

ENVIRONMENTAL CHEMISTRY OF SOILS

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New York Oxford
OXFORD UNIVERSITY PRESS
1994

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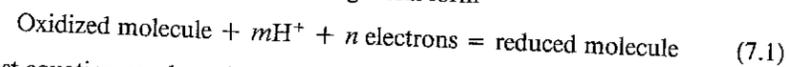
Oxidation-Reduction Reactions

The importance of pH as a "master variable" controlling chemical reactions in soils has been stressed in previous chapters. However, soils subjected to fluctuations in water content come under the influence of another master variable: the *reduction-oxidation* (or redox) *potential*. Under conditions of water saturation, the lack of molecular oxygen can result in a sequence of redox reactions that changes the soil pH. In this sense the redox state of the soil exerts control over the pH. The nature of redox reactions will be discussed in this chapter, as these reactions profoundly influence metal ion solubility and the chemical form of ions and molecules dissolved in soil solution. The reader is referred to section 1.2f in Chapter 1 for a review of the basic chemical principles necessary for the understanding of redox reactions.

7.1. REDOX POTENTIALS

7.1a. Theory

For any electron-transfer half-reaction of general form



the Nernst equation can be written:

$$E_h = E_h^0 - \frac{0.059}{n} \log \frac{(\text{reduced molecule})}{(\text{oxidized molecule})(\text{H}^+)^m} \quad (7.2)$$

where:

- E_h = potential for the half-reaction (volts, V)
- E_h^0 = standard state potential for the half-reaction (volts, V)
- n = moles of electrons involved in the reaction as written
- m = moles of protons involved in the reaction as written

and the parentheses denote chemical activities of the reduced and oxidized molecules.

Table 7.1 lists a number of half-reactions important in soils and their corresponding standard-state potentials. The more positive the E_h^0 , the stronger the tendency for

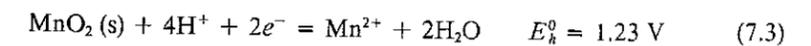
Table 7.1. Standard-State Reduction Potentials of Half-Reactions Involving Important Elements in Soils

Reaction	E_h^0 (volts) ^a
$\text{Mn}^{3+} + e^- = \text{Mn}^{2+}$	1.51
$\text{MnOOH(s)} + 3\text{H}^+ + e^- = \text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.45
$\frac{1}{2}\text{NO}_3^- + \frac{1}{2}\text{H}^+ + e^- = \frac{1}{2}\text{N}_2(\text{g}) + \frac{1}{2}\text{H}_2\text{O}$	1.245
$\frac{1}{2}\text{MnO}_2(\text{s}) + 2\text{H}^+ + e^- = \frac{1}{2}\text{Mn}^{2+} + \text{H}_2\text{O}$	1.23
$\frac{1}{2}\text{O}_2(\text{g}) + \text{H}^+ + e^- = \frac{1}{2}\text{H}_2\text{O}$	1.229
$\text{Fe(OH)}_3(\text{s}) + 3\text{H}^+ + e^- = \text{Fe}^{2+} + 3\text{H}_2\text{O}$	1.057
$\frac{1}{2}\text{NO}_3^- + \text{H}^+ + e^- = \frac{1}{2}\text{NO}_2^- + \frac{1}{2}\text{H}_2\text{O}$	0.834
$\text{Fe}^{3+} + e^- = \text{Fe}^{2+}$	0.711
$\frac{1}{2}\text{O}_2(\text{g}) + \text{H}^+ + e^- = \frac{1}{2}\text{H}_2\text{O}_2$	0.682
$\frac{1}{2}\text{SO}_4^{2-} + \frac{1}{2}\text{H}^+ + e^- = \frac{1}{2}\text{H}_2\text{S} + \frac{1}{2}\text{H}_2\text{O}$	0.303
$\frac{1}{2}\text{N}_2(\text{g}) + \frac{1}{2}\text{H}^+ + e^- = \frac{1}{2}\text{NH}_4^+$	0.274
$\frac{1}{2}\text{CO}_2(\text{g}) + \text{H}^+ + e^- = \frac{1}{2}\text{CH}_4(\text{g}) + \frac{1}{2}\text{H}_2\text{O}$	0.169
$\text{H}^+ + e^- = \frac{1}{2}\text{H}_2(\text{g})$	0.000

^aThe E_h^0 can be converted to the equilibrium constant for the half-reaction, K , using the equation $E_h^0 = (0.059/n) \log K$.

these half-reactions to proceed as written. This principle is evident from equation 7.2. Since the stipulation of standard-state conditions fixes the activities of the reduced molecule, oxidized molecule, and proton at unity (by definition), then the last term in equation 7.2 is zero, and $E_h = E_h^0$. That is, the reaction's potential, E_h , is equal to its standard-state potential, E_h^0 , only under conditions where the activities of the molecules and the proton in reaction 7.1 are unity. Such conditions are obviously not realistic in soils, where activities of electron-donating and -accepting ions are typically below 10^{-4} and the pH ranges from 4 to 9. It is more useful, then, to present the potentials of Table 7.1 in graphic form, where the H^+ activity is seen as an independent variable with an important effect on redox potential.¹ This is done in Figure 7.1, imposing the additional constraint that most dissolved ions and molecules be assigned an activity of 10^{-5} . (The exception here is the dissolved gases, O_2 , N_2 , CH_4 , CO_2 , and H_2 . The first two are given partial pressures of 0.2 and 0.8 atmosphere, respectively, while the last three are assigned a partial pressure of 0.001 atmosphere). While these activity values are arbitrary, they are more realistic than the unit activities of standard-state conditions.

Consider the reduction of Mn oxide to soluble Mn^{2+} as an example half-reaction:



Then, according to the Nernst equation:

$$E_h = E_h^0 - \frac{0.059}{2} \log \frac{(\text{Mn}^{2+})}{(\text{H}^+)^4} \quad (7.4)$$

1. Since E_h can affect pH directly through reaction 7.1, it may be arbitrary whether E_h or pH is chosen as the dependent (y -axis) variable. But soil pH is sometimes determined by processes unrelated to the redox reaction itself, in which case pH is justifiably selected to be the independent (x -axis) variable.

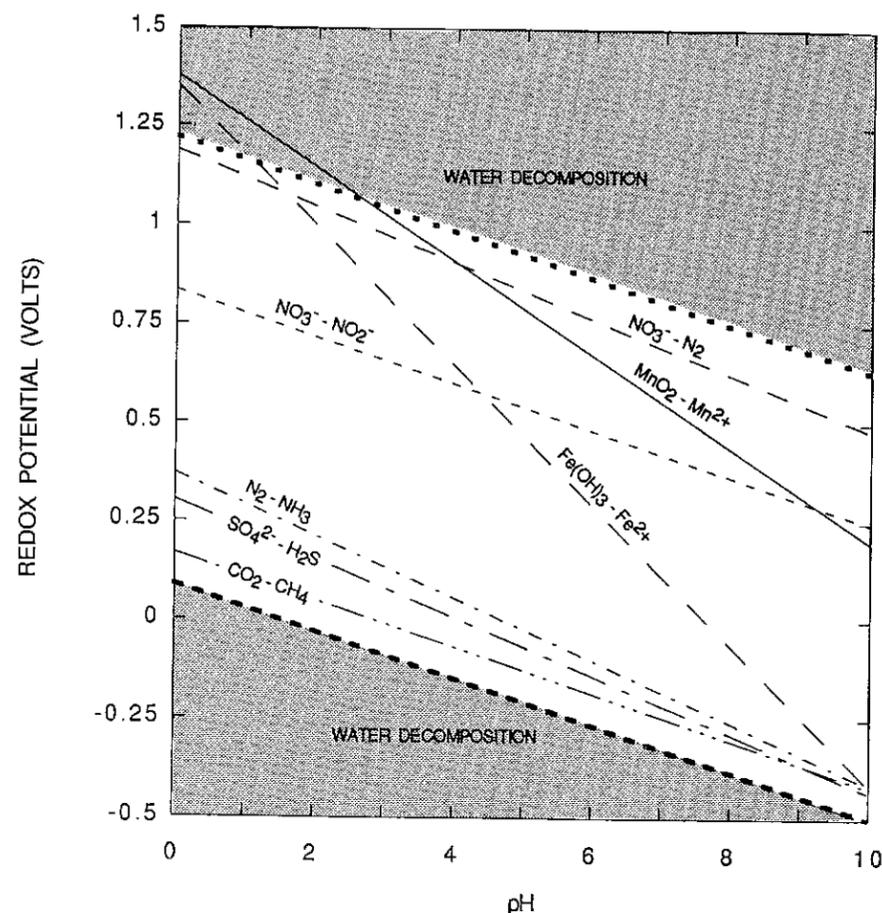


Figure 7.1. The relationship of redox potential, E_h , to pH for important half-cell reactions in water. The bold broken lines denote the E_h at which water is oxidized to O_2 (upper line) or reduced to H_2 (lower line).

That is:

$$E_h = 1.23 - 0.0295 \log (Mn^{2+}) - 0.118 \text{ pH} \quad (7.5)$$

And, assuming that $(Mn^{2+}) = 10^{-5}$, then:

$$E_h = 1.378 - 0.118 \text{ pH} \quad (7.6)$$

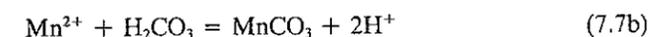
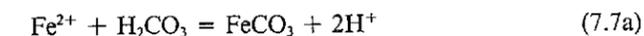
This equation describes a straight line on the E_h -pH axis system, and is plotted in Figure 7.1 along with the analogous equations for several other half-reactions of interest. It should be noted that the slope of each line is determined by the stoichiometric ratio of protons to electrons in the particular half-reaction, specified by the value of m/n in reaction 7.1. For $m/n = 1$, the slope is -59 mV/pH unit . In general, for any value of m/n , the slope is $(m/n) \times (-59 \text{ mV/pH unit})$.

7.1b. Reduction Reaction Sequence and E_h in Waterlogged Soils

Figure 7.1 is useful in understanding the sequence of reactions likely to occur as a soil becomes waterlogged and molecular oxygen, O_2 , is depleted in the soil due to its low solubility in water ($8 \mu\text{g/ml}$) and its consumption by continued biological activity. Before the soil is fully depleted of oxygen, residual O_2 , even under much less than fully aerated conditions, should maintain the redox potential of the soil solution at a high (strongly oxidizing) value. This means that all half-reactions listed below the O_2 - H_2O reaction in Table 7.1, if they are at equilibrium with ("coupled to") the O_2 - H_2O reaction, are driven from right to left. For example, essentially all of the iron in the soil would be maintained in oxidized forms (Fe oxides), and the activity of Fe^{2+} would be extremely low. This situation implies equilibrium and a spatially constant redox potential, unlikely in practice because of slow diffusion of O_2 into water-filled micropores of soil aggregates, and because redox reactions in general tend to be sluggish. The O_2 molecule, despite being a potentially powerful oxidant, often reacts very slowly with substrates because of kinetic limitations. Thus, certain reduced species such as Mn^{2+} and Fe^{2+} are often present in soil solution along with dissolved oxygen, an indication that conditions of nonequilibrium are common.

Microbial activity changes from aerobic to anaerobic when the dissolved oxygen diminishes to trace levels (about $10^{-6} M$). The observable change that follows waterlogging, once O_2 is consumed in the water-saturated soil by biological activity, is a decrease in redox potential accompanied by a rise in pH toward 7. Most reduction reactions consume H^+ , accounting for this pH change. In fact, it is CO_2 in the reduced soil that buffers pH in the 6 to 7 range via the H_2CO_3 - HCO_3^- reaction. Without CO_2 , the soil pH would go well above 7 as reduction progressed and continued to consume H^+ . If, however, the pH of the aerated soil is initially higher than 7, as is the case in calcareous and sodic soils, then reduction reactions actually lower the pH toward 7 because metal ions made soluble by reduction can precipitate as carbonates, hydroxides, or sulfides. For example Mn^{2+} and Fe^{2+} precipitate as $MnCO_3$ and $FeCO_3$ (see reactions 7.7a and b), generating protons to counter those consumed by reduction.

Anaerobic organisms are able to use oxidized chemical species such as nitrate (NO_3^-) as electron acceptors in place of molecular oxygen. Consequently, microbial reduction of nitrate to N_2 (a process termed "denitrification") occurs in the early stages of soil reduction, as does Mn oxide reduction to Mn^{2+} . Reduced species such as nitrite (NO_2^-) and Mn^{2+} then appear in solution. As more extreme reducing conditions develop, ammonium (NH_4^+) accumulates from nitrogen reduction reactions, and iron solubility increases in the form of Fe^{2+} . The elevated iron and manganese solubility is ultimately limited by precipitation of the rather insoluble carbonates of Fe (siderite) and Mn (rhodochrosite) if the soil pH is not too low:



These reactions prevent the pH from rising much above 7 even as reduction reactions continue in the soil. The process of Fe reduction in soils dissolves silica and phosphate adsorbed on ferric oxides and precipitated in Fe^{3+} -rich minerals. The fainter

colors of reduced mineral forms of Fe and Mn compared with their oxidized counterparts account for the pallid appearance of waterlogged soils.

Ultimately, prolonged anoxic conditions cause sulfate to be reduced to sulfide, which then precipitates with Fe^{2+} and other metals as insoluble sulfide minerals such as pyrite (FeS_2). Manganese sulfides form if the reducing conditions are extreme; otherwise MnCO_3 is the more likely precipitated form of reduced Mn in anaerobic soils. Consequently, *prolonged* waterlogging of soils tends to bring Fe and Mn solubilities back down to low levels. If the redox potential decreases to low positive or somewhat negative values (< 200 mV), organic carbon can undergo reduction, forming methane. At these extreme conditions of soil reduction, hydrogen gas may be generated in the soil.

When considering the actual processes by which electrons are transferred in these reduction reactions, it should not be assumed that all reductions are caused directly by microorganisms. For example, bacteria may exude organic chemicals such as polyphenols, which in turn chemically reduce Mn oxides and other easily reducible compounds. Therefore, Mn oxide may in this sense be an indirect electron acceptor, whereas NO_3^- accepts electrons by a direct enzymatically catalyzed reaction within the cell.

Whether the process is direct or indirect, all of the reduction reactions require soil flooding to saturate pores combined with organic matter to support microbial activity and create anaerobic conditions. However, once water is drained out of the soil, many of the reduction reactions reverse. As O_2 reenters pores, the redox potential increases and iron and manganese oxidize to darkly colored oxides, forming red, brown, and black stains and deposits in the soil. In contrast to reduction, oxidation reactions as a group are H^+ -generating, so that soil aeration generally causes the pH to shift lower. Only if the soil is alkaline prior to flooding can subsequent aeration be expected to raise the pH.

Reduction-oxidation episodes in soils cause appreciable redistribution of elements as some minerals dissolve and new minerals precipitate. It is unlikely that the surface chemical properties of the soil are preserved through the reduction and oxidation processes. In particular, freshly precipitated Fe and Mn oxides seem to provide recently reoxidized soils with new reactive surfaces for heavy metal and organic sorption.

E_h , or redox potential, is a measure of the *intensity* of the reducing or oxidizing conditions; that is, the tendency of the soil solution to donate electrons to or accept electrons from a chemical species or electrode introduced into the solution. Conversely, the *capacity* of the soil to be reduced or oxidized is measured by the quantities of potentially reactive electron donors (e.g., S^{2-} , Fe^{2+} , Mn^{2+}) and acceptors (e.g., $\text{Fe}(\text{OH})_3$, MnO_2 , NO_3^- , SO_4^{2-}) in the soil. Once a soil is flooded and O_2 is consumed, the redox potential (E_h) begins to decrease. How much the E_h decreases depends on the quantity of reactive electron acceptors in the soil compared with the quantity of electrons generated by biological reactions, particularly organic matter oxidation. A large reserve of electron acceptors such as Mn^{4+} or Fe^{3+} in the form of oxides means that the redox potential tends to maintain a more nearly constant value as reduction of acceptors continues; the system is then said to be "well poised" with regard to E_h in much the same way that pH is well buffered in soils having a large capacity to donate or accept protons. Even so, a high organic matter level in soils

usually means that the electron acceptors are overwhelmed by microbial activity, and the E_h decreases rapidly.

7.1c. Redox Potential Measurement in Soil by Electrode

The potentials listed in Table 7.1 and plotted in Figure 7.1 are thermodynamic values and do not necessarily correspond to actual values measured in solutions, for reasons that will be discussed in this section. For example, aerobic soil solutions typically have measured E_h values of about 400 to 500 mV, and O_2 disappears from the soil at about 350 mV. These are much lower values than expected theoretically, since dissolved O_2 should in principle maintain potentials closer to 1000 mV (see Figure 7.1). To understand discrepancies between theory and measurement, some knowledge of the principles involved in redox potential measurement is needed.

The commonest method of measuring redox potential is to immerse a platinum (Pt) electrode along with a reference electrode into a solution; the electrodes are connected to a potentiometer that measures the potential difference between the two electrodes. Reduced species in solution tend to donate electrons to the conducting Pt electrode, while oxidized species tend to accept electrons from the electrode. This creates electron flow in the electrode. However, to cause any *detectable* movement of electrons in the electrode, the reaction between the oxidized (ox) and reduced (red) form of an element in solution:



must be shifted away from equilibrium. At the steady state of equilibrium, the forward reaction rate of equation 7.8 equals the backward rate, and the *net* electron flow (net current) is zero. Even at equilibrium, however, electron flow *in either direction*, termed the *exchange current*, i_0 , is not zero.

A very small shift of the electrode potential away from its equilibrium value causes the half-reaction (equation 7.8) to proceed either to the left or right, as illustrated in Figure 7.2, thereby creating a net current that can be measured. How precisely this measurement can determine the equilibrium potential of a particular half-reaction depends on how steeply the net current deviates from zero near the equilibrium potential. The greater the magnitude of the exchange current, i_0 , the more steep is the net current function. This, in turn, is a function of the concentration of reduced and oxidized species near the electrode surface, as is illustrated in Figure 7.2 for the example of the $\text{Fe}^{3+} - \text{Fe}^{2+}$ couple at two different concentrations. For this particular half-reaction, if either Fe species is at a concentration less than about $10^{-5} M$, the exchange current is sufficiently low to prevent accurate measurement of the redox potential using the Pt electrode.

In the particular case of the $\text{O}_2 - \text{H}_2\text{O}$ half reaction:



it is found that, even when the Pt electrode is shifted well away from the equilibrium potential, relatively little exchange current is generated, as shown in Figure 7.3. This

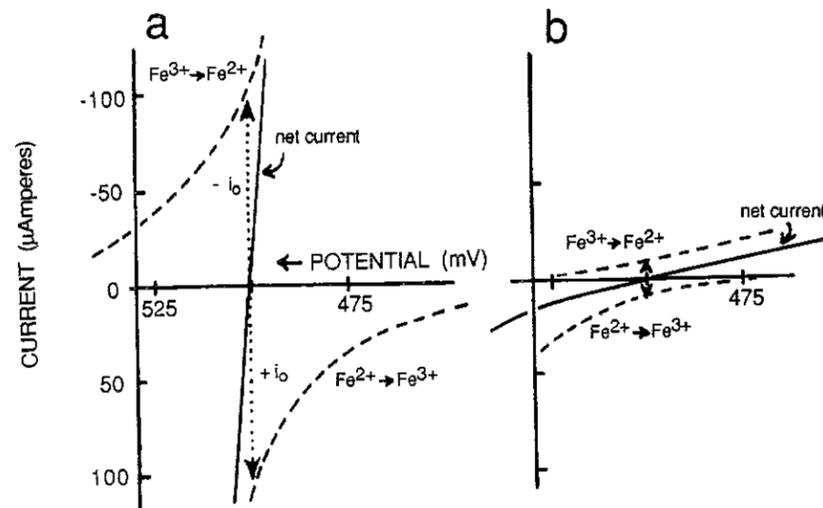


Figure 7.2. Measurement of the platinum electrode potential in relation to the electrode current for the Fe^{3+} - Fe^{2+} redox pair at pH 2 in water, under conditions of (a) $[\text{Fe}^{3+}] = [\text{Fe}^{2+}] = 10^{-3} \text{ M}$, and (b) $[\text{Fe}^{3+}] = [\text{Fe}^{2+}] = 10^{-4} \text{ M}$. (Adapted from W. Stumm and J. J. Morgan. 1981. *Aquatic Chemistry*. 2nd ed. New York: Wiley. Used with permission.)

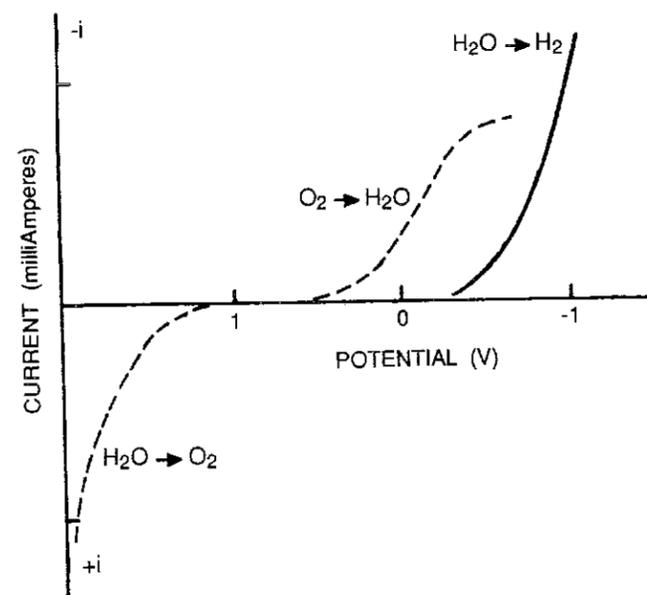


Figure 7.3. Electrode current in pure water (aerated) as a function of potential. Net current is close to zero over a wide range of electrode potential, making it difficult to locate the equilibrium potential, E_h . (Adapted from W. Stumm and J. J. Morgan. 1981. *Aquatic Chemistry*. 2nd ed. New York: Wiley. Used with permission.)

makes it difficult, if not impossible, to determine the value of the equilibrium potential (E_h) for the O_2 - H_2O reaction.

A further problem in complex systems such as soil solutions, in which several redox couples coexist, is that it is quite possible that the exchange current in either direction is the sum of the exchange currents for two or more half-reactions. Consider the Fe^{3+} - Fe^{2+} and O_2 - H_2O redox couples, which can occur together in soil solutions. As Figure 7.4 illustrates, the measured potential, E_m , at which the net current is zero might then be the potential at which the rate of O_2 reduction at the electrode surface equals the rate of Fe^{2+} oxidation. This situation would be likely if the concentration of Fe^{2+} in solution exceeded that of Fe^{3+} (which is usually the case in reduced soils because of the generally low solubility of Fe^{3+}). In instances such as this, the two redox couples are not in equilibrium with one another, and the measured potential is termed a *mixed potential*, E_m , representing neither the E_h of the O_2 - H_2O nor the Fe^{3+} - Fe^{2+} couple. Thus, this measured potential is not informative about the extent of oxidation or reduction for *individual* redox couples at equilibrium. Because of this problem of interpreting mixed potentials, and because many redox couples (such as CO_2 - CH_4 and NO_3^- - NO_2^-) do not react in a reversible manner at the electrode surface, redox potentials measured in soil solution cannot be relied on to reflect the thermodynamic reaction potentials such as those listed in

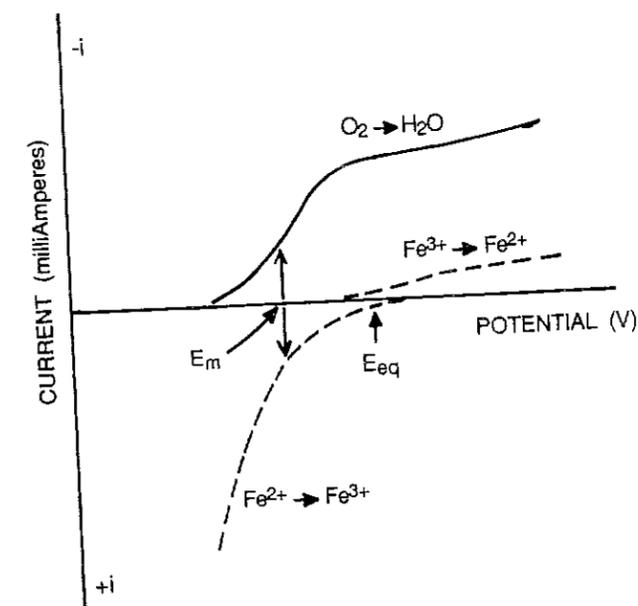


Figure 7.4. Electrode current in aerated water containing Fe^{2+} . The measured "equilibrium" potential is a mixed potential, E_m , obscuring the true equilibrium potential, E_{eq} , of the Fe reaction. The mixed potential is not subject to the usual interpretation because the Fe^{2+} - Fe^{3+} and O_2 - H_2O redox pairs are not in equilibrium. (Adapted from W. Stumm and J. J. Morgan. 1981. *Aquatic Chemistry*. 2nd ed. New York: Wiley. Used with permission.)

Table 7.1. This may be why, in aerated soil solutions, measured electrode potentials tend to be around 500 mV, while theoretical O_2 reduction potentials are considerably higher.

We find, then, that the Pt electrode responds well to some redox couples (such as $Fe^{3+} - Fe^{2+}$) and not to others. If all couples were at equilibrium with one another, each would "report" the same potential to the electrode. That is, all redox couples would be leveled to a single E_h value by electron exchange among them. In reality, certain couples fail to enter into this equilibrium because of inert behavior. A good example is the $NO_3^- - N_2$ couple; nitrate is expected to be a strong oxidant by virtue of the high reduction potential of this half reaction (see Table 7.1). However, because this reaction is extremely slow, the theoretical E_h (calculated from equation 7.2) of the $NO_3^- - N_2$ couple has no influence on the redox potentials of soil solutions. Otherwise, redox potentials of soil solutions containing measurable nitrate would always be high. Actual reduction of NO_3^- to N_2 in soils tends to begin at an electrode-measured E_h below 400 mV, much lower than theoretical. Figure 7.5 compares the theoretical E_h of important redox pairs (solid lines) with the electrode-measured E_h range over which these pairs are found to be active in accepting or donating electrons in soils (open and shaded boxes). It is notable that NO_3^- disappears from anaerobic soils at a considerably higher E_h than that at which NH_4^+ appears. The reason for this is the favorability of the denitrification reaction ($NO_3^- \rightarrow N_2$) over NO_3^- reduction to NH_4^+ . As a result, only a small fraction of the NO_3^- in a soil is converted to NH_4^+ on waterlogging; most of the nitrogen is lost as gaseous products (N_2O , N_2).

The $O_2 - H_2O$ couple is the redox pair controlling reactions in aerated solutions, so that re-aeration of anoxic soils drives reduced species (e.g., Fe^{2+}) toward the oxidized state. The range of redox potentials over which Fe^{2+} , Mn^{2+} , and NH_4^+ have been found to oxidize and disappear on aeration of a reduced soil are denoted by the open boxes in Figure 7.5. Nitrate reappearance on aeration is also depicted by an open box. The measured redox potentials that follow re-aeration do not directly reflect the $O_2 - H_2O$ equilibrium state but rather the status of redox couples having faster electron exchange rates. Furthermore, while each redox couple would be expected (in theory) to undergo complete conversion to the reduced form (in flooded soils) or to the oxidized form (in re-aerated soils) before the adjacent redox couple on the E_h scale became active, actual behavior in soils is much less ideal. Several redox reactions are typically active simultaneously. This may reflect spatial variability in the aeration (and redox potential) of soil aggregates, caused by slow diffusion processes in micropores.

Large discrepancies between theoretical and measured E_h are obvious in Figure 7.5 for the $O_2 - H_2O$, $NO_3^- - N_2$, and Mn oxide- Mn^{2+} couple. Although the first two are explained by inert behavior of O_2 , NO_3^- , and N_2 at the Pt electrode, the discrepancy for the Mn couple may have more to do with an inappropriate choice of Mn oxide (MnO_2) to represent soil Mn in the oxidized state. The exact nature of this Mn is not known, but if it is in the form of Mn oxides, they are likely to be impure, noncrystalline, and of mixed oxidation state (between +3 and +4), with ill-defined reduction potentials.

It is clear, after considering all of the factors likely to affect electrode-measured redox potentials, that these potentials are unlikely to be quantitatively meaningful

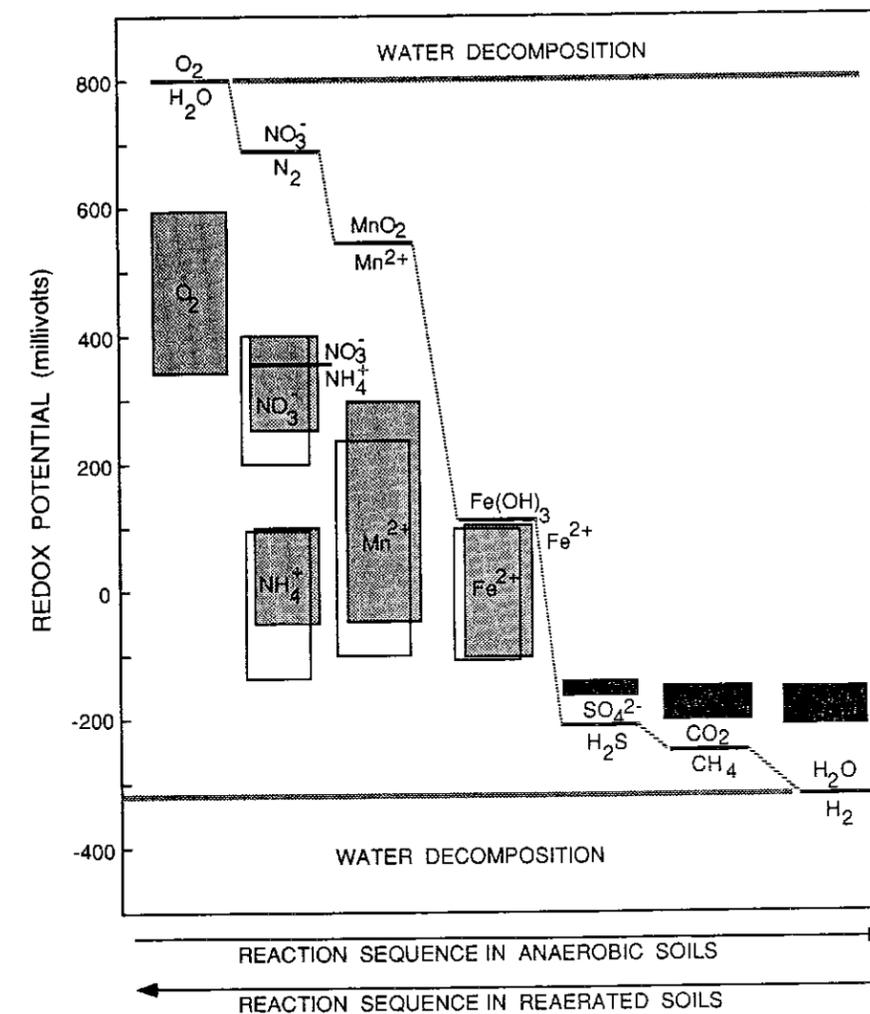
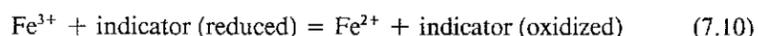


Figure 7.5. The reduction and oxidation sequence in soil solutions at pH 7. Theoretical potentials are indicated by solid lines, assuming equal activities of reduced and oxidized species unless otherwise noted (the pressure of H_2 is arbitrarily set at 10^{-3} atmosphere). Measured ranges of soil potentials over which the indicated species react (change concentration) during soil reduction and oxidation are specified by boxes (shaded for reduction, open for oxidation, black for initial appearance of the reduced form during reduction). (Data, in part, from W. H. Patrick and A. Jugsujinda. 1992. Sequential reduction and oxidation of inorganic nitrogen, manganese, and iron in flooded soil. *Soil Sci. Soc. Am. J.* 56:1071-1073.)

for soil solutions. Consequently, thermodynamic calculations of equilibrium states based only on these measurements should be viewed with suspicion.

7.1d. E_h Measurement by Redox Indicators

Given the problems inherent to the electrode measurement of E_h in soil solution, it would seem desirable to consider other methods of estimating E_h . Theoretically, one could analyze the soil solution for the reduced and oxidized species of a redox couple, say dissolved Fe^{2+} and Fe^{3+} , and use the Nernst relation (equation 7.2) to calculate E_h . Usually, however, there are difficulties with this approach. In the case of the Fe couple, Fe^{3+} solubility in all but very acid soil solutions is extremely low (below detection), so that an assumption must be made about the activity of the free Fe^{3+} ion. It might reasonably be assumed that the solubility product of Fe oxide limits this activity, but Fe oxides have a rather wide range of solubilities depending on oxide crystallinity, structure, and purity. A better approach to measuring E_h would be to use an "indicator" chemical that undergoes reversible electron transfer with natural redox couples in soil solution, that is,



The color of an ideal indicator would depend on the fraction of this chemical in the reduced and oxidized state, allowing a visual estimation of redox potential in much the same way that pH indicators are used to estimate pH. The quantity of indicator present must be sufficiently small that the electron transfer between indicator and solution does not in itself significantly alter the E_h of the solution.

The oxidized form of the indicator usually reacts with protons upon conversion to the reduced form, as is the case for quinone (Q) reduction to the phenol, hydroquinone (HQ):



The involvement of H^+ ions in most reduction reactions of this kind means that the solution pH as well as E_h affects the fraction of indicator in the reduced and oxidized state. This is made evident by applying the Nernst equation to reaction 7.11:

$$E_h = E_h^0 - 0.059 \text{ pH} - (0.059/2) \log \left[\frac{(HQ)}{(Q)} \right] \quad (7.12)$$

Since E_h^0 , the standard-state potential for the Q-HQ redox couple, is a constant (0.699 volt), equation 7.12 reveals that the ratio of reduced to oxidized indicator at any particular pH is determined by the E_h of the solution. At a fixed pH, for example, this equation becomes

$$E_h = E_h^0 - (0.059/2) \log \left[\frac{(HQ)}{(Q)} \right] \quad (7.13)$$

where E_h^0 is the sum of the first two terms on the right side of equation 7.12. At pH 7, $E_h^0 = 0.699 - 0.413 = 0.286$ volt. In general, for redox indicators with unknown standard-state potentials, the value of E_h^0 can be obtained by preparing mixtures containing known amounts of the oxidized and reduced indicator in pH buffers, mea-

suring E_h by the Pt electrode method, and using an equation like 7.13 to calculate E_h^0 for that particular pH.

The E_h^0 values for a number of indicators useful in measuring redox potentials of soil solutions are listed in Table 7.2. The E_h^0 value (adjusted for pH) represents the approximate solution E_h range for which that indicator is diagnostic. Outside of its range, any particular indicator is fully in the reduced or oxidized state; for the Q-HQ indicator, this would mean that the last term in equation 7.13 could not be quantified. In that event, the solution E_h could not be measured by this single indicator; it would be possible to state only that the E_h is above the E_h^0 value (if the indicator is fully oxidized) or below the E_h^0 value (if the indicator is fully reduced).

In practice, to measure the redox potential of a solution by an indicator, first the pH must be measured. The E_h^0 value is then calculated for the indicator at that pH. Then E_h is estimated by an equation of the same form as equation 7.13 but specific for the indicator being used. This estimation is made by using the color of the solution to gauge the ratio of reduced to oxidized indicator. According to equation 7.13, when the indicator is equally in the reduced and oxidized form, $E_h = E_h^0$.

Suppose that in a particular soil solution all indicators with E_h^0 values above +200 millivolts converted to their reduced forms (which tend to be colorless), but all indicators with E_h^0 below +200 millivolts remained in the oxidized (colored) form. The E_h of the solution must then have been very near +200 millivolts. Methylene blue, which is intensely colored in the oxidized state, has been used as an indicator of the onset of strongly reducing conditions in soil solutions. It becomes colorless at an E_h of about +11 millivolts, assuming a pH of 7 (see Table 7.2).

Other indicators of the redox state of the soil include complexing ligands (organic and inorganic) that produce different colors in the presence of Fe^{3+} and Fe^{2+} . Ammo-

Table 7.2. Redox Indicators Ranked by Their E_h^0 Values at pH 7^a

Indicator	E_h^0 (millivolts)
Phenol blue	+224
o-Cresol Indophenol	+191
Thymol indophenol	+174
1-Naphthol-2-sodium sulfonate indophenol	+123
Toluylene blue	+115
Thionine	+63
Methylene blue	+11
Potassium indigo trisulfonate	-81
Potassium indigo disulfonate	-125
Diazine green	-255
Rosinduline	-281
Neutral red	-325
Benzyl viologen	-359

^aCaution must be exercised in using these redox indicators because many of them are also pH indicators. This means that their color in the oxidized state may vary depending on the pH of the solution.

Source: P. R. Hesse. 1971. *A Textbook of Soil Chemical Analysis*. New York: Chemical Publishing.

niium thiocyanate, for example, forms a red color in the presence of Fe^{3+} , while o-phenanthroline forms a red complex with Fe^{2+} but not with Fe^{3+} . These are not true redox indicators because they specifically sense the oxidation state of only the iron redox pair. But if the Fe redox couple is in equilibrium with the other redox couples in soil solution (a questionable assumption), such Fe-specific indicators should report a redox status consistent with the E_h measured by true redox indicators.

Practical difficulties have limited the use of redox indicators in soils. In clear, colorless solutions that are well poised (i.e., have significant concentrations of reduced and oxidized species), redox indicators work well. In soils, however, indicators are much more difficult to use. They may adsorb at colloid surfaces or complex with metal cations, profoundly changing their redox properties, color, and detectability. Separating the soil solution from the soil solids by filtration or other methods solves some of these problems, but increases the chance that anaerobic solutions become aerated (unless extreme care is taken to exclude oxygen gas during the process). Fortunately, oxygen reacts rather slowly with many indicators in their reduced form, so that colorimetric detection of redox potential may be possible before aeration compromises the measurement. Nevertheless, the use of redox indicators has not been accepted in soil chemistry as a generally satisfactory method, even though clever experimental designs might circumvent the known drawbacks.

7.1e. The Concept of p_e in Soil Solutions

Although free electrons do not exist in aqueous solutions, one can still quantify the degree of electron availability, sometimes termed the virtual electron activity, by the parameter p_e :

$$p_e = -\log(e^-) \quad (7.14)$$

where (e^-) symbolizes electron activity measured in terms of the tendency of the solution to accept or donate electrons. Reducing solutions have a high value of (e^-) , and consequently a low or negative p_e . Conversely, oxidizing solutions have a low electron activity and a high (positive) p_e .

For the general case of redox half-reactions:



the virtual "equilibrium" expression¹ is

$$K = \frac{(\text{red})}{(\text{ox})(e^-)^n} \quad (7.16)$$

which in logarithmic form, considering the definition of p_e , becomes

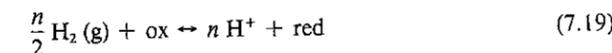
$$\log K - n p_e = \log \left[\frac{(\text{red})}{(\text{ox})} \right] \quad (7.17)$$

1. No such reaction can attain equilibrium in isolation, since at least one other redox pair must be present to donate or accept the electron(s). The "equilibrium constant" should then be thought of as a virtual or operational constant only.

Now the redox potential, E_h , is conventionally defined in terms of the potential of a cell composed of two half-cells: the half-cell of particular interest (given in general terms by reaction 7.15) and the standard hydrogen half-cell (with E_h and p_e assigned values of zero). The reaction in the latter case is



which, when combined with the second half-cell reaction (7.15), gives the overall cell reaction:



The Nernst equation, applied to this reaction, produces the relationship:

$$E = E^0 - \frac{RT}{nF} \ln \frac{(\text{H}^+)^n (\text{red})}{(P_{\text{H}_2})^{n/2} (\text{ox})} \quad (7.20)$$

where R is the gas constant and F is the Faraday constant ($F = 96,490$ coulombs/mole). Because the hydrogen half-cell is defined to be at standard-state conditions, $(\text{H}^+) = 1.0$, $P_{\text{H}_2} = 1.0$ atmosphere, and the potential of this half-cell is 0.00 volt, meaning that E and E^0 in equation 7.20 can be taken as the measured and standard half-cell potential, respectively, of reaction 7.15. But the Nernst equation for half-cell reaction 7.15 is

$$E_h = E_h^0 - \left(\frac{RT}{nF} \right) \ln \left[\frac{(\text{red})}{(\text{ox})} \right] \quad (7.21)$$

Using equation 7.17, equation 7.21 can be reexpressed in terms of the equilibrium constant for the half-cell reaction:

$$E_h = E_h^0 - \left(\frac{2.303 RT}{nF} \right) (\log K - n p_e) \quad (7.22)$$

But the free energy of reaction, ΔG_r , is related to the reaction potential, E , by

$$\Delta G_r = -nFE \quad (7.23)$$

so that the standard-state free energy is given by

$$\Delta G_r^0 = -nFE^0 \quad (7.24)$$

Thermodynamics provides the relationship between ΔG_r^0 and the equilibrium constant (see Chapter 1):

$$\Delta G_r^0 = -RT \ln K \quad (7.25)$$

so it follows that

$$nFE^0 = RT \ln K \quad (7.26)$$

and consequently

$$E^0 = \frac{(2.303 RT \log K)}{nF} \quad (7.27)$$

which at room temperature can be written as

$$E^0 \text{ (volts)} = \left(\frac{0.059}{n}\right) \log K \quad (7.28)$$

This provides the useful conversion between standard potentials and equilibrium constants of redox reactions.

Because the standard-state half-cell potential, E_h^0 , is measured *relative* to the zero potential of the hydrogen half-cell, $E^0 = E_h^0$, and the definition of E^0 given by equation 7.27 is substituted into equation 7.22 to give

$$E_h = \left(\frac{2.303 RT}{nF}\right) \log K - \left(\frac{2.303 RT}{nF}\right) (\log K - n p\epsilon) = \left(\frac{2.303 RT}{nF}\right) p\epsilon \quad (7.29)$$

At room temperature, this equation relating $p\epsilon$ to E_h becomes simply

$$E_h \text{ (volts)} = 0.059 p\epsilon \quad (7.30)$$

so that E_h and $p\epsilon$ for half-reactions are seen to be easily interchangeable, related by the Nernst constant. The choice of E_h (volt units) or $p\epsilon$ (unitless) in measuring redox status is a matter of preference and convenience.

In soils, $p\epsilon$ values lie in the range of -6 (strongly reduced) to $+12$ (strongly oxidized). However, these $p\epsilon$ values (and E_h values as well) are negatively correlated with pH. Such a correlation is expected from consideration of the individual redox reactions occurring in soils (see Figure 7.1).

Using the $\text{MnO}_2 - \text{Mn}^{2+}$ reaction as an example, equation 7.5, written in terms of $p\epsilon$, provides the $p\epsilon$ -pH relationship:

$$p\epsilon = 20.8 - 0.5 \log (\text{Mn}^{2+}) - 2 \text{ pH} \quad (7.31)$$

If the Mn^{2+} activity in soil solution were more or less constant (perhaps controlled by ion exchange processes), then $p\epsilon$ and pH would, as observed, be negatively correlated. Closer scrutiny of the $p\epsilon$ -pH relationship in soils, however, reveals that the slope of the function tends to be near 1. This would be predicted if the controlling redox reaction(s) in the soil involved equal numbers of protons and electrons (that is, $m = n$ in reaction 7.1). This is clearly not the case for the $\text{MnO}_2 - \text{Mn}^{2+}$ reaction, whose $p\epsilon$ -pH function has a slope of 2. For the $\text{O}_2 - \text{H}_2\text{O}$ and several other important redox couples in soils, however, the expected slope is at or near unity (Table 7.1 lists redox couples along with the number of protons and electrons consumed by reduction).

For the $\text{O}_2 - \text{H}_2\text{O}$ reaction in an aerated soil with $P_{\text{O}_2} = 0.2$ atmosphere, the Nernst equation gives

$$E_h = 1.219 - 0.059 \text{ pH} \quad (7.32)$$

or equivalently in terms of $p\epsilon$

$$p\epsilon + \text{pH} = 20.66 \quad (7.33)$$

Actual $p\epsilon$ -pH correlations obtained by Pt electrode measurements in wet, aerobic soils give a somewhat different relationship:

$$p\epsilon + \text{pH} \approx 15 \quad (7.34)$$

plotted as the shaded band in Figure 7.6. The slope of this band, but not the intercept, is consistent with behavior of the $\text{O}_2 - \text{H}_2\text{O}$ and several other redox half-reactions. It is known that the $\text{O}_2 - \text{H}_2\text{O}$ redox couple does not behave in an ideal manner at the Pt electrode surface, so that the discrepancy between the expected and observed $p\epsilon + \text{pH}$ value may be due to Pt electrode potential readings below the theoretical E_h value for aerated water. Despite this discrepancy, it is generally believed that the $\text{O}_2 - \text{H}_2\text{O}$ couple controls the $p\epsilon$ -pH relationship in aerated soil systems.

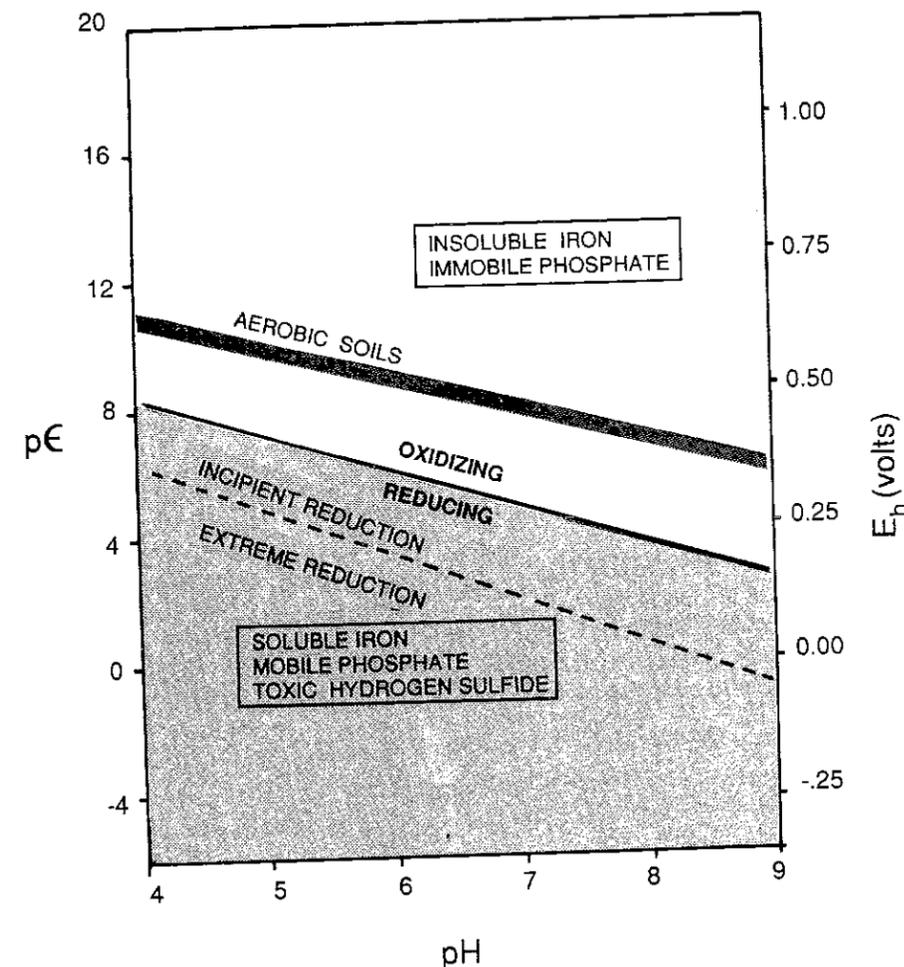


Figure 7.6. Estimated degrees of soil oxidation and reduction, based on $p\epsilon$ -pH or E_h -pH values. The broad line labeled "aerobic soils" is the $p\epsilon$ -pH relationship measured by electrode in aerated soils. (Data from P. R. Hesse, 1971. *A Textbook of Soil Chemical Analysis*. New York: Chemical Publishing; and W. L. Lindsay, 1979. *Chemical Equilibria in Soils*. New York: Wiley.)

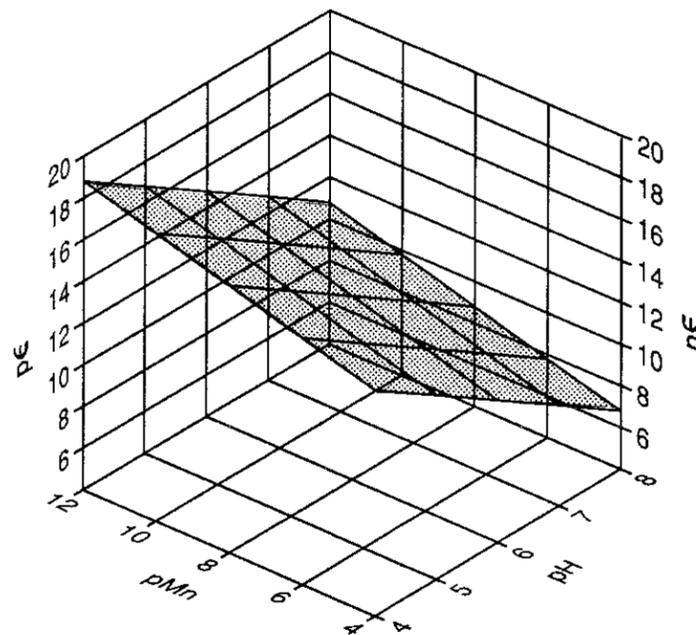


Figure 7.7. Theoretical dependence of p_e on pH and dissolved Mn^{2+} activity ($pMn = -\log(Mn^{2+})$).

Holding the pH of a redox reaction system constant does not necessarily fix the p_e of the system, although equations such as 7.33 and 7.34 suggest this. In the case of the MnO_2-Mn^{2+} couple, the Mn^{2+} activity influences the p_e -pH relation according to equation 7.31. The Mn^{2+} - p_e -pH relation is depicted graphically in Figure 7.7, indicating that, at a given pH, higher Mn^{2+} activity results in a lower p_e of solution. Consequently, the oxidative strength of Mn oxides is lowered as Mn^{2+} is dissolved and builds up in the process of oxidizing other chemical species. Similarly, lower O_2 partial pressures in poorly aerated soils reduce the p_e according to the equation:

$$p_e = 20.8 - pH + 0.25 \log P_{O_2} \quad (7.35)$$

In general, as reaction products of spontaneous redox reactions accumulate, they lower the p_e of the redox couple that provides the oxidant and raise the p_e of the redox couple that provides the reductant. When the two p_e values converge, equilibrium is reached.

7.2. CHEMISTRY OF IMPORTANT REDOX COUPLES IN SOILS

7.2a. The H_2O-O_2 Couple

The four-electron reduction of O_2 to water has a very favorable potential of +1.229 volts (see Table 7.1), making O_2 a powerful oxidant, at least in principle. Two-electron reduction to hydrogen peroxide (H_2O_2) is much less favorable ($E_h = +0.68$

REDOX REACTIONS

volt). As the subsequent two-electron reduction of H_2O_2 to H_2O is slow, the effective redox potential of O_2 may be only +0.68 volt. In biologically mediated oxidations, enzymes catalyze what appears to be synchronous two- and four-electron reduction of O_2 , and the O_2-H_2O and $O_2-H_2O_2$ reaction potentials may be relevant. In chemical oxidations, however, there is no evidence for reduction of O_2 in either four- or two-electron steps. Instead, oxidation of substrates by O_2 inevitably proceeds through a series of one-electron steps, which means that the full oxidative potential of O_2 is not necessarily exploited.

The one-electron reduction of O_2 to the superoxide radical ion, O_2^- , is unfavorable, with a potential of -0.56 volt. This means that single electron oxidation of molecules by O_2 itself is unlikely. The superoxide ion is a moderately effective *reducing* agent, but a poor oxidizing agent. However, the superoxide ion reacts with water to form peroxide ions, HO_2^- and O_2^{2-} . These are thought to be the operative oxidizing species in aerated water.

There are further reasons that O_2 demonstrates a surprisingly weak ability to oxidize organic molecules in spite of its high reduction potential. In its ground (unexcited) electronic state, O_2 has an electron spin of $S = 1$ (referred to as the triplet state, caused by two unpaired electrons). It can be excited by ultraviolet light to the $S = 0$ (singlet) state, in which there are no unpaired electrons. Most organic substrates are also in the singlet electronic state under normal conditions, and since electron transfer between molecules in different spin states is a spin-forbidden process, molecular oxygen in its normal (unexcited) electronic state is not expected to react with most organic molecules. In contrast, singlet oxygen, formed by photochemical excitation of triplet oxygen, is an extremely potent organic oxidant but is of very limited importance in soil chemistry because ultraviolet light is a factor only at the soil surface.

Molecular oxygen, if bonded to certain transition metal ions in solution or at oxide surfaces, can be more reactive than dissolved free oxygen. This property may contribute to the catalytic activity of metal oxide minerals in oxidation reactions.

All of these considerations of O_2 reduction mechanisms suggest that the four-electron reduction of O_2 , with its very favorable potential, overestimates the oxidative power of O_2 in chemical systems. This should be kept in mind in the following discussions of redox reactions if O_2 is the oxidant.

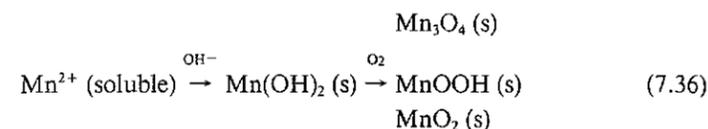
Strong oxidation potentials can arise in aqueous solutions from sources other than dissolved O_2 , at least if these solutions are irradiated with light. Low-energy ultraviolet light (wavelength ≈ 300 nm) induces the photoreduction of hydrolyzed Fe^{3+} species such as dissolved $FeOH^{2+}$ or colloidal Fe hydroxide by the $O_2^{2-} \rightarrow Fe^{3+}$ electron transfer. This reaction produces Fe^{2+} and $\cdot OH$, the hydroxy radical. The hydroxy radical is one of the most powerful and reactive oxidants known to occur in water, oxidizing most natural organics (carboxylic acids, phenols, etc.) and many metals.

7.2b. The $Mn^{2+}-Mn$ Oxide System

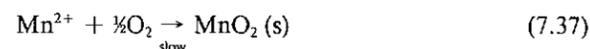
Microorganisms can facilitate and use energy from redox reactions (without a net cost in energy) only if these reactions are favored thermodynamically. Microbes catalyze, via enzyme systems, the reduction of O_2 to H_2O . In the process, they may directly or indirectly promote Mn from oxidation state +2 to +3 or +4. In effect,

the oxidative power of O_2 is converted into the form of Mn(+3,+4) oxides. Mn oxides are perhaps the most potent oxidizing solids in soils.

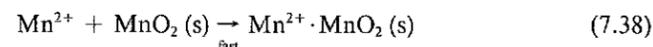
Chemically, oxidation of Mn^{2+} occurs spontaneously in alkaline aerated solutions, as the initially precipitated manganous hydroxide rapidly reacts with O_2 to produce a variety of oxide products depending on pH, the concentration of O_2 , presence of cations, and other factors:



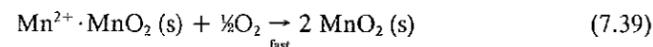
Although Mn^{2+} in solution is thermodynamically unstable with respect to oxidation by O_2 at any pH higher than 4, the *rate* of uncatalyzed oxidation is not appreciable unless the pH is well above 8. The Mn oxidation reaction is *autocatalytic*; that is, the initial oxidation step:



is followed by selective adsorption of Mn^{2+} onto the freshly formed Mn oxide:



and the adsorbed Mn^{2+} is then oxidized relatively quickly:

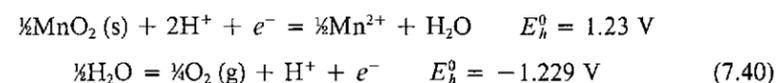


Consequently, as Mn oxides precipitate, oxidation accelerates in response to the increased surface available for selective adsorption of Mn^{2+} .

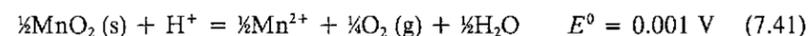
In soils, autocatalytic oxidation of Mn^{2+} by Mn oxides seems to be a mechanism by which the formation of Mn oxides can be explained at pH values well below 8. There is also evidence that Mn and Fe tend to co-precipitate in oxides, possibly because iron oxide surfaces also catalyze the oxidation of Mn^{2+} . In any event, the oxidizing agent for Mn^{2+} is molecular oxygen, either by a direct or indirect reaction path. The reason for this is clear from Figure 7.5. Except for NO_3^- , which tends to be kinetically inert, O_2 is the only sufficiently strong and common oxidant in soil to be able to oxidize Mn^{2+} .

Example Problem: What is the equilibrium concentration of Mn^{2+} in an aerated soil solution at pH 4, assuming that MnO_2 is the solid phase formed by Mn oxidation?

Solution: From Table 7.1, the relevant half-reactions might be:



since Mn^{2+} in aerated soil solutions can be assumed to be oxidized by dissolved molecular oxygen. If these two half-reactions are coupled (in equilibrium), the overall reaction is written as their sum:



The Nernst relation for this reaction at room temperature is

$$E = E^0 - 0.059 \log \frac{(P_{O_2})^{1/4} (Mn^{2+})^{1/2}}{(H^+)} \quad (7.42)$$

which becomes

$$E = 0.001 - 0.01475 \log P_{O_2} - 0.0295 \log (Mn^{2+}) - 0.059 \text{ pH} \quad (7.43)$$

Now for aerated water at pH 4, $P_{O_2} \approx 0.2$ atmosphere, and equation 7.43 simplifies to

$$E = -0.225 - 0.0295 \log (Mn^{2+}) \quad (7.44)$$

Since this redox system is taken to be at equilibrium, there is no potential for the reaction to do work; that is, $E = 0$ (or equivalently, from equation 7.23, $\Delta G = 0$). Thus equation 7.44 can be used to solve for the equilibrium activity of Mn^{2+} :

$$(Mn^{2+}) = 10^{-7.63} \quad (7.45)$$

This means that the solution concentration of free Mn^{2+} ions at pH 4 should be less than 10^{-7} molar (neglecting corrections for activity coefficients). But much higher concentrations than this are usual in aerated soil solutions; it appears that equilibrium between Mn oxides and dissolved O_2 is not the usual situation. Disequilibrium could be attributed to the sluggish participation of O_2 in electron transfer reactions despite its potential to force reaction 7.41 strongly to the left. However, other explanations for the higher than expected Mn^{2+} concentrations in soils are possible, including:

1. Reduced zones within the generally aerated soil matrix
2. Control of redox reactions by forms of oxidized Mn that are quite different from MnO_2
3. Failure of reaction 7.40 to measure the operative chemical oxidation potential of molecular oxygen (see discussion about O_2 in section 7.2a)
4. Coupling of the Mn reduction to kinetically active reducing agents such as polyphenols.

The predominant stable forms of Mn in soils under different prevailing solution conditions of pH and E_h can be summarized in a pH- E_h or pH- p_e diagram. For example, equation 7.31 provides a relationship between p_e and pH for any particular activity of Mn^{2+} in solution. If a realistic Mn^{2+} activity, say 10^{-5} , is chosen to represent soil solution, equation 7.31 becomes simply

$$p_e = 23.3 - 2 \text{ pH} \quad (7.46)$$

Plotted on a p_e -pH axis system, this is a straight line specifying the redox and acidity conditions in the solution that allow MnO_2 and approximately $10^{-5} M Mn^{2+}$ to co-exist in equilibrium. Below this line (lower p_e), Mn^{2+} concentrations are higher than 10^{-5} ; above this line (higher p_e), Mn^{2+} concentrations are lower. In Figure 7.8, this line, along with other lines separating different chemical forms of Mn, is plotted. Areas enclosed by lines envelope p_e and pH conditions favorable to the formation of specific chemical forms of manganese. It is apparent from the figure that the predom-

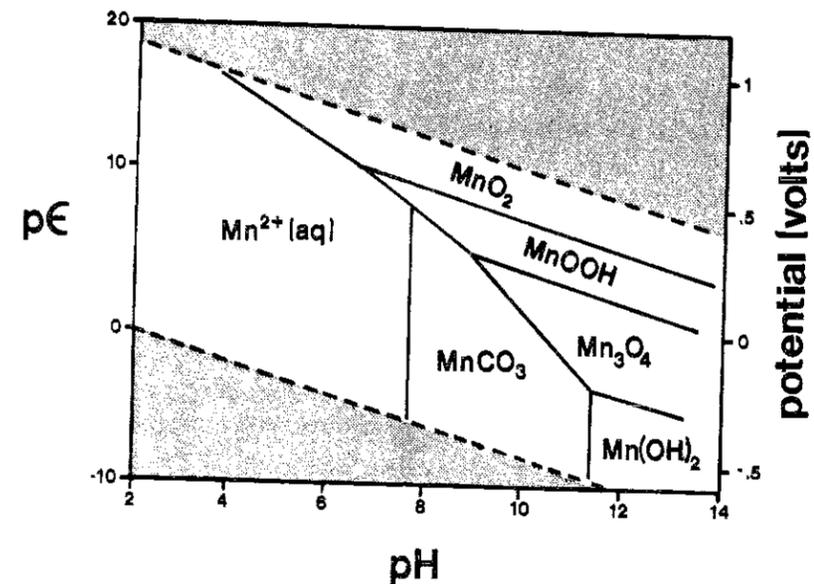


Figure 7.8. Stability field diagram for soluble and solid forms of Mn under a range of redox potential and pH conditions, assuming a dissolved CO_2 concentration of 10^{-3} M. Shaded areas delineate conditions that are unattainable because of water decomposition. (Adapted from W. Stumm and J. J. Morgan, 1981. *Aquatic Chemistry*, 2nd ed. New York: Wiley.)

inant form of Mn below pH 7 should be soluble Mn^{2+} unless the solution is strongly oxidizing (aerated). At higher pH, Mn^{2+} is expected to precipitate as MnCO_3 under reducing conditions, or to oxidize to an insoluble oxide under oxidizing conditions.

7.2c. The Fe^{2+} –Fe Oxide System

Ferrous iron (Fe^{2+}) appears later than Mn^{2+} in soils that have been subjected to prolonged waterlogging because, as Table 7.1 shows, the reduction potential of Fe^{3+} in oxides (and probably in many other soil minerals as well) is lower than that of Mn(+3,+4) in Mn oxides. Since Fe^{2+} , like Mn^{2+} , is rather soluble, it can reach appreciable concentrations in poorly aerated soil solutions. The introduction of dissolved oxygen causes rapid oxidation of Fe^{2+} and precipitation of ferric hydroxide if the solution pH is much higher than 6. The rate law of oxidation of dissolved Fe^{2+} is known to be

$$\frac{-d[\text{Fe}^{2+}]}{dt} = k[\text{Fe}^{2+}][\text{OH}^-]^2 P_{\text{O}_2} \quad (7.47)$$

where $k \approx 8.0 \times 10^{13} \text{ min}^{-1} \text{ atm}^{-1} \text{ mole}^{-2} \text{ liter}^2$ at 20°C . The sensitivity of oxidation rate to pH is evident from this equation; Fe^{2+} persists for no more than a few minutes in aerated solutions of pH 7 or higher.

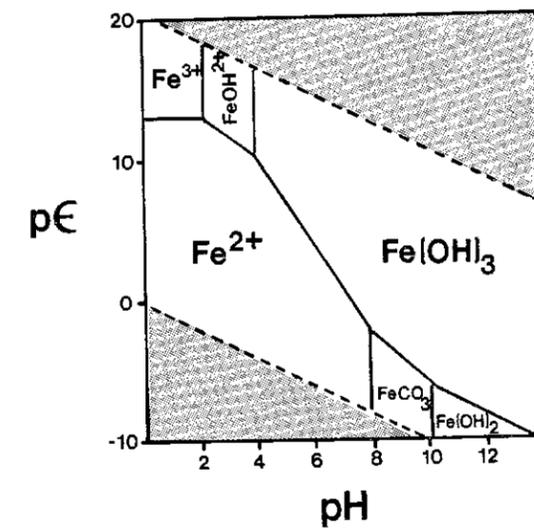
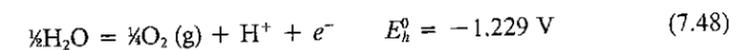
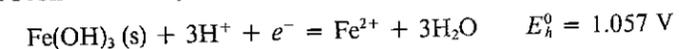


Figure 7.9. Stability field diagram for soluble and solid forms of Fe under a range of redox potential and pH conditions, assuming a dissolved CO_2 concentration of 10^{-3} M. Shaded areas delineate conditions that are unattainable because of water decomposition. (Adapted from W. Stumm and J. J. Morgan, 1981. *Aquatic Chemistry*, 2nd ed. New York: Wiley.)

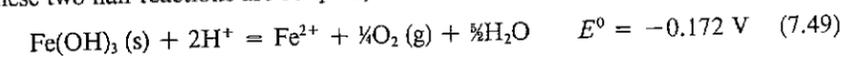
The pE -pH diagram in Figure 7.9 depicts the thermodynamically stable forms of Fe under a range of conditions in solution. This shows that, if reducing conditions prevail in solution, soluble Fe^{2+} should be stable only if the pH is below about 8. If the pH is higher than 8, as may be the case in calcareous or sodic soils, solid FeCO_3 would be the predominant form of iron. Under oxidizing conditions, the highly insoluble ferric hydroxides and oxides are the most stable forms of iron over a wide pH range.

Example Problem: Since O_2 reacts directly with Fe^{2+} to limit iron solubility in aerated water, what is the equation relating Fe^{2+} activity to pH in aerobic soils?

Solution: From Table 7.1, the relevant half-reactions are



If these two half-reactions are coupled, the overall reaction is written as their sum:



From the Nernst equation for this reaction at room temperature:

$$E = E^0 - 0.059 \log \frac{(P_{\text{O}_2})^{1/4} (\text{Fe}^{2+})}{(\text{H}^+)^2} \quad (7.50)$$

which becomes

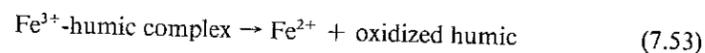
$$E = -0.172 - \frac{1}{2}(0.059) \log P_{O_2} - 0.059 \log (Fe^{2+}) - 2(0.059)pH \quad (7.51)$$

Since $E = 0$ at equilibrium, and aerated conditions allow P_{O_2} to be assigned a partial gas pressure of about 0.2 atmosphere, equation 7.51 can be simplified to give the desired relationship between Fe^{2+} activity and pH:

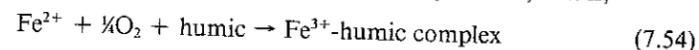
$$\log (Fe^{2+}) = -2.74 - 2 pH \quad (7.52)$$

This result shows that, even in acid soil solutions, the equilibrium activity of Fe^{2+} would be far below detectable levels if the soil is aerated. Furthermore, as is easily shown by equation 7.51, traces of dissolved oxygen in solution would be sufficient to keep the Fe^{2+} concentration well below detection. That these predictions are not borne out in soils may suggest, as for the Mn case, that equilibrium is not usually attained with O_2 in soil solution and that soluble organics may reduce Fe^{3+} even when O_2 is present. Alternatively, reduced zones may exist in aerated soils because of slow O_2 diffusion into micropores, or the O_2-H_2O half-reaction may not be the appropriate one to express the oxidative potential of O_2 (see discussion in section 7.2a).

Various natural polyphenols in soils, including those in humic acids, can reduce Fe^{3+} to Fe^{2+} , for example:



Processes such as this one maintain detectable concentrations of Fe^{2+} in many soil solutions despite the presence of dissolved O_2 . Commonly, though, Fe^{2+} reacts *faster* with oxygen when these humics are present than when they are not, that is,



When reactions 7.53 and 7.54 are combined, it is seen that no net change in the oxidation state of Fe has occurred. Instead, the $Fe^{3+}-Fe^{2+}$ system has merely acted as a catalyst for the oxidation of the humic acid by O_2 .

Metal-complexing ligands, including humic and fulvic acids, by preferentially complexing with Fe^{3+} or Fe^{2+} actually shift the redox potential of soil solutions. This fact can be illustrated simply by considering the Nernst equation for the Fe^{3+}/Fe^{2+} redox couple (see Table 7.1):

$$E_h = E_h^0 (Fe^{3+}-Fe^{2+}) - 0.059 \log \left[\frac{(Fe^{2+})}{(Fe^{3+})} \right] \quad (7.55)$$

The redox potential of solution, E_h , is solely determined by the Fe^{2+}/Fe^{3+} activity ratio in this case. If the pH is kept very low so that dissolved Fe^{3+} does not hydrolyze to form Fe-hydroxy species, then this activity ratio in solution is approximated closely by the ratio of the total dissolved Fe^{2+} to Fe^{3+} . Once a complexing ligand is put in solution, the activity of one of the metal ions is lowered relative to the other, and the redox potential changes. For example, fluoride complexes much more strongly with Fe^{3+} than with Fe^{2+} , lowering the activity of Fe^{3+} relative to Fe^{2+} . According to equation 7.55, the consequence

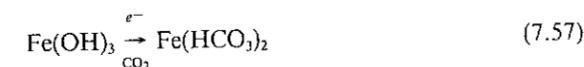
is a *decrease* in the redox potential. In chemical terms, this means that the tendency of Fe^{3+} to be reduced is diminished because complexation stabilizes the oxidized state of iron. Most natural organic complexing agents in soil solutions, being "hard" bases with oxygen ligands, would similarly stabilize oxidized iron and decrease the redox potential.

Realistically, it should be recognized that precipitated forms of Fe^{3+} are present in the soil in addition to soluble Fe^{3+} and Fe^{2+} . That is, the more appropriate half-reaction is the $Fe^{2+}-Fe(OH)_3$ couple (see Table 7.1). For this couple, the Nernst equation gives

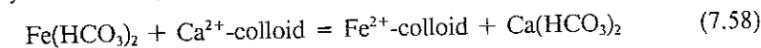
$$E_h = E_h^0 (Fe(OH)_3-Fe^{2+}) - 0.059 \log \left[\frac{(Fe^{2+})}{(H^+)^3} \right] \quad (7.56)$$

Now we find that the redox potential is pH dependent because the Fe^{3+} activity is controlled by the solubility product of $Fe(OH)_3$ (or some other very insoluble mineral of Fe^{3+}). If the solution pH is increased, precipitation stabilizes the oxidized form of iron and the redox potential of the Fe system is lowered. If a ligand capable of forming soluble complexes with Fe^{3+} is added to the system, it will dissolve part of the $Fe(OH)_3$, increasing the total soluble Fe^{3+} . However, because this dissolution has no effect on the activity of the free Fe^{3+} and Fe^{2+} ions (free Fe^{3+} is controlled by solubility of the ferric oxide), the redox potential in this case is unaffected by the complexing ligand—at least, once equilibrium is established.

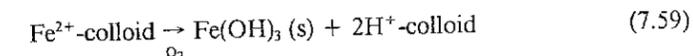
Fluctuating water tables are common in many soils, creating alternating aerobic and anaerobic conditions. During wet periods, iron oxides undergo reduction, with organic matter (directly or indirectly) supplying the electrons:



The Fe^{2+} ions may then occupy a significant fraction of exchange sites on the soil colloids (clays and humus):



Because $Ca(HCO_3)_2$ is a soluble salt that can be leached out of the soil, there may be a tendency for exchangeable Fe^{2+} to accumulate as base cations are lost. Once the soil drains, aerobic conditions again prevail, and Fe^{2+} oxidation generates acid soils:



The overall process of soil acidification by alternating iron reduction and oxidation, diagrammed in Figure 7.10, is termed *ferrolysis*. A hardpan of iron oxide may build up at the interface of the aerobic and anaerobic zones if the water table tends to perch at a particular position in the soil profile. Magnetite, Fe_3O_4 , a black oxide containing iron in both the reduced and oxidized state, is sometimes formed at this interface. In the Fe stability diagram (Figure 7.9), magnetite would appear above pH 6 over a narrow range of p_e at the interface of the reduced and oxidized forms of Fe.

The accumulation of acidity in the surface soil by ferrolysis is a localized process, enabled by the spatial separation of acid-generating Fe^{2+} from the alkaline bicarbonate ion. It occurs only where drainage permits bicarbonate to leach through the soil profile.

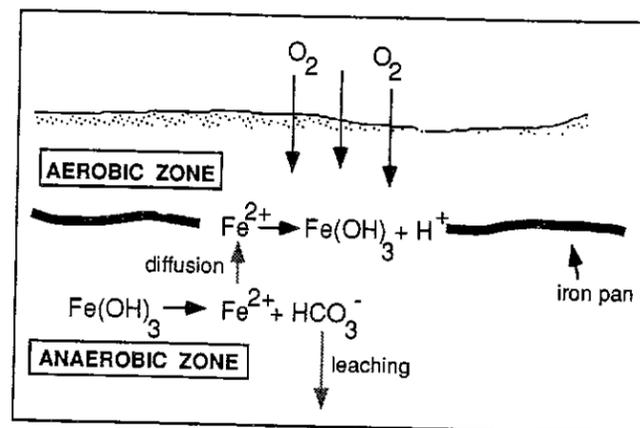


Figure 7.10. Schematic description of ferrolysis in a soil with a perched water table.

7.2d. The Carbon Cycle

Solar radiation, by the process of photosynthesis,¹ provides the energy to create simultaneously within plant cells both molecular oxygen (positive p_e) and pockets of strongly reducing conditions (negative p_e). This is a state of extreme disequilibrium at the subcellular level. The localized reducing conditions converts CO_2 to reduced organic compounds possessing high energy C-H (as well as organic N, S, and P) bonds. In effect, solar energy raises the oxidation state of oxygen atoms while lowering that of carbon atoms, as illustrated schematically in Figure 7.11. Nonphotosynthetic organisms then use O_2 to oxidize the energy-rich organics, returning the system to "equilibrium."

In aerobic soils, in fact, the only stable forms of carbon are CO_2 , HCO_3^- , and CO_3^{2-} ; all soil organic matter is potentially susceptible to oxidation by O_2 . While the persistence of humus in soils for years, even centuries, may seem to belie this statement, the redox reaction moves slowly but inexorably in the direction of equilibrium. The reduced forms of carbon in the soil organic matter provide the energy (and electrons) that drives the "engine" of chemical reduction under water-saturated conditions.

7.2e. The Nitrogen Cycle

The most stable chemical form of nitrogen in aerated soil solutions is nitrate (NO_3^-), yet N_2 gas is prevalent in the air of soil pores. Oxidation of N_2 to nitrate, a thermodynamically favored reaction in aerated soils, is made difficult by the high bond order of N_2 . The N-N triple bond has a formidably high dissociation energy of 225 kcal/mole, and biological organisms have not evolved enzymatic systems to

1. Photosynthesis is a complex sequence of catalyzed redox reactions, using the energy of photons absorbed by plant pigments. Clusters of Mn atoms in +3 and +4 oxidation states are now known to catalyze the water splitting reaction that generates O_2 .

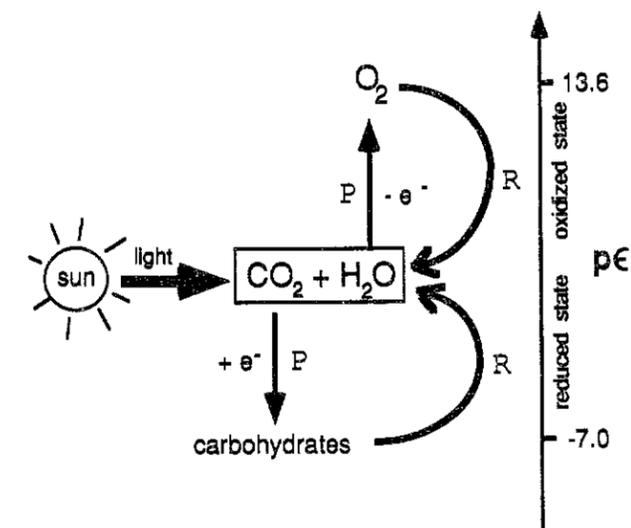


Figure 7.11. Schematic description of the carbon cycle, placing respiration (R) and photosynthesis (P) on a redox scale.

achieve the difficult oxidation to NO_3^- . On the other hand, the reverse reaction, reduction of NO_3^- to N_2 , is favored under moderately reducing conditions ($-4 < p_e < 12$). Termed *denitrification*, it proceeds by an indirect pathway through intermediates including nitrite (NO_2^-) and N_2O . Denitrification accounts for significant losses of nitrogen from wet, but not necessarily flooded, soils.

Under strongly reducing conditions ($p_e < -4$), N_2 reduction to ammonium (NH_4^+) is thermodynamically possible, and when it occurs as an enzyme-catalyzed reaction in plants and algae is referred to as *nitrogen fixation*. In these N-fixing organisms, extreme reducing conditions are maintained at the subcellular level to permit the enzymatic system to catalyze N_2 reduction. Enabling this reaction is costly to the plant in terms of the energy invested. With the high energy required to break the triple N-N bond, only a few organisms have evolved with enzymes capable of reducing N_2 .

Although chemical reduction of N_2 to ammonium by reaction with H_2 gas is thermodynamically possible at room temperature, the reduction proceeds only at very high temperature. Consequently, abiotic nitrogen fixation is not feasible even in strongly reduced soils.

The various nitrogen redox reactions are depicted in Figure 7.12, illustrating the oxidation state of the possible chemical forms.

7.2f. The Sulfur Cycle

In aerobic soils, sulfate (SO_4^{2-}) is the stable form of sulfur. Strongly reducing conditions cause sulfate to be reduced biologically to hydrogen sulfide (H_2S), a foul-smelling gas that dissolves readily in water according to the reaction:

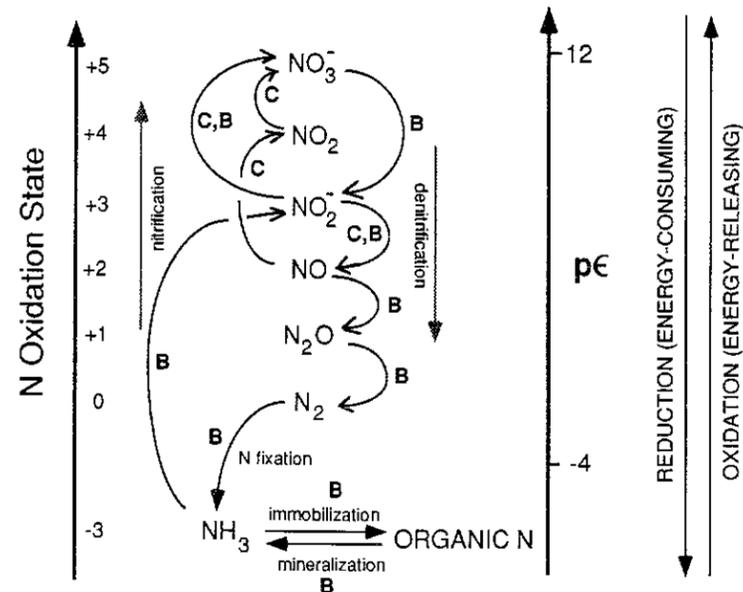
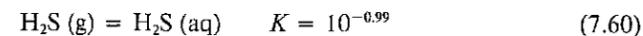
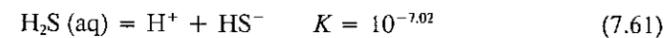


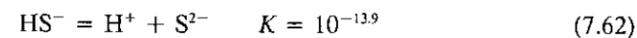
Figure 7.12. Schematic description of the nitrogen cycle, placed on a redox scale.



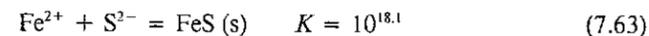
and dissociates in nonacid solutions:



A further dissociation step produces the sulfide anion:



which forms highly insoluble precipitates in anaerobic soils by reaction with Fe²⁺ and a number of other transition and heavy metals. For example, the reaction:



limits Fe²⁺ solubility to very low levels in strongly reduced soils, whereas in moderately reduced soils, *siderite* (FeCO₃) may limit solubility to a degree determined by the CO₂ partial pressure.

Submerged soils commonly contain iron sulfides, or *pyrites*, with formulas ranging from FeS to FeS₂, which, once the soils are exposed to air by a fluctuating water table or drainage, begin to oxidize by biological and chemical means. The reaction pathway in soils and sediments submerged in sulfate-rich water, typically found on coastal margins of oceans, is illustrated in Figure 7.13. The acidity generated by sulfide oxidation, once these sediments are drained, can produce extremely low pH (3.0–3.5) along with sulfate minerals such as jarosite and gypsum. Soils showing evidence of acidifying weathering reactions and the associated sulfate minerals are called *acid sulfate soils*. Although usually located on coastal margins, these soils can occur

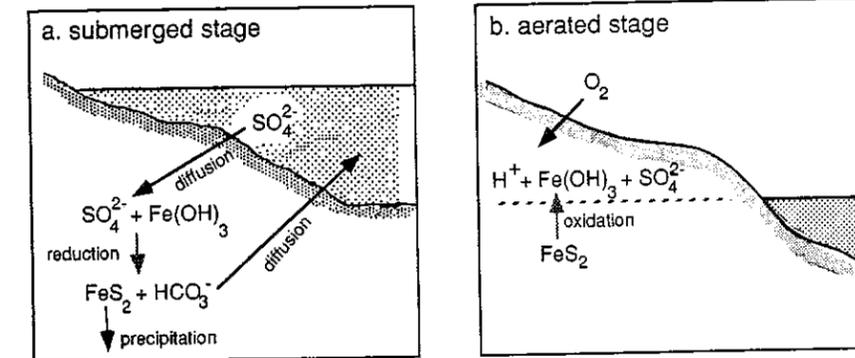
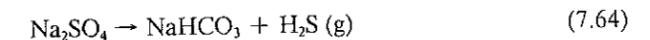


Figure 7.13. Process of sulfide accumulation (submerged stage) and acid sulfate generation (aerated stage) on a seacoast.

inland because pyrite-rich sedimentary deposits may be located along old coastlines. Furthermore, mining operations often bring pyritic tailings to the surface where oxidation generates extreme acidity in the form of sulfuric acid (see Figure 7.13b). Leachate from such sites poses a hazard because the acid dissolves and mobilizes toxic heavy metals in the rock (e.g., lead, cadmium, copper).

In semiarid climates, sulfate deposits in the soil are sometimes reduced under conditions of poor drainage. The conditions necessary for reduction are created in natural basins where water accumulates due to the very low water permeability of sodic soils. The sulfate reduction reaction:



allows hydrogen sulfide to escape to the atmosphere, while alkalinity in the form of NaHCO₃ accumulates as water evaporates at the soil surface. In this situation of poor drainage, the sulfate-sulfide reduction reaction has the overall effect of adding alkalinity to the soil. (The reverse reaction of iron sulfide oxidation adds acidity, but occurs in situations of better drainage.)

Wetlands of humid climatic zones often emit H₂S, as is evident from the rotten-egg odor of marshes and swamps. As long as the dominant exchangeable base cations are Ca²⁺ and Mg²⁺, which is the case in most freshwater wetlands, H₂S formation should not cause the soils to become strongly alkaline. In these nonsodic soils, alkalinity generated by reduction forms precipitates of Ca (and Mg) carbonates. The low solubility of these carbonates prevents the pH from rising much above 8. In sodic soils, however, reaction 7.64 causes alkalinity to build up in the form of soluble Na carbonates (see Chapter 8, Section 8.1).

7.3. REDOX REACTIONS AT MINERAL SURFACES

Clays and oxides have the ability to promote certain redox reactions such as the oxidation of phenols and aromatic amines. These are surface reactions, involving an adsorption step and electron transfer step, unlike many of the chemical reactions

discussed in the previous sections of this chapter which were assumed to be redox processes of homogeneous solutions. Soil minerals known to be reactive as electron acceptors include ferric oxides, manganese oxides, and Fe^{3+} -bearing layer silicate clays.

Surface-localized redox reactions can be viewed as the transfer of an electron between one particular surface metal ion and an adsorbed molecule, with a change in the oxidation state of the metal ion. This is a reasonable description if electrons have no mobility in the mineral; that is, if the mineral is an *insulator*. However, some minerals are *semiconductors* or *conductors*, in which case electron transfer might be better described as insertion of electrons into (or extraction of electrons from) the overlapping electronic orbitals of the solid. The resultant electron excess or deficit is then delocalized over the solid, not associated with one particular metal ion at one surface location.

In the *band theory* of solids, the overlapping atomic orbitals of the solid form "bands" of many energy levels, rather than a single energy level, as diagrammed in Figure 7.14. The orbitals occupied by the valence electrons constitute the *valence band*, while the first excited state of the electrons, normally unoccupied, is the *conduction band* of the solid. The bands of even higher excited states generally overlap the conduction band, creating a continuum of allowed electronic energy levels from E_c , the energy level at the bottom of the conduction band, out to infinite energy.

Most silicate clays and oxides are insulators and semiconductors, types of solids that possess a *band gap*—a nonallowed region of energy, E_g , between the filled valence band and empty conduction band (see Figure 7.14). This gap prevents electron flow in these minerals, so that they are nonconducting. In the solid, the *Fermi*

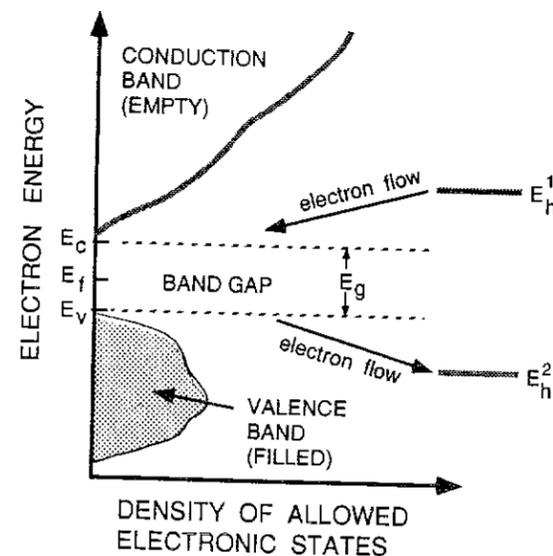


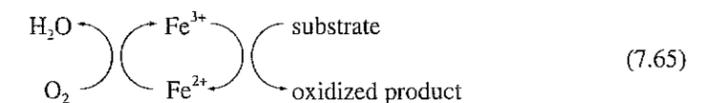
Figure 7.14. Scheme of electronic energy levels in semi-conducting solids. E_h^1 and E_h^2 refer to electronic energy levels of molecules in solution that may, respectively, donate electrons to or accept electrons from the solid.

energy, E_f , defines the electrochemical (redox) potential of the electrons; it is the energy level above which all levels are unoccupied and below which all levels are filled. For insulators and semiconductors, since the valence band is almost completely filled while the conduction band is essentially unoccupied, the Fermi energy falls within the bandgap region. This E_f of the solid is somewhat analogous to the E_h of redox couples in solution, so that the relative energy levels of E_f and E_h tend to determine the direction of electron flow between the solid and reducible or oxidizable molecules in solution. The electron flow, depicted schematically in Figure 7.14, must ultimately reach an equilibrium such that E_f and E_h are equalized. If, for example, the solid is initially able to oxidize molecules adsorbed from solution, electrons flowing into the solid from the molecules cause the Fermi energy to rise. Reduction of the solid continues until the Fermi energy rises enough to balance the solution redox potential.

Many soil minerals of interest, including Fe oxides, behave as insulators. However, minerals characterized by metals with mixed oxidation states, such as Mn oxides,¹ are often semiconductors or conductors, in which case electron flow through the conduction band of the solid is possible. Oxidation of dissolved molecules by these types of solids can be viewed as the transfer of electrons from solution and insertion into the conduction band. For example, Mn oxides can oxidize NO_2^- to NO_3^- without release of Mn^{2+} to solution. The electrons accepted by the oxide from NO_2^- are delocalized in the solid so that no Mn^{2+} is released.

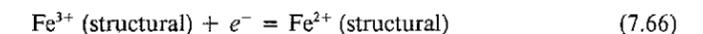
Mn oxides are versatile oxidants. They can oxidize Co^{2+} to Co^{3+} , Cr^{3+} to Cr^{6+} (chromate), As^{3+} to As^{5+} , and phenols and aromatic amines to polymeric products. Some of the organic degradation reactions are discussed in more detail in Chapter 10.

In many cases in which structural or adsorbed Mn and Fe of minerals act as oxidizing agents, the mineral is only the catalyst, because O_2 ultimately reoxidizes the reduced Mn or Fe in the mineral, as follows:



The reaction is much faster with the mineral present, although the reasons for this are not fully understood. After all, O_2 as an oxidant is theoretically more powerful than $\text{Fe}(\text{OH})_3$ and as powerful as MnO_2 (see Table 7.1)

It is interesting to speculate about why the mineral surface should react much more rapidly than molecular oxygen with a substrate. One explanation might be that Mn^{3+} in oxides has a higher reduction potential than O_2 (see Table 7.1). However, such comparisons of reduction potentials should be made with caution. In the case of O_2 , the half-cell reaction is that of a homogeneous solution-gas mixture. In the case of metals such as Fe^{3+} in the octahedral sites of silicate clays, the reduction is a solid-state reaction:



1. Manganese in the structure of these oxides can have a mixture of oxidation states +2, +3, and +4.

which is quite different from the $\text{Fe}^{3+} - \text{Fe}^{2+}$ half-cell reaction in solution whose potential is given in Table 7.1. In fact, the reduction potential for reaction 7.66 is not known.¹ Similarly, the potentials for reduction of structural Mn^{4+} or Mn^{3+} in Mn oxides to lower oxidation states *within the solid* are unknown. The $\text{Fe}(\text{OH})_3 - \text{Fe}^{2+}$ and $\text{MnO}_2 - \text{Mn}^{2+}$ reaction potentials given in Table 7.1 are appropriate only for those particular solid forms of iron hydroxide and manganese oxide in which reduction releases Fe^{2+} or Mn^{2+} to solution. Electron transfer processes within the solid state are not described by standard-state potentials such as those listed in Table 7.1. They are complicated by the electron-conducting properties of the solids, and involve intermediate states of reduction or oxidation within the solids. The band theory of solids indicates that electron transfers in conducting and semiconducting minerals can occur without any particular atom changing valence by an integral amount. This property facilitates electron flow into and out of the mineral, and may account for the ease with which part of the structural Fe^{3+} in Fe-rich smectites is reduced to Fe^{2+} .

In solids, the immediate structural environment (crystal field) of a metal ion is likely to alter its reduction potential. For example, Fe^{3+} substituted in a silicate has a potential different from Fe^{3+} in $\text{Fe}(\text{OH})_3$, and different again from Fe^{3+} in solution. Structures that stabilize Fe^{3+} relative to Fe^{2+} lower the reduction potential of Fe^{3+} in the solid. Solution properties such as pH are likely to affect these potentials in a manner different from the way they affect solution potentials. It is interesting that, in a recent study of biotite subjected to weathering in the presence of Cu^{2+} , the reduction of adsorbed Cu^{2+} to metallic copper (Cu^0) has been demonstrated (Earley et al., 1992). Reduction of Cu^{2+} by Fe^{2+} in soil clays is also known to occur. Although Cu^{2+} reduction by solution Fe^{2+} is not favorable, structural Fe^{2+} in the octahedral sheet of 2:1 silicate minerals seems to be a much more potent oxidant than aqueous Fe^{2+} . This is explained by the high stability of Fe^{3+} relative to Fe^{2+} in octahedral sites of silicates and oxides.

It appears from the above discussion that the reduction potentials of many solid phases in soils, such as Mn oxides of mixed oxidation state or Fe^{3+} -bearing layer silicates cannot be gauged by classical electrochemical concepts. The question of whether molecular oxygen or a particular mineral is the more potent oxidizing agent in soils is a complex one, since kinetic as well as thermodynamic factors come into play. That is, properties other than intrinsic reduction potential probably contribute to the effectiveness of Fe- and Mn-bearing minerals as oxidants relative to O_2 . As opposed to dissolved O_2 , which oxidizes molecules through chance encounters in three-dimensional solutions, mineral surfaces may attract substrate molecules electrostatically or by some other form of bonding, thereby concentrating them in two dimensions. The probability of electron transfer with adjacent structural Fe or Mn ions is then enhanced, as is the chance of direct reaction with dissolved O_2 . Examples of reactions that seem to be promoted in this way include: (1) Benzidine oxidation by birnessite (a Mn oxide) and smectites, (2) phenol oxidation by Mn and Fe oxides, and (3) Cr^{3+} oxidation by Mn oxides. In each case, the substrate is adsorbed to the surface prior to electron exchange, either by electrostatic attraction (in the case of benzidine cations), complexation with surface metal cations (in the case of phenols), or coordination to surface oxyanions (in the case of Cr^{3+}). Intimate association at the surface is probably a necessary preliminary step to electron transfer between dissolved molecules and minerals.

1. Part of the structural Fe^{3+} in smectites can be reduced to Fe^{2+} by dithionite and other moderate reducing agents.

Mineral surfaces containing structural Fe^{3+} and Mn^{3+} , besides increasing the probability for reductant-oxidant encounter, are facile one-electron acceptors, unlike molecular oxygen.¹ Oxidation of organics at these mineral surfaces seems not to be constrained by the rule of spin parity that limits the reactivity of O_2 (see section 7.2a). Again, chemical factors besides the magnitude of reduction potentials appear to favor heterogeneous oxidations by soil colloids over homogeneous oxidations by molecular oxygen.

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Suggested Additional Reading

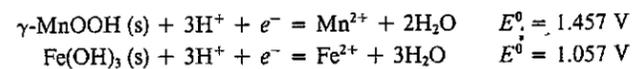
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Questions

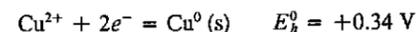
- Why is the oxidation of most organic compounds energetically favorable? Which are the best electron acceptors for the biological oxidation of organic matter in soil?
- Part of the soluble iron in soil solutions of spodosols is in the form of Fe^{2+} .
 - Calculate the expected "half-life" of 10^{-4} molar Fe^{2+} , assuming the solution is aerated and at pH 6. Repeat the calculation for pH 5 (use equation 7.47).
 - Explain the persistence of soluble Fe^{2+} in these well-drained soils, given that they contain significant dissolved organic matter.
- Why are electrode-measured redox potentials and thermodynamically defined redox potentials not necessarily the same in soil solutions?
- A soil solution at pH 5 contains $10 \mu\text{g}/\text{ml}$ of NO_3^- and $1 \mu\text{g}/\text{ml}$ of Fe as Fe^{2+} . No soluble Fe^{3+} is detected.
 - Are the ions in this solution at thermodynamic equilibrium?
 - Can a theoretical redox potential be defined for this solution?
 - Estimate the E_h that a Pt electrode would report for this solution.

1. The Mn^{4+} ion in pyrolusite (MnO_2) is rather inert in oxidation reactions, evidently because the one-electron $\text{Mn}^{4+} - \text{Mn}^{3+}$ reduction step is not a very favorable reaction.

5. For the following systems of waterlogged soils, estimate the p_e assuming that the redox reactions are at equilibrium:
- Soil solution with traces of dissolved O_2 ; pH is 7.
 - Soil containing both $Fe(OH)_3$ and $FeCO_3$; pH is 6.
 - Soil solution containing sulfate at $10^{-4} M$ and with the smell of hydrogen sulfide gas; pH is 6.
 - Soil containing MnO_2 ; solution has $10^{-5} M Mn^{2+}$ and pH is 7.
 - Soil air contains nearly equal amounts of carbon dioxide and methane.
6. The following reactions in some cases can control the solubility of Fe^{2+} and Mn^{2+} in soil solutions:

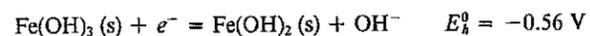


- Derive an equation that defines the relationship between soluble Fe^{2+} and Mn^{2+} in soil solution at equilibrium with $MnOOH$ and $Fe(OH)_3$. What does this equation predict the activity of Fe^{2+} to be when the activity of Mn^{2+} is 10^{-5} ?
 - Calculate the E_h and p_e of this soil if the pH is 7 and Mn^{2+} activity is 10^{-5} .
 - If molecular oxygen were introduced into this anaerobic soil system, what would be the likely sequence of chemical processes?
 - Mn oxides are often intimately associated with Fe oxides in soils. Can you develop a plausible mechanism to explain this association?
7. Should Fe^{2+} in soil solution be able to reduce nitrate to nitrite? If so, what pH would be favorable to reduction?
8. A recent observation (Bartlett and James, 1992) was made that a solution at pH 4.2, containing hydrolyzed Fe^{3+} and Cr^{3+} , formed Fe^{2+} and chromate (CrO_4^{2-}) simultaneously on exposure to light. Dissolved O_2 did not seem to be necessary for the reaction.
- Propose a mechanism for this reaction.
 - What would you expect to happen when the light is turned off?
9. Biotite is an Fe^{2+} -rich mica that weathers easily to release K^+ from the interlayer regions. When it is weathered in the presence of Cu^{2+} , the reduction of adsorbed Cu^{2+} to metallic copper (Cu^0) in the interlayer has been demonstrated (Earley et al., 1992).
- Calculate the potential and free energy of the $2Fe^{2+} + Cu^{2+} = 2Fe^{3+} + Cu^0$ reaction in solution under standard-state conditions, using the known reduction equation:



Is the reaction favorable in solution?

- Since the electron transfer actually involves Fe in the solid state, the reduction equation:



seems to be an appropriate model for the biotite reaction. Calculate the potential and the free energy of the $2Fe(OH)_2 + Cu^{2+} = 2Fe(OH)_3 + Cu^0$ reaction at pH 7, assuming the solution activity of Cu^{2+} is maintained at 0.01. Is the formation of metallic Cu by $Fe(OH)_2$ a favorable reaction?

- How does actual Fe^{2+} oxidation in biotite differ from the model $Fe(OH)_2 \rightarrow Fe(OH)_3$ reaction?