Chapter 4 Oxidation–Reduction Reactions

Oxidation–reduction reactions (often referred to as *redox* reactions) involve the gain or loss of electrons. The species involved in the reactions may be atoms, molecules, or ions. A ***cation*** is a *positively charged ion* (fewer electrons than the number of protons in the nucleus), and an ***anion*** is a *negatively charged ion* (more electrons than the number of protons in the nucleus). For many elements, the oxidation state is an important factor in determining their behavior in the natural environment. For example, Fe^{2+} is more soluble in water than Fe^{3+}. If water in which iron occurs as the Fe^{2+} cation is exposed to higher oxygen concentrations, as might occur when groundwater is pumped to the surface, some of the iron would be oxidized to Fe^{3+} and an iron hydroxide would precipitate from solution. Hence, the oxidation–reduction characteristics of the natural environment play a key role in the transport and ultimate fate of various contaminants.

BASIC PRINCIPLES

Electrochemical Cells

Consider the following simple experiment (Figure 4–1). Zinc and copper metal bars are connected by wires to a voltmeter. The bars are immersed in a container that is divided into two compartments by a porous partition. The zinc bar is immersed in a $ZnSO_4$ solution and the copper bar is immersed in a $CuSO_4$ solution. The porous partition very cleverly allows SO_4^{2-} anions to pass from one side to the other, but does not allow metal cations to pass from one side to the other. The experiment we have set up is an electrochemical (or galvanic) cell. After the metal bars are immersed in the solution, several changes occur. The Zn^{2+} cations increase in the left-hand side of the container and the concentration of Cu^{2+} cations decreases in the right-hand side of the container. SO_4^{2-} anions move from right to left through the porous partition, thus maintaining the charge balance in both halves of the container. Immediately after immersing the bars, a voltage is recorded by the voltmeter. With time, this voltage decreases to zero. What has occurred is an oxidation–reduction reaction that with time achieved equilibrium.

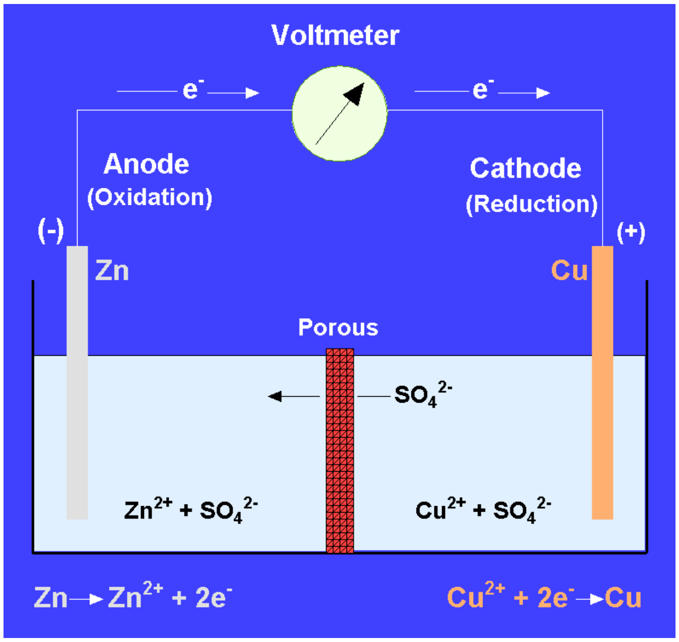


Figure 4–1 Diagram of a Zn-Cu electrochemical cell. Zn and Cu metal electrodes are immersed in a $CuSO_4$ solution. Electrons flow from left to right and a potential is recorded by the voltmeter. With time, this potential decreases to zero, the concentration of Zn^{2+} increases in the left-hand half of the cell, and the concentration of Cu^{2+} decreases in the right-hand half of the cell. After Faure (1998).

Let us consider the various components of this reaction. In the left-hand side of the container, Zn metal has gone into solution as Zn^{2+} cations. Because there has been a loss of electrons, we say that the Zn has been oxidized. In the right-hand side of the container, Cu^{2+} cations have precipitated onto the Cu electrode as copper metal. Because there has been a gain in electrons, we say that the Cu^{2+} cations have been reduced. The oxidation of Zn is the source of electrons for the system and Zn is referred to as a *reducing agent.* During reduction of the copper cations, electrons are removed from the system and copper is referred to as an *oxidizing agent.* This nomenclature is sometimes a major stumbling block for students. Remember ***oxidation*** is the *loss of electrons* and ***reduction*** is the *gain of electrons.* A ***reducing agent*** is an *electron donor* (it loses electrons and is oxidized), and an ***oxidizing agent*** is an *electron acceptor* (it gains electrons and is reduced). In terms of our example, the complete electrochemical reaction is

$$\mathrm{Zn} + \mathrm{Cu}^{2+} \rightarrow \mathrm{Zn}^{2+} + \mathrm{Cu}$$

Table 4–1 Oxidation–Reduction Reactions

Reaction	ΔG_R^0 (kJ mol^{-1})
$Zn + Fe^{2+} \rightleftharpoons Zn^{2+} + Fe$	−68.4
$Fe + Cu^{2+} \rightleftharpoons Fe^{2+} + Cu$	−144.4
$Cu + 2Ag^{+} \rightleftharpoons Cu^{2+} + 2Ag$	−88.7

Zn is oxidized and acts as a reducing agent, and Cu is reduced and acts as an oxidizing agent. This reaction can be divided into two half-reactions

$$\mathrm{Zn} \rightarrow \mathrm{Zn}^{2+} + 2\mathrm{e}^{-} \text{ and } \mathrm{Cu}^{2+} + 2\mathrm{e}^{-} \rightarrow \mathrm{Cu}$$

Half-reactions (often called ***electrodes)*** will be further considered in subsequent sections.

Electromotive Series

Three oxidation-reduction reactions, and their free energies, are listed in Table 4–1. Each reaction has a negative free energy. Thus, the reactions proceed spontaneously to the right. In the first reaction, Zn acts as a reducing agent and Fe acts as an oxidizing agent. In the second reaction, Fe acts as a reducing agent and Cu acts as an oxidizing agent. In the third reaction, Cu acts as a reducing agent and Ag acts as an oxidizing agent. For these four elements, in terms of their strength as reducing agents from strongest to weakest, the order is Zn, Fe, Cu, and Ag. The electromotive series is a listing of the elements (as half-reactions) in terms of their decreasing strengths as reducing agents. The electromotive series for a number of elements, and some of their oxidation states, is given in Table 4–2.

Electromotive Force

Returning to the experiment illustrated in Figure 4–1, the voltage generated by the electrons flowing from the zinc bar to the copper bar is referred to as the ***electromotive force (emf).*** The electromotive force is related to the free energy of an oxidation-reduction reaction as follows:

$$\Delta G_R = -n\mathscr{F}E \qquad (4\text{–}1)$$

where ΔG_R is the free energy of the reaction in any state, E is the corresponding electromotive force, n is the number of electrons transferred in the reaction, and F is Faraday's constant (96,489 coulombs mol^{-1}, 23.06 kcal volt^{-1} gram equivalent^{-1}, or, in SI units, 96.42 kJ volt^{-1} gram equivalent^{-1}).

EXAMPLE 4–1 Calculate the *standard emf (E°)* for the oxidation-reduction reaction illustrated in Figure 4–1. In the standard state [Zn^{2+}] = [Cu^{2+}] = 1.0, P = 1 atm, and T = 25°C. The reaction is written

$$\text{Zn} + \text{Cu}^{2+} \rightleftharpoons \text{Zn}^{2+} + \text{Cu}$$

Calculating the free energy using the values in Appendix II, source 3, gives

$$\Delta G_{\text{R}}^{0} = [(-147.3) + (0.00)] - [(0.00) + (65.5)] = -212.8 \text{ kJ mol}^{-1}$$

Calculating the emf gives

$$E^{\circ} = \frac{-\Delta G_{\text{R}}^{0}}{n\mathscr{F}} = \frac{-(-212.8)}{(2)(96.42)} = 1.10 \text{ V}$$

The number of electrons transferred in the reaction is 2; therefore, n = 2.

Table 4–2 Electromotive Series for Selected Half-Reactions Arranged in Order of Decreasing Strengths as Reducing Agents*

Oxidizing agent		Reducing agent	Standard electrode potential, V
Li^{+}	$+1e^{-}$ →	Li	−3.045
Na^{+}	$+1e^{-}$ →	Na	−2.714
Pu^{3+}	$+3e^{-}$ →	Pu	−2.07
Th^{4+}	$+4e^{-}$ →	Th	−1.90
Np^{3+}	$+3e^{-}$ →	Np	−1.86
Al^{3+}	$+3e^{-}$ →	Al	−1.66
U^{4+}	$+4e^{-}$ →	U	−1.38
Mn^{2+}	$+2e^{-}$ →	Mn	−1.18
V^{3+}	$+3e^{-}$ →	V	−0.87
Zn^{2+}	$+2e^{-}$ →	Zn	−0.763
S	$+2e^{-}$ →	S^{2-}	−0.44

Oxidizing agent		Reducing agent	Standard electrode potential, V
Fe^{2+}	$+2e^- \rightarrow$	Fe	−0.41
Cd^{2+}	$+ 2e^- \rightarrow$	Cd	−0.403
Co^{2+}	$+2e^- \rightarrow$	Co	−0.277
Ni^{2+}	$+2e^- \rightarrow$	Ni	−0.250
Sn^{2+}	$+2e^- \rightarrow$	Sn	−0.140
Pb^{2+}	$+2e^- \rightarrow$	Pb	−0.126
$2H^+$	$+2e^- \rightarrow$	H_2	0.00
Ti^{4+}	$+1e^- \rightarrow$	Ti^{3+}	0.04
Sn^{4+}	$+ 2e^- \rightarrow$	Sn^{2+}	0.15
Cu^{2+}	$+2e^- \rightarrow$	Cu	0.337
Cu^+	$+1e^- \rightarrow$	Cu	0.521
Se	$+2e^- \rightarrow$	Se^{2-}	0.67
Fe^{3+}	$+1e^- \rightarrow$	Fe^{2+}	0.771
Ag^+	$+1e^- \rightarrow$	Ag	0.799
Pu^{4+}	$+1e^- \rightarrow$	Pu^{3+}	0.97
Au^{3+}	$+3e^- \rightarrow$	Au	1.50
Co^{3+}	$+1e^- \rightarrow$	Co^{2+}	1.82

*Data from Daniels and Alberty (1967) and Faure (1998).

Note: By international convention half-cell reactions are written so that the electrons appear on the left-hand side of the equation; i.e., the reduced form of the element appears on the right and the oxidized form appears on the left. Not all textbooks (or professional papers) follow this convention, an added difficulty for the student attempting to understand a conceptually difficult subject.

It is impossible to measure only the electromotive force of a half-reaction. In order to measure the potential of a half-reaction (electrode), another metallic electrode is required. This is done by arbitrarily assigning a potential to one electrode (half-reaction) and comparing all other electrodes to this electrode. The universally accepted reference electrode is the ***standard hydrogen electrode (SHE)*** for which the value of $E°$ is arbitrarily set equal to 0.00 V (at $P = 1$ atm and $T = 25°C$). This electrode is written

$$H^{+} + e^{-} \rightarrow \frac{1}{2} H_{2\,(g)}$$

If $E°$ = 0.00 V, then $\Delta G_R^0 = 0.00$, from which it follows that $G°(H^+) = G°(e^-) = 0.00$. Also, for a hydrogen half-cell in the standard state, $[H^+] = [H_2] = 1$. It is now possible to determine the emf of any half-reaction by comparison to the standard hydrogen electrode. The results of these determinations are tabulated in Table 4–2 (the electromotive series).

EXAMPLE 4–2 Calculate the standard electrode potential for the oxidation of scandium. During oxidation, scandium gives up three electrons. Remember the convention is that the electrons appear on the left-hand side of the equation. The reaction with the hydrogen electrode is written

$$Sc^{3+} + 1.5H_{2\,(g)} \rightleftharpoons Sc + 3H^{+}$$

Calculating the free energy using the values in Appendix II, source 4, gives

$$\Delta G_R^0 = [(0.00) + (3)(0.00)] - [(-586.6) + (1.5)(0.00)] = 586.6 \text{ kJ mol}^{-1}$$

Calculating the emf gives

$$E^{\circ} = \frac{-\Delta G_R^0}{n\mathscr{F}} = \frac{-(586.6)}{(3)(96.42)} = -2.03 \text{ V}$$

A hydrogen electrode is difficult to prepare and maintain. In its stead, a calomel electrode is often used. The reaction for this electrode is

$$Hg_2Cl_2 + 2e^{-} \rightleftharpoons 2Hg + 2Cl^{-}$$

For a normal calomel electrode (one molar solution of potassium chloride) the potential is 0.2802 V, and for a saturated calomel electrode (saturated in potassium chloride) the potential is 0.2444 V, both relative to the standard hydrogen electrode. The saturated calomel electrode is the one most frequently used when making environmental measurements of oxidation-reduction potentials.

The electromotive force for an oxidation-reduction reaction can be determined by combining the appropriate half-reactions. Consider the reaction between Zn and Cu electrodes that we used as an example at the beginning of this chapter. Referring to Table 4–2, we see that Zn is the stronger reducing agent. Thus, Zn will be oxidized and Cu will be reduced (as we observed in the experiment). We can write the half-reactions and combine them as follows:

$$\begin{array}{ll}
\mathrm{Zn} \rightarrow \mathrm{Zn}^{2+} + 2\mathrm{e}^- & E^\circ = 0.763 \\
\mathrm{Cu}^{2+} + 2\mathrm{e}^- \rightarrow \mathrm{Cu} & E^\circ = 0.337 \\
\hline
\mathrm{Zn} + \mathrm{Cu}^{2+} \ \square \ \mathrm{Zn}^{2+} + \mathrm{Cu} & E^\circ = 1.100\ \mathrm{V}
\end{array}$$

Because Zn is oxidized, we have reversed the Zn half-reaction and reversed the sign for the electromotive force. Thus, the Zn half-reaction has a positive value.

Balancing Oxidation–Reduction Equations

The oxidation-reduction reactions we have considered so far are relatively simple. Most reactions are more complicated and we will need to balance complex equations. The following rules are used when balancing oxidation-reduction equations:

1. Determine the valence numbers (charge) for all elements involved in the reaction.
2. Determine the number of electrons given off and taken up in the reaction. Balance the transfer of electrons.
3. Balance the elements, except oxygen and hydrogen, on both sides of the equation.
4. Balance the number of oxygen atoms by adding H_2O.
5. Balance the number of hydrogens by adding H^+.

EXAMPLE 4–3 Acid mine drainage is caused by the oxidation of pyrite when it comes in contact with water containing dissolved oxygen. The elements of interest are Fe and S. The reaction is written as follows:

$$\mathrm{FeS}_{2\ \mathrm{pyrite}} + \mathrm{O}_2 \rightarrow \mathrm{Fe(OH)}_{3\ \mathrm{(ppt)}} + \mathrm{SO}_4^{2-}$$

Both Fe and S are oxidized. Fe is oxidized from Fe^{2+} to Fe^{3+}, releasing 1 electron in the process. S is oxidized from S^- in pyrite to S^{6+} in the sulfate ion, releasing 7 electrons in the process. We have now determined the valences for the elements involved in the reaction (rule 1). The breakdown of one pyrite molecule releases a total of 15 electrons, 1 from Fe oxidation and 14 (2 × 7) from S oxidation. Each oxygen receives 2 electrons to become O^{2-}. Thus, 4 electrons are consumed by the O_2 molecule. In summary, 15 electrons are released by FeS_2 and 4 are consumed by O_2. We could balance the transfer of electrons by setting $\mathrm{FeS_2} = \frac{4}{15}$. However, this would leave us with some very nasty fractions in the equation. It is preferable to work with simple whole numbers. We accomplish this by cross-multiplying these two numbers, which gives the following (rule 2):

$$4\mathrm{FeS_2} + 15\mathrm{O_2} \rightarrow \mathrm{Fe(OH)_3} + \mathrm{SO_4^{2-}}$$

The electrons released and consumed are now in balance, 4 × 15 = 15 × 4. We now balance all the elements except hydrogen and oxygen (rule 3).

$$4\mathrm{FeS_2} + 15\mathrm{O_2} \rightarrow 4\mathrm{Fe(OH)_3} + 8\mathrm{SO_4^{2-}}$$

We now balance the number of oxygens by adding H_2O (rule 4).

$$4\mathrm{FeS_2} + 15\mathrm{O_2} + 14\mathrm{H_2O} \rightarrow 4\mathrm{Fe(OH)_3} + 8\mathrm{SO_4^{2-}}$$

Lastly, we balance the number of hydrogens by adding H^+ (rule 5).

$$4\mathrm{FeS}_{2\ \mathrm{pyrite}} + 15\mathrm{O_2} + 14\mathrm{H_2O} \rightarrow 4\mathrm{Fe(OH)}_{3\ \mathrm{(ppt)}} + 8\mathrm{SO_4^{2-}} + 16\mathrm{H^+}$$

Note that during the oxidation of pyrite a substantial number of H^+ ions are produced; i.e., for each mole of pyrite that is oxidized 4 mol of H^+ ions are released. It is these H^+ ions that are responsible for the very low pH of waters draining from coal and base-metal mines (acid mine drainage).

The Nernst Equation and Eh

Consider the following generalized oxidation-reduction reaction:

$$\mathrm{aA_{ox}} + \mathrm{bB_{red}} \rightleftharpoons \mathrm{cC_{red}} + \mathrm{dD_{ox}} \qquad (4\text{–}2)$$

As we did in Chapter 2 (equation 2–25), we can write this reaction in terms of free energy.

$$\Delta G_\mathrm{R} = \Delta G_\mathrm{R}^0 + RT\ln\frac{[\mathrm{C_{red}}]^\mathrm{c}[\mathrm{D_{ox}}]^\mathrm{d}}{[\mathrm{A_{ox}}]^\mathrm{a}[\mathrm{B_{red}}]^\mathrm{b}} \qquad (4\text{–}3)$$

Substituting for $\Delta G_\mathrm{R} = -n\mathscr{F}E$ and $\Delta G_\mathrm{R}^0 = -n\mathscr{F}E^\circ$ gives

$$E = E^\circ - \frac{RT}{n\mathscr{F}} \ln \frac{[\mathrm{C_{red}}]^\mathrm{c}[\mathrm{D_{ox}}]^\mathrm{d}}{[\mathrm{A_{ox}}]^\mathrm{a}[\mathrm{B_{red}}]^\mathrm{b}} = E^\circ - \frac{RT}{n\mathscr{F}} \ln K \qquad (4\text{–}4)$$

Equation 4–4 is referred to as the ***Nernst equation*** and can be used to calculate the emf of an oxidation-reduction reaction under any conditions. $E°$ is the emf of the reaction in the standard state, R is the gas constant (8.314×10^{-3} kJ deg^{-1} mol^{-1}), T is the temperature (K), n is the number of electrons transferred in the reaction, F is the Faraday constant (96.42 kJ volt^{-1} gram equivalent^{-1}), and K is the equilibrium constant.

We usually work in base 10, rather than base *e,* so it is useful to write this equation in terms of base 10 logarithms. Assuming that the reaction occurs at 25°C, the Nernst equation can be written

$$\begin{aligned} E &= E^\circ - \frac{RT}{n\mathscr{F}} \ln K = E^\circ - \frac{(8.314\times 10^{-3})(298.15)(2.303)}{(n)(96.42)} \log K \\ &= E^\circ - \frac{0.0592}{n} \log K \end{aligned} \qquad (4\text{–}5)$$

If we are measuring the emf of a half-cell relative to the hydrogen electrode (or a proxy, such as the calomel electrode), the Nernst equation is usually written so that the activity product of the oxidized species is in the numerator. What this means is that the sign is reversed in the Nernst equation, giving

$$E = E^\circ + \frac{0.0592}{n} \log \left(\frac{\text{Activity product of oxidized species}}{\text{Activity product of reduced species}} \right) \qquad (4\text{–}6)$$

This has the potential to be a very confusing complication. How the calculation is carried out is illustrated in Example 4–4.

EXAMPLE 4–4 Calculate the emf for the half-reaction

$$\mathrm{Mn^{3+} + e^- \rightarrow Mn^{2+}}$$

Combining this half-reaction with the hydrogen electrode yields

$$\mathrm{Mn^{3+}} + \frac{1}{2}\mathrm{H_{2\,(g)}} \rightleftharpoons \mathrm{Mn^{2+} + H^+}$$

For this reaction,

$$\Delta G_{\mathrm{R}}^{0} = [(-228.1) + (0.00)] - [(-84.8) + \left(\frac{1}{2}\right)(0.00)] = -143.3\ \mathrm{kJ\ mol^{-1}}$$

$$E^{\circ} = \frac{-\Delta G_{\mathrm{R}}^{0}}{n\mathscr{F}} = -\frac{-(-143.3)}{(1)(96.42)} = 1.49\ \mathrm{V}$$

The Nernst equation for the reaction is

$$E = E^{\circ} + \frac{0.0592}{n}\log K = 1.49 + 0.0592\log\frac{[\mathrm{Mn^{3+}}][\mathrm{H_{2\,(g)}}]^{½}}{[\mathrm{Mn^{2+}}][\mathrm{H^{+}}]}$$

For the hydrogen half-cell in the standard state, $[\mathrm{H^+}] = [\mathrm{H_2}] = 1$. Thus, the $[\mathrm{Mn^{3+}}]/[\mathrm{Mn^{2+}}]$ ratio is determined by the electromotive force of the system. For example, groundwater has $E = 0.00$ V, and surface water has $E = 0.80$ V. What would happen when groundwater is pumped to the surface? At $E = 0.00$ V,

$$\log\frac{[\mathrm{Mn^{3+}}]}{[\mathrm{Mn^{2+}}]} = \frac{E - 1.49}{0.0592} = \frac{0.00 - 1.49}{0.0592} = -25.2$$

and at $E = 0.80$ V,

$$\log\frac{[\mathrm{Mn^{3+}}]}{[\mathrm{Mn^{2+}}]} = \frac{E - 1.49}{0.0592} = \frac{0.80 - 1.49}{0.0592} = -11.7$$

When the groundwater is exposed to the oxidizing surface environment, $\mathrm{Mn^{3+}}$ increases relative to $\mathrm{Mn^{2+}}$. Because the solubility of $\mathrm{Mn^{3+}}$ is less than that of $\mathrm{Mn^{2+}}$, this may lead to the precipitation of manganese.

We can define a special type of electromotive force, Eh. **Eh** is *the electromotive force of any reaction measured relative to the standard hydrogen electrode.* What was determined in Example 4–4 was Eh. Eh is an environmental parameter that reflects the overall oxidation-reduction potential of a natural system relative to the hydrogen electrode. Because the hydrogen electrode is not easily transported, measurements in the field are usually made between a Pt electrode and a reference electrode. The measurements are then corrected, using equation 4–7, to the value that would be observed if the reference electrode was a hydrogen electrode.

$$\mathrm{Eh} = E_{\mathrm{meas}} - E_{\mathrm{ref}} \qquad (4–7)$$

The most commonly used reference electrode is the calomel electrode, for which E_{ref} = 244.4 mV

(25°C). Ionic equilibria calculated from the Nernst equation using the measured Eh often are not in good agreement with the measured ionic equilibria. Thus, except in certain circumstances, Eh measurements are only used in a qualitative sense. The reasons for this disagreement are numerous, and the student should consult standard reference works, such as Langmuir (1997) and Stumm and Morgan (1996), for further details. In practice, it is best to determine Eh based on specific oxidation-reduction reactions (see Example 4–5).

EXAMPLE 4–5 Calculate the Eh for a water sample at 25°C for which $[\mathrm{Mn}^{2+}] = 10^{-3}$ mol L^{-1} and $[\mathrm{Mn}^{3+}] = 10^{-14}$ mol L^{-1}. Using the data from Example 4–4,

$$\begin{aligned} \mathrm{Eh} &= 1.49 + 0.0592\ \log[\mathrm{Mn}^{3+}] - 0.0592\ \log[\mathrm{Mn}^{2+}] \\ &= 1.49 + 0.0592\ \log[10^{-14}] - 0.0592\ \log[10^{-3}] = 0.84\ \mathrm{V} \end{aligned}$$

A direct Eh measurement is made using a calomel electrode as the reference electrode. The measured Eh is 901 mV. The corrected Eh is

$$\mathrm{Eh} = E_{\mathrm{meas}} - E_{\mathrm{ref}} = 901 - 244 = 657\ \mathrm{mV} = 0.657\ \mathrm{V}$$

The measured environmental Eh suggests that there should be significantly less Mn^{3+} present than the amount measured. Mn is an example of an electroactive species, and electrons are easily exchanged at the surface of an Eh electrode. If the water sample was largely composed of electroactive species, there should be good agreement between the measured Eh and the Eh calculated from the Mn reaction. The lower measured Eh suggests that there are also nonelectroactive species present that cannot easily exchange electrons at the surface of the Eh electrode. C, N, O, H, and oxidized sulfur are examples of such species. The presence of nonelectroactive species gives rise to mixed potentials because these species are not in equilibrium with the Eh electrode. In these cases, the Eh measurement is not environmentally significant.

Oxidation-Reduction Reactions and pe

An alternative way to look at oxidation-reduction is through the concept of electron activity, p*e*. This approach is often used by chemists and engineers and is algebraically simpler than the Nernst equation. Geo- and environmental scientists still tend to use Eh. Consider the half-reaction

$$\mathrm{Fe}^{3+} + \mathrm{e}^{-} \rightleftharpoons \mathrm{Fe}^{2+}$$

We can write this reaction as follows:

$$K = \frac{[\mathrm{Fe}^{2+}]}{[\mathrm{Fe}^{3+}][\mathrm{e}^{-}]} \tag{4–8}$$

The electrons appear explicitly in this equation. However, this should not be interpreted as a concentration of electrons, but rather as the tendency to accept or release electrons. Similar to pH,

$$\mathrm{p}e = -\log[\mathrm{e}^{-}] \tag{4–9}$$

Rewriting equation 4–8 in logarithmic form and substituting for e using equation 4–9 gives

$$\log K = \log[\mathrm{Fe}^{2+}] - \log[\mathrm{Fe}^{3+}] - \log[\mathrm{e}^{-}] = \log[\mathrm{Fe}^{2+}] - \log[\mathrm{Fe}^{3+}] + \mathrm{p}e \tag{4–10}$$

Solving equation 4–10 for p*e* gives

$$\mathrm{p}e = \log K + \log[\mathrm{Fe}^{3+}] - \log[\mathrm{Fe}^{2+}] \tag{4–11}$$

Note that in the standard state, $[\mathrm{Fe}^{2+}] = [\mathrm{Fe}^{3+}] = 1$ and $\mathrm{p}e^{\circ} = \log K$. For the reaction illustrated by equation 4–11, only one electron is transferred. A more general statement of the relationship between p*e*° and *K* is

$$\mathrm{p}e^{\circ} = \frac{1}{n}\log K \tag{4–12}$$

where p*e*° is the standard state and *n* is the number of electrons transferred in the reaction. For the general case when *n* numbers of electrons are transferred at conditions other than the standard state,

$$\mathrm{p}e = \mathrm{p}e^{\circ} + \frac{1}{n}\log\left(\frac{\text{Activity product of oxidized species}}{\text{Activity product of reduced species}}\right) \tag{4–13}$$

Note that in terms of p*e* this is analogous to the general form of the Nernst equation (4–6).

EXAMPLE 4–6 At 25°C, calculate p*e*° for the reaction

$$\mathrm{Zn} + \mathrm{Fe}^{2+} \rightleftharpoons \mathrm{Zn}^{2+} + \mathrm{Fe}$$

From Table 4–1, $\Delta G_{\mathrm{R}}^{0} = -68.4\ \mathrm{kJ\ mol}^{-1}$

$$\log K = \frac{-\Delta G_{\mathrm{R}}^{0}}{5.708} = \frac{-(-68.4)}{5.708} = 11.98$$

and

$$\mathrm{p}e^{\circ} = \frac{1}{n}\log K = \frac{1}{2}\times 11.98 = 5.99$$

If $[\mathrm{Fe}^{2+}] = 10^{-3}$ and $[\mathrm{Zn}^{2+}] = 10^{-6}$, calculate the p*e*.

$$\begin{aligned}\mathrm{p}e &= \mathrm{p}e^{\circ} + \frac{1}{n}\log[\mathrm{Zn}^{2+}] - \frac{1}{n}\log[\mathrm{Fe}^{2+}] = \mathrm{p}e^{\circ} + \frac{1}{2}\log[10^{-6}] - \frac{1}{2}\log[10^{-3}] \\ &= 6 - 3 + 1.5 = 4.5\end{aligned}$$

Eh and p*e* are related as follows:

$$\mathrm{Eh} = \frac{2.303RT}{\mathscr{F}}\,\mathrm{p}e \qquad (4\text{–}14)$$

and at 25°C,

$$\mathrm{Eh} = 0.059\ \mathrm{p}e \qquad (4\text{–}15)$$

OXIDATION–REDUCTION DIAGRAMS

The stability of many species in solution and the solubility of solid phases is controlled by the oxidation-reduction potential of the environment. In many cases, H^+ ions are involved in these reactions; hence, they are also pH sensitive. Diagrams that represent the range of stability for various species in terms of Eh and pH can be constructed from thermodynamic data. These graphical representations are used to make first-order inferences about the distribution of species in various natural environments. The pioneering work in this area was that of Garrels and Christ (1965). More recently, Brookins (1988) has prepared a number of Eh–pH diagrams for geologically and environmentally important systems. The basic principles used to construct these diagrams and their interpretation are considered in this section.

Stability of Water

Although one does not often think of water in terms of oxidation-reduction, limits for the breakdown of water can be derived in terms of Eh and pH. Consider the following reaction (referred to as the ***water electrode***):

$$2\mathrm{H}^+ + \frac{1}{2}\mathrm{O}_{2\,(g)} + 2\mathrm{e}^- \rightleftharpoons \mathrm{H}_2\mathrm{O}_{(1)} \tag{4–16}$$

In this reaction, the oxygen in the water molecule is converted to a gas, the valence number of oxygen changes from −2 to 0, and two electrons are released to solution. This is an oxidation reaction and its emf can be determined by reference to the standard hydrogen electrode. The emf of the standard hydrogen electrode is, by definition, zero, so we only need to calculate the emf for the water half-reaction. The Nernst equation for this reaction is

$$\mathrm{Eh} = E^\circ + \frac{0.0592}{2}\log([\mathrm{O}_2]^{½}[\mathrm{H}^+]^2) \tag{4–17}$$

We calculate $E°$, at 25°C, from the standard free energy for reaction 4–16.

$$\begin{aligned}\Delta G^0_\mathrm{R} &= [-237.14] - [(2)(0.00) + \left(\frac{1}{2}\right)(0.00) + (2)(0.00)] \\ &= -237.14\ \mathrm{kJ\ mol}^{-1}\end{aligned} \tag{4–18}$$

and

$$E^\circ = \frac{-(-237.14)}{(2)(96.42)} = 1.23\ \mathrm{V} \tag{4–19}$$

The Eh equation is

$$\mathrm{Eh} = 1.23 + \frac{0.0592}{2}\log([\mathrm{O}_2]^{½}[\mathrm{H}^+]^2) \tag{4–20}$$

However, we would like to write this equation in terms of Eh and pH because pH is what we determine when we measure $[\mathrm{H}^+]$ in solution. We can rewrite equation 4–20 as follows:

$$\mathrm{Eh} = 1.23 + \frac{0.0592}{2}\left(\frac{1}{2}\right)\log[\mathrm{O}_2] + \frac{0.0592}{2}(2)\log[\mathrm{H}^+] \tag{4–21}$$

Recall that the definition of pH is pH = $-\log[\mathrm{H}^+]$. Substituting for pH in equation 4–21, and carrying out the appropriate multiplications, gives

$$\mathrm{Eh} = 1.23 + 0.0148\ \log[\mathrm{O}_2] - 0.0592\ \mathrm{pH} \tag{4–22}$$

which is the Eh–pH equation for the water electrode.

The limits of the natural Eh–pH environment are determined by the conditions under which water will break down into its gaseous components. We can write the following equilibrium reaction:

$$2H_2O_{(1)} \rightleftharpoons O_{2\,(g)} + 2H_{2\,(g)}$$

The equilibrium constant for this reaction is

$$K = [O_2][H_2]^2 = 10^{-83.1} \qquad (4–23)$$

Clearly, the pressure of neither gas can exceed 1 atm. If we set H_2 = 1 atm, then $O_2 = 10^{-83.1}$ atm; and if we set O_2 = 1 atm, then $H_2 = 10^{-41.65}$ atm. Substituting the two extreme values for O_2 yields the limits of the natural environment. At $O_{2\,(g)}$ = 1 atm,

$$\mathrm{Eh} = 1.23 + 0.0148\ \log[1] - 0.0592\ \mathrm{pH} = 1.23 - 0.0592\ \mathrm{pH} \qquad (4–24)$$

and at $O_{2(g)} = 10^{-83.1}$,

$$\mathrm{Eh} = 1.23 + 0.0148\ \log[10^{-83.1}] - 0.0592\ \mathrm{pH} = -0.0592\ \mathrm{pH} \qquad (4–25)$$

If we use the present-day atmospheric partial pressure of O_2 = 0.2 atm, *E*° in equation 4–24 is 1.22. The limits for the natural environment, in terms of Eh and pH, are shown in Figure 4–2. These natural limits are the starting point for the construction of Eh–pH diagrams. Also shown on Figure 4–2 are the Eh–pH ranges for some natural waters.

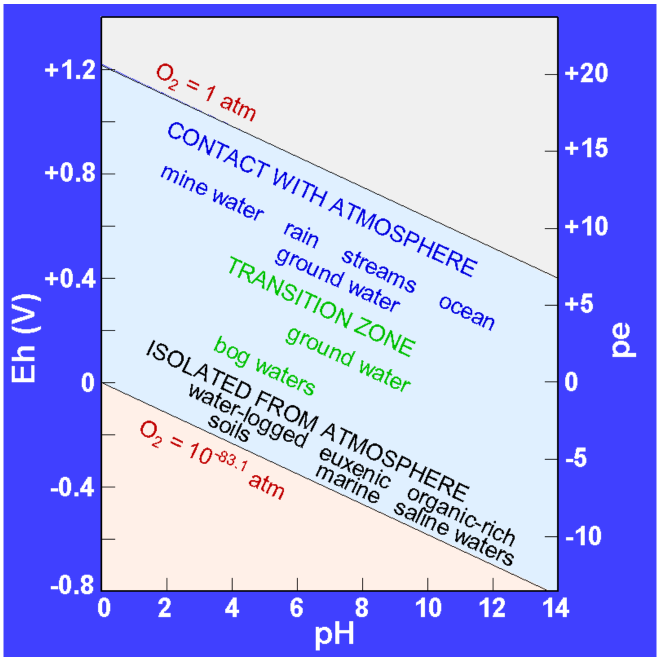


Figure 4–2 Stability limits for natural waters at the earth's surface in terms of Eh and pH at 25°C. The limits are based on partial pressures of oxygen of 1 and $10^{-83.1}$ atm. Also shown is the emf in p*e* units. The range of Eh and pH conditions for various natural environments is modified from Garrels and Christ (1965).

We can also plot this diagram in terms of p*e*, and the p*e* units are shown on the right-hand side of Figure 4–2. To further illustrate the relationship between Eh and p*e*, we will derive the p*e*–pH equations for the limits of the natural environment. For the water electrode (equation 4–16), $\Delta G_{\mathrm{R}}^{0} = -237.14 \text{ kJ mol}^{-1}$, from which we can calculate the equilibrium constant for the reaction at 25°C.

$$\log K = \frac{-\Delta G_{\mathrm{R}}^{0}}{5.708} = \frac{-(-237.14)}{5.708} = 41.55 = \frac{[\mathrm{H_2O_{(l)}}]}{[\mathrm{H^+}]^2[\mathrm{O_{2\,(g)}}]^{1/2}[\mathrm{e^-}]^2} \qquad (4\text{–}26)$$

Writing the equilibrium equation 4–26 using p*e* gives

$$\log K = -\frac{1}{2}\log P_{\mathrm{O_2}} + 2\ \mathrm{p}e + 2\ \mathrm{pH} = 41.55 \qquad (4\text{–}27)$$

Note that $[\mathrm{e^-}]$ has been replaced by p*e* and $[\mathrm{H^+}]$ has been replaced by pH. Rewriting equation 4–27 in terms of p*e* gives

$$\mathrm{p}e = \frac{1}{4}\log P_{\mathrm{O_2}} - \mathrm{pH} + 20.775 \qquad (4\text{–}28)$$

Substituting $P_{\mathrm{O_2}} = 1$ atm gives

$$\mathrm{p}e = 20.775 - \mathrm{pH} \qquad (4\text{–}29)$$

and substituting $P_{\mathrm{O_2}} = 10^{-83.1}$ atm gives

$$\mathrm{p}e = -\mathrm{pH} \qquad (4\text{–}30)$$

In p*e* units, equations 4–29 and 4–30 are analogous to equations 4–24 and 4–25, respectively.

In the previous equations we have dealt with oxygen in terms of its partial pressure in the atmosphere. At 25°C the relationship between the partial pressure of oxygen, in atm, and the oxygen dissolved in water, in mol L^{-1}, is (Stumm and Morgan, 1996)

$$\frac{[O_{2\,(aq)}]}{[O_{2\,(g)}]} = 10^{-2.9} \qquad (4\text{–}31)$$

Solving equation 4–31 for oxygen dissolved in water gives

$$[O_{2\,(aq)}] = [O_{2\,(g)}](10^{-2.9}) \qquad (4\text{–}32)$$

EXAMPLE 4–7 A groundwater sample, at 25°C, has Eh = 0.6 and pH = 6.0. Assuming the system is at equilibrium, calculate the amount of dissolved oxygen in the groundwater sample.

Rearrange equation 4–22 to solve for $[O_{2\,(g)}]$.

$$0.0148\ \log[O_{2\,(g)}] = \text{Eh} - 1.23 + 0.0592\ \text{pH} = 0.6 - 1.23 + (0.0592)(6)$$
$$[O_{2\,(g)}] = 10^{-18.57}\ \text{atm}$$

The amount of dissolved oxygen in the groundwater is

$$[O_{2\,(aq)}] = [O_{2\,(g)}](10^{-2.9}) = [10^{-18.57}](10^{-2.9}) = 10^{-21.47}\ \text{mol L}^{-1}$$

In ppm, the amount of dissolved oxygen is

$$\begin{aligned}(10^{-21.47}\ \text{mol L}^{-1})(32\ \text{g mol}^{-1}) &= 1.08\times10^{-20}\ \text{g L}^{-1}\\ &= 1.08\times10^{-17}\ \text{mg L}^{-1} = 1.08\times10^{-17}\ \text{ppm}\end{aligned}$$

This is an incredibly small amount of dissolved oxygen given that we have an oxidizing environment. Thus, even in oxidizing environments the amount of dissolved oxygen can be very low. To put this calculation into perspective, fish require on the order of 5 to 7 ppm dissolved oxygen, so this environment would not support fish or other higher forms of aquatic life.

Constructing Eh–pH Diagrams

This topic is covered in detail in a number of textbooks, and one of the most complete descriptions is found in the classic text by Garrels and Christ (1965). In this section we will consider two types of Eh–pH interactions—those between minerals and dissolved species, as illustrated by the Fe system, and those between dissolved species and gases, as illustrated by the nitrogen system. Further examples are found in the problem set at the end of the chapter.

The Iron Eh–pH Diagram The iron Eh–pH diagram will be constructed for surface conditions and T = 25°C. Iron can exist in the natural environment in three oxidation states, 0, +2, and +3. Native iron, Fe, has 0 valence. The two stable oxides are Fe_3O_4, in which iron has both +2 and +3 valence, and Fe_2O_3, in which iron has +3 valence. We will start by plotting the boundaries for these three solid phases on the Eh–pH diagram. Native iron is oxidized to magnetite according to the following half-reaction:

$$\mathrm{Fe_3O_4 + 8e^- \rightarrow 3Fe}$$

A total of 8 electrons are released because in the magnetite molecule two of the Fe atoms are in the +3 valence state and one is in the +2 valence state. In order to balance the number of oxygens on the left-hand side of the equation, we add 4 water molecules to the right-hand side, which results in $8H^+$ on the left-hand side of the equation.

$$\mathrm{Fe_3O_4 + 8e^- + 8H^+} \;\square\; \mathrm{3Fe + 4H_2O}$$

Relative to the hydrogen electrode, we can write the following Nernst equation. In this, and all subsequent calculations, we will use the hydrogen electrode as the reference electrode. This will not be explicitly stated.

$$\mathrm{Eh} = E^\circ + \frac{0.0592}{8}\log\left(\frac{[\mathrm{Fe_3O_4}][\mathrm{H^+}]^8}{[\mathrm{Fe}]^3[\mathrm{H_2O}]^4}\right) \qquad (4\text{–}33)$$

The activities of the solid phases and water are unity, assuming that the water is nearly pure. We will make this assumption in subsequent calculations, and the Nernst equations will include only species that have an activity other than unity.

$$\mathrm{Eh} = E^\circ + \frac{0.0592}{8}\log[\mathrm{H^+}]^8 \qquad (4\text{–}34)$$

For this reaction, $\Delta G_\mathrm{R}^0 = 64.2\ \mathrm{kJ\ mol^{-1}}$ and $E°$ = −0.083 V. Substituting into equation 4–34 and converting $[H^+]$ to pH gives

$$\mathrm{Eh} = -0.083 - 0.0592\ \mathrm{pH} \qquad (4\text{–}35)$$

The half-reaction for the oxidation of Fe_3O_4 to Fe_2O_3 is

$$\mathrm{3Fe_2O_3 + 2e^- \rightarrow 2\ Fe_3O_4}$$

Only 2 electrons are released in this reaction because in the Fe_3O_4 molecule two of the Fe atoms already have a +3 valence. Adding water to balance the number of oxygens gives

$$3Fe_2O_3 + 2e^- + 2H^+ \rightleftharpoons 2Fe_3O_4 + H_2O$$

For this reaction, $\Delta G_R^0 = -34.2\ \text{kJ mol}^{-1}$ and $E°$ = 0.18 V. The Nernst equation is

$$\text{Eh} = E^\circ + \frac{0.0592}{2}\log[\text{H}^+]^2 = 0.18 - 0.0592\ \text{pH} \qquad (4–36)$$

Equations 4–35 and 4–36 are plotted in Figure 4–3. Note that the boundary between metallic iron and magnetite falls outside of the stability field of water. Hence, metallic iron is not stable in the surficial environment. What this means in practice is that native iron is inherently unstable in the presence of water and readily oxidizes. You are familiar with one of these oxidation products, rust. With reference to Figure 4–2, one would expect that magnetite would be the stable form of iron oxide only in reducing environments isolated from the atmosphere.

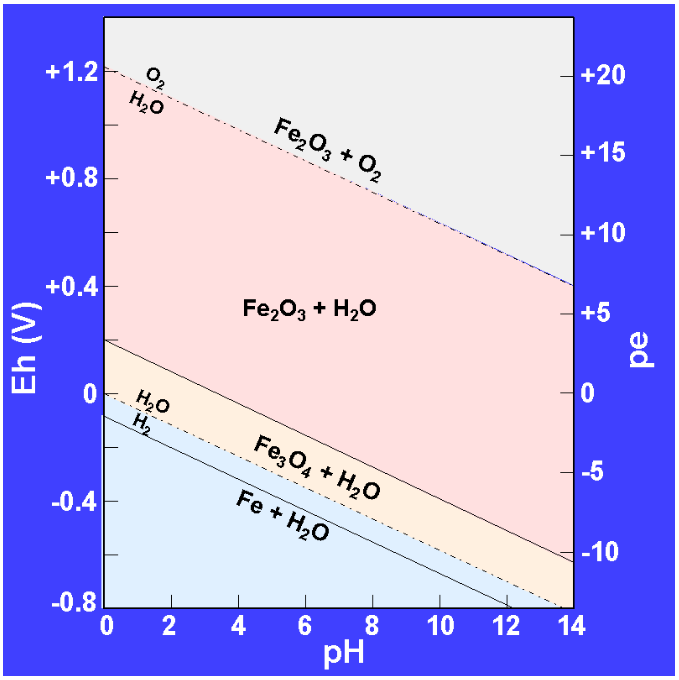


Figure 4–3 Eh–pH diagram showing the stability limits of hematite, magnetite, and metallic iron at 25°C in the presence of water.

Magnetite and hematite are slightly soluble in the surficial environment and coexist in equilibrium with Fe^{2+} and Fe^{3+} ions in solution. We will first consider equilibrium reactions involving magnetite, hematite, and Fe^{3+}. For hematite, we can write

$$\mathrm{Fe_2O_3 + 6H^+ \rightleftharpoons 2Fe^{3+} + 3H_2O}$$

Note that in hematite, iron has a +3 valence. There is no change in valence in going from hematite to Fe^{3+} and this reaction is only pH dependent; i.e., it is not an oxidation-reduction reaction. This often comes as a surprise to students because we are plotting Eh–pH diagrams and the presumption is made that both variables must be involved in all calculations. Later we will write a reaction that is dependent only on Eh; i.e., pH is not a variable. We can write the reaction in terms of an equilibrium constant:

$$K_{\mathrm{eq}} = \frac{[\mathrm{Fe^{3+}}]^2}{[\mathrm{H^+}]^6} \tag{4–37}$$

For this reaction, $\Delta G^0_{\mathrm{R}} = 22.2\ \mathrm{kJ\ mol^{-1}}$ and $K = 10^{-3.89}$. Writing equation 4–37 in logarithmic form, we get

$$2\ \log[\mathrm{Fe^{3+}}] - 6\ \log[\mathrm{H^+}] = -3.89 \tag{4–38}$$

or

$$\log[\mathrm{Fe^{3+}}] + 3\ \mathrm{pH} = -1.95 \tag{4–39}$$

Note that the boundary between hematite and Fe^{3+} is fixed either by the concentration of Fe^{3+} ions in solution or the pH. This boundary has been plotted in Figure 4–4 for various values of $[Fe^{3+}]$. For magnetite, the reaction is

$$\mathrm{3Fe^{3+} + 4H_2O + e^- \rightleftharpoons Fe_3O_4 + 8H^+}$$

$$\Delta G^0_{\mathrm{R}} = -50.4\ \mathrm{kJ\ mol^{-1}}\ \text{ and } E° = 0.52\ \mathrm{V}.$$

The Nernst equation for this reaction is

$$\mathrm{Eh} = 0.52 + \frac{0.0592}{1}\log\left(\frac{[\mathrm{Fe^{3+}}]^3}{[\mathrm{H^+}]^8}\right) = 0.52 + 0.177\ \log[\mathrm{Fe^{3+}}] + 0.473\ \mathrm{pH} \tag{4–40}$$

This boundary is also plotted in Figure 4–4 for various values of $[Fe^{3+}]$.

The boundaries we have drawn in Figure 4–4 are actually activity contour lines. Each represents a particular activity of Fe^{3+} in solution coexisting with either hematite or magnetite.

Note that only under very acidic conditions is a significant amount of Fe^{3+} found in solution and that the equilibrium concentration of Fe^{3+} in solution increases with decreasing pH (increased acidity). Under any Eh–pH conditions there will be some Fe^{3+} in a solution coexisting with hematite or magnetite, but at other than very low pH the Fe^{3+} in solution will be infinitesimal. For any Eh–pH calculation that involves the activity of ions other than H^+, an activity value must be selected in order to draw the Eh–pH boundary.

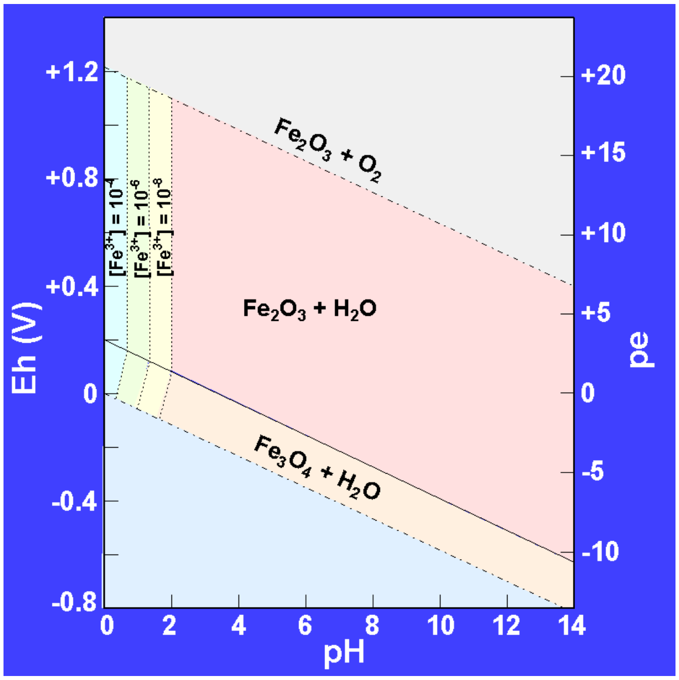


Figure 4–4 Eh–pH diagram showing the variation in $[Fe^{3+}]$, in mol L^{-1}, for a solution coexisting with hematite or magnetite. Only at very low pH values does Fe^{3+} have a significant activity.

We now repeat the preceding calculations, but in this case for Fe^{2+} in equilibrium with hematite or magnetite. For hematite, we can write the following reaction:

$$\mathrm{Fe_2O_3} + 2\mathrm{e^-} \rightleftharpoons 2\mathrm{Fe^{2+}}$$

Adding appropriate amounts of H_2O and H^+ gives

$$\mathrm{Fe_2O_3} + 6\mathrm{H^+} - 2\mathrm{e^-} \rightleftharpoons 2\mathrm{Fe^{2+}} + 3\mathrm{H_2O}$$

For this reaction, $\Delta G_R^0 = -126.4\ \mathrm{kJ\ mol^{-1}}$ and $E° = 0.66$ V. The resulting Nernst equation is

$$\mathrm{Eh} = 0.66 + \frac{0.0592}{2}\log\left(\frac{[\mathrm{H}^+]^6}{[\mathrm{Fe}^{2+}]^2}\right) = 0.66 - 0.177\ \mathrm{pH} - 0.0592\ \log[\mathrm{Fe}^{2+}] \tag{4–41}$$

Similarly for magnetite,

$$\mathrm{Fe_3O_4} + 8\mathrm{H}^+ + 2\mathrm{e}^- \rightleftharpoons 3\mathrm{Fe}^{2+} + 4\mathrm{H_2O}$$

For this reaction, $\Delta G_\mathrm{R}^0 = -172.5\ \mathrm{kJ\ mol^{-1}}$ and $E° = 0.89$ V. The Nernst equation is

$$\mathrm{Eh} = 0.89 + \frac{0.0592}{2}\ \log\left(\frac{[\mathrm{H}^+]^8}{[\mathrm{Fe}^{2+}]^3}\right) = 0.89 - 0.237\ \mathrm{pH} - 0.0888\ \log[\mathrm{Fe}^{2+}] \tag{4–42}$$

As was the case for [Fe^{3+}], in Figure 4–5 the Eh–pH boundaries for these equilibria are plotted using [Fe^{2+}] = 10^{-4}, 10^{-6}, and 10^{-8} mol L^{-1}.

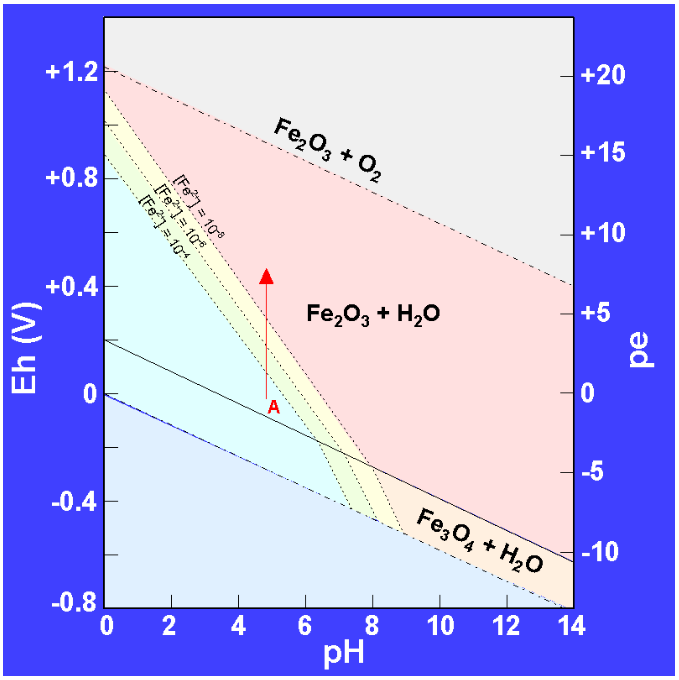


Figure 4–5 Eh–pH diagram showing the variation in [Fe^{2+}], in mol L^{-1}, for a solution coexisting with hematite or magnetite. The arrow indicates increasing oxidation. See text for discussion.

In both Figure 4–4 and Figure 4–5 we have in essence drawn contour lines showing the activity of Fe^{3+} and Fe^{2+} for solutions in equilibrium with hematite or magnetite. Note that these are for solutions in equilibrium with the solid phases. For example, within the field of hematite as shown in Figure 4–3, hematite is always present. Consider Figure 4–5. To the left of the activity contour labeled $[Fe^{2+}] = 10^{-8}$, Fe^{2+} is present in solution and has an activity of greater than 10^{-8} mol L^{-1}. These solutions are in equilibrium with either hematite or magnetite.

What would happen to the activity of Fe^{2+} if the oxidation-reduction potential of an environment was changed? Referring to Figure 4–5, let us suppose that local groundwater had the Eh and pH indicated by point A and was in equilibrium with hematite. For this sample, $[Fe^{2+}] = 10^{-2}$ mol L^{-1}. The groundwater is pumped to the surface and exposed to atmospheric oxygen. The Eh of the sample would change in the direction shown by the arrow. Note that the activity of Fe^{2+} decreases in this direction and the solution would be supersaturated in Fe^{2+} with respect to hematite. Thus, ignoring kinetic factors, we would expect that Fe would precipitate as hematite. Note that this is an oxidation-reduction reaction, because the valence of Fe must change from +2 to +3.

We can now combine Figures 4–3, 4–4, and 4–5 into a single diagram, referred to as a *composite diagram* (Figure 4–6). With reference to Figures 4–4 and 4–5, you will note that in the upper left-hand corner of the diagram, $[Fe^{3+}] > [Fe^{2+}]$. Thus, there is a field in which Fe^{3+} is the dominant iron cation. The boundary for this field is represented by the reaction

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$$

For this reaction, $\Delta G_R^0 = -74.3 \text{ kJ mol}^{-1}$ and $E° = 0.77$ V. The Nernst equation is

$$Eh = 0.77 + \frac{0.0592}{1}\log\left(\frac{[Fe^{3+}]}{[Fe^{2+}]}\right) \qquad (4–43)$$

When $[Fe^{3+}] = [Fe^{2+}]$, the Nernst equation reduces to

$$Eh = 0.77 \text{ V} \qquad (4–44)$$

This is only an oxidation-reduction reaction, so the boundary is independent of pH. The $[Fe^{3+}]$ field occupies a small area in the upper left corner of the water stability field (Figure 4–6). To reem-phasize an earlier point, for the Eh–pH conditions represented by the field labeled Fe^{3+}, waters that plot in this field and that are in equilibrium with hematite would contain both Fe^{2+} and Fe^{3+}, but $[Fe^{3+}] > [Fe^{2+}]$. Waters that plot in the field labeled Fe^{2+} and that are in equilibrium with either hematite or magnetite would have $[Fe^{2+}] > [Fe^{3+}]$. By convention, the diagrams are constructed with ionic activities = 10^{-6} mol L^{-1}.

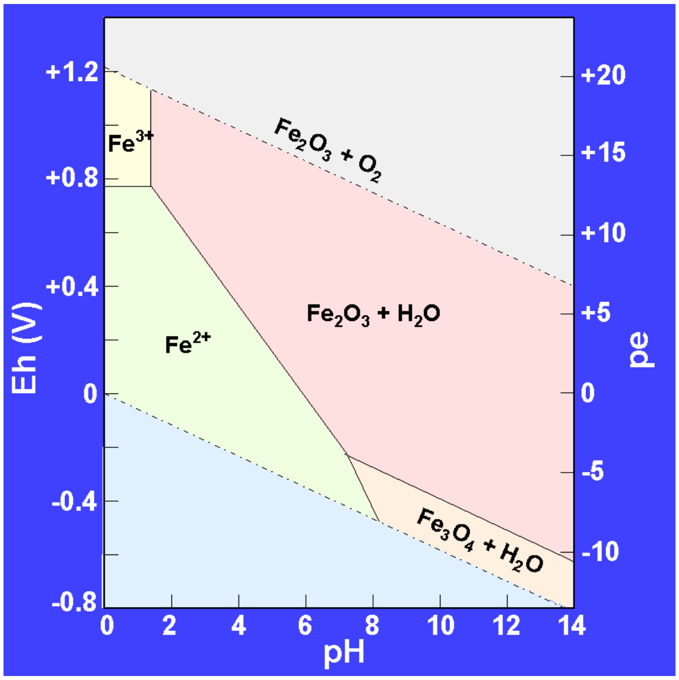


Figure 4–6 Composite diagram showing the stability fields for hematite and magnetite as a function of Eh and pH. The boundary for the ionic species is drawn with activity = 10^{-6} mol L^{-1}. In the field labeled Fe^{2+}, $[Fe^{2+}] > [Fe^{3+}]$. In the field labeled Fe^{3+}, $[Fe^{3+}] > [Fe^{2+}]$. For a system containing hematite or magnetite, the solution is in equilibrium with the solid phase.

Iron also occurs in the natural environment as the iron carbonate mineral siderite ($FeCO_3$). This introduces another complication into our analysis in that the fugacity of CO_2 gas or the activity of carbonate species must also be considered.

For a solution in equilibrium with $CO_{2\,(g)}$ and magnetite, we can write the following reaction:

$$Fe_3O_4 + 3CO_{2\,(g)} + 2H^+ + 2e^- \rightleftharpoons 3FeCO_3 + H_2O$$

For this reaction, $\Delta G^0_R = -41.4\ \text{kJ mol}^{-1}$ and $E° = 0.215$ V. The Nernst equation is

$$\text{Eh} = 0.215 + \frac{0.0592}{2}\log([H^+]^2[CO_2]^3) = 0.215 - 0.0592\ \text{pH} + 0.0888\ \log[CO_2] \qquad (4\text{–}45)$$

The partial pressure of CO_2 in the earth's atmosphere is $10^{-3.5}$ atm. Substituting this value into equation 4–45 gives

$$\text{Eh} = -0.096 - 0.0592\ \text{pH} \qquad (4\text{–}46)$$

This Eh–pH equation yields values that are slightly less than that of the water breakdown boundary. Thus, siderite is not stable at the earth's surface in water in equilibrium with atmospheric CO_2; i.e., if siderite is present, it is a metastable phase. Two points to consider are that the difference is very small and that kinetic factors always need to be taken into account. In practice, siderite is found in natural waters and thus persists despite the thermodynamic limitations. Most authors set CO_2 — 10^{-2} atm, a pressure greater than that of atmospheric CO_2, in order to plot siderite on the iron Eh–pH diagram. Using this value for CO_2, the Eh–pH equation for the siderite-magnetite boundary becomes

$$\mathrm{Eh} = 0.0374 - 0.0592\ \mathrm{pH} \qquad (4\text{–}47)$$

The dissolution of siderite to yield Fe^{2+} ions in solution can be written

$$\mathrm{FeCO_3} + 2\mathrm{H^+} \rightleftharpoons \mathrm{Fe^{2+}} + \mathrm{CO_2} + \mathrm{H_2O}$$

This is not an oxidation-reduction reaction. The equilibrium constant is written

$$K = \frac{[\mathrm{CO_2}][\mathrm{Fe^{2+}}]}{[\mathrm{H^+}]^2} \qquad (4\text{–}48)$$

For this reaction, $\Delta G^0_{\mathrm{R}} = -43.7\ \mathrm{kJ\ mol^{-1}}$, which gives $K = 10^{7.656}$. Taking the logs and substituting pH for $-\log[H^+]$ gives

$$7.656 = \log[\mathrm{CO_2}] + \log[\mathrm{Fe^{2+}}] + 2\ \mathrm{pH} \qquad (4\text{–}49)$$

Setting $[CO_2] = 10^{-2}$ atm and $[Fe^{2+}] = 10^{-6}$ mol L^{-1} gives pH = 7.83. The siderite field under these conditions is shown in Figure 4–7.

If the solution is not in equilibrium with $CO_{2\,(g)}$—i.e., it is a closed system—we must take into consideration the more complex equilibria of the carbonate system. This topic was covered in Chapter 3. In brief, we have three carbonate species, $\mathrm{H_2CO_{3\,(aq)}}$, $\mathrm{HCO_3^-}$, and $\mathrm{CO_3^{2-}}$, and the relative abundances of these species is a function of the pH. Thus, the reactions involving magnetite, hematite, and the dissolved carbonate species will be dependent upon pH. For example, at low pH the dominant species is $H_2CO_{3\,(aq)}$ and the reactions used to construct the boundaries between magnetite, hematite, and siderite would involve this particular carbonate species. This topic will not be considered further here. The interested student can find a complete discussion in

Garrels and Christ (1965) and Faure (1998).

Another important group of iron-containing minerals is the sulfides. As was the case for the iron carbonates, sulfur species such as $H_2S_{(aq)}$, HS^-, HSO_4^-, and SO_4^{2-} must be considered when writing Eh–pH equations involving iron sulfides. Under normal surface conditions, pyrite (FeS_2) is the stable iron sulfide and its stability field is controlled by the activity of the sulfur-containing species. We will not consider these calculations here. The interested student can consult Garrels and Christ (1965) or Faure (1998) for the solutions to the stability limits in the iron sulfide system. A final composite diagram for the iron system, including the minerals hematite, magnetite, siderite, and pyrite, is shown in Figure 4–8. Note that pyrite is stable over a fairly broad range of pH values at low Eh.

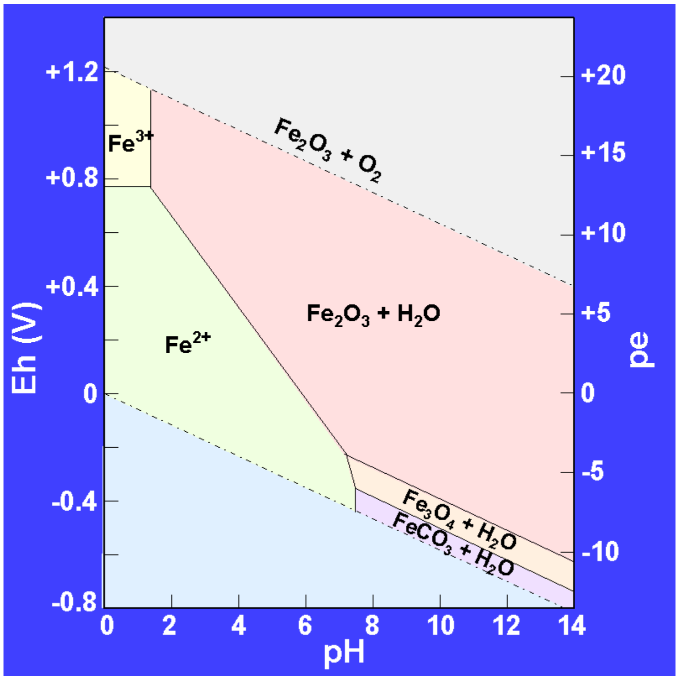


Figure 4–7 Composite Eh–pH diagram showing the stability fields of hematite, magnetite, and siderite as a function of Eh and pH. For ionic species, activity = 10^{-6} mol L^{-1}. $P_{co2} = 10^{-2}$ atm, a partial pressure greater than that of the earth's atmosphere. At $P_{CO2} = 10^{-3.5}$ atm, the actual partial pressure, siderite would plot below the stability limit of liquid H_2O.

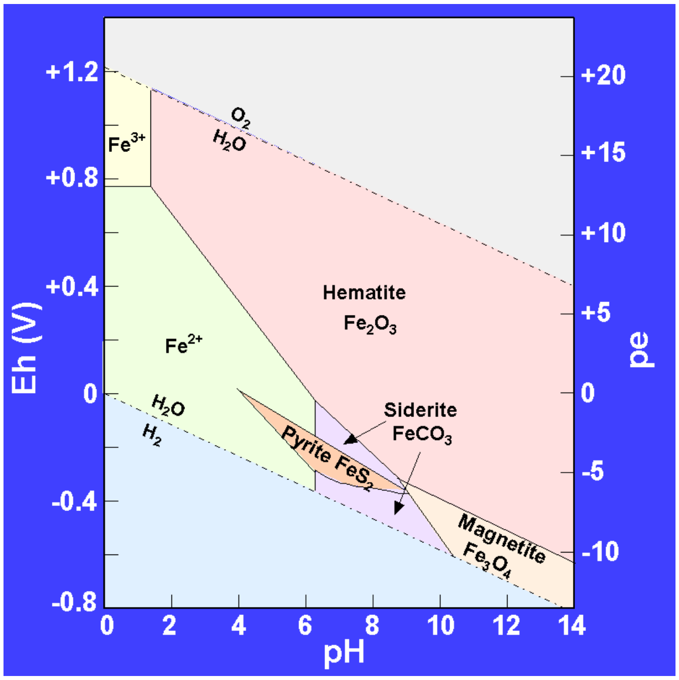


Figure 4–8 Composite Eh–pH diagram showing the stability relations for the iron oxides, carbonates, and sulfides in water at 25°C. Activity of Fe species = 10^{-6} mol L^{-1} total dissolved carbonate = 1 mol L^{-1}, and total dissolved sulfur = 10^{-6} mol L^{-1}. After Garrels and Christ (1965).

The Nitrogen Eh–pH Diagram As a second example of an Eh–pH diagram, this one containing only gases and aqueous species, we will draw the diagram for the nitrogen system under surface conditions at 25°C. The extensive use of nitrogen in fertilizers has led to an interest in the fate of nitrogen species in ground and surface waters. Nitrogen can show a variety of valences from $+5\ (NO_3^-)$ to $-3\ (NH_4^+)$. The major nitrogen species in surface and ground waters are $N_{2\,(g)}$, $NH_{3\,(g)}$, NO_2^-, NO_3^-, and NH_4^+. Because nitrogen minerals are readily soluble, they are rarely found in nature and will, therefore, not be included in our Eh–pH calculations.

Oxidation of N_2 to NO_3^- is represented by the following reaction:

$$2NO_3^- + 10e^- \rightarrow N_2$$

Balancing the equation gives

$$2NO_3^- + 12H^+ + 10e^- \square\ N_2 + 6H_2O$$

For this reaction, $\Delta G_{\mathrm{R}}^{0} = -1199.6\ \mathrm{kJ\ mol^{-1}}$ and $E°$ = 1.24 V. The Nernst equation is

$$\mathrm{Eh} = 1.24 + \frac{0.0592}{10}\log\left(\frac{[\mathrm{H}^+]^{12}[\mathrm{NO}_3^-]^2}{[\mathrm{N}_2]}\right) \tag{4–50}$$

The partial pressure of nitrogen in the earth's atmosphere is 0.77 atm, thus $[\mathrm{N_2}]$ = 0.77 atm. In the following calculations we will assume that the waters are in equilibrium with atmospheric nitrogen. Note that in many groundwaters $\mathrm{N_2}$ partial pressure is less than 0.77 atm. This will change the position, but not the slopes, of the various stability boundaries calculated here. Nitrate concentrations in groundwater are on the order of 10^{-3} mol $\mathrm{L^{-1}}$, thus $[\mathrm{NO}_3^-] = 10^{-3}\ \mathrm{mol\ L^{-1}}$. Substituting these values gives the following Eh–pH equation:

$$\mathrm{Eh} = 1.21 - 0.071\ \mathrm{pH} \tag{4–51}$$

Oxidation of NH_4^+ to $\mathrm{N_2}$ is represented by the following reaction:

$$\mathrm{N_2} + 8\mathrm{H}^+ + 6\mathrm{e}^- \rightleftharpoons 2\mathrm{NH}_4^+$$

For this reaction, $\Delta G_{\mathrm{R}}^{0} = -158.8\ \mathrm{kJ\ mol^{-1}}$ and $E°$ = 0.27 V. The resulting Nernst equation is

$$\mathrm{Eh} = 0.27 + \frac{0.0592}{6}\log\left(\frac{[\mathrm{N}_2][\mathrm{H}^+]^8}{[\mathrm{NH}_4^+]^2}\right) \tag{4–52}$$

Setting $[\mathrm{NH}_4^+] = 10^{-3}\ \mathrm{mol\ L^{-1}}$ and $\mathrm{N_2}$ = 0.77 atm gives

$$\mathrm{Eh} = 0.33 - 0.0791\ \mathrm{pH} \tag{4–53}$$

Oxidation of $\mathrm{NH_3}$ to $\mathrm{N_2}$ is represented by the following reaction:

$$\mathrm{N_2} + 6\mathrm{H}^+ + 6\mathrm{e}^- \rightleftharpoons 2\mathrm{NH}_3$$

For this reaction, $\Delta G_{\mathrm{R}}^{0} = -53.2\ \mathrm{kJ\ mol^{-1}}$ and $E°$ = 0.09 V. The resulting Nernst equation is

$$\mathrm{Eh} = 0.09 + \frac{0.0592}{6}\log\left(\frac{[\mathrm{N}_2][\mathrm{H}^+]^6}{[\mathrm{NH}_3]^2}\right) \tag{4–54}$$

Setting $[\mathrm{NH_3}] = 10^{-3}$ mol $\mathrm{L^{-1}}$ and $\mathrm{N_2}$ = 0.77 atm gives

$$\mathrm{Eh} = 0.15 - 0.0592\ \mathrm{pH} \tag{4–55}$$

Lastly, consider the relationship between NH_4^+ and NH_3. This is not an oxidation-reduction reaction because there is no change in the valence of nitrogen. The reaction can be written

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$

For this reaction, $\Delta G_R^0 = 52.8\ \text{kJ mol}^{-1}$ and $K = 10^{-9.25}$. Writing this reaction in terms of the equilibrium constant,

$$K = \frac{[NH_3][H^+]}{[NH_4^+]} = 10^{-9.25} \tag{4–56}$$

Setting $[NH_3] = [NH_4^+] = 1$ gives pH = 9.25 for the boundary between these two species when they are at equal activity.

We can now plot an Eh–pH diagram (Figure 4–9) for the nitrogen species. The relationship between N_2 and NO_3^- is given by equation 4–51, the relationship between N_2 and NH_4^+ is given by equation 4–53, and the relationship between N_2 and NH_3 is given by equation 4–55. The boundary between NH_4^+ and NH_3 is independent of Eh and is at a constant pH = 9.25 (equation 4–56). We first plot equation 4–51. We then plot equations 4–53 and 4–55. Note that the slopes of the lines calculated from the latter two equations are different. The change in slope corresponds to the change from the NH_4^+ dominant field to the NH_3-dominant field.

NO_2^- is also found in groundwater. We will now calculate the Eh–pH relationship for this species. NO_2^- is intermediate in the oxidation-reduction sequence between NO_3^- and N_2. We can write the following equation to represent the oxidation of NO_2^- to NO_3^-:

$$NO_3^- + 2H^+ + 2e^- \rightleftharpoons NO_2^- + H_2O$$

For this reaction, $\Delta G_R^0 = -160.6\ \text{kJ mol}^{-1}$ and $E° = 0.83$ V. The Nernst equation is

$$\text{Eh} = 0.83 + \frac{0.0592}{2}\log\left(\frac{[NO_3^-][H^+]^2}{[NO_2^-]}\right) \tag{4–57}$$

Setting $[NO_3^-] = 10^{-3}\ \text{mol L}^{-1}$ and solving equation 4–57 for Eh, given $[NO_3^-]/[NO_2^-]$ ratios of 1 and 10^4, gives, respectively, the following Eh–pH equations:

$$\mathrm{Eh} = 0.83 - 0.0592\ \mathrm{pH} \qquad (4\text{–}58)$$

and

$$\mathrm{Eh} = 0.95 - 0.0592\ \mathrm{pH} \qquad (4\text{–}59)$$

These two curves are plotted in Figure 4–9. The significance of these results is that the stability field for NO_2^- falls within the field of N_2 stability, a more reduced form of nitrogen. The conclusion is that NO_2^- is a metastable species. It occurs in water as a kinetic intermediary species formed during the reduction of NO_3^- to N_2.

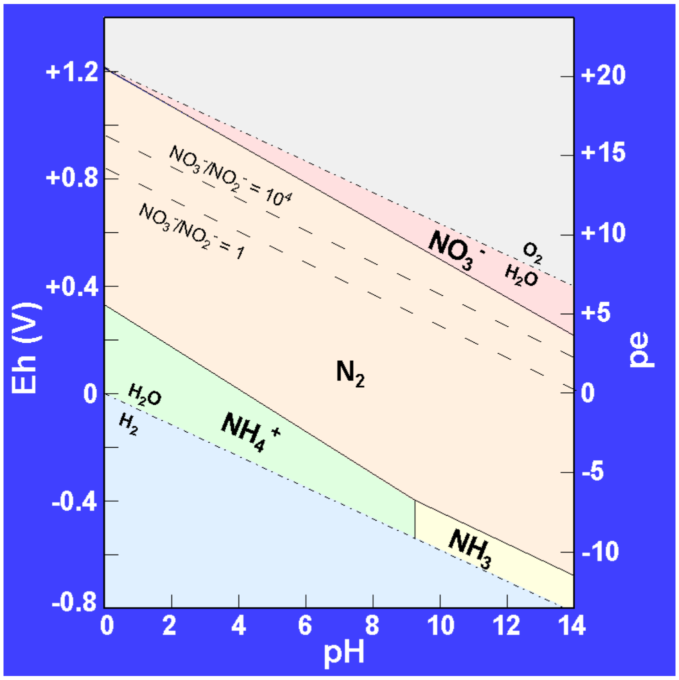


Figure 4–9 Eh–pH diagram for the nitrogen system at 25°C N_2 = 0.77 atm and activity of the dissolved species = 10^{-3} mol L^{-1}. The dashed lines indicate the boundary between NO_3^- and NO_2^- for activity ratios of 1 and 10^4. Because N_2 is a more reduced form of nitrogen, NO_2^- must exist metastably in this region. Only at very low concentrations of NO_2^- would it be the stable species relative to N_2.

To reemphasize an earlier point, consider the boundary in Figure 4–9 between N_2 and NO_3^-.

On the more oxidizing side of this boundary, NO_3^- activities are 10^{-3} mol L^{-1} or greater (as the system becomes more oxidizing). However, N_2 is also present in the system under these conditions. This boundary does not represent the disappearance of N_2, but rather the occurrence of NO_3^- with activites of 10^{-3} mol L^{-1}or greater.

Case Study 4–1 illustrates an environmental application of Eh–pH diagrams. In the case study we are concerned with acidic runoff from a coal mine and the factors that affect the concentrations of dissolved iron and manganese in the runoff.

CASE STUDY 4–1

Sources of High Dissolved Manganese Concentrations in Mildly Acidic Runoff from a Coal Mine in Eastern Tennessee

Larsen and Scarbrough (2000) investigated the sources of dissolved manganese in mildly acidic runoff from a coal mine. The mined coal is low in sulfur, and the presence of overburden with a large neutralization capacity (as a consequence of the common occurrence of siderite cement) indicated that acid mine drainage should not be a problem at this site. However, within a year of opening the mine the mildly acidic (pH = 4) mine waters contained significant quantities (up to 60 mg L^{-1}) of dissolved manganese. Because these manganese concentrations exceeded those permitted for the mine effluent, a study was undertaken to determine the source of the manganese and the steps that might be taken to reduce its concentration in the effluent.

Mineralogical and extraction studies were conducted on samples from the mine site to identify the source of the ex-tractable manganese. Two sources were identified: exchangeable manganese on clay minerals (mainly illite + muscovite and chlorite) in the shales and mudstones and manganese in siderite concretions and cement. The study suggested that the siderite was the major source of the dissolved manganese. The proposed mechanism was that sulfuric acid formed by the oxidation of pyrite in the mine spoils reacted with the siderite. The acid was neutralized by the hydrolysis of the siderite, with the concomitant release of Ca, Mg, Mn, and Fe to the solutions percolating through the mine spoils. Because these are electroactive species (refer to Example 4–5), an environmental Eh measurement should be meaningful in this case. The Eh–pH range of the spoil solution is plotted in the iron Eh–pH diagram (Figure 4–C1–1) and the manganese Eh–pH diagram (Figure 4–C1–2). Note that the spoil solution plots within the $Fe(OH)_{3\ ppt}$ field in Figure 4–C1–1, indicating that iron should be removed as an iron-hydroxide flocculate. Manganese, on the other hand, is soluble in the Eh–pH range of the spoil solution (Figure 4–C1–2) and will remain in solution.

Potential methods to control the manganese concentration in the spoil solution are (1) limiting oxidation of the pyrite in the spoils in order to minimize the acid contribution to the spoil solution, (2) keeping the siderite-rich spoils separate and up the hydraulic gradient from the pyrite-rich spoils thus limiting siderite dissolution, and (3) increasing the pH and Eh of the effluent to induce Mn-hydroxide flocculation.

Source: Larsen and Scarbrough (2000).

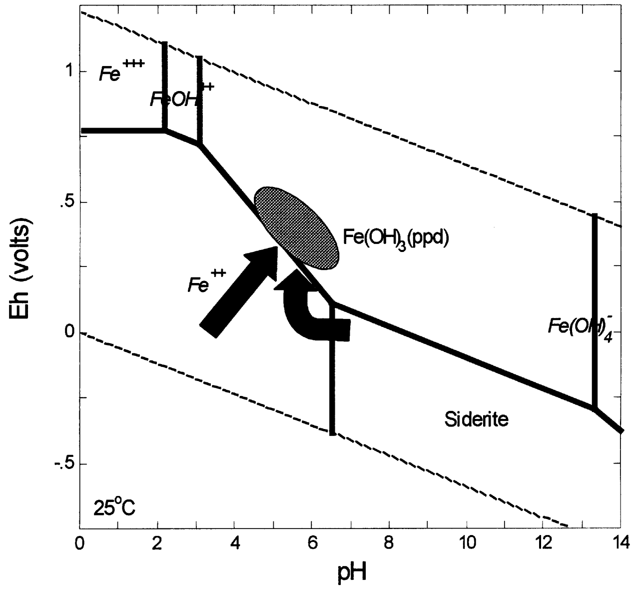


Figure 4–C1-1 Iron Eh–pH diagram at 25°C and 1.013 bars. The ellipsoidal field is the range in Eh–pH values for the spoil solution. The straight and curved arrows show hypothetical reaction paths for waters reacting with the pyritic and sideritic spoils, respectively. The spoil waters fall within the Fe-hydroxide field, and iron is apparently removed from solution as an Fe-hydroxide flocculate. Personal communication, D. Larsen, 2000.

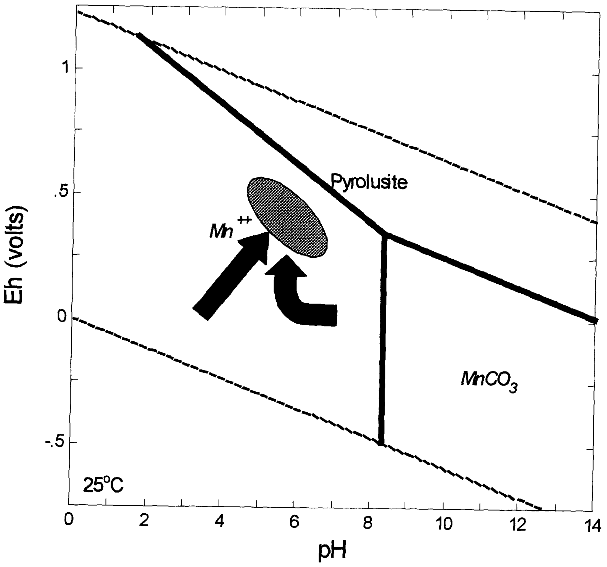


Figure 4–C1-2 Manganese Eh–pH diagram at 25°C and 1.013 bars. Field and arrows same as Figure 4–C1–1. The spoil waters fall within the Mn^{2+} field, and manganese remains in solution. If the pH and Eh were increased, the manganese would be removed from solution as a Mn-hydroxide flocculate. Personal communication, D. Larsen, 2000.

THE ROLE OF MICROORGANISMS IN OXIDATION-REDUCTION REACTIONS

So far, we have considered inorganic processes that can lead to changes in the oxidation state of various species. In the natural environment, microorganisms play an important role in facilitating a number of chemical reactions. In this section we will consider the role of microorganisms in mediating oxidation-reduction reactions. A more complete discussion of the role of microorganisms in the natural environment can be found in Ehrlich (1996) and Banfield and Nealson (1997). Consider the following reaction in which ammonium is oxidized to nitrate:

$$\mathrm{NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+}$$

For this reaction, $\Delta G_R^0 = -266.5\ \mathrm{kJ\ mol^{-1}}$. Given the large negative free energy, one would expect that this reaction would readily occur. However, an aqueous solution containing ammonium ions and exposed to the air is very stable. In contrast, this reaction proceeds at a measurable rate in natural waters that contain microorganisms. In this case, the bacteria *Nitrosomonas* sp. and *Nitrobacter* sp. use the ammonium ion as a substrate for their metabolism. In effect, the microorganisms act as a catalyst. In the natural environment many oxidation-reduction reactions are mediated by microorganisms.

It is important to understand that the microorganisms simply act as catalysts; i.e., they facilitate the transfer of electrons. The types of reactions that occur are still controlled by what is thermodynamically possible. For example, the oxidation of ammonium to nitrate can only occur in the Eh–pH range in which nitrate is the stable form of nitrogen. Hence, all the thermodynamic calculations we have done in the preceding section, and the Eh–pH diagrams constructed from these calculations, are still an accurate description of what reactions are possible under any given conditions of Eh, pH, and concentration of individual species.

Microorganisms and Energy Pathways

Microorganisms belong to one of three groups: procaryotes, eucaryotes, and viruses. Viruses are important in terms of the transmission of diseases, but they do not play a role in facilitating chemical reactions and will not be considered further. ***Procaryotes*** have a *simple cellular structure with rigid cell walls and lack a nucleus.* These are the most primitive life-forms and are believed to have been the first life-forms to arise on earth. The procaryotes include all types of bacteria. ***Archaebacteria*** (a subgroup of the procaryotes) *inhabit extreme environments, similar to those that may have existed early in earth history, and are considered to represent ancient life-forms.* The archaebacteria include ***methanogens*** *(bacteria that produce methane),* ***halophiles*** *(bacteria that exist in high-salinity environments),* ***thermophiles*** *(bacteria that exist in high-temperature environments),* and ***thermoacidophiles*** *(bacteria that exist in high-temperature and low-pH environments).* ***Eucaryotes*** have a *true nucleus and a more complex structure than procaryotes.* This more complex structure is represented by the presence of mitochondria, chloroplasts, and vacuoles and the compartmentalization of some key metabolic processes. Algae, fungi, and protozoa are members of the eucaryote group.

Microorganisms are classified in various ways depending on how they obtain their carbon and energy. ***Autotrophs*** *obtain their carbon from* CO_2, HCO_3^-, *or* CO_3^{2-} *and use external energy for the synthesis of organic compounds.* ***Photosynthesizers*** *use sunlight as the external energy source,* and ***chemo synthesizers*** *use chemical reactions involving various inorganic molecules as the external energy source.* ***Photolithotrophs*** are *photosynthetic autotrophs,* and ***chemolithotrophs*** are *chemosynthetic autotrophs.* ***Heterotrophs*** *derive their energy from the* *oxidation of organic compounds and use previously synthesized carbon as their source of carbon.* Microorganisms can be either ***aerobes,*** *microorganisms that directly use molecular oxygen as the electron acceptor for their oxidation reactions,* or ***anaerobes,*** *microorganisms that use other electron-poor species* $\left(SO_4^{2-},\ NO_3^-\right)$ *as the electron acceptor for their oxidation reactions.* ***Obligate anaerobes*** can *only function in the absence of oxygen;* ***facultative anaerobes*** can *use either oxygen or other electron acceptors for oxidation.*

Organisms themselves use catalysts, called *enzymes,* to facilitate the transfer of electrons. ***Enzymes*** are *proteins that facilitate a reaction by forming a complex with the reactants that brings the reactants into close proximity*. Enzymes are usually specific to a particular substrate. ***Oxygenases*** are *enzymes that facilitate oxidation reactions,* and ***reductases*** are *enzymes that facilitate reduction reactions.* An important characteristic of microorganisms is their ability to synthesize a new enzyme that can utilize a previously unavailable substrate. This characteristic is particularly important in microbial remediation of pollutants. The pollutant is often a new organic chemical not previously found in the environment. The synthesis of an enzyme that can utilize this new substrate is the key step in the remediation process.

Five groups of microorganisms, important in mediating oxidation-reduction reactions, are briefly described here.

Bacteria are single-celled organisms ranging in size from 0.2 to 50 μm in diameter, but commonly less than 5 μm. They are the most abundant microorganisms in water and soil. The shape of bacterial cells is usually spherical, straight-rod, or curved-rod. Because of their small size, they have a large surface-to-volume ratio and usually have a negative surface charge. Bacteria can exist in aerobic and/or anaerobic environments. Bacteria obtain their carbon either directly from carbonate species (autotrophs) or from organic compounds (heterotrophs). Most bacteria are chemoautotrophs and derive their energy from chemical oxidation reactions. Bacteria prefer neutral to slightly alkaline environments.

Actinomycetes are a class of unicelluar organisms that show similarities to both fungi and bacteria. They typically form branched filamentous colonies and are found in both aquatic and terrestrial environments. Their principle role is the degradation of existing organic compounds. Like bacteria, actinomycetes prefer alkaline environments.

Fungi are multinucleate and do not have internal cell boundaries. The living mass of a fungus is bounded externally by a rigid wall composed of cellulose or chitin. The basic structure is a tubular, often branched filament. Fungi use organic compounds as their carbon source and play a key role in the degradation of litter in the soil. Fungi prefer acidic environments.

Algae range from unicellular to complex multicellular varieties and vary in size from microscopic to large, plant-like structures. The main differences between the types of algae are biochemical: (1) types of chlorophyll and other pigments, (2) chemical composition of the cell wall, and (3) chemical nature of stored foods. Algae convert inorganic carbon into organic compounds.

Protozoa are mostly unicellular organisms with animal-like characteristics and are commonly 5–50 μm in size. They are found either in water or in thin films of water on the surface of particles and are most abundant in warm, well-oxygenated environments of intermediate pH.

Examples of Oxidation–Reduction Reactions Mediated by Microorganisms

Aerobic degradation is the decomposition of dead plant and microbial material in the presence of oxygen. The reaction can be written

$$\mathrm{CH_2O}_{\,(\mathrm{aq})} + \mathrm{O}_{2\,(\mathrm{g})} \rightarrow \mathrm{CO}_{2\,(\mathrm{g})} + \mathrm{H_2O}$$

and at 25°C, $\Delta G_{\mathrm{R}}^{0} = -501.8\ \mathrm{kJ\ mol^{-1}}$. Thermodynamically, the reaction is highly favored. However, in practice, without the presence of microorganisms this reaction occurs very slowly. Microorganisms that facilitate aerobic degradation are heterotrophic species of bacteria, fungi, protozoa, and actinomycetes. As an example, consider the secondary treatment of sewage effluent. At a sewage treatment facility you may have seen large circular or rectangular tanks filled with gravel. Following primary treatment (which removes particulate matter), sewage effluent is trickled onto this gravel bed. The community of microorganisms that exist on the gravel mediate the aerobic oxidation of the dissolved organic matter in the effluent. A problem that occasionally rises at sewage treatment facilities is the destruction of this microorganism community by harmful chemicals in the effluent. When this happens, the microbial community has to be reestablished in order for aerobic oxidation of dissolved organic matter to occur.

Anaerobic degradation occurs in an environment without measurable oxygen or nitrate and sulfate (other possible oxidizing agents). The reaction can be written

$$2CH_2O_{\,(aq)} \rightarrow CH_{4\,(g)} + CO_{2\,(g)}$$

and at 25°C, $\Delta G_R^0 = -185.7\ \text{kJ mol}^{-1}$. Thermodynamically, the reaction is not as strongly favored as aerobic oxidation, but the reaction should proceed spontaneously. Species of actinomycetes are the major anaerobes responsible for mediating this reaction. This type of biomass degradation typically occurs in swamps and other wetlands and releases methane to the atmosphere. Methane is a greenhouse gas (Chapter 8), and anaerobic degradation is one of the major sources of atmospheric methane.

Nitrification is the oxidation of ammonium ion to nitrate ion. It is a two-step process, and both steps are mediated by autotrophic bacteria.

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + H_2O + 2H^+ \quad \text{and} \quad NO_2^- + 0.5O_2 \rightarrow NO_3^-$$

The net reaction is

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$$

For the first step, $\Delta G_R^0 = -190.0\ \text{kJ mol}^{-1}$, and for the second step, $\Delta G_R^0 = -76.5\ \text{kJ mol}^{-1}$. The nitrification of ammonium ion is thermodynamically favored. However, as in the previous examples, it is the presence of microorganisms (the bacteria *Nitrosomonas* and *Nitrobacter*, respectively) that facilitates these reactions.

Denitrification is the reduction of nitrogen in nitrate to nitrogen gas, nitrous oxide, or ammonium ion. Which pathway occurs depends on the Eh and pH of the environment. In an aerobic environment, denitrification is represented by the following reaction:

$$4NO_3^- + 5CH_2O_{(aq)} + 4H^+ \rightarrow 2N_2 + 7H_2O + 5CO_2$$

For this reaction, $\Delta G_R^0 = -2548.4\ \text{kJ mol}^{-1}$, indicating that the reaction is thermodynamically strongly favored. The reaction is mediated by facultative heterotrophic bacteria, such as species of *Pseudomonas* and *Achromobacter*. When small amounts of oxygen are present, the reaction follows a different pathway, leading to the production of nitrous oxide. This reaction is written

$$2NO_3^- + 2CH_2O_{(aq)} + 2H^+ \rightarrow N_2O + 3H_2O + 2CO_2$$

For the reaction, $\Delta G_R^0 = -919.1\ \text{kJ mol}^{-1}$. From an environmental point of view, this is an interesting reaction because there has been a recent increase in the N_2O content of the atmosphere. This increase may be due, in part, to an increase in the use of fertilizers, which leads to more denitrification.

Sulfide oxidation occurs under aerobic conditions. This oxidation is usually micro-bially mediated. These sulfide oxidation reactions are important in a number of environmental settings. Consider the following reaction in which sulfide formed during the decomposition of organic matter is oxidized:

$$HS^- + 2O_2 \rightarrow SO_4^{2-} + H^+$$

For this reaction, $\Delta G_R^0 = -756.6\ \text{kJ mol}^{-1}$. The reaction is mediated by chemoautotrophic bacteria, such as *Thiobacillus thiooxidans.*

In organic-rich environments, such as mangrove swamps and other types of swamps, the large quantity of organic matter leads to a strongly reducing environment and the precipitation of metal sulfides. Soils formed under these conditions contain abundant sulfide minerals. If these soils are drained, thus exposing them to atmospheric oxygen, the sulfide minerals are oxidized, with the release of metal ions, sulfate, and hydrogen ions. The release of hydrogen ions leads to decreasing pH, i.e., acidification of the soils. Similar oxidation reactions occur when sulfide minerals in spoils, either from coal mining or the mining of sulfide ore deposits, are exposed to the atmosphere. The oxidation of FeS_2 (pyrite) can be written

$$2FeS_{2\,\text{pyrite}} + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+$$

For this reaction, $\Delta G_R^0 = -2327.8\ \text{kJ mol}^{-1}$. The Fe^{2+} is oxidized to Fe^{3+} as follows:

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$$

For this reaction, $\Delta G_R^0 = -177.4\ \text{kJ mol}^{-1}$. The reaction is biologically mediated by the acid-tolerant, iron-oxidizing bacteria *Thiobacillus ferrooxidans.* The Fe^{3+} acts as an oxidizing agent and oxidizes additional pyrite according to the reaction

$$\mathrm{FeS_{2\,pyrite}} + 14\mathrm{Fe^{3+}} + 8\mathrm{H_2O} \rightarrow 15\mathrm{Fe^{2+}} + 2\mathrm{SO_4^{2-}} + 16\mathrm{H^+}$$

For this reaction, $\Delta G_R^0 = -543.0\ \mathrm{kJ\ mol^{-1}}$. For the oxidation sequence consisting of the latter two reactions, the rate-limiting step is the oxidation of Fe^{2+} to Fe^{3+}. Because of the positive feedback loop, the oxidation of pyrite is a self-accelerating process.

Sulfate reduction occurs in organic-rich reducing environments. An example of a sulfate reduction reaction is

$$\mathrm{SO_4^{2-}} + 2\mathrm{CH_2O_{(aq)}} + \mathrm{H^+} \rightarrow \mathrm{HS^-} + 2\mathrm{CO_2} + 2\mathrm{H_2O}$$

For this reaction, $\Delta G_R^0 = -247.0\ \mathrm{kJ\ mol^{-1}}$. The reaction is mediated by sulfate-reducing bacteria, such as *Desulfovibrio desulfuricans*, an obligate anaerobe that grows at pH values greater than 5.5.

As an example of a biologically mediated oxidation-reduction reaction, Case Study 4–2 investigates the role of bacteria in the reduction of arsenate to arsenite in a hypersaline lake.

OXIDATION–REDUCTION PROCESSES IN NATURAL SYSTEMS

In the previous sections we developed the thermodynamic basis for oxidation-reduction reactions and looked at the role of microorganisms in oxidation-reduction reactions. In the natural environment the major oxidizing agent is atmospheric oxygen and the major reducing agent is organic carbon. Most carbon compounds are unstable in water; i.e., their stability field falls below the H_2O-H_2 boundary. The oxidation of organic matter first utilizes the dissolved oxygen in the system. If the amount of dissolved oxygen is limited, either because the system is isolated from the atmosphere or the rate of replenishment of dissolved oxygen is less than its rate of consumption by organic matter, the decomposition of organic matter proceeds with the reduction of $\mathrm{NO_3^-}$, $\mathrm{NO_2^-}$, and $\mathrm{SO_4^{2-}}$. A further decrease in oxidation-reduction potential can lead to the bacterial reduction of carbonate species and fermentation, resulting in the production of methane.

Table 4–3 lists reduction and oxidation reactions that may be combined to produce biologically mediated redox reactions. These reactions are combined in different ways as the overall Eh of the environment changes. The sequence of biologically mediated oxidation-reduction reactions is shown graphically in Figure 4–10. The calculations required to construct this diagram were done at pH = 7 and $\mathrm{HCO_3^-} = 1\times10^{-3}\ \mathrm{mol\ L^{-1}}$. The box in Figure 4–10 lists examples of various redox reactions that are combinations of the reduction and oxidation reactions listed in Table 4–3. With decreasing oxygen content, and a corresponding decrease in Eh, reactions will proceed in the order aerobic respiration → denitrification → nitrate reduction → fermentation → sulfate reduction → methane fermentation. If MnO_2 is present, it should be reduced to Mn^{3+} in the same Eh range as nitrate reduction, and if $FeOOH_{(s)}$ or $Fe(OH)_{3\,(s)}$ is present, it will be reduced to Fe^{2+} at Eh's similar to those for fermentation. The oxidation-reduction reaction sequence is paralleled by an ecological succession of microorganisms: aerobic heterotrophs → denitrifiers → fermentors → sulfate reducers → methane bacteria. The sequence illustrated here might occur in a lake undergoing eutrophication. As the organic content of the lake increases, and oxidizing agents are utilized in the decomposition of the organic matter, the series of reactions outlined here would occur in the deep waters of the lake. Under extreme conditions, the production of methane might be possible. Such a result might be expected when a lake evolves to a swamp or marsh.

Table 4–3 Reduction and Oxidation Reactions That May Be Combined to Produce Biologically Mediated Redox Reactions*

	Reduction		Oxidation
A	$O_{2(g)} + 4H^+ + e^- \rightarrow 2H_2O$	L	$CH_2O_{(aq)} + H_2O \rightarrow CO_{2\,(g)} + 4H^+ + 4e^-$
B	$2NO_3^- + 12H^+ + 10e^- \rightarrow N_{2\,(g)} + 6H_2O$	L-l	$HCOO^- \rightarrow CO_{2\,(g)} + H^+ + 2e^-$
C	$MnO_{2\,(s)} + HCO_3^- + 3H^+ + 2e^- \rightarrow MnCO_{3\,(s)} + 2H_2O$	L-2	$CH_2O_{(aq)} + H_2O \rightarrow HCOO^- + 3H^+ + 2e^-$
D	$NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O$	L-3	$CH_3OH_{(aq)} \rightarrow CH_2O_{(aq)} + 2H^+ + 2e^-$
E	$FeOOH_{(s)} + HCO_3^- + 2H^+ + e^- \rightarrow FeCO_{3\,(s)} + 2H_2O$	L-4	$CH_{4\,(g)} + H_2O \rightarrow CH_3OH_{(aq)} + 2H^+ + 2e^-$
F	$CH_2O_{(aq)} + 2H^+ + 2e^- \rightarrow CH_3OH_{(aq)}$	M	$HS^- + 4H_2O \rightarrow SO_4^{2-} + 9H^+ + 8e^-$
G	$SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O$	N	$FeCO_{3\,(s)} + 2H_2O \rightarrow FeOOH_{(s)} + HCO_3^- + 2H^+ + e^-$
H	$CO_{2\,(g)} + 8H^+ + 8e^- \rightarrow CH_{4\,(g)} + 2H_2O$	O	$NH_4^+ + 3H_2O \rightarrow NO_3^- + 10H^+ + 8e^-$
J	$N_{2\,(g)} + 8H^+ + 6e^- \rightarrow 2NH_4^+$	P	$MnCO_{3\,(s)} + 2H_2O \rightarrow MnO_{2\,(s)} + HCO_3^- + 3H^+ + 3e^-$

* Modified from Stumm and Morgan (1996).

CASE STUDY 4–2

Bacterial Dissimilatory Reduction of Arsenate and Sulfate in Mono Lake, California

Mono Lake, California, is an alkaline and hypersaline lake with high concentrations (~200 *μ*mol

L^{-1}) of dissolved inorganic arsenic. For Mono Lake, pH = 9.8, salinity = 75 to 90 g L^{-1} dissolved solids, and dissolved carbonates = 0.4 mol L^{-1}. Oremland et al. (2000) studied the change in speciation from As^{5+} (arsenate) to As^{3+} (arsenite) that occurred in the transition from oxic (oxygen-rich) surface waters to anoxic (oxygen-depleted) bottom waters. The distinction between arsenic species is important because arsenate is strongly adsorbed to mineral surfaces, whereas arsenite is much more mobile and toxic. Arsenic is derived from both anthropogenic sources, such as drainage from mines and mine tailings, pesticides, and biocides and from natural sources, such as hydrothermal leaching or solution of arsenic-containing minerals in rocks. Numerous studies have documented the change from arsenate to arsenic species, with depth, in stratified lakes. Two possible biochemical reduction pathways have been identified: (1) the reduction of As by a reductase present in the cytoplasm of certain bacteria that leads to the rapid expulsion of As from the cell and (2) a respiratory *(dissimilatory)* As^{5+} reductase present in certain anaerobes that enables them to conserve energy produced by the oxidation of organic substrates.

For Mono Lake the authors measured the change in a number of parameters as a function of depth (Figure 4–C2–1). The rapid decrease in oxygen between 11 and 17 m represents the transition from the oxic surface layer to the anoxic deep layer. In the surface waters, arsenic occurs as As^{5+} and sulfide and methane are absent. In the deep waters, arsenic occurs predominantly as As^{3+} and sulfide and methane are present in significant amounts. Total cell counts show a significant increase in the deep waters. Relative to shallow waters (5 m depth), deep waters (24 m depth) contained significant amounts of sulfate-respiring and arsenate-respiring bacteria (~50X increase for sulfate-respiring bacteria and ~100X increase for arsenate-respiring bacteria).

Previous studies found that the arsenic-respiring bacteria *B. selenitireducens* and *B. arsenicoselenatis* occurred in the Mono Lake sediments. The first species was used to develop a radioassay technique to measure the reduction of As^{5+} to As^{3+}. A radioassay technique was also used to measure the reduction of sulfate. In the surface waters, the rate constants for the reduction of arsenate are essentially zero, but in the deepest waters, the rate constants vary between 0.277 and 0.290 d^{-1}. Similar observations were made for the reduction of sulfate, with the surface waters having rate constants of zero and the deepest waters having rate constants that varied between 5×10^{-6} and 2×10^{-5} d^{-1}. For the 1999 measurements, the integrated reduction rates were sulfate, 12.6 mmol m^{-2} d^{-1} between 21 and 28 m depth, and arsenate, 17.3 mmol m^{-2} d^{-1} between 18 and 28 m depth.

The authors considered two reactions for the oxidation of organic carbon, one involving arsenate reduction and the other sulfate reduction. The two reactions are

$$\mathrm{CH_2O + 2H_2AsO_4^- \rightarrow HCO_3^- + 2H_2AsO_3^- + H^+}$$

and

$$\mathrm{2CH_2O + SO_4^{2-} \rightarrow 2HCO_3^- + HS^- + H^+}$$

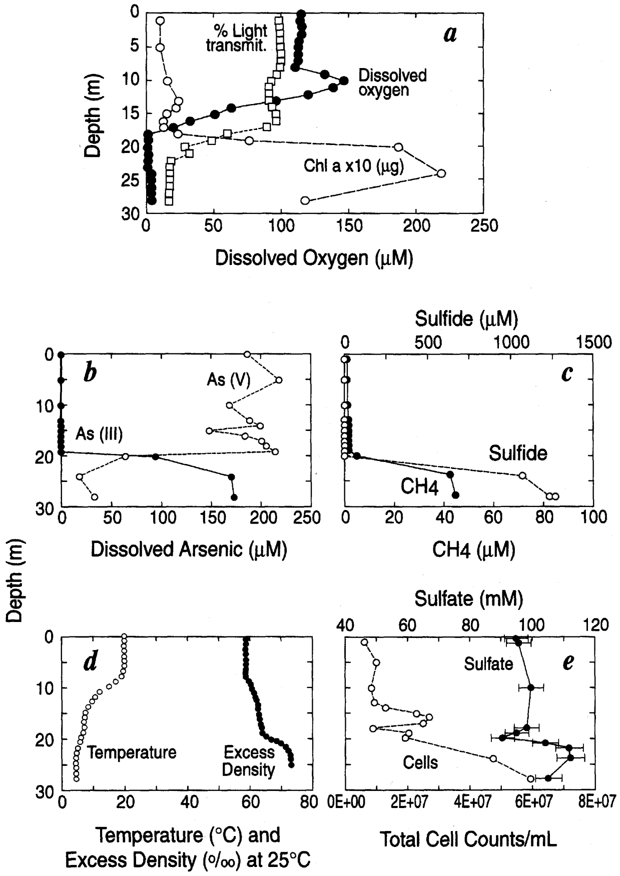


Figure 4–C2–1 Variations with depth of various physical, chemical, and biological parameters for Mono Lake in July, 1999. From Oremland et al. (2000).

Using the integrated daily reduction values for arsenate and sulfate, the authors concluded that these two processes could account for the oxidation of 32 to 55% of the organic matter produced annually by photosynthesis in the surface waters.

The authors also made the provocative suggestion that arsenate-reducing bacteria might be found on Mars. They noted that in hypersaline environments there is a high energy requirement for the maintenance of osmotic pressure. In a situation such as this, arsenate reduction would be favored over sulfate reduction. For example, consider the following reactions calculated for an ion concentration of 1 μmol L^{-1}, pH = 7, and $P_{H_2} = 10^{-6.6}$ atm:

$$SO_4^{2-} + H^+ + 4H_2 \rightarrow HS^- + 4H_2O \quad (\Delta G' = -0.42 \text{ kJ mol electrons}^{-1})$$

and

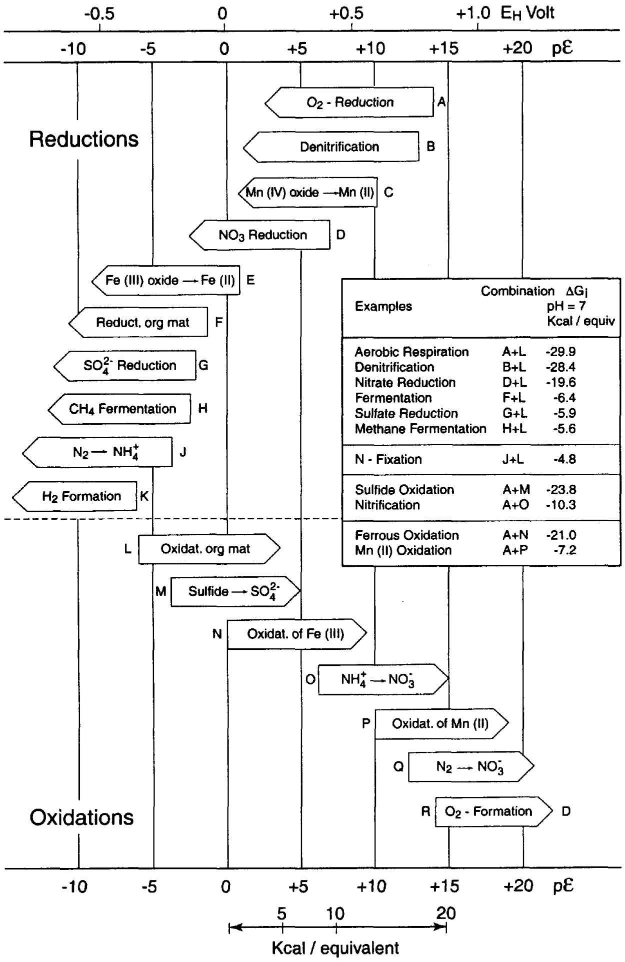
$$H_2AsO_4^- + H^+ + H_2 \rightarrow H_3AsO_3 + H_2O \quad (\Delta G' = -23.0 \text{ kJ mol electrons}^{-1})$$

The free energy for arsenate reduction is much greater than that for sulfate reduction. Hence, this reaction would be energetically favored. During the late stages of the “drying up” of Mars, hypersaline lakes would represent the last biome. Hydrothermal activity associated with Martian shield volcanoes would introduce arsenic into these lakes. If some oxygen was present, a biogeochemical cycle might develop in which the cycling of arsenic between the +3 and +5 oxidation states would provide the energy for anaerobic decomposition of organic matter.

Source: Oremland et al. (2000).

Redox Buffering

Similar to pH buffering discussed in Chapter 3 is the concept of ***redox buffering.*** When oxygen is present in water, the Eh is controlled by the oxygen-water half-reaction. During the oxidation of organic matter, as long as measurable oxygen is present, there is very little change in Eh. Recall from our earlier discussion that relatively large variations in dissolved oxygen lead to only small variations in Eh. When dissolved oxygen is no longer significant, there is a rapid drop in Eh until the sulfate and nitrate oxidation-reduction reactions become important. The sulfate and nitrate serve as electron acceptors for the oxidation of organic matter. In these reactions sulfate is reduced to HS^- and nitrate to nitrite, ammonium ion, or N_2, depending on the environmental conditions. After the sulfate and nitrate are exhausted (i.e., there are no additional oxidants), there is a further small decline in Eh until fermentation (anaerobic biodegradation) becomes important. Because of these processes, natural waters tend to fall into two main Eh ranges, referred to as high and low Eh (or p*e)* environments (Figure 4–11).



Examples	Combination	ΔG_l pH = 7 Kcal / equiv
Aerobic Respiration	A+L	-29.9
Denitrification	B+L	-28.4
Nitrate Reduction	D+L	-19.6
Fermentation	F+L	-6.4
Sulfate Reduction	G+L	-5.9
Methane Fermentation	H+L	-5.6
N - Fixation	J+L	-4.8
Sulfide Oxidation	A+M	-23.8
Nitrification	A+O	-10.3
Ferrous Oxidation	A+N	-21.0
Mn (II) Oxidation	A+P	-7.2

Figure 4–10 Sequence of microbially mediated redox processes. Letters refer to reactions in Table 4–3. From AQUATIC CHEMISTRY, 3rd Edition by W. Stumm and J. J. Morgan. Copyright © 1996. This material is used by permission of John Wiley & Sons, Inc.

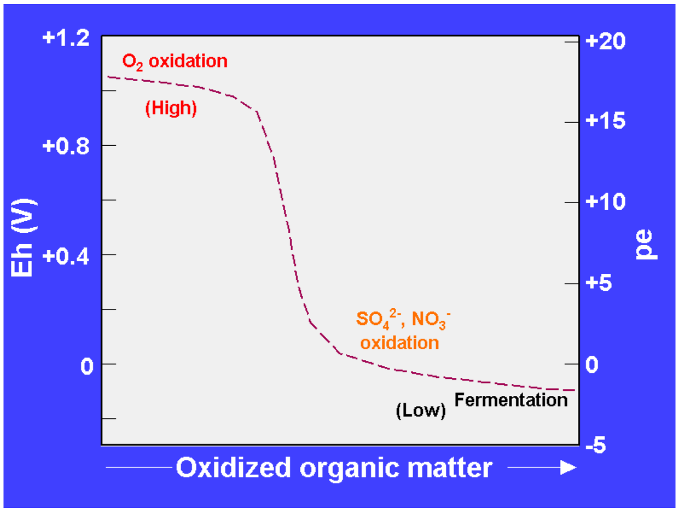


Figure 4–11 Schematic representation of redox buffering regions in acidic waters. Modified from vanLoon and Duffy (2000).

Classification of Oxidation–Reduction Environments

When the Eh concept was first introduced earlier in this chapter, the comment was made that there was often a discrepancy between the measured Eh and the observed oxidation–reduction equilibria. Because of the difficulty of measuring a thermodynamically meaningful Eh, Berner (1981b) suggested a simplified scheme. The initial distinction is between environments that contain *significant dissolved oxygen* (***oxic***) and those that have *no significant dissolved oxygen* (***anoxic***)**.** Subsequent modification led to the recognition of a third environment, ***suboxic,*** which *contains some dissolved oxygen.* The anoxic environment is subdivided into two environments, one that *contains significant dissolved sulfide* (***sulfidic***) and the other with *minimal dissolved sulfide* (***nonsulfidic***). The nonsulfidic environment is subdivided on the basis of whether or not sulfate reduction and methane production can occur. These different oxidation-reduction environments and their characteristics are summarized in Table 4–4. Also included in the table are phases that characterize each of these environments.

Table 4–4 Oxidation-Reduction Classification of Natural Environments*

Environment	Dissolved gases (10^{-6} mol L^{-1})	Characteristic phases
Oxic	$O_2 > 30$	Hematite, goethite, ferrihydrite, MnO_2-type phases, no organic matter
Suboxic	$O_2 < 30$ and ≥ 1	Hematite, goethite, ferrihydrite, MnO_2-type phases, minor organic matter
Anoxic	$O_2 < 1$	
Sulfidic	$H_sS \geq 1$	Pyrite, marcasite, rhodocrosite, organic matter
Nonsulfidic	$H_2S < 1$	
Postoxic		Low-temperature Fe^{2+} and Fe^{3+} silicates, siderite, vivianite, rhodocrosite, no sulfide minerals, minor organic matter
Methanic		Siderite, vivanite, rhodocrosite, earlier formed sulfide minerals, organic matter

*After Berner (1981b) and Anderson et al. (1994) as modified by Langmuir (1997).

Oxidative and Reductive Capacity

Oxidative and reductive capacity was defined by Scott and Morgan (1990). It is essentially a measure of the net oxidation or reduction potential of an environment. The mathematical expression is

$$\mathrm{OXC} = \Sigma\, n_i[\mathrm{Ox}]_i - \Sigma\, n_i[\mathrm{Red}]_i = -\mathrm{RDC} \tag{4–60}$$

where OXC is the oxidative capacity, RDC is the reductive capacity, $[\mathrm{Ox}]_i$ and $[\mathrm{Red}]_i$ are the molar concentrations of the oxidants and reductants, respectively, including both dissolved and solid species, and $\Sigma\, n_i$ is the number of electrons transferred in the oxidation-reduction reactions. Given these units, capacity is expressed in moles of electrons per liter; i.e., capacity is a measure of the excess or deficiency of electrons in the environment.

EXAMPLE 4–8 A groundwater sample is collected from an aquifer overlain by cultivated fields.

For this sample $[O_{2\,(aq)}] = 2 \times 10^{-4}$ mol L^{-1}, $[NO_3^-] = 1 \times 10^{-3}$ mol L^{-1} colloidal $Fe(OH)_{3\,(s)} = 1 \times 10^{-4}$ mol L^{-1}, and dissolved organic carbon (DOC) as $CH_2O = 1 \times 10^{-3}$ mol L^{-1}. We did not consider the iron hydroxides when we constructed the iron Eh–pH diagram, but they are common in natural systems as metastable phases intermediate to the iron oxides.

We can write four possible reactions that control the concentrations of these species:

$$
\begin{aligned}
&4H^+ + O_{2\,(g)} + 4e^- \rightleftharpoons 2H_2O \\
&NO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}N_2 + 3H_2O \\
&Fe(OH)_3 + 3H^+ + e^- \rightleftharpoons Fe^{2+} + 3H_2O \\
&HCO_3^- + 5H^+ + 4e^- \rightleftharpoons CH_2O\ (\text{organic matter}) + 2H_2O
\end{aligned}
$$

Substituting into the OXC equation (4–60) gives

$$
\begin{aligned}
\text{OXC} &= (n_i)[O_{2\,(aq)}] + (n_i)[NO_3^-] + (n_i)[Fe(OH)_3] - (n_i)[CH_2O] \\
&= (4)(2 \times 10^{-4}) + (5)(1 \times 10^{-3}) + (1)(1 \times 10^{-4}) - (4)(1 \times 10^{-3}) \\
&= 1.9 \times 10^{-3}\ \text{mol electrons L}^{-1}
\end{aligned}
$$

The environment has excess oxidizing capacity; i.e., all the dissolved organic matter will be oxidized and there will still be some oxidative capacity left in the groundwater system.

Oxidation-Reduction Ladders

An ***oxidation-reduction ladder*** is *a graphical representation of oxidation-reduction reactions arranged in order of decreasing oxidation potential*; i.e., species of couples higher on the ladder can oxidize species of couples lower on the ladder. Eh depends on both pH and concentrations of individual species, so this information must be specified when constructing an Eh ladder. Figure 4–12 is an example of an Eh ladder on which has been plotted the Eh for the various reactions described in the section on the construction of Eh–pH diagrams. These calculations are done at pH = 5.7 (the pH of surface waters in equilibrium with atmospheric CO_2) and activity of ionic species = 1×10^{-3} mol L^{-1}. Plotted on this ladder are two reactions that were not previously described, i.e., the oxidation reaction between dissolved methane and bicarbonate ion and the oxidation reaction between dissolved CH_2O (a proxy for dissolved organic carbon, DOC) and bicarbonate ion. For dissolved methane the reaction is

$$HCO_3^- + 9H^+ + 8e^- \rightleftharpoons CH_{4\,(aq)} + 3H_2O$$

For this reaction, $\Delta G_R^0 = -158.8 \text{ kJ mol}^{-1}$ and $E°$ = 0.206 V. The Nernst equation is

$$E = 0.206 + \frac{0.0592}{8}\log\left(\frac{[HCO_3^-][H^+]^9}{[CH_{4\,(aq)}]}\right) \tag{4–61}$$

If we set $[HCO_3^-] = [CH_{4\,(aq)}]$, the Eh–pH equation becomes

$$\text{Eh} = 0.206 - 0.0666 \text{ pH} \tag{4–62}$$

The reaction between $CH_2O_{(aq)}$ and bicarbonate ion is

$$HCO_3^- + 5H^+ + 4e^- \rightleftharpoons CH_2O_{(aq)} + 2H_2O$$

For this reaction, $\Delta G_R^0 = -17.1 \text{ kJ mol}^{-1}$ and $E°$ = 0.044 V. The Nernst equation is

$$E = 0.044 + \frac{0.0592}{4}\log\left(\frac{[HCO_3^-][H^+]^5}{[CH_2O_{(aq)}]}\right) \tag{4–63}$$

If we set $[HCO_3^-] = [CH_2O_{(aq)}]$, the Eh–pH equation becomes

$$\text{Eh} = 0.044 - 0.0740 \text{ pH} \tag{4–64}$$

At pH = 5.7, Eh = −378 mV for reaction 4–61. At this pH, the Eh for the breakdown of water to H_2 gas is −337 mV. Thus, $CH_2O_{(aq)}$ is only stable under conditions more reducing than those that lead to the breakdown of water. What this means is that $CH_2O_{(aq)}$ exists metastably in water and should readily oxidize. Whether or not complete oxidation of DOC will take place depends on the total oxidizing capacity of the environment.

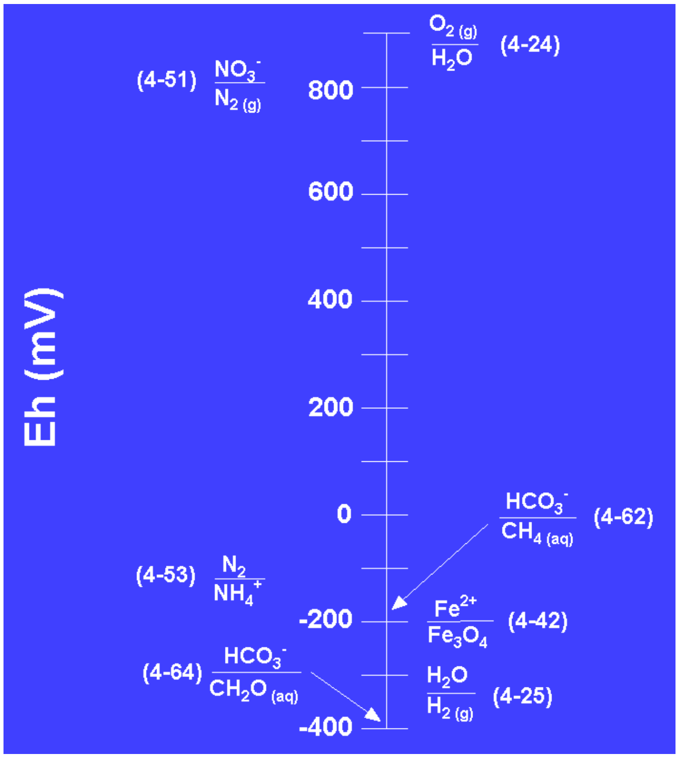


Figure 4–12 Eh ladder plot at pH = 5.7 for some of the reactions previously described in the chapter. $O_{2\ (g)}$ = 0.21 atm, $N_{2\ (g)}$ = 0.77 atm, activities of aqueous species = 1×10^{-3} mol L^{-1}. Numbers in parentheses refer to equations in the text.

We can use the Eh ladder to predict what would happen during changes in the natural system. For example, if oxygen was added to the system, the first reaction to occur would be the oxidation of $CH_2O_{\ (aq)}$ to HCO_3^- because the greatest difference in oxidation-reduction potential exists between these two couples. If dissolved oxygen was still present after the completion of this reaction, the next step would be the oxidation of Fe^{2+}, resulting in the precipitation of Fe_3O_4 (magnetite). If the dissolved oxygen was exhausted during this process, the next step would be the reduction of NO_3^- to N_2. Thus, reactions would proceed in a stepwise fashion, moving down the ladder as each oxidant was exhausted and moving up the ladder as each reductant was exhausted. The oxidation-reduction processes would be completed when the only remaining couples had the same Eh. If DOC was added to the system, the first step would be the removal of dissolved O_2, then reduction of N_2, and so on. Thus, additions of oxygen (or other oxidants) to the system or the addition of organic matter (or other reductants) leads to changes in the species present in a system.

Because there is also a kinetic factor—i.e., reactions don't occur instantaneously— one can envision that the Eh of a system can change with time. For example, groundwater entering an aquifer will initially be in equilibrium with atmospheric oxygen. Once the groundwater is isolated from the atmosphere (we will assume a closed system), various oxidation reactions will begin to utilize dissolved oxygen. As these reactions proceed, moving down the Eh ladder, the Eh of the system will change toward some final equilibrium value. Thus, with distance from the recharge area, which is proportional to the time since the water was in equilibrium with the atmosphere, the Eh of the groundwater will change.

The changes in Eh-sensitive species in a system can be used to determine the impact of an anthropogenic input. For example, let us suppose that landfill leachate is entering a stream. This organic-rich leachate will cause a series of reduction reactions to occur in the stream. In the immediate vicinity of the landfill, there will be significant reduction and $CH_{4\ (aq)}$ and NH_4^+ may occur in the stream given sufficient organic input. In the downstream direction, the addition of atmospheric oxygen will lead to a series of oxidation reactions that will, at some distance, return the stream to its more or less natural conditions. Monitoring the Eh-sensitive species would allow us to construct a model of this stream rejuvenation process. Similarly, Case Study 4–3 describes the reactions that took place when septic system effluent was discharged into a groundwater system.

CASE STUDY 4–3

Effect of Septic System Effluent on Groundwater

Robertson and Blowes (1995) investigated the impact of septic system effluent discharged to a silt-fine-sand aquifer. Given the nature of the aquifer material, there was not a great deal of buffering capacity. Hence, it was possible to achieve acidic conditions in the effluent plume. Partial oxidation of sulfide minerals in the aquifer sediments and the oxidation of DOC and NH_4^+ released H^+ ions to solution. The oxidation of organic carbon can be represented by the following equation:

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^-$$

and the oxidation of NH_4^+ by

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$$

The effluent had pH = 6.4, and pH values in the effluent plume ranged down to pH = 4.4. The latter value can be compared with the natural groundwater pH of 5.6 to 5.9. NH_4^+ and NO_3^- occurred in approximately equal amounts in the effluent plume. The persistence of NH_4^+, relatively high DOC levels compared to aerobic septic system plumes, and high Fe concentrations, presumably as the more soluble Fe^{2+} species, led the authors to conclude that the plume must be anaerobic.

Assuming that Cl^- is a conservative species, i.e., a species whose concentration is not changed by processes occurring in the system, the authors found that there was a significant decrease with time (distance) in the total nitrogen content of the effluent plume; i.e., the N/Cl ratio decreased. This decrease could be due to reduction reactions involving either dissolved organic carbon and/or sulfide minerals present in the aquifer.

For DOC,

$$5CH_2O + 2NO_3^- \rightarrow 5CO_2 + 2N_2 + 3H_2O + 4OH^-$$

Note that this reaction would tend to raise the pH. For sulfide minerals,

$$FeS_2 + 2NO_3^- + 2H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + N_2 + 4H^+$$

Sulfate concentrations were elevated in the NO_3^--depleted zone and also increased along the flow path, suggesting that the latter reaction might be important in the reduction of nitrate.

Fe, Mn, Ni, Cr, Zn, and Co concentrations were found to be greater in the effluent plume than in the noncontaminated groundwater. The authors suggested that these metals were added to the system either during oxidation of sulfide minerals (previous equation) or during reduction reactions, as illustrated by the following equations:

$$MnO_{2\,\text{birnesite}} + CH_2O \rightarrow Mn^{2+} + CO_2 + H_2O$$

and

$$Fe(OH)_3 + CH_2O \rightarrow Fe^{2+} + CO_2 + 2H_2O + H^+$$

The introduction of DOC and dissolved ammonia by septic system discharge to a groundwater system resulted in a number of oxidation-reduction reactions that significantly modified groundwater chemistry. These modifications included a decrease in pH, an increase in dissolved sulfate ion, and an increase in dissolved metals. These changes were monitored by measuring variations in Eh-sensitive species.

Source: Robertson and Blowes (1995).

The Redox Interface

The ***redox interface*** or ***redox front*** is a *zone of rapidly changing Eh.* This zone may be sharp and extend over a distance of only several millimeters (see Case Study 4–4) or it may extend over a distance of many meters or tens of meters. Redox interfaces occur where environments of very different oxidation-reduction potentials come into contact. As one example, consider the interface between seawater and the seafloor. Ocean waters are generally aerobic at all depths, whereas pore waters in bottom sediments, depending on the organic carbon content of the sediments, are often suboxic to anoxic. This change can occur over a distance of several to 10 millimeters and is reflected by an increase in reduced species in the pore waters relative to the overlying seawater. As a second example, consider the discharge of organic-rich waste to the environment, as described in Case Study 4–3. In the immediate vicinity of the discharge, the high DOC produces anoxic waters. As one moves away from the discharge site, mixing with groundwater adds oxygen to the system and the waters become oxic. This transition occurs over a distance of several meters, and the transition zone is marked by several subzones of varying Eh. As a third example, consider groundwater flow through an aquifer. Where the water enters the aquifer, the aquifer is near the surface and unconfined, and the waters are well aerated and oxic. As the waters move through the aquifer, the aquifer deepens and becomes confined; i.e., impermeable layers prevent exchange of oxygen with the atmosphere, and the waters become anoxic due to O_2-consuming redox reactions. In terms of Eh-sensitive species and Eh, Figure 4–13 schematically shows the changes that might be expected in crossing a redox interface. Note the increase in Fe and Mn in solution. The lower Eh would favor Fe^{2+} and Mn^{2+}, species that are more soluble. Mn- and Fe-containing minerals in the aquifer would begin to decompose, releasing these ions to solution.

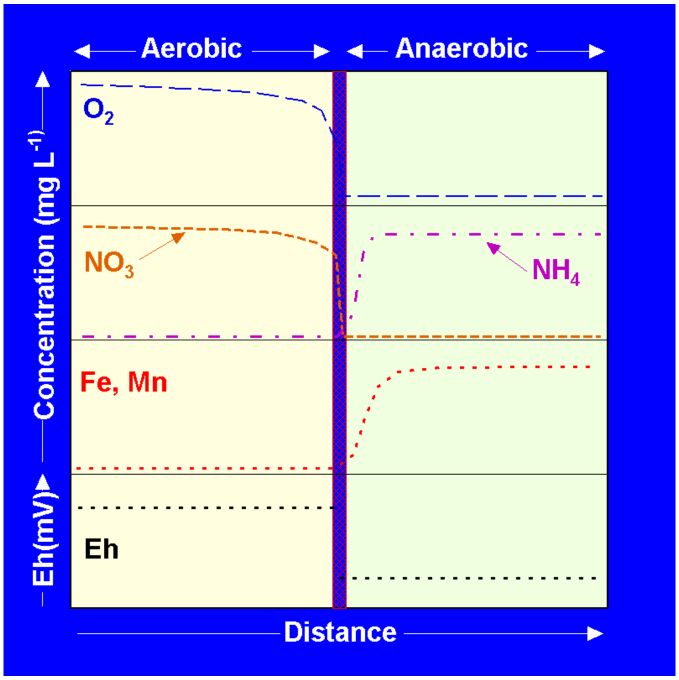


Figure 4–13 Schematic representation of changes that would occur across a redox interface between aerobic and anaerobic groundwater.

CASE STUDY 4–4

Corrosion of Brass in a Marine Environment

An interesting example of the significance of the redox front is a study on the corrosion of brass shells done by Stoffyn-Egli et al. (1998). In 1942 a British munitions ship caught fire in Halifax Harbour and was sunk by naval gunfire using sand-filled shells. A most unusual, but effective, way to put out a fire. In 1994 brass (30% Zn, 70% Cu) ammunition shells were retrieved from the seafloor around the vessel. These shells were 10 cm in diameter and 30 cm long and had a wall thickness of approximately 1 mm. The shells were partially embedded in the soft, organic-rich clayey-silts that comprise the bottom sediments of this portion of Halifax Harbour. A sharp redox front occurs between the oxygenated marine waters of Halifax Harbour and the pore waters of the anaerobic bottom sediments. The redox front extends vertically over a distance of 10 cm and the partially buried brass shells straddled the redox front. The surface of the brass shell embedded in the bottom sediments had a coating of native copper (Cu) and djurleite ($Cu_{1.96}S$). The portion of the shell protruding above the bottom had a coating of cuprite, atacamite, and a new copper sulfate mineral that appeared to have a stability field similar to that of connellite. Thus, the sequence of minerals on the surface of the shell matched the changing Eh–pH conditions of the surrounding environment (Figure 4–C4–1). The arrow in Figure 4–C4–1 indicates the changing Eh–pH conditions in going from the sediment pore waters to marine waters. A similar pattern was observed for the corrosion coating on the inside of the hollow shells: Native copper and djurlite were found immediately above the brass while the surface layers consisted of atacamite and the new copper sulfate mineral. The more oxidized coatings tended to act as a protective cover on the brass shells, and the more reduced coatings tended to peel off the brass shells, thus exposing more material to corrosion. The authors suggest that this may be an important observation because Cu-based canisters have been considered as containers for high-level nuclear wastes. The results of this study suggest that reducing, sulfur-rich waters could accelerate corrosion of these types of canisters.

Source: Stoffyn-Egli et al. (1998).

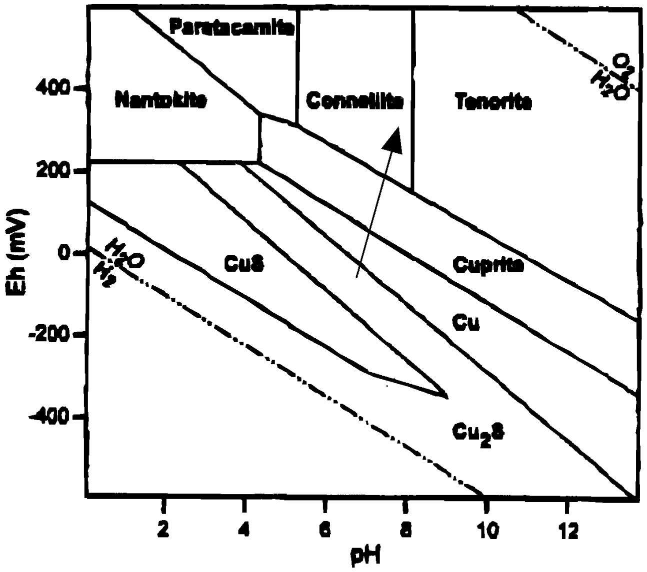


Figure 4–C4–1 Eh–pH diagram for copper. Arrow shows Eh–pH trend for redox front. From Stoffyn-Egli et al. (1998).

In this chapter the basic principles needed to understand and describe oxidation-reduction reactions have been developed. Oxidation and reduction processes play a role in a number of different environments, and further descriptions of redox processes will be found in the chapters on fresh and marine waters. This chapter concludes with case studies that illustrate the importance of redox processes in the distribution and degradation of contaminants.

Case Study 4–5 considers changes that occur across the oxic/postoxic boundary in marine sediments. The significant observation is that under certain conditions Hg can be immobilized in selenide minerals, thus inhibiting its release to the environment.

Case Study 4–6 concerns the effect of a hydrocarbon spill that entered an aquifer on the geochemistry of the aquifer sediments and the implications of the resulting changes in terms of hydrocarbon degradation and migration.

CASE STUDY 4–5

A Coupled Natural Immobilization Mechanism for Mercury and Selenium in Deep-Sea Sediments

Mercone et al. (1999) investigated the distribution of Hg and Se, among other elements, across the oxic/postoxic boundary (Berner's classification of redox environments) in marine sediments. Three different deep-sea sediment sequences (turbidite, sapropel, and glacial/interglacial transition) were investigated. Sapropels are dark, very organic-rich (>2 wt% organics) sediments. In each of these sequences the oxic/postoxic boundary has persisted in a narrow depth zone for thousands of years. Sediment samples collected across this boundary showed an enrichment in Hg, Se, Cd, V, Sb, and Tl just below (on the postoxic side) the boundary. Hg maxima were either coincident with, or very close to, the Se maxima, and in several cases a similar relationship was noted for Cd and Pt. The underlying postoxic sediments contained sulfide minerals that are absent above the redox boundary. The authors suggested that oxidation of sulfide minerals was the source of the trace metals. The sulfide released from the sulfide minerals was oxidized to sulfate, while the metals migrated downward across the redox boundary. In the reducing, sulfide-poor postoxic environment, these metals were reprecipitated as selenide minerals such as tiemannite (HgSe). These minerals will not form in the presence of sulfide, but the sulfide-deficient pore waters are a suitable environment. The minerals will persist under oxidizing conditions, thus immobilizing Hg and other associated metals. The authors suggest that this mechanism may be important during the weathering of sulfide wastes that contain significant Hg. The presence of Se in these wastes can retard the loss of Hg to the environment as long as sulfide is oxidized to sulfate.

Source: Mercone et al. (1999).

CASE STUDY 4–6

The Effect of a Hydrocarbon Spill on the Sediments of the Contaminated Aquifer

A glacial-outwash, sandy aquifer near Bemidji, Minnesota (Figure 4–C6–1) was contaminated in 1979 by a high-pressure oil pipeline burst. Oil was sprayed onto the land surface and a 1-m-thick oil slick was found floating on the water table in the vicinity of the spill. This is now a USGS Toxic Substance Hydrology study site. Previous studies have outlined the extent of the contaminant plume and its redox conditions (Figure 4–C6–1). These studies have largely focused on the groundwater chemistry. The degradation of the organic compounds largely occurs by microbial activity, during which Fe^{3+} is reduced to Fe^{2+}. This inference is supported by the observations that within the anoxic part of the plume Fe^{2+} and Mn^{2+} are abundant and the DOC is a complex mixture containing notable amounts of low-molecular-weight aliphatic and aromatic organic acids, metabolic intermediates in the degradation of hydrocarbons. The source of the Fe^{3+} is iron-containing minerals in the aquifer.

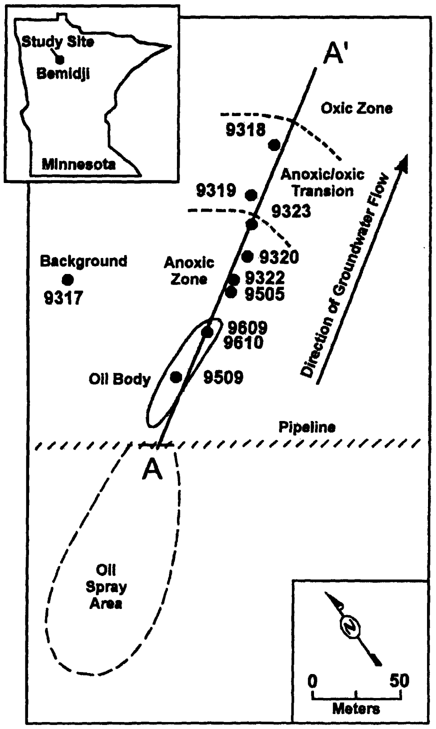


Figure 4–C6-1 Location of study site, redox zones, and locations of core samples. From Tuccillo et al. (1999).

Tuccillo et al. (1999) investigated the impact of these processes on the sediment geochemistry. A series of sediment core samples were collected along the plume axis (Figure 4–C6–2). A series of selective iron extractions were done and sediment mineralogy was determined. The purpose of the selective iron extractions was to determine the relative importance of the various Fe-containing phases that were contributing iron to the oxidation–reduction process. It was found that there was a rough inverse correlation between the Fe^{2+} concentration in the pore waters and the Fe^{3+} loss from the sediment. The samples collected closest to the oil spill had the highest Fe^{2+} in the pore waters and the greatest Fe^{3+} loss from the sediments. These data supported the microbial degradation of hydrocarbons according to reactions such as the following for the degradation of toluene:

$$C_7H_8 + 36Fe(OH)_3 + 65H^+ \rightarrow 7HCO_3^- + 36Fe^{2+} + 87H_2O$$

The continued availability of Fe^{3+} is required for this reaction. Once Fe^{3+} is exhausted, other degradation reactions become important.

The authors also noted that there was an increase in Fe^{2+} in the affected sediments relative to background values. This was ascribed to the precipitation of an iron-containing carbonate. One possible reaction is

$$0.2Ca^{2+} + 0.8Fe^{2+} + HCO_3^- \rightarrow Fe_{0.8}Ca_{0.2}CO_3 + H^+$$

There may also be some precipitation of Fe^{2+} as an iron hydroxide.

Finally, it was observed that there was a significant increase in the iron content of the sediments in the anoxic/oxic transition zone. This was believed to be due to the reoxidation (Fe^{2+} to Fe^{3+}) and precipitation of iron as Fe^{3+} oxyhydroxides. These oxyhydroxides may be efficient adsorbers of organic compounds and thus act as a barrier to the migration of the hydrocarbons.

Source: Tuccillo et al. (1999).

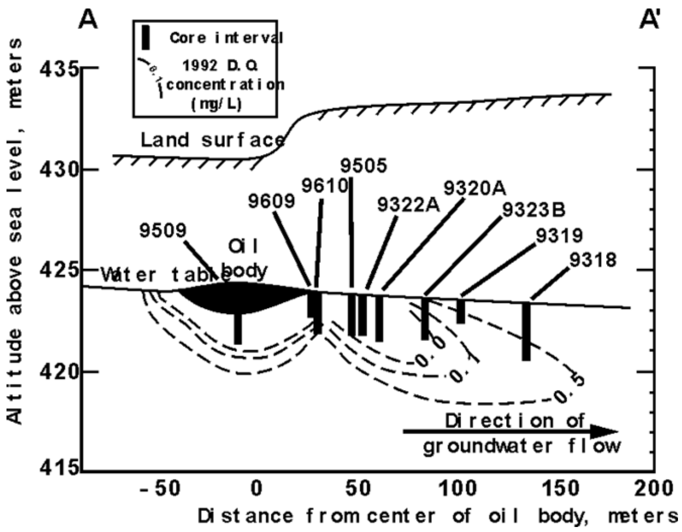


Figure 4–C6–2 Cross-section showing the extent of the anoxic plume, dissolved oxygen content, and location of the core samples. From Tuccillo et al. (1999).

QUESTIONS AND PROBLEMS

1. Define *anion* and *cation.*

2. Define *oxidation* and *reduction.*

3. Define *reducing agent* and *oxidizing agent.*

4. For the following oxidation–reduction reaction, identify the reducing agent, the oxidizing agent, the species that is oxidized, and the species that is reduced.

$$\mathrm{Ce} + \mathrm{Pu}^{3+} \rightarrow \mathrm{Ce}^{3+} + \mathrm{Pu}$$

5. What is the *electromotive series*?

6. Define *standard hydrogen electrode* and *saturated calomel electrode.* How are the two electrodes related?

7. Define *Eh*.

8. What is the relationship between Eh and p*e*?

9. Why must we select a value for the activity of ionic species when we draw Eh–pH diagrams?

10. What is an *electroactive* species?

11. Case Study 4–1 dealt with the release of Mn in a spoil solution draining a coal mine waste dump.

One suggested solution to the problem was to increase the pH so that Mn-hydroxide would precipitate from solution. With reference to this case study, explain why increasing pH would produce this result. Note that a field for Mn-hydroxide is not shown in Figure 4–C1-2. Reference to Figure 4–C1-1, and the construction of the Fe Eh–pH diagram described in the text, might give you a hint about how to answer this question.

12. Microorganisms play an important role in mediating chemical reactions. Consider the following reaction:

$$NO_3^- + H_2O + H^+ \rightarrow NH_4^+ + 2O_2$$

For this reaction, $\Delta G_R^0 = 266.5 \text{ kJ mol}^{-1}$. Will the presence of microorganisms facilitate this reaction? Explain.

13. What are the characteristics that distinguish *procaryotes* from *eucaryotes*?

14. Distinguish among *methanogens, halophiles, thermophiles,* and *thermoacidophiles.*

15. Distinguish between *autotrophs* and *heterotrophs.*

16. Distinguish between *photolithotrophs* and *chemolithotrophs.*

17. How do *obligate anaerobes* differ from *facultative anaerobes*?

18. What is the role of enzymes?

19. How does *aerobic degradation* of biomass differ from *anaerobic degradation* of biomass?

20. Soils in the Mekong delta have been continuously submerged and used for rice growing. These soils developed on pynte-rich former marine deposits. What might happen if these soils were drained so that they could be used for other types of agriculture?

21. With reference to Case Study 4–2, what is *dissimilatory reduction*?

22. What is a *radioassay*? To answer this question, you should refer to the article used for Case Study 4–2.

23. Refer to Figure 4–C2–1. From the plots of dissolved oxygen, As(III), As(V), sulfide, and methane concentrations as a function of depth, what can you conclude about the processes that determine the oxidation state of arsenic and sulfur in Mono Lake?

24. Relate the reaction order shown in Figure 4–10 to the presence of different types of microorganisms.

25. Define *Eh buffering* and give an example of an Eh buffer.

26. Describe and discuss Berner's oxidation-reduction classification of natural environments.

27. Define *oxidative capacity.* What is the significance of this concept?

28. What are *oxidation-reduction* ladders, and why are they useful when investigating oxidation-reduction reactions in natural environments?

29. What is a *redox interface,* and why is it important?

30. Describe what happens, in terms of Eh and species in solution, when an organic-rich effluent enters aerobic groundwater.

31. What might happen to a Cu-based canister used to store radioactive materials if it came in contact with reducing saline groundwater? Refer to Case Study 4–4 to answer this question.

32. With reference to Case Study 4–5, explain how the presence of Se in sulfide wastes might retard the loss of Hg to the environment.

33. With reference to Case Study 4–6, explain why the highest Fe^{2+} concentrations in the pore waters corresponded with the lowest $Fe^{3\,+}$ concentrations in the sediment.

34. Balance the following oxidation-reduction reactions:

$$\begin{gathered}
PbO_{2\,(s)} \rightarrow Pb^{2+} + O_2 \\
Fe^{2+} + MnO_{2\,(s)} \rightarrow Fe^{3+} + Mn^{2+} \\
As_2S_{3\,(s)} + NO_3^- \rightarrow HAsO_4^{2-} + S^0 + NO_2^- \\
CH_2O_{(aq)} + NO_3^- \rightarrow N_2 + HCO_3^- + CO_{2\,(g)} \\
FeS_{2\text{ pyrite}} + NO_3^- \rightarrow N_{2\,(g)} + FeOOH_{\text{goethite}} + SO_4^2 \\
C_2HCl_3 + O_2 \rightarrow CO_2 + Cl^- \\
Mn^{2+} + O_2 + Co^{2+} \rightarrow MnO_{2\,(s)} + Co_3O_{4\,(s)}
\end{gathered}$$

35. For the following reaction, at 25°C,

$$Ce_{\text{metal}} + Pu^{3+} \rightarrow Ce^{3+} + Pu_{\text{metal}}$$

calculate:

a. The standard-state free energy. Use the thermodynamic data from Appendix II, source 4 or source 5, as appropriate.

b. The standard-state electromotive force.

c. The K_{eq} value for the reaction and the $[Ce^{3+}]/[Pu^{3+}]$ ratio at equilibrium.

36. a. Calculate the standard electrode potentials, at 25°C, for each of the following half-reactions. Use the thermodynamic data from Appendix II, source 4 or source 5, as appropriate.

$$\begin{array}{ll} Np^{3+} + 3e^- \rightarrow Np & Ce^{3+} + 3e^- \rightarrow Ce \\ Pu^{3+} + 3e^- \rightarrow Pu & Th^{4+} + 4e^- \rightarrow Th \end{array}$$

b. Arrange the half-reactions in the order strongest reducing agent to weakest reducing agent.

37. Using the results from problem 36,

a. Calculate the standard electromotive force for the reaction $Pu + Np^{3+} \rightarrow Pu^{3+} + Np$.

b. Calculate K_{eq} for this reaction.

c. If $[Np^{3+}] = 10^{-6}$ mol L^{-1}, calculate the activity of Pu^{3+} at equilibrium.

38. In order for fish to survive, the dissolved oxygen content of a lake or stream must be at least 3 μg mL^{-1}. A particular lake has pH = 6.5 and T = 25°C.

a. Calculate the minimum Eh required for this lake to support a fish population.

b. There are a number of summer homes around this lake and each has its own septic system. The effluent from the septic systems drains into the lake and this supports a summer algal bloom. In early spring, the lake has an Eh = 0.90 V, but by late summer Eh = 0.4 V. What would you conclude about the health of the fish in this lake?

39. a. Derive the Eh–pH equation at standard conditions for the reaction $Co^{3+} + e^- \rightarrow Co^{2+}$. Use the thermodynamic data from Appendix II, source 4.

b. Given $[Co^{2+}] = 10^{-4}$ mol L^{-1}, calculate $[Co^{3+}]$ when Eh = 0.95.

40. Construct an Eh–pH diagram, at standard conditions, based on the progressive oxidation of Co to form oxides, starting with metallic Co. The appropriate reactions are

$CoO + 2H^+ + 2e^- \rightarrow Co + H_2O$ and $Co_3O_4 + 2H^+ + 2e^- \rightarrow 3CoO + H_2O$

For each of these reactions derive the Eh–pH equation and plot the resulting equation. Use the thermodynamic data from Appendix II, source 4.

41. Derive the Eh–pH equations, at standard conditions, for the solution of the oxide minerals of

Co to form Co^{2+}. Plot these equations on the same Eh–pH diagram you used for problem 40. Set $[Co^{2+}] = 10^{-6}$ mol L^{-1}. Use the thermodynamic data from Appendix II, source 4.

$Co^{2+} + 2e^- \rightarrow Co$

$CoO + 2H^+ \rightarrow Co^{2+} + H_2O$

$Co_3O_4 + 8H^+ 2e^- \rightarrow 3Co^{2+} + 4H_2O$

42. Calculate the Eh for acid mine drainage (pH = 4) and ocean water (pH = 8.3) in equilibrium with atmospheric oxygen $(P_{O_2} = 0.2 \text{ atm})$ at T = 25°C.

43. In Case Study 4–3, the impact of septic system effluent on groundwater was described. Assume the groundwater temperature is 25°C. Use the thermodynamic data from Appendix II, source 4.

a. Considering the portion of the plume that had pH = 4.4, calculate the Eh of the water. $[NH_4^+] = [NO_3^-]$, and the Eh–pH equation relating these two species is $NO_3^- + 8e^- + 10H^+ \rightarrow NH_4^+ + 3H_2O$.

b. At this Eh, calculate the concentration of dissolved oxygen in the water.

c. A direct measurement of the oxidation-reduction potential of the plume water, using a calomel electrode as the reference electrode, gives Eh = 974 mV. Calculate the corrected Eh value. How does this compare to the Eh determined in part (a)?

44. The iron hydroxides were ignored when we constructed the iron Eh–pH diagram. This was done because the hydroxides are metastable phases that will convert with time to hematite and magnetite. However, they can and do occur in natural systems in a metastable state. Construct an Eh–pH diagram, at standard conditions, for the Fe hydroxides, $Fe(OH)_2$ and $Fe(OH)_3$. Use the thermodynamic data from Appendix II, source 4. Set the activity of dissolved species = 10^{-6} mol L^{-1}. The aqueous species $Fe(OH)^{2+}$ can occur in this system, but for this problem ignore this species. Using the equations developed for the diagram plus the diagram itself, what will happen at constant pH = 7 if the Eh of the environment increases from 0 V to 0.6 V?

45. Construct an Eh–pH diagram, at standard conditions, for the sulfur species. The species are $S_{(s)}$, SO_4^{2-}, HSO_4^-, HS^-, and $H_2S_{(aq)}$. Set the activity of all the dissolved species = 10^{-3} mol

L^{-1}. Use the thermodynamic data from Appendix II, source 2.

46. The oxidation of pyrite can be represented by the reaction $4FeS_{2\ \text{pyrite}} + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_{3\ \text{ferrihydrite}} + 8SO_4^{2-} + 16H^+$.

a. Write the p*e* equation for this reaction at 25°C. Remember that when calculating the free energy the reaction is written so that the oxidized forms are on the left and the reduced forms are on the right. Use the thermodynamic data from Appendix II, source 4.

b. Calculate the p*e* when $\text{pH} = 4,\ SO_4^{2-} = 10^{-3}\ \text{mol L}^{-1}$, and the reaction is in equilibrium with atmospheric oxygen $(P_{O_2} = 0.2\ \text{atm})$.

47. Fredrickson et al. (2000) investigated the microorganism (*Shewanella putrefaciens*)-mediated reduction of U^{6+} to U^{4+}. U^{6+} is soluble and uranium is transported in solution in the oxidized form, whereas U^{4+} is relatively insoluble. Hence, the oxidation state of uranium is an important factor in determining the mobility of uranium in surface and ground waters. One of the investigated reactions was $0.5UO_2(CO_3)_3^{4-} + H^+ + e^- \rightarrow 0.5UO_{2\ \text{uraninite}} + 1.5HCO_3^-$.

a. Calculate *E*° for this reaction at 25°C. Use the thermodynamic data from Appendix II, source 4 or source 5, as appropriate.

b. Calculate the Eh for this reaction at $\text{pH} = 5.7,\ UO_2(CO_3)_3^{4-} = 1 \times 10^{-5}\ \text{mol L}^{-1}$, and total carbonate, $C_T = 3 \times 10^{-2}$ mol L^{-1}. You will first have to calculate the amount of C_T that exists as at the given pH.

c. Based on these calculations, comment on the solubility of uranium in acidic waters such as those found in swamps and marshes.

48. One of the microorganism-mediated reduction reactions considered in Case Study 4–2 is $CH_2O_{(aq)} + 2H_2AsO_4^- \rightarrow HCO_3^- + 2H_2AsO_3^- + H^+$.

a. Calculate *E*° for this reaction at 25°C. Use the thermodynamic data from Appendix II, source 4.

b. Write the Nernst equation for this reaction and calculate the ratio of $H_2AsO_4^-$ to $H_2AsO_3^-$ when Eh = 0.57 V and Eh = 0.28 V. In order to do this calculation, set $CH_2O = 1 \times 10^{-4}$ mol L^{-1}. Use the pH and total carbonate, C_T, given in the case study. Remember to determine the proportion of total carbonate that occurs as HCO_3^-.

c. Based on these two calculations, would you expect As^{5+} or As^{3+} to be the dominant ionic form of arsenic in a bog? Test your hypothesis by calculating the Eh when the two arsenic species are in equal abundance given pH = 4, $C_T = 1 \times 10^{-3}$ mol L^{-1}, and $CH_2O = 1 \times 10^{-2}$ mol L^{-1}.

49. Oxidation of organic matter can be represented by the reaction $CH_2O_{(aq)} + O_{2\,(g)} \rightarrow CO_{2\,(g)} + H_2O$. It was suggested earlier that as long as measurable amounts of oxygen are present in a system, the Eh will remain relatively constant during oxidation of organic matter (redox buffering). Suppose the system becomes isolated from the atmosphere and the oxygen content decreases by roughly 10 orders of magnitude. Calculate the Eh of a system when $P_{O_2} = 0.2$ atm and $P_{O_2} = 10^{-10}$ atm. Initially, $P_{CO_2} = 10^{-3.5}$ atm. At the lower partial pressure of oxygen, $P_{CO_2} = 10^{-2.5}$ atm. Set $CH_2O_{(aq)} = 1 \times 10^{-4}$ mol L^{-1}. Use the thermodynamic data from Appendix II, source 4. Based on these calculations, does the system tend to act as a buffer?

50. A lake is in equilibrium with atmospheric oxygen $(P_{O_2} = 0.2\ \text{atm})$. A chemical analysis of a water sample from the lake gives $NO_3^- = 1\times10^{-3}$ mol L^{-1}, $SO_4^{2-} = 1\times10^{-4}$ mol L^{-1}, and $CH_2O_{(aq)} = 1 \times 10^{-3.5}$ mol L^{-1}. Four possible reactions that control the concentrations of these species are

$$O_{2\,(g)} + 4H^+ + 4e^- \rightarrow 2H_2O$$
$$NO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}N_2 + 3H_2O$$
$$SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O$$
$$CO_{2\,(g)} + 4H^+ + 4e^- \rightarrow CH_2O_{(aq)} + H_2O$$

Calculate the oxidative capacity of the lake water. You will need to use Henry's law to determine the amount of dissolved O_2. Assume T = 25°C. Will all of the organic matter in the lake be oxidized? Explain.