

Table 4. Mean composition of the atmosphere

[After Mirtov (1961)]

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

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

PRINCIPLES AND PROCESSES CONTROLLING COMPOSITION OF NATURAL WATER

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

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

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

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

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

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

Thermodynamics of Aqueous Systems

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

In spite of these limitations, the second law of thermodynamics remains a fundamental concept of great

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

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

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

Chemical Reactions

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

Reversible and Irreversible Reactions in Water Chemistry

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

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

and reverse reactions are occurring simultaneously, at least on a micro scale, and at comparable rates when reaction affinities are small.

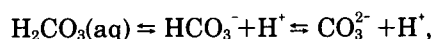
These definitions are not entirely satisfactory for our purposes. It has already been pointed out that some reactions do not take place to a significant extent, even though they may be favored thermodynamically, owing to energy barriers in some of the reaction pathways. If such a condition applies to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

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

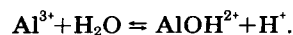
The ease with which a particular reaction can be reversed is important because readily reversible processes can be expected generally to approach chemical equilibrium closely. Irreversible processes can reach a steady state, but thermodynamic principles apply to them in a different way. Easily reversed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

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

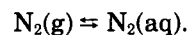
An example of an easily reversed process is the formation of complex ions or similar homogeneous (single-phase) reactions. Dissolved carbon dioxide, represented as H_2CO_3 , dissociates reversibly:



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



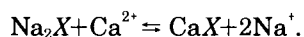
Some heterogeneous reactions, such as the solution of unreactive gases, are readily reversible, for example,



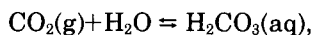
The association of N_2 molecules with water molecules that occurs in this reaction is implied in the notation $\text{N}_2(\text{aq})$ but is not specifically indicated by the equation. Other symbols used here to indicate the phase of reactants

or products are: (c)=solid, (l)=liquid, and (g)=gas. Dissolved ions and their electronic charges are designated by superscript + and - signs. Unless otherwise indicated H₂O is assumed to be in the liquid state.

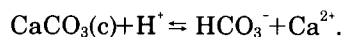
Many sorption-desorption or ion-exchange reactions are readily reversed—for example,



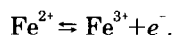
Some solution-dissolution processes can be considered readily reversible, for example, the solution of carbon dioxide gas,



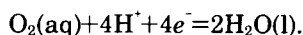
and reactions involving calcite and some other carbonates apparently can be reversed rather easily in many natural systems:



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

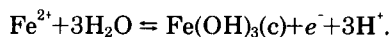


The reduction of aqueous oxygen is less readily reversible:



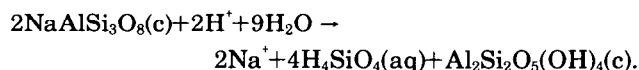
(This reaction takes place in steps and is more complicated than this statement indicates.)

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



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

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



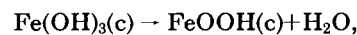
The kaolinite may dissolve reversibly:



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

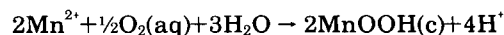
Energy barriers of various kinds may inhibit reversibility. Precipitation reactions may be slowed or stopped by the energy demand imposed by the formation of the nucleus of a crystal. Oxidation-reduction reactions, especially those involving sulfur or nitrogen, may be very slow unless biota are present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

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



the reaction affinity will be greater than zero as long as any Fe(OH)₃ remains.

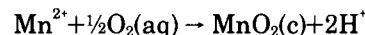
Processes whose reversibility is hindered may occur in steps. It has been suggested (Hem and others, 1982) that an irreversible process for alteration of manganese oxide to a more stable form can give a nonequilibrium steady state Mn²⁺ concentration if it occurs in an open system. The two steps in the process are



and



These add up to



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

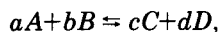
The most important single factor that makes many of the reactions in natural aqueous systems irreversible is the openness of many systems to fluxes of reactants that may totally control the thermodynamics and may drive the reactions in one direction only.

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

Chemical Equilibrium—The Law of Mass Action

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

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



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

$$R_1 = k_1' [A]^a [B]^b$$

and

$$R_2 = k_2' [C]^c [D]^d,$$

where bracketed terms represent active masses. The quantities k_1' and k_2' are proportionality constants for the forward and reverse reactions. When $R_1 = R_2$, the system will be in a state of dynamic equilibrium and no change in active concentrations (represented by the bracketed quantities) will occur. This leads to the expression

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

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

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

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

A further flaw in the derivation is that it implies reactions proceeding in opposition to each other, when values for A for both processes must be near zero. How-

ever, this difficulty can be avoided by deriving the mass law from fundamental thermodynamic concepts. This derivation is based on the convention that the bracketed terms given above represent "activities" of reactants and products. The activity, " α ," is related to thermodynamic quantities by the relationship

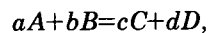
$$\mu = \mu^\circ + RT \ln \alpha.$$

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

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

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

For the reaction



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

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

At standard states,

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

As shown above,

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

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

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

This rearranges to

$$\Delta\mu_R = \Delta G^\circ_R + RT \ln \frac{\alpha_C^c \times \alpha_D^d}{\alpha_A^a \times \alpha_B^b}.$$

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

$$-\Delta G^{\circ}_R = RT \ln \frac{\alpha^c_C \times \alpha^d_D}{\alpha^a_A \times \alpha^b_B} .$$

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

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

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

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

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

and

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

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

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

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

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

Ionic Activity

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

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

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

The solutes in aqueous systems do not display thermodynamically ideal behavior—that is, concentrations

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

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

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

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

where α_i is activity of ionic species i , C_i is its concentration on the molal (moles of i /kg H_2O) or molar (moles of i /L) scale, and γ_i is the activity coefficient. The use of brackets to denote activity is the convention followed in this book. Molar activities will be used throughout. In dilute solutions, molal and molar scales are nearly the same.

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

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

The form of the Debye-Hückel equation used here is

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

where

γ_i is the activity coefficient of the ion,

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

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

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

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

a_i	Ions
11	Th ⁴⁺ , Sn ⁴⁺ .
9	Al ³⁺ , Fe ³⁺ , Cr ³⁺ , H ⁺ .
8	Mg ²⁺ , Be ²⁺ .
6	Ca ²⁺ , Cu ²⁺ , Zn ²⁺ , Sn ²⁺ , Mn ²⁺ , Fe ²⁺ , Ni ²⁺ , Co ²⁺ , Li ⁺ .
5	Fe(CN) ₆ ⁴⁻ , Sr ²⁺ , Ba ²⁺ , Cd ²⁺ , Hg ²⁺ , S ²⁻ , Pb ²⁺ , CO ₃ ²⁻ , SO ₃ ²⁻ , MoO ₄ ²⁻ .
4	PO ₄ ³⁻ , Fe(CN) ₆ ³⁻ , Hg ₂ ²⁺ , SO ₄ ²⁻ , SeO ₄ ²⁻ , CrO ₄ ²⁻ , HPO ₄ ²⁻ , Na ⁺ , HCO ₃ ⁻ , H ₂ PO ₄ ⁻ .
3	OH ⁻ , F ⁻ , CNS ⁻ , CNO ⁻ , HS ⁻ , ClO ₄ ⁻ , K ⁺ , Cl ⁻ , Br ⁻ , I ⁻ , CN ⁻ , NO ₂ ⁻ , NO ₃ ⁻ , Rb ⁺ , Cs ⁺ , NH ₄ ⁺ , Ag ⁺ .

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

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

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

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

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

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

Figure 1 is a graph for determining γ when I is known for the various major ions, and some minor ions, of natural water. The graph was prepared using the Debye-Hückel equation and assumes a temperature of 25°C. Ions listed in table 5 that have the same ionic charge and a_i value plot on the same line (Al³⁺ and Fe³⁺, for example). Figure 1 can therefore be used for many species besides those specifically identified on the graph.

Calculation of Activity Coefficients at Higher Ionic Strength

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

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

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

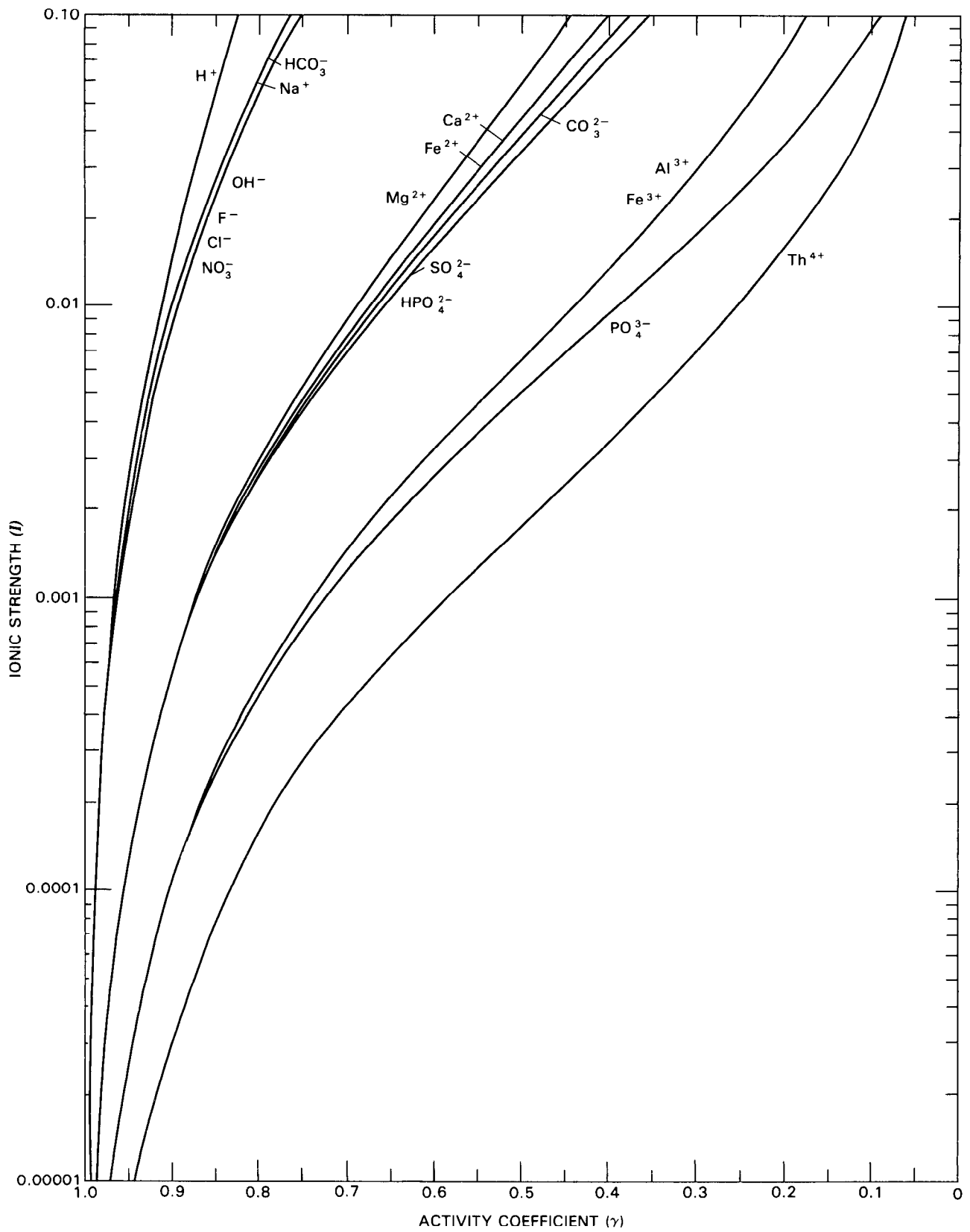


Figure 1. Relation of activity coefficients for dissolved ions to ionic strength of solution (25°C)

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

Effects of Temperature and Pressure on Chemical Equilibria

Many of the calculations and examples given in this book were made by assuming standard conditions (25°C and 1 atmosphere pressure). The effects of moderate departures from standard conditions (a few atmospheres pressure and $\pm 10^\circ$ 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 (ΔH°) 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 ΔH°_R by a summation like that used to compute ΔG°_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:

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

where the temperature values T_1 and T_2 are in Kelvins and ΔH°_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 ΔH° 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:

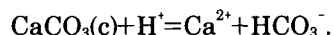
$$\frac{\text{Volume percent} \times \text{total pressure (atmospheres)}}{100}$$

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



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

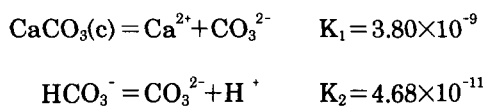
$$K = \frac{[\text{Ca}^{2+}][\text{HCO}_3^-]}{[\text{CaCO}_3(\text{c})][\text{H}^+]}$$

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

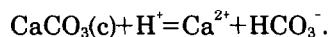
The requirement that specified solids actually must be present is easily overlooked, and information on

solids is obviously not given in the usual water analysis. Without reasonable assurance that solids specified are present, the application of equilibrium calculations may be misleading.

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



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



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

$$\frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{[\text{CaCO}_3(\text{c})]} \div \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} = \frac{3.80 \times 10^{-9}}{4.68 \times 10^{-11}} = 0.81 \times 10^2$$

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

$$\frac{[\text{Ca}^{2+}][\text{HCO}_3^-]}{0.81 \times 10^2} = [\text{H}^+]$$

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

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

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

$$\text{pH}(\text{meas}) - \text{pH}(\text{equil}) = \text{S.I.}$$

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

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

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

Free Energy and the Equilibrium Constant

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

$$-\Delta G_R^\circ = RT \ln K,$$

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

$$-\Delta G_R^\circ = 1.364 \log K,$$

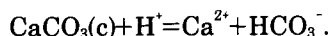
when ΔG_R° is in kilocalories per mole. For data given in kilojoules per mole, the expression becomes

$$-\Delta G_R^\circ = 5.707 \log K.$$

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

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

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



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

<i>Species</i>	ΔG°_f
CaCO ₃ (c) (calcite)	-269.80 kcal/mol
H ⁺	0 (reference state)
Ca ²⁺	-132.30
HCO ₃ ⁻	-140.26

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

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

$$K = 1.05 \times 10^2$$

This value for the equilibrium constant compares with 0.81×10^2 for 25°C computed from solubility studies by Jacobson and Langmuir (1974). Differences of this sort are large enough to be of concern for many purposes. However, the compilations of free energy data can be used to make many useful theoretical evaluations of chemical processes that might control natural-water composition. Where appropriate, extensive arrays of equilibria may be set up and solved simultaneously, or a given water composition can be tested for possible equilibrium with a long list of mineral species. Computations of this type are routine tasks for modern computer technology, and a large number of programs have been set up to perform them (Nordstrom, Plummer, and others,

1979). Most such computations, however, postulate the widespread existence of equilibrium in the natural systems being modeled. The extent to which such assumptions may be valid remains uncertain and controversial. Ways of treating various kinds of systems with respect to equilibrium thermodynamics will be considered more closely later in this book.

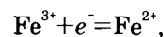
The attractiveness of thermodynamic models and calculations is evident in current literature, but it must be remembered that actual measurements and observations are preferable to computed numbers when it is possible to make them. Some properties of natural systems are difficult to measure, but there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

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

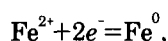
An important caveat should be noted here. Thermodynamic data compilations like the ones referred to above are produced for the most part from calorimetric measurements and data, beginning with simple systems and using the results to develop values for the more complex ions or compounds. The computation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

Electrochemical Equilibrium

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



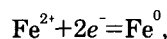
where ferric iron is reduced to the ferrous state. A further reduction,



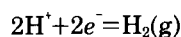
would carry the ferrous ion to metallic iron. The symbol “ e^- ” represents the electron, or unit negative charge.

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

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



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



taken as zero.

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

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

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

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

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

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

$$\Delta G_R^\circ = \Sigma \Delta G_{\text{red}}^\circ - \Delta G_{e^-}^\circ - \Sigma \Delta G_{\text{ox}}^\circ$$

and

$$\Delta G_{e^-}^\circ = 0.$$

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

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

$$-\Delta G_R = nFE$$

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

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

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

$$E = E_h = E^\circ + \frac{RT}{nF} \ln \frac{[\text{oxidized}]}{[\text{reduced}]}.$$

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

$$+\Delta G_R^\circ = nFE^\circ.$$

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

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

$$E_h = E^\circ + \frac{0.0592}{n} \log \frac{[\text{oxidized}]}{[\text{reduced}]}.$$

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

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

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

$$-\Delta G^{\circ}_R = nFE^{\circ},$$

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

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

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

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

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

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

$$pE = Eh/0.0592.$$

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

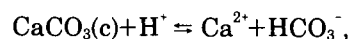
Disequilibrium Indices

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

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

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

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



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

The reaction affinity A which was defined earlier as

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

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

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

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

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

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

Thermodynamics of Nonequilibrium Systems

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

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

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

lished by Helgeson (1968) and by Helgeson and others (1969) and, more recently, by Lasaga and Kirkpatrick (1981).

Rates of Chemical Reactions

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

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

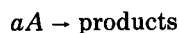
A mechanical analogy to this kind of feedback effect is evident in a long freight train traversing a mountain pass. As the locomotive reaches the summit and starts downgrade, the kinetic energy of that part of the train moving downhill becomes available to help move the remaining part of the train still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

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

Rate Constants: Order of Reaction

The rate at which a chemical reaction occurs can be observed in a controlled system by noting the rate at which a reactant disappears or the rate at which a product is formed. In an irreversible chemical process (one in which products are removed from the reaction site or

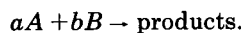
back-reaction effects, for whatever reason, do not influence the system significantly)



the rate of reaction of A can be represented as

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

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



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

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

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

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

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

Such a process might occur when the concentration of A is always very small compared with that of another reacting substance. There are some processes whose rate is controlled by availability of reaction sites at a solid

surface. These could display zero-order kinetics if the number of sites is always large compared to the concentration of A .

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

Integration of the first-order rate expression leads to

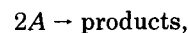
$$kt = 2.303 \log \frac{[A]_0}{[A]_t},$$

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

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

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

For the second-order reaction of the type



the expression for the rate of loss of A is

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

Integration of this equation leads to

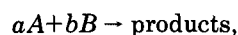
$$kt = \frac{1}{[A]_t} - \frac{1}{[A]_0} = \frac{[A]_0 - [A]_t}{[A]_0 [A]_t}.$$

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

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

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

For a second-order process of the type



the rate expression after integration gives

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

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

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

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

Effect of Temperature on Reaction Rate

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

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

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

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

Chemical Kinetics and the Law of Mass Action

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

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

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

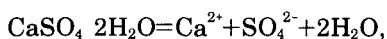
Solubility Concepts

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

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

Solubility Product

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

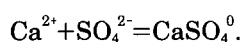


and the corresponding solubility product expression is (with water having unit activity)

$$[\text{Ca}^{2+}][\text{SO}_4^{2-}] = K_{\text{SO}}.$$

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

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



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

$$K = \frac{[\text{Ca}^{2+}][\text{SO}_4^{2-}]}{[\text{CaSO}_4^0]}.$$

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

$$C_{\text{Ca}(\text{total})} = \frac{[\text{Ca}^{2+}]}{\gamma_{\text{Ca}^{2+}}} + \frac{[\text{CaSO}_4^0]}{\gamma_{\text{CaSO}_4^0}}$$

and

$$C_{\text{SO}_4(\text{total})} = \frac{[\text{SO}_4^{2-}]}{\gamma_{\text{SO}_4^{2-}}} + \frac{[\text{CaSO}_4^0]}{\gamma_{\text{CaSO}_4^0}}.$$

If no other ions are present to form complexes with calcium or sulfate, the three equations containing activity (bracketed) terms above should describe the aqueous chemical species adequately. The equilibrium constants needed can be found in data compilations such as that of Smith and Martell (1976), $C_{\text{Ca}^{2+}}$ and $C_{\text{SO}_4^{2-}}$ are known, and $\gamma_{\text{CaSO}_4^0}$, the activity coefficient for the uncharged ion pair, can be assumed to be unity. There remain five unknown terms, including two activity coefficients, for which initial estimates can be made by ignoring CaSO_4 ion pairing. Thus, there are three unknowns to be determined and three equations that may be solved simultaneously. The activity of CaSO_4^0 thus obtained can be used to correct the initial estimate of ionic strength, and the whole computation repeated until further recycling does not change the calculated activities of calcium and sulfate. These can then be used to compute an activity product for comparison with the solubility product for gypsum.

When other cations and anions are present in large amounts, more ion pairs must be taken into account by adding them as terms to the equations for $C_{\text{Ca}^{2+}}$ and $C_{\text{SO}_4^{2-}}$ and by including stability equilibria for them in the calculations. In principle, the method is applicable to highly complicated systems, and it becomes desirable in practice to program the equations for an electronic computer.

Reactions at Interfaces

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

Gas-Liquid Interfaces

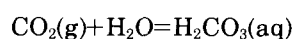
The surface of a body of water in contact with the atmosphere at standard pressure and temperature is rather rigidly maintained by intermolecular forces, as shown by the surface tension of water, which is 72.2 dynes per centimeter at 20°C, a value higher than that of most liquids. Water molecules, however,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

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

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

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

For carbon dioxide, the solubility relationship may be written



$$K_h = \frac{[\text{H}_2\text{CO}_3]}{P_{\text{CO}_2}}$$

The further reaction of $\text{H}_2\text{CO}_3(\text{aq})$ produces other dissolved species, but the amount of dissolved carbon dioxide in undissociated form is accurately predicted by the value of K_h , which is known for a wide range of temperatures. Values for K_h in table 33 entail the conventional assignment of all undissociated aqueous CO_2 to the H_2CO_3 form.

Liquid-Solid Interfaces

Interactions that occur at interfaces between solid and solution phases obviously are important. Any reaction involving dissolution or precipitation of a solid ultimately occurs at such an interface. Also of interest here, however,

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

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

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

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

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

Purely thermodynamic theoretical models of adsorption at mineral surfaces are beyond the scope of this discussion. This transition from the solution phase to the solid phase, however, can be represented in terms of energy, and this has useful implications in solution or deposition processes. A very finely divided precipitate, for example, may have a greater solubility than a precipitate that is identical in composition and structure but is present in larger crystals. This difference can be assigned to the surface free energy of the solid. The magnitude of this quantity (generally a few tens or hundreds of ergs per square centimeter) is too small to be noticed until the

area per unit weight of solid becomes very large, as it would be, for example, if the mean diameter of solid particles were $0.1 \mu\text{m}$ or less. Some observations of this effect have been reported by Schindler (1967), Hostetler (1963), and many other investigators.

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

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

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

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

chemistry is covered in the well-known text by Adamson (1976).

Adsorption Equations

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

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

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

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

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

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

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

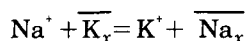
where θ is the fraction of adsorption capacity that is occupied by \overline{A}_x . This isotherm can be applied over a considerable range of concentrations.

Cation Exchange Capacity, Selectivity

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

In any event, the reversibility of the process suggests that a mass law model might be used, and a substantial number of water-chemistry studies have used this ap-

proach. For solutions containing sodium and potassium, the equation would be



or

$$K_s = \frac{[\text{K}^+] [\overline{\text{Na}_x}]}{[\overline{\text{K}_x}] [\text{Na}^+]}$$

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

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

Electrical Double-Layer Models

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

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

Membrane Effects

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

$$\pi = \frac{RT}{V} \ln \frac{\alpha_{1\text{H}_2\text{O}}}{\alpha_{2\text{H}_2\text{O}}}$$

where

R = gas constant (for conversion of units),

T = temperature, in Kelvins,

V = molar volume of water,

$\alpha_{1\text{H}_2\text{O}}$ = activity of water in more dilute solution, and

$\alpha_{2\text{H}_2\text{O}}$ = activity of water in more concentrated solution.

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

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

where, on the molar scale,

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

P_0 = vapor pressure of solvent,

and P = vapor pressure of solution.

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

Semipermeable or selectively permeable membranes are used in industrial water purification; in such processes, the osmotic effect is used in reverse, with pressure being

applied to the solution from which one wishes to extract water, leaving solutes behind.

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

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

Clays as Semipermeable Membranes

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

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

was less well defined. The possible importance of clay membrane filtration in concentrating solutes in subsurface brines was pointed out by Bredehoeft and others (1962). Field studies of such effects in the Kettleman North Dome oil field in California were reported by Kharaka and Berry (1974).

Relationships Among Environmental Factors and Natural-Water Composition

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

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

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

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

Climate

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

Certain of the major ionic constituents of natural water are influenced more strongly than others by climatic effects. Bicarbonate, for example, tends to predominate in water in areas where vegetation grows profusely. Some metals are accumulated by vegetation and may reach peak concentrations when plant-decay cycles cause

extra amounts of these metals to enter the circulating water. These effects are most readily observed in river water, because most of the runoff that enters the streams has spent some time within soils of the drainage basin and also may contact fallen leaves and other plant debris.

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

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

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

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

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

Geologic Effects

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

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

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

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

White (1957b) also defined "magmatic water" as water released when rocks deep within the crust or mantle are converted to a molten state. An older term

used by some geochemists is "juvenile water," meaning water that has not previously been involved in the circulating system of the hydrologic cycle. The water that is, or has recently been, in circulation is termed "meteoric." The difficulty in ascertaining whether any fraction of a natural water is juvenile makes this classification virtually useless. Some water of meteoric origin may remain in storage in aquifers for very long periods of time.

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

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

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

Biochemical Factors

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

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

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

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

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

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

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

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

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

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

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

Influence of Soil and Soil-Forming Processes

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

The major features of the chemical composition of many natural waters are the result of soil-forming proc-

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

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

Aquatic Biota

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

Many of the chemical processes occurring in soil also occur in freshwater bodies. Photosynthesis by plant species rooted in the pond or stream bottom, as well as by floating species, produces oxygen and consumes carbon dioxide, and respiration and decay consume oxygen and produce carbon dioxide. A well-defined diurnal cyclic fluctuation of pH often can be observed in near-surface water of lakes and streams (Livingstone, 1963, p. 9). Aquatic plants also require nutrient elements, especially nitrogen and phosphorus, which they may take up through roots in the bottom sediment or may assimilate directly from the water. The photosynthesizing biota help provide food and oxygen for other life forms in the water where they grow. Cycles of growth and decay produce organic

debris that is partly precipitated to the bottom of the water body, where it may serve as food for other kinds of organisms. Diatoms extract silica from water in which they grow. Other solutes, including some trace constituents, are essential nutrients for certain species of biota. As a result, the concentrations of some trace elements may be controlled by biological processes. Biological effects on iron concentrations were noted by Oborn and Hem (1962).

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

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

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

The Hydrologic Cycle

A characteristic property of the free water of the Earth is its continual motion, imparted primarily by the input of radiant energy from the Sun. This energy input causes some liquid water, wherever a water surface is exposed to the atmosphere, to be converted to the vapor state and carried off by wind. When atmospheric condi-

tions become favorable, the vapor returns to the liquid state with a release of energy, first forming the very small droplets of clouds and then, if temperatures are low enough, tiny ice crystals. Rain or snow may be produced if the condensation proceeds under favorable conditions. The amounts of energy involved in water circulation in the atmosphere are very large in total and when concentrated, as in tropical storms, may have spectacular consequences. The water reaching the land surface by precipitation moves downgradient in the general direction of the ocean or a point of minimum gravitational energy.

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

Sources of Solutes in the Atmosphere

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

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

Some elements form solids or liquids with a significant vapor pressure at ordinary temperatures. Certain boron compounds, for example (Gast and Thompson, 1959), tend to evaporate from the ocean to a significant extent for this reason. The elements iodine and mercury

have appreciable vapor pressures at low temperature, but those elements are comparatively rare and do not influence air or rainfall composition appreciably.

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

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

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

Composition of Atmospheric Precipitation

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

Gorham (1955) made extensive observations of rainfall composition in the English Lake District, an area about 50 km east of the Irish Sea. These data showed a resemblance to seawater in the ratios of sodium to chloride and magnesium to chloride. Gorham (1961) discussed the general influence of atmospheric factors on water

quality in a later paper. Some of the rather voluminous data from work done in the U.S.S.R. were summarized by Drozdova and Makhon'ko (1970). The occurrence of minor constituents, for example fluoride (Mikey, 1963), in rainfall was studied in some of this work.

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

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

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

The reported composition of rainfall is influenced by the methods used to obtain samples for analysis. The samples collected for some investigations represent only

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

The values given in table 6 show that rainfall composition is highly variable, not only from place to place,

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

Constituent	1	2	3	4	5	6
SiO ₂	0.0	1.2	0.3	0.1
Al01
Fe00015
Ca0	.65	1.2	.8	1.41	.075
Mg2	.14	.7	1.2027
Na6	.56	.0	9.4	.42	.220
K6	.11	.0	.0072
NH ₄0
HCO ₃	3	7	4
SO ₄	1.6	2.18	.7	7.6	2.14	1.1
Cl2	.57	.8	17	.22
NO ₂0200	.02
NO ₃1	.62	.2	.0
Total dissolved solids	4.8	8.2	38
pH	5.6	6.4	5.5	4.9

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

but also from storm to storm in a single area—and within individual storm systems as well. A very large volume of air passes through a storm system. The very nature of the conditions that often produce rain, a mingling of air masses of different properties and origins, ensures a high degree of vertical and horizontal non-homogeneity. Analyses 3 and 4 in table 6 represent samples of rain collected successively during a rainy period at Menlo Park, Calif. The later sample shows a considerably higher concentration of solutes than the earlier. Analyses 2 and 6 in table 6 represent bulk precipitation, and analysis 1 probably can be assumed to have been influenced by dry fallout. The other data in the table represent composition of rainfall unaffected by dry fallout. The variability of solute concentrations in rain at Menlo Park and at a site about 550 km further north was studied intensively by Kennedy and others (1979) during parts of 1971 and 1972.

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

Influence of Humans

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

Chemical Thermodynamic Models Applied to Natural Water

The foregoing discussion of environmental factors that influence natural-water composition indicates clearly that many complications exist. Nevertheless, the theoretical concepts and application techniques briefly described in earlier sections hold much promise for evaluating and

understanding these processes and their effects. At this point it is worthwhile to review some recent efforts to apply equilibrium thermodynamics to develop models of natural-water chemistry, and the ways in which the models have been used in different kinds of systems.

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

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

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

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

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

A description of many chemical models and a discussion of their applicability to various situations was published by Nordstrom, Plummer, and others (1979).

A description of the approaches used in the U.S. Geological Survey model development process was published by Plummer and others (1983). Coupling of water quality to water-transport models is considered elsewhere in this book.

The Phase Rule

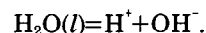
Systems in which natural waters occur are heterogeneous—that is, they include more than one phase (solids, liquid water, and gases). In evaluating the degree to which the solute concentrations of water in such systems can vary independently, it is sometimes helpful to apply the phase rule formulated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

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

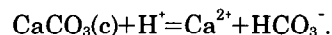
Phases in this context represent the parts of the system that are homogeneous within themselves and have definable boundary surfaces. Components are the minimum number of independent chemical constituents derived from or constituting the phases that must be present to reproduce the system. The degrees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

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

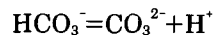
1. Dissociation of water:



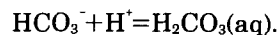
2. Reaction of calcite with aqueous H^+ :



3. Interactions among dissolved carbonate species:



or



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

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

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

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

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

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

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

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

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

Some Characteristics of Ground-Water Systems

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

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

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

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

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

Surface Water Systems—Rivers

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

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

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

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

Chemical equilibria probably control a few properties of water in flowing streams. For example, the ion-exchange reactions of solutes with suspended sediment probably are rapid enough that they usually are at equilibrium. Kennedy and Brown (1966) found that sodium-

saturated natural sediments from Brandywine Creek, Del., exchanged 90 percent of their adsorbed sodium for calcium in 3–7 minutes in laboratory experiments. Certain oxidations, ferrous to ferric iron, for example, also normally may reach equilibrium quickly. The equilibrium approach, however, seems inadequate for studies of most biologically mediated processes such as use and production of carbon dioxide and oxygen. A river is by nature a dynamic system, and kinetic principles would seem much better suited to stream chemistry than the steady-state equilibrium approach. For example, the processes whereby biota consume organic-pollution loads of streams often can be most effectively studied by application of kinetics and nonequilibrium models.

Lakes and Reservoirs

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

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

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

Estuaries

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

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

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

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

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

In subsequent years, the Geological Survey conducted extensive studies in several other estuaries, notably in San Francisco Bay, Calif. and in the Potomac River estuary, and many data compilations and research reports have been produced. Examples of individual estuarine research studies are given in the annual volumes of "Geological Survey Research" (U.S. Geological Survey, 1980a, p. 159-162; 1980b, p. 167-174). An overview of water-quality aspects of an intensive study of the Potomac Estuary and the section of the Potomac River affected by tides is given by Callender and others (1984). Much of

the information obtained in estuarine studies is unique to the system where it was collected, but some broad understanding of processes is gained from such studies.

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

Water Chemistry and Movement in the Unsaturated Zone

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

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

ed to appear, eventually, in shallow ground water in such areas.

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

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

Geochemical Cycles

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

For many years, geochemists have been interested in these circulation patterns, and some have tried to deduce the Earth's erosional history from differences in distribution of elements between igneous rocks on one hand and the sedimentary rocks and the ocean on the other. If the premise is accepted that the sediments were derived from erosion of igneous rocks having an average composition similar to the igneous rocks now available for sampling, and that the surplus of eroded elements not

accounted for in the observable present volume of sediments was left in the ocean, it is possible to estimate how much erosion of the outer crust has taken place. Goldschmidt (1933, 1937, 1954) made a series of such estimates on the basis of the distribution of sodium among igneous and sedimentary rocks and the water of the oceans. His figure, which is widely known and quoted, is that the equivalent of 160 kg of igneous rock has been eroded from each square centimeter of the Earth's surface.

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

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

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

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

Amounts of some of the elements that are contributed annually to the ocean by rivers are still imperfectly known. Goldberg and Arhennius (1958), however, prepared estimates of removal rates and residence times of a large number of elements by determining the composition and rate of accumulation of sediment in the ocean. This approach uses the same fundamental concept as Barth's, and residence times agreed reasonably well where they could be computed for some of the elements by both

methods. The residence times of the elements determined by Goldberg (1963a) are given in table 7. These range from 2.6×10^8 years for sodium to only 100 years for aluminum. Similar results were reported by MacKenzie and Garrels (1966).

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

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

Cycles of some elements are interrelated. Lasaga (1980) evaluated some aspects of coupling between the cycles of carbon and oxygen, using concepts of thermodynamics of irreversible processes. This approach has interesting possibilities for future theoretical studies, be-

cause one can predict stable states that are not at thermodynamic equilibrium.

EVALUATION OF WATER COMPOSITION

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

Collection of Water Samples

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

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

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

Table 7. Average residence time of elements in the ocean

[After Goldberg (1963a)]

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