Water-Quality Principles
QW1022–TEL

Lesson 7—Reduction-Oxidation (Redox) Chemistry

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Electrochemical Equilibrium (p.20)

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

$$Fe^{3+} + e^{-} = Fe^{2+},$$

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

$$Fe^{2+}+2e^{-}=Fe^{0},$$

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

$$Fe^{2+}+2e^{-}=Fe^{0},$$

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,

$$2H^{+}+2e^{-}=H_2(g)$$

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 Eh, 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

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

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,

$$\Delta G^{\circ}_R=\Sigma\Delta G^{\circ}_{\text{red}}-\Delta G^{\circ}_{e^-}-\Sigma\Delta G^{\circ}_{\text{ox}}$$

and

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

The thermodynamic equilibrium condition for the couple requires that $\alpha^{\circ}_{e^-}=1$ 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,

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

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

$$+\Delta G^{\circ}_R=nFE^{\circ}.$$

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 "Eh" 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

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

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,

$$\text{pE} = \text{Eh}/0.0592.$$

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:

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

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

$$CaCO_3(c) + H^+ \rightleftharpoons Ca^{2+} + HCO_3^-,$$

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

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

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

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

Redox Potential

In the section "Electrochemical Equilibrium" the concept of the redox potential, or Eh, of an aqueous system was introduced. It was shown that when the oxidation and reduction processes within the system are at a state of equilibrium, the Eh of the system is a function of the standard potential of the reduction half-reaction and the activities of participating species. This relationship, the Nernst equation, was used in the discussion of iron chemistry to develop pH-Eh diagrams that summarize the redox chemistry of the element.

The redox potential is a numerical index of the intensity of oxidizing or reducing conditions within a system, with the hydrogen-electrode potential serving as a reference point of zero volts. Positive potentials indicate that the system is relatively oxidizing, and negative potentials indicate that it is relatively reducing. In the notation used in this book, Eh values are given in volts. As noted earlier, the calculated pH-Eh relationships are useful for predicting and defining equilibrium behavior of multivalent elements.

If an inert metal electrode is immersed in a solution containing oxidized and reduced species, it should attain an electrical potential matching that of the redox couples in the system—assuming that a reversible equilibrium among electron-donating and electron-accepting species and the electrode surface exists. The size and sign of the potential can be evaluated if a standard electrode, having a known potential, is also immersed in the solution and both electrodes are connected to a sensitive electrometer. Most pH meters are capable of these measurements. Potentiometric measurements have been used for a long time in analytical chemistry, to determine the end point in redox titrations, for example. The inert metal electrode generally is one made of platinum.

If all the necessary requirements are fulfilled, it should be possible to measure redox potentials in natural-water systems. Such measured values would then represent the redox intensity in a manner completely analogous to the calculated or theoretical values based on ratios of solute activities and the Nernst equation. Many investigators have made measurements of this type and have interpreted them, or attempted to interpret them, with various degrees of success. ZoBell (1946) was one of the first investigators to make measurements in materials of geologic interest. A large number of published measurements on various kinds of water and sediment-water mixtures were compiled by Baas-Becking and others (1960). Measurements have been made in connection with studies of ground-water composition, especially with respect to iron chemistry (Back and Barnes, 1961, 1965; Barnes and Back, 1964b) in connection with water-treatment plant operations (Weart and Margrave, 1957), as an indication of the conditions in sewage digestors, and in numerous studies of soils, biochemical systems, and lake and ocean sediments. Redox data also were used by Clarke (1966) and by Barnes and Clarke (1969) in describing and studying causes of corrosion and encrustation of well casings. Measurements in ground water in the U.S.S.R. were described by Germanov and others (1959). A theoretical evaluation of measured redox potentials in aqueous iron systems by Doyle (1968) suggested that ferric oxyhydroxide is deposited on the platinum electrode during the measurement, giving a stable potential that is in accord with the one predicted by the Nernst equation.

The measurement of electrode potentials in natural aqueous systems that correspond to theoretical Eh values encounters many difficulties. Many redox couples do not behave in a reversible fashion at the platinum-electrode surface. Some systems may be perturbed by the presence of the electrodes, and others give mixed potentials that are influenced by several different couples. Some of these limitations were described by Stumm and Morgan (1981, p. 490–495) and by Bricker (1982, p. 59–65).

Factors that stabilize the redox potential in an aqueous system are similar to those involved in stabilizing other properties of solutions in these systems. A system whose Eh is stabilized toward the effects of minor environmental changes is said to be "poised." The poising effect can be exerted by large reserves of reactants, in the same way pH may be stabilized by buffering through reserves of reactants that interact with H^+ ions.

In its natural environment, a ground water may be poised by reactive solids or adsorbed species on solid surfaces. When brought to the land surface and into contact with air, the unpoised redox system in the water may be quickly overwhelmed by reactions involving oxygen. Solutions in contact with air give a measurable redox potential, but one that is far from the thermodynamically predicted value for the H_2O–O_2(aq) couple. The mechanism establishing this potential has been ascribed to several different effects, but the effect of oxygen tends to be the dominant control on measurements of redox potential in natural water in contact with air.

Difficulty of measurement of redox potential in ground-water systems has led to suggestions by some investigators that a calculated value would be more dependable. Such calculated values can be obtained by applying the Nernst equation to determined data on activities of species participating in redox couples, with the further assumption that these activities were equilibrium values. Cherry and others (1979) suggested, for example, the use of determined values for arsenic solute species to compute Eh. Dissolved-iron concentrations can be used for this purpose in some waters (Hem and Cropper, 1959, p.17–20).

Measured redox potentials have been shown to be useful in studies of systems that can be well characterized, or that are controlled in the laboratory and in which the reactants behave reversibly. Studies related to iron chemistry have already been cited. Bricker (1965) used Eh measurements in studies of manganese chemistry. Berner (1963) and Boulegue and Michard (1979) used such measurements in evaluating reduced sulfur species.

Whether Eh values are measured or calculated, they relate to ratios of solute activities and give little or no indication of the quantitative capacity of the system to oxidize or reduce material that might be introduced from outside. Other characteristics of the system must be evaluated to apply predictive redox models.

Whatever the experimental difficulties in measuring Eh values, the usefulness of the Nernst equation and the pH-Eh diagram in generalized theoretical studies of redox equilibria in natural water is well established. The diagram is an indication of limiting conditions and is a clear, simple, and convenient means of evaluating the chemical-equilibrium status of multivalent elements in a specified environment. Techniques for preparing such diagrams are given in the discussion of iron chemistry in an earlier section of this book.