

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 $[\text{HCO}_3^-]:[\text{H}_2\text{CO}_3]$ will be near 100:1 at pH 4.4, and the ratio $[\text{HCO}_3^-]:[\text{CO}_3^{2-}]$ 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 ($\delta^{13}\text{C}$) data.

From studies of $\delta^{13}\text{C}$ 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 that 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 , $\text{H}_2\text{CO}_3(\text{aq})$, 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 CO₂ species distribution diagram. The lines on this graph were computed from the first and second dissociation equilibrium expressions,

$$\frac{[\text{H}_2\text{CO}_3^*]}{[\text{H}_2\text{CO}_3]} = K_1 [\text{H}^+]^{-1}$$

and

$$\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = K_2 [\text{H}^+]^{-1},$$

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 HCO₃⁻:H₂CO₃ 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 H₂CO₃. 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

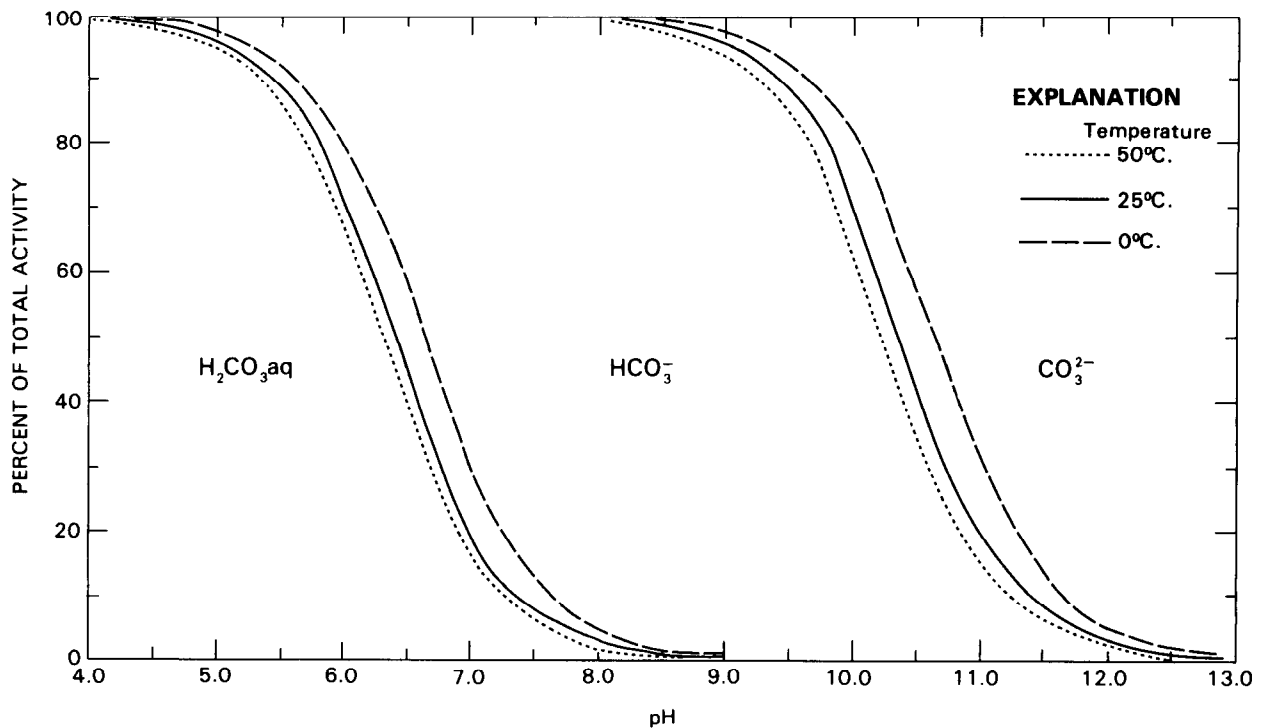


Figure 19. Percentages of dissolved carbon dioxide species activities at 1 atmosphere pressure and various temperatures as a function of pH.

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 $2\frac{1}{2}$ 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 non-carbonate 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 CaCO₃ or H₂SO₄. 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 H₂CO₃ 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 ₂ SO ₄ (total)					913					

¹Probably about 0.6 meq/L of the total alkalinity is actually present in the form H₃SiO₄.

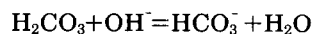
²Density, 1.046 g/mL.

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 H₂S and SO₂ 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 NH₄, 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



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 stream-flow 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.

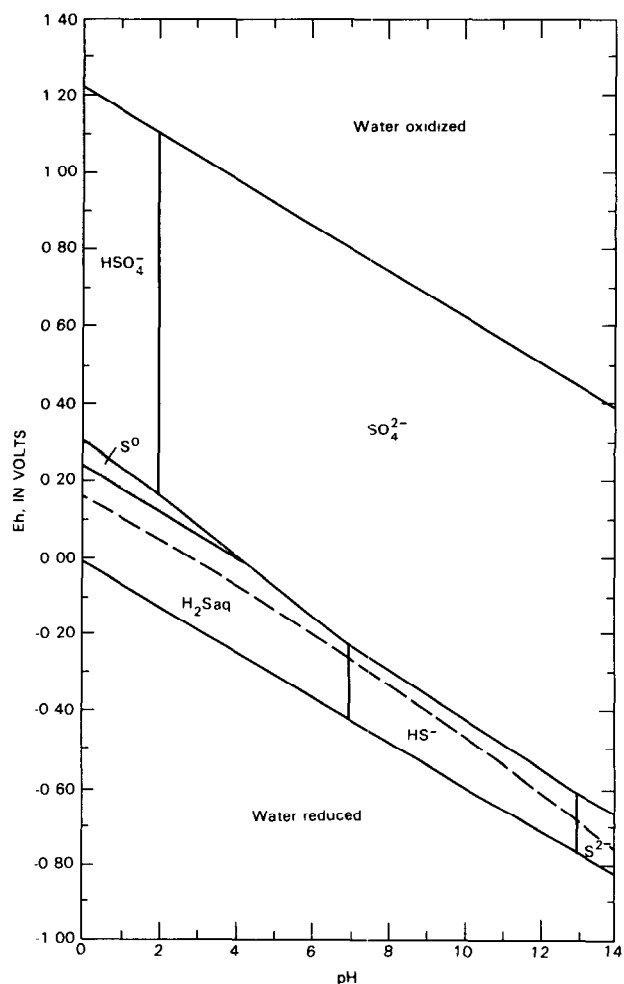


Figure 20. Fields of dominance of sulfur species at equilibrium at 25°C and 1 atmosphere pressure. Total dissolved sulfur activity 96 mg/L as SO_4^{2-} . Dashed line represents redox equilibrium between dissolved CO_2 species and methane ($CH_4(aq)$).

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) attributed 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

$$[H^+][SO_4^{2-}] = [HSO_4^-] \times 10^{-1.99}$$

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 ($\sim 1,000$ – 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 calculated 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 $25^\circ C$. 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 $25^\circ C$ 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-

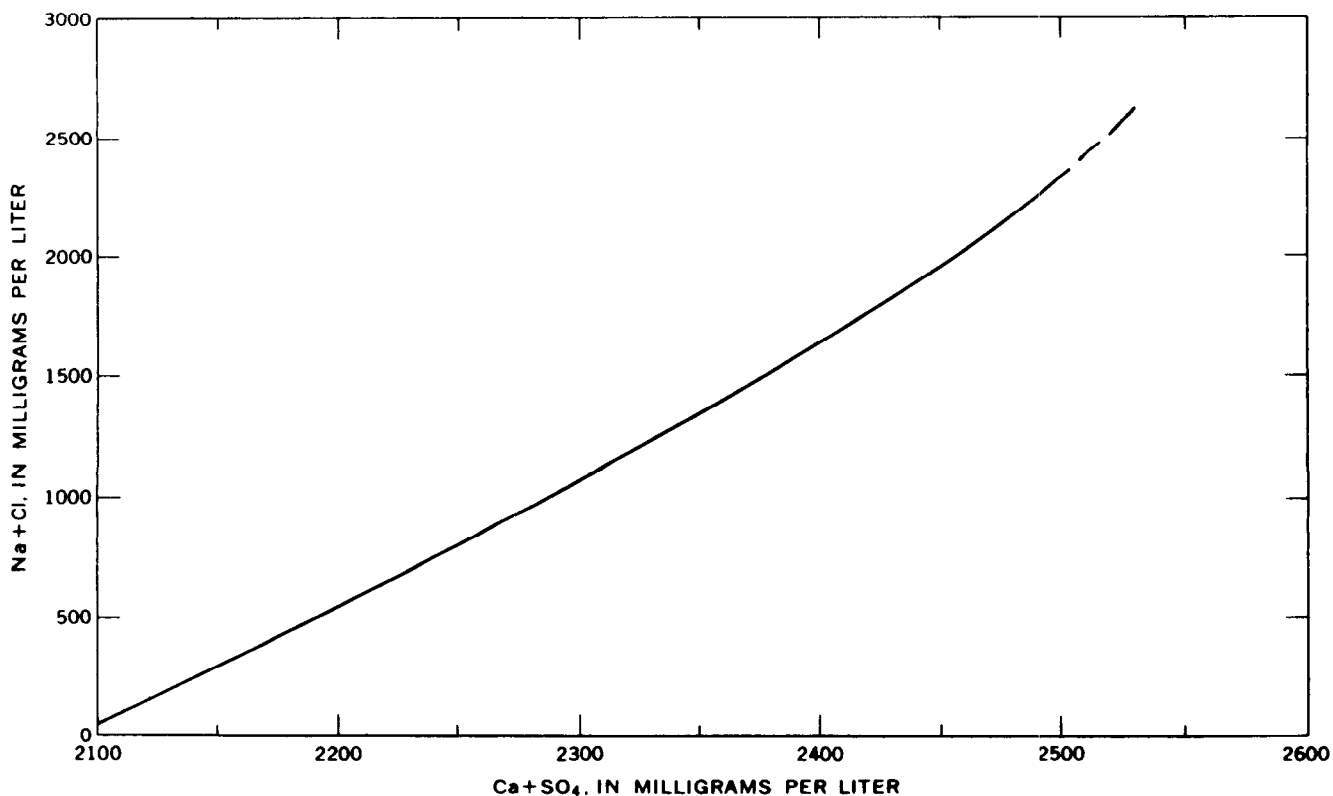


Figure 21. Solubility of gypsum in sodium chloride solutions at 25°C and 1 atmosphere pressure.

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, $\text{Na}_8[\text{Cl}_2(\text{AlSiO}_4)_6]$, 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 sources 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 concentration 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. Gambell and Fisher suggested that this indicates a substantial contribution of chloride from erosion of the crystalline 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 mi² 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, $\text{Ca}_5(\text{Cl},\text{F},\text{OH})(\text{PO}_4)_3$, 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 $\text{NaMgAl}(\text{F},\text{OH})_6 \cdot \text{H}_2\text{O}$ to $\text{Al}_2(\text{F},\text{OH})_6 \cdot \text{H}_2\text{O}$, 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

$$[\text{F}^-]^2 = 10^{-10.58} \times 10^{3.00}$$

and

$$[\text{F}^-] = 10^{-3.79} = 3.1 \text{ mg/L.}$$

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 $\text{Al}(\text{OH})_3$ 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 Rober-son and Hem (1969) indicate that in a solution containing 2,300 mg/L Na⁺ and 2.7 mg/L Al³⁺ 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		2		3		4	
	Apr. 29, 1941		Aug. 14, 1952		Sept. 16, 1947		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)								
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, Salva 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 H₂S, 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: $\text{H}_3\text{PO}_4(\text{aq})$, 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

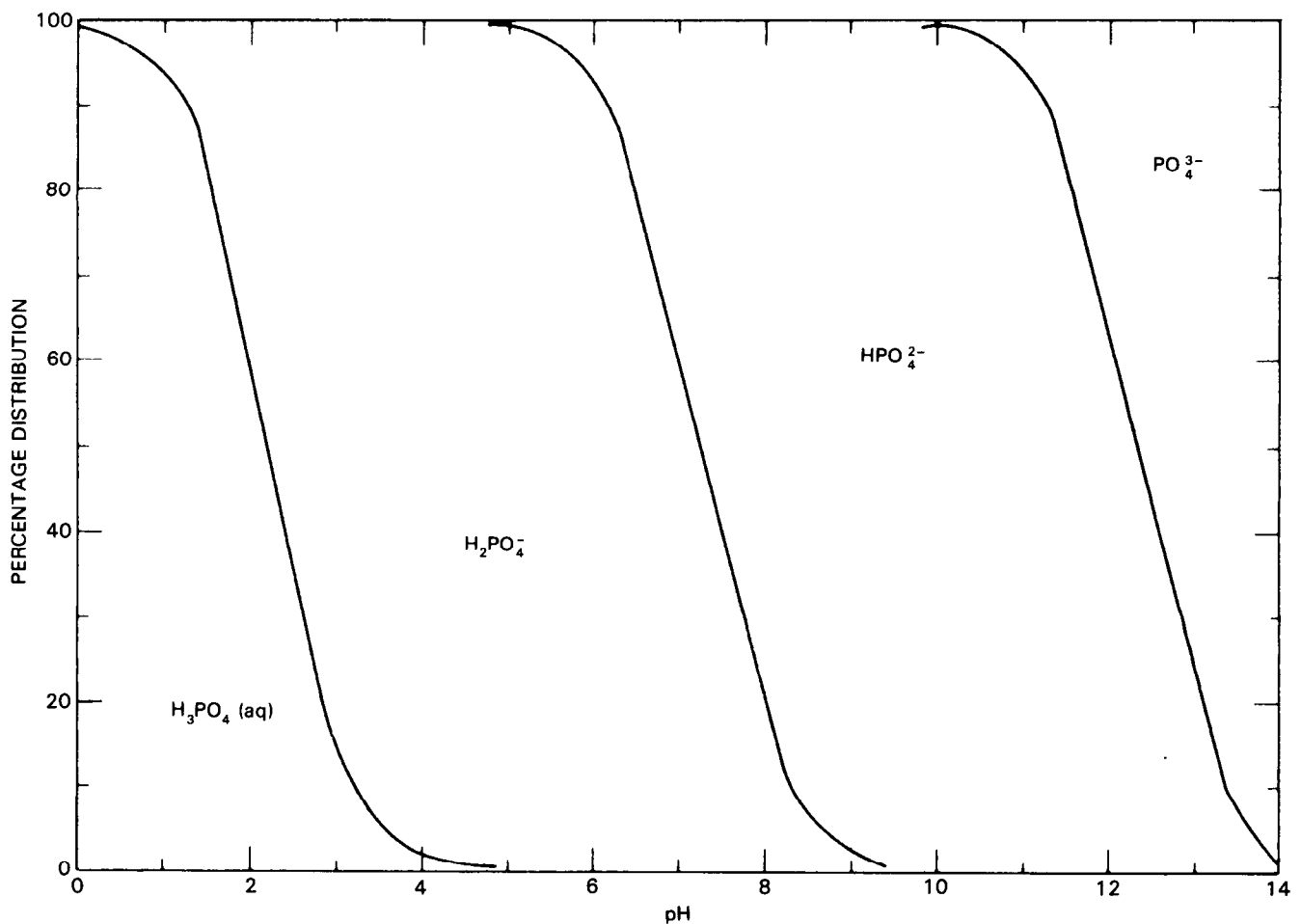


Figure 22. Percentages of dissolved phosphate species activity as a function of pH at 25°C and 1 atmosphere pressure.

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 north-eastern 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 ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) 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 $\mu\text{g/L}$ as P and total dissolved phosphorus about 25 $\mu\text{g/L}$. 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. Meybeck's estimates indicate that dissolved inorganic phosphorus 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, $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$, and kernite, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$. 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 $\text{B}(\text{OH})_3(\text{aq})$, 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 $\text{B}(\text{OH})_4^-$ 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 that 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 $\mu\text{g/L}$.

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 $\mu\text{g/L}$). 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 $0.10 \mu\text{g/L}$ 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 metalloid 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 know 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 interpretable 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 Administration 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 constit-

uents 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, $\text{LiAl}(\text{Si}_2\text{O}_6)$, amblygonite ($\text{Li,Na} \text{Al}(\text{PO}_4)(\text{F,OH})$), and lepidolite, a lithium mica whose composition is $\text{K}_2\text{Li}_3\text{Al}_3(\text{OH, F})_4(\text{AlSi}_3\text{O}_{10})_2$. 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 mag-

nesium 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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$, 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 $\mu\text{g/L}$ versus 1.1 $\mu\text{g/L}$). Durfor and Becker (1964), however, reported a median value of 2.0 $\mu\text{g/L}$ for lithium and 1.05 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$, but only a few rubidium concentrations exceeded 200 $\mu\text{g/L}$. 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 beryllium 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).

Beryllium 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 $\mu\text{g/L}$. In systems in which the dissolved species Be^{2+} , BeOH^+ , $\text{Be(OH)}_2(\text{aq})$, and Be(OH)_3^- are the only significant forms, the equilibrium solubility at pH 6.0 would be near 100 $\mu\text{g/L}$ 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 $\mu\text{g/m}^3$ 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 irriga-

tion-water limit of 100 $\mu\text{g/L}$ for continuous use on all soils and of 500 $\mu\text{g/L}$ 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 $\mu\text{g/L}$). Beryllium concentrations were below the detection limit (0.3 $\mu\text{g/L}$) 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 (celestite) 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

$$\frac{[\text{HCO}_3^-][\text{Sr}^{2+}]}{[\text{H}^+]} = K$$

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		2		3		4		5	
	May 2, 1952		About 1911		About 1917		Mar. 29, 1963		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 ₂ SO 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 (BaSO₄), 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 Ba²⁺ 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 $\text{Ti}(\text{OH})_2^{2+}$. 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, $\text{Ti}(\text{OH})_4(\text{aq})$, has been proposed. Its solubility between pH 4 and pH 8, according to data accepted by Baes and Mesmer, is about 150 $\mu\text{g/L}$. 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 evaluate 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 $\mu\text{g/L}$ for river water.

The median concentration of titanium in major rivers of North America reported by Durum and Haffty (1963) was 8.6 $\mu\text{g/L}$. 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 $\mu\text{g/L}$." 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 $\mu\text{g/L}$ 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 $5 \mu\text{g/L}$ total V and the equivalent of approximately $10 \text{ mg/L SO}_4^{2-}$ 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 $70 \mu\text{g/L}$ were found in the study of U.S. public water supplies by Durfor and Becker (1964). However, the median value was reported as $<4.3 \mu\text{g/L}$. Turekian (1969, p. 314) estimated an average concentration of $0.9 \mu\text{g/L}$ 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 $10 \mu\text{g/L}$.

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+} , $\text{Cr}(\text{OH})_2^+$, and $\text{Cr}(\text{OH})_4^-$. Anionic forms, present under oxidizing conditions, include dichromate $\text{Cr}_2\text{O}_7^{2-}$ and chromate CrO_4^{2-} . The dissolved forms that

predominate in reduced systems between pH 5 and pH 9 probably are CrOH^{2+} and $\text{Cr}(\text{OH})_2^+$.

A metastable hydroxide, $\text{Cr}(\text{OH})_3$, has a minimum solubility near $5 \mu\text{g/L}$ 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 $1 \mu\text{g/L}$ 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 $50 \mu\text{g/L}$ 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 $10 \mu\text{g/L}$. The median value for the public water supplies studied by Durfor and Becker (1964, p. 78) was $0.43 \mu\text{g/L}$ as Cr, and for North American rivers reported by Durum and Haffty (1963), $5.8 \mu\text{g/L}$. In more recent studies Kharkar and others (1968) estimated an average for river waters of $1.4 \mu\text{g/L}$. Durum and others (1971) found concentrations exceeding $5 \mu\text{g/L}$ 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 $200 \mu\text{g/L}$ 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 $\text{Co}(\text{OH})_2$ 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 $\mu\text{g}/\text{L}$. 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 $\mu\text{g}/\text{L}$. 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 $\mu\text{g}/\text{L}$ 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 $\mu\text{g}/\text{L}$ (which was the detection limit for the analytical procedure used). Maliuga (1950) reported average concentrations of 20 $\mu\text{g}/\text{L}$ 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 $\text{Ni}(\text{OH})_3$.

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 developed 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 $\text{Ni}(\text{OH})_2$ is more stable than the corresponding cobalt species and might maintain activities of Ni^{2+} below 100 $\mu\text{g}/\text{L}$ 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 $\mu\text{g}/\text{L}$. A value of "less than 2.7 $\mu\text{g}/\text{L}$ " 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 than cobalt. Maliuga (1950) found an average of 40 $\mu\text{g}/\text{L}$ 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 $\mu\text{g/L}$, slightly greater than his estimate of 0.2 $\mu\text{g/L}$ 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, $\text{H}_2\text{MoO}_4(\text{aq})$. 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 $\mu\text{g/L}$ 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 Runnells (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 $\mu\text{g/L}$ for continuous use and 50 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ Mo. It is rather easy, however, to find higher concentrations. Voegeli and King (1969) found more than 1 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ were present. The median value for public water supplies reported by Durfor and Becker (1964) was 1.4 $\mu\text{g/L}$. A study by Barnett and others (1969) showed molybdenum concentrations exceeding 100 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ and where anomalous concentrations useful for geochemical prospecting ranged from 10 $\mu\text{g/L}$ 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 $\mu\text{g/L}$. The maximum value reported was 1.1 mg/L, and concentrations of more than 100 $\mu\text{g/L}$ were observed rather frequently. The mean concentration for the samples that contained measurable amounts was 68 $\mu\text{g/L}$.

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 ($2\text{Cu}^+ \rightarrow \text{Cu}^0 + \text{Cu}^{2+}$) favor the more oxidized form. Cupric ions form complexes with many different ligands. In solutions above neutral pH the form $\text{Cu}(\text{OH})_3^-$ may predominate. A strong $\text{CuCO}_3(\text{aq})$ 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 $10 \mu\text{g/L}$, 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 public 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 $10 \mu\text{g/L}$ can be commonly expected in river water. Data published by Duror and Becker (1964) gave

a median value of $8.3 \mu\text{g/L}$ 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 $100 \mu\text{g/L}$ 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 $10 \mu\text{g/L}$ in most natural water. Kharkar and others (1968) suggested an average of $0.3 \mu\text{g/L}$ in river water.

Silver has been proposed as a disinfectant for water, and Woodward (1963) quoted data showing that as little as $10 \mu\text{g/L}$ 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 $.01 \mu\text{g/L}$ (1 to 10 nanograms/L (ng/L)). In seeded precipitation the silver concentration may be as high as $1 \mu\text{g/L}$. 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 $5 \mu\text{g/L}$ 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 $\mu\text{g/L}$.

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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$. More extensive results for the U.S. streams studied by Durum and others (1971) gave a median value of 20 $\mu\text{g/L}$ for samples from 726 sites. Bowen (1966 p. 164) estimated an average concentration of 10 $\mu\text{g/L}$ in all surface water. Streams affected by mine drainage commonly contain 100 $\mu\text{g/L}$ or more. For example, the dissolved zinc concentration in monthly composites of daily samples from the Allegheny River at Oakmont, Pa., exceeded 100 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$, 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 $\mu\text{g/L}$ (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, $\text{Hg}(\text{aq})$ (Hem, 1970), which has an equilibrium solubility of 25 $\mu\text{g/L}$ 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 $50 \mu\text{g/L}$ (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 $50 \mu\text{g/L}$ 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 $50 \mu\text{g/L}$ 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 $100 \mu\text{g/L}$ or more in areas subject to substantial air pollution down to $1.0 \mu\text{g/L}$ or less in more remote areas. Lazrus and others (1970) reported an average of $34 \mu\text{g/L}$ 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 $200 \mu\text{g/L}$ to less than $1.0 \mu\text{g/L}$. Part of the lead could generally be removed by filtration through $0.10\text{-}\mu\text{m}$ -porosity filter membranes. Lead concentrations of Greenland snow in that general time period (1966–74) were between about 0.1 and $0.2 \mu\text{g/kg}$ (Herron and others, 1977). These authors found concentrations of a few hundredths $\mu\text{g/L}$ 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 $1.0 \mu\text{g/L}$ 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 $1 \mu\text{g/L}$ were more common in the western part of the United States. However, concentrations above $10 \mu\text{g/L}$ were observed in a substantial number of the samples from all regions except the northwest.

Occasional concentrations of dissolved lead in excess of $10 \mu\text{g/L}$ 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 $50 \mu\text{g/L}$ 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 $\text{HAsO}_2(\text{aq})$. 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 ($(\text{CH}_3)_2\text{AsOOH}$ and $\text{CH}_3\text{AsO}(\text{OH})_2$, 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 $\mu\text{g/L}$) in 79 percent of the samples analyzed. However, concentrations greater than 50 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ in streams in the Southeastern United States.

Cherry and others (1979) proposed the use of the $\text{As}^{5+}:\text{As}^{3+}$ 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 $\mu\text{g/L}$ (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 $\mu\text{g/L}$ for average river water appears to have been strongly influenced by a sample from the Amazon that was reported to contain about 5 $\mu\text{g/L}$, 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 $\mu\text{g/L}$. The average concentration in stream water estimated by Goldberg and others (1971) is 0.2 $\mu\text{g/L}$. Dall'Aglio and others (1978) reported values below 0.1 $\mu\text{g/L}$ for most Italian rivers sampled. Anderson and others (1961) reported 80 $\mu\text{g/L}$ 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 $\mu\text{g/L}$, 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 $\mu\text{g/L}$. Konovalov (1959) reported concentrations ranging from 42.4 to 3.3 $\mu\text{g/L}$ 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 (^3H) 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 scalars, 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 ($\text{curies} \times 10^{-12}$, 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 $\mu\text{g/L}$ 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 $^{40}\text{K}-^{40}\text{Ar}$ are used for dating geologic formations. It seems likely, however, that few aqueous systems 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 800 pCi/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 atmo-

sphere 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 fresh-water probably is only from 0.01 to 1 $\mu\text{g/L}$.

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 fission 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 down dip 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 $^{239+240}\text{Pu}$ was estimated to be 8.1 ± 0.1 pCi/m²/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 mate-

rial, 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.

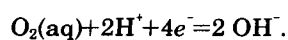
Oxygen

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



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 $\mu\text{g/L}$ 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 hydrolo-

gists 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

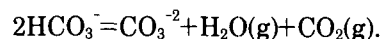
of an aliquot of the water sample. Total solids, total dissolved solids, and dissolved solids are terms used more or less synonymously for this value. The dissolved solids also may be calculated if the concentrations of major ions are known, and it is not always clearly indicated whether the value given 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:



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:

	<i>Dissolved solids (mg/L)</i>
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 ($\text{mg/L HCO}_3^- \times 0.4917 = \text{mg/L CO}_3$) 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 ($\text{pH} < 4.5$), 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,

ity (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 with 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 aque-

ous 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 poisoning 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 H₂O–O₂(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.

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

$$\text{SAR} = \frac{(\text{Na}^+)}{\sqrt{1/2[(\text{Ca}^{2+}) + (\text{Mg}^{2+})]}}$$

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 $\pm\delta$ values computed from the formula

$$\delta_x = \frac{R_x - R_{\text{STD}}}{R_{\text{STD}}} \times 1,000$$

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 $\delta^2\text{H}$ or $\delta^{18}\text{O}$ departure above or below $\text{SMOW}=0$, 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."