CHAPTER

9

OXIDATION AND REDUCTION

The reddish-brown coloration of many weathered rock surfaces is a familiar sight. The color is generally caused by fine-grained Fe(III) compounds, formed by reaction of Fe(II) minerals with oxidizing agents in rain and air. Reactions of this sort, involving a change in oxidation state, are referred to as oxidation–reduction reactions. They occur not only during rock weathering, but in diagenetic, metamorphic, and magmatic processes as well. Oxidation–reduction reactions have a controlling influence on the solubility and transport of some minor elements in seawater, groundwater, and hydrothermal solutions. The stability of many ore minerals and the sequence of mineral crystallization in magmas are sensitive functions of oxidation state. In this chapter we explore the chemistry of oxidation–reduction reactions and develop methods to represent their equilibria graphically.

Oxidation means an increase in oxidation state, reduction a decrease. For example, when zinc displaces copper from a solution of copper sulfate,

$$\mathrm{Zn} + \mathrm{Cu}^{2+} \rightarrow \mathrm{Zn}^{2+} + \mathrm{Cu}, \tag{9-1}$$

the zinc is oxidized (change in oxidation state from 0 to +2) and the copper is reduced (+2 to 0). When chlorine displaces bromine from a solution of sodium bromide,

$$\mathrm{Cl}_2 + 2\mathrm{Br}^- \rightarrow 2\mathrm{Cl}^- + \mathrm{Br}_2, \tag{9-2}$$

chlorine is reduced (0 to −1) and bromine is oxidized (−1 to 0). And when gold is dissolved by the action of MnO_2 in hydrochloric acid solution,

$$3MnO_2 + 2Au + 12H^+ + 8Cl^- \rightarrow 3Mn^{2+} + 2AuCl_4^- + 6H_2O, \qquad (9\text{-}3)$$

manganese is reduced (+4 to +2) and gold is oxidized (0 to +3). Alternatively, oxidation may be described as a loss of electrons and reduction as a gain; in the zinc–copper reaction, for example, each Zn atom loses two electrons to a copper ion. Note that any reaction of this sort must involve both an oxidation and a reduction, and that the total changes in oxidation state must balance (see Appendix X for methods of balancing oxidation–reduction reactions).

Conditions of equilibrium for reactions like these can be described using the methods of the preceding chapter. But in addition to equilibrium constants and free energy, another device is available for describing the tendency of one substance to react with another when the reaction involves changes in oxidation state. This device, called the oxidation potential or oxidation–reduction potential, often provides the most convenient method of getting the desired quantitative information.

9-1 OXIDATION POTENTIALS

Any oxidation–reduction reaction, theoretically at least, can be set up so that the transfer of electrons from one element to another will take place along a wire. For the zinc–copper reaction the arrangement is very simple: pieces of the two metals are connected by a wire and submerged in copper sulfate solution. The piece of zinc slowly dissolves, fresh copper from the solution plates out on the copper metal, and a current flows through the wire. The process occurring at the zinc electrode may be symbolized

$$Zn \rightarrow Zn^{2+} + 2e^-, \qquad (9\text{-}4)$$

where e^- indicates an electron. The liberated electrons move along the wire to the copper electrode, where they are used in the reaction

$$Cu^{2+} + 2e^- \rightarrow Cu. \qquad (9\text{-}5)$$

Reactions of this kind, showing the processes that occur as electrons are produced or consumed at an electrode, are called *half-reactions*, or *electrode reactions*. Addition of two half-reactions gives the complete oxidation–reduction reaction; thus Eq. (9-5) added to Eq. (9-4) gives Eq. (9-1). For a more complicated illustration, the electrode reactions corresponding to Eq. (9-3) are:

$$3MnO_2 + 12H^+ + 6e^- \rightarrow 3Mn^{2+} - 6H_2O \qquad (9\text{-}6)$$

and

$$2Au + 8Cl^- \rightarrow 2AuCl_4^- + 6e^-. \qquad (9\text{-}7)$$

The potential difference between the electrodes of our zinc–copper cell can be measured by adding a galvanometer to the circuit. The amount of the potential difference depends on a great many variables, but we arrange to keep most of these constant. Thus we fix the activity of both Cu^{2+} and Zn^{2+} at 1; we make sure that the metal of the electrodes is pure and has a clean surface; we hold the temperature at 25°C and the pressure at 1 bar; and we arrange to have as small a flow of current as possible. Under such conditions the measurement of potential difference is reproducible and may be compared with potential differences measured similarly for other oxidation–reduction reactions. (We pass over the technical difficulties in such measurements, which for some reactions are very troublesome.)

If we set up a number of cells similar to the zinc–copper cell, using various metals in contact with solutions of metal ions, we find that the metals can be arranged in a series according to their ability to displace one another from solution and according to the size of the potential difference produced by different pairs. Thus zinc displaces copper, copper displaces silver, and silver displaces gold; and the potential difference of a zinc–silver or a zinc–gold cell is greater than the potential difference of a zinc–copper cell. On the other hand, the reverse reactions do not take place appreciably: silver placed in copper sulfate solution or in zinc sulfate solution causes no detectable reaction. Experiments of this sort give us the familiar *electromotive series* of metals, according to which we express the chemical reactivities of various metals with respect to one another.

The electromotive series can be made quantitative by assigning a potential difference to each half-reaction. This requires that one half-reaction be chosen as a standard and given an arbitrary potential of zero, so that other half-reactions can be measured against it. A convenient choice is the hydrogen couple,

$$\tfrac{1}{2}H_2 \rightarrow H^+ + e^- \qquad E^\circ = 0.00 \text{ volt.} \qquad (9\text{-}8)$$

If we arrange a cell with zinc as one electrode and hydrogen as the other (by letting hydrogen at 1 bar and 25°C bubble over a platinum rod), and use a solution containing H^+ and Zn^{2+} both at an activity of 1, we obtain the potential difference for the overall reaction,

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2 \qquad E^\circ = -0.76 \text{ volt,} \qquad (9\text{-}9)$$

and we use this number as the potential for the zinc electrode reaction:

$$Zn \rightarrow Zn^{2+} + 2e^- \qquad E^\circ = -0.76 \text{ volt.} \qquad (9\text{-}10)$$

There is no way of measuring potentials for half-reactions independently. We get them only as differences between pairs of half-reactions, so that the actual numbers are no more than relative voltages compared with the hydrogen electrode.

Electrode potentials and potential differences for complete reactions are both designated by the symbol E. For electrode reactions like Eq. (9-10) the potential E is also called the *electromotive force*. The symbol E° refers to *standard* potentials or potential differences, for reactions that take place with all substances at unit activities; most commonly it refers to reactions at 25°C and 1 bar, but may be used for other specified temperatures or pressures. Standard electrode potentials for some reactions of geologic interest are tabulated in Appendix IX.

Several details about the arrangement in this table should be noted. Each half-reaction is given with the reduced form of the element on the left and the oxidized form on the right. Strong reducing agents appear toward the top of the table, strong oxidizing agents near the bottom. Some reactions follow different courses in acid and basic solutions, because certain precipitates and complex ions are stable in one kind of solution but not in the other; hence it is necessary to include an auxiliary table for those reactions that occur only in an alkaline environment. The + and − signs given to the voltages are purely arbitrary, and unfortunately are not uniform from one reference to another. In this book, we follow the usual practice in geochemical literature, making voltages more reducing than the hydrogen electrode negative and those more oxidizing than the hydrogen electrode positive.

Qualitatively, the table tells us at a glance what reactions are possible and what are not. The reduced form of any couple will react with the oxidized form of any couple *below* it, but not with the oxidized form of a couple above it. Thus Pb will reduce Ag^+ but not Al^{3+}. Two reactions close together in the table will reach equilibrium with all substances present in appreciable amounts; thus metallic lead and tin are stable in contact with a solution containing fairly large amounts of both Pb^{2+} and Sn^{2+}. Technically, of course, all possible reactions indicated by the table are equilibrium processes. When we say "Pb will not reduce Al^{3+}," we mean more precisely that Pb will react until a very small amount of Pb^{2+} is formed, but that the ratio $a_{Al^{3+}}/a_{Pb^{2+}}$ is very large at equilibrium.

To use the table quantitatively to find the potential difference for a particular reaction, we need only subtract one half-reaction from another and subtract the corresponding voltages. Each reaction must be multiplied by a coefficient that will make the electron changes the same, for no free electrons can appear in the overall reaction. *The voltages, however, are not multiplied by the coefficients*; unlike free energies and enthalpies, the voltages are measurements of potential only and do not change with amount of substance present. For example, to find the potential for the oxidation of Fe^{2+} by MnO_2 in acid solution, we look up the two electrode reactions

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \qquad E^\circ = +0.77 \text{ volt}, \tag{9-11}$$

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^- \qquad E^\circ = +1.23 \text{ volt}. \tag{9-12}$$

To make the electron changes balance, we multiply the iron half-reaction by 2, and then subtract the manganese half-reaction. The standard potential for the overall reaction is found by subtracting the half-reaction potentials without multiplication:

$$MnO_2 + 4H^+ + 2Fe^{2+} \rightleftharpoons Mn^{2+} + 2H_2O + 2Fe^{3+} \qquad E^\circ = -0.46 \text{ volt}. \tag{9-13}$$

The convention regarding + and − signs means that a reaction which takes place spontaneously must have a negative voltage, and one that requires outside energy has a positive voltage—a convention similar to the one we have used for free energy and enthalpy.

9-2 RELATION OF OXIDATION POTENTIAL TO FREE ENERGY

Since the potential difference for a reaction computed from the data of Appendix IX is a measure of how far the reaction mixture is from equilibrium, it must clearly be related to the free energy change of reaction (ΔG). The relation is simple,

$$\Delta G = \mathbf{nf}\,E. \tag{9-14}$$

Here **n** is the number of electrons that the equation shows shifting from one kind of atom to another, E is the potential difference, and **f** is the Faraday constant. This constant is a number which, when multiplied by voltage, gives energy; the usual expression for it is 96,485 coulombs, the corresponding energies being expressed in volt-coulombs, or joules. For example, the standard free energy change in the manganese–iron reaction just discussed is

$$\Delta G^\circ = \mathbf{nf}\,E^\circ = 2 \times 96{,}485(-0.46) = -88{,}766 \text{ joules} = -88.8 \text{ kJ}. \tag{9-15}$$

This checks well with the figure −88.4 kJ which is obtained by adding up free energies of formation in the usual way. Note that a potential difference of half a volt corresponds to a fairly large free energy change.

It should be emphasized again that free energies depend on how the equation is written—i.e., on whether the coefficients are doubled or tripled or halved—while the potential does not. The difference is taken care of in Eq. (9-14) by the factor **n**, which, of course, changes if the coefficients change. By convention, the equality of Eq. (9-14) refers to electrode reactions where electrons appear on the right-hand side, as in the generalized reaction,

$$\textit{reduced state} \rightleftharpoons \textit{oxidized state} + \mathbf{n}e^-. \tag{9-16}$$

So far we have talked exclusively about standard potentials, which are potentials for unit activities at a temperature of 25°C. To find the potential difference for a reaction under different conditions, we make use of the relations developed earlier for free energies. By combining Eqs. (9-15) and (8-42), we obtain for the hypothetical reaction of Eq. (8-44),

$$E = \frac{\Delta G}{\mathbf{nf}} = \frac{\Delta G^\circ}{\mathbf{nf}} + \frac{RT}{\mathbf{nf}} \ln \frac{a_Z^z a_Q^q}{a_X^x a_Y^y}, \tag{9-17}$$

$$= E^\circ + \frac{2.303RT}{\mathbf{nf}} \log \frac{a_Z^z a_Q^q}{a_X^x a_Y^y}, \tag{9-18}$$

an expression called the Nernst equation. For reactions at 25°C the combination of constants before the logarithm is 0.059/**n**, so that

$$E = E^\circ + \frac{0.059}{\mathbf{n}} \log \frac{a_Z^z a_Q^q}{a_X^x a_Y^y}. \tag{9-19}$$

For example, to find the potential for the manganese–iron reaction [Eq. (9-13)] in a solution with pH 3 and unit concentrations of other ions:

$$\begin{aligned} E &= -0.46 + \frac{0.059}{2} \log \frac{a_{Mn^{2+}} a_{Fe^{3+}}^2}{a_{H^+}^4 a_{Fe^{2+}}^2}, \\ &= -0.46 + 0.03 \log \frac{1}{(10^{-3})^4}, \\ &= -0.46 + 12 \times 0.03 = -0.10 \text{ volt}. \end{aligned} \tag{9-20}$$

The smaller negative value for E means that the reaction would have less tendency to take place, as we would expect when the concentration of one of the reactants is reduced. (If the Nernst equation is used to calculate potentials at temperatures other than 25°C, the E° term refers to the standard potential at temperature T, not at 25°C.)

The relation of the oxidation potential to the equilibrium constant for a reaction may be formulated by combining Eqs. (9-15) and (8-51):

$$\mathrm{E}^\circ = \frac{\Delta G^\circ}{\mathbf{nf}} = -\frac{2.303RT \log K}{\mathbf{nf}} = -\frac{0.059}{\mathbf{n}} \log K. \tag{9-21}$$

To find oxidation potentials at elevated temperatures and pressures we simply use values of ΔG° or K computed for the conditions of interest using methods outlined in Chapter 8.

What advantages can be claimed for oxidation potentials as opposed to free energies in handling problems of equilibrium? Their chief merit is convenience: from a table of potentials like Appendix IX one can see at a glance, with no calculation except a mental note of how far apart two half-reactions are in the table, whether a given oxidation-reduction process can be expected to take place and approximately how far the reaction will go. If a more quantitative estimate is needed, the calculation involves only two figures rather than several.

9-3 REDOX POTENTIALS

One further advantage of oxidation potentials is their usefulness in treating problems which concern not only specific reactions but also the general oxidizing or reducing characteristics of a geologic environment. It is common knowledge, for example, that dissolved sulfur is largely in the form of SO_4^{2-} in water of the open sea, where conditions are oxidizing, but chiefly in the form of H_2S in the stagnant bottom waters of enclosed basins. Oxidation potentials make it possible to refine such qualitative statements and to estimate semi-quantitatively just what concentrations of the various ions and compounds of sulfur can exist in these environments.

The ability of a natural environment to oxidize sulfur, or bring about any other oxidation or reduction process, is measured by a quantity called its *redox potential*. Experimentally this is determined by immersing an inert electrode, usually platinum, in the environment—say in a sample of seawater, swamp muck, or soil–and determining the potential difference between the platinum and a hydrogen electrode or some other electrode of known potential. Measured redox potentials of seawater, for example, range between +0.3 volt for aerated water to −0.5 volt for water from bottom sediments containing organic matter. The term redox potential is used by some geochemists also as a synonym for oxidation potential, applicable to potentials of individual half-reactions as well as to potentials of environments. In either usage it is commonly given the symbol Eh to remind us that the potential difference is measured relative to the standard hydrogen electrode [Eq. (9-8)].

As an example, suppose we find the redox potential of a sample of water to be +0.5 volt, and inquire as to the dominant form of dissolved iron in this environment. If the solution is acid, the choice lies between Fe^{2+} and Fe^{3+} (neglecting possible complexes). For the standard potential of the Fe^{2+}–Fe^{3+} couple [(Eq. (9-11)] we read from Appendix IX a value +0.77 volt. The measured potential is more reducing than this; hence we would expect qualitatively to find Fe^{2+} the chief ion. To get a quantitative value for the Fe^{2+}/Fe^{3+} ratio, we substitute in Eq. (9-19), using 0.77 as E° and 0.5 as E (equivalent to Eh as defined above):

$$\mathrm{Eh} = \mathrm{E} = 0.5 = 0.77 + \frac{0.059}{1} \log \frac{a_{\mathrm{Fe}^{3+}}}{a_{\mathrm{Fe}^{2+}}},$$

$$\log \frac{a_{\mathrm{Fe}^{3+}}}{a_{\mathrm{Fe}^{2+}}} = -\frac{0.27}{0.059} = -4.58, \tag{9-22}$$

$$\frac{a_{\mathrm{Fe}^{3+}}}{a_{\mathrm{Fe}^{2+}}} = 10^{-4.58} = 2.6 \times 10^{-5}.$$

In this water, therefore, the equilibrium activity of Fe^{2+} is nearly 40,000 times that of Fe^{3+}. [Note that the activity of the electron which appears in Eq. (9-11) can be omitted from Eq. (9-22) because the electrode potential is measured against the hydrogen electrode, with activities of H_2 and H^+ assumed equal to 1; cf. Eqs. (9-9) and (9-10).]

Redox potential in many ways is analogous to pH. It measures the ability of an environment to supply electrons to an oxidizing agent, or to take up electrons from a reducing agent, just as the pH of an environment measures its ability to supply protons (hydrogen ions) to a base or to take up protons from an acid. In a complex solution like seawater or water in a soil the redox potential is determined by a number of reactions, just as pH is determined by the combined effects of the carbon dioxide system, the boric acid system, and various organic acids. The particular reactions are difficult to identify, and are less important than the overall ability of the environment to maintain its Eh and pH constant when small amounts of foreign material are added.

Although usually expressed, like E°, as a voltage with reference to a standard hydrogen electrode, redox potential may also be described by a number more explicitly analogous to pH, a number called *electron activity* and symbolized *pe*. This is the negative logarithm of an assumed activity of electrons in a solution, just as pH is the negative logarithm of the activity of protons in the solution. As an example, for the Eh of a solution containing the ions Fe^{2+} and Fe^{3+} we generally write

$$\mathrm{Eh} = \mathrm{E}^\circ + \frac{2.303RT}{\mathbf{f}} \log \left(a_{\mathrm{Fe}^{3+}}/a_{\mathrm{Fe}^{2+}}\right), \tag{9-23}$$

where E° is the standard potential of the half-reaction of Eq. (9-11), and where the activity of the electron is omitted from the logarithmic term even though it appears in the expression for the reaction in Eq. (9-11). This is permissible, as noted above, because the potential is measured relative to the standard hydrogen electrode, so that Eq. (9-11) is actually

$$\mathrm{Fe}^{2+} + \mathrm{H}^+ \rightleftharpoons \mathrm{Fe}^{3+} + \tfrac{1}{2}\mathrm{H}_2. \tag{9-24}$$

Because $a_{H^+} = a_{H_2} = 1$ in the standard hydrogen electrode, the activity product of Eq. (9-24) is

$$\frac{a_{Fe^{3+}} a_{H_2}^{1/2}}{a_{Fe^{2+}} a_{H^+}} = \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}}. \qquad (9\text{-}25)$$

Alternatively we could focus attention on the simple expression of Eq. (9-11) without the hydrogen terms and regard e^- as a substance in solution, so that the equilibrium constant would be expressed

$$K = \frac{a_{Fe^{3+}} a_{e^-}}{a_{Fe^{2+}}}, \qquad (9\text{-}26)$$

or in logarithmic form

$$\log K = \log (a_{Fe^{3+}}/a_{Fe^{2+}}) + \log a_{e^-}, \qquad (9\text{-}27)$$

where a_{e-} is the activity of the electrons.

The relationship between Eh and a_{e-} is obtained by first rearranging Eq. (9-27):

$$\log (a_{Fe^{3+}}/a_{Fe^{2+}}) = \log K - \log a_{e^-}, \qquad (9\text{-}28)$$

and combining Eqs. (9-15) and (8-49),

$$E^\circ = \frac{2.303RT}{\mathbf{f}} \log K. \qquad (9\text{-}29)$$

Substitution of these equations [Eq. (9-29) and (9-28)] in Eq. (9-23) gives

$$\mathrm{Eh} = \frac{-2.303RT}{\mathbf{f}} \log K + \frac{2.303RT}{\mathbf{f}} \log K - \frac{2.303RT}{\mathbf{f}} \log a_{e^-}, \qquad (9\text{-}30)$$

$$\mathrm{Eh} = +\frac{2.303RT}{\mathbf{f}} pe, \qquad (9\text{-}31)$$

where the symbol $pe \equiv -\log a_{e-}$. For a system at 25°C, then, $\mathrm{Eh} = (2.303 \times 8.314 \times 298/96{,}485)pe = 0.059pe$. Thus the two numbers for expressing redox potential are proportional, but the proportionality constant changes with temperature. Either Eh or *pe* can be used to represent redox potential, and little advantage can be claimed for choosing one over the other. The main difference is that the slopes of lines representing redox reactions on an Eh–pH diagram are determined, in part, by temperature [Eq. (9-18)], but for diagrams using *pe* as a descriptive variable the slopes of reaction lines are solely a function of reaction stoichiometry.

Unfortunately, redox potentials in nature cannot be determined as simply and unambiguously as this discussion has implied. The difficulty is that some of the reactions that determine redox potentials are slow, so that instantaneous readings with a platinum electrode do not give valid equilibrium potential differences. This is particularly true for reactions involving oxygen, which, of course, include a great many of the most important oxidation reactions in nature. Most reactions in which oxygen plays a role take place by a series of steps, and one of the steps is very slow. Hence redox potentials measured in oxygen-containing environments are generally lower than equilibrium values, and there is no simple way to apply a correction factor. This means that most redox potential measurements in nature give us only qualitative or semi-quantitative information. It is useful nevertheless to make calculations based on the measured values and on theoretical potentials, since such calculations can at least set limits to the processes we may expect in natural environments.

9-4 LIMITS OF pH AND Eh IN NATURE

To make predictions about geologic processes, we need at least a rough idea as to the ranges of natural Eh and pH values. The ranges will obviously be more restricted than those with which the chemist is accustomed to deal in the laboratory.

The limits of pH we have mentioned in earlier discussions. The solutions of highest acidity found in nature are those formed by the dissolving of volcanic gases and by the weathering of ores containing pyrite. Locally such solutions may attain pH's less than zero ($m_{H^+} > 1$). Acidities of this magnitude are quickly lowered by reaction with adjacent rocks, and the rocks are thereby drastically altered, as is evident in the bleached and porous zones commonly found near fumaroles, hot springs, and pyritic ore deposits. Given enough time, contact with ordinary silicate or carbonate rocks would neutralize the solutions. Complete neutralization is generally prevented by dissolution of carbon dioxide from the atmosphere and of organic acids formed by decaying organic matter; these two are the source of acidity in most near-surface waters, giving pH's commonly in the range 5 to 6. Lower pH's are found in the A horizons of pedalfer soils, especially podzols, where values as low as 3.5 are sometimes recorded (see Sec. 13-10 for soil classification). Disregarding the possible extremes, we can reasonably select a figure of 4 as the *usual* lower limit of pH's in natural environments.

At the other end of the scale, CO_2-free water in contact with carbonate rocks can acquire by hydrolysis a pH of about 10, and in contact with the silicates of ultramafic rocks a pH of nearly 12. Similar high values may be found in desert basins, where fractional crystallization and fractional solution have segregated alkaline salts like sodium carbonate and sodium borate. But most surface waters have sufficient contact with the atmosphere that such high alkalinities are not attained, and a reasonable upper limit of pH in *most* near-surface environments is about 9.

The strongest oxidizing agent commonly found in nature is the oxygen of the atmosphere. Stronger agents than this cannot persist, for the reason that they would react with water to liberate oxygen. Thus the upper limit of redox potentials is defined by the reaction

$$H_2O \rightleftharpoons \tfrac{1}{2}O_2 + 2H^+ + 2e^- \qquad E^\circ = +1.23 \text{ volts}. \qquad (9\text{-}32)$$

The potential of this half-reaction clearly depends on the pH, as shown by the expression of Eq. (9-19) for Eq. (9-32):

$$\mathrm{Eh} = 1.23 + 0.03 \log a_{O_2}^{0.5} \cdot a_{H^+}^2. \qquad (9\text{-}33)$$

For the usual concentration of O_2 we may use 0.2 atm (or approximately 0.2 bar), since oxygen makes up about one-fifth of the atmosphere by volume. Hence

$$\begin{aligned} \mathrm{Eh} &= 1.23 + 0.03 \log (0.2)^{0.5} + 0.059 \log a_{\mathrm{H}^+}, \\ &= +1.22 - 0.059\ \mathrm{pH}. \end{aligned} \qquad (9\text{-}34)$$

Slowness of reaction ("overvoltage effects") should make it possible for stronger oxidizing agents to exist locally and temporarily. Actually, however, measured oxidizing potentials in nature are always well below this limit, so that the empirical equation

$$\mathrm{Eh} = 1.04 - 0.059\ \mathrm{pH} \qquad (9\text{-}35)$$

is a more realistic upper boundary (Baas Becking et al., 1960). The discrepancy probably means that oxidation reactions involving O_2 have complicated mechanisms, possibly with a slow step in which traces of hydrogen peroxide act as an intermediate (Sato, 1960).

Reducing agents likewise are limited to substances that do not react with water, the reaction this time resulting in liberation of hydrogen. The limiting redox potential is that of the hydrogen electrode reaction,

$$H_2 \rightleftharpoons 2H^+ + 2e^- \qquad E^\circ = 0.00\ \text{volt}, \qquad (9\text{-}36)$$

for which

$$\begin{aligned} \mathrm{Eh} &= 0.00 + 0.03 \log a^2_{\mathrm{H}^+} - 0.03 \log a_{\mathrm{H}_2}, \\ &= -0.059\ \mathrm{pH} - 0.03 \log a_{\mathrm{H}_2}. \end{aligned} \qquad (9\text{-}37)$$

Since the pressure of hydrogen gas in near-surface environments cannot exceed 1 atm, the maximum possible reducing potential in the presence of water would be

$$\mathrm{Eh} = -0.059\ \mathrm{pH} - 0.03 \log (1) = -0.059\ \mathrm{pH}. \qquad (9\text{-}38)$$

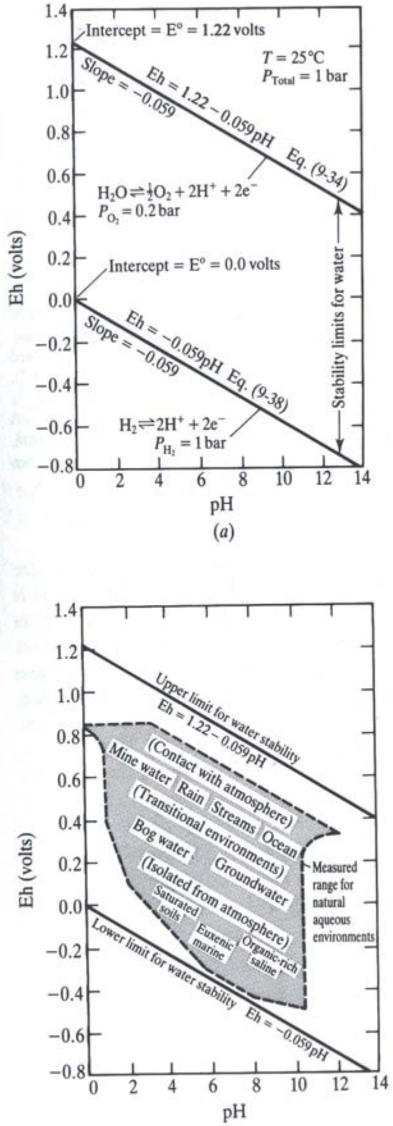
Conceivably local conditions might permit stronger reducing reactions, particularly within bodies of organic material (coal or petroleum) out of contact with water.

9-5 Eh–pH DIAGRAMS

The usual limits of Eh and pH that we have just discussed may be conveniently plotted on a graph with Eh as ordinate and pH as abscissa (Fig. 9-1). Fig. 9-1(*a*) shows the stability of water as described by the lines for Eqs. (9-34) and (9-38). The shaded area in Fig. 9-1(*b*) outlines the range of measurements in many kinds of surface and near-surface environments.

To show the conditions under which various oxidation–reduction processes may be expected to occur in nature, potentials for these processes are plotted on graphs like those in Fig. 9-1. For example, Fig. 9-2 shows one method of diagramming some of the oxidation reactions of iron in solution. Consider first the couple

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^- \qquad E^\circ = +0.77\ \text{volt}. \qquad (9\text{-}11)$$



(*a*)

(*b*)

FIGURE 9-1
Framework of Eh–pH diagrams. Diagonal lines in (*a*) define the upper [Eq. (9-34)] and lower [Eq. (9-38)] stability limits for water at 25°C and 1 bar. The shaded area in (*b*) shows the measured limits of Eh and pH in natural environments. (Reprinted by permission from Baas Becking et al., 1960.)

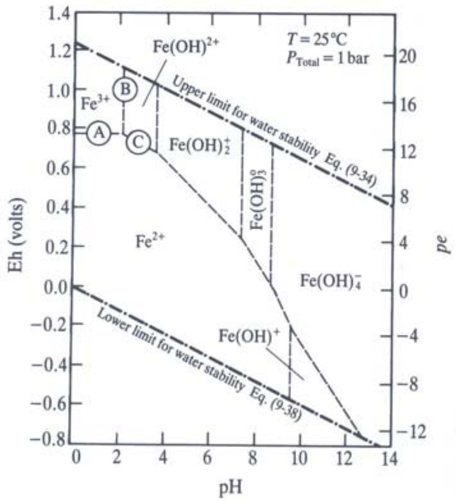


FIGURE 9-2
Eh-pH diagram for the simple ions of iron at 25°C and 1 bar. The dashed lines denote Eh and pH conditions for equal activities of the aqueous species. Lines marked A, B, and C represent equal activities of iron species determined from Eq. (9-11), (2-27), and (9-42), respectively. Redox potential is expressed as volts (Eh) on the left side and as *pe* on the right side. (Reprinted by permission from Nordstrom and Munoz, 1985.)

This reaction is independent of pH, since neither H^+ nor OH^- appears in the equation, so that its standard potential may be plotted as a horizontal line (A). This line corresponds to the Eh where the activity of Fe^{3+} equals the activity of Fe^{2+} in the solution, a requirement of Eq. (9-23) when Eh = E°. At any pair of Eh–pH values above the line the ratio $a_{Fe^{3+}}/a_{Fe^{2+}}$ is greater than 1, at any pair below the line less than 1. The line cannot be continued far into the diagram because Fe^{3+} reacts with water to form $Fe(OH)^{2+}$:

$$Fe^{3+} + H_2O \rightleftharpoons Fe(OH)^{2+} + H^+ \qquad \log K = -2.2. \tag{2-27}$$

For unit activity of water the equilibrium constant is

$$\log K = \log \frac{a_{Fe(OH)^{2+}}}{a_{Fe^{3+}}} + \log a_{H^+}, \tag{9-39}$$

$$= \log \frac{a_{Fe(OH)^{2+}}}{a_{Fe^{3+}}} - pH, \tag{9-40}$$

and setting the ratio $a_{Fe(OH)^{2+}}/a_{Fe^{3+}}$ equal to one gives

$$\log K = -pH = -2.2. \tag{9-41}$$

Eq. (9-41) plots as the vertical line marked B in Fig. 9-2. The area in the figure outlined by the upper stability limit for water and lines A and B is the range of Eh and pH values where Fe^{3+} is the predominant (most abundant) species of iron. In Chapter 2 we used similar methods for defining the range of pH for the predominant carbonate (Fig. 2-3) and sulfur (Fig. 2-4) species in solution.

The next step is to construct a line showing equal activities of Fe^{2+} and $Fe(OH)^{2+}$, by adding reactions (9-11) and (2-27):

$$Fe^{2+} + H_2O \rightleftharpoons Fe(OH)^{2+} + H^+ + e^-. \tag{9-42}$$

The standard potential for this reaction, E° = 0.900, is determined by calculating the standard free energy of reaction (9-11) from its standard potential using Eq. (9-15), and by adding to this the standard free energy for Eq. (2-27) as computed from Eq. (8-49). The resultant standard free energy for Eq. (9-42) (86,853 J mol^{-1}) then gives the standard potential, by use of Eq. (9-15). A line representing equal activities of Fe^{2+} and $Fe(OH)^{2+}$ is now derived from the Nernst equation (9-19),

$$Eh = E° + 0.059 \log \frac{a_{Fe(OH)^{2+}}}{a_{Fe^{2+}}} + \log a_{H^+}, \tag{9-43}$$

by substituting E° = 0.900, $a_{Fe^{2+}} = a_{Fe(OH)^{2+}}$, and $-\log a_{H^+} = pH$:

$$Eh = 0.900 - pH. \tag{9-44}$$

This equation, plotted as line C in Fig. 9-2, has a slope of −1 and an intercept of 0.900. The point where lines A, B, and C intersect represents Eh and pH values where the three species Fe^{3+}, Fe^{2+}, and $Fe(OH)^{2+}$ have equal activities. Using these methods, similar lines can be constructed for the other species of Fe(III) and Fe(II) in solution.

The completed diagram shows that the change from Fe(II) to Fe(III) falls approximately in the middle of the field representing conditions in nature [Fig. 9-1(*b*)], so that we would expect to find changes from one to the other very frequent, depending on slight shifts in the pH or Eh of the environment. This obviously corresponds with everyday experience. We find iron compounds reduced in the organic-rich surface layer of a soil and oxidized beneath, reduced in bottom sediments of the sea and oxidized in seawater itself, and so on. The diagram also indicates that oxidation of iron takes place much more completely in alkaline solution than in acid, which fits the observation that larger amounts of dissolved iron are commonly present in slightly acid stream waters than in the faintly alkaline water of the oceans because of the low solubility of hydrous Fe(III) compounds.

One other kind of information can be given on Eh–pH diagrams: the concentration of Fe^{2+} or of total Fe^{2+} plus Fe^{3+} in equilibrium with various minerals at different Eh–pH conditions. This is accomplished first by setting up equations for the electrode potentials of reactions between minerals such as magnetite and hematite,

$$\underset{\text{magnetite}}{2Fe_3O_4} + H_2O \rightleftharpoons \underset{\text{hematite}}{3Fe_2O_3} + 2H^+ + 2e^- \qquad E° = +0.22 \text{ volts}. \tag{9-45}$$

For unit activity of water and solids the Nernst equation is

$$Eh = E° + \frac{0.059}{2} \log a_{H^+}^2 \tag{9-46}$$

or

$$Eh = 0.22 - 0.059 \text{ pH}, \tag{9-47}$$

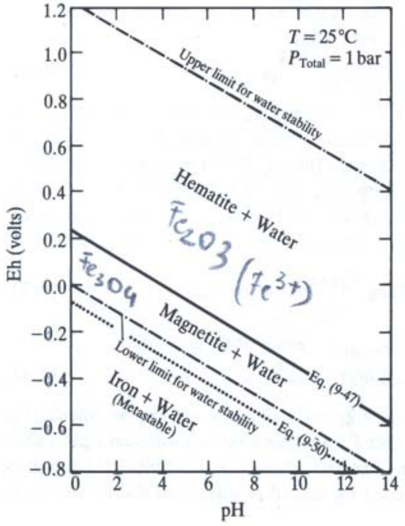


FIGURE 9-3
Eh–pH diagram showing hematite–magnetite–water equilibrium (solid line) and metastable equilibrium of magnetite–native iron–water (dotted line).

which plots as the solid straight line in Fig. 9-3. This line defines Eh–pH conditions for hematite–magnetite equilibrium. A line for equilibrium between magnetite and native iron is constructed in a similar manner:

$$\underset{\text{iron}}{3Fe} + 4H_2O \rightleftharpoons \underset{\text{magnetite}}{Fe_3O_4} + 8H^+ + 8e^- \qquad E° = -0.08 \text{ volts}, \tag{9-48}$$

$$Eh = -0.08 + \frac{0.059}{8} \log a_{H^+}^8, \tag{9-49}$$

and

$$Eh = -0.08 - 0.059 \text{ pH}. \tag{9-50}$$

Eq. (9-50) plots below the lower stability limit of water in Fig. 9-3, meaning that metallic iron is not to be expected in sedimentary environments because its presence would require too low a redox potential.

To compute the concentration of iron species in equilibrium with hematite and magnetite we combine the relationships derived in Figs. 9-2 and 9-3. For example, the activity of Fe^{2+} in a solution saturated with hematite is derived from the reaction

$$2Fe^{2+} + 3H_2O \rightleftharpoons \underset{\text{hematite}}{Fe_2O_3} + 6H^+ + 2e^-, \tag{9-51}$$

$$Eh = E° + 0.03 \log \frac{a_{H^+}^6}{a_{Fe^{2+}}^2}. \tag{9-52}$$

The standard potential E° given in tables is 0.65 volts. Hence

$$Eh = 0.65 - 0.18 \text{ pH} - 0.059 \log a_{Fe^{2+}}. \tag{9-53}$$

Rearrangement gives $\log a_{Fe}^{2+}$ as a function of pH and Eh:

$$\log a_{Fe^{2+}} = \frac{0.65 - 0.18 \text{ pH} - Eh}{0.059}. \tag{9-54}$$

In the field where hematite is the stable iron mineral, hematite cannot precipitate unless the activity of Fe^{2+} exceeds values given by this equation.

Eq. (9-54) defines a planar three-dimensional surface in terms of the variables $\log a_{Fe^{2+}}$, Eh, and pH. Any fluid that plots on this surface is saturated with hematite. Such a three-dimensional plot would be similar in form to the one shown in Fig. 4-11 for feldspar–solution equilibrium. To graphically represent the concentration of Fe^{2+} in equilibrium with hematite on a two-dimensional Eh–pH diagram, we first specify a concentration of Fe^{2+} (assuming that $a_{Fe^{2+}} = m_{Fe^{2+}}$) and use Eq. (9-54) to compute the equilibrium line in terms of Eh and pH. One such line is shown in Fig. 9-4 (dotted line marked D) for a concentration of $Fe^{2+} = 10^{-6}m$. A similar line may be derived for magnetite–solution equilibrium (dotted line marked E in Fig. 9-4). At Eh values greater than 0.77 volt, where Fe^{3+} is the predominant iron species, we can use the equation

$$2Fe^{3+} + 3H_2O \rightleftharpoons \underset{\text{hematite}}{Fe_2O_3} + 6H^+ \tag{9-55}$$

to compute the vertical line marked F in the figure to complete the diagram.

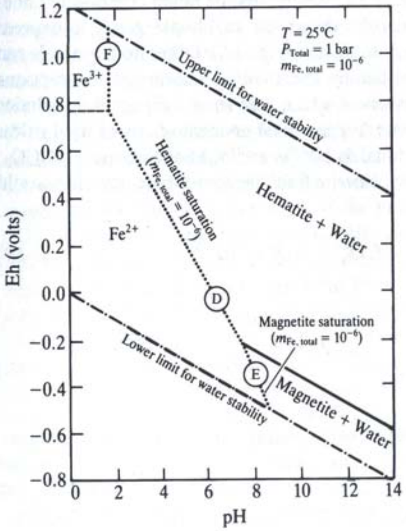


FIGURE 9-4
Eh–pH diagram showing equilibrium conditions for iron oxides and a solution containing $10^{-6}m$ total iron (dotted line marked $m_{Fe,total} = 10^{-6}$). The dashed line separates the predominance areas for aqueous Fe^{3+} and Fe^{2+} (Fig. 9-2), and the solid line denotes equilibrium between hematite and magnetite (Fig. 9-3).

The dotted line (F-D-E) in Fig. 9-4 represents the Eh and pH conditions for equilibrium of hematite or magnetite with a solution containing $10^{-6}m$ Fe^{2+} at Eh values less than +0.77 volt, and $10^{-6}m$ Fe^{3+} at Eh values greater than +0.77 volt. Because the dotted line lies within the predominance areas of these two iron species in Fig. 9-2, we can say that the dotted line in Fig. 9-4 represents iron oxide equilibria with a solution containing $10^{-6}m$ total iron ($m_{\mathrm{Fe,total}} = 10^{-6}$). For a total iron concentration greater than this the computed line would plot to the left of the one shown in the figure, and for a lower concentration the line would plot to the right. In the latter case the calculations can be simplified by taking into account the predominance areas of other iron species in solution (Fig. 9-2).

Eh–pH diagrams may be made geologically more realistic by plotting fields of stability for other common rock-forming minerals. Suppose we inquire, for example, as to the Eh–pH conditions under which siderite would be deposited in preference to hematite. The equation relating the two minerals is

$$\underset{\text{siderite}}{2FeCO_3} + 3H_2O \rightleftharpoons \underset{\text{hematite}}{Fe_2O_3} + 2H_2CO_3 + 2H^+ + 2e^- . \qquad (9\text{-}56)$$

From free energies we calculate the E° value, +0.30 volt, and then set up the equation for Eh at various concentrations:

$$\mathrm{Eh} = \mathrm{E}^\circ + 0.03 \log a^2_{H_2CO_3} a^2_{H^+}, \qquad (9\text{-}57)$$

$$\mathrm{Eh} = 0.30 + 0.059 \log a_{H_2CO_3} - 0.059\ \mathrm{pH}. \qquad (9\text{-}58)$$

For any given total concentration of dissolved CO_2, $a_{H_2CO_3}$ is a function of pH alone (Fig. 2-3). Hence Eh can be expressed as a function (albeit a rather complicated one) of pH, and the corresponding line can be drawn on an Eh–pH graph to express equilibrium between siderite and hematite (line A, Fig. 9-5). Other iron minerals can be included by setting up similar equations and making reasonable assumptions about total dissolved sulfur, total dissolved silica, and so on. Figure 9-5 includes hematite, siderite, magnetite, and pyrite, for assumed concentrations of total sulfur (H_2S, HS^-, S^{2-}, HSO_4^-, and SO_4^{2-}) equal to $10^{-6}m$ and of total carbonate (H_2CO_3, HCO_3^-, and CO_3^{2-}) equal to $1m$. For the siderite field the appropriate equation would be

$$\underset{\text{siderite}}{FeCO_3} \rightleftharpoons Fe^{2+} + CO_3^{2-} \qquad K = 10^{-10.7}, \qquad (9\text{-}59)$$

whence

$$a_{Fe^{2+}} = \frac{10^{-10.7}}{a_{CO_3^{2-}}} . \qquad (9\text{-}60)$$

The concentration of CO_3^{2-} would then be expressed as a function of total carbonate and pH, and substitution in this equation gives values of $a_{Fe^{2+}}$. In Fig. 9-5 the dotted line showing siderite equilibrium with a solution where the Fe^{2+} activity is 10^{-6} is parallel to the Eh axis, since the equation involves no oxidation or reduction.

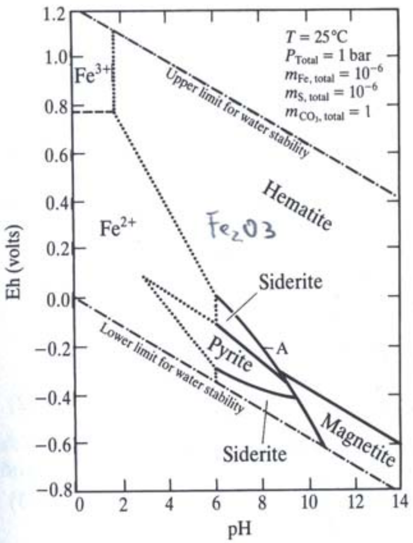


FIGURE 9-5
Eh–pH diagram showing fields of common iron minerals. Total concentration of dissolved carbonate $1m$, of dissolved sulfur $10^{-6}m$. The dotted boundaries on the left side of the diagram represent equilibrium of hematite, siderite, and pyrite with a solution containing $10^{-6}m$ total iron. (Reprinted by permission from Garrels and Christ, 1965.)

The Eh–pH relations in Fig. 9-5 may be interpreted as follows: Hematite is the stable mineral of iron in all moderately and strongly oxidizing environments. In reducing environments the stable mineral may be pyrite, siderite, or magnetite, depending on concentrations of sulfur and carbonate in the solution. For the conditions of high total carbonate ($1m$) and low total sulfur ($10^{-6}m$) shown in Fig. 9-5, siderite has two fields of stability separated by the field of pyrite, and magnetite is stable only in contact with strongly basic solutions. If dissolved carbonate is smaller and dissolved sulfur is higher, the field of pyrite expands until it fills nearly all the lower part of the diagram; a small field in which pyrrhotite is stable may appear at the extreme lower edge of the natural Eh range. If both carbonate and sulfur are very low, the field of magnetite extends into near-neutral environments. All the mineral transitions involving oxidation are favored by basic solutions, so that, for example, hematite may form from siderite in response to an increase in either pH or Eh. The occurrence of siderite is practically restricted to neutral and basic environments; it can precipitate from weakly acid solutions only if the concentration of dissolved iron is abnormally high. Within narrow ranges of Eh and pH most pairs of iron minerals are stable together—magnetite–hematite, hematite–siderite, magnetite–siderite, siderite–pyrite. Even the pair hematite–pyrite, although forbidden by the low total sulfur of Fig. 9-5, has a stable existence in environments with higher sulfur. Most of these conclusions are familiar enough as geological deductions based on field associations of iron minerals, but the diagram displays the underlying chemistry and makes the conclusions more quantitative.

9-6 FUGACITY DIAGRAMS

Eh and *pe* are the variables commonly employed to express redox conditions in sedimentary and groundwater environments, i.e., for equilibria under usual conditions of temperature and pressure. These variables can be used also at higher temperatures and/or pressures, by making the necessary corrections to Gibbs free energies and equilibrium constants by the methods described in Chapter 8, but other variables are often more convenient.

One example is the fugacity of oxygen, f_{O_2}, a gas that can be assumed present in contact with any redox equilibrium and whose fugacity will change as redox conditions change. Consider the equilibrium between hematite and magnetite

$$\underset{\text{hematite}}{6Fe_2O_3} \rightleftharpoons \underset{\text{magnetite}}{4Fe_3O_4} + O_2. \tag{9-61}$$

For pure hematite and magnetite the equilibrium constant is [Eq. (8-49)]

$$\log K = \frac{-\Delta G^\circ}{2.303RT} = \log a_{O_2}, \tag{9-62}$$

or expressed in terms of fugacity using the definition of Eq. (8-35),

$$\log K = \log \frac{f_{O_2}}{f^\circ_{O_2}}. \tag{9-63}$$

If we choose a standard state for oxygen as unit fugacity of the pure gas at 1 bar and any temperature ($f^\circ_{O_2} = 1$ bar), Eq. (9-63) reduces to

$$\log K = \log f_{O_2}, \tag{9-64}$$

where the term "f_{O_2}" is actually the ratio of the fugacity of oxygen (measured in bars) to its fugacity in the standard state (1 bar) and the equilibrium constant is a dimensionless number (see Sec. 8-4).

The hematite–magnetite reaction [Eq. (9-61)] is endothermic, so oxygen fugacity increases with increasing temperature [see Eq. (8-61)]. This increase is illustrated by the curve marked HM in Fig. 9-6. The fugacity of oxygen in equilibrium with hematite and magnetite is very small, about 10^{-80} bar at low temperatures, increasing to values of about 10^{-10} bar at magmatic temperatures. If H_2O is present, the equilibrium can also be represented by

$$\underset{\text{hematite}}{3Fe_2O_3} + H_2 \rightleftharpoons \underset{\text{magnetite}}{2Fe_3O_4} + H_2O, \tag{9-65}$$

and the equilibrium constant is

$$\log K = \log\left(f_{H_2O}/f_{H_2}\right). \tag{9-66}$$

For this reaction the oxidation state of the system is expressed by the fugacity ratio of H_2O to H_2.

An equilibrium curve like the one for hematite and magnetite in Fig. 9-6 is sometimes referred to as an oxygen buffer because the presence of these minerals in a rock may control the oxidation state as temperature (and pressure) change. Also

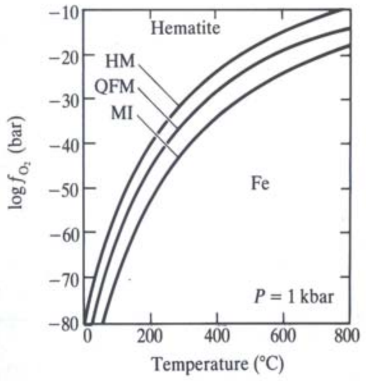


FIGURE 9-6
Oxygen fugacity for equilibria of hematite–magnetite [HM, Eq. (9-61)], quartz–fayalite–magnetite [QFM, Eq. (9-67)], and magnetite–iron [MI, Eq. (9-68)], as a function of temperature at a pressure of 1 kbar.

shown in Fig. 9-6 are equilibrium curves for the assemblage quartz, magnetite, and fayalite, and for magnetite and native iron, as represented by the reactions

$$\underset{\text{magnetite}}{2Fe_3O_4} + \underset{\text{quartz}}{3SiO_2} \rightleftharpoons \underset{\text{fayalite}}{3Fe_2SiO_4} + O_2 \tag{9-67}$$

and

$$\underset{\text{magnetite}}{\tfrac{1}{2}Fe_3O_4} \rightleftharpoons \underset{\text{iron}}{\tfrac{3}{2}Fe} + O_2. \tag{9-68}$$

The oxidation states of most geologic systems lie between the curves for hematite stability [Eq. (9-61), oxidizing conditions] and for native iron [Eq. (9-68), reducing conditions].

For further illustration, we look at oxidation–reduction relations among the simple compounds of sulfur. We start with a standard Eh–pH diagram for sulfur at 25°C and 1 bar [Fig. 9-7(*a*)], assuming a dilute solution with a total concentration of dissolved sulfur species of 0.001*m*. The diagram shows fields of stability for the common oxidation states of sulfur in ordinary environments: −2 for sulfides, 0 for the native element, +6 for sulfates. The narrow wedge marked S_{rh} on the left-hand side of the diagram means that native sulfur (rhombic) is stable in contact with near-surface solutions over a small range of Eh and pH. The other fields are marked with the formulas of the principal ions or molecules present. Over most of the area of any one field, the designated species makes up more than 99% of the total concentration of sulfur in solution, hence it has a concentration of approximately 0.001*m*. Near any boundary line the concentration diminishes; the line itself is drawn through points where the two species on either side have equal concentrations, approximately 0.0005*m*. Note that the important sulfur-containing ion in oxidizing solutions in SO_4^{2-}, that reducing solutions have chiefly H_2S at pH's less than 7 and chiefly HS^- at pH's greater than 7, and that S^{2-} is not a major constituent of

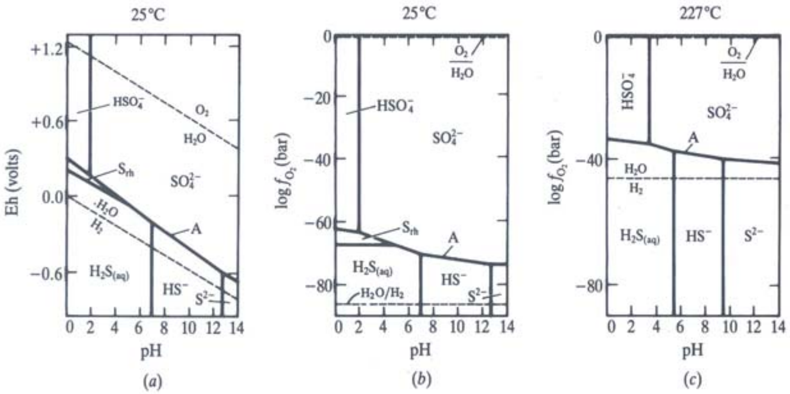


FIGURE 9-7
Eh–pH and f_{O_2}–pH diagrams for stable sulfur species. Total concentration of dissolved sulfur species 0.001*m*. (*a*): Eh–pH, 25°C, 1 bar. (*b*): f_{O_2}–pH, 25°C, 1 bar. (*c*): f_{O_2}–pH, 227°C, pressure equal to liquid–vapor equilibrium for H_2O.

any geologically important solution. These are simply quantitative expressions of our general knowledge about the chemical behavior of sulfur.

The diagram, like any Eh–pH diagram, has stringent limitations. The boundaries are calculated for equilibrium conditions, and take no account of slow reactions or metastable forms of sulfur. Actually the reduction of sulfate to sulfide is so slow as to be undetectable unless bacteria are present, so that SO_4^{2-} may have at least a temporary existence in strongly reducing solutions. Ions that are metastable under these conditions (for example, SO_3^{2-}, S_2^{2-}, $S_2O_3^{2-}$) do not appear at all. A number of heavy metals form complex ions with various sulfur species, and if these are present the diagram would be more complicated. Fig. 9-7(*a*) thus shows only the bare bones of sulfur chemistry, but for present purposes this is adequate.

Converting Fig. 9-7(*a*) to a f_{O_2}–pH diagram requires that the equation for each line be expressed as a reaction involving O_2 as an oxidizing agent. Take, for example, the line marked A on Fig. 9-7(*b*), separating fields of SO_4^{2-} and HS^-. The appropriate equation is

$$HS^- + 2O_2 \rightleftharpoons SO_4^{2-} + H^+. \qquad (9\text{-}69)$$

Free energies of formation (Appendix VIII) are +12.1 kJ mol^{-1} for HS^-, −744.5 kJ mol^{-1} for SO_4^{2-}, and 0 for $2O_2$ and H^+, so that $\Delta G°$ for the reaction is −756.6 kJ mol^{-1}. From this figure the equilibrium constant can be calculated and expressed as a quotient of activities [Eq. (8-49)]:

$$\log K = -(-756.6/5.708) = +132.6,$$
$$= \log a_{SO_4^{2-}} - \text{pH} - \log a_{HS^-} - 2\log f_{O_2}. \qquad (9\text{-}70)$$

At the boundary, by definition, $a_{SO_4^{2-}} = a_{HS^-}$, so that the equation reduces to

$$\log f_{O_2} = -\tfrac{1}{2}\text{pH} - 66.3. \qquad (9\text{-}71)$$

For comparison, the corresponding line on Fig. 9-7(*a*), also marked A, is drawn by calculating the standard Gibbs free energy of reaction and thence E° and Eh for the reaction

$$HS^- + 4H_2O \rightleftharpoons SO_4^{2-} + 9H^+ + 8e^-. \qquad (9\text{-}72)$$

Thus each line on one diagram has a matching line on the other. The stability fields have different shapes, but the relations among them are identical. It should be noted that the absurdly low values for oxygen fugacity indicated on Fig. 9-7(*b*), down to 10^{-80} bar, have no meaning as actual, measurable gas pressures, but are simply numerical indices of the oxidation state of the system.

To adapt the diagram to a higher temperature, we need only modify the values of the equilibrium constant obtained from the equation for each line, using the methods outlined in Chapter 8, and from these get values of $\log f_{O_2}$ as a function of pH. A diagram for the sulfur system at a temperature of 227°C, constructed in this manner, is shown as Fig. 9-7(*c*). Note that the field of native sulfur has vanished and that the field boundaries have shifted somewhat, but general relations among the sulfur species are still much the same.

As on the Eh–pH diagram of Fig. 9-5, we can also represent mineral stabilities on f_{O_2}–pH diagrams. One example is shown in Fig. 9-8 for iron sulfide and iron oxide minerals at 250°C, where the solution contains 0.1*m* total dissolved sulfur. Phase diagrams like the ones given in Figs. 9-5 and 9-8 provide a useful basis for description and interpretation of mineral stabilities in terms of pH and oxidation state. In later chapters we will use diagrams of this sort to estimate conditions for

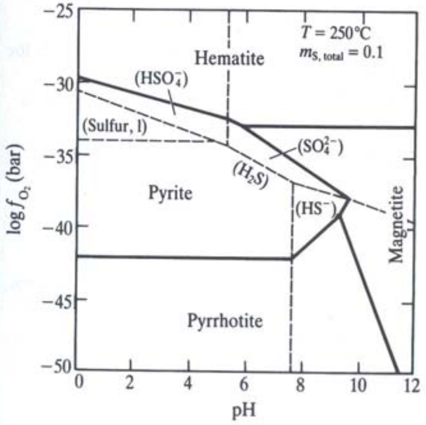


FIGURE 9-8
Oxygen fugacity–pH diagram for mineral stabilities in the system Fe–S–O (stability fields are shown by the thick solid lines) at 250°C for solutions with a total concentration of dissolved sulfur of 0.1*m*. Dashed lines show relationships among the predominant sulfur species in solution. (Diagram simplified from Crerar, D. A., and H. L. Barnes: "Ore solution chemistry. V. Solubilities of chalcopyrite and chalcocite assemblages in hydrothermal solutions at 200°C to 350°C," *Economic Geology*, vol. 71, pp. 772–794, 1976.)

diagenesis (Chap. 14) and for the formation of hydrothermal ore deposits (Chap. 19).

This same procedure, obviously, can be used to show relations between any two variables that are sensitive to change in acidity or oxidation potential—or to any other significant properties of a system. For example, the phase relations given in Fig. 9-8 could also be represented by the variables of sulfur fugacity and oxygen fugacity, or sulfur fugacity and the fugacity ratio of H_2O to H_2. The best variables to use in any particular case depend on the conditions of an experiment, or of a natural environment, and on the ease with which the variables can be measured. At high temperatures, as illustrated by the examples above, fugacities of gases are often the variables of choice.

Whatever variables are used, the limitations of such stability diagrams must be kept in mind. They are drawn to show equilibrium relations, and equilibrium is often not attainable in reasonable time. Usually other variables play a role, besides the two that are selected; a three-dimensional figure can be tried, to accommodate a third, but is generally inconvenient; variables beyond three can be handled only by cumbersome partial sections. And there is always the limitation posed by uncertainty in the thermodynamic data. With all these qualifications, are diagrams of this sort worth the time and effort they take to construct? The same question can be asked about any quantitative representation of geologic relations based on laboratory data for simple compounds and solutions. The answer must come from experience: Do the diagrams in fact summarize geologic and experimental observations realistically, and do they lead to predictions that can be tested against field occurrences? Many such diagrams do indeed lead to successful predictions, and serve as a convenient way to summarize large accumulations of data, but their correspondence with geologic observation is often far from perfect.

PROBLEMS

1. Complete and balance the following oxidation–reduction equations. (One method for balancing such equations is outlined in Appendix X.)

$Fe^{2+} + UO_2^{2+} \rightleftharpoons Fe^{3+} + U^{4+}$ (strongly acid solution)

$Cl^- + MnO_4^- \rightleftharpoons Cl_2 + MnO_2$ (weakly acid solution)

$V(OH)_3 + O_2 \rightleftharpoons VO_4^{-3}$ (alkaline solution)

$CH_4 + SO_4^{2-} \rightleftharpoons CO_2 + S$ (acid solution)

2. From the data of Appendix IX, find E° and calculate $\Delta G°$ for the following reactions:
(*a*) $Mn + Cu^{2+} \rightleftharpoons Mn^{2+} + Cu$.
(*b*) $MnO_2 + PbO + H_2O \rightleftharpoons Mn(OH)_2 + PbO_2$.
(*c*) $3Cu + 2NO_3^- + 8H^+ \rightleftharpoons 3Cu^{2+} + 4H_2O + 2NO$.
(*d*) $3HgS + 2NO_3^- + 8H^+ \rightleftharpoons 3Hg^2 + 4H_2O + 2NO + 3S$.
(*e*) $2Ag + \frac{1}{2}O_2 + 2Cl^- + 2H^+ \rightleftharpoons 2AgCl + H_2O$.

3. On an Eh–pH diagram like Fig. 9-4, plot curves for the following half-reactions:
(*a*) $I^-–IO_3^-$.
(*b*) $Cr^{3+}–Cr_2O_7^{2-}$ and $Cr(OH)_3–CrO_4^{2-}$.
(*c*) $Sn–Sn^{2+}$ and $Sn–Sn(OH)_3^-$.
(*d*) $V^{3+}–VO^{2+}$ and $V(OH)_3–VO(OH)_2$.
(*e*) $H_2S–S$, $HS^-–S$, and $S^{2-}–S$.
(*f*) $H_2SO_3–SO_4^{2-}$ and $SO_3^{2-}–SO_4^{2-}$.
Where it is necessary to assume an activity for some ion other than H^+ and OH^-, use 10^{-5}.

4. In lake water at a pH of 5 and a redox potential of +0.30 volt, what concentration of Cu^{2+} could exist in contact with metallic copper?

5. What redox potential must an environment possess in order for the activities of Fe^{2+} and Fe^{3+} to be equal?

6. The following questions refer to Fig. 9-5:
(*a*) Describe the sequence of iron minerals that would form from a solution at a constant Eh of −0.2 volt, if its pH increases slowly from an initial value of 4.
(*b*) Describe the sequence of oxidation products of siderite in contact with a solution whose pH is maintained at 9 while oxidation occurs.
(*c*) Does the simple Fe(III) ion, Fe^{3+}, play a role in ordinary near-surface solutions? In what sort of geologic environment might its concentration become appreciable?

7. Arrange the following, insofar as possible, in order of (*a*) decreasing pH and (*b*) decreasing Eh. In places where the order is ambiguous, explain why.
A. Seawater from near the surface in the tropics.
B. Water from a temporary playa lake in Death Valley.
C. Water from a lake in New York State.
D. Water in a small stream draining an area of schist containing abundant pyrite.
E. Water from a swamp in northern Canada.

8. Which of the following can be formed and continue to exist in near-surface environments? For those which cannot, give reasons to justify your answer.

$Ca(OH)_2$ MnO_4^- $CoCl_3$ Ag
UO_2^{2+} K_2S H_2CO_3 SiO
SO_4^{2-} Zn Al^{3+} Mn

9. Construct Eh–pH and log f_{O_2}–pH diagrams for solution–mineral phase relations in the system Fe–S–O–H at 25°C and 1 bar, for total dissolved sulfur of 0.1*m* and unit activity of water. Use data in Appendices VIII and IX to compute phase boundaries and lines of equal activities of aqueous species, and Figs. 9-5 and 9-8 as guides to constructing the diagrams.

REFERENCES AND SUGGESTIONS FOR FURTHER READING

Baas Becking, L. G. M., I. R. Kaplan, and D. Moore: "Limits of the natural environment in terms of pH and oxidation–reduction potentials," *Jour. Geology*, vol. 68, pp. 243–284, 1960. A tabulation of recorded measurements of Eh and pH in natural environments, and a discussion of the factors that limit these variables in different geologic situations.