

TABLE 4.1
pE° Values of Redox Reactions Important in Natural Waters (at 25°C)

Reaction	pE°	pE° (W) ^a
1. $\frac{1}{2} \text{O}_2(\text{g}) + \text{H}^+(\text{W}) + e^- \rightleftharpoons \frac{1}{2} \text{H}_2\text{O}$	+20.75	+13.75
2. $\frac{1}{5} \text{NO}_3^- + \frac{1}{5} \text{H}^+ + e^- \rightleftharpoons \frac{1}{10} \text{N}_2 + \frac{1}{5} \text{H}_2\text{O}$	+12.65	+21.05
3. $\frac{1}{2} \text{MnO}_2 + \frac{1}{2} \text{HCO}_3^-(1 \times 10^{-3} \text{ M}) + \frac{1}{2} \text{H}^+(\text{W}) + e^- \rightleftharpoons \frac{1}{2} \text{MnCO}_3(\text{s}) + \frac{1}{2} \text{H}_2\text{O}$	—	+8.5 ^b
4. $\frac{1}{2} \text{NO}_3^- + \text{H}^+(\text{W}) + e^- \rightleftharpoons \frac{1}{2} \text{NO}_2^- + \frac{1}{2} \text{H}_2\text{O}$	+14.15	+7.15
5. $\frac{1}{8} \text{NO}_3^- + \frac{1}{4} \text{H}^+(\text{W}) + e^- \rightleftharpoons \frac{1}{8} \text{NH}_4^+ + \frac{1}{4} \text{H}_2\text{O}$	+14.90	+6.15
6. $\frac{1}{8} \text{NO}_3^- + \frac{1}{4} \text{H}^+(\text{W}) + e^- \rightleftharpoons \frac{1}{8} \text{NH}_4^+ + \frac{1}{4} \text{H}_2\text{O}$	+15.14	+5.82
7. $\frac{1}{2} \text{CH}_3\text{OH} + \text{H}^+(\text{W}) + e^- \rightleftharpoons \frac{1}{2} \text{CH}_4(\text{g}) + \frac{1}{2} \text{H}_2\text{O}$	+9.88	+2.88
8. $\frac{1}{4} \text{CH}_3\text{O} + \text{H}^+(\text{W}) + e^- \rightleftharpoons \frac{1}{4} \text{CH}_4(\text{g}) + \frac{1}{4} \text{H}_2\text{O}$	+6.94	-0.06
9. $\text{FeOOH}(\text{g}) + \text{HCO}_3^-(1 \times 10^{-3} \text{ M}) + 2\text{H}^+(\text{W}) + e^- \rightleftharpoons \text{FeCO}_3(\text{s}) + 2\text{H}_2\text{O}$	—	-1.67 ^b
10. $\frac{1}{2} \text{CH}_3\text{O} + \text{H}^+(\text{W}) + e^- \rightleftharpoons \frac{1}{2} \text{CH}_3\text{OH}$	+3.99	-3.01
11. $\frac{1}{8} \text{SO}_4^{2-} + \frac{1}{4} \text{H}^+(\text{W}) + e^- \rightleftharpoons \frac{1}{8} \text{S}(\text{s}) + \frac{1}{4} \text{H}_2\text{O}$	+6.03	-3.30
12. $\frac{1}{8} \text{SO}_4^{2-} + \frac{1}{4} \text{H}^+(\text{W}) + e^- \rightleftharpoons \frac{1}{8} \text{H}_2\text{S}(\text{g}) + \frac{1}{4} \text{H}_2\text{O}$	+5.75	-3.50
13. $\frac{1}{8} \text{SO}_4^{2-} + \frac{1}{4} \text{H}^+(\text{W}) + e^- \rightleftharpoons \frac{1}{8} \text{HS}^- + \frac{1}{4} \text{H}_2\text{O}$	+4.13	-3.75
14. $\frac{1}{2} \text{S}(\text{s}) + \text{H}^+(\text{W}) + e^- \rightleftharpoons \frac{1}{2} \text{H}_2\text{S}(\text{g})$	+2.89	-4.11
15. $\frac{1}{4} \text{CO}_2 + \text{H}^+ + e^- \rightleftharpoons \frac{1}{4} \text{CH}_4 + \frac{1}{4} \text{H}_2\text{O}$	+2.87	-4.13
16. $\frac{1}{2} \text{N}_2 + \frac{1}{2} \text{H}^+(\text{W}) + e^- \rightleftharpoons \frac{1}{2} \text{NH}_4^+$	+4.68	-4.65
17. $\text{H}^+(\text{W}) + e^- \rightleftharpoons \frac{1}{2} \text{H}_2(\text{g})$	0.00	-7.00
18. $\frac{1}{4} \text{CO}_2(\text{g}) + \text{H}^+(\text{W}) + e^- \rightleftharpoons \frac{1}{4} \text{CH}_2\text{O} + \frac{1}{4} \text{H}_2\text{O}$	-1.20	-8.20

Source: Stumm, Werner and James J. Morgan, *Aquatic Chemistry*, John Wiley and Sons, New York, 1970, p. 318.

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

^b These data correspond to $a_{\text{HCO}_3^-} = 1.00 \times 10^{-3} \text{ M}$ rather than unity and, hence, are not exactly pE°(W); they represent typical aquatic conditions more exactly than pE° values do.

4.9 THE LIMITS OF pE IN WATER

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



or reduced as



These two reactions determine the limits of pE in water. On the oxidizing side (relatively more positive pE values), the pE value is limited by the oxidation of water, half-reaction 4.45. The evolution of hydrogen, Half-reaction 4.46, limits the pE value on the reducing side.

The condition under which oxygen from the oxidation of water has a pressure of 1.00 atm can be regarded as the oxidizing limit of water, whereas a hydrogen pressure of 1.00 atm may be regarded as the reducing limit of water. These are *boundary conditions* that enable calculation of the stability boundaries of water. Writing the reverse of Reaction 4.45 for one electron and setting $P_{\text{O}_2} = 100$ yield



Thus, Equation 4.49 defines the pH-dependent oxidizing limit of water. At a specified pH, pE values more positive than the one given by Equation 4.49 cannot exist at equilibrium in water in contact with the atmosphere.

$$pE = pE^0 + \log(P_{\text{O}_2}^{1/4} [\text{H}^+]) \quad (4.48)$$

$$pE = 20.75 - \text{pH} \quad (4.49)$$

The pE -pH relationship for the reducing limit of water taken at $P_{\text{H}_2} = 1$ atm is given by the following derivation:



$$pE = pE^0 + \log[\text{H}^+] \quad (4.51)$$

$$pE = -\text{pH} \quad (4.52)$$

For neutral water ($\text{pH} = 7.00$), substitution into Equations 4.52 and 4.49 yields -7.00 to 13.75 for the pE range of water. The pE -pH boundaries of stability for water are shown by the dashed lines in Figure 4.4 of Section 4.11.

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

4.10 pE VALUES IN NATURAL WATER SYSTEMS

Although it is not generally possible to obtain accurate pE values by direct potentiometric measurements in natural aquatic systems, in principle, pE values may be calculated from the species present in water at equilibrium. An obviously significant pE value is that of neutral water in thermodynamic equilibrium with the atmosphere. In water under these conditions, $P_{\text{O}_2} = 0.21$ atm and $[\text{H}^+] = 1.00 \times 10^{-7}$ M. Substitution into Equation 4.48 yields

$$pE = 20.75 + \log\{(0.21)^{1/4} \times 1.00 \times 10^{-7}\} = 13.8 \quad (4.53)$$

According to this calculation, a pE value of around +13 is to be expected for water in equilibrium with the atmosphere, that is, an oxic water. At the other extreme, consider anoxic water in which

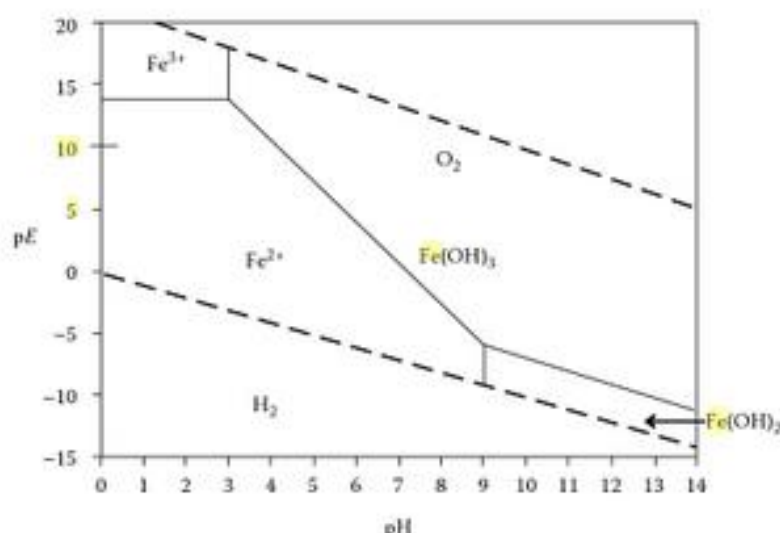


FIGURE 4.4 Simplified pE - pH diagram for iron in water. The maximum soluble iron concentration is 1.00×10^{-5} M.

methane and CO_2 are being produced by microorganisms. Assume $P_{CO_2} = P_{CH_4}$ and that $pH = 7.00$. The relevant half-reaction is



for which the Nernst equation is

$$pE = 2.87 + \log \frac{P_{CO_2}^{1/8} [H^+]}{P_{CH_4}^{1/8}} = 2.87 + \log [H^+] = 2.87 - 7.00 = -4.13 \quad (4.55)$$

Note that the pE value of -4.13 does not exceed the reducing limit of water at $pH 7.00$, which from Equation 4.52 is -7.00 . It is of interest to calculate the pressure of oxygen in neutral water at this low pE value of -4.13 . Substitution into Equation 4.48 yields

$$-4.13 = 20.75 + \log (P_{O_2}^{1/4} \times 1.00 \times 10^{-7}) \quad (4.56)$$

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

4.11 pE - pH DIAGRAMS

The examples cited so far have shown the close relationships between pE and pH in water. This relationship may be expressed graphically in the form of a pE - pH diagram. Such diagrams show the regions of stability and the boundary lines for various species in water. Because of the numerous species that may be formed, such diagrams may become extremely complicated. For example, if a metal is being considered, several different oxidation states of the metal, hydroxy

complexes, and different forms of the solid metal oxide or hydroxide may exist in different regions described by the pE - pH diagram. Most waters contain carbonate, and many contain sulfates and sulfides, so that various metal carbonates, sulfates, and sulfides may predominate in different regions of the diagram. In order to illustrate the principles involved, however, a simplified pE - pH diagram is considered here. The reader is referred to more advanced works on geochemistry and aquatic chemistry for more complicated (and more realistic) pE - pH diagrams.^{1,2}

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



$$K_{sp} = \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^2} = 8.0 \times 10^{12} \quad (4.59)$$



$$K'_{sp} = \frac{[\text{Fe}^{3+}]}{[\text{H}^+]^3} = 9.1 \times 10^3 \quad (4.61)$$

[The constants K_{sp} and K'_{sp} are derived from the solubility products of $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$, respectively, and are expressed in terms of $[\text{H}^+]$ to facilitate the calculations.] Note that the formation of species such as $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_2^+$, and solid FeCO_3 or FeS , all of which might be of significance in a natural water system, is not considered. Rapid hydrolysis of iron(III) in solution yields solid ferrihydrite, a hydrated iron(III) hydroxide/oxide with a high surface area and strong affinity to coprecipitate metals other than iron.

In constructing the pE - pH diagram, several boundaries must be considered. The first two of these are the oxidizing and reducing limits of water (see Section 4.9). At the high pE end, the stability limit of water is defined by Equation 4.49 derived previously:

$$pE = 20.75 - pH \quad (4.49)$$

The low pE limit is defined by Equation 4.52:

$$pE = -pH \quad (4.52)$$

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

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

$$pE = 13.2 + \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \quad (4.62)$$

$$[\text{Fe}^{3+}] = [\text{Fe}^{2+}] \quad (4.63)$$

$$pE = 13.2 \quad (\text{independent of } pH) \quad (4.64)$$

At pE exceeding 13.2, as the pH increases from very low values, $\text{Fe}(\text{OH})_3$ precipitates from a solution of Fe^{3+} . The pH at which precipitation occurs depends, of course, upon the concentration

of Fe^{3+} . In this example, a maximum soluble iron concentration of $1.00 \times 10^{-5} \text{ M}$ has been chosen so that at the $\text{Fe}^{3+}/\text{Fe}(\text{OH})_3$ boundary, $[\text{Fe}^{3+}] = 1.00 \times 10^{-5} \text{ M}$. Substitution in Equation 4.61 yields

$$[\text{H}^+]^3 = \frac{[\text{Fe}^{3+}]}{K'_{\text{sp}}} = \frac{1.00 \times 10^{-5}}{9.1 \times 10^3} \quad (4.65)$$

$$\text{pH} = 2.99 \quad (4.66)$$

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

$$[\text{H}^+]^2 = \frac{[\text{Fe}^{2+}]}{K_{\text{sp}}} = \frac{1.00 \times 10^{-5}}{8.0 \times 10^{12}} \quad (4.67)$$

$$\text{pH} = 8.95 \quad (4.68)$$

Throughout a wide pE - pH range, Fe^{2+} is the predominant soluble iron species in equilibrium with the solid hydrated iron(III) oxide, $\text{Fe}(\text{OH})_3$. The boundary between these two species depends upon both pE and pH . Substituting Equation 4.61 into Equation 4.62 yields

$$\text{pE} = 13.2 + \frac{K'_{\text{sp}}[\text{H}^+]^3}{[\text{Fe}^{2+}]} \quad (4.69)$$

$$\begin{aligned} \text{pE} &= 13.2 + \log 9.1 \times 10^3 - \log 1.00 \times 10^{-5} + 3 \times \log[\text{H}^+] \\ \text{pE} &= 22.2 - 3 \text{ pH} \end{aligned} \quad (4.70)$$

The boundary between the solid phases $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ likewise depends upon both pE and pH , but it does not depend upon an assumed value for total soluble iron. The required relationship is derived from substituting both Equations 4.59 and 4.61 into Equation 4.62:

$$\begin{aligned} \text{pE} &= 13.2 + \log \frac{K'_{\text{sp}}}{K_{\text{sp}}[\text{H}^+]^2} [\text{H}^+]^3 \\ \text{pE} &= 13.2 + \log \frac{9.1 \times 10^3}{8.0 \times 10^{12}} + \log[\text{H}^+] \end{aligned} \quad (4.71)$$

$$\text{pE} = 4.3 - \text{pH} \quad (4.72)$$

All of the equations needed to prepare the pE - pH diagram for iron in water have now been derived. To summarize, the equations are (Equation 4.49), O_2 - H_2O boundary; (Equation 4.52), H_2 - H_2O boundary; (Equation 4.64), Fe^{3+} - Fe^{2+} boundary; (Equation 4.66), Fe^{3+} - $\text{Fe}(\text{OH})_3$ boundary; (Equation 4.68), Fe^{2+} - $\text{Fe}(\text{OH})_2$ boundary; (Equation 4.70), Fe^{2+} - $\text{Fe}(\text{OH})_3$ boundary; and (Equation 4.72), $\text{Fe}(\text{OH})_2$ - $\text{Fe}(\text{OH})_3$ boundary.

The pE - pH diagram for the iron system in water is shown in Figure 4.4. In this system, at a relatively high hydrogen-ion activity and high electron activity (an acidic reducing medium), iron(II) ion, Fe^{2+} , is the predominant iron species; some groundwaters contain appreciable levels of iron(II) under these conditions. (In most natural water systems the solubility range of Fe^{2+} is relatively narrow because

of the precipitation of FeS or FeCO_3 .) At a very high hydrogen-ion activity and low electron activity (an acidic oxidizing medium), Fe^{3+} ion predominates. In an oxidizing medium at lower acidity, solid $\text{Fe}(\text{OH})_3$ is the primary iron species present. Finally, in a basic reducing medium, with low hydrogen-ion activity and high electron activity, solid $\text{Fe}(\text{OH})_2$ can be stable.

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

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

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



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

$$pE = -7.45 + \frac{1}{2} \log [\text{Fe}^{2+}] \quad (4.74)$$

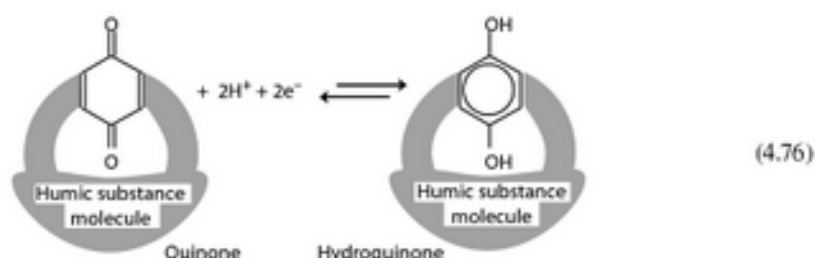
For iron metal in equilibrium with $1.00 \times 10^{-5} \text{ M Fe}^{2+}$, the following pE value is obtained:

$$pE = -7.45 + \frac{1}{2} \log 1.00 \times 10^{-5} = -9.95 \quad (4.75)$$

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

4.12 HUMIC SUBSTANCES AS NATURAL REDUCTANTS

Humic substances (see Section 3.17) are oxidation–reduction-active species that may be significant as reducing species in chemical and biochemical processes that occur in natural water and wastewater systems. The capability of humic substances to act as reductants is due primarily to the presence of the quinone/hydroquinone group that acts as an oxidation–reduction couple as follows:



There is some evidence suggesting that soluble humic substances can act as intermediates in the reduction of species in water by solid reductants, such as solid iron(II) species.