Water-Quality Principles
QW1022–TEL

Lesson 4—Governing Principles of Aqueous Systems

Source:

Hem, J.D., 1985, Study and interpretation of the chemical characteristics of natural water: U.S. Geological Survey Water Supply Paper 2254, p. 10–12, 14–15, 23.

U.S. Department of the Interior
U.S. Geological Survey

PRINCIPLES AND PROCESSES CONTROLLING COMPOSITION OF NATURAL WATER

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

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

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

Thermodynamic principles may also be useful in correlating chemical processes with biological or physical processes. However, for many environmental effects it is not usually possible to use this approach very rigorously. The statements here about nonchemical factors are generalized and somewhat qualitative. Nevertheless, the interrelationships of water chemistry and water environment constitute the principal theme of this book, and an improved understanding of them is the goal of workers in this field.

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

Thermodynamics of Aqueous Systems

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Chemical Reactions

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

Reversible and Irreversible Reactions in Water Chemistry

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

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

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

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

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

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

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

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

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

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

Chemical Equilibrium—The Law of Mass Action

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

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

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

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

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

and

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

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

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

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

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

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

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

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

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

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

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

For the reaction

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

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

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

At standard states,

$$c\Delta G^\circ{}_C+d\Delta G^\circ{}_D-a\Delta G^\circ{}_A-b\Delta G^\circ{}_B=\Delta G^\circ{}_R.$$

As shown above,

$$\mu_A=\Delta G^\circ{}_A+RT\ \ln\alpha_A,$$

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

$$c(\Delta G^\circ{}_C+RT\ln\alpha_C)+d(\Delta G^\circ{}_D+RT\ln\alpha_D)$$
$$-a(\Delta G^\circ{}_A+RT\ln\alpha_A)-b(\Delta G^\circ{}_B+RT\ln\alpha_B)=\Delta\mu_R.$$

This rearranges to

$$\Delta\mu_R=\Delta G^\circ{}_R+RT\ln\frac{\alpha^c{}_C\times\alpha^d{}_D}{\mu^a{}_A\times\alpha^b{}_B}.$$

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

$$-\Delta G^{\circ}_R = RT \ln \frac{\alpha^c{}_C \times \alpha^d{}_D}{\alpha^a{}_A \times \alpha^b{}_B} \quad .$$

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/kgH_2O) or molar (moles of i/L) scale, and γ_i is the activity coefficient. The use of brackets to denote activity is the convention followed in this book. Molar activities will be used throughout. In dilute solutions, molal and molar scales are nearly the same.

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

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

The form of the Debye-Hückel equation used here is

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

where

γ_i is the activity coefficient of the ion,

Thermodynamics of Nonequilibrium Systems

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

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

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

Rates of Chemical Reactions

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

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

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

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