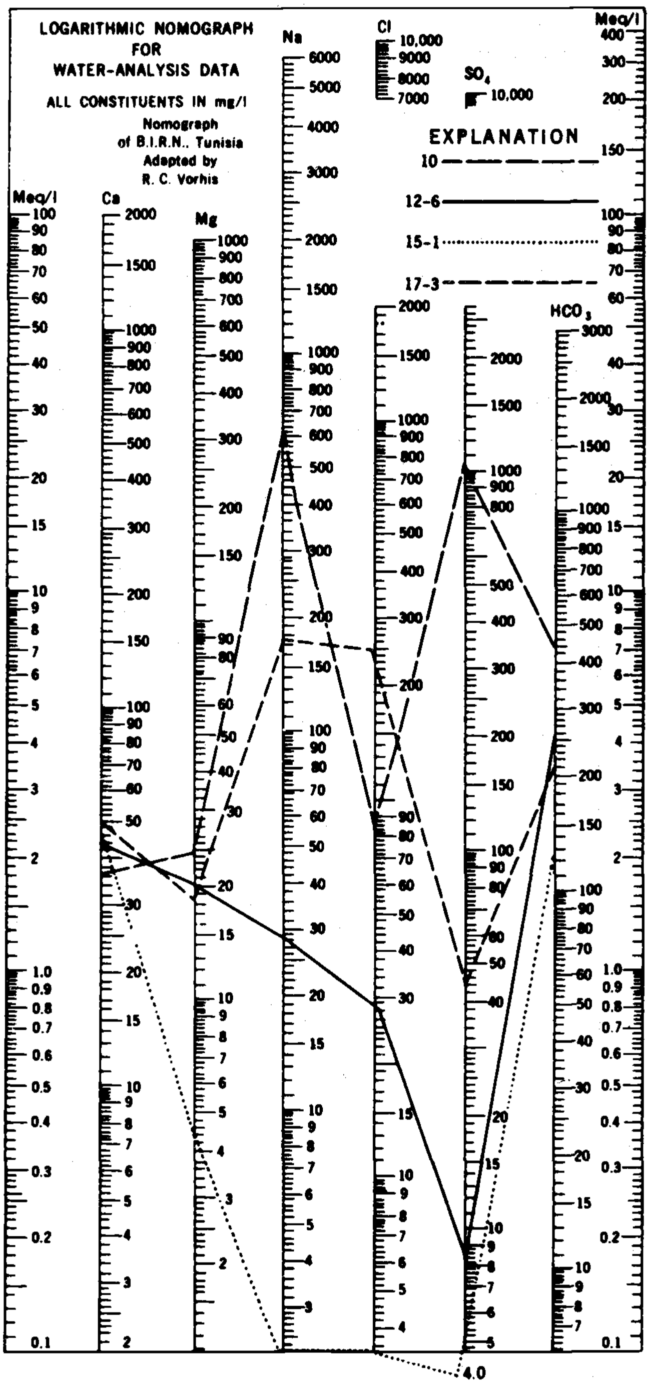


Figure 35. Analyses represented by logarithmic plotting of concentration in milligrams per liter. Numbers under "Explanation" indicate source of data in tables 10, 12, 15, and 17 (e.g., "12-6"=table 12, analysis 6).

plotted point falls. Similar classification and plotting schemes have appeared in other countries, especially in the U.S.S.R.

A considerable number of authors have described trilinear plots in which the cation and anion triangles are combined or projected in several ways. The expression of analyses by two points on separate graphs is obviously rather inconvenient. By further combining the variables, it is possible to express the water composition in terms of two groups of cationic and two groups of anionic components, with the proviso that because all are percentages, the sums of cations and anions must equal 100. This is equivalent to specifying two variables and permits the analysis to be expressed as a single point on a two-coordinate diagram.

The first trilinear diagram incorporating this combination of the anion and cation fields to be published in the United States was that of Hill (1940). In the Hill diagram, the anion and cation triangles occupy positions at the lower left and lower right; the bases of the triangles aline vertically and the vertices point toward each other. The upper central portion of the diagram is diamond shaped. In using this diagram, the proportions of anions and cations are plotted as points in each of the lower triangles. The points are then extended into the central plotting field by projecting them along lines parallel to the upper edges of the central field. The intersection of these projections represents the composition of the water with respect to the combination of ions shown. Hill's original diagram was so arranged that bicarbonates and sulfate were grouped together, and the point in the central field amounted to a plot of sodium percentage versus chloride percentage. Hill also divided the central plotting field into 10 areas and proposed a classification scheme involving 10 types of water, depending on the area in which the analysis is plotted. In later revisions of his procedure, Hill (1941, 1942) combined sulfate with chloride rather than with bicarbonate.

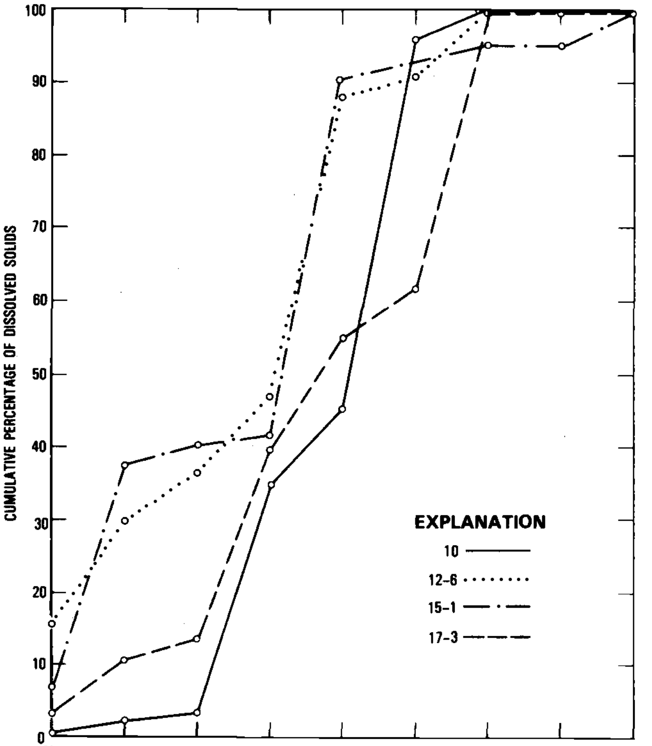


Figure 36. Analyses represented by linear plotting of cumulative percentage composition based on milligrams per liter. Numbers under "Explanation" indicate source of data in tables 10, 12, 15 and 17 (e.g., "12-6"=table 12, analysis 6).

Langelier and Ludwig (1942) proposed a diagram using rectangular coordinates in which percent sodium plus potassium was represented on the ordinate and percent carbonate plus bicarbonate on the abscissa. This diagram had no cation or anion triangles.

Piper (1944) suggested the form of the trilinear diagram that is represented by figure 37. The circles plotted in the central field have areas proportional to dissolved-solids concentrations and are located by extending the points in the lower triangles to points of intersection. The diagram is fundamentally the same as Hill's; however, Piper developed his diagram independently.

A number of forms of the trilinear diagram have appeared in literature of the U.S.S.R. The procedure of Durov (1948) is similar to that of Piper. Filatov (1948) proposed a two-point system with cation and anion triangles having a common side.

All trilinear plotting techniques are, in a sense, descendants of the geochemical classification scheme of Palmer (1911). In Palmer's classification, the composition of a water was expressed by percentage of total ions, with consideration, in effect, of the proportions of sodium to total cations and of bicarbonate to total anions. Palmer, however, was apparently thinking more in terms of combined salts in solution than more modern chemists do, and his classification scheme is of only historical interest today.

The trilinear diagram constitutes a useful tool in water-analysis interpretation. Most of the graphical procedures described here are of value in pointing out features of analyses and arrays of data that need closer study. The graphs themselves do not constitute an adequate means of making such studies, however, unless they can demonstrate that certain relationships exist among individual samples. The trilinear diagrams sometimes can be used for this purpose.

Applications of the diagram pointed out by Piper include testing groups of water analyses to determine whether a particular water may be a simple mixture of others for which analyses are available or whether it is affected by solution or precipitation of a single salt. It can be shown easily that the analysis of any mixture of waters A and B will plot on the straight line AB in the plotting field (where points A and B are for the analyses of the two components) if the ions do not react chemically as a result of mixing. Or, if solutions A and C define a straight line pointing toward the NaCl vertex, the more concentrated solution represents the more dilute one spiked by addition of sodium chloride.

Plotting of analyses of samples from wells successively downslope from each other may show linear trends and other relationships that can be interpreted geochemically. Poland and others (1959) used trilinear diagrams extensively in studying contamination of ground water by seawater and other brines along the California coast near Los Angeles. The relationships shown by the diagrams usually constitute supporting evidence for conclusions regarding water sources that also have other bases of support.

Trilinear diagrams continue to be used in papers dealing with natural-water chemistry and geochemistry. A few examples are cited here to indicate the varieties of applications. Maderak (1966) used trilinear diagrams to show trends in composition as streamflow volume changed at several sampling points on the Heart River in

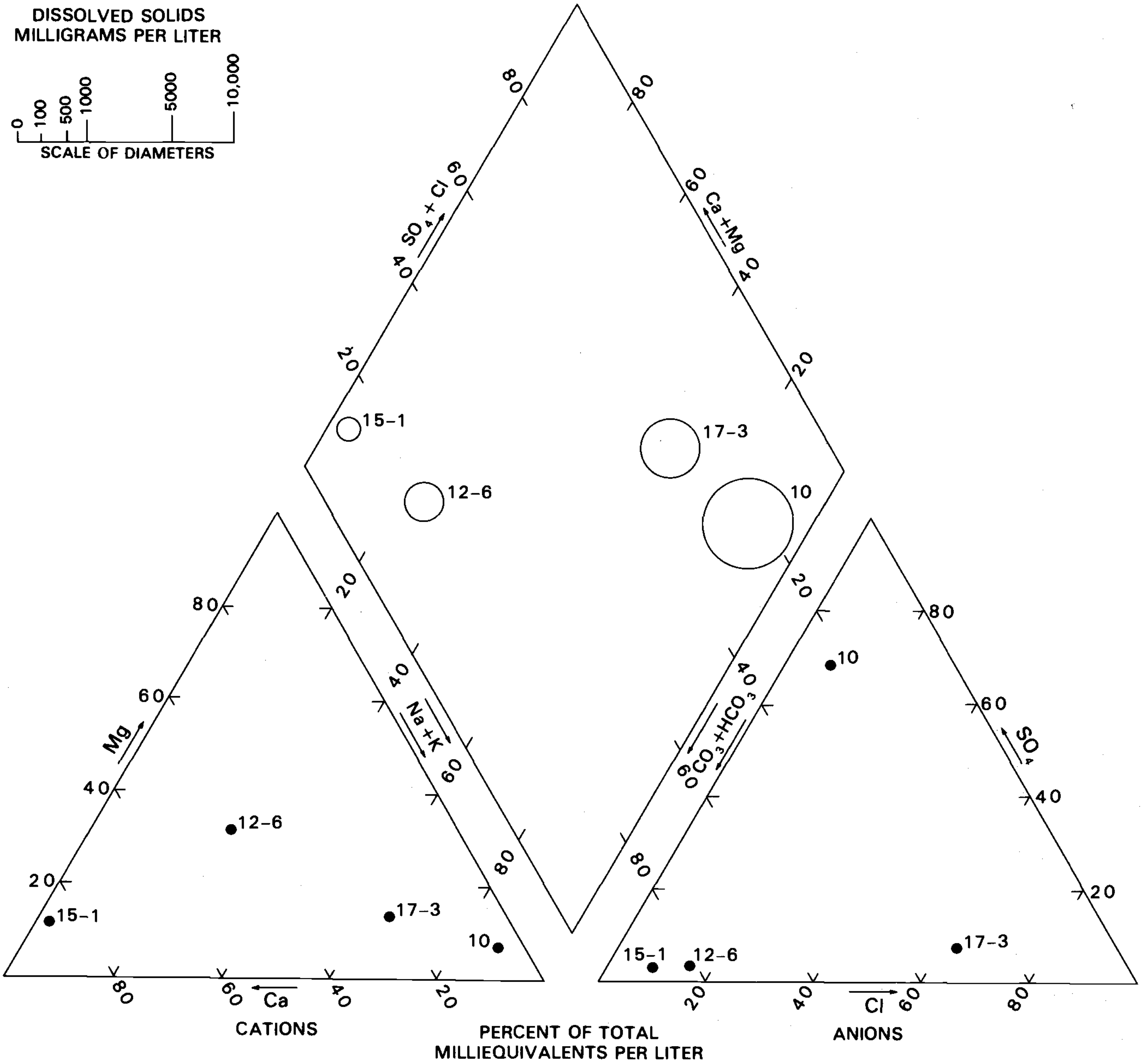


Figure 37. Trilinear diagram showing analyses represented by three-point plotting method. Numbers near circles indicate source of data in tables 10, 12, 15, and 17 (e.g., "12-6"=table 12, analysis 6).

western North Dakota. Hendrickson and Krieger (1964) and Feth and others (1964) used the diagram as a means of generally indicating similarities and differences in the composition of water from certain geologic and hydrologic units. Bradford and Iwatsubo (1978) used the diagrams to show effects of logging and other factors on stream-water composition in the area of Redwood National Park, Calif. Trilinear diagrams were used by White and others (1980) to help correlate rock and water composition in the ground water of Ranier Mesa, Nev. Many other papers could be cited. The trilinear diagram has been widely used by U.S. Geological Survey hydrologists.

A compilation of methods for graphical representation of water analyses that had been described in the literature up to that time, was prepared by Zaporozec (1972).

Methods of Extrapolating Chemical Data

A considerable part of the task of interpreting water-quality data can be extrapolating or interpolating. For example, a few analyses of river-water samples taken at irregular intervals may need to be used to estimate a continuous record, or analytical records may need to be extended backward or forward in time by correlating the analyses with some other measured variable. For ground-water studies, variations in time generally are less important than variations from place to place in the composition of a ground-water body, and procedures are needed for extrapolating analyses representing individual wells or springs to cover the whole volume of ground water of an area.

The extension of individual observations of river-water composition can be accomplished by several averaging techniques or other statistical treatments already discussed. As the technology of on site observations of water quality has matured, more complete chemical records are being computed from continuously measured specific conductance. This sort of calculation can provide fairly dependable values for major ions, at least for many streams. The accuracy of the calculated value depends on how good a correlation of the measured with the calculated properties can be established from previous records of a more complete nature.

Water-Quality Hydrographs

A graph showing the changes over a period of time of some property of water in a stream, lake, or underground reservoir is commonly termed a "hydrograph." Hydrographs showing variability of a property of river water with time are often used as illustrations in reports. An example is figure 4, which shows the change with time of the conductivity of water in the Rio Grande at San Acacia, N.M. For a stream, where changes with time can be large and can occur rapidly, an accurate extrapolation cannot be made on the basis of time alone. On that basis, it is possible to state only approximately what the composition of water would be at different times of the year. In contrast, streams that are controlled by storage reservoirs (the Colorado River below Hoover Dam, for example), streams that derive most or all of their flow from ground-water sources (the Niobrara River, for example, which drains the sandhill region of northwestern Nebraska), and streams that have very large discharge rates (the Mississippi River at New Orleans, for example) may exhibit only minor changes in composition from day to day or even from year to year.

Streams whose flow patterns have been altered extensively by humans may show definite long-term trends as the water quality adjusts to the new regime. The Gila River at Gillespie Dam, Ariz., for example, showed a deteriorating quality over many years of record as irrigation depleted the upstream water supply (Hem, 1966).

In ground water, the changes in quality with time are normally slow. The illustrations already given in this paper, however, show that both long-term and short-term trends can be observed. The slow increase in dissolved solids that occurred in the ground water of the Wellton-Mohawk area of Arizona (fig. 7) represents a condition related to water use and development, but shorter term fluctuations may be related to well construction and operation (fig. 5) or to changing recharge rates, evapotranspiration, or other factors that often influence water near the water table observed in shallow wells or seasonal springs (fig. 6). Deep wells that obtain water from large ground-water bodies that are not too extensively exploited and many thermal springs may yield water of constant composition for many years. Analyses published by George and others (1920) for Poncha Springs near Salida, Colo., represented samples collected in 1911. A sample of a spring in this same group collected in 1958 (White and others, 1963) gave an analysis that did not differ by more than ordinary analytical error from the one made 47 years before, with the exception of the sodium and potassium. The potassium values reported by George and others (1920) appear too high and sodium too low, in comparison with the modern analysis, but the total of the two alkali metals is nearly identical in both analyses.

Water Quality in Relation to Stream Discharge

The concentration of dissolved solids in the water of a stream is related to many factors, but it seems obvious that one of the more direct and important factors is the variable volume of liquid water from rainfall available for dilution and transport of weathering products. Presumably, therefore, the dissolved-solids concentration should be an inverse function of the rate of discharge of water over all or at least most of the recorded range. In discussing averaging of river-water chemical analyses, some of the complications that influence discharge versus dissolved-solids concentration relationships have been pointed out. There will no doubt, however, be a continuing demand to know how well the composition of a river water can be computed from the water-discharge rate and some previous record of composition. Some further consideration of the subject, therefore, is needed. The goal would be to obtain a dissolved-solids rating curve for a stream-measuring station: a graph of dissolved-solids concentration versus water-discharge rate, expressing their correlation.

The development of such a correlation requires a preliminary assessment that might be termed a "conceptual model." The model can then be tested for validity and to determine what kinds of information might be required to develop it completely. A consistent relationship between water discharge and total solute concentration ought to be observed in a stream that receives a large part of its mineral load from a rather constant saline inflow upstream from the measuring point and whose runoff from other sources is constant and low in dissolved-solids concentration. A finite relationship can be expected to hold for any single unreactive dissolved component. No stream meets these specifications completely, and few streams that might approach them have been studied closely.

The simplest dilution model for a particular solute in a reach of river assumes, then, that a constant total load of solute is entering upstream and that the observed concentration of that solute at the sampling point varies owing to dilution by runoff. If other factors are insignificant, this condition can be evaluated from a simplified solute-balance equation:

$$C_1Q_1+C_2Q_2-C_3(Q_1+Q_2)=0,$$

where

C_1=concentration of solute before dilution,
Q_1=volume of flow before dilution,
C_2=concentration of solute in diluting water, and
Q_2=volume of dilution water,
C_3=final concentration observed.

The three terms in this equation represent loads of solute, and an inflow-outflow balance is assumed (that is, it is assumed there is no change in storage).

If the concentration of solute in the diluting water is zero, then C_2Q_2 drops out and

$$C_3=\frac{C_1Q_1}{Q_1+Q_2}.$$

C_1Q_1 is constant and can also be represented as W_1, the total original solute load. This is the equation of a hyperbola. If expressed in logarithmic form, however,

$$\log C_3=\log W_1-\log (Q_1+Q_2),$$

it has the form of a straight line, with slope -1.0. Thus, the degree to which a particular set of concentration and stream-discharge data fits the simple dilution model can be tested by plotting these variables on log-log paper.

Of course, most natural systems can display a simple dilution mechanism only over a limited range of concentration. Normally, the dilution water contains some of the same solute as the water being diluted, and this will cause the high-discharge end of the plot to approach a minimum near the concentration present in the diluting water. At the low-discharge end, Q_2 approaches zero and the value of C_3 will become equal to the concentration of solute in the inflow source. The solubility of the ion being considered, or other factors independent of discharge, also may limit the ion's concentration at low discharge, so the slope of the curve will tend to flatten at very low discharge. It is obvious that complexities in most natural systems tend to make the equation considerably more complicated. For example, if some of the solute being considered is present in the runoff, the value of C_2 will not be zero, and the final equation will have the form

$$C_3=\frac{W_1+C_2Q_2}{Q_1+Q_2}.$$

If expressed in logarithmic terms, this equation would give a curved line, as C_2Q_2 is unlikely to be constant and probably will vary in response to discharge.

A practical difficulty inherent in the use of the log-log type of plot is that observed solute concentrations commonly show a rather narrow range of variation, and considerable clustering of points may occur. It is of interest, however, to use this approach to explore the relationships between discharge and solute concentration obtainable from existing records.

In past years, in studies by the U.S. Geological Survey, the only chemical determination made for each daily sample usually was specific conductance, and many of these data have never been published. Discharge information readily available for use with these determinations is the published daily mean rate of flow. An instantaneous sample may not be a good representation of the daily mean conductivity, and some values thus may be poorly suited for establishing a meaningful discharge-conductivity relationship. However, if a well-defined relationship exists, it will not be completely obscured, although individual points may be scattered. Records collected for the specific purpose of exploring water-quality–water-discharge relationships must be obtained carefully with the aim of getting fully compatible data for both variables. This is perhaps most effectively accomplished by simultaneous continuous measurement of water-discharge rate and solute concentration.

A sampling station whose characteristics might be suitable for establishing a dissolved-solids versus discharge relationship was operated for a time by the U.S. Geological Survey on the San Francisco River at Clifton, in southeastern Arizona. About 60 percent of the annual dissolved-solids load of the river there was contributed by saline inflow from the Clifton Hot Springs, a short distance above the gaging station and about 1½ miles above the sampling section. The varying amounts of discharge from the direct runoff and a more constant amount of dilute base flow of the river above the springs might be considered dilution factors controlling the concentration observed at the sampling point.

Specific conductance of water at this station should approach a high limiting value near the conductance of the spring inflow (about 16,000 μmho/cm) at low discharge, and a minimum value fixed by the conductance of runoff, which has had only a brief opportunity to react with near-surface rock and soil minerals, at high discharge. The lower limiting value can be estimated only approximately from the sampling record, but it is probably about 200 μmho.

Figure 38 is a logarithmic plot of specific conductance of daily samples versus daily mean discharge for the 1944 water year for the San Francisco River at Clifton, Ariz. Some daily values were omitted where the points are closely grouped. The scatter of points is substantial, and it would be difficult to fit them to a straight line. Furthermore, the slope of such a line is not -1.0. Both facts suggest that the simple dilution equation derived in the earlier discussion is not directly applicable.

From other information about the quality of water at this point, however, it is possible to derive a more pertinent relationship. The solute load at the sampling point may be considered to have three components, represented by C_nQ_n terms, in which C represents con-

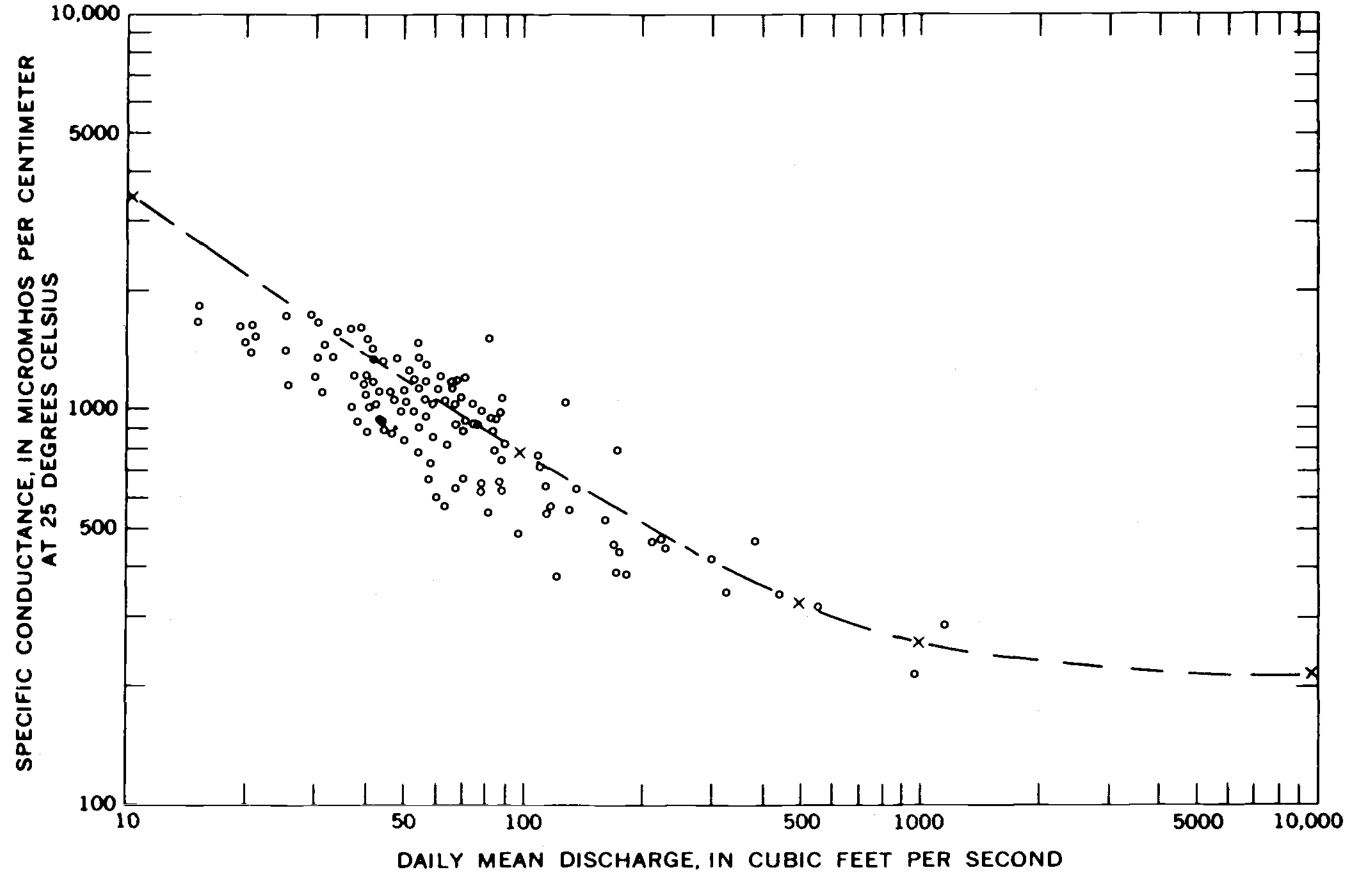


Figure 38. Specific conductance of daily samples and daily mean discharge, San Francisco River at Clifton, Ariz., October 1, 1943, to September 30, 1944. Circles represent observed values. Symbols "x" are calculated values based on postulated relationship in text.

ductance in micromhos and Q represents discharge of water in cubic feet per second (cfs). C_1Q_1 represents the solute load brought in by spring inflow. This water has a specific conductance of about 16,000 μmho, and the flow is considered constant at 2 cfs (Hem, 1950). C_2Q_2 represents base solute load of the river above the springs that dilutes the spring inflow. For simplicity, this water is assumed from available analyses of samples taken above the inflow zone to have a specific conductance of 500 μmho and a maximum flow rate of 100 cfs. C_3Q_3 represents flood runoff, constituting all flow above 102 cfs, and is assigned a specific conductance of 200 μmho. The mixture of all these is represented by concentration C_F. The equation for predicting concentration at this station from water-discharge data becomes

$$C_F = \frac{C_1Q_1 + C_2Q_2 + C_3Q_3}{Q_1 + Q_2 + Q_3}.$$

Substituting appropriate values from quantities postulated above gives the points with the symbol "x" in figure 38. The dashed curve fitted to these points smooths out some of the irregularities that would result if more calculated points were used, but demonstrates an approximate fit of the model to actually observed conditions.

The scatter of observed points is substantial; therefore, there would be substantial uncertainty in conductance values calculated from discharge by means of any curve fitted to the points. Some of the spread in points in figure 38 may have resulted from changes in rate of spring inflow, and some might have been caused by incomplete mixing of the inflow with the river water at the sampling point. Most of the scatter, however, is probably related to the failure of individual samples to represent the average composition of the river for a whole day.

The San Francisco River is subject to rapid changes in stage, especially during the summer when heavy local thunderstorms often occur in the afternoon and early evening. The resulting runoff events commonly occur at night, and the river stage was frequently near the low point for the day when samples were collected. Sampling was always done during the daytime, and the probability of a sample's representing the day's average composition was not always good during the summer storm period.

Another approach to the construction of discharge-concentration models has been to develop a mathematical relationship that best fits a set of observed points. For example, Steele (1968a, b) studied the relationships of dissolved-ion concentration to water discharge of Pescadero Creek, a small northern California coastal stream, and reported that his data fitted the relation $CQ^N=K$, or $\log C = \log K - N \log Q$. The exponent N can be evaluated from the slope of the regression line. This exponent does not, however, represent a simple hydrologic parameter. It is empirical and represents several kinds of hydrologic effects.

Other investigators who have developed dissolved-solids rating curves include Durum (1953), who found a reasonably good correlation between chloride concentration and discharge for the Saline River near Russell, Kans., and Hendrickson and Krieger (1964), who found reasonably consistent relationships between specific conductance and discharge for the Salt River at Shepherdsville, Ky., for low-flow periods.

In streams for which runoff patterns and solute-load sources are more complicated, a poorly defined relationship between discharge and dissolved-solids concentration is to be expected. An interesting feature observed in many streams, although closely studied in only a few places, is a tendency for the water of a rising stage to have a considerably higher dissolved-solids concentration than the water passing the sampling point at an equal flow rate after the peak discharge has passed. Hendrickson and Krieger (1964 p. 123) presented a semilog graph of conductance (on the x-axis) versus log of discharge which shows a counterclockwise loop that ideally would be characteristic of observations during a flood event. At first the conductance is nearly constant as discharge rises; then the conductance begins to decrease as the peak stage is reached, continues to decrease after the flow begins to recede, and, finally, increases with falling stage until the starting point on the graph is again reached. Flood observations showing several looping cycles were presented by these investigators for the Salt River at Shepherdsville, Ky.

Toler (1965) observed a clockwise loop in his study of the relation of dissolved solids to discharge for Spring Creek in southwestern Georgia. The effect was attributed to an increasing contribution from ground water during falling stages that resulted from the rapid circulation of water through the limestone of the drainage basin.

The factors that control the concentration of water early in a flood event obviously are different for different streams and sampling points. In general, however, when a sudden large inflow of water occurs upstream from a sampling point, the flood wave moving down the channel tends to push water already in the channel ahead of it. If the stream had a low or moderate flow rate before the rise began, the water in the channel would be relatively high in dissolved-solids concentration, and as the wave moved downstream a large volume of this more highly mineralized water might accumulate in the wave front.

The effect of water-discharge rate on water composition may obscure the effect of other factors one might wish to evaluate. The analysis of long-term records to evaluate water-quality trends can be accomplished by establishing a correlation between discharge and solute concentration and then looking for systematic departures from the relationship. Some procedures for detecting long-term trends were described by Harned and others (1981), by Hirsch and others (1982), and by Smith and others (1982).

As noted earlier, there are long-term water-quality records for many streams in U.S. Geological Survey data files. As a part of an intensive study of the hydrology of the lower Colorado River basin (legally defined as that part of the drainage basin downstream from Lees Ferry, Ariz.), Irelan (1971) reviewed and summarized water-quality records and related data up to 1965. Some of the sampling points on the Colorado River have continuous sampling records dating back to the mid 1920's. These continuing studies were federally financed and were intended to aid in planning for development and use of the water resources of the basin. Further reference to the Colorado River data and their interpretation will be made in a later section of this book under the topic "Water-Management Concepts and Problems." Support and justification for such long-term data-collection programs has come from various sources. One of the frequently cited justifications is that of establishing a "base line" that can be used to evaluate subsequent trends of improvement or degradation in water quality. Actual documentation of trends or of methods for study of records to discern trends has not always kept pace with the rate of record accumulation. Some of the difficulties in correlating discharge with water composition have already been noted. Contrary to the intuitive supposition that the longer the record, the better the understanding of the system, it often can be demonstrated that a briefer, more intensive investigation of hydrology and chemistry of a stream can form a more useful model than one derived from many years of routinely collected data.

Summaries of two long-term records based on daily sampling have been made here using published annual average discharge and annual discharge-weighted average dissolved-solids concentrations. Figure 39 is a log-log plot of discharge-weighted average dissolved-solids concentrations versus mean water discharge for each year of record for two daily sampling records from New Mexico. Data for the Rio Grande at San Acacia have also been used for other purposes in this book and the record covers a period, in all, of 17 years beginning with 1940. The record for the Pecos River near Artesia began with the water year 1938, and points in figure 39 cover a period of 40 years. In 1978 the schedule of sampling and analysis was changed, and subsequent records are not directly comparable with the earlier ones.

The points for the Rio Grande station could be considered to define either a straight regression line or a curved one similar to that in figure 38. The years of highest discharge are those having a large spring snowmelt component, which also has a low dissolved-solids concentration. As noted earlier, high summer flows at this point commonly are rather high in solute concentration, and as a result the annual discharge versus dissolved-solids relationship is ill defined if a significant amount of summer runoff occurs. A more stringent type of data analysis would be needed to detect any long-term trends at this sampling station.

The data points for the Pecos River station appear to indicate a trend, because points representing the last 20 years of the record are displaced downward. A least-squares linear regression for successive 10-year periods shows an increased negative slope of the lines, particularly for the 1968–77 period. Correlation coefficients for these regressions range from 0.92 to 0.71. Because the water discharge is used to compute the weighted-average dissolved-solids value, a certain amount of correlation is inherently present in this relationship. It is of interest to note that the minimum average dissolved-solids concentration, which occurred in 1958, corresponds to a flow less than one-fourth as great as the flow in 1941, the year of highest runoff. In 1974, a concentration nearly the same as that of 1958 was attained with an even lower average discharge. There appears to be a trend toward convergence of the four regression lines at their upper ends, near a concentration of 4,000 mg/L dissolved solids.

Although further mathematical analyses of the Pecos River data in figure 39 could be carried out, their value for hydrologic interpretation without supplementary information is rather limited. Apparently the inflow of rather saline ground water from upstream sources which dominates the river water composition in years of low discharge declined in quantity, especially in the 1960's and 1970's, while remaining about the same in dissolved-solids concentration during the period of record. Only a few long-term records with this degree of detail exist, but it seems likely that the trends shown here could have been evaluated by other means that might be as quantitative, and more efficient, than the 40-year daily sampling program. There will, however, be a continuing need for long-term studies of stream-water composition for such purposes as surveillance of pollution, maintenance of stream-quality standards, and observation of the long-term influence of changing land-use or water-use patterns. Some of these studies may require considerable detailed sampling and analysis. This type of work obviously is expensive in money and professional talent. A program involving the collection of large volumes of data tends to develop a momentum of its own and can degenerate into a repetitive exercise of routine operations. Data must be continuously examined and studied in a logical framework, mathematically designed if possible, and not allowed to accumulate without interpretation and evaluation.

In further emphasis of the need for logical interpretation, it is desirable to use methods of graphing data that can be shown as likely to fit the mathematics of the relationships that are possible. The log-log plot tends to deemphasize the scatter of points that may appear when one or both axes are cartesian, but it fits the mathematical characteristics that can be expected for concentration versus discharge relationships. The use of semilog plots for this relationship should be avoided.

Natural processes in which time is satisfactorily considered as the independent variable may sometimes be well represented by semilog plotting, with time being plotted on the linear axis. Chemical-reaction rates and solute-transport rates may involve this kind of variation. One of the graphical approaches that can be used to analyze detailed water-quality data is the cumulative-mass plot. Several examples were published by Irelan (1971). This requires computing annual or shorter period dissolved loads and adding them together chronologically. The cumulative totals, year by year, are plotted against time. A change in slope of the line indicates a change in some significant factor large and persistent enough to be discerned by this technique.

Methods of correlating water-quality patterns observed in synoptic studies were described by Rickert and others (1976). Various methods used to define base-line conditions and trends for North Carolina streams were described by Simmons and Heath (1982) and by Harned and Meyer (1983). Peters (1984) used data from 56 stream sampling stations in the NASQAN network in a statistical study to evaluate correlations among major-ion runoff-yields (in kg/km^2/year) and environmental factors, including bedrock type, annual precipitation, population density, and average stream temperature. The most important environmental factors were found to be annual precipitation and rock type.

Water-Quality Maps

A useful procedure in the study of water-quality data is to enter the information on a map of the area being investigated. A map of this kind is most likely to be useful in the study of underground water in single, widespread aquifers, but mapping also may have some value in surface-water studies. If a systematic areal distribution of water-quality features is observed, correlations with other characteristics of the ground-water system can be made. If the map is started early in the investigation of an area and information is added as it is obtained, the areas needing closer field study often can be identified.

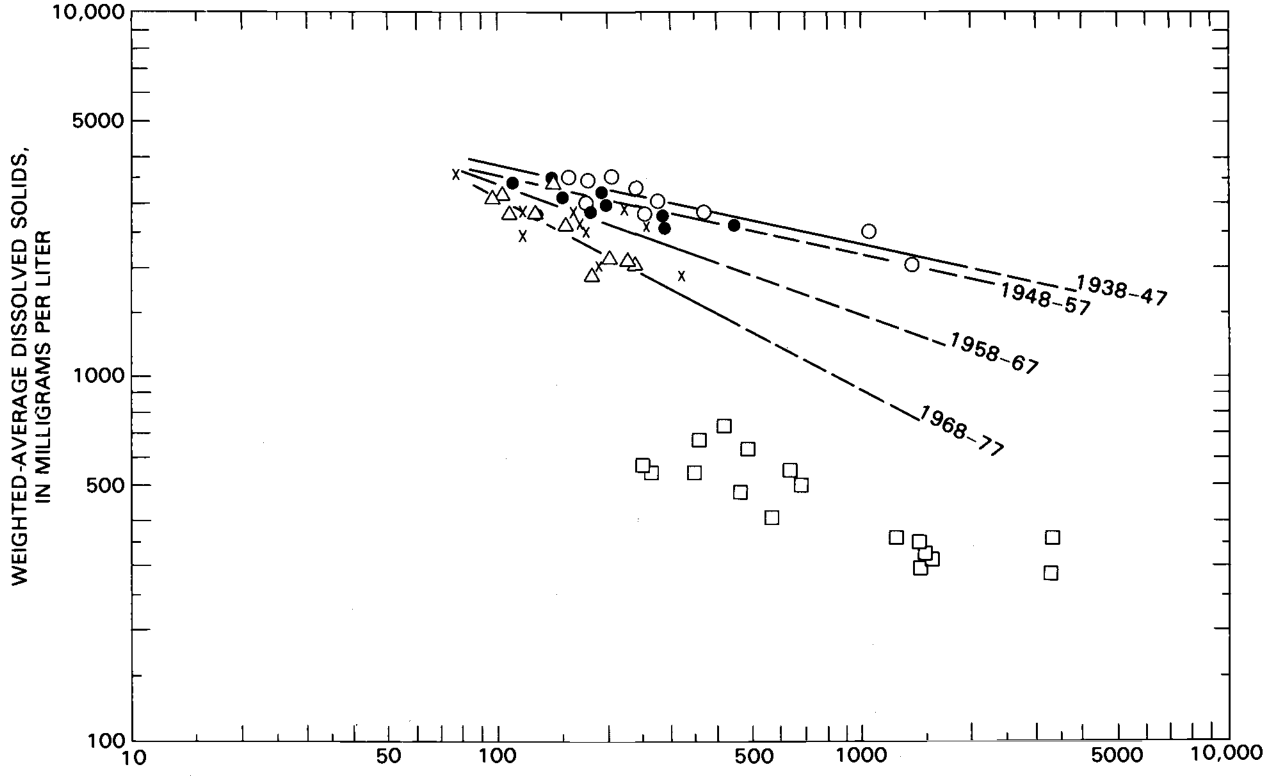


Figure 39. Weighted-average dissolved solids and annual mean discharge, Rio Grande at San Acacia, N. Mex., and Pecos River near Artesia, N. Mex. (Squares represent Rio Grande data, 1940-57. All other symbols represent Pecos River data: open circles, 1938-47; shaded circles, 1948-57; X's, 1958-67; triangles, 1968-77. Lines are least-squares regressions for each 10-year period.)

Usually, a map of the quality of ground water is prepared by entering numbers or symbols at well and spring locations to represent concentrations of constituents, and the areal distribution of solutes thus can be observed in a general way. If many of the wells are open in more than one aquifer or the water of the aquifers tends to vary in composition with distance below the land surface, these variations may well obscure any lateral changes in water quality in a single aquifer. If the sample sites represent only a few of the existing wells and springs, extrapolation of data between sampling sites may be unwise. If the investigator has many analyses, however, and can reasonably assume they represent a water body that is close to being uniform in composition through a vertical section at all well locations, the results may be best expressed in the form of an isogram map. This type of map extrapolates data between sampling points and often gives useful hydrologic and geologic clues. It may help show areas of recharge and discharge, areas of leakage from other aquifers, and directions of water movement.

Map Symbols

One type of water-quality map is prepared by entering a symbol at each sampling point to represent the quality observed there. The symbol can be a bar graph, a pattern diagram, or perhaps a distinctive color traced along a stream. Figures 40 and 41 are two types of symbol maps.

Figure 40, published in a report by Sever (1965) on ground water in parts of southwestern Georgia, shows iron content of wells in a single aquifer and the tendency for the higher iron concentrations to occur in one area, under the influence of geologic and topographic variations. Figure 41 shows the composition of water from wells at Minot, N. Dak., by "pie" diagrams. According to Pettyjohn (1967), the similarities and differences in composition in areas A–D on the map can be correlated with sources of recharge and nature of aquifer materials.

Maps showing the occurrence of iron in ground water were used by Langmuir (1969a) in a paper describing the geochemical behavior of iron at Camden, N.J. A series of maps was used by Feder (1979) to summarize a large amount of information on water in the State of Missouri.

Many water-quality maps have appeared in the U.S. Geological Survey Hydrologic Atlas series, for example, maps showing stream-water quality in the Western United States by Feth (1965), saline ground-water resources of the United States by Feth and others (1965), and river-water quality in the United States by Rainwater (1962). Some European hydrologists also have published water-quality maps (Langguth, 1966).

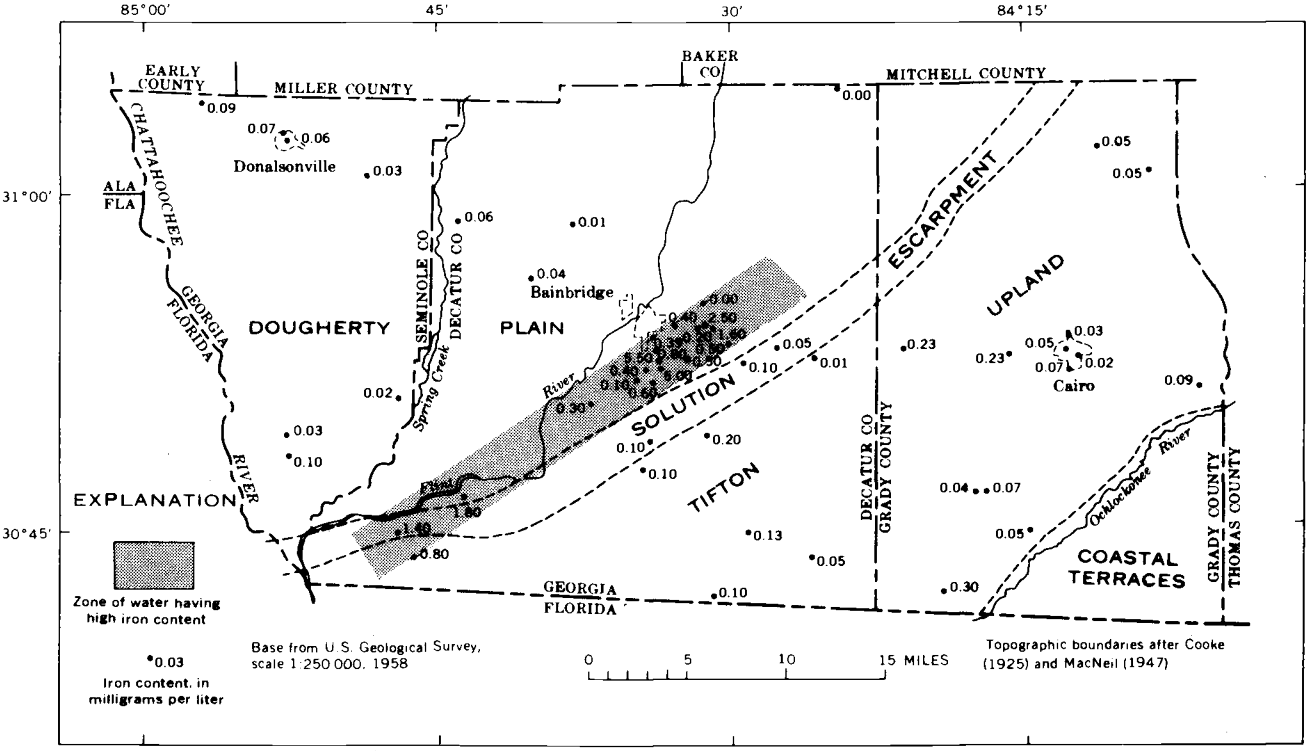


Figure 40. Iron content of ground water from the principal artesian aquifer and topographic regions, southwestern Georgia (Sever, 1965).

Isogram Maps

The technique of mapping ground-water characteristics by drawing lines of equal concentration of dissolved solids or of single ions has been used in reports published by various investigators since the early 1900's. A related procedure identifies concentration ranges by distinctive colors or by shading.

The applicability of this technique depends mainly on two factors: the homogeneity of water composition in the vertical direction at any given point and the spacing between sampling points. An isogram map is particularly useful in studies of ground water in large single-aquifer systems. In alluvial fill of the basins within the Basin and Range physiographic province of the Western United States, water-bearing zones tend to be lenticular but in many places are closely enough interconnected to constitute single hydrologic systems over large areas. Isogram maps have been used successfully in studying several areas of this type.

Figure 42 consists of two isogram maps selected from a series of similar maps in a report by Moore (1965). These maps show the iron concentration and pH of water from the "500-foot" sand of the Claiborne Group in the western part of Tennessee. The outcrop area of the sand, where recharge occurs, is also shown. Both iron and pH increase as water moves away from the outcrop area. A similar increase in hardness of the water occurs downdip, as the recharge attacks minerals in the aquifer.

In a study of the Phoenix, Ariz., area, McDonald and others (1947) prepared a map showing ground-water quality over a large area. Subsequent work has shown considerably more variation of composition with depth than had been supposed in 1947, and the importance of this effect seems to have been increased by declining ground-water levels; nevertheless, isogram maps have been useful in water-resources studies of that region. A more recent map of part of this area used both isograms and symbols to show ground-water composition (Kister and Hardt, 1966). An isogram map of ground-water quality in the Douglas basin, Arizona, was published by Coates and Cushman (1955), and other reports using this device are numerous.

Detailed hydrologic studies in the lower part of Safford Valley, Ariz., were described by Gatewood and others (1950). Quality of ground water in the alluvial fill of Holocene geologic age, which lies adjacent to the Gila River and constitutes a fairly well defined hydrologic unit, is shown by a map in that report, part of which is reproduced here (pl. 3). During the investigation many shallow observation wells were installed in the river-bottom land, and the concentration of dissolved solids in

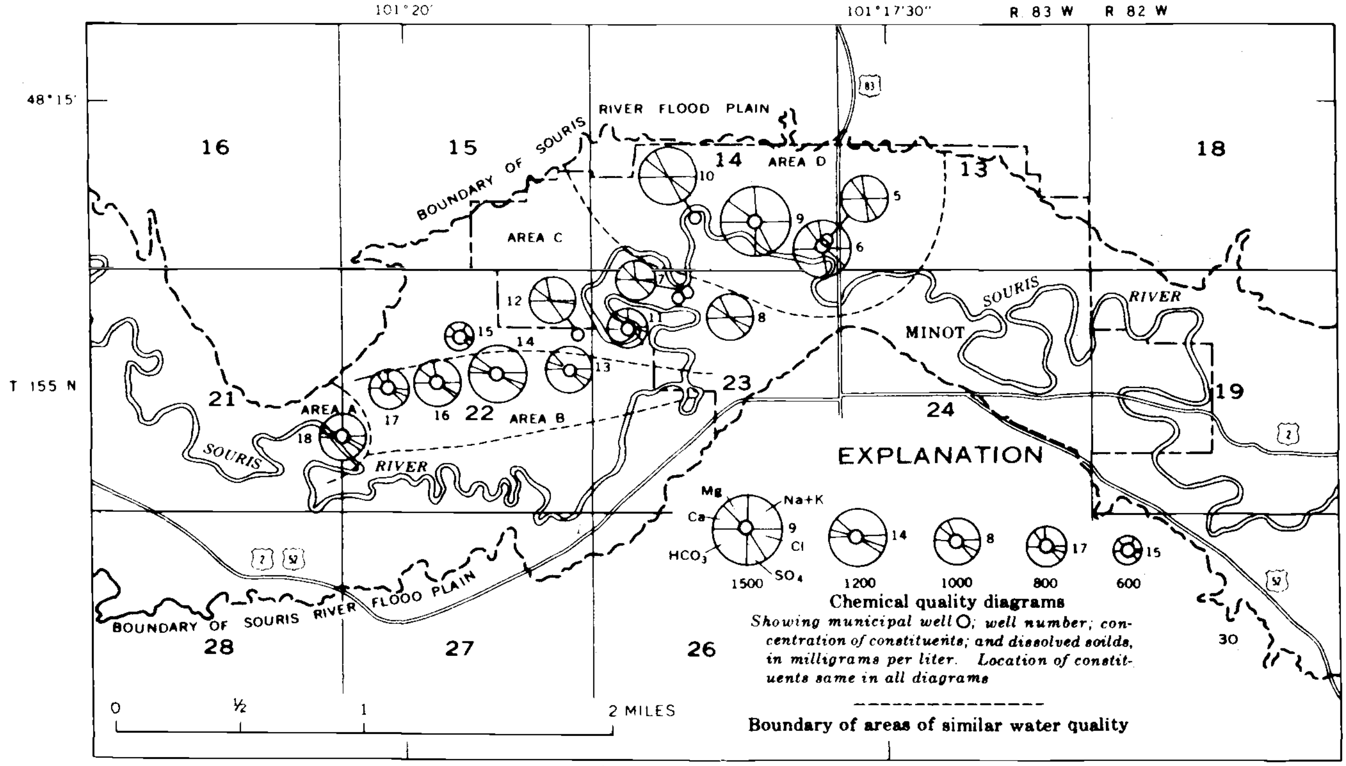


Figure 41. Chemical quality of water and dissolved solids in the Minot aquifer, North Dakota (Pettyjohn, 1967).

ground water of the area can be interpolated between wells with reasonable confidence. The map shows that there is saline ground water throughout the river-bottom area at the upstream end of the reach. Farther downstream, in the vicinity of Geronimo, the saline water appears to have been entirely replaced by much more dilute water. This dilute inflow to the system comes from underflow of Goodwin Wash and other ephemeral tributaries that drain a large area to the south. The effect of this underflow on water levels in the area also is substantial, and maps of the water-table elevation used along with water-quality maps afford a better means of gaining a good understanding of hydrologic conditions in the area than does either type of map used alone.

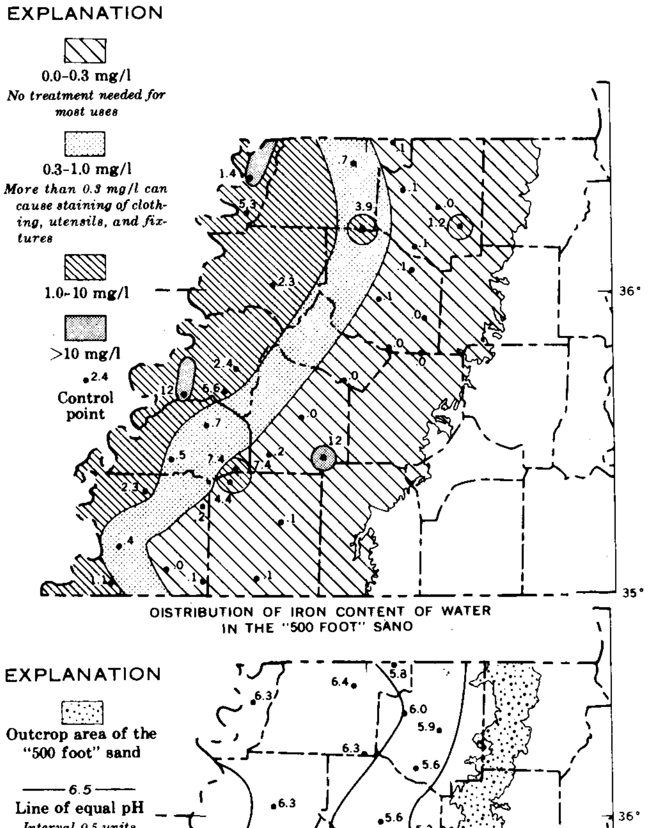


Figure 42. Distribution of iron and pH in water from the "500 foot" sand, western Tennessee (Moore, 1965).

Another study farther downstream on the Gila which was made in the 1960's and 1970's also obtained detailed information on ground-water composition near the river and summarized it with a large-scale map (Laney, 1977).

Maps of water quality were generated in a detailed mathematical model of potential effects of oil-shale development described by Robson and Saulnier (1981).

Water-Quality Profiles

A diagram showing differences in water quality along a cross section through a stream or through a surface or underground water body may be a useful way of imparting information. For the purposes of this discussion, such diagrams are called "water-quality profiles." The differences in water composition across the Susquehanna River at Harrisburg, Pa., are shown in figure 2, and the lack of mixing in the river there has already been noted and explained. Another kind of profile could be a diagram showing river-water composition over a distance along the channel. McCarren (1967) used a diagram covering a long distance on the Allegheny River to show changes in composition from sampling station to sampling station. Profile diagrams may be used in studies of estuaries where water composition tends to change frequently in response to streamflow and tidal effects.

Stratification in lakes and storage reservoirs caused by temperature differences may bring about depletion of dissolved oxygen and can affect many other constituents. Reservoir-profile diagrams are commonly used to show some of these effects. A less common type of reservoir stratification caused by differences in salinity of inflow in Lake Whitney and Possum Kingdom Reservoir on the Brazos River in Texas was shown in a profile diagram in a report by Irelan and Mendieta (1964). Figure 43 shows dissolved-solids concentration and temperature of water observed by Howard (1960) at depths at two locations in Lake Mead, the reservoir behind Hoover Dam on the Colorado River. A warm layer of dilute water was present near the surface at both sites during the August observation.

Profile diagrams are not commonly used for ground-water reservoirs. Where a considerable difference in water composition occurs with depth, however, some sort of three-dimensional diagram representing water-quality conditions is useful. The "fence" diagram commonly used by geologists can be adapted to this purpose. Diagrams of this type were used by Back (1960) to show the distribution of anions and cations in ground water of the Atlantic Coastal Plain in the Eastern United States and have been used in many other papers since then. Back introduced the concept of "hydrochemical facies" to describe the patterns of ground-water solute distributions in aquifers, in parallel to the lithofacies concept widely used in geology.

RELATION OF WATER QUALITY TO LITHOLOGY

Much of what has already been discussed in this book has to do with water-rock interaction, but the topic has been considered mainly from chemical or hydrologic viewpoints. The geologist and petrologist are perhaps more likely to approach this topic with the query, Given some knowledge of the type of rocks and their composition within a study area, what chemical properties and constituents should we expect to find in the surface and underground water? This approach to natural-water chemistry will be explored briefly in this section.

To begin with, not all the solutes in natural water come from dissolution of rock minerals. For example, the bicarbonate present in most water is derived in large part from carbon dioxide that has been extracted from the air and liberated in the soil through biochemical activity. Some rocks serve as sources of chloride and sulfate through direct solution. The circulation of sulfur, however, may be greatly influenced by biologically mediated oxidation and reduction, and atmospheric circulation of chloride and other ions may be a significant factor influencing the anion content of many natural waters. The anions in rainfall are balanced by cations, partly H^+ but also other cations. Consequently, a part of the cation content of natural water may be derived from nonlithologic sources. The importance of this effect on major-cation concentrations is usually rather small.

Many rock minerals may be viewed as hydrogen-ion acceptors, as indicated in the reactions shown previously. Hydrogen ions that participate in weathering

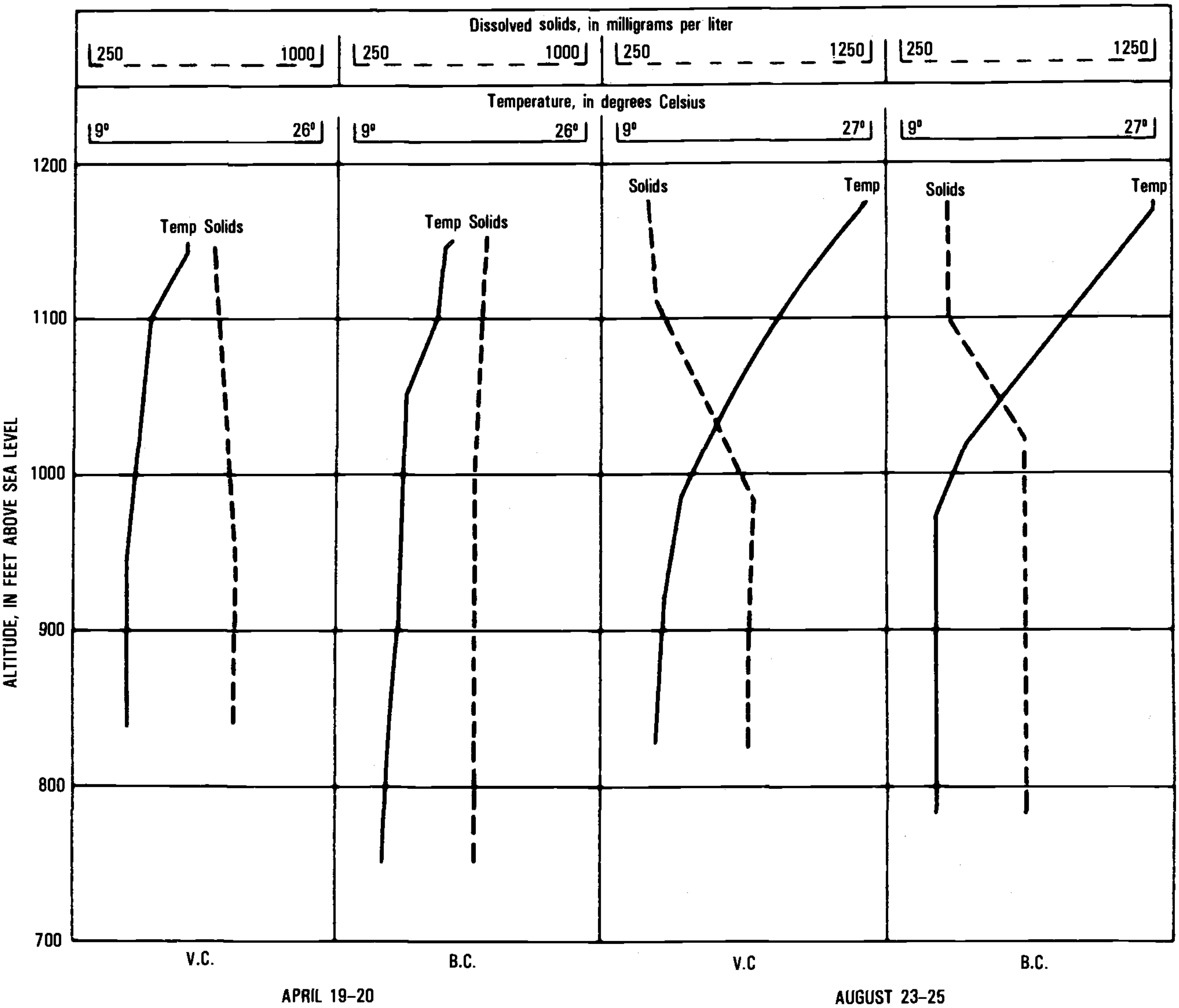


Figure 43. Temperature and dissolved solids of water in Lake Mead in Virgin and Boulder Canyons, 1948. Virgin Canyon=V.C.; Boulder Canyon=B.C. (Howard 1960)

reactions are produced in the respiration and decay of organic matter and in the oxidation of sulfides. Ideally, half the bicarbonate dissolved in water associated with carbonate rock came from the rock, and the remainder from soil air or from other similar carbon dioxide sources. In noncarbonate-rock environments, the hydrogen ions introduced through solution of carbon dioxide react with rock minerals but are mostly retained in solid residual species formed in the reaction, such as clay minerals. In a sense, the hydrogen ions release cations from the rock minerals, and the cations finally released into weathering solutions are balanced in solution by equivalent quantities of bicarbonate. Some of the H^+ and OH^- in the reaction is also derived from hydrolysis. An excellent summary of weathering reactions by Keller (1957) pointed out the significance of hydrolysis in these reactions. More recently, Drever (1982, p. 138–199) reviewed the influence of weathering processes on natural-water chemistry and demonstrated the application of various techniques with examples from published literature.

A general relationship between the mineral composition of a natural water and that of the solid minerals with which the water has been in contact is certainly to be expected. This relationship may be comparatively simple and uncomplicated, as in the case of an aquifer that receives direct recharge by rainfall and from which water is discharged without contacting any other aquifer or other water. Or the situation may be rendered complex by the influence of one or more interconnected aquifers of different composition, the mixing of unlike waters, chemical reactions such as cation exchange, adsorption of dissolved ions, and biological influences. Processes involved in soil formation and the soil composition of the area may have considerable influence on composition of both surface and underground water.

Most rocks are complex mixtures of minerals that differ widely in their stability toward, or solubility in, water. Most rocks except the evaporites, however, are made up of minerals that are not readily soluble. The classification to which a particular rock is assigned is decided on the basis of its principal components. Such a classification may not adequately reflect the presence of the more soluble components that may exert an influence on the composition of water circulating through the rock. In some kinds of rock, minor components may control major features of the composition of circulating ground water. A carbonate-cemented sandstone composed largely of silica in the form of quartz, for example, might yield a water containing mostly calcium and bicarbonate ions. Resistate and hydrolyzate rocks may contain remnants of highly mineralized connate water, and this may strongly affect the quality of ground water or surface water associated with the rocks.

The complexity of rock-water-air systems obviously imposes difficulties in applying a strict chemical-equilibrium model. Some rock species, the carbonates, for example, do lend themselves to this approach, but water associated with other rock types may be better considered as influenced by reaction rates and irreversible mechanisms. Garrels and MacKenzie (1967) described some of the effects that might be anticipated from the solution of igneous-rock minerals. If the dissolution of feldspars, for example, is viewed as an irreversible reaction, one might expect stoichiometric relationships among silica and cations in solution to resemble those in the original rock if water-rock contact time is short. Upper limits on most of the solute species would represent saturation with respect to some new solid phase, and the stoichiometry thus might be altered after long contact time of the solution with the rock minerals.

In spite of the acknowledged difficulties, many investigators have wished for a classification system for waters based on the chemical composition of the rocks from which the waters have dissolved their load of mineral matter. Regarding such a classification, Clarke (1924a, p. 8), in a paper on the composition of river and lake water, stated: "A classification of waters according to their origin is something quite different *** its purpose is geologic and although no complete scheme for it has yet been developed, the analyses as arranged in this memoir give some suggestions as to what may be possible." Clarke went on to mention limestone and dolomite waters and siliceous water, which "might be termed granitic or feldspathic, at least until a better name can be found."

In "The Data of Geochemistry," Clarke (1924b) cited a considerable number of studies, made mostly in central and western Europe, in which the writers had determined river-water composition and correlated it with drainage-basin geology. Some of these studies were made as early as the middle of the 19th century; hence, interest in this subject cannot be said to be a recent development.

It is certainly unrealistic to expect that any correlation system can succeed without considering the wide differences in weathering products and weathering rates that characterize similar rock terranes exposed in different climatic environments. If extreme conditions are left out, however, some systematic evaluation is possible. The analyses presented here show general trends and represent conditions occurring within the United States. The analyses were selected from tables given earlier in this report, and part of the basis for their selection was that their composition clearly showed the properties one might expect on a theoretical basis. More exacting studies, in which both the water and associated rock species are analyzed, have been made for granitic terranes in the California Sierra Nevada by Feth and others (1964) and for granitic and other terranes in a mountainous area near Sante Fe, N. Mex., by Miller (1961) and in Wyoming by Miller and Drever (1977). Several such studies were reviewed by Drever (1982, p. 163–199). The general findings of these investigators and of Garrels (1967), who studied published data from several sources, are in accord with the statements about water from igneous terranes made in the first edition of this book, and the discussion is, therefore, repeated here with only minor changes. The analyses shown probably represent somewhat idealized situations, but they may aid the reader in cultivating an understanding of the composition of water that might be expected from different rock types.

Igneous Rocks

Rocks of igneous origin may be classified as extrusive or intrusive. The extrusive rocks include those ejected at the land surface as lava flows and the pyroclastic deposits resulting from explosive volcanic activity. The latter include such forms as volcanic ash and cinders, tuff, and breccia. Some of the extrusive deposits are permeable enough to permit rapid and extensive circulation of water and can be good aquifers. The intrusive rocks include batholiths, stocks, dikes, sills, and other forms that are intruded below the surface of the Earth and typically are dense and nearly impermeable to water except along fractures. Both the extrusive and intrusive rocks are further classified by geologists on the basis of chemical and mineral composition, texture, and other characteristics. The chemical and mineral composition is of principal importance in the relationships to be discussed here, and classifications based on other characteristics will not be considered. Extrusive rocks and intrusive rocks of the same chemical and mineral composition have different names but tend to yield similar weathering products to water. As a class, the extrusive rocks react more readily than the intrusive rocks for two reasons: (1) the extrusive rocks generally expose more surface area for reaction and (2) many are partly glassy—that is, not crystalline.

Igneous rocks consist predominantly of silicate minerals, although in glassy species the crystal organization may be poorly developed. The classification scheme for silicate minerals presented earlier aids somewhat in understanding the bases of the classification of igneous rocks. If oxygen is relatively abundant compared with silicon, minerals having neso- and inosilicate structures tend to be formed as the molten mass crystallizes. If oxygen is relatively depleted and silicon is abundant, the structures of minerals will more likely have the tectosilicate pattern. The intermediate classes of silicate structures will be formed in systems lying between the extremes. The crystallization process is complex, however, and products formed depend on availability of other elements and on temperature and pressure. The subject cannot be considered here, but it is discussed more extensively in geochemical textbooks. (See Krauskopf, 1979, p. 287-367.)

Generally, rock analyses are expressed in terms of oxides. These can be recalculated to a statement that shows the proportions of the principal mineral species in the rock. Analyses in this form are the basis for the classification scheme used here.

Rocks of igneous origin exhibit a wide range of mineral compositions, for rock masses are generally mixtures of many different mineral species. Although it is not possible to design a simple classification scheme for these rocks, a general basis for the commonly used names for different rock types can be shown readily in terms of the major mineral components. Readers unfamiliar with petrology may thus gain some understanding of the meaning of such terms as granite or basalt and of the possible significance of the rock composition thus indicated in predicting the chemical composition of solutions of weathering products. The classification scheme used here is in general that of Peterson (1961), who considered it to represent a consensus of authorities on the subject. All rocks form a continuous series having a wide range of compositions and textures, and any assignment of classification and name must be entirely arbitrary.

The proportion of pure silica, generally in the form of quartz, that is present forms a convenient base from which to begin a rock-classification scheme: (1) rocks rich in quartz ($>$10 percent), (2) rocks impoverished in quartz and in feldspathoids (both $<$10 percent), and (3) rocks rich in feldspathoids and impoverished in quartz. Feldspathoids, a class of aluminosilicate minerals chemically similar to feldspar, form from melts enriched in soldium and potassium but containing too small an amount of silicon to produce tectosilicate feldspar structures. Rock masses belonging to the third class above are not common and will not be considered further in this book.

The second property used here in classifying igneous rocks is derived from the amount and type of feldspar present. The feldspar group is a very important class of igneous-rock minerals in which Al^{3+} ions substitute for some of the Si^{4+} ions in the tectosilicate structure. To compensate for the loss of positive charges, additional cations are bound in the structure, most commonly K^+, Na^+, or Ca^{2+}. The potassium feldspar $KAlSi_3O_8$ may occur in two different crystal forms, orthoclase or microcline. The plagioclase feldspars form an isomorphous series—a solid solution—whose composition ranges between the end members albite, $NaAlSi_3O_8$, and anorthite, $CaAl_2Si_2O_8$.

Rocks rich in quartz and having a large proportion of feldspar of which more than two-thirds is of the potassium or sodium type would be called granite if intrusive in origin and rhyolite if extrusive. A rock rich in quartz and feldspar in which plagioclase predominates and the proportion of albite to anorthite is greater than 1:1 would be called quartz diorite if intrusive and dacite if extrusive. Both these two kinds of rock should contain less calcium than sodium and potassium.

Rocks impoverished in quartz but rich in feldspar, more than two-thirds of which is of the sodium or potassium type, are called syenite if intrusive and trachyte if extrusive. Rocks impoverished in quartz but rich in feldspar in which plagioclase predominates and the proportion of albite to anorthite is greater than 1:1 are called diorite if intrusive and andesite if extrusive. Rocks relatively impoverished in quartz and containing more than 10 percent feldspar, mostly plagioclase in which anorthite predominates, are called gabbro or diabase if intrusive and basalt if extrusive.

Rocks in the latter class generally contain considerable amounts of ferromagnesian inosilicate and nesosilicate minerals such as hornblende, amphibole, and olivine. In the peridotite rocks, quartz and feldspar are virtually absent and the ferromagnesian species of minerals predominate. Rocks of this type are commonly called ultrabasic.

Further information concerning the classification of rocks can be found in standard texts on petrology and geochemistry. In practice, the application of any system requires careful examination of the rocks, and the classification given to a particular rock based only on examination in the field may not always be as indicative of its composition as the foregoing scheme might suggest.

In considering igneous rocks in relation to water composition, the texture and structure of the rocks are significant because they determine the surface area of solid rock that may be exposed to attack. Ground water may be recovered in large amounts from some of the extrusive igneous rocks that contain shrinkage cracks and other joints, interflow zones, or other openings through which water may move. Most igneous rocks, however, are rather impermeable. Surface water originating in areas where igneous rocks are exposed is low in dissolved solids because, in general, the weathering attack on igneous rocks is slow. Concentrations are likely to be a function of contact time and area of solid surface exposed per unit volume of water. Where vigorous soil-forming processes and plant growth are occurring, an enhanced supply of carbon dioxide and, hence, hydrogen ions becomes available to circulating water. The amount of attack that occurs is related to the availability of H^+, as well as the other factors cited.

Surface water in areas of igneous rocks may display the effects of rock solution less distinctly than underground waters that have better opportunity to participate in reactions with the rock minerals. A considerable and usually uncertain fraction of the solute load in a very dilute river or lake water may be related to solutes in rainfall or to dust and other atmospheric fallout transported from other localities. The examples cited later in this section are mostly underground waters.

Detritus may be derived from igneous rocks by erosional processes that are largely mechanical, and subsequent circulation of water through detritus of this type can give rise to an assemblage of solutes closely similar to that to be expected from the unaltered rock. The detrital material, however, has greatly increased surface area where reactions with water can occur.

From the above generalizations, a much simplified view of the process of attack by water may be expressed in terms of chemical equations. The reaction of carbon dioxide and water supplies hydrogen ions:

$$CO_2(aq)+H_2O=HCO_3^-+H^+.$$

Hydrogen ions aid in the attack on feldspars that causes the feldspars to be changed to clay minerals, here represented by kaolinite, and silica and cations are released:

$$2NaAlSi_3O_8+9H_2O+2H^+ =Al_2Si_2O_5(OH)_4+2Na^++4H_4SiO_4$$

and

$$CaAl_2Si_2O_8+H_2O+2H^+=Al_2Si_2O_5(OH)_4+Ca^{2+}.$$

In tropical climates the clay minerals may break down or fail to form, leaving a residue of bauxite or of other metal oxides, if significant amounts of these metals were present in the original rock. Attack on ferromagnesian species may be represented by the decomposition of forsterite to form antigorite, silica, and magnesium ions:

$$5Mg_2SiO_4+8H^++2H_2O=Mg_6(OH)_8Si_4O_{10}+4Mg^{2+}+H_4SiO_4.$$

The alteration of forsterite by this process requires much H^+ and, as shown by Barnes and O'Neil (1969), may result in water having a very high pH. A good many other similar reactions could be written for other mineral species, but for this discussion it is not necessary to go into further detail. The direct solution of quartz to give H_4SiO_4 is a possible source of silica in water also, but this is a slow reaction and is generally a less significant source than silicate decomposition.

The weathering solutions must maintain a cation-anion charge balance. Equations given above include HCO_3^- as the only anionic species, and it generally is the principal one in these dilute solutions. Atmospheric sources of Cl^- and SO_4^{2-} are generally less important, but some accessory mineral species may provide larger quantities of these anions.

All these reactions involving dissolution of silicates probably are more complicated than the equations imply, but the equations can serve as a basis for some useful generalizations. The reactions as written are not reversible, but the rate at which the reaction proceeds will be speeded if H^+ activity increases and will tend to be retarded by the attainment of high activities of the dissolved products. The rate of reaction may also be a function of the area of surface of solids exposed per unit volume of solution and of the rates of ion transport away from the solid surfaces by water movement through the reaction sites. The reaction rate also is increased by increased temperature.

As the solutions move through the soil and the underlying rock, the composition of the water should be expected to change. At first the composition may reflect the stoichiometry of the initial weathering process. At later stages, saturation with respect to amorphous silica may be attained so that no further increase in dissolved-silica concentration can occur. Garrels and MacKenzie (1967) postulated that water from feldspathic terranes would, as it became more concentrated owing to evaporation, evolve to high-pH sodium carbonate solutions like some of the playa lakes on the east side of the Sierra Nevada of California.

Specific rates of reaction of feldspar have been studied in the laboratory rather extensively (Busenberg and Clemency, 1976; Petrović, 1976). Work also has been done on kinetics and mechanisms of reaction of other silicate rocks and minerals (Helgeson, 1971; White and Claassen, 1978; Clemency and Lin, 1981; Lin and Clemency, 1981). This research and work of others aids in understanding the mechanisms of silicate dissolution.

For the purpose of this discussion the stoichiometric relationships, and other considerations displayed in the simple equations, can be used to draw certain inferences. For example, it would appear that because sodium feldspar contains more silica than other rock minerals considered, water influenced by disintegration of this mineral to form solutes and kaolinite should have a high silica concentration. If the feldspar is a pure albite, the molarity of silica released to the water would be about double that of the sodium. If the clay mineral form is higher in silica content than kaolinite, the ratio would be lower.

In figure 44, analyses of several waters known to be associated with igneous rocks of different kinds are shown graphically. Analysis 12–2 (corresponding to analysis 2 in table 12) represents water from a spring issuing from rhyolitic terrane; the effect of dissolution of sodium-rich silicate minerals typical of this rock type is demonstrated both by the high silica content and by the high molar ratios of silica to sodium and silica to bicarbonate, although the theoretical maxima for albite dissolution are not reached. The water represented by this analysis issues

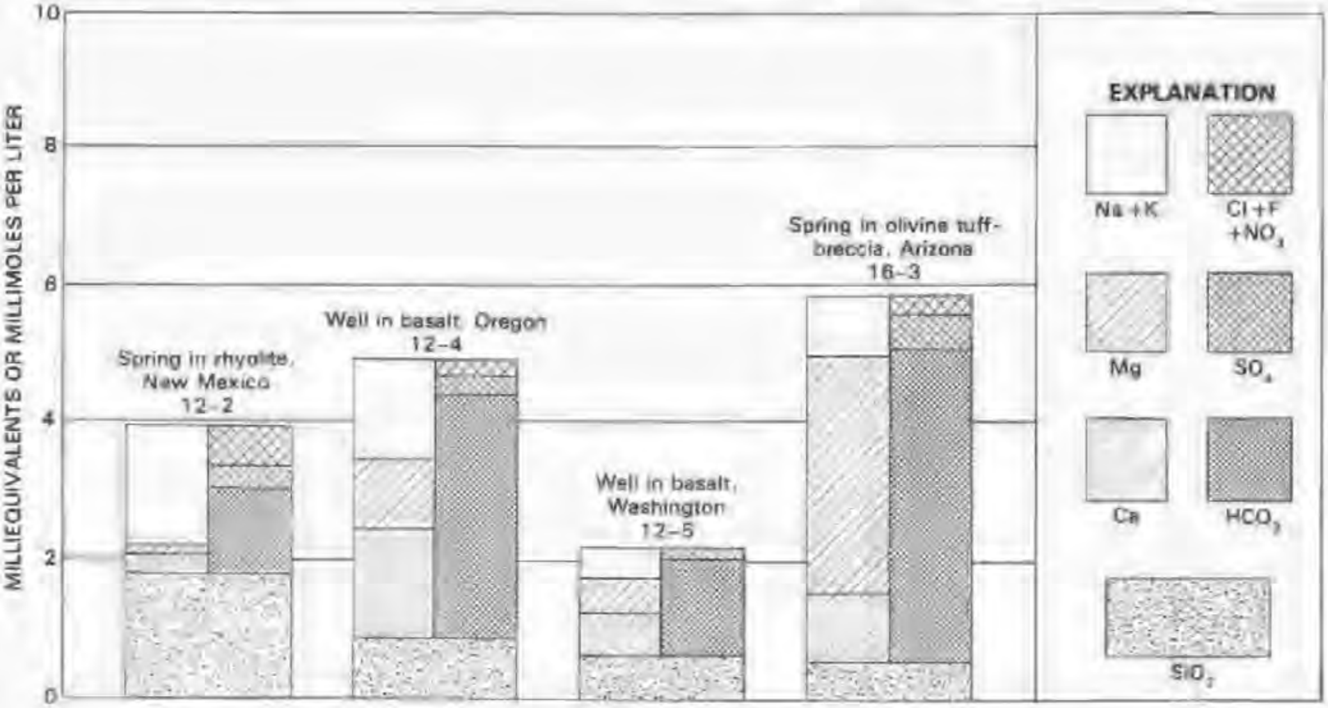


Figure 44. Composition of ground water obtained from igneous rocks. Numbers above bars indicate source of data in tables 12 and 16 (e.g., "12-2"=table 12, analysis 2).

from the ground at a temperature of 38°C. The elevated temperature increases the solubility of silica and also probably causes a more rapid attack on the rhyolitic glass and feldspars and a higher concentration of sodium than might otherwise be observed.

Analysis 16–3 represents water from a spring issuing from an ultrabasic rock. The molar ratio of magnesium to silica in this water is 3.3, which is a fairly close approach to the theoretical value of 4 suggested by the equation for dissolution of olivine. This water probably had a rather short contact time with the rock. A more unusual example is given in analysis 18–5 (fig. 50), which represents a water from an area where peridotite is being altered to serpentinite. Additional reactions related to this process that may control calcium and magnesium concentrations in the water were described by Barnes and others (1972).

In general, the amount of silica produced per hydrogen ion used up in water-rock interaction is higher for sodium-rich feldspar than for the other rock minerals considered. Thus, one might expect higher silica concentrations in relation to total ion content for water from granite or rhyolite than for water associated with basalt or ultrabasic rock in which sodium-rich feldspar would be rare or absent. Ideally, the ratio of calcium to sodium in water from feldspar-rich rocks should be related to the composition of the plagioclase feldspar present. Also, the proportion of magnesium to the other cations in the water could be an index to the relative abundance of ferromagnesian rock minerals in the rock environment.

Garrels (1967) made a number of generalizations, like the ones above, that he believed useful in considering broadly the geochemistry of natural water. It is evident, of course, that this is only a starting point in considering the highly complex systems commonly found in nature.

Analyses 12–4 and 12–5 represented in figure 44 are for water associated with a basalt transitional between the rhyolite of 12–2 and the ultrabasic rock of 16–3. The decreasing relative importance of sodium and the decrease in the SiO_2:HCO_3 ratio is evident in the change in the rock type to a form less likely to contain alkali feldspar; however, the relationship is obscured to some extent by the differences in total ion content among the different waters.

Sedimentary Rocks

The classification scheme for sedimentary rocks used in this section was introduced in an earlier chapter dealing with the composition of the Earth's crust. In a strict sense, most of the ground water and surface waters of the Earth are associated with sedimentary material for most or all of the time they spend in that part of the hydrologic cycle. Chemical characterization of these materials by any existing classification scheme can be only approximate. As noted previously, resistates include sandstone and other species made up of relatively unaltered fragments of other rocks. Hydrolyzates are fine-grained species made up, in large part, of clay minerals. Precipitates are, for the most part, carbonate rocks. Evaporites consist of readily soluble minerals, such as gypsum and halite, that were deposited from water that became concentrated owing to evaporation.

Resistates

As the name implies, resistate sediments are composed principally of residual unaltered fragments of a precursor rock body. These fragments survived the weathering process because they were resistant to chemical attack; however, the intensity of weathering processes has a wide range, and the composition of mineral particles in this type of sediment reflects this fact. The particles also may range in size from boulders to submicrometer fragments, but generally these sediments have been reworked by moving water and the finest grain sizes are rare or absent.

An ideal resistate might be a sandstone composed of quartz grains and other highly resistant mineral fragments such as garnet, tourmaline, and zircon. In many resistate sediments, chemical attack may not have been strong enough to break down feldspars or even some of the less resistant minerals. Some sands and gravels are made up principally of comminuted fragments of the original rock that have undergone little chemical change. These fragments are subject to later attack and solution by water in the same way the original rock was, but perhaps at an accelerated rate owing to the increased surface area per unit weight of rock.

The consolidated resistate sedimentary rocks, such as sandstone, contain cementing material deposited on the grain surfaces and within the openings among grains. This cementing material normally is deposited from water that has moved through the rock at some past time and can be redissolved. The most common cementing materials include calcium carbonate, silica, and ferric oxyhydroxide or ferrous carbonate, with admixtures of other materials such as clay minerals.

Many resistate sedimentary rocks are permeable and may, therefore, easily receive and transmit solutes acquired by water from some other type of rock. In the course of moving through the sedimentary formations, several kinds of alteration processes may occur that may influence the composition of the transmitted water. One of these processes has already been mentioned—the precipitation of cementing material. This process is commonly a reversible one, but it may be more complicated than simple bulk precipitation and re-solution of a solid. For example, the electrostatic field in a solution near a mineral surface is different from the field farther away from the surface. This influences solute ion behavior, and precipitation of solids may be catalyzed by this effect. The precipitation of a coating on the grain surfaces of a detrital rock may alter the composition of water that has reached the rock from some other formation. As this "foreign" water passes through its new environment, the coating of grain surfaces will progress slowly in the direction of water movement until all the active surfaces in the formation are covered, a process that may require a long time and a large volume of water. During the time this process is taking place, an advancing front of chemical change will occur. Many species of metal ions can be incorporated in the coatings by coprecipitation effects. The coprecipitation of certain metals with calcite has been studied by Alekin and Moricheva (1960). The possibility that coprecipitation might occur with some other kinds of cementing material, notably ferric oxyhydroxides, seems at least as great (Hem, 1977b).

Other factors that may control concentrations of major, as well as minor, constituents of water circulating through resistate sediments are adsorption and ion exchange. Most mineral surfaces exposed to water at near-neutral pH have a net negative electrostatic charge. Some sites on the surface have rather intense charges owing to imperfections in crystallinity and to broken chemical bonds of ions held in the lattice, and cations from solution will be attracted to and held at these sites. Less commonly, there may be sites with net positive charges, at which solute anions may be retained. Ions associated with the charge sites participate in equilibrium reactions with species in solution in the process of ion exchange. "Adsorption" is a more general term for retention of solutes at surfaces and sometimes is applied to all such effects, in contrast to "ion exchange," which is considered to occur at specific sites. The processes that are involved have been described earlier. Because some ion always is present at an exchange site, the reactions are replacements whereby ions from solution are adsorbed and sorbed ions are released, in a manner approximately predictable from equilibrium theory.

A sandstone that is deposited under marine conditions or that is later intruded by seawater would be expected to have sodium ions adsorbed on most exchange sites. Freshwater entering the sandstone at some later period can be expected to have its cation composition altered by ion-exchange reactions. Commonly, this takes the form of removal of most of the divalent cations from the entering water and their replacement by sodium present in exchange positions on the mineral surfaces. This natural softening effect has been observed in many aquifers. One would expect that an aquifer having this property would show general behavior like that of an ion-exchange column or of a water softener and would have a characteristic breakthrough point at which the exchange capacity became exhausted.

Adsorptive capacity for anions may well involve hydroxide groups that can occur at some charge sites. Hydroxide groups were shown by Halevy (1964) to be available at certain sites on kaolinite particles. These hydroxide ions could perhaps be replaced by fluoride ions because they have the same charge and the same approximate shape. Bower and Hatcher (1967) showed that such a process can occur in soils. Some ground waters high in pH show high concentrations of fluoride, possibly owing to the reversal of this effect (analysis 1, table 18). Other anions generally are larger than the fluoride ion and seem less likely to be involved in ion-exchange equilibria, although Yamabe (1958) believed the reaction could involve carbonate ions.

The participation of clay minerals in ion-exchange reactions has been indicated in some of the foregoing discussion. These minerals have high exchange capacity per unit weight and are present in considerable amounts in some resistate sediments, although the clay minerals are more characteristically found in hydrolyzates. Exchange reactions also are important, of course, in water in hydrolyzate sediments. Exchange processes are by no means confined to clay minerals. When exchange capacities of minerals are computed on the basis of sites per unit of effective surface area, the importance of clays as exchange substrates in ground-water systems can be viewed more realistically. Much of their effectiveness as cation exchangers in soils is due to the large surface area per unit weight that clay minerals have.

Neither the surface area encountered by a unit volume of ground water in an aquifer nor the exchange capacity per unit area is commonly determined. A realistic model for solute behavior may require attention to these factors, however (Hem, 1977b).

Many resistate sediments form in anaerobic environments and contain organic material or other solids that can maintain reducing conditions for long periods of time. The rock also may contain some reduced mineral species, such as pyrite. The solutions moving through the sedimentary rock at later periods in its history may bring in oxygen and may participate in oxidation or reduction reactions. Many such reactions may be biologically mediated—that is, they may be intimately involved with life processes of micro-organisms. Oxidation reactions can be expected in the part of the rock lying above the water table and to some extent at greater depth, depending on the availability of oxygen. Species stable in reduced environments, such as pyrite, will be altered by oxidation, with a release of energy. The sulfur of pyrite, for example, will be oxidized to sulfate, and ferrous iron will be released. Reduction processes that can occur where oxygen is depleted may convert sulfate to sulfur or sulfide, and both oxidation and reduction reactions involving nitrogen may be significant. Any of these reactions for which an outside source of energy is needed either require some other material that bacteria can use for food or must occur where biota can obtain radiant energy from sunlight.

Figure 45 describes graphically the analyses of four waters from resistate sediments. Analysis 12–7 represents water from the Santa Fe Formation which underlies the Rio Grande valley at Albuquerque, N. Mex. The high silica concentrations and other properties suggest that the water has attacked particles of igneous rock included in this formation. The ground water associated with a pure quartz sand can be among the lowest in dissolved-solids content of any ground water. For example, water from wells in quartz sand aquifers on Long Island, N.Y., may contain less than 30 mg/L of dissolved solids (Kimmel and Braids, 1980).

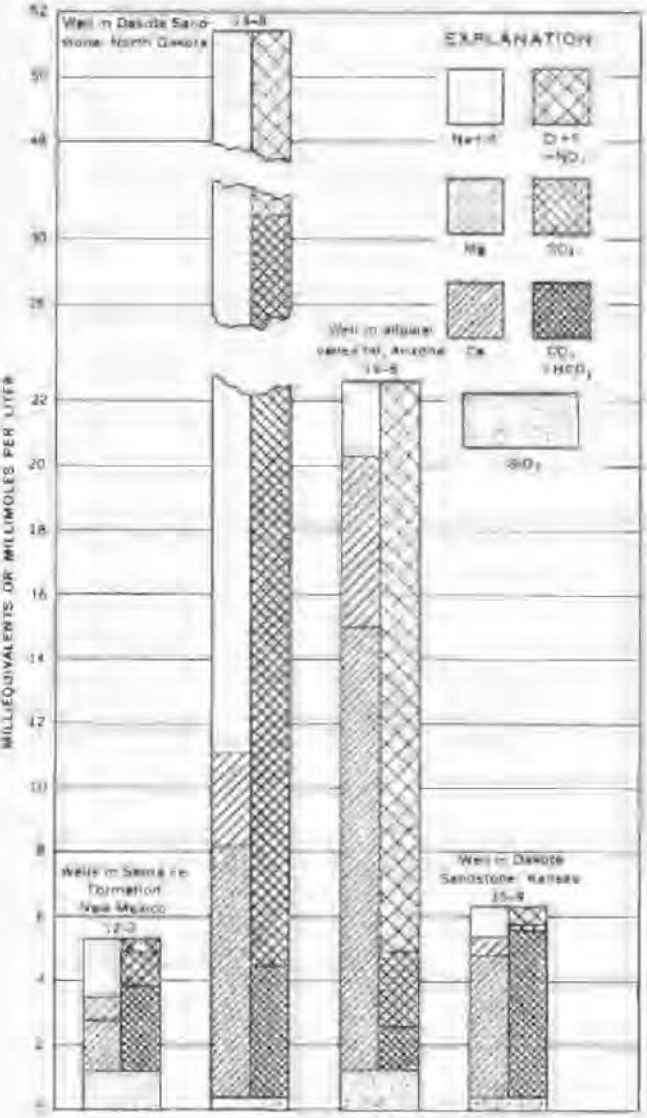


Figure 45. Composition of ground water obtained from resistate sedimentary rock types. Numbers above bars indicate source of data in tables 12, 14, and 15 (e.g., "12-7"=table 12, analysis 7).

Analysis 14–8 is for a much more highly mineralized water from the Dakota Sandstone in North Dakota, where the concentrations of sodium, chloride, and sulfate are high. These ions can best be explained as having migrated into the sandstone from other rock formations associated with the sandstone. The sluggish circulation of water in the sandstone retards flushing of solutes.

Analysis 15–6 represents water from valley fill at Phoenix, Ariz., that reflects the influence of irrigation-drainage water. The proportions of cations in this water probably have been altered by ion-exchange reactions in the overlying soil.

Some rock formations yield notable concentrations of unusual constituents to ground water and thus provide a natural tracer by which the lithologic source of the water can be recognized. One of the more outstanding examples of such an effect is the occurrence of strontium in water from certain sandstones and other rock formations in Wisconsin, as noted Nichols and McNall (1957).

Because of the many ways in which their composition may be affected, the water from resistate rocks has a wide range of chemical quality. Although water from a particular aquifer may have distinctive properties, these must generally be determined by actual sampling and analysis and can seldom be predicted solely from the knowledge that the water is associated with resistate sediments.

Hydrolyzates

Shale and other fine-grained sedimentary rocks are composed, in large part, of clay minerals and other fine-grained particulate matter that has been formed by chemical reactions between water and silicates. Almost all hydrolyzate rocks also contain finely divided quartz and other minerals characteristic of resistates, but such minerals are present as smaller particles. Shale and similar rocks are porous but do not transmit water readily because openings are very small and are poorly interconnected. Many such rocks were originally deposited in saltwater, and some of the solutes may remain in the pore spaces and attached to the particles for long periods after the rock has been formed. As a result, the water obtained from a hydrolyzate rock may contain rather high concentrations of dissolved solids. Because environmental conditions commonly change from time to time during deposition, many hydrolyzate sediments contain layers of coarser material, and water may be transmitted in those layers at a rate sufficient to supply a well or spring. Even where the material is too fine grained to transmit water to wells in useful amounts, the very wide lateral exposure of such formations to more porous overlying, and underlying, layers may result in a significant migration of water and solutes from the hydrolyzates into the aquifers with which they are interbedded. These effects can be noted in many places and can become important

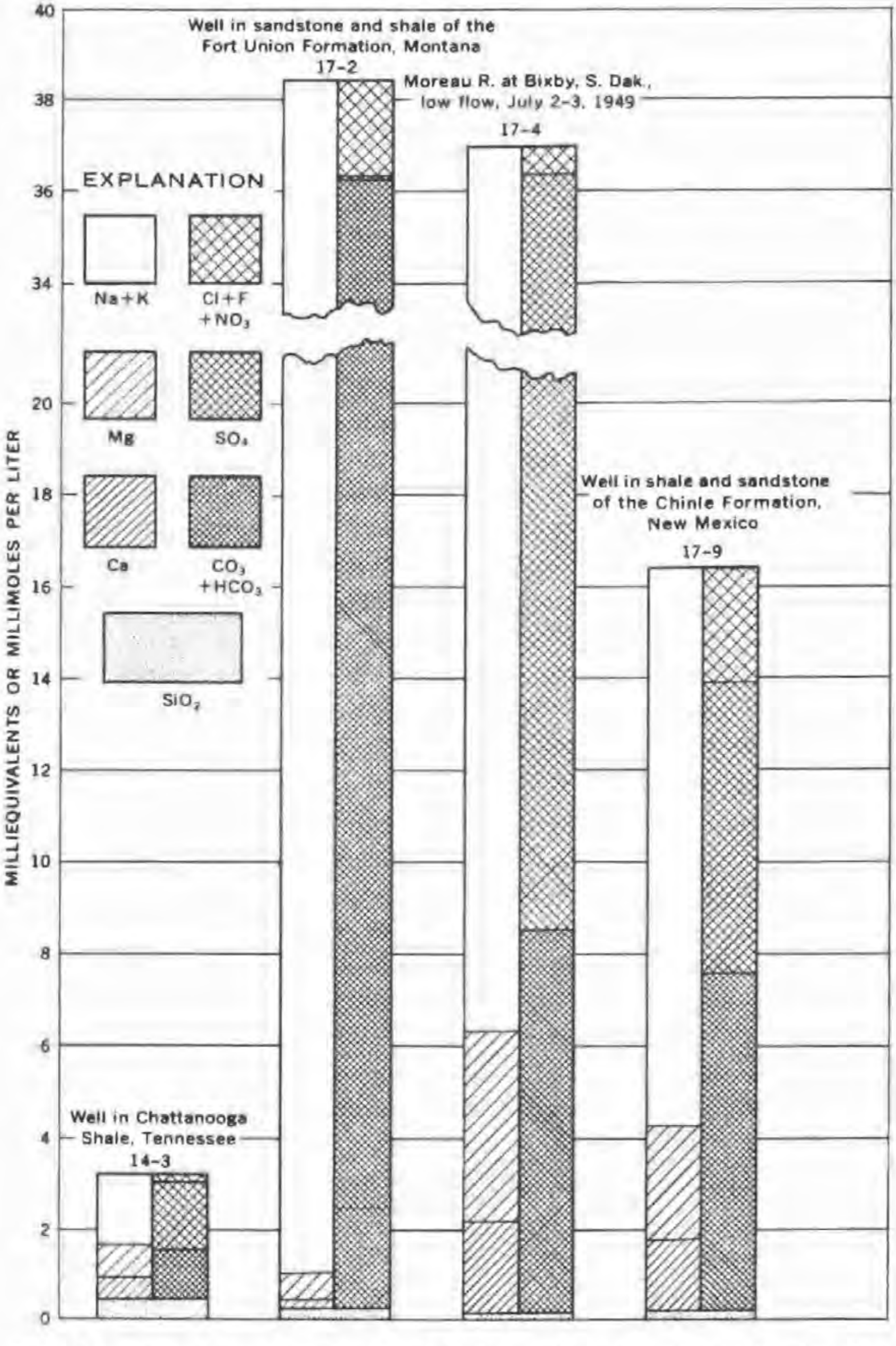


Figure 46. Composition of water obtained from hydrolyzate sedimentary rock types. Numbers above bars indicate source of data in tables 14 and 17 (e.g., "14-3"=table 14, analysis 3).

and damaging when hydrostatic pressures in the zone of saturation are changed extensively by withdrawals of ground water. Lofgren (1975) described extensive subsidence of irrigated land in San Joaquin Valley, Calif., following ground-water extraction. Similar effects have been observed in other areas. The effect of shale beds containing solutes on quality of surface runoff is worth noting, also.

Davis (1961), in a study of surface-water composition, noted that the runoff from areas underlain by certain geologic formations in California was characterized by low ratios of bicarbonate to sulfate. He correlated this fact with the presence of sulfide minerals in the sedimentary formations. These minerals formed when the sediments were laid down in reducing environments. Weathering caused the oxidation of the sulfide to sulfate. Reduced iron minerals, notably pyrite, are commonly associated with hydrolyzates.

Analyses in figure 46 represent four waters associated with hydrolyzate sediments. They share one dominant characteristic: sodium is their principal cation. This is not necessarily true of all water associated with hydrolyzates, however, as some contain large concentrations of calcium and magnesium. Clay minerals can have high cation-exchange capacities and may exert a considerable influence on the proportionate concentrations of the different cations in water associated with them. Direct solution of the hydrolyzate minerals themselves, however, is a less significant factor except in environments in which water circulation is rapid (in instances of high rainfall, for example) or in which a low pH is maintained in the circulating water.

Analysis 14–3 represents water from the Chattanooga Shale that has a low dissolved-solids concentration because of the abundant supply of water from rainfall. The rather high silica concentration in this water is somewhat unusual for water from hydrolyzates and may be the result of solution of unaltered silicate minerals. Analysis 17–2 represents water from sandstone and shale in the Fort Union Formation. This analysis shows the effect of both cation-exchange softening and sulfate reduction. The former process has increased the sodium concentration at the expense of the calcium and magnesium. The latter process has caused the bicarbonate to increase, partly at the expense of the sulfate.

The composition of water at very low flow in the Moreau River at Bixby, S. Dak., is shown by analysis 17–4. The drainage basin of this stream contains a high proportion of hydrolyzate rocks. Analysis 17–9 represents water from the Chinle Formation, which is sandy enough in some places to yield small amounts of water.

The effect of hydrolyzates containing readily soluble material can be observed in floodwaters of some streams, for example, in the basin of the Rio Puerco, which is a tributary to the Rio Grande above San Acacia, N. Mex. Floodwaters from this tributary are heavily laden with suspended sediment and dissolved solids. Figure 47 shows the average analyses for normal flow and for summer-flood periods for the Rio Grande at San Acacia. The difference between the averages is in large part the effect of inflow from the Rio Puerco. Somewhat similar effects can be demonstrated for other streams draining hydrolyzate sediments, for example, the Powder River of Montana. The chemical relationships in that basin were described by Swenson (1953).

Precipitates

The sedimentary rocks termed "precipitates," for the purposes of this discussion, are composed of the common alkaline earth carbonates: limestone, which is mainly calcium carbonate, and dolomite, which is principally the compound $CaMg(CO_3)_2$. The magnesium limestones have a wide range of Ca:Mg ratios, up to equimolar.

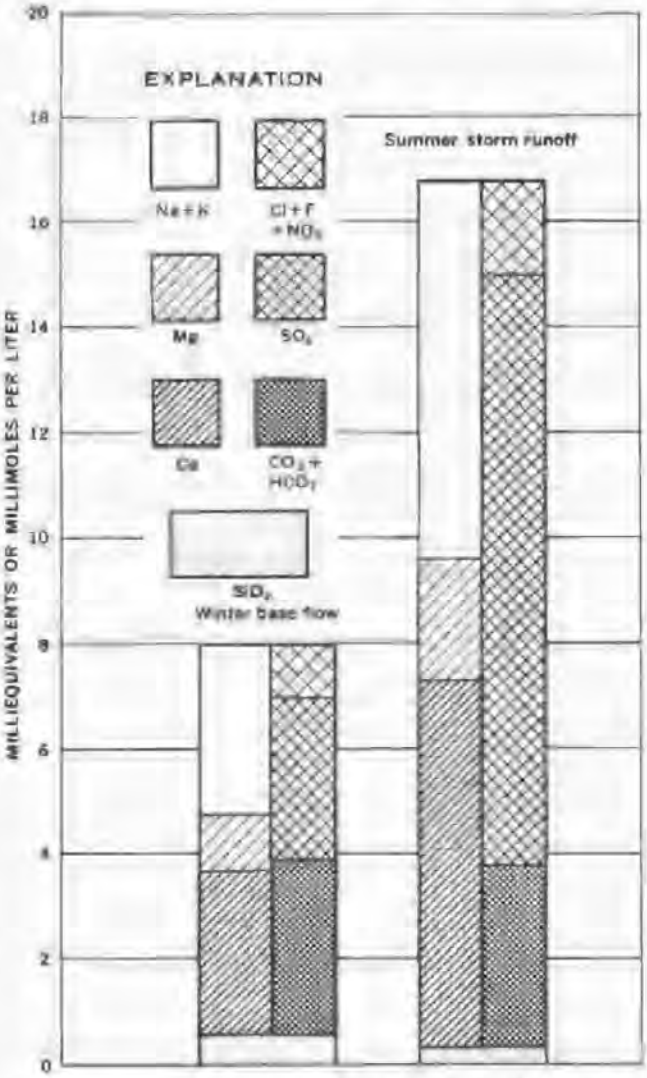


Figure 47. Average composition of water from Rio Grande during two periods in 1945 and 1946.

There are no massive carbonate-rock formations in which magnesium is more abundant than calcium, but several magnesium carbonate minerals with and without added hydroxide do exist. Carbonate minerals other than those of calcium and magnesium occur as impurities in many limestones and dolomites. As a class, the carbonate rocks can be viewed as fairly simple chemical substances compared with the silicate rocks.

The solution of limestone is principally the process of solution of calcium carbonate, which already has been discussed at length. The kinetics of dissolution and precipitation of calcite have been studied extensively. Both processes are fast enough to make it reasonable to evaluate limestone hydrochemistry by an equilibrium approach. However, the circulation systems in limestone are generally not entirely closed to the entry of outside reactants. Calcite equilibria are discussed more extensively in the section of this book dealing with calcium. The proportion of magnesium to calcium in water from limestone may reflect to some extent the composition of the limestone. This interpretation must be made cautiously, however, because there are many complications that can influence the calcium-to-magnesium ratio. Silica is normally a minor constituent of water from limestone.

Analysis 15-1 in figure 48 represents water from a rather pure limestone. According to the calcite-solubility graph (pl. 2), this water is a little below saturation with respect to calcite. The source is a spring of large discharge in a region where water is plentiful. The predominance of calcium and bicarbonate in the analysis, however, is obvious. This analysis also is shown graphically in figures 30-37.

Dolomite does not dissolve reversibly—that is, the conditions required for direct precipitation of dolomite are not generally reached, at least in the kind of environment in which ground water of potable quality occurs. As noted for limestone, however, the ratio of calcium to magnesium in water from dolomite tends to reflect the 1:1 composition of those ions in the rock, so long as the solution is not subjected to too many influences that might cause some calcium carbonate precipitation. Calcite precipitation from such a water can decrease the Ca:Mg ratio to values below 1. Analysis 16-1 in figure 48 represents water from the Knox Dolomite. It has Ca:Mg ratio near 1.0, and judging from its pH it seems to be virtually at saturation with respect to calcite. The influence

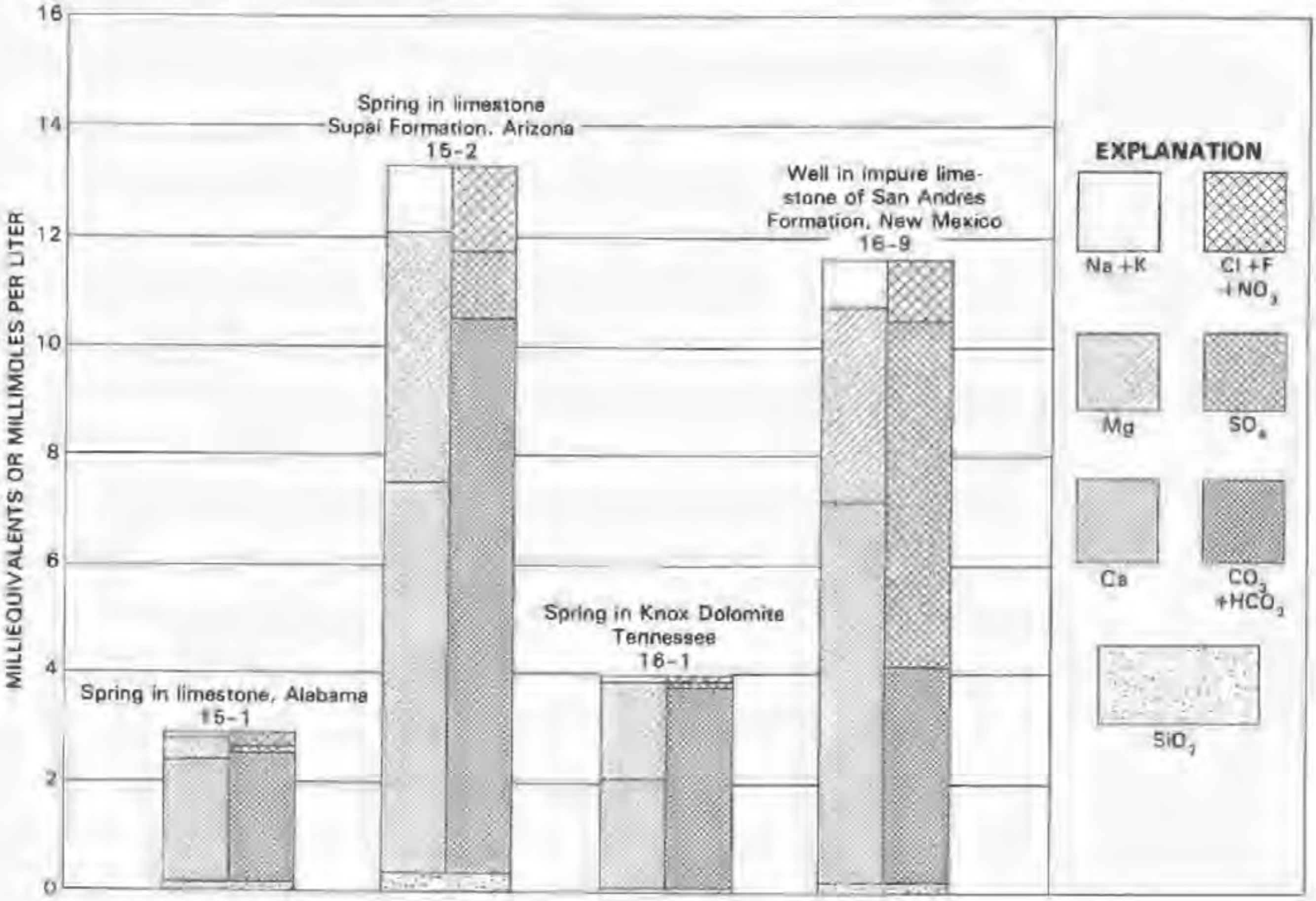


Figure 48. Composition of ground water obtained from precipitate sedimentary rock types. Numbers above bars indicate source of data in tables 15 and 16 (e.g., "15-1"=table 15, analysis 1).

of impurities in the rocks on these two analyses evidently is insignificant. The bicarbonate concentration is very nearly equal to the sum of calcium and magnesium in the two bar graphs, and sodium, chloride, and sulfate are all present in minor amounts.

Analysis 16–9 is for a water from impure limestone that contains both gypsum and dolomite; the water also has been influenced by solution of sodium chloride. The hydrology of the aquifer from which this water came, the San Andres Limestone of the Roswell basin, New Mexico, was first described by Fiedler and Nye (1933).

Water that moves for long distances through impure limestone and dolomite may participate in irreversible processes. Calcite saturation may be reached first, after which gypsum and dolomite continue to dissolve along the flow path while calcite is precipitated (Plummer and Back, 1980). The influence of gypsum is indicated by the large proportion of sulfate in solution in analysis 16–9, and the bicarbonate content is barely larger than that of analysis 16–1, although calcium and magnesium are much greater.

Analysis 15–2 represents a water from limestone in the deeply buried Supai Formation in the Grand Canyon region, Arizona. The constituents other than calcium, magnesium, and bicarbonate in this water may originate from other formations, as little is known of the circulation of the water in this aquifer. A point of interest, however, is the high degree of supersaturation with respect to calcite. The water deposits calcite on exposure to air. Obviously, at some point in its circulation path, this water achieved a considerably greater capacity than most waters for solution of limestone. Carbon dioxide released by metamorphic processes could supply additional solvent power. Orfanidi (1957) suggested that metamorphic alteration of carbonate rocks at depth could help explain the composition of some ground waters in the U.S.S.R. Barnes, Irwin, and White (1978) reviewed the metamorphic sources of CO_2 in other areas. In some terranes the bacterially mediated reduction of sulfate coupled to oxidation of organic matter also can produce substantial amounts of CO_2.

Readers interested in pursuing the subject of relationships between carbonate rocks and water composition will find more details in discussions in this book in the sections titled "Calcium," "Magnesium," "Alkalinity," and "Hydrogen-Ion Activity" and in the large literature on this subject that is available elsewhere (for example, Garrels and Christ, 1964, p. 74–92).

Evaporites

The highly soluble nature of evaporite sediments causes water associated with them to have high dissolved-solids concentrations. Gypsum and anhydrite are the least soluble of the rocks considered here as evaporites, and gypsum can transmit water through solution channels as limestone does. A water moving through gypsum eventually becomes saturated with respect to that solid and has a composition like the one shown in analysis 15–3, figure 49. The distribution of solutes in two nearly saturated brines from southeastern New Mexico is shown graphically by two analyses in figure 49. One of these, analysis 17–8, is essentially a saturated $Na^+ + Cl^-$ solution. The other, analysis 16–6, has a high proportion of Mg^{2+}

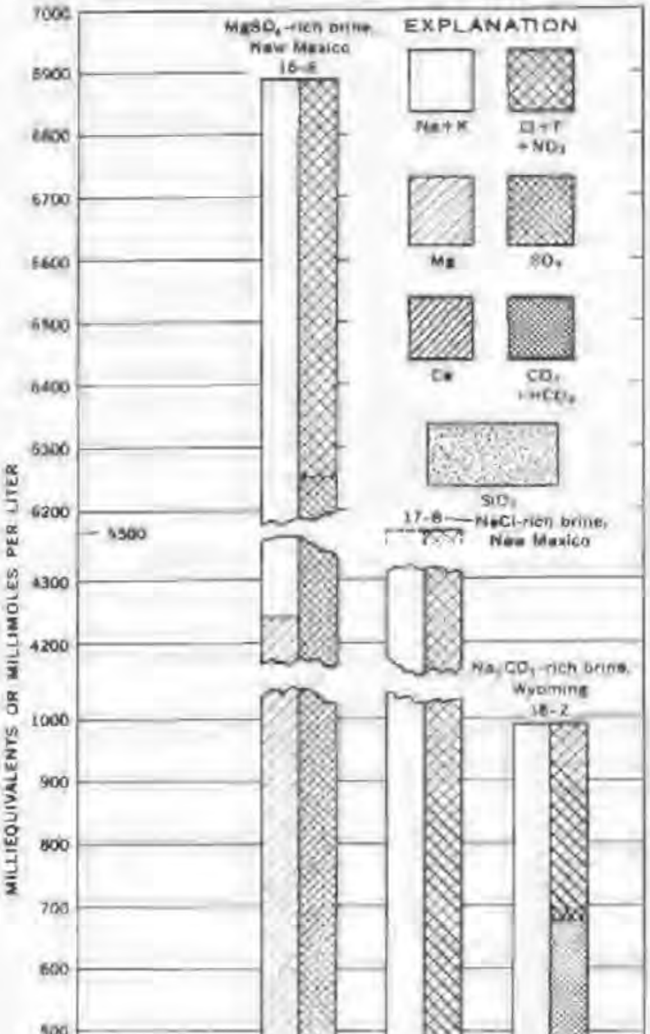


Figure 49. Composition of ground water obtained from evaporite sedimentary rock types. Numbers above bars indicate source of data in tables 15-18 (e.g., "15-3"=table 15, analysis 3).

and SO_4^{2-}. Analysis 18–2 is for a water associated with a Wyoming Na_2CO_3 deposit. The vertical scale in figure 49 is condensed by a factor of 50 as compared with figures 44–48; hence the graphs are not directly comparable. The scale used in figure 49 causes the graph for analysis 15–3, a water that has more than 30 meq/L of cations, to appear small even though the water is above the usual concentration limit for potability.

The composition of natural brines generally is closely related to the composition of the evaporite deposits from which they are derived and may include minerals of economic value. Some of the elements commercially recovered from such brines are magnesium, potassium, boron, lithium, and bromine. Many analyses of natural brines have been published by White and others (1963).

Metamorphic Rocks

Rocks of any kind may be metamorphosed. The process as considered here consists of the alteration of rock by heat and pressure to change the physical properties and, sometimes, the mineral composition. All degrees of alteration may occur, up to complete reassembly of rock components into new minerals. Considering the wide possible variety of original rocks, it is evident that few simple generalizations about the composition of water to be expected in association with metamorphic rocks can be made.

If sedimentary rocks are subjected to sufficiently intense heat and pressure, they can be completely melted into a new igneous mass. Gneiss and schist result from heat and pressure that do not completely reorganize the initial rock. Although these rock types may be dense and non-water-bearing, there are places where ground water is recovered from them. Water from such formations generally can be expected to be low in solute concentrations and to resemble more closely the water from igneous terranes than the water from the sediments as they existed before being metamorphosed. Analysis 12–9, represented graphically in figure 50, is for water from schist. Analysis 13–5 represents water from a granitic gneiss. The rather high proportion of silica in both these waters shows the influence of silicate minerals.

The dense structures of slate, a metamorphosed form of shale, and of quartzite, a metamorphosed form of quartzose sandstone, tend to restrict water movement to fracture zones and thereby prevent contact of ground

Figure 50. Composition of ground water obtained from metamorphic rocks. Numbers above bars indicate source of data in tables 12, 13, 16, and 18 (e.g., "12-9"=table 12, analysis 9).

water with surface areas of minerals as large as is normally expected in shale or in sandstone. The opportunity for water to pick up solutes from these metamorphosed rocks is, therefore, small, and water from slate or quartzite also is likely to contain low concentrations of solutes. Analysis 16–8, figure 50, represents water from a quartzite in Alabama. Limestone may be converted to marble without much chemical change, and the processes of solution in such a marble are much the same as those in limestone. If the original limestone was impure, however, it could yield a marble containing some minerals less soluble than calcite.

Processes of metamorphism generally involve aqueous solutions, and the alteration products that result may include hydrolyzate minerals. The release of water from some types of rocks during metamorphic processes can be expected. White (1957a) examined natural waters for possible features of their composition that could be attributed to metamorphism of rocks. Among the properties cited by White as possible indications of a metamorphic influence on water composition were high concentrations of sodium, bicarbonate, and boron and relatively low concentrations of chloride. Analysis 18–5 is for water described by Barnes and others (1967) to issue from a zone of alteration of ultrabasic rock to serpentinite.

The first three analyses in figure 50 represent waters that passed through metamorphosed rocks long after the processes of metamorphism were completed. In contrast, the water represented by analysis 18–5 is actively participating in the ongoing metamorphic process.

INFLUENCE OF ACTIVITIES OF HUMANS

All life forms interact with their environments in various ways. As a result of these interactions, complex ecologic structures have evolved, structures in which diverse life forms interact with one another in supportive as well as in predatory ways. One might view the present-day Earth-surface environment as having been shaped in many ways through these life processes interacting with their surroundings over the span of geologic time. Certainly this is true for the development of soils—and it has been thought by many geochemists that the atmosphere has attained much or all of its oxygen from activity of photosynthetic organisms. A more extreme view was expressed by Lovelock and Margulis (1974), who suggested that the life processes of organisms established and continue to maintain the composition of the atmosphere at an optimum for living species to thrive. It is perhaps less clear how natural waters might have been made more hospitable over a long time span by such processes, but one may readily observe ways in which organic processes currently maintain water bodies in a state favorable for life (oxygen and nutrient balances, for example).

Many human activities have adverse consequences for the environment. As human populations increase and civilizations become more and more technologically developed, the adverse effects become obvious, and they have been a matter of deep concern to thoughtful observers for more than a century. When human activities cause a decline in the quality of natural waters we use the term "pollution." This word has deep connotations and water pollution is difficult to define scientifically. For the purpose of this discussion it is defined as man-caused deterioration of water quality that is sufficiently severe to decrease substantially the usefulness of the resource, either by humans or by some other life form deemed to be beneficial.

In a broad general sense one can describe the interaction of life forms with their environment in the terms of thermodynamics. Life processes themselves, for example, involve an expenditure of energy to produce a form of internal order (decreased entropy). When the organisms die, the second law of thermodynamics predicts that this order will be largely destroyed and its stored energy partly released, with an increase in entropy in the products of decay. The energy loss is not total, however, and over geologic time large amounts of available energy have been stored, in coal and petroleum, for example.

The rise of modern civilization has brought with it a large and increasing use of energy, from fossil sources and more recently from nuclear fission. Much of this energy is employed in ways that influence the physical environment, as in agriculture, timber harvesting, and mining. These activities could be likened to increases in degree of order—at least humans generally consider the results beneficial. The side effects on natural water may sometimes be severe enough to constitute pollution as defined here. This general view of pollution problems has been discussed by Stumn and Morgan (1981, p. 724–725).

Some of the energy expended by an industrial civilization is used to produce entropy decreases that can be more exactly defined thermodynamically. The conversion of iron oxide ore to metallic iron, and the recovery of other metals from ores, give products that are thermodynamically unstable (that is, low in entropy). Their conversion to more stable forms can be a source of water pollution as the metals react with their environment. Production and use of synthetic organic chemical compounds also pose a pollution threat, one that may be difficult to evaluate because these substances would not be present in the environment under natural conditions.

From these considerations a generalization can be made: Industrial civilizations can be expected to have substantial intrinsic environmental effects, and some may bring about pollution of natural water as this has been defined here. Some parts of the definition are subjective. Specifically, the definition requires that judgments be made as to what constitutes a substantial impairment of usability of the water and which of such impaired uses are sufficiently beneficial to justify concern. It is in these areas that conflicts occur, and generally they cannot be resolved by scientific methods alone.

Much of the subject of water-pollution control and problems relating to it are beyond the scope of this book. However, there are many ways in which natural-water chemistry, as discussed here, can be applied to help understand, predict, and remedy pollution problems. It is necessary to recognize that environmental change attributable to humans is unavoidable and that some deterioration in water quality may be acceptable if alternatives entail unacceptable social costs.

Detection of lower and lower levels of organic or inorganic pollutants has become relatively easy. The improved ability to identify such materials in solution has resulted from improved technology and application of analytical chemistry. The fact that a particular substance is present does not, however, establish the existence of pollution as it is defined here. Various other aspects need to be considered. The major tasks to which scientific contributions can be made include such things as determining form, stability, and transport rates and mechanisms for pollutant species, predicting the probable effects of current or forseeable practices in waste disposal or product use, assessing the impacts of artificial sources versus natural sources, and providing methods for identifying the most significant existing and potential pollution problems.

Stumm and Stumm-Zollinger (1971) discussed the subject of water pollution and presented a thoughtful analysis of many ecologic aspects and implications of the subject. Some aspects of the topic are discussed further here, and some were touched earlier in this book.

High densities of populations of human or other biological species inevitably encounter metabolic-waste-disposal problems, and these problems may be greatly magnified in industrial civilizations that produce large volumes of waste products. Waste accumulations in excessive amounts may occur in colonies of some of the lower forms of life and may cause the colonies to die out. The intelligence of humans as individuals is certainly sufficient to recognize, understand, and cope with problems related to waste management. Unfortunately, as in many other aspects of human behavior, the intelligence and ethical standards of social groups seem to lag far behind the levels attainable by individuals. Thus, many aspects of both cause and cure of water pollution lie in the area of the social rather than the physical or biological sciences.

Waste-disposal practices may be classified into three major categories on the basis of the general aim of the process: (1) processes that convert the waste to innocuous or reusable material, (2) processes that disperse the waste into a diluting medium, and (3) processes in which wastes are stored in a place where it is supposed they cannot later become a nuisance or a hazard. Failure of any of these processes to work satisfactorily can cause pollution problems.

Techniques of waste disposal in which organic waste is converted to innocuous forms are commonly used in sewage-disposal plants. Natural processes that produce similar results occur in oxygenated river water; however, heavy loading of streams with organic waste produces many undesirable effects, and the natural process of purification may easily become overwhelmed. Many inorganic wastes must either be dispersed into the environment in such a way as to avoid objectionable concentrations in any locality or be stored where they can do no harm.

Some common ionic species may be dispersed into the environment with no serious problems. Chloride, for example, may not be objectionable if maintained at a low enough concentration, and it can be conveyed to the ocean, where it will cause no significant effects. Some other solutes, however, may tend to accumulate and become concentrated in such places as stream sediment or biota and can be released from such accumulations in unexpected ways to cause troublesome local concentrations.

A method of disposal used in some places for obnoxious wastes is to inject them into deep aquifers that contain salty water. This generally amounts to storing the waste, but it is a method of storage whereby control over the material cannot be maintained. More positive controls generally are required for the highly dangerous wastes produced in some nuclear processes. Highly radioactive material is presently being stored in tanks or in solid form, which minimizes the possibility of escape.

Whatever the technique of waste disposal used, the increasing density of population in many areas makes it more and more likely that any water sampled will be affected in some way by the activities of humans. The added material may not fit the term "pollution" in the sense that the water becomes unusable, but it may have a measurable effect on major or minor dissolved-ion concentrations. Addition of organic matter to ground water may provide a reductant for oxidized minerals and may cause changes in the geochemical balance of the system, and changes in pH may cause rock minerals to dissolve.

Although some polluted surface waters can be restored to reasonable quality fairly rapidly by decreasing waste loads or concentrations, the process can be costly. A polluted ground water, on the other hand, may be so slow to recover that it becomes necessary to think of the pollution of aquifers as almost irreversible once it has occurred. For this reason, great care is needed to protect ground-water aquifers. Incidents of contamination of ground water from septic tanks, sewage and industrial waste-disposal systems, solid-waste disposal practices, and natural-gas and petroleum-storage leaks as well as other topics related to the general subject of ground-water pollution have been receiving attention for a long time. Many were described at a pioneering symposium sponsored by the U.S. Public Health Service (U.S. Public Health Service, 1961). Control and abatement of the pollution of ground water that has resulted from faulty waste-disposal practices has been a growing problem in urban and rural areas. A bibliography of papers on ground-water contamination prepared by Bader and others (1973) included more than 700 references.

Continued concern about ground-water contamination is evidenced by the number of papers on this topic published in professional journals—a total of 19 in the 1984 volume of the journal "Ground Water," for example. Increased interest in and research on this and other aspects of environmental pollution in recent years also is evident in the number of popular articles in mass media and the new scientific and technical journals, such as "Environmental Science and Technology," "Journal of Environmental Quality," "Water, Air and Soil Pollution," and others that publish research in this field.

During recent decades the usual and preferred procedure for disposal of solid wastes has been to bury them in so-called sanitary landfills. Although, in theory, wastes in a properly designed and managed landfill should not be a contamination threat, in practice many of these landfills have not been protected from infiltration of water from the surface or from lateral movement of ground water through them, and leachate has contaminated neighboring ground water and surface water. Examples on Long Island, N.Y., cited by Kimmel and Braids (1980), showed that such leachates commonly are high in bicarbonate, chloride, and sodium and can have excessive amounts of dissolved metals, especially iron. Effects of landfill leaching also have been studied extensively in Europe (Golwer and others, 1975). Landfill leachates may also contain a wide variety of organic compounds. A case study relating to ground water contamination from a landfill in the Atlantic City, N.J., area (Sharefkin and others, 1984) illustrates the chemical complexity of potential leachates. These authors point out the high costs of correcting this type of problem.

In a society with highly developed industrial and agricultural technologies, a large number of organic and inorganic products are manufactured and used that would not be able to enter the environment naturally. Inevitably, some of these products, or their residues or byproducts, enter the hydrosphere. When their presence is discovered a surge of publicity and general concern may follow, along with pressures for various kinds of action to correct or lessen the problem. During the past several decades attention has been drawn, for example, to lead and mercury in the aqueous environment and to various common and exotic organic substances, as already noted. A matter of more recent concern worldwide is the occurrence of rainfall having a low pH—the "acid rain" problem. Most of these environmental releases are forms of indirect pollution in the sense that the objectionable material was not being formally consigned to receiving water as a waste effluent.

One aspect of a form of indirect pollution of water mentioned above is the intrusion of seawater. This subject has been selected for further diuscussion here because it illustrates some of the subtleties of pollution effects and is an area in which both hydrologic and chemical knowledge is essential in achieving control.

Saltwater Intrusion

Both surface and underground waters may be contaminated by saline water where opportunity for contact occurs. The activities of humans may aid in bringing about contamination but are by no means required. Along seacoasts there is a saltwater-freshwater contact zone both in streams and in aquifers that extend under the sea.

The relation between seawater and freshwater in aquifers along the seacoast generally can be described by hydraulic relationships. The effect of man's withdrawal of water from the landward parts of these aquifers may have far-reaching effects on the position of the saltwater-freshwater interface. The hydraulics of coastal aquifers have been studied extensively in the field and by means of laboratory models. It is generally agreed by hydrologists that the boundaries between freshwater and saltwater in coastal aquifers depend on the balance of forces in a dynamic system. Normally, freshwater moves seaward continuously at a rate that is related to the head above mean sea level in the freshwater aquifer. As Hubbert (1940) pointed out, the result of this movement is that in an unconfined system freshwater discharges into the sea through the saturated zone from the high-tide line for some distance offshore. Cooper (1959) described how the movements of fresh- and saltwater along a contact zone tend to produce a diffuse zone of mixing rather than a sharp interface.

In a confined or semiconfined aquifer that is open to the sea at some distance offshore, a similar dynamic circulation pattern can be expected. So long as a high head of freshwater inland is maintained in the aquifer, freshwater will discharge into the ocean at the outcrop of the aquifer and will maintain the zone of contact with salty water in the aquifer a considerable distance offshore. Pumping inland will reduce the head of the freshwater, and because head changes are transmitted rapidly through the system, the flow of freshwater seaward will be decreased. The head may decline enough to stop entirely the seaward flow of freshwater past the interface. With the decreased freshwater flow, the system will be unstable, and saltwater will invade the aquifer. The saltwater front will move inland to the point where the reduced freshwater head is again sufficient to produce a balancing seaward movement of freshwater past the interface.

Overdevelopment of coastal aquifers can greatly decrease the freshwater head and can bring about conditions favorable for the migration of saltwater inland. The migration of the saltwater front, however, is rather slow, as it represents actual movement of water in the system under low gradients with high resistance. The appearance of salty water in a well may not occur until some years after the head decline has reached serious proportions. The rate of movement of some of the ions in the saltwater front will be influenced by ion exchange, and diffusion and head fluctuation will cause the interface to become a transitional zone rather than a sharp front.

Saltwater intrusion into highly developed aquifers is a serious problem in many places along continental margins and has occurred in other places where nonoceanic saltwater was drawn into an aquifer when hydraulic heads were altered. Hydrologists are frequently confronted with the need to recognize incipient stages of saltwater intrusion so that steps can be taken to correct the situation.

The composition of average seawater is given in table 2. Chloride is the major anion, and it moves through aquifers at nearly the same rate as the intruding water. Increasing chloride concentrations may well be the first indication of the approach of a seawater contamination front. In an area where no other source of saline contamination exists, high chloride concentrations in ground water can be considered rather definite proof of seawater contamination. If important amounts of chloride could come from other sources, however, the establishment of definite proof of the seawater source may be difficult.

Components of seawater other than chloride may be used to identify contamination, but difficulties are encountered in using them. Magnesium is present in seawater in much greater concentration than is calcium. A low calcium:magnesium ratio may sometimes be indicative of seawater contamination. The presence of sulfate in anionic proportion similar to that of seawater also might be indicative. Because of possible cation-exchange reactions and sulfate reduction in the aquifers that can be expected to occur when seawater is introduced, the proportions of anions and cations in the first contaminated water to reach the sampling point cannot be expected to be exactly the same as those of a simple mixture of seawater and freshwater. It is indeed likely that even after moving only a short distance through an aquifer the water in the advancing saltwater front will have little superficial resemblance to a simple mixture. After the exchange capacity of the aquifer has been satisfied and equilibrium reestablished, the water transmitted inland will be virtually unaltered seawater; however, a considerable volume of water may need to pass before this stage is reached. Because of the cation-exchange effects, the removal of the introduced ions from a contaminated aquifer by restoring seaward movement of freshwater also will tend to be slow.

Minor constituents of seawater may, in some instances, aid in determining whether a particular aquifer has been contaminated by seawater or by some other saline source. Incipient stages of contamination cannot generally be detected by these constituents. Piper and others (1953) were confronted with the need to differentiate seawater contamination of an aquifer from contamination by connate brine and had some success in doing this by comparing iodide, boron, and barium concentrations in the suspected water. The constituents that might be expected to be useful in identifying sources should be selected by using knowledge of the composition of contaminating solution and by considering the chemical and exchange behavior of the solutes.

Table 22 gives analyses of water from a well in the Los Angeles, Calif., area before and after contamination by seawater. The calcium concentration in the contami-

Table 22. Analyses showing the effects of seawater contamination in the Gaspur water-bearing zone, Dominguez Gap, Los Angeles County, California

[Date below sample number is date of collection. Source of data: Piper, Garrett, and others (1953, p. 227)]

Constituent	1 Jan. 8, 1923		2 Apr. 4, 1928	
	mg/L	meq/L	mg/L	meq/L
Silica (SiO_2)			20	
Iron (Fe)			.97	
Calcium (Ca)	27	1.35	438	21.86
Magnesium (Mg)	11	.90	418	34.38
Sodium (Na)	82	3.57	1,865	81.10
Potassium (K)			56	1.43
Bicarbonate (HCO_3)	235	3.85	193	3.16
Sulfate (SO_4)	40	.83	565	11.76
Chloride (Cl)	40	1.13	4,410	124.38
Fluoride (F)			.0	.00
Nitrate (NO_3)			1.8	.03
Dissolved solids:				
Calculated	318		8,200	
Hardness as $CaCO_3$	113		2,810	
Noncarbonate	0		2,650	

1. Well 4/13-35 M3, Southern California Edison Co., West Gaspur Well, Los Angeles, Calif., before contamination by seawater.
2. Same well; water contaminated by intrusion of seawater.

nated water is higher than would be expected from a simple admixture of seawater sufficient to produce the observed chloride concentration in the contaminated water, probably owing to the exchange of calcium held on exchange sites on aquifer minerals for sodium in solution in the advancing saltwater front.

Detection and tracing of seawater contamination using stable isotopes of hydrogen and oxygen, or long-lived radioactive isotopes such as carbon-14, should have a considerable potential. Hanshaw, Back, Rubin, and Wait (1965) described this technique.

Large withdrawals of ground water from wells near the shoreline of Los Angeles County, Calif., has caused extensive inland contamination of ground water by seawater intrusion. Remedial measures undertaken there since the 1940's to control the situation have been described in many published reports, for example, that of Banks and others (1957). Seawater intrusion was controlled by injecting freshwater through wells into the contaminated aquifer close to the shoreline so as to build up a freshwater barrier. More recently, a similar procedure has been used farther south, in Orange County, Calif. (Hammer and Elser, 1980).

APPLICATION OF WATER-QUALITY MEASUREMENTS TO QUANTITATIVE HYDROLOGY

Certain types of water-quality determinations can be used to measure or estimate water-discharge rates or quantities of stored water. Various kinds of "chemical" measuring techniques suitable for surface streams have been in use for many years (Corbett and others, 1945, p. 88–90; Rantz and others, 1983, p. 211–259). One of these has been applied extensively to determine the rate of solute movement, or time of travel of water through a reach of a river, a value that cannot be estimated accurately from stream-discharge records. In this procedure, a readily detectable solute is added to the stream in the form of a concentrated slug, and the length of time required for the material to appear at a downstream point is measured. In recent years, many measurements of this kind have been made with dyes such as rhodamine WT in response to the need for time-of-travel data in pollution studies and for other applications. Inorganic materials also can be used as tracers, and Nelson and others (1966) used radioactive materials introduced into the Columbia River by nuclear facilities at Hanford, Wash., to trace the flow times in that stream. An index of U.S. Geological Survey time-of-travel studies was assembled by Boning (1973).

The salt-dilution method of measuring flow rate of a stream consists of adding, at a constant rate, a known quantity of tracer, usually sodium chloride, and measuring the concentration of chloride in the water upstream from the point of addition and far enough downstream that mixing is complete. The flow must remain constant during the time the measurements are being made, and enough time must be allowed so that the concentration at the downstream point is stable. This provides enough information for calculating the discharge rate of the stream. The method can be used in systems in which other procedures are impossible because of inaccessibility or extremes of turbulence or velocity. Amounts of salt added need not be large enough to affect water quality adversely.

The mathematical basis for calculating discharge by the tracer method is the mass-balance equation cited previously in connection with the relation of stream-water quality to discharge. The water discharges in a system of this type are related by the equation

$$q_1+q_2=q_3,$$

where q_1 is the discharge upstream, q_2 is the discharge of the tagging solution, and q_3 is the discharge downstream from the point of addition of q_2. To express the discharge rate for the tracer ion, one may write the equation

$$c_1q_1+c_2q_2=c_3q_3,$$

where the c terms are the concentrations known or observed at the points at which the q values are taken. When the technique is used as described above, all the c terms and q_2 are known: hence, the two equations provide values for q_1 and q_3.

This procedure for evaluating discharges has potential hydrologic uses that seem not to have been used widely. Water-quality changes occur in river systems owing to inflows of water of a different composition, and a combination of sampling and flow measurement might be used to help determine quantities that cannot be measured directly.

A simple example of a system that can be evaluated this way is a stream low in dissolved-solute concentrations that receives inflow from a saltwater spring. If the spring inflow is accessible for measurement, the streamflow can be measured by analyzing samples of water collected from the spring and from the stream above the inflow point and from the stream far enough below the inflow to assure complete mixing, and then determining the springflow. If the springflow cannot be measured directly, as is more commonly the case, a single measurement of riverflow and analysis of samples at the three necessary points can provide a basis for calculating spring inflow.

It is true that the usual procedure would be to measure flow above and below the inflow zone and to determine inflow by calculating the difference. If the riverflows are fairly large, however, the probable magnitude of the measuring error may easily exceed the quantity of inflow.

At Clifton, Ariz., the San Francisco River receives enough inflow from hot saline springs that issue from gravel in the streambed to alter the composition of the river water considerably at normal stages of flow. The composition of the inflowing water was determined by sampling one point of spring discharge that was above the river level, and samples of river water were obtained upstream and downstream from the inflow zone. The discharge was measured by means of a current meter at the downstream site. Table 23 contains the analyses and the calculated and measured discharges. Although the calculated inflow is a little more than 2 ft^3/s, almost all this amount occurs below the water surface in the stream, where it is not noticeable to the casual observer and is not measurable by direct means. The correlation of dissolved-solids and discharge data for the San Francisco River below the inflow zone at Clifton was discussed earlier.

In areas where interconnections between groundwater and surface-water systems are of interest, detailed studies often include seepage measurements. These consist of a series of measurements of riverflow and tributary inflow taken in a downstream direction, with unmeasured gains and losses between measuring points being ascribed to ground-water inflows or losses of streamflow to the ground-water reservoir. Such measurements can provide considerably more information if water samples are taken at all measuring sites. The analyses of the samples help show where both inflow and outflow may be occurring between measuring points and help refine the investigator's understanding of the hydrologic system. Data of this kind were used, for example, to help evaluate details of the hydrology of the Safford Valley, Ariz. (Gatewood and others, 1950).

In studies of surface streams and related inflows and outflows, enough measurements and observations usually can be made to provide for a detailed evaluation. Although it would be helpful to be able to estimate ground-water flow rates and the contributions from point and diffuse sources of recharge by chemical techniques, the inherent complexity of ground-water chemistry and flow patterms and the difficulty of obtaining truly representative samples severely limit the tracer approach.

For example, there are serious problems inherent in deciding whether ground-water samples from wells ade-

Table 23. Analyses of water from Clifton Hot Springs and from the San Francisco River above and below Clifton, Arizona

[Date below sample number is date of collection. c, calculated. Source of data: Hem (1950)]

Constituent	1 Jan. 10, 1944		2 Jan. 10, 1944		3 Jan. 10, 1944	
	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
Silica (SiO_2)					58	
Iron (Fe)					.19	
Calcium (Ca)	44	2.20	72	3.59	860	42.91
Magnesium (Mg)	12	.99	13	1.07	41	3.37
Sodium (Na)	58	2.52	156	6.78	2,670	116.10
Potassium (K)					142	3.63
Bicarbonate (HCO_3)	204	3.34	206	3.38	109	1.79
Sulfate (SO_4)	17	.35	19	.40	153	3.19
Chloride (Cl)	70	1.97	270	7.62	5,800	163.58
Fluoride (F)	.8	.04	.8	.04	3.0	.16
Nitrate (NO_3)	.2	.00	.5	.01	7.5	.12
Dissolved solids: Calculated	302		633		9,790	
Hardness as $CaCO_3$	160		233		2,310	
Noncarbonate	0		64		2,220	
Specific conductance (micromhos at 25°C).	547		1,160		16,500	
Discharge (cfs)	58(c)		60		2.1(c)	

1. San Francisco River, 2 mi above Clifton, Ariz.
2. San Francisco River at gaging station at Clifton, Ariz.
3. Clifton Hot Springs seep opposite Southern Pacific Lines depot. Temperature, 43.4°C.

quately represent the entire thickness of aquifer penetrated and whether the tracer ions used move with the same speed as the water itself. There are, however, a number of examples that can be cited in which chemical techniques of measurement have been useful.

Many investigations of direction and rates of ground-water movement have been made by studies that involved injection of slugs of salt, dye, or radioactive material. The idea is by no means new. Slichter (1902) conducted a number of studies in which salt solution was added to one well and its appearance monitored in adjacent wells; he referred to similar work done in Europe at earlier times by Adolph Thiem. More recent experiments of this type were described by Kaufman and Orlob (1956).

Any tracer material that may be added must be similar in density and temperature to that of the ground water, and large amounts might constitute objectionable pollution. Where movement is through large fissures or cavernous openings, a tracer technique becomes more simple and useful. Additions of organic dye have been used to trace water movement through limestone and to identify pollution sources in such systems.

Material that is naturally present is also potentially useful for tracing flow and for estimating rates of movement. Radioactive material present naturally includes tritium, carbon-14, and lead-210. The half-life of lead-210 and its chemical properties limit its usefulness as a ground-water tracer. The use of isotopes, both radioactive and stable, has produced an extensive literature already referred to (Rodehamel and others, 1971; Friedman and O'Neil, 1977).

Some of the water stored in McMillan Reservoir in the Pecos River north of Carlsbad, N. Mex., escapes through solution openings in gypsum, but the outflow apparently is all or nearly all returned to the river through springs located a few miles downstream from the reservoir. Many investigations of this system have been made. Theis and Sayre (1942, p. 54–58) used the observed pattern of chloride concentrations in the reservoir and spring water to develop an empirical equation relating water emerging at the springs to water that had been stored in the reservoir at earlier times. From this, the volume of storage in the ground-water system feeding the springs was estimated. At a section of the river a few miles farther downstream, Claassen (1981) calculated the rate of enlargement, by dissolution in the circulating water, of channels in gypsum beds using data on quality of river water and ground water.

Kaufman and Orlob (1956) observed that chloride ions seemed to move at effectively the same rate as water through porous material. In fact, the retardation of chloride in their experiment was a little less than that of tritium, which participated to some extent in exchange reactions, even though the tritium actually was incorporated in water molecules.

Some aquifers can be considered conduits having fairly well defined boundaries. Water moving down such channels may show quality changes related to side inflows or to other factors. Plate 3, a water-quality map of part of Safford Valley, Ariz., shows how the composition of ground water in the alluvial fill, which was considered by Gatewood and others (1950) to be a hydrologic unit, changes downstream. The inflow of fresher water from the south side of this section of the valley is evidently large compared with the amount of rather saline water moving downstream in the fill at the upstream end of the reach. The relative magnitudes of flow can be estimated by the composition of the influent water and the mixture.

Admittedly, the effects of other factors, such as river stage and pumping for irrigation, may influence the results of calculations. Where the data can be obtained, however, water-quality maps offer a method of extending estimates of both ground-water flows and the relative amounts of water contributed from different sources.

In an early study of ground-water and surface-water relationships along the Illinois River at Peoria, Ill., Larson (1949) used water-quality data to estimate the proportions of river water and ground water in a pumped well near the stream. Chemical studies to evaluate sources of water in wells along the Platte River in Nebraska were described by Barnes and Bentall (1968). Konikow and Bredehoeft (1974) prepared maps of water quality for ground water in the Arkansas River valley downstream from Pueblo, Colo. This study used mathematical modeling to compute probable future water quality in the aquifer.

Mathematical Simulations—Flow Models

The simple equation of conservation of mass introduced earlier is an underlying physical principle from which much more detailed mathematical simulations of flow in single or multiphase systems can be derived. The increase in emphasis on mathematical treatment of hydrologic systems is probably the most significant development in the field of hydrology during the past 20 years.

Hydrologic systems are dynamic in the sense that water, solutes, and energy are in motion within them, influenced in various ways by the physical properties of the channels or passages through which the motion occurs and by those effects that relate to the driving energy, or hydraulic head. Interrelationships of this kind can be represented by systems of partial differential equations based on the principle of conservation of mass, which, for example, might be capable of predicting how a ground-water system would be affected in space and time by postulated local head changes. These equations can be designed to show propagation of such changes in space along two or even three coordinates. Solutions for systems of partial differential equations like these can be readily produced by modern computer techniques. They would be prohibitively laborious if done by other methods.

More closely related to the subject of water chemistry are the various types of transport models that deal with fluid and solute movement. These also consist of arrays of partial differential equations that relate rates of movement of water in one or more dimensions to change in transported substances associated with the water. Factors treated by such models commonly include dispersion, or mixing, advective transport, diffusion along concentration gradients, and behavior of sources and sinks in the system for the material being transported.

These mathematical models are based on principles of physics. The incorporation of chemical factors is generally necessary to simulate successfully the behavior of dissolved material being transported. For a few types of material it can reasonably be assumed that the solute does not participate in chemical or adsorptive interactions with anything else in the system, and its behavior then can be modeled accurately by means of the physical transport equations.

A slug of nonreactive (conservative) solute added to a river, as in a chemical spill, will be perceived at a downstream point as an increase in concentration of that solute with time to a peak, followed by a decrease to background levels. Characteristically, the concentration plotted against time for sites short distances downstream from the spill will display a sharp rise to a peak, followed by a slower decline to background. As the distance downstream increases the peak is attenuated, finally becoming very faint. The shape of the peak and the degree of attenuation are related to the hydraulic characteristics of the system as well as to the extent of interaction of solute with other components of the system. A prediction of height and duration of the downstream peak obviously is possible if the system is characterized well enough.

In practice, the modeling of solute transport in streams is complicated by chemical interactions and by difficulties in evaluating physical parameters. Nevertheless, many stream system models have been developed, often by using results of field experiments and observations on the particular reach of stream that is being modeled. Theoretical concepts may define the general structure of the model, but some of the necessary numbers must be obtained by fitting and by trial and error. This may produce a model that can be used only for the stream for which it was developed, but such models have been used effectively for predicting the response of streams to sewage effluents and some of the related biochemical effects that can be observed in rivers. A review of some of the work on modeling of phytoplankton in rivers and other water bodies was given by DiToro and others (1971). Development of a model for transport of added tracers in a small mountain stream having "pool-and-riffle" characteristics was described by Bencala and Walters (1983).

In most ground water systems the flow characteristics are materially different from those in open channels. A large area of solid surface generally is encountered by each unit volume of water moving through the system. In a fine-grained sediment, the surface area contacted by each liter of water transmitted may amount to thousands of square meters per meter of travel. The quantity of cations in exchange sites on this large area may well be as large as, or larger than, the quantity in solution in a liter of water. With the slow rates of water movement that might be expected in some systems—perhaps only a few tens of meters a year—there is a maximum of opportunity for completion of any interaction that might occur between solutes and surfaces. Cations will be adsorbed or dissolved in accordance with selectivity behavior of the sites, but it can be expected that such systems will extract introduced trace metal cations effectively because so many sites are available. Even where the proportion of sites occupied at equilibrium by adsorbed trace metals is small, their low initial concentration can easily be decreased to undetectable levels.

Many models of transport of conserved solutes in ground water are described in the literature. Robertson (1977), for example, modeled the transport of tritium in basalt and associated soils in Idaho, and Bredehoeft and Pinder (1973) described a model they applied to a chloride-contamination problem in a limestone aquifer in Georgia.

Where there is solute-solid interaction, an approach that has been used is to assume that a local equilibrium condition is rapidly attained. A model by Rubin and James (1973) for an ion-exchange process in ground water used this approach coupled to a physical-transport model. A general review with some mathematical methods for studying transport of solutes in aqueous systems was given by Lerman (1979). The broader subject of mathematical modeling of ground water was reviewed briefly by Appel and Bredehoeft (1976), who gave a substantial number of literature references to solute-transport models for ground water. A review of water-quality-assessment model techniques for surface-water systems was prepared by Hines and others (1975).

In general terms, ground-water systems and water in such environments as soil or unsaturated zones or lakebed sediments are characterized by slow water movement and by very much slower movement of many solutes. Models of such systems need to give major emphasis to evaluating the chemical and related processes that cause this differential, and the mathematical structure of the model should be appropriate to the chemistry of the system (Rubin, 1979, 1983).

A study by Jackson and Inch (1980) of the movement of the radioactive nuclides strontium-90 and cesium-137 through a sand aquifer demonstrated the use of several kinds of chemical and transport models. The rate of movement observed for strontium-90 was about 3 percent, and the rate of cesium-137 movement, about 0.3 percent of the ground-water movement rate in that system.

In surface-water systems the bulk of the water moves much more rapidly than in the systems cited above. However, the modeling of solute transport in such systems is complicated by the additional effect of a moving solid phase (suspended and bed sediment) interacting with solutes, as well as by much more important photochemical and biochemical factors.

As noted in earlier sections of this book dealing with chemical equilibrium, solids that participate in an equilibrium are usually assumed to be at standard state (activity$\equiv$1). Therefore, models using equilibrium assumptions are somewhat limited in their capacity to evaluate systems in which the changing nature and quantity of participating solids at various places in the system is a matter of concern.

In those ground-water systems in which chemical processes may represent a more sensitive aspect of the model than physical transport, the appropriate models to use may be those in which chemical rather than physical processes are emphasized. Wigley and others (1978) and Plummer and Back (1980) demonstrated that one can describe flow rates in regional limestone aquifer systems and can develop much other information on their hydrologic properties by studies of major element chemistry, mass balances, and isotopic distributions. The principles used in these models were reviewed by Plummer and others (1983).

In theory, at least, the modeling of solute behavior in a carbonate system can be based on fairly simple equilibrium chemistry. The modeling of reactive solutes in granular aquifer material is a much more difficult task, and one that has by no means been reduced to a routine exercise.

The development of a mathematical model that has predictive usefulness is a substantial contribution to applied hydrologic science, but it is necessary to tailor the model to the specific system to which it is to be applied. A proper perspective needs to be maintained, for some evaluations of hydrologic systems can be made with less detailed models than others. The term "model" need not imply a massive computer-programmed approach. In any event, a conceptual model laid out in rather simple terms must always precede it. The more detailed model is then developed to fulfill the requirements of the study.

RELATION OF QUALITY OF WATER TO USE

An immediate purpose of the usual quality-of-water study is to determine if the water is satisfactory for a proposed use. Accordingly, the subject of water-analysis interpretation must often include some consideration of standards and tolerances that have been established for water that is to be used for various purposes. Standards for water to be used for drinking and other domestic purposes have been established in many countries. Published literature contains tolerance levels and related data for constituents of water to be used in agriculture, in industry, for propagation of fish, and for a number of other specific purposes.

Water that is to be used as a public supply may be employed for many purposes. Therefore, the standards used to evaluate the suitability of water for public supply generally are more restrictive than those that would be applied to water for a small domestic or farm supply, although not necessarily more rigorous for individual components than the limits that apply for many industrial uses.

Water from mineral and hot springs is used medicinally in many places, and the mystic qualities of natural warm springs have been of great interest to man since prehistoric time. Medicinal uses have been summarized by Licht (1963) and will not be considered here.

An extensive survey of water-quality standards and review of the literature on the effects of solutes on uses of water was prepared by McKee and Wolf (1963). More recently, the U.S. Environmental Protection Agency sponsored a thorough study of water-quality and water-use interrelationships by a committee named by the National Academy of Science (NAS–NAE, 1972). Water uses for which standards were suggested include (1) recreation and aesthetics, (2) public water supplies, (3) freshwater aquatic life and wildlife, (4) marine aquatic life and wildlife, (5) agricultural uses, and (6) industrial water supplies. The subject can be considered only rather briefly here.

Domestic Uses and Public Supplies

Besides being chemically safe for human consumption, water to be used in the home should be free of undesirable physical properties such as color or turbidity and should have no unpleasant taste or odor. Harmful micro-organisms should be virtually absent; however, they are not usually considered in ordinary chemical analyses. The presence of harmful micro-organisms is considerably more difficult to ascertain than most other properties of water, but it is a highly important consideration. Over the years, great progress has been made in decreasing the incidence of waterborne disease, especially typhoid fever and cholera, and in the United States these two diseases have become rare.

Filtration of water taken from surface-water sources and disinfection, usually by addition of chlorine, have been the most effective means of controlling harmful organisms. In recent years increasing attention has been given to the occurrence in water of the protozoan *Giardia lamblia,* which can cause intestinal disturbances (giardiasis). This organism can be transported in an inactive cyst form that is resistant to chlorine (Lin, 1985). It is thought that waterborne giardiasis has become the most common waterborne disease in the United States (Lin, 1985).

The standard sanitary test for bacteriologic quality is the determination of total coliform bacteria concentration. The common species *Escherichia coli* occurs in great numbers in the intestinal tracts of warmblooded animals, and the presence of these and related bacteria in water is generally considered an index of fecal pollution. The coliform bacilli are not themselves directly harmful, but their presence in excessive numbers is considered suggestive of the possible presence of other species that are pathogenic. Although direct determination of pathogens is often advocated, the problems involved are large, and the substitution of such determinations for the simple coliform count is not likely to occur. As noted above, the sanitary condition of a water is not indicated by chemical testing alone. Thus, a water that is safe for drinking on the basis of its chemical composition may not be safe bacteriologically. This subject is not considered in detail here. Standards for the sanitary condition of public water supplies have been set and enforced at State or local governmental levels in the United States in past years. More recently, an increasing Federal involvement in establishing water-quality standards and arranging for their enforcement has developed.

Mandatory standards for dissolved constituents believed to be harmful to humans were first established in the United States in 1914 by the U.S. Public Health Service. These standards applied only to water used for drinking or preparing food in interstate common carriers. The standards were revised several times in ensuing years and were widely recognized as defining a safe water supply. However, they did not have a legal status except for water used in interstate commerce. This situation changed during the 1970's with passage of Federal legislation (1974 Safe Drinking Water Act). Standards for inorganic constituents in public water supplies that became effective in 1977 are given in tables 24 and 25. Concentrations indicated are not to be exceeded in water furnished to the public by water utility systems. The limits given are similar to those in the earlier (U.S. Public Health Service, 1962) standards and generally are similar to standards in other countries and recommended by the World Health Organization (1971). They generally follow recommendations given in the previously mentioned publication "Water Quality Criteria, 1972" (NAS-NAE, 1972). These interim standards are to be succeeded sometime in the future by more comprehensive standards.

When water supplies are found to exceed the limits given in tables 24 and 25, remedial action is required. Technology available for removal of the substances was summarized by Sorg (1978, 1979), by Sorg and Logsdon (1978, 1980), and by Sorg and others (1978). For some solutes in these standards, notably nitrate nitrogen, removal by treatment processes may be impractical, and new sources of water may be required.

Besides the mandatory limits given in table 24, the 1962 U.S. Public Health Service standards (U.S. Public Health Service, 1962) also included secondary limits which were to be followed unless no better quality supply was available. Some of the constituents in this list are considered objectionable because they have undesirable physical effects, such as staining of laundry or scaling of water heating units, and none were thought to be health related. The limits for these substances are given in table 26 along with corresponding "potable water-quality goals" recommended by the American Water Works Association (American Water Works Association, 1981, p.71).

Table 24. National Interim Primary Drinking Water Regulations (U.S. Environmental Protection Agency, 1976)

Contaminant	Maximum contaminant level (mg/L, or as indicated)
Arsenic (As)	0.05
Barium (Ba)	1.0
Cadmium (Cd)	.01
Chromium (Cr)	.05
Lead (Pb)	.05
Mercury (Hg)	.002
Nitrate (as N)	10
(as NO_3)	44
Selenium (Se)	.01
Silver (Ag)	.05
Radium-226 and -228 (Ra)	5 pCi/L
Gross alpha activity	15 pCi/L
Gross beta activity	4 millirem/yr[1]

[1] Based on 2-L/d drinking-water intake except for tritium and strontium-90. Average annual concentrations for these elements that are assumed to result in 4-millirem/yr exposure are ^{90}Sr=8 pCi/L and ^{3}H=20,000 pCi/L.

Table 25. National Interim Primary Drinking Water Regulations—Fluoride

Average annual maximum temperature		Maximum fluoride concentration (mg/L)
°F	°C	
53.7 or less	12.0 or less	2.4
53.8 - 58.3	12.1 - 14.6	2.2
58.4 - 63.8	14.7 - 17.6	2.0
63.9 - 70.6	17.7 - 21.4	1.8
70.7 - 79.2	21.5 - 26.2	1.6
79.2 - 90.5	26.3 - 32.5	1.4

In many areas of the United States the American Water Works Association goals for dissolved solids are not attainable, and in some places all available water supplies exceed 500 mg/L in dissolved solids. As a matter of fact, residents of some areas have used water containing more than 1,000 mg/L of dissolved solids all their lives. Although detailed medical data are not available, there do not seem to be any obvious detrimental effects on public health that can be attributed to such water supplies. Some of the undesirable impurities listed in the tables may be ingested in larger quantities from sources in the diet other than drinking water. The limits given in table 24, however, refer to substances known or thought to be toxic at low concentrations and should be followed as closely as possible.

The limits for radioactive substances in drinking water are viewed somewhat differently from those for nonradioactive solutes. It is generally agreed that the effects of radioactivity are harmful, and unnecessary exposure should be avoided. The limits given in table 24 are particularly strict for radium and for strontium-90.

Strontium-90 is a fission product, but radium occurs naturally and in some waters may exceed the limit. Both nuclides are preferentially absorbed in bone structure and are, therefore, especially undesirable in drinking water.

The lower limit of detection of solutes in water by taste is, of course, a function of individual sensitivity. Some substances can be detected in very low concentrations, however. Certain organic compounds impart taste when present at very low levels, and the taste and odor may be intensified by chlorination. Chlorophenols impart a noticeable taste when only a few micrograms per liter are present (Burttschell and others, 1959). Free-chlorine concentrations of a few tenths of a milligram per liter are usually noticeable, also. On the other hand, many common solute ions cannot be detected by taste until concentrations of tens or even hundreds of milligrams per liter are attained. Chloride concentrations of 400 mg/L impart a noticeable salty taste for most people. Users may become accustomed to waters containing high concentrations of major ions, however, and prefer the taste of such water to the "tastelessness" of more dilute solutions.

Table 26. Nonmandatory standards and goals for dissolved substances

Substance	USPHS standard[1] (mg/L)	AWWA potable water quality goals[2] (mg/L)
Aluminum (Al)		<0.05
Chloride (Cl)	250	
Copper (Cu)	1.0	<.2
Iron (Fe)	.3	<.05
Manganese (Mn)	.05	<.01
Sulfate (SO_4)	250	
Zinc (Zn)	5	<1
Total dissolved solids	500	<200
Total hardness		80

[1] U.S. Public Health Service (1962).

[2] American Water Works Association (1981, p. 71).

A considerable literature exists on the subject of taste effects in drinking water. Taste thresholds for zinc, copper, iron, and manganese were explored by Cohen and others (1960). Bruvold and others (1967) made a statistical study of consumer attitudes toward tastes imparted by major ions.

The possible hazards presented by organic compounds that are in solution in drinking water are incompletely known or understood. Recently, techniques have been developed that are capable of detecting specific compounds at nanogram-per-liter concentrations, and a list of compounds that might be considered particularly undesirable has been proposed (Keith and Telliard, 1979). The actual establishment of limits had not been done by the end of 1984, however. This topic is considered further in the section "Synthetic Organics."

Among the classes of compounds that have been thought to be particularly undesirable are chlorinated or brominated hydrocarbons. It has been shown that compounds of this type are synthesized when water containing naturally derived organic material is chlorinated for disinfection.

The water-supply industry of the United States is justifiably proud of the fact that waterborne disease has been brought to an extremely low level of incidence in this country, and the practice of chlorination of water supplies has played an important role in this. Substitution of other disinfecting processes to minimize the still-uncertain risk of chlorinated hydrocarbons remains a rather warmly debated issue.

Some waters are corrosive toward metals in pipelines and water tanks, and as a result the water from the user's tap may at times be excessively high in lead, zinc, copper, cadmium, iron, or other metals. The extent to which this may represent a health problem is not well known because information on metal content of water actually consumed by the final users is sparse.

Damage to plumbing done by corrosive water represents a major expense to utilities and water users. Properties of water that might indicate its potential for corrosive effects are not generally considered in setting water quality criteria, and the whole subject of corrosion of metals by water remains inadequately understood. A review by Singley (1981) described a few past efforts to devise indices of corrosivity for water supplies.

Agricultural Use

Water required for nondomestic purposes on farms and ranches includes that consumed by livestock and that used for irrigation.

Water to be used by stock is subject to quality limitations of the same type as those relating to quality of drinking water for human consumption. Most animals, however, can tolerate water that is considerably higher in dissolved-solids concentration than that which is considered satisfactory for humans. There are few references in published literature that give maximum concentrations for water to be used for livestock. Range cattle in the Western United States may get accustomed to highly mineralized water and can be seen in some places drinking water that contains nearly 10,000 mg/L of dissolved solids. To be used at such a high concentration, however, these waters must contain mostly sodium and chloride. Water containing high concentrations of sulfate are much less desirable. An upper limit of dissolved solids near 5,000 mg/L for water to be used by livestock is recommended by some investigators, and it would seem obvious that for best growth and development of the animals their water supply should have concentrations considerably below the upper limit.

In the report by McKee and Wolf (1963), the upper limits of concentration for stock water include the following:

Stock	*Concentration (mg/L)*
Poultry	2,860
Pigs	4,290
Horses	6,435
Cattle (dairy)	7,150
Cattle (beef)	10,100
Sheep (adult)	12,900

These, in turn, were quoted from a publication of the Department of Agriculture of Western Australia. The 1972 Water Quality Criteria (NAS-NAE, 1972) give similar but somewhat lower maximum concentrations for major ions.

"Water Quality Criteria, 1972" also quotes limits for most of the minor elements listed in table 24 and for some others. Most of these suggested limits are well above values likely to be encountered in natural potable water except for fluoride, for which an upper limit of 2.0 mg/L is recommended. It is interesting to note that this is below the maximum fluoride limit listed in table 25 as tolerable for water for human consumption.

The chemical quality of water is an important factor to be considered in evaluating its usefulness for irrigation. Features of the chemical composition that need to be considered include the total concentration of dissolved matter in the water, the concentrations of certain potentially toxic constituents, and the relative proportions of some of the constituents present. Whether a particular water can be used successfully for irrigation, however, depends on many factors not directly associated with water composition. A brief discussion of some of these factors is included here to show the complexity of the problem of deciding whether or not a given water is suitable. Readers interested in the subject can find more information in the other publications to which reference is made.

The part of the irrigation water that is actually consumed by plants or evaporated is virtually free of dissolved material. The growing plants do selectively retain some nutrients and a part of the mineral matter originally dissolved in the water, but the amount of major cations and anions so retained is not a large part of their total content in the irrigation water. Eaton (1954, p. 12) determined the quantity of mineral matter retained by crop plants and showed that it consists mostly of calcium and magnesium salts. The bulk of the soluble material originally present in the water that was consumed remains behind in the soil, normally in solution in residual water. The concentration of solutes in soil moisture cannot be allowed to rise too high because excessive concentrations interfere with the osmotic process by which plant root membranes are able to assimilate water and nutrients. Some substances of low solubility, especially calcium carbonate, may precipitate harmlessly in the soil as solute concentrations are increased, but the bulk of the residual solutes presents a disposal problem that must be solved effectively to maintain the productivity of irrigated soil. The osmotic processes by which plants are able to absorb water through their roots are discussed in the section titled "Membrane Effects."

The extent and severity of salt-disposal problems in irrigated areas depend on several factors. Among these factors are the chemical composition of the water supply, the nature and composition of the soil and subsoil, the topography of the land, the amounts of water used and the methods of applying it, the kinds of crops grown, the climate of the region, especially the amount and distribution of rainfall, and the nature of the ground-water and surface-water drainage system.

In most areas, the excess soluble material left in the soil from previous irrigations is removed by leaching the topsoil and permitting part of the resulting solution to percolate below the root zone and thence to move downward toward the ground-water reservoir. In areas where the water table beneath the irrigated land can be kept far enough below the surface, this process of drainage is reasonably effective. The necessary leaching may be accomplished by rainfall in areas where the precipitation is sufficient to saturate the soil deeply. The leaching process also occurs during the irrigation season, either with this purpose specifically in mind or when extra amounts of water are added in an effort to store an extra supply of water in the soil or to use unusually large supplies of water that happen to be available. The need for leaching the soil is generally recognized by farmers who use highly mineralized irrigation water.

In areas where natural drainage is inadequate, the irrigation water that infiltrates below the root zone eventually will cause the water table to rise excessively, a process resulting in serious problems. "Seeped" (waterlogged) land in which the water table is at or near the land surface has become common in many irrigated areas of the United States and elsewhere. Such land has little value for agriculture but often provides a site for water-loving vegetation. Transpiration by such vegetation and direct evaporation from wet soil and open water surfaces can result in waste of large and economically significant quantities of water; also, the soil in such areas soon becomes highly charged with residual salts.

Although waterlogged areas generally have extensive saline accumulations, the quality of the water available was not always the primary cause of abandonment of the land. The reasons for failure of ancient irrigation enterprises include some things unrelated to water-management practices. According to Eaton (1950), however, failure to provide proper drainage to remove excess water and solutes must have played a large part in the decline of areas along the Tigris and Euphrates Rivers in what is now Iraq and may have been important elsewhere, also.

In most large irrigated areas it has become necessary to provide some means of facilitating the drainage of ground water so that the water table is held well below the land surface. In some areas this is accomplished by systems of open drainage ditches or by buried tile systems. In many places, the excess ground water is pumped out by means of wells. The extracted drainage water is higher in dissolved-solids concentration than the original irrigation water, owing to the depletion of the water itself and the leaching of soil and subsoil of saline material, fertilizers, and soil amendments. The concentration of solutes in the drainage water, however, is commonly small enough that the water can be reused for irrigation. In areas of intensive development, several such cycles can occur before the water is finally released.

For long-term successful operation of an irrigation project, all the ions present in the irrigation water that were not extracted by plants must be disposed of either by flowing away from the area in drainage or by storage in an innocuous form within the area. The relationship among total ion loads in an irrigated area can be expressed in terms of the ion inflow-outflow or salt-balance equation:

$$W_i - W_o \pm \Delta W_s = 0.$$

In this equation, the W_i and W_o terms represent total ion loads into and out of the area over a finite time period, and the ΔW_s term represents the change in storage within the area during that period. Although this equation tends to obscure the importance of the time factor and is certainly an oversimplification, it has frequently been used to evaluate the performance of irrigation developments.

Scofield (1940) termed this general relationship the "salt balance" and made calculations of solute inflow and outflow on the basis of streamflow and water analyses. Scofield did not attempt to evaluate changes in ion storage except to term the salt balance unfavorable when storage was increasing and favorable when it was decreasing.

In the more highly developed irrigated areas where most of the water comes from a surface supply, as along the Rio Grande from the San Luis Valley in Colorado to Fort Quitman, Tex., and along the Gila River and its tributaries in Arizona, the drainage water returned to the stream by the upper irrigated areas is used again for irrigation in the next area downstream. The cycle of use and reuse may be repeated six times or more until the residual drainage is too small in quantity and too saline to have any further value.

Deterioration of ground-water quality associated with irrigation development is commonly observed. Moreover, the rate of deterioration is increased when water pumped from wells for drainage is reused in the vicinity for irrigation, for this practice increases the intensity of recycling and converts part of what would have been ion outflow into stored ions. If large amounts of water are pumped, the ground-water circulation pattern in the affected area may come to resemble a closed basin having no outflow. Obviously, the result of such overdevelopment will be ground water too saline for continued use for irrigation. The rates of movement of solutes through systems of this kind, however, are generally not well enough understood to permit a prediction of how long a period of time might be required to attain that result. In some areas the decline of the water table from pumping may be more rapid than the rate at which residual solutes move downward from the soil zone. Abandonment of ground-water-irrigated areas in the United States in recent years has generally been brought about by declining water levels, which resulted in decreased yields from wells. As energy costs have climbed, this decreased yield makes the cost of water from this source uneconomic.

Besides the general increase in major solute ion concentrations that irrigation drainage may cause in ground water underlying irrigated land, there may be additions of specific solutes that are undesirable. A major problem in some irrigated regions has been the increasing concentration of nitrate in ground water that has received drainage from fertilized irrigated fields. Some types of pesticides also may persist in drainage water. The occurrence of selenium in irrigation drainage was noted in a preceding section of this book "Minor and Trace Constituents."

The need for consideration of details of the processes and concepts involved in the salt-balance equation is obvious. The storage term in the equation includes material held in the soil and subsoil, that in the saturated zone, and that in the material between. It includes dissolved ions and initially dissolved material that has precipitated as sparingly soluble minerals, as well as ions held by adsorption on mineral surfaces. The length of time required for a given addition to the storage term to be felt as a change in salinity of some specific fraction of the water supply can be estimated only when rates of the processes involved are approximately known. Some fairly sophisticated attempts to model solute circulation through irrigated areas have been made. A study of this type by Orlob and Woods (1967) pointed up the need for more information to improve ability to predict the effect of changes in water use on the quality of residual water. A digital computer model for an irrigated area in the Arkansas River valley in Colorado was developed by Konikow and Bredehoeft (1974). This model incorporated both hydrologic and water-quality parameters and was used to evaluate effects of hydrologic stress on total-solute concentrations in ground water and surface drainage.

The conservation of irrigation water by using the smallest possible quantity runs the risk of encouraging solute accumulation. Water conservation is, of course, a desirable goal, but the need for solute removal must not be overlooked.

Dry-land agriculture is not without problems of salinity. In parts of the Northern Plains of the United States and adjacent areas of Canada, for example, grain crops are grown successfully by allowing lands to lie fallow in alternate years. Moisture from rain and snowmelt is partly conserved in the fallow ground for use by the crop in the succeeding year. In places this stored moisture has mobilized soluble material and issues from hydraulically favorable sites as saline seeps in which the water may contain high solute concentrations (Thompson and Custer, 1976).

In addition to problems caused by excessive concentrations of dissolved solids, certain constituents in irrigation water are especially undesirable, and some may be damaging even when present in only small concentrations. One of these constituents that has recieved considerable attention is boron. This element is essential in plant nutrition and is sometimes added to fertilizer in small amounts because some soils in humid regions are deficient in boron. A small excess over the needed amount, however, is toxic to some types of plants.

Work done around 1930 by the U.S. Department of Agriculture showed that the plants most sensitive to excess boron included citrus fruit trees and walnut trees.

Table 27. Relative tolerance of crop plants to boron

[In each group, the plants first named are considered more sensitive, and the last named more tolerant. After U.S. Dept. of Agriculture Handbook 60 (U.S. Salinity Laboratory staff, 1954)]

Sensitive	Semitolerant	Tolerant
Lemon	Lima bean	Carrot
Grapefruit	Sweetpotato	Lettuce
Avocado	Bell pepper	Cabbage
Orange	Pumpkin	Turnip
Thornless blackberry	Zinnia	Onion
Apricot	Oat	Broadbean
Peach	Milo	Gladiolus
Cherry	Corn	Alfalfa
Persimmon	Wheat	Garden beet
Kadota fig	Barley	Mangel
Grape (Sultanina and Malaga)	Olive	Sugar beet
Apple	Raggedrobin rose	
Pear	Fieldpea	Palm *(Phoenix canariensis)*
Plum	Radish	Date palm *(P. dactylifera)*
	Sweetpea	Athel *(Tamarix aphylla)*
American elm		Asparagus
Navy bean	Tomato	
Jerusalem-artichoke	Pima cotton	
Persian (English) walnut	Acala cotton	
Black walnut	Potato	
Pecan	Sunflower (native)	

Later work summarized by the U.S. Salinity Laboratory Staff (1954) is shown in part in table 27. The Salinity Laboratory also developed a rating table that indicates the permissible boron concentrations in irigation water for three classes of plants (table 28).

The toxicities of other minor constituents of irrigation water generally have received less attention than boron. However, experiments with plants growing in nutrient solutions and in test plots have shown that certain other elements may be damaging to plants, even in very low concentrations (NAS–NAE, 1972, p. 338-345). Some of these elements, notably molybdenum, selenium, and cadmium, may accumulate in plant tissues and cause toxicity when the plants or seeds are consumed by animals. Lithium in water in small concentrations (0.06 to 0.10 mg/L) has been shown to be damaging to citrus trees (Bradford, 1963).

The term "alkali" is commonly used throughout the Western United States to refer to efflorescent deposits of white material or salt crusts that appear where water evaporates from soil surfaces. The word does not necessarily imply anything about the composition of the material. In some irrigated soils, patches of dark-colored alkali are present, and this material is commonly called black alkali. The dark color is caused by organic material leached from the soil. Black alkali is mostly sodium carbonate, and soil where it occurs has a high pH along with other undesirable properties. White alkali deposits commonly are predominantly sodium sulfate and chloride but may also contain calcium and magnesium. Soils of high salinity interfere with crop growth, and a high pH may decrease the solubility of some essential elements.

The process of cation exchange already has been discussed. It occurs in irrigated soil and may influence soil properties, especially when concentrations of solutes are high. An irrigation water having a high proportion of sodium to total cations tends to place sodium ions in the exchange positions on the soil-mineral particles, and water having mostly divalent cations reverses this process. The particles in the soil having the highest exchange capacity per unit weight are the clay minerals. These minerals preferentially adsorb divalent ions, and when their exchange sites are occupied by calcium and magnesium, the physical properties of the soil are optimal for plant growth and cultivation. If the exchange positions become saturated with sodium, however, the soil tends to become deflocculated and impermeable to water. A soil of this type is difficult to cultivate and may not support plant growth.

The cation-exchange process is reversible and can be controlled either by adjusting the composition of the water, when this is possible, or by using soil amendments. The condition of a sodium-saturated soil can be improved by applying gypsum, which releases calcium to occupy exchange positions. The soil also may be treated with sulfur, sulfuric acid, ferrous sulfate, or other chemicals that tend to lower the pH of the soil solution. The lower pH brings calcium into solution by dissolving carbonates or other calcium minerals.

The tendency of a water to replace adsorbed calcium and magnesium with sodium can be expressed by the sodium-adsorption ratio, which has been discussed in the section titled "Sodium-Adsorption Ratio (SAR)."

Investigators agree that deposition of some of the dissolved ions in irrigation water can occur as a result of concentration effects and related changes and that some of the calcium and bicarbonate can be expected to precipitate as calcium carbonate. Such a reaction might be considered a form of ion storage in the salt-balance equation. Doneen (1954) pointed out that gypsum also could be deposited from irrigation water without doing any harm to soils. Neither of these precipitation reactions can be expected to remove all the ionic species involved, and rather than make arbitrary subtractions of these ions from inflow or outflow terms in the salt-balance equation, as most writers have done, it might be better to incorporate them into the storage term. A working salt-balance equation complete enough to have practical usefulness should contain a storage term that includes a number of different components, including the precipitates.

In considering the effects that might follow from precipitation of carbonates from irrigation water, Eaton (1950) suggested that if much of the calcium and magnesium originally present were precipitated, the residual water would be considerably higher in proportion of sodium to the other cations than it had been originally.

Table 28. Rating of irrigation water for various crops, on the basis of boron concentration in the water

Class of water		Sensitive crops (mg/L)	Semitolerant crops (mg/L)	Tolerant crops (mg/L)
Rating	Grade			
1	Excellent	<0.33	<0.67	<1.00
2	Good	.33–0.67	.67–1.33	1.00–2.00
3	Permissible	.67–1.00	1.33–2.00	2.00–3.00
4	Doubtful	1.00–1.25	2.00–2.50	3.00–3.75
5	Unsuitable	>1.25	>2.50	>3.75

Some waters in which the bicarbonate content is greater than an amount equivalent to the total of the calcium and magnesium could thus evolve into solutions containing mostly sodium and bicarbonate and would have a high pH and a potential for deposition of black alkali.

Although the relationships suggested above are somewhat oversimplified, the U.S. Salinity Laboratory Staff (1954, p. 75) made studies showing that some additional hazard does exist when waters high in bicarbonate and low in calcium are used for irrigation. It was proposed, therefore (U.S. Salinity Laboratory Staff, 1954, p. 81), that waters containing more than 2.5 meq/L of residual sodium carbonate are not suited for irrigation, that those containing 1.25–2.5 meq/L are marginal, and that those containing less than 1.25 meq/L are probably safe. (Residual sodium carbonate is defined as twice the amount of carbonate or bicarbonate a water would contain after subtracting an amount equivalent to the calcium plus the magnesium.)

The residual sodium carbonate concept appears to ignore two major factors in the chemical behavior of carbonate species that must have some influence. As pointed out in earlier sections of this book, calcium carbonate tends to precipitate independently and thus leaves magnesium in solution. Although the conditions in irrigated soils might favor deposition of mixed carbonates, their existence does not seem to have been demonstrated. A more recent paper by Eaton and others (1968) suggested that precipitation of magnesium might occur by combination with silica. The second factor is the production of carbon dioxide in the soil by plants. This is a major source of bicarbonate ions and in some irrigated soils may provide much more of this material than the irrigation water originally contained.

From this brief discussion it should be evident that the relationships between water quality and the feasibility of using water for irrigation are not simple. Increasing difficulties that can be expected as salinity of the water supply increases could be translated into economic effects. A decrease in crop yield accompanied by increased costs in water and land management occurs as the water becomes less suitable.

Generalizations regarding sensitivity of crops to salinity of water supply were made by the U.S. Salinity Laboratory Staff (1954, p.67). A list of crops arranged in three groups with respect to their tolerance toward salinity shows that, generally, crops tolerant to boron also are tolerant to salinity. According to this list, the more sensitive species include fruit trees and beans and the more tolerant include the date palm, asparagus, beets, Bermuda grass, cotton, sugar beets, and barley. Most vegetables and field and forage crops are included in the moderately tolerant group.

A diagram widely used for evaluating waters for irrigation, published by the U.S. Salinity Laboratory (1954, p.80), is reproduced in figure 51. Specific conductance, as an index of dissolved-solids concentration, is plotted on one axis, and the sodium-adsorption ratio on the other. The diagram is divided into 16 areas that are used to rate the degree to which a particular water may give rise to salinity problems and undesirable ion-exchange effects in soil.

Water having a specific conductance greater than 5,000 μmho/cm is used with some success in certain areas, where soil conditions, crops grown, and irrigation techniques are suitable. The hydrologist needs to consider local experience before arbitrarily stating whether a given water is usable or not. Salinity problems, however, may be slow to develop and may be observable only in decreased crop yields or in other respects less easy to evaluate. A water of high salinity must always be viewed with suspicion until proof of its safety for a specific use is obtained.

Industrial Use

The quality requirements for industrial water supplies range widely, and almost every industrial application has its own standards. For some uses such as single-pass condensing of steam or for cooling or for concentrating ores, chemical quality is not particularly critical and almost any water may be used. At the opposite extreme, water approaching or equaling the quality of distilled water is required for processes such as the manufacture of high-grade paper or pharmaceuticals, where impurities in the water would seriously affect the quality of the product. Modern maximum-pressure steam boilers may require makeup water less concentrated than the average distilled water of commerce, and very pure water is desirable in nuclear reactors to minimize radioactivity induced by neutron activation of the dissolved species.

It is not the purpose of this book to review the subject of industrial water-quality standards in any detail. Some idea as to the varied nature of the requirements for certain industries can be obtained from table 29. This table is based on data presented by the U.S. Federal Water Pollution Control Administration (1968). Additional consideration of industrial water-quality requirements was given by McKee and Wolf (1963). The NAS-NAE (1972) publication "Water Quality Criteria, 1972" includes a section on industrial water that describes both quality and quantity requirements.

The standards given in table 29 represent maximum values permitted in the water at the point of use, after any necessary treatment but before adding any internal conditioners that may be needed during the process. The increasing stringency of requirements for boiler-feed water as the steam pressure increases is particularly noticeable. The absence of an entry in the table indicates either that no limit for the constituent or characteristic has been given or that the constituent cannot attain objectionable

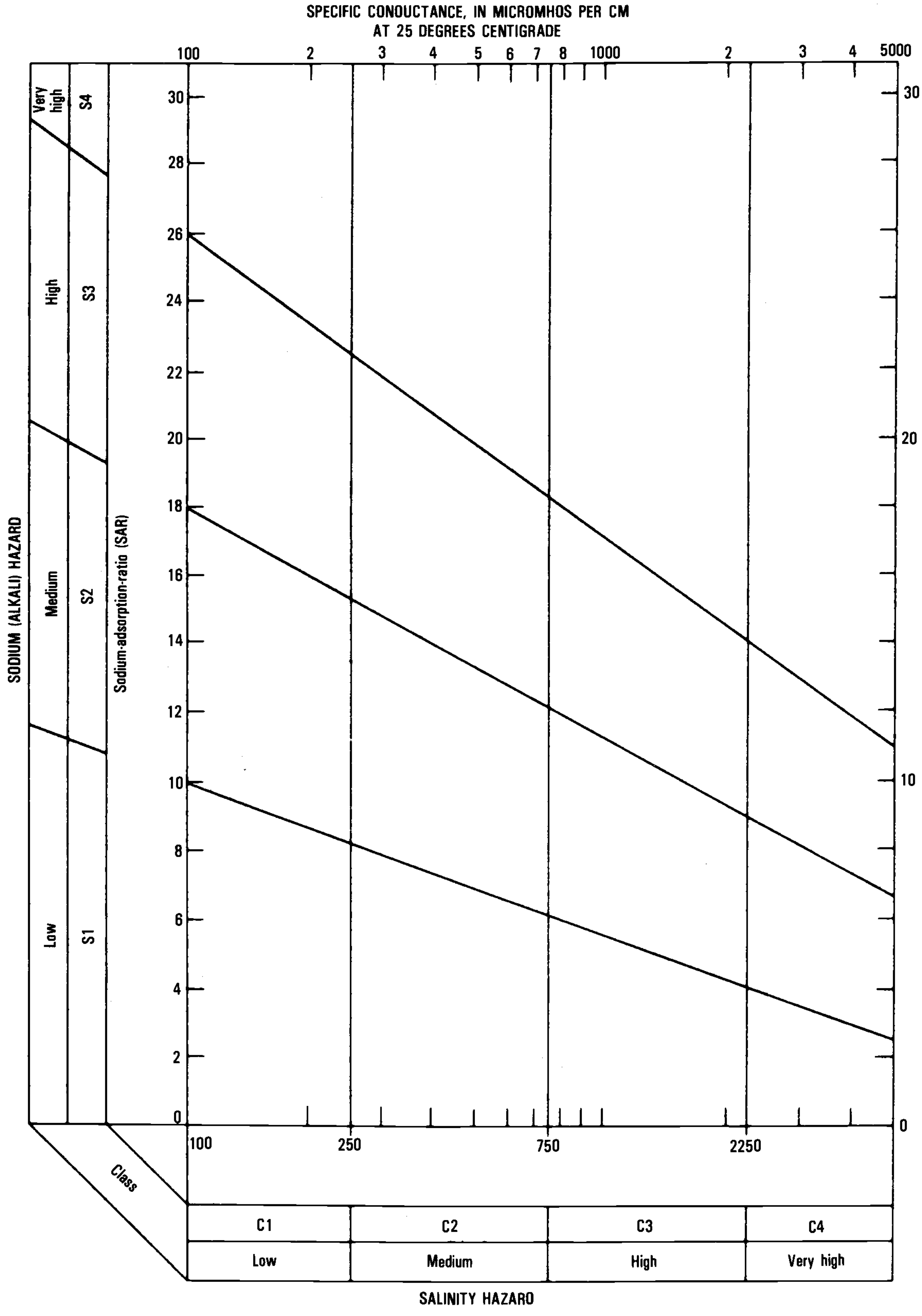


Figure 51. Diagram for use in interpreting the analysis of irrigation water. Adapted from U.S. Salinity Laboratory staff (1954).

levels if the water meets the other specifications. Water used for processing food or beverages must also meet drinking-water standards.

It is technically possible to treat any water to give it a composition suitable for special uses. If the water requires extensive treatment, however, especially if large amounts of water are involved, it may not be economically feasible to use some supply sources. Industrial plants having large water requirements are commonly located with reference to availability of water.

Although water temperature is not a chemical property and has not received much consideration here, the temperature of a supply and the seasonal fluctuation of that temperature are major considerations in the use of water for cooling by industry. In some areas, ground water is used extensively for this purpose because its temperature is uniform and is below air temperatures during warm weather. Some industries have recharged ground-water aquifers with cold water from surface streams each winter and have withdrawn the cool stored water in the summer when the regularly used surface supply is too warm for efficient cooling. In the past there were instances of industrial plants located along the same stream using and reusing the water for cooling until the temperature of the water for many miles of river was far above normal levels. Excessively high temperatures deplete dissolved oxygen and interfere with normal stream ecology, an effect sometimes called thermal pollution. In recent years these practices have been regulated to prevent undesirable ecologic stress.

Industrial expansion has contributed greatly to increasing per capita use of water in the United States. Much of the industrial use, however, is nonconsumptive. That is, the water is not evaporated or incorporated into the finished product, but is released after use without significant change in quantity, possibly with an increased load of dissolved or suspended material or perhaps with very little change from its original composition. As water supplies have become more fully used, however, many industries have found it necessary to conserve and reuse water that in former years would have been allowed to flow down a sewer or back to a surface stream. In some places, reclaimed sewage has been used for certain noncritical industrial purposes.

Recirculation of water that is depleted by evaporation, as in a cooling tower, introduces concentration factors, and intensified reuse can be expected to raise the average solute concentration in effluents.

Recreational and Esthetic Uses

Considerable attention is now being paid to recreational uses of rivers and lakes for such purposes as swimming, fishing, and boating and for simple esthetic enjoyment. The cost of restoring water bodies that have lost their value for such purposes because of pollution may be substantial, but there is strong public support in many places for the aim of creating or protecting waters for these purposes.

Water for swimming and other sports in which water is in contact with the skin obviously must conform to sanitary requirements. Fish that are sought by anglers require clean water and a good supply of dissolved oxygen. Certain metal ions may be lethal to fish and other aquatic life forms when present at levels near or below the limits given for public water supplies. Copper, zinc, and aluminum, which are not among the metals for which limits are prescribed for public water supplies, are toxic to fish and many other species of aquatic life. The absence of fish from low-pH lakes in Europe and North America is believed to be the result of aluminum brought into solution by precipitation having a low pH ("acid rain") (Cronan and Schofield, 1979).

One of the important factors in the assimilation of dissolved metal ions by aquatic biota is the tendency for increasing concentrations in species higher in the food chain. One of the more insidious effects of mercury-containing waste that enters rivers and lakes is an increase in mercury content of fish to the extent that they become dangerous to eat. Some species of fish are more sensitive than others to ions and organic solutes, and certain combinations of ions may exert synergistic effects. McKee and Wolf (1963) compiled many references on the effects of dissolved material on fish. Water-quality requirements for fish have been summarized by NAS–NAE (1972).

Although highly impure water is attractive in appearance when viewed from a distance, it is obvious that even the lowest standards of pollution control must aim to produce a product reasonably pleasing to the senses of the viewer from close at hand, while walking along the shore or riding over the water in a boat. The surroundings of the water body are an important part of this esthetic impression.

WATER-MANAGEMENT CONCEPTS AND PROBLEMS

The term "water-quality management" is frequently used in recent literature. Sometimes it is used as a synonym for "pollution control." Most of the time, however, it implies the use and development of water resources in a way that maintains water quality at the optimum level. This may involve many administrative and engineering activities concerned with decreasing the pollution loads contributed to streams through better and more complete sewage treatment, cleaning up existing pollution by dredging and other means, and designing and building storage facilities to increase low flows of streams and thus to decrease quality fluctuations, or any of a number of related activities. The use of the term also implies that enough is known about the natural-water circulation systems so that quality indeed can be effectively managed.

"Clean water" legislation in the United States, and the accompanying emphasis on pollution abatement, resulted in large expenditures during the 1960's and 1970's aimed at decreasing "point sources" of contaminants. These point sources were taken to be sewage outfalls and industrial waste streams. It is generally agreed that substantial improvement in the quality of stream water resulted in many places. However, it has become evident that "nonpoint sources" have a major impact and that control of these sources poses a much more difficult problem. Some aspects of this topic have been discussed in this book in different contexts. The effects of agricultural practices—fertilization, use of pesticides, and cultivation techniques, for example—may have profound influences on water quality both in surface streams and underground.

Pollution, as the term was defined in the preceding section, entails a level of contamination that is harmful, and pollution control, therefore, would have as a goal keeping the concentrations of contaminating substances at relatively low levels, though not necessarily eliminating them altogether. A different goal has often been advocated—the elimination of pollution altogether, thereby restoring waters to a pristine state. For various reasons, such a goal is unrealistic, not to mention unattainable. One of the best ways of controlling pollution is through conservation of resources, reuse of processed materials, and increased vigilance at all levels to prevent loss by leaks and spills. Perfection in this effort cannot be expected. Moreover, for some uses of processed material, recovery of the material is impracticable. For example, the recovery of lead after leaded gasoline had been burned or after paint had been spread, if not impossible, would require prohibitively large expenditures of energy.

The maintenance of a healthy industrial economy appears to require a large and probably increasing per capita energy use. The rapid increase in energy cost that occurred during the 1970's made it evident that there may be an economic limit to energy use as well as a limit

Table 29. Water-quality requirements

[Concentrations, which represent upper limits for water at point of use before addition of internal conditioners, are in milligrams per liter except as indicated (U.S.

Constituent	Boiler feedwater pressure (pounds per square inch gauge)				Textiles (scouring, bleaching, and dyeing)
	0–150	150–700	700–1,500	1,500–5,000	
Silica (SiO_2)	30	10	0.7	0.01	
Aluminum (Al)	5	.1	.01	.01	
Iron (Fe)	1	.3	.05	.01	.1
Manganese (Mn)	.3	.1	.01		.01
Calcium (Ca)		0	0		
Magnesium (Mg)		0	0		
Ammonium (NH_4)	.1	.1	.1	.7	
Copper (Cu)	.5	.05	.05	.01	.01
Zinc (Zn)		0	0		
Bicarbonate (HCO_3)	170	120	48		
Sulfate (SO_4)					
Chloride (Cl)					
Fluoride (F)					
Nitrate (NO_3)					
Hardness as $CaCO_3$	20	0	0	0	25
Alkalinity as $CaCO_3$	140	100	40	0	
Acidity as $CaCO_3$	0	0	0	0	
pH	8.0–10.0	8.2–10.0	8.2–9.0	8.8–9.2	([3])
Dissolved solids	700	500	200	.5	100
Color (units)					5
Organics:					
CCl_4 extract	1	1	.5	0	
Methylene-blue active substances	1	1	.5	0	
Chemical oxygen demand	5	5	.5	0	
Dissolved oxygen	2.5	.007	.007	.007	
Temperature (°F)					
Suspended solids	10	5	0	0	5

[1] Not to exceed U.S. Public Health Service drinking-water standards.

[2] Limit for noncarbonate hardness, 70 mg/L as $CaCO_3$.

[3] Ranges from 2.5 to 10.5, depending on process and product.

related to the finite availability of fossil fuel. There may be an environmental limit as well—a point at which the environmental damage from high energy use becomes too great to be tolerated.

The concept of water-quality management is related in a general way to broader concepts of management of water resources for full and efficient use by humans. This kind of water use may involve extensive storage and transport facilities to make water available when and where it is needed. Sometimes a considerable degree of chemical control is required to make the quality of the water satisfactory, as in the treatment of public water supplies.

As the intensiveness of development of water supplies increases, the interweaving of chemical effects with the various physical processes in the circulation of water becomes more and more evident and of greater and greater practical importance. Some of the chemical effects of water storage in reservoirs have already been mentioned. There are some undesirable chemical effects in many impoundments; perhaps most significant is the tendency for water to become stratified at times and for previously accumulated sediments to contribute undesirable impurities to the water near the reservoir bottom. In arid climates, however, a more visible and generally objectionable feature of large open-storage reservoirs is the loss of water by evaporation. Evaporation losses from Lake Mead on the Colorado River average 849,000 acre-ft per year (Meyers, 1962, p. 94), equivalent to a depth of more than 6 ft over the surface of the lake.

A means of storage that avoids some of the disadvantages and inefficiencies of surface reservoirs would have considerable appeal. The method most frequently suggested, and one that is generally believed to have the greatest promise, is the injection of surface water into the ground-water body for later removal by pumping. The integration of surface-water and ground-water systems that would result if this technique were adopted on a large scale has a very logical appeal to the water-resources planner.

for selected industries and processes

Federal Water Pollution Control Administration, 1968)]

Chemical pulp and paper		Wood chemicals	Synthetic rubber	Petroleum products	Canned, dried, and frozen fruits and vegetables	Soft-drinks bottling	Leather tanning (general finishing processes)	Hydraulic cement manufacture
Unbleached	Bleached							
50	50	50			50			35
1.0	.1	.3	.1	1	.2	.3	.3	25
.5	.05	.2	.1		.2	.05	.2	.5
20	20	100	80	75		100		
12	12	50	36	30				
		250						
		100			250	500	250	250
200	200	500		300	250	500	250	250
					1	(1)		
		5			10			
100	100	900	350	[2]350	250		soft	
		200	150		250	85		400
					0			0
6–10	6–10	6.5–8.0	6.2–8.3	6.0–9.0	6.5–8.5		6.0–8.0	6.5–8.5
		1,000		1,000	500			600
30	10	20	20		5	10	5	
					.2	(4)	(5)	1
	95							
10	10	30	5	10	10			500

[4] Carbon chloroform extract limit, 0.2 mg/L; also specified to be free of taste and odor.

[5] Carbon chloroform extract limit, 0.2 mg/L.

It should be evident from the descriptions of chemical systems and influences in surface streams and in ground-water bodies that the two environments are very different. Conversion of a surface water to a ground water in large quantity at a rapid rate and with a minimum of effort and expense is necessary in successful artificial recharge of ground-water reservoirs. Chemical factors that appear subtle and unimportant to the casual observer may create great difficulties in the recharging process.

Recharging techniques most commonly used include spreading water on the land surface and allowing it to percolate to the water table and injecting water directly through wells, in a reversal of the usual pumping process. Some success has, of course, been attained in both ways, partly inadvertently. For example, most irrigation projects have brought about extensive ground-water recharge by infiltration from irrigated fields as well as from unlined ditches and canals. "Water flooding" as a means of recovering petroleum is practiced extensively, and highly unfavorable chemical conditions have been overcome as brines are pumped back down wells in these operations.

Extensive withdrawals of ground water have resulted in some areas in the subsidence of the land surface (Poland and Green, 1962; Holzer and others, 1979). Poland (1981) showed that the land-subsidence problem is substantial. In 17 affected areas of the United States the measured subsidence ranged from 0.3 to 9.0 m. Areas affected included 16,000 km^2 in California, 12,000 km^2 in Texas, and 2,700 km^2 in Arizona.

Subsidence of the city of Venice, Italy, related to ground-water withdrawals in an adjacent industrial area has been studied extensively. Gambolati and others (1974) concluded that subsidence between 1930 and 1973 has been 15 cm. Water from surface sources was substituted for some of the industrial wells during the 1970's. Apparently subsidence had stopped by 1979 (Volpi and others, 1979). Even a small amount of subsidence can add significantly to flood hazards in Venice. The aquifer storage space lost by subsidence probably cannot be regained. However, a more conservative management policy under which water pumped out is replaced periodically can at least prevent or minimize future subsidence.

The subsidence effects noted above have generally been attributed to compaction of sediments when they were dewatered. The finer grained material in some ground-water systems might contain water differing in chemical composition from the bulk solution present in the coarser material. The normal pattern of water movement in such systems concentrates flow through the coarser fraction. It seems possible that the composition of ground water pumped from wells where subsidence is occurring might be affected as the fine-grained material that usually does not yield much water is "squeezed dry." Such effects do not seem to have been documented, but might be discernible if they were looked for.

Whether recharge is accomplished by spreading or by injection, some consideration of chemical and biological factors is required to enable recharging to continue over extended periods. From descriptions in the literature, it is evident that most attempts at injection through wells have encountered difficulties. Often, insufficient thought has been given to the effects on water compositions of injecting the water into a new environment or to reactions that might occur between native and introduced solutes. Changes in Eh and in pH might occur, altering the solubility of solutes such as calcium and iron and causing precipitates that might clog openings around the injection well. Or the new solution might dissolve objectionable amounts of impurities from solids that were stable in the previous environment, or create environments promoting or sustaining biological growths in and near the injection well.

There is an extensive literature on the nonchemical aspects of artificial recharge. An introduction to earlier literature can be obtained from the bibliography by Todd (1959). More recent papers describing recharging experiments in which some consideration was given to chemistry include one by Reed and others (1966) on work done at Kalamazoo, Mich., and two reports on experiences in Oregon and Washington by Price and others (1965) and by Foxworthy and Bryant (1967). Artificial-recharge experiments in the Grand Prairie region of Arkansas included some chemical considerations described by Sniegocki (1963). More recently, U.S. Geological Survey studies of recharging techniques and effects, both chemical and physical, were made in the Ogallala aquifer of western Texas (Wood and Signor, 1975; Brown and others, 1978; Wood, 1978) and at Bay Park, Long Island, N.Y. (Vecchioli and Ku, 1972; Ragone, 1977). Microbiologic factors were also studied (Ehrlich and others, 1979) at Bay Park.

Wise management of water resources could be said to have the following goals: providing sufficient quantities of water of acceptable quality for all beneficial uses, using fair methods of allocation when total supplies are temporarily inadequate, and, insofar as possible, developing resources in such a way as to avoid overcommitments so that in the long term there will be no continuous shortages or significant continuous water-quality impairment.

Sources of freshwater are renewable but are finite in quantity, and their availability is variable both in time and from place to place. Obviously, the goals of management mentioned above cannot be fully attained, and, indeed, in some ways the goals are incompatible. Metropolitan areas require large supplies of water. Commonly, these supplies have been obtained from surface- or ground-water sources in the surrounding area; in some instances, water has been imported from drainage basins or ground-water systems hundreds of kilometers distant.

Water-development projects for other purposes, notably for the irrigation of agricultural land in arid or semiarid regions, may involve much larger quantities of water. All such developments have costs as well as benefits. The benefits are generally self-evident, but many of the costs are intangible, including environmental effects both in the areas of water use and in areas from which water is taken.

A part of the environmental cost is the deterioration of water quality resulting from water use and waste disposal in the impacted areas. The kinds of effects that might be anticipated and their time frame generally have not been well understood. An improved ability to predict water-quality changes related to water-resource development is one goal toward which research in chemistry of natural aqueous systems must be directed. Although utopia will never be reached, a more complete grasp of the water-quality-related costs of water-resource development will certainly help in making wiser decisions.

A few decades ago, public opinion seemed willing to support development of water resources on a broad scale and there were various far-reaching proposals for transferring large amounts of water from one region to another. Proposals for supplementing water supplies in water-short regions of the Southwestern United States where population was increasing were among the more seriously considered. During the 1960's, the State of California began to implement a plan to transfer water from streams in the northern part of the State south to parts of the San Joaquin Valley and over the Tehachapi Mountains into water-short areas farther south. Water deliveries to the Los Angeles area began in the mid-1970's.

Economic and political factors play important roles in water-transfer plans of this type, and the future of such plans in the field of water-resources management is difficult to predict. The Colorado River basin in the Southwestern United States is an example of an area in which water use has been increasing. A brief review of management efforts and water-quality factors affecting the Colorado River is indicative of the present limited ability to cope with large-scale water-distribution problems.

Hydrologic studies of the Colorado River have been carried on by the U.S. Geological Survey since the bureau was formed in 1879. Water-quality data, much of it based on daily sampling, have been obtained at some points in the lower part of the basin (downstream from Lees Ferry, Ariz., which is near the Arizona–Utah border) continuously since 1925. A review of these records up to 1965 was made by Irelan (1971). His observations and those of contemporaries offer some insight into the changes in water quality that the development of water resources in the basin have brought about. They also provide some indications of the factors that affect the usefulness of records of this kind for predicting trends.

Prior to the completion of Hoover Dam on the Colorado River near Las Vegas, Nev., the riverflow was essentially uncontrolled. As noted by Irelan (1971, p. E4), dissolved solids at points downstream from the Grand Canyon reached 1,500 mg/L during the fall and winter low-flow periods in most years, and in some years the maximum was near 1,800 mg/L. Hoover Dam was completed in 1935 and, subsequently, two additional dams, Davis and Parker, were constructed downstream. The construction of Glen Canyon Dam forming Lake Powell just upstream from Lees Ferry was completed in 1963. Reservoir storage capacity in the four impoundments is equivalent to several years of average river discharge.

The storage reservoirs mix high- and low-flow water and damp out the annual fluctuation of solute concentrations. Some calcium carbonate is precipitated out in the reservoirs, as noted earlier, and evaporation tends to increase solute concentrations. Also, some solutes are added by dissolution of soluble rock strata in the reservoirs. Irelan's (1971, p. E10) compilation showed that water released from Lake Mead, the reservoir formed by Hoover Dam, from 1937 to 1964 ranged in dissolved solids from near 600 to a little over 800 mg/L (annual discharge-weighted averages). Water diverted into the Colorado River Aqueduct at Parker Dam, for use by the Metropolitan Water District of Southern California, had about the same composition. From 1941 to 1965, the annual weighted average hardness of this water ranged from 286 to 388 mg/L as $CaCO_3$ (Irelan, 1971, p. E11).

It has long been recognized that the Colorado River water is higher in dissolved-solids concentration than would be considered fully satisfactory for a public supply in other parts of the United States, and that successful use of the water for irrigation requires good drainage to avoid solute accumulation in the soil (Howard, 1930, p. 6). The Metropolitan Water District of Southern California (MWD) has successfully used the water after treatment to decrease its hardness. Other sources available to MWD provide water of substantially lower solute concentration. Other large-scale users in the lower part of the basin have no such alternatives, however.

As noted by Irelan (1971, p. E31), saline drainage water pumped from wells in the Wellton-Mohawk area east of Yuma, Ariz., brought about deterioration in the quality of the river water crossing the International Boundary in 1961. Remedial measures of various kinds have been required since then to maintain the quality of water delivered to Mexico at acceptable levels.

Other water-development projects in the Colorado River basin, both above and below Lees Ferry, have been planned or are under construction. They can be expected to bring about some further increases in solute concentrations in the water available from the river in the lower part of the basin, but there is no agreement as to probable timing or magnitude of such increases. Irelan (1971, p.

E39) concluded that some increases probably would occur after projects proposed but not in operation in 1969 were completed. Hill (1965) predicted that the hardness of water diverted from the river for use by the MWD might reach 435 mg/L (as $CaCO_3$) by 1990. A later prediction by Valantine (1974) called for dissolved-solids concentrations at the Parker Dam (Lake Havasu) diversion point to average 800 mg/L by 1990, and 980 mg/L by the year 2000.

Irelan's (1971, p. E39) short-term prediction was that mineral concentrations in the water of the lower river would be stabilized temporarily at concentrations less than those of 1965. The filling of Lake Powell, behind Glen Canyon Dam, decreased downstream flow in that year. Records published in the series "Water Resources Data for Arizona" for the years 1971–82 and 1966–70, in the U.S. Geological Survey Water-Supply Paper series, show that this prediction was accurate. The dissolved-solids concentration in Lake Havasu averaged 811 mg/L in 1965. In 1968, the dissolved-solids concentrations generally were a little less than 700 mg/L and subsequently, through 1982, ranged from near or a little less than 700 to about 750 mg/L. Hardness concentrations during the 1969–83 period were generally lower than in 1965 and were below 350 mg/L most of the time.

Data of the type available for the Colorado River permit relatively accurate computation of annual solute loads transported past sampling points. Evaluation techniques used by Irelan (1971) included many such calculations. One approach is the cumulative mass diagram in which the cumulative solute load is plotted on the ordinate against time on the abscissa. A change in slope of this line may indicate a perturbation in the stream regimen. It is evident that differences in total flow produced by wet and dry years have a substantial influence and that other factors tend to be obscured by such differences. The Colorado, at least in its lower reaches, is definitely a managed stream in many respects. Still, the effects of management actions on water quality are difficult to discern closely without careful studies.

The Colorado River system is large in terms of area, flow, and solute load. The relative importance of different factors that influence the system is difficult to determine, and because of the system's size the results of perturbations may be slow to appear. The effects on water composition caused by seasonal and year-to-year variations in precipitation and runoff, as noted in preceding discussions of river-water chemistry, tend to be decreased in streams controlled by storage reservoirs. An example given in the section "Frequency Distributions" demonstrated that the seasonal changes in dissolved-solids concentration that were characteristic of the lower Colorado River before the construction of storage reservoirs no longer occur. The total storage capacity of Lakes Powell, Mead, Mohave, and Havasu is more than 54 million acre-feet. Hely (1969) reported that annual discharge of the river at Lees Ferry ranged from a maximum of 22 million to a minimum of 4.4 million acre-feet during the period 1896–1962. The mean annual discharge was about 13.4 million acre-feet during that period. Thus, the storage capacity is sufficient to hold about 4 years of average runoff, and effects of single abnormally wet or dry years on the composition of water in the lower river should be rather small, although some of the inflow to the larger reservoirs in wet years may pass through them without completely mixing with previously stored water. A succession of wet years, however, could cause major changes, especially if they followed a dry period in which stored water had been depleted extensively.

Predictions of dissolved-solids values to be expected in future years cannot take into account the effects of major long-term fluctuations in annual discharge, as such events cannot be foreseen accurately. The Lake Havasu predictions cited earlier in this discussion assumed a continuation of discharges near the recent average. As Hely (1969) and other investigators have noted, the average annual Colorado River discharge for the first 30 years of the 20th century was more than 4 million acre-feet greater than the average for the second 30 years, possibly indicating some long-term cyclic effect.

During 1983 and 1984 the flow of the Colorado River above Lake Powell was very much above normal, and as a result large volumes of stored water were spilled from all the reservoirs. By late 1984 the diluting effect of high flows had become distinctly noticeable in the lowermost reservoir, Lake Havasu. Dissolved-solids concentration of stored water in the lake in the early part of 1985 was substantially below 600 mg/L (U.S. Geological Survey, unpub. data, 1985). This dilution effect can be expected to influence the composition of water in the lower part of the Colorado River for several years.

Owing to the unpredictable nature of large fluctuations in flow, long-term predictions of stored-water quality have a large element of uncertainty. Water users dependent on the lower Colorado River would obviously welcome a return to more abundant supplies if, indeed, the apparent dry cycle is coming to an end. Development based on overly optimistic estimates, however, would seem from the historical record to be very unwise.

The long record of hydrologic data available for the Colorado River offers many opportunities for studying the effects of natural and human-induced processes. One of the purposes of this book is to provide the background as well as encouragement for such studies. The value of long-term records cannot by fully realized without a concurrent emphasis on interpretation.

Smaller scale studies of natural-water chemistry may offer greater opportunity for evaluating and understanding the effects of some of the processes and chemically activated controls on the occurrence and behavior of individual elements. Applications of theoretical chemistry that have been described here and further research in these areas remain a challenge for present and future students of natural-water chemistry.

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TABLES 30–33

Table 30. Chemical thermodynamic data for carbon, oxygen, and sulfur species

[From Wagman and others (1968)]

Species	ΔG_f° (kcal/mol)
$CH_4(g)$	-12.13
$CH_4(aq)$	-8.22
$CO_2(g)$	-91.254
$CO_2(aq)$	-92.26
$H_2CO_3(aq)$	-148.94
HCO_3^-	-140.26
CO_3^{2-}	-126.17
$O_2(aq)$	3.9
OH^-	-37.594
$H_2O(l)$	-56.69
S^{2-}	20.5
HS^-	2.88
$H_2S(g)$	-8.02
$H_2S(aq)$	-6.66
HSO_4^-	-180.69
SO_4^{2-}	-177.97

Table 32. Chemical thermodynamic data for manganese species

Species	ΔG_f° (kcal/mol)	Source
$Mn^{2+}(aq)$	-54.5	Wagman and others (1969).
$MnOH^+(aq)$	-96.8	Do.
$Mn(OH)_3^-(aq)$	-177.9	Do.
$Mn(OH)_2$ (amorphous)	-147.0	Do.
$MnCO_3$ (rhodochrosite)	-195.0	Robie and others (1978).
MnS (alabandite)	-52.14	Do.
Mn_3O_4 (hausmannite)	-306.7	Wagman and others (1969).
β-MnOOH (feitknechtite)	-129.8	Hem and others (1982).
γ-MnOOH (manganite)	-133.3	Bricker (1965).
δ-MnO_2 (birnessite)	-108.3	Do.
γ-MnO_2 (nsutite)	-109.1	Do.

Table 31. Chemical thermodynamic data for iron species

[c, calculated]

Species	ΔG_f° (kcal/mol)	Source
$Fe^{2+}(aq)$	-18.85	Robie and others (1978).
$FeOH^+(aq)$	-62.58(c)	Baes and Mesmer (1976).
$Fe(OH)_3^-(aq)$	-147	Wagman and others (1969).
FeO (stoichiometric)	-60.03	Robie and others (1978).
FeS_2 (pyrite)	-38.3	Do.
FeS	-24.22	Do.
$FeCO_3$ (siderite)	-159.35	Wagman and others (1969).
$Fe^{3+}(aq)$	-1.1	Robie and others (1978).
$FeOH^{2+}(aq)$	-54.83	Wagman and others (1969).
$Fe(OH)_2^+(aq)$	-106.7(c)	Baes and Mesmer (1976).
$Fe(OH)_4^-(aq)$	-198.4	Do.
$Fe(OH)_3$ (amorphous)	-166	Feitknecht and Schindler (1963).
FeOOH (goethite)	-116.77	Robie and others (1978).
Fe_2O_4 (magnetite)	-242.01	Do.

Table 33. Equilibrium constants for temperatures from 0° to 50°C for the system $CaCO_3+H_2O+CO_2$

[Ionic strength, 0.0]

T(°C)	Log K_{H_2O} 1	Log K_h 2	Log K_1 3	Log K_2 4	Log K_s 5
0	-14.955	-1.114	-6.579	-10.625	2.274
10	-14.534	-1.270	-6.464	-10.490	2.131
20	-14.161	-1.406	-6.381	-10.377	1.983
30	-13.833	-1.521	-6.327	-10.290	1.837
40	-13.533	-1.620	-6.298	-10.220	1.685
50	-13.263	-1.705	-6.285	-10.172	1.537

1. Dissociation of water: $K_{H_2O} = [H^+][OH^-]$ (Ackerman, 1958).
2. Henry's law constant for solution of CO_2 in water: $K_h = [H_2CO_3]/P_{CO_2}$ (Harned and Davis, 1943).
3. First dissociation constant for carbonic acid: $K_1 = [HCO_3^-][H^+]/[H_2CO_3]$ (Harned and Davis, 1943).
4. Second dissociation constant for carbonic acid: $K_2 = [CO_3^{2-}][H]/[HCO_3]$ (Harned and Scholes, 1941).
5. Solubility constant for calcite: $K_s = [Ca^{2+}][HCO_3^-]/[H^+]$ (calculated from data of Jacobson and Langmuir, 1974).

INDEX

[Major references are underscored]

Explanatory Note to Plate 2

Nomograph for evaluating calcite equilibria $T=0°C$ to $50°C$, $I=0.0$ to 0.5

This nomograph provides a means of estimating the calcite saturation index (S.I.) for waters of known ionic strength (*I*) for temperatures (*T*) between 0° and 50°C. Besides the values for *T* and *I* it is necessary to know the concentrations (mg/L) of HCO_3 and Ca and the pH. Preferably pH and HCO_3 measurements should be made at the time samples are collected. Ionic strength can be computed using plate 1 if all major dissolved ion concentrations are known. For some waters an approximate value for *I* can be computed from the specific conductance of the water (Lind, 1970).

Instructions for use:

1. Place overlay (pl. 2*B*) on Ca vs HCO_3 grid (pl. 2*A*) so that match lines coincide.
2. While keeping the match lines exactly superimposed, move 2*B* until the determined value of *I* read on the ionic strength scale coincides with the temperature (measured at time of sample collection) value read on the temperature scale on 2*A*.
3. Locate in 2*A* the point of intersection of Ca and HCO_3 concentrations (in mg/L). The position of this point on the pH grid (2*B*) is the equlibrium pH for calcite saturation at these *T* and *I* values.
4. Compute calcite saturation index from the formula

$$\text{S.I.}=\text{pH}_{\text{measured}} - \text{pH}_{\text{equilib}}.$$

A positive value for S.I. indicates supersaturation. Importance of simplifying assumptions and related factors that may affect accuracy of S.I. values obtained with the nomograph are discussed under the topic headings "Calcium—Chemical Controls on Calcium Concentrations" in the text.

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