Water-Quality Principles
QW1022–TEL

Lesson 5, Part 1: Field-Measured Properties and Major Ions: Field Measurements

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U.S. Department of the Interior
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Effects of Temperature and Pressure on Chemical Equilibria

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

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

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

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

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

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

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

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

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

Solution of Calcite

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

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

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

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

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

Hydrogen-Ion Activity (pH)

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

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

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

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

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

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

By convention, the activity of the liquid water is taken to be unity in this very dilute solution, and the constant K_w is then equal to the product of the activities of H^+ and OH^-. This ion-activity product for water at 25°C is, in exponential terms, $10^{-14\,000}$ (Covington and others, 1966). The two-place log of K_w is −14.00. At neutrality, by definition $[H^+]=[OH^-]$ and therefore pH=7.00.

At higher temperatures, K_w increases and the neutral value of pH becomes smaller; the value for 30°C given by Covington and others (1966) is $10^{-13\,837}$. Neutral pH at 30°C therefore would be 6.92. The value of K_w at 0°C was given by Ackerman (1958) as $10^{-14.955}$, which means that neutral pH at that temperature is 7.48. The strong effect of temperature on hydrogen-ion behavior has considerable geochemical significance and must be taken into account in measurements of pH and in calculations using pH data.

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

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

Range of pH of Natural Water

(p.63)

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.

Specific Electrical Conductance

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

Units for Reporting Conductance

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

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

Physical Basis of Conductance

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

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

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

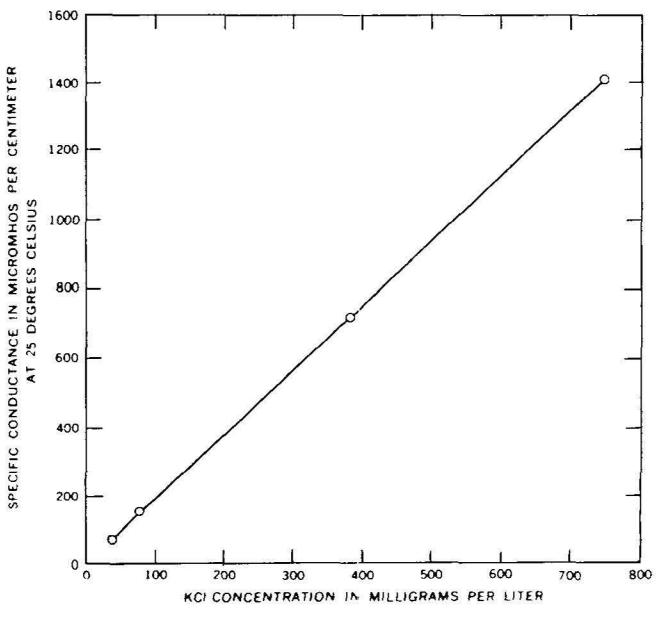

Figure 8. Specific conductance of potassium chloride solutions.

Alkalinity and Acidity

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

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

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

Alkalinity

The alkalinity of a solution may be defined as the capacity for solutes it contains to react with and neutralize acid. The property of alkalinity must be determined by titration with a strong acid, and the end point of the titration is the pH at which virtually all solutes contributing to alkalinity have reacted. The end-point pH that should be used in this titration is a function of the kinds of solute species responsible for the alkalinity and their concentrations. However, the correct titration end point for a particular solution can be identified from the experimental data when the species involved are unknown. It is the point at which the rate of change of pH per added volume of titrant (dpH/dV_{acid}) is at a maximum. As dissociation constants in table 33 show, the ratio $[HCO_3]$:$[H_2CO_3]$ will be near 100:1 at pH 4.4, and the ratio $[HCO_3^-]$:$[CO_3^{2-}]$ will have a similar value at pH 8.3 at temperatures near 20°C. The best values for the end points for a particular sample depend on ionic strength and temperature. Analytical procedures may specify a pH value between 5.1 and 4.5, or that of the methyl-orange end point (about pH 4.0-4.6). Sometimes, however, an alkalinity above the phenolphthalein end point (about pH 8.3) is also specified. Thus one may find terms such as "methyl-orange alkalinity," or its equivalent, "total alkalinity," and "phenolphthalein alkalinity." Dilute solutions such as rainwater require special procedures for this determination (Stumm and Morgan, 1981, p. 226–229).

Several different solute species contribute to the alkalinity of water as defined above, and titration with acid does not specifically identify them. The property of alkalinity can be expressed in quantitative terms in various ways. The most common practice is to report it in terms of an equivalent amount of calcium carbonate. It could also be expressed in milliequivalents per liter, where meq/L is 1/50 times mg/L $CaCO_3$.

In almost all natural waters the alkalinity is produced by the dissolved carbon dioxide species, bicarbonate and carbonate, and the end points mentioned above were selected with this in mind. Analyses in this book, and most others in current geochemical literature, follow the convention of reporting titrated alkalinity in terms of the equivalent amount of bicarbonate and carbonate.

The more important noncarbonate contributors to alkalinity include hydroxide, silicate, borate, and organic ligands, especially acetate and propionate. Rarely, other species such as NH_4OH or HS^- may contribute significantly to alkalinity. If alkalinity is expressed in milliequivalents per liter, or as $CaCO_3$, the contributions from these species will affect the cation-anion balance of the analysis only if some of them are determined by other methods and are thus included in the balance computation in two places.

Except for waters having high pH (greater than about 9.50) and some others having unusual chemical composition, especially water associated with petroleum and natural gas or water having much dissolved organic carbon, the alkalinity of natural waters can be assigned entirely to dissolved bicarbonate and carbonate without serious error. The important contribution of short-chain aliphatic acid anions to titratable alkalinity in water from certain oil fields was pointed out by Willey and others (1975).

Sources of Alkalinity

The principal source of carbon dioxide species that produce alkalinity in surface or ground water is the CO_2 gas fraction of the atmosphere, or the atmospheric gases present in the soil or in the unsaturated zone lying between the surface of the land and the water table. The CO_2 content of the atmosphere is near 0.03 percent by volume. Soil-zone and unsaturated-zone air can be substantially enriched in carbon dioxide, usually owing to respiration by plants and the oxidation of organic matter.

In some natural systems there may be sources of carbon dioxide other than dissolution of atmospheric or soil-zone CO_2. Possible major local sources include biologically mediated sulfate reduction and metamorphism of carbonate rocks. In some areas, outgassing from rocks in the mantle 15 km or more below the surface has been suggested (Irwin and Barnes, 1980). Indications of source can sometimes be obtained from stable isotope ($\delta^{13}C$) data.

From studies of $\delta^{13}C$ values in dissolved HCO_3^- in 15 oil and gas fields, Carothers and Kharaka (1980) concluded that the decarboxylation of acetate and other short-chain aliphatic acids was an important CO_2 source in these waters. This process also produces methane and other hydrocarbon gases.

Carbon dioxide species are important participants in reactions tht control the pH of natural waters. Various aspects of this fact were discussed in the section on pH. Reactions among the alkalinity-related species, aqueous CO_2, $H_2CO_3(aq)$, HCO_3^-, and CO_3^{2-}, and directly pH-related species, OH^- and H^+, are relatively fast and can be evaluated with chemical equilibrium models. Rates of equilibration between solute species and gaseous CO_2 across a phase boundary are slower, and water bodies exposed to the atmosphere may not be in equilibrium with it at all times. The oceans are a major factor in maintaining atmospheric CO_2 contents. It may be of interest to note that carbonic acid, H_2CO_3, is conventionally used to represent all the dissolved undissociated carbon dioxide. In actuality, only about 0.01 percent of the dissolved carbon dioxide is present in this form. We will use the H_2CO_3 convention in discussing these systems, however, as the choice of terminology has no practical effect on final results.

Oxygen

The equilibrium concentration of dissolved oxygen (DO) in water in contact with air is a function of temperature and pressure, and to a lesser degree, of the concentration of other solutes. Tabulated values for DO in water in equilibrium with water-saturated air at 101.3 kilopascals (1 atmosphere) at temperatures from 0° to 50°C, and having 0 to 20,000 mg/L dissolved Cl^-, are given in "Standard Methods for the Examination of Water and Waste Water" (American Public Health Association and others, 1980, p. 392). At 5°C in freshwater the equilibrium DO value is 12.75 mg/L. At 30°C the concentration is 7.54 mg/L. Values for DO in water analyses may be given in milligrams per liter or as a percentage of saturation at the temperature of measurement.

The higher forms of aquatic life require oxygen for survival, and the DO determination is used widely in evaluations of the biochemistry of streams and lakes. The DO concentration may be depleted by processes that consume dissolved, suspended, or precipitated organic matter, and values above equilibrium can be produced in systems containing actively photosynthesizing biota. These aspects of water chemistry are not a primary object of concern in this book, important though they may be in many ways. The extent to which a supply of oxygen can be maintained in a polluted stream or lake depends in part on the hydraulic properties that influence rates at which atmospheric oxygen can be supplied in the water column; the stream can assimilate more organic or other oxidizable material without significant degradation when the rate is rapid than when it is slow (Langbein and Durum, 1967). Various mathematical models of these kinds of systems have been constructed (for example, Bauer and Bennett, 1976).

Electrodes for determining DO can be used for obtaining continuous records at field sites. The oxygen concentration in a surface water body is a dynamic indicator of the balance between oxygen-consuming and oxygen-producing processes at the moment of sampling.

Abiotic chemical reactions involving dissolved oxygen are also important, and some have already been discussed. Atmospheric oxygen is the principal electron sink for redox processes in the hydrosphere. A statement of the dissolved oxygen redox process may be written

$$O_2(aq)+2H^++4e^-=2\ OH^-.$$

In aerated water under standard conditions, this relationship predicts an Eh only a short distance below the upper water-stability line in the pH-Eh diagram. The equation, however, implies a multielectron transfer which is likely to proceed in a step-wise fashion. The mechanisms by which aqueous oxygen participates in redox processes seem not to be fully understood, but a rather complicated route involving peroxide intermediate species is commonly postulated (Latimer, 1952, p. 39–44). The oxidation intensity in aerated systems, as indicated by the apparent equilibrium distributions of oxidizable species such as iron, is much below the value predicted by the summarizing equation but is in more reasonable agreement with values predicted by the peroxide mechanism.

According to Cooper and Zika (1983), hydrogen peroxide (H_2O_2) is present in aerated natural waters exposed to sunlight, and these investigators believed its presence is related to photochemical processes mediated by organic solutes (humic material). Concentrations greater than 100 μg/L of H_2O_2 were observed in surface-water samples exposed to sunlight (1.0 watt-hour/m^2). The samples contained from 12 to 18 mg/L TOC. Similar results were obtained using ground-water samples.

Thermodynamic data of Wagman and others (1968, p. 11–13) indicate that the equilibrium concentration of H_2O_2 in aerated water is about 12 orders of magnitude smaller than the concentrations reported by Cooper and Zika (1983). However, other investigators referenced in Cooper and Zika's paper have found H_2O_2 in rainwater and seawater. Implications of these results for natural-water chemistry need further exploration. A review of the photochemical processes occurring in natural water was published by Zafiriou and others (1984).

Oxygen is supplied to ground water through recharge and by movement of air through unsaturated material above the water table. This oxygen reacts with oxidizable material encountered along the flow path of the water. Water containing measurable amounts of dissolved oxygen may penetrate long distances into the system if little reactive material is available. The principal reacting species are organic materials and reduced inorganic minerals such as pyrite and siderite. As time passes the oxidizable material in the aquifer will be removed or altered for long distances from the point of recharge.

Oxygen Demand and Other Evaluations of Organic Pollution Load (p157)

The dissolved-oxygen concentration of a water body represents the status of the system at the point and moment of sampling. The processes by which organic debris, or other kinds of material in the water, react with oxygen are relatively slow. The processes generally are

biological, which means a suitable incubation and growth period is required for the organism involved. As the organisms multiply, the rate at which they use oxygen may exceed the rate at which the dissolved oxygen in the water can be replenished from the atmosphere, and the dissolved-oxygen concentration may decrease—perhaps drastically. After the processes have attained virtual completion, the normal oxygen level of the water can be reestablished. If the oxidizable load is light, the oxygen level may not be depleted much at any time. If considerable oxidizable material is present, however, the oxygen may be substantially depleted while the digestive processes are going on. A system may be so overloaded by pollutants that oxygen levels fall practically to zero and aerobic organisms are destroyed. Because considerable time may be required for the natural purification processes to become effective again, the polluted water may move through many miles of river channel with very low oxygen concentrations.

Various methods have been used to estimate the requirement of a given water for oxygen or to evaluate the organic pollution load in a quantitative way. These include measurement of biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon. The latter has already been discussed.

Biochemical Oxygen Demand (BOD)

The BOD determination is commonly made by diluting portions of a sample with oxygenated water and measuring the residual dissolved oxygen after a period of incubation (usually 5 days at 20°C). The results are commonly expressed in terms of weight of oxygen required per unit volume of the initial sample. Sometimes the pollution load of a given waste stream is expressed in terms of the human population level whose normal domestic sewage production would equal the BOD of the stream. The determination is slow to make and has no particularly direct geochemical significance, but it is extensively applied in pollution studies. It is generally considered to be a useful way of expressing stream-pollution loads and of comparing one set of conditions with another.

Chemical Oxygen Demand (COD)

To determine pollution or oxidizable material loads more quickly, wet oxidations with strong oxidizing agents have been used extensively. The results can be expressed in terms of oxygen equivalent. Heating the sample with an aliquot of standard permanganate or dichromate is one such procedure. The results of COD determinations obviously do not correspond to values obtained by BOD determinations, but they may be helpful in comparing conditions in a stream at one time with those at another time.

Hardness

The concept of hardness as an evaluation of certain chemical properties of water has become deeply imbedded in the literature of water analysis and in the habits of thought of almost everyone concerned with water quality. In spite of wide usage, however, the property of hardness is difficult to define exactly, and several definitions are in common use.

The terms "hard" and "soft" are contained in a discourse on water quality by Hippocrates (460–377 B.C.), quoted as follows by Baker (1949): "Consider the waters which the inhabitants use, whether they be marshy and soft, or hard and running from elevated and rocky situations***." The use of the terms there could have some of the modern meaning; at least limestone was probably present in many of the upland regions familiar to Hippocrates. Over the years, the property of hardness has been associated with effects observed in the use of soap or with the encrustations left by some types of water when they are heated. If the reactions with soap are the only ones considered, one might say that hardness represents the soap-consuming capacity of a water. The effect results from cations that form insoluble compounds with soap. In the mid-19th century, a procedure was developed for titration of hardness with standard soap solution.

Because most of the effect observed with soap results from the presence of calcium and magnesium, hardness is now generally defined in terms of these constituents alone, with some rather indefinite reservations about interferences (American Society for Testing and Materials, 1964, p. 391). The other ions that might precipitate soap include H^+ and all polyvalent metal cations, but they are present mostly in insignificant amounts in waters of the type that are usable domestically and for which hardness data might be obtained.

Because hardness is a property not attributable to a single constituent, some convention has to be used for expressing concentrations in quantitative terms. Usually, this consists of reporting hardness in terms of an equivalent concentration of calcium carbonate. In practical water analysis, the hardness is computed by multiplying the sum of milliequivalents per liter of calcium and magnesium by 50. The hardness value resulting is generally called "hardness as $CaCO_3$" in tabulated data. The same quantity is sometimes referred to as "calcium+magnesium hardness" or "total hardness." The usual wet-chemical procedures for determining calcium and magnesium include an amount of these metals approximately equivalent to any other alkaline-earth metals; hence, a reasonable, practical definition of hardness is "the effect of alkaline-earth cations."

Carbonate hardness, when reported, includes that part of the hardness equivalent to the bicarbonate+carbonate (or alkalinity). If the hardness exceeds the alkalin-

ity (in milligrams per liter of $CaCO_3$ or other equivalent units), the excess is termed "noncarbonate hardness" and frequently is reported in water analyses. In some older reports the terms "temporary" and "permanent" are used instead of "carbonate" and "noncarbonate" in speaking of these subdivisions of hardness. All hardness concentrations given in this book are in terms of equivalent quantities of $CaCO_3$ in milligrams per liter.

Hardness values are reported in some European countries in terms of "degrees." One French degree is equivalent to 10 mg/L, one German degree to 17.8 mg/L, and one English or Clark degree to 14.3 mg/L, all in terms of calcium carbonate.

The soap procedure for titration of hardness has been supplanted by chelation methods for titration of the alkaline-earth metal and by spectrophotometric procedures for the individual elements. Analyses made since the late 1940's can generally be assumed not to have used the soap procedure. Modern methods give results that are far more reliable than the old procedure.

Hardness determinations have a limited value in geochemical studies. Modern analytical procedures can provide separate calcium and magnesium values practically as easily as combined ones, and the increase in usefulness of the results is well worth the trouble. In most water analyses in current literature hardness values, if reported, are probably calculated from calcium and magnesium concentrations.

RANGE OF HARDNESS CONCENTRATION

The adjectives "hard" and "soft" as applied to water are inexact, and some writers have tried to improve on this situation by adding qualifying adverbs. Durfor and Becker (1964, p.27) used the following classification:

Hardness range (mg/L of $CaCO_3$)	*Description*
0–60	Soft.
61–120	Moderately hard.
121–180	Hard.
More than 180	Very hard.

In some areas of the United States, however, where most water has a low dissolved-solids content, a water containing 50 mg/L of hardness would be considered hard by most residents.

The standards by which water hardness is judged have tended to become more rigorous over the years. Many public water supplies now are softened to less than 100 mg/L of hardness. The U.S. Public Health Service (1962) and later U.S. drinking water standards do not specify any value for hardness. The World Health Organization (1971) suggested an upper limit of 500 mg/L. According to the American Water Works Association (Bean, 1962), however, "ideal" water should not contain more than 80 mg/L of hardness.

Hardness in water used for ordinary domestic purposes does not become particularly objectionable until it reaches a level of 100 mg/L or so. Hardness can greatly exceed this level, and in many places—especially where waters have been in contact wihth limestone or gypsum—200 or 300 mg/L or more of hardness is common. Hardness becomes noticeable in all uses at these levels, and becomes increasingly troublesome as the concentration rises. In water from gypsiferous formation, 1,000 mg/L or more of hardness may be present.

In recent years, some authors have reported apparent statistical correlations between the hardness or other properties of drinking-water supplies and the death rates from cardiovascular diseases. Muss (1962) reviewed literature on this subject and expressed the belief that in a very general way the lower death rates from heart and circulatory diseases occurred in States where the public water supplies are highest in hardness. Kobayashi (1957) reported that the geographical distribution of high death rates for apoplexy in Japan seemed to suggest the high rates occurred in areas where the river waters had low alkalinity and relatively high sulfate content. All these Japanese waters, however, were relatively soft. Because many other factors affect these apparent correlations, their significance is uncertain.

A paper by Neri and others (1975) presented data from Canada supporting the hypothesis that hard water provided some protection from heart disease because of its increased magnesium content. Hopps (1979) reviewed the general subject of health in relation to the geochemical environment.