Chapter 13

13-3, 13-5, 13-10, 13-14, 13-15, 13-17, 13-20, 13.21, 13-22, 13-26, 13-29, 13.35, 13.47

13-3

a)

(16 mol O_2)*((4 mol e^-)/(mol O_2))*((9.649*10^4 C)/(mol e-)) = 6.2*10^6 C

I = (6.2*10^6 C)/((1 day)*(24 hr/day)*(3600 s/hr)) = 71 A

b)

I = P/E = (5.00*10^2 W)/(115 V) = 4.35 A

c)

P = EI = (1.1 V)(71 A) = 78 W

13-5

To find the re-dox pairs for a given reaction, You must look for species that contain the same element in different oxidation states. In this case S(+2) in $S_2O_3^{2-}$ is being oxidized to S(+1) in $S_4O_6^{2-}$. I(0) in I_2 is being reduced to I(-1) in I^-.

a)

Lose Electrons (Oxidation)

$2S_2O_3^{2-} \leftrightarrow 2e- + S_4O_6^{2-}$

b)

Gain Electrons Reduction

$I_2 + 2e- \leftrightarrow 2I^-$

I_2 is the oxidant and $S_2O_3^{2-}$ is the reductant

c)

(1.00 g $S_2O_3^{2-}$)*(112.12 g/mol) = 8.92 mmol $S_2O_3^{2-}$ = 8.92 mmol e-

d) [(8.92 *10^{-3} mol e-)*(9.649*10^4 C)/(mol e-))]/(60s) = 14.3 A

13.10

a)

By convention the oxidation is always written on the left side of the cell notation and the reduction is written on the right side.

$Zn(s) \leftrightarrow Zn^{+2} + 2e-$ oxidation

$Cl_2(l) + 2e- \leftrightarrow 2Cl^-$ reduction

Electrons flow from the Zn electrode.

b)

$(1.00*10^3 \text{ C/s})*(3600 \text{ s/hr})*(1 \text{ mol e-}/9.649*10^4 \text{ C})*(1\text{mol } Cl_2/2 \text{ mol e-})$

$(70.90 \text{ g } Cl_2/1\text{mol } Cl_2)(1\text{kg }/1000\text{g}) = 1.32 \text{ kg } Cl_2$ consumed

13-13

The larger the E^0, the greater the equilibrium constant.

$$E^0 = (0.05916/n)\log K$$

With the reaction, $Fe(CN)_6^{3-} + e- \leftrightarrow Fe(CN)_6^{4-}$, you still have Fe^{+2} going to Fe^{3+} because the each CN^- carries one negative charge.

Since E^0 for this reaction is less than that for the uncomplexed reaction, the equilibrium constant must be smaller and Fe^{+3} (the reactant) must be stabilized to a greater extent by CN^- complexation relative to Fe^{2+}.

The E^0 for the phenathroline complex reaction is greater than that for the uncomplexed reaction. Therefore, the equilibrium constant is greater and Fe^{2+} (the product) must be stabilized to a greater extent by CN^- complexation relative to Fe^{3+}.

13-14

E is the cell potential under any given set of conditions. At equilibrium E = 0.

E^0 is the cell potential only under the special case where all activities of all species that make up the cell are at unity. This is a constant at standard pressure and temperature.

13-16

The half reaction is already written as a reduction. So…

a)

$$E = E^0 - (0.05914/3) \log\{P_{AsH3}/[H^+]^3\}$$

b)

$$= -0.238 - (0.05914/3) \log\{(1\text{torr}/760)/(10^{-3})^3\}$$
$$= -0.36 \text{ V}$$

13-18

The only aqueous specie that participates in the reaction is [OH-], and it is both consumed and produced in the overall redox reaction. Also, because both reactants are solids, there is no need for separate anode and cathode compartments. Therefore, the [OH-] remains constant.

The Nernst equation for the cathode reaction is

$E_R = E^0 – 0.05916 \log[OH-]$

$E_O = E^0 – 0.05916 \log\{1/[OH^-]\}$

As a result, the E_{cell} is independent of the concentrations of the reactants or products

13-19

This problem is designed to illustrate that many times a given half-cell can be written correctly as more than one half reaction.

a)

for the reduction: $2AgCl(s) + 2e- \leftrightarrow 2Ag(s) + 2Cl^-$

E+ $= E^0 – (0.05914) \log[Cl^-]$

$= 0.222 - (0.05914) \log(0.10) = 0.281$ V

for the oxidation: $PbF_2(s) + 2e- \leftrightarrow Pb(s) + 2F^-$

E^- $= E^0 – (0.05914/2) \log([F^-]^2)$

$= -0.350 – (0.05914/2) \log((0.10)^2) = -0.291$ V

Ecell $= E^+ - E^- = 0.281 – (-.291) = 0.572$ V

b)

for the reduction: $2Ag^+ + 2e- \leftrightarrow 2Ag(s)$

E+ $= E^0 – (0.05914) \log(1/[Ag^+])$

$[Ag^+] = Ksp_{(AgCl)}/[Cl^-]$

E+ $= E^0 – (0.05914) \log([Cl^-]/(1.8*10^{-10}))$

$= 0.7993 - (0.05914) \log((0.1/(1.8*10^{-10})) = 0.281$ V

for the oxidation: $Pb^{+2} + 2e- \leftrightarrow Pb(s)$

E- $= E^0 – (0.05914) \log(1/[Pb^{+2}])$

$[Pb^{+2}] = Ksp_{PbF2}/[F^-]^2$

$= -0.126 – (0.05914/2) \log([F^-]^2/Ksp_{PbF2})$

$= -0.126 – (0.05914/2) \log([0.10]^2/(3.6*10^{-8}) = -0.287$ V

Ecell = E^+ - E^- = 0.281 – (-0.287) = 0.568 V

The two calculations are in reasonable agreement!!!!
Whether you write the half reaction in terms of AgCl, Ag, and Cl- or just in terms of Ag, and Ag^+, you obtain a E^+ of 0.281 V. If you look at the difference between the two Nernst equations for E-, you will see that the only difference if the Ksp factor in the log term. This Ksp factor is built into E^0(AgCl).

13.20
Dr. Harris has already written out the Nernst equation for the whole reaction for you. It is truly a chug and plug type of problem. But you must first find the ionic strength and the activity coeeficients.

μ in each half-cell = ½ (.01 +.01) = .01 M
by interpolation
$\gamma_{(H+@ m=0.01)} = 0.914$

$\gamma_{(Ag+@ m=0.01)} = 0.898$

0.7983 $= E^0 –$
$0.05916 \log\{((0.01)*.914)/((727.2/760)^{.5}*(.01*.898))\}$
$= E^0 – 0.00102$

$E^0 = 0.7993$ V

13.21

You must determine which reactions you must to add together to obtain the reaction in question.

$HOBr \rightarrow Br_{2(aq)}$
$Br_{2(aq)} \rightarrow 2Br^-_{(aq)}$

$HOBr \rightarrow 2Br^-_{(aq)}$

balanced reaction between HOBr and Br^- in an acidic solution

balancing the half-cell reaction:
step 1: add H^+ to the reactant side and water to the product side

$HOBr + H^+ \leftrightarrow Br^- + H_2O$

Step 2: Stoichiometrically balance the reaction.

It already is in this case!

Step 3: balance the charge by adding electrons

$HOBr + 2e- + H^+ \leftrightarrow Br^- + H_2O$

Repeat for the reactions that you must add to obtain the above rxn. When you add to half-rxns to obtain a third half-rxn, the safe thing to do is to add the ΔGs.

$HOBr + H^+ + e- \leftrightarrow 1/2Br_2 + H_2O$	$\Delta G_1 = -F(1.584)$
$1/2Br_2 + e- \leftrightarrow Br^-$	$\Delta G_2 = -F(1.098)$
$HOBr + 2e- + H^+ \leftrightarrow Br^- + H_2O$	$\Delta G_3 = \Delta G_1 + \Delta G_1 = -2F(E^0)$

$$-F(1.584) + -F(1.098) = -2FE^0$$

$$E^0 = (1.584 + 1.098)/2 = 1.341 \text{ V}$$

13.25

a)

Break the reaction into two half-cell reactions

When adding a reduction rxn to an oxidation rxn to obtain a whole cell reaction, E^0s are simply additive.

Reduction	from Appendix H
$4Co^{+3} + 4e- \leftrightarrow 4Co^{+2}$	$E_+^0 = 1.92$
Oxidation	
$O_2(g) + 4H^+ + 4e- \leftrightarrow 2H_2O$	$E_-^0 = 1.229$

$$E^0 = E_+^0 + E_-^0 = 0.69 \text{ V}$$

$$\Delta G^0 = -nFE^0 = -4(9.649*10^4 \text{C/mol})(0.69 \text{ V}) = -2.7*10^5 \text{ J}$$

$$K = 10^{(nE0/0.05916)} = 10^{(4(.69)/0.05916)} = 10^{46.653} = 10^{47}$$

b)

Break the reaction into 2 half-cell reaction

Reduction	from Appendix H
$Ag(S_2O_3)_2^{3-} + e- \leftrightarrow Ag(s) + 2S_2O_3^{2-}$	$E_+^0 = 0.017$ V
Oxidation	
$Fe(CN)_6^{3-} + e- \leftrightarrow Fe(CN)_6^{2-}$	$E_-^0 = 0.356$

$$E^0 = E_+^0 + E_-^0 = -0.339 \text{ V}$$

$$\Delta G^0 = -nFE^0 = -(1)(9.649*10^4 \text{C/mol})(-0.339 \text{ V}) = 3.27*10^4 \text{ J}$$

$$K = 10^{(nE0/0.05916)} = 10^{(4(-.339)/0.05916)} = 1.9*10^{-6}$$

13-26

14-26

You got a solution containing

$[Ce^{3+}] = 0.100$ M
$[Ce^{4+}] = 1.00*10^{-4}$ M
$[MnO_4^-] = 0.100$ M
$[Mn^{2+}] = 1.00*10^{-4}$ M
$[H^+] = 1.00$ M

a)

$$5[Ce^{4+} + e- \leftrightarrow Ce^{3+}] \qquad E_+^0 = 1.70 \text{ V}$$

$$- \quad MnO_4^- + 8H^+ + 5e- \leftrightarrow Mn^{2+} + 4H_2O \qquad E_-^0 = 1.507 \text{ V}$$

$$Mn^{2+} + 4H_2O + 5Ce^{4+} \leftrightarrow MnO_4^- + 8H^+ + 5Ce^{3+}$$

$$E = (E_+^0 - E_-^0) - 0.05916/5 \log\{[H^+]^8[MnO_4^-][Ce^{3+}]^5/[Mn^{2+}][Ce^{4+}]\}^5$$

b)
At equilibrium E = 0 and Q = K

$$(E_+^0 - E_-^0) = 0.05916/5 \log K$$
$$5(1.70-1.507)/.05916 = \log K$$
$$K = 10^{16.3117} = 2*10^{16}$$

$\Delta G^0 = -RT\ln K \quad = -(8.314 \text{ J/Kmol})(298 \text{ K})\ln(2*10^{16})$

$= -9.3*10^4$ J/mol or 93 kJ/mol

c)

$E = 0.193 – 0.05916/5 \log\{[1.00]^8[0.1][0.1]^5/[10^{-4}][10^{-4}]^5\}$

$E = 0.193 – 0.05916/5 \log\{[10^3]^6\} = 0.02$ V

d)

$\Delta G = -nFE = -(5)(9.649*10^4$ C/mol e-)(0.02 V)
$= 9649$ J or 10 kJ

at equilibrium

$(1.70-1.507) = – 0.05916/5 \log\{[H^+]^8[0.1][0.1]^5/[10^{-4}][10^{-4}]^5\}$

$10^{5(1.70-1.507)/.05916} = \{[H^+]^8[0.1][0.1]^5/[10^{-4}][10^{-4}]^5\}$

$(10^{5(1.70-1.507)/.05916})/10^{18} = [H^+]^8$

$\{(10^{5(1.70-1.507)/.05916})/10^{18}\}^{1/8} = [H^+] = 0.62$ M

$pH = -\log[H^+] = 0.21$

13-28

You are forming a half-reaction. It is safest to add together multiply Ks (or add ΔGs).

$Pd(OH)_2(s) \leftrightarrow Pd^{+2} + 2OH^-$ $Ksp = 3*10^{-28}$

$Pd^{+2} + 2e- \leftrightarrow Pd(s)$ $K_1 = 10^{(nE0/.05916)} = 8.9*10^{30}$

$Pd(OH)_2(s) +2e- \leftrightarrow Pd(s) + 2OH^-$ $K = Ksp*K_1$

$K = 3*10^3$

$\text{Log } K = -nE^0/0.05916$

$E^0 = -(0.05916/2)\log(3*10^3) = 0.103$ V

13-32

The following two equations add to give the overall reduction reaction. You add the ΔG^0, when adding equations to form half reactions.

$Cu^{2+} + e^- \leftrightarrow Cu^+$	$E^0 = 0.161$ V	$\Delta G^0 = -1F(0.161)$
$Cu^+ + I^- \leftrightarrow CuI(s)$	$1/Ksp = 1\cdot10^{12}$	$\Delta G^0 = -RT\ln(1/Ksp)$

$Cu^{2+} + I^- + e^- \leftrightarrow CuI(s)$

$\Delta G^0 = -1(0.161) - RT\ln(1/Ksp) = -84000$ J/mol
$E^0 = \Delta G^0/-nF = 0.870$ V

Now use the E^0 for the half reactions to calculate E_{cell}.

Reduction $Cu^{2+} + I^- + e^- \leftrightarrow CuI(s)$
Oxidation $Q + 2H^+ + 2e^- \leftrightarrow HQ$ $\quad E^0 = 0.700$ V

$E^0_{cell} = 0.870 – 0.700 = 0.170$ V
$\Delta G^0_{cell} = -(2)FE^0_{cell} = -32900$ J/mol $= -32.9$ kJ/mol
$K = e^{-\Delta G0/RT} = 6\cdot10^5$

OR

$Cu^{2+} + 2e^- \leftrightarrow Cu(s)$	$E^0 = 0.339$ V	$\Delta G^0 = -2F(0.339)$
$Cu(s) + I^- \leftrightarrow CuI(s)$	$E^0 = 0.185$V	$\Delta G^0 = -1F(0.185)$

$Cu^{2+} + I^- + e^- \leftrightarrow CuI(s)$

$E^0 = 2(.339) + 0.185 = 0.863$ V

Now use the E^0 for the half reactions to calculate E_{cell}.

Reduction Cu^{2+} + I- + e- ↔ CuI(s)
Oxidation Q + $2H^+$ + 2e- ↔ HQ $E^0 = 0.700$ V

$E^0_{cell} = 0.863 - 0.700 = 0.163$ V
$\Delta G^0_{cell} = -(2)FE^0_{cell}$ = -31500 J/mol = -31.5 kJ/mol
$K = e^{-\Delta G0/RT} = 3 \cdot 10^5$

The difference between the two answers is just a reflection of the precision in which the E^0's and Ksp's are known.

13-33

$E_{left} = E^0_{(MgF2)} - 0.05916/2 \log\{[F^-]^2/pO_2^{1/2}\}$
$E_{right} = E^0_{(MgF2)} - 0.05916/2 \log\{[F^-]^2/pO_2^{1/2}\}$

Net Rxn
$MgO_{(s)} + Al_2O_{3(s)} \leftrightarrow MgAl_2O_{4(s)}$

$E = E^0$ because all reactants and products in the Nernst Eq are solids (in std state)

$\Delta G^0 = -2F(0.1529) = 2.951 \cdot 10^4$ J/mol = 29.51 kJ/mol

Use the formula given to calculate E0 at 900 and 1250. Convert the E^0 to ΔG^0 ($\Delta G^0 = -nFE^0$). Plot E^0 as a function of T. The negative of the slope give ΔS^0 and the intercept gives ΔH^0.

	E^0	ΔG^0				
900	1.50E-01	-2.89E+04	slope	-5.90519	5.905188	ΔS^0
1250	1.61E-01	-3.10E+04	intercept	-23601.5		ΔH^0

13.35

a)

Reduction

$2AgCl(s) + 2e- \leftrightarrow 2Ag(s) + 2Cl^-$ $E_+^0 = 0.222$ V

Oxidation

\- $2H^+ + 2e- \leftrightarrow H_2(g)$ $E_-^0 = 0$ V

$2AgCl(s) + H_2(g) \leftrightarrow 2Ag(s) + 2Cl^- + 2H^+$

$E^0_{cell} = E_+^0 - E_-^0 = 0.222 \text{ V} - 0 \text{ V} = 0.222 \text{ V}$

Nerst eq for this cell

$E_{cell} = E^0_{cell} - 0.05916/n \log K$

$0.485 = 0.222 - 0.05916/n \log\{[Cl^-]^2[H^+]^2/p_{H2}\}$

$0.263 = -0.05916/2 \log\{[Cl^-]^2[10^{-3.60}]^2/1.00 \text{ atm}\}$

$-(0.263)(2)/(0.05916) = \log\{[Cl^-]^2[10^{-3.60}]^2/1.00 \text{ atm}\}$

$10^{-(0.263*2/0.05916)} = [Cl^-]^2[10^{-3.60}]^2/1.00$

$[Cl^-]^2 = \{1/10^{-3.6})^2\}10^{-(0.263*2/0.05916)} = 0.0204$

$[Cl^-] = 0.143$ M

13-39

(aragonite) $PbCO_{3(s)} + 2e- \leftrightarrow Pb_{(s)} + CO_3^{2-}{}_{(aq)}$

(calcite) $PbCO_{3(s)} + 2e- \leftrightarrow Pb_{(s)} + CO_3^{2-}{}_{(aq)}$

$E = E^0\text{cell} -0.05916 \log\{[CO_3^{2-}]_{arg}/[CO_3^{2-}]_{cal}\}$

$-0.0018 = 0.000 - 0.05916/2\log\{[CO_3^{2-}]_{arg}/[CO_3^{2-}]_{cal}\}$

$[CO_3^{2-}]_{arg}/[CO_3^{2-}]_{cal} = 1.15$
$[CO_3^{2-}]_{cal}/[CO_3^{2-}]_{arg} = 0.869$
$[Ca^{2+}]_{cal}/[Ca^{2+}]_{arg} = 0.869$

Ksp(CaCO3)calc/Ksp(CaCO3)arg = (0.869)(.869) = 0.76

13.47

$HPO_4^{2-} + 2H^+ + 2e^- \leftrightarrow HPO_3^{2-} + H_2O$ $\quad E^0 = -0.234$ V
$K_1 = 10^{nE0/.05916} = 1.2*10^{-8}$

$H_2PO_4^- \leftrightarrow HPO_4^{2-} + H^+$ $\quad K_2 = 6.32*10^{-8}$

$H_2PO_4^- + H^+ + 2e^- \leftrightarrow HPO_3^{2-} + H_2O$ $\quad K = K_1K_2 = 7.6*10^{-16}$

$E^0 = 0.05914/2 \log K = -0.447$ V