Oxidation-Reduction (Redox) Reactions

Eh, Ph, and the chemistry of natural waters
Important equations and terms for redox reactions:

\[ \Delta G_R = nFE \]
\[ \Delta G_R = \Delta G_R^\circ + RT\ln Q \]
\[ \text{Eh} = E = E^\circ + \left(\frac{2.303RT}{nF}\right)\log Q = \left(\frac{0.05916}{n}\right)\log Q \]
\[ E^\circ = -\left(\frac{0.05916}{n}\right)\log K \]
\[ \text{Eh} = 1.23 + 0.01479\log[O_2] - 0.05916\text{pH} \]

\[ R = 1.987 \times 10^{-3} \text{ kcal/mol}^\circ \]
\[ T = 298.15^\circ \text{K} \]
\[ F = 23.06 \text{ kcal/V} \]
\[ n = \text{number of electrons transferred in the reaction} \]
\[ Q = \text{reaction quotient} \]
\[ E^\circ = \text{standard potential for a half-reaction} \]
\[ \text{Eh} = \text{electromotive force (emf) generated between an electrode in any state and the H}_2\text{ electrode (the reference hydrogen scale Eh)} \text{ in standard state (theoretical voltage)} \]
Zn(s) + Cu^{2+} (aq) \rightleftharpoons Zn^{2+} (aq) + Cu(s)

Each metal has a different relative preference for electrons

Electrode Potential
Separate the reaction into half-reactions and add the e-

\[ \text{Zn}(s) + \text{Cu}^{2+} (aq) \rightleftharpoons \text{Zn}^{2+} (aq) + \text{Cu}(s) \]

\[ \text{Zn}(s) \rightleftharpoons \text{Zn}^{2+} (aq) + 2e^- \]

\[ \text{Cu}^{2+} (aq) + 2e^- \rightleftharpoons \text{Cu}(s) \]

There will be Energy gained or lost by the exchange of e-

Unfortunately, such measurements are not possible (nor would these reactions occur in the natural environment: electrons are not given up except to another element or species).

This requires the establishment of an arbitrary reference value.
Hydrogen Scale Potential Eh

\[
\frac{1}{2} H_2(g) \rightleftharpoons H^+(aq) + e^-
\]

The potential measured for the entire reaction is then assigned to the half-cell reaction of interest:

\[
\text{Zn}(s) \rightleftharpoons \text{Zn}^{2+}(aq) + 2e^- \quad \text{becomes}
\]

\[
\text{Zn}^{2+}(aq) + H_2(g) \rightleftharpoons \text{Zn}(s) + 2H^+
\]

The potential for this reaction = -0.763 V

So the Eh of the reduction of Zn\(^{2+}\) to Zn (s) = -0.763 V
\[ Zn^{2+}(aq) + H_2(g) \rightleftharpoons Zn(s) + 2H^+ \]

(+) \( Eh \) means reaction moves left to right
(-) \( Eh \) means reaction moves right to left

\[ Eh = E = E^\circ + (2.303RT/nF)\log Q = (0.05916/n)\log Q \]

(+) \( Eh \) means the metal ion is reduced by \( H_2(g) \) to the metal
(-) \( Eh \) means the metal will be oxidized to the ion and \( H^+ \) is reduced
Calculating the Eh of Net Reactions

We can calculate Eh values by algebraic combinations of the reactions and potentials that are listed in Table 14.3 of the text.

There is, however, a “catch”

Calculate the Eh for the reaction:
\[ \text{Fe}^{3+}(aq) + 3\text{e}^- \rightleftharpoons \text{Fe(s)} \]
This reaction is the algebraic sum of two reactions listed in Table 14.3

\[ \text{Fe}^{3+}(aq) + e^- \leftrightarrow \text{Fe}^{2+}(aq) \]
\[ \text{Fe}^{2+}(aq) + 2e^- \leftrightarrow \text{Fe}(s) \]

Since the reactions sum, we might assume that we can simply sum the Eh values to obtain the Eh of the net reaction.

Doing so, we obtain an Eh of 0.33 V.
However, the true Eh of this reaction is -0.037 V.

**What did we do wrong?**
We have neglected to take into consideration the number of electrons exchanged.

\[
\begin{align*}
\text{Fe}^{3+}(aq) + \text{e}^- & \rightleftharpoons \text{Fe}^{2+}(aq) \\
\text{Fe}^{2+}(aq) + 2\text{e}^- & \rightleftharpoons \text{Fe}(s)
\end{align*}
\]

In the algebraic combination of Eh values, we need to multiply the Eh for each component reaction by the number of electrons exchanged.

We then divide the sum of these values by number of electrons exchanged in the net reaction to obtain the Eh of the net reaction

\[
Eh_{(net)} = \frac{1}{z_{net}} \sum_i z_i Eh_i
\]
\[ Eh(\text{net}) = \frac{1}{z_{\text{net}}} \sum_{i} z_{i}Eh_{i} \]

where the sum is over the component reactions \( i \).

By Hess’s Law, the \( \Delta G \) of the net reaction must be the simple sum of the component reaction \( \Delta G \)’s

…but Eh values are obtained by multiplying \( \Delta G \) by \( z \).

\[ \Delta G_{R} = nFE \]
\[ Eh nett = \frac{1}{z_{net}} \sum_{i} z_i Eh_i \]

\[
Eh = \frac{1}{3} (1 \times 0.77 + 2 \times -0.44) = \frac{1}{3} (0.77 - 0.88) = \frac{1}{3}(-0.11) = -0.037
\]

Fe\(^{3+}\)(aq) + e\(-\) \rightleftharpoons Fe\(^{2+}\)(aq)

Fe\(^{2+}\)(aq) + 2e\(-\) \rightleftharpoons Fe(s)
\[
\text{Eh(volts)} = E^\circ + \frac{RT}{nF} \ln \left( \frac{(A)^a(B)^b}{(C)^c(D)^d} \right)
\]

\[
\text{Eh} = E^\circ + (2.303RT/nF)\log Q = (0.05916/n)\log Q
\]

\[
aA + bB + ne^- = cC + dD
\]

oxidized \hspace{1cm} \text{reduced}
If an environment is characterized by a certain redox reaction, it has a characteristic Eh.

\[ \text{Eh} = 1.23 + 0.01479\log[O_2] - 0.05916\text{pH} \]

\[ [O_2] = 10^{-8.31}\text{atm} \]

From Garrels & Christ (1965)

Similar to Fig. 14.4 on p. 238
1) write the equation for the reaction

\[ H_2O(l) \leftrightarrow \frac{1}{2} O_2(g) + H_2(g) \]

2) “electrode” the equation

\[ H_2O(l) \leftrightarrow 2H^+ + \frac{1}{2} O_2(g) + 2e^- \]

O in H₂O gives up 2e-

2e-
3) 
\[ Eh = E^\circ + \frac{0.05916}{2} \log\left(\frac{[O_2]}{[H^+]^2}\right) \]

4) get \( E^\circ \) from \( \Delta G_r^\circ \)

\[ \Delta G_r^\circ = \left[2G_f^\circ(H^+) + 1/2 G_f^\circ(O_2) + 2G_f^\circ(e^-)\right] - \left[G_f^\circ(H_2O(l))\right] \]

\[ G_f^\circ H^+ = G_f^\circ O_2 = G_f^\circ e^- = 0 \]

\[ \Delta G_r^\circ = -G_f^\circ H_2O = +56.687 \text{ kcal} \]

\[ E^\circ = + \frac{56.687}{2 \times 23.06} = +1.23V \]
6) 

\[
Eh = 1.23 + \frac{0.05916}{2} \log \left( [O_2]^{1/2} [H^+]^2 \right)
\]

\[
Eh = 1.23 + 0.01479 \log [O_2] - 0.05916 \text{pH}
\]

This demonstrates the Eh - pH relationship as shown in figure 14.4 p. 238 and is the equation for the lines limiting the minimum and maximum [O₂] for natural waters.
Figure 14.11 on p. 248