Due: Monday, 11/10 by 5 p.m.

1. Problem 16.1 in the text (p. 379)
   A. Chlorine exists in seven oxidation states. Determine the oxidation state of each compound and order them from the most negative oxidation state to the most positive oxidation state.

<table>
<thead>
<tr>
<th>Substance</th>
<th>formula</th>
<th>Chlorine oxidation state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride</td>
<td>Cl⁻</td>
<td>-1</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Cl₂</td>
<td>0</td>
</tr>
<tr>
<td>Hypochlorous acid</td>
<td>HOCl</td>
<td>+1</td>
</tr>
<tr>
<td>Chlorite</td>
<td>ClO₂⁻</td>
<td>+3</td>
</tr>
<tr>
<td>Chlorine dioxide</td>
<td>ClO₂</td>
<td>+4</td>
</tr>
<tr>
<td>Chlorate</td>
<td>ClO₃⁻</td>
<td>+5</td>
</tr>
<tr>
<td>Perchlorate</td>
<td>ClO₄⁻</td>
<td>+7</td>
</tr>
</tbody>
</table>

   B. Write a balanced half reaction for the conversion of each oxidation state to the next highest oxidation state at low pH.

   1. \( \text{Cl}^- \leftrightarrow \frac{1}{2} \text{Cl}_2 + e^- \)
   2. \( \text{Cl}_2 + \text{H}_2\text{O} \leftrightarrow \text{HOCl} + e^- + \text{H}^+ \)
   3. \( \text{HOCl} + \text{H}_2\text{O} \leftrightarrow \text{ClO}_2^- + 2e^- + 3\text{H}^+ \)
   4. \( \text{ClO}_2^- \leftrightarrow \text{ClO}_2 + e^- \)
   5. \( \text{ClO}_2 + \text{H}_2\text{O} \leftrightarrow \text{ClO}_3^- + e^- + 2\text{H}^+ \)
   6. \( \text{ClO}_3^- + \text{H}_2\text{O} \leftrightarrow \text{ClO}_4^- + 2e^- + 2\text{H}^+ \)

2. Problem 16.3 in the text (p. 379)
   Dissolved oxygen, \( \text{O}_2(\text{aq}) \) or DO, can be measured by a wet-chemical technique called the Winkler method which consists of the steps listed below. For each step, write the balanced overall reaction.

   **Step 1. Addition of Mn(II) in alkaline solution**
   \[
   2(\text{Mn}^{2+} + 3\text{H}_2\text{O} \leftrightarrow \text{MnO(OH)}_{2(\text{s})} + 2e^- + 4\text{H}^+) \\
   \text{O}_2 + 4e^- + 4\text{H}^+ \leftrightarrow 2\text{H}_2\text{O} \\
   2\text{Mn}^{2+} + \text{O}_2 + 4\text{H}_2\text{O} \leftrightarrow 2\text{MnO(OH)}_{2(\text{s})} + 4\text{H}^+ 
   \]

   **Step 2. Iodide addition**
   \[
   \text{MnO(OH)}_{2(\text{s})} + 2e^- + 4\text{H}^+ \leftrightarrow \text{Mn}^{2+} + 3\text{H}_2\text{O} \\
   2\text{I}^- \leftrightarrow \text{I}_2 + 2e^- \\
   \text{MnO(OH)}_{2(\text{s})} + 2\text{I}^- + 4\text{H}^+ \leftrightarrow \text{Mn}^{2+} + \text{I}_2 + 3\text{H}_2\text{O} 
   \]
Step 3. Titration of I₂ with S₂O₃²⁻

\[ I_2 + 2e^- \leftrightarrow 2I^- \]
\[ 2S_2O_3^{2-} \leftrightarrow S_4O_6^{2-} + 2e^- \]
\[ I_2 + 2S_2O_3^{2-} \leftrightarrow 2I^- + S_4O_6^{2-} \]

D. Combine the steps and write the overall reaction for the Winkler method. Is the overall reaction equation consistent with 1 mg/L DO in a 200 mL requiring 1 mL of 0.025 M Na₂S₂O₃ titrant?

**ANSWER:** The overall reaction is:

\[ O_2 + 4S_2O_3^{2-} + 4H^+ \leftrightarrow 2H_2O + 2S_4O_6^{2-} \]

One mole of oxygen requires 4 moles of thiosulfate. Therefore 1 mg/L of DO in 200 mL (equal to 0.00625 mmoles) should require 0.025 millimoles of thiosulfate which is consistent with adding 1 mL of 0.025 M Na₂S₂O₃.

3. Problem 16.4 in the text (p. 380)

A. If the oxidation state of H in hydrogen peroxide (H₂O₂) is +1, what is the oxidation state of oxygen?

**ANSWER:** The oxidation state of each oxygen must be -1 to balance the charges of the two hydrogens.

B. Write the half reactions and overall reaction for the conversion of hydrogen peroxide to molecular oxygen and water.

**SOLUTION:**

\[ H_2O_2 \leftrightarrow O_2 + 2H^+ + 2e^- \]
\[ 2H^+ + H_2O_2 + 2e^- \leftrightarrow 2H_2O \]

Net reaction:

\[ 2H_2O_2 \leftrightarrow O_2 + 2H_2O \]

C. Is the overall reaction a disproportionation or a comproportionation reaction or neither?

**ANSWER:** The overall reaction is a disproportionation reaction in which a single oxidation state of oxygen reacts to yield two different oxidation states.

4. Problem 16.5 in the text (p. 380)

A. A drinking water treatment plant is using ozone for disinfection. Plant personnel want to use ozone also to oxidize reduced manganese, Mn²⁺, to MnO₂(s). Find the required ozone dose (g O₃ per g Mn²⁺ oxidized) if ozone is reduced to oxygen.

**SOLUTION:** The two half reactions are:

\[ Mn^{2+} + 2H_2O \leftrightarrow MnO_2(s) + 4H^+ + 2e^- \]
\[ O_3 + 2H^+ + 2e^- \leftrightarrow O_2 + H_2O \]
Net reaction: \( \text{Mn}^{2+} + \text{O}_3 + \text{H}_2\text{O} \leftrightarrow \text{MnO}_2(s) + \text{O}_2 + 2\text{H}^+ \)

One mole of Mn requires one mole of ozone. Therefore 1 g of Mn which equals 0.0182 moles requires 0.0182 moles of ozone which is equal to 0.874 g \( \text{O}_3 \).

5. **Problem 16.9 in the text (P. 380)**

Reproduce the \( \text{pH} \)-\( \text{pE} \) diagram for the aqueous chlorine system shown in Figure 16.12. The pertinent equilibria are:

- \( \text{HOCl} + \text{H}^+ + \text{e}^- \leftrightarrow \frac{1}{2} \text{Cl}_2(aq) + \text{H}_2\text{O} \quad \text{Log } K = 26.6 \)
- \( \frac{1}{2} \text{Cl}_2(aq) + \text{e}^- \leftrightarrow \text{Cl}^- \quad \text{Log } K = 23.6 \)
- \( \text{HOCl} \leftrightarrow \text{OCl}^- + \text{H}^+ \quad \text{Log } K = -7.54 \)

**SOLUTION:**

The species to consider are \( \text{Cl}_2, \text{HOCl}, \text{OCl}^- \) and \( \text{Cl}^- \). For each pair of species, we want to write a half reaction for which the Nernst equation will be written in log form as the equation of a straight line.

1. **HOCl and Cl\(_2\)**

   \[
   \text{HOCl} + \text{H}^+ + \text{e}^- \leftrightarrow \frac{1}{2} \text{Cl}_2(aq) + \text{H}_2\text{O} \quad \text{Log } K = 26.6
   \]

   \[
   \text{pe} = \text{pe}^0 - \frac{1}{\text{n}} \log \left( \frac{\text{[reduced]}}{\text{[oxidized]}} \right) \\
   \text{pe} = \text{pe}^0 - \frac{1}{\text{n}} \cdot \log \left( \frac{\{\text{Cl}_2\}^{0.5}}{\{\text{HOCl}\} \cdot \{\text{H}^+\}} \right) = \text{pe}^0 - \frac{1}{\text{n}} \cdot \log \left( \frac{\{\text{HOCl}\} \cdot \{\text{H}^+\}}{\{\text{Cl}_2\}^{0.5}} \right) - \frac{1}{\text{n}} \cdot \text{pH}
   \]

   When the ratio \( \{\text{Cl}_2\}/\{\text{HOCl}\} = 1 \) the middle term on the left-hand side of the equation equals zero, and can be neglected. Thus, along the line \( \text{pe} = 26.6 - \text{pH} \) the activities of \( \text{Cl}_2 \) and \( \text{HOCl} \) are equal (at equilibrium).

2. **OCl\(^-\) and Cl\(_2\)**

   \[
   \text{OCl}^- + 2\text{H}^+ + \text{e}^- \leftrightarrow \frac{1}{2} \text{Cl}_2 + \text{H}_2\text{O} \quad \text{Log } K = 34.14
   \]

   \[
   \text{pe} = \text{pe}^0 - \frac{1}{\text{n}} \cdot \log \left( \frac{\{\text{Cl}_2\}^{0.5}}{\{\text{OCl}^-\}} \right) - 2\text{pH} \\
   \text{pe} = 34.14 - 2\text{pH}
   \]

3. **Cl\(_2\) and Cl\(^-\)**

   \[
   \frac{1}{2} \text{Cl}_2(aq) + \text{e}^- \leftrightarrow \text{Cl}^- \quad \text{Log } K = 23.6
   \]

   \[
   \text{pe} = \text{pe}^0 - \frac{1}{\text{n}} \cdot \log \left( \frac{\{\text{Cl}_2\}^{0.5}}{\{\text{Cl}^-\}} \right) \\
   \text{pe} = \text{pe}^0 - 23.6
   \]

4. **HOCl and Cl\(^-\)**

   \[
   \text{HOCl} + \text{H}^+ + \text{e}^- \leftrightarrow \frac{1}{2} \text{Cl}_2(aq) + \text{H}_2\text{O} \quad \text{Log } K = 26.6
   \]

   \[
   \frac{1}{2} \text{Cl}_2(aq) + \text{e}^- \leftrightarrow \text{Cl}^- \quad \text{Log } K = 23.6
   \]

   \[
   \text{HOCl} + \text{H}^+ + 2\text{e}^- \leftrightarrow \text{Cl}^- + \text{H}_2\text{O} \quad \text{Log } K = 50.2
   \]

   \[
   \text{pe} = \text{pe}^0 - \frac{1}{\text{n}} \cdot \log \left( \frac{\{\text{Cl}^-\} \cdot \{\text{H}^+\}^2}{\{\text{HOCl}\}} \right) \\
   \text{pe} = \text{pe}^0 - 25.1 - 0.5 \cdot \text{pH}
   \]

5. **OCl\(^-\) and Cl\(^-\)**

   \[
   \text{HOCl} + \text{H}^+ + 2\text{e}^- \leftrightarrow \text{Cl}^- + \text{H}_2\text{O} \quad \text{Log } K = 50.2
   \]

   \[
   \text{OCl}^- + \text{H}^+ \leftrightarrow \text{HOCl} \quad \text{Log } K = 7.54
   \]

   \[
   \text{OCl}^- + 2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{Cl}^- + \text{H}_2\text{O} \quad \text{Log } K = 57.74
   \]
\[ pe = \frac{pH}{n} \log \left( \frac{\text{Cl}^-}{\text{OCl}^-} \right) \]
\[ pe = p_e^0 - 1/n \log \left( \frac{\text{Cl}^-}{\text{OCl}^-} \right) - \frac{2}{2pH} \]
\[ pe = 28.87 - 2/2pH = 28.87 - pH \]

We now have the equations for all necessary lines, it only remains to decide which lines are appropriate to include over what range of pH and pe. The graph with all lines is shown below.

Many of the regions in this graph make no sense. For instance, the red line represents the situation where \( \{\text{OCl}^-\} = \{\text{Cl}_2\} \). However, since \( \{\text{OCl}^-\} \) becomes miniscule below where \( pH = pKa \) (7.56), it makes no sense to depict this line between pH 0 and 7.56. Above pH 7.56, the red line suggests that \( \text{Cl}_2 \) should exist below the line; however, below the red line is in the region where any \( \text{Cl}_2 \) would be reduced to \( \text{Cl}^- \) (indicated by the region below the green line). Hence the entire red line should be omitted. Once all the extraneous lines are removed, the graph simplifies to the figure shown below and in the text.
6. An aluminum pot is filled with tap water at pH 7.0 that contains 25 mg/L Cl\(^{-}\) and 1 mg/L HOCl as Cl\(_2\). What is the total dissolved Aluminum concentration in the solution after it equilibrates? You may assume that the reaction proceeds until all the HOCl is consumed.

**SOLUTION:** To answer this question, we must first write a balanced equation for the redox reaction that occurs. HOCl will be reduced and in the process will oxidize Al\(^0\) to Al\(^{3+}\).

\[
3\text{HOCl} + 3\text{H}^+ + 2\text{e}^- \rightarrow \text{Cl}^- + \text{H}_2\text{O} \quad 2\text{Al}^0 \leftrightarrow \text{Al}^{3+} + 3\text{e}^- \\
3\text{HOCl} + 3\text{H}^+ + 2\text{Al}^0 \leftrightarrow 2\text{Al}^{3+} + 3\text{Cl}^- + 3\text{H}_2\text{O}
\]

The equation indicates that for every mole of HOCl reduced, 2/3 of a mole of Al will be released from the pot into the water. We are told that there is initially 1 mg/L HOCl as Cl\(_2\) present, and that all of it will react. 1 mg/L Cl\(_2\) is equal to 0.014 moles/L; hence, the initial 0.014 moles can liberate 0.0094 moles/L Al\(^{3+}\).

The next question is whether this much Al\(^{3+}\) will remain in solution at pH 7, or whether it will precipitate as Al(OH)\(_3\)(s). That question is beyond your capability to answer right now. It turns out that most of the Al\(^{3+}\) would precipitate out of solution; the solubility of gibbsite at pH 7 is only 6x10\(^{-8}\) mole/L.

7. Once H\(_2\)S is formed in an anaerobic sediment or bottom water, it may react with dissolved oxygen in the overlying aerobic water. The contact between the two reactants might result from simultaneous diffusion of sulfide up and oxygen down, creating a sharp interface where they meet, or from the mixing of oxygenated water with sulfide-bearing sediment as a result of a storm or burrowing benthic organisms. The reaction is often mediated by bacteria, although it also occurs in the absence of microorganisms. A lake water at pH 6.5 contains 10\(^{-3}\) M SO\(_4^{2-}\) and 10\(^{-5}\) M reduced sulfur (S(-2)). Assuming the solution is at equilibrium with respect to redox reactions, determine the pe of the water. What is the equilibrium value of dissolved oxygen (pO\(_2\))?

**SOLUTION:**

We must use the Nernst equation to find the pe of the lake water. The half reaction to use is the reduction of sulfate to sulfide:

\[
10\text{H}^+ + \text{SO}_4^{2-} + 8\text{e}^- \leftrightarrow \text{H}_2\text{S} + 4\text{H}_2\text{O}
\]

Because the pH is below the pK\(_a\), the equation is written with H\(_2\)S rather than HS\(^-\) as the product. As a first approximation, we can assume that all of the S(-II) is in the form of H\(_2\)S. In that case, the Nernst equation becomes:

\[
\text{pe} = \text{pe}^0 + 1/\text{n} \cdot \log(\text{oxidized})/(\text{reduced})
\]
We need to find the pe° or log K for the reaction above, but to do that we need to add the two reactions provided in Table 16.3:

\[
\begin{align*}
\text{SO}_4^{2-} + 8\text{H}^+ + 6\text{e}^- & \rightleftharpoons \text{S(s)} + 4\text{H}_2\text{O} & \log K = 36.2 \\
\text{S(s)} + 2\text{H}^+ + 2\text{e}^- & \rightleftharpoons \text{H}_2\text{S} & \log K = 4.8 \\
\text{SO}_4^{2-} + 10\text{H}^+ + 8\text{e}^- & \rightleftharpoons \text{H}_2\text{S} + 4\text{H}_2\text{O} & \log K = 41.0 \quad \text{pe}^0 = 5.125
\end{align*}
\]

\[
\text{pe} = \text{pe}^0 + \frac{1}{n} \cdot \log \left( \frac{\text{SO}_4^{2-}}{\text{H}^+} \right)^\frac{10}{\text{H}_2\text{S}}
\]

\[
\text{pe} = 5.125 + \frac{1}{8} \cdot \log (10^{-3})(10^{-6.5})^{10}/(10^{-5}) = -2.75
\]

This is a very low pe value, indicative of highly reducing conditions. We could refine the calculation by calculating the exact concentration of H\(_2\)S from the pK\(_a\) of 7.1.

\[
\begin{align*}
\text{C}_T &= [\text{H}_2\text{S}] + [\text{HS}^-] \\
K_a &= \frac{[\text{HS}^-][\text{H}^+]}{[\text{H}_2\text{S}]} \\
K_a &= \frac{(C_T-[\text{H}_2\text{S}])}{[\text{H}_2\text{S}]} \\
[H_2S] &= \frac{\gamma_1[H^+]C_T}{K_a + \gamma_1[H^+]} = 0.93 \cdot 10^{-6.5} \cdot 10^{-5} = 10^{-5.1}
\end{align*}
\]

Obviously, this small change in H\(_2\)S concentration is not going to affect the calculate pe much; it raises it to -2.74.

At this pe we should expect extremely little dissolved oxygen. The concentration of dissolved oxygen in equilibrium at this pe would be determined from the half reaction:

\[
\text{O}_2 + 4\text{e}^- + 4\text{H}^+ \rightleftharpoons 2\text{H}_2\text{O} \quad \text{pe}^0 = 20.78
\]

\[
\begin{align*}
\text{pe} &= \text{pe}^0 + \frac{1}{n} \cdot \log (\text{O}_2\text{(g)})/[\text{H}_2\text{O}]^4 \\
-2.75 &= 20.78 + \frac{1}{4} \cdot \log (\text{pO}_2 \cdot (10^{-6.5})^4) \\
-94.12 &= \log (\text{pO}_2 \cdot (10^{-6.5})^4) \\
10^{-94.12}/10^{-26} &= \text{pO}_2 = 10^{-68.12} \text{ atm}
\end{align*}
\]

This is a very small amount of oxygen, essentially none.