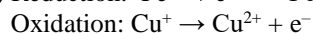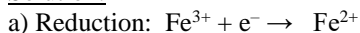# CHAPTER 19 ELECTROCHEMISTRY: CHEMICAL CHANGE AND ELECTRICAL WORK

CHEMICAL CONNECTIONS BOXED READING PROBLEMS

B19.1   <u>Plan:</u> Reduction is the gain of electrons while oxidation is the loss of electrons.
        <u>Solution:</u>
        a) Reduction: $Fe^{3+} + e^- \rightarrow Fe^{2+}$
           Oxidation: $Cu^+ \rightarrow Cu^{2+} + e^-$

        b) Overall: $Fe^{3+} + Cu^+ \rightarrow Fe^{2+} + Cu^{2+}$

END–OF–CHAPTER PROBLEMS

19.1   Oxidation is the loss of electrons (resulting in a higher oxidation number), while reduction is the gain of electrons (resulting in a lower oxidation number). In an oxidation-reduction reaction, electrons transfer from the oxidized substance to the reduced substance. The oxidation number of the reactant being oxidized increases while the oxidation number of the reactant being reduced decreases.
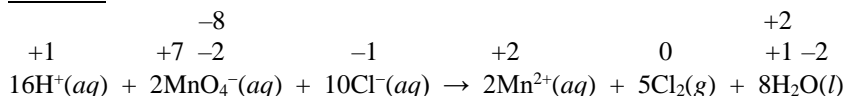
19.3   **No**, one half-reaction cannot take place independently of the other because there is always a transfer of electrons from one substance to another. If one substance loses electrons (oxidation half-reaction), another substance must gain those electrons (reduction half-reaction).

19.6   To remove protons from an equation, add an equal number of hydroxide ions to both sides to neutralize the H^+ and produce water: $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$.

19.8   (a) Spontaneous reactions, $\Delta_{sys}G < 0$, take place in voltaic cells, which are also called galvanic cells.
        (b) Nonspontaneous reactions take place in electrolytic cells and result in an increase in the free energy of the cell ($\Delta_{sys}G > 0$).

19.10   <u>Plan:</u> Assign oxidation numbers; the species with an atom whose oxidation number has increased is being oxidized and is the reducing agent. The species with an atom whose oxidation number has decreased is being reduced and is the oxidizing agent. Electrons flow from the reducing agent to the oxidizing agent. To write the molecular equation, pair K^+ ions with anions and SO_4^{2-} ions with cations to form neutral molecules.
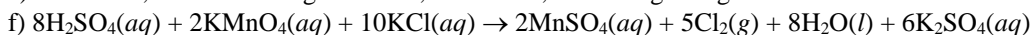   <u>Solution:</u>

$$\overset{+1}{\underset{}{}}\quad \overset{+7\ -2}{\underset{}{}}\quad \overset{-8}{\underset{}{}}\quad \overset{-1}{\underset{}{}}\quad \overset{+2}{\underset{}{}}\quad \overset{0}{\underset{}{}}\quad \overset{+2}{\underset{+1\ -2}{}}$$

$16H^+(aq) + 2MnO_4^-(aq) + 10Cl^-(aq) \rightarrow 2Mn^{2+}(aq) + 5Cl_2(g) + 8H_2O(l)$
       a) To decide which reactant is oxidized, look at oxidation numbers. **Cl⁻** is oxidized because its oxidation number increases from –1 in Cl^- to 0 in Cl_2.
       b) **MnO₄⁻** is reduced because the oxidation number of Mn decreases from +7 in MnO_4^- to +2 in Mn^{2+}.
       c) The oxidizing agent is the substance that causes the oxidation by accepting electrons. The oxidizing agent is the substance reduced in the reaction, so **MnO₄⁻** is the oxidizing agent.
       d) **Cl⁻** is the reducing agent because it loses the electrons that are gained in the reduction.
       e) **From Cl⁻**, which is losing electrons, **to MnO₄⁻**, which is gaining electrons.
       f) $8H_2SO_4(aq) + 2KMnO_4(aq) + 10KCl(aq) \rightarrow 2MnSO_4(aq) + 5Cl_2(g) + 8H_2O(l) + 6K_2SO_4(aq)$

19.12   <u>Plan:</u> Divide the reaction into the two half-reactions, balance elements other than oxygen and hydrogen, and then balance oxygen by adding H_2O and hydrogen by adding H^+. Balance the charge by adding electrons and multiply each half-reaction by an integer so that the number of electrons lost equals the number of electrons gained. Add the half-reactions together, canceling substances that appear on both sides. For basic solutions, add
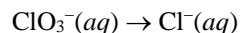
one OH⁻ ion to each side of the equation for every H⁺ ion present to form H_2O and cancel excess H_2O molecules. The substance that gains electrons is the oxidizing agent while the substance that loses electrons is the reducing agent.
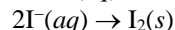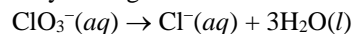
Solution:

a) Divide into half-reactions:

$ClO_3^-(aq) \rightarrow Cl^-(aq)$

$I^-(aq) \rightarrow I_2(s)$
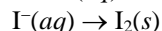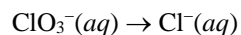
Balance elements other than O and H:

$ClO_3^-(aq) \rightarrow Cl^-(aq)$	chlorine is balanced
$2I^-(aq) \rightarrow I_2(s)$	iodine now balanced

Balance O by adding H_2O:

$ClO_3^-(aq) \rightarrow Cl^-(aq) + 3H_2O(l)$	add three waters to add three O atoms to product
$2I^-(aq) \rightarrow I_2(s)$	no change
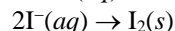
Balance H by adding H⁺:
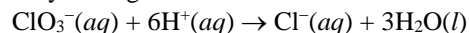
$ClO_3^-(aq) + 6H^+(aq) \rightarrow Cl^-(aq) + 3H_2O(l)$	add six H⁺ to reactants
$2I^-(aq) \rightarrow I_2(s)$	no change
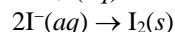
Balance charge by adding e⁻:
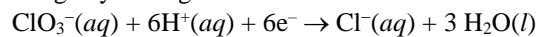
$ClO_3^-(aq) + 6H^+(aq) + 6e^- \rightarrow Cl^-(aq) + 3\ H_2O(l)$	add 6e⁻ to reactants for a −1 charge on each side
$2I^-(aq) \rightarrow I_2(s) + 2e^-$	add 2e⁻ to products for a −2 charge on each side
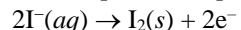
Multiply each half-reaction by an integer to equalize the number of electrons:

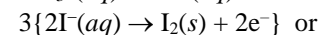|	
$ClO_3^-(aq) + 6H^+(aq) + 6e^- \rightarrow Cl^-(aq) + 3H_2O(l)$	multiply by one to give 6e⁻
$3\{2I^-(aq) \rightarrow I_2(s) + 2e^-\}$ or	multiply by three to give 6e⁻
$6I^-(aq) \rightarrow 3I_2(s) + 6e^-$	
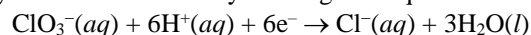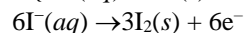
Add half-reactions to give balanced equation in acidic solution:

$$ClO_3^-(aq) + 6H^+(aq) + 6I^-(aq) \rightarrow Cl^-(aq) + 3H_2O(l) + 3I_2(s)$$
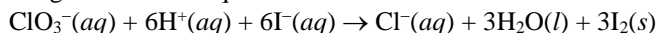
Check balancing:

	Reactants:		Products:	
	1 Cl			1 Cl
	3 O			3 O
	6 H			6 H
	6 I			6 I
	−1 charge			−1 charge

Oxidizing agent is ClO₃⁻ and reducing agent is I⁻.

b) Divide into half-reactions:
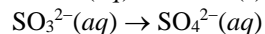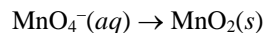
$MnO_4^-(aq) \rightarrow MnO_2(s)$

$SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq)$

Balance elements other than O and H:

$MnO_4^-(aq) \rightarrow MnO_2(s)$	Mn is balanced
$SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq)$	S is balanced
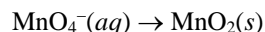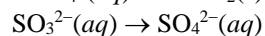
Balance O by adding H_2O:
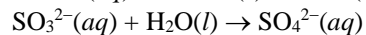
$MnO_4^-(aq) \rightarrow MnO_2(s) + 2H_2O(l)$	add two H_2O to products
$SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq)$	add one H_2O to reactants

Balance H by adding H⁺:

$MnO_4^-(aq) + 4H^+(aq) \rightarrow MnO_2(s) + 2H_2O(l)$	add four H⁺ to reactants
$SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2H^+(aq)$	add two H⁺ to products
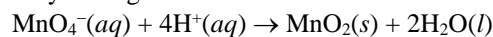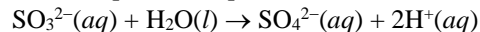
Balance charge by adding e⁻:
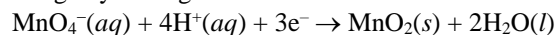
$MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightarrow MnO_2(s) + 2H_2O(l)$	add 3e⁻ to reactants for a 0 charge on each side
$SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$	add 2e⁻ to products for a −2 charge on each side

Multiply each half-reaction by an integer to equalize the number of electrons:

|	
$2\{MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightarrow MnO_2(s) + 2H_2O(l)\}$ or	multiply by two to give 6e⁻
$2MnO_4^-(aq) + 8H^+(aq) + 6e^- \rightarrow 2MnO_2(s) + 4H_2O(l)$	
$3\{SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-\}$ or	multiply by three to give 6e⁻
$3SO_3^{2-}(aq) + 3H_2O(l) \rightarrow 3SO_4^{2-}(aq) + 6H^+(aq) + 6e^-$	

Add half-reactions and cancel substances that appear as both reactants and products:

2 $MnO_4^-(aq)$ + ~~8H$^+$~~(aq) + 3$SO_3^{2-}(aq)$ + ~~3H$_2$O(l)~~ → 2$MnO_2(s)$ + ~~4~~$H_2O(l)$ + 3$SO_4^{2-}(aq)$ + ~~6H$^+$(aq)~~

The balanced equation in acidic solution is:

$2MnO_4^-(aq) + 2H^+(aq) + 3SO_3^{2-}(aq) \rightarrow 2MnO_2(s) + H_2O(l) + 3SO_4^{2-}(aq)$
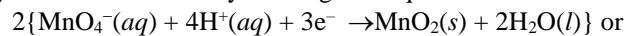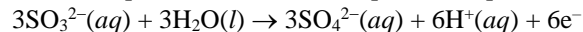
To change to basic solution, add OH$^-$ to both sides of equation to neutralize H$^+$

$2MnO_4^-(aq) + 2H^+(aq) + 2OH^-(aq) + 3SO_3^{2-}(aq) \rightarrow 2MnO_2(s) + H_2O(l) + 3SO_4^{2-}(aq) + 2OH^-(aq)$

$2MnO_4^-(aq)$ + ~~2~~$H_2O(l)$ + 3$SO_3^{2-}(aq)$ → 2$MnO_2(s)$ + ~~H$_2$O(l)~~ + 3$SO_4^{2-}(aq)$ + 2$OH^-(aq)$
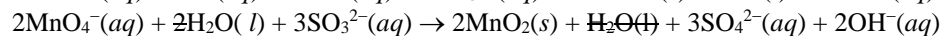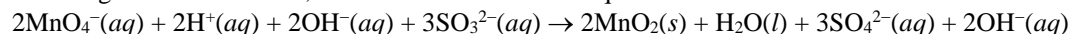
Balanced equation in basic solution:

$2MnO_4^-(aq) + H_2O(l) + 3SO_3^{2-}(aq) \rightarrow 2MnO_2(s) + 3SO_4^{2-}(aq) + 2OH^-(aq)$
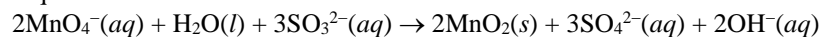
Check balancing:

	Reactants:		Products:	
	2 Mn		2 Mn	
	18 O		18 O	
	2 H		2 H	
	3 S		3 S	
	–8 charge		–8 charge	

Oxidizing agent is MnO_4^- and reducing agent is SO_3^{2-}.

c) Divide into half-reactions:

$MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$

$H_2O_2(aq) \rightarrow O_2(g)$

Balance elements other than O and H:
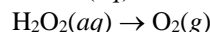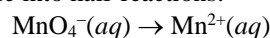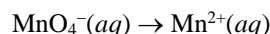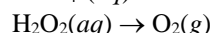
$MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$	Mn is balanced
$H_2O_2(aq) \rightarrow O_2(g)$	No other elements to balance

Balance O by adding H_2O:
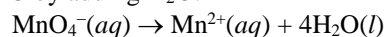
$MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	add four H_2O to products
$H_2O_2(aq) \rightarrow O_2(g)$	O is balanced
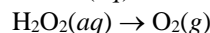
Balance H by adding H$^+$:

$MnO_4^-(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	add eight H$^+$ to reactants
$H_2O_2(aq) \rightarrow O_2(g) + 2H^+(aq)$	add two H$^+$ to products
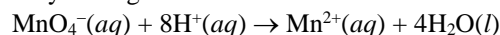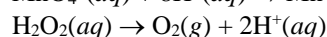
Balance charge by adding e$^-$:
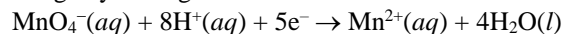
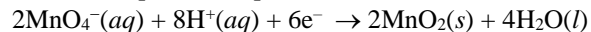| $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	add 5e$^-$ to reactants for +2 on each side
$H_2O_2(aq) \rightarrow O_2(g) + 2H^+(aq) + 2e^-$	add 2e$^-$ to products for 0 charge on each side
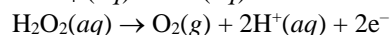
Multiply each half-reaction by an integer to equalize the number of electrons:

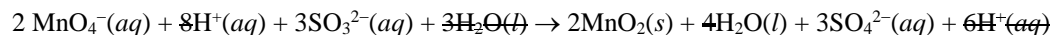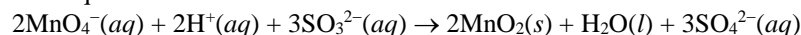| $2\{MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)\}$ or	multiply by two to give 10e$^-$
$2MnO_4^-(aq) + 16H^+(aq) + 10e^- \rightarrow 2Mn^{2+}(aq) + 8H_2O(l)$	
$5\{H_2O_2(aq) \rightarrow O_2(g) + 2H^+(aq) + 2e^-\}$ or	multiply by five to give 10e$^-$
$5H_2O_2(aq) \rightarrow 5O_2(g) + 10H^+(aq) + 10e^-$	

Add half-reactions and cancel substances that appear as both reactants and products:

$2MnO_4^-(aq)$ + ~~16~~H$^+(aq)$ + 5$H_2O_2(aq)$ → 2$Mn^{2+}(aq)$ + 8$H_2O(l)$ + 5$O_2(g)$ + ~~10H$^+$(aq)~~

The balanced equation in acidic solution:

$2MnO_4^-(aq) + 6H^+(aq) + 5H_2O_2(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g)$
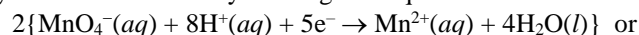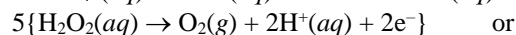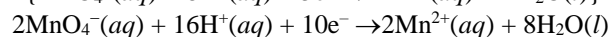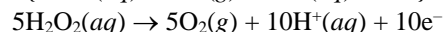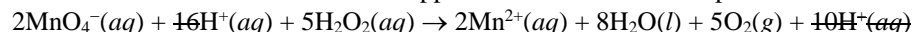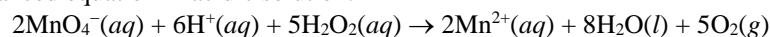
Check balancing:

	Reactants:		Products:	
	2 Mn		2 Mn	
	18 O		18 O	
	16 H		16 H	
	+4 charge		+4 charge	

Oxidizing agent is MnO_4^- and reducing agent is H_2O_2.

19.14   Plan: Divide the reaction into the two half-reactions, balance elements other than oxygen and hydrogen, and then balance oxygen by adding H_2O and hydrogen by adding H$^+$. Balance the charge by adding electrons and multiply each half-reaction by an integer so that the number of electrons lost equals the number of electrons gained. Add the half-reactions together, canceling substances that appear on both sides. For basic solutions, add one OH$^-$ ion to each side of the equation for every H$^+$ ion present to form H_2O and cancel excess H_2O molecules. The substance that gains electrons is the oxidizing agent while the substance that loses electrons is the reducing agent.

Solution:
a) Balance the reduction half-reaction:

$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)$ balance Cr

$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ balance O by adding H_2O

$Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ balance H by adding H^+

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ balance charge by adding $6e^-$

Balance the oxidation half-reaction:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ balance charge by adding $2e^-$

Add the two half-reactions multiplying the oxidation half-reaction by three to equalize the electrons:
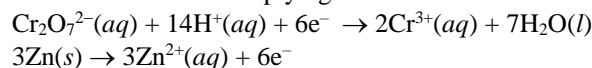
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

$3Zn(s) \rightarrow 3Zn^{2+}(aq) + 6e^-$

Add half-reactions and cancel substances that appear as both reactants and products:

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 3Zn(s) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3Zn^{2+}(aq)$

Oxidizing agent is $Cr_2O_7^{2-}$ and reducing agent is Zn.

b) Balance the reduction half-reaction:

$MnO_4^-(aq) \rightarrow MnO_2(s) + 2H_2O(l)$ balance O by adding H_2O

$MnO_4^-(aq) + 4H^+(aq) \rightarrow MnO_2(s) + 2H_2O(l)$ balance H by adding H^+

$MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightarrow MnO_2(s) + 2H_2O(l)$ balance charge by adding 3 e^-

Balance the oxidation half-reaction:

$Fe(OH)_2(s) + H_2O(l) \rightarrow Fe(OH)_3(s)$ balance O by adding H_2O

$Fe(OH)_2(s) + H_2O(l) \rightarrow Fe(OH)_3(s) + H^+(aq)$ balance H by adding H^+

$Fe(OH)_2(s) + H_2O(l) \rightarrow Fe(OH)_3(s) + H^+(aq) + e^-$ balance charge by adding $1e^-$
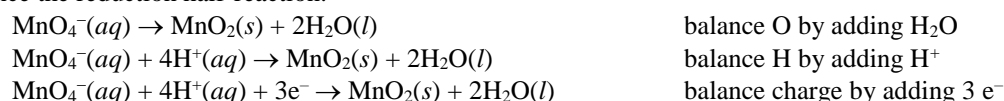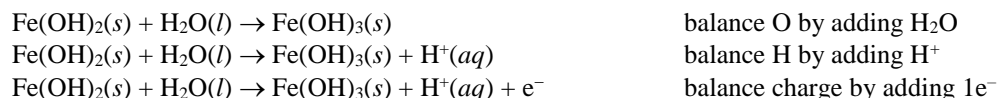
Add half-reactions after multiplying oxidation half-reaction by 3:
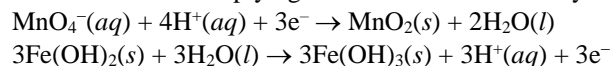
$MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightarrow MnO_2(s) + 2H_2O(l)$

$3Fe(OH)_2(s) + 3H_2O(l) \rightarrow 3Fe(OH)_3(s) + 3H^+(aq) + 3e^-$

Add half-reactions and cancel substances that appear as both reactants and products:

$MnO_4^-(aq) + \cancel{4}H^+(aq) + 3Fe(OH)_2(s) + \cancel{3}H_2O(l) \rightarrow MnO_2(s) + \cancel{2H_2O(l)} + 3Fe(OH)_3(s) + \cancel{3H^+(aq)}$

$MnO_4^-(aq) + \ H^+(aq) + 3Fe(OH)_2(s) + H_2O(l) \rightarrow MnO_2(s) + 3Fe(OH)_3(s)$
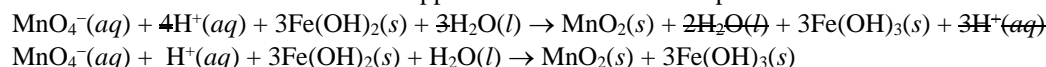
Add OH^- to both sides to neutralize the H^+ and convert $H^+ + OH^- \rightarrow H_2O$:

$MnO_4^-(aq) + \ H^+(aq) + OH^-(aq) \ + 3Fe(OH)_2(s) + H_2O(l) \rightarrow MnO_2(s) + 3Fe(OH)_3(s) + OH^-(aq)$

$MnO_4^-(aq) + 3Fe(OH)_2(s) + 2H_2O(l) \rightarrow MnO_2(s) + 3Fe(OH)_3(s) + OH^-(aq)$
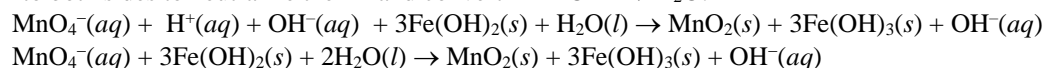
Oxidizing agent is MnO_4^- and reducing agent is $Fe(OH)_2$.

c) Balance the reduction half-reaction:

$2NO_3^-(aq) \rightarrow N_2(g)$ balance N

$2NO_3^-(aq) \rightarrow N_2(g) + 6H_2O(l)$ balance O by adding H_2O

$2NO_3^-(aq) + 12H^+(aq) \rightarrow N_2(g) + 6H_2O(l)$ balance H by adding H^+

$2NO_3^-(aq) + 12H^+(aq) + 10e^- \rightarrow N_2(g) + 6H_2O(l)$ balance charge by adding $10e^-$

Balance the oxidation half-reaction:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ balance charge by adding $2e^-$
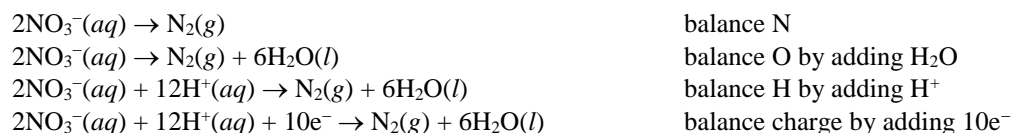
Add the half-reactions after multiplying the reduction half-reaction by one and the oxidation half-reaction by five:
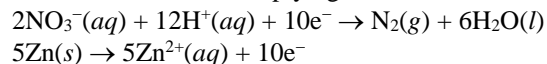
$2NO_3^-(aq) + 12H^+(aq) + 10e^- \rightarrow N_2(g) + 6H_2O(l)$

$5Zn(s) \rightarrow 5Zn^{2+}(aq) + 10e^-$

Add half-reactions and cancel substances that appear as both reactants and products:

$2NO_3^-(aq) + 12H^+(aq) + 5Zn(s) \rightarrow N_2(g) + 6H_2O(l) + 5Zn^{2+}(aq)$
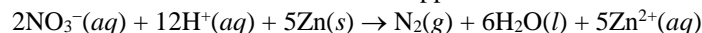
Oxidizing agent is NO_3^- and reducing agent is Zn.

19.16   Plan: Divide the reaction into the two half-reactions, balance elements other than oxygen and hydrogen, and then balance oxygen by adding H_2O and hydrogen by adding H^+. Balance the charge by adding electrons and multiply each half-reaction by an integer so that the number of electrons lost equals the number of electrons gained. Add the half-reactions together, canceling substances that appear on both sides. For basic solutions, add one OH^- ion to each side of the equation for every H^+ ion present to form H_2O and cancel excess H_2O molecules. The substance that gains electrons is the oxidizing agent while the substance that loses electrons is the reducing agent.

Solution:
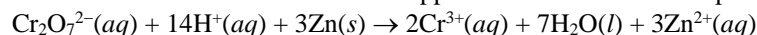a) Balance the reduction half-reaction:

$NO_3^-(aq) \rightarrow NO(g) + 2H_2O(l)$ balance O by adding H_2O

$NO_3^-(aq) + 4H^+(aq) \rightarrow NO(g) + 2H_2O(l)$ balance H by adding H^+

$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$ balance charge by adding $3e^-$

Balance oxidation half-reaction:

$4Sb(s) \rightarrow Sb_4O_6(s)$ balance Sb

$4Sb(s) + 6H_2O(l) \rightarrow Sb_4O_6(s)$ balance O by adding H_2O

$4Sb(s) + 6H_2O(l) \rightarrow Sb_4O_6(s) + 12H^+(aq)$ balance H by adding H^+

$4Sb(s) + 6H_2O(l) \rightarrow Sb_4O_6(s) + 12H^+(aq) + 12e^-$ balance charge by adding $12e^-$

Multiply each half-reaction by an integer to equalize the number of electrons:

$4\{NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)\}$ multiply by four to give $12e^-$

$1\{4Sb(s) + 6H_2O(l) \rightarrow Sb_4O_6(s) + 12H^+(aq) + 12e^-\}$ multiply by one to give $12e^-$

This gives:

$4NO_3^-(aq) + 16H^+(aq) + 12e^- \rightarrow 4NO(g) + 8H_2O(l)$

$4Sb(s) + 6H_2O(l) \rightarrow Sb_4O_6(s) + 12H^+(aq) + 12e^-$

Add half-reactions. Cancel common reactants and products:

$4 NO_3^-(aq) + \cancel{16H^+(aq)} + 4Sb(s) + \cancel{6H_2O(l)} \rightarrow 4NO(g) + \cancel{8}H_2O(l) + Sb_4O_6(s) + \cancel{12H^+(aq)}$

Balanced equation in acidic solution:

$4NO_3^-(aq) + 4H^+(aq) + 4Sb(s) \rightarrow 4NO(g) + 2H_2O(l) + Sb_4O_6(s)$
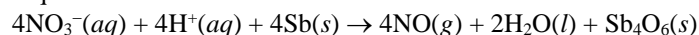
Oxidizing agent is NO_3^- and reducing agent is Sb.
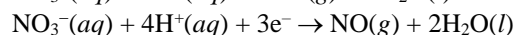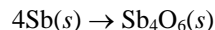
b) Balance reduction half-reaction:

$BiO_3^-(aq) \rightarrow Bi^{3+}(aq) + 3H_2O(l)$ balance O by adding H_2O

$BiO_3^-(aq) + 6H^+(aq) \rightarrow Bi^{3+}(aq) + 3H_2O(l)$ balance H by adding H^+
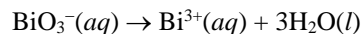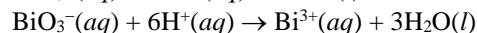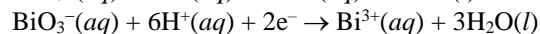
$BiO_3^-(aq) + 6H^+(aq) + 2e^- \rightarrow Bi^{3+}(aq) + 3H_2O(l)$ balance charge to give +3 on each side

Balance oxidation half-reaction:

$Mn^{2+}(aq) + 4H_2O(l) \rightarrow MnO_4^-(aq)$ balance O by adding H_2O

$Mn^{2+}(aq) + 4H_2O(l) \rightarrow MnO_4^-(aq) + 8H^+(aq)$ balance H by adding H^+
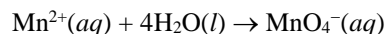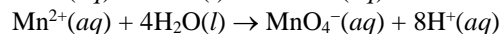
$Mn^{2+}(aq) + 4H_2O(l) \rightarrow MnO_4^-(aq) + 8H^+(aq) + 5e^-$ balance charge to give +2 on each side

Multiply each half-reaction by an integer to equalize the number of electrons:

$5\{BiO_3^-(aq) + 6H^+(aq) + 2e^- \rightarrow Bi^{3+}(aq) + 3H_2O(l)\}$ multiply by five to give $10e^-$
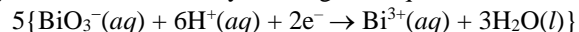
$2\{Mn^{2+}(aq) + 4H_2O(l) \rightarrow MnO_4^-(aq) + 8H^+(aq) + 5e^-\}$ multiply by two to give $10e^-$

This gives:

$5BiO_3^-(aq) + 30H^+(aq) + 10e^- \rightarrow 5Bi^{3+}(aq) + 15H_2O(l)$

$2Mn^{2+}(aq) + 8H_2O(l) \rightarrow 2MnO_4^-(aq) + 16H^+(aq) + 10e^-$
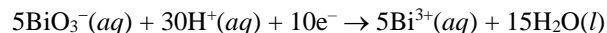
Add half-reactions. Cancel H_2O and H^+ in reactants and products:
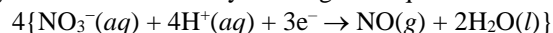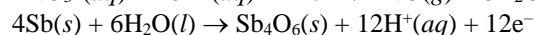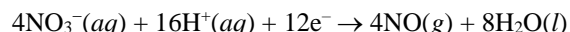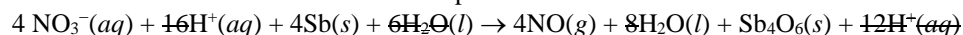
$5BiO_3^-(aq) + \cancel{30}H^+(aq) + 2Mn^{2+}(aq) + \cancel{8H_2O(l)} \rightarrow 5Bi^{3+}(aq) + \cancel{15}H_2O(l) + 2MnO_4^-(aq) + \cancel{16H^+(aq)}$

Balanced reaction in acidic solution:

$5BiO_3^-(aq) + 14H^+(aq) + 2Mn^{2+}(aq) \rightarrow 5Bi^{3+}(aq) + 7H_2O(l) + 2MnO_4^-(aq)$
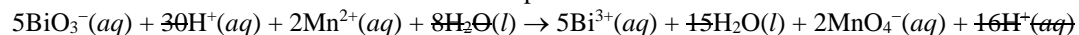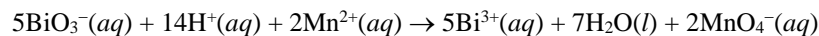
BiO_3^- is the oxidizing agent and Mn^{2+} is the reducing agent.

c) Balance the reduction half-reaction:

$Pb(OH)_3^-(aq) \rightarrow Pb(s) + 3H_2O(l)$ balance O by adding H_2O

$Pb(OH)_3^-(aq) + 3H^+(aq) \rightarrow Pb(s) + 3H_2O(l)$ balance H by adding H^+
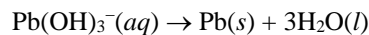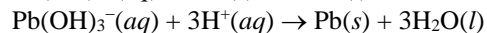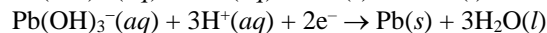
$Pb(OH)_3^-(aq) + 3H^+(aq) + 2e^- \rightarrow Pb(s) + 3H_2O(l)$ balance charge to give 0 on each side

Balance the oxidation half-reaction:
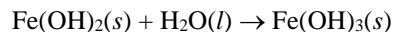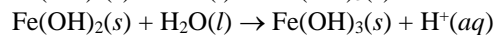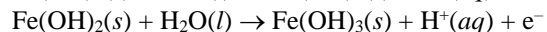
$Fe(OH)_2(s) + H_2O(l) \rightarrow Fe(OH)_3(s)$ balance O by adding H_2O

$Fe(OH)_2(s) + H_2O(l) \rightarrow Fe(OH)_3(s) + H^+(aq)$ balance H by adding H^+

$Fe(OH)_2(s) + H_2O(l) \rightarrow Fe(OH)_3(s) + H^+(aq) + e^-$ balance charge to give 0 on each side

Multiply each half-reaction by an integer to equalize the number of electrons:

$1\{Pb(OH)_3^-(aq) + 3H^+(aq) + 2e^- \rightarrow Pb(s) + 3H_2O(l)\}$ multiply by 1 to give $2e^-$
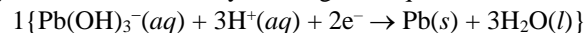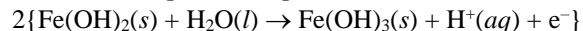
$2\{Fe(OH)_2(s) + H_2O(l) \rightarrow Fe(OH)_3(s) + H^+(aq) + e^-\}$ multiply by 2 to give $2e^-$

This gives:

$Pb(OH)_3^-(aq) + 3H^+(aq) + 2e^- \rightarrow Pb(s) + 3H_2O(l)$

$2Fe(OH)_2(s) + 2H_2O(l) \rightarrow 2Fe(OH)_3(s) + 2H^+(aq) + 2e^-$

Add the two half-reactions. Cancel H_2O and H^+:

$Pb(OH)_3^-(aq) + \cancel{3}H^+(aq) + 2Fe(OH)_2(s) + \cancel{2H_2O(l)} \rightarrow Pb(s) + \cancel{3}H_2O(l) + 2Fe(OH)_3(s) + \cancel{2H^+(aq)}$

$Pb(OH)_3^-(aq) + H^+(aq) + 2Fe(OH)_2(s) \rightarrow Pb(s) + H_2O(l) + 2Fe(OH)_3(s)$
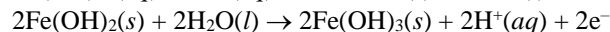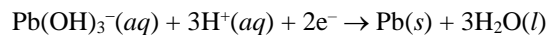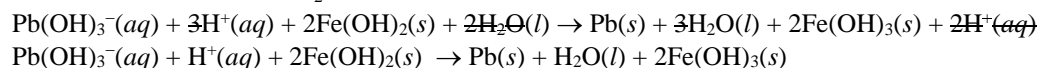
Add one OH^- to both sides to neutralize H^+:

$Pb(OH)_3^-(aq) + H^+(aq) + OH^-(aq) + 2Fe(OH)_2(s) \rightarrow Pb(s) + H_2O(l) + 2 Fe(OH)_3(s) + OH^-(aq)$

$Pb(OH)_3^-(aq) + \cancel{H_2O(l)} + 2Fe(OH)_2(s) \rightarrow Pb(s) + \cancel{H_2O(l)} + 2Fe(OH)_3(s) + OH^-(aq)$

Balanced reaction in basic solution:

$Pb(OH)_3^-(aq) + 2Fe(OH)_2(s) \rightarrow Pb(s) + 2Fe(OH)_3(s) + OH^-(aq)$
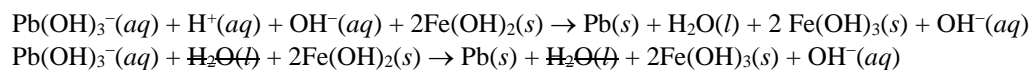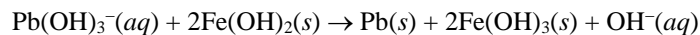
$Pb(OH)_3^-$ is the oxidizing agent and $Fe(OH)_2$ is the reducing agent.

19.18 Plan: Divide the reaction into the two half-reactions, balance elements other than oxygen and hydrogen, and then balance oxygen by adding H_2O and hydrogen by adding H^+. Balance the charge by adding electrons and multiply each half-reaction by an integer so that the number of electrons lost equals the number of electrons gained. Add the half-reactions together, canceling substances that appear on both sides. For basic solutions, add one OH^- ion to each side of the equation for every H^+ ion present to form H_2O and cancel excess H_2O molecules. The substance that gains electrons is the oxidizing agent while the substance that loses electrons is the reducing agent.

Solution:

a) Balance reduction half-reaction:

$MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	balance O by adding H_2O
$MnO_4^-(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	balance H by adding H^+
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	balance charge by adding $5e^-$

Balance oxidation half-reaction:

$As_4O_6(s) \rightarrow 4AsO_4^{3-}(aq)$	balance As
$As_4O_6(s) + 10H_2O(l) \rightarrow 4AsO_4^{3-}(aq)$	balance O by adding H_2O
$As_4O_6(s) + 10H_2O(l) \rightarrow 4AsO_4^{3-}(aq) + 20H^+(aq)$	balance H by adding H^+
$As_4O_6(s) + 10H_2O(l) \rightarrow 4AsO_4^{3-}(aq) + 20H^+(aq) + 8e^-$	balance charge by adding $8e^-$
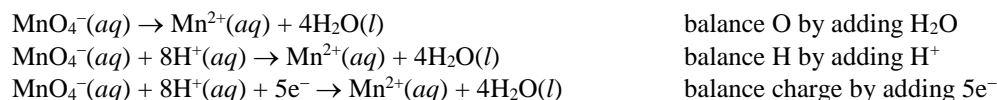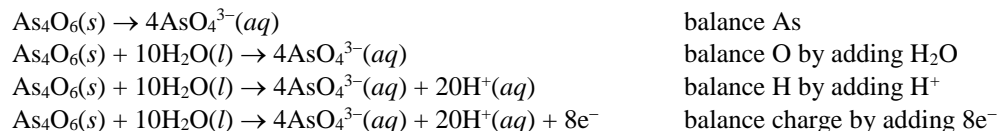
Multiply reduction half-reaction by 8 and oxidation half-reaction by 5 to transfer 40 e^- in overall reaction.
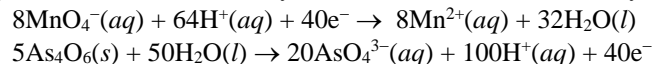
$8MnO_4^-(aq) + 64H^+(aq) + 40e^- \rightarrow 8Mn^{2+}(aq) + 32H_2O(l)$

$5As_4O_6(s) + 50H_2O(l) \rightarrow 20AsO_4^{3-}(aq) + 100H^+(aq) + 40e^-$

Add the half-reactions and cancel H_2O and H^+:

$5As_4O_6(s) + 8MnO_4^-(aq) + \cancel{64H^+(aq)} + \cancel{50}H_2O(l) \rightarrow 20AsO_4^{3-}(aq) + 8Mn^{2+}(aq) + \cancel{32H_2O(l)} + \cancel{100}H^+(aq)$

Balanced reaction in acidic solution:

$5As_4O_6(s) + 8MnO_4^-(aq) + 18H_2O(l) \rightarrow 20AsO_4^{3-}(aq) + 8Mn^{2+}(aq) + 36H^+(aq)$
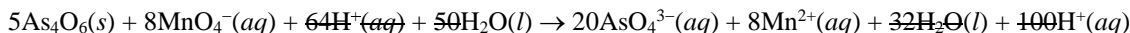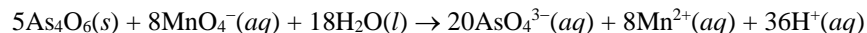
Oxidizing agent is MnO_4^- and reducing agent is As_4O_6.

b) The reaction gives only one reactant, P_4. Since both products contain phosphorus, divide the half-reactions so each includes P_4 as the reactant.

Balance reduction half-reaction:
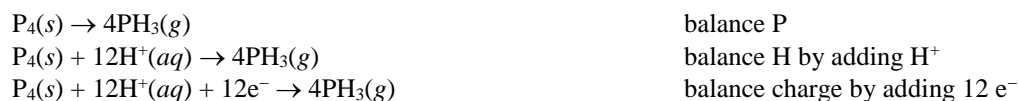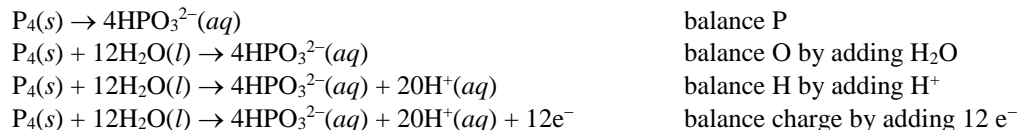
$P_4(s) \rightarrow 4PH_3(g)$	balance P
$P_4(s) + 12H^+(aq) \rightarrow 4PH_3(g)$	balance H by adding H^+
$P_4(s) + 12H^+(aq) + 12e^- \rightarrow 4PH_3(g)$	balance charge by adding 12 e^-

Balance oxidation half-reaction:

$P_4(s) \rightarrow 4HPO_3^{2-}(aq)$	balance P
$P_4(s) + 12H_2O(l) \rightarrow 4HPO_3^{2-}(aq)$	balance O by adding H_2O
$P_4(s) + 12H_2O(l) \rightarrow 4HPO_3^{2-}(aq) + 20H^+(aq)$	balance H by adding H^+
$P_4(s) + 12H_2O(l) \rightarrow 4HPO_3^{2-}(aq) + 20H^+(aq) + 12e^-$	balance charge by adding 12 e^-

Add two half-reactions and cancel H^+:

$2P_4(s) + \cancel{12H^+(aq)} + 12H_2O(l) \rightarrow 4HPO_3^{2-}(aq) + 4PH_3(g) + \cancel{20}H^+(aq)$

Balanced reaction in acidic solution:

$2P_4(s) + 12H_2O(l) \rightarrow 4HPO_3^{2-}(aq) + 4PH_3(g) + 8H^+(aq)$ or

$P_4(s) + 6H_2O(l) \rightarrow 2HPO_3^{2-}(aq) + 2PH_3(g) + 4H^+(aq)$
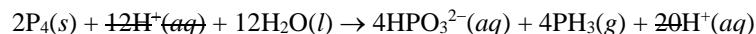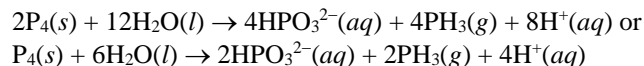
P_4 is both the oxidizing agent and reducing agent.

c) Balance the reduction half-reaction:
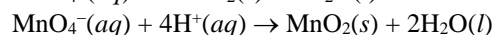
$MnO_4^-(aq) \rightarrow MnO_2(s) + 2H_2O(l)$ balance O by adding H_2O

$MnO_4^-(aq) + 4H^+(aq) \rightarrow MnO_2(s) + 2H_2O(l)$ balance H by adding H^+

$MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightarrow MnO_2(s) + 2H_2O(l)$ balance charge by adding $3e^-$

Balance oxidation half-reaction:

$CN^-(aq) + H_2O(l) \rightarrow CNO^-(aq)$ balance O by adding H_2O

$CN^-(aq) + H_2O(l) \rightarrow CNO^-(aq) + 2H^+(aq)$ balance H by adding H^+
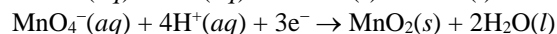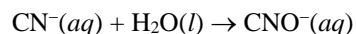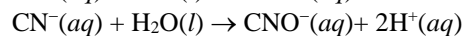
$CN^-(aq) + H_2O(l) \rightarrow CNO^-(aq) + 2H^+(aq) + 2e^-$ balance charge by adding $2e^-$

Multiply the oxidation half-reaction by three and reduction half-reaction by two to transfer $6e^-$ in overall reaction.

$2MnO_4^-(aq) + 8H^+(aq) + 6e^- \rightarrow 2MnO_2(s) + 4H_2O(l)$

$3CN^-(aq) + 3H_2O(l) \rightarrow 3CNO^-(aq) + 6H^+(aq) + 6e^-$
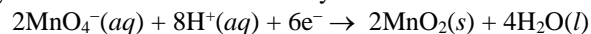
Add the two half-reactions. Cancel the H_2O and H^+:

$2MnO_4^-(aq) + 3CN^-(aq) + \cancel{8}H^+(aq) + \cancel{3H_2O}(l) \rightarrow 2MnO_2(s) + 3CNO^-(aq) + \cancel{6H^+(aq)} + \cancel{4}H_2O(l)$

$2MnO_4^-(aq) + 3CN^-(aq) + 2H^+(aq) \rightarrow 2MnO_2(s) + 3CNO^-(aq) + H_2O(l)$
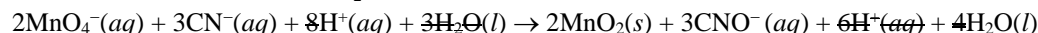
Add 2 OH^- to both sides to neutralize H^+ and form H_2O:

$2MnO_4^-(aq) + 3CN^-(aq) + 2H^+(aq) + 2OH^-(aq) \rightarrow 2MnO_2(s) + 3CNO^-(aq) + H_2O(l) + 2OH^-(aq)$

$2MnO_4^-(aq) + 3CN^-(aq) + \cancel{2}H_2O(l) \rightarrow 2MnO_2(s) + 3CNO^-(aq) + \cancel{H_2O(l)} + 2OH^-(aq)$

Balanced reaction in basic solution:

$2MnO_4^-(aq) + 3CN^-(aq) + H_2O(l) \rightarrow 2MnO_2(s) + 3CNO^-(aq) + 2OH^-(aq)$
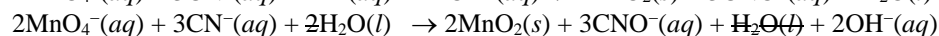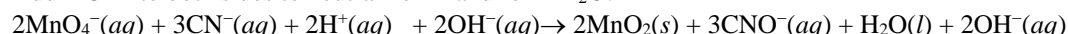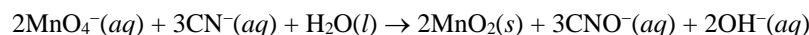
Oxidizing agent is MnO_4^- and reducing agent is CN^-.

19.21   a) Balance reduction half-reaction:
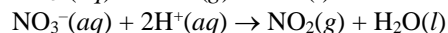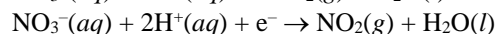
$NO_3^-(aq) \rightarrow NO_2(g) + H_2O(l)$ balance O by adding H_2O

$NO_3^-(aq) + 2H^+(aq) \rightarrow NO_2(g) + H_2O(l)$ balance H by adding H^+

$NO_3^-(aq) + 2H^+(aq) + e^- \rightarrow NO_2(g) + H_2O(l)$ balance charge to give 0 on each side

Balance oxidation half-reaction:

$Au(s) + 4Cl^-(aq) \rightarrow AuCl_4^-(aq)$ balance Cl
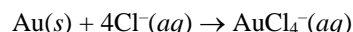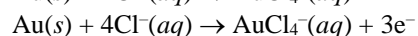
$Au(s) + 4Cl^-(aq) \rightarrow AuCl_4^-(aq) + 3e^-$ balance charge to –4 on each side

Multiply each half-reaction by an integer to equalize the number of electrons:
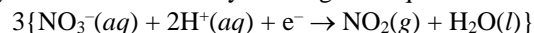
$3\{NO_3^-(aq) + 2H^+(aq) + e^- \rightarrow NO_2(g) + H_2O(l)\}$ multiply by three to give $3e^-$
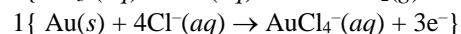
$1\{Au(s) + 4Cl^-(aq) \rightarrow AuCl_4^-(aq) + 3e^-\}$ multiply by one to give $3e^-$

This gives:

$3NO_3^-(aq) + 6H^+(aq) + 3e^- \rightarrow 3NO_2(g) + 3H_2O(l)$

$Au(s) + 4Cl^-(aq) \rightarrow AuCl_4^-(aq) + 3e^-$

Add half-reactions:

$Au(s) + 3NO_3^-(aq) + 4Cl^-(aq) + 6H^+(aq) \rightarrow AuCl_4^-(aq) + 3NO_2(g) + 3H_2O(l)$
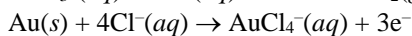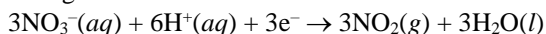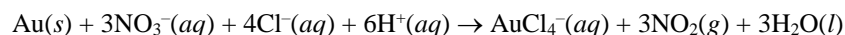
b) Oxidizing agent is **NO_3^-** and reducing agent is **Au**.

c) The HCl provides chloride ions that combine with the unstable gold ion to form the stable ion, $AuCl_4^-$.

19.22   <u>Plan:</u> The oxidation half-cell (anode) is shown on the left while the reduction half-cell (cathode) is shown on the right. Remember that oxidation is the loss of electrons and electrons leave the oxidation half-cell and move towards the positively charged cathode. If a metal is reduced, it will plate out on the cathode.
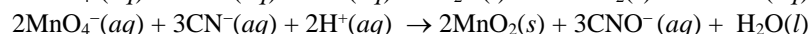
<u>Solution:</u>

a) **A** is the anode because by convention the anode is shown on the left.

b) **E** is the cathode because by convention the cathode is shown on the right.

c) **C** is the salt bridge providing electrical connection between the two solutions.

d) **A** is the anode, so oxidation takes place there. Oxidation is the loss of electrons, meaning that electrons are leaving the anode.

e) **E** is assigned a positive charge because it is the cathode.

f) **E** gains mass because the reduction of the metal ion produces the solid metal which plates out on E.

19.25   (a) An active electrode is a reactant or product in the cell reaction, whereas an inactive electrode is neither a reactant nor a product. (b) An inactive electrode is present only to conduct electricity when the half-cell reaction does not include a metal. (c) Platinum and graphite are commonly used as inactive electrodes.

19.26   a) The metal **A** is being oxidized to form the metal cation. To form positive ions, an atom must always lose electrons, so this half-reaction is always an oxidation.
b) The metal ion **B** is gaining electrons to form the metal **B**, so it is displaced.
c) The anode is the electrode at which oxidation takes place, so metal **A** is used as the anode.
d) Acid oxidizes metal **B** and metal **B** oxidizes metal **A**, so acid will oxidize metal **A** and **bubbles will form** when metal **A** is placed in acid. The same answer results if strength of reducing agents is considered. The fact that metal **A** is a better reducing agent than metal **B** indicates that if metal **B** reduces acid, then metal **A** will also reduce acid.

19.27   Plan: The anode, at which the oxidation takes place, is the negative electrode. Electrons flow from the anode to the cathode. Anions from the salt bridge flow into the oxidation half-cell, while cations from the salt bridge flow into the reduction half-cell.
Solution:
a) If the zinc electrode is negative, it is the anode and oxidation takes place at the zinc electrode:
$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$
Reduction half-reaction: $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$
Overall reaction: $Zn(s) + Sn^{2+}(aq) \rightarrow Zn^{2+}(aq) + Sn(s)$
b)
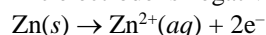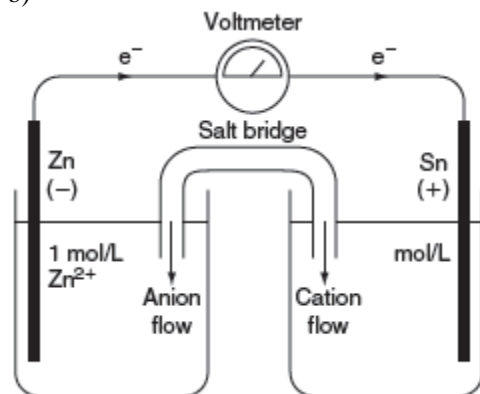
19.29   Plan: The oxidation half-cell (anode) is shown on the left while the reduction half-cell (cathode) is shown on the right. Remember that oxidation is the loss of electrons and electrons leave the oxidation half-cell and move towards the positively charged cathode. Anions from the salt bridge flow into the oxidation half-cell, while cations from the salt bridge flow into the reduction half-cell.
Solution:
a) Electrons flow from the anode to the cathode, so **from the iron half-cell to the nickel half-cell**, left to right in the figure. By convention, the anode appears on the left and the cathode on the right.
b) Oxidation occurs at the anode, which is the electrode in the **iron** half-cell.
c) Electrons enter the reduction half-cell, the **nickel** half-cell in this example.
d) Electrons are consumed in the reduction half-reaction. Reduction takes place at the cathode, **nickel** electrode.
e) The anode is assigned a negative charge, so the **iron** electrode is negatively charged.
f) Metal is oxidized in the oxidation half-cell, so the **iron** electrode will decrease in mass.
g) The solution must contain nickel ions, so any nickel salt can be added. **1 mol/L NiSO₄** is one choice.
h) KNO₃ is commonly used in salt bridges, the ions being **K⁺ and NO₃⁻**. Other salts are also acceptable answers.
i) **Neither**, because an inactive electrode could not replace either electrode since both the oxidation and the reduction half-reactions include the metal as either a reactant or a product.
j) Anions will move towards the half-cell in which positive ions are being produced. The oxidation half-cell produces Fe^{2+}, so salt bridge anions move **from right** (nickel half-cell) **to left** (iron half-cell).
k)   Oxidation half-reaction: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$
            Reduction half-reaction: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$
            Overall cell reaction: $Fe(s) + Ni^{2+}(aq) \rightarrow Fe^{2+}(aq) + Ni(s)$

19.31   Plan: The cathode, at which the reduction takes place, is the positive electrode. Electrons flow from the anode to the cathode. Anions from the salt bridge flow into the oxidation half-cell, while cations from the salt bridge flow into the reduction half-cell.

Solution:
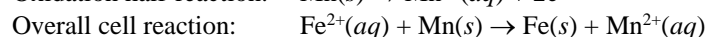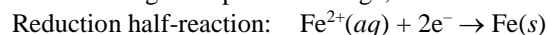a) The cathode is assigned a positive charge, so the iron electrode is the cathode.

Reduction half-reaction: $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$

Oxidation half-reaction: $Mn(s) \rightarrow Mn^{2+}(aq) + 2e^-$

Overall cell reaction: $Fe^{2+}(aq) + Mn(s) \rightarrow Fe(s) + Mn^{2+}(aq)$

b)
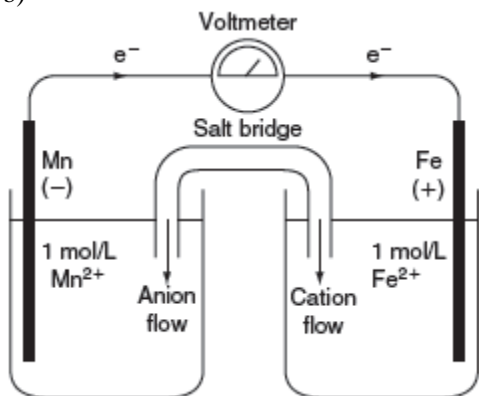
19.33   <u>Plan:</u> In cell notation, the oxidation components of the anode compartment are written on the left of the salt bridge and the reduction components of the cathode compartment are written to the right of the salt bridge. A double vertical line separates the anode from the cathode and represents the salt bridge. A single vertical line separates species of different phases. Anode || Cathode

Solution:

a) Al is oxidized, so it is the anode and appears first in the cell notation. There is a single vertical line separating the solid metals from their solutions.

$Al(s) \mid Al^{3+}(aq) \parallel Cr^{3+}(aq) \mid Cr(s)$
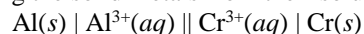
b) Cu^{2+} is reduced, so Cu is the cathode and appears last in the cell notation. The oxidation of SO_2 does not include a metal, so an inactive electrode must be present. Hydrogen ion must be included in the oxidation half-cell.

$Pt \mid SO_2(g) \mid SO_4^{2-}(aq), H^+(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$

19.36   (a) A negative E°_{cell} indicates that the cell reaction is not spontaneous, $\Delta G^\circ > 0$. (b) The reverse reaction is spontaneous with $E^\circ_{cell} > 0$.

19.37   (a) Similar to other state functions, the sign of E° changes when a reaction is reversed. (b) Unlike ΔG°, ΔH° and S°, E° is an intensive property, the ratio of energy to charge. When the coefficients in a reaction are multiplied by a factor, the values of ΔG°, ΔH° and S° are multiplied by the same factor. However, E° does not change because both the energy and charge are multiplied by the factor and their ratio remains unchanged.

19.38   <u>Plan:</u> Divide the balanced equation into reduction and oxidation half-reactions and add electrons. Add water and hydroxide ion to the half-reaction that includes oxygen. Use the relationship $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$ to find the unknown E° value.

Solution:

a) Oxidation: $Se^{2-}(aq) \rightarrow Se(s) + 2e^-$

Reduction: $2SO_3^{2-}(aq) + 3H_2O(l) + 4e^- \rightarrow S_2O_3^{2-}(aq) + 6OH^-(aq)$
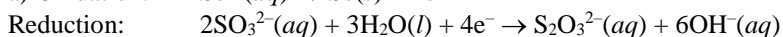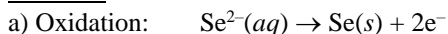
b) $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$E^\circ_{anode} = E^\circ_{cathode} - E^\circ_{cell} = -0.57 \text{ V} - 0.35 \text{ V} = \mathbf{-0.92 \text{ V}}$

19.40   Plan: The greater (more positive) the reduction potential, the greater the strength as an oxidizing agent.
         Solution:
         a) From Appendix D:
         $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ $E° = 0.77$ V
         $Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$ $E° = 1.07$ V
         $Cu^{2+}(aq) + e^- \rightarrow Cu(s)$ $E° = 0.34$ V
         When placed in order of decreasing strength as oxidizing agents: **Br_2 > Fe^{3+} > Cu^{2+}.**
         b) From Appendix D:
         $Ca^{2+}(aq) + 2e- \rightarrow Ca(s)$ $E° = -2.87$ V
         $Cr_2O_7^{2-}(aq) + 14H^+(aq)$ $6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ $E° = 1.33$ V
         $Ag^+(aq) + e^- \rightarrow Ag(s)$ $E° = 0.80$ V
         When placed in order of increasing strength as oxidizing agents: **Ca^{2+} < Ag^+ < $Cr_2O_7^{2-}$.**

19.42   Plan: Use the relationship $E°_{cell} = E°_{cathode} - E°_{anode}$. $E°$ values are found in Appendix D. Spontaneous reactions
         have $E°_{cell} > 0$.
         Solution:
         a)   Oxidation: $Co(s) \rightarrow Co^{2+}(aq) + 2e^-$ $E° = -0.28$ V
                 Reduction: $2H^+(aq) + 2e^- \rightarrow H_2(g)$ $E° = 0.00$ V
                 Overall reaction: $Co(s) + 2H^+(aq) \rightarrow Co^{2+}(aq) + H_2(g)$
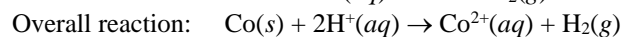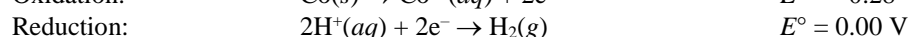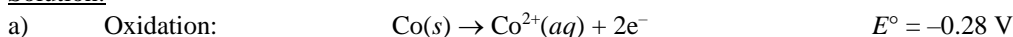
                                                                          $E°_{cell} = 0.00$ V$-$ $(-0.28$ V$) =$ **0.28 V**

                 Reaction is **spontaneous** under standard-state conditions because $E°_{cell}$ is positive.
         b)   Oxidation: $2\{Mn^{2+}(aq) + 4H_2O(l) \rightarrow MnO_4^-(aq) + 8H^+(aq) + 5e^-\}$ $E° = +1.51$ V
                 Reduction: $5\{Br_2(l) + 2e^- \rightarrow 2 Br^-(aq)\}$ $E° = +1.07$ V
                 Overall: $2Mn^{2+}(aq) + 5Br_2(l) + 8H_2O(l) \rightarrow 2MnO_4^-(aq) + 10Br^-(aq) + 16H^+(aq)$
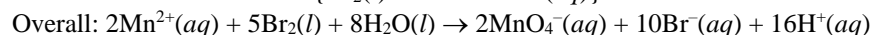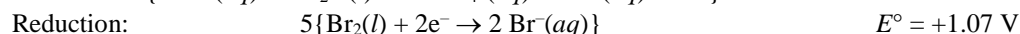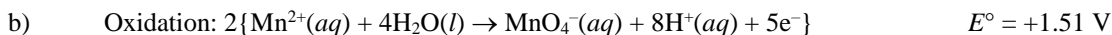
                                                                          $E°_{cell} = 1.07$ V $- 1.51$ V $=$ **–0.44 V**

                 Reaction is **not spontaneous** under standard-state conditions with $E°_{cell} < 0$.
         c)   Oxidation: $Hg_2^{2+}(aq) \rightarrow 2Hg^{2+}(aq) + 2e^-$ $E° = +0.92$ V
                 Reduction: $Hg_2^{2+}(aq) + 2e^- \rightarrow 2Hg(l)$ $E° = +0.85$ V
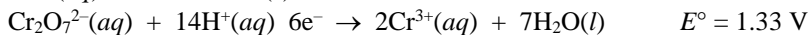   Overall: $2Hg_2^{2+}(aq) \rightarrow 2Hg^{2+}(aq) + 2Hg(l)$

                 or $Hg_2^{2+}(aq) \rightarrow Hg^{2+}(aq) + Hg(l)$ $E°_{cell} = 0.85$ V$- 0.92$ V $=$ **–0.07 V**
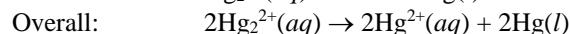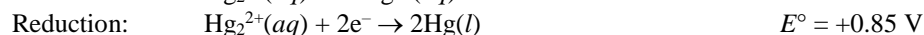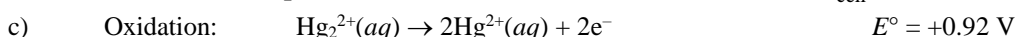
                 Negative $E°_{cell}$ indicates reaction is **not spontaneous** under standard-state conditions.

19.44   Plan: Use the relationship $E°_{cell} = E°_{cathode} - E°_{anode}$. $E°$ values are found in Appendix D. Spontaneous reactions
         have $E°_{cell} > 0$.
         Solution:
         a)   Oxidation: $2\{Ag(s) \rightarrow Ag^+(aq) + e^-\}$ $E° = +0.80$ V
                 Reduction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E° = +0.34$ V
                 Overall: $2Ag(s) + Cu^{2+}(aq) \rightarrow 2Ag^+(aq) + Cu(s)$
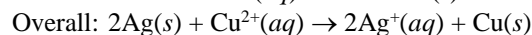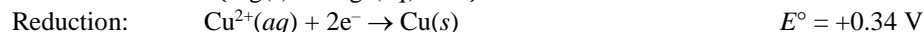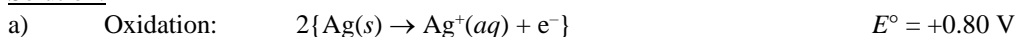
                                                                          $E°_{cell} = +0.34$ V $- 0.80$ V $=$ **–0.46 V**

                 The reaction is **not spontaneous**.
         b)   Oxidation: $3\{Cd(s) \rightarrow Cd^{2+}(aq) + 2e^-\}$ $E° = -0.40$ V
                 Reduction: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ $E° = +1.33$ V
                 Overall: $Cr_2O_7^{2-}(aq) + 3Cd(s) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3Cd^{2+}(aq) + 7H_2O(l)$
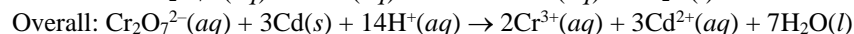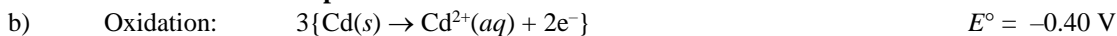
                                                                          $E°_{cell} = +1.33$ V$- (-0.40$ V$) =$ **+1.73 V**

                 The reaction is **spontaneous**.

c) Oxidation: $Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$ $\qquad\qquad\qquad\qquad E° = -0.13$ V
Reduction: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ $\qquad\qquad\qquad\qquad E° = -0.25$ V
Overall: $Pb(s) + Ni^{2+}(aq) \rightarrow Pb^{2+}(aq) + Ni(s)$
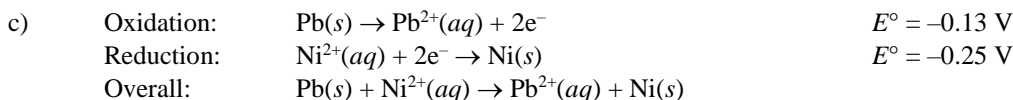
$$E°_{cell} = -0.25 \text{ V} - (-0.13 \text{ V}) = \textbf{-0.12 V}$$

The reaction is **not spontaneous**.

19.46 <u>Plan:</u> Spontaneous reactions have $E°_{cell} > 0$. All three reactions are written as reductions. When two half-reactions are paired, one half-reaction must be reversed and written as an oxidation. Reverse the half-reaction that will result in a positive value of $E°_{cell}$ using the relationship $E°_{cell} = E°_{cathode} - E°_{anode}$. To balance each reaction, multiply each half-reaction by an integer so that the number of electrons lost equals the number of electrons gained and then add the half-reactions. The greater (more positive) the reduction potential, the greater the strength as an oxidizing agent.
<u>Solution:</u>
Adding (1) and (2) to give a spontaneous reaction involves converting (1) to oxidation:
Oxidation: $2\{Al(s) \rightarrow Al^{3+}(aq) + 3e^-\}$ $\qquad\qquad\qquad E° = -1.66$ V
Reduction: $3\{N_2O_4(g) + 2e^- \rightarrow 2NO_2^-(aq)\}$ $\qquad\qquad E° = +0.867$ V
$3N_2O_4(g) + 2Al(s) \rightarrow 6NO_2^-(aq) + 2Al^{3+}(aq)$

$$E°_{cell} = 0.867 \text{ V} - (-1.66 \text{ V}) = \textbf{2.53 V}$$

Oxidizing agents: $N_2O_4 > Al^{3+}$; reducing agents: $Al > NO_2^-$
Adding (1) and (3) to give a spontaneous reaction involves converting (1) to oxidation:
Oxidation: $2\{Al(s) \rightarrow Al^{3+}(aq) + 3e^-\}$ $\qquad\qquad\qquad\qquad E° = -1.66$ V
Reduction: $3\{SO_4^{2-}(aq) + H_2O(l) + 2e^- \rightarrow SO_3^{2-}(aq) + 2OH^-(aq)\}$ $\quad E° = +0.93$ V
$2Al(s) + 3SO_4^{2-}(aq) + 3H_2O(l) \rightarrow 2Al^{3+}(aq) + 3SO_3^{2-}(aq) + 6OH^-(aq)$
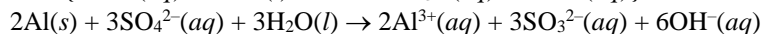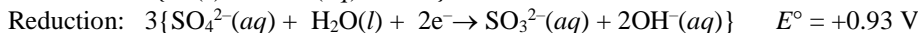
$$E°_{cell} = 0.93 \text{ V} - (-1.66 \text{ V}) = \textbf{2.59 V}$$

Oxidizing agents: $SO_4^{2-} > Al^{3+}$; reducing agents: $Al > SO_3^{2-}$
Adding (2) and (3) to give a spontaneous reaction involves converting (2) to oxidation:
Oxidation: $2NO_2^-(aq) \rightarrow N_2O_4(g) + 2e^-$ $\qquad\qquad\qquad E° = 0.867$ V
Reduction: $SO_4^{2-}(aq) + H_2O(l) + 2e^- \rightarrow SO_3^{2-}(aq) + 2OH^-(aq)$ $\qquad E° = 0.93$ V
$SO_4^{2-}(aq) + 2NO_2^-(aq) + H_2O(l) \rightarrow SO_3^{2-}(aq) + N_2O_4(g) + 2OH^-(aq)$
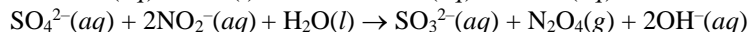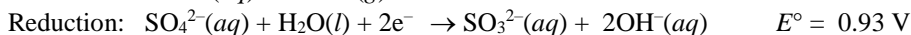
$$E°_{cell} = 0.93 \text{ V} - 0.867 \text{ V} = \textbf{0.06 V}$$

Oxidizing agents: $SO_4^{2-} > N_2O_4$; reducing agents: $NO_2^- > SO_3^{2-}$
Rank oxidizing agents (substance being reduced) in order of increasing strength:
$\qquad$ **$Al^{3+} < N_2O_4 < SO_4^{2-}$**
Rank reducing agents (substance being oxidized) in order of increasing strength:
$\qquad$ **$SO_3^{2-} < NO_2^- < Al$**
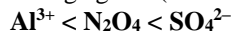
19.48 <u>Plan:</u> Spontaneous reactions have $E°_{cell} > 0$. All three reactions are written as reductions. When two half-reactions are paired, one half-reaction must be reversed and written as an 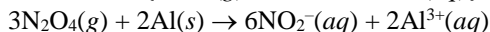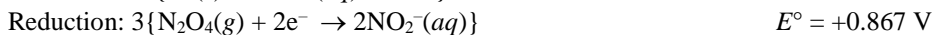oxidation. Reverse the half-reaction that will result in a positive value of $E°_{cell}$ using the relationship $E°_{cell} = E°_{cathode} - E°_{anode}$. To balance each reaction, multiply each half-reaction by an integer so that the number of electrons lost equals the number of electrons gained and then add the half-reactions. The greater (more positive) the reduction potential, the greater the strength as an oxidizing agent.
<u>Solution:</u>
Adding (1) and (2) to give a spontaneous reaction involves converting (2) to oxidation:
Oxidation: $Pt(s) \rightarrow Pt^{2+}(aq) + 2e^-$ $\qquad\qquad\qquad\qquad E° = +1.20$ V
Reduction: $2HClO(aq) + 2H^+(aq) + 2e^- \rightarrow Cl_2(g) + 2H_2O(l)$ $\qquad E° = +1.63$ V
$2HClO(aq) + Pt(s) + 2H^+(aq) \rightarrow Cl_2(g) + Pt^{2+}(aq) + 2H_2O(l)$

$$E°_{cell} = 1.63 \text{ V} - 1.20 \text{ V} = \textbf{0.43 V}$$

Oxidizing agents: $HClO > Pt^{2+}$; reducing agents: $Pt > Cl_2$
Adding (1) and (3) to give a spontaneous reaction involves converting (3) to oxidation:

Oxidation: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$ $E° = -0.31$ V

Reduction: $2HClO(aq) + 2H^+(aq) + 2e^- \rightarrow Cl_2(g) + 2H_2O(l)$ $E° = +1.63$ V

       $2HClO(aq) + Pb(s) + SO_4^{2-}(aq) + 2H^+(aq) \rightarrow Cl_2(g) + PbSO_4(s) + 2H_2O(l)$
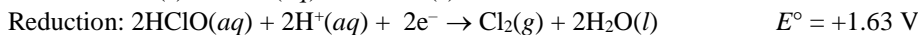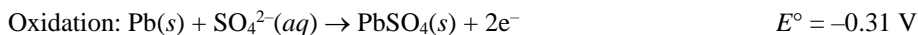
       $E°_{cell} = 1.63$ V $- (-0.31$ V$) = $ **1.94 V**

       Oxidizing agents: $HClO > PbSO_4$; reducing agents: $Pb > Cl_2$

Adding (2) and (3) to give a spontaneous reaction involves converting (3) to oxidation:

Oxidation: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$ $E° = -0.31$ V

Reduction: $Pt^{2+}(aq) + 2e^- \rightarrow Pt(s)$ $E° = 1.20$ V

       $Pt^{2+}(aq) + Pb(s) + SO_4^{2-}(aq) \rightarrow Pt(s) + PbSO_4(s)$
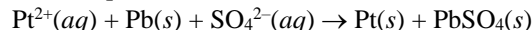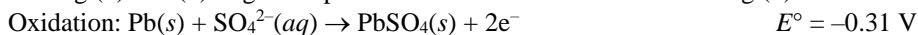
       $E°_{cell} = 1.20$ V $- (-0.31$ V$) = $ **1.51 V**

       Oxidizing agents: $Pt^{2+} > PbSO_4$; reducing agents: $Pb > Pt$

Order of increasing strength as oxidizing agent: **$PbSO_4 < Pt^{2+} < HClO$**

Order of increasing strength as reducing agent: **$Cl_2 < Pt < (Pb + SO_4^{2-})$**

19.50   Metal A + Metal B salt $\rightarrow$ solid coloured product on metal A

       Conclusion: Product is solid metal B. B is undergoing reduction and plating out on A. A is a better reducing agent than B.

     Metal B + acid $\rightarrow$ gas bubbles

       Conclusion: Product is H_2 gas produced as result of reduction of H^+. B is a better reducing agent than acid.

     Metal A + Metal C salt $\rightarrow$ no reaction

       Conclusion: C is not undergoing reduction. C must be a better reducing agent than A.

     Since C is a better reducing agent than A, which is a better reducing agent than B and B reduces acid, then **C would also reduce acid to form H_2 bubbles**.

     The order of strength of reducing agents is: **C > A > B**.

19.53   At the negative (anode) electrode, oxidation occurs so the overall cell reaction is

     $A(s) + B^+(aq) \rightarrow A^+(aq) + B(s)$ with $Q = [A^+]/[B^+]$.
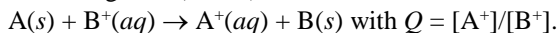
     a) The reaction proceeds to the right because with $E_{cell} > 0$ (voltaic cell), the spontaneous reaction occurs. As the cell operates, **$[A^+]$ increases and $[B^+]$ decreases**.

     b) **E_{cell} decreases** because the cell reaction takes place to approach equilibrium, $E_{cell} = 0$.

     c) E_{cell} and $E°_{cell}$ are related by the Nernst equation: $E_{cell} = E°_{cell} - \dfrac{RT}{zF} \ln \dfrac{[A^+]}{[B^+]}$.

     $E_{cell} = E°_{cell}$ when $\dfrac{RT}{zF} \ln \dfrac{[A^+]}{[B^+]} = 0$. This occurs when $\ln \dfrac{[A^+]}{[B^+]} = 0$. Recall that $e^0 = 1$, so **$[A^+]$ must equal $[B^+]$**

     for E_{cell} to equal $E°_{cell}$.

     d) **Yes**, it is possible for E_{cell} to be less than $E°_{cell}$ when **$[A^+] > [B^+]$**.

19.55   In a concentration cell, the overall reaction takes place to decrease the concentration of the more concentrated electrolyte. The more concentrated electrolyte is reduced, so it is in the **cathode** compartment.

19.56   <u>Plan:</u> The equilibrium constant can be found by using $\ln K = \dfrac{zFE°_{cell}}{RT}$. Use $E°$ values from Appendix D to

     calculate $E°_{cell}$ ($E°_{cell} = E°_{cathode} - E°_{anode}$) and then calculate K. The substances given in the problem must be the reactants in the equation.

     <u>Solution:</u>

     a) Oxidation: $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$ $E° = -0.25$ V

       Reduction: $2\{Ag^+(aq) + 1e^- \rightarrow Ag(s)\}$ $E° = +0.80$ V

$$Ni(s) + 2Ag^+(aq) \rightarrow Ni^{2+}(aq) + 2Ag(s)$$
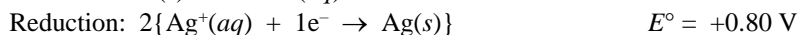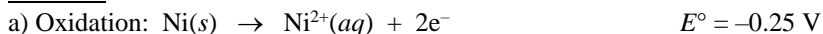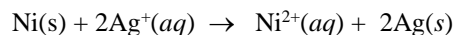
$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.80$ V $- (-0.25$ V$) = 1.05$ V; two electrons are transferred.

$$\ln K = \frac{zFE^\circ_{cell}}{RT} = \frac{2(96485 \text{ C/mol e}^-)(1.05 \text{ V})}{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})} = 81.78107$$

$K = e^{81.78107}$

$K = 3.28904 \times 10^{35} = \mathbf{3 \times 10^{35}}$

b) Oxidation: $3\{Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-\}$ $E^\circ = -0.44$ V

    Reduction: $2\{Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)\}$ $E^\circ = -0.74$ V

        $3Fe(s) + 2Cr^{3+}(aq) \rightarrow 3Fe^{2+}(aq) + 2Cr(s)$
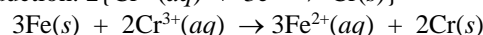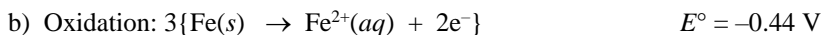
$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = -0.74$ V $- (-0.44$ V$) = -0.30$ V; six electrons are transferred.

$$\ln K = \frac{zFE^\circ_{cell}}{RT} = \frac{6(96485 \text{ C/mol e}^-)(-0.30 \text{ V})}{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})} = -70.09806$$

$K = e^{-70.09806}$

$K = 3.604 \times 10^{-31} = \mathbf{4 \times 10^{-31}}$

19.58   <u>Plan:</u> The equilibrium constant can be found by using $\ln K = \dfrac{zFE^\circ_{cell}}{RT}$. Use E° values from Appendix D to calculate E°_{cell} ($E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$) and then calculate K. The substances given in the problem must be the reactants in the equation.

<u>Solution:</u>

a) Oxidation: $2\{Ag(s) \rightarrow Ag^+(aq) + 1e^-\}$ $E^\circ = +0.80$ V

    Reduction: $Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$ $E^\circ = -1.18$ V

        $2Ag(s) + Mn^{2+}(aq) \rightarrow 2Ag^+(aq) + Mn(s)$
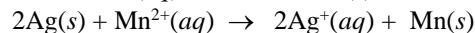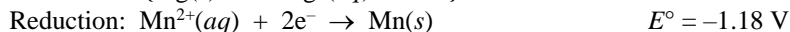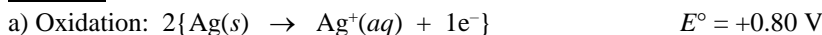
        $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = -1.18$ V $- (0.80$ V$) = -1.98$V; two electrons are transferred.

$$\ln K = \frac{zFE^\circ_{cell}}{RT} = \frac{2(96485 \text{ C/mol e}^-)(-1.98 \text{ V})}{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})} = --154.2157$$

        $K = e^{-154.2157}$

        $K = 1.05914 \times 10^{-67} = \mathbf{1 \times 10^{-67}}$

b) Oxidation: $2Br^-(aq) \rightarrow Br_2(l) + 2e^-$ $E^\circ = 1.07$ V

    Reduction: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ $E^\circ = 1.36$ V

        $2Br^-(aq) + Cl_2(g) \rightarrow Br_2(l) + 2Cl^-(aq)$
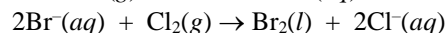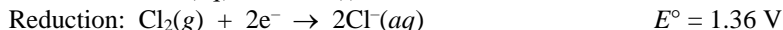
        $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 1.36$ V $- 1.07$ V $= 0.29$ V; two electrons transferred.

$$\ln K = \frac{zFE^\circ_{cell}}{RT} = \frac{2(96485 \text{ C/mol e}^-)(0.29 \text{ V})}{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})} = 22.58715$$

        $K = e^{22.58715}$ $K = 6.44876 \times 10^9 = \mathbf{6 \times 10^9}$

19.60   <u>Plan:</u> Use $\Delta G^\circ = -nFE^\circ_{cell}$ to calculate ΔG°. Substitute J/C for V in the unit for E°_{cell}. The units of ΔG° remain as J/mol as a reminder that the value is for a reaction as written.

<u>Solution:</u>

a) $\Delta G^\circ = -zFE^\circ_{cell} = -(2 \text{ mol e}^-)(96{,}485 \text{ C/mol e}^-)(1.05 \text{ J/C}) = -2.026185 \times 10^5$ J $= \mathbf{-2.03 \times 10^5}$ **J/mol**

b) $\Delta G^\circ = -zFE^\circ_{cell} = -(6 \text{ mol e}^-)(96{,}485 \text{ C/mol e}^-)(-0.30 \text{ J/C}) = 1.73673 \times 10^5$ J $= \mathbf{1.7 \times 10^5}$ **J/mol**

19.62   Plan: Use $\Delta G° = -zFE°_{cell}$ to calculate $\Delta G°$. Substitute J/C for V in the unit for $E°_{cell}$. The units of $\Delta G°$ remain as
        J/mol as a reminder that the value is for a reaction as written.
        Solution:
        a) $\Delta G° = -zFE°_{cell} = -$ (2 mol e$^-$)(96,485 C/mol e$^-$)(–1.98 J/C) = 3.820806x10^5 J= **3.82x10^5 J/mol**

        b) $\Delta G° = -zFE°_{cell} = -$ (2 mol e$^-$)(96,485 C/mol e$^-$)(0.29 J/C) = –5.59613x10^4 J= **–5.6x10^4 J/mol**

19.64   Plan: Use $E°_{cell} = \dfrac{RT}{zF} \ln K$ to find $E°_{cell}$ and then $\Delta G° = -RT \ln K$ to find $\Delta G°$.

        Solution:
        $T = (273 + 25)K = 298$ K
        $E°_{cell} = \dfrac{RT}{zF} \ln K = \dfrac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(1)(96485 \text{ C/mol})} \ln\left(5.0\text{x}10^4\right) = 0.277834$ V= **0.28 V**

        $\Delta G° = -RT \ln K = -$ (8.314 J/mol•K)(298 K) ln (5.0x10^4) = –2.68067797x10^4 J/mol= **–2.7x10^4 J/mol**

19.66   Plan: Use $E°_{cell} = \dfrac{RT}{zF} \ln K$ to find $E°_{cell}$ and then $\Delta G° = -RT \ln K$ to find $\Delta G°$.

        Solution:
        $T = (273 + 25)K = 298$ K
        $E°_{cell} = \dfrac{RT}{zF} \ln K = \dfrac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln\left(65\right) = 0.0535956$ V= **0.054 V**

        $\Delta G° = -RT \ln K = -$ (8.314 J/mol•K)(298 K) ln (65) = –1.03423x10^4 J/mol= **–1.0x10^4 J/mol**

19.68   Plan: The standard reference half-cell is the H_2/H^+ cell. Since this is a voltaic cell, a spontaneous reaction is
        occurring. For a spontaneous reaction between H_2/H^+ and Cu/Cu^{2+}, Cu^{2+} must be reduced and H_2 must be

        oxidized. Write the balanced reaction and calculate $E°_{cell}$. Use the Nernst equation, $E_{cell} = E°_{cell} - \dfrac{RT}{zF} \ln Q$,

        to find [Cu^{2+}] when $E_{cell} = 0.22$ V.
        Solution:
        Oxidation: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$ $E° = 0.00$ V
        Reduction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E° = 0.34$ V
               $Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2H^+(aq)$
        $E°_{cell} = E°_{cathode} - E°_{anode} = 0.34$ V – 0.00 V = 0.34 V
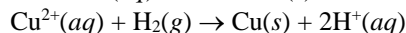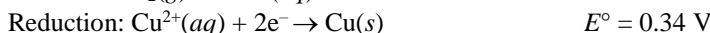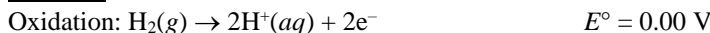
        $E_{cell} = E°_{cell} - \dfrac{RT}{zF} \ln Q$

        $E_{cell} = E°_{cell} - \dfrac{RT}{zF} \ln \dfrac{\left[H^+\right]^2}{\left[Cu^{2+}\right] p_{H_2}}$

             For a standard hydrogen electrode [H^+] = 1.0 mol/L and p_{H_2} = 1.0 bar.

        0.22 V $= 0.34$ V $- \dfrac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln \dfrac{1.0}{\left[Cu^{2+}\right]1.0}$

        0.22 V $- 0.34$ V $= - \dfrac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln \dfrac{1.0}{\left[Cu^{2+}\right]1.0}$

        -0.12 V $= - \dfrac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln \dfrac{1.0}{\left[Cu^{2+}\right]1.0}$

$$9.34641 = \ln \frac{1.0}{\left[Cu^{2+}\right]1.0} \qquad \text{Raise each side to } e^x.$$

$$1.14576 \times 10^4 = \frac{1}{[Cu^{2+}]}$$

$[Cu^{2+}] = 8.72783 \times 10^{-5} = \mathbf{8.7 \times 10^{-5} \ mol/L}$

19.70   Plan: Since this is a voltaic cell, a spontaneous reaction is occurring. For a spontaneous reaction between Ni/Ni^{2+} and Co/Co^{2+}, Ni^{2+} must be reduced and Co must be oxidized. Write the balanced reaction and calculate E°_{cell}.

Use the Nernst equation, $E_{cell} = E^{\circ}_{cell} - \dfrac{RT}{zF} \ln Q$, to find E_{cell} at the given ion concentrations. Then the Nernst equation can be used to calculate $[Ni^{2+}]$ at the given E_{cell}. To calculate equilibrium concentrations, recall that at equilibrium $E_{cell} = 0.00$.

Solution:

a) Oxidation: $Co(s) \rightarrow Co^{2+}(aq) + 2e^-$ $E^{\circ} = -0.28$ V

Reduction: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ $E^{\circ} = -0.25$ V

        $Ni^{2+}(aq) + Co(s) \rightarrow Ni(s) + Co^{2+}(aq)$
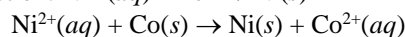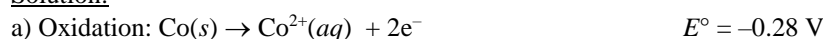
          $E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode} = -0.25$ V $- (-0.28$ V$) = 0.03$ V

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{zF} \ln Q$$

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{zF} \ln \frac{\left[Co^{2+}\right]}{\left[Ni^{2+}\right]} \qquad\qquad z = 2e^-$$

$$E_{cell} = 0.03 \text{ V} - \frac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln\left(\frac{0.20}{0.80}\right)$$

$E_{cell} = 0.04779885$ V $= \mathbf{0.05 \ V}$

b) From part a), notice that an increase in $[Co^{2+}]$ leads to a decrease in cell potential. Therefore, the concentration of cobalt ion must increase further to bring the potential down to 0.03 V. Thus, the new concentrations will be $[Co^{2+}] = 0.20$ mol/L $+ x$ and $[Ni^{2+}] = 0.80$ mol/L $- x$ (there is a 1:1 mole ratio).

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{zF} \ln \frac{\left[Co^{2+}\right]}{\left[Ni^{2+}\right]}$$

$$0.03 \text{ V} = 0.03 \text{ V} - \frac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln\left(\frac{0.20 + x}{0.80 - x}\right)$$

$$0 = -\frac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln\left(\frac{0.20 + x}{0.80 - x}\right)$$

$$0 = \ln \frac{(0.20 + x)}{(0.80 - x)} \qquad\qquad \text{Raise each side to } e^x.$$

$$e^0 = 1 = \frac{(0.20 + x)}{(0.80 - x)}$$

$0.20 + x = 0.80 - x$

$x = 0.30$ mol/L

$[Ni^{2+}] = 0.80 - x = 0.80 - 0.30 = \mathbf{0.50 \ mol/L}$

c) At equilibrium $E_{cell} = 0.00$; to decrease the cell potential to 0.00, $[Co^{2+}]$ increases and $[Ni^{2+}]$ decreases.

$$0.00 \text{ V} = 0.03 \text{ V} - \frac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln\left(\frac{0.20 + x}{0.80 - x}\right)$$

$$-0.03 \text{ V} = -\frac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln\left(\frac{0.20 + \text{x}}{0.80 - \text{x}}\right)$$

$$2.3366 = \ln\left(\frac{0.20 + \text{x}}{0.80 - \text{x}}\right) \qquad \text{Raise each side to } e^x.$$

$$10.3460 = \left(\frac{0.20 + \text{x}}{0.80 - \text{x}}\right)$$

x = 0.71186 $[Co^{2+}] = 0.20 + 0.71186 = 0.91186 =$ **0.91 mol/L**
$[Ni^{2+}] = 0.80 - 0.71186 = 0.088135 =$ **0.09 mol/L**

19.72   Plan: The overall cell reaction proceeds to increase the 0.10 mol/L H^+ concentration and decrease the 2.0 mol/L
H^+ concentration. Use the Nernst equation to calculate E_{cell}. $E^{\circ}_{cell} = 0$ V for a concentration cell since the half-
reactions are the same.
Solution:
Half-cell **A is the anode** because it has the lower concentration.
Oxidation: $H_2(g; 0.95 \text{ bar}) \rightarrow 2H^+(aq; 0.10 \text{ mol/L}) + 2e^-$ $E^{\circ} = 0.00$ V
Reduction: $2H^+(aq; 2.0 \text{ mol/L}) + 2e^- \rightarrow H_2(g; 0.60 \text{ bar})$ $E^{\circ} = 0.00$ V
       $2H^+(aq; 2.0 \text{ mol/L}) + H_2(g; 0.95 \text{ bar}) \rightarrow 2H^+(aq; 0.10 \text{ mol/L}) + H_2(g; 0.60 \text{ bar})$
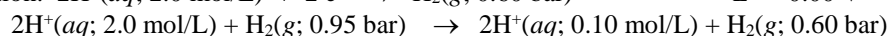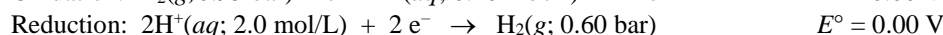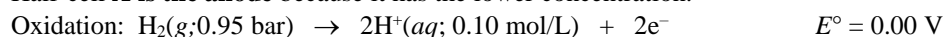
               $E^{\circ}_{cell} = 0.00$ V $z = 2e^-$

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{zF} \ln Q$$

Q for the cell equals $\dfrac{\left[H^+\right]^2_{\text{anode}} \, p_{H_2(\text{cathode})}}{\left[H^+\right]^2_{\text{cathode}} \, p_{H_2(\text{anode})}} = \dfrac{(0.10)^2 (0.60)}{(2.0)^2 (0.95)} = 0.00157895$

$$E_{cell} = 0.00 \text{ V} - \frac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln (0.00157895) = 0.082821 \text{ V} = \textbf{0.083 V}$$

19.74   Electrons flow from the anode, where oxidation occurs, to the cathode, where reduction occurs. The electrons
always flow from the anode to the cathode, no matter what type of cell.

19.76   A D-sized battery is much larger than an AAA-sized battery, so the D-sized battery contains a greater amount of
the cell components. (a) The potential, however, is an intensive property and does not depend on the amount of
the cell components. (Note that amount is different from concentration.) (b) The total amount of charge a battery
can produce does depend on the amount of cell components, so the D-sized battery produces more charge than the
AAA-sized battery.

19.78   The Teflon spacers keep the two metals separated so the copper cannot conduct electrons that would promote the
corrosion of the iron skeleton. Oxidation of the iron by oxygen causes rust to form and the metal to corrode.

19.81   Plan: Sacrificial anodes are metals with E° values that are more negative than that for iron, –0.44 V, so they are
more easily oxidized than iron.
Solution:
a) E°(aluminum) = –1.66 V. Yes, except aluminum resists corrosion because once a coating of its oxide covers it,
no more aluminum corrodes. Therefore, it would not be a good choice.
b) E°(magnesium) = –2.37 V. Yes, magnesium is appropriate to act as a sacrificial anode.
c) E°(sodium) = –2.71 V. Yes, except sodium reacts with water, so it would not be a good choice.
d) E°(lead) = –0.13 V. No, lead is not appropriate to act as a sacrificial anode because its E° value is too high.
e) E°(nickel) = –0.25 V. No, nickel is inappropriate as a sacrificial anode because its E° value is too high.
f) E°(zinc) = –0.76 V. Yes, zinc is appropriate to act as a sacrificial anode.
g) E°(chromium) = –0.74 V. Yes, chromium is appropriate to act as a sacrificial anode.

19.83 $3Cd^{2+}(aq) + 2Cr(s) \rightarrow 3Cd(s) + 2Cr^{3+}(aq)$
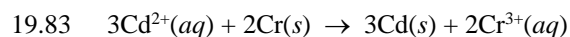
$E^{\circ}_{cell} = -0.40 \text{ V} - (-0.74 \text{ V}) = 0.34 \text{ V}$

To reverse the reaction requires 0.34 V with the cell in its standard state. A 1.5 V supplies more than enough potential, so the cadmium metal oxidizes to Cd^{2+} and chromium plates out.

19.85   The oxidation number of nitrogen in the nitrate ion, NO_3^-, is +5 and cannot be oxidized further since nitrogen has only five electrons in its outer level. In the nitrite ion, NO_2^-, on the other hand, the oxidation number of nitrogen is +3, so it can be oxidized at the anode to the +5 state.

19.87   Plan: Oxidation occurs at the anode, while reduction occurs at the cathode.
Solution:
a) At the anode, bromide ions are oxidized to form bromine (**Br₂**). $2Br^-(l) \rightarrow Br_2(l) + 2e^-$
b) At the cathode, sodium ions are reduced to form sodium metal (**Na**). $Na^+(l) + e^- \rightarrow Na(s)$

19.89   Plan: Oxidation occurs at the anode, while reduction occurs at the cathode. Decide which anion is more likely to be oxidized and which cation is more likely to be reduced. The less electronegative anion holds its electrons less tightly and is more likely to be oxidized; the cation with the higher ionization energy has the greater attraction for electrons and is more likely to be reduced.
Solution:
Either iodide ions or fluoride ions can be oxidized at the anode. The ion that more easily loses an electron will form. Since I is less electronegative than F, I^- will more easily lose its electron and be oxidized at the anode. The product at the **anode is I₂** gas. The iodine is a gas because the temperature is high to melt the salts.
Either potassium or magnesium ions can be reduced at the cathode. Magnesium has greater ionization energy than potassium because magnesium is located up and to the right of potassium on the periodic table. The greater ionization energy means that magnesium ions will more readily add an electron (be reduced) than potassium ions. The product at the cathode is **magnesium** (liquid).

19.91   Plan: Oxidation occurs at the anode, while reduction occurs at the cathode. Decide which anion is more likely to be oxidized and which cation is more likely to be reduced. The less electronegative anion holds its electrons less tightly and is more likely to be oxidized; the cation with the higher ionization energy has the greater attraction for electrons and is more likely to be reduced.
Solution:
Bromine gas forms at the anode because the electronegativity of bromine is less than that of chlorine. **Calcium** metal forms at the cathode because its ionization energy is greater than that of sodium.

19.93   Plan: Compare the electrode potentials of the species with those of water. The reduction half-reaction with the more positive electrode potential occurs at the cathode, and the oxidation half-reaction with the more negative electrode potential occurs at the anode.
Solution:
Possible reductions:
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E^{\circ} = +0.34 \text{ V}$
$Ba^{2+}(aq) + 2e^- \rightarrow Ba(s)$ $E^{\circ} = -2.90 \text{ V}$
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$ $E^{\circ} = -1.66 \text{ V}$
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E = -1 \text{ V}$ with overvoltage
Copper can be prepared by electrolysis of its aqueous salt since its reduction half-cell potential is more positive than the potential for the reduction of water. The reduction of copper is more spontaneous than the reduction of water. Since the reduction potentials of Ba^{2+} and Al^{3+} are more negative and therefore less spontaneous than the reduction of water, these ions cannot be reduced in the presence of water since the water is reduced instead.
Possible oxidations:
$2Br^-(aq) \rightarrow Br_2(l) + 2e^-$ $E^{\circ} = +1.07 \text{ V}$
$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $E = 1.4 \text{ V}$ with overvoltage
Bromine can be prepared by electrolysis of its aqueous salt because its reduction half-cell potential is more negative than the potential for the oxidation of water with overvoltage. The more negative reduction potential for Br^- indicates that its oxidation is more spontaneous than the oxidation of water.

19.95   Plan: Compare the electrode potentials of the species with those of water. The reduction half-reaction with the
        more positive electrode potential occurs at the cathode, and the oxidation half-reaction with the more negative
        electrode potential occurs at the anode.
        Solution:
        Possible reductions:
        $Li^+(aq) + e^- \rightarrow Li(s)$ $E° = -3.05$ V
        $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $E° = -0.76$ V
        $Ag^+(aq) + e^- \rightarrow Ag(s)$ $E° = 0.80$ V
        $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E = -1$ V with overvoltage
        Zinc and silver can be prepared by electrolysis of their aqueous salt solutions since their reduction half-cell
        potentials are more positive than the potential for the reduction of water. The reduction of zinc and silver is more
        spontaneous than the reduction of water. Since the reduction potential of Li^+ is more negative and therefore less
        spontaneous than the reduction of water, this ion cannot be reduced in the presence of water since the water is
        reduced instead.
        Possible oxidations:
        $2I^-(aq) \rightarrow I_2(l) + 2e^-$ $E° = +0.53$ V
        $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $E = 1.4$ V with overvoltage
        Iodine can be prepared by electrolysis of its aqueous salt because its reduction half-cell potential is more negative
        than the potential for the oxidation of water with overvoltage. The more negative reduction potential for I^-
        indicates that its oxidation is more spontaneous than the oxidation of water.

19.97   Plan: Compare the electrode potentials of the species with those of water. The reduction half-reaction with the
        more positive electrode potential occurs at the cathode, and the oxidation half-reaction with the more negative
        electrode potential occurs at the anode.
        Solution:
        a) Possible oxidations:
                $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $E = 1.4$ V with overvoltage
                $2F^- \rightarrow F_2(g) + 2e^-$ $E° = 2.87$ V
        Since the reduction potential of water is more negative than the reduction potential for F^-, the oxidation of water
        is more spontaneous than that of F^-. The oxidation of water produces oxygen gas (**O_2**), and hydronium ions
        (**H_3O^+**) at the anode.
        Possible reductions:
                $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E = -1$ V with overvoltage
                $Li^+(aq) + e^- \rightarrow Li(s)$ $E° = -3.05$ V
        Since the reduction potential of water is more positive than that of Li^+, the reduction of water is more spontaneous
        than the reduction of Li^+. The reduction of water produces **H_2** gas and **OH^-** at the cathode.
        b) Possible oxidations:
                $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $E = 1.4$ V with overvoltage
        The oxidation of water produces oxygen gas (**O_2**), and hydronium ions (**H_3O^+**) at the anode.
        The SO_4^{2-} ion cannot oxidize as S is already in its highest oxidation state in SO_4^{2-}.
        Possible reductions:
                $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E = -1$ V with overvoltage
                $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$ $E° = -0.14$ V
                $SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow SO_2(g) + 2H_2O(l)$ $E = -0.63$ V (approximate)
        The potential for sulfate reduction is estimated from the Nernst equation using standard-state concentrations and
        pressures for all reactants and products except H^+, which in pure water is 1×10^{-7} mol/L.
                $E = 0.20$ V $- (0.0592$ V/2$)$ ln $[1/(1\times10^{-7})^4] = -0.6288$ V$= -0.63$ V
        The most easily reduced ion is Sn^{2+} with the most positive reduction potential, so **tin metal** forms at the cathode.
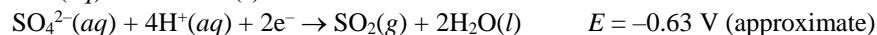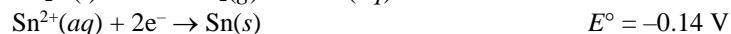
19.99   Plan: Compare the electrode potentials of the species with those of water. The reduction half-reaction with the
        more positive electrode potential occurs at the cathode, and the oxidation half-reaction with the more negative
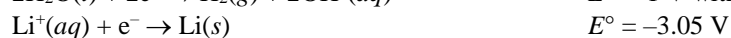   electrode potential occurs at the anode.
        Solution:
        a) Possible oxidations:
                $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $E = 1.4$ V with overvoltage
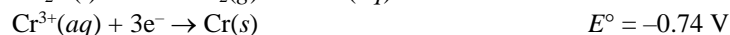
The oxidation of water produces oxygen gas (O_2), and hydronium ions (H_3O^+) at the anode.
NO_3^- cannot oxidize since N is in its highest oxidation state in NO_3^-.
Possible reductions:

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $\qquad$ $E = -1$ V with overvoltage

$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$ $\qquad$ $E° = -0.74$ V

$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$ $\qquad$ $E = +0.13$ V (approximate)

The potential for nitrate reduction is estimated from the Nernst equation using standard-state concentrations and pressures for all reactants and products except H^+, which in pure water is 1×10^{-7} mol/L.

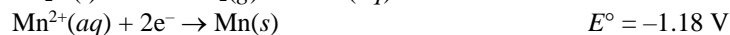$E = 0.96$ V $- (0.0592$ V$/2)$ log $[1/(1 \times 10^{-7})^4] = 0.1312$ V$= 0.13$ V

The most easily reduced ion is NO_3^-, with the most positive reduction potential so **NO gas** is formed at the cathode.

b) Possible oxidations:

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $\qquad$ $E = 1.4$ V with overvoltage

$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ $\qquad$ $E° = 1.36$ V

The oxidation of chloride ions to produce **chlorine gas** occurs at the anode. Cl^- has a more negative reduction potential showing that it is more easily oxidized than water.
Possible reductions:

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $\qquad$ $E = -1$ V with overvoltage

$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$ $\qquad$ $E° = -1.18$ V

It is easier to reduce water than to reduce manganese ions, so **hydrogen gas and hydroxide ions** form at the cathode. The reduction potential of Mn^{2+} is more negative than that of water showing that its reduction is less spontaneous than that of water.

19.101 $\underline{\text{Plan:}}$ Write the half-reaction for the reduction of Mg^{2+}. Convert mass of Mg to amount (mol) and use the mole ratio in the balanced reaction to find the amount (mol) of electrons required for every mole of Mg produced. The Faraday constant is used to find the charge of the electrons in coulombs. To find the current, the charge is divided by the time in seconds.
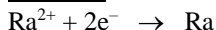$\underline{\text{Solution:}}$
$Mg^{2+} + 2e^- \rightarrow Mg$
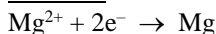
a) Amount (mol) of electrons $= \left(45.6 \text{ g Mg}\right)\left(\dfrac{1 \text{ mol Mg}}{24.31 \text{ g Mg}}\right)\left(\dfrac{2 \text{ mol e}^-}{1 \text{ mol Mg}}\right) = 3.751542575$ mol$=$ **3.75 mol e$^-$**

b) Charge $= \left(3.751542575 \text{ mol e}^-\right)\left(\dfrac{96,485 \text{ C}}{\text{mol e}^-}\right) = 3.619676 \times 10^5$ C$=$ **3.62x10^5 C**

c) Current $= \left(\dfrac{3.619676 \times 10^5 \text{ C}}{3.50 \text{ h}}\right)\left(\dfrac{1 \text{ h}}{3600 \text{ s}}\right)\left(\dfrac{A}{C/s}\right) = 28.727587$ A $=$ **28.7 A**

19.103 $\underline{\text{Plan:}}$ Write the half-reaction for the reduction of Ra^{2+}. Use the Faraday constant to convert charge in coulombs to amount (mol) of electrons provided; the balanced reduction reaction converts amount (mol) of electrons to amount (mol) of radium produced. Multiply amount (mol) of radium by its molar mass to obtain grams.
$\underline{\text{Solution:}}$
$Ra^{2+} + 2e^- \rightarrow Ra$
In the reduction of radium ions, Ra^{2+}, to radium metal, the transfer of two electrons occurs.

Mass (g) of Ra $= \left(235 \text{ C}\right)\left(\dfrac{1 \text{ mol e}^-}{96,485 \text{ C}}\right)\left(\dfrac{1 \text{ mol Ra}}{2 \text{ mol e}^-}\right)\left(\dfrac{226 \text{ g Ra}}{1 \text{ mol Ra}}\right) = 0.275224$ g$=$ **0.275 g Ra**

19.105 $\underline{\text{Plan:}}$ Write the half-reaction for the reduction of Zn^{2+}. Convert mass of Zn to amount (mol)s and use the mole ratio in the balanced reaction to find the amount (mol) of electrons required for every mole of Zn produced. The Faraday constant is used to find the charge of the electrons in coulombs. To find the time, the charge is divided by the current.

Solution:
$$Zn^{2+} + 2e^- \rightarrow Zn$$
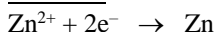
Time (s) $= \left(65.5 \text{ g Zn}\right)\left(\dfrac{1 \text{ mol Zn}}{65.41 \text{ g Zn}}\right)\left(\dfrac{2 \text{ mol e}^-}{1 \text{ mol Zn}}\right)\left(\dfrac{96,485 \text{ C}}{1 \text{ mol e}^-}\right)\left(\dfrac{1}{21.0 \text{ A}}\right)\left(\dfrac{1 \text{ A}}{C/s}\right) = 9.20169 \times 10^3 \text{ s} = \textbf{9.20x10}^3 \textbf{ s}$

19.107 a) The sodium sulfate ionizes to produce Na^+ and SO_4^{2-} ions which make the water conductive; therefore the current will flow through the water to complete the circuit, increasing the rate of electrolysis. Pure water, which contains very low (10^{-7} mol/L) concentrations of H^+ and OH^-, conducts electricity very poorly.
b) The reduction of H_2O has a more positive half-potential (–1 V) than the reduction of Na^+ (–2.71 V); the more spontaneous reduction of water will occur instead of the less spontaneous reduction of sodium ion. The oxidation of H_2O is the only oxidation possible because SO_4^{2-} cannot be oxidized under these conditions. In other words, it is easier to reduce H_2O than Na^+ and easier to oxidize H_2O than SO_4^{2-}.

19.109 Plan: Write the half-reaction for the reduction of Zn^{2+}. Find the charge in coulombs by multiplying the current by the time in units of seconds. Use the Faraday constant to convert charge in coulombs to amount (mol) of electrons provided; the balanced reduction reaction converts amount (mol) of electrons to amount (mol) of zinc produced. Multiply amount (mol) of zinc by its molar mass to obtain grams.
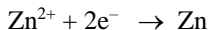Solution:
$$Zn^{2+} + 2e^- \rightarrow Zn$$

Mass (g) of Zn $= \left(0.855 \text{ A}\right)\left(\dfrac{C/s}{A}\right)\left(2.50 \text{ day}\right)\left(\dfrac{24 \text{ h}}{1 \text{ day}}\right)\left(\dfrac{3600 \text{ s}}{1 \text{ h}}\right)\left(\dfrac{1 \text{ mol e}^-}{96,485 \text{ C}}\right)\left(\dfrac{1 \text{ mol Zn}}{2 \text{ mol e}^-}\right)\left(\dfrac{65.41 \text{ g Zn}}{1 \text{ mol Zn}}\right)$

$= 62.59998 \text{ g} = \textbf{62.6 g Zn}$

19.111 Plan: Write the reduction half-reaction for H^+. Use the ideal gas law to find the amount (mol) of H_2 produced. The mole ratio in the balanced reduction reaction gives the moles of electrons required for that amount of H_2 and the Faraday constant converts the amount (mol) of electrons to charge in coulombs. To convert coulombs to energy in joules, remember that 1 V equals 1 J/C; multiply the charge in coulombs by volts to obtain joules. Convert this energy to units of kilojoules and use the given conversion factor between mass of oil and energy to find the mass of oil combusted to provide the needed amount of energy.
Solution:
The half-reaction is: $2H^+(aq) + 2e^- \rightarrow H_2(g)$
a) First, find the amount (mol) of hydrogen gas.
$$n = \dfrac{PV}{RT} = \dfrac{\left(12.0 \text{ bar}\right)\left(3.5 \times 10^6 \text{ L}\right)}{\left(0.08314 \dfrac{L \cdot bar}{mol \cdot K}\right)\left((273 + 25)K\right)} = 1.695208 \times 10^6 \text{ mol H}_2$$

Then, find the coulombs knowing that there are two electrons transferred per mol of H_2.
$$\text{Coulombs} = \left(1.695208 \times 10^6 \text{ mole H}_2\right)\left(\dfrac{2 \text{ mol e}^-}{1 \text{ mol H}_2}\right)\left(\dfrac{96485 \text{ C}}{1 \text{ mol e}^-}\right) = 3.27124287760 \times 10^{11} = \textbf{3.3x10}^{11} \textbf{ C}$$

b) Energy (J) $= \left(\dfrac{1.44 \text{ J}}{C}\right)\left(3.27124287760 \times 10^{11} \text{ C}\right) = 4.71058974 \times 10^{11} = \textbf{4.7x10}^{11} \textbf{ J}$

c) Mass (kg) $= \left(4.71058974 \times 10^{11} \text{ J}\right)\left(\dfrac{1 \text{ kJ}}{10^3 \text{ J}}\right)\left(\dfrac{1 \text{ kg}}{4.0 \times 10^4 \text{ kJ}}\right) = 1.177647 \times 10^4 = \textbf{1.2x10}^4 \textbf{ kg}$

19.114 Plan: Write balanced half-reactions for the reduction of each metal ion. From the current, 65.0% of the amount (mol) of product will be copper and 35.0% zinc. Assume a current of exactly 100 C. The amount of current used to generate copper would be (65.0%/100%)(100 C) = 65.0 C, and the amount of current used to generate zinc would be (35.0%/100%)(100 C) = 35.0 C. Convert each coulomb amount to amount (mol) of electrons using the Faraday constant and use the balanced reduction reactions to convert the amount (mol) of electrons to amount

(mol) and then mass of each metal. Divide the mass of copper produced by the total mass of both metals produced and multiply by 100 to obtain mass percent.

Solution:

The half-reactions are: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ and $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$

$$\text{Mass (g) of copper} = (65.0\ C)\left(\frac{1\ mol\ e^-}{96,485\ C}\right)\left(\frac{1\ mol\ Cu}{2\ mol\ e^-}\right)\left(\frac{63.55\ g\ Cu}{1\ mol\ Cu}\right) = 0.021406177\ g\ Cu$$

$$\text{Mass (g) of zinc} = (35.0\ C)\left(\frac{1\ mol\ e^-}{96,485\ C}\right)\left(\frac{1\ mol\ Zn}{2\ mol\ e^-}\right)\left(\frac{65.41\ g\ Zn}{1\ mol\ Zn}\right) = 0.01186376\ g\ Zn$$

$$\text{Mass \% of copper} = \frac{0.021406177\ g\ Cu}{0.021406177\ g\ Cu + 0.01186376\ g\ Zn}(100\%) = 64.340900\ \% = \textbf{64.3\% Cu}$$

19.115 Plan: Write the reduction half-reaction for Au^{3+}. Use the equation for the volume of a cylinder to find the volume of gold required; use the density to convert volume of gold to mass and then amount (mol) of gold. The mole ratio in the balanced reduction reaction is used to convert the amount (mol) of gold to amount (mol) of electrons required and the Faraday constant is used to convert amount (mol) of electrons to coulombs. Divide the coulombs by the current to obtain time in seconds, which is converted to time in days. To obtain the cost, start by multiplying the amount (mol) of gold from part a) by four to get the amount (mol) of gold needed for the earrings. Convert this amount (mol) to grams, then to troy ounces, and finally to dollars.

Solution:

The reaction is: $Au^{3+}(aq) + 3e^- \rightarrow Au(s)$

a) $V = \pi r^2 h$

$$V\ (cm^3) = \pi\left(\frac{4.00\ cm}{2}\right)^2(0.25\ mm)\left(\frac{10^{-3}\ m}{1\ mm}\right)\left(\frac{1\ cm}{10^{-2}\ m}\right) = 0.314159265\ cm^3$$

$$\text{Amount (mol) of Au} = (0.314159265\ cm^3)\left(\frac{19.3\ g\ Au}{1\ cm^3}\right)\left(\frac{1\ mol\ Au}{197.0\ g\ Au}\right) = 0.03077804\ mol\ Au$$

$$\text{Time (days)} = (0.03077804\ mol\ Au)\left(\frac{3\ mol\ e^-}{1\ mol\ Au}\right)\left(\frac{96,485\ C}{1\ mol\ e^-}\right)\left(\frac{A}{C/s}\right)\left(\frac{1}{0.013\ A}\right)\left(\frac{1\ h}{3600\ s}\right)\left(\frac{1\ day}{24\ h}\right)$$

$$= 7.931675\ days = \textbf{8 days}$$

b) The time required doubles once for the second earring of the pair and doubles again for the second side, thus it will take four times as long as one side of one earring.

$$\text{Time} = (4)(7.931675\ days) = 31.7267\ days = \textbf{32 days}$$

c) $$\text{Cost} = (4)(0.03077804\ mol\ Au)\left(\frac{197.0\ g\ Au}{1\ mol\ Au}\right)\left(\frac{1\ troy\ oz}{31.10\ g}\right)\left(\frac{\$1615}{troy\ oz}\right) = \$1259.45 = \textbf{\$1300}$$

19.118 Plan: Write the half-reactions and cell reaction for the silver battery. Convert mass of zinc to amount (mol) of zinc, keeping in mind that only 80% of the zinc will react; from the amount (mol) of zinc, the amount (mol) of electrons required is obtained. The Faraday constant is used to convert the amount (mol) of electrons to charge in coulombs which is divided by the current to obtain the time in seconds. The amount (mol) of zinc is also used to find the amount (mol) of Ag_2O consumed and the amount of Ag needed for that amount of Ag_2O. Convert this mass of silver to troy ounces and then to dollars.

Solution:

The half-reactions and the cell reaction are:

$$Zn(s) + \cancel{2OH^-}\ \cancel{(aq)} \rightarrow ZnO(s) + \cancel{H_2O(l)} + \cancel{2e^-}$$
$$\underline{Ag_2O(s) + \cancel{H_2O(l)} + \cancel{2e^-} \rightarrow 2Ag(s) + \cancel{2OH^-}\ \cancel{(aq)}}$$
$$Zn(s) + Ag_2O(s) \rightarrow ZnO(s) + 2Ag(s)$$
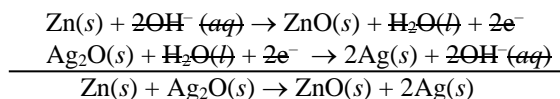
$$\text{Amount (mol) of Zn} = (0.75\ g\ Zn)\left(\frac{80\%}{100\%}\right)\left(\frac{1\ mol\ Zn}{65.41\ g\ Zn}\right) = 0.00917291\ mol\ Zn$$

a) Time (days) = $\left(0.00917291 \text{ mol Zn}\right)\left(\dfrac{2 \text{ mol e}^-}{1 \text{ mol Zn}}\right)\left(\dfrac{96{,}485 \text{C}}{1 \text{ mol e}^-}\right)\left(\dfrac{A}{C/_S}\right)\left(\dfrac{1 \ \mu A}{10^{-6} \text{ A}}\right)\left(\dfrac{1}{0.85 \ \mu A}\right)\left(\dfrac{1 \text{ h}}{3600 \text{ s}}\right)\left(\dfrac{1 \text{ day}}{24 \text{ h}}\right)$
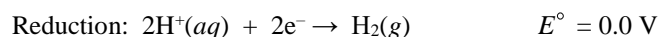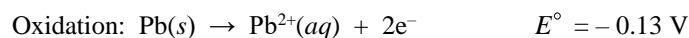
$= 2.410262 \times 10^4$ days = **2.4×10^4 days**

b) Mass (g) of Ag = $\left(0.00917291 \text{ mol Zn}\right)\left(\dfrac{1 \text{ mol Ag}_2\text{O}}{1 \text{ mol Zn}}\right)\left(\dfrac{100\%}{95\%}\right)\left(\dfrac{2 \text{ mol Ag}}{1 \text{ mol Ag}_2\text{O}}\right)\left(\dfrac{107.9 \text{ g Ag}}{1 \text{ mol Ag}}\right)$

$= 2.0836989$ g= **2.1 g Ag**

c) Cost = $\left(2.0836989 \text{ g Ag}\right)\left(\dfrac{95\%}{100\%}\right)\left(\dfrac{1 \text{ troy oz}}{31.10 \text{ g Ag}}\right)\left(\dfrac{\text{CAD } 27.48}{\text{troy oz}}\right)\left(\dfrac{1}{2.410262 \times 10^4 \text{ days}}\right)$

$= 7.25689 \times 10^{-5}$ = **CAD 7.3×10^{-5}/day**

19.121 Plan: Since the cells are voltaic cells, the reactions occurring are spontaneous and will have a positive E°_{cell}.
Write the two half-reactions. When two half-reactions are paired, one half-reaction must be reversed and written
as an oxidation. Reverse the half-reaction that will result in a positive value of E°_{cell} using the relationship

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$. E° values are found in Appendix D. The oxidation occurs at the negative electrode
(the anode).   Use the Nernst equation to find cell potential at concentrations other than 1 mol/L.
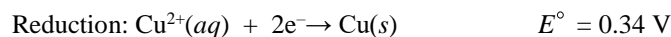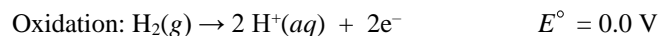Solution:
a) Cell with SHE and Pb/Pb^{2+}:

Oxidation: $\text{Pb}(s) \rightarrow \text{Pb}^{2+}(aq) + 2\text{e}^-$ $E^\circ = -0.13$ V

Reduction: $2\text{H}^+(aq) + 2\text{e}^- \rightarrow \text{H}_2(g)$ $E^\circ = 0.0$ V

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.0 \text{ V} - (-0.13 \text{ V}) = \textbf{0.13 V}$
Cell with SHE and Cu/Cu^{2+}:

Oxidation: $\text{H}_2(g) \rightarrow 2 \text{ H}^+(aq) + 2\text{e}^-$ $E^\circ = 0.0$ V

Reduction: $\text{Cu}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Cu}(s)$ $E^\circ = 0.34$ V

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.34 \text{ V} - 0.00 \text{ V} = \textbf{0.34 V}$
b) The anode (negative electrode) for the cell with SHE and Pb/Pb^{2+} is **Pb**.
The anode for the cell with SHE and Cu/Cu^{2+} is **platinum** in the SHE.
c) The precipitation of PbS decreases [Pb^{2+}]. Use Nernst equation to see how this affects potential. Cell reaction
is:

$\text{Pb}(s) + 2\text{H}^+(aq) \rightarrow \text{Pb}^{2+}(aq) + \text{H}_2(g)$ $E_{cell} = E^\circ_{cell} - \dfrac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{z(96485 \text{ C/mol})} \ln Q$

$E_{cell} = E^\circ_{cell} - \dfrac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln \dfrac{[\text{Pb}^{2+}]p_{\text{H}_2}}{[\text{H}^+]^2}$ $z = 2\text{e}^-$

Decreasing the concentration of lead ions makes the following term more negative:

$\dfrac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln \dfrac{[\text{Pb}^{2+}]p_{\text{H}_2}}{[\text{H}^+]^2}$

When this more negative value is subtracted from E°_{cell}, cell potential **increases**.
d) The [H$^+$] = 1.0 mol/L , [Cu^{2+}] = 1×10^{-16} mol/L and the H$_2$ = 1 bar in the SHE.

Cell reaction: $\text{Cu}^{2+}(aq) + \text{H}_2(g) \rightarrow \text{Cu}(s) + 2\text{H}^+(aq)$

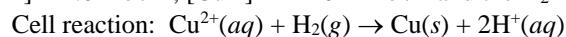$E_{cell} = E^\circ_{cell} - \dfrac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{z(96485 \text{ C/mol})} \ln Q$

$$E_{cell} = E_{cell}^{\circ} - \frac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln \frac{[\text{H}^+]^2}{[\text{Cu}^{2+}]p_{\text{H}_2}} \qquad z = 2e^-$$

$$E_{cell} = 0.34 \text{ V} - \frac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln \frac{(1)^2}{\left(1\text{x}10^{-16}\right)(1\ )}$$

$$E_{cell} = -0.133012 \text{ V} = \textbf{-0.13 V}$$

19.124 The three steps equivalent to the overall reaction $\text{M}^+(aq) + \text{e}^- \rightarrow \text{M}(s)$ are:

1) $\text{M}^+(aq) \rightarrow \text{M}^+(g)$ Energy is $-\Delta_{\text{hydration}}H$

2) $\text{M}^+(g) + \text{e}^- \rightarrow \text{M}(g)$ Energy is $-$IE or $-\Delta_{\text{ionization}}H$

3) $\text{M}(g) \rightarrow \text{M}(s)$ Energy is $-\Delta_{\text{atomization}}H$

The energy for step 3 is similar for all three elements, so the difference in the energy for the overall reaction depends on the values for $-\Delta_{\text{hydration}}H$ and $-$IE. The lithium ion has a more negative hydration energy than Na^+ and K^+ because it is a smaller ion with large charge density that holds the water molecules more tightly. The amount of energy required to remove the waters surrounding the lithium ion offsets the lower ionization energy to make the overall energy for the reduction of lithium larger than expected.

19.125 The key factor is that the table deals with electrode potentials in aqueous solution. The very high and low standard electrode potentials involve extremely reactive substances, such as F_2 (a powerful oxidant), and Li (a powerful reductant). These substances react directly with water, rather than according to the desired half-reactions. An alternative (essentially equivalent) explanation is that any aqueous cell with a voltage of more than 1.23 V has the ability to electrolyze water into hydrogen and oxygen. When two electrodes with 6 V across them are placed in water, electrolysis of water will occur.

19.127 Plan: Write the half-reaction for the reduction of Al^{3+}. Convert mass of Al to amount (mol) and use the mole ratio in the balanced reaction to find the amount (mol) of electrons required for every mole of Al produced. The Faraday constant is used to find the charge of the electrons in coulombs. To find the time, the charge is divided by the current. To calculate the electrical power, multiply the time by the current and voltage, remembering that 1 A = 1 C/s (thus, 100,000 A is 100,000 C/s) and 1 V = 1 J/C (thus, 5.0 V = 5.0 J/C). Change units of J to kW • h. To find the cost of the electricity, use the kW • h per 1000 kg of aluminum calculated in part b) to find the power (kW • h) for the mass of aluminum, keeping in mind the 90.% efficiency.
Solution:
a) Aluminum half-reaction: $\text{Al}^{3+}(aq) + 3 \text{ e}^- \rightarrow \text{Al}(s)$, so $n = 3$. Remember that 1 A = 1 C/s.

$$\text{Time (s)} = \left(1000 \text{ kg Al}\right)\left(\frac{10^3 \text{ g}}{1 \text{ kg}}\right)\left(\frac{1 \text{ mol Al}}{26.98 \text{ g Al}}\right)\left(\frac{3 \text{ mol e}^-}{1 \text{ mol Al}}\right)\left(\frac{96,485 \text{ C}}{1 \text{ mol e}^-}\right)\left(\frac{\text{A}}{\text{C}/\text{s}}\right)\left(\frac{1}{100,000 \text{ A}}\right)$$

         = 1.0728503x10^5 s= **1x10^5 s**
         The mass and current limit the answer to 1 significant figure.
b) 5 V = 5 J/C

$$\text{Power} = \left(1.0728503\text{x}10^5\text{s}\right)\left(\frac{100,000 \text{ C}}{\text{s}}\right)\left(\frac{5.0 \text{ J}}{\text{C}}\right)\left(\frac{1 \text{ kJ}}{10^3 \text{ J}}\right)\left(\frac{1 \text{ kW} \cdot \text{h}}{3.6\text{x}10^3 \text{ kJ}}\right) = 1.4900699\text{x}10^4 = \text{kW} \cdot \text{h } \textbf{1.5x}10^4 \textbf{ kW} \cdot \textbf{h}$$

$$\text{c) Cost} = \left(454 \text{ g Al}\right)\left(\frac{1 \text{ kg}}{1000 \text{ g}}\right)\left(\frac{1.4900699\text{x}10^4 \text{ kW} \cdot \text{h}}{1000 \text{ kg Al}}\right)\left(\frac{\text{CAD} 0.177}{1 \text{ kW} \cdot \text{h}}\right)\left(\frac{100\%}{90.\%}\right) = \$1.3304 = \textbf{\$1.3}$$

19.129 Plan: When considering two substances, the stronger reducing agent will reduce the other substance.
Solution:
Statement: Metal D + hot water → reaction   Conclusion: D reduces water to produce $\text{H}_2(g)$. D is a stronger reducing agent than H^+.
Statement: D + E salt → no reaction   Conclusion: D does not reduce E salt, so E reduces D salt. E is better reducing agent than D.

Statement: D + F salt → reaction   Conclusion: D reduces F salt. D is better reducing agent than F.
If E metal and F salt are mixed, the salt F would be reduced producing F metal because E has the greatest reducing strength of the three metals (E is stronger than D and D is stronger than F). The ranking of increasing reducing strength is **F < D < E**.

19.131 Plan: Examine the change in oxidation numbers in the equations to find n, the amount (mol) of electrons transferred. Use $\Delta G = -nFE$ to calculate ΔG. Substitute J/C for V in the unit for E. Convert ΔG to units of kJ and divide by the
total mass of reactants to obtain the ratio.
Solution:
a) Cell I: Oxidation number (O.N.) of H changes from 0 to +1, so one electron is lost from each of four hydrogen atoms for a total of four electrons. O.N. of oxygen changes from 0 to –2, indicating that two electrons are gained by each of the two oxygen atoms for a total of four electrons. There is a transfer of **four mole of electrons** in the reaction.

$$\Delta G = -zFE = -(4 \text{ mol e}^-)(96{,}485 \text{ C/mol e}^-)(1.23 \text{ J/C}) = -4.747062 \times 10^5 \text{ J/mol} = \mathbf{-4.75 \times 10^5 \text{ J/mol}}$$

Cell II: In $Pb(s) \to PbSO_4$, O.N. of Pb changes from 0 to +2 and in $PbO_2 \to PbSO_4$, O.N. of Pb changes from +4 to +2. There is a transfer of **two mole of electrons** in the reaction.

$$\Delta G = -zFE = -(2 \text{ mol e}^-)(96{,}485 \text{ C/mol e}^-)(2.04 \text{ J/C}) = -3.936588 \times 10^5 \text{ J/mol} = \mathbf{-3.94 \times 10^5 \text{ J/mol}}$$

Cell III: O.N. of each of two Na atoms changes from 0 to +1 and O.N. of Fe changes from +2 to 0. There is a transfer of **two mole of electrons** in the reaction.

$$\Delta G = -zFE = -(2 \text{ mol e}^-)(96{,}485 \text{ C/mol e}^-)(2.35 \text{ J/C}) = -4.534795 \times 10^5 \text{ J/mol} = \mathbf{-4.53 \times 10^5 \text{ J/mol}}$$

b) Cell I: Mass of reactants $= \left(2 \text{ mol H}_2\right)\left(\dfrac{2.016 \text{ g H}_2}{1 \text{ mol H}_2}\right) + \left(1 \text{ mol O}_2\right)\left(\dfrac{32.00 \text{ g O}_2}{1 \text{ mol O}_2}\right) = 36.032 \text{ g}$

$$\frac{w_{max}}{\text{reactant mass}} = \left(\frac{-4.747062 \times 10^5 \text{ J}}{36.032 \text{ g}}\right)\left(\frac{1 \text{ kJ}}{10^3 \text{ J}}\right) = -13.17457 \text{ kJ/g} = \mathbf{-13.2 \text{ kJ/g}}$$

Cell II: Mass of reactants $=$

$$\left(1 \text{ mol Pb}\right)\left(\frac{207.2 \text{ g Pb}}{1 \text{ mol Pb}}\right) + \left(1 \text{ mol PbO}_2\right)\left(\frac{239.2 \text{ g PbO}_2}{1 \text{ mol PbO}_2}\right) + \left(2 \text{ mol H}_2\text{SO}_4\right)\left(\frac{98.09 \text{ g H}_2\text{SO}_4}{1 \text{ mol H}_2\text{SO}_4}\right)$$
$$= 642.58 \text{ g}$$

$$\frac{w_{max}}{\text{reactant mass}} = \left(\frac{-3.936588 \times 10^5 \text{ J}}{642.58 \text{ g}}\right)\left(\frac{1 \text{ kJ}}{10^3 \text{ J}}\right) = -0.612622 \text{ kJ/g} = \mathbf{-0.613 \text{ kJ/g}}$$

Cell III: Mass of reactants $= \left(2 \text{ mol Na}\right)\left(\dfrac{22.99 \text{ g Na}}{1 \text{ mol Na}}\right) + \left(1 \text{ mol FeCl}_2\right)\left(\dfrac{126.75 \text{ g FeCl}_2}{1 \text{ mol FeCl}_2}\right) = 172.73 \text{ g}$

$$\frac{w_{max}}{\text{reactant mass}} = \left(\frac{-4.534795 \times 10^5 \text{ J}}{172.73 \text{ g}}\right)\left(\frac{1 \text{ kJ}}{10^3 \text{ J}}\right) = -2.625366 \text{ kJ/g} = \mathbf{-2.63 \text{ kJ/g}}$$

Cell I has the highest ratio (most energy released per gram) because the reactants have very low mass while Cell II has the lowest ratio because the reactants are very massive.

19.135 Plan: Write the balanced equation. Multiply the current and time to calculate total charge in coulombs. Remember that the unit 1 A is 1 C/s, so the time must be converted to seconds. From the total charge, the number of electrons transferred to form copper is calculated by dividing total charge by the Faraday constant. Each mole of copper deposited requires two moles of electrons, so divide the amount (mol) of electrons by two to get amount (mol) of copper. Then convert to grams of copper. The initial concentration of Cu^{2+} is 1.00 mol/L (standard condition) and initial volume is 345 mL. Use this to calculate the initial amount (mol) of copper ions, then subtract the amount (mol) of copper ions converted to copper metal and divide by the cell volume to find the remaining $[Cu^{2+}]$.
Solution:
a) Since the cell is a voltaic cell, write a spontaneous reaction. The reduction of Cu^{2+} is more spontaneous than the reduction of Sn^{2+}: $Cu^{2+}(aq) + Sn(s) \to Cu(s) + Sn^{2+}(aq)$

$$\text{Mass (g) of Cu} = (0.17 \text{ A})\left(\frac{C/s}{A}\right)\left(\frac{3600 \text{ s}}{1 \text{ h}}\right)(48.0 \text{ h})\left(\frac{1 \text{ mol e}^-}{96,485 \text{ C}}\right)\left(\frac{1 \text{ mol Cu}}{2 \text{ mol e}^-}\right)\left(\frac{63.55 \text{ g Cu}}{1 \text{ mol Cu}}\right)$$

$$= 9.674275 \text{ g} = \textbf{9.7 g Cu}$$

b) Initial amount (mol) of $Cu^{2+} = \left(1.00\frac{\text{mol Cu}^{2+}}{\text{L}}\right)(345 \text{ mL})\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right) = 0.345 \text{ mol Cu}^{2+}$

Amount (mol) of Cu^{2+} reduced $= (9.674275 \text{ g Cu})\left(\frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}}\right) = 0.1522309205 \text{ mol Cu}^{2+}$

Remaining amount (mol) of Cu^{2+} = initial amount (mol) – amount (mol) reduced = 0.345 mol – 0.1522309205 mol= 0.1927691 mol Cu^{2+}

Concentration (mol/L) $Cu^{2+} = \dfrac{0.1927691 \text{ mol Cu}^{2+}}{(345 \text{ mL})\left(\dfrac{10^{-3} \text{ L}}{1 \text{ mL}}\right)} = 0.558751 \text{ mol/L} = \textbf{0.56 mol/L Cu}^{2+}$

19.137 Plan: Examine each reaction to determine which reactant is the oxidizing agent; the oxidizing agent is the reactant that gains electrons in the reaction, resulting in a decrease in its oxidation number.
Solution:
From reaction between $U^{3+} + Cr^{3+} \rightarrow Cr^{2+} + U^{4+}$, find that Cr^{3+} oxidizes U^{3+}.
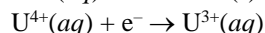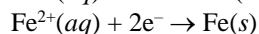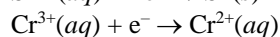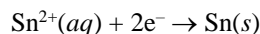From reaction between $Fe + Sn^{2+} \rightarrow Sn + Fe^{2+}$, find that Sn^{2+} oxidizes Fe.
From the fact that there is no reaction that occurs between Fe and U^{4+}, find that Fe^{2+} oxidizes U^{3+}.
From reaction between $Cr^{3+} + Fe \rightarrow Cr^{2+} + Fe^{2+}$, find that Cr^{3+} oxidizes Fe.
From reaction between $Cr^{2+} + Sn^{2+} \rightarrow Sn + Cr^{3+}$, find that Sn^{2+} oxidizes Cr^{2+}.
Notice that nothing oxidizes Sn, so Sn^{2+} must be the strongest oxidizing agent. Both Cr^{3+} and Fe^{2+} oxidize U^{3+}, so U^{4+} must be the weakest oxidizing agent. Cr^{3+} oxidizes iron so Cr^{3+} is a stronger oxidizing agent than Fe^{2+}.
The half–reactions in order from strongest to weakest oxidizing agent:
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$
$Cr^{3+}(aq) + e^- \rightarrow Cr^{2+}(aq)$
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$
$U^{4+}(aq) + e^- \rightarrow U^{3+}(aq)$

19.141 Plan: Write a balanced equation that gives a positive E_{cell}° for a spontaneous reaction. Calculate the E_{cell}° and use the Nernst equation to find the silver ion concentration that results in the given E_{cell}.
Solution:
a) The calomel half-cell is the anode and the silver half-cell is the cathode. The overall reaction is:
$$2Ag^+(aq) + 2Hg(l) + 2Cl^-(aq) \rightarrow 2Ag(s) + Hg_2Cl_2(s)$$
$E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ} = 0.80 \text{ V} - 0.24 \text{ V} = 0.56 \text{ V}$ with $z = 2$.
Use the Nernst equation to find $[Ag^+]$ when $E_{cell} = 0.060$ V.
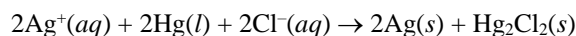
$$E_{cell} = E_{cell}^{\circ} - \frac{(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})}{z(96485 \text{ C/mol})}\ln Q$$

$$0.060 \text{ V} = 0.56 \text{ V} - \frac{(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})}\ln\frac{1}{\left[Ag^+\right]^2\left[Cl^-\right]^2}$$

$-$

The problem suggests assuming that $[Cl^-]$ is constant. Assume it is 1.00 mol/L.

$$-0.50 \text{ V} = -\frac{(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})}\ln\frac{1}{\left[Ag^+\right]^2(1.00)^2}$$

$$38.94337 = \ln \frac{1}{\left[\text{Ag}^+\right]^2 (1.00)^2}$$

$$e^{38.94337} = \frac{1}{\left[\text{Ag}^+\right]^2}$$

$$8.18258 \times 10^{16} = \frac{1}{\left[\text{Ag}^+\right]^2}$$

$8.18258 \times 10^{16}[\text{Ag}^+]^2 = 1$

$[\text{Ag}^+]^2 = 1.22211 \times 10^{-17}$

$[\text{Ag}^+] = 3.49587 \times 10^{-9}$ mol/L = **3.5x10⁻⁹ mol/L**

b) Again use the Nernst equation and assume $[\text{Cl}^-] = 1.00$ mol/L.

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln \frac{1}{\left[\text{Ag}^+\right]^2 \left[\text{Cl}^-\right]^2}$$

$$0.53 \text{ V} = 0.56 \text{ V} - \frac{(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln \frac{1}{\left[\text{Ag}^+\right]^2 \left[\text{Cl}^-\right]^2}$$

$$-0.03 \text{ V} = -\frac{(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln \frac{1}{\left[\text{Ag}^+\right]^2 \left[\text{Cl}^-\right]^2}$$

$$2.33660 = \ln \frac{1}{\left[\text{Ag}^+\right]^2 (1.00)^2}$$

$$e^{2.33660} = \frac{1}{\left[\text{Ag}^+\right]^2}$$

$$10.3460 = \frac{1}{\left[\text{Ag}^+\right]^2}$$

$10.3460 \, [\text{Ag}^+]^2 = 1$

$[\text{Ag}^+]^2 = 0.0966555$

$[\text{Ag}^+] = 0.31089$ mol/L = **0.3 mol/L**

19.143   <u>Plan:</u> Use the Nernst equation to write the relationship between E°_{cell} and the cell potential for both the waste stream and for the silver standard.

<u>Solution:</u>

a) The reaction is $\text{Ag}^+(aq) \rightarrow \text{Ag}(s) + 1e^-$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})}{(z)(96485 \text{ C/mol})} \ln Q$$

Nonstandard cell: $\qquad E_{\text{waste}} = E^{\circ}_{\text{cell}} - \dfrac{(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})}{(1)(96485 \text{ C/mol})} \ln \left[\text{Ag}^+\right]_{\text{waste}}$

Standard cell: $\qquad E_{\text{standard}} = E^{\circ}_{\text{cell}} - \dfrac{(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})}{(1)(96485 \text{ C/mol})} \ln \left[\text{Ag}^+\right]_{\text{standard}}$

b) To find $[\text{Ag}^+]_{\text{waste}}$: $\qquad E^{\circ}_{\text{cell}} = E_{\text{standard}} + \dfrac{(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})}{(1)(96485 \text{ C/mol})} \ln \left[\text{Ag}^+\right]_{\text{standard}}$

$$= E_{\text{waste}} + \frac{(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})}{(1)(96485 \text{ C/mol})} \ln \left[\text{Ag}^+\right]_{\text{waste}}$$

$$E_{\text{standard}} - E_{\text{waste}} = \frac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(1)(96485 \text{ C/mol})} \, (\ln [Ag^+]_{\text{waste}} - \ln [Ag^+]_{\text{standard}})$$

$$\frac{E_{\text{standard}} - E_{\text{waste}}}{0.0256783} = (\ln [Ag^+]_{\text{waste}} - \ln [Ag^+]_{\text{standard}})$$

$$\ln [Ag^+]_{\text{waste}} = \frac{E_{\text{standard}} - E_{\text{waste}}}{0.0256783} + \ln [Ag^+]_{\text{standard}}$$

$$[Ag^+]_{\text{waste}} = \left[e^{\left(\frac{E_{\text{standard}} - E_{\text{waste}}}{0.0256783} \right)} \right] \left(\left[Ag^+ \right]_{\text{standard}} \right)$$

c) Convert mol/L to ng/L for both $[Ag^+]_{\text{waste}}$ and $[Ag^+]_{\text{standard}}$:

$$E_{\text{waste}} - E_{\text{standard}} = - \frac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(1)(96485 \text{ C/mol})} \ln \frac{[Ag^+]_{\text{waste}}}{[Ag^+]_{\text{standard}}} \quad \text{Remember: } \ln A - \ln B = \ln (A/B)$$

If both silver ion concentrations are in the same units, in this case ng/L, the "conversions" cancel and the equation derived in part b) applies if the standard concentration is in ng/L.

$$[Ag^+]_{\text{waste}} = \left[e^{\left(\frac{E_{\text{standard}} - E_{\text{waste}}}{0.0256783} \right)} \right] \left(\left[Ag^+ \right]_{\text{standard}} \right)$$

d) Plug the values into the answer for part c).

$$[Ag^+]_{\text{waste}} = \left[e^{\left(\frac{-0.003}{0.0256783} \right)} \right] (1000. \text{ ng/L}) = 889.7363 \text{ ng/L} = \textbf{900 ng/L}$$

e) Temperature is included in the RT/zF term, in which we have been using T = 298 K. To account for different temperatures, insert the required T value in RT/zF term.

$$E_{\text{standard}} + \left(\frac{RT_{\text{standard}}}{zF} \right) \ln [Ag^+]_{\text{standard}} = E_{\text{waste}} + \left(\frac{RT_{\text{waste}}}{zF} \right) \ln [Ag^+]_{\text{waste}}$$

$$E_{\text{standard}} - E_{\text{waste}} = \frac{RT_{\text{waste}}}{zF} \ln [Ag^+]_{\text{waste}} - \frac{RT_{\text{standard}}}{zF} \ln [Ag^+]_{\text{standard}}$$

$$E_{\text{standard}} - E_{\text{waste}} = \frac{R}{zF} \, (T_{\text{waste}} \ln [Ag^+]_{\text{waste}} - T_{\text{standard}} \ln [Ag^+]_{\text{standard}})$$

$$(E_{\text{standard}} - E_{\text{waste}}) \left(\frac{zF}{R} \right) = T_{\text{waste}} \ln [Ag^+]_{\text{waste}} - T_{\text{standard}} \ln [Ag^+]_{\text{standard}}$$

$$(E_{\text{standard}} - E_{\text{waste}}) \left(\frac{zF}{R} \right) + T_{\text{standard}} \ln [Ag^+]_{\text{standard}} = T_{\text{waste}} \ln [Ag^+]_{\text{waste}}$$

$$\ln [Ag^+]_{\text{waste}} = \left(\frac{(E_{\text{standard}} - E_{\text{waste}})(zF/R) + T_{\text{standard}} \ln \left[Ag^+ \right]_{\text{standard}}}{T_{\text{waste}}} \right)$$

$$[Ag^+]_{\text{waste}} = e^{\left(\frac{(E_{\text{standard}} - E_{\text{waste}})(zF/R) + T_{\text{standard}} \ln \left[Ag^+ \right]_{\text{standard}}}{T_{\text{waste}}} \right)}$$

19.145 <u>Plan:</u> Multiply the current in amperes by the time in seconds to obtain coulombs. Convert coulombs to amount (mol) of electrons with the Faraday constant and use the mole ratio in the balanced half-reactions to convert amount (mol) of electrons to amount (mol) and then mass of reactants. Divide the total mass of reactants by the mass of the battery to find the mass percentage that consists of reactants.
<u>Solution:</u>
a) Determine the total charge the cell can produce.

$$\text{Capacity (C)} = \left(300.\ \text{mA·h}\right)\left(\frac{10^{-3}\ \text{A}}{1\ \text{mA}}\right)\left(\frac{3600\ \text{s}}{1\ \text{h}}\right)\left(\frac{1\ \text{C}}{1\ \text{A·s}}\right) = \textbf{1.08x10}^{\textbf{3}}\ \textbf{C}$$

b) The half-reactions are:
$$Cd^0 \rightarrow Cd^{2+} + 2e^- \quad \text{and} \quad NiO(OH) + H_2O(l) + e^- \rightarrow Ni(OH)_2 + OH^-$$
Assume 100% conversion of reactants.

$$\text{Mass (g) of Cd} = \left(1080\ \text{C}\right)\left(\frac{1\ \text{mol e}^-}{96,485\ \text{C}}\right)\left(\frac{1\ \text{mol Cd}}{2\ \text{mol e}^-}\right)\left(\frac{112.4\ \text{g Cd}}{1\ \text{mol Cd}}\right) = 0.62907\ \text{g} = \textbf{0.629 g Cd}$$

$$\text{Mass (g) of NiO(OH)} = \left(1080\ \text{C}\right)\left(\frac{1\ \text{mol e}^-}{96,485\ \text{C}}\right)\left(\frac{1\ \text{mol NiO(OH)}}{1\ \text{mol e}^-}\right)\left(\frac{91.70\ \text{g NiO(OH)}}{1\ \text{mol NiO(OH)}}\right)$$
$$= 1.026439\ \text{g} = \textbf{1.03 g NiO(OH)}$$

$$\text{Mass (g) of H}_2\text{O} = \left(1080\ \text{C}\right)\left(\frac{1\ \text{mol e}^-}{96,485\ \text{C}}\right)\left(\frac{1\ \text{mol H}_2\text{O}}{1\ \text{mol e}^-}\right)\left(\frac{18.02\ \text{g H}_2\text{O}}{1\ \text{mol H}_2\text{O}}\right) = 0.20170596\ \text{g} = \textbf{0.202 g H}_2\textbf{O}$$

Total mass of reactants = 0.62907 g Cd + 1.026439 g NiO(OH) + 0.20170596 g H₂O
$$= 1.857215\ \text{g} = \textbf{1.86 g reactants}$$

c) Mass % reactants = $\dfrac{1.85721\ \text{g}}{18.3\ \text{g}}\left(100\%\right)$ = 10.14872 % = **10.1%**

19.147 <u>Plan:</u> For a list of decreasing reducing strength, place the elements in order of increasing (more positive) $E°$. Metals with potentials lower than that of water (–0.83 V) can displace hydrogen from water by reducing the hydrogen in water. Metals with potentials lower than that of hydrogen (0.00 V) can displace hydrogen from acids by reducing the H^+ in acid. Metals with potentials above that of hydrogen (0.00 V) cannot displace (reduce) hydrogen.
<u>Solution:</u>
Reducing agent strength: Li > Ba > Na > Al > Mn > Zn > Cr > Fe > Ni > Sn > Pb > Cu > Ag > Hg > Au
These can displace H₂ from water: Li, Ba, Na, Al, and Mn.
These can displace H₂ from acid: Li, Ba, Na, Al, Mn, Zn, Cr, Fe, Ni, Sn, and Pb.
These cannot displace H₂: Cu, Ag, Hg, and Au.

19.150 a) The reference half-reaction is: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E° = 0.34$ V
Before the addition of the ammonia, $E_{cell} = 0$. The addition of ammonia lowers the concentration of copper ions through the formation of the complex $Cu(NH_3)_4{}^{2+}$. The original copper ion concentration is $[Cu^{2+}]_{original}$, and the copper ion concentration in the solution containing ammonia is $[Cu^{2+}]_{ammonia}$.
The Nernst equation is used to determine the copper ion concentration in the cell containing ammonia.
The reaction is $Cu^{2+}_{initial}(aq) + Cu(s) \rightarrow Cu(s) + Cu^{2+}_{ammonia}(aq)$.
The half-cell with the larger concentration of copper ion (no ammonia added) is the reduction and the half-cell with the lower concentration of copper ion due to the addition of ammonia and formation of the complex is the oxidation.

$$E_{cell} = E°_{cell} - \frac{(8.314\ \text{J/mol·K})(298\ \text{K})}{(z)(96485\ \text{C/mol})}\ln Q$$

$$0.129\ \text{V} = 0.00\ \text{V} - \frac{(8.314\ \text{J/mol·K})(298\ \text{K})}{(2)(96485\ \text{C/mol})}\ln \frac{\left[Cu^{2+}\right]_{ammonia}}{\left[Cu^{2+}\right]_{original}}$$

$$0.129 \text{ V} = -\frac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln \frac{\left[\text{Cu}^{2+} \right]_{\text{ammonia}}}{\left[\text{Cu}^{2+} \right]_{\text{original}}}$$

$$-10.04739 = \ln \frac{\left[\text{Cu}^{2+} \right]_{\text{ammonia}}}{(0.0100)}$$

$$4.329865 \times 10^{-5} = \frac{\left[\text{Cu}^{2+} \right]_{\text{ammonia}}}{(0.0100)}$$

$[\text{Cu}^{2+}]_{\text{ammonia}} = 4.329865 \times 10^{-7}$ mol/L

This is the concentration of the copper ion that is not in the complex. The concentration of the complex and of the uncomplexed ammonia must be determined before K_f may be calculated.

The original amount (mol) of copper and the original amount (mol) of ammonia are found from the original volumes and concentrations:

$$\text{Original amount (mol) of copper} = \left(\frac{0.0100 \text{ mol Cu(NO}_3)_2}{\text{L}} \right) \left(\frac{1 \text{ mol Cu}^{2+}}{1 \text{ mol Cu(NO}_3)_2} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (90.0 \text{ mL})$$

$$= 9.00 \times 10^{-4} \text{ mol Cu}^{2+}$$

$$\text{Original amount (mol) of ammonia} = \left(\frac{0.500 \text{ mol NH}_3}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (10.0 \text{ mL}) = 5.00 \times 10^{-3} \text{ mol NH}_3$$

Determine the amount (mol) of copper still remaining uncomplexed.

$$\text{Remaining amount (mol) of copper} = \left(\frac{4.329865 \times 10^{-7} \text{ mol Cu}^{2+}}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (100.0 \text{ mL})$$

$$= 4.329865 \times 10^{-8} \text{ mol Cu}$$

The difference between the original amount (mol) of copper and the copper ion remaining in solution is the copper in the complex (= amount (mol) of complex). The concentration (mol/L) of the complex may now be found.

Amount (mol) of copper in complex = $(9.00 \times 10^{-4} - 4.329865 \times 10^{-8})$ mol Cu^{2+} = 8.9995670×10^{-4} mol Cu^{2+}
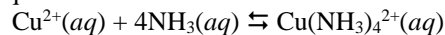
$$\text{Concentration (mol/L) of complex} = \left(\frac{8.9995670 \times 10^{-4} \text{ mol Cu}^{2+}}{100.0 \text{ mL}} \right) \left(\frac{1 \text{ mol Cu(NH}_3)_4^{2+}}{1 \text{ mol Cu}^{2+}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right)$$

$$= 8.9995670 \times 10^{-3} \text{ mol/L Cu(NH}_3)_4^{2+}$$

The concentration of the remaining ammonia is found as follows:

Concentration (mol/L) of ammonia =

$$\left(\frac{\left(5.00 \times 10^{-3} \text{ mol NH}_3 \right) - \left(8.9995670 \times 10^{-4} \text{ mol Cu}^{2+} \right) \left(\frac{4 \text{ mol NH}_3}{1 \text{ mol Cu}^{2+}} \right)}{100.0 \text{ mL}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right)$$

$$= 0.014001732 \text{ mol/L ammonia}$$

The K_f equilibrium is:

$$\text{Cu}^{2+}(aq) + 4\text{NH}_3(aq) \rightleftharpoons \text{Cu(NH}_3)_4^{2+}(aq)$$

$$K_f = \frac{\left[\text{Cu(NH}_3)_4^{2+} \right]}{\left[\text{Cu}^{2+} \right] \left[\text{NH}_3 \right]^4} = \frac{\left[8.9995670 \times 10^{-3} \right]}{\left[4.329865 \times 10^{-7} \right] \left[0.014001732 \right]^4} = 5.407795 \times 10^{11} = \mathbf{5.4 \times 10^{-11}}$$

b) The K_f will be used to determine the new concentration of free copper ions.

Amount(mol) of uncomplexed ammonia before the addition of new ammonia =
$(0.014001732 \text{ mol NH}_3/\text{L})(10^{-3} \text{ L}/1 \text{ mL})(100.0 \text{ mL}) = 0.0014001732 \text{ mol NH}_3$

Amount(mol) of ammonia added = 5.00×10^{-3} mol NH_3 (same as original amount (mol) of ammonia)

From the stoichiometry:

	$Cu^{2+}(aq)$	+	$4NH_3(aq)$	$\rightarrow$	$Cu(NH_3)_4^{2+}(aq)$
Initial amount (mol)	4.329865×10^{-8} mol		0.0014001732 mol		8.9995670×10^{-4} mol
Added amount (mol)			5.00×10^{-3} mol		
Cu^{2+} is limiting	$-(4.329865 \times 10^{-8}$ mol)		$-4(4.329865 \times 10^{-8}$ mol)		$+(4.329865 \times 10^{-8}$ mol)
After the reaction	0		0.006400 mol		9.00000×10^{-4} mol

Determine concentrations before equilibrium:

$[Cu^{2+}] = 0$

$[NH_3] = (0.006400$ mol $NH_3/110.0$ mL)$(1$ mL$/10^{-3}$ L$) = 0.0581818$ mol/L NH_3

$[Cu(NH_3)_4^{2+}] = (9.00000 \times 10^{-4}$ mol $Cu(NH_3)_4^{2+}/110.0$ mL)$(1$ mL$/10^{-3}$ L$)$

$\quad\quad = 0.008181818$ mol/L $Cu(NH_3)_4^{2+}$

Now allow the system to come to equilibrium:

	$Cu^{2+}(aq)$	+	$4NH_3(aq)$	$\leftrightarrows$	$Cu(NH_3)_4^{2+}(aq)$
Initial molarity	0		0.0581818		0.008181818
Change	+x		+4x		−x
Equilibrium	x		0.0581818 + 4 x		0.008181818 – x

$$K_f = \frac{\left[Cu(NH_3)_4^{2+}\right]}{\left[Cu^{2+}\right]\left[NH_3\right]^4} = \frac{[0.008181818 - x]}{[x][0.0581818 + 4x]^4} = 5.34072 \times 10^{11}$$

Assume – x and + 4x are negligible when compared to their associated numbers:

$$K_f = 5.34072 \times 10^{11} = \frac{[0.008181818]}{[x][0.0581818]^4}$$

$x = [Cu^{2+}] = 1.3369 \times 10^{-9}$ mol/L Cu^{2+}

Use the Nernst equation to determine the new cell potential:

$$E = 0.00 \text{ V} - \frac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln \frac{\left[Cu^{2+}\right]_{ammonia}}{\left[Cu^{2+}\right]_{original}}$$

$$E = - \frac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln \left(\frac{1.3369 \times 10^{-9}}{0.0100} \right)$$

$E = 0.203215$ V= **0.20 V**

c) The first step will be to do a stoichiometry calculation of the reaction between copper ions and hydroxide ions.

$$\text{Amount (mol) of OH}^- = \left(\frac{0.500 \text{ mol NaOH}}{\text{L}} \right)\left(\frac{1 \text{ mol OH}^-}{1 \text{ mol NaOH}} \right)\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right)(10.0 \text{ mL}) = 5.00 \times 10^{-3} \text{ mol OH}^-$$

The initial moles of copper ions were determined earlier: 9.00×10^{-4} mol Cu^{2+}

The reaction:

	$Cu^{2+}(aq)$	+	$2OH^-(aq)$	$\rightarrow$	$Cu(OH)_2(s)$
Initial amount (mol)	9.00×10^{-4} mol		5.00×10^{-3} mol		
Cu^{2+} is limiting	$-(9.00 \times 10^{-4}$ mol)		$-2(9.00 \times 10^{-4}$ mol)		
After the reaction	0		0.0032 mol		

Determine concentrations before equilibrium:

$[Cu^{2+}] = 0$

$[NH_3] = (0.0032$ mol $OH^-/100.0$ mL)$(1$ mL$/10^{-3}$ L$) = 0.032$ mol/L OH^-

Now allow the system to come to equilibrium:

	$Cu(OH)_2(s)$	$\leftrightarrows$	$Cu^{2+}(aq)$	+	$2OH^-(aq)$
Initial molarity			0.0		0.032
Change			+x		+2x
Equilibrium			x		0.032 + 2 x

$K_{sp} = 2.2 \times 10^{-20} = [Cu^{2+}][OH^-]^2$

$K_{sp} = 2.2 \times 10^{-20} = [x][0.032 + 2x]^2$

Assume 2x is negligible compared to 0.032 mol/L.

$K_{sp} = 2.2 \times 10^{-20} = [x][0.032]^2$

$x = [Cu^{2+}] = 2.1484375 \times 10^{-17} = 2.1 \times 10^{-17}$ mol/L

Use the Nernst equation to determine the new cell potential:

$$E = 0.00 \text{ V} - \frac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln \frac{\left[Cu^{2+}\right]_{\text{hydroxide}}}{\left[Cu^{2+}\right]_{\text{original}}}$$

$$E = - \frac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln \left(\frac{2.1484375 \times 10^{-17}}{0.0100} \right)$$

$$E = 0.433630 \text{ V} = \textbf{0.43 V}$$

d) Use the Nernst equation to determine the copper ion concentration in the half-cell containing the hydroxide ion.

$$E = 0.00 \text{ V} - \frac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln \frac{\left[Cu^{2+}\right]_{\text{hydroxide}}}{\left[Cu^{2+}\right]_{\text{original}}}$$

$$0.340 = - \frac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln \frac{\left[Cu^{2+}\right]_{\text{hydroxide}}}{(0.0100)}$$

$$-26.48149 = \ln \frac{\left[Cu^{2+}\right]_{\text{hydroxide}}}{(0.0100)}$$

$$3.15671 \times 10^{-12} = \frac{\left[Cu^{2+}\right]_{\text{hydroxide}}}{(0.0100)}$$

$[Cu^{2+}]_{\text{hydroxide}} = 3.15671 \times 10^{-14}$ mol/L

Now use the K_{sp} relationship:

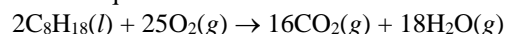$K_{sp} = [Cu^{2+}][OH^-]^2 = 2.2 \times 10^{-20}$

$K_{sp} = 2.2 \times 10^{-20} = [3.2622257 \times 10^{-14}][OH^-]^2$

$[OH^-]^2 = 6.96928 \times 10^{-7}$

$[OH^-] = 8.3482 \times 10^{-4} = 8.3 \times 10^{-4}$ mol/L $OH^- = \textbf{8.3} \times \textbf{10}^{-4}$ **mol/L NaOH**

19.153   a) The chemical equation for the combustion of octane is:

$2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g)$

The heat of reaction may be determined from heats of formation.

$$\Delta_r H^\circ = \sum m \, \Delta_{f \text{ (products)}} H^\circ - \sum n \, \Delta_{f \text{ (reactants)}} H^\circ$$

$$\Delta_r H^\circ = [(16)(\Delta_f H^\circ \text{ of } CO_2) + (18)(\Delta_f H^\circ \text{ of } H_2O)]$$
$$- [(2)(\Delta_f H^\circ \text{ of } C_8H_{18}) + (25)(\Delta_f H^\circ \text{ of } O_2)]$$

$$\Delta_r H^\circ = [(16)(-393.5 \text{ kJ/mol}) + (18)(-241.826 \text{ kJ/mol})]$$
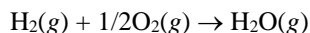$$- [(2)(-250.1 \text{ kJ/mol}) + (25)(0 \text{ kJ/mol})]$$

$$\Delta_r H^\circ = -10148.868 \text{ kJ/mol} = -10148.9 \text{ kJ per two moles of octane}$$

The energy from 4.00 L of gasoline is:

$$\text{Energy (kJ)} = (4.00 \text{ L}) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left(\frac{0.7028 \text{ g}}{\text{mL}} \right) \left(\frac{1 \text{ mol } C_8H_{18}}{114.22 \text{ g } C_8H_{18}} \right) \left(\frac{-10148.9 \text{ kJ}}{2 \text{ mol } C_8H_{18}} \right)$$

$$= -1.2489313 \times 10^5 = -\textbf{1.25} \times \textbf{10}^5 \text{ \textbf{kJ}}$$

b) The energy from the combustion of hydrogen must be found using the balanced chemical equation and the heats of formation.

$$H_2(g) + 1/2O_2(g) \rightarrow H_2O(g)$$

With the reaction written this way, the heat of reaction is simply the heat of formation of water vapour (since the heats of formation of the pure elements are zero). .

$$\Delta H° = -241.826 \text{ kJ/mol}$$

The amount (mol) of hydrogen needed to produce the energy from part a) is:

$$\text{Amount (mol) of } H_2 = \left(-1.2489313 \times 10^5 \text{ kJ / mol}\right)\left(\frac{1 \text{ mol } H_2}{-241.826 \text{ kJ / mol}}\right) = 516.45867 \text{ mol}$$

Finally, use the ideal gas equation to determine the volume.

$$V = \frac{nRT}{p} = \frac{\left(516.45867 \text{ mol } H_2\right)\left(0.08314 \frac{\text{L•bar}}{\text{mol•K}}\right)\left((273 + 25)K\right)}{\left(1.00 \text{ bar}\right)} = 1.27956 \times 10^4 = \textbf{1.28x10}^\textbf{4} \textbf{ L}$$

c) This part of the problem requires the half-reaction for the electrolysis of water to produce hydrogen gas.

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$
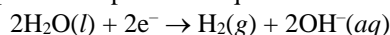
Use 1 A = 1 C/s

$$\text{Time (s)} = \left(516.45867 \text{ mol } H_2\right)\left(\frac{2 \text{ mol } e^-}{1 \text{ mol } H_2}\right)\left(\frac{96,485 \text{ C}}{1 \text{ mol } e^-}\right)\left(\frac{s}{1.00 \times 10^3 C}\right) = 9.966103 \times 10^4 = \textbf{9.97x10}^\textbf{4} \textbf{ seconds}$$

d) Find the coulombs involved in the electrolysis of 516 moles of H_2.

$$\text{Coulombs} = \left(516.45867 \text{ mol } H_2\right)\left(\frac{2 \text{ mol } e^-}{1 \text{ mol } H_2}\right)\left(\frac{96485 \text{ C}}{1 \text{ mol } e^-}\right) = 99,661,030 \text{ C}$$

Joules = C x V = 99,661,030 C x 6.00 V = 597,966,177 J

$$\text{Power (kW • h)} = \left(597,966,177 \text{ J}\right)\left(\frac{1 \text{ kW•h}}{3.6 \times 10^6 \text{ J}}\right) = 166.102 \text{ kW•h} = \textbf{166 kW•h}$$
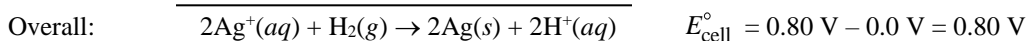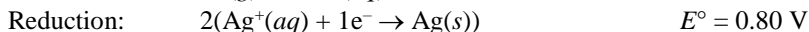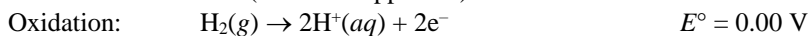
e) The process is only 88.0% efficient, additional electricity is necessary to produce sufficient hydrogen. This is the purpose of the (100%/88.0%) factor.

$$\text{Cost} = \left(166.102 \text{ kW•h}\right)\left(\frac{100\%}{88\%}\right)\left(\frac{\$0.123}{1 \text{ kW•h}}\right) = \$23.2165 = \textbf{\$23.2}$$

19.154 Plan: Write the half-reactions and the overall reaction. Calculate $E^°_{cell}$ by using $E^°_{cell} = E^°_{cathode} - E^°_{anode}$ and then use the Nernst equation to find [H^+] at a cell potential of 0.915 V. pH is obtained from [H^+].
Solution:
The half-reactions are (from the Appendix):

Oxidation: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$ $E° = 0.00$ V
Reduction: $\underline{2(Ag^+(aq) + 1e^- \rightarrow Ag(s))}$ $E° = 0.80$ V
Overall: $2Ag^+(aq) + H_2(g) \rightarrow 2Ag(s) + 2H^+(aq)$ $E^°_{cell} = 0.80$ V – 0.0 V = 0.80 V

The hydrogen ion concentration can now be found from the Nernst equation.

$$E_{cell} = E^°_{cell} - \frac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln Q$$

$$0.915 \text{ V} = 0.80 \text{ V} - \frac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln \frac{\left[H^+\right]^2}{\left[Ag^+\right]^2 p_{H_2}}$$

$$0.915 \text{ V} - 0.80 \text{ V} = - \frac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln \frac{\left[H^+\right]^2}{(0.100)^2 (1.00)}$$

$$0.115 \text{ V} = -\frac{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln \frac{\left[\text{H}^+\right]^2}{(0.100)^2 (1.00)}$$

$$-8.9570 = \ln \frac{\left[\text{H}^+\right]^2}{(0.0100)}$$

$$1.28835 \times 10^{-4} = \frac{\left[\text{H}^+\right]^2}{(0.0100)}$$

$[\text{H}^+] = 1.135 \times 10^{-3}$ mol/L

pH $= -\log [\text{H}^+] = -\log (1.1413851 \times 10^{-3}) = 2.94498 = \textbf{2.94}$