
OXIDATION AND REDUCTION

Oxidation and reduction dramatically change the behavior of the chemical elements. *Oxidation* is the loss or donation of electrons by an element; *reduction* is the gain or acceptance of electrons. Oxidation of one substance and reduction of another always occur together—free electrons do not exist in chemical reactions. A substance can donate electrons only if another substance can accept them. The importance of oxidation–reduction (*redox*) reactions is that energy, the energy of life, is transferred by these electron transfers. Oxygen, carbon, nitrogen, and sulfur—and to a lesser extent, iron and manganese—are the primary elements that carry out electron transfer, energy transfer, in the metabolism of living organisms and in soils.

The hydrogen ion H^+ and the electron e^- have been called the two master variables that govern chemistry. Together, the availability of H^+ and e^- determines the direction and rate of almost all organic and many inorganic reactions. The availability of H^+ and that of e^- are similar conceptually but different in reality. The H^+ availability, or potential, is related to its concentration in water and can be measured by the familiar pH glass electrode. The glass membrane around the electrode shields the electrode from other possible reactions. The measurement is so good that some people define pH as the H^+ potential, even though ions cannot be measured unequivocally. The measured pH is probably very close to the H^+ potential, but we cannot know for certain. The pH electrode is the best example of *ion-selective electrodes*, where a selective membrane isolates the electrode from all substances but the desired substance in an aqueous solution.

In contrast, the e^- availability and e^- potential are measurable under some conditions, but there is no concentration of free electrons that corresponds to the H^+ concentration. Someone calculated that the concentration of free electrons is about 10^{-45} M, or about 1 free electron per galaxy. Also in contrast to H^+ , the measurement of the e^- potential is qualitative in natural systems. Because the measuring

electrode is nonselective and has no shield analogous to the glass membrane of the pH electrode, many ions and molecules can donate and accept electrons from the measuring electrode. Each substance has its own degree of electron availability and hence its own potential at the electrode. The electrode's voltage is therefore a mixed potential, a weighted sum of the potentials of all the electron transfers at the electrode surface. The potential does not represent the e^- potential of any ion or molecule at the electrode. When only one substance is present in the system, the electron's potential may be measurable if the kinetics of electron transfer between the substance and the electrode surface are favorable.

Virtually all biological reactions and many inorganic reactions in soils are redox reactions. Dioxygen O_2 is the major and final electron acceptor (*oxidizing agent*) in nature and therefore buffers the e^- availability in *aerobic* systems (where O_2 is available). Dioxygen diffuses through soil pores to plant roots, soil microbes, and inorganic substances from the atmosphere. Until the soil becomes quite wet and/or the oxygen demand is high, the oxygen diffusion rate is usually rapid enough to maintain adequate oxygen availability. Even if only the larger soil pores are open to the atmosphere, the oxygen supply can be sufficient because gas diffusion through the gas phase is 10 000 times faster than gas diffusion through water.

If the diffusion path length from the soil surface through the soil solution is long, combined with a high oxygen demand from actively metabolizing roots and microbes, oxygen may be lacking. Oxygen deprivation (*anaerobic* conditions) slows the rates of root metabolism and ion uptake, weakens plant resistance to soil pathogens, and increases the concentration of undesirable reduced ions in the soil solution. Oxygen dissolved in water in a flooded soil can supply oxygen for about 24 hours to plants.

Much of the earth's soils are flooded or very wet for part or all of the year, subsoils have restricted water drainage and low oxygen concentrations, and the interior pores of soil aggregates in aerobic soils can have considerably lower oxygen concentrations than does the atmosphere. The ocean depths have restricted access to atmospheric oxygen. We think of aerobiosis as the ideal and common state of nature, but that is egocentrism. Most of the living earth has a limited oxygen supply.

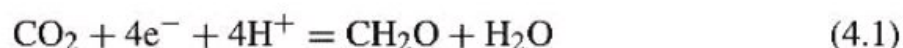
Carbon dioxide is formed when oxygen accepts electrons from carbon compounds during metabolism. The CO_2 diffuses away in the same way as oxygen diffuses toward the reaction site. If diffusion rates are slow, as in flooded soils, the CO_2 and H_2CO_3 concentrations increase and they begin to buffer pH. The pH range of oxygen-deprived regions and poorly drained soils is therefore narrower than that of well-drained soils.

Agricultural practices can change the soil's ability to supply oxygen. Irrigation, cultivation, introduced crops, lower plant densities, and the shorter growing season of agricultural crops change the soil's water content and therefore change the pore space available for gas transfer between the root zone and the atmosphere. For example, large areas of the midwestern North America have tile drains to remove the water that accumulates during the crop season and reduces oxygen availability to roots. The cultivated plants are less dense and have a shorter growing season than native plants so water accumulates more. The native plant population transpires more

water and lessens water accumulation in the soil. Cultivation destroys the large soil pores through which gases and water move most rapidly. Cultivation also destroys the organic matter content, which maintains an open soil structure and improves permeability.

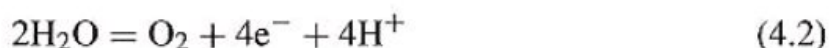
4.1 SOIL OXIDATION–REDUCTION

Redox reactions in the soil are mostly the result of a cycle started by photosynthesis. One part of the reaction is

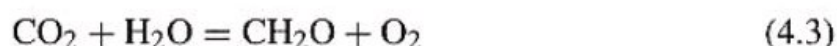


where CH_2O represents a carbohydrate. Carbon in CO_2 accepts electrons and its oxidation state changes from the C^{4+} in CO_2 to C^0 in carbohydrate $(\text{CH}_2\text{O})_n$.

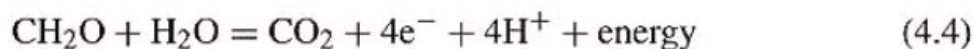
Simultaneously, the O^{2-} in water gives up electrons as it oxidizes to O^0 in O_2 :



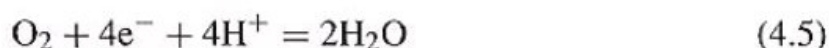
In these reactions O^{2-} is the *electron donor*, and C^{4+} is the *electron acceptor*. Equations 4.1 and 4.2 are called *half-reactions* because they describe only half of the reaction. Although half-reactions appear to imply that free electrons exist, half-reactions imply only that the other half of the reaction is unspecified. The overall reaction of photosynthesis is the sum of the half-reactions:



Respiration (oxidation) in plants and animals and oxidation in soils complete the photosynthetic cycle by utilizing the energy stored in the carbohydrates and organic compounds derived from the carbohydrates, by disposing of organic wastes, and by producing the CO_2 needed for more photosynthesis by the reaction:



To obtain the energy and complete the reaction, organisms must find an electron acceptor to accept the electrons. If oxygen is available, the half-reaction of aerobic electron acceptance is the reverse of Eq. 4.2:



Equation 4.4 summarizes the many steps of the intricate Krebs or citric acid cycle that organisms utilize to obtain the energy in a useful form. Equation 4.5 also oversimplifies the intricate mechanism of electron acceptance by oxygen in living organisms.

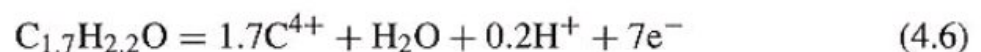
A key to obtaining the energy in organic compounds, and thus to sustain life, is to obtain an electron acceptor. Higher plants and animals can utilize only O_2 as an electron acceptor, but microbes in soils and elsewhere can also utilize the oxidized states

of nitrogen, sulfur, iron, manganese, and other elements as electron acceptors. These electron acceptors do not release all of the photosynthetic energy and retain some of the energy in the reduced states. The energy content of these reduced states makes them reactive and potential pollutants in our concept of a healthy, that is, aerobic, environment. Reacting further with O_2 changes the partially oxidized compounds to higher, more benign, oxidation states.

Redox reactions of C, N, and S compounds are catalyzed by enzymes. Catalysis is necessary because most elements exchange electrons reluctantly. Enzymes lower the activation energy of electron transfer and increase reaction rates enormously. The reluctance of C, N, and S compounds to reach equilibrium creates the metastability of carbon compounds and prevents you the reader and the paper of this page from immediately oxidizing to CO_2 . The irreversibility of electron transfer is a nuisance for physical chemists who like the simplicity of equilibrium, but is essential for life.

4.2 ELECTRON DONORS

The major electron donors in soils are the carbon compounds in living roots and microbes, in dead plant matter, and in soil organic matter (SOM). Table 4.1 shows the approximate C, H, and O contents of the two largest plant components, cellulose and lignin, and of typical SOM. For simplicity, Table 4.1 ignores the amounts of N, S, P, and other elements in these materials. Assuming that plant matter contains 1/3 lignin and 2/3 cellulose, an empirical formula for "plant matter" is approximately $C_{1.7}H_{2.2}O$. Assuming further that all the carbon in this material oxidizes to C^{4+} in CO_2 , the half-reaction of plant matter oxidation is



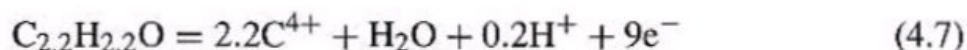
The reaction does not go to completion immediately. Some carbon remains as SOM—microbial biomass and partially metabolized by-products.

The SOM in Table 4.1 is richer in carbon than is plant matter. SOM tends to contain more aromatic (cyclic and resonating carbon-carbon bond) compounds, and contains less oxygen, than the plant matter from which it is derived. Alternatively, because cellulose oxidizes faster than lignin, the aromatic groups may represent an accumulation of aromatic carbon from unreacted lignin. All of these materials eventually oxidize in soils, but each succeeding oxidative step is much slower. The half-

Table 4.1. Approximate C, H, and O composition of lignin, cellulose, and soil organic matter (nitrogen, sulfur, and other elements are ignored)

	C(%)	H(%)	O(%)	Empirical Formula
Lignin	61–64	5–6	30	$C_{2.8}H_{2.9}O$
Cellulose	44.5	6.2	49.3	$C_{1.2}H_2O$
Soil organic matter	58	5	36	$C_{2.2}H_{2.2}O$

reaction for the oxidation of soil organic matter is



Soil organic matter contains amino ($-\text{NH}_2$) and sulfhydryl ($-\text{SH}$) groups, which also are electron donors.

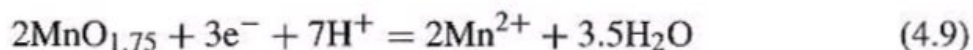
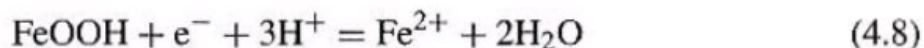
Inorganic electron donors in soils are generally in much smaller amounts and include sulfide S^{2-} , sulfur S^0 , Fe^{2+} , $\text{Mn}^{2+,3+}$, and ammonia N^{3-} . The reduced oxidation states of the trace elements Cr, Cu, Mo, Hg, As, and Se are also electron donors in soils.

4.3 ELECTRON ACCEPTORS

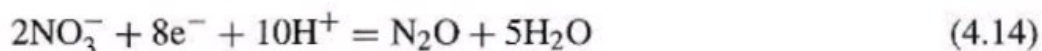
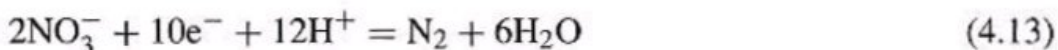
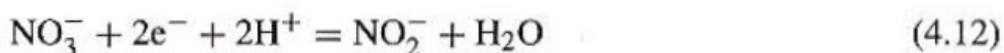
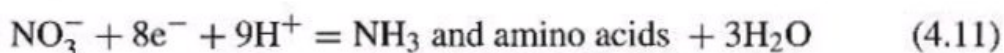
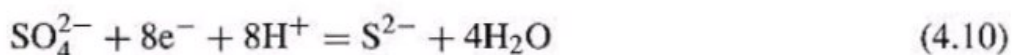
The role of soil in the oxidation of reduced C compounds is to provide electron acceptors for plant roots and microbes. Oxygen is the strongest electron acceptor in nature and yields the most energy from oxidation (Eq. 4.5). Oxygen is also the only electron acceptor that plant roots can utilize. Oxygen is made available by diffusion through soil pores and by being dissolved in the soil solution. At soil temperatures, the dissolved O_2 concentration is about 10 mg L^{-1} so that the O_2 in air and water are about the same, on a volume basis.

The O_2 supply can be insufficient because soil pores are water-filled. The O_2 supply in unsaturated soils can also be less than the microbial and plant root demand due to a large supply of readily decomposable organic matter. Plant root demand for O_2 is relatively constant while microbial demand fluctuates widely in response to organic inputs. High oxygen demand, relative to oxygen supply, also occurs in soils affected by leaks from natural gas pipes or used for organic waste disposal. Since oxygen diffusion from the surface is relatively slow, oxygen becomes deficient.

Soil microorganisms, in contrast to higher plants and animals, can utilize other electron acceptors if O_2 is unavailable. The prominent secondary electron acceptors in soils and their half-reactions are



where $\text{MnO}_{1.75}$ signifies the complex Mn(III-IV) oxides in soils.



The conditions that govern the endproducts of the nitrogen reactions are not yet well understood. The formation of N_2O (nitrous oxide) is of interest because it is a long-lived "greenhouse" gas in the atmosphere and its concentration is increasing. Nitrous oxide is often released initially after nitrate fertilizers are added to soils.

In addition to yielding less energy than O_2 , these secondary electron acceptors also yield products unfavorable to agriculture and aquaculture. The reduced oxidation states are more toxic than the oxidation states that are stable in the presence of O_2 . Ammonia and nitrite, for example, are more toxic than nitrate; H_2S is more toxic than sulfate. Reduction of Fe(III) and Mn(III–IV) can cause phytotoxic Fe^{2+} and Mn^{2+} concentrations in rice paddies. Reduction of NO_3^- to gaseous N_2 and N_2O is agriculturally undesirable because soil nitrogen is lost.

If both oxygen and secondary electron acceptors are absent, microorganisms in soils and other systems can still extract some energy from photosynthetically produced compounds by *fermentation*. Microbes can rearrange carbon compounds into more stable structures and release about 10% of the total energy in the initial compound. The products of fermentation include ethanol (C_2H_5OH), methane (CH_4), peat, and CO_2 . In geologic time, further nonmicrobial reactions produce coal and petroleum. The fermentation products retain about 90% of the original energy and are useful fuels.

Fermentation and reduction of secondary electron acceptors are temporary expedencies for soil microbes. The resulting products are unstable in the presence of oxygen and eventually oxidize further when oxygen becomes available. SOM is a beneficial result of incomplete oxidation and fermentation. The SOM content reflects the difference of the rates of organic matter addition vs. oxidation rates. The rate of addition is essentially the rate of net photosynthesis. The oxidation rate is governed by temperature and by the rate of oxygen supply.

4.4 REDOX REACTIONS

The tendency of a substance to donate or accept electrons, and the measure of the electron's availability, is given by its *electrode potential*. In principle, electrode potentials can be measured directly by an electrode and a voltmeter. All chemical elements can transfer electrons and thus change their oxidation states. Table 4.2 shows the standard electrode potentials of the half-reactions of several elements. The general reaction is



where Ox is an oxidized state of the element and Red is a reduced state.

High electrode potentials mean that Ox is available and readily accepts electrons. The halogen gases, for example, have high electrode potentials and thus are strong oxidizing agents; they want to accept electrons and be reduced. Low electrode potentials mean that Red is available and readily donates electrons. The alkali metals are strong electron donors, are strong reducing agents, and are avid electron donors.

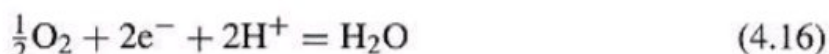
Table 4.2. Electrode potentials (reduction potentials) of selected half-reactions at 25° C. (The dashed lines show the limits of electrode potential in aqueous systems).

Reaction	Eh^0 (V)
$F_2 + 2e^- = 2F^-$	+2.87
$Cl_2 + 2e^- = 2Cl^-$	1.36
$NO_3^- + 6H^+ + 5e^- = \frac{1}{2}N_2 + 3H_2O$	1.26

$O_2 + 4H^+ + 4e^- = 2H_2O$	1.23
$NO_3^- + 2H^+ + 4e^- = NO_2^- + H_2O$	0.85
$Fe^{3+} + e^- = Fe^{2+}$	0.77
$SO_4 + 10H^+ + 8e^- = H_2S + 4H_2O$	0.31
$CO_2 + 4H^+ + 4e^- = C + 2H_2O$	0.21
$N_2 + 6H^+ + 6e^- = 2NH_3$	0.09
$2H^+ + 2e^- = H_2$	0

$Fe^{2+} + 2e^- = Fe$	-0.44
$Zn^{2+} + 2e^- = Zn$	-0.76
$Al^{3+} + 3e^- = Al$	-1.66
$Mg^{2+} + 2e^- = Mg$	-2.37
$Na^+ + e^- = Na$	-2.71
$Ca^{2+} + 2e^- = Ca$	-2.87
$K^+ + e^- = K$	-2.92

The range of electrode potentials possible in soils is limited by the stability of water with respect to oxidation and reduction. High electrode potentials can oxidize water to O_2 . Low electrode potentials can reduce water to H_2 . If a solution contains an oxidizing agent such as Cl_2 with an electrode potential greater than that of the H_2O-O_2 couple, or half-reaction, the oxidizing agent can oxidize water to O_2 :



The oxidation of water to O_2 prevents the electrode potential from rising above the electrode potential of Eq. 4.6. Strong oxidizing agents (high electrode potential) such as hypochlorite (ClO^-) and Cl_2 are unstable and decompose in soils and water by reducing to Cl^- as they oxidize water to O_2 . Although oxidizing agents stronger than O_2 should not in principle be formed in an aqueous system, N_2O is an apparent exception. Nitrous oxide has a high electrode potential, but nitrogen electron transfers are sluggish and irreversible. Not only is N_2O formed in soils, it is somewhat stable in soils and is stable for many years in the atmosphere.

Strong reducing agents, in contrast, can reduce water to H_2 :



The H^+ ion is reduced rather than H_2O , but H^+ is always present in aqueous solutions because water dissociates. The H^+-H_2 couple (Eq. 4.17) is the lower limit of electrode potential in aqueous systems and soils.

The stability of water with respect to oxidation to O_2 , and reduction to H_2 , limits the range of electrode potentials and the oxidation states possible in any system containing water. These limits are the dashed lines in Table 4.2. Dissolved F_2 and Cl_2 gases are unstable because of their high electrode potentials. The reduced states F^- and Cl^- are the stable states in water because they have accepted an electron and thereby discharged their oxidizing power. Metals are likewise unstable in water and soils because of their tendency to oxidize, to donate electrons. Their oxidized states (Al^{3+} , Ca^{2+} , K^+ , etc.) are stable in water. Table 4.2 implies correctly that the common metals are unstable and will corrode. Exceptions such as aluminium and zinc metals are metastable; an oxide layer that forms initially on their surfaces inhibits further oxidation. Soils and seawater catalyze the breakdown of these protective layers and speed up their corrosion (oxidation). Iron and steel do not form this protective layer.

For the redox couples between the dashed lines in Table 4.2, both states are stable in water and soil, depending on the electron availability. Under reducing conditions Fe^{2+} , sulfide, and ammonia are stable. If O_2 is available, $Fe(III)$, SO_4^{2-} , and NO_3^- are stable.

Soil microorganisms utilize the strongest electron acceptors available, in order to obtain the maximum energy from their food substrate. If the O_2 supply is insufficient, the next strongest electron acceptor available in soils is nitrate. The manganese(IV,III-II) redox couple may be stronger, but $Mn(IV,III)$ oxides are solids, which cannot diffuse to the microbes, so their availability is low. Nitrate reduces to amino acids, N_2 or N_2O . After oxygen and nitrate have been exhausted, $Fe(III)$ and $Mn(IV,III)$ hydroxyoxides can be reduced, and Fe^{2+} and Mn^{2+} concentrations in the soil solution increase. If the rate of electron acceptance by these acceptors is less than the availability of food sources, even stronger reducing conditions result. Microbes can reduce sulfate to sulfur or sulfide, ferment organic matter to CO_2 and methane or peat, and in extreme cases reduce water to H_2 .

The stepwise order of reduction in Table 4.3 is idealized. The rate of electron availability is usually much faster than the rate at which electron acceptors can dissolve and diffuse to the soil microbes. The reactions then overlap and several proceed simultaneously.

Under slower conditions in the laboratory, the order of utilization of electron acceptors follows the order of electron potentials at pH 7, as listed in the second column of Table 4.3. The standard electrode potentials of Table 4.2 are at pH 0. Most electrode potentials change similarly with pH, however, so the order of standard electrode potentials and of utilization of electron acceptors are similar. Appendix 4.1 describes how the pH dependence of electrode potentials can be calculated.

The third column of Table 4.3 lists the measured ranges of potentials over which each reaction occurs in soils. The potentials are measured with a platinum electrode whose potential responds roughly to the electron availability. Reasons for the difference between electrode and redox potentials are discussed in Appendix 4.2. In

Table 4.3. Order of utilization of principal electron acceptors in soils, equilibrium potentials of these half-reactions at pH 7, and measured potentials of these reactions in soils

Reaction	<i>Eh</i> at pH 7 (V)	Measured Redox Potential in Soils (V)
O ₂ disappearance $\frac{1}{2} \text{O}_2 + 2\text{e}^- + 2\text{H}^+ = \text{H}_2\text{O}$	0.82	0.6 to 0.4
NO ₃ ⁻ disappearance $\text{NO}_3^- + 2\text{e}^- + 2\text{H}^+ = \text{NO}_2^- + \text{H}_2\text{O}$	0.54	0.5 to 0.2
Mn ²⁺ formation $\text{MnO}_2 + 2\text{e}^- + 4\text{H}^+ = \text{Mn}^{2+} + 2\text{H}_2\text{O}$	0.4	0.4 to 0.2
Fe ²⁺ formation $\text{FeOOH} + \text{e}^- + 3\text{H}^+ = \text{Fe}^{2+} + 2\text{H}_2\text{O}$	0.17	0.3 to 0.1
HS ⁻ formation $\text{SO}_4^{2-} + 9\text{H}^+ + 6\text{e}^- = \text{HS}^- + 4\text{H}_2\text{O}$	-0.16	0 to -0.15
H ₂ formation $\text{H}^+ + \text{e}^- = \frac{1}{2}\text{H}_2$	-0.41	-0.15 to -0.22
CH ₄ formation (example of fermentation) $(\text{CH}_2\text{O})_n = n/2 \text{CO}_2 + n/2 \text{CH}_4$	—	-0.15 to -0.22

addition, part of the reason for the range in Table 4.3 is that the potentials were measured at soil pH values other than 7, and redox potentials are pH dependent.

Redox conditions in soils vary widely over short distances because O₂ must diffuse through pores of various sizes and water-filled pores. In aerobic soils the interior of soil aggregates may be partially anaerobic. The change from oxygen sufficiency to deficiency can occur within a few millimeters. In wet soils, only the largest pores are open to gas diffusion from the atmosphere.

Redox conditions in saturated and flooded soils can be more homogenous and redox measurements with the platinum electrode tend to be more reliable. Some water-loving plants such as rice, however, can conduct oxygen through the stem to the root. The soil immediately surrounding such roots is oxidized compared to the rest of the flooded soil. Convection currents in overlying water also bring oxygen downward, so that submerged sediments are often topped by a thin oxidized layer.

4.5 FLOODED SOILS

Ponnamperuma (1972) reviewed the chemistry of flooded soils. This research has understandably concentrated on the soil conditions of paddy rice agriculture. Only some generalizations are mentioned here. The behavior of C, N, S, Fe, and Mn generally follows that shown in Table 4.3. When rice paddies are drained before harvest, redox potentials rise, Fe²⁺ and Mn²⁺ concentrations decrease, and C, N, and S oxidize. When the soils are flooded again, the reactions reverse.

Phosphate apparently precipitates as Fe(III) and Al phosphates during the dry part of the rice culture cycle. Under subsequent reducing conditions, the Fe(III) phosphate is reduced to more soluble Fe(II) phosphate. This reduction can account for the rather high availability of phosphate for centuries in paddy soils. The Fe(III) phosphate may be slightly more stable than Al phosphate so the Al phosphate that precipitates initially slowly transforms to Fe(III) phosphate. Similar aerobic soils often supply inadequate phosphate to plants because Fe(III) phosphate remains insoluble.

A second noteworthy flooded soil is *acid sulfate* soil. Sediments along tropical and subtropical coastlines and river deltas may contain significant quantities of Fe(II) sulfides. When drained, these sulfides oxidize to H_2SO_4 and the acidic Fe^{3+} ion. The soil acidity can increase to pH 2. Such conditions are highly phytotoxic and can be remedied under aerobic conditions only by extensive leaching and lime applications. If resubmerged, acid sulfate soils revert rapidly to near neutrality as the Fe(III) and sulfate are reduced back to Fe(II) sulfides.

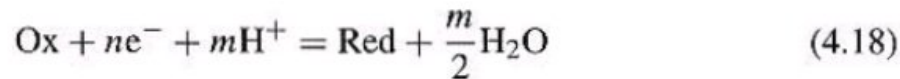
A third example of flooded soils is the extensive areas of soils rich in organic matter, peat and muck soils, or *Histosols*. The slow rate of organic matter oxidation is due to slow O_2 diffusion through stagnant water; to low concentrations of mineral nutrients; and, in the most extensive areas of *Histosols* in Canada and Siberia, to low temperatures. Peat soils are to some degree self-perpetuating. They have a high water-holding capacity, which allows them to spread up slight slopes above the water table. In warm seasons the high specific heat of water slows the warming rate of the peat. During occasional dry seasons the high thermal resistivity of peat slows warming below the immediate surface.

APPENDIX 4.1 ELECTROCHEMISTRY

Electrode, electron, reversible, and equilibrium potentials and electron activity are closely related terms for the equilibrium potential of the electron, where potential means availability and driving force. Equilibrium implies that all electron transfers are reversible, that a small change of electron potential will bring about a corresponding electron transfer. Table 4.2 lists such reversible potentials for half-reactions of some common ions. Reversible electron transfers, however, are rare. Irreversible reactions (Appendix 4.3), in which the electron transfer is hindered by an activation energy barrier, are the norm. This barrier can be overcome by extra energy or *over-voltage*. Enzyme catalysis and soil surface catalysis can reduce, but not completely remove, this activation energy barrier. As a result of irreversibility, redox reactions in soils respond sluggishly to changes in electron potential. The irreversibility is relatively low for iron reactions; carbon and nitrogen electron transfers are exceedingly irreversible.

Oxidation–reduction equilibrium also implies that the electrode potentials of all redox couples in the system are equal. Because of irreversibility, this condition is rare in mixtures of redox couples, especially in mixtures containing organic and nitrogen compounds such as the soil solution.

Despite these limitations, equilibrium is a convenient starting point from which to study redox reactions. A generalized redox half-reaction is



where Ox is the oxidized species and Red is the reduced species of the redox couple. The equilibrium equation for this reaction is

$$K = \frac{\text{Red}}{\text{Ox}(e^-)^n(\text{H}^+)^m} \quad (4.19)$$

where (e^-) has been called *electron availability*, *electrode potential*, and *electron activity*. The electron activity has no relation to ion activities in solution because the concentration of free electrons in solution is vanishingly small.

Electron (or electrode) potential is given the symbol Eh , while electron activity is associated with pe . Equation 4.19 can be transformed into the Nernst equation:

$$Eh - Eh^0 = \frac{RT}{nF} \log \frac{\text{Red}}{(\text{Ox})(\text{H}^+)^m} = -\frac{0.059}{n} \log \frac{\text{Red}}{\text{Ox}} - \frac{0.059}{n/m} \text{pH} \quad (4.20)$$

where Eh^0 is the standard electrode potential, R is the gas constant, T is absolute temperature, F is the Faraday constant, and 0.059 is the quotient of the constants at 25° C. The standard potential must be defined in terms of an arbitrary reference state because, like free energy, the absolute potential cannot be defined. The Eh^0 is related to the standard Gibbs free energy by

$$G^0 = -nF Eh^0 = -96.48n Eh^0 \quad (4.21)$$

where G^0 is in joules.

The electron potential pe is an alternative expression of electron availability. From Eq. 4.19,

$$pe + \text{pH} = \log K - \log(\text{Red}) + \log(\text{Ox}) \quad (4.22)$$

when $n = m$. Adding pe and pH is advantageous because the sum can be used as one axis of a two-dimensional graph, while the activities of the reduced and oxidized species are plotted on the other axis. Adding $pe + \text{pH}$ also makes arithmetic sense because the numerical range of pe and pH are similar. Each has approximately equal weight in the sum, in accord with their joint importance at equilibrium. Adding $pe + \text{pH}$, however, implies that both are at equilibrium, and that is rarely the case for pe . Nonetheless, $pe + \text{pH}$ diagrams can summarize a great deal of thermodynamic data and provide a picture of the behavior of chemical elements in nature.

At 25°C,

$$pe = 0.059 Eh \quad (4.23)$$

APPENDIX 4.2 *Eh* AND *pe*

The range of electrode potentials in systems containing water is limited by the stability of water with respect to oxidation and reduction (Eqs. 4.16 and 4.17). Substituting into the Nernst equation (Eq. 4.20) yields

$$Eh = Eh^0 - \frac{0.0059}{4} \log \frac{1}{P_{O_2}} - 0.059 \text{ pH} \quad (4.24)$$

for the upper limit of oxidizing conditions in soils and water, and for the lower limit,

$$Eh = Eh^0 - \frac{0.059}{2} \log \frac{1}{P_{H_2}} - 0.059 \text{ pH} \quad (4.25)$$

where P_{O_2} and P_{H_2} are the partial pressures of oxygen and hydrogen gases. Gases are essentially ideal at low pressures so the partial pressure and activity are equal. The Eh is dependent on the pH and the gas concentration but changes only 15 mV per tenfold change of P_{O_2} and 30 mV per tenfold change of P_{H_2} . The Eh limits of water, and therefore of soil and biological systems, are plotted in an Eh -pH diagram (Fig. 4.1a) at unit partial pressures of O_2 and H_2 . Water is stable between the lines; dioxygen is stable at oxidizing conditions and electrode potentials above the upper line. Dihydrogen is stable at potentials below the lower line.

Equation 4.19 can be transformed to

$$K = \frac{(H_2O)^{1/2}}{(H^+)(e^-)(P_{O_2})^{1/4}} \quad (4.26)$$

and

$$pe + pH = 20.78 + \frac{1}{4} \log P_{O_2} \quad (4.27)$$

The $pe + pH$ values range from 20.78 at highly oxidizing conditions at $pO_2 = 1$ and pH 0, to $pe + pH = 0$ at strongly reducing conditions when $pH_2 = 1$ (Fig. 4.1b).

Carbon, nitrogen, sulfur, and iron are elements that lend themselves to redox considerations. Interested readers should consult Pourbaix (1966) and Garrels and Christ (1965) for Eh -pH diagrams for other elements, or Lindsay for $pe + pH$ plots. All of these diagrams assume equilibrium and that Eh can be measured accurately. Both assumptions are questionable, but some success has been obtained measuring changes in Fe chemistry in soils. Carbon Eh -pH and $pe + pH$ diagrams are not very interesting. The stability of CO_2 totally dominates the diagrams. Carbon compounds are stable only in a narrow strip near the H^+ - H_2 boundary, that is, they are stable only under strong reducing conditions.

A4.2.1 Nitrogen

Eh -pH and $pe + pH$ diagrams can qualitatively describe nitrogen chemistry at the earth's surface, including simple interactions with biological systems. The chemistry

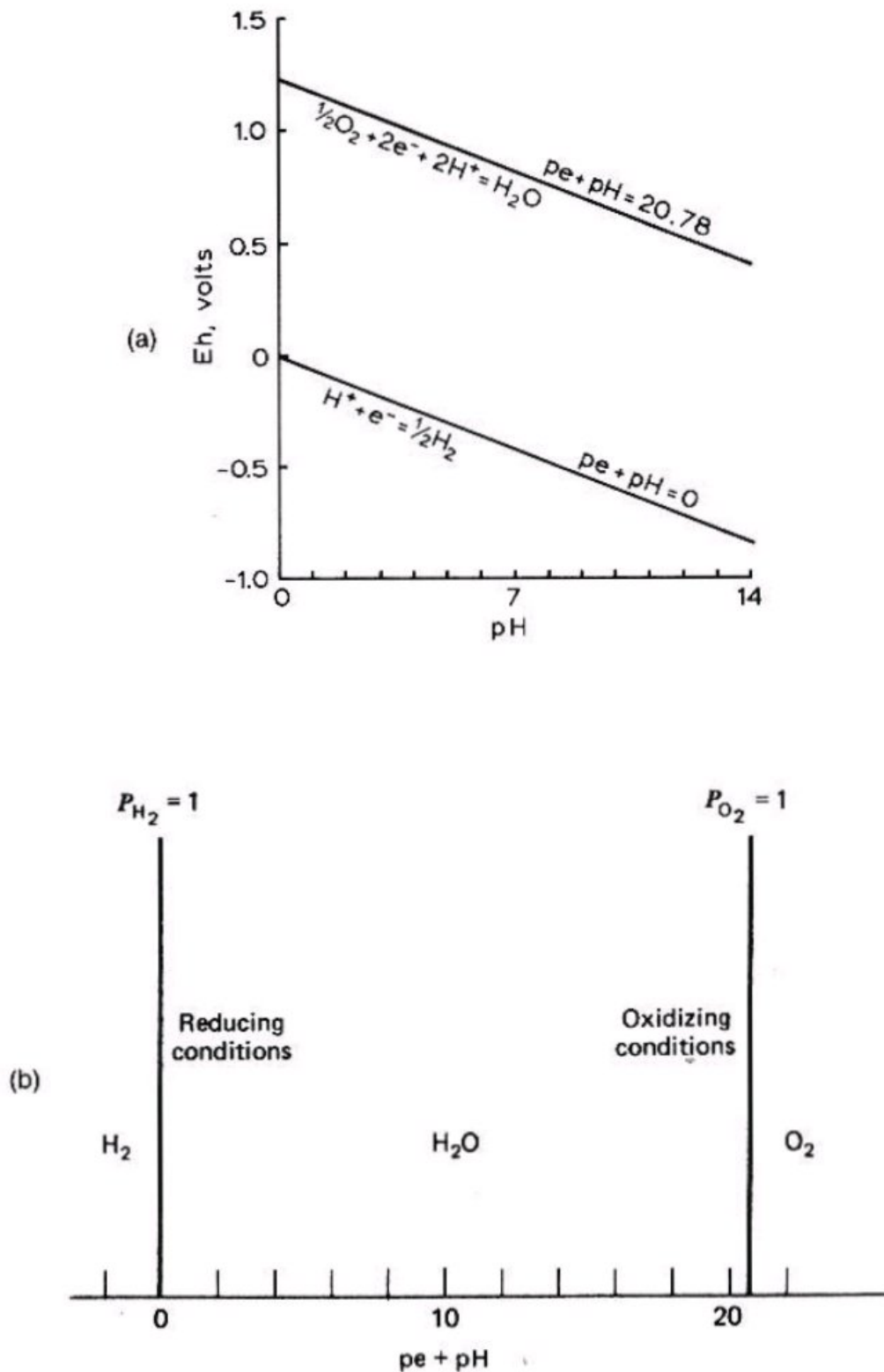


FIGURE 4.1. The range of oxidizing and reducing conditions as shown in (a) *Eh*-pH and (b) *pe* and pH diagrams. The range is defined by the breakdown of water to H_2 or O_2 .

of nitrogen is usually discussed in terms of the microorganisms and the reaction mechanisms that they carry out. Microbes and enzymes are only catalysts, however, and perform only those redox reactions that electron availability permits. *Eh* and *pe* describe that electron availability.

Nitrogen has many oxidation states that might be stable within the redox stability range of water. By comparing the electrode potentials of all possible redox couples,

the stable oxidation states can be sorted out. For example, nitrate is reduced to nitrite (NO_2^-) at $Eh^0 = 0.95$ volts (V), and nitrite reduces to N_2 at $Eh^0 = 1.25$ V. Those potentials mean that if a reducing agent is added to a nitrate solution, all of the nitrate will reduce to N_2 before the electrode potential increases enough to reduce nitrate to nitrite. Nitrite ions are therefore unstable and should spontaneously decompose to N_2 . Nitrite solutions are indeed unstable but decompose only slowly, because nitrogen redox equations are invariably irreversible.

The stable oxidation states of nitrogen within the stability limits of water turn out to be nitrate, N_2 , and ammonia. Their oxidation–reduction relationships are shown in Fig. 4.2. The stability region is dominated by N_2 . Nitrate is stable only at strongly oxidizing conditions and $\text{pH} > 3$. Ammonia is stable only under reducing conditions. Although not shown, the stability regions of NO_3^- and NH_3 are concentration dependent, increasing slightly as the their solution concentrations decrease.

Figure 4.2 also shows the stability region of the amino acid alanine ($\text{CH}_3\text{—CHNH}_2\text{—COOH}$), whose stability is typical of other amino acids. Nitrogen in alanine is more stable to oxidation than is ammonia. This accounts for the rarity of ammonia in nature compared to amino nitrogen. Ammonia is liberated when the carbon required for amino compounds disappears, such as in the composting of manure and in wastewater treatment. The alanine– N_2 boundary is shown as a dashed line because it is not a true equilibrium. Alanine is unstable with respect to oxidation to CO_2 . The alanine– N_2 boundary is a steady state and is maintained by the continuous production of amino acid precursors by photosynthesis.

A protein– N_2 boundary unfortunately cannot be calculated, because the energies of formation of proteins are not yet known. Proteins are presumably more stable than amino acids, because free amino acids such as alanine are rare in nature, while proteins are common. The protein– N_2 boundary would represent the highest potential

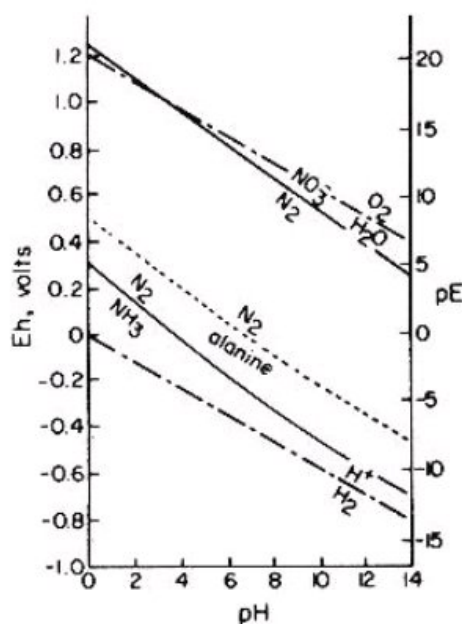


FIGURE 4.2. Eh - pH diagram of the $\text{N-H}_2\text{O-O}_2$ -amino acid system.

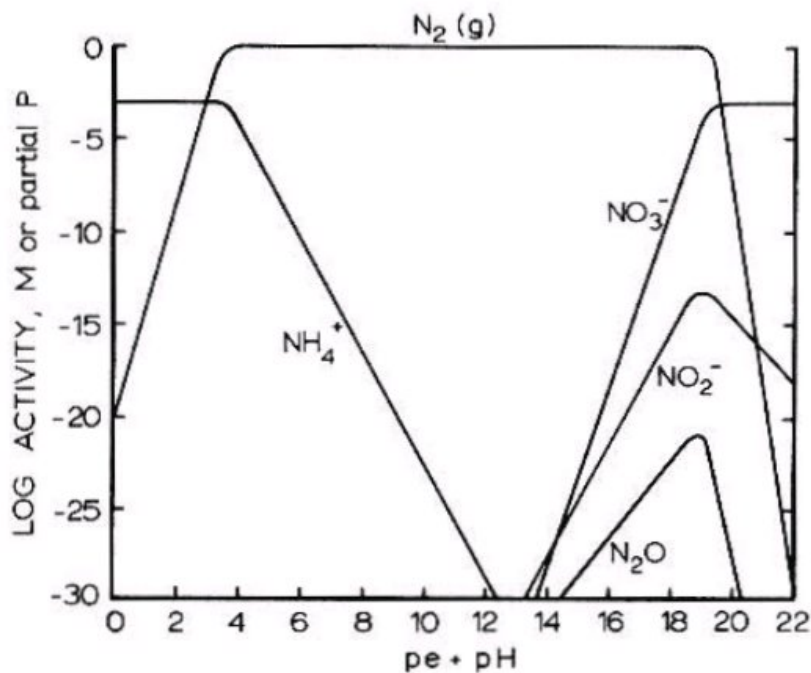


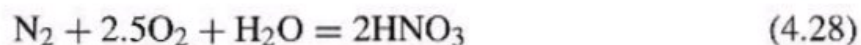
FIGURE 4.3. Distribution of soluble and gaseous nitrogen species. Total soluble nitrogen is assumed to be 10^{-3} M. (Adapted from Lindsay (1979).)

(the strongest oxidizing condition), at which N_2 could be converted to protein by soil microorganisms or other means during nitrogen fixation.

Figure 4.3 shows some $pe + pH$ relations of nitrogen. This diagram has the advantage of being able to plot the concentration dependence of the redox equilibria. The vertical axis is the aqueous activity of dissolved ions or the partial pressure of gases. The concentration of soluble nitrogen is assumed to total 10^{-3} M and the N_2 partial pressure is assumed to be that of the atmosphere, 0.78. Nitrite and nitrous oxide can be present in only exceedingly low concentrations at equilibrium. Higher concentrations of NO_2^- and N_2O (and NO and the $NO_2^- - N_2O_4$ pair) are unstable; they will tend to degrade to NH_3 , N_2 , or NO_3^- .

The Eh - pH diagram shows only the "stable" nitrogen species over the range of electron potentials in aqueous systems. The $pe + pH$ diagram shows that the "stable" species are actually only the most prominent ones. The "unstable" species are also present but in much lower concentrations.

The overall distribution of nitrogen compounds roughly follows the distribution suggested by Figs. 4.2 and 4.3. Most of the world's nitrogen exists as N_2 . Some also exists as amino nitrogen in reduced carbon compounds, living organisms, and dead organic matter. A very small fraction exists as nitrates. If equilibrium existed, the nitrate fraction would be much larger because of oxidation of organic N, and oxidation of atmospheric N_2 to NO_3^- :



Almost all the O_2 in the atmosphere would be consumed. The remaining atmosphere would contain perhaps 99% N_2 and 1% O_2 , and the oceans, rain, and "freshwaters" would be dilute HNO_3 . The reaction is fortunately hindered by the general

irreversibility of nitrogen reactions. Reaction 4.28 proceeds in the atmosphere to a limited extent when lightning provides sufficient activation energy.

Nitrogen reactions are generally highly irreversible, and enzymatic catalysis is necessary for nitrogen conversions in soils. Redox irreversibility is unfortunate from the standpoint of studying redox reactions, but is absolutely necessary for life. Reversibility would bring with it equilibrium, and all organisms would be transformed into CO_2 , N_2 , NO_3^- , and H_2O .

Irreversibility means that more energy is required to carry out, and less energy is derived from, reactions. While natural reactions are remarkably conservative of chemical energy, energy optimization is not the only criterion that determines which reactions occur. Unstable compounds, such as nitrite and nitrous oxide (N_2O), for example, would not be produced if soil microorganisms were concerned only with optimal utilization of available chemical energy. Spring thaw can bring about temporary nitrite accumulation in soils, apparently because microbial nitrite reducers respond slower to increased temperature than do the microbes that reduce nitrate to nitrite. In addition, nitrate fertilization or wetting of dry soil initially stimulates N_2O production, so that up to 25 to 50% of the nitrogen lost by denitrification can be lost as N_2O . Both N_2O and nitrite production appear to be temporary maladjustments during a flurry of microbial activity after a sudden environmental change.

A4.2.2 Sulfur

Figures 4.4 and 4.5 show the equilibrium relations of the sulfur oxidation states—sulfate, elemental sulfur, and sulfide—which are stable within the stability limits of water. The stable oxidation states are similar to those of nitrogen. Elemental sulfur, however, is much less stable than is elemental nitrogen and is stable only under acid conditions.

Figure 4.4 shows the sulfur stability regions for unit activity of sulfate and sulfide. The region of sulfur stability diminishes with decreasing sulfate and sulfide concentrations. Sulfur in the amino acid cysteine ($\text{HS}-\text{CH}_2-\text{CHNH}_2-\text{COOH}$) is more stable against oxidation than is the nitrogen in alanine. The cysteine sulfate boundary is shown as a dashed line because it is unstable at $Eh^0 = 0.31$ V with respect to CO_2 . Like alanine, the stability of cysteine is a steady state dependent on continuing production of organic compounds. The stability region of cysteine increases with increasing concentrations of sulfate compounds.

Figure 4.5 is a $pe + pH$ diagram of sulfur at pH 7 and 10^{-3} M soluble sulfur species. Only SO_4^{2-} and HS^- are stable, with the HS^- stable only under strongly reducing conditions. The soluble sulfur concentration is too low and the pH is too high to permit elemental sulfur stability. Figure 4.5 ignores organic sulfur compounds.

Sulfur redox reactions seem to be more reversible than those of nitrogen. Intermediate compounds in the reaction series from sulfate to sulfur or sulfide, and vice versa, do not appear in soils. Sulfur also differs from nitrogen in that little sulfur volatilizes from soils. Although H_2S is a gas, apparently any H_2S formed in soils reacts rapidly with Fe and other transition metal oxides to form sulfides. Some organic

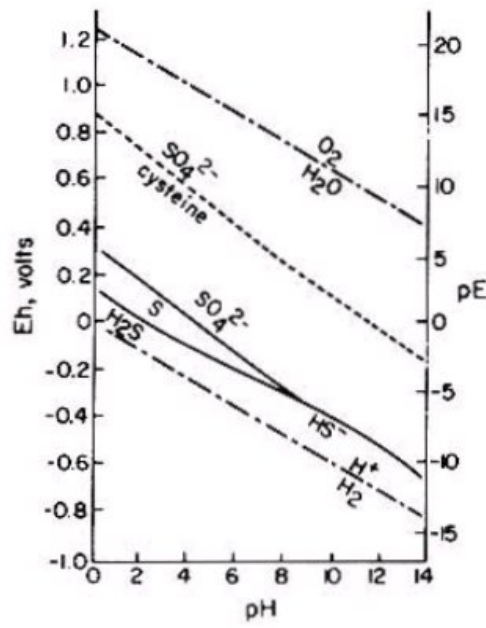


FIGURE 4.4. Eh-pH diagram of the S-H₂O-O₂-amino acid system.

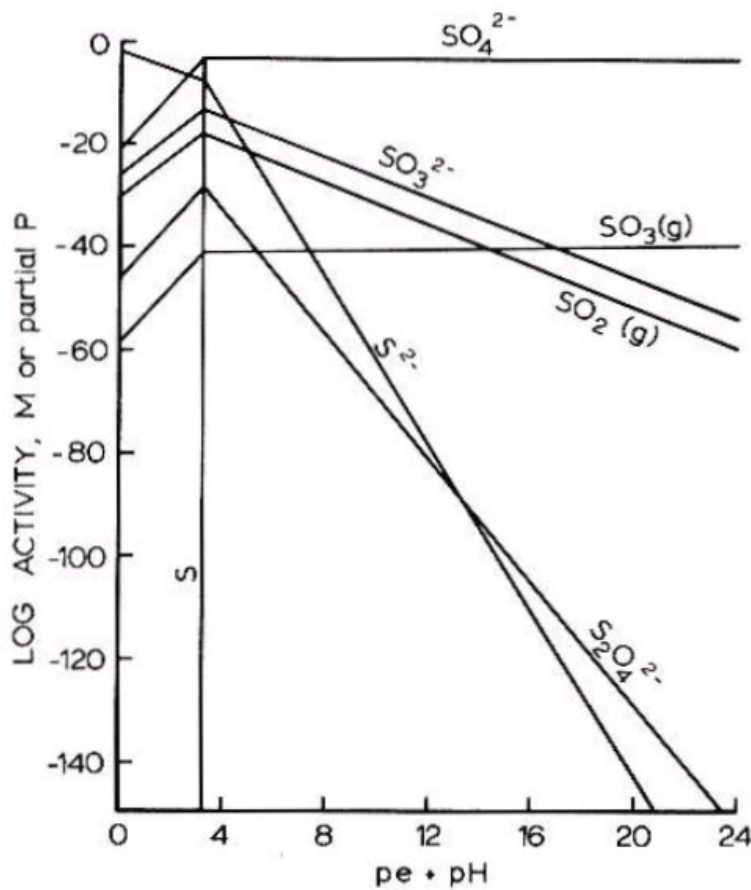


FIGURE 4.5. Distribution of solid, gaseous, and aqueous sulfur species at pH 7 and 10⁻³ M total soluble sulfur. (Adapted from Lindsay (1979).)

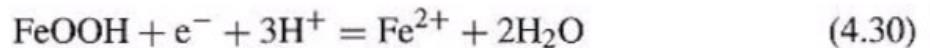
gases containing —SH groups are occasionally liberated during decomposition of fresh organic matter, but the amounts are small.

A4.2.3 Iron

Electron exchange of iron(II–III) tends to be more reversible than is electron exchange between nitrogen, sulfur, or carbon states. Iron redox reactions occur in soils without enzymatic catalysis. The Fe(II) minerals in parent material rocks oxidize spontaneously, though slowly, in aerobic soils. The electron availability for subsequent Fe redox reactions in soils is determined by microbial oxidation of carbon compounds. The reduction of Fe(III) in acid solutions is



The concentration of Fe(III) at soil pH levels is very low because of the insolubility of Fe(III) hydroxyoxides. As a result Eq. 4.29 consumes a negligible number of electrons. The major reaction by which Fe(III) accepts electrons in soils is the reduction of solid-phase Fe(III) hydroxyoxide:



Substituting Eq. 4.30 into the Nernst equation (4.20) yields

$$Eh = Eh^0 - 0.059 \left[\log(\text{Fe}^{2+}) + 3 \text{pH} \right] \quad (4.31)$$

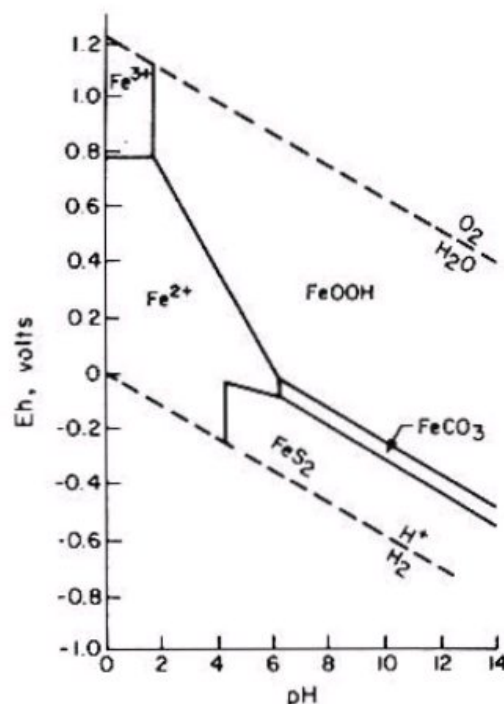


FIGURE 4.6. The *Eh*-pH diagram of various iron ions and compounds.

Equations 4.31 and the Nernst form of Eq. 4.29 are two of the boundaries in the Eh -pH diagram for Fe (Fig. 4.6). The diagram shows that FeOOH dissolves to Fe^{2+} under reduced and moderately acidic conditions. The Fe^{3+} ion predominates under strongly acidic and oxidizing conditions. Fe^{2+} and FeOOH are the predominant states in typical well-aerated soils. Goethite (FeOOH) is less stable at equilibrium than hematite (Fe_2O_3) in many free-energy tabulations, but goethite seems to govern the solution chemistry of Fe in soils.

The electrode potential of Eq. 4.31 depends on the Fe^{2+} concentration. The lines shown in Fig. 4.6 are for 10^{-6} activity of soluble Fe. Higher activities shift the equilibrium boundaries to the left. Under strongly reducing conditions FeOOH is unstable with respect to $Fe(OH)_2$, magnetite (Fe_3O_4), siderite ($FeCO_3$), and pyrite (FeS_2). The region of $FeCO_3$ stability increases with increasing P_{CO_2} . The region shown corresponds to $P_{CO_2} = 0.01$, which is not unreasonable for moist field soils.

APPENDIX 4.3 REDOX POTENTIAL MEASUREMENTS

Applying models of equilibrium oxidation–reduction, such as Figs. 4.2, 4.4, and 4.6, quantitatively to soils requires that the electrode potential be known. From the electrode potential one could then calculate the soil solution concentrations of Fe^{2+} , Mn^{2+} , and NO_3^- and the sulfate/sulfide ratio from Eq. 4.20. Ideally, the potential of an inert electrode in the system should equal the electrode potential, because the electrode should take on a potential corresponding to the electron availability. This measurement is called the *redox potential*.

Redox potential measurements are even simpler than pH measurements. A platinum electrode with its necessary reference electrode is inserted into a soil or suspension and the potential is measured with a sensitive potentiometer, such as a pH meter. Platinum is the preferred inert electrode material because of its greater response to change in redox conditions.

Table 4.3 shows, however, that redox potentials often differ greatly from electrode potentials. Ion activities are only qualitatively related to redox potentials, except in rare circumstances. One reason is that the Nernst equation applies only to equilibrium. Redox reactions in soils are nonequilibria, though in some cases for highly reduced soils, a steady state may be reached approximating equilibrium. Then only a few redox couples in the soil affect the platinum electrode and the result may approach a pseudo-equilibrium.

Second, equilibrium implies that the electrode potentials of all redox couples in the system are equal. Electrons would exchange between all redox couples until the potentials of all the available electrons are equal. In aerobic soils, this would mean that the potentials of all redox couples would have to equal the potential of the O_2 - H_2O couple because it would be a major factor. Measuring the redox potential would be unnecessary.

Third, redox couples do not necessarily transfer electrons equally or reversibly with platinum or other inert electrodes. Electron transfers between ions or molecules and electrodes are usually irreversible even in pure solutions. Reversibility is unlikely

to be greater in a mixed system such as soils. The inert electrode responds more readily to reversible redox couples than to irreversible couples. The Fe(II–III) and H^+ – H_2 couples are relatively reversible at platinum surfaces, so, if present, they strongly influence the potential of the electrode.

Fourth, the relative effect of a redox couple on the redox potential increases with the couple's concentration. A high concentration affects the potential more because the likelihood of electron transfer with the electrode is greater. The redox potential is a measure both of the amount of electron transfer and of the electrode potential. In aerobic soils the O_2 – H_2O couple is influential, despite its irreversibility, because the O_2 concentration is high.

The potential of the platinum electrode in a mixture of redox couples is a poorly defined, weighted average of the potentials of all the redox couples present. The contribution of each couple to the average potential is an unknown function of its concentration, irreversibility, and equilibrium electrode potential. The potential of a nonequilibrium mixture of redox couples is not the potential of any single couple and is a mixed potential.

Under aerobic conditions the redox potential deviates widely from the potentials of soil redox couples. In anaerobic soils, redox potentials may be more quantitatively related to ion activities. The Fe^{2+} and perhaps Mn^{2+} concentrations are high and tend to dominate the redox potential. The range of redox potentials that have been measured in soils is shown in Fig. 4.7. The envelope around those data was considered by the investigators to be the extreme limits of likely redox potentials and pH values in soils and natural waters. Redox potentials can closely approach the H^+ – H_2 potential, because it is nearly reversible at the platinum electrode.

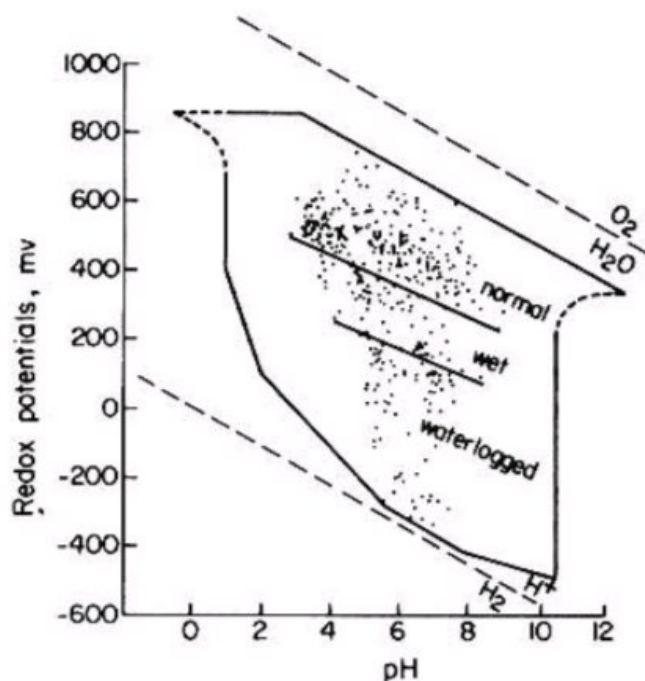


FIGURE 4.7. The range of redox potentials and pH values in soils. (From L. G. M. Bass Becking, I. R. Kaplan, and D. Moore. 1960. *J. Geol.* 68:243.)

The redox potential is pH-sensitive and should be measured in conjunction with pH. To convert redox potentials to a common pH, the conversion factor of -59 mV per unit pH is usually employed, although the change of redox potential with pH can be as great as -200 mV per unit pH during rapid redox changes. The value of -59 mV per unit pH is probably reasonable for most measurements. Reporting both the measured redox potential and the pH avoids the conversion problem. Because redox potentials are most often mixed potentials, measurements more precise than ± 10 mV have little significance.

The redox potential, like the pH, is an intensity measurement. In theory, it measures the availability rather than the quantity of electrons. Because the redox potential is governed by the potential rate of electron donation versus the rate of electron acceptance, however, it is also a crude estimate of the number of electron donors (reducing agents) present. The qualitative nature of redox measurements has discouraged their use. Redox measurements, however, are used frequently in wastewater treatment to indicate the extent of treatment necessary.

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QUESTIONS AND PROBLEMS

1. Why do redox potentials measured in soils differ from electrode potentials?
2. What electrochemical properties for redox measurements would the ideal electrode have?
3. From the elemental analyses in Table 4.1, derive the empirical formula for SOM.
4. Write the balanced reactions for the oxidation of plant matter (Eq. 4.6) and SOM (Eq. 4.7) by oxygen.
5. Write balanced half-reactions and Nernst equations for the reduction NO_3^- to N_2 and for N_2 to NH_3 .
6. What would you expect the redox potential to be in a soil of pH 7 at field moisture capacity? If the soil were at equilibrium, what should the electron potential be? Calculate the exact potential from Eq. 4.21

7. From the hydrolysis reactions of iron given in Chapter 3 and from the Nernst equation (Eq. 4.20), derive the equation for the Fe(II–III) potential as a function of H^+ activity from pH 0 to pH 14.
8. Assuming equilibrium, what is the Eh value of the O_2 – H_2O water couple at $P_{O_2} = 0.21$ (normal air), 0.20 (typical soil air), and 0.01 (perhaps typical of the air in an anaerobic soil aggregate)? What ranges of redox potentials might a platinum electrode measure in these three situations? Why do the redox potentials differ from the electrode potential?
9. Describe the likely chemical changes in a soil as it becomes increasingly anaerobic.
10. If oxidizing agents with electrode potentials greater than the H_2O/O_2 couple should not persist in aqueous solutions, why are solutions $KMnO_4$ and $NaOCl$, which are common in the laboratory and home, rather stable?
11. What redox reactions tend to “poise” the redox potentials of most soils in the “normal” region of Fig. 4.7?