1. Exercises 6.6, 6.8, 6.11, 6.12, 6.13, 6.18

6.6 In general terms the Nernst equation is

\[ E = E^* - \left( \frac{RT}{NF} \right) \ln Q \]

where \( Q \) is the reaction quotient.

(a) For the reduction of oxygen, \( \text{O}_2(g) + 4 \text{H}^+(aq) + 4 e^- \rightarrow 2 \text{H}_2\text{O}(l) \), first we must solve for \( Q \), given the partial pressure of oxygen and the pH.

\[ Q = \frac{1}{p(O_2)[H^+]^4} = \frac{1}{(0.2\text{bar})(1\times10^{-7})^4} = 5 \times 10^{28} \]

Substituting into the Nernst equation, we find

\[ E = 1.229V - \frac{0.059V}{4} \ln(5 \times 10^{28}) = 1.229V - 0.42V = 0.81V \]

(b) For the reduction of \( \text{Fe}_2\text{O}_3(s) \),

\[ Q = \frac{1}{[H^+]^6} \]

and

\[ E = E^* - \left( \frac{RT}{NF} \right) \ln \left( \frac{1}{[H^+]^6} \right) = E^* + \left( \frac{RT}{NF} \right) \ln([H^+]^6) = E^* + 6 \left( \frac{RT}{NF} \right) \ln([H^+]) \]

\[ E = E^* - 6 \left( \frac{RT}{NF} \right) (2.3)(-\log([H^+])) = E^* - 13.8 \left( \frac{RT}{NF} \right) \text{pH} \]

6.8 (a) For basic solutions, we follow the dotted line in Figure 6.16. If the points for \( \text{Cl}^- \) and \( \text{ClO}_4^- \) are connected by a straight line, \( \text{Cl}_2 \) lies above it. Therefore, \( \text{Cl}_2 \) is thermodynamically susceptible to disproportionation to \( \text{Cl}^- \) and \( \text{ClO}_4^- \) when it is dissolved in aqueous base. In practice, the oxidation of \( \text{ClO}^- \) is slow, so a solution of \( \text{Cl}^- \) and \( \text{ClO}_4^- \) is formed when \( \text{Cl}_2 \) is dissolved in aqueous base.
(b) Now looking at the solid line in Figure 6.16, if we draw a straight line from Cl to HClO₄, we see that Cl₂ is (slightly) below the line. Therefore, Cl₂ will not spontaneously disproportionate; however, $E^\circ$ for the Cl₂/Cl⁻ couple is 1.36 V. This value is more positive than $E^\circ$ for the O₂/H₂O couple, 1.23 V. Therefore, Cl₂ is thermodynamically capable of oxidizing water (although the reaction is very slow).

$$\text{Cl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{Cl}^-(\text{aq}) + 2 \text{H}^+(\text{aq}) + \frac{1}{2} \text{O}_2(\text{l})$$

(c) The point for ClO₃⁻ in acidic solution on the Frost diagram in Figure 6.16 lies above the single straight line connecting the points for Cl₂ and ClO₄⁻. Therefore, since ClO₃⁻ is thermodynamically unstable with respect to disproportionation in acidic solution (i.e. it should disproportionate), the failure of it to exhibit any observable disproportionation must be due to a kinetic barrier.

6.11 (a) The transformation of reactants into products can be envisioned to take place by the simple atom transfer of an “I⁺⁺” ion from HOI to I. Therefore, this is probably an atom transfer reaction.

(b) This reaction takes place without any net change in the coordination spheres of the two metal ions (Co³⁺ and Cr³⁺ are kinetically inert to substitution). The cobalt ion has three phenanthroline (phen) ligands whether it is +3 or +2 and the chromium ion has three bipyridine (bipy) ligands whether it is +2 or +3. Therefore, this is probably a simple outer-sphere electron transfer reaction.

(c) Each of the I₃⁻ ions is formed by reaction of I⁻ with I₂. It is unlikely that I₂ could be formed by a simple single-step reaction of I⁻ with IO₃⁻, since IO₃⁻ must lose all thee of its oxygen atoms. Therefore, this is probably a multistep mechanism.

6.12 The Latimer diagram for chlorine is given in Appendix 2, and the relevant portion is reproduced below:

$$\begin{align*}
\text{ClO}_4^- & \rightarrow 1.201V \rightarrow \text{ClO}_3^- \rightarrow 1.181V \rightarrow \text{HClO}_2 \rightarrow 1.674V \rightarrow \text{HClO} \rightarrow 1.630V \rightarrow \text{Cl}_2 \\
+7 & \rightarrow +5 \rightarrow +3 \rightarrow +1 \rightarrow 0
\end{align*}$$

To determine the potential for any couple, you must calculate the weighted average of the potentials of the intervening couples. In general terms, it is

$$\frac{n_1E_{+1}^* + n_2E_{+2}^* + \ldots + n_nE_{+n}^*}{(n_1 + n_2 + \ldots + n_n)}$$

In this specific case, it is

$$\frac{(2)(1.201V) + (2)(1.181V) + (2)(1.674V) + (1)(1.630V)}{2 + 2 + 2 + 1} = 1.392V$$
Thus, the standard potential for the ClO$_4^-$/Cl$_2$ couple is 1.392 V. The balanced half-reaction (prove this for yourself) for this reduction is

$$2 \text{ClO}_4^-(aq) + 16 \text{H}^+(aq) + 14 \text{e}^- \rightarrow \text{Cl}_2(g) + 8 \text{H}_2\text{O}(l)$$

Note that the point for ClO$_4^-$ at pH 0 in the Frost diagram shown in Figure 6.16 has a y value of ~9.7, which is $NE^o/V$ or 7(1.392).

6.13 To calculate an equilibrium constant using thermodynamic data, you can make use of the expressions $\Delta G = -RT\ln K$ and $\Delta G = -\nu FE$. Since the overall reaction is just the sum of two reactions, we can invoke Hess’s Law to find $\Delta G$.

$$\begin{align*}
\text{Au}^+(aq) + \text{e}^- & \rightarrow \text{Au}(s) \quad E^o = +1.69 \text{ V} \\
\text{Au}(s) + 2 \text{CN}^-(aq) & \rightarrow [\text{Au(CN)}_2]^-(aq) + \text{e}^- \quad E^o = +0.60 \text{ V} \\
\text{Au}^+(aq) + 2\text{CN}^- \quad & \rightarrow [\text{Au(CN)}_2]^-(aq)
\end{align*}$$

Now we solve for $\Delta G$

$$\Delta G = F(\nu_1E^o_1 + \nu_2E^o_2) = (96.485kJ \cdot mol^{-1}V^{-1})[(1)(1.69V) + (1)(0.60V)] = 221kJ \cdot mol^{-1}$$

From this, we assume $T = 298K$ (room temperature) and solve for $K$.

$$K = \exp\left(-\frac{\Delta G}{RT}\right) = \exp\left(-\frac{221kJ \cdot mol^{-1}}{8.31J \cdot K^{-1} \cdot mol^{-1}}(298)\right) = \exp(89.2) = 5.7 \times 10^{38}$$

6.18 If the metal ion is coordinated by only water molecules, then the potential measured from the cyclic voltammogram (i.e. the midpoint measured between the cathodic and anodic peak potentials) should be equal to the value derived from standard potentials, taking into account the pH of the solution. However, if other ligands are present, the measured potential will not correspond to the standard value. Instead, the reduction potential will be either higher or lower than the standard value depending on whether the ligands coordinate more strongly to the reduced metal ion or to the oxidized metal ion.

2. Problems 6.2, 6.4, 6.9, 6.10

6.2 Since the identity of the hydrogen isomer affect the rate of the reaction, we can surmise that a protonation / deprotonation must be involved in the rate-determining-step of the reaction. This should not affect the rate of simple electron transfer, since that mechanism does not at all relate to the identity of the solvent. Simple atom transfer—a special case of inner-sphere electron transfer—involves the atoms coordinated to the complex. Again, unless the atom transfer involves a water molecule, the rate should not be affected by the identity of the solvent.
6.4 The oxygen reaction (from Table 6.1) is
\[ \text{O}_2 + 4 \text{H}^+ + 4 e^- \rightarrow 2 \text{H}_2\text{O} \quad +1.23 \text{ V} \]
Using the equation, \( \Delta G = \nu F E^\circ \) (with \( \nu = 4 \)), we find \( \Delta G = 475 \text{ kJ mol}^{-1} \). The atomic weight of \( \text{O}_2 \) is 32 g mol\(^{-1}\), so, for 1.00 g of oxygen, we have
\[ \left( \frac{475 \text{kJ}}{1 \text{mol}} \right) \left( \frac{1 \text{mol}}{32 \text{g}} \right) (1.00 \text{g}) = 14.8 \text{kJ} \]
For iron, \( E^\circ = 1.67 \text{ V} \) and \( \nu = 1 \), so \( \Delta G = 161 \text{ kJ mol}^{-1} \). The atomic weight of FeO(OH) is 88.9 g mol\(^{-1}\).
\[ \left( \frac{161 \text{kJ}}{1 \text{mol}} \right) \left( \frac{1 \text{mol}}{88.9 \text{g}} \right) = 1.81 \text{kJ g}^{-1} \]
Now we take the ratio of these two numbers to find how many grams of the iron compound are needed to produce as much energy as oxygen.
\[ \left( \frac{14.8 \text{kJ}}{1.81 \text{kJ g}^{-1}} \right) = 8.18 \text{g} \]

6.9 To construct the Frost diagram, we must first figure out the value of all of the points. The elemental mercury has an oxidation number of 0, and is the first point of our graph. The remainder of the points is determined from their distance from \( \text{Hg}_0 \). For \( \text{Hg}^{2+} \), with a +1 oxidation state, \( NE^\circ = 0.796 \text{ V} \). For \( \text{Hg}^{2+} \), in the +2 oxidation state, the potential from elemental Hg is \((0.911 + 0.706)/2 = 0.854 \text{ V}\), so \( NE^\circ = 1.707 \text{ V} \). We then plot these values to obtain the graph, below.

![Frost Diagram](image)

From this graph, we see that \( \text{Hg}_2^{2+} \) is slightly below the line that would connect Hg and \( \text{Hg}_2^{2+} \), so we would predict that it would not spontaneously disproportionate. In fact, we would predict that Hg and \( \text{Hg}^{2+} \) would comproportionate to form \( \text{Hg}_2^{2+} \). None of the slopes are especially steep, so we would not expect any of the species to be especially good oxidizing or reducing agents.
6.10 If we first write out the two half-reactions that make up the disproportionation reaction, we can assign each a potential from the Latimer diagram.

\[
\begin{align*}
\text{HO}_2 & \rightarrow \text{O}_2 + \text{H}^+ + e^- & E^\circ = 0.125 \text{ V (Note the sign)} \\
\text{HO}_2 + \text{H}^+ + e^- & \rightarrow \text{H}_2\text{O}_2 & E^\circ = 1.510 \text{ V}
\end{align*}
\]

The net \(E^\circ\) is simply the sum of the individual \(E^\circ\) values of the half-reactions: \(E^\circ = 0.125 \text{ V} + 1.510 \text{ V} = 1.735 \text{ V}\). Since \(E^\circ > 0\), we expect this to be a spontaneous reaction.

3. The corrosion of steel in seawater is a common problem for both the pleasure boater as well as the U.S. Navy. While it is a complex process involving water and an electrolyte, one key electrochemical step is the oxidation of the iron in steel to the ferrous state.

\[
\text{Fe(II)} + 2e^- \rightarrow \text{Fe(s)} \quad E^\circ = -0.44 \text{ V}
\]

Under anaerobic conditions the Fe(II) precipitates as Fe(II)(OH)\(_2\), while under aerobic conditions the Fe(II) further oxidizes to yield Fe\(_{2}\)O\(_3\)·H\(_2\)O (rust).

\[
\begin{align*}
\text{O}_2(g) + 2 \text{H}_2\text{O}(l) + 4e^- & \rightarrow 4 \text{OH}^- & E^\circ = +0.82 \text{ V (pH 7)} \\
2\text{H}^+ + 2e^- & \rightarrow \text{H}_2(g) & E^\circ = -0.41 \text{ V (pH 7)}
\end{align*}
\]

One popular method of preventing the steel corrosion is attachment of a block of zinc as a sacrificial anode.

\[
\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn(s)} \quad E^\circ = -0.76 \text{ V}
\]

(a) How many kJ/mol more favorable is the oxidation of zinc compared to iron?

For zinc,

\[
\Delta G_{\text{zinc}} = vFE^\circ = (2)(96.485 \text{kJ} \cdot \text{mol}^{-1}V^{-1})(-0.76 \text{V}) = -147 \text{kJ}
\]

For iron,

\[
\Delta G_{\text{iron}} = vFE^\circ = (2)(96.485 \text{kJ} \cdot \text{mol}^{-1}V^{-1})(-0.44 \text{V}) = -85 \text{kJ}
\]

Thus, the difference is

\[
\Delta \Delta G = \Delta G_{\text{zinc}} - \Delta G_{\text{iron}} = -147 \text{kJ} + 85 \text{kJ} = -62 \text{kJ}
\]

(b) How would passivation of the Zn anode (formation of a ZnO layer) effect the corrosion of the steel?

Passivation would stop corrosion of the steel. The ZnO would coat the surface and not allow further corrosion to take place, similar to the Al\(_2\)O\(_3\) coating on aluminum cans.
(c) According to the following reduction half-equations, which metals could be used in place of zinc?

\[
\begin{align*}
    \text{K}^+_{(aq)} + e^- & \rightarrow \text{K} (s) & \quad E^\circ = -2.93 \text{ V} \\
    \text{Mg}^{2+} + 2 e^- & \rightarrow \text{Mg} (s) & \quad E^\circ = -2.37 \text{ V} \\
    \text{Al}^{3+} + 3 e^- & \rightarrow \text{Al} (s) & \quad E^\circ = -1.66 \text{ V} \\
    \text{Cu}^{2+} + 2 e^- & \rightarrow \text{Cu} (s) & \quad E^\circ = +0.15 \text{ V} \\
    \text{Ag}^+ + e^- & \rightarrow \text{Ag} (s) & \quad E^\circ = +0.80 \text{ V} \\
    \text{Co}^{3+} + 1 e^- & \rightarrow \text{Co}^{2+} & \quad E^\circ = +1.92 \text{ V}
\end{align*}
\]

All of the elements with \( E^\circ \) values less than –0.44V could be used in place of zinc. Each of these would be preferentially oxidized before iron.

(d) Considering the solvent (salty sea water) which metal, besides Zn, is the best choice and why?

Clearly, the aqueous K\(^+\) ion is not a good choice as an anode in salty sea water, as it would simply mix with the water. For the other two options, magnesium and aluminum, we need to consider the proton-to-hydrogen-gas reaction. Magnesium is such a good reductant that it begins to produce hydrogen gas from protons at a very high rate (because of the very large overpotential). The overpotential for this reaction is \(-2.37 \text{ V} + 0.41 \text{ V} = -1.96 \text{ V}\). An overpotential of greater than 0.6 V leads to a very fast reaction. Aluminum is also capable of this reaction, but since its potential is lower, the reaction does not occur nearly as quickly.