CHEM 1202 - Homework # 9 & 10

ANSWER KEY

Redox & Electrochemistry

Due Friday, Dec 8th, 2006 by Noon

Check the box to the right if you want your graded homework to be placed out in the public rack outside Prof. Stanley's office. Otherwise you will have to pick up your homework from Prof. Stanley in person: ☐

1. (5 pts) Which of the following substances is the best ***reducing*** agent?

a) F^- [✓ b) Mg] c) Li^+ d) Ag^+ e) Zn

2. (5 pts) Which of the following substances is the best ***oxidizing*** agent?

a) F^- b) Mg^{2+} [✓ c) O_3] d) Ag^+ e) Cu

3. (10 pts) Balance the following reaction in **acidic** solution.

1st determine ox states: **+2 –2** **–2 +1** **+2, +3** **–2** **–1**

$$2\ S_2O_3^{2-}(aq) + OCl^-(aq) \rightleftharpoons S_4O_6^{2-}(aq) + Cl^-(aq)$$

Two of the sulfur atoms have +2 oxidation state while the other two have +3, only the two that are oxidized should be used in figuring the # of e- transferred.

Use the half-cell method. Write out the oxidation and reduction half cells and balance based on # of electrons:

Oxidation half cell: $2S_2O_3^{2-}(aq) \rightleftharpoons S_4O_6^{2-}(aq) + 2e-$
Reduction half cell: $OCl^-(aq) + 2e- \rightleftharpoons Cl^-(aq)$

*We need **two** $S_2O_3^{2-}$ to produce **one** $S_4O_6^{2-}$. At least four redox active sulfur atoms on each side are needed to balance the rxn*

Since we have the same # of electrons on each side of the reaction, we can simply add them together to get our core redox-balanced rxn (otherwise we would have to multiply each rxn by an integer # to get the same # of e- on each side):

$$2S_2O_3^{2-}(aq) + OCl^-(aq) \rightleftharpoons S_4O_6^{2-}(aq) + Cl^-(aq)$$

Now we need to balance the oxygen atoms on each side by adding H_2O's to the side missing oxygen atoms and the appropriate # of H^+ to the opposite side of the rxn. The product side is missing 1 oxygen atom so we need to add one water and then 2 H^+ to the reactant side. This gives us our final balanced equation:

$$\boxed{2H^+(aq) + 2S_2O_3^{2-}(aq) + OCl^-(aq) \rightleftharpoons S_4O_6^{2-}(aq) + Cl^-(aq) + H_2O}$$

4. (10 pts) Balance the following reaction in **basic** solution:

1st determine ox states: **+5 –2** **+3** **+3** **+6 –2**

$$BiO_3^-(aq) + Cr^{3+}(aq) \rightleftharpoons Bi^{3+}(aq) + CrO_4^{2-}(aq)$$

Write out the oxidation and reduction half cells and balance based on # of electrons:

Oxidation half cell: $Cr^{3+}(aq) \rightleftharpoons CrO_4^{2-}(aq) + 3e-$
Reduction half cell: $BiO_3^-(aq) + 2e- \rightleftharpoons Bi^{3+}(aq)$

Since we do NOT have the same # of electrons on each side of the reaction, we to multiply each rxn by an integer # to get the same # of e- on each side. 6e- is the common factor, so we need to multiply the Cr^{3+} half cell by 2 and the BiO_3^- half cell by 3 and add them together to get the core redox-balanced rxn:

$$3BiO_3^-(aq) + 2Cr^{3+}(aq) \rightleftharpoons 3Bi^{3+}(aq) + 2CrO_4^{2-}(aq)$$

We now need to balance the oxygen atoms and H^+, then convert to **basic solution** by adding the same # of OH^- anions to each side of the rxn as we have H^+, reacting them to make 2 H_2O molecules, then canceling out the redundant H_2O's:

ACID solution: $2H^+(aq) + 3BiO_3^-(aq) + 2Cr^{3+}(aq) \rightleftharpoons 3Bi^{3+}(aq) + 2CrO_4^{2-}(aq) + H_2O$

BASIC Solution: $\boxed{H_2O\ (aq) + 3BiO_3^-(aq) + 2Cr^{3+}(aq) \rightleftharpoons 3Bi^{3+}(aq) + 2CrO_4^{2-}(aq) + 2OH^-(aq)}$

5. (5 pts) Write the oxidation state for the underlined element in the box following each compound.

a) LiAl**H**$_4$	**–1**	b) Ba$_3$(**As**O$_4$)$_2$	**+5**	c) Na$_2$**Ni**Cl$_4$	**+2**
d) Ca**S**O$_3$	**+4**	e) H$_2$**O**$_2$	**–1**		

6. (15 pts) Calculate the redox potentials for the following reactions. Show the two half cell reactions, written in the proper direction and their potentials used to calculate your answer.

a) $H_2(g) + 2Li(s) \rightleftharpoons 2H^-(soln) + 2Li^+(soln)$

$H_2 + 2e^- \longrightarrow 2H^-$ E° = –2.25 V
$2Li \longrightarrow 2Li^+ + 2e^-$ E° = +3.05 V

E° = + 0.80 V

b) $4H^+(aq) + O_2(g) + 2Cu(s) \rightleftharpoons 2H_2O + 2Cu^{2+}(aq)$

$4H^+ + O_2 + 4e^- \longrightarrow 2H_2O$ E° = +1.23 V
$2Cu \longrightarrow 2Cu^{2+} + 4e^-$ E° = –0.34 V

E° = + 0.89 V

c) $F_2(g) + 2Cl^-(aq) \rightleftharpoons 2F^-(aq) + Cl_2(g)$

$F_2 + 2e^- \longrightarrow 2F^-$ E° = +2.87 V
$2Cl^- \longrightarrow Cl_2 + 2e^-$ E° = –1.36 V

E° = + 1.51 V

d) $Cu(s) + 2Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$

$2Ag^+ + 2e^- \longrightarrow 2Ag$ E° = +0.80 V
$Cu \longrightarrow Cu^{2+} + 2e^-$ E° = –0.34 V

E° = + 0.46 V

e) $3Pb^{2+}(aq) + 2Al(s) \rightleftharpoons 3Pb(s) + 2Al^{+3}(aq)$

$3Pb^{2+} + 6e^- \longrightarrow 3Pb$ E° = –0.13 V
$2Al \longrightarrow 2Al^{3+} + 6e^-$ E° = +1.66 V

E° = + 1.53 V

7. (10 pts) ***Library/web research topic:*** Describe in your own words the chemistry (with formulas) involved in a lithium-ion battery. Is lithium metal used? What is the voltage of this electrochemical reaction? List two main advantages and two main disadvantages of lithium-ion batteries with BRIEF explanations. DO NOT COPY DIRECTLY FROM ANY REFERENCE (except for chemical formulas). List your primary reference used at the end.

Lithium ion rechargeable batteries have anodes composed of carbon/graphite (represented by C_6 in the formula below) while the cathode is composed of $Li^+[CoO_2]^-$ (Co^{3+} oxidation state) or $LiMn_2O_4$ (mixed Mn^{3+}/Mn^{4+}). When the battery is charged some of the carbon anode is reduced to $[C_6]^{x-}$ (where x = # of electrons transferred) and some of the Co^{3+} in the cathode is oxidized to a +4 oxidation state. Enough Li^+ cations migrate to the anode to balance the negative charge build-up. This forms a mixture of $[Li^+]_x[C_6]^{x-}$ at the anode (electron source) and oxidized CoO_2 at the cathode (electron acceptor). **Li metal is NOT formed unless something goes wrong during the charging process!** When the battery discharges (produces electricity) the electrons flow from the reduced anode to the oxidized cathode through the external circuit (wire) reducing the CoO_2 to $[CoO_2]^-$. The Li^+ cations migrate back from the carbon anode to the cathode to reform $LiCoO_2$. There is an electrolyte typically composed of either a polar organic gel and a lithium salt or a nano-porous polymer (Li-polymer-ion). This makes the Li^+ cation migration possible between the anode and cathode.

Reaction: $[Li^+]_x[C_6]^{x-} + xCoO_2 \rightleftharpoons C_6 + xLiCoO_2$

The voltage produced is about **3.6 V**.

Advantages: light weight & high power density (voltage & amps; very good for small electronic devices); no memory effect (doesn't matter how often you charge or discharge, charging after light use does not reduce the battery capacity); low self-discharge (built-in computer chip for monitoring battery stats does slowly drain battery).

Disadvantages: limited lifetime (aging will gradually deactivate regardless of level of use, typically 3 years); heat sensitive (faster deactivation at higher temps); not good for high power drain devices; built-in computer chip and protection circuit to monitor charging and discharging, temp, etc. (adds to cost); internal short-circuit can cause fire due to high power density (recent fires and recalls for notebook computer batteries).

Refs: http://electronics.howstuffworks.com/lithium-ion-battery1.htm
http://www.buchmann.ca/Article5-Page1.asp
http://en.wikipedia.org/wiki/Lithium_ion_battery