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

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

$$Fe^{3+}+H_2O \rightleftharpoons FeOH^{2+}+H^+.$$
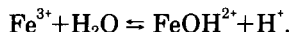
The $Fe^{3+}$ and $OH^-$ in this unit are chemically bound to each other. If the concentration of ferric iron is high enough, the formation of complex species may also involve association of monomeric units to give dimers

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

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

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

$$Ca^{2+}+SO_4^{2-} \rightleftharpoons CaSO_4(aq).$$
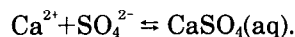
In this complex, the $Ca^{2+}$ and $SO_4^{2-}$ components are believed to be separated by one or more layers of intervening water molecules. Some authors have used the term "ion pair" in a less rigorous context.

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

## SIGNIFICANCE OF PROPERTIES AND CONSTITUENTS REPORTED IN WATER ANALYSES

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

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

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

| Constituent | mg/L or ppm | meq/L or epm | mM/L | Gravimetric percent | Percentage of epm | Grains per U.S. gallon |
|---|---|---|---|---|---|---|
| Silica (SiO₂) | 7.9 | | 0.131 | 0.40 | | 0.46 |
| Iron (Fe) | .17 | | .003 | .01 | | .01 |
| Calcium (Ca) | 37 | 1.85 | .925 | 1.87 | 6.1 | 2.16 |
| Magnesium (Mg) | 24 | 1.97 | .985 | 1.21 | 6.5 | 1.40 |
| Sodium (Na) ⎱ Potassium (K) ⎰ | 611 | 26.58 | 26.58 | 30.80 | 87.4 | 35.69 |
| Bicarbonate (HCO₃) | 429 | 7.03 | 7.03 | [1]10.63 | 23.1 | 25.06 |
| Sulfate (SO₄) | 1,010 | 21.03 | 10.52 | 50.90 | 69.2 | 59.00 |
| Chloride (Cl) | 82 | 2.31 | 2.31 | 4.14 | 7.6 | 4.79 |
| Fluoride (F) | .6 | .03 | .032 | .03 | .1 | .04 |
| Nitrate (NO₃) | .0 | .00 | .000 | .00 | .0 | .00 |
| Boron (B) | .2 | | .019 | .01 | | .01 |
| Dissolved solids: Calculated | 1,980 | 60.80 | 48.535 | 100.00 | 200.00 | 115.65 |
| Hardness as CaCO₃: Total | 191 | | 1.91 | | | 11.16 |
| Noncarbonate | 0 | | .00 | | | 0 |
| Specific conductance (micromhos at 25°C). | 2,880 | 2,880 | 2,880 | 2,880 | 2,880 | 2,880 |
| pH | 7.3 | 7.3 | 7.3 | 7.3 | 7.3 | 7.3 |

[1]As carbonate (CO₃).

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

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

## Nature of the Dissolved State

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

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

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

## Characterization of Suspended Particulate Material

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

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

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

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

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

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

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

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

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

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

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

oxidizing acids, and, finally, dissolution in hydrofluoric acid mixtures or through alkali fusion procedures used in rock analysis.

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

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

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

## Hydrogen-Ion Activity (pH)

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

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

Even when no other solutes are present, a few of the $H_2O$ molecules in liquid water will be broken up into $H^+$

and $OH^-$ ions. This process of dissociation is a chemical equilibrium that may be written

$$H_2O(l)=H^+ + OH^-.$$
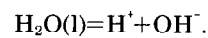
In mass-law form, the equilibrium can be expressed as the equation

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

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

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

The hydrogen-ion content of a natural water computed in moles per liter (milligrams per liter for $H^+$ is nearly the same as millimoles per liter) is usually in the "trace constituent" range. At pH 7, only $1\times10^{-7}$ moles per liter of hydrogen ion is present, for example. The major constituents of most waters are in the concentration range of $10^{-4}$ moles per liter and up. Thus the hydrogen-ion content does not begin to approach the status of a major component of the solution until the pH goes below 4.0. A pH of less than 0 or greater than 14 can be attained in concentrated acid or base solutions.

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

The reaction of dissolved carbon dioxide with water, which is one of the most important in establishing pH in natural-water systems, is represented by the three steps
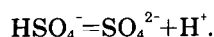
$$CO_2(g) + H_2O(l) = H_2CO_3(aq),$$

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

and

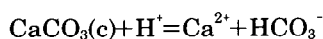$$HCO_3^- = H^+ + CO_3^{2-}.$$
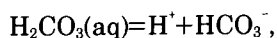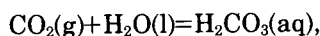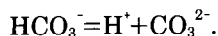
Both the second and third steps produce $H^+$ and influence the pH of the solution. Other reactions involving dissociations of acidic solutes include
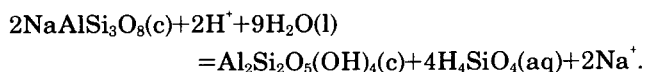
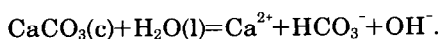$$H_2PO_4^- = HPO_4^{2-} + H^+,$$

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

and

$$HSO_4^- = SO_4^{2-} + H^+.$$
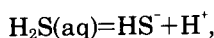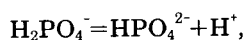
Many of the reactions between water and solid species consume $H^+$; for example,

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

and

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

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

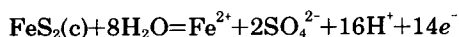$$CaCO_3(c) + H_2O(l) = Ca^{2+} + HCO_3^- + OH^-.$$

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

Certain reactions in which precipitates are formed, such as

$$Fe^{3+} + 3H_2O = Fe(OH)_3(c) + 3H^+,$$
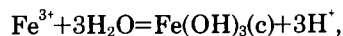
influence pH, and most oxidation reactions are pH related,

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

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

$$7/2O_2 + 14e^- + 14H^+ = 7H_2O.$$
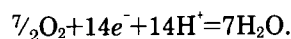
Adding these together gives

$$FeS_2 + 7/2O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+.$$
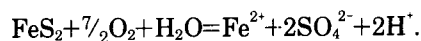
If a particular reaction or set of reactions involving water, hydrogen ions, other solutes, and solids or gases has attained equilibrium, the pH that should be attained can be computed by the mass law and a set of simultaneous equations. General procedures for making such computations have already been outlined.

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

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

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

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

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

and

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

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

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

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

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

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

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

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

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

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

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

### Buffered Solutions

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

Some insight into the mechanisms can be obtained by briefly reviewing the carbon dioxide–water equilibria

just discussed. If the principal solutes are $H_2CO_3$ and $HCO_3^-$ the first dissociation of carbonic acid,
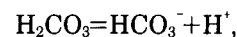
$$H_2CO_3 = HCO_3^- + H^+,$$

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

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

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

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

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

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

### Range of pH of Natural Water

As stated previously, the pH of pure water at 25°C is 7.00. Most ground waters found in the United States

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

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

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

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

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

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

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

## Measurement and Interpretation of pH

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

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

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

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

The measured pH is a very important piece of information in many types of geochemical equilibrium or solubility calculations, and values that are inaccurate or unrepresentative are a substantial source of error in

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

**Table 11.** Analyses of waters with unstable pH

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

| Constituent | 1 Jan. 5, 1967 | | 2 Jan. 5, 1967 | | 3 June 14, 1950 | |
|---|---|---|---|---|---|---|
| | mg/L | meq/L | mg/L | meq/L | mg/L | meq/L |
| Silica (SiO₂) | 22 | | 22 | | 19 | |
| Iron (Fe) | .02 | | .00 | | .01 | |
| Manganese (Mn) | .01 | | | | | |
| Zinc (Zn) | .02 | | | | | |
| Calcium (Ca) | 93 | 4.64 | 22 | 1.10 | 264 | 13.17 |
| Magnesium (Mg) | 58 | 4.77 | 54 | 4.44 | 79 | 6.50 |
| Sodium (Na) | 15 | .65 | 15 | .65 | 513 | 22.31 |
| Potassium (K) | 1.2 | .03 | 1.1 | .03 | 23 | .59 |
| Strontium (Sr) | .50 | .01 | | | | |
| Carbonate (CO₃) | | | | | 0 | |
| Bicarbonate (HCO₃) | 556 | 9.02 | 297 | 4.87 | 964 | 15.80 |
| Sulfate (SO₄) | 50 | 1.04 | 55 | 1.15 | 147 | 3.06 |
| Chloride (Cl) | 16 | .45 | 17 | .48 | 815 | 22.99 |
| Fluoride (F) | .3 | .02 | | | .2 | .01 |
| Nitrate (NO₃) | .1 | .00 | | | 3.2 | .05 |
| Boron (B) | .02 | | | | | |
| Dissolved solids: Calculated | 530 | | 332 | | 2,340 | |
| Residue at 180°C | | | | | | |
| Hardness as CaCO₃ | 470 | | 277 | | 984 | |
| Noncarbonate | 19 | | 34 | | 194 | |
| Specific conductance (micromhos at 25°C). | | | | | 3,940 | |
| pH | 7.54 | | 8.40 | | 6.5 | |

1. Spring on headwaters of Blackbird Creek, SE1/4 sec. 6, T. 6 S., R. 5 E., San Mateo County, Calif Temperature, 7°C. pH measured at time of collection. Calcium determined on acidified sample.

2 Reanalysis of unacidified fraction of sample 1 after 6 months of storage in laboratory.

3. Spring discharging into Little Colorado River, 13 mi from mouth, Coconino County, Ariz One of a group known as Blue Springs Water-bearing formation Redwall Limestone. Water contains CO₂ and deposits travertine Discharge of group, about 200 cfs, temperature, 20 6°C pH measured in laboratory.

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

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

## Specific Electrical Conductance

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

### Units for Reporting Conductance

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

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

### Physical Basis of Conductance

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

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

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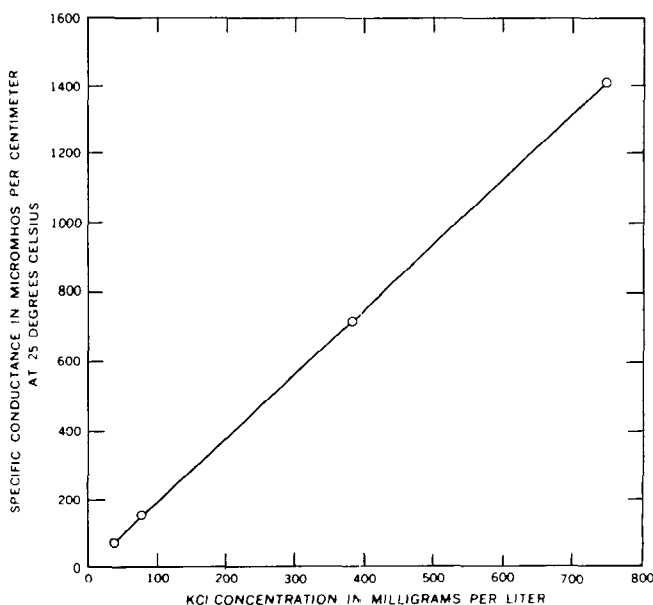


Figure 8. Specific conductance of potassium chloride solutions.

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

To conduct a current, solute ions actually must move through the solution to transfer charges, and the effectiveness of a particular ion in this process depends on its charge, its size, the way it interacts with the solvent, and other factors. The property called "ionic mobility" represents the velocity of an ion in a potential gradient of 1 V/cm. (It should be noted that this is not the same property as the geochemical mobility of an element, a concept relating to the ease of transport of elements in geochemical cycles). Ionic mobility is decreased by increasing concentration owing to interferences and interactions among the ions. Limiting values attained in solutions of very low concentration for the major ions in natural water are in the vicinity of $6\times10^{-4}$ cm/s at 25°C (Glasstone and Lewis, 1960, p. 445).

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

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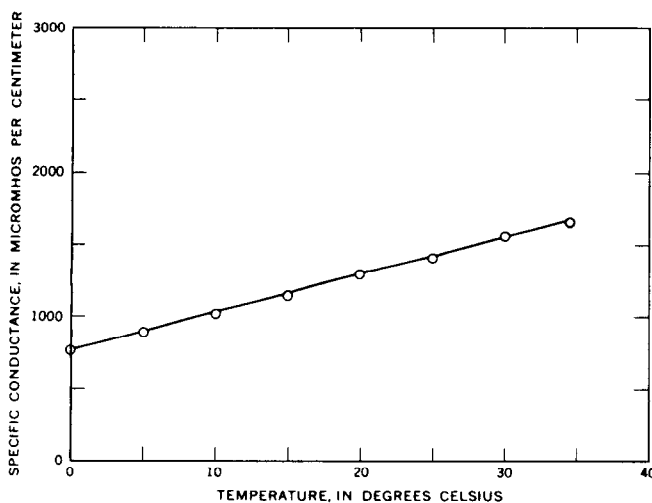
ably well defined relationship is indicated for the range; thus, for any given conductance value a dissolved-solids value can be estimated with an uncertainty of only about ±100 mg/L, using the curve, which was fitted by eye to the points in figure 10. The whole set of data fit a straight line regression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

$$KA=S$$

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

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



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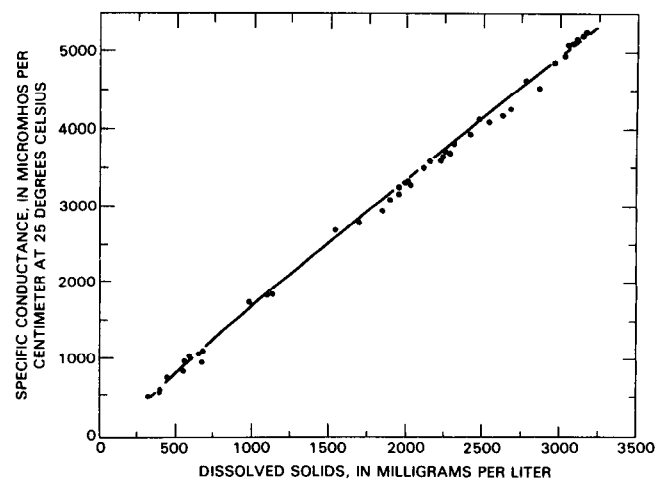


**Figure 10.** Dissolved solids and specific conductance of composites of daily samples, Gila River at Bylas, Ariz., October 1, 1943, to September 30, 1944.

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

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

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

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

### Range of Conductance Values

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

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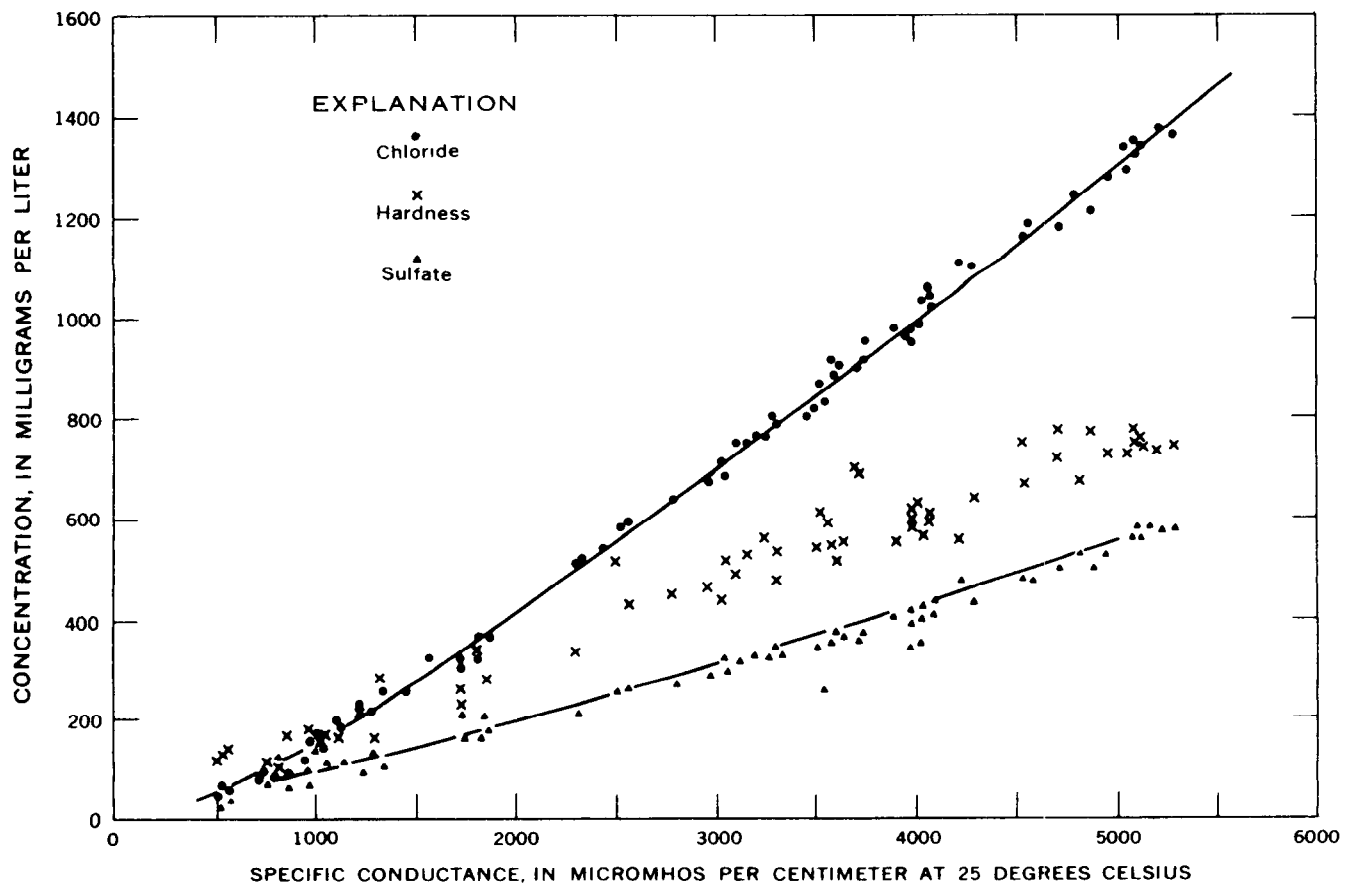


Figure 11. Relation of conductance to chloride, hardness, and sulfate concentrations, Gila River at Bylas, Ariz., October 1, 1943, to September 30, 1944.

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

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

### Accuracy and Reproducibility

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

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

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

## Silica

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

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

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

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

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

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

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

**Table 12. Analyses of waters**

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

| Constituent | 1 Nov. 23, 1953 | | 2 Aug. 1, 1947 | | 3 Oct. 16, 1957 | | 4 June 13, 1952 | |
|---|---|---|---|---|---|---|---|---|
| | mg/L | meq/L | mg/L | meq/L | mg/L | meq/L | mg/L | meq/L |
| Silica (SiO₂) | 99 | | 103 | | 363 | | 49 | |
| Aluminum (Al) | | | | | .2 | | | |
| Iron (Fe) | .04 | | .0 | | .06 | | .01 | |
| Manganese (Mn) | | | | | .0 | | .00 | |
| Calcium (Ca) | 2.4 | .120 | 6.5 | .324 | .8 | .04 | 32 | 1.597 |
| Magnesium (Mg) | 1.4 | .115 | 1.1 | .090 | .0 | .00 | 12 | .987 |
| Sodium (Na) | 100 | 4.348 | 40 | 1.729 | 352 | 15.30 | 30 | 1.305 |
| Potassium (K) | 2.9 | .074 | | | 24 | .61 | 5.2 | .133 |
| Carbonate (CO₃) | 24 | ¹.800 | 0 | 0 | (²) | 3.86 | 0 | .0 |
| Bicarbonate (HCO₃) | 111 | 1.819 | 77 | 1.262 | | | 220 | 3.605 |
| Sulfate (SO₄) | 30 | .625 | 15 | .312 | 23 | .48 | 11 | .299 |
| Chloride (Cl) | 10 | .282 | 17 | .479 | 405 | 11.42 | 7.9 | .223 |
| Fluoride (F) | 22 | 1.158 | 1.6 | .084 | 25 | 1.32 | .2 | .011 |
| Nitrate (NO₃) | .5 | .008 | .4 | .006 | 1.8 | .03 | 2.9 | .047 |
| Boron (B) | .19 | | .0 | | 4.4 | | .08 | |
| Dissolved solids: | | | | | | | | |
|   Calculated | 348 | | 222 | | 1,310 | | 225 | |
|   Residue on evaporation | | | | | | | 257 | |
| Hardness as CaCO₃ | 12 | | 20 | | 2 | | 129 | |
|   Noncarbonate | 0 | | 0 | | 0 | | 0 | |
| Specific conductance (micromhos at 25°C). | 449 | | 167 | | 1,790 | | 358 | |
| pH | 9.2 | | 6.7 | | 9.6 | | 7.8 | |
| Color | | | | | | | 10 | |

¹Includes some silicate ion, probably H₃SiO₄, calculated at 0.389 meq/L.

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

1. Flowing well 7S 6E-9ba2, Owyhee County, Idaho. Depth, 960 ft; temperature, 50.0°C.

2. Spring on the Rio San Antonio, SW1/4 sec. 7, T. 20 N., R. 4 E. (unsurveyed), Sandoval County, N. Mex. Flow, about 25 gpm; temperature, 38°C Water from rhyolite.

3. Spring, 650 ft south of Three Sisters Springs in Upper Geyser Basin, Yellowstone National Park, Wyo. Temperature, 94°C. Also reported: 1.5 mg/L As, 5.2 mg/L Li, 1.5 mg/L Br, 0.3 mg/L I, 1.3 mg/L PO₄⁻³, and 2.6 mg/L H₂S.

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

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

## Forms of Dissolved Silica

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

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

containing high proportions of silica

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

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

4. Drilled well, NW1/4 sec. 10, T. 2 N., R. 32 E., Umatilla County, Oreg. Depth, 761 ft. Water from basalt of the Columbia River Group.
5. Flowing well, SE1/4 sec 16, T. 12 N., R. 17 E., Yakima County, Wash. Depth, 1,078 ft; temperature, 17 2 °C. Water from basalt.
6 Eagle Creek at P-D pumping plant near Morenci, Greenlee County, Ariz Mean discharge for composite period, 9.9 cfs. Drainage basin of about 600-mi² area in which virtually all rocks exposed are extrusive volcanic rocks
7. Main pump station, Albuquerque, N. Mex Public supply. Seven wells, 250 to 716 ft deep. Water from the Santa Fe Formation (valley fill).
8. Middle Loup River at Dunning, Nebr. Discharge, 394 cfs Drainage from Nebraska sand hills, flow maintained by ground water.
9. Well at Valdese General Hospital, Rutherford College, Burke County, N C Depth, 400 ft; temperature, 15.0°C. Water from mica schist.

$$H_4SiO_4(aq) = H^+ + H_3SiO_4^-.$$
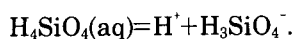
Values collected by Sillen and Martell (1964, p. 145) for the equilibrium constant for this reaction at 25°C range from $10^{-9.41}$ to $10^{-9.91}$. These values indicate that the first dissociation step is half completed at a pH value somewhere between 9.41 and 9.91, and silicate ions ($H_3SiO_4^-$) might constitute no more than 10 percent of the total dissolved silica species at a pH between 8.41 and 8.91. Any silicate ions that might be present are converted to silicic acid in the alkalinity titration and appear in the analysis as an equivalent amount of carbonate or bicarbonate. As a result, the ionic balance is maintained in the analysis, and there is no obvious indication that the ionic species are incorrectly identified. In any detailed interpretation of the chemistry of high-pH waters, the contribution of $H_3SiO_4^-$ to the alkalinity must be taken into account.

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

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

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

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

### Solubility Controls

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

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

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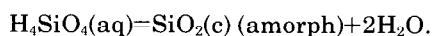
The dissolution of the sodium feldspar, albite, can be summarized

$$2NaAlSi_3O_8(c)+2H^++9H_2O(l)$$
$$=Al_2Si_2O_5(OH)_4(c)+4H_4SiO_4(aq)+2Na^+.$$
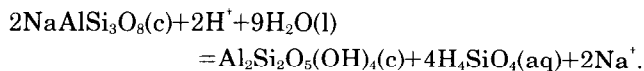
If the clay mineral produced dissolves reversibly,

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

An upper limit for silica concentration might be fixed by

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

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

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

### Occurrence in Natural Water

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

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

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

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

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

## Aluminum

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

### Sources of Aluminum in Water

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

On weathering of igneous rocks, the aluminum is mostly retained in new solid species, some of which may be greatly enriched in aluminum. Nearly pure aluminum hydroxide in the form of gibbsite is a fairly common mineral, and less common hydroxides include nordstrandite and bayerite, whose composition and structure are similar to that of gibbsite. In low-pH environments aluminum may be precipitated as an aluminum hydroxysulfate. The most common of the sedimentary aluminum-enriched minerals are clays. The clay minerals have a layered structure in which aluminum octahedrally co-

ordinated with six oxide or hydroxide ions (gibbsite structure) forms one type of layer, and silicon tetrahedrally coordinated with oxygen forms a second type of layer. These layers alternate in various ways, forming the various clay structures. The layers are bound together by Si–O–Al bonds. Diagrams of the structures of the common clay minerals have been given by many investigators, including Grim (1968, p. 51–125) and Robinson (1962, p. 31–58). Clays are present in most natural-water environments and are abundant in most soils and in hydrolyzate sedimentary rocks.

### Species in Solution

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

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

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

In the presence of fluoride, strong complexes of aluminum and fluoride are formed. The ions $AlF^{2+}$ and

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

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

### Solubility Controls

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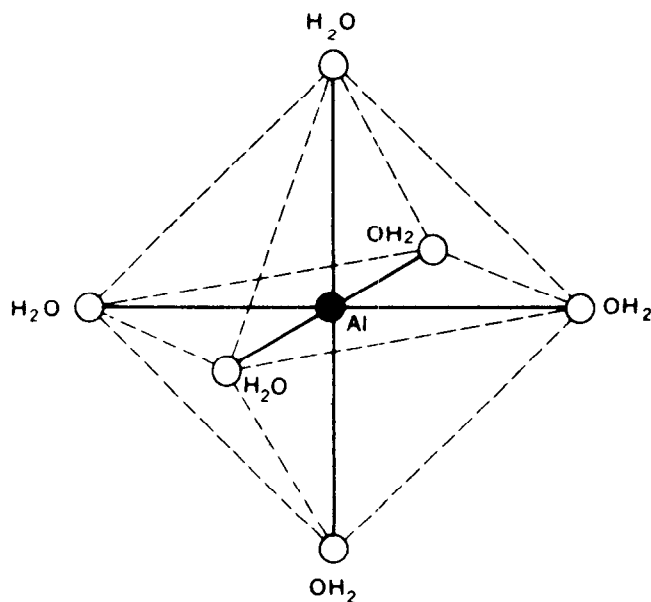


**Figure 12.** Schematic diagram of hydrated aluminum ion, $Al(H_2O)_6^{3+}$. (From Hem, 1968b, in "Trace Inorganics in Water," Advances in Chemistry Series, 73, copyright American Chemical Society, 1968, used by permission.)

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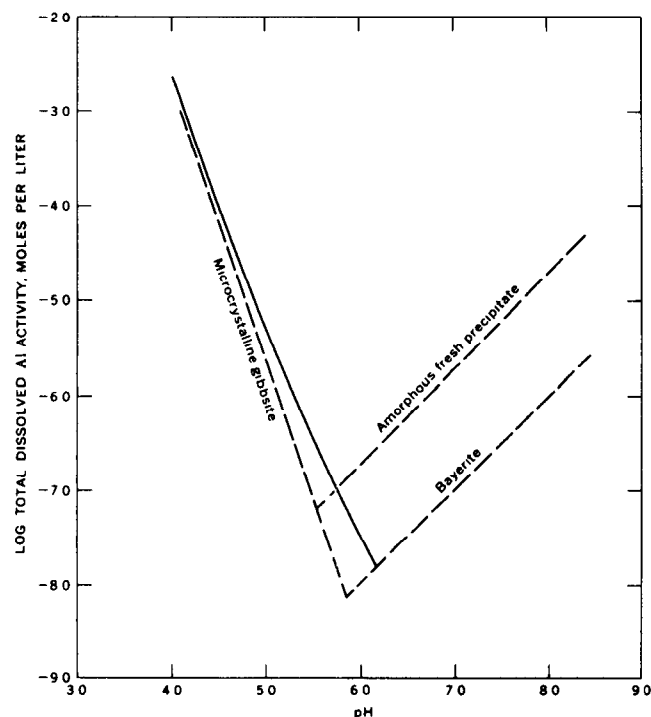


Figure 13. Equilibrium activities of free aluminum for three forms of aluminum hydroxide (dashed lines) and calculated activity of $Al^{3+}+AlOH^{2+}$ (solid line).

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

## Occurrence of Aluminum in Water

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

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

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

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

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

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

## Iron

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

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

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

| Constituent | 1 Dec. 13, 1955 | | 2 Dec. 3, 1955 | | 3 Aug. 31, 1958 | | 4 Mar. 1–6, 8–10, 1963 | | 5 Mar. 25, 1953 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | mg/L | meq/L | mg/L | meq/L | mg/L | meq/L | mg/L | meq/L | mg/L | meq/L |
| Silica (SiO$_2$) | 98 | | 10 | | 92 | | 9.7 | | 31 | |
| Aluminum (Al) | 28 | | 1 | | .35 | | 3.5 | | .2 | |
| Iron (Fe) | .88 | | .04 | | .02 | | .10 | | 2 7 | |
| Manganese (Mn) | 9.6 | | 1.3 | | .31 | | 2.5 | | .22 | |
| Calcium (Ca) | 424 | 21.16 | 58 | 2 89 | 67 | 3.34 | 32 | 1.60 | 28 | 1 40 |
| Magnesium (Mg) | 194 | 15.96 | 13 | 1 07 | .0 | .00 | 11 | .90 | 1.9 | .16 |
| Sodium (Na) | 416 | 18.10 | 23 | 1 00 | 477 | 20.75 | 12 | .52 | 6.8 | .30 |
| Potassium (K) | 11 | .28 | 2 8 | .07 | 40 | 1.02 | 3.7 | .09 | 4.2 | 11 |
| Hydrogen (H) | | 10 | | | | | | .16 | | |
| Carbonate (CO$_3$) | 0 | | 0 | | 0 | .00 | 0 | | | |
| Bicarbonate (HCO$_3$) | 0 | | 101 | 1.66 | 1,020 | 16.72 | 0 | | 121 | 1.98 |
| Sulfate (SO$_4$) | 2,420 | 50.38 | 116 | 2.42 | 169 | 3.52 | 171 | 3.56 | 1 4 | .03 |
| Chloride (Cl) | 380 | 10.72 | 39 | 1.10 | 206 | 5.81 | 5.0 | .14 | 1.0 | .03 |
| Fluoride (F) | 1.8 | .09 | .0 | | 6.8 | .36 | .1 | .01 | .1 | .01 |
| Nitrate (NO$_3$) | 3.1 | .05 | .6 | .01 | 1 8 | .03 | 5.3 | .09 | .2 | .00 |
| Orthophosphate (PO$_4$) | .0 | | .1 | | .11 | | | | .0 | |
| Boron (B) | | | | | 2.8 | | | | | |
| Dissolved solids: Calculated | 3,990 | | 314 | | 1,570 | | 256 | | 137 | |
| Residue at 180°C | 4,190 | | 338 | | 1,560 | | 260 | | | |
| Hardness as CaCO$_3$ | 1,860 | | 198 | | 168 | | 125 | | 78 | |
| Noncarbonate | 1,860 | | 115 | | 0 | | 125 | | 0 | |
| Specific conductance (micromhos at 25°C). | 4,570 | | 517 | | 2,430 | | 507 | | 192 | |
| pH | 4.0 | | 7.0 | | 6.7 | | 3.8 | | 6.9 | |

1. Well, 7 mi northeast of Monticello, Drew County, Ark. Depth, 22 ft. Water-bearing formation, shale, sand, and marl of the Jackson Group. Also contained radium (Ra), 1 7 pCi/L, and uranium (U), 17 µg/L.

2. Composite from two radial collector wells at Parkersburg, Kanawha County, W. Va Depth, 52 ft Water from sand and gravel Also contained copper (Cu), 0 01 mg/L, and zinc (Zn), 0 01 mg/L

3. Wagon Wheel Gap hot spring, Mineral County, Colo Discharge, 20 gpm; temperature, 62.2°C. Associated with vein of the Wagon Wheel Gap fluorite mine Also contained 2.3 mg/l. Li, 0 9 mg/L NH$_1$, 0 3 mg/L Br, and 0 3 mg/L I

4 Kiskiminitas River at Leechburg (Vandergrift), Pa. Composite of nine daily samples Mean discharge for period, 10,880 cfs.

5 Well, 167 ft deep, Baltimore County, Md. Water-bearing formation, Port Deposit granitic gneiss Also contained 0 01 mg/L copper (Cu).

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

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

## Sources of Iron

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

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

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

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

in processes of oxidation and reduction of iron, and some species may use these reactions as energy sources.

### Species of Iron in Natural Water

The most common form of iron in solution in ground water is the ferrous ion $Fe^{2+}$. Like aluminum and many other metal ions, this ion has an octahedral hydration shell of six water molecules. Except where hydration may have special significance, water of hydration shells will not be shown in the formula of this or other ions that follow. The monohydroxide complex $FeOH^+$ can be predominant above a pH of about 9.5 (Baes and Mesmer, 1976, p. 100) and may be significant at somewhat lower pH's. Above a pH of 11, the anion $Fe(OH)_3^-$ or $HFeO_2^-$ can exist in water in appreciable concentrations, but such a high pH is rarely attained in natural systems. An ion pair $FeSO_4(aq)$ reported in Sillen and Martell (1964, p. 240) could be important in solutions that have more than a few hundred milligrams of sulfate per liter. Ferrous complexes are formed by many organic molecules, and some of the complexes may be considerably more resistant to oxidation than free ferrous ions would be. Organic compounds containing iron are particularly important in life processes, such as photosynthesis, and in the functions of hemoglobin in the blood of animals.

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

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

The only anionic ferric species for which data are available is $Fe(OH)_4^-$. Langmuir (1969b) indicated that his value for its $\Delta G_f°$ was a rough estimate. The value used here was calculated from a stability constant esti-

mated by Baes and Mesmer (1976, p. 104). The effect of $Fe(OH)_4^-$ on iron solubility is not significant, in any event, unless the pH is 10 or greater.

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

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

### Solubility Calculations: pH-Eh Diagrams

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

The pH-Eh diagram wes extensively developed by Marcel Pourbaix in Belgium in the years prior to World War II. The diagrams began to be used in geochemistry after a compilation (Pourbaix, 1949) and applications by R.M. Garrels (1960) in the United States made Pourbaix's work more widely known. Details of preparation of the diagrams are given in various publications (Hem and Cropper, 1959; Garrels and Christ, 1964; Hem, 1965). Application of these diagrams to iron systems has been used as a textbook example, and a general agreement between theoretical calculations and field behavior of iron has been demonstrated by Barnes and Back (1964b) and many other investigators. Experience, therefore, suggests that reactions represented in the theoretical model for iron commonly approach chemical equilibrium in the real world closely enough that the most important processes are reasonably well represented in such a model.

This is perhaps less likely for most other elements that are subject to redox reactions owing either to unfavorable kinetics or to lack of, or failure to include, some of the fundamental thermodynamic data and reactions in the model. Nevertheless, the pH-Eh diagram is a very useful method of clarifying complicated chemical relationships and illustrating boundary conditions and thermodynamically permissible reactions and products.

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

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

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

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

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

$$2H^++2e^-=H_2(g).$$
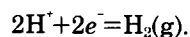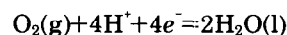
Chemical thermodynamic data needed for construction of figures 14 and 15 and references to sources of data are given in tables 30 and 31 (appendix). From the standard free energies, $\Delta G^\circ_R$ is computed for the first equation (as stated in the discussion of electrochemical equilibrium, the standard free energy of the electron must be taken as zero):

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

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

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

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

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

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

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

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

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

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

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

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

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

$$FeOH^{2+} + H^+ + e^- = Fe^{2+} + H_2O.$$
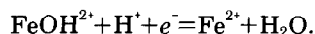
The value of $\Delta G_R°$ is determined for this half-reaction as indicated above and is used to derive the standard potential $E°$, which in this case is equal to 0.898V. The Nernst equation gives the value for Eh as follows:

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

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

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

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

$$Fe^{3+} + H_2O = FeOH^{2+} + H^+.$$
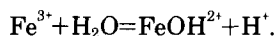
The equilibrium constant is obtained from

$$\frac{-\Delta G°_R}{2.303\,RT} = \log K_{eq}.$$

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

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

Again specifying that

$$[FeOH^{2+}] = [Fe^{3+}]$$

leads to

$$[H] = 10^{-2.17},$$

which is the vertical boundary between the two domains. These boundaries obviously terminate when they intersect. If the mathematics are done correctly, changes in slope of the horizontal or sloping boundaries should occur only where they intersect or are intersected by a vertical boundary.

Lines designating stability domains of solids are located by similar reasoning. For a boundary between $Fe(OH)_3(c)$ and $Fe^{2+}$,

$$Fe(OH)_3(c) + 3H^+ + e^- = Fe^{2+} + 3H_2O.$$
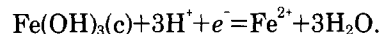
The standard potential for this half-reaction is 0.994 V and

$$Eh = 0.994 + 0.0592 \log \frac{[H^+]^3}{[Fe^{2+}]}$$

A value for $[Fe^{2+}]$ must be specified to fix this boundary. For $[Fe^{2+}] = 10^{-6.00}$ moles/L (56 $\mu$g/L),

$$Eh = 1.349 - 0.178 \text{ pH.}$$

Activities of solids and of $H_2O(l)$ are assigned values of 1.0 throughout and do not appear in the Nernst equation. The boundaries for some solids may involve activities of dissolved sulfur species, for example,

$$Fe^{2+} + 2SO_4^{2-} + 16H^+ + 14e^- = FeS_2(c) + 8H_2O,$$
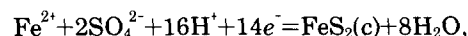
or dissolved carbon dioxide species,

$$Fe^{2+} + HCO_3^- = FeCO_3(c) + H^+.$$
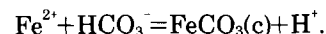
A specified total concentration for sulfate was used in drawing figure 14. The mass-law statement for siderite

precipitation must be supplemented with equilibrium equations for carbon dioxide species to derive from the total amount specified the fraction that is present as $HCO_3^-$ at the pH of the boundary.

Thermodynamic data used in drawing figures 14 and 15 were mostly taken from Wagman and others (1968) or from Robie and others (1978), and some differ slightly from values used in the earlier edition of this book. As noted earlier in this book, some writers have preferred to use a notation "pE" (Sillen, 1967b, p. 52) or "pε" (Stumm and Morgan, 1981, p. 422–436) in place of Eh. The rationale for this notation is primarily that it simplifies calculations in which redox and other types of chemical equilibria must be considered simultaneously. In this writer's opinion, the concept of pE as a measure of molar activity of electrons tends to obscure the electrochemical factors involved in redox processes and the greater mathematical simplicity is not very important in an age of electronic computers. However, the value of the diagrams for summarizing chemical relationships is not affected by the choice of notation.

Figure 14 represents a system containing a constant total amount of dissolved sulfur and carbon dioxide species equivalent to 96 mg/L as $SO_4^{2-}$ and 61 mg/L as $HCO_3^-$. Boundaries are drawn for a dissolved iron activity of $10^{-6.00}$ molar (56 μg/L). Solids indicated by the shaded areas would be thermodynamically stable in their designated domains. Boundaries between solute species are not sensitive to specified dissolved iron activity, but the domains of solid species will increase in area if more dissolved iron is present.

The boundaries for sulfides and elemental iron shown in figure 14 extend below the water stability boundary and were extended to that area only to show what conditions are required for thermodynamic stability of elemental iron. These conditions include the absence of liquid water.

Under the conditions specified for figure 14, siderite $(FeCO_3)$ saturation is not reached. Therefore, $FeCO_3$ is not a stable phase and it does not have a stability domain in the diagram. The more stable ferric or mixed valence oxyhydroxides (magnetite, goethite, hematite, etc.) were not considered as likely equilibrium species in aqueous systems at low temperatures.

Figure 15 is an iron solubility diagram for which most conditions are the same as those for figure 14. The lower solubility of $10^{-7.00}$ molar is equivalent to 5.6 μg/L and the upper limit shown is $10^{-3.00}$ molar, equivalent to 56 mg/L. The contours are plotted as the stability boundaries for solids when the indicated activities of dissolved iron are present. Calculations can be extended to show higher and lower iron solubilities, but there is little practical significance in doing so. As iron content becomes greater, the solubility of ferrous iron is controlled by siderite precipitation rather than by FeO. The bound-

ary between FeO and $FeCO_3$ in the presence of the specified bicarbonate activity would be at pH 8.55. This corresponds to an $Fe^{2+}$ activity of about 100 μg/L. The solubility of iron in the siderite-controlled area is also a function of the bicarbonate species activity specified.

Figure 15 demonstrates that there are two general Eh-pH conditions under which iron solubility is very low. One of these is a condition of strong reduction in the presence of sulfur and covers a wide pH range, within the field of stability for pyrite. The second is a condition of moderate oxidation above a pH of 5 and is in the ferric hydroxide stability region. Between these regions, and especially at low pH, iron is relatively soluble. The high-solubility regions at high pH are outside the range that is common in natural systems.

It is evident from the solubility diagram that exposing an equilibrated system to relatively small shifts in Eh or pH can cause great changes in iron solubility. Thus,
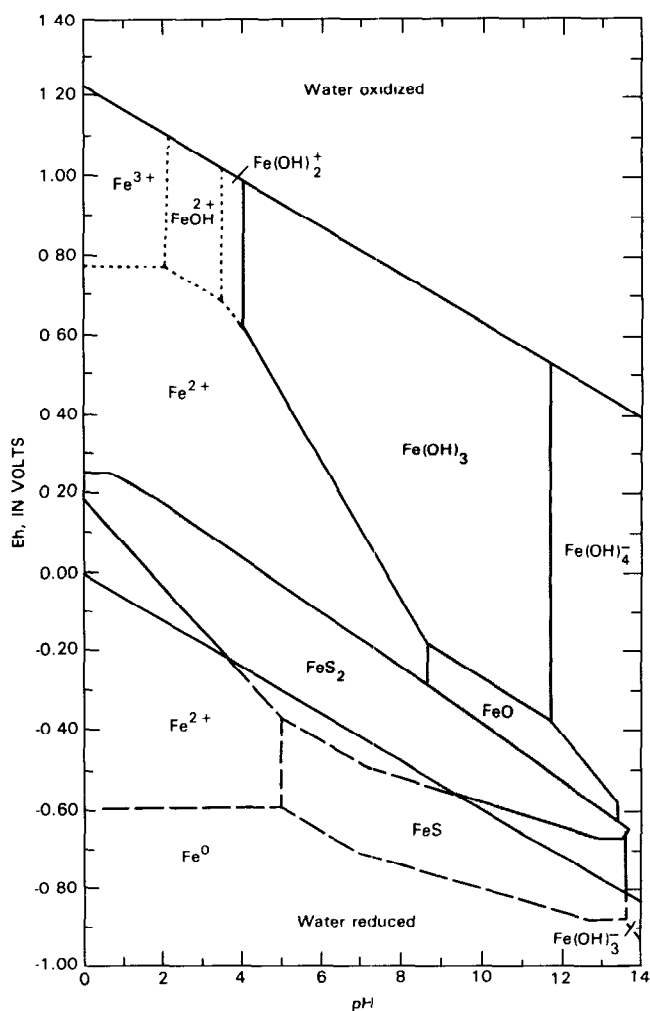


**Figure 14.** Fields of stability for solid and dissolved forms of iron as a function of Eh and pH at 25°C and 1 atmosphere pressure. Activity of sulfur species 96 mg/L as $SO_4^{2-}$, carbon dioxide species 61 mg/L as $HCO_3^-$, and dissolved iron 56 μg/L.

when pyrite is exposed to oxygenated water or ferric hydroxide is in contact with reducing substances, iron will tend to go into solution. It also is evident that if pH and dissolved iron activity and the nature of the solid are known, an equilibrium Eh of the system can be calculated, or at least a range of possible values can be given.

Within the usual pH range of natural water (pH 5–9), the maintenance of an Eh below 0.20 and above −0.10 V (or lower if sulfide is absent) can permit a considerable ferrous iron concentration in equilibrium. This goes a long way toward explaining the behavior of iron in underground water, where a relatively low Eh can be attained owing to chemical reactions that may deplete dissolved oxygen. The reaction of oxygen with pyrite is itself such a process, and the reaction products $SO_4^{2-}$ and $Fe^{2+}$ may be transported stably in the moving solution after the oxygen that might react with $Fe^{2+}$ to
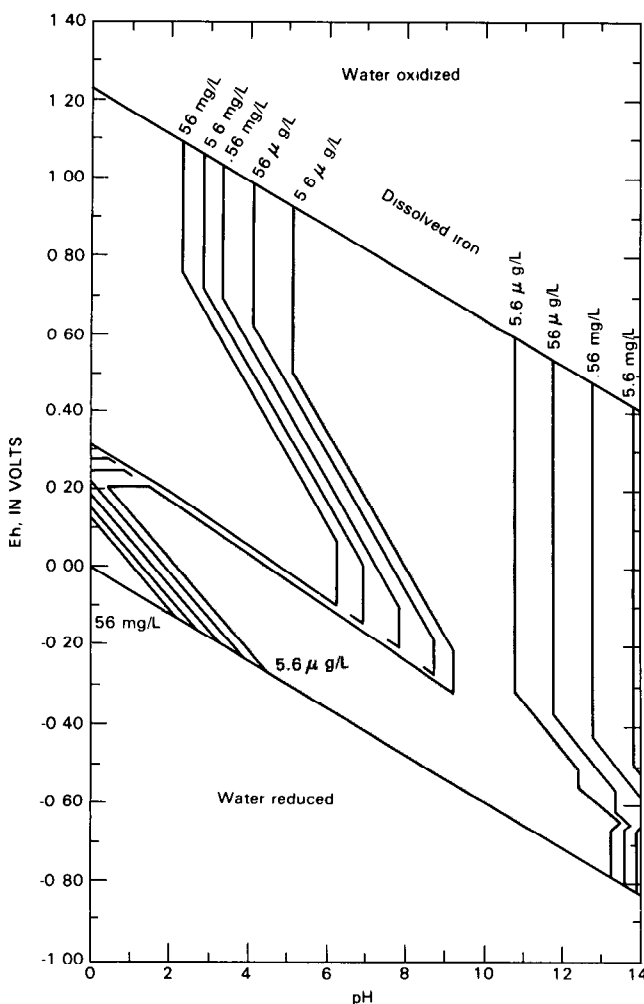


Figure 15. Equilibrium activity of dissolved iron as a function of Eh and pH at 25°C and 1 atmosphere pressure. Activity of sulfur species 96 mg/L as $SO_4^{2-}$, and carbon dioxide species 61 mg/L as $HCO_3^-$.

convert it to $Fe^{3+}$ has been used up. It is notable also that in a considerable part of this range of Eh, the solubility of iron may be controlled by precipitation of ferrous carbonate. In this part of the system, iron solubility is a function of pH and dissolved bicarbonate species but is independent of Eh. Thermodynamics of siderite control of ferrous iron solubility were discussed by the writer in earlier papers (Hem, 1960, 1965). If an iron-bearing ground water of this type dissolves oxygen from the air, however, iron is oxidized to the ferric form, which may precipitate as ferric hydroxide.

The positions of solubility contours like those in figure 15 are strongly influenced by the thermodynamic properties of the postulated solids. The free energy value used for $Fe(OH)_3(c)$ in figure 15 is −166.0 kcal/mole, which represents a poorly crystallized precipitate that has undergone some aging. According to Langmuir and Whittemore (1971), natural fresh precipitates may have $\Delta G°$ values as high as −164.5 kcal/mole, but more stable material is produced on aging. Attainment of significant crystallinity may be very slow and, according to these authors, could take thousands of years if dissolved iron activity is below 50 $\mu$g/L. More stable oxyhydroxides such as hematite and goethite have very low solubilities, but their roles in equilibrium control of iron solubility in freshwater natural systems probably are seldom major.

Redox equilibrium calculations are useful in some other aspects of the aqueous chemistry of iron. Barnes and Clarke (1969), for example applied such calculations in studies of the tendency of waters to corrode or encrust steel well casings and screens, and much of the impetus for the development of pH-Eh diagrams by Pourbaix was the need for a better theoretical understanding of metal-corrosion processes.

Nevertheless, the field application of redox principles and of pH-Eh diagrams is fraught with many uncertainties and complexities, which can lead to erroneous interpretations. Some errors stem from uncertainties about what is producing the potential one might measure in a natural water using a reference and inert metal electrode pair. Such potentials will not be rigorously related to specific dissolved metal ion activities if reversible equlibrium is not attained. But nonequilibrium conditions are widely prevalent in natural aqueous systems. Some of the problems in interpreting such potentials were discussed by Stumm and Morgan (1981, p. 490). Interpretations based on measured potentials are likely to be very uncertain unless the system can be well characterized by other information.

Although the pH-potential diagram is an effective means of summarizing redox equilibria, the simplifications that are required to prepare the diagram should be kept in mind. Some of the limitations of the diagrams merit attention.

Standard temperature and pressure (25°C and 1

atmosphere) are generally specified. However, diagrams could be prepared for other conditions if thermodynamic data used are appropriate for those conditions. As a rule, the departures from 25°C that are observed in natural water systems, other than geothermal systems, do not introduce enough deviation from standard conditions to justify correcting for them. The effect of ionic strength cannot be readily incorporated in the diagrams and thermodynamic activities rather than concentrations must be used.

A diagram such as figure 14 or 15 is an imperfect representation of a real-world system in other important ways. The prescribed constant total dissolved carbon and sulfur species, for example, implies, incorrectly, that one can evaluate the effect of changing some other variable, such as pH, independently without concern about its probable influence on total carbonate availability. The mingling of open- and closed-system concepts that is required for preparation of these diagrams limits their applicability to natural conditions. The numerical value of Eh, or pE, is an indicator of redox intensity, but it has little value as an indicator of redox capacity. This constraint also applies in some degree to pH values.

## Reaction Rates

The requirement that rates of the reactions modeled in pH-Eh diagrams be relatively fast has been noted. Kinetics of relevant processes in the iron system have been evaluated by many investigators.

Precipitation of ferric oxyhydroxide by oxygenation of ferrous solutions is rapid at near-neutral pH. Data compiled by Sung and Morgan (1980) and determined from their own investigations suggest that the process has a half-time of about 18 minutes in aerated solutions with ionic strengths of 0.02 or less at 25°C and pH 6.84 in the presence of about 550 mg/L $HCO_3^-$. The rate is very sensitive to temperature and to $OH^-$ activity and above about pH 5 (Stumm and Morgan, 1970, p. 538) is second-order in $[OH^-]$. That is, the rate increases by a factor of 100 for each unit increase in $\log [OH^-]$. Below pH 3, the uncatalyzed rate of conversion of $Fe^{2+}$ to $Fe^{3+}$ is very slow. The rate also is slowed by complexing of $Fe^{2+}$, especially by organic material (Theis and Singer, 1974).

Oxidation rates of pyrite and other sulfides are slow in sterile systems but are greatly speeded by bacteria. Biological mediation is generally necessary to reach equilibrium in sulfide systems. Measurements of rates and evaluation of mechanisms, especially the oxidation of pyrite by $Fe^{3+}$, were reported by Nordstrom, Jenne, and Ball (1979).

Kinetic studies of ferric oxyhydroxide aging in relation to iron solubility were made by Langmuir and Whittemore (1971).

## Roles of Bacteria in Solution and Precipitation of Iron

The ways in which microbiota may influence the occurrence of iron in water appear to be widely misunderstood. One result is a semi-"folklore" interpretation that blames all high concentrations of iron in water on activities of bacteria and leads to laborious and expensive efforts to eliminate bacteria, and thus the troublesome iron problem, by disinfecting wells, pipelines, and well-drilling equipment. These activities may have temporary effects but do not eliminate all iron problems.

From a thermodynamic point of view, the ways in which bacteria may be involved in the behavior of iron in water include the following:

1. Processes in which bacteria exert a catalytic effect to speed reactions that are thermodynamically favorable but occur rather slowly in the absence of bacteria. The biota may derive energy from them but may not use the iron otherwise.
2. Processes that require a contribution of energy from another source to alter the iron status and can be promoted by bacteria that consume some other substance as a source of energy.

Processes of the first type are involved in the oxidation of dissolved ferrous iron by *Gallionella, Crenothrix,* and *Leptothrix.* These genera require oxygen; hence, they live in environments in which ferrous iron is unstable. The bacteria may become established in wells and remove some iron by precipitation of ferric hydroxide before the water gets to the surface of the ground. Sulfur-oxidizing bacteria may exert an indirect effect on iron behavior by catalyzing reactions that bring iron into solution, the oxidation of pyrite, for example Bacterial catalysis may increase the rate of conversion of $Fe^{2+}$ to $Fe^{3+}$ in acid solutions in the presence of pyrite by as much as six orders of magnitude and can be a major factor in generation of acid mine drainage (Nordstrom, Jenne, and Ball, 1979).

Processes of the second type typically involve iron- and sulfur-reducing species which require an oxidizable substance, usually organic, as a source of food and energy. Reduction or oxidation of iron may occur incidentally, and iron may play no essential role in the life processes of the bacteria. Some species of bacteria that have been shown to influence the precipitation of iron were discussed by Clark and others (1967). There have been many studies in microbiology concerning the roles of iron in the lives of these microorganisms (Neilands, 1974).

The net effect of bacteria may be either to increase or to decrease dissolved-iron concentrations in water after it is intercepted by a well. Bacterial colonies in wells and pipelines may be partly dislodged by moving water from time to time and thus give rise to occasional releases of accumulated ferric hydroxide. The occurrence of iron

in ground water, however, is primarily a chemical phenomenon and cannot be ascribed solely to the bacteria. The biota associated with iron solution and deposition may aggravate some types of problems related to iron-bearing water. These biota are abundant and will inevitably become established in favorable situations.

Different types of bacteria may live together in a symbiotic relationship, with one species providing food for another. Sulfur reducing and oxidizing species may establish such relationships and greatly aggravate problems with well performance and corrosion of iron pipe or well casing and other exposed metallic iron in water-supply systems.

## Occurrence of Iron in Water

Water in a flowing surface stream that is fully aerated should not contain more than a few micrograms per liter of uncomplexed dissolved iron at equilibrium in the pH range of about 6.5 to 8.5. The higher concentrations sometimes reported in such waters are generally particulates (Kennedy and others, 1974) small enough to pass through 0.45 $\mu$m porosity filter membranes. A typical river-water concentration of 10 $\mu$g/L is given in analysis 8, table 12. The effect of organic complexing is indicated by analysis 4, table 14, which is for a stream in northeastern Minnesota. The reported color for this water is 140 units, indicating a large amount of dissolved organic material. The iron in solution, 1.4 mg/L, is presumably complexed or stabilized by this material.

Another condition is shown in analysis 7, table 14, which is for a Pennsylvania stream carrying drainage from coal mines. The water has a pH of 3.0 and 15 mg/L of iron. Lower pH and higher iron concentration can occur in coal-mine drainage water. The water represented by analysis 6 in table 14, which is from a Michigan iron mine, has a pH of 7.5 and an iron content of only 0.31 mg/L. Iron ores in the Lake Superior region are primarily ferric oxides and silicates not readily soluble in water. Analysis 3, table 18, represents water having a pH of 1.9 and 33 mg/L of iron.

In lakes and reservoirs in which a stratified condition becomes established, water at and near the bottom may become enriched in organic matter and depleted in oxygen and may attain a low Eh. Ferrous iron can be retained in solution in water of this type to the extent of many milligrams per liter (Livingstone, 1963, p. G11). The iron content of lake water also can be influenced by aquatic vegetation, both rooted and free-floating forms (Oborn and Hem, 1962).

Occurrence of iron in ground waters of near-neutral pH can generally be at least qualitatively explained by chemical reactions that have been described and summarized in the pH-Eh diagrams. Deviations from these

simple models generally can be ascribed to water circulation and mixing mechanisms.

When it reaches the ground-water body, recharge can be expected to contain oxygen acquired from exposure to air. Dissolved-oxygen activity of $10^{-3.5}$ moles/L represents approximate atmospheric saturation at ordinary air temperatures. If this amount of oxygen is depleted by reacting with pyrite, the final solution could contain about 5 mg/L of ferrous iron and about 17 mg/L of sulfate. A once-through continuous-flow system in which oxygen is not replenished after this reaction has occurred should have a final iron concentration in the water approaching 5 mg/L. Higher iron concentrations in such systems are common, however—perhaps owing to faster transport of oxygen than water in the unsaturated zone or to occasional flow reversals accompanied by reactions between ferric iron and pyrite.

Higher iron concentrations in simple hydraulic systems could result from interactions between oxidized iron minerals and organic matter or by dissolution of $FeCO_3$. Such waters should be relatively low in sulfate. The latter effect may not be diagnostic, however, because sulfate produced by pyrite oxidation may be reduced again in some systems and lost from solution.

Analyses 1, 2, and 3 in table 14 probably typify iron-containing ground water where a pyrite-oxidation mechanism is plausible. Regional development of a zone of oxidation near the surface overlying a zone of reduction at depth was described for interbedded sands of the Mississippi Embayment in northeastern Texas by Broom (1966). The ground water in this region is characterized by low iron concentrations in the upper oxidized and lower reduced strata, but iron concentrations are high near the contact between zones at intermediate depth where oxidation is currently active (Hem, 1965). Chemical zonations of iron in a lateral pattern in confined or semiconfined aquifers in parts of New Jersey were described by Langmuir (1969a).

Ground water having a pH of between 6 and 8 can be sufficiently reducing to retain as much as 50 mg/L of ferrous iron at equilibrium, when bicarbonate activity does not exceed 61 mg/L. In many areas, the occurrence of 1.0–10 mg/L of iron in ground water is common. This type of water is clear when first drawn from the well but soon becomes cloudy and then brown from precipitating ferric hydroxide. Wells that yield water of this type may appear to be erratically distributed around an area, and some exhibit changes in composition of their water with time that are difficult for hydrologists to explain. For example, in eastern Maryland and at other localities of the Atlantic Coastal Plain, the permeability of some coastal sedimentary beds is much greater than others, and a well may encounter solutions with different oxidation-reduction potentials at different depths. Mingling of these waters at contacts between strata and particularly

where the strata are locally short-circuited, either naturally or by a well that penetrates them, can cause deposition or solution of iron minerals. In many wells, corrosion of the iron casing adds iron to the water pumped out, and iron may be precipitated in various forms within the well under some conditions.

Brines such as that represented by analysis 5, table 14, can retain iron that is stabilized by complex ion formation.

Because of the unstable nature of ferrous iron in samples of alkaline ground water, the iron orignially present may have been oxidized and precipitated by the time the analysis is made. To ensure that concentrations of iron reported in analyses represent the amounts in solution at the time of sampling, waters suspected of containing iron should be filtered at the time of sampling, and an aliquot of the filtrate acidified to prevent precipitation. The iron in untreated portions of samples repre-

sented by analyses 1–3, 8, and 9, table 14, had largely been lost from solution before analysis. Concentrations of iron reported are the totals originally present in a filtered, acidified fraction of the sample. The oxidation and precipitation reactions decreased the pH and altered the alkalinity originally present in the unacidified solutions used for the rest of the analysis. Although it might be possible to reconstruct these data to give the original composition of the water at the time of sampling, it is not common practice to do so. The effect of precipitation of iron may be readily noticeable in dilute solutions such as the one represented by analysis 9, table 14.

## Manganese

Although manganese is one of the more abundant metallic elements, there is only about one-fiftieth as

**Table 14.** Analyses of

[Analyses by U S Geological Survey. Date below sample number is date of collection. Sources of data: 1, 5, and 6, U S. Geological Survey, unpublished data, 2, 3, 21), 8, Simpson (1929, p. 298)]

| Constituent | 1 May 28, 1952 | | 2 Mar. 8, 1952 | | 3 Feb. 27, 1952 | | 4 Oct. 1–31, 1962 | |
|---|---|---|---|---|---|---|---|---|
| | mg/L | meq/L | mg/L | meq/L | mg/L | meq/L | mg/L | meq/L |
| Silica ($SiO_2$) | 20 | | 12 | | 26 | | 11 | |
| Aluminum (Al) | | | 1.2 | | 1.2 | | | |
| Iron (Fe) | 2.3 | | 2.9 | | 10 | | 1.4 | |
| Manganese (Mn) | .00 | | | | | | | |
| Calcium (Ca) | 126 | 6.29 | 2.7 | .135 | 8.8 | .439 | 18 | .898 |
| Magnesium (Mg) | 43 | 3.54 | 2.0 | .164 | 8 4 | .691 | 8.0 | .658 |
| Sodium (Na) | 13 | .56 | 35 | 1.522 | 34 | 1.478 | 9.3 | .40 |
| Potassium (K) | 2.1 | .05 | 1.7 | .044 | 2.9 | .074 | | |
| Bicarbonate ($HCO_3$) | 440 | 7.21 | 100 | 1.639 | 65 | 1.065 | 69 | 1.131 |
| Sulfate ($SO_4$) | 139 | 2.89 | 5.6 | .117 | 71 | 1.478 | 29 | .604 |
| Chloride (Cl) | 8.0 | 23 | 2.0 | .056 | 2.0 | .056 | 6 4 | .181 |
| Fluoride (F) | .7 | .04 | .1 | .005 | .3 | .016 | | |
| Nitrate ($NO_3$) | .2 | .00 | .6 | .010 | .0 | .000 | 2.9 | .046 |
| Dissolved solids: | | | | | | | | |
| Calculated | 594 | | 113 | | 187 | | | |
| Residue on evaporation | 571 | | 101 | | 180 | | 156 | |
| Hardness as $CaCO_3$ | 490 | | 15 | | 56 | | 78 | |
| Noncarbonate | 131 | | 0 | | 3 | | 21 | |
| Specific conductance (micromhos at 25°C). | 885 | | 162 | | 264 | | 188 | |
| pH | 7.6 | | 7.4 | | 6.4 | | 6.9 | |
| Color | 1 | | 23 | | 7 | | 140 | |
| Acidity as $H_2SO_4$ (total) | | | | | | | | |

1. Well 3, Nelson Rd., Water Works, Columbus, Ohio. Depth, 117 ft, temperature, 13.3°C. Water from glacial outwash.
2. Well 79·8-50, public supply, Memphis, Tenn. Depth, 1,310 ft, temperature, 22 2°C. Water from sand of the Wilcox Formation
3. Well 5.290-1, 6 mi southeast of Maryville, Blount County, Tenn. Depth, 66 ft; temperature, 14 4°C Water from the Chattanooga Shale
4. Partridge River near Aurora, Minn. Composite sample. Mean discharge, 30.8 cfs.
5. Brine produced with oil from well in NW1/4 sec. 3, T. 11 N , R 12 E , Okmulgee County, Okla Depth, 2,394 ft Water from the Gilcrease sand of drillers, Atoka Formation.

much manganese in the Earth's crust as there is iron. Manganese is not an essential constituent of any of the more common silicate rock minerals, but it can substitute for iron, magnesium, or calcium in silicate structures.

The chemistry of manganese is somewhat like that of iron in that both metals participate in redox processes in weathering environments. Manganese, however, has three possible valence states in such environments rather than two (2+, 3+, and 4+) and can form a wide variety of mixed-valence oxides. The 3+ species are unstable in that they may disproportionate. That is, two $Mn^{3+}$ ions may interact spontaneously to produce one $Mn^{2+}$ and one $Mn^{4+}$ ion, and these products are more stable thermodynamically than the original $Mn^{3+}$ species. This ability has a number of interesting ramifications in the chemistry of the element in natural water.

Manganese is an undesirable impurity in water supplies, mainly owing to a tendency to deposit black oxide stains. The recommended upper limit for manganese in public water supplies in the United States is 0.05 mg/L (50 $\mu g/L$) (NAS-NAE, 1972). No mandatory limit is specified for this element by the U.S. Environmental Protection Agency. It is an essential element for both plant and animal life forms.

## Sources of Manganese

Many igneous and metamorphic minerals contain divalent manganese as a minor constituent. It is a significant constituent of basalt and many olivines and of pyroxene and amphibole. Small amounts commonly are present in dolomite and limestone, substituting for calcium. The silicate, rhodonite ($MnSiO_3$), and the carbonate, rhodochrosite ($MnCO_3$), are pink to red minerals sometimes used as gemstones.

When divalent manganese is released to aqueous solution during weathering, it is somewhat more stable

waters containing iron

and 9, Scott and Barker (1962, p. 63, 101); 4, U.S. Geological Survey Water-Supply Paper 1948 (p 297); 7, U.S. Geological Survey Water-Supply Paper 1022 (p

| 5 Mar. 11, 1952 | | 6 Jan. 30, 1952 | | 7 Aug. 8, 1944 | | 8 June 24, 1921 | | 9 Oct. 26, 1954 | |
|---|---|---|---|---|---|---|---|---|---|
| ppm | epm | mg/L | meq/L | mg/L | meq/L | mg/L | meq/L | mg/L | meq/L |
| 9.1 | | 8.1 | | 21 | | 23 | | 7.9 | |
| | | | | 29 | 3.23 | | | .6 | |
| 32 | | .31 | | 15 | .81 | 4.8 | | 11 | |
| | | .34 | | 10 | .36 | | | .32 | |
| 7,470 | 372.75 | 264 | 13.17 | 119 | 5.94 | 136 | 6.79 | 8.4 | .419 |
| 1,330 | 109.37 | 17 | 1.40 | 68 | 5.59 | 35 | 2.88 | 1.5 | .123 |
| { 43,800 | 1,940.59 | 52 | 2.26 } | 17 | .74 | 960 | 41.74 | { 1.5 | .065 |
| { 129 | 3.30 | 31 | .80 } | | | | | { 3.6 | .092 |
| 76 | 1.25 | 61 | 1.00 | 0 | .00 | 249 | 4.08 | 30 | .492 |
| 47 | .98 | 757 | 15.76 | 817 | 17.01 | 1,260 | 26.23 | 5.9 | .123 |
| 83,800 | 2,363.43 | 24 | 68 | 22 | .62 | 734 | 20.70 | 1.8 | .051 |
| 0 | | .8 | .04 | .1 | .01 | | | .1 | .005 |
| | | .0 | .00 | .4 | .01 | 7.5 | .12 | .4 | .006 |
| 137,000 | | 1,280 | | 1,260 | | 3,280 | | 47 | |
| 140,000 | | 1,180 | | | | 3,450 | | 44 | |
| 24,200 | | 730 | | 845 | | 484 | | 27 | |
| 24,100 | | 679 | | 845 | | 280 | | 2 | |
| 146,000 | | 1,460 | | 1,780 | | | | 68.8 | |
| 7.4 | | 7.5 | | 3.0 | | | | 6.3 | |
| 15 | | 2 | | 8 | | | | 3 | |
| | | | | 342 | | | | | |

6. Drainage at collar, drill hole 89, 7th level, Mather A iron mine, Ishpeming, Mich Temperature, 15.1°C.
7. Shamokin Creek at Weighscale, Pa. Discharge, 64 2 cfs, affected by drainage from coal mines
8 Flowing well, Minneapolis, St. Paul, and Sault Ste. Marie R.R , Enderlin, Ramsom County, N. Dak Depth, 613 ft Water from the Dakota Sandstone.
9. City well 4, Fulton, Miss. Depth, 210 ft; temperature, 17 2°C Water from the Tuscaloosa Formation

toward oxidation than is ferrous iron. Generally, however, if it is in contact with the atmosphere, it will be precipitated, at sites where pH is high enough, as a crust of manganese 4+ oxide. These encrustations generally contain a substantial quantity of coprecipitated iron and, under some conditions, significant amounts of other metal ions as well, especially cobalt, lead, zinc, copper, nickel and barium. A particularly favorable substrate for manganese oxide precipitation is a previously existing manganese oxide surface. Thus the deposit may become thicker with time and form nodules around some central nucleus, as on the bottoms of certain lakes and at many localities on the ocean bottom. Small, discrete particles of oxide or coatings on other particles are widely distributed in stream sediments and soils. Coatings of manganese oxides in streambeds occur in many places. These coatings generally do not become very thick, owing to mechanical erosion and changes in water properties. In some areas manganese oxide may accumulate with other material in the form of a bog. The deposits in streams and bogs in New Brunswick, Canada, were described by Brown (1964). Other descriptions of streambed deposits concern streams in Sweden (Ljunggren, 1952, 1953, 1955), Colorado (Theobald and others, 1963), and Maine (Canney and Post, 1964; Nowlan, 1976). The mechanisms that produce these deposits are different. The deposits studied by Ljunggren seemed to be associated with an aquatic moss. In the other areas, however, the deposition seemed to occur without any organic intervention. Moran and Wentz (1974) and Wentz (1974) studied Colorado mountain streams affected by drainage from mines. There, as in the area described by Theobald and others, a low-pH, metal-enriched water is neutralized by mixing with normal stream water, and much of the dissolved-metal load is precipitated.

Manganese nodules in Oneida Lake, N.Y., were described by Dean and Greeson (1979). Literature on all aspects of marine manganese oxide nodules is voluminous and growing.

In lakes and reservoirs where thermal stratification develops, the bottom sediments may become anoxic and manganese oxide previously deposited may be reduced and dissolved. Water drawn from the deeper part of the supply reservoir may at times contain significant concentrations of dissolved $Mn^{2+}$. Reduction of manganese oxides at depth in buried sediment may be a factor in accumulations of manganese nodules in many environments. Diffusing $Mn^{2+}$ can be redeposited as oxide when it reaches the surface of the sediment layer and encounters oxygenated water (Callender and Bowser, 1980).

Manganese is an essential element in plant metabolism, and it is to be expected that organic circulation of manganese can influence its occurrence in natural water. Specific mention of manganese accumulation in tree leaves appears in published literature. Some species of trees are much more effective accumulators than others. Bloss and Steiner (1960) found considerable quantities in the leaves of the chestnut oak, and Ljunggren (1951) reported similar findings for the needles of spruce trees in southern Sweden. Aquatic plants were noted by Oborn (1964) to be accumulators of manganese. Manganese in plant parts that die back or are shed becomes available for solution in runoff and soil moisture. The importance of this source of manganese in river water is not completely known, although some preliminary studies by Slack and Feltz (1968) of the effects of fallen leaves on the water quality of a small stream in Virginia showed it could be important at times.

Lateritic weathering processes have produced manganese oxide accumulations of economic importance in many locations, and manganese oxides are a constituent of the dark stain ("desert varnish") present on rocks in arid regions (Hem, 1964, p. 10).

## Form of Dissolved Manganese

Under conditions to be expected in natural-water systems, any dissolved manganese will be in the 2+ oxidation state. The ion $Mn^{2+}$ will predominate in most situations. The hydroxide complex $MnOH^+$ becomes the principal form above pH 10.5, and anionic forms will be significant at pH 12.0 or higher. The complex ion $MnHCO_3^+$ can be important in solutions having bicarbonate concentrations near 1,000 mg/L as $HCO_3$ (Hem, 1963a, b). The $MnSO_4(aq)$ ion pair could be important in solutions in which sulfate activity is greater than a few hundred milligrams per liter, judging from stability data reported by Nair and Nancollas (1959). Organic complexes of manganese may play a significant role in its transport in some situations. In general, however, the $Mn^{2+}$ ion is considerably more stable than $Fe^{2+}$ in aerated water, and it can be transported at higher concentrations without the protection of complexation.

Some $Mn^{3+}$ species may be stable in strongly acid solutions, and stable organic complexes of $Mn^{3+}$ are known to exist under some conditions. However, the role of $Mn^{3+}$ in natural systems probably is related more closely to the instability of this form of the element with respect to disproportionation.

Manganese at higher oxidation states than $Mn^{4+}$ is not likely to occur to a significant extent in natural aqueous systems. Very small amounts of such species could theoretically occur at very high pH. Permanganate ($MnO_4^-$) is used extensively in water treatment as an oxidant for removal of iron, manganese, and organic material. The $MnO_2$ produced in such interactions is removed by filtration.

### Quantification of Manganese Redox Processes

Equilibria among dissolved and solid forms of manganese in the 2+, 3+, and 4+ oxidation states can be

conveniently summarized in an pH-Eh diagram (fig. 16). Use of the diagram to explain natural aqueous systems, however, is not as simple and straightforward as in the case of iron. The two pH-Eh diagrams for iron specify oxyhydroxides that are not the most stable species known. However, natural systems appear to be well enough controlled by equilibria involving these metastable species to justify their use in the model.

For manganese, the situation is less clear cut. The common, naturally occurring oxides are generally forms of $MnO_2$, when the manganese is at the $Mn^{4+}$ oxidation state, or mixed-valence oxides in which the oxidation state of manganese is less than +4.0 but substantially above +3.0. Species where the oxidation state is +3.0 as in $MnOOH$ or below 3.0 as in $Mn_3O_4$ are readily produced when $Mn^{2+}$ solutes are oxidized by air in laboratory experiments. Although these oxides do occur naturally, they are relatively uncommon.
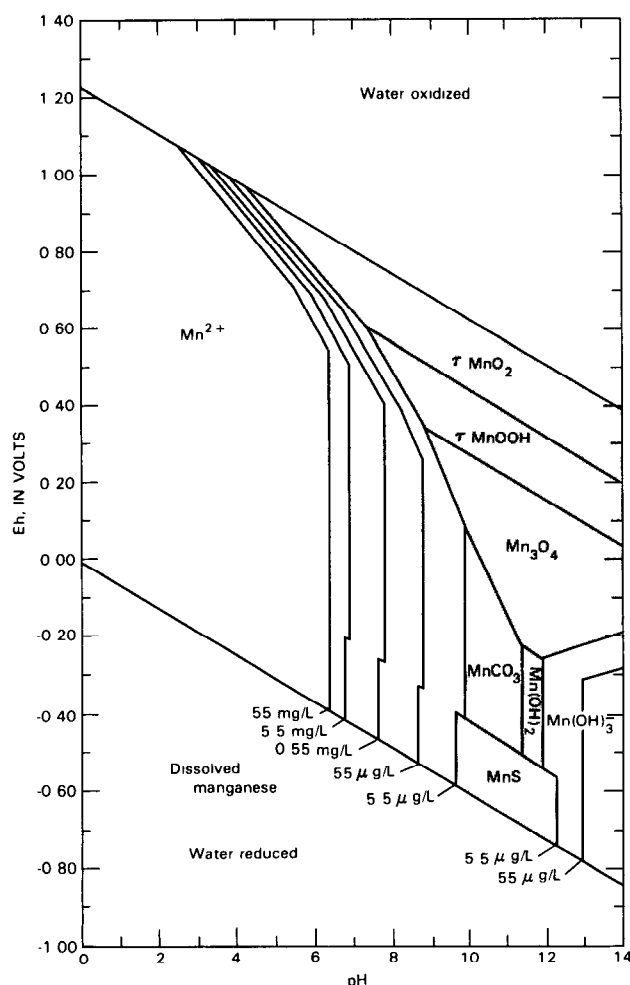


Figure 16. Fields of stability of manganese solids and equilibrium dissolved manganese activity as a function of Eh and pH at 25°C and 1 atmosphere pressure. Activity of sulfur species 96 mg/L as $SO_4^{2-}$, and carbon dioxide species 61 mg/L as $HCO_3$.

Thermodynamic data used for preparing figure 16 are given in tables 30 and 32. If certain other forms of oxyhydroxides or other published stability data are used, the boundaries in the figure would be shifted somewhat, but the general features would remain about the same. The total activities of sulfur and carbon dioxide species are $10^{-3.00}$ molar throughout, as in figure 14 and 15. The manganous sulfide, alabandite, does not have as important an effect as the iron sulfides, but the manganese carbonate, rhodochrosite, appears to have more influence than the corresponding ferrous carbonate, siderite. Figure 16 shows solid stability domains and equilibrium manganese activities from $10^{-3.00}$ to $10^{-7.00}$ moles/L (55 mg/L to 5.5 $\mu$g/L).

Natural oxygenated water commonly contains manganese concentrations near those predicted by figure 16 for equilibria involving $\gamma MnOOH$ but does not usually have the extremely small concentrations that are permitted in much of the $MnO_2$ stability field. For example, the chemical reaction

$$Mn^{2+}+\tfrac{1}{2}O_2(aq)+H_2O=MnO_2(c)+2H^+$$
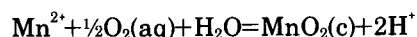
gives an equilibrium activity of dissolved $Mn^{2+}$ of less than 1 nanogram/L (ng/L) at pH 7.00 in aerated water. Apparently this simple equilibrium mechanism does not control manganese activity in such systems.

A chemical mechanism for manganese oxidation in aerated water that may help explain the generally observed behavior of this element has been proposed (Hem, 1978). In this model, precipitation of the oxide occurs in an open system and manganese will ultimately attain a steady-state concentation that is a function of kinetics of oxidation and of disproportionation of an $Mn^{3+}$ intermediate. Essentially, this mechanism proposes a first step in which an oxide containing $Mn^{3+}$ is produced and a second step immediately following in which two of the $Mn^{3+}$ ions still at the solid-solution interface disproportionate. The $Mn^{4+}$ ion that is formed enters the oxide crystal structure and the $Mn^{2+}$ ion again becomes available for interaction with $O_2(aq)$.

The coupled oxidation-disproportionation mechanism can be summarized graphically by plotting equilibrium lines for the reactions, for example,

$$1.\ 3Mn^{2+}+\tfrac{1}{2}O_2(aq)+3H_2O=Mn_3O_4(c)+6H^+$$

and

$$2.\ Mn_3O_4(c)+4H^+=MnO_2(c)+2H_2O+2Mn^{2+}$$
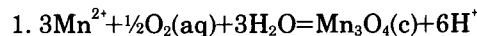
on a pH versus log $[Mn^{2+}]$ grid (fig. 17).

In the region between lines 1 and 2 in figure 17, both reactions are thermodynamically favored to go to the right as written. If the process occurs in an open

system, that is, a system in which dissolved oxygen is brought in by flowing water, and if there are continuing supplies of $Mn^{2+}$ and continuing removal of surplus $H^+$, a steady-state control of $Mn^{2+}$ concentration can be maintained. Figure 17 shows that for the solid species specified, activity of $Mn^{2+}$ could range from about $10^{-6.2}$ to $10^{-8.3}$ molar at pH 7.5 (about 34 to about 0.3 $\mu g/L$).

If a less stable $Mn^{3+}$ oxide is the initial form, the positions of the lines would be shifted somewhat to the right and solubilities would be greater, but the general range of concentrations observed in oxygenated natural waters are in reasonable accord with values this precipitation mechanism forecasts.

Information available on the sources of samples whose analyses are in tables 12–20 is not adequate to evaluate the applicability of this model closely. However, 7 of the 13 analyses that include specific manganese concentrations and pH values are plotted in figure 17. Of these, 6 plot between lines 1 and 2 and the other is just outside line 2. Four of the remaining 6 analyses not shown in figure 17 represent water having a pH of 4.0 or less that clearly should not be expected to precipitate manganese oxide. The other 2 are substantially higher in manganese than the oxidation model would predict.
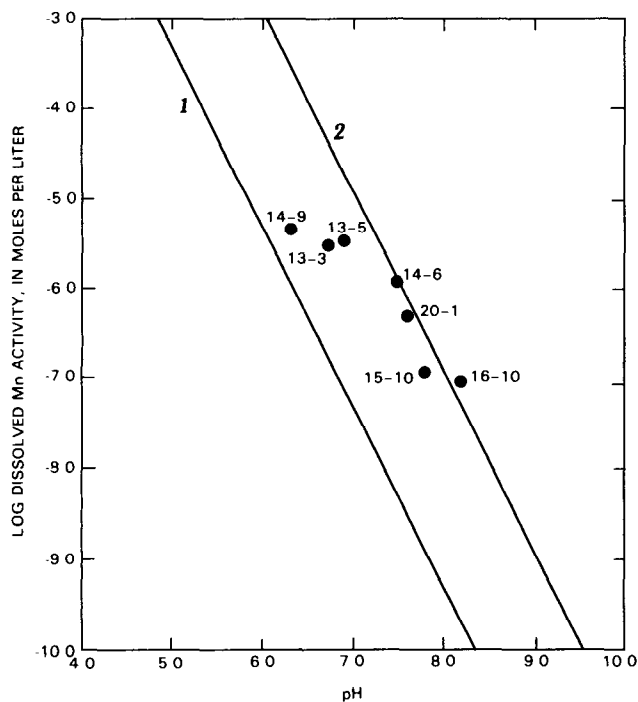


Figure 17. Activity of dissolved manganese at equilibrium at 25°C and 1 atmosphere pressure as a function of pH in aerated water. Line 1, oxidation of $Mn^{2+}$ to form $Mn_3O_4$. Line 2, disproportionation of $Mn_3O_4$ to form $\gamma MnO_2$ and $Mn^{2+}$. Plotted points represent analytical data from tables 13-16 and 20 (e.g., "14-9"=table 14, analysis 9).

One of these (analysis 2, table 13) probably represents a reduced system, and both it and the other (analysis 2, table 18) have about the manganese activity one would predict for equilibrium with rhodochrosite. These evaluations take into account effects of ionic strength and complex-ion formation but are inexact because of uncertainties in the applicability of the laboratory pH determinations.

Research by Morgan (1967), Wilson (1980), and Sung and Morgan (1981) on kinetics of manganese oxidation has demonstrated the importance of solid surfaces as sites for oxidation and precipitation. Manganese oxide surfaces are especially favorable for catalysis of the oxidation process. These surfaces have a high density of negative charge sites and are capable of adsorbing large numbers of cations per unit area, when conditions favor this process (Murray, 1974).

Whether the processes of adsorption or of coprecipitation are the more important depends on the composition of water in contact with the manganese oxides. The oxides, in any event, are effective scavengers (Jenne, 1968, 1975) and may be useful as indicators in geochemical prospecting for ore deposits (Chao and Anderson, 1974; Nowlan, 1976).

The rate of manganese oxidation in aerated solutions displays a second-order dependence on $OH^-$ activity and is relatively slow in laboratory systems below pH 9.0. In river waters in which favorable surfaces are plentiful, the kinetic behavior may be pseudo-first-order; half-times of the order of a few days were observed in the Susquehanna River in Pennsylvania (Lewis, 1976) at near-neutral pH and temperatures of 5° to 20°C.

The rate of oxidation also is strongly temperature dependent, and lower temperatures (near 0°C) seem to favor the formation of more fully oxidized species (Hem, 1981; Hem and others, 1982) as initial precipitates ($\beta MnOOH$ rather than $Mn_3O_4$).

Bacteria may influence the rates of manganese oxidation, probably in a manner similar to the effects of bacteria in oxidation of ferrous iron. Tyler and Marshall (1967) found Hyphomicrobium in deposits of manganese oxide in pipelines. Schweisfurth has conducted extensive research on manganese oxidizing bacteria and has published many papers in Germany (for example, Schweisfurth, 1973; Jung and Schweisfurth, 1976).

## Occurence of Manganese in Water

Manganese is often present to the extent of more than 1 mg/L in streams that have received acid drainage from coal mines. Manganese usually persists in the water for greater distances downstream from the pollution source than the iron contained in the drainage inflows.

As the acidity is gradually neutralized, ferric hydroxide precipitates first. Manganese, however, also disappears from solution after a longer time. These effects can be noted for streams in the Ohio River basin (U.S. Geological Survey Water-Supply Paper 1948). Analysis 4, table 13, presents water from a river influenced by acid mine drainage from which most of the iron has been precipitated. Analysis 7, table 14, is for water affected by mine drainage in which much iron was still present. Manganese concentrations exceeding 1 mg/L have been measured in water from small streams in the Northern United States during winter low-flow conditions (U.S. Geological Survey, 1969, p. 240, for example). During long periods of ice cover the dissolved-oxygen concentration in the water is depleted and manganese may be extracted from organic-rich sediment. Records of composition of many U.S. streams collected since about 1970 include manganese concentrations. These data indicate that concentrations up to a few hundred micrograms per liter occur in many streams at times. Some of the manganese reported in these analyses may be particulate material that can pass through 0.45 $\mu$m filter pores. Data obtained by Kennedy and others (1974), however, suggest that this is a much less important effect for manganese than it is for iron or aluminum.

Ground waters may contain more than 1.0 mg/L of manganese under some circumstances. High iron concentrations may accompany the manganese, but this is not invariably true. Analysis 1, table 13, is for a low-pH water that is very high in manganese, but some of the iron that might originally have been in solution in the water could have been lost by precipitation of ferric hydroxide in the sample after collection.

Analysis 2, table 13, represents water pumped from two radial collector wells located along the Ohio River at Parkersburg, W. Va. The manganese concentration of this water is 1.3 mg/L, compared with only 40 $\mu$g/L of iron. Excessive manganese concentrations also have been reported in other localities where wells were located with the aim of withdrawing water from gravel deposits adjacent to or within stream channels. Streambed materials may include sand grains and pebbles having manganese oxide coatings. The coatings may be reduced and dissolved by water of different composition that reaches them. Dissolved organic solutes, for example, may reduce the oxide and liberate $Mn^{2+}$. Anaysis 5 in table 13 and analysis 9 in table 14 represent ground waters high in iron that also contain several hundred micrograms per liter of manganese. The manganese may well have come from the same initial source as the iron.

Many of the ground waters reported to carry large manganese concentrations are from thermal springs. White and others (1963, p. F50) reported some examples of these. In many places these springs seem to be closely associated with manganese oxide deposits. Analysis 3,

table 13, represents water from a thermal spring that contains 0.31 mg/L of manganese.

## Calcium

Calcium is the most abundant of the alkaline-earth metals and is a major constituent of many common rock minerals. It is an essential element for plant and animal life forms and is a major component of the solutes in most natural water. Calcium has only one oxidation state, $Ca^{2+}$. Its behavior in natural aqueous systems is generally governed by the availability of the more soluble calcium-containing solids and by solution- and gas-phase equilibria that involve carbon dioxide species, or by the availability of sulfur in the form of sulfate. Calcium also participates in cation-exchange equilibria at aluminosilicate and other mineral surfaces. Solubility equilibrium models have been used widely in studying the chemical behavior of calcium.

### Sources of Calcium

Calcium is an essential constituent of many igneous-rock minerals, especially of the chain silicates pyroxene and amphibole, and the feldspars. The plagioclase feldspar group of minerals represents mixtures in various proportions of the end members albite, $NaAlSi_3O_8$, and anorthite, $CaAl_2Si_2O_8$. Calcium also occurs in other silicate minerals that are produced in metamorphism. Some calcium is, therefore, to be expected in water that has been in contact with igneous and metamorphic rock. The concentration generally is low, however, mainly because the rate of decomposition of most igneous-rock minerals is slow. The decomposition of anorthite can be represented as

$$CaAl_2Si_2O_8+H_2O+2H^+=Al_2Si_2O_5(OH)_4+Ca^{2+}$$
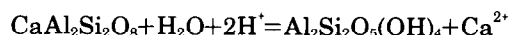
The normal composition of plagioclase feldspar lies between the pure sodium and pure calcium forms, and decomposition will, therefore, generally yield both calcium and sodium and some soluble silica. Under some conditions the solution may attain saturation with respect to calcium carbonate.

The most common forms of calcium in sedimentary rock are carbonates. The two crystalline forms, calcite and aragonite, both have the formula $CaCO_3$, and the mineral dolomite can be represented as $CaMg(CO_3)_2$. Limestone consists mostly of calcite with admixtures of magnesium carbonate and other impurities. A carbonate rock is commonly termed "dolomite" if the magnesium

is present in amounts approaching the theoretical 1 : 1 mole ratio with calcium. Other calcium minerals common in sediments include the sulfates gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$), and, more rarely, the fluoride, fluorite ($CaF_2$). Calcium is also a component of some types of zeolites and montmorillonite.

In sandstone and other detrital rocks, calcium carbonate commonly is present as a cement between particles or a partial filling of interstices. Calcium also is present in the form of adsorbed ions on negatively charged mineral surfaces in soils and rocks. Because divalent ions are held more strongly than monovalent ions at surface charge sites, and because calcium is generally the dominant divalent ion in solution, most such sites are occupied by calcium ions in the usual river or ground-water system.

## Solute Species

Calcium ions are rather large, having an ionic radius near 1 angstrom. The charged field around the ion is therefore not as intense as the fields of smaller divalent ions. Calcium ions have a less strongly retained shell of oriented water molecules surrounding them in solution. The usual dissolved form can be simply represented as the ion $Ca^{2+}$. Calcium does form complexes with some organic anions, but the influence of such species on the concentrations of calcium in natural water is probably not important. In some solutions, complexes such as $CaHCO_3^+$ can exist. Data published by Greenwald (1941) show that about 10 percent of the calcium might be in this form if the bicarbonate concentration were near 1,000 mg/L. The ion pair $CaSO_4(aq)$ is more important. In solutions in which sulfate concentrations exceed 1,000 mg/L, more than half the calcium could be present in the form of the $CaSO_4$ ion pair. Both of these generalizations assume that the calcium concentration is small compared with the bicarbonate or sulfate concentrations.

Garrels and Christ (1964, p. 96) also mentioned hydroxide and carbonate ion pairs with calcium. These species could be present in appreciable concentrations in strongly alkaline solutions. Other calcium ion pairs, such as those with phosphate, are known but are not likely to influence the behavior of calcium in natural water to a significant extent. However, small amounts of phosphate are sometimes added in water treatment to inhibit $CaCO_3$ precipitation and phosphate is a constituent of many types of wastewater.

## Chemical Controls of Calcium Concentration

Equilibria involving carbonates are the major factor in limiting the solubility of calcium in most natural water. The calcite dissolution-precipitation and dissolved carbon dioxide species equilibria were introduced earlier to demonstrate chemical equilibrium calculations, and

the discussion of pH. Calculations required to determine whether a particular solution may be in thermodynamic equilibrium with calcite require values for activities of $Ca^{2+}$, $HCO_3^-$ and $H^+$ and solution temperature. Analytical concentrations must be corrected for ionic strength effects and complexing, and equilibrium constants used must be appropriate for the temperature of the system.

Computer programs such as WATEQ (Truesdell and Jones, 1974) can perform all the necessary computations. For many interim or preliminary studies of water chemistry data, however, it may be convenient to evaluate the calcite equilibrium by a graphical procedure. Two forms of the calcite-solubility relationship are given here, as plate 2a and 2b and in figure 18. Both entail some simplifying assumptions that limit their applicability range to some extent.

Plate 2 is for a system lacking a gas phase and is based on the calcite-solubility equilibrium equation already extensively discussed:

$$\frac{[Ca^{2+}][HCO_3^-]}{[H^+]} = K_s{}^1.$$

[1] The symbol $K_s$ represents the solubility equilibrium constant for calcite in the reaction $CaCO_3 + H^+ = HCO_3^- + Ca^{2+}$

The illustration consists of two parts, a log-log grid of calcium concentration versus bicarbonate concentration (both in mg/L) and a pH-grid overlay. When in use, the overlay is alined on the log-log plot so that the x-axes match.

Equilibrium constants at various temperatures, based on data in published literature, are given in table 33. The equilibrium solubility of calcite has a strong temperature dependence in this range. The solubility at 0° is more than five times as great as at 50°. To determine equilibrium conditions for a single temperature in this range when the effect of ion activity corrections can be ignored (ionic strength $\simeq 0.0$), the overlay may be moved right or left until the extension of the pH 8.0 line intersects the appropriate point on the temperature scale of the log-log base sheet. A saturation index for a water sample having this temperature can be obtained by plotting the point of intersection of the calcium and bicarbonate concentrations given in the analysis and reading the equilibrium pH from the pH grid. This pH is subtracted from the measured pH given in the analysis to give the S.I. value. A positive value for S.I. indicates supersaturation.

To permit the use of the graph for ionic strengths >0.0, conversion of stoichiometric concentrations to thermodynamic activities was incorporated in plate 2 by including activity coefficients in the equilibrium constant. The mass-law expression in terms of concentrations, $C_{i^+}$, may be written

$$\frac{C_{Ca^{2+}}\ \gamma_{Ca^{2+}} \times C_{HCO_3^-}\ \gamma_{HCO_3^-}}{[H]} = K_s$$

or

$$\frac{C_{Ca^{2+}} \times C_{HCO_3^-}}{[H]} = \frac{K_s}{\gamma_{Ca^{2+}}\ \gamma_{HCO_3^-}} .$$

The activity coefficients (gamma terms) were evaluated by means of the Davies equation for values of $I$ from 0.0 to 0.5. This relationship is

$$-\log \gamma_i = 0.509 Z_i^2\ \frac{\sqrt{I}}{1+\sqrt{I}} - 0.2I ,$$

where $Z_i$ is the ionic charge and $I$ is ionic strength (Butler, 1964, p. 473).

The ionic-strength scale on the pH-grid overlay represents the positions to which the pH 8.0 line would be shifted by increased ionic strength. Simultaneous calibration of the graph for temperature and ionic-strength effects is accomplished by positioning the pH grid at the point where the temperature of the solution matches its ionic strength, using the scales on the match line in the lower parts of the two sheets.

Plate 2 provides a simple means of checking chemical analyses for possible conformance to calcite equilibrium. The only computation required is for ionic strength, and this can be obtained by using plate 1; as noted earlier, it also may be possible to estimate a usable number from the specific conductance. The graph does have some practical and theoretical limitations, however, and it is not applicable to all natural waters. Chemical analyses report calcium as a total $Ca^{2+}$, which includes any calcium complexes or ion pairs that are present. Any equilibrium calculation, however, must be based on the actual species of the solutes involved. Calcium forms complexes with bicarbonate and sulfate. The calcium bicarbonate complexes do not affect the usefulness of plate 2 because the basic data of Jacobson and Langmuir (1974) that were used compensate for these complexes. However, the effect of the calcium sulfate ion pair can be substantial, and waters that contain more than a few hundred milligrams of sulfate per liter require a more comprehensive mathematical treatment. Determinations of $HCO_3^-$ by titration are subject to uncertainties noted in the discussion of alkalinity in a later section of this book. The bicarbonate concentration required when using plate 2 is that fraction of the alkalinity present as $HCO_3$ (not total alkalinity as $HCO_3^-$).

The Davies equation does not include a temperature effect on the ion activity. Such a effect is indicated in the extended Debye-Hückel expression used elsewhere in

this book. The design of plate 2 of necessity requires that temperature does not affect the activity coefficient calculation. This simplification probably does not introduce important errors compared with those resulting from other factors that are inherent in applying simple equilibrium models, however.

The system postulated does not contain a gas phase, and an equilibrium among dissolved $CO_2$ species is assumed. Measurements of pH and bicarbonate concentration must be as closely representative of the actual system as possible. This generally requires measurement of both properties in the field at the sampling site, at the temperature of the water source (Barnes, 1964). The calcium concentration in a sample can be stabilized by acidifying the sample at the time of collection so that this property can be measured later in the laboratory. Enough additional determinations must be made to permit calculation of ionic strength.

A less readily controllable requirement for applying calcite equilibrium calculations is that the solid involved is pure calcite and the reaction is directly reversible. The calcium carbonate in most limestones has significant amounts of other divalent cations substitued for $Ca^{2+}$ in the lattice. A congruent reversible equilibrium may not be attainable in such a system, especially if the attacking solution has a Ca:Mg ratio substantially different from the solution in which the initial limestone was produced. However, in many if not most practical systems, a relatively pure secondary calcite precipitate can exist, and its behavior may indeed approximate reversibility well enough to make the model useful. In some environments films of organic matter may form on calcium carbonate surfaces and inhibit precipitation or dissolution.

Plummer and Busenberg (1982) have provided additional solubility data for calcium carbonates that can be used over the temperature range $0°-90°C$. A saturation index (S.I.) for a water can be derived using plate 2 as noted above. Most investigators seem to have thought that experimental and other uncertainties in S.I. values are unlikely to be less than $\pm 0.10$ (Langmuir, 1971) and any system in which the graphically estimated S.I. value is in the range $\pm 0.3$ is probably close to equilibrium.

The determination of S.I. is useful as an indicator of chemical stability and of probable behavior of ground water encountered in wells, where there may be concern over possible deposition of carbonate precipitates on well screens, gravel packs, and water-yielding rock faces. Some aspects of this were discussed by Barnes and Clarke (1969). Such precipitates may be mixtures of various solids and can be expected if waters of differing chemical composition enter the well during operation of the pump.

The occurrence of siderite ($FeCO_3$) in carbonate precipitates that form in pipelines where some iron is available either from the water itself or the distribution

system was noted by Sontheimer and others (1981). These authors suggested that siderite formation was an essential step in the development of a protective calcium carbonate coating, which prevents corrosion of water-distribution pipes.

In the presence of a gas phase containing $CO_2$, computations of calcite solubility can be made in terms of the partial pressure of $CO_2$ and pH. This requires consideration of carbon dioxide solubility, from Henry's Law

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

and the first dissociation of carbonic acid

$$\frac{[HCO_3^-][H^+]}{[H_2CO_3]} = K_1.$$

The activity of $H_2CO_3$ is assumed to include any uncombined dissolved $CO_2$ as well, in accord with conventional practice. Combining these equations with the one for calcite solubility gives, when all three are at equilibrium:

$$\frac{[Ca^{2+}] K_1 K_h P_{CO_2}}{[H^+]^-} = K_s.$$

Values of the equilibrium constants from 0° to 50°C are given in table 33.

This expression gives an indication of the $CO_2$ content of the gas phase that provided a water with its capacity for dissolving calcite. It might be interpreted for ground water as indicative of the partial pressure of $CO_2$ in the unsaturated zone through which recharge passed as it moved toward the water table. Subsequent reaction between $CO_2$ species and calcite would presumably have occurred in the absence of a gas phase, and no replenishment of $CO_2$ could occur. Depending on the nature of water circulation and water table fluctuations, this may or may not be a valid assumption. Some replenishment of the dissolved $CO_2$ in the zone of saturation might occur in some systems, owing to $SO_4^{2-}$ reduction.

Observations and calculations were made by Deines and others (1974), on the basis of $^{13}C$ contents and the foregoing equilibria, on ground-water systems in limestone in the Nittany Valley of Pennsylvania. The $P_{CO_2}$ values for these waters ranged from $10^{-1.3}$ to $10^{-1.8}$ atmospheres. It appeared that after equilibrating with the gas phase the water generally reacted with calcite under closed-system conditions like those postulated for plate 2.

In the discussions of pH and of the phase rule it was shown that a closed system containing water, carbon dioxide gas, and calcite would have 1 degree of freedom.

The activity of dissolved calcium in such a system is therefore specified if a value for $P_{CO_2}$ is specified. The equations required for computing the activity of $Ca^{2+}$ include five chemical equilibria and a cation-anion balance equation, and enough information to permit calculating activity coefficients. Temperature effects can be included by using appropriate equilibrium constants from table 33. The final product could be a graph of calcium concentration versus $P_{CO_2}$ for specified temperature and ionic strength. Calculations of this type were described by Garrels and Christ (1964, p. 81–83).

Natural systems contain other solutes and solids, and this kind of calculation has a somewhat limited practical applicability. Figure 18 is a graph of calcite solubility in terms of calcium concentration and $CO_2$ partial pressure based on laboratory experimental data at 25°C that were published by Frear and Johnston (1929).

The $CO_2$ content of normal air is 0.03 percent (by volume), or 0.0003 atmosphere. At this $P_{CO_2}$, the solubility indicated by the Frear and Johnston data in figure 18 for calcium in water in contact with air is about 20 mg/L. Garrels and Christ (1964, p. 83), using other
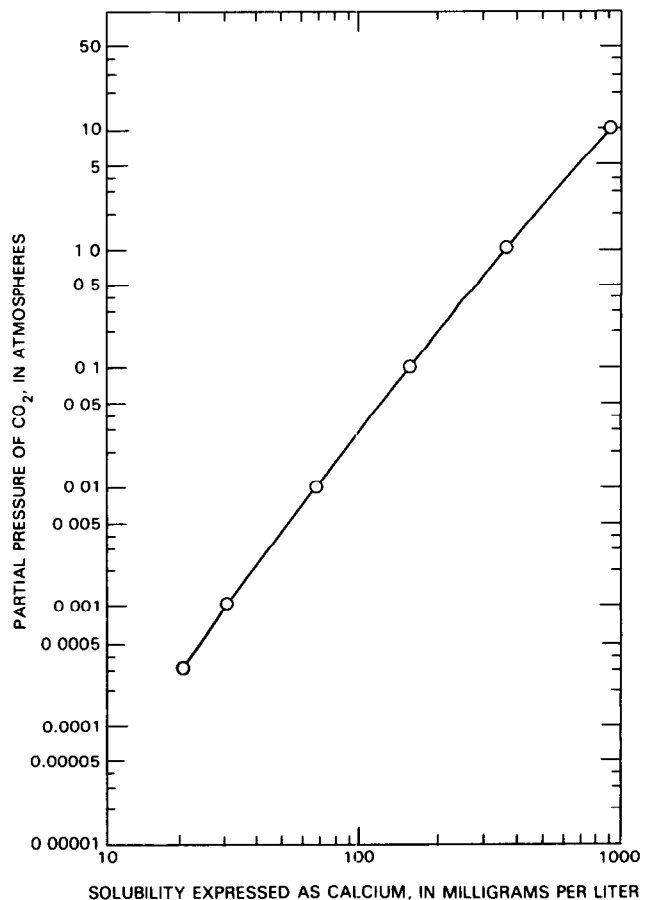


Figure 18. Solubility of calcium carbonate (calcite) in water at 25°C as a function of partial pressure of $CO_2$.

published thermodynamic data, calculated a solubility of 16 mg/L under these conditions.

If the input of $H^+$ is solely from the water itself and carbon dioxide is absent, the solubility of calcite is 5.4 mg/L of calcium (Askew, 1923). It is of interest to note that this solution would have a pH between 9.0 and 10.0. Garrels and Christ (1964, p. 81) observed this experimentally. They further calculated (p. 88) that rainwater that had dissolved all the carbon dioxide possible through equilibrium with air and then was equilibrated with calcite in the absence of a gas phase could dissolve hardly any more calcium than pure water and would also reach a high pH. Such a solution is not a very effective solvent for calcite in a stoichiometric sense. However, other solutes that may be present in rainwater ("acid rain") may substantially increase its solvent power.

From figure 18 it is evident that the concentrations of calcium that are common in waters in regions where carbonate rocks occur generally are well above the level specified for the partial pressure of carbon dioxide in the atmosphere. Water percolating through the soil and the unsaturated zone above the water table, however, is exposed to air in pore spaces in the soil, which is greatly enriched in carbon dioxide. Partial pressures of carbon dioxide in soil air are commonly 10–100 times the levels reached in the atmosphere (Bolt and Bruggenwert, 1978, p. 11). The carbon dioxide content of soil air for the most part results from plant respiration and from decay of dead plant material and can be expected to be greatest in environments that support dense stands of vegetation.

Observations and calculations of $P_{CO_2}$ for groundwater systems commonly give values between $10^{-1.0}$ and $10^{-2.5}$ for $P_{CO_2}$ in the gas phase. Values reported by Deines and others (1974) already cited are typical of systems in temperate regions where vegetation is abundant. Other souces of $CO_2$ such as sulfate reduction and oxidation of lignite fragments may be significant in some systems.

For dolomitic terranes, a reversible equilibrium is more difficult to attain, but a model postulating equilibrium has been shown by some workers to predict composition of ground water reasonably well (Barnes and Back, 1964a; Langmuir, 1971). This equilibrium will be considered more fully in discussing magnesium in the next section.

In environments in which hydrogen ions are supplied for rock weathering by processes other than dissociation of dissolved carbon dioxide species, for example, by oxidation of sulfur or sulfides, calcium may be brought into solution in amounts greater than the stoichiometric equivalent of bicarbonate. In such a system, or where water is in contact with solid gypsum or anhydrite, the maximum calcium concentration that could be reached would generally be determined by equilibria in which gypsum is a stable solid. Systems in which calcium solubility might be controlled by fluoride, phosphate, or other anions likely to occur only at low concentrations can be postulated but are likely to be rare in the real world.

The effect of cation-exchange processes on calcium concentrations in water differs from mineral dissolutions or precipitations in that only cations are directly involved. The requirement of anion-cation balance in the reacting solution thus prevents simple cation exchange or desorption from increasing or decreasing the total ionic load. Cation-exchange processes can bring about changes in the ratio of calcium to other cations in solution. Also, this effect in systems in which each liter of the water is in contact with an extensive area of solid surface tends to maintain a relatively constant Ca:Na ratio.

Reaction rates for calcium carbonate precipitation have been studied rather extensively. The presence of a favorable solid surface is a substantial aid in starting precipitation from a solution that is supersaturated. The rate of attainment of calcite saturation in ground water moving through a limestone aquifer depends on the nature of the flow system and the intimacy of contact of the water with calcite surfaces as well as on chemical factors. Studies in Pennsylvania showed that water of "conduit type" springs where residence time of the water was short (days or weeks) commonly is unsaturated. Water from "diffuse type" springs where residence time is measured in months is generally near saturation (Deines and others, 1974).

Studies by Plummer and Back (1980) showed that a continuing irreversible dissolution of dolomite and gypsum with some precipitation of calcite occurred along flow paths in the Floridan aquifer in Florida, and in the Madison limestone in South Dakota.

### Occurrence of Calcium in Water

Applicability of the chemical models for calcium to natural waters can be illustrated with some of the tabulated analyses in this paper.

Generally calcium is the predominant cation in river water. Analysis 7 in table 15 is for the Cumberland River at Smithland, Ky., near the point where it joins the Ohio River. The pH of river water is influenced by many factors, especially by photosynthesizing organisms. These organisms commonly cause diurnal and seasonal fluctuations, with higher pH values on summer days and lower values at night and during other periods of low photosynthetic activity. The measured pH in river water is generally not well correlated with calcium and bicarbonate activities. However, the calcium concentration of the Cumberland River water, 25 mg/L, is not greatly above that which could occur in water in equilibrium with calcite in contact with air (20 mg/L, as shown in fig. 18). It is interesting to note that the average concentration of

calcium in river water, shown as 13.4 to 15 mg/L in table 3, is also not far from an equilibrium value for a system containing calcite in contact with air. At equilibrium, however, a pH much greater than is usually observed in river water would be predicted.

Rivers in more arid regions, especially where some of the more soluble rock types are exposed, tend to have much higher dissolved-calcium concentrations. Analysis 8, table 15, is a discharge-weighted average of the composition observed for a year in the Pecos River at Artesia in southeastern New Mexico. It shows clearly the influence of gypsum, which is abundant in the Pecos drainage basin.

When river water is impounded in a storage reservoir, changes may occur in calcium content as a result of calcium carbonate precipitation. The increased pH near the water surface, caused by algae and plankton, may bring about supersaturation, and precipitation can occur on solid surfaces around the edges of the water body. A conspicuous white deposit developed around the edges of Lake Mead on the Colorado River between Arizona and Nevada as a result of this process. In part, the deposition in that reservoir also was related to inflows that are high in calcium and to the solution of gypsum beds exposed in the reservoir in the first few decades after the beginning of the storage of water (Howard, 1960, p. 119–124). A quantitative study of the changes that occurred in stored water composition, owing to gypsum solution and calcium carbonate deposition, was made by Bolke (1979) on the Flaming Gorge reservoir on the Green River in Wyoming and Utah. During the period 1963–75, there was a net gain of 1,947,000 metric tons in dissolved-solids load of the river attributable to effects of this kind within the reservoir. The freshwater deposit called marl, which is formed in many lakes, is made up partly of calcium carbonate.

**Table 15. Analyses of waters in which**

[Analyses by U.S Geological Survey. Date below sample number is date of collection. Sources of data: 1, 4, and 9, Scott and Barker (1962, p. 19, 47, 59); 2,

| Constituent | 1 Mar. 28, 1952 | | 2 May 20, 1950 | | 3 Nov. 25, 1949 | | 4 Mar. 26, 1952 | |
|---|---|---|---|---|---|---|---|---|
| | mg/L | meq/L | mg/L | meq/L | mg/L | meq/L | mg/L | meq/L |
| Silica (SiO$_2$) | 8.6 | | 22 | | 29 | | 130 | |
| Iron (Fe) | .05 | | | | | | 41 | |
| Manganese (Mn) | | | | | | | | |
| Calcium (Ca) | 48 | 2.395 | 144 | 7.19 | 636 | 31.74 | 93,500 | 4,665.65 |
| Magnesium (Mg) | 3.6 | .296 | 55 | 4.52 | 43 | 3.54 | 12,100 | 995.35 |
| Sodium (Na) | } 2.1 | .091 | 29 | 1.24 | 17 | .74 { | 28,100 | 1,222.35 } |
| Potassium (K) | } | | | | | { | 11,700 | 299.17 } |
| Bicarbonate (HCO$_3$) | 152 | 2.491 | 622 | 10.19 | 143 | 2.34 | 0 | .00 |
| Sulfate (SO$_4$) | 3.2 | .067 | 60 | 1.25 | 1,570 | 32.69 | 17 | .35 |
| Chloride (Cl) | 8.0 | .226 | 53 | 1.49 | 24 | .68 | 255,000 | 7,193.55 |
| Fluoride (F) | .0 | | .4 | .02 | | | | |
| Nitrate (NO$_3$) | | | .3 | .00 | 18 | .29 | | |
| Dissolved solids: | | | | | | | | |
| Calculated | 148 | | 670 | | 2,410 | | [1]408,000 | |
| Residue on evaporation | | | | | | | 415,000 | |
| Hardness as CaCO$_3$ | 135 | | 586 | | 1,760 | | | |
| Noncarbonate | 10 | | 76 | | 1,650 | | | |
| Specific conductance (micromhos at 25°C). | 269 | | 1,120 | | 2,510 | | ([3]) | |
| pH | 7.5 | | | | | | 5.29 | |
| Color | | | | | | | | |

[1]Includes strontium (Sr) 3,480 mg/L, 79.43 meq/L; bromide (Br) 3,720 mg/L, 46.56 meq/L; iodide (I) 48 mg/L, 0.38 meq/L.
[2]Includes 0.70 mg/L lithium (Li) and 0.03 mg/L zinc (Zn).
[3]Density at 46°C, 1.275 g/mL.

1. Big Spring, Huntsville, Ala Temperature, 16.1°C. Water-bearing formation, Tuscumbia Limestone.
2 Spring on Havasu Creek near Grand Canyon, Ariz. Flow, 100 gpm; temperature, 19.4°C. Water-bearing formation, limestone in the Supai Formation. Water deposits travertine.
3. Jumping Springs, SE1/4 sec. 17, T. 26 S., R. 26 E., Eddy County, N. Mex. Flow, 5 gpm. Water-bearing formation, gypsum in the Castile Formation.
4. Brine well 3 Monroe, SE1/4 sec. 27, T. 14 N., R. 2 E , Midland, Mich. Depth, 5,150 ft; temperature, 46.1°C. Water-bearing formation, Sylvania Sandstone.

In closed basins, water can escape only by evaporation, and the residual water can be expected to change in composition after a fairly well defined evolutionary pattern. The less soluble substances, including calcium carbonate, are lost first, followed by calcium sulfate (Swenson and Colby, 1955, p. 24–27). The Salton Sea in Imperial Valley, Calif., is fed by irrigation drainage, and since its origin, during flooding by the Colorado River in 1907, it has become rather highly mineralized. Hely and others (1966) concluded that the water of the Salton Sea in 1965 was at saturation with respect to gypsum because the water seemed incapable of dissolving powdered gypsum in a laboratory experiment.

Equilibrium solubilities can be expected to control calcium concentrations in many ground-water systems. Unfortunately, many published chemical analyses of such waters are unsuitable for rigorous testing of calcite-solubility models owing to lack of accurate onsite measurements for pH and alkalinity. Most of the analyses in

calcium is a major constituent

the tables in this book also have this shortcoming. However, if the acceptable uncertainty in saturation index calculations is broadened, the application of calcite equilibria to some of the ground-water analyses may be useful here. Approximations of this kind often are of value in water-analysis interpretation.

Analysis 1 in table 15 represents a large limestone spring, and as might be expected the water evidently is not far from calcite equilibrium. The calculated S.I. value for this solution is -0.21. The water represented by analysis 9 in table 16 also came from a limestone. Although this solution is less dominated by calcium and bicarbonate, it also is near calcite equilibrium, with an S.I. of +0.20.

Springs that form deposits of travertine are common in many areas of the United States (Feth and Barnes, 1979). Analysis 3, table 11, represents the water from such a spring which issues from Redwall Limestone in the Grand Canyon region of Arizona. Such waters are

6, and 10, U.S Geological Survey, unpublished data; 3 and 5, Hendrickson and Jones (1952); 8, U.S. Geological Survey Water-Supply Paper 1163 (p. 360)]

| 5 Jan. 26, 1948 | | 6 June 23, 1949 | | 7 May 19, 1952 | | 8 1948 and 1949 | | 9 June 6, 1954 | | 10 Dec. 8, 1954 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| mg/L | meq/L | mg/L | meq/L | mg/L | meq/L | mg/L | meq/L | mg/L | meq/L | mg/L | meq/L |
|  |  | 74 |  | 4.9 |  | 17 |  | 24 |  | 15 |  |
|  |  |  |  | .04 |  |  |  | .02 |  | 1.0 |  |
|  |  |  |  |  |  |  |  | .00 |  | .01 |  |
| 99 | 4.94 | 277 | 13.82 | 25 | 1.248 | 394 | 19.66 | 88 | 4.39 | 96 | 4.790 |
| 28 | 2.30 | 64 | 5.26 | 3.9 | .321 | 93 | 7.65 | 7.3 | .60 | 19 | 1.562 |
| 4.1 | .18 | 53 | 2.29 { | 4.5 | .196 } | 333 | 14.48 { | 19 | .83 | 18 | .783 |
|  |  |  |  | 1.4 | .036 } |  |  | 2.8 | .07 | 1.5 | .038 |
| 287 | 4.70 | 85 | 1.39 | 90 | 1.475 | 157 | 2.57 | 320 | 5.24 | 133 | 2.180 |
| 120 | 2.50 | 113 | 2.35 | 12 | .250 | 1,150 | 23.94 | 6.7 | .14 | 208 | 4.330 |
| 6 | .17 | 605 | 17.06 | 2.2 | .062 | 538 | 15.17 | 13 | .37 | 25 | .705 |
|  |  | .2 | .01 | .1 | .005 |  |  | .3 | .02 | .4 | .021 |
| 2.8 | .05 | 35 | .56 | 1.9 | .031 | 5.0 | .08 | 4.6 | .07 | .4 | .006 |
| 401 |  | 1,260 |  | 100 |  | 2,610 |  | 323 |  | [2]449 |  |
|  |  |  |  | 99 |  |  |  | 322 |  | 468 |  |
| 362 |  | 954 |  | 78 |  | 1,370 |  | 250 |  | 318 |  |
| 127 |  | 884 |  | 5 |  | 1,240 |  | 0 |  | 209 |  |
| 651 |  | 2,340 |  | 172 |  | 3,540 |  | 543 |  | 690 |  |
|  |  |  |  | 6.7 |  |  |  | 7.5 |  | 7.8 |  |
|  |  |  |  | 5 |  |  |  | 2 |  | 3 |  |

5. Rattlesnake Spring, sec. 25, T. 24 S., R 23 E., Eddy County, N. Mex. Flow, 2,500 gpm  Water-bearing formation, alluvium, probably fed by the Capitan Limestone.
6 Irrigation well, NE1/4 sec 35, T. 1 S., R. 6 E., Maricopa County, Ariz. Temperature, 25.6°C. Water-bearing formation, alluvium
7. Cumberland River at Smithland, Ky. Discharge, 17,100 cfs.
8. Pecos River near Artesia, N. Mex. Discharge-weighted average, 1949 water year; mean discharge, 298 cfs.
9 City well at Bushton, Rice County, Kans. Depth, 99 ft. Water-bearing formation, Dakota Sandstone.
10. Industrial well, Willimansett, Mass. Depth, 120 ft; temperature, 12.2°C. Water-bearing formation, Portland Arkose.

substantially supersaturated at normal atmospheric pressure. Reaching the calcium activity in this analysis by solution of calcite would require a partial pressure of $CO_2$ near 0.4 atmosphere (fig. 18). The S.I. calculated for this analysis is +0.13. Other travertine-depositing springs are represented by analyses given by White and others (1963, p. F54).

Analysis 9 in table 15 represents water from sandstone with calcareous cement that has given the solution a character typical of saturation with calcite. The S.I. for this solution is +0.28.

Analysis 3 in table 15 is for a spring that issues from gypsum. From the expressions

$$[Ca^{2+}][SO_4^{2-}]=10^{-4.625}$$

and

$$\frac{[CaSO_4]}{[Ca^{2+}][SO_4^{2-}]}=10^{2.31}$$

(equilibrium constants for 25°C from Sillen and Martell, 1964) the saturation index for this water can be calculated, by the procedure outlined under the heading "Solubility Product." The S.I. value obtained is −0.025, indicating a close approach to equilibrium. The effect of temperature departure from 25°C was not considered in this calculation but is less important for gypsum that it would be for calcite equilibria. Evaluations for gypsum saturation pose few measurement or sample-stability problems, but calculations are tedious if done by hand.

Equilibrium with respect to gypsum is obviously to be expected in ground water from a gypsiferous aquifer. The water represented by analysis 3, table 15, is predominantly a solution of calcium and sulfate. As the amount of other solutes increases, the solubility of gypsum will tend to increase owing to greater ionic strength and smaller activity coefficients. In a solution containing 2,500 mg/L of chloride and about 1,500 mg/L of sodium, the equilibrium concentration of calcium would be near 700 mg/L. These calculations presuppose nearly equivalent concentrations of calcium and sulfate. Frequently, this does not occur in natural water. When the solution is in equilibrium with gypsum, however, any increase in sulfate activity would be matched by a decrease in calcium as $CaSO_4$ precipitates (see also fig. 21).

Natural brines in which the predominant dissolved ions are calcium and chloride are fairly common. An example is represented by analysis 4 in table 15. There is no general agreement as to how such a composition is reached. Water that has been trapped underground for a long time could be altered from its original composition by selective permeability of strata for different solutes, by the bacterial reduction of sulfate and other dissolved ions, and by adsorption or desorption of dissolved ions,

as well as by chemical solution or precipitation of minerals. The formation of calcium chloride brine was ascribed by Valyashko and Vlasova (1965) to a combination of concentration and ion-exchange processes.

The process of cation exchange in ground-water bodies has been observed extensively since early studies by Renick (1924) called attention to natural softening of ground water by cation exchange in sediments underlying the northern Great Plains area of the United States. Ground water that has exchanged calcium for sodium is common in many areas (see analyses 1 and 2, table 17). The reverse effect, exchange of sodium for calcium, also can be expected but is less well documented. In localities near the ocean where seawater has entered freshwater aquifers, the advancing saltwater front commonly carries higher proportions of calcium to sodium than are characteristic of seawater (Poland and others, 1959, p. 193), owing to release of calcium from exchange positions by the sodium brought in by the advancing saltwater.

In irrigated areas, the exchange of calcium for sodium in soil moisture may proceed forward or in reverse at different times and in any specific spot may fluctuate extensively. The residual solutes from the irrigation water that was used by the crop or evaporated from the soil, however, will partly reappear in drainage water. The water of the Salt River, which is extensively used for irrigation in the Phoenix, Ariz., area, is shown by analysis 5, table 17, to contain nearly twice as many milliequivalents per liter of $Na^+$ as of $Ca^{2+}+Mg^{2+}$. The ion ratio in the effluent, principally drainage of residual irrigation water, is represented by analysis 6, table 17; it has a slightly higher proportion of the divalent ions, and this suggests that the exchange reactions are occurring, even though a good deal of the calcium present in the initial water probably is precipitated as carbonate or, possibly, sulfate in the irrigated area. The effect is more strongly shown by analysis 6, table 15, which represents water from a well in the area irrigated with Salt River water, where recharge is composed of irrigation drainage water. The milliequivalents per liter concentration of sodium in the water is far lower than that of calcium.

Water that is strongly influenced by irrigation return flow may approach simultaneous equilibrium with both calcite and gypsum. Water of the Gila River at Gillespie Dam near Gila Bend, Ariz., and the Rio Grande at Fort Quitman, Tex., shows these properties at times (Hem, 1966). Whether analysis 3, table 15, depicts equilibrium with both solids cannot be determined because the pH is not known.

## Magnesium

Magnesium is an alkaline-earth metal and has only one oxidation state of significance in water chemistry, $Mg^{2+}$. It is a common element and is essential in plant and animal nutrition.

In some aspects of water chemistry, calcium and magnesium may be considered as having similar effects, as in their contributions to the property of hardness. The geochemical behavior of magnesium, however, is substantially different from that of calcium. Magnesium ions are smaller than sodium or calcium ions and can be accommodated in the space at the center of six octahedrally coordinated water molecules, an arrangement similar to that described for aluminum. The hydration shell of the magnesium ion is not as strongly held as that of aluminum ions, but the effect of hydration is much greater for magnesium than for the larger ions of calcium and sodium. The tendency for precipitated crystalline magnesium compounds to contain water or hydroxide is probably related to this hydration tendency.

## Sources of Magnesium

In igneous rock, magnesium is typically a major constituent of the dark-colored ferromagnesian minerals. Specifically, these include olivine, the pyroxenes, the amphiboles, and the dark-colored micas, along with various less common species. In altered rocks, magnesian mineral species such as chlorite and serpentine occur. Sedimentary forms of magnesium include carbonates such as magnesite and hydromagnesite, the hydroxide brucite, and mixtures of magnesium with calcium carbonate. Dolomite has a definite crystal structure in which calcium and magnesium ions are present in equal amounts.

The alteration of magnesian olivine (forsterite) to serpentinite can be written

$$5Mg_2SiO_4+8H^++2H_2O$$
$$=Mg_6(OH)_8Si_4O_{10}+4Mg^{2+}+H_4SiO_4.$$
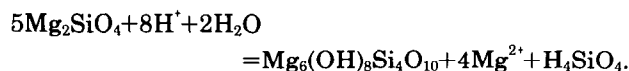
This is somewhat analogous to the reactions shown previously for weathering of feldspar and produces a solid alteration product, serpentinite. The reaction, like that for the alteration of other silicates, is not reversible and cannot be treated as a chemical equilibrium. Released products, however, can be expected to participate in additional reactions.

## Form of Dissolved Magnesium

The magnesium ion, $Mg^{2+}$, will normally be the predominant form of magnesium in solution in natural water. Data given by Sillen and Martell (1964, p. 41–42) show that the complex $MgOH^+$ will not be significant below about pH 10. The ion pair $MgSO_4(aq)$ has about the same stability as the species $CaSO_4(aq)$, and magnesium complexes with carbonate or bicarbonate have approximately the same stability as the similar species of calcium. The sulfate ion pair and the bicarbonate complex will be significant if the solution contains more than 1,000 mg/L of sulfate or bicarbonate.

## Chemical Controls of Magnesium Concentration

Carbonate equilibria involving magnesium are more complicated that those governing calcium activities. There are several different forms of magnesium carbonates and hydroxycarbonates and they may not dissolve reversibly. Magnesite, $MgCO_3$, from solubility products given by Sillen and Martell (1964, p. 136, 137), seems to be about twice as soluble as calcite. However, the hydrated species nesquehonite, $MgCO_3 \cdot 3H_2O$, and lansfordite, $MgCO_3 \cdot 5H_2O$, are considerably more soluble than magnesite. The basic carbonate hydromagnesite, $Mg_4(CO_3)_3$ $(OH)_2 \cdot 3H_2O$, may be the least soluble species under some conditions. Magnesite apparently is not usually precipitated directly from solution, and, as noted by Hostetler (1964), a considerable degree of supersaturation with respect to all magnesium carbonate species may be required before precipitation can occur. In any event, such species are rarely significant factors in limiting magnesium content of water.

Magnesium occurs in significant amounts in most limestones. The dissolution of this material obviously brings magnesium into solution, but the process is not readily reversible—that is, the precipitate that forms from a solution that has attacked a magnesian limestone may be nearly pure calcite. Magnesium concentration would tend to increase along the flow path of a ground water undergoing such processes, until a rather high [Mg]:[Ca] ratio is reached.

Conditions under which direct precipitation of dolomite from solution occurs are not commonly found in natural-water (nonmarine) environments. Dolomite precipitates have been found in saline lakes in various places. Hostetler (1964) cited reports of its occurrence from South Australia, Austria, Utah, and the U.S.S.R. but noted that the concentrations of magnesium, calcium, and carbonate ions in water associated with the dolomite seemed to be above theoretical saturation limits in many instances.

Recent workers seem to be in fairly general agreement that the solubility product for dolomite is near $10^{-17\ 0}$ at 25 °C. Langmuir (1971) accepted this value and calculated values of $10^{-16\ 56}$ at 0°, $10^{-16\ 71}$ at 10°, and $10^{-16.89}$ at 20°C. Earlier, several investigators (Hsu, 1963; Barnes and Back, 1964a; Holland and others, 1964) used analyses of ground water in association with dolomite to calculate an ion-activity product near $10^{-16\ 5}$. The general characteristics of ground water from dolomitic terrane suggest that saturation with respect to calcite also occurs in many such waters. Yanat'eva (1954) reported that dolomite was somewhat more soluble than calcite under a partial pressure of $CO_2$ approaching that of ordinary air.

The attainment of a relatively stable value for the activity product is possible in a system in which calcite is precipitated while dolomite dissolves. Long residence times of water in such systems would produce [Mg]:[Ca] ratios above 1.0 and a high pH, with both tending to increase along the flow path. This mechanism is treated quantitatively in the mass-balance model that Plummer and Back (1980) applied to the Floridan and the Madison Limestone aquifers. Carbon dioxide could be replenished within these systems through sulfate reduction and, theoretically at least, very high magnesium concentrations might ultimately be reached. Magnesium hydroxide (brucite) occurs naturally, and the solubility product at 25°C is between $10^{-10}$ and $10^{-11}$ (Sillen and Martell, 1964, p. 41–42). Precipitation of this solid implies a high pH and a solution impoverished in dissolved carbon dioxide species.

The cation-exchange behavior of magnesium is similar to that of calcium. Both ions are strongly adsorbed by clay minerals and other surfaces having exchange sites.

Some magnesium silicate minerals can be synthesized readily in the laboratory at 25°C. Siffert (1962), for example, prepared sepiolite ($Mg_3Si_4O_{11}\cdot4H_2O$) by precipitation from solutions of $Si(OH)_4$ and $MgCl_2$ at a pH of 8.73 or higher. This mineral or a related species may have a significant effect on magnesium concentration in weathering solutions acting on magnesium-rich igneous rock.

Eaton and others (1968) proposed that the solubility of magnesium in irrigation drainage water might be limited by precipitation of a magnesium silicate of unspecified composition in the soil. A magnesium sink is needed to explain the loss of magnesium that is commonly observed in such waters.

Table 7, which shows residence times of the elements in the ocean, points up another factor of some importance: Magnesium has a very long residence time compared

**Table 16.** Analyses of waters in which

[Analyses by U.S. Geological Survey except as indicated. Date under sample number is date of collection. Sources of data: 1, 3–7, and 9, U.S. Geological Survey,

| Constituent | 1 Feb. 27, 1952 | | 2 April 11, 1952 | | 3 Sept. 29, 1948 | | 4 Oct. 18, 1957 | |
|---|---|---|---|---|---|---|---|---|
| | mg/L | meq/L | mg/L | meq/L | mg/L | meq/L | mg/L | meq/L |
| Silica (SiO₂) | 8.4 | | 18 | | 31 | | 175 | |
| Aluminum (Al) | 1.4 | | | | | | | |
| Iron (Fe) | .24 | | 1.4 | | | | | |
| Calcium (Ca) | 40 | 1.996 | 94 | 4.69 | 20 | 1.00 | 34 | 1.70 |
| Magnesium (Mg) | 22 | 1.809 | 40 | 3.29 | 42 | 3.45 | 242 | 19.90 |
| Sodium (Na) | .4 | .017 | 17 | .74 | 19 | .83 | 184 | 8.00 |
| Potassium (K) | 1.2 | .031 | 2.2 | .06 | | | 18 | .46 |
| Carbonate (CO₃) | 0 | | 0 | | 0 | | 0 | |
| Bicarbonate (HCO₃) | 213 | 3.491 | 471 | 7.72 | 279 | 4.57 | 1,300 | 21.31 |
| Sulfate (SO₄) | 4.9 | .102 | 49 | 1.02 | 22 | .46 | 6.6 | .14 |
| Chloride (Cl) | 2.0 | .056 | 9.0 | .25 | 7 | .20 | 265 | 7.47 |
| Fluoride (F) | .0 | .000 | .8 | .04 | .2 | .01 | 1.0 | .05 |
| Nitrate (NO₃) | 4.8 | .077 | 2.4 | .04 | 2.5 | .04 | .2 | .00 |
| Dissolved solids: | | | | | | | | |
| Calculated | 190 | | 466 | | 281 | | [1]1,580 | |
| Residue on evaporation | 180 | | 527 | | | | | |
| Hardness as CaCO₃ | 190 | | 400 | | 222 | | 1,080 | |
| Noncarbonate | 16 | | 13 | | 0 | | 14 | |
| Specific conductance (micromhos at 25°C). | 326 | | 764 | | 458 | | 2,500 | |
| pH | 7.4 | | 6.7 | | 8.2 | | 6.5 | |
| Color | 5 | | 5 | | | | | |

[1]Includes 18 mg/L of boron (B).

[2]Contains 0.01 mg/L of manganese (Mn) and 0 9 mg/L of lithium (Li).

[3]Density, 1,345 g/mL.

1. Spring 2½ mi northwest of Jefferson City, Tenn. Flow, 5,000 gpm; temperature, 14 4°C. From the Knox Dolomite.

2. Well number 5, City of Sidney, Ohio. Depth, 231 ft; temperature, 11.7°C. Water-bearing formation, Niagara Group.

3. Spring in Buell Park, Navajo Indian Reservation, Ariz. Flow, 18 gpm; temperature 12.2°C. Water-bearing formation, olivine tuff-breccia.

4. Main spring at Siegler Hot Springs, NE1/4 sec. 24, T. 12 N., R. 8 W., Lake County, Calif. Water issues from contact with serpentine and sedimentary rocks. Temperature, 52.5°C.

with calcium. Organisms that require calcium for shell or skeletal parts represent an important factor in calcium precipitation. Such demands on magnesium are much smaller.

### Occurrence of Magnesium in Water

Analyses in table 16 can be used to demonstrate some of the effects of dolomite dissolution on magnesium content and other properties of natural water. As noted earlier, the calculation of S.I. values from these data is subject to an unknown but probably substantial uncertainty because the reported pH values are laboratory determinations. Analyses 1, 2, and 10 represent ground waters from dolomitic terranes and analysis 9 is for ground water from limestone containing dolomite.

Before it reaches saturation with respect to either dolomite or calcite, a water passing through dolomite should dissolve equal molar amounts of calcium and magnesium. Analyses 1 and 2 in table 16 have negative values for S.I. for calcite and for dolomite. Analysis 1 has nearly equal meq/L values for calcium and magnesium. The greater proportion of calcium in analysis 2 may reflect the fact that the rocks of the Niagara Group, from which the water comes, include limestone as well as dolomite.

Water represented by analysis 10, table 16, has substantial supersaturation with respect to calcite (S.I.=+0.40) and a calculated S.I. for dolomite of +0.99. Dissolved magnesium exceeds calcium in this water, and this can be explained by calcite precipitation after reaching supersaturation. As noted earlier, dolomite does not precipitate readily under these conditions. Analysis 5 in table 16 illustrates this behavior even more strongly. This water is from a pool in Carlsbad Caverns, N. Mex., in which calcite is precipitating. The dolomite S.I. in this solution is +1.58.

magnesium is a major constituent

unpublished data; 2, 8, and 10, Scott and Barker (1962, p. 19, 87, 113)]

| 5 Apr. 20, 1945 | | 6 Feb. 7, 1939 | | 7 May 21, 1952 | | 8 May 27, 1952 | | 9 Mar. 11, 1952 | | 10 Oct. 29, 1954 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| mg/L | meq/L | mg/L | meq/L | mg/L | meq/L | mg/L | meq/L | mg/L | meq/L | mg/L | meq/L |
| 11 | | | | 4.2 | | 12 | | 13 | | 18 | |
| | | | | | | 1.0 | | | | .2 | |
| .04 | | | | .13 | | .03 | | .01 | | .39 | |
| 16 | .80 | 130 | 6.49 | 18 | .898 | 23 | 1.148 | 140 | 6.99 | 35 | 1.747 |
| 71 | 5.84 | 51,500 | 4,236.39 | 8.5 | .699 | 12 | .987 | 43 | 3.54 | 33 | 2.714 |
| 7.8 | .34 | 59,000 | 2,566.60 | 2.5 | .109 | 1.7 | .074 | 21 | .91 | 28 | 1.218 |
| | | 2,810 | 71.85 | 2.4 | .061 | 1.6 | .041 | | | 1.3 | .033 |
| 21 | .70 | | | 0 | | 0 | | 0 | | 0 | .000 |
| 320 | 5.25 | 1,860 | 30.49 | 90 | 1.475 | 127 | 2.081 | 241 | 3.95 | 241 | 3.950 |
| 21 | .44 | 299,000 | 6,225.18 | 9.5 | .198 | 1.6 | .033 | 303 | 6.31 | 88 | 1.832 |
| 8 | .23 | 22,600 | 637.55 | 1.5 | .042 | 2.0 | .056 | 38 | 1.07 | 1.0 | .028 |
| 1.0 | .05 | | | .0 | .000 | .0 | .000 | .8 | .04 | .9 | .047 |
| 19 | .31 | | | .8 | .013 | .9 | .014 | 4.1 | .07 | 1.2 | .019 |
| 333 | | 436,000 | | 92 | | 119 | | 682 | | ²326 | |
| 321 | | 510,000 | | 106 | | 108 | | 701 | | 329 | |
| 332 | | | | 80 | | 107 | | 526 | | 224 | |
| 34 | | | | 6 | | 3 | | 329 | | 27 | |
| 570 | | (³) | | 165 | | 197 | | 997 | | 511 | |
| 8.3 | | | | 7.0 | | 7.6 | | 7.4 | | 8.2 | |
| | | | | 35 | | 5 | | | | | |

5. Green Lake in Carlsbad Caverns, N. Mex. Pool of ground-water seepage.

6. Test well one, SW1/4 sec. 24, T. 25 S., R. 26 E., Eddy County, N. Mex. Water from 142–195 ft.

7. Wisconsin River at Muscoda, Grant County, Wis. Flows through area of magnesian limestone.

8. Spring, SW1/4 sec. 26, T. 16 S., R. 7 E., Calhoun County, Ala. Supplies city of Anniston. Flow, 46 cfs; temperature, 17.8°C. Water-bearing formation, quartzite.

9. Oasis flowing well, SW1/4 sec. 15, T. 11 S., R. 25 E., Chaves County, N. Mex. Depth, 843 ft; flow, more than 9,000 gpm when drilled. Water-bearing formation, San Andreas Limestone (limestone and dolomitic limestone, with minor amounts of sandstone, gypsum, and anhydrite). Temperature, 20.6°C.

10. Drilled well, NW1/4 sec. 6, T. 6 N., R. 21 E., Milwaukee County, Wis. Depth, 500 ft; temperature, 10.0°C. Water-bearing formation, Niagara Dolomite.

A similar effect may be noted by comparing analyses 1 and 2 in table 11. These represent "before and after" composition of a water that lost calcium from solution by formation of a calcium carbonate precipitate inside the sample bottle during storage.

Analysis 9 in table 16 represents water from the Roswell artesian system in southeastern New Mexico. This water is in contact with limestone and dolomite and appears to be near saturation with respect to both calcite and dolomite; computed values for S.I. are +0.20 and +0.18, respectively.

Analysis 7 in table 16 represents water from the Wisconsin River. The rather high proportion of magnesium to calcium in streams of that region was pointed out many years ago by Clarke (1924a).

The chemical reaction written earlier in this discussion for the conversion of olivine to serpentinite indicates that the process consumes much $H^+$. This could also be considered equivalent to production of $OH^-$. Barnes and others (1967) called attention to ground waters of unusual composition that they observed in association with fresh or partly serpentinized peridotite or dunite. An example is given as analysis 5, table 18. This water had a pH of 11.78 and carbonate species were below detection. The magnesium concentration is very small owing to precipitation of brucite ($Mg(OH)_2$). At the calcium concentration reported in the analysis, only a few tenths of a milligram of $CO_3^{2-}$ per liter could be present at equilibrium with $CaCO_3$. Barnes, O'Neil, and Trescases (1978) have cited other examples of these "ultrabasic" waters, from Oman, New Caledonia, and Yugoslavia. The hydroxide concentration in analysis 5, table 18, was calculated from the pH value, which was measured in the field at the time of sample collection. Some of the calcium is probably present as the $CaOH^+$ complex, and the silica and aluminum would be present in anionic form at this pH. With these factors taken into account, the cation-anion balance is satisfactory.

## Sodium

Sodium is the most abundant member of the alkali-metal group of the periodic table. The other naturally occurring members of this group are lithium, potassium, rubidium, and cesium. In igneous rocks, sodium is slightly more abundant than potassium, but in sediments, sodium is much less abundant. The amounts of sodium held in evaporite sediments and in solution in the ocean are an important part of the total. All the alkali metals occur in the 1+ oxidation state and do not participate in redox processes. Sodium ions have a radius somewhat greater than 1 angstrom and are not strongly hydrated.

When sodium has been brought into solution, it tends to remain in that status. There are no important precipitation reactions that can maintain low sodium concentrations in water, in the way that carbonate precipitation controls calcium concentrations. Sodium is retained by adsorption on mineral surfaces, especially by minerals having high cation-exchange capacities such as clays. However, the interaction between surface sites and sodium, and with monovalent ions generally, is much weaker than the interactions with divalent ions. Cation-exchange processes in freshwater systems tend to extract divalent ions from solution and to replace them with monovalent ions.

### Sources of Sodium

According to Clarke's (1924a, p. 6) estimate, about 60 percent of the body of igneous rock in the Earth's outer crust consists of feldspar minerals. The feldspars are tectosilicates, with some aluminum substituted for silica and with other cations making up for the positive-charge deficiency that results. The common feldspars are orthoclase and microcline, which have the formula $KAlSi_3O_8$, and the plagioclase series ranging in composition from albite, $NaAlSi_3O_8$, to anorthite, $CaAl_2Si_2O_8$. Some sodium may be present, substituting for potassium in orthoclase and microcline.

Potassium feldspar is resistant to chemical attack. However, species containing sodium and calcium are somewhat more susceptible to weathering; they yield the metal cation and silica to solution and commonly form a clay mineral with the aluminum and part of the original silica. Besides the kaolinite shown as a product in earlier discussions of this reaction in this book, other clays such as illite or montmorillonite may be formed. Feth and others (1964), in studies of water in the feldspar-rich granitic terrane of the Sierra Nevada of California and Nevada, found that, in general, calcium and sodium ions were the most important cations in stream and spring water and that these tended to reflect abundance of the ions in the type of rock and the rate at which the minerals were attacked.

In resistate sediments, sodium may be present in unaltered mineral grains, as an impurity in the cementing material, or as crystals of readily soluble sodium salts deposited with the sediments or left in them by saline water that entered them at some later time. The soluble salts go into solution readily and are rather quickly removed from coarse-grained sediments after environmental changes, such as an uplift of land surface or a decline of sea level, impose a freshwater leaching regimen. During the early stages of the leaching process, the water leaving the formation may have high concentrations of sodium in solution. The last traces of marine salt or connate water may persist for long periods where circulation of water is impaired.

In hydrolyzate sediments, the particles normally are very small, and the circulation of water through the

material is impaired. Thus, the water trapped in the sediment when it was laid down may be retained with its solute load for long periods. The hydrolyzates include a large proportion of clay minerals having large cation-exchange capacities. Where sands and clays are interbedded, water and sodium may be retained longer in the less permeable strata during leaching and flushing by freshwater circulation. When such interbedded sections are penetrated by wells, water will be drawn mainly from more permeable sections at first. Long-continued withdrawals and water-table declines can be expected to alter water-circulation patterns, and saline solutions can be induced to move from the clay and shale layers. When this occurs on a large scale, a substantial increase in sodium concentration of the pumped water will occur. Kister and Hardt (1966) observed this effect in irrigation wells of the Santa Cruz basin in Arizona, where extensive declines in water levels had occurred.

Human activities can have a significant influence on the concentrations of sodium in surface water and ground water. The use of salt for deicing highways in winter and the disposal of brine pumped or flowing from oil wells, for example, have had direct, noticeable regional effects. Somewhat less directly, the reuse of water for irrigation commonly leaves a residual that is much higher in sodium concentration than was the original water. Pumping of ground water, which alters hydraulic gradients, can induce lateral movement of seawater into freshwater coastal aquifers.

Ion-exchange and membrane effects associated with clays were described under the topic "Membrane Effects." Some of these factors may influence sodium concentrations. Hanshaw (1964), for example, showed that when compacted, clays may preferentially adsorb sodium, but when dispersed in water, they may preferentially adsorb calcium.

### Dissolved Species

The sodium of dilute waters in which dissolved-solids concentrations are below 1,000 mg/L is generally in the form of the $Na^+$ ion. In more concentrated solutions, however, a variety of complex ions and ion pairs is possible. Species for which stability constants are given in Sillen and Martell (1964, p. 136, 235) include $NaCO_3^-$, $NaHCO_3(aq)$, and $NaSO_4^-$. These and other ion pairs or complexes involving sodium are substantially less stable than the ones involving divalent cations such as calcium or magnesium.

### Solubility Controls

Because of the high sodium concentrations that can be reached before any precipitate is formed, the sodium concentrations in natural water can have a very wide range, from less than 1 mg/L in rainwater and dilute stream runoff in areas of high rainfall to very high levels in brines associated with evaporite deposits and in brines of closed basins, where more than 100,000 mg/L may be present.

Sodium bicarbonate is one of the less soluble of the common sodium salts. At ordinary room temperature, however, a pure solution of this salt could contain as much as about 15,000 mg/L of sodium. In natural water, the conditions required for precipitation of pure sodium bicarbonate are unlikely to be attained, although water in some closed basins may attain high concentrations of carbonate and bicarbonate and leave a residue of solid forms of sodium carbonate. These are somewhat more soluble than the bicarbonate.

Sodium carbonate residual brines occur in some closed basins in California, Oregon, and Washington and elsewhere. Garrels and MacKenzie (1967) described a sequence of concentration and precipitation of solids from water that originally obtained its solute contents from weathering of silicate minerals in igneous rock. These processes may lead to solutions having a pH of more than 10.

A higher solubility limit on sodium concentration is exerted by the separation of solid sodium chloride, or halite. When saturated with respect to halite, a solution could have as much as 150,000 mg/L of sodium and about 230,000 mg/L of chloride, but concentrations this high are seldom reached in natural environments. Inclusions of brine are present in some halite formations. It can be shown, theoretically at least, that such inclusions may be able to migrate through the salt if a temperature gradient exists, by dissolving salt at the warmer end of the inclusion and precipitating it at the cooler end.

Sodium sulfate solubility is strongly influenced by temperature. The solid precipitated may contain various amounts of water, ranging from mirabilite or Glauber's salt with the formula $Na_2SO_4 \cdot 10H_2O$, through the heptahydate with seven molecules of water and the anhydrous form. Closed-basin lakes in cool climates may precipitate mirabilite during cool weather, which may be redissolved at higher temperatures. Mitten and others (1968) discribed such effects in eastern Stump Lake, N. Dak. Sodium concentrations in the lake during a 5-year period of intermittent sampling generally were between 20,000 and 30,000 ppm. An apparent decrease of about 25 percent in sodium concentration and a corresponding loss of sulfate was reported over a 1-week period when the water temperature decreased from 11° to 3°C (Mitten and others, 1968, p. 26). Somewhat similar deposition of mirabilite has been observed in Great Salt Lake, Utah (Eardley, 1938).

### Occurrence of Sodium in Water

In table 17 and some other places in this book are analyses that illustrate the various features of sodium behavior in natural aqueous systems.

Analysis 2 in table 12 represents water from rhyolitic volcanic rock and indicates the predominance of sodium over other cations that ought to be observed in water that has attacked albite. Waters that are low in dissolved solids, and in which calcium and magnesium have been depleted and sodium increased through cation exchange, are common in sediments of the Atlantic Coastal Plain and the Mississippi embayment. Analysis 2 in table 14 is for a dilute water from the Wilcox Formation showing this effect. A more strongly influenced example is analysis 1 in table 17, which represents a well in Atlantic Coastal Plain sediments. Analysis 2 in table 17 also shows the influence of cation exchange.

Some effects on surface-stream chemistry of solutes retained in fine-grained sediment are demonstrated by analysis 4, table 17. This analysis represents a stream in western South Dakota where the country rock is fine grained and contains soluble material. In the process of weathering, the exposed surfaces of these rocks may develop noticeable efflorescences of salts by evaporation of water between rainy periods. Aqueous precipitation heavy enough to wash away these deposits occurs occasionally, and at the same time the layer of leached sediment at the surface also may be stripped away. Colby and others (1953) have discussed these effects in greater detail.

Wells that penetrate clay and shale to reach lower, more permeable beds may at times obtain water high in dissolved solids directly from the shale layers, as seems indicated in analysis 9, table 17. Analysis 8, table 14,

**Table 17. Analyses of water in which**

[Analyses by U.S. Geological Survey. Date below sample number is date of collection. Sources of data: 1, 3, 7, and 8, U.S. Geological Survey, unpublished data; 2, 214); 9, Griggs and Hendrickson (1951, p. 111)]

| Constituent | 1 June 3, 1952 | | 2 Oct. 3, 1949 | | 3 May 13, 1952 | | 4 July 2-3, 1949 | |
|---|---|---|---|---|---|---|---|---|
| | mg/L | meq/L | mg/L | meq/L | mg/L | meq/L | mg/L | meq/L |
| Silica (SiO₂) | 22 | | 16 | | 22 | | 8.2 | |
| Iron (Fe) | .20 | | .15 | | .00 | | .04 | |
| Calcium (Ca) | 2.5 | .12 | 3.0 | .15 | 49 | 2.45 | 40 | 2.00 |
| Magnesium (Mg) | 2.1 | .17 | 7.4 | .61 | 18 | 1.48 | 50 | 4.11 |
| Sodium (Na) | 1,182 | 7.90 | 857 | 37.28 | 168 | 7.29 | 699 | 30.40 |
| Potassium (K) | | | 2.4 | .06 | | | 16 | .41 |
| Carbonate (CO₃) | 30 | 1.00 | 57 | 1.90 | 0 | | 26 | .87 |
| Bicarbonate (HCO₃) | 412 | 6.75 | 2,080 | 34.09 | 202 | 3.31 | 456 | 7.47 |
| Sulfate (SO₄) | 3.5 | .07 | 1.6 | .03 | 44 | .92 | 1,320 | 27.48 |
| Chloride (Cl) | 9.5 | .27 | 71 | 2.00 | 246 | 6.94 | 17 | .48 |
| Fluoride (F) | 1.7 | .09 | 2.0 | .11 | .1 | .01 | 1.0 | .05 |
| Nitrate (NO₃) | .6 | .01 | .2 | .00 | 2.2 | .04 | 1.9 | .03 |
| Boron (B) | | | .40 | | | | .60 | |
| Dissolved solids: | | | | | | | | |
| Calculated | 457 | | 2,060 | | 649 | | 2,400 | |
| Residue on evaporation | 452 | | | | 651 | | 2,410 | |
| Hardness as CaCO₃ | 15 | | 38 | | 196 | | 306 | |
| Noncarbonate | 0 | | 0 | | 31 | | 0 | |
| Specific conductance (micromhos at 25°C). | 718 | | 2,960 | | 1,200 | | 3,140 | |
| pH | 8.7 | | 8.3 | | 7.7 | | 8.2 | |
| Color | 1 | | | | 2 | | | |

¹Density, 1.019 g/mL at 20°C.
²Density, 1.21 g/mL.

1. Well at the Raleigh-Durham Airport, Wake County, N.C. Depth, 184 ft. Water-bearing formation, Coastal Plain sedimentary rocks.
2. Well, SE1/4 NE1/4 sec. 2, T. 22 N., R. 59 E., Richland County, Mont. Depth, 500 ft. Water-bearing formation, Fort Union Formation (sandstone and shale).
3. Irrigation well, SE1/4 sec. 3, T. 1 N., R. 5 E., Maricopa County, Ariz. Depth, 500 ft.; temperature, 20.5°C. Water-bearing formation, valley fill.

shows the composition of water obtained from the Dakota Sandstone in southeastern North Dakota. The water is high in sodium and in sulfate. Solute contents of water in the formation in this region may be derived from overlying and underlying finer grained materials (Swenson, 1968).

Water associated with evaporite formations generally has a very high sodium concentration. Analysis 2 in table 18 represents a sodium carbonate brine from Wyoming. Sodium carbonate evaporite deposits occuring in southern Wyoming are mined as a source of soda ash.

Water affected by solution of halite is represented by analyses 7 and 8 in table 17. Analysis 8 displays near-saturation with respect to sodium chloride. The source of the salinity in the Salt Banks spring is not evident at the surface. Inflows of this type have a signifi-

cant influence on the water of the Salt River, which is impounded for use in irrigation of the area near Phoenix, Ariz. The composition of this supply is represented by analysis 5 in table 17.

Anthropogenic effects on sodium concentrations are demonstrated by high sodium concentration of residual drainage from the Salt River Valley irrigated area (analysis 6, table 17). Somewhat higher average concentrations occurred at this sampling point during the 10 years following 1952. Most of the increase was in sodium, chloride, and sulfate. The water at low flow is near saturation with respect to calcite and gypsum (Hem, 1966). Analysis 3, table 17, represents a well in the irrigated area upstream where recharge is virtually all brought about by applied irrigation water. The analysis

sodium is a major constituent

Torrey and Kohout (1956, p. 44); 4, U.S. Geological Survey Water-Supply Paper 1162 (p. 457); 5 and 6, U.S. Geological Survey Water-Supply Paper 1253 (p. 205,

| 5 1951 –52 | | 6 1951 –52 | | 7 Dec. 8, 1951 | | 8 Jan. 31, 1938 | | 9 Oct. 15, 1946 | |
|---|---|---|---|---|---|---|---|---|---|
| mg/L | meq/L | mg/L | meq/L | mg/L | meq/L | mg/L | meq/L | mg/L | meq/L |
| 18 | ............ | 31 | ............ | 46 | ............ | | ............ | 13 | ............ |
| .01 | ............ | .01 | ............ | | | | | | |
| 48 | 2.40 | 353 | 17.61 | 505 | 25.20 | 722 | 36.03 | 30 | 1.50 |
| 14 | 1.15 | 149 | 12.25 | 291 | 23.94 | 2,490 | 204.83 | 31 | 2.55 |
| 150 | 6.52 | 1,220 | 53.05 | 10,100 | 439.35 | 121,000 | 5,263.50 } | 279 | 12.13 |
| 5.8 | .15 | 9.8 | .25 | 170 | 4.35 | 3,700 | 94.61 } | | |
| 0 | ............ | 0 | ............ | 0 | ............ | 63 | 2.10 | 0 | ............ |
| 153 | 2.51 | 355 | 5.82 | 1,520 | 24.91 | 40 | .66 | 445 | 7.29 |
| 50 | 1.04 | 1,000 | 20.82 | 899 | 18.72 | 11,700 | 243.59 | 303 | 6.31 |
| 233 | 6.57 | 1,980 | 55.84 | 16,200 | 457.00 | 189,000 | 5,331.69 | 80 | 2.26 |
| .4 | .02 | 1.9 | .10 | | | | | 1.2 | .06 |
| 2.4 | .04 | 24 | .39 | | | | | 17 | .27 |
| .15 | ............ | 2.4 | ............ | 17 | ............ | | | | |
| 597 | ............ | 4,940 | ............ | [1]29,000 | ............ | [2]329,000 | ............ | 973 | ............ |
| 611 | ............ | | | | | | | | |
| 178 | ............ | 1,490 | ............ | 2,460 | ............ | | | 202 | ............ |
| 52 | ............ | 1,200 | ............ | 1,210 | ............ | | | 0 | ............ |
| 1,090 | ............ | 7,620 | ............ | 41,500 | ............ | 225,000 | ............ | 1,510 | ............ |
| | | | | 7.1 | | | | | |

4. Moreau River at Bixby, S. Dak.; composite of two daily samples. Mean discharge, 1 7 cfs. Drains the Pierre Shale, the Fox Hills Sandstone, and the Hell Creek Formation.

5. Salt River below the Stewart Mountain Dam, Ariz. Discharge-weighted average, 1952 water year; mean discharge, 362 cfs.

6. Gila River at the Gillespie Dam, Ariz. Discharge-weighted average, 1952 water year; mean discharge, 71 1 cfs.

7. Spring entering the Salt River at Salt Banks near Chrysotile, Ariz. Temperature, 21 1°C. Water-bearing formation, quartzite and diabase.

8. Test well 3, sec. 8, T. 24 S., R. 29, E., Eddy County N. Mex. Depth, 292 ft. Brine from the Salalado Formation and the Rustler Formation.

9  Well in SW1/4 sec. 7, T. 17 N., R. 26 E., San Miguel County, N. Mex. Depth, 50 ft. Water-bearing formation, shale of the Chinle Formation.

is nearly the same as that for the river water (analysis 5, table 17). The effect of seawater encroachment in a coastal aquifer near Los Angeles, Calif. is shown by analyses in table 22.

Many water analyses in the earlier literature report a computed value for sodium rather than an actually determined one. The computed value represents the difference between the sum of the determined anions, in milliequivalents per liter, and the determined cations, expressed in the same units. Obviously, the computation cannot be made unless all the other major ions have been determined. Potassium is commonly lumped with sodium in the computation, and the value reported as "sodium and potassium, as sodium." The principal reason for omitting sodium from the analysis in former years was that the determination was difficult, tedious, and expensive by the procedures then available. After about 1955, the flame photometer and related flame spectrochemical methods made the sodium determination one of the quickest and easiest in the analytical chemists' repertoire, and, thus, analyses with computed sodium values are no longer common. The principal objection to the computation of sodium is that it prevents any really effective check of the accuracy of the determinations of the major dissolved components; therefore, analyses reporting computed sodium values are more likely to contain major errors.

## Potassium

As shown in table 1, potassium is slightly less common than sodium in igneous rock but more abundant in all the sedimentary rocks. In the ocean the concentration of potassium, though substantial, is far less than that of sodium. The figures point up the very different behavior of these two alkali metals in natural systems. Sodium tends to remain in solution rather persistently once it has been liberated from silicate-mineral structures. Potassium is liberated with greater difficulty from silicate minerals and exhibits a strong tendency to be reincorporated into solid weathering products, especially certain clay minerals. In most natural water, the concentration of potassium is much lower than the concentration of sodium.

Another important factor in the hydrochemical behavior of potassium is its involvement in the biosphere, especially in vegetation and soil. Potassium is an essential element for both plants and animals. Maintenance of optimum soil fertility entails providing a supply of available potassium. The element is present in plant material and is lost from agricultural soil by crop harvesting and removal as well as by leaching and runoff acting on organic residues.

### Sources of Potassium

The principal potassium minerals of silicate rocks are the feldspars orthoclase and microcline ($KAlSi_3O_8$),

the micas, and the feldspathoid leucite ($KAlSi_2O_6$). The potassium feldspars are resistant to attack by water. Presumably they are altered to silica, clay, and potassium ions by the same process as other feldspars, only more slowly.

In sediments, the potassium commonly is present in unaltered feldspar or mica particles or in illite or other clay minerals. Evaporite rocks may locally include beds of potassium salts and constitute a source for high potassium concentration in brines.

Average content of potassium in living plants, according to data given by Mason (1952, p. 199), is near 0.3 percent. Concentrations in dry plant material and in ash are substantially greater. Wood ashes have been used by humans as a potash source for many centuries.

### Control Mechanisms for Potassium Concentration

Although potassium is an abundant element and its common salts are highly soluble, it seldom occurs in high concentrations in natural water. Chemical mechanisms that might be expected to bring about such a result, however, are not of a type that is readily quantified. The broad generalizations already stated suggest that potassium concentrations in water are low partly because of the high degree of stability of potassium-bearing aluminosilicate minerals. Unaltered potassium feldspar grains occur in many sandstones.

The potassium ion is substantially larger than the sodium ion, and it would normally be expected to be adsorbed less strongly than sodium in ion-exchange reactions. Actually, however, potassium is incorporated in a special way into some clay-mineral structures. In illite, potassium ions are incorporated in spaces between crystal layers, and they cannot be removed by further ion-exchange reactions.

Potassium ions assimilated by plants become available for re-solution when the plants mature and die, or when leaves and other parts are shed at the end of the growing season. In the natural recycling that occurs in forests and grasslands, this potassium is leached into the soil by rains during the dormant season or made available by the gradual decay of the organic material. Some leakage of potassium to ground water and runoff during these processes would be expected.

There are indications that biological factors may be important in controlling the availability of potassium for solution in river water and ground water. Records of quality of surface waters of the United States show that at times of relatively high water discharge many streams in the central part of the country carry potassium concentrations nearly as high as (or higher than) they do at times of low discharge. This may be the result of soil leaching by runoff. Similar effects were noted by Steele (1968b), in Pescadero Creek, Calif., and by Kennedy and Malcolm (1977), who made very detailed studies of

discharge and solute contents of the Mattole River in northern California. Slack (1964) observed increased potassium in water of pools in the Cacapon River of West Virginia during autumn, when the water was affected by the leaching of recently fallen tree leaves.

Some closed-basin lakes in the Sand Hills region of northern Nebraska contain water having notable concentrations of potassium (Clarke, 1924a) and were considered possible domestic commercial sources of potash (Hicks, 1921) before the discovery of potassium-rich evaporite deposits in New Mexico. The reasons for potassium accumulation in these lake waters have not been fully established. Hicks (1921) hypothesized that the leaching of potassium from the ashes of grass destroyed in prairie fires was a possible source. Such an exotic mechanism is perhaps unnecessary. The concentration of potassium in at least some of the near-surface strata in the entire High Plains region of western Nebraska and Kansas is greater than the sodium concentration, as indicated by rock analyses tabulated by Hill and others (1967). Ground water in the Ogallala and some other formations in the region may also have relatively high proportions of potassium to sodium (Johnson, 1960). These waters are uniformly low in dissolved solids, as the rock formations do not contain readily soluble minerals. However, where water circulation is impaired and the water table intersects the surface, evaporation could eventually build up potassium concentrations in the water to levels observed in the Nebraska lakes. Mobilization of potassium by grasses growing on the highly permeable soil may also play a significant role.

### Occurrence of Potassium in Water

In dilute natural waters in which the sum of sodium and potassium is less than 10 mg/L, it is not unusual for the potassium concentration to equal or even exceed the sodium concentration. This can be seen in analysis 9, table 14, which represents water from sandstone, and analyses 1 and 8, table 16, representing water from dolomite and quartzite, respectively. Analysis 7, table 16, for the Wisconsin River, also shows this property.

Water containing 10 to 20 mg/L of sodium and nearly equal concentrations of potassium appears to be fairly common in the Ogalala Formation in southwestern Nebraska (Johnson, 1960). However, in most other freshwater aquifers, if the sodium concentration substantially exceeds 10 mg/L the potassium concentration commonly is half or a tenth that of sodium. Concentrations of potassium more than a few tens of milligrams per liter are decidedly unusual except in water having high dissolved-solids concentration or in water from hot springs. The concentrations of potassium in the two most saline waters represented in table 17 (analyses 7 and 8) are high, but potassium:sodium molar ratios are less than 0.02.

Seawater contains 390 mg/L of potassium (table 2). Analysis 6, table 14, representing mine water, and analysis 3, table 18, representing an acidic thermal spring, both have rather high potassium to sodium ratios.

There are deficiencies in the basic information about the chemistry of potassium in water. Many of the available chemical analyses of water and some of the analyses included in this book do not include potassium determinations. Some of the old wet-chemical methods for potassium required considerable analytical skill, and the accuracy of some of the earlier published values for potassium concentrations obtained using these methods appears to be questionable. In more recent years, better methods have become available, but potassium has remained one of the more difficult ions to analyze accurately. Research aimed at attaining a better understanding of the chemical behavior of potassium in natural aqueous systems is needed.

## Alkalinity and Acidity

The properties of alkalinity and acidity are important characteristics of natural and polluted waters and are almost always included in the chemical determinations. However, these properties differ in important ways from most of the other determinations reported in the analysis. Both are defined as "capacity" functions—that is, the capacity of the solution to neutralize acid or base. Both properties may be imparted by several different solute species, and both are evaluated by acid-base titration, to appropriate end points. Systems having these properties are commonly referred to by chemists as "buffered systems."

Most quantities determined in chemical analyses are "intensity" functions—that is, they are actual concentrations of a particular dissolved species at the time of analysis. The measurement of pH provides values of concentrations of $H^+$ and $OH^-$ in solution. These species contribute, of course, to acidity or alkalinity, but within the pH range commonly seen in natural water they are minor constituents, at concentrations of $10^{-5.00}$ molar or lower. The principal solutes that constitute alkalinity are imparted to natural water during its passage in liquid form through the hydrologic cycle. They reflect the history of the water, as an imprint left by these encounters. The properties of alkalinity or acidity also evaluate the potential of the solution for some kinds of water-rock interaction or interaction with other material the water may contact.

Most natural waters contain substantial amounts of dissolved carbon dioxide species, which are the principal source of alkalinity and can conveniently be evaluated by acid titrations. Undissociated dissolved carbon dioxide contributes to acidity rather than to titratable alkalinity and can also be determined by titration using a basic solution.