# Redox equilibria in natural waters

A Chem1 Reference Text

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## Contents

Electron-transfer reactions provide the energetic basis for the life process, and through this, play a crucial role in the geochemical cycle of the elements. It all begins, of course, with photosynthesis

$$\mathrm{CO_2} \;+\; \mathrm{H_2O} \;\longrightarrow\; \{\mathrm{CH_2O}\} \;+\; \mathrm{O_2} \qquad \Delta H^\circ = +478\ \mathrm{kJ\,mol^{-1}} \tag{1}$$

in which $\{CH_2O\}$ represents the reduced carbon of glucose and its polymers. Living organisms are thermodynamically unstable and require a continual source of free energy merely to survive. This they obtain either from sunlight or from chemical free energy sources such as the carbohydrate products of the above reaction. The metabolic activities of organisms are largely centered around the stepwise breakdown of these foodstuffs in a way that transfers smaller increments of free energy to intermediates (mainly ADP) that are able to efficiently convey it to sites of synthesis or mechanical movement where it can be utilized. The overall effect can be summarized as the transfer of electrons from the reduced carbon of $\{CH_2O\}$ to an electron acceptor such as $O_2$ (this is the reverse of photosynthesis) or to $SO_3^{2-}$ or $NO_3^-$ , accompanied by the release of $CO_2$ to the environment.

It is largely through these processes that the major bio-active elements carbon, nitrogen, sulfur, iron and manganese (but not phosphorus) are moved through their geochemical cycles. From the global geochemical standpoint, the $O_2$ produced by photosynthetic organisms maintains an electron deficiency in the atmosphere and in waters in contact with the atmosphere; respiration and reactions with the reduced components of the lithosphere (including volcanic gases, substances introduced at sites of seafloor spreading, and substances leached into natural waters) act to maintain a non-equilibrium, more or less steady state between global electron sources and electron sinks.

At the same time there are some other natural redox processes that are not directly connected with the biosphere. Direct absorption of light by $Fe^{3+}$ in surface waters, for example, can result in its photochemical reduction to $Fe^{2+}$ even in the presence of oxygen, which would normally tend to drive the reaction the other way. The vents at geothermally active oceanic ridges emit considerable amounts of reduced compounds which react with oxidants such as $O_2$, $SO_3^{2-}$ and $Fe^{3+}$(all originally of biologic origin) which initiate processes which alter the composition and oxidation state of the oceans.

In order to understand these processes we will begin by reviewing the fundamental ideas of oxidation and reduction and electrochemical potentials. We will extend these concepts somewhat beyond what you may recall from earlier chemistry courses, and discuss electron activity, the electron free energy scale, and pE. This will provide the basis for the major subject of this chapter which deals with the redox state of the aquatic environment and its relation to the geobiochemistry of some of the major element. In doing so, two general principles should be kept in mind:

- Redox reactions tend to be kinetically inhibited, and are often extremely slow. As a consequence of this, redox equilibrium is rarely achieved, either in natural waters or on the Earth as a whole.
- This kinetic sluggishness, upon which life itself depends, can be overcome by suitable enzymes. Thus the major redox processes of the geochemical cycle are mediated by organisms.

# 1 Electron transfer and oxidation state

The oxidation number of an atom is a somewhat hypothetical yet useful quantity, representing essentially the electric charge the atom would possess if it were to dissociate itself from the formula unit, carrying with it only those electrons shared with other atoms having a smaller electronegativity.

The usefulness of oxidation numbers lies in the fact that many chemical reactions can be represented as involving the transfer of just the number of electrons required to change the oxidation number of the element from one characteristic value to another.

The Gibbs free energy change $\Delta G$ represents the maximum work, other than $PV$ work, that a process can deliver to the surroundings at constant pressure and temperature. In the case of an electron-transfer reaction, the oxidation and reduction steps can in principle be carried out in separate locations, so that the electrons yielded by the oxidation step are made to travel through an external circuit to the site of the reduction. The experimental arrangement in which the process is carried out in this way is known as an *electrochemical cell.* The work in this case is *electrical work*, which is the product of the charge and the potential difference through which it is transported. If the process is carried out reversibly, then the work is given by

$$\Delta G = -n\mathcal{F}E \tag{2}$$

in which $\mathcal{F}$ is 96500 C $\text{mol}^{-1}$, $E$ is the potential difference and $n$ is the number of moles of charge transported[1].

The above equation can also be written

$$E = \frac{-\Delta G}{nF}$$

which serves to emphasize the physical significance of cell potentials as intensive units expressing the number of Joules of work per mole of electrons transferred. (This is the reason that $E^\circ$ values of half reactions are *not* multiplied by stoichiometric factors when determining $E^\circ$ for an overall reaction; the presence of $n$ in the denominator of Eq 2 means that $E$ values always refer to the transfer of *one* electron.)

The various oxidation states of a given element are best listed in a manner that reveals their relative stabilities under standard conditions. The two clearest ways of doing this are by means of *Latimer diagrams* (Figure 2) and plots of standard free energies of compounds of an element in various oxidation states (1).

## 1.1 Latimer diagrams

Considerable insight into the chemistry of a single element can be had by comparing the standard electrode potentials (and thus the relative free energies) of the various oxidation states of the element. The most convenient means of doing this is shown in Fig. 2. The formulas of the species that represent each oxidation state of the element are written from left to right in order of increasing oxidation number, and the standard potential for the oxidation of each species to the next on the right is written in between the formulas. (Note that the signs of these potentials are opposite to those in Table 1 because we are writing these as oxidation instead of reduction reactions.) Potentials for reactions involving hydrogen ions will be pH dependent, so separate diagrams are usually provided for acidic and alkaline solutions (effective hydrogen ion concentrations of 1 $M$ and $10^{-14}$ $M$).

If the potential to the right of a species is more positive than the one on the left, then the its oxidation is thermodynamically favored; if the signs are reversed, then reduction is spontaneous.

An important condition to recognize is when the potential on right of a species is more positive than that on the left. This indicates that the species will tend to undergo *disproportionation*, or self-oxidation and reduction. As an example, consider $Cl_2$ in alkaline solution. Although the potential for its oxidation is negative, the potential for its *reduction* to $Cl^-$ is *positive* (+1.35 v), so the free energy necessary for the oxidation of one atom of chlorine to hypochlorite can be supplied by the reduction of another to chloride ion. Thus elemental chlorine is thermodynamically unstable with respect to disproportionation in alkaline solution, and the same it true of the oxidation product, $HClO^-$.

This might be a good time to point out that many oxidation-reduction reactions, unlike most acid-base reactions, tend to be very slow, so the fact that a species is thermodynamically unstable does not always

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[1] To relate the joule to electrical units, recall that the coulomb is one amp-sec, and that *power*, which is the *rate* at which work is done, is measured in *watts*, which is the product of amps and volts. Thus

$$1 \text{ J} = 1 \text{ watt-sec} = 1 \text{ (amp-sec)} \times \text{volts}$$

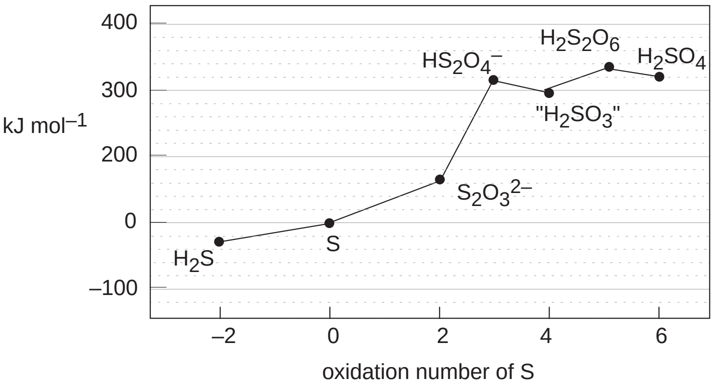
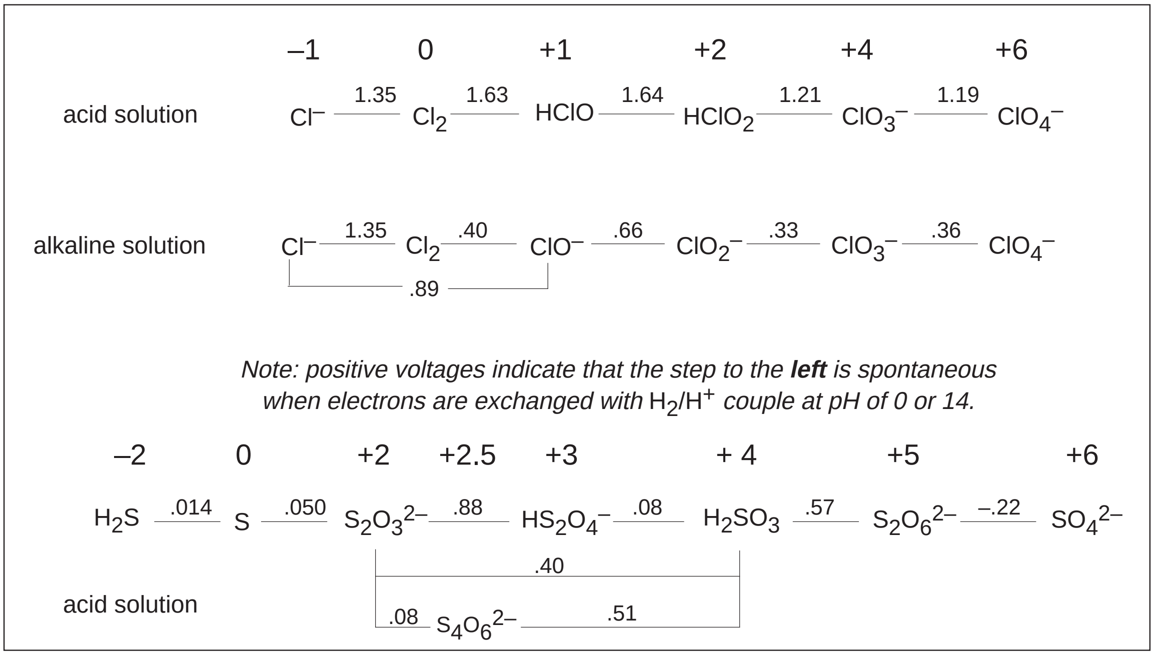


Figure 1: Free energy of sulfur in various oxidation states. (J. Chem. Ed. **54** 485 1977)



*Note: positive voltages indicate that the step to the* ***left*** *is spontaneous when electrons are exchanged with* $H_2/H^+$ *couple at pH of 0 or 14.*

Figure 2: Latimer diagrams for chlorine and sulfur in aqueous solution.

mean that it will quickly decompose. Thus the disproportionion of chlorine mentioned above occurs only very slowly. Interestingly, this process is catalyzed by light, and this is why extra chlorine has to be used to disinfect outdoor swimming pools on sunny days.

## 1.2 The fall of the electron

A table of standard half-cell potentials such as in Table 1 (page 11) summarizes a large amount of chemistry, for it expresses the relative powers of various substances to donate electrons by listing reduction half-reactions in order of increasing $E°$ values, and thus of increasing spontaniety. The greater the value of $E°$, the greater the tendency of the substance on the left to acquire electrons, and thus the stronger this substance is as an oxidizing agent.

One can draw a useful analogy between acid-base and oxidation-reduction reactions. Both involve the transfer of a species from a source, the donor, to a sink, the acceptor. The source and sink nomenclature implies that the tendency of the proton (in the case of acids) or of the electron (for reducing agents) to undergo transfer is proportional to the fall in free energy. From the relation $\Delta G° = -RT \ln K_a$, you can see that the acid dissociation constant is a measure of the fall in free energy of the proton when it is transfered from a donor HA to the solvent $H_2O$, which represents the reference (zero) free energy level of the proton in aqueous solution.

In the same way, a standard half-cell potential is a measure of the drop in the free energy of the electron when it "falls" from its source level to the hydrogen ion, which by virtue of the defined value of $E° = 0$ for $H^+/H_2$, can also be regarded as the zero free energy level of the electron.

Fig. 3 shows a number of redox couples on an electron free-energy scale. Several conclusions of wide practical importantce can be drawn from this table.

- Thus, in Fig. 3 it is seen that $Fe^{3+}$, representing a rather low-lying empty level, can accept electrons from, and thus oxidize, $I^-$, Cu*(s)*, or any higher reductant. Similarly, if $Fe^{3+}$ and $I_3^-$ are both present, one would expect a higher reductant to reduce $Fe^{3+}$ before $I_3^-$, as long the two reactions take place at similar rates.
- *Water* can undergo both oxidation and reduction. In the latter role, water can serve as an electron sink to any metal listed above it. These metals are all thermodynamically unstable in the presence of water. A spectacular example of this is the action of water on metallic sodium.
- Water can *donate* electrons to any acceptor *below* it. For example, an aqueous solution of $Cl_2$ will slowly decompose into hypochlorous acid (HOCl) with the evolution of oxygen.
- Only those substances that appear *between* the two reactions involving water will be stable in aqueous solution in both their oxidized and reduced forms.
- A metal that is above the $H^+/H_2$ couple will react with *acids*, liberating $H_2$; these are sometimes known as the "active" metals. Such metals will also of course react with water.

# 2 The Nernst equation and $E_{\mathrm{H}}$

By combining Eq 2 with the definition

$$\Delta G = \Delta G° + RT \ln Q \tag{3}$$

then for a reaction involving the transfer of $n$ moles of electrons, we can obtain the *Nernst equation*

$$E = E° - \tfrac{RT}{n\mathcal{F}} \ln Q \tag{4}$$

This diagram shows the relationship between various redox pairs somewhat more clearly than does the more traditional table of standard potentials in Table 1. Electron donors (otherwise known as reducing agents or reductants) are shown on the left, and their conjugate oxidants (acceptors) on the right.

The vertical location of each redox couple represents the free energy of an electron in the reduced form of the couple, relative to the free energy of the electron when attached to the hydrogen ion (and thus in $H_2$).

Three scales of free energy are shown. The one on the left corresponds to the standard reduction potential of the couple, which is the free energy per electron-mole (recall the relation $\Delta G^\circ = -n\mathcal{F}E^\circ$). The rightmost scale gives the corresponding energy in kilo-Joules per mole of electrons transferred, so it applies directly only to a half reaction written as a one-electron reduction. The p$E^\circ$ scale is described elsewhere in this chapter; it corresponds to $(1/n)\log K$ for the reduction of the oxidant by $H_2$. The p$E$ scale has another significance: just as pH is a measure of the availability of protons in the solution, so the p$E$ represents the availability of electrons; thus the more negative the p$E$, the more "reducing" is the solution, and the greater will be the fraction of each couple in its reduced form, with the lower ones being most strongly affected.

An oxidant can be regarded as a substance possessing unoccupied electron levels. If a reductant is added to a solution containing several oxidants, the various empty levels will be filled from the lowest up. Note however, that electron transfer reactions can be very slow, so kinetic factors may alter the order in which these steps actually take place.

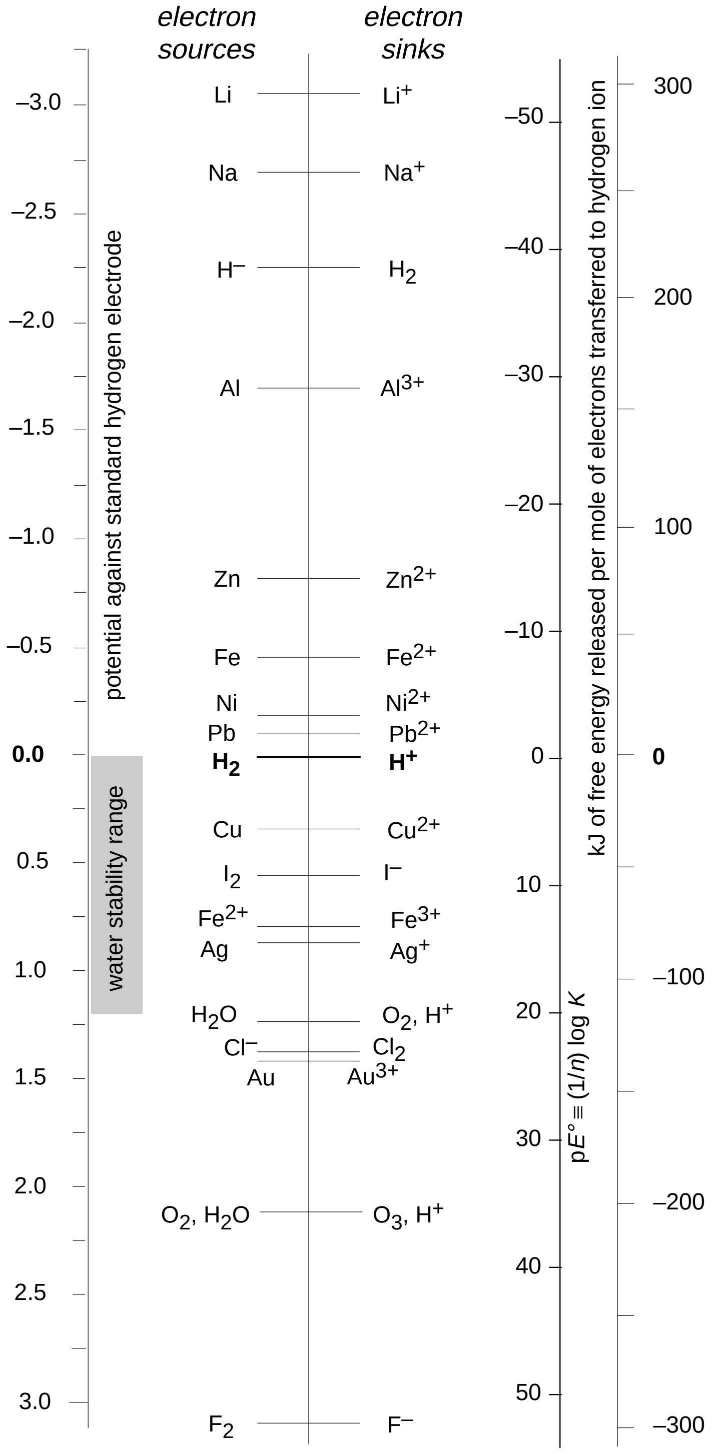


Figure 3: Electron free energy diagram for aqueous solutions.

which, at 25 °C, is commonly written

$$\boxed{E = E^\circ - \tfrac{.05915}{n}\log Q} \tag{5}$$

The potentials $E$ and $E^\circ$ can apply to half-reactions (oxidation or reduction) or to a net reaction, but only for the latter can potentials be determined experimentally, since single-electrode potentials are not measurable.

If an electrode system involving the divalent metal M is defined by the reaction

$$\mathrm{M^{2+}} \ + \ 2\,\mathrm{e^-} \ \longrightarrow \ \mathrm{M} \tag{6}$$

then it can form part of the galvanic cell represented by

$$\mathrm{Pt}\,|\,\mathrm{H_2}(\mathit{1\ atm})\,|\,\mathrm{H^+}(a = \mathit{1})\,||\ \mathrm{M^{2+}}(a = \mathit{1})\,|\,\mathrm{M}(s) \tag{7}$$

whose net reaction is

$$\mathrm{M^{2+}} \ + \ \mathrm{H_2} \ \longrightarrow \ 2\,\mathrm{H^+} \ + \ \mathrm{M}(s) \tag{8}$$

The EMF (i.e., the electrical potential difference between the Pt and M electrodes) of this cell is defined as

$$E = V_{\mathrm{M^{2+},M}} - V_{\mathrm{H^+,H_2}} \tag{9}$$

If the left half of the cell consists of a *standard hydrogen electrode* whose EMF is by definition zero, then

$$E \equiv E_{\mathrm{H}} = V_{\mathrm{M^{2+},M}} \tag{10}$$

and the Nernst equation for the $\mathrm{M^{2+}/M}$ half-cell becomes

$$E_{\mathrm{H}} = E_{M^{2+},M} = E^\circ{}_{M^{2+},M} + \frac{.05915}{2}\log\{\mathrm{M^{2+}}\} \tag{11}$$

Standard electrode potentials can be combined in order to find the EMF of a cell composed of any pair of oxidation-reduction systems. The standard EMF of the cell is defined as

$$E_{\mathrm{cell}} = E_{\mathrm{right}} - E_{\mathrm{left}} \tag{12}$$

in which the reaction at the *left* electrode is always written as an *oxidation*, while that at the right electrode is a *reduction.*

The Nernst Equation (5) predicts that a cell potential will change by 59 millivolts per ten-fold change in the concentration of a substance involved in a one-electron oxidation or reduction; for $n$-electron processes, the variation will be $59 \div n$ mv per decade concentration change. As illustrated in Fig. 4, these predictions are only fulfilled at low concentrations, not just of the electroactive ion, but of all ionic species. The greater the charge of the ion, the lower the concentration must be. At concentrations in excess of about $10^{-3}M$ for singly-charged cations, it is necessary to use *activities* in place of concentrations in the Nernst Equation.

The *sign* of a half-cell $E_{\mathrm{H}}$ corresponds to the polarity the electrode system would have relative to a standard hydrogen electrode; thus a $\mathrm{Ag^+/Ag}$ electrode system would withdraw electrons from a standard hydrogen electrode: the Ag metal would be positive with respect to the Pt.

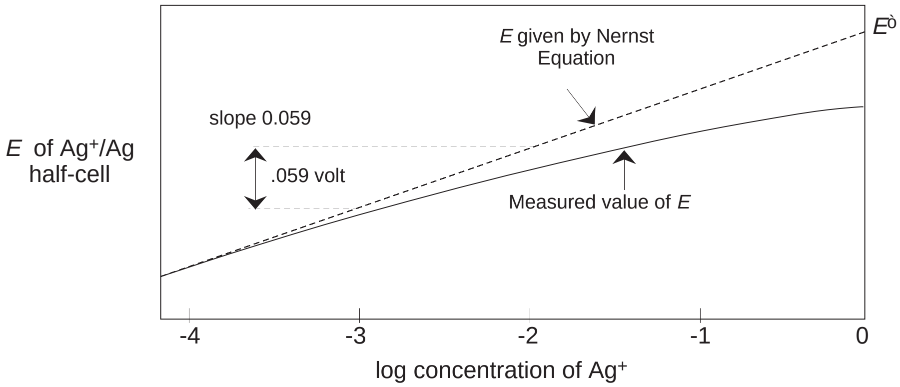


Figure 4: Concentration-dependence of half-cell potentials

## 3 $E$ as a determinant of system composition

According to the Nernst equation (4), the potential $E$ of a half cell reaction is determined by the ratio of the activities of the conjugate oxidant and reductant. In many applications, particularly in geochemistry and environmental chemistry, it is convenient to regard $E$ as an independent variable in its own right; to emphasize that we are refering these potentials to the standard hydrogen electrode, rather to one of the more commonly used reference electrodes, the more explicit symbol $E_\mathrm{H}$ is frequently used. $E_\mathrm{H}$ can be thought of as a master variable that controls the equilibrium distribution of the various oxidation states of an element, in very much the same way that the hydrogen ion concentration controls the relative concentrations of the conjugate acid-base species. This relationship is commonly expressed as a log-$C$ (or log-activity) plot vs $E$, for a fixed total concentration of the element.

As an example, we will consider a system in which the maximum total concentration of dissolved Fe is .01 $M$. If the ionic strength is 0.1 $M$(a value approximating that of seawater), a standard formula for estimating ionic activity coefficients predicts the values $\gamma_{Fe^{2+}} = .405$ and $\gamma_{Fe^{3+}} = .18$. The two couples of interest are: $\mathrm{Fe^{2+}} + 2\,\mathrm{e^-} = \mathrm{Fe}$; $E^\circ = -.440$ V , for which we have

$$E_\mathrm{H} = -.440 + .0295 \log\{\mathrm{Fe^{2+}}\}$$

$$\log\{\mathrm{Fe^{2+}}\} = 33.81\,E^\circ + 14.87$$

and $\mathrm{Fe^{3+}} + \mathrm{e^-} = \mathrm{Fe^{2+}}$; $E^\circ = .771$ V with

$$E_\mathrm{H} = .771 - .059 \log \frac{\{\mathrm{Fe^{2+}}\}}{\{\mathrm{Fe^{3+}}\}}$$

so that the value of $E_\mathrm{H}$ in the solution controls the ratio of the two ions:

$$\frac{\{\mathrm{Fe^{2+}}\}}{\{\mathrm{Fe^{3+}}\}} = 10^{\frac{E^\circ_\mathrm{H} - .771}{.059}}$$

These relations are plotted in Fig. 5, in which the following points should be noted:

- Fe*(s)* always exists at unit activity, and only when $[\mathrm{Fe^{2+}}]$ falls below its maximum value (for this solution) of .01 $M$.
- Fe*(s)*and $\mathrm{Fe^{2+}}$ cannot be in equilibrium under any conditions because they cannot both be present in sufficient quantity to satisfy the equilibrum condition $\mu_\mathrm{Fe} = \mu_{\mathrm{Fe^{2+}}}$.

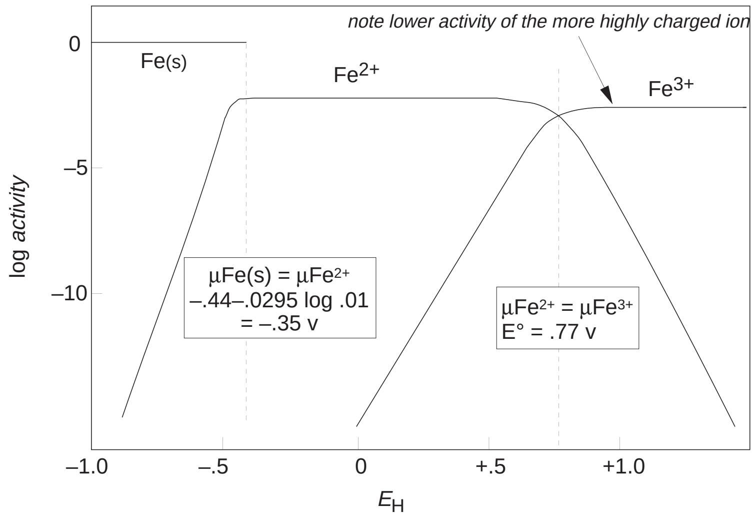


Figure 5: Distribution of Fe species as a function of $E$.

- At the $Fe^{2+}/Fe^{3+}$ crossover point, the activities of these two ions are identical, but their *concentrations* are different:

$$[Fe^{2+}](.405) = [Fe^{3+}](.18)$$

$$[Fe^{2+}] + [Fe^{3+}] = .01$$

$$[Fe^{2+}] = .00308\,M \qquad\qquad [Fe^{3+}] = .00692\,M$$

# 4 Electron activity and pE

For a half reaction such as

$$\mathbf{Ox} + n\,e^- \longrightarrow \mathbf{Red}$$

in which **Ox** and **Red** represent the upper and lower oxidation states of a redox pair such as $Fe^{3+}$ and $Fe^{2+}$, we can define a formal equilibrium constant

$$K = \frac{\{\mathbf{Red}\}}{\{\mathbf{Ox}\}\{e^-\}^n} \tag{13}$$

in which the activity of the electron appears explicitly. Although the electron has no independent existence in aqueous solutions, its *activity*, which is a direct measure of its free energy, represents a very real quantity: the *availability* of electrons (to an electron accepting substance) in the solution. Thus the *concentration* term $[e^-]$ would have no physical meaning, but the *activity* $\{e^-\}$ is an expression of the availability of electrons in the solution and thus of its *reducing power*. This is exactly analogous to the way in which the hydrogen ion activity expresses the ability of the solution to supply protons to a base.

We can solve the foregoing equation for $\{e^-\}$:

$$\{e^-\} = \left(\frac{1}{K}\frac{\{\mathbf{Red}\}}{\{\mathbf{Ox}\}}\right)^{1/n}$$

which bears a strong resemblence to the equation used to calculate $\{H^+\}$ in an acid-base buffer solution.

Continuing the analogy with the hydrogen ion activity, we can define $\mathrm{p}E \equiv -\log\{e^-\}$ and write

$$\mathrm{p}E = \frac{1}{n}\left(\log K - \log\frac{\{\mathbf{Ox}\}}{\{\mathbf{Red}\}}\right)$$

or

$$\boxed{\mathrm{p}E = \tfrac{1}{n}(\log K - \log Q)} \tag{14}$$

For the special case when $Q = 1$ we can define

$$\boxed{\mathrm{p}E^\circ = \tfrac{1}{n}\log K} \tag{15}$$

and thus from Eq 14

$$\boxed{\mathrm{p}E = \mathrm{p}E^\circ - \tfrac{1}{n}\log Q} \tag{16}$$

From the relations $\Delta G^\circ = -RT\ln K$ and $\Delta G^\circ = -n\mathcal{F}E^\circ$ we can write

$$\ln K = 2.3\log K = \frac{\Delta G^\circ}{RT}$$

and express $\mathrm{p}E^\circ$ in Eq 15 as

$$\mathrm{p}E^\circ = \frac{1}{n}\log K = \frac{1}{n}\frac{-\Delta G^\circ}{2.3RT} = \frac{\mathcal{F}E^\circ}{2.3RT} \qquad (\Delta G^\circ\text{in J, } E^\circ\text{in volts}) \tag{17}$$

Thus at 25 °C we have the relations

$$\mathrm{p}E^\circ = 16.9E^\circ = -\frac{.175\Delta G^\circ}{n} \qquad (\Delta G^\circ\text{in kJ}) \tag{18}$$

You should understand that the quantities $\mathrm{p}E^\circ$, K, $E^\circ$ and $\Delta G^\circ$are all different ways of expressing the free energy change of the reaction. In particular, the $\mathrm{p}E^\circ$ is proportional to the fall in free energy

| *couple* | $E^\circ$(v) | $\Delta G^\circ$ kJ | $\log K_{\text{red}}$ | p$E^\circ$ |
|---|---|---|---|---|
| $Na^+ + e^- \longrightarrow Na(s)$ | −2.71 | 261.5 | −45.8 | −45.8 |
| $Ca^{2+} + 2e^- \longrightarrow Ca(s)$ | −2.67 | 515.2 | −97.0 | −48.5 |
| $Al^{3+} + 3e^- \longrightarrow Al(s)$ | −1.66 | 480.5 | −84.3 | −28.1 |
| $Zn^{2+} + 2e^- \longrightarrow Zn(s)$ | −.76 | 146.7 | −25.79 | −12.9 |
| $Fe^{2+} + 2e^- \longrightarrow Fe(s)$ | −0.44 | 84.91 | −14.8 | −7.4 |
| $Cr^{3+} + e^- \longrightarrow Cr^{2+}$ | −0.41 | 39.56 | −6.9 | −6.9 |
| $Cd^{2+} + 2e^- \longrightarrow Cd(s)$ | −0.40 | 77.19 | −13.61 | −6.8 |
| $Pb^{2+} + e^- \longrightarrow Pb(s)$ | −0.13 | 25.09 | −4.27 | −2.1 |
| $\mathbf{H^+ + e^- \longrightarrow \frac{1}{2} H_2}(g)$ | **0** | **0** | **0** | **0** |
| $Cu^{2+} + e^- \longrightarrow Cu(s)$ | +0.34 | −65.61 | 11.44 | 5.7 |
| $Fe^{3+} + e^- \longrightarrow Fe^{2+}$ | +0.77 | 25.09 | 13.0 | 13.0 |
| $Fe(OH)_3(s) + 3H^+ + e^- \longrightarrow Fe^{2+} + 3H_2O$ | +1.06 | −102.3 | 17.9 | 17.9 |
| $O_2(g) + 4H^+ + 4e^- \longrightarrow 2H_2O$ | +1.23 | −474.7 | 83.10 | 20.8 |
| $NO_3^- + 6\,H^+ + 5\,e^- \longrightarrow \frac{1}{2}\,N_2(g) + 3\,H_2O$ | +1.24 | −598.2 | 105.2 | 21 |
| $2HOCl + 2H^+ + 2\,e^- \longrightarrow Cl_2(g) + 2H_2O$ | +1.60 | −308.8 | 54.0 | 27.0 |

Table 1: Standard EMF's and p$E^\circ$ values for some common redox couples.

accompanying the transfer of one mole of electrons from an electron source (reducing agent) to $H^+$ (both species at unit activity).

Perhaps more usefully, Eq 15 shows that p$E^\circ$ is the base-10 logarithm of the equilibrium constant for the one-electron reduction of a species by hydrogen ion. For this reason, when working with p$E^\circ$ and p$E$ values, it is common practice to write reactions in terms of one electron-mole. While this usually leads to rather unwieldy fractional coefficients as in

$$\tfrac{1}{8}\,NO_3^+ + \tfrac{5}{4}H^+ + e^- \longrightarrow \tfrac{1}{8}\,NH_4^+$$

it has the advantage of allowing free energy changes to be compared on a common basis. Also, the relation (15) is simplified to p$E^\circ = \log K$. Of course, since the $K$'s derived from ordinary standard EMF tables

$$K = \exp\frac{n\mathcal{F}E^\circ}{RT} \tag{19}$$

refer to $n$-electron reactions, they will be $e^n$ as large as the one-electron $K$'s that we need here.

In a table of standard EMF's, as given in Table 1, the half reactions are normally shown in order of increasing electron-donor (reducing) tendency. This means that the reduced form of any couple will tend to remove electrons from (oxidize) an equimolar concentration of the reduced form of any other couple appearing below it. From Eq 17 it is clear that p$E^\circ$ will increase as one goes to couples of greater oxidizing power. Just as low pH implies a high proton-donating tendency in aqueous solution, so does low p$E$ imply a high electron-donating (reducing) tendency.

**Problem Example 1**

Find the p$E^\circ$ for the $S/H_2S$ couple, for which $E^\circ = +.14$ v.

$$S(s) + 2\,H^+ + 2\,e^- \longrightarrow H_2S$$

$$pE^\circ = \frac{\log K}{n} = \frac{nE^\circ}{n \times .059} = \frac{(.14)}{.059} = \underline{2.37}$$

## 4.1 Redox equilibrium and p$E$

The p$E^\circ$ of a half reaction expresses the electron activity required to maintain reactants and products at unit activities. Thus for the reduction

$$\mathrm{Fe^{3+}} + \mathrm{e^-} \longrightarrow \mathrm{Fe^{2+}} \qquad \mathrm{K} = 10^{13}$$

the electron activity of the solution must be held to the very low value of $10^{-13}$ (p$E = 13$) to maintain equal activities of the two ions; this corresponds to what is usually referred to as an oxidizing environment.

The value of $K = 10^{13}$ actually refers, of course, to the reaction

$$\mathrm{Fe^{3+}} + \mathrm{H_2} \longrightarrow \mathrm{Fe^{2+}} + 2\,\mathrm{H^+}$$

with

$$K = \frac{\{\mathrm{Fe^{2+}}\}\{\mathrm{H^+}\}}{\{\mathrm{Fe^{3+}}\}P_{\mathrm{H_2}}^{.5}} = 10^{13}$$

so that the equilibrium condition $\{\mathrm{Fe^{3+}}\} = \{\mathrm{Fe^{2+}}\}$ would require a pH of 13 at unit pressure of $\mathrm{H_2}$ or a hydrogen partial pressure of $10^{26}$ atm at zero pH. Fortunately, far better electron acceptors than $\mathrm{H^+}$ are available; otherwise $\mathrm{Fe^{3+}}$ would likely be an unknown species!

In complex mixtures such as natural waters and cellular fluids, a variety of redox couples are usually present. In most cases of practical interest one couple will dominate all the other redox equilibria by virtue of its greater concentration. Just as the pH of a solution containing a mixture of weak acid-base systems can be considered as a master variable that defines the composition of the system (which can then be manipulated by addition of strong acid or strong base), so the p$E$ of a dominant redox system can be regarded as a similar master variable that controls the redox balance of the other couples in the system.

There is one major distinction in this analogy between the pH and the p$E$ that cannot be too strongly emphasized, however. Whereas proton-transfer reactions are among the most rapid ones known, electron-transfer reactions are frequently extremely slow, so in the absence of catalytic mediation, one cannot depend on redox systems to be anywhere near equilibrium.

One other difference between acid-base and redox equilibria should be noted. Redox equilibria are very frequently characterized by very large (or small) equilibrium constants. Thus the corrosion of iron can be described by the reaction

$$2\,\mathrm{Fe}(s) + \frac{3}{2}\,\mathrm{O_2}(g) \longrightarrow \mathrm{Fe_2O_3}(s)$$

for which $K = 10^{130}$. This reaction will be spontaneous whenever the partial pressure of oxygen exceeds $10^{-87}$ atm. Although a pressure such as this is perfectly valid as a thermodynamic quantity, it has no physical meaning in terms of an actual establishment of equilibrium, even if the kinetics are favorable; all it means is that the reaction can be considered “quantitative”.

# 5 p$E$ in water and natural aquatic systems

## 5.1 Using tables of pE° and pE°($W$)

The values given in tables of standard EMFs and p$E^\circ$’s refer to solutions in which the activities of any $\mathrm{H^+}$ or $\mathrm{OH^-}$ ions involved in the reaction are unity, corresponding to a “1 $M$ ideal solution”. In electrochemistry, *formal potentials* $E^{\circ\prime}$ are frequently used; these are experimentally-determined values for couples in solutions of high ionic strength such as 1 $M$ $\mathrm{HClO_4}$ or 1 $M$ HCl.

The pH of natural waters and of intracellular fluids is closer to 7 than to 0, so it is often convenient to correct $E^\circ$ and p$E^\circ$ values to pH = 7.0 when considering reactions that take place in these media. The corrected p$E^\circ$ is denoted by p$E^\circ$(W):

$$\mathrm{p}E^\circ(\mathrm{W}) = \mathrm{p}E^\circ + \frac{\mathrm{n_H}}{2}\log K_w \tag{20}$$

in which $n_\mathrm{H}$ is the number of protons exchanged per electron transferred.

## 5.2 Limits of pE in water

Water can be oxidized

$$2\,\mathrm{H_2O} \longrightarrow \mathrm{O_2}\textit{(g)} + 4\,\mathrm{H^+} + 4\,\mathrm{e^-} \qquad -E^\circ = -1.229 \text{ v} \tag{21}$$

and it can be reduced

$$2\,\mathrm{H_2O} + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2} + 2\,\mathrm{OH^-} \qquad E^\circ = -.8277 \text{ v} \tag{22}$$

This means that the equilibrium composition of the system $\mathrm{O_2} - \mathrm{H_2O} - \mathrm{H_2}$ depends on the pE, as well as on the pH and the dissolved $\mathrm{O_2}$ concentration.

**Problem Example 2**

Find the pE of a lake at 10 °C whose pH is 6.4 and whose waters are in equilibrium with atmospheric oxygen at $P_{\mathrm{O_2}} = .21$ atm.
*Solution:* From Eq 17 we have

$$\mathrm{p}E^\circ = \frac{\mathcal{F}}{2.3RT}E^\circ = 5046\frac{E^\circ}{T} = 5046 \times \frac{1.23}{283} = 21.9$$

From Eq 16 this gives

$$pE = 21.9 - \frac{1}{4}\log(P_{\mathrm{O_2}}[\mathrm{H^+}]^4 = 21.9 - 6.6 = \underline{15.3}$$

At sufficiently high or low p$E$, the stable form of the system will be $\mathrm{O_2}$ or $\mathrm{H_2}$, rather than $\mathrm{H_2O}$. The stability of water can be expressed in terms of the pressures of $\mathrm{H_2}$ and $\mathrm{O_2}$ in equilibrium with $\mathrm{H_2O}$. These equilibria can be expressed in two equivalent ways, depending on whether $\mathrm{H_2O}$ or $\mathrm{H^+}$ is considered a source or sink for $\mathrm{H_2}$:

$$2\,\mathrm{H_2O} + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2}\textit{(g)} + 2\,\mathrm{OH^-} \qquad K = 10^{-28} \tag{23}$$

$$2\,\mathrm{H^+} + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2}\textit{(g)} \qquad K = 1 \tag{24}$$

$$\mathrm{O_2}\textit{(g)} + 4\,\mathrm{H^+} + 4\,\mathrm{e^-} \longrightarrow 2\,\mathrm{H_2O} \qquad K = 10^{83.1} \tag{25}$$

$$\mathrm{O_2} + 2\,\mathrm{H_2O} + 4\,\mathrm{e^-} \longrightarrow 4\,\mathrm{OH^-} \qquad K = 10^{27.1} \tag{26}$$

In logarithmic form and in terms of pH, these relations become

$$\log\, P_{\mathrm{H_2}} = 0 - 2\,\mathrm{pH} - 2\,\mathrm{p}E \tag{27}$$

$$\log\, P_{\mathrm{O_2}} = 4\,\mathrm{pH} + 4\,\mathrm{p}E - 83.1 \tag{28}$$

If water is defined as the stable phase whenever the equilibrium partial pressure of $\mathrm{O_2}$ is less than 1 atm,

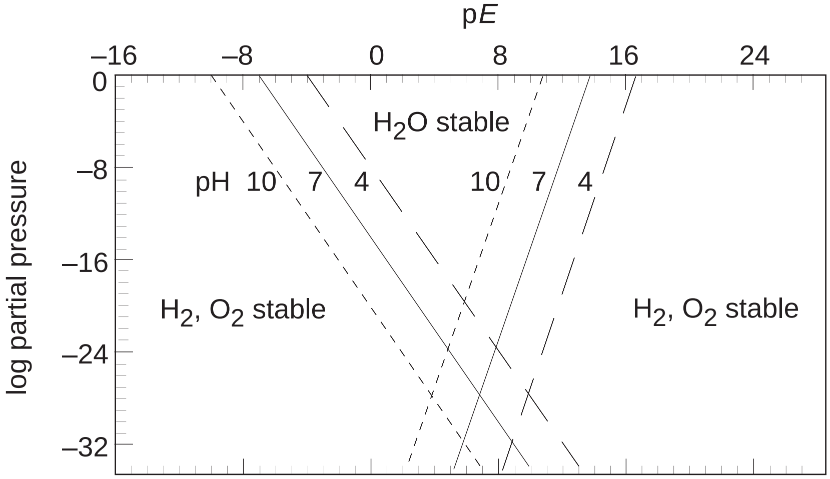


Figure 6: pE range of water stability at different pH values.

we can use the p$E^\circ$ value for the reverse of the water oxidation reaction

$$\tfrac{1}{4}\,O_2 \;+\; H^+ \;+\; e^- \;\longrightarrow\; \tfrac{1}{2}H_2O \quad pE^\circ = +20.75 \tag{29}$$

The p$E$ of water in contact with oxygen will depend on both the partial pressure of the oxygen and on the pH:

$$pE = pE^\circ + \log(P_{O_2}^{\frac{1}{4}}[H^+]) \tag{30}$$

For normal air, this becomes

$$pE = 20.75 - pH \tag{31}$$

Any oxidant having a p$E$ more positive than the value given by Eq 31 will be thermodynamically unstable in aqueous solution.

Similarly, the reduction of $H^+$ is given by

$$H^+ \;+\; e^- \;\longrightarrow\; \tfrac{1}{2}H_2 \tag{32}$$

for which

$$pE = pE^\circ + \log{[H^+]} = 0 + \log{[H^+]} = -pH \tag{33}$$

Any substance having p$E$ more negative than −pH will tend to reduce water. In general, the range of pE's permitted in natural waters within the range of commonly countered pH values extends from about −10 to +17. It should be noted, however, that the decomposition reactions shown above are usually very slow, so many oxidants or reductants whose pE's lie outside this range can exist in aqueous solutions in significant amounts.

## 5.3 pE in natural waters

For waters in equilibrium with air in which $P_{O_2} = .21$ atm, substitution into (31) yields a value +13.75 if the pH is 7.0. Thus natural water in contact with the atmosphere should exhibit a p$E$ of around 13. It is not always the case, however, that the reaction of Eq 29 is fast enough to control the pE, so values both above and below 13 are commonly encountered.

# 6 log-$C$ vs p$E$ diagrams

Logarithmic plots of oxidant-reductant concentrations as a function of p$E$ can be constructed in analogy to the log-$C$ vs pH plots of acid-base chemistry. Taking the $Fe^{3+}/Fe^{2+}$ system as an example, we start with the equilibrium and mass conservation expressions:

$$\frac{\{Fe^{2+}\}}{\{Fe^{3+}\}\{e^-\}} = K \tag{34}$$

$$[Fe^{2+}] + [Fe^{3+}] = C_{T,Fe} \tag{35}$$

Combining these, we obtain the relations

$$[Fe^{3+}] = \frac{C_{T,Fe}}{\{e^-\}K + 1} = \frac{C_{T,Fe}K^{-1}}{\{e^-\} + K^{-1}} \tag{36}$$

$$[Fe^{2+}] = \frac{C_{T,Fe}}{\{e^-\}} \tag{37}$$

When the p$E$ is well above or below p$E°$, we can make approximations that yield simplified logarithmic expressions:

| | | |
|---|---|---|
| $pE < pE^\circ$ | $[Fe^{3+}] \sim \frac{C_{T,Fe}K^{-1}}{\{e^-\}}$ | $\log[Fe^{3+}] = \log C_{T,Fe} + pE - pE^\circ$ |
| | $[Fe^{2+}] \sim \frac{C_{T,Fe}\{e^-\}}{\{e^-\}}$ | $\log[Fe^{2+}] = \log C_{T,Fe}$ |
| $pE > pE^\circ$ | $[Fe^{3+}] = \frac{C_{T,Fe}K^{-1}}{K^{-1}}$ | $\log[Fe^{3+}] = \log C_{T,Fe}$ |
| | $[Fe^{2+}] = \frac{C_{T,Fe}\{e^-\}}{K^{-1}}$ | $\log[Fe^{2+}] = \log C_{T,Fe} + pE^\circ - pE$ |

These relations are plotted in Fig. 7 for a system in which the pH is 2.

**The sulfate-sulfide system at pH 10** This system has a more complicated stoichiometry, leading to log-$C$ plots of different slopes. At this pH, the only significant −2 form of sulfur is the hydrosulfide ion, $HS^-$ .

$$SO_3^{2-} + 9\,H^+ + 8\,e^- \longrightarrow HS^- + 4\,H_2O\mathit{(l)} \qquad \Delta G^\circ = -194.2 \text{ kJ/mol} \tag{38}$$

The p$E$ of this system is defined by

$$pE = \frac{1}{8}\log K + \frac{1}{8}\log\frac{[SO_3^{2-}][H^+]^9}{[HS^-]} \tag{39}$$

The equilibrium constant for reaction (38) is $K = 10^{34}$. Substituting this value into the above expression, we have

$$pE = 4.25 - 1.125\,pH + \frac{1}{8}\log[SO_3^{2-}] - \frac{1}{8}\log[HS^-] \tag{40}$$

At pH = 10, this becomes

$$pE = -7 + \frac{1}{8}\log[SO_3^{2-}] - \frac{1}{8}\log[HS^-] \tag{41}$$

This equation is plotted in Fig. 8 for the condition $[SO_3^{2-}] + [HS^-] = 10^{-4}\,M$. This plot also shows the partial pressures of $O_2$ and of $H_2$ in equilibrium with $H_2O$ as a function of pE at this pH. From this diagram it is apparent that $SO_3^{2-}$ is stable with respect to the −2 oxidation state of sulfur over most of the p$E$ range shown; the hydrosulfide ion will predominate only under highly anaerobic conditions (high electron activity) where $P_{O_2} < 10^{-68}$ atm.

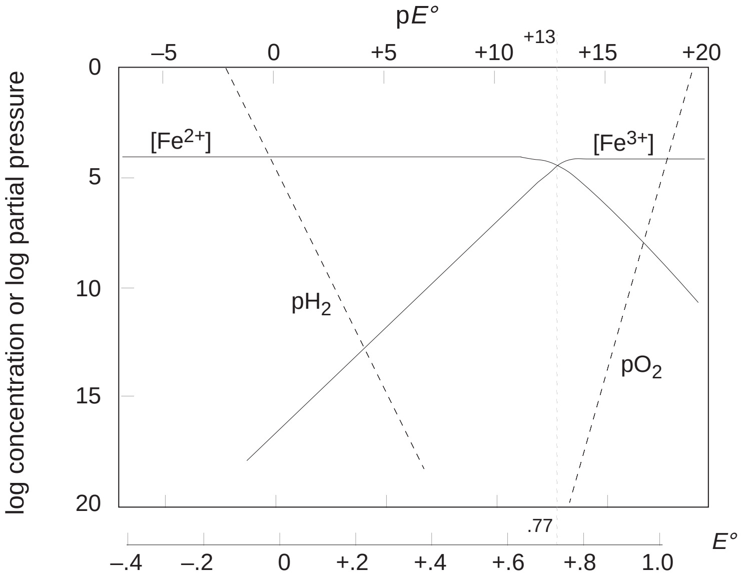


Figure 7: Log-$C$ vs p$E$ diagram for iron at pH= 2. (From Snoeyink and Jenkins)

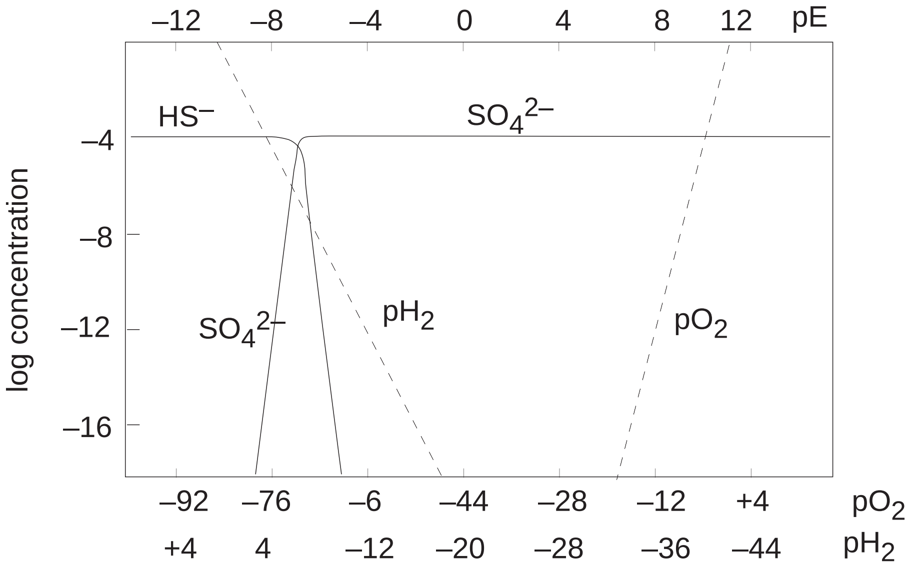


Figure 8: Log-$C$ vs p$E$ diagram for sulfur at pH= 10. (From Stumm and Morgan)

Inclusion of oxidation states involving solids is best done by considering activity ratios, taking unit activity of one of the solids as a reference. Thus in order to investigate the conditions under which elemental sulfur (which is found in marine sediments) can exist, we need the reactions

$$\begin{array}{lcl}
(a) & SO_3^{2-} \; + \; 9\,H^+ + 8\,e^- \longrightarrow HS^- + 4\,H_2O & \log K = 34.0 \\
(b) & H_2S(aq) \longrightarrow S(s) + 2\,H^+ + 2\,e^- & \log K = -4.8 \\
(c) & H^+ + HS^- \longrightarrow H_2S(aq) & \log K = 36.2 \\
\hline
(d) & SO_3^{2-} \; + \; 8\,H^+ \; + \; 6\,e^- \longrightarrow S(s) \; + \; 4\,H_2O & \log K = 36.2
\end{array}$$

From *(b)* and *(c)* above we obtain

$$(e) \quad S^{2-} \longrightarrow S(s) \; + \; H^+ \; + \; 2\,e^- \quad \log K = 2.2$$

From *(d)* and *(e)* we can construct the activity ratios

$$\log \frac{[SO_3^{2-}]}{\{S\}} = -36.2 + 8\,pH + 6\,pE \tag{42}$$

$$\log \frac{[HSO_3^-]}{\{S\}} = -2.2 - pH - 2\,pE \tag{43}$$

By plotting this equation for pH= 10 it can be shown that the activity of solid sulfur is always less than those of $SO_3^{2-}$ and $HS^-$ , so that the element will not be formed at any value of pE.

For acidic solutions, in which $H_2S$ rather than $HS^-$ is the major form of −2 sulfur, we use *(b)* and (42) to obtain a ratio for $H_2S$:

$$\log \frac{[H_2S]}{\{S\}} = 4.8 - 2\,pH - 2\,pE \tag{44}$$

A similar plot, done at pH= 4, reveals a very narrow range of stability of the solid between pE's of about −0.6 and +0.4. Note that this does not mean that elemental sulfur will not be found in sediments outside this pH range; the solid may originally have been formed under other conditions, and remains as a metastable phase. Also, a solid can be stable at less than unit activity if it is present as a solid solution.

A log-$C$ vs pH plot for the $SO_3^{2-}$ –$S(s)$–$H_2S$ system can be constructed by combining the data given above with the equation

$$(f) \quad SO_3^{2-} \; + \; 3\,H_2S(aq) \; + \; 2\,H^+ \longrightarrow 4\,S(s) \; + \; 4\,H_2O \quad \log K = 21.8$$

## 7 Oxidizing-reducing capacity

In analogy with pH, p$E$ is an intensive property which measures the oxidizing (or reducing) *tendency*, rather than *capacity*. The oxidizing capacity expresses the moles per litre of electrons that must be added or removed in order to attain a given pE. This is entirely analogous to the acid-base concepts of acid- or base neutralizing capacity.

For a system containing a number of different redox species, the oxidizing capacity at a given p$E$ is found by subtracting the equivalent sum of all reductants that lie above this p$E$ from the sum of all oxidants lying below it. Thus for a solution containing $Fe^{3+}$, $I_3^-$, $O_2$, $H_2$, and $Cu^{2+}$, the oxidizing capacity with respect to p$E = 5$ is given by

$$2\,[Cu^{2+}] + 2\,[I_3^-] + [Fe^{3+}] + 4\,[O_2] - 2\,[H_2] \tag{45}$$

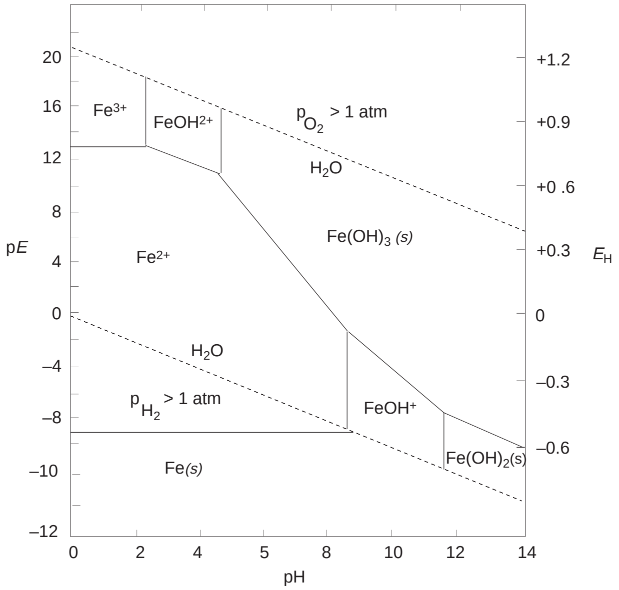


Figure 9: pE - pH diagram for the aqueous $Fe^{3+}$-$Fe^{2+}$ system.

# 8 pE - pH diagrams

The equilibrium composition of a redox system involving $H^+$ depends on both the pH and the pE. The interplay of these two factors is best illustrated by constructing a phase diagram in which the various lines represent states of (pE,pH) at which equilibria occur. Diagrams of this kind are widely employed in geochemistry, oceanographic chemistry and in corrosion engineering. States not falling on lines correspond to the predominance of a single species. Horizontal lines correspond to redox couples in which protons are not involved, while vertical lines represent acid-base reactions without electron transfer. In establishing a line separating a solid from a dissolved species, it is necessary to define the equilibrium concentration at which the dissolved species is so low that is is considered to be the unstable form. This concentration is of course entirely arbitrary, and is selected according to the application one has in mind. A value of $10^{-7}\,M$ is used in the diagram for the $Fe^{3+}$–$Fe^{2+}$ system in Fig. 9.

# 9 Redox reactions in the aquatic environment

The major elements found in natural waters that enter into redox reactions are C, N, O, S, Fe, and Mn. It is noteworthy that all of these elements are present in living cells, whose average composition is approximated by the formula $C_{106}H_{263}O_{110}N_{16}P$ . More significantly, redox reactions involving these elements are capable of supplying free energy to organisms. These reactions are all catalyzed by enzymes and take place in local intracellular environments where the pH and p*E* are such that the reactions are thermodynamically favorable.

The ultimate source of biochemical free energy is of course solar radiation. It is estimated that about .004% of the insolation reaching the earth's surface is used for photosynthesis. Of this energy, a small fraction (15-20% in phytoplankton) is utilized by the organism; the remainder is bound into carbohydrate, lipid, and protein, where it becomes available to heterotrophic consumers and decomposers.

The conversion of $CO_2$ to glucose can only take place in a highly reducing microenvironment where negative p*E* values prevail (reaction 20 of Table 3). The other half of the biochemical cycle consists of

**anaerobic conditions**

| *process* | *typical reaction* | $\Delta G^\circ$(W), kJ/mol |
|---|---|---|
| denitrification | $CH_2O + NO_3^- \longrightarrow CO_2 + H^+ + N_2$ | 18 |
| nitrate reduction | $CH_2O + NO_3^- \longrightarrow CO_2 + NH_4^+$ | −82 |
| fermentation | $CH_2O + 2\,H_2 \longrightarrow CH_4 + H_2O$ | −23 |
| nitrogen fixation | $CH_2O + N_2 \longrightarrow CO_2 + NH_4^+$ | −23 |

**aerobic conditions**

| | | |
|---|---|---|
| respiration | $CH_2O + O_2 \longrightarrow CO_2 + H_2O$ | −125 |
| sulfide oxidation | $CH_2O + HS^- \longrightarrow SO_4^{2-} + H^+$ | −96 |
| nitrification | $CH_2O + NH_4^+ \longrightarrow NO_3^- + H^+$ | −43 |

Table 2: Sequence of biologically mediated redox reactions.

various respiratory, fermentative, and other autotrophic processes that release free energy, increase the average p$E$ level, and generally act to restore the system to a state that is closer to equilibrium with the environment. This restoration is never complete; inspection of p$E^\circ$(W) values in Table 3 shows that equilibrium concentrations of organic compounds in oxygen-saturated waters should be less than $10^{-35}$ $M$, [$Fe^{2+}$] less than $10^{-18}$ $M$, and most nitrogen should be in the form of nitrate. The fact that the observed concentrations of these substances differ markedly from the equilibrium values is due entirely to kinetics, and well illustrates the crucial role that organism play in maintaining the dynamic steady state of the aquatic environment.

The entire scheme is nicely summarized by the diagram of Fig. 10, which can be regarded as an "electron ladder" in which electrons, elevated by photosynthesis to the highly negative p$E$ of carbohydrate, trickle down to lower-lying electron sinks. Which particular sink will be most likely to receive the electrons from a higher level? This depends ultimately on the kinetics of the various enzyme-mediated reactions. It turns out, however, that organisms that are able to capture more free energy from this process tend to dominate a local environment; this is indeed the reason that oxygen-consuming eukaryotes dominate aerobic waters and soils. Thus at successively deeper (and more deoxygnated) levels within such bodies, successively higher electron sinks come into play as the major respiratory agents (Fig. 11).

The profound effects of biochemical processes on the redox chemistry of the environment have been discussed in detail by Stumm and Morgan, from whose book the $\log C$ vs pE diagrams of figures 12-15 are taken. The following points should be noted in relation to the four major elements involved in the environmental redox cycle.

## 9.1 Nitrogen

The concentration of $N_2$*(aq)* in equilibrium with the atmosphere is 0.0005 $M$. According to 12*(a)*, $N_2$ is the stable species over the greater part of the p$E$ range. *Nitrogen fixation* (conversion of $N_2$ to $NH_4^+$) is thermodynamically favored at negative p$E$'s, but it is kinetically limited, probably by the activation energy associated with scission of the N≡N bond. Thus processes involving $N_2$ together with other forms of nitrogen are not well coupled, and it is more useful to consider a diagram as in *(b)* in which $N_2$ is not considered. The effect is to produce a p$E$ region extending from about 4 to 12 in which all three of the major ionic forms of nitrogen can coexist. The highly facile nature of the interconversions between these species within the nitrogen cycle may well reflect the overlap of these predominance regions.

| | Reaction | pE° | pE°(*W*) |
|---|---|---|---|
| 1 | $\frac{1}{4}O_2 + H^+ + e^- \longrightarrow \frac{1}{2}H_2O$ | +20.75 | +13.75 |
| 2 | $\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^- \longrightarrow \frac{1}{16}N_2(g) + \frac{3}{5}H_2O$ | +21.05 | +12.65 |
| 3 | $\frac{1}{2}MnO_2\mathit{(s)} + \frac{1}{2}HCO_3^- + \frac{3}{2}H_2O + e^- \longrightarrow \frac{1}{2}MnCO_3\mathit{(s)} + H_2O$ | – | +8.9 |
| 4 | $\frac{1}{2}NO_3^- + H^+ + e^- \longrightarrow \frac{1}{2}NO_2^- + \frac{1}{2}H_2O$ | +14.15 | +7.15 |
| 5 | $\frac{1}{8}NO_3^- + \frac{5}{4}H^+ + e^- \longrightarrow \frac{1}{8}NH_4^+ + \frac{3}{8}H_2O$ | +14.9 | +6.15 |
| 6 | $\frac{1}{6}NO_2^- + \frac{4}{3}H^+ + e^- \longrightarrow \frac{1}{6}NH_4^+ + \frac{1}{3}H_2O$ | +15.14 | +5.82 |
| 7 | $\frac{1}{2}CH_3OH + H^+ + e^- \longrightarrow \frac{1}{2}CH_4(g) + \frac{1}{2}H_2O$ | +9.88 | +2.88 |
| 8 | $\frac{1}{4}CH_2O + H^+ + e^- \longrightarrow \frac{1}{4}CH_4(g) + \frac{1}{4}H_2O$ | +6.94 | −0.06 |
| 9 | $FeOOH(s) + HCO_3^- + 2H^+ + e^- \longrightarrow FeCO_3\mathit{(s)} + 2H_2O$ | – | −0.08 |
| 10 | $\frac{1}{2}CH_3O + H^+ + e^- \longrightarrow \frac{1}{2}CH_3OH$ | +3.99 | −3.01 |
| 11 | $\frac{1}{6}SO_3^{2-} + \frac{4}{3}H^+ + e^- \longrightarrow \frac{1}{6}S(s) + \frac{2}{3}H_2O$ | +6.03 | −3.30 |
| 12 | $\frac{1}{8}SO_3^{2-} + \frac{5}{4}H^+ + e^- \longrightarrow \frac{1}{8}H_2\mathit{(g)} + \frac{1}{2}H_2O$ | +5.25 | −3.50 |
| 13 | $\frac{1}{8}SO_3^{2-} + \frac{9}{8}H^+ + e^- \longrightarrow \frac{1}{8}HS^- + \frac{1}{2}H_2O$ | +4.25 | −3.75 |
| 14 | $\frac{1}{2}S\mathit{(s)} + H^+ + e^- \longrightarrow \frac{1}{8}H_2S\mathit{(g)} + \frac{1}{2}H_2O$ | +2.89 | −4.81 |
| 15 | $\frac{1}{8}CO_2 + H^+ + e^- \longrightarrow \frac{1}{8}CH_4\mathit{(g)} + \frac{1}{4}H_2O$ | +2.87 | −4.13 |
| 16 | $\frac{1}{6}N_2\mathit{(g)} + \frac{4}{3}H^+ + e^- \longrightarrow \frac{1}{3}NH_4^+$ | +4.68 | −4.68 |
| 17 | $\frac{1}{2}ADP^+ + \frac{1}{2}H^+ + e^- \longrightarrow \frac{1}{2}ADPH$ | −2.0 | −5.5 |
| 18 | $H^+ + e^- \longrightarrow \frac{1}{2}H_2\mathit{(g)}$ | 0.0 | 0.0 |
| 19 | oxidized ferridoxin + $e^-$ $\longrightarrow$ reduced ferridoxin | −7.1 | −7.1 |
| 20 | $\frac{1}{4}CO_2\mathit{(g)} + H^+ + e^- \longrightarrow \frac{1}{14}C_6H)_{12}O_6 + \frac{1}{4}H_2O$ | −0.2 | −7.2 |
| 21 | $\frac{1}{2}HCOO^- + \frac{3}{2}H^+ + e^- \longrightarrow \frac{1}{2}CH_2O + \frac{1}{2}H_2O$ | +2.82 | −7.68 |
| 22 | $\frac{1}{4}CO_2\mathit{(g)} + H^+ + e^- \longrightarrow \frac{1}{4}CH_2O + \frac{1}{4}H_2O$ | −1.20 | −8.20 |
| 23 | $\frac{1}{2}CO_2\mathit{(g)} + \frac{1}{2}H^+ + e^- \longrightarrow \frac{1}{2}HCOO^-$ | −4.33 | −8.33 |

This data is reproduced from Stumm & Morgan's *Aquatic Chemistry.* The p*E*(W) values refer to pH 7.0 and 25 °C. Oxidants and reductants are assumed to be at unit activities, except for $HCO_3^-$, which is at 0.001 *M* concentration.

Table 3: p*E*° values for reactions in the aquatic environment.

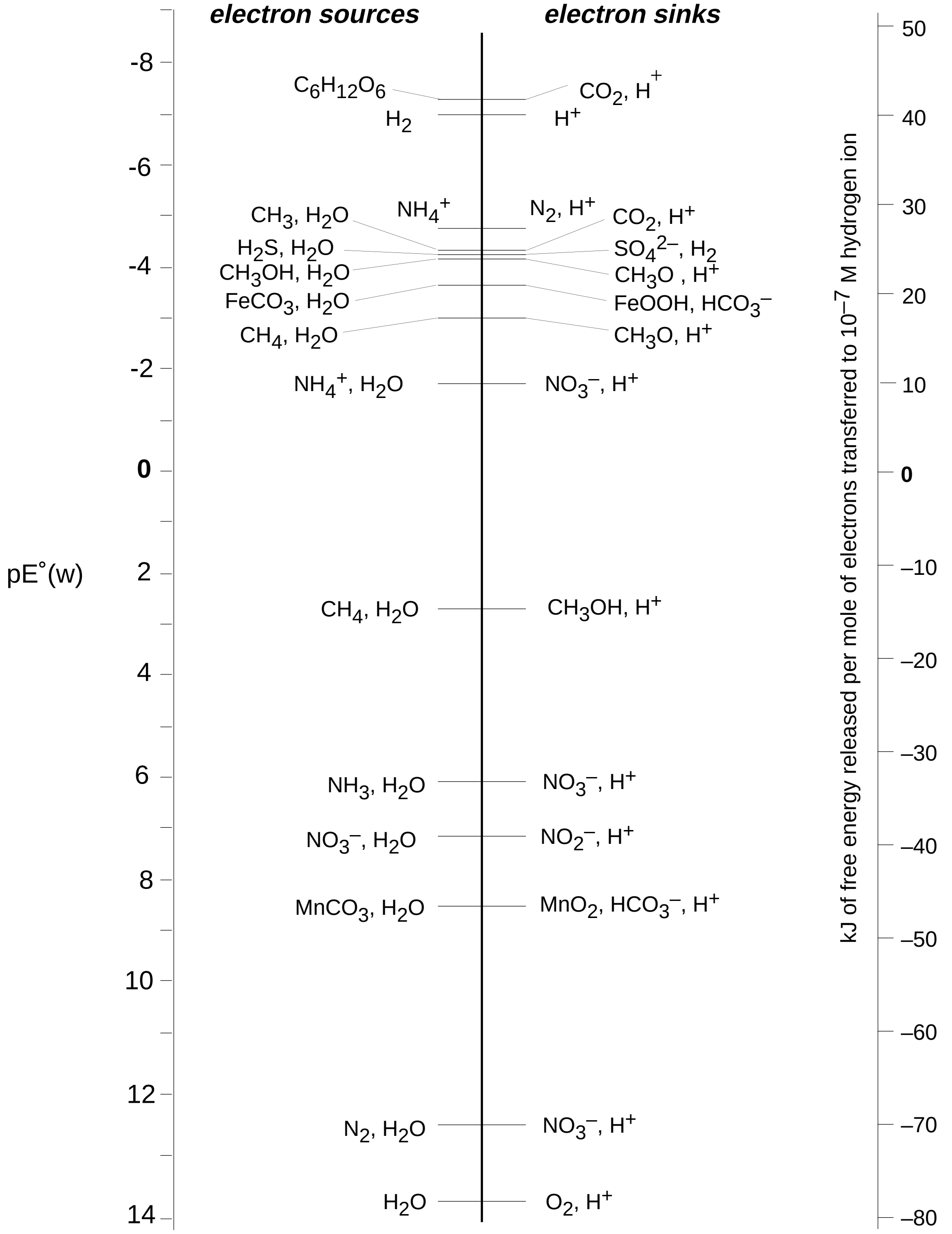


Figure 10: Electron free energy diagram for some reactions of biogeochemical importance.

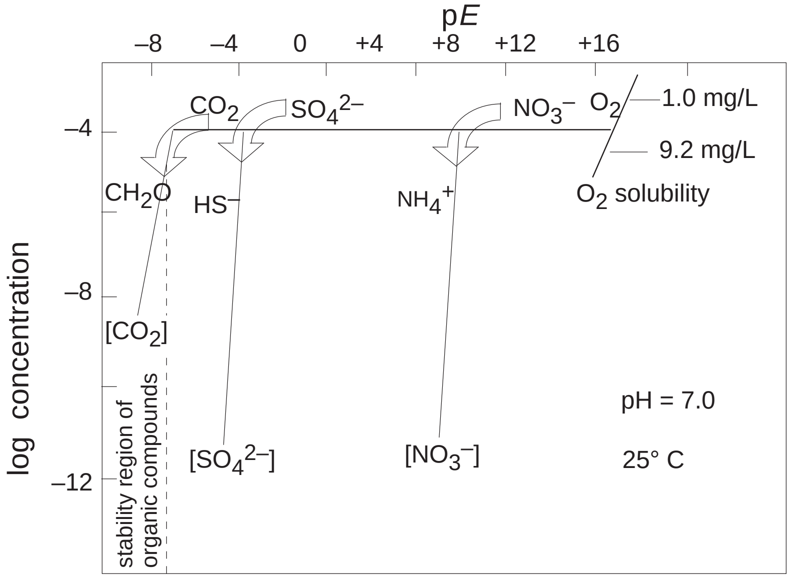
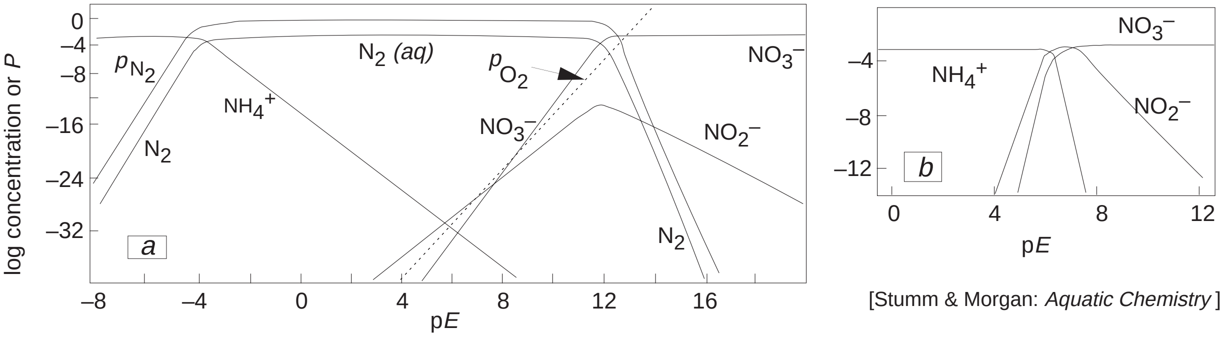


Figure 11: Succession of electron acceptors in environments of varying p$E$



[Stumm & Morgan: *Aquatic Chemistry*]

Figure 12: log-$C$ vs p$E$ diagrams for nitrogen

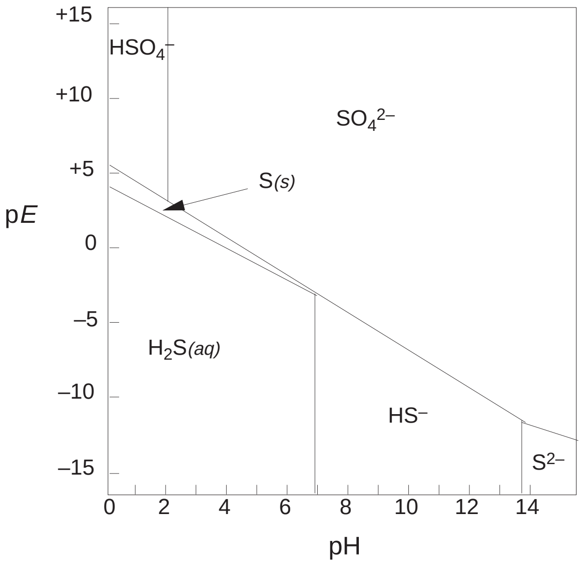


Figure 13: pE and activity ratio predominance diagrams for sulfur

Compare this with the log-$C$ vs. p$E$ diagram in Fig. 8 on page 16.

## 9.2 Sulfur

The sulfate ion can become the primary electron acceptor in waters and sediments in which oxygen gas been depleted by reaction with organic matter. The odor of $H_2S$ is often apparent in perpetually wet muds, for example. The major reaction of interest is

$$SO_3^{2-} \;+\; 9\,H^+ \;+\; 8e^- \;\longrightarrow\; HS^- \;+\; 4\,H_2O \qquad (\Delta G^\circ = -294 \text{ kJ mol}^{-1}) \tag{46}$$

for which $K = 10^{34}$; thus

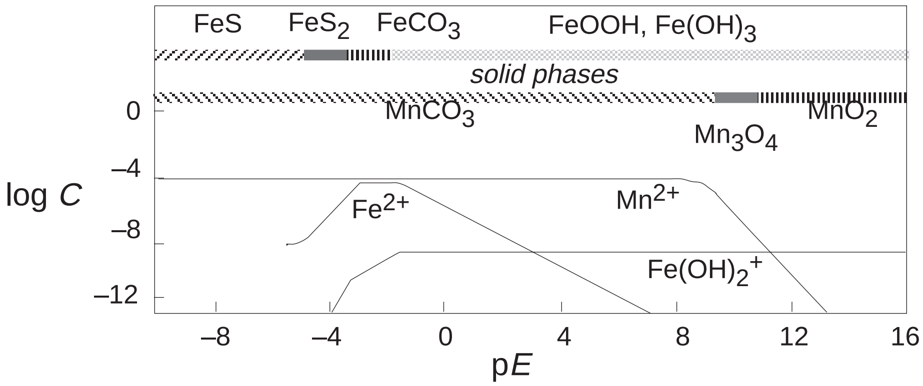
$$pE = 4.25 - 1.125\,\text{pH} + \frac{1}{8}\log[SO_3^{2-}] - \frac{1}{8}\log[HS^-] \tag{47}$$

This relation is plotted in Fig. 13 for a solution having a pH of 10 and a total sulfur species concentration of $10^{-4}$ $M$. It is apparent that $SO_3^{2-}$ is the favored species if any detectable amount of oxygen is present.

Elemental sulfur is one of several oxidation intermediates of sulfur that is often found in the natural environment. It is the stable form of sulfur only within a very narrow range of p$E$and pH, and is probably formed by the reaction

$$SO_4^{2-} \;+\; 2H^+ \;+\; 3H_2S \;\longrightarrow\; 4S(s) + 4H_2O \qquad \log \text{K(W)} = 4.86$$

which is favored by low pH.



[Stumm & Morgan: *Aquatic Chemistry*]

Figure 14: log-$C$ vs p$E$ diagram for iron and manganese

## 9.3 Iron and manganese

The solid oxides are the only stable forms of these elements at pE's in excess of 11 Fig. 14; soluble Fe and Mn species should have concentrations smaller than $10^{-9}$ *M*in oxygenated waters. In the absence of $O_2$, these concentrations will be limited by the solubilities of the carbonates; $[HCO_3^-] = 10^{-3}$ *M* is assumed in the Figure.

## 9.4 Carbon

The five major oxidation states of organic carbon are represented by the the following substances:

| *name* | methane | methanol | formaldehyde | formate | carbon dioxide |
|---|---|---|---|---|---|
| *formula* | $CH_4$ | $CH_3OH$ | $CH_2O$ | $HCOO^-$ | $CO_2$ |
| *oxidation number* | −4 | −2 | 0 | +2 | +4 |
| *reduction pE° (W)* | *(reference)* | +2.88 | −.06 | | −4.13 |

From Fig. 15 it is apparent that the the first and last of these are stable in water. Methane is thus the only organic solute found in natural waters that is thermodynamically stable in the presence of oxygen; all other organics should decompose into $CH_4$ or $CO_2$, except near the crossover p$E$ of −4.13, where the formation of graphite is theoretically possible but is not observed. Note that from a thermodynamic standpoint, anaerobic conditions are no more conducive to the preservation of organic substances than are aerobic conditions.

The microbially-mediated conversion of carbon compounds into $CO_2$ or $CH_4$ is known as *fermentation.* In *alcoholic* fermentation, carbohydrate, represented by $C_6H_{12}O_6$ (i.e., $(CH_2O)_n$) undergoes disproportionation:

$$CH_2O + 2\,CH_2O + H_2O \longrightarrow 2\,CH_3OH + CO_2(g) \tag{48}$$

$$C_6H_{12}O_6 \longrightarrow 2\,C_2H_5OH + 2\,CO_2(g) \tag{49}$$

*Methane fermentation* occurs when $H_2$ is available:

$$4\,H_2(g) + CO_2(g) \longrightarrow CH_4 + 2\,H_2O \tag{50}$$

The hydrogen can be produced by various processes, such as the $\beta$-oxidation of fatty acids:

$$CH_3CH_2CH_2COO^- + H_2O \longrightarrow 2\,CH_3COO^- + H^+ \tag{51}$$

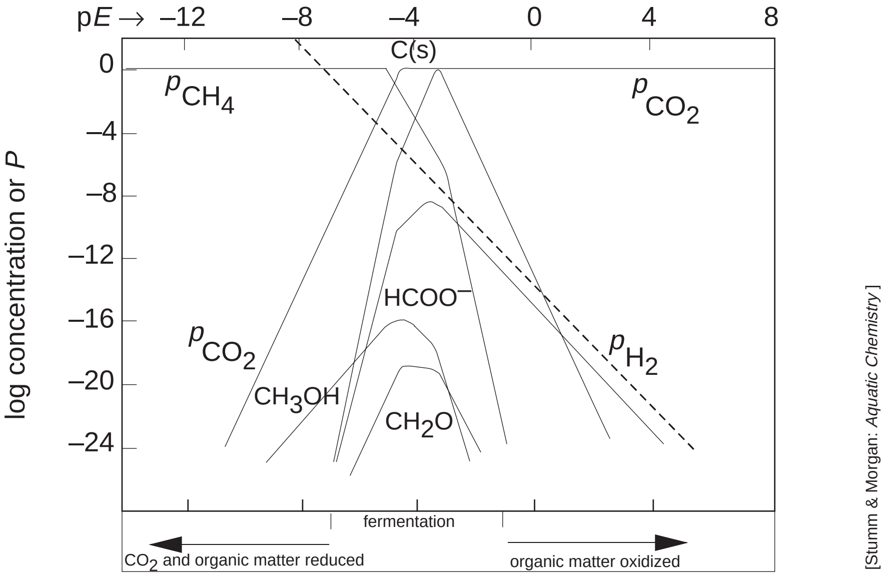


Figure 15: log-$C$ vs p$E$ diagram for carbon

## 9.5 Field measurements of $E_H$ and p$E$

In theory, one can simply dip a platinum electrode and a reference electrode into a moist soil or a body of water, and determine the local $E_H$ by measuring the voltage between the two. Numerous considerations cast suspicion on the reliability of such measurements[2], but a very large number have been made. In general, the results agree with what one would predict; $E_H$ diminishes with depth in lakes and impounded waters, and is very low in bogs and in many lake-bottom mud cores.

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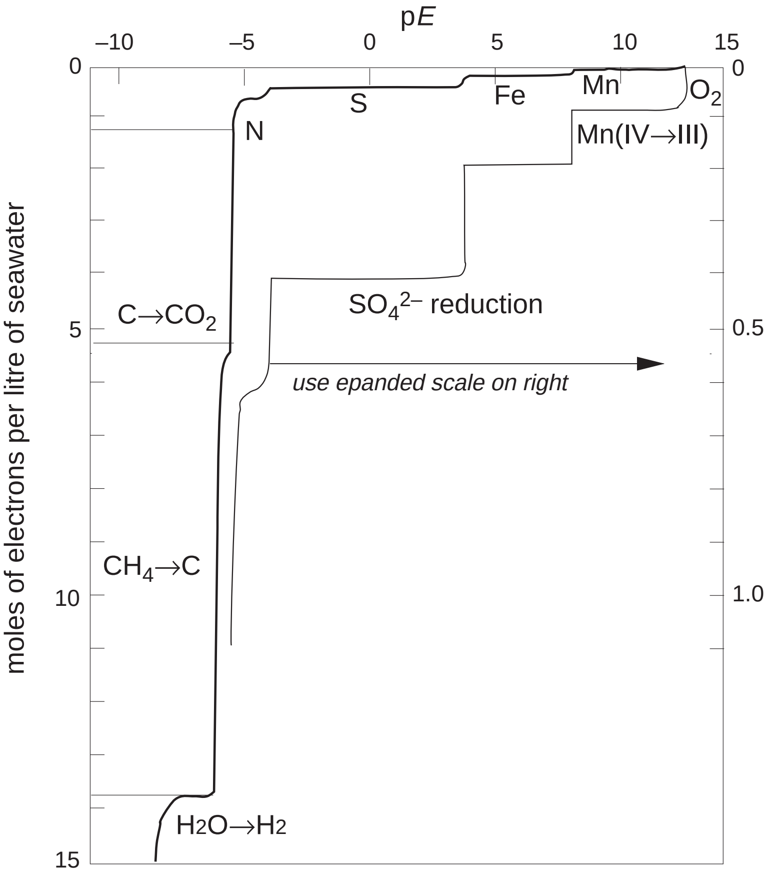
[2] See, for example, M. Whitfield, *Limnol. Oceanog.* 1974:19(857).

# 10 Oxidation and evolution

Suppose that electrons could be freely exchanged amongst the various components of a closed aqueous system containing dissolved organic material (represented by $CH_2O$) together with $NO_3^-$ , $SO_4^{2+}$, and other oxidized substances. The observed sequence of reactions would would correspond to a redox titration of the organic material by successively weaker electron acceptors as listed in Fig. 10; the result would be a "titration curve" whose general form is depicted in Fig. 16.

This sequence of reactions is roughly descriptive of what is actually observed as one examines the vertical distribution of substances in a eutrophic lake, and in soils and sediments. The time sequence of reactions in an anaerobic fermentation unit or batch digester also follows the same general scheme. Since these reactions are all enzyme-catalyzed, there is an ecological sequence of microorganisms (aerobic heterotrophs, denitrifiers, fermentors, sulfate reducers, and methanogenic bacteria) that reflects the chemical sequence.

Moreover, the succession of organisms on the evolutionary scale corresponds to a general tendency to utilize reactions yielding larger amounts of energy; recall that the appearance of respiratory organisms was a comparatively recent development. This has led to the suggestion that the titration of the environment by electrons would correspond to a backwards movement in geological time.



This graph shows how the p$E$ of a model seawater system will vary with the number moles of electrons added by a reducing agent. The top of the diagram represents the zero level with p$E = 12.5$, which corresponds to the present oceanic environment. The two curves are shown at different scales, the scale of the thinner curve being magnified tenfold with respect to the other. From L.G. Sillén, *Ark. Kem.* **25**, 159 (1965).

Figure 16: Environmental redox “titration curve”

# References

[1] Morel, François and Hering, Janet *Principles and applications of aquatic chemistry* 1993: Wiley Written as a textbook, with many end-of-chapter problems.

[2] Snoeyink, Vernon and Jenkins, David *Water chemistry* 1980: Wiley This textbook is more readable than Stumm and Morgan, and has a good chapter on carbonate equilibria.

[3] Stumm, Werner and Morgan, James *Aquatic chemistry* 3rd Ed 1995: Wiley This was first published in 1970, and is the classic work on the chemistry of natural waters, and probably the best-known reference in the field. A bit difficult to read in places, but very through and with some worked examples and a few problems. Chapter 8 of this book is devoted to oxidation-reduction.

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