Chapter 19: Electrochemistry

Electrochemistry is the interconversion of chemical energy and electrical energy; it is applied oxidation-reduction (electron transfer) chemistry.

Redox reactions:
- You should know the definitions of oxidation, reduction, and electron transfer as well as how electron transfer relates to redox reaction.
- You should be able to:
  - identify an oxidation/reduction reaction based on changes in oxidation states
  - write oxidation and reduction half reactions
  - determine oxidation numbers of elements within species and a reaction
  - identify oxidizing and reducing agents
  - balance redox reactions by the method of balancing each half reaction individually and combining them for reactions that take place in acidic solution.

Galvanic Cells:
- You should understand
  - how Galvanic cells are set up including the difference between the anode and the cathode in terms of what chemistry occurs
  - the direction of electron flow
  - the importance of the salt bridge and ion flow
  - use of line notation as short-hand representation of the Galvanic cell set-up
  - complete description of a Galvanic Cell includes the balanced cell reaction, the cell potential (see below) and a description of the physical set up of the cell (line notation)

Standard Reduction Potentials and Cell Potentials:
- You should understand
  - standard reduction potentials are measured and reported relative to the standard hydrogen electrode
  - potentials are assigned and reported for reduction half reactions
  - there is a relationship between the magnitude of the standard reduction potential and the strength of a species as an oxidizing agent
  - if you reverse a half reaction you must reverse the sign of the potential
  - if you multiply a half reaction by some factor you do NOTHING to the potential
  - \( E_{\text{cell}}^\circ = E_{\text{ox}}^\circ + E_{\text{red}}^\circ \)
  - a Galvanic cell will always run spontaneously in the direction that produces a + cell potential

Cell Potential, Electrical Work, and Free Energy
- When an electrochemical cell produces a current it can do work
  \[ w = -nFE_{\text{cell}} \] where \( n \) = mol of electrons transferred, and \( F \) is the Faraday constant defining the charge on one mol of electrons as 96,485 C/mol e−
- For a process at constant T and P, \( \Delta G = w \), so \( \Delta G^\circ = -nFE_{\text{cell}}^\circ \)
- Cell potential is dependent on concentration (because \( \Delta G \) is dependent on composition), and this dependence is given by the Nernst Equation: \( E = E^\circ - (RT/nF)(\ln Q) \) or, at 25°C: \( E = E^\circ - (0.0592/n)(\log Q) \)
- At equilibrium \( E = 0 \) and \( Q = K \), so the Nernst equation can be used to calculate the value of the equilibrium constant for a redox reaction: \( E^\circ = (0.0592/n)\log K \) at 25°C

Electrolysis - forces a chemical change that wouldn't happen spontaneously
- You should be able to quantify how much chemical change occurs with current flow of a specified time by relating
current (in amp or C/s) and time of current flow to quantity of charge (in C). The Faraday constant relates quantity of charge to mol of electrons, and the balanced oxidation or reduction half reaction relates mol of electrons to mol of chemical compound.

A few problems:

1. Write the net cell reaction and sketch the cell diagram for each of the following galvanic cells:
   a. H\textsuperscript{+}/H\textsubscript{2} redox couple in combination with a Ag\textsuperscript{+}/Ag redox couple
   b. Cl\textsubscript{2}/Cl\textsuperscript{−} redox couple in combination with a AgCl/Ag, Cl\textsuperscript{−} redox couple

2. Write the cathode and anode half reactions and the cell reaction for each of the following galvanic cells:
   a. C (graphite) \| Fe\textsuperscript{2+} (aq), Fe\textsuperscript{3+} (aq) \| NO\textsubscript{3}\textsuperscript{−} (aq), H\textsuperscript{+} (aq) \| NO (g) \| Pt (s)
   b. U \| U\textsuperscript{3+} (aq) \| Y\textsuperscript{2+} (aq) \| V

3. Write the cathode and anode half-reactions, the balanced cell reaction, and the line notation for galvanic cells with the following skeletal reactions:
   a. Ni\textsuperscript{2+} (aq) + Zn (s) \rightarrow Ni (s) + Zn\textsuperscript{2+} (aq)
   b. Au\textsuperscript{+} (aq) \rightarrow Au (s) + Au\textsuperscript{3+} (aq)

4. Calculate the standard cell potential (E\textsuperscript{o}) for each of the following galvanic cells:
   a. Pt \| Cr\textsuperscript{3+} (aq), Cr\textsuperscript{2+} (aq) \| Cu\textsuperscript{2+} (aq) \| Cu
   b. C(graphite) \| Sn\textsuperscript{4+} (aq), Sn\textsuperscript{2+} (aq) \| Pb\textsuperscript{4+} (aq), Pb\textsuperscript{2+} (aq) \| Pt (For Pb\textsuperscript{4+} + 2e\textsuperscript{−} \rightarrow Pb\textsuperscript{2+};
   E\textsuperscript{o} = +1.67 V, For Sn\textsuperscript{4+} + 2 e\textsuperscript{−} \rightarrow Sn\textsuperscript{2+}; E\textsuperscript{o} = +0.15 V)

5. Calculate the standard cell potential (E\textsuperscript{o}) and ΔG\textsuperscript{o} for galvanic cells with the following cell reactions:
   a. Zn (s) + Fe\textsuperscript{2+} (aq) \rightarrow Zn\textsuperscript{2+} (aq) + Fe (s)
   b. Ag\textsuperscript{+} (aq) + Cl\textsuperscript{−} (aq) \rightarrow AgCl (s)
   c. 3 Au\textsuperscript{+} (aq) \rightarrow 2 Au (s) + Au\textsuperscript{3+} (aq) (Au\textsuperscript{+} + e\textsuperscript{−} \rightarrow Au; E\textsuperscript{o} =1.69V, Au\textsuperscript{3+} + 3 e\textsuperscript{−} \rightarrow Au, E\textsuperscript{o} = 1.50 V)

6. Arrange the following species in order of increasing strength as oxidizing agents:
   a. Co\textsuperscript{3+}, Cl\textsubscript{2}, Ce\textsuperscript{4+}
   b. NO\textsubscript{3}−, IO\textsubscript{3}−, Cr\textsubscript{2}O\textsubscript{7}2−; all in acidic solution
   c. H\textsubscript{2}O\textsubscript{2}, O\textsubscript{2}, MnO\textsubscript{4}−, IO\textsubscript{4}−; all in acidic solution

7. Identify the spontaneous reactions among the following reactions and, for the spontaneous reactions, write balanced reduction & oxidation half-reactions. Show that these rxns are spontaneous by calculating ΔG\textsuperscript{o}.
   a. I\textsubscript{2} + H\textsubscript{2} \rightarrow
   b. Mg\textsuperscript{2+} + Cu \rightarrow
   c. Al + Pb\textsuperscript{2+} \rightarrow

8. Determine the equilibrium constant for the reactions taking place in the following galvanic cells:
   a. Pt \| Cr\textsuperscript{3+} (aq), Cr\textsuperscript{2+} (aq) \| Cu\textsuperscript{2+} (aq) \| Cu
   b. Mn (s) + Ti\textsuperscript{2+} (aq) \rightarrow Mn\textsuperscript{2+} (aq) + Ti (s) (For Ti\textsuperscript{2+} + 2 e\textsuperscript{−} \rightarrow Ti; E\textsuperscript{o}=−1.63 V)
   c. A Pb\textsuperscript{2+}/Pb redox couple in combination with a Hg\textsubscript{2}2+/Hg redox couple

9. Calculate the reaction quotient (Q) for the following cell reactions given the cell potential:
   a. Pt \| Sn\textsuperscript{4+} (aq), Sn\textsuperscript{2+} (aq) \| Pb\textsuperscript{4+} (aq), Pb\textsuperscript{2+} (aq) \| C (graphite); E = 1.33 V (See prob. #4b for info)
   b. Pt \| O\textsubscript{2} (g) \| H\textsuperscript{+} (aq) \| Cr\textsubscript{2}O\textsubscript{7}2− (aq), H\textsuperscript{+} (aq), Cr\textsuperscript{3+} (aq) \| Pt; E = 0.10 V
10. Determine $E$ for the following galvanic cells:
   a.  $\text{Zn} \mid \text{Zn}^{2+} (\text{aq}, 0.10 \text{ M}) \parallel \text{Ni}^{2+} (\text{aq}, 0.0010 \text{ M}) \mid \text{Ni}$
   b.  $\text{Pt} \mid \text{Cl}_2 (\text{g}, 100 \text{ Torr}) \parallel \text{HCl} (\text{aq}, 1.0 \text{ M}) \parallel \text{HCl} (\text{aq}, 0.010 \text{ M}) \parallel \text{H}_2 (\text{g}, 450 \text{ Torr}) \parallel \text{Pt}$

11. a.  How much time is required to electroplate 4.4 mg of silver from a silver nitrate solution, using a current of 0.50 A?
   b.  Calculate the mass of copper that can be electroplated from CuSO$_4$ (aq) using the same current and time.

12. a.  What current is required to electroplate 6.66 µg of gold in 30.0 min from AuCl$_3$ (aq)?
   b.  How much time is required to electroplate 6.66 µg of chromium from a potassium dichromate solution with a current of 100 mA?  The net cell reaction you need to consider is:
      \[ \text{Cr}_2\text{O}_7^{2-} (\text{aq}) + 14 \text{H}^+ (\text{aq}) + 12 \text{e}^- \rightarrow 2 \text{Cr} (\text{s}) + 7 \text{H}_2\text{O} (\text{l}) \]

13. When a titanium chloride solution was electrolyzed for 500 s with a 120 mA current, 15.0 mg of titanium was deposited.  What is the oxidation number of the titanium in the titanium chloride?

Answers to Review Problems:
1.  a.  $\text{Pt(s)} \parallel \text{H}^+ (\text{aq}) \parallel \text{H}_2 (\text{g}) \parallel \text{Ag}^+ (\text{aq}) \parallel \text{Ag(s)}$
   b.  $\text{Ag (s)} \parallel \text{Cl}^- (\text{aq}) \parallel \text{AgCl (s)} \parallel \text{Cl}^- (\text{aq}) \parallel \text{Pt (s)}$
2.  a.  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^- \text{ anode}, \text{NO}_3^- + 4 \text{H}^+ + 3 \text{e}^- \rightarrow \text{NO} + 2 \text{H}_2\text{O cathode,} \quad 3 \text{Fe}^{2+} + \text{NO}_3^- + 4 \text{H}^+ \rightarrow 3 \text{Fe}^{3+} + \text{NO} + 2 \text{H}_2\text{O overall}$
   b.  $\text{U} \rightarrow \text{U}^{3+} + 3 \text{e}^- \text{ anode, V}^{2+} + 2 \text{e}^- \rightarrow \text{V cathode, 2 U + 3 V}^{2+} \rightarrow 2 \text{U}^{3+} + 3 \text{ V overall}$
3.  a.  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^- \text{ anode, Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni cathode, Ni}^{2+} + \text{Zn} \rightarrow \text{Zn}^{2+} + \text{Ni overall,}$
   \[ \text{Zn (s)} \parallel \text{Zn}^{2+} (\text{aq}) \parallel \text{Ni}^{2+} (\text{aq}) \parallel \text{Ni (s)} \]
   b.  $\text{Au}^+ + \text{e}^- \rightarrow \text{Au cathode, Au}^+ \rightarrow \text{Au}^{3+} + 2\text{e}^- \text{ anode, 3 Au}^+ \rightarrow 2 \text{Au} + \text{Au}^{3+} \text{ overall,}$
   \[ \text{Pt(s)} \parallel \text{Au}^+, \text{Au}^{3+} (\text{aq}) \parallel \text{Au}^+ (\text{aq}) \parallel \text{Au (s)} \]
4.  a.  0.84 V, b.  1.52 V
5.  a.  0.32 V, $\Delta G^\circ = -61.8 \text{ kJ}$; b.  0.58 V, $-56.0 \text{ kJ}$; c.  0.19 V, $-55.0 \text{ kJ}$
6.  a.  $\text{Cl}_2 < \text{Ce}^{4+} < \text{Co}^{3+}$; b.  $\text{NO}_3^- < \text{IO}_3^- < \text{Cr}_2\text{O}_7^{2-}$; c.  $\text{O}_2 < \text{IO}_3^- < \text{MnO}_4^- < \text{H}_2\text{O}_2$
7.  a.  $\text{I}_2 + 2\text{e}^- \rightarrow 2 \text{I}^-, \text{H}_2 \rightarrow 2 \text{H}^+ + 2\text{e}^-, \text{I}_2 + \text{H}_2 \rightarrow 2 \text{H}^+ + 2 \text{I}^-, E^\circ = .54 \text{ V, } \Delta G^\circ = -104 \text{ kJ}$
   b.  non-spontaneous
   c.  $\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-,$  $\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}, 2 \text{Al} + 3 \text{ Pb}^{2+} \rightarrow 2 \text{ Al}^{3+} + 3 \text{ Pb}, E^\circ=1.53 \text{ V, } \Delta G^\circ=-886 \text{ kJ}$
8.  a.  $E^\circ = 0.84, K = 2.4 \times 10^{35}$; b.  $E^\circ = -0.45, K = 6.3 \times 10^{-16}$; c.  $E^\circ = 0.93, K = 2.6 \times 10^{31}$
9.  a.  2.62 x $10^6$, b.  1
10. a.  0.18 V, b.  0.47 V, c.  $-1.45 \text{ V}$
11. a.  7.8 s, b.  1.28 mg
12. a.  $5.44 \times 10^{-6}$ amp, b.  0.742 s
13. +2