Manahan, Stanley E. "OXIDATION-REDUCTION"
Environmental Chemistry
Boca Raton: CRC Press LLC, 2000

4 OXIDATION-REDUCTION

4.1. THE SIGNIFICANCE OF OXIDATION-REDUCTION

Oxidation-reduction (**redox**) reactions are those involving changes of oxidation states of reactants. Such reactions are easiest to visualize as the transfer of electrons from one species to another. For example, soluble cadmium ion, Cd^{2+}, is removed from wastewater by reaction with metallic iron. The overall reaction is

$$Cd^{2+} + Fe \rightarrow Cd + Fe^{2+} \tag{4.1.1}$$

This reaction is the sum of two **half-reactions**, a reduction half-reaction in which cadmium ion accepts two electrons and is reduced,

$$Cd^{2+} + 2e^{-} \rightarrow Cd \tag{4.1.2}$$

and an oxidation half-reaction in which elemental iron is oxidized:

$$Fe \rightarrow Fe^{2+} + 2e^{-} \tag{4.1.3}$$

When these two half-reactions are added algebraically, the electrons cancel on both sides and the result is the overall reaction given in Equation 4.1.1.

Oxidation-reduction phenomena are highly significant in the environmental chemistry of natural waters and wastewaters. In a lake, for example, the reduction of oxygen (O_2) by organic matter (represented by $\{CH_2O\}$),

$$\{CH_2O\} + O_2 \rightarrow CO_2 + H_2O \tag{4.1.4}$$

results in oxygen depletion which can be fatal to fish. The rate at which sewage is oxidized is crucial to the operation of a waste treatment plant. Reduction of insoluble iron(III) to soluble iron(II),

$$Fe(OH)_3(s) + 3H^+ + e^- \rightarrow Fe^{2+} + 3H_2O \quad (4.1.5)$$

in a reservoir contaminates the water with dissolved iron, which is hard to remove in the water treatment plant. Oxidation of NH_4^+ to NO_3^- in water,

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \quad (4.1.6)$$

converts ammonium nitrogen to nitrate, a form more assimilable by algae in the water. Many other examples can be cited of the ways in which the types, rates, and equilibria of redox reactions largely determine the nature of important solute species in water.

This chapter discusses redox processes and equilibria in water. In so doing, it emphasizes the concept of pE, analogous to pH and defined as the negative log of electron activity. Low pE values are indicative of reducing conditions and high pE values reflect oxidizing conditions.

Two important points should be stressed regarding redox reactions in natural waters and wastewaters. First, as is discussed in Chapter 6, “Aquatic Microbial Biochemistry,” many of the most important redox reactions are catalyzed by microorganisms. Bacteria are the catalysts by which molecular oxygen reacts with organic matter, iron(III) is reduced to iron(II), and ammonia is oxidized to nitrate ion.

The second important point regarding redox reactions in the hydrosphere is their close relationship to acid-base reactions. Whereas the activity of the H^+ ion is used to express the extent to which water is acidic or basic, the activity of the electron, e^-, is used to express the degree to which an aquatic medium is oxidizing or reducing. Water with a high hydrogen ion activity, such as runoff from “acid rain”, is *acidic.* By analogy, water with a high *electron* activity, such as that in the anaerobic digester of a sewage treatment plant, is said to be *reducing.*Water with a low H^+ ion activity (high concentration of OH^-)—such as landfill leachate contaminated with waste sodium hydroxide—is *basic*, whereas water with a low electron activity—highly chlorinated water, for example—is said to be *oxidizing.* Actually, neither free electrons nor free H^+ ions as such are found dissolved in aquatic solution; they are always strongly associated with solvent or solute species. However, the concept of electron activity, like that of hydrogen ion activity, remains a very useful one to the aquatic chemist.

Many species in water undergo exchange of both electrons and H^+ ions. For example, acid mine water contains the hydrated iron(III) ion, $Fe(H_2O)_6^{3+}$, which readily loses H^+ ion

$$Fe(H_2O)_6^{3+} \leftrightarrows Fe(H_2O)_5OH^{2+} + H^+ \quad (4.1.7)$$

to contribute acidity to the medium. The same ion accepts an electron

$$Fe(H_2O)_6^{3+} + e^- \leftrightarrows Fe(H_2O)_6^{2+} \quad (4.1.8)$$

to give iron(II).

Generally, the transfer of electrons in a redox reaction is accompanied by H^+ ion transfer, and there is a close relationship between redox and acid-base processes. For example, if iron(II) loses an electron at pH 7, three hydrogen ions are also lost to form highly insoluble iron(II) hydroxide,

$$Fe(H_2O)_6^{2+} \leftarrow\rightarrow e^- + Fe(OH)_3(s) + 3H_2O + 3H^+ \qquad (4.1.9)$$

an insoluble, gelatinous solid.

The stratified body of water shown in Figure 4.1 can be used to illustrate redox phenomena and relationships in an aquatic system. The anaerobic sediment layer is so reducing that carbon can be reduced to its lowest possible oxidation state, -4 in CH_4. If the lake becomes anaerobic, the hypolimnion may contain elements in their reduced states: NH_4^+ for nitrogen, H_2S for sulfur, and soluble $Fe(H_2O)_6^{2+}$ for iron. Saturation with atmospheric oxygen makes the surface layer a relatively oxidizing medium. If allowed to reach thermodynamic equilibrium, it is characterized by the more oxidized forms of the elements present: CO_2 for carbon, NO_3^- for nitrogen, iron as insoluble $Fe(OH)_3$, and sulfur as SO_4^{2-}. Substantial changes in the distribution of chemical species in water resulting from redox reactions are vitally important to aquatic organisms and have tremendous influence on water quality.

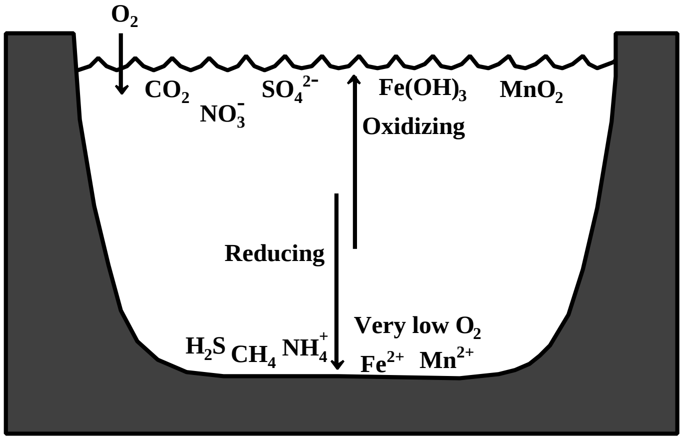

Figure 4.1. Predominance of various chemical species in a stratified body of water that has a high oxygen concentration (oxidizing, high pE) near the surface and a low oxygen concentration (reducing, low pE) near the bottom.

It should be pointed out that the systems presented in this chapter are assumed to be at equilibrium, a state almost never achieved in any real natural water or wastewater system. Most real aquatic systems are dynamic systems that may approach a steady-state, rather than true equilibrium. Nevertheless, the picture of a system at equilibrium is very useful in visualizing trends in natural water and wastewater systems, yet the model is still simple enough to comprehend. It is important to realize the limitations of such a model, however, especially in trying to make measurements of the redox status of water.

4.2. THE ELECTRON AND REDOX REACTIONS

In order to explain redox processes in natural waters it is necessary to have an understanding of redox reactions. In a formal sense such reactions can be viewed as the transfer of electrons between species. This section considers such reactions in a simple system. All redox reactions involve changes in the oxidation states of some of the species that take part in the reaction. Consider, for example, a solution containing iron(II) and iron(III) that is sufficiently acidic to prevent precipitation of solid $Fe(OH)_3$; such a medium might be acid mine water or a steel pickling liquor waste. Suppose that the solution is treated with elemental hydrogen gas over a suitable catalyst to bring about the reduction of iron(III) to iron(II). The overall reaction can be represented as

$$2Fe^{3+} + H_2 \rightleftarrows 2Fe^{2+} + 2H^+ \tag{4.2.1}$$

The reaction is written with a double arrow, indicating that it is *reversible* and could proceed in either direction; for normal concentrations of reaction participants, this reaction goes to the right. As the reaction goes to the right, the hydrogen is *oxidized* as it changes from an *oxidation state* (number) of 0 in elemental H_2 to a higher oxidation number of +1 in H^+. The oxidation state of iron goes from +3 in Fe^{3+} to +2 in Fe^{2+}; the oxidation number of iron decreases, which means that it is *reduced*.

All redox reactions such as this one can be broken down into a reduction *half-reaction*, in this case

$$2Fe^{3+} + 2e^- \rightleftarrows 2Fe^{2+} \tag{4.2.2}$$

(for one electron, $Fe^{3+} + e^- \rightleftarrows Fe^{3+}$) and an oxidation half-reaction, in this case

$$H_2 \rightleftarrows 2H^+ + 2e^- \tag{4.2.3}$$

Note that adding these two half-reactions together gives the overall reaction. *The addition of an oxidation half-reaction and a reduction half-reaction, each expressed for the same number of electrons so that the electrons cancel on both sides of the arrows, gives a whole redox reaction.*

The equilibrium of a redox reaction, that is, the degree to which the reaction as written tends to lie to the right or left, can be deduced from information about its constituent half-reactions. To visualize this, assume that the two half-reactions can be separated into two half-cells of an electrochemical cell as shown for Reaction 4.2.1 in Figure 4.2.

If the initial activities of H^+, Fe^{2+}, and Fe^{3+} were of the order of 1 (concentrations of 1 M), and if the pressure of H_2 were 1 atm, H_2 would be oxidized to H^+ in the left half-cell, Fe^{3+} would be reduced to Fe^{2+} in the right half-cell, and ions would migrate through the salt bridge to maintain electroneutrality in both half-cells. The net reaction occurring would be Reaction 4.2.1.

If a voltmeter were inserted in the circuit between the two electrodes, no significant current could flow and the two half-reactions could not take place. However, the voltage registered by the voltmeter would be a measure of the relative tendencies of the two half-reactions to occur. In the left half-cell the oxidation half-reaction,

$$H_2 \rightleftarrows 2H^+ + 2e^- \tag{4.2.3}$$

will tend to go to the right, releasing electrons to the platinum electrode in the half-cell and giving that electrode a relatively negative (-) potential. In the right half-cell the reduction half-reaction,

$$Fe^{3+} + e^{-} \leftrightarrows Fe^{2+} \qquad (4.2.2)$$

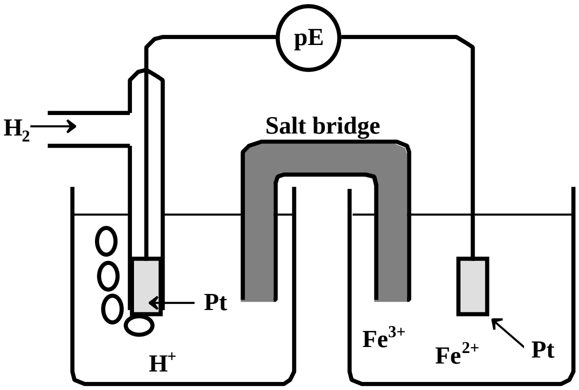

Figure 4.2. Electrochemical cell in which the reaction $2Fe^{3+} + H_2 \leftrightarrows 2Fe^{2+} + 2H^{+}$ can be carried out in two half-cells.

will tend to go to the right, taking electrons from the platinum electrode in the half-cell and giving that electrode a relatively positive (+) potential. The difference in these potentials is a measure of the "driving force" of the overall reaction. If each of the reaction participants were at unit activity, the potential difference would be 0.77 volts.

The left electrode shown in Figure 4.2 is the standard electrode against which all other electrode potentials are compared. It is called the **standard hydrogen electrode**, **SHE**. This electrode has been assigned a potential value of exactly 0 volts by convention, and its half-reaction is written as the following:

$$2H^{+} + 2e^{-} \leftrightarrows H_2 \qquad E^0 = 0.00 \text{ volts} \qquad (4.2.4)$$

The measured potential of the right-hand electrode in Figure 4.2.1 versus the standard hydrogen electrode is called the **electrode potential, E.** If the Fe^{2+} and Fe^{3+} ions in solution are both at unit activity, the potential is the **standard electrode potential** (according to IUPAC convention, the **standard reduction potential**), $\mathbf{E^0}$. The standard electrode potential for the Fe^{3+}/Fe^{2+} couple is 0.77 volts expressed conventionally as follows:

$$Fe^{3+} + e^{-} \leftrightarrows Fe^{2+} \qquad E^0 = +0.77 \text{ volts} \qquad (4.2.5)$$

4.3. ELECTRON ACTIVITY AND pE

In this book, for the most part, pE and pE^0 are used instead of E and E^0 to more clearly illustrate redox equilibria in aquatic systems over many orders of magnitude of electron activity in a manner analogous to pH. Numerically, pE and pE^0 are simply the following:

$$pE = \frac{E}{\frac{2.303RT}{F}} = \frac{E}{0.0591} \text{ (at 25˚C)} \qquad (4.3.1)$$

$$pE^0 = \frac{E^0}{\frac{2.303RT}{F}} = \frac{E^0}{0.0591} \text{ (at 25˚C)} \qquad (4.3.2)$$

where R is the molar gas constant, T is the absolute temperature, and F is the Faraday constant. The “pE concept” is explained below.

Just as pH is defined as

$$pH = -\log(a_{H^+}) \qquad (4.3.3)$$

where a_{H^+} is the activity of hydrogen ion in solution, pE is defined as

$$pE = -\log(a_{e^-}) \qquad (4.3.4)$$

where a_{e^-} is the activity of the electron in solution. Since hydrogen ion concentration may vary over many orders of magnitude, pH is a convenient way of expressing a_{H^+} in terms of manageable numbers. Similarly, electron activities in water may vary over more than 20 orders of magnitude so that it is convenient to express a_{e^-} as pE.

Values of pE are defined in terms of the following half-reaction for which pE^0 is defined as exactly zero:*

$$2H^+(aq) + 2e^- \leftrightarrows H_2(g) \qquad E^0 = +0.00 \text{ volts} \qquad pE^0 = 0.00 \qquad (4.3.5)$$

Whereas it is relatively easy to visualize the activities of ions in terms of concentration, it is harder to visualize the activity of the electron, and therefore pE, in similar terms. For example, at 25˚C in pure water, a medium of zero ionic strength, the hydrogen ion concentration is 1.0×10^{-7} M, the hydrogen-ion *activity* is 1.0×10^{-7}, and the pH is 7.0. The electron activity, however, must be defined in terms of Equation 4.3.5. When $H^+(aq)$ at unit activity is in equilibrium with hydrogen gas at 1 atmosphere pressure (and likewise at unit activity), the activity of the electron in the medium is exactly 1.00 and the pE is 0.0. If the electron activity were increased

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* Thermodynamically, the free energy change for this reaction is defined as exactly zero when all reaction participants are at unit activity. For ionic solutes, activity — the effective concentration in a sense — approaches concentration at low concentrations and low ionic strengths. The activity of a gas is equal to its partial pressure. Furthermore, the free energy, G, decreases for spontaneous processes occurring at constant temperature and pressure. Processes for which the free energy change, ΔG, is zero have no tendency toward spontaneous change and are in a state of equilibrium. Reaction 4.2.4 is the one upon which free energies of formation of all ions in aqueous solution is based. It also forms the basis for defining free energy changes for oxidation-reduction processes in water.

by a factor of 10 (as would be the case if H^+(*aq*) at an activity of 0.100 were in equilibrium with H_2 at an activity of 1.00), the electron activity would be 10 and the pE value would be -1.0.

4.4. THE NERNST EQUATION

The **Nernst equation** is used to account for the effect of different activities upon electrode potential. Referring to Figure 4.2, if the Fe^{3+} ion concentration is increased relative to the Fe^{2+} ion concentration, it is readily visualized that the potential and the pE of the right electrode will become more positive because the higher concentration of electron-deficient Fe^{3+} ions clustered around it tends to draw electrons from the electrode. Decreased Fe^{3+} ion or increased Fe^{2+} ion concentration has the opposite effect. Such concentration effects upon E and pE are expressed by the **Nernst equation**. As applied to the half-reaction

$$Fe^{3+} + e^- \rightleftarrows Fe^{2+} \qquad E^0 = +0.77 \text{ volts} \qquad pE^0 = 13.2 \qquad (4.4.1)$$

the Nernst equation is

$$E = E^0 + \frac{2.303RT}{nF}\log\frac{[Fe^{3+}]}{[Fe^{2+}]} = E^0 + \frac{0.0591}{n}\log\frac{[Fe^{3+}]}{[Fe^{2+}]} \qquad (4.4.2)$$

where n is the number of electrons involved in the half-reaction (1 in this case), and the activities of Fe^{3+} and Fe^{2+} ions have been taken as their concentrations (a simplification valid for more dilute solutions, which will be made throughout this chapter). Considering that

$$pE = \frac{E}{\frac{2.303RT}{F}} \quad \text{and} \quad pE^0 = \frac{E^0}{\frac{2.303RT}{F}}$$

the Nernst equation can be expressed in terms of pE and pE^0

$$pE = pE^0 + \frac{1}{n}\log\frac{[Fe^{3+}]}{[Fe^{2+}]} \quad \text{(In this case n = 1)} \qquad (4.4.3)$$

The Nernst equation in this form is quite simple and offers some advantages in calculating redox relationships.

If, for example, the value of $[Fe^{3+}]$ is 2.35×10^{-3} M and $[Fe^{2+}] = 7.85 \times 10^{-5}$ M, the value of pE is

$$pE = 13.2 + \log\frac{2.35 \times 10^{-3}}{7.85 \times 10^{-5}} = 14.7 \qquad (4.4.4)$$

As the concentration of Fe^{3+} increases relative to the concentration of Fe^{2+}, the value of pE becomes higher (more positive) and as the concentration of Fe^{2+} increases relative to the concentration of Fe^{3+}, the value of pE becomes lower (more negative).

4.5. REACTION TENDENCY: WHOLE REACTION FROM HALF-REACTIONS

This section discusses how half-reactions can be combined to give whole reactions and how the pE^0 values of the half-reactions can be used to predict the directions in which reactions will go. The half-reactions discussed here are the following:

$$Hg^{2+} + 2e^- \rightleftarrows Hg \qquad pE^0 = 13.35 \tag{4.5.1}$$

$$Fe^{3+} + e^- \rightleftarrows Fe^{2+} \qquad pE^0 = 13.2 \tag{4.5.2}$$

$$Cu^{2+} + 2e^- \rightleftarrows Cu \qquad pE^0 = 5.71 \tag{4.5.3}$$

$$2H^+ + 2e^- \rightleftarrows H_2 \qquad pE^0 = 0.00 \tag{4.5.4}$$

$$Pb^{2+} + 2e^- \rightleftarrows Pb \qquad pE^0 = -2.13 \tag{4.5.5}$$

Such half-reactions and their pE^0 values can be used to explain observations such as the following: A solution of Cu^{2+} flows through a lead pipe and the lead acquires a layer of copper metal through the reaction

$$Cu^{2+} + Pb \rightarrow Cu + Pb^{2+} \tag{4.5.6}$$

This reaction occurs because the copper(II) ion has a greater tendency to acquire electrons than the lead ion has to retain them. This reaction, which can be carried out in two separate half-cells as shown in Figure 4.3, can be obtained by subtracting the lead half-reaction, Equation 4.5.5, from the copper half-reaction, Equation 4.5.3:

$$\begin{array}{lll} Cu^{2+} + 2e^- \rightleftarrows Cu & pE^0 = 5.71 & (4.5.3) \\ -(Pb^{2+} + 2e^- \rightleftarrows Pb & pE^0 = -2.13) & (4.5.5) \\ \hline Cu^{2+} + Pb \rightleftarrows Cu + Pb^{2+} & pE^0 = 7.84 & (4.5.7) \end{array}$$

The positive values of pE^0 for this reaction, 7.84, indicate that the reaction tends to go to the right as written. This occurs when lead metal directly contacts a solution of copper(II) ion. Therefore, if a waste solution containing copper(II) ion, a relatively innocuous pollutant, comes into contact with lead in plumbing, toxic lead may go into solution.

In principle, half-reactions may be allowed to occur in separate electrochemical half-cells, as could occur for Reaction 4.5.7 in the cell shown in Figure 4.3 if the meter (pE) were bypassed by an electrical conductor; they are therefore called **cell reactions.**

If the activities of Cu^{2+} and Pb^{2+} are not unity, the direction of the reaction and value of pE are deduced from the Nernst equation. For Reaction 4.5.7 the Nernst equation is

$$pE = pE^0 + \frac{1}{n}\log\frac{[Cu^{2+}]}{[Pb^{2+}]} = 7.84 + \frac{1}{2}\log\frac{[Cu^{2+}]}{[Pb^{2+}]} \qquad (4.5.8)$$

By combining the appropriate half-reactions it can be shown that copper metal will not cause hydrogen gas to be evolved from solutions of strong acid (hydrogen ion has less attraction for electrons than does copper(II) ion), whereas lead metal, in contrast, will displace hydrogen gas from acidic solutions.

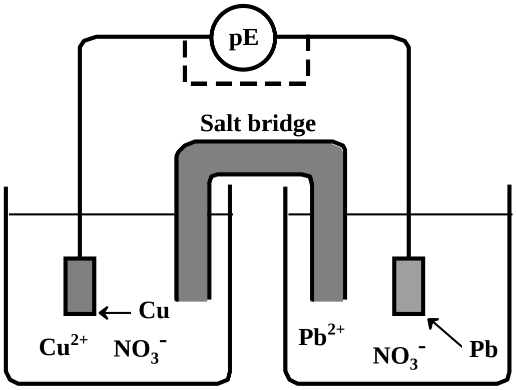

Figure 4.3. Cell for the measurement of pE between a lead half-cell and a copper half-cell. In this configuration "pE" has a very high resistance and current cannot flow.

4.6. THE NERNST EQUATION AND CHEMICAL EQUILIBRIUM

Refer again to Figure 4.3. Imagine that instead of the cell being set up to measure the potential between the copper and lead electrodes, the voltmeter, V, was removed and the electrodes directly connected with a wire so that the current might flow between them. The reaction

$$Cu^{2+} + Pb \rightleftarrows Cu + Pb^{2+} \qquad pE^0 = 7.84 \qquad (4.5.7)$$

will occur until the concentration of lead ion beomes so high, and that of copper ion so low, that the reaction stops. The system is at equilibrium and, since current no longer flows, pE is exactly zero. The equilibrium constant K for the reaction is given by the expression

$$K = \frac{[Pb^{2+}]}{[Cu^{2+}]} \qquad (4.6.1)$$

The equilibrium constant can be calculated from the Nernst Equation, noting that under equilibrium conditions pE is zero and $[Cu^{2+}]$ and $[Pb^{2+}]$ are at equilibrium concentrations:

$$pE = pE^0 + \frac{1}{n}\log\frac{[Cu^{2+}]}{[Pb^{2+}]} = pE^0 + \frac{1}{n}\log\frac{1}{K}$$

$$pE = 0.00 = 7.84 - \frac{1}{2}\log\frac{[Pb^{2+}]}{[Cu^{2+}]} = 7.84 - \frac{1}{2}\log K \qquad (4.6.2)$$

Note that the reaction products are placed over reactants in the log term, and a minus sign is placed in front to put the equilibrium constant in the correct form (a purely mathematical operation). The value of log K obtained from solving the above equation is 15.7.

The equilibrium constant for a redox reaction involving n electrons is given in terms of pE simply by

$$\log K = n(pE^0) \qquad (4.6.3)$$

4.7. THE RELATIONSHIP OF pE TO FREE ENERGY

Aquatic systems and the organisms that inhabit them — just like the steam engine or students hoping to pass physical chemistry — must obey the laws of thermodynamics. Bacteria, fungi, and human beings derive their energy from acting as mediators (catalysts) of chemical reactions and extracting a certain percentage of useful energy from them. In predicting or explaining the behavior of an aquatic system, it is helpful to be able to predict the useful energy that can be extracted from chemical reactions in the system, such as microbially mediated oxidation of organic matter to CO_2 and water, or the fermentation of organic matter to methane by anaerobic bacteria in the absence of oxygen. Such information may be obtained by knowing the free-energy change, ΔG, for the redox reaction; ΔG, in turn, may be obtained from pE for the reaction. The free-energy change for a redox reaction involving n electrons at an absolute temperature of T is given by

$$\Delta G = -2.303nRT(pE) \qquad (4.7.1)$$

where R is the gas constant. When all reaction participants are in their standard states (pure liquids, pure solids, solutes at an activity of 1.00) ΔG is the standard free energy change, ΔG^0, given by

$$\Delta G^0 = -2.303nRT(pE^0) \qquad (4.7.2)$$

4.8. REACTIONS IN TERMS OF ONE ELECTRON-MOLE

For comparing free energy changes between different redox reactions, it is most meaningful to consider the reactions in terms of the transfer of exactly 1 mole of electrons. This concept may be understood by considering two typical and important redox reactions that occur in aquatic systems — nitrification

$$NH_4^+ + 2O_2 \leftrightarrows NO_3^- + 2H^+ + H_2O \qquad pE^0 = 5.85 \qquad (4.8.1)$$

and oxidation of iron(II) to iron(III):

$$4Fe^{2+} + O_2 + 10H_2O \leftrightarrows 4Fe(OH)_3(s) + 8H^+ \qquad pE^0 = 7.6 \qquad (4.8.2)$$

What do reactions written in this way really mean? If any thermodynamic calculations are to be made involving the reactions, Reaction 4.8.1 means that one mole of ammonium ion reacts with two moles of oxygen to yield one mole of nitrate ion, two moles of hydrogen ion, and one mole of water. Reaction 4.8.2 is taken to mean that four moles of iron(II) ion react with one mole of oxygen and ten moles of water to produce four moles of $Fe(OH)_3$ and eight moles of hydrogen ions. The free-energy changes calculated for these quantities of reaction participants do not enable meaningful comparisons of their free energy changes. Such comparisons may be made, though, on the common basis of the transfer of one mole of electrons, writing each reaction in terms of one electron-mole. The advantage of this approach is illustrated by considering Reaction 4.8.1, which involves an eight-electron change, and Reaction 4.8.2, which involves a four-electron change. Rewriting Equation 4.8.l for one electron-mole yields

$$\tfrac{1}{8}NH_4^+ + \tfrac{1}{4}O_2 \leftrightarrows \tfrac{1}{8}NO_3^- + \tfrac{1}{4}H^+ + \tfrac{1}{8}H_2O \qquad pE^0 = 5.85 \tag{4.8.3}$$

whereas Reaction 4.8.2, when rewritten for one electron-mole rather than four, yields:

$$Fe^{2+} + \tfrac{1}{4}O_2 + \tfrac{5}{2}H_2O \leftrightarrows Fe(OH)_3(s) + 2H^+ \qquad pE^0 = 7.6 \tag{4.8.4}$$

From Equation 4.7.2, the standard free energy change for a reaction is

$$\Delta G^0 = -2.303nRT(pE^0) \tag{4.7.2}$$

which, for a one electron-mole reaction is simply

$$\Delta G^0 = -2.303RT(pE^0) \tag{4.7.2}$$

Therefore, for reactions written in terms of one electron-mole, a comparison of pE^0 values provides a direct comparison of ΔG^0 values.

As shown in Equation 4.6.3 for a redox reaction involving *n* electrons, pE^0 is related to the equilibrium constant by

$$\log K = n\,(pE^0) \tag{4.8.5}$$

which for a one electron-mole reaction becomes simply

$$\log K = pE^0 \tag{4.8.6}$$

Reaction 4.8.3, the nitrification reaction written in terms of one electron-mole, has a pE^0 value of +5.85. The equilibrium-constant expression for this reaction is,

$$K = \frac{[NO_3^-]^{1/8}[H^+]^{1/4}}{[NH_4^+]^{1/8}P_{O_2}^{1/4}} \tag{4.8.7}$$

a computationally cumbersome form for which log K is given very simply as the following:

$$\log K = pE^0 = 5.85 \text{ or } K = 7.08 \times 10^5 \tag{4.8.8}$$

Table 4.1 is a compilation of pE^0 values for redox reactions that are especially important in aquatic systems. Most of these values are calculated from thermodynamic data rather than from direct potentiometric measurements in an electrochemical cell, as shown in Figure 4.2. Most electrode systems that might be devised do not give potential responses corresponding to the Nernst equation; that is, they do not behave *reversibly*. It is true that one may place a platinum electrode and a reference electrode in water and measure a potential. This potential, referred to the standard hydrogen electrode, is the so-called **E_H value**. Furthermore, the measured potential will be more positive (more oxidizing) in an oxidizing medium, such as the aerobic surface layers of a lake, than in a reducing medium, such as the anaerobic bottom regions of a body of water. However, attaching any quantitative significance to the E_H value measured directly with an electrode is a very dubious practice. Acid mine waters containing relatively high levels of sulfuric acid and dissolved iron give reasonably accurate E_H values by direct measurement, but most aquatic systems do not yield meaningful values of E_H.

4.9. THE LIMITS OF pE IN WATER

There are pH-dependent limits to the pE values at which water is thermodynamically stable. Water may be both oxidized

$$2H_2O \leftarrow\rightarrow O_2 + 4H^+ + 4e^- \tag{4.9.1}$$

or it may be reduced:

$$2H_2O + 2e^- \leftarrow\rightarrow H_2 + 2OH^- \tag{4.9.2}$$

These two reactions determine the limits of pE in water. On the oxidizing side (relatively more positive pE values), the pE value is limited by the oxidation of water, Half-reaction 4.9.1. The evolution of hydrogen, Half-reaction 4.9.2, limits the pE value on the reducing side.

The condition under which oxygen from the oxidation of water has a pressure of 1.00 atm can be regarded as the oxidizing limit of water whereas a hydrogen pressure of 1.00 atmosphere may be regarded as the reducing limit of water. These are **boundary conditions** that enable calculation of the stability boundaries of water. Writing the reverse of Reaction 4.9.1 for one electron and setting $P_{O_2} = 1.00$ yields:

$$1/4O_2 + H^+ + e^- \leftarrow\rightarrow 1/2H_2O \quad pE^0 = 20.75 \text{ (from Table 4.1)} \tag{4.9.3}$$

Thus, Equation 4.9.5 defines the pH-dependent oxidizing limit of water. At a specified pH, pE values more positive than the one given by Equation 4.9.5 cannot exist at equilibrium in water in contact with the atmosphere.

Table 4.1. pE^0 Values of Redox Reactions Important in Natural Waters (at 25˚C)

Reaction	pE^0	$pE^0(W)$[1]
(1) $1/4\,O_2(g) + H^+(W) + e^- \leftrightarrows 1/2\,H_2O$	+20.75	+13.75
(2) $1/5\,NO_3^- + 6/5\,H^+ + e^- \leftrightarrows 1/10\,N_2 + 3/5\,H_2O$	+21.05	+12.65
(3) $1/2\,MnO_2 + 1/2\,HCO_3^-(10^{-3}) + 3/2\,H^+(W) + e^- \leftrightarrows 1/2\,MnCO_3(s) + H_2O$	—	+8.5[2]
(4) $1/2\,NO_3^- + H^+(W) + e^- \leftrightarrows 1/2\,NO_2^- + 1/2\,H_2O$	+14.15	+7.15
(5) $1/8\,NO_3^- + 5/4\,H^+(W) + e^- \leftrightarrows 1/8\,NH_4^+ + 3/8\,H_2O$	+14.90	+6.15
(6) $1/6\,NO_2^- + 4/3\,H^+(W) + e^- \leftrightarrows 1/6\,NH_4^+ + 1/3\,H_2O$	+15.14	+5.82
(7) $1/2\,CH_3OH + H^+(W) + e^- \leftrightarrows 1/2\,CH_4(g) + 1/2\,H_2O$	+9.88	+2.88
(8) $1/4\,CH_2O + H^+(W) + e^- \leftrightarrows 1/4\,CH_4(g) + 1/4\,H_2O$	+6.94	-0.06
(9) $FeOOH(g) + HCO_3^-(10^{-3}) + 2H^+(W) + e^- \leftrightarrows FeCO_3(s) + 2H_2O$	—	-1.67[2]
(10) $1/2\,CH_2O + H^+(W) + e^- \leftrightarrows + 1/2\,CH_3OH$	+3.99	-3.01
(11) $1/6\,SO_4^{2-} + 4/3\,H^+(W) + e^- \leftrightarrows 1/6\,S(s) + 2/3\,H_2O$	+6.03	-3.30
(12) $1/8\,SO_4^{2-} + 5/4\,H^+(W) + e^- \leftrightarrows 1/8\,H_2S(g) + 1/2\,H_2O$	+5.75	-3.50
(13) $1/8\,SO_4^{2-} + 5/4\,H^+(W) + e^- \leftrightarrows 1/8\,H_2S(g) + 1/2\,H_2O$	+4.13	-3.75
(14) $1/2\,S + H^+(W) + e^- \leftrightarrows 1/2\,H_2S$	+2.89	-4.11
(15) $1/8\,CO_2 + H^+ + e^- \leftrightarrows 1/8\,CH_4 + 1/4\,H_2O$	+2.87	-4.13
(16) $1/6\,N_2 + 4/3\,H^+(W) + e^- \leftrightarrows 1/3\,NH_4^+$	+4.68	-4.65
(17) $H^+(W) + e^- \leftrightarrows 1/2\,H_2(g)$	0.00	-7.00
(18) $1/4\,CO_2(g) + H^+(W) + e^- \leftrightarrows 1/4\,CH_2O + 1/4\,H_2O$	-1.20	-8.20

[1] (W) indicates $a_{H^+} = 1.00 \times 10^{-7}\ M$ and $pE^0(W)$ is a pE^0 at $a_{H^+} = 1.00 \times 10^{-7}\ M$.

[2] These data correspond to $a_{HCO_3^-} = 1.00 \times 10^{-3}\ M$ rather than unity and so are not exactly $pE^0(W)$; they represent typical aquatic conditions more exactly than pE^0 values do.

Source: Stumm, Werner and James J. Morgan, *Aquatic Chemistry*, John Wiley and Sons, New York, 1970, p. 318. Reproduced by permission of John Wiley & Sons, Inc.

$$pE = pE^0 + \log(P_{O_2}^{1/4}[H^+]) \qquad (4.9.4)$$

$$pE = 20.75 - pH \qquad (4.9.5)$$

The pE-pH relationship for the reducing limit of water taken at P_{H_2} = exactly 1 atm is given by the following derivation:

$$H^+ + e^- \leftarrow\rightarrow {}^1/_2H_2 \qquad pE^0 = 0.00 \qquad (4.9.6)$$

$$pE = pE^0 + \log [H^+] \qquad (4.9.7)$$

$$pE = -pH \qquad (4.9.8)$$

For neutral water (pH = 7.00), substitution into Equations 4.9.8 and 4.9.5 yields -7.00 to 13.75 for the pE range of water. The pE-pH boundaries of stability for water are shown by the dashed lines in Figure 4.4 of Section 4.11.

The decomposition of water is very slow in the absence of a suitable catalyst. Therefore, water may have temporary nonequilibrium pE values more negative than the reducing limit or more positive than the oxidizing limit. A common example of the latter is a solution of chlorine in water.

4.10. pE VALUES IN NATURAL WATER SYSTEMS

Although it is not generally possible to obtain accurate pE values by direct potentiometric measurements in natural aquatic systems, in principle, pE values may be calculated from the species present in water at equilibrium. An obviously significant pE value is that of neutral water in thermodynamic equilibrium with the atmosphere. In water under these conditions, P_{O_2} = 0.21 atm and $[H^+] = 1.00 \times 10^{-7}$ M. Substitution into Equation 4.9.4 yields:

$$pE = 20.75 + \log \{(0.21)^{1/4} \times 1.00 \times 10^{-7}\} = 13.8 \qquad (4.10.1)$$

According to this calculation, a pE value of around +13 is to be expected for water in equilibrium with the atmosphere, that is, an aerobic water. At the other extreme, consider anaerobic water in which methane and CO_2 are being produced by microorganisms. Assume $P_{CO_2} = P_{CH_4}$ and that pH = 7.00. The relevant half-reaction is

$$^1/_8CO_2 + H^+ + e^- \leftarrow\rightarrow {}^1/_8CH_4 + {}^1/_4H_2O \qquad (4.10.2)$$

for which the Nernst equation is

$$pE = 2.87 + \log\frac{P_{CO_2}^{1/8}[H^+]}{P_{CH_4}^{1/8}[H^+]} = 2.87 + \log[H^+] = 2.87 - 7.00 = -4.13 \qquad (4.10.3)$$

Note that the pE value of - 4.13 does not exceed the reducing limit of water at pH 7.00, which from Equation 4.9.8 is -7.00. It is of interest to calculate the pressure of oxygen in neutral water at this low pE value of - 4.13. Substitution into Equation 4.9.4 yields

$$-4.13 = 20.75 + \log(P_{O_2}^{1/4} \times 1.00 \times 10^{-7}) \qquad (4.10.4)$$

from which the pressure of oxygen is calculated to be 3.0 × 10^{-72} atm. This impossibly low figure for the pressure of oxygen means that equilibrium with respect to oxygen partial pressure is not achieved under these conditions. Certainly, under any condition approaching equilibrium between comparable levels of CO_2 and CH_4, the partial pressure of oxygen must be extremely low.

4.11. pE-pH DIAGRAMS

The examples cited so far have shown the close relationships between pE and pH in water. This relationship may be expressed graphically in the form of a **pE-pH diagram.** Such diagrams show the regions of stability and the boundary lines for various species in water. Because of the numerous species that may be formed, such diagrams may become extremely complicated. For example, if a metal is being considered, several different oxidation states of the metal, hydroxy complexes, and different forms of the solid metal oxide or hydroxide may exist in different regions described by the pE-pH diagram. Most waters contain carbonate, and many contain sulfates and sulfides, so that various metal carbonates, sulfates, and sulfides may predominate in different regions of the diagram. In order to illustrate the principles involved, however, a simplified pE-pH diagram is considered here. The reader is referred to more advanced works on geochemistry and aquatic chemistry for more complicated (and more realistic) pE-pH diagrams[1,2].

A pE-pH diagram for iron may be constructed assuming a maximum concentration of iron in solution, in this case 1.0 × 10^{-5} M. The following equilibria will be considered:

$$Fe^{3+} + e^{-} \leftrightarrows Fe^{2+} \qquad pE^{0} = +13.2 \qquad (4.11.1)$$

$$Fe(OH)_2(s) + 2H^{+} \leftrightarrows Fe^{2+} + 2H_2O \qquad (4.11.2)$$

$$K_{sp} = \frac{[Fe^{2+}]}{[H^{+}]^2} = 8.0 \times 10^{12} \qquad (4.11.3)$$

$$Fe(OH)_3(s) + 3H^{+} \leftrightarrows Fe^{3+} + 3H_2O \qquad (4.11.4)$$

$$K_{sp}' = \frac{[Fe^{3+}]}{[H^{+}]^3} = 9.1 \times 10^{3} \qquad (4.11.5)$$

(The constants K_{sp} and K_{sp}' are derived from the solubility products of $Fe(OH)_2$ and $Fe(OH)_3$, respectively, and are expressed in terms of $[H^+]$ to facilitate the calculations.) Note that the formation of species such as $Fe(OH)^{2+}$, $Fe(OH)_2{}^{+}$, and solid $FeCO_3$ or FeS, all of which might be of significance in a natural water system, is not considered.

In constructing the pE-pH diagram, several boundaries must be considered. The first two of these are the oxidizing and reducing limits of water (see Section 4.9). At the high pE end, the stability limit of water is defined by Equation 4.9.5 derived previously:

$$pE = 20.75 - pH \tag{4.9.5}$$

The low pE limit is defined by Equation 4.9.8:

$$pE = -pH \tag{4.9.8}$$

The pE-pH diagram constructed for the iron system must fall between the boundaries defined by these two equations.

Below pH 3, Fe^{3+} may exist in equilibrium with Fe^{2+}. The boundary line that separates these two species, where $[Fe^{3+}] = [Fe^{2+}]$, is given by the following calculation:

$$pE = 13.2 + \log\frac{[Fe^{3+}]}{[Fe^{2+}]} \tag{4.11.6}$$

$$[Fe^{3+}] = [Fe^{2+}] \tag{4.11.7}$$

$$pE = 13.2 \text{ (independent of pH)} \tag{4.11.8}$$

At pE exceeding 13.2, as the pH increases from very low values, $Fe(OH)_3$ precipitates from a solution of Fe^{3+}. The pH at which precipitation occurs depends, of course, upon the concentration of Fe^{3+}. In this example, a maximum soluble iron concentration of 1.00×10^{-5} M has been chosen so that at the $Fe^{3+}/Fe(OH)_3$ boundary, $[Fe^{3+}] = 1.00 \times 10^{-5}$ M. Substitution in Equation 4.11.5 yields:

$$[H^+]^3 = \frac{[Fe^{3+}]}{K_{sp}'} = \frac{1.00 \times 10^{-5}}{9.1 \times 10^3} \tag{4.11.9}$$

$$pH = 2.99 \tag{4.11.10}$$

In a similar manner, the boundary between Fe^{2+} and solid $Fe(OH)_2$ may be defined, assuming $[Fe^{2+}] = 1.00 \times 10^{-5}$ M (the maximum soluble iron concentration specified at the beginning of this exercise) at the boundary:

$$[H^+]^2 = \frac{[Fe^{2+}]}{K_{sp}} = \frac{1.00 \times 10^{-5}}{8.0 \times 10^{12}} \text{ (from Equation 4.11.3)} \tag{4.11.11}$$

$$pH = 8.95 \tag{4.11.12}$$

Throughout a wide pE-pH range, Fe^{2+} is the predominant soluble iron species in equilibrium with the solid hydrated iron(III) oxide, $Fe(OH)_3$. The boundary between these two species depends upon both pE and pH. Substituting Equation 4.11.5 into Equation 4.11.6 yields:

$$pE = 13.2 + \log\frac{K_{sp}'[H^+]^3}{[Fe^{2+}]} \qquad (4.11.13)$$

$$pE = 13.2 + \log 9.1 \times 10^3 - \log 1.00 \text{ x } 10^{-5} + 3 \times \log [H^+]$$

$$pE = 22.2 - 3\,pH \qquad (4.11.14)$$

The boundary between the solid phases $Fe(OH)_2$ and $Fe(OH)_3$ likewise depends upon both pE and pH, but it does not depend upon an assumed value for total soluble iron. The required relationship is derived from substituting both Equation 4.11.3 and Equation 4.11.5 into Equation 4.11.6:

$$pE = 13.2 + \log\frac{K_{sp}'[H^+]^3}{[Fe^{2+}]} \qquad (4.11.13)$$

$$pE = 13.2 + \log\frac{K_{sp}'[H^+]^3}{K_{sp}[H^+]^2} \qquad (4.11.15)$$

$$pE = 13.2 + \log\frac{9.1 \times 10^3}{8.0 \times 10^{12}} + \log [H^+]$$

$$pE = 4.3 - pH \qquad (4.11.16)$$

All of the equations needed to prepare the pE-pH diagram for iron in water have now been derived. To summarize, the equations are (4.9.5), O_2-H_2O boundary; (4.9.8), H_2–H_2O boundary; (4.11.8), Fe^{3+}-Fe^{2+} boundary; (4.11.10), Fe^{3+}-$Fe(OH)_3$ boundary; (4.11.12), Fe^{2+}-$Fe(OH)_2$ boundary; (4.11.14), Fe^{2+}-$Fe(OH)_3$ boundary; and (4.11.16), $Fe(OH)_2$-$Fe(OH)_3$ boundary.

The pE-pH diagram for the iron system in water is shown in Figure 4.4. In this system, at a relatively high hydrogen ion activity and high electron activity (an acidic reducing medium), iron(II) ion, Fe^{2+}, is the predominant iron species; some groundwaters contain appreciable levels of iron(II) under these conditions. (In most natural water systems the solubility range of Fe^{2+} is very narrow because of the precipitation of FeS or $FeCO_3$.) At a very high hydrogen ion activity and low electron activity (an acidic oxidizing medium), Fe^{3+} ion predominates. In an oxidizing medium at lower acidity, solid $Fe(OH)_3$ is the primary iron species present. Finally, in a basic reducing medium, with low hydrogen ion activity and high electron activity, solid $Fe(OH)_2$ is stable.

Note that within the pH regions normally encountered in a natural aquatic system (approximately pH 5 to 9) $Fe(OH)_3$ or Fe^{2+} are the predominant stable iron species. In fact, it is observed that in waters containing dissolved oxygen at any appreciable level (a relatively high pE), hydrated iron(III) oxide ($Fe(OH)_3$ is essentially the only inorganic iron species found. Such waters contain a high level of suspended iron, but any truly soluble iron must be in the form of a complex (see Chapter 3).

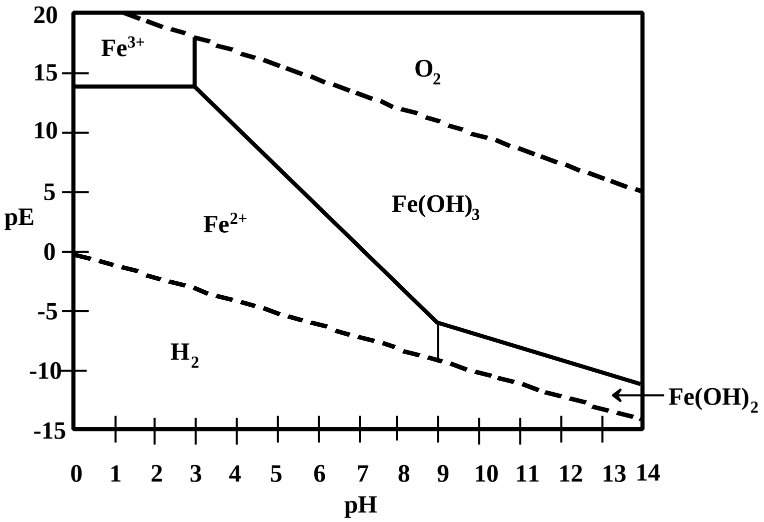

Figure 4.4. Simplifed pE-pH diagram for iron in water. The maximum soluble iron concentration is 1.00 × 10^{-5} M.

In highly anaerobic, low pE water, appreciable levels of Fe^{2+} may be present. When such water is exposed to atmospheric oxygen, the pE rises and $Fe(OH)_3$ precipitates. The resulting deposits of hydrated iron(III) oxide can stain laundry and bathroom fixtures with a refractory red/brown stain. This phenomenon also explains why red iron oxide deposits are found near pumps and springs that bring deep, anaerobic water to the surface. In shallow wells, where the water may become aerobic, solid $Fe(OH)_3$ may precipitate on the well walls, clogging the aquifer outlet. This usually occurs through bacterially-mediated reactions, which are discussed in Chapter 6.

One species not yet considered is elemental iron. For the half-reaction

$$Fe^{2+} + 2e^{-} \rightleftarrows Fe \qquad pE^0 = -7.45 \qquad (4.11.17)$$

the Nernst equation gives pE as a function of $[Fe^{2+}]$

$$pE = -7.45 + {}^1/_2 \log[Fe^{2+}] \qquad (4.11.18)$$

For iron metal in equilibrium with 1.00 × 10^{-5} M Fe^{2+}, the following pE value is obtained:

$$pE = -7.45 + {}^1/_2 \log 1.00 \times 10^{-5} = -9.95 \qquad (4.11.19)$$

Examination of Figure 4.4 shows that the pE values for elemental iron in contact with Fe^{2+} is below the reducing limit of water. This shows that iron metal in contact with water is thermodynamically unstable with respect to reducing water and going into solution as Fe^{2+}, a factor that contributes to the tendency of iron to undergo corrosion.

4.12. CORROSION

One of the most damaging redox phenomena is **corrosion**, defined as the destructive alteration of metal through interactions with its surroundings. In addition to its multibillion dollar annual costs due to destruction of equipment and structures, corrosion introduces metals into water systems and destroys pollution control equipment and waste disposal pipes; it is aggravated by water and air pollutants and some kinds of hazardous wastes (see corrosive wastes in Chapter 19, Section 19.6).

Thermodynamically, all commonly-used metals are unstable relative to their environments. Elemental metals tend to undergo chemical changes to produce the more stable forms of ions, salts, oxides, and hydroxides. Fortunately, the rates of corrosion are normally slow, so that metals exposed to air and water may endure for long periods of time. However, protective measures are necessary. Sometimes these measures fail; for example, witness the gaping holes in automobile bodies exposed to salt used to control road ice.

Corrosion normally occurs when an electrochemical cell is set up on a metal surface. The area corroded is the anode, where the following oxidation reaction occurs, illustrated for the formation of a divalent metal ion from a metal, M:

$$M \rightarrow M^{2+} + 2e^- \tag{4.12.1}$$

Several cathodic reactions are possible. One of the most common of these is the reduction of H^+ ion:

$$2H^+ + 2e^- \rightarrow H_2 \tag{4.12.2}$$

Oxygen may also be involved in cathodic reactions, including reduction to hydroxide, reduction to water, and reduction to hydrogen peroxide:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{4.12.3}$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{4.12.4}$$

$$O_2 + 2H_2O + 2e^- \rightarrow 2OH^- + H_2O_2 \tag{4.12.5}$$

Oxygen may either accelerate corrosion processes by participating in reactions such as these, or retard them by forming protective oxide films. As discussed in Chapter 6, bacteria are often involved with corrosion.

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QUESTIONS AND PROBLEMS

1. The acid-base reaction for the dissociation of acetic acid is

   $$HOAc + H_2O \rightarrow H_3O^+ + OAc^-$$

   with $K_a = 1.75 \times 10^{-5}$. Break this reaction down into two half-reactions involving H^+ ion. Break down the redox reaction

   $$Fe^{2+} + H^+ \rightarrow Fe^{3+} + {}^1/_2H_2$$

   into two half-reactions involving the electron. Discuss the analogies between the acid-base and redox processes.

2. Assuming a bicarbonate ion concentration [HCO_3^-] of 1.00×10^{-3} *M* and a value of 3.5×10^{-11} for the solubility product of $FeCO_3$, what would you expect to be the stable iron species at pH 9.5 and pE -8.0, as shown in Figure 4.4?
3. Assuming that the partial pressure of oxygen in water is that of atmospheric O_2, 0.21 atm, rather than the 1.00 atm assumed in deriving Equation 4.9.5, derive an equation describing the oxidizing pE limit of water as a function of pH.
4. Plot log P_{O_2} as a function of pE at pH 7.00.
5. Calculate the pressure of oxygen for a system in equilibrium in which [NH_4^+] = [NO_3^-] at pH 7.00.
6. Calculate the values of [Fe^{3+}], pE, and pH at the point in Figure 4.4 where Fe^{2+} is at a concentration of 1.00×10^{-5} M, $Fe(OH)_2$, and $Fe(OH)_3$ are all in equilibrium.
7. What is the pE value in a solution in equilibrium with air (21% O_2 by volume) at pH 6.00?
8. What is the pE value at the point on the Fe^{2+}–$Fe(OH)_3$ boundary line (see Figure 4.4) in a solution with a soluble iron concentration of 1.00×10^{-4} M at pH 6.00?
9. What is the pE value in an acid mine water sample having [Fe^{3+}] = 7.03×10^{-3} M and [Fe^{2+}] = 3.71×10^{-4} M?
10. At pH 6.00 and pE 2.58, what is the concentration of Fe^{2+} in equilibrium with $Fe(OH)_2$?
11. What is the calculated value of the partial pressure of O_2 in acid mine water of pH 2.00, in which [Fe^{3+}] = [Fe^{2+}] ?
12. What is the major advantage of expressing redox reactions and half-reactions in terms of exactly one electron-mole?
13. Why are pE values that are determined by reading the potential of a platinum electrode versus a reference electrode generally not very meaningful?
14. What determines the oxidizing and reducing limits, respectively, for the thermodynamic stability of water?
15. How would you expect pE to vary with depth in a stratified lake?
16. Upon what half-reaction is the rigorous definition of pE based?