Homework week 12 (electrochemistry, batteries, corrosion and balancing equations)

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".

---

1. Given the electrochemical cell used for the determination of Cu in the test solution:

   SCE || Cu^{2+} (?? M) | Cu where SCE is a saturated calomel reference electrode, E^o_{SCE} = +0.241 V.

   a) What is the cell potential if the $[Cu^{2+}] = 1x10^{-3}$ M?

   b) Make a plot of E_{cell} vs some function of $[Cu^{2+}]$ such that the plot results in a straight line. (What "function of would you use? What is the slope of the line?) ***Hint***

2. Consider an automobile's lead-acid storage battery consisting of 6 cells, i.e., assume E_{Batt} = 12.0 V.
   a) How many amp-hours of energy can be generated per kg of $Pb_{(s)}$? ***Hint***

   b) Show that units of amp-hours are units of energy, e.g., show how to convert from amp-hours to Joules. (Any assumptions being made?)

3. a) Use the E^o tables to argue that a 1.0 M solution of Cu^+ will or will not disproportionate into $Cu_{(s)}$ and Cu^{2+}. ***Hint***

   b) Etimate the ratio of $[Cu^{2+}]/[Cu^+]$ if $CuNO_3$ were initially dissolved in solution? ***Hint***

4. What prevents a typical dry cell battery from being recharged?

5. Draw a typical H_2/O_2 fuel cell and explain how electricity is generated.

6. A Zn plate is often bolted to the hull of metal ships and serves as a "sacrificial anode".
   a) Explain chemically how this functions to protect the ships iron hull from rusting. ***Hint***

   b) Try transforming this into an electrochemical cell notation to illustrate what is taking place with and without the Zn plate presence. (Assume the $O_{2(aq)}$ is the oxidizing agent.) ***Hint***

7. So… you feel pretty comfortable balancing equations, eh? Want to try a couple of them? (All are done in aqueous solution so you have H_2O, H^+ and OH^- that you can include in the reaction as needed to balance it.) *Remember*: If you have been successful, the final equation will be mass and charged balanced, i.e., number of moles of particular elements is the same on left and right side of equation and the total charge on the left equals the charge on the right. ***Hint***

   $FeS + HCl \rightarrow FeCl_2 + H_2S$

   $Cu_2S + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + S$

   $NO_2- \rightarrow NO_3- + NO$

   $FeSO_4 + KClO_3 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + K_2SO_4 + Cl_2$

   $U(SO_4)_2 + KMnO_4 \rightarrow UO_2SO_4 + MnSO_4 + KHSO_4$
   (For this reaction, write it to imply that occurs in a neutral solution but results in an acidic solution. Then write it to imply that it is run in an alkaline solution.)

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

Half-reaction	$\mathscr{E}°$ (V)	Half-reaction	$\mathscr{E}°$ (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

Hints

1b Write out the Nernst equation for this cell and transpose it into a y = mx + b format where x = f([Cu^{2+}]).

2a Consider what basic SI units that amp-hours could represent.

3a Write the balanced equation and then break it into 2 half-cell reactions. Determine E^o_{cell} to make a conclusion.

b Consider the full Nernst equation where Q=K and E_{cell}=0.

6a You may have to go to the internet or text to explore this topic.
b Your cell will take on the general form of X | Y, etc. || Z, etc. | W

7 If you're having trouble, the following may assist you in approaching the problems:

General rules for balancing equations

- Dissociate all soluble salts (strong electrolytes), e.g., Na^+, K^+, Cl^-, etc.
- Do not include these in the equation to be balanced ***unless*** they are involved in an electron transfer, a precipitation or complexation reaction (i.e., exclude "spectator ions")
- Final equation must balance in **mass** and **charge**

When no electron transfer occurs...

- Most can be done by inspection
- Balance mass
- Check to insure that charge is also balanced

With electron transfer (oxidation-reduction reactions)

1. Identify species being reduced
2. Write half reaction with that species
3. Mass balance (except for H and O)
4. Add O as H_2O and balance H on other side (if needed) by adding H^+.
5. Balance charge with e^- addition

   ----
6. Repeat steps 2-5 above for the species being oxidized
7. See if number of electrons consumed or generated in the balanced half reactions are the same. If not, multiply equations by appropriate so free electrons will balance.
8. Add the two half reactions
9. Add spectator ions as needed. (must be added to both sides of reaction equation)