Homework week 11 (electrochemistry)

In some cases, there are "hints" at the bottom of the problem set. In these cases the word *Hint* is shown after the question. Try struggling with the question for a while before jumping to the hint which, by the way, is often not a "big hint".

Some suggested problem from your text (Oxtoby et al., 7th ed.; Chapter 17): 1, 5, 11, 15, 21, 25, 31, 35, 51, 53, 57 (Also, some "interesting problems" and some "real world problems" if your curiosity remains high: 41, 73, 81, 87 95)

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1. A 10 ml solution is used as an electrolytic cell for the reduction of Cu^{2+} to $Cu_{(s)}$ at an electrode. The solution contains $3x10^{-5}$ M Cu^{2+}. The coulometric determination is run at a constant current of 3.00 mA.

   a) Is the copper deposited at the anode or cathode of this cell?

   b) How long must the electrolysis run to quantitatively reduce the Cu^{2+}?

   c) Let's assume that you have a means of determining the time for >99.9% of the copper to be deposited. If a more easily reduced metal was co-deposited with the copper, would your calculations for the amount of copper in the solution (based on the current-time information) give you an erroneously high or low value?

2. Given the following electrochemical cell:

   Ag | AgI | K^+ (0.003M), I^- (0.003 M) || Ag^+ (0.001 M), NO_3^- (0.001 M) | Ag

   a) Write the half-cell reactions (expressed as reductions) and give their E^o values. (Note: The left hand electrode is a Ag wire with coating of $AgI_{(s)}$ on it.)

   b) Write the overall chemical reaction implied by this cell.

   c) What is E^o_{cell}? What is E_{cell}? (You may have to go to source outside your text for Ag/AgI standard reduction potential and its half reaction.)

   d) Circle the anode in the cell notation above.

   e) What is ΔG^o for the reaction implied by the cell?

   f) Could ΔG^o be <0 and yet the cell reaction not proceed spontaneously as written? If so, how could that be?

   g) Which species is serving as the reducing agent as implied by the reaction? The oxidizing agent?

3. a) Could 1 F HCl be used to dissolve (i.e., oxidize) Cu(s)? (When thinking about this, assume the P_{H2} = 1 atm)?

   b) HNO3 is considered a stronger oxidizing acid than HCl. Can you look at tables of standard reduction potentials and figure out how you could have deduced that on your own? (see additional E^o values on last page of this set.) Where does perchloric acid ($HClO_4$) rank relative to these other two acids for oxidizing power? (You may have to go to the web to get some information to answer this.)

   c) Potassium permanganate ($KMnO_4$) is considered a strong ______ (reducing?... or oxidizing?) agent. How would you use your electrochemical knowledge to justify and explain this to a fellow classmate.

4. The conversion of methane to methanol is an important reaction with regard to “energy”, e.g., methanol is a liquid at room temperature while methane is a gas and not as easy to store. If the reaction involves methane reacting with water to form methanol and an acidic solution, is this a redox reaction? What if the product includes $H_{2(g)}$ as well as methanol? (Write the reactions in both cases.)

5. How is a fuel cell different from a more conventional battery, e.g., your car battery or the Lithium-ion battery?

6. Here’s a bit of a challenging question: Use the information in the reduction potential table given below to determine the K_{sp} for $Hg_2Cl_{2(s)}$. (*Hint*: Break the solubility reaction down into 2 half-cell reaction which, when put together, yields the reaction you’d write for the dissolution of $Hg_2Cl_{2(s)}$. Then consider how to use electrochemical data to get the desired equilibrium constant. (Note: Reaction for dissolution of this compound is $Hg_2Cl_{2(s)} \leftrightarrows Hg_2^{2+} + 2\,Cl^-$ where Hg_2^{2+} is the stable solution species for Hg(I).)

Standard Reduction Potentials at 25°C (298 K) for Many Common Half-reactions

Half-reaction	$\mathcal{E}°$ (V)	Half-reaction	$\mathcal{E}°$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$IO_4^- + 2H^+ + 2e^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	−2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	−2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	−2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	−3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

SCE: $Hg_2Cl_2 + 2e \rightarrow 2Hg + 2\,Cl^-$ (sat’d KCl) $E^o = +0.241$ V