CHAPTER 21 ELECTROCHEMISTRY: CHEMICAL CHANGE AND ELECTRICAL WORK

21.1 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.

21.2 An electrochemical process involves electron flow. At least one substance must lose electron(s) and one substance must gain electron(s) to produce the flow. This electron transfer is a redox process.

21.3 **No**, one half-reaction cannot take place independent 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).

21.4 O^{2-} is too strong a base to exist in H_2O. The reaction $O^{2-} + H_2O \rightarrow 2OH^-$ occurs. Only species actually existing in solution can be present when balancing an equation.

21.5 Multiply each half-reaction by the appropriate integer to make e^- lost equal to e^- gained.

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

21.7 **No**, add spectator ions to the balanced ionic equation to obtain the balanced molecular equation.

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

21.9 a) **True**
b) **True**
c) **True**
d) **False**, in a voltaic cell, the system does work on the surroundings.
e) **True**
f) **False**, the electrolyte in a cell provides a solution of mobile ions to maintain charge neutrality.

21.10 a) To decide which reactant is oxidized, look at oxidation numbers. **Cl^-** is oxidized because its oxidation number increases from -1 to 0.
b) **MnO_4^-** is reduced because the oxidation number of Mn decreases from +7 to +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 **MnO_4^-** 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 MnO_4^-**, which is gaining electrons.
f) $8\ H_2SO_4(aq) + 2\ KMnO_4(aq) + 10\ KCl(aq) \rightarrow 2\ MnSO_4(aq) + 5\ Cl_2(g) + 8\ H_2O(l) + 6\ K_2SO_4(aq)$

21.11 $2\ CrO_2^-(aq) + 2\ H_2O(l) + 6\ ClO^-(aq) \rightarrow 2\ CrO_4^{2-}(aq) + 3\ Cl_2(g) + 4\ OH^-(aq)$

a) The CrO_2^- is the oxidized species because Cr increases in oxidation state from +3 to +6.
b) The ClO^- is the reduced species because Cl decreases in oxidation state from +1 to 0.
c) The oxidizing agent is ClO^-; the oxidizing agent is the substance reduced.
d) The reducing agent is CrO_2^-; the reducing agent is the substance oxidized.
e) Electrons transfer from CrO_2^- to ClO^-.
f) $2\ NaCrO_2(aq) + 6\ NaClO(aq) + 2\ H_2O(l) \rightarrow 2\ Na_2CrO_4(aq) + 3\ Cl_2(g) + 4\ NaOH(aq)$

21.12 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
$2\ I^-(aq) \rightarrow I_2(s)$ iodine now balanced
Balance O by adding H_2O
$ClO_3^-(aq) \rightarrow Cl^-(aq) + 3\ H_2O(l)$ add 3 waters to add 3 O's to product
$2\ I^-(aq) \rightarrow I_2(s)$ no change
Balance H by adding H^+
$ClO_3^-(aq) + 6\ H^+(aq) \rightarrow Cl^-(aq) + 3\ H_2O(l)$ add 6 H^+ to reactants
$2\ I^-(aq) \rightarrow I_2(s)$ no change
Balance charge by adding e^-
$ClO_3^-(aq) + 6\ H^+(aq) + 6\ e^- \rightarrow Cl^-(aq) + 3\ H_2O(l)$ add 6 e^- to reactants
$2\ I^-(aq) \rightarrow I_2(s) + 2\ e^-$ add 2 e^- to products
Multiply each half-reaction by an integer to equalize the number of electrons
$ClO_3^-(aq) + 6\ H^+(aq) + 6\ e^- \rightarrow Cl^-(aq) + 3\ H_2O(l)$ multiply by 1 to give 6 e^-
$3\{2\ I^-(aq) \rightarrow I_2(s) + 2\ e^-\}$ multiply by 3 to give 6 e^-
Add half-reactions to give balanced equation in acidic solution.

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

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 ClO_3^- 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
$MnO_4^-(aq) \rightarrow MnO_2(s) + 2\ H_2O(l)$ add 2 H_2O to products
$SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq)$ add 1 H_2O to reactants
Balance H by adding H^+
$MnO_4^-(aq) + 4\ H^+(aq) \rightarrow MnO_2(s) + 2\ H_2O(l)$ add 4 H^+ to reactants
$SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2\ H^+(aq)$ add 2 H^+ to products
Balance charge by adding e^-
$MnO_4^-(aq) + 4\ H^+(aq) + 3\ e^- \rightarrow MnO_2(s) + 2\ H_2O(l)$ add 3 e^- to reactants
$SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2\ H^+(aq) + 2\ e^-$ add 2 e^- to products
Multiply each half-reaction by an integer to equalize the number of electrons
$2\{MnO_4^-(aq) + 4\ H^+(aq) + 3\ e^- \rightarrow MnO_2(s) + 2\ H_2O(l)\}$ multiply by 2 to give 6 e^-
$3\{SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2\ H^+(aq) + 2\ e^-\}$ multiply by 3 to give 6 e^-

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

$2\ MnO_4^-(aq) + \cancel{8}\ H^+(aq) + 3\ SO_3^{2-}(aq) + \cancel{3\ H_2O(l)} \rightarrow 2\ MnO_2(s) + \cancel{4}\ H_2O(l) + 3\ SO_4^{2-}(aq) + \cancel{6\ H^+(aq)}$

The balanced equation in acidic solution is:

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

To change to basic solution, add OH to both sides of equation to neutralize H^+.

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

Balanced equation in basic solution:

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

Check balancing:

Reactants:	2 Mn	Products:	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 - Mn is balanced

Balance O by adding H_2O

$MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)$ add 4 H_2O to products

Balance H by adding H^+

$MnO_4^-(aq) + 8\ H^+(aq) \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)$ add 8 H^+ to reactants

$H_2O_2(aq) \rightarrow O_2(g) + 2\ H^+(aq)$ add 2 H^+ to products

Balance charge by adding e^-

$MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^- \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)$ add 5 e^- to reactants

$H_2O_2(aq) \rightarrow O_2(g) + 2\ H^+(aq) + 2\ e^-$ add 2 e^- to products

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

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

$5\{H_2O_2(aq) \rightarrow O_2(g) + 2\ H^+(aq) + 2\ e^-\}$ multiply by 5 to give 10 e^-

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

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

The balanced equation in acidic solution

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

Check balancing:

Reactants:	2 Mn	Products:	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.

21.13 a) $3\ O_2(g) + 4\ NO(g) + 2\ H_2O(l) \rightarrow 4\ NO_3^-(aq) + 4\ H^+(aq)$

Oxidizing agent is O_2 and reducing agent: NO

b) $2\ CrO_4^{2-}(aq) + 8\ H_2O(l) + 3\ Cu(s) \rightarrow 2\ Cr(OH)_3(s) + 3\ Cu(OH)_2(s) + 4\ OH^-(aq)$

Oxidizing agent is CrO_4^{2-} and reducing agent: Cu

c) $AsO_4^{3-}(aq) + NO_2^-(aq) + H_2O(l) \rightarrow AsO_2^-(aq) + NO_3^-(aq) + 2\ OH^-(aq)$

Oxidizing agent is AsO_4^{3-} and reducing agent: NO_2^-.

21.14 a) Balance the reduction half-reaction:

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

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

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

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

Balance the oxidation half-reaction:

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

Add the two half-reactions multiplying the oxidation half-reaction by 3 to equalize the electrons.

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

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

b) Balance the reduction half-reaction:

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

Balance the oxidation half-reaction

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

Add half-reactions after multiplying oxidation half-reaction by 3.

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

Add OH^- to both sides to neutralize the H^+ and convert $H^+ + OH^- \rightarrow H_2O$

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

Oxidizing agent is MnO_4^- and reducing agent is $Fe(OH)_2$.

c) Balance the reduction half-reaction:

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

Balance the oxidation half-reaction:

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

Add the half-reactions after multiplying the reduction half-reaction by 1 and the oxidation half-reaction by 5.

$2\ NO_3^-(aq) + 12\ H^+(aq) + 5\ Zn(s) \rightarrow N_2(g) + 6\ H_2O(l) + 5\ Zn^{2+}(aq)$

Oxidizing agent is NO_3^- and reducing agent is Zn.

21.15 a) $3\ BH_4^-(aq) + 4\ ClO_3^-(aq) \rightarrow 3\ H_2BO_3^-(aq) + 4\ Cl^-(aq) + 3\ H_2O(l)$

Oxidizing agent is ClO_3^- and reducing agent: BH_4^-

b) $2\ CrO_4^{2-}(aq) + 3\ N_2O(g) + 10\ H^+(aq) \rightarrow 2\ Cr^{3+}(aq) + 6\ NO(g) + 5\ H_2O(l)$

Oxidizing agent is CrO_4^{2-} and reducing agent: N_2O

c) $3\ Br_2(l) + 6\ OH^-(aq) \rightarrow BrO_3^-(aq) + 5\ Br^-(aq) + 3\ H_2O(l)$

Oxidizing agent is Br_2 and reducing agent is Br_2.

21.16 a) Balance the reduction half-reaction:

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

Balance oxidation half-reaction:

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

Multiply reduction half-reaction by 4 and add half-reactions. Cancel common reactants and products.

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

Balanced equation in acidic solution:

$4\ NO_3^-(aq) + 4\ H^+(aq) + 4\ Sb(s) \rightarrow 4\ NO(g) + 2\ H_2O(l) + Sb_4O_6(s)$

Oxidizing agent is NO_3^- and reducing agent is Sb.

b) Balance reduction half-reaction:

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

$BiO_3^-(aq) + 6\ H^+(aq) \rightarrow Bi^{3+}(aq) + 3\ H_2O(l)$ balance H

$BiO_3^-(aq) + 6\ H^+(aq) + 2\ e^- \rightarrow Bi^{3+}(aq) + 3\ H_2O(l)$ balance charge

Balance oxidation half-reaction:

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

$Mn^{2+}(aq) + 4\ H_2O(l) \rightarrow MnO_4^-(aq) + 8\ H^+(aq)$ balance H

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

Multiply reduction half-reaction by 2 and oxidation half-reaction by 2 to transfer 10 e^- in the overall reaction. Cancel H_2O and H^+ in reactants and products.

$5\ BiO_3^-(aq) + \cancel{30}\ H^+(aq) + 2\ Mn^{2+}(aq) + \cancel{8\ H_2O}(l) \rightarrow 5\ Bi^{3+}(aq) + \cancel{15}\ H_2O(l) + 2\ MnO_4^-(aq) + \cancel{16\ H^+(aq)}$

Balanced reaction in acidic solution:

$5\ BiO_3^-(aq) + 14\ H^+(aq) + 2\ Mn^{2+}(aq) \rightarrow 5\ Bi^{3+}(aq) + 7\ H_2O(l) + 2\ MnO_4^-(aq)$

BiO_3^- is the oxidizing agent and Mn^{2+} is the reducing agent.

c) Balance the reduction half-reaction:

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

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

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

Balance the oxidation half-reaction

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

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

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

Multiply oxidation half-reaction by 2 and add two half-reactions. Cancel H_2O and H^+.

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

Add OH^- to both sides to neutralize H^+.

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

Balanced reaction in basic solution:

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

$Pb(OH)_3^-$ is the oxidizing agent and $Fe(OH)_2$ is the reducing agent.

21.17 a) $1[2\ OH^-(aq) + NO_2(g) \rightarrow NO_3^-(aq) + H_2O(l) + 1\ e^-]$

$1[NO_2(g) + 1\ e^- \rightarrow NO_2^-(aq)]$

Overall: $2\ NO_2(g) + 2\ OH^-(aq) \rightarrow NO_3^-(aq) + NO_2^-(aq) + H_2O(l)$

Oxidizing agent is NO_2 and reducing agent is NO_2.

b) $4[Zn(s) + 4\ OH^-(aq) \rightarrow Zn(OH)_4^{2-}(aq) + 2\ e^-]$

$1[NO_3^-(aq) + 6\ H_2O(l) + 8\ e^- \rightarrow NH_3(aq) + 9\ OH^-(aq)$

Overall: $4\ Zn(s) + 16\ OH^-(aq) + NO_3^-(aq) + 6\ H_2O(l) + 8\ e^- \rightarrow 4\ Zn(OH)_4^{2-}aq) + NH_3(aq) + 9\ OH^-(aq) + 8\ e^-$

$4\ Zn(s) + 7\ OH^-(aq) + NO_3^-(aq) + 6\ H_2O(l) \rightarrow 4\ Zn(OH)_4^{2-}(aq) + NH_3(aq)$

Oxidizing agent is NO_3^- and reducing agent is Zn.

c) $3[8\ H_2S(g) \rightarrow S_8(s) + 16\ H^+(aq) + 16\ e^-]$

$16[3\ e^- + NO_3^-(aq) + 4\ H^+(aq) \rightarrow NO(g) + 2\ H_2O(l)]$

Overall: $24\ H_2S(g) + 16\ NO_3^-(aq) + 64\ H^+(aq) + 48\ e^- \rightarrow 3\ S_8(s) + 48\ H^+(aq) + 48\ e^- + 16\ NO(g) + 32\ H_2O(l)$

$24\ H_2S(g) + 16\ NO_3^-(aq) + 16\ H^+(aq) \rightarrow 3\ S_8(s) + 16\ NO(g) + 32\ H_2O(l)$

Oxidizing agent is NO_3^- and reducing agent is H_2S.

21.18 a) Balance reduction half-reaction:

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

$MnO_4^-(aq) + 8\ H^+(aq) \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)$ balance H

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

Balance oxidation half-reaction:

$As_4O_6(s) \rightarrow 4\ AsO_4^{3-}(aq)$ balance As

$As_4O_6(s) + 10\ H_2O(l) \rightarrow 4\ AsO_4^{3-}(aq)$ balance O

$As_4O_6(s) + 10\ H_2O(l) \rightarrow 4\ AsO_4^{3-}(aq) + 20\ H^+(aq)$ balance H

$As_4O_6(s) + 10\ H_2O(l) \rightarrow 4\ AsO_4^{3-}(aq) + 20\ H^+(aq) + 8\ e^-$ balance charge

Multiply reduction half-reaction by 8 and oxidation half-reaction by 5 to transfer 40 e^- in overall reaction. Add the half-reactions and cancel H_2O and H^+.

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

Balanced reaction in acidic solution:

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

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 include P_4 as the reactant.

Balance reduction half-reaction:

$P_4(s) \rightarrow 4\ PH_3(g)$ balance P

$P_4(s) + 12\ H^+(aq) \rightarrow 4\ PH_3(g)$ balance H

$P_4(s) + 12\ H^+(aq) + 12\ e^- \rightarrow 4\ PH_3(g)$ balance charge

Balance oxidation half-reaction:

$P_4(s) \rightarrow 4\ HPO_3^{2-}(aq)$ balance P

$P_4(s) + 12\ H_2O(l) \rightarrow 4\ HPO_3^{2-}(aq)$ balance O

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

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

Add two half-reactions and cancel H^+.

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

Balanced reaction in acidic solution:

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

$P_4(s) + 6\ H_2O(l) \rightarrow 2\ HPO_3^{2-}(aq) + 2\ PH_3(g) + 4\ H^+(aq)$

P_4 is both the oxidizing agent and reducing agent.

c) Balance the reduction half-reaction:

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

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

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

Balance oxidation half-reaction:

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

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

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

Multiply the oxidation half-reaction by 3 and reduction half-reaction by 2 to transfer 6 e^- in overall reaction. Add two half-reactions. Cancel the H_2O and H^+.

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

Add 2 OH^- to both sides to neutralize H^+ and form H_2O.

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

Balanced reaction in basic solution:

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

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

21.19 a) $SO_3^{2-}(aq) + 2\ OH^-(aq) \rightarrow SO_4^{2-}(aq) + H_2O(l) + 2\ e^-$
$Cl_2(g) + 2\ e^- \rightarrow 2\ Cl^-(aq)$
Overall: $SO_3^{2-}(aq) + 2\ OH^-(aq) + Cl_2(g) \rightarrow SO_4^{2-}(aq) + 2\ Cl^-(aq) + H_2O(l)$
Oxidizing agent is Cl_2 and reducing agent is SO_3^{2-}.

b) $7[Fe(CN)_6^{3-}(aq) + 1\ e^- \rightarrow Fe(CN)_6^{4-}(aq)]$
$1[Re(s) + 8\ OH^-(aq) \rightarrow ReO_4^-(aq) + 4\ H_2O(l) + 7\ e^-]$
Overall: $7\ Fe(CN)_6^{3-}(aq) + Re(s) + 8\ OH^-(aq) + 7\ e^- \rightarrow 7\ Fe(CN)_6^{4-}(aq) + ReO_4^-(aq) + 4\ H_2O(l) + 7\ e^-$
Oxidizing agent is $Fe(CN)_6^{3-}$ and reducing agent is Re.

c) $2[MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^- \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)]$
$5[HCOOH(aq) \rightarrow CO_2(g) + 2\ H^+(aq) + 2\ e^-]$
Overall: $2\ MnO_4^-(aq) + 5\ HCOOH(aq) + 16\ H^+(aq) + 10\ e^- \rightarrow$
$2\ Mn^{2+}(aq) + 5\ CO_2(g) + 8\ H_2O(l) + 10\ H^+(aq) + 10\ e^-$
$2\ MnO_4^-(aq) + 5\ HCOOH(aq) + 6\ H^+(aq) \rightarrow 2\ Mn^{2+}(aq) + 5\ CO_2(g) + 8\ H_2O(l)$
Oxidizing agent is MnO_4^- and reducing agent is $HCOOH$.

21.20 $5\ Fe^{2+}(aq) + MnO_4^-(aq) + 8\ H^+(aq) \rightarrow Mn^{2+}(aq) + 5\ Fe^{3+}(aq) + 4\ H_2O(l)$

21.21 a) Balance reduction half-reaction:

$NO_3^-(aq) \rightarrow NO_2(g) + H_2O(l)$	balance O
$NO_3^-(aq) + 2\ H^+(aq) \rightarrow NO_2(g) + H_2O(l)$	balance H
$NO_3^-(aq) + 2\ H^+(aq) + e^- \rightarrow NO_2(g) + H_2O(l)$	balance charge

Balance oxidation half-reaction:

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

Multiply reduction half-reaction by 3 and add half-reactions.
$Au(s) + 3\ NO_3^-(aq) + 4\ Cl^-(aq) + 6\ H^+(aq) \rightarrow AuCl_4^-(aq) + 3\ NO_2(g) + 3\ H_2O(l)$

b) Oxidizing agent is $\mathbf{NO_3^-}$ and reducing agent is **Au**.

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

21.22 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 produced the metal.

21.23 Unless the oxidizing and reducing agents are physically separated, the redox reaction will not generate electrical energy. This electrical energy is produced by forcing the electrons to travel through an external circuit.

21.24 The purpose of the salt bridge is to maintain charge neutrality by allowing anions to flow into the anode compartment and cations to flow into the cathode compartment.

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

21.26 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.

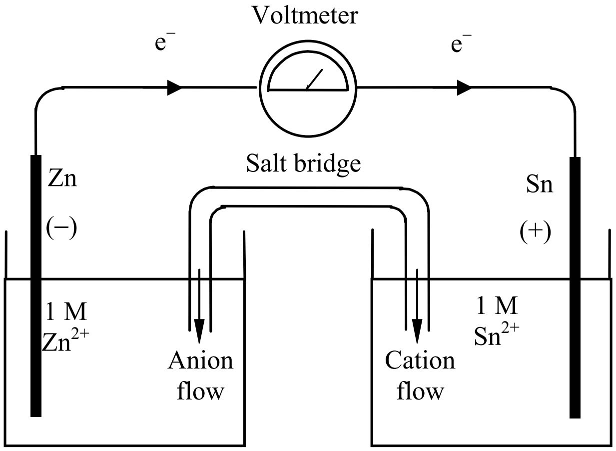
21.27 a) If the zinc electrode is negative, oxidation takes place at the zinc electrode:

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

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

Overall reaction: $\mathrm{Zn}(s) + \mathrm{Sn}^{2+}(aq) \rightarrow \mathrm{Zn}^{2+}(aq) + \mathrm{Sn}(s)$

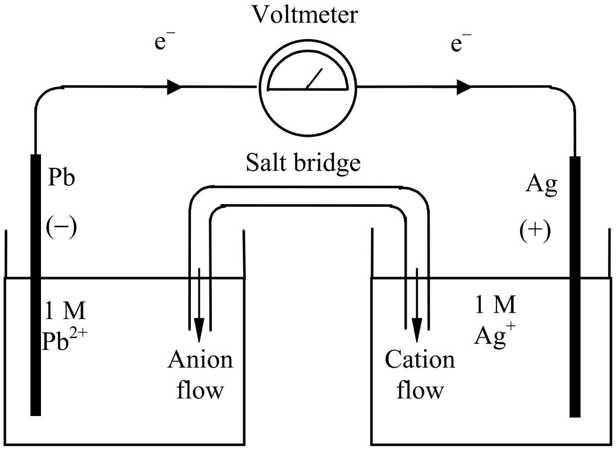
b)



21.28 a)

(red half-rxn)	$\mathrm{Ag}^+(aq) + 1\ \mathrm{e}^- \rightarrow \mathrm{Ag}(s)$
(ox half-rxn)	$\mathrm{Pb}(s) \rightarrow \mathrm{Pb}^{2+}(aq) + 2\ \mathrm{e}^-$
(overall rxn)	$2\ \mathrm{Ag}^+(aq) + \mathrm{Pb}(s) \rightarrow 2\ \mathrm{Ag}(s) + \mathrm{Pb}^{2+}(aq)$

b)



21.29 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 *M* $NiSO_4$** is one choice.

h) KNO_3 is commonly used in salt bridges, the ions being **K^+ and NO_3^-**. 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 toward 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: $Fe(s) \rightarrow Fe^{2+}(aq) + 2\ e^-$
Reduction half-reaction: $Ni^{2+}(aq) + 2\ e^- \rightarrow Ni(s)$
Overall cell reaction: $Fe(s) + Ni^{2+}(aq) \rightarrow Fe^{2+}(aq) + Ni(s)$

21.30 a) The electrons flow **left to right**.

b) Reduction occurs at the electrode on the **right**.

c) Electrons leave the cell from the **left** side.

d) The **zinc** electrode generates the electrons.

e) The **cobalt** electron has the positive charge.

f) The **cobalt** electrode increases in mass.

g) The anode electrolyte could be **1 *M* $Zn(NO_3)_2$**.

h) One possible pair would be K^+ and NO_3^-.

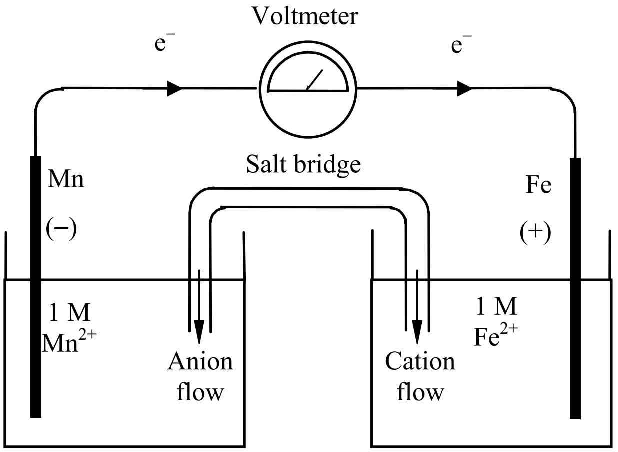
i) **Neither** electrode could be replaced because both electrodes are part of the cell reaction.

j) The cations move from **left to right** to maintain charge neutrality.

k) Reduction: $Co^{2+}(aq) + 2\ e^- \rightarrow Co(s)$
Oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$
Overall: $Zn(s) + Co^{2+}(aq) \rightarrow Co(s) + Zn^{2+}(aq)$

21.31 a) The cathode is assigned a positive charge, so the iron electrode is the cathode.
Reduction half-reaction: $Fe^{2+}(aq) + 2\ e^- \rightarrow Fe(s)$
Oxidation half-reaction: $Mn(s) \rightarrow Mn^{2+}(aq) + 2\ e^-$
Overall cell reaction: $Fe^{2+}(aq) + Mn(s) \rightarrow Fe(s) + Mn^{2+}(aq)$

b)

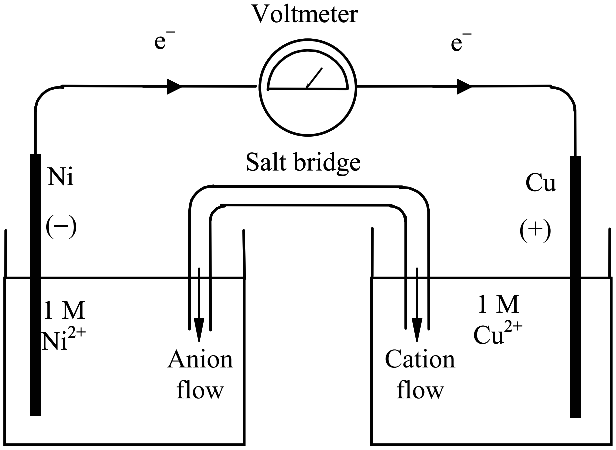


21.32 a) (red half-rxn) $Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$

(ox half-rxn) $Ni(s) \rightarrow Ni^{2+}(aq) + 2\ e^-$

(overall rxn) $Cu^{2+}(aq) + Ni(s) \rightarrow Cu(s) + Ni^{2+}(aq)$

b)



21.33 a) Al is oxidized, so it is the anode and appears first in the cell notation:

$Al(s)|Al^{3+}(aq)||Cr^{3+}(aq)|Cr(s)$

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.

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

21.34 a) $Mn(s) + Cd^{2+}(aq) \rightarrow Mn^{2+}(aq) + Cd(s)$

b) $3\ Fe(s) + 2\ NO_3^-(aq) + 8\ H^+(aq) \rightarrow 3\ Fe^{2+}(aq) + 2\ NO(g) + 4\ H_2O(l)$

21.35 An isolated reduction or oxidation potential cannot be directly measured. However, by assigning a standard half-cell potential to a particular half-reaction, the standard potentials of other half-reactions can be determined relative to this reference value. The standard reference half-cell is a standard hydrogen electrode defined to have an $E°$ value of 0.000 V.

21.36 A negative E^o_{cell} indicates that the cell reaction is not spontaneous, $\Delta G° > 0$. The reverse reaction is spontaneous with $E^o_{cell} > 0$.

21.37 Similar to other state functions, the sign of $E°$ changes when a reaction is reversed. Unlike $\Delta G°$, $\Delta H°$ 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 $\Delta G°$, $\Delta H°$ 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.

21.38 a) 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.

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

Reduction: $2\ SO_3^{2-}(aq) + 3\ H_2O(l) + 4\ e^- \rightarrow S_2O_3^{2-}(aq) + 6\ OH^-(aq)$

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

21.39 a) (red half-rxn) $O_3(g) + 2\,H^+(aq) + 2\,e^- \rightarrow O_2(g) + H_2O(l)$

(ox half-rxn) $Mn^{2+}(aq) + 2\,H_2O(l) \rightarrow MnO_2(s) + 4\,H^+(aq) + 2\,e^-$

b) $E^o_{cell} = E^\circ_{\text{ozone}} - E^\circ_{\text{manganese}}$

$E^\circ_{\text{manganese}} = E^\circ_{\text{ozone}} - E^o_{cell}$

$= 2.07\text{ V} - 0.84\text{ V}$

$= \mathbf{1.23\ V}$

21.40 a) The greater the reduction potential, the greater the strength as an oxidizing agent. When placed in order of decreasing strength as oxidizing agents: $\mathbf{Br_2 > Fe^{3+} > Cu^{2+}}$.

b) When placed in order of increasing strength as oxidizing agents: $\mathbf{Ca^{2+} < Ag^{+} < Cr_2O_7^{2-}}$.

21.41 a) When placed in order of decreasing strength as reducing agents: $\mathbf{SO_2 > MnO_2 > PbSO_4}$

b) When placed in order of increasing strength as reducing agents: **Hg < Sn < Fe**

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

Reduction: $2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)$ $\quad E^\circ = 0.00\text{ V}$

Overall reaction: $Co(s) + 2\,H^+(aq) \rightarrow Co^{2+}(aq) + H_2(g)$ $\quad E^o_{cell} = \mathbf{0.28\ V}$

Reaction is **spontaneous** under standard state conditions because E^o_{cell} is positive.

b) Oxidation: $2\{Mn^{2+}(aq) + 4\,H_2O(l) \rightarrow MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^-\}$ $\quad -E^\circ = -1.51\text{ V}$

Reduction: $5\{Br_2(l) + 2\,e^- \rightarrow 2\,Br^-(aq)\}$ $\quad E^\circ = +1.07\text{ V}$

Overall: $2\,Mn^{2+}(aq) + 5\,Br_2(l) + 8\,H_2O(l) \rightarrow 2\,MnO_4^-(aq) + 10\,Br^-(aq) + 16\,H^+(aq)$ $\quad E^o_{cell} = \mathbf{-0.44\ V}$

Reaction is **not spontaneous** under standard state conditions with $E^o_{cell} < 0$.

c) Oxidation: $Hg_2^{2+}(aq) \rightarrow 2\,Hg^{2+}(aq) + 2\,e^-$ $\quad -E^\circ = -0.92\text{ V}$

Reduction: $Hg_2^{2+}(aq) + 2\,e^- \rightarrow 2\,Hg(l)$ $\quad E^\circ = +0.85\text{ V}$

Overall: $2\,Hg_2^{2+}(aq) \rightarrow 2\,Hg^{2+}(aq) + 2\,Hg(l)$ $\quad E^o_{cell} = \mathbf{-0.07\ V}$

or $Hg_2^{2+}(aq) \rightarrow Hg^{2+}(aq) + Hg(l)$

Negative E^o_{cell} indicates reaction is **not spontaneous** under standard state conditions.

21.43 a) $Cl_2(g) + 2\,Fe^{2+}(aq) \rightarrow 2\,Cl^-(aq) + 2\,Fe^{3+}(aq)$

$E^o_{cell} = E^\circ_{Cl_2} - E^\circ_{Fe^{3+}}$

$= 1.36\text{ V} - (0.77\text{ V})$

$= 0.59\text{ V}$

The reaction is **spontaneous**.

b) $Mn^{2+}(aq) + 2\,H_2O(l) + 2\,Co^{3+}(aq) \rightarrow MnO_2(s) + 4\,H^+(aq) + 2\,Co^{2+}(aq)$

$E^o_{cell} = E^\circ_{Co^{3+}} - E^\circ_{MnO_2}$

$= 1.82\text{ V} - (1.23\text{ V})$

$= 0.59\text{ V}$

The reaction is **spontaneous**.

c) $3\,AgCl(s) + NO(g) + 2\,H_2O(l) \rightarrow 3\,Ag(s) + 3\,Cl^-(aq) + NO_3^-(aq) + 4\,H^+(aq)$

$E^o_{cell} = E^\circ_{AgCl} - E^\circ_{NO_3^-}$

$= 0.22\text{ V} - (0.96\text{ V})$

$= -0.74\text{ V}$

The reaction is **nonspontaneous**.

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

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

Overall: $2\ \text{Ag}(s) + \text{Cu}^{2+}(aq) \rightarrow 2\ \text{Ag}^{+}(aq) + \text{Cu}(s)$ E^{o}_{cell} = **-0.46 V**

The reaction is **not spontaneous**.

b) Oxidation: $\text{Cd}(s) \rightarrow \text{Cd}^{2+}(aq) + 2\ e^{-}$ $-E^\circ = +0.40\text{ V}$

Reduction: $\text{Cr}_2\text{O}_7^{2-}(aq) + 14\ \text{H}^{+}(aq) + 6\ e^{-} \rightarrow 2\ \text{Cr}^{3+}(aq) + 7\ \text{H}_2\text{O}(l)$ $E^\circ = +1.33\text{ V}$

Overall: $\text{Cr}_2\text{O}_7^{2-}(aq) + 3\ \text{Cd}(s) + 14\ \text{H}^{+}(aq) \rightarrow 2\ \text{Cr}^{3+}(aq) + 3\ \text{Cd}^{2+}(aq) + 7\ \text{H}_2\text{O}(l)$

The reaction is **spontaneous**. E^{o}_{cell} = **$+1.73$ V**

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

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

Overall: $\text{Pb}(s) + \text{Ni}^{2+}(aq) \rightarrow \text{Pb}^{2+}(aq) + \text{Ni}(s)$ E^{o}_{cell} = **-0.12 V**

The reaction is **not spontaneous**.

21.45 a) $2\ \text{Cu}^{+}(aq) + \text{PbO}_2(s) + 4\ \text{H}^{+}(aq) + \text{SO}_4^{2-}(aq) \rightarrow 2\ \text{Cu}^{2+}(aq) + \text{PbSO}_4(s) + 2\ \text{H}_2\text{O}(l)$

$E^{o}_{cell} = E^\circ_{\text{PbO}_2} - E^\circ_{\text{Cu}^{2+}}$

$= 1.70\text{ V} - (0.15\text{ V})$

$= 1.55\text{ V}$

The reaction is **spontaneous**.

b) $\text{H}_2\text{O}_2(aq) + \text{Ni}^{2+}(aq) \rightarrow 2\ \text{H}^{+}(aq) + \text{O}_2(g) + \text{Ni}(s)$

$E^{o}_{cell} = E^\circ_{\text{Ni}^{2+}} - E^\circ_{\text{O}_2}$

$= -0.25\text{ V} - (0.68\text{ V})$

$= -0.93\text{ V}$

The reaction is **nonspontaneous**.

c) $3\ \text{Ag}^{+}(aq) + \text{MnO}_2(s) + 4\ \text{OH}^{-}(aq) \rightarrow 3\text{Ag}(s) + \text{MnO}_4^{-}(aq) + 2\ \text{H}_2\text{O}(l)$

$E^{o}_{cell} = E^\circ_{\text{Ag}^{+}} - E^\circ_{\text{MnO}_4^{-}}$

$= 0.80\text{ V} - (0.59\text{ V})$

$= 0.21\text{ V}$

The reaction is **spontaneous**.

21.46 Adding (1) and (2) to give a spontaneous reaction involves converting (1) to oxidation:

$3\ \text{N}_2\text{O}_4(g) + 2\ \text{Al}(s) \rightarrow 6\ \text{NO}_2^{-}(aq) + 2\ \text{Al}^{3+}(aq)$ $E^{o}_{cell} = 0.867\text{ V} - (-1.66\text{ V}) =$ **2.53 V**

Reverse (1), and then add (1) and (3) to give a spontaneous reaction.

$2\ \text{Al}(s) + 3\ \text{SO}_4^{2-}(aq) + 3\ \text{H}_2\text{O}(l) \rightarrow 2\ \text{Al}^{3+}(aq) + 3\ \text{SO}_3^{2-}(aq) + 6\ \text{OH}^{-}(aq)$

$E^{o}_{cell} = 0.93\text{ V} - (-1.66\text{ V}) =$ **2.59 V**

Reverse (2), then add (2) and (3) for the spontaneous reaction:

$\text{SO}_4^{2-}(aq) + 2\ \text{NO}_2^{-}(aq) + \text{H}_2\text{O}(l) \rightarrow \text{SO}_3^{2-}(aq) + \text{N}_2\text{O}_4(g) + 2\ \text{OH}^{-}(aq)$

$E^{o}_{cell} = 0.93\text{ V} - 0.867\text{ V} =$ **0.06 V**

Rank oxidizing agents (substance being reduced) in order of increasing strength:

$\text{Al}^{3+} < \text{N}_2\text{O}_4 < \text{SO}_4^{2-}$

Rank reducing agents (substance being oxidized) in order of increasing strength:

$\text{SO}_3^{2-} < \text{NO}_2^{-} < \text{Al}$

21.47 $3\ N_2O(g) + 6\ H^+(aq) + 2\ Cr(s) \rightarrow 3\ N_2(g) + 3\ H_2O(l) + 2\ Cr^{3+}(aq)$
E^{o}_{cell} = 1.77 V - (-0.74 V) = 2.51 V
Oxidizing agents: $N_2O > Cr^{3+}$; reducing agents: $Cr > N_2$
$3\ Au^+(aq) + Cr(s) \rightarrow 3\ Au(s) + Cr^{3+}(aq)$
E^{o}_{cell} = 1.69 V - (-0.74 V) = 2.43 V
Oxidizing agents: $Au^+ > Cr^{3+}$; reducing agents: $Cr > Au$
$N_2O(g) + 2\ H^+(aq) + 2\ Au(s) \rightarrow N_2(g) + H_2O(l) + 2\ Au^+(aq)$
E^{o}_{cell} = 1.77 V - (1.69 V) = 0.08 V
Oxidizing agents: $N_2O > Au^+$; reducing agents: $Au > N_2$
Oxidizing agents: $N_2O > Au^+ > Cr^{3+}$; reducing agents: $Cr > Au > N_2$

21.48 Spontaneous reaction results when (2) is reversed and added to (1):
$2\ HClO(aq) + Pt(s) + 2\ H^+(aq) \rightarrow Cl_2(g) + Pt^{2+}(aq) + 2\ H_2O(l)$
E^{o}_{cell} = 1.63 V - 1.20 V = **0.43 V**
Spontaneous reaction results when (3) is reversed and added to (1):
$2\ HClO(aq) + Pb(s) + SO_4^{2-}(aq) + 2\ H^+(aq) \rightarrow Cl_2(g) + PbSO_4(s) + 2\ H_2O(l)$
E^{o}_{cell} = 1.63 V - (-0.31 V) = **1.94 V**
Spontaneous reaction results when (3) is reversed and added to (2):
$Pt^{2+}(aq) + Pb(s) + SO_4^{2-}(aq) \rightarrow Pt(s) + PbSO_4(s)$
E^{o}_{cell} = 1.20 V - (-0.31 V) = **1.51 V**
Order of increasing strength as oxidizing agent: $\mathbf{PbSO_4 < Pt^{2+} < HClO}$
Order of increasing strength as reducing agent: $\mathbf{Cl_2 < Pt < (Pb + SO_4^{2-})}$

21.49 $S_2O_8^{2-}(aq) + 2\ I^-(aq) \rightarrow 2\ SO_4^{2-}(aq) + I_2(s)$
E^{o}_{cell} = 2.01 V - (0.53 V) = 1.48 V
Oxidizing agents: $S_2O_8^{2-} > I_2$; reducing agents: $I^- > SO_4^{2-}$
$Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ I^-(aq) \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l) + 3\ I_2(s)$
E^{o}_{cell} = 1.33 V - (0.53 V) = 0.80 V
Oxidizing agents: $Cr_2O_7^{2-} > I_2$; reducing agents: $I^- > Cr^{3+}$
$3\ S_2O_8^{2-}(aq) + 2\ Cr^{3+}(aq) + 7\ H_2O(l) \rightarrow 6\ SO_4^{2-}(aq) + Cr_2O_7^{2-}(aq) + 14\ H^+(aq)$
E^{o}_{cell} = 2.01 V - (1.33 V) = 0.68 V
Oxidizing agents: $S_2O_8^{2-} > Cr_2O_7^{2-}$; reducing agents: $Cr^{3+} > SO_4^{2-}$
Oxidizing agents: $S_2O_8^{2-} > Cr_2O_7^{2-} > I_2$; reducing agents: $I^- > Cr^{3+} > SO_4^{2-}$

21.50 Metal A + Metal B salt → solid colored product on metal A
Conclusion: Product is solid metal B. A is better reducing agent than B.
Metal B + acid → gas bubbles
Conclusion: Product is H_2 gas produced as result of reduction of H^+. B is better reducing agent than acid.
Metal A + Metal C salt → no reaction
Conclusion: 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 $\mathbf{H_2}$ bubbles**.
The order of strength of reducing agents is: **C > A > B**.

21.51 a) **Copper** metal is coating the iron.

b) The oxidizing agent is **Cu^{2+}** and the reducing agent is **Fe**.

c) Yes, this reaction, being spontaneous, may be made into a voltaic cell.

d) $Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$

e)
$$\begin{aligned} E^{o}_{cell} &= E^{\circ}_{Cu^{2+}} - E^{\circ}_{Fe^{2+}} \\ &= 0.34\text{ V} - (-0.44\text{ V}) \\ &= 0.78\text{ V} \end{aligned}$$

21.52 $E_{\text{cell}} = -\dfrac{0.0592\text{ V}}{n}\log\left(\dfrac{Q}{K}\right)$ and $\Delta G = -nFE_{\text{cell}}$

a) When $Q / K < 1$, $E_{\text{cell}} > 0$ and $\Delta G < 0$.
When $Q / K = 1$, $E_{\text{cell}} = 0$ and $\Delta G = 0$.
When $Q / K > 1$, $E_{\text{cell}} < 0$ and $\Delta G > 0$.

b) Only when $Q / K < 1$ will the reaction proceed spontaneously and be able to do work.

21.53 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 $E_{\text{cell}} > 0$ (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, $E_{\text{cell}} = 0$.

c) E_{cell} and E^{o}_{cell} are related by the Nernst equation: $E_{\text{cell}} = E^{o}_{cell} - (RT / nF)\ln([A^{+}] / [B^{+}])$.
$E_{\text{cell}} = E^{o}_{cell}$ when $(RT / nF)\ln([A^{+}] / [B^{+}]) = 0$. This occurs when $\ln([A^{+}] / [B^{+}]) = 0$. Recall that $e^{0} = 1$, so **$[A^{+}]$ must equal $[B^{+}]$** for E_{cell} to equal E^{o}_{cell}.

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

21.54 a) Examine the Nernst equation: $E_{\text{cell}} = E^{o}_{cell} - \dfrac{2.303\text{ RT}}{nF}\log Q$

$$E_{\text{cell}} = \frac{2.303\text{ RT}}{nF}\log K - \frac{2.303\text{ RT}}{nF}\log Q$$

$$E_{\text{cell}} = \frac{2.303\text{ RT}}{nF}\left(\log\frac{K}{Q}\right) = -\frac{2.303\text{ RT}}{nF}\left(\log\frac{K}{Q}\right)$$

If $Q / K < 1$, E_{cell} will decrease with a decrease in cell temperature. If $Q / K > 1$, E_{cell} will increase (become less negative) with a decrease in cell temperature.

b) $E_{\text{cell}} = E^{o}_{cell} - \dfrac{2.303\text{ RT}}{nF}\log\dfrac{[\text{Active ion at anode}]}{[\text{Active ion at cathode}]}$

E_{cell} will decrease as the concentration of an active ion at the anode increases.

c) E_{cell} will increase as the concentration of an active ion at the cathode increases.

d) E_{cell} will increase as the pressure of a gaseous reactant in the cathode compartment increases.

21.55 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.

21.56 The equilibrium constant can be found by combining two equations: $\Delta G° = -nFE°$ and $\Delta G° = -RT \ln K$,

We get: $\ln K = \frac{nFE°}{RT}$ or $\log K = \frac{nE°}{0.0592}$

a) $E^o_{cell} = E^o_{cathode} - E^o_{anode}$ = 0.80 V - (-0.25 V) = 1.05 V; 2 electrons are transferred.

$$\log K = \frac{nE°}{0.0592} = \frac{2(1.05\ \text{V})}{0.0592\ \text{V}} = 35.47297 \text{ (unrounded)}$$

$K = 2.97146 \times 10^{35}$ = $\mathbf{3 \times 10^{35}}$

b) E^o_{cell} = -0.74 V - (-0.44 V) = -0.30 V; 6 electrons are transferred.

$$\log K = \frac{nE°}{0.0592} = \frac{6(-0.30\ \text{V})}{0.0592\ \text{V}} = -30.4054 \text{ (unrounded)}$$

$K = 3.9318 \times 10^{-31}$ = $\mathbf{4 \times 10^{-31}}$

21.57 a) $2\ Al(s) + 3\ Cd^{2+}(aq) \rightarrow 2\ Al^{3+}(aq) + 3\ Cd(s)$ n = 6

E^o_{cell} $= E°_{Cd^{2+}} - E°_{Al^{3+}}$
= -0.40 V - (-1.66 V)
= 1.26 V

$$\log K = \frac{nE°}{0.0592} = \frac{6(1.26\ \text{V})}{0.0592\ \text{V}} = 130.7432 \text{ (unrounded)}$$

$K = 5.5360 \times 10^{130}$ = $\mathbf{6 \times 10^{130}}$

b) $I_2(s) + 2\ Br^-(aq) \rightarrow Br_2(l) + 2\ I^-(aq)$ n = 2

E^o_{cell} $= E°_{I_2} - E°_{Br_2}$
= 0.53 V - (1.07 V)
= -0.54 V

$$\log K = \frac{nE°}{0.0592} = \frac{2(-0.54\ \text{V})}{0.0592\ \text{V}} = -18.24324 \text{ (unrounded)}$$

$K = 5.7116 \times 10^{-19}$ = $\mathbf{6 \times 10^{-19}}$

21.58 a) E^o_{cell} = -1.18 V - 0.80 V = -1.98 V; 2 electrons transferred.

$$\log K = \frac{nE°}{0.0592} = \frac{2(-1.98\ \text{V})}{0.0592\ \text{V}} = -66.89189 \text{ (unrounded)}$$

$K = 1.2826554 \times 10^{-67}$ = $\mathbf{1 \times 10^{-67}}$

b) E^o_{cell} = 1.36 V - 1.07 V = 0.29 V; 2 electrons transferred.

$$\log K = \frac{nE°}{0.0592} = \frac{2(0.29\ \text{V})}{0.0592\ \text{V}} = 9.797297 \text{ (unrounded)}$$

$K = 6.2704253 \times 10^{9}$ = $\mathbf{6 \times 10^{9}}$

21.59 a) $2\ Cr(s) + 3\ Cu^{2+}(aq) \rightarrow 2\ Cr^{3+}(aq) + 3\ Cu(s)$ n = 6

E^o_{cell} $= E°_{Cu^{2+}} - E°_{Cr^{3+}}$
= 0.34 V - (-0.74 V)
= 1.08 V

$$\log K = \frac{nE°}{0.0592} = \frac{6(1.08\ \text{V})}{0.0592\ \text{V}} = 109.45945946 \text{ (unrounded)}$$

$K = 2.880444 \times 10^{109}$ = $\mathbf{3 \times 10^{109}}$

b) $Sn(s) + Pb^{2+}(aq) \rightarrow Sn^{2+}(aq) + Pb(s)$ n = 2

$E° = E°_{Pb^{2+}} - E°_{Sn^{2+}}$

$= -0.13\ V - (-0.14\ V)$

$= 0.01V$

$$\log K = \frac{nE°}{0.0592} = \frac{2(0.01\ V)}{0.0592\ V} = 0.3378 \text{ (unrounded)}$$

$K = 2.1767 = \mathbf{2}$

21.60 Substitute J / C for V.

a) $\Delta G° = -nFE° = -(2\text{ mol e}^-)(96485\text{ C / mol e}^-)(1.05\text{ J / C}) = -2.026185 \times 10^5 = \mathbf{-2.03 \times 10^5\ J}$

b) $\Delta G° = -nFE° = -(6\text{ mol e}^-)(96485\text{ C / mol e}^-)(-0.30\text{ J / C}) = 1.73673 \times 10^5 = \mathbf{1.73 \times 10^5\ J}$

21.61 Substitute J / C for V.

a) $\Delta G° = -nFE° = -(6\text{ mol e}^-)(96485\text{ C / mol e}^-)(1.26\text{ J / C}) = -7.294266 \times 10^5 = \mathbf{-7.29 \times 10^5\ J}$

b) $\Delta G° = -nFE° = -(2\text{ mol e}^-)(96485\text{ C / mol e}^-)(-0.54\text{ J / C}) = 1.042038 \times 10^5 = \mathbf{1.0 \times 10^5\ J}$

21.62 Substitute J / C for V.

a) $\Delta G° = -nFE° = -(2\text{ mol e}^-)(96485\text{ C / mol e}^-)(-1.98\text{ J / C}) = 3.820806 \times 10^5 = \mathbf{-3.82 \times 10^5\ J}$

b) $\Delta G° = -nFE° = -(2\text{ mol e}^-)(96485\text{ C / mol e}^-)(0.29\text{ J / C}) = -5.59613 \times 10^4 = \mathbf{-5.6 \times 10^4\ J}$

21.63 Substitute J / C for V.

a) $\Delta G° = -nFE° = -(6\text{ mol e}^-)(96485\text{ C / mol e}^-)(1.08\text{ J / C}) = -6.252228 \times 10^5 = \mathbf{-6.25 \times 10^5\ J}$

b) $\Delta G° = -nFE° = -(2\text{ mol e}^-)(96485\text{ C / mol e}^-)(0.01\text{ J / C}) = -1.9297 \times 10^3 = \mathbf{-2 \times 10^3\ J}$

21.64 Find $\Delta G°$ from the fact that $\Delta G° = -RT \ln K$. Then use $\Delta G°$ value to find E^o_{cell}, and $E°$ from $\Delta G° = -nFE°$.

T = (273 + 25)K = 298 K

$\Delta G° = -RT \ln K = -(8.314\text{ J/mol•K})(298\text{ K}) \ln(5.0 \times 10^3) = -2.1101959 \times 10^4 = \mathbf{-2.1 \times 10^4\ J}$

$E° = -\Delta G° / nF = -(-2.1101959 \times 10^4\text{ J}) / (1\text{ mol e}^-)(96485\text{ C / mol e}^-)[V / (J / C)] = 0.218707 = \mathbf{0.22\ V}$

21.65 Find $\Delta G°$ from the fact that $\Delta G° = -RT \ln K$. Then use $\Delta G°$ value to find E^o_{cell}, and $E°$ from $\Delta G° = -nFE°$.

T = (273 + 25)K = 298 K

$\Delta G° = -RT \ln K = -(8.314\text{ J/mol•K})(298\text{ K}) \ln(5.0 \times 10^{-6}) = 3.0241423 \times 10^4 = \mathbf{3.0 \times 10^4\ J}$

$E° = -\Delta G° / nF = -(3.0241423 \times 10^4\text{ J}) / (1\text{ mol e}^-)(96485\text{ C / mol e}^-)[V / (J / C)] = -0.31343 = \mathbf{-0.31\ V}$

21.66 Use $\log K = \frac{nE_{cell}°}{0.0592}$ and $\Delta G° = -nFE°$. T = (273 + 25)K = 298 K

$E^o_{cell} = (0.0592 / n) \log K = (0.0592 / 2) \log 75 = 0.055501813 = \mathbf{0.056\ V}$

$\Delta G° = -RT \ln K = -(8.314\text{ J/mol•K})(298\text{ K}) \ln(75) = -1.0696887 \times 10^4 = \mathbf{-1.1 \times 10^4\ J}$

21.67 Use $\log K = \frac{nE_{cell}°}{0.0592}$ and $\Delta G° = -nFE°$. T = (273 + 25)K = 298 K

$E^o_{cell} = (0.0592 / n) \log K = (0.0592 / 2) \log 0.075 = -0.033298 = \mathbf{-0.033\ V}$

$\Delta G° = -RT \ln K = -(8.314\text{ J/mol•K})(298\text{ K}) \ln(0.075) = 6.4175734 \times 10^3 = \mathbf{6.4 \times 10^3\ J}$

21.68 The cell reaction is: $Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2\ H^+(aq)$

$$E^o_{cell} = E^o_{Cu^{2+}} - E^o_{H^+}$$
$$= 0.34\ V - 0.00\ V$$
$$= 0.34\ V$$

$$E_{cell} = E^o_{cell} - \frac{0.0592}{n} \log \frac{\left[H^+\right]^2}{\left[Cu^{2+}\right]\left[H_2\right]}$$

For a standard hydrogen electrode $[H^+] = 1.0\ M$ and $[H_2] = 1.0$ atm

$$0.25\ V = 0.34\ V - \frac{0.0592}{2} \log \frac{1.0}{\left[Cu^{2+}\right]1.0}$$

$$(0.25\ V - 0.34\ V)\ (-2 / 0.0592) = \log \frac{1.0}{\left[Cu^{2+}\right]1.0} = 3.04054 \text{ (unrounded)}$$

$[Cu^{2+}] = 9.1087755 \times 10^{-4} = \mathbf{9 \times 10^{-4}}\ \boldsymbol{M}$

21.69 The cell reaction is: $Pb^{2+}(aq) + Mn(s) \rightarrow Pb(s) + Mn^{2+}(aq)$

$$E^o_{cell} = E°_{Pb^{2+}} - E°_{Mn^{2+}}$$
$$= -0.13\ V - (-1.18\ V)$$
$$= 1.05\ V$$

$$E_{cell} = E^o_{cell} - \frac{0.0592}{n} \log \frac{\left[Mn^{2+}\right]}{\left[Pb^{2+}\right]}$$

$$0.42\ V = 1.05\ V - \frac{0.0592}{2} \log \frac{[1.3]}{\left[Pb^{2+}\right]}$$

$$(0.42\ V - 1.05\ V)\ (-2 / 0.0592) = \log \frac{[1.3]}{\left[Pb^{2+}\right]} = 21.28378 \text{ (unrounded)}$$

$[Pb^{2+}] = 6.7633142 \times 10^{-22} = \mathbf{7 \times 10^{-22}}\ \boldsymbol{M}$

21.70 The spontaneous reaction (voltaic cell) is $Ni^{2+}(aq) + Co(s) \rightarrow Ni(s) + Co^{2+}(aq)$ with

$E^o_{cell} = -0.25\ V - (-0.28\ V) = 0.03\ V$

a) Use the Nernst equation: $E_{cell} = E^o_{cell} - (0.0592\ V / n) \log Q$

$E_{cell} = 0.03\ V - (0.0592\ V / 2) \log ([Co^{2+}] / [Ni^{2+}])$

$= 0.03\ V - (0.0592\ V / 2) \log (0.20\ M / 0.80\ M)$

$= 0.047820975\ V = \mathbf{0.05\ V}$

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

$[Co^{2+}] = 0.20\ M + x$ and $[Ni^{2+}] = 0.80\ M - x$

$0.03\ V = 0.03\ V - (0.0592\ V / 2) \log [(0.20 + x) / (0.80 - x)]$

$x = 0.20$

$[Ni^{2+}] = 0.80 - 0.20 = \mathbf{0.60}\ \boldsymbol{M}$

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

$0.00\ V = 0.03\ V - (0.0592\ V / 2) \log [(0.20 + x) / (0.80 - x)]$

$x = 0.711629955$ (unrounded)

$[Co^{2+}] = 0.20 + 0.711629955 = 0.911629955 = \mathbf{0.91}\ \boldsymbol{M}$

$[Ni^{2+}] = 0.80 - 0.711629955 = 0.088370044 = \mathbf{0.09}\ \boldsymbol{M}$

21.71 The spontaneous reaction (voltaic cell) is $Cd^{2+}(aq) + Mn(s) \rightarrow Cd(s) + Mn^{2+}(aq)$ with

E^o_{cell} = -0.40 V - (-1.18 V) = 0.78 V.

a) Use the Nernst equation: $E_{cell} = E^o_{cell}$ - (0.0592 V / n) log *Q*.

E_{cell} = 0.78 V - (0.0592 V / 2) log ($[Mn^{2+}]$ / $[Cd^{2+}]$)

= 0.78 V - (0.0592 V / 2) log (0.090 *M* / 0.060 *M*)

= 0.774787698 V = **0.77 V**

b) For the $[Cd^{2+}]$ to decrease from 0.060 *M* to 0.050 *M*, a change of 0.010 *M*, the $[Ni^{2+}]$ must increase by the same amount, from 0.090 *M* to 0.100 *M*.

E_{cell} = 0.78 V - (0.0592 V / 2) log (0.100 *M* / 0.050 *M*)

= 0.771089512 V = **0.77 V**

c) Increase the manganese and decrease the cadmium by equal amounts.

0.055 V = 0.78 V - (0.0592 V / 2) log ($[Mn^{2+}]$ / $[Cd^{2+}]$)

($[Mn^{2+}]$ / $[Cd^{2+}]$) = 3.1134596×10^{24} (unrounded)

$[Mn^{2+}] + [Cd^{2+}]$ = 0.150 *M*

$[Cd^{2+}]$ = 4.81779×10^{-26} *M* (unrounded)

$[Mn^{2+}]$ = 0.150 *M* - $[Cd^{2+}]$ = **0.150 *M***

d) At equilibrium E_{cell} = 0.00.

0.00 V = 0.78 V - (0.0592 V / 2) log ($[Mn^{2+}]$ / $[Cd^{2+}]$)

($[Mn^{2+}]$ / $[Cd^{2+}]$) = 2.2456979×10^{26} (unrounded)

$[Mn^{2+}] + [Cd^{2+}]$ = 0.150 *M*

$[Cd^{2+}]$ = $6.6794377 \times 10^{-28}$ = **7×10^{-28} *M***

$[Mn^{2+}]$ = 0.150 *M* - $[Cd^{2+}]$ = **0.150 *M***

21.72 The overall cell reaction proceeds to increase the 0.10 *M* H^+ concentration and decrease the 2.0 *M* H^+ concentration. Therefore, half-cell **A is the anode** because it has the lower concentration.

$$Q \text{ for the cell equals } \frac{\left[H^+\right]^2_{anode}\ P_{H(cathode)}}{\left[H^+\right]^2_{cathode}\ P_{H(anode)}} = \frac{(0.10)^2(0.50)}{(2.0)^2(0.90)} = 0.001388889 \text{ (unrounded)}$$

E_{cell} = 0.00 V - (0.0592 V / 2) log (0.001388889) = 0.084577 = **0.085 V**

21.73 $Sn^{2+}(0.87\ M) \rightarrow Sn^{2+}(0.13\ M)$

Half-cell **B is the cathode**.

E_{cell} = 0.00V - (0.0592 V / 2) log (0.13 / 0.87) = 0.024437 = **0.024 V**

21.74 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.

21.75 The electrodes are separated by an electrolyte paste, which for the ordinary dry cell battery contains $ZnCl_2$, NH_4Cl, MnO_2, starch, graphite, and water.

21.76 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. 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.) 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.

21.77 a) Alkaline batteries = (6.0 V) (1 alkaline battery / 1.5 V) = **4 alkaline batteries**.

b) Voltage = (6 Ag batteries) (1.6 V / Ag battery) = **9.6 V**

c) The usual 12 volt car battery consists of six 2 volt cells. If two cells are shorted only four cells remain.

Voltage = (4 cells) (2 V / cell) = **8 V**

21.78 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.

21.79 Bridge supports rust more rapidly at the water line due to the presence of large concentrations of both O_2 and H_2O.

21.80 Chromium, like iron, will corrode through the formation of a metal oxide. Unlike the iron oxide, which is relatively porous and easily cracks, the chromium oxide forms a protective coating, preventing further corrosion.

21.81 Sacrificial anodes are metals with $E°$ less than that for iron, -0.44 V, so they are more easily oxidized than iron.
a) $E°$(aluminum) = -1.66. 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 value is too high.
e) $E°$(nickel) = -0.25 V. No, nickel is inappropriate as a sacrificial anode because its 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.

21.82 a) Oxidation occurs at the **left** electrode (anode).
b) Elemental M forms at the **right** electrode (cathode).
c) Electrons are being released by ions at the **left** electrode.
d) Electrons are entering the cell at the **right** electrode.

21.83 $3\ Cd^{2+}(aq) + 2\ Cr(s) \rightarrow 3\ Cd(s) + 2\ Cr^{3+}(aq)$

$$E^o_{cell} = -0.40\ V - (-0.74\ V) = 0.34\ V$$

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.

21.84 The $E_{\text{half-cell}}$ values are different than the $E°_{\text{half-cell}}$ values because in pure water, the $[H^+]$ and $[OH^-]$ are 1.0×10^{-7} *M* rather than the standard-state value of 1 *M*.

21.85 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 to the +5 state.

21.86 Due to the phenomenon of overvoltage, the products predicted from a comparison of electrode potentials are not always the actual products. When gases (such as $H_2(g)$ and $O_2(g)$) are produced at metal electrodes, there is an overvoltage of about 0.4 to 0.6V more than the electrode potential indicates. Due to this, if H_2 or O_2 is the **expected** product, another species may be the true product.

21.87 a) At the anode, bromide ions are oxidized to form bromine (**Br_2**).
b) At the cathode, sodium ions are reduced to form sodium metal (**Na**).

21.88 a) At the negative electrode (cathode) barium ions are reduced to form barium metal (**Ba**).
b) At the positive electrode (anode), iodide ions are oxidized to form iodine (**I_2**).

21.89 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 I_2** 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).

21.90 Liquid strontium (**Sr**) forms at the negative electrode, and gaseous bromine (**Br_2**) forms at the positive electrode.

21.91 **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.

21.92 Liquid calcium forms at the negative electrode and chlorine gas forms at the positive electrode.

21.93 **Copper and bromine** can be prepared by electrolysis of their aqueous salts because their half-cell potentials are more positive than the potential for the electrolysis of water with overvoltage, about 1 V for reduction of water and about 1.4 V for the oxidation of water.

21.94 Strontium is too electropositive to form from the electrolysis of an aqueous solution. The elements that electrolysis will separate from an aqueous solution are **gold, tin, and chlorine**.

21.95 **Iodine, zinc, and silver** can be prepared by electrolysis of their salt solutions because water is less readily oxidized than iodide ions and less readily reduced than zinc ions and silver ions.

21.96 Electrolysis will separate both **iron and cadmium** from a aqueous solution.

21.97 a) Possible oxidations:

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

$2\ F^- \rightarrow F_2(g) + 2\ e^-$ $-E° = -2.87$ V

The oxidation of water produces oxygen gas (**O_2**), and hydronium ions (**H_3O^+**) at the anode.

Possible reductions:

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

$Li^+(aq) + e^- \rightarrow Li(s)$ $E° = -3.05$ V

The reduction of water produces **H_2** gas and **OH^-** at the cathode.

b) Possible oxidations:

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

The oxidation of water produces oxygen gas (**O_2**), and hydronium ions (**H_3O^+**) at the anode.

Possible reductions:

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

$Sn^{2+}(aq) + 2\ e^- \rightarrow Sn(s)$ $E° = -0.14$ V

$SO_4^{2-}(aq) + 4\ H^+(aq) + 2\ e^- \rightarrow SO_2(g) + 2\ H_2O(l)$ $E = -0.63$ 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} *M*.

$E = 0.20\ V - (0.0592 / 2) \log [1 / (1 \times 10^{-7})^4] = -0.6288 = -0.63\ V$

The most easily reduced ion is Sn^{2+}, so **tin metal** forms at the cathode.

21.98 a) Solid zinc (**Zn**) forms at the cathode and liquid bromine (**Br_2**) forms at the anode.

b) Solid copper (**Cu**) forms at the cathode and both oxygen gas (**O_2**) and aqueous hydrogen ions (**H^+**) form at the anode.

21.99 a) Possible oxidations:

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

The oxidation of water produces oxygen gas (**O_2**), and hydronium ions (**H_3O^+**) at the anode.

Possible reductions:

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

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

$NO_3^-(aq) + 4\ H^+(aq) + 3\ e^- \rightarrow NO(g) + 2\ H_2O(l)$ $E = +0.13$ 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} *M*.

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

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

b) Possible oxidations:

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

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

The oxidation of chloride ions to produce **chlorine gas** occurs at the anode.

Possible reductions:

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

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

It is easier to reduce water than to reduce manganese ions, so **hydrogen gas and hydroxide ions** form at the cathode.

21.100 a) Solid iron (**Fe**) forms at the cathode, and solid iodine (**I_2**) forms at the anode.
b) Gaseous hydrogen (**H_2**) and aqueous hydroxide ion (**OH^-**) form at the cathode, while gaseous oxygen (**O_2**) and aqueous hydrogen ions (**H^+**) form at the anode.

21.101 $Mg^{2+} + 2\ e^- \rightarrow Mg$

a) (35.6 g Mg) (1 mol Mg / 24.31 g Mg) (2 mol e^- / 1 mol Mg) = 2.92883587 = **2.93 mol e^-**

b) (2.92883587 mol e^-) (96485 C / mol e^-) = 2.8258872 x 10^5 = **2.83 x 10^5 coulombs**

c) $$\left(\frac{2.8258872 \text{ x } 10^5 \text{ C}}{2.50 \text{ h}}\right)\left(\frac{1 \text{ h}}{3600 \text{ s}}\right)\left(\frac{\text{A}}{\text{C}/\text{s}}\right) = 31.3987 = \mathbf{31.4\ A}$$

21.102 $Na^+ + 1\ e^- \rightarrow Na$

a) (215 g Na) (1 mol Na / 22.99 g Na) (1 mol e^- / 1 mol Na) = 9.351892127 = **9.35 mol e^-**

b) (9.351892127 mol e^-) (96485 C / mol e^-) = 9.0231731 x 10^5 = **9.02 x 10^5 coulombs**

c) $$\left(\frac{9.0231731 \text{ x } 10^5 \text{C}}{9.50 \text{ h}}\right)\left(\frac{1 \text{ h}}{3600 \text{ s}}\right)\left(\frac{\text{A}}{\text{C}/\text{s}}\right) = 26.383547 = \mathbf{26.4\ A}$$

21.103 $Ra^{2+} + 2\ e^- \rightarrow Ra$

In the reduction of radium ions, Ra^{2+}, to radium metal, the transfer of two electrons occurs.

$$(215 \text{ C})\left(\frac{1 \text{ mol e}^-}{96485 \text{ C}}\right)\left(\frac{1 \text{ mol Ra}}{2 \text{ mol e}^-}\right)\left(\frac{226 \text{ g Ra}}{1 \text{ mol Ra}}\right) = 0.25180 = \mathbf{0.282\ g\ Ra}$$

21.104 $Al^{3+} + 3\ e^- \rightarrow Al$

In the reduction of aluminum ions, Al^{3+}, to aluminum metal the transfer of three electrons occurs.

$$(305 \text{ C})\left(\frac{1 \text{ mol e}^-}{96485 \text{ C}}\right)\left(\frac{1 \text{ mol Al}}{3 \text{ mol e}^-}\right)\left(\frac{26.98 \text{ g Al}}{1 \text{ mol Al}}\right) = 0.028428944 = \mathbf{0.0284\ g\ Al}$$

21.105 $Zn^{2+} + 2\ e^- \rightarrow Zn$

$$\text{Time} = (85.5 \text{ g Zn})\left(\frac{1 \text{ mol Zn}}{65.41 \text{ g Zn}}\right)\left(\frac{2 \text{ mol e}^-}{1 \text{ mol Zn}}\right)\left(\frac{96485 \text{ C}}{1 \text{ mol e}^-}\right)\left(\frac{1}{23.0 \text{ A}}\right)\left(\frac{1 \text{ A}}{\text{C}/\text{s}}\right) = 1.0966901 \text{ x } 10^4 = \mathbf{1.10 \text{ x } 10^4\ seconds}$$

21.106 $Ni^{2+} + 2\ e^- \rightarrow Ni$

$$\text{Time} = (1.63 \text{ g Ni})\left(\frac{1 \text{ mol Ni}}{58.69 \text{ g Ni}}\right)\left(\frac{2 \text{ mol e}^-}{1 \text{ mol Ni}}\right)\left(\frac{96485 \text{ C}}{1 \text{ mol e}^-}\right)\left(\frac{1}{13.7 \text{ A}}\right)\left(\frac{1 \text{ A}}{\text{C}/\text{s}}\right) = 391.1944859 = \mathbf{391\ seconds}$$

21.107 a) The sodium sulfate makes the water conductive, so the current will flow through the water to complete the circuit, increasing the rate of electrolysis. Pure water, which contains very low (10^{-7} *M*) concentrations of H^+ and OH^-, conducts electricity very poorly.
b) The reduction of H_2O has a more positive half-potential than the reduction of Na^+; the oxidation of H_2O is the only reduction 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-}.

21.108 Iodine is formed first since its oxidation potential ($E^\circ_{ox}(I^-)$) is more positive than the oxidation potential ($E^\circ_{ox}(Br^-)$) of bromide.

21.109 $Zn^{2+} + 2\ e^- \rightarrow Zn$

$$\text{Mass} = (0.755\ \text{A})\left(\frac{\text{C}/\text{s}}{\text{A}}\right)\left(\frac{3600\ \text{s}}{1\ \text{h}}\right)\left(\frac{24\ \text{h}}{1\ \text{day}}\right)(2.00\ \text{day})\left(\frac{1\ \text{mol e}^-}{96485\ \text{C}}\right)\left(\frac{1\ \text{mol Zn}}{2\ \text{mol e}^-}\right)\left(\frac{65.41\ \text{g Zn}}{1\ \text{mol Zn}}\right)$$

= 44.222678 = **44.2 g Zn**

21.110 $Mn^{2+}(aq) + 2\ H_2O(l) \rightarrow MnO_2(s) + 4\ H^+(aq) + 2\ e^-$

$$\text{Time} = (1.00\ \text{kg MnO}_2)\left(\frac{10^3\ \text{g}}{1\ \text{kg}}\right)\left(\frac{1\ \text{mol MnO}_2}{86.94\ \text{g MnO}_2}\right)\left(\frac{2\ \text{mol e}^-}{1\ \text{mol MnO}_2}\right)\left(\frac{96485\ \text{C}}{1\ \text{mol e}^-}\right)\left(\frac{1}{25.0\ \text{A}}\right)\left(\frac{\text{A}}{\text{C}/\text{s}}\right)\left(\frac{1\ \text{h}}{3600\ \text{s}}\right)$$

= 24.66196 = **24.7 hours**

The MnO_2 product forms at the **anode**, since the half-reaction is an oxidation.

21.111 The half-reaction is: $2\ H^+(aq) + 2\ e^- \rightarrow H_2(g)$
a) First, find the moles of hydrogen gas.

$$n = PV / RT = \frac{(10.0\ \text{atm})(2.5 \times 10^6\ \text{L})}{\left(0.0821\frac{\text{L} \bullet \text{atm}}{\text{mol} \bullet \text{K}}\right)((273 + 25)\text{K})} = 1.0218345 \times 10^6\ \text{mol H}_2\ \text{(unrounded)}$$

Then, find the coulombs knowing that there are two electrons transferred per mol of H_2.

$$(1.0218345 \times 10^6\ \text{mole H}_2)\left(\frac{2\ \text{mol e}^-}{1\ \text{mol H}_2}\right)\left(\frac{96485\ \text{C}}{1\ \text{mol e}^-}\right) = 1.9718341 \times 10^{11} = \mathbf{2.0 \times 10^{11}\ coulombs}$$

b) Remember that 1 V equals 1 J / C.
(1.24 J / C) (1.9718341 x 10^{11} C) = 2.4450743 x 10^{11} = **2.4 x 10^{11} J**
c) (2.4450743 x 10^{11} J) (1 kJ / 10^3 J) (1 kg / 4.0 x 10^4 kJ) = 6.1126858 x 10^3 = **6.1 x 10^3 kg**

21.112 a) The half reactions are:
$H_2O(l) + Zn(s) \rightarrow ZnO(s) + 2\ H^+(aq) + 2\ e^-$
and $2\ e^- + 2\ H^+(aq) + MnO_2(s) \rightarrow Mn(OH)_2(s)$.
2 moles of electrons flow per mole of reaction.

$$\text{b) Mass of MnO}_2 = (2.50\ \text{g Zn})\left(\frac{1\ \text{mol Zn}}{65.41\ \text{g Zn}}\right)\left(\frac{1\ \text{mol MnO}_2}{1\ \text{mol Zn}}\right)\left(\frac{86.94\ \text{g MnO}_2}{1\ \text{mol MnO}_2}\right) = 3.322886 = \mathbf{3.32\ g\ MnO_2}$$

$$\text{Mass of H}_2\text{O} = (2.50\ \text{g Zn})\left(\frac{1\ \text{mol Zn}}{65.41\ \text{g Zn}}\right)\left(\frac{1\ \text{mol H}_2\text{O}}{1\ \text{mol Zn}}\right)\left(\frac{18.02\ \text{g H}_2\text{O}}{1\ \text{mol H}_2\text{O}}\right) = 0.6887326 = \mathbf{0.689\ g\ H_2O}$$

c) Total mass of reactants = 2.50 g Zn + 3.322886 g MnO_2 + 0.6887326 g H_2O = 6.5116186 = **6.51 g**

$$\text{d) Charge} = (2.50\ \text{g Zn})\left(\frac{1\ \text{mol Zn}}{65.41\ \text{g Zn}}\right)\left(\frac{2\ \text{mol e}^-}{1\ \text{mol Zn}}\right)\left(\frac{96485\ \text{coulombs}}{1\ \text{mol e}^-}\right) = 7.3754013 \times 10^3 = \mathbf{7.38 \times 10^3\ coulombs}$$

e) An alkaline battery consists of more than just reactants. The case, electrolyte paste, cathode, absorbent, and unreacted reactants (less than 100% efficient) also contribute to the mass of an alkaline battery.

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

Mass Ag = 1.8016 g - 1.7854 g = 0.0162 g Ag produced

$$\text{Coulombs} = (0.0162\ \text{g Ag})\left(\frac{1\ \text{mol Ag}}{107.9\ \text{g Ag}}\right)\left(\frac{1\ \text{mol e}^{-}}{1\ \text{mol Ag}}\right)\left(\frac{96485\ \text{coulombs}}{1\ \text{mol e}^{-}}\right) = 14.48616 = \mathbf{14.5\ coulombs}$$

21.114 From the current 70.0% of the moles of product will be copper and 30.0% zinc. Assume a current of exactly 100 coulombs. The amount of current used to generate copper would be (70.0% / 100%) (100 C) = 70.0 C, and the amount of current used to generate zinc would be (30.0% / 100%) (100 C) = 30.0 C.

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

$$\text{Mass copper} = (70.0\ \text{C})\left(\frac{1\ \text{mol e}^{-}}{96485\ \text{C}}\right)\left(\frac{1\ \text{mol Cu}}{2\ \text{mol e}^{-}}\right)\left(\frac{63.55\ \text{g Cu}}{1\ \text{mol Cu}}\right) = 0.023052806\ \text{g Cu (unrounded)}$$

$$\text{Mass zinc} = (30.0\ \text{C})\left(\frac{1\ \text{mol e}^{-}}{96485\ \text{C}}\right)\left(\frac{1\ \text{mol Zn}}{2\ \text{mol e}^{-}}\right)\left(\frac{65.41\ \text{g Zn}}{1\ \text{mol Zn}}\right) = 0.010168938\ \text{g Zn (unrounded)}$$

$$\text{Mass \% copper} = \left(\frac{0.023052806\ \text{g Cu}}{(0.023052806\ +\ 0.010168938)\text{g Sample}}\right) \text{x } 100\% = 69.3907 = \mathbf{69.4\%\ Cu}$$

21.115

	Voltaic Cell	Electrolytic Cell
a)	ΔG is negative	ΔG is positive
b)	Oxidation	Oxidation
c)	Reduction	Reduction
d)	(-)	(+)
e)	Anode	Anode

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

a) Moles of gold plated = (volume of gold) (density of gold) (1 / molar mass of gold)

The volume of the gold is the volume of a cylinder (see the inside back cover of the text)

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

$$(\pi)\left(5.00\ \text{cm}/2\right)^2 (0.20\ \text{mm})\left(\frac{10^{-3}\ \text{m}}{1\ \text{mm}}\right)\left(\frac{1\ \text{cm}}{10^{-2}\ \text{m}}\right)\left(\frac{19.3\ \text{g Au}}{\text{cm}^3}\right)\left(\frac{1\ \text{mol Au}}{197.0\ \text{g Au}}\right) = 0.03847255\ \text{mol Au (unrounded)}$$

$$\text{Time} = (0.03847255\ \text{mol Au})\left(\frac{3\ \text{mol e}^{-}}{1\ \text{mol Au}}\right)\left(\frac{96485\ \text{C}}{1\ \text{mol e}^{-}}\right)\left(\frac{\text{A}}{\text{C}/\text{s}}\right)\left(\frac{1}{0.010\ \text{A}}\right)\left(\frac{1\ \text{h}}{3600\ \text{s}}\right)\left(\frac{1\ \text{day}}{24\ \text{h}}\right)$$

$$= 12.88897 = \mathbf{13\ days}$$

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.

Time = (4) (12.88897 days) = 51.5558887 = **5.2 x 10^1 days**

c) Start by multiplying the moles of gold from part (a) by four to get the moles for the earrings. Convert this moles to grams, then to troy ounces, and finally to dollars.

$$\text{Cost} = (4)(0.03847255\ \text{mol Au})\left(\frac{197.0\ \text{g Au}}{1\ \text{mol Au}}\right)\left(\frac{1\ \text{Troy Ounce}}{31.10\ \text{g}}\right)\left(\frac{\$320}{\text{Troy Ounce}}\right) = 311.936917 = \mathbf{\$310}$$

21.117 a) The half-reaction is: $2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4\ e^-$

Determine the moles of oxygen from the ideal gas equation. Use the half-reaction and the current to convert the moles of oxygen to time.

$$n = PV / RT = \left(\frac{(99.8\ \text{kPa})(10.0\ \text{L})}{\left(0.0821 \frac{\text{L} \bullet \text{atm}}{\text{mol} \bullet \text{K}}\right)((273 + 28)\text{K})}\right)\left(\frac{1\ \text{atm}}{1.01325\ \text{x}\ 10^5\ \text{Pa}}\right)\left(\frac{10^3\ \text{Pa}}{1\ \text{kPa}}\right)$$

$= 0.398569696$ mol O_2 (unrounded)

$$\text{Time} = (0.398569696\ \text{mol}\,O_2)\left(\frac{4\ \text{mol e}^-}{1\ \text{mol}\ O_2}\right)\left(\frac{96485\ \text{C}}{1\ \text{mol e}^-}\right)\left(\frac{\text{A}}{\text{C}/\text{s}}\right)\left(\frac{1}{1.3\ \text{A}}\right)\left(\frac{1\ \text{min}}{60\ \text{s}}\right)$$

$= 1.97210 \times 10^3 =$ **2.0×10^3 min**

b) The balanced chemical equation is: $2\ H_2O(l) \rightarrow 2\ H_2(g) + O_2(g)$

The moles of oxygen determined previously and this chemical equation leads to the mass of hydrogen.

Mass H_2 = (0.398569696 mol O_2) (2 mol H_2 / 1 mol O_2) (2.016 g H_2 / 1 mol H_2)

= 1.60703 = 1.61 g H_2

21.118 Corrosion is an oxidation process. This would be favored by the metal being in contact with the moist ground. To counteract this, electrons should flow into the rails and away from the overhead wire, so the overhead wire should be connected to the positive terminal.

21.119 The half-reactions and the cell reaction are:

$Zn(s) + 2\ OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2\ e^-$

$Ag_2O(s) + H_2O(l) + 2\ e^- \rightarrow 2\ Ag(s) + 2\ OH^-(aq)$

$Zn(s) + Ag_2O(s) \rightarrow ZnO(s) + 2\ Ag(s)$

The key is the moles of zinc. From the moles of zinc, the moles of electrons and the moles of Ag_2O may be found.

Moles Zn = (16.0 g Zn) (80% / 100%) (1 mol Zn / 65.41 g Zn) = 0.195688732 mol Zn (unrounded)

The 80% is assumed to have two significant figures.

$$\text{a) Time} = (0.195688732\ \text{mol Zn})\left(\frac{2\ \text{mol e}^-}{1\ \text{mol Zn}}\right)\left(\frac{96485\text{C}}{1\ \text{mol e}^-}\right)\left(\frac{\text{A}}{\text{C}/\text{s}}\right)\left(\frac{1\ \text{mA}}{10^{-3}\ \text{A}}\right)\left(\frac{1}{4.8\ \text{mA}}\right)\left(\frac{1\ \text{h}}{3600\ \text{s}}\right)\left(\frac{1\ \text{day}}{24\ \text{h}}\right)$$

= 91.054337 = **91 days**

$$\text{b) Mass Ag} = (0.195688732\ \text{mol Zn})\left(\frac{100\%}{80\%}\right)\left(\frac{2\ \text{mol Ag}^-}{1\ \text{mol Zn}}\right)\left(\frac{95\%}{100\%}\right)\left(\frac{107.9\ \text{g Ag}}{1\ \text{mol Ag}}\right) = 50.14768 = \textbf{50. g Ag}$$

c) Cost = (50.14768 g Ag) (1 troy oz / 31.10 g) ($5.50 g / troy oz) = 8.86856 = **$ 8.9**

21.120 $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

$$\text{Theoretical amount of copper} = (5.8\ \text{A})\left(\frac{\text{C}/\text{s}}{\text{A}}\right)\left(\frac{3600\ \text{s}}{1\ \text{h}}\right)(10\ \text{h})\left(\frac{1\ \text{mol e}^-}{96485\ \text{C}}\right)\left(\frac{1\ \text{mol Cu}}{2\ \text{mol e}^-}\right)\left(\frac{63.55\ \text{g Cu}}{1\ \text{mol Cu}}\right)$$

= 68.7632 g Cu (unrounded)

$$\text{Efficiency} = \left(\frac{\text{Actual Yield}}{\text{Theoretical Yield}}\right) \text{x}\ 100\% = \left(\frac{53.4\ \text{g Cu}}{68.7632\ \text{g Cu}}\right) \text{x}\ 100\% = 77.6578 = \textbf{78\%}$$

The final assumes that 10 hours has two significant figures.

21.121

	a) Molten Electrolysis	b) Aqueous Electrolysis
Anode product	$Cl_2(g)$	$Cl_2(g)$
Cathode product	$Na(l)$	$H_2(g)$ and $OH^-(aq)$
Species reduced	$Na^+(l)$	$H_2O(l)$
Species oxidized	$Cl^-(l)$	$Cl^-(aq)$

21.122 a) $E°$ for standard hydrogen electrode is 0.00 V, for Pb / Pb^{2+} -0.13 V and for Cu / Cu^{2+} 0.34. Cell with SHE and Pb / Pb^{2+}: E^o_{cell} = **0.13 V**

Cell with SHE and Cu / Cu^{2+}: E^o_{cell} = **0.34 V**

b) The anode (negative electrode) in cell with SHE and Pb / Pb^{2+} is **Pb**.

The anode in 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

$$Pb(s) + 2\ H^+(aq) \rightarrow Pb^{2+}(aq) + H_2(g)$$

$$E_{cell} = E^o_{cell} - (0.0592\ V / 2) \log ([Pb^{2+}]\ P_{H_2}\ /\ [H^+]^2)$$

Decreasing the concentration of lead ions gives a negative value for the term $(0.0592\ V / 2) \log ([Pb^{2+}]\ P_{H_2}\ /\ [H^+]^2)$.

When this negative value is subtracted from E^o_{cell}, cell potential **increases**.

d) The H^+ and the H_2 in the SHE are both one.

Cell reaction: $Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2\ H^+(aq)$

$$E_{cell} = 0.34\ V - (0.0592\ V / 2) \log ([H^+]^2 / [Cu^{2+}]\ P_{H_2})$$

$$= 0.34\ V - (0.0592\ V / 2) \log\{1 / (1 \times 10^{-16})\}$$

$$= -0.1336 = \mathbf{-0.13\ V}$$

21.123 a) $\text{Volume} = \left(2.0\ cm^2\right)\left(7.0 \times 10^{-6}\ m\right)\left(\dfrac{1\ cm}{10^{-2}\ m}\right) = \mathbf{0.0014\ cm^3}$

b) Mass = (0.0014 cm^3) (10.5 g Ag / 1 cm^3) = 0.0147 = **0.015 g**

c) $\text{Time} = \left(0.0147\ g\ Ag\right)\left(\dfrac{1\ mol\ Ag}{107.9\ g\ Ag}\right)\left(\dfrac{1\ mol\ e^-}{1\ mol\ Ag}\right)\left(\dfrac{96485\ C}{1\ mol\ e^-}\right)\left(\dfrac{A}{C/s}\right)\left(\dfrac{1\ mA}{10^{-3}\ A}\right)\left(\dfrac{1}{10.0\ mA}\right)\left(\dfrac{1\ min}{60\ s}\right)$

= 21.908 = **22 min**

d) $\text{Cost} = \left(0.0147\ g\ Ag\right)\left(\dfrac{1\ Troy\ Ounce}{31.10\ g\ Ag}\right)\left(\dfrac{\$5.50}{1\ Troy\ Ounce}\right)\left(\dfrac{100\ cents}{\$1}\right) = 0.2599678 = \mathbf{0.26\ ¢}$

21.124 The reduction of H_2O to H_2 and OH^- is easier than the reduction of Al^{3+} to Al.

21.125 The three steps equivalent to the overall reaction $M^+(aq) + e^- \rightarrow M(s)$ are

1) $M^+(aq) \rightarrow M^+(g)$ Energy is $-\Delta H_{hydration}$
2) $M^+(g) + e^- \rightarrow M(g)$ Energy is -IE or $-\Delta H_{ionization}$
3) $M(g) \rightarrow M(s)$ Energy is $-\Delta H_{atomization}$

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 $-\Delta H_{hydration}$ and -IE. The lithium ion has a much 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.

21.126 a) The half-reaction is: $Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$

$\text{Mass Cu} = \left(5.0\,A\right)\left(\dfrac{C/s}{A}\right)\left(\dfrac{3600\,s}{1\,h}\right)\left(1.25\,h\right)\left(\dfrac{1\ mol\ e^-}{96485\,C}\right)\left(\dfrac{1\ mol\ Cu}{2\ mol\ e^-}\right)\left(\dfrac{63.55\ g\ Cu}{1\ mol\ Cu}\right) = 7.40983 = \mathbf{7.4\ g\ Cu}$

b) Thickness = (7.40983 g Cu) (1 cm^3 / 8.95 g Cu) (1 / 50.0 cm^2) = 0.016558 = **0.017 cm**

21.127 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), 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.

21.128 Wherever the tin surface is scratched to expose the iron, the iron corrosion occurs more rapidly because iron is a better reducing agent (compare $E°$ values). An electrochemical cell is set up where iron becomes the anode and tin the cathode. A coating on the inside of the can separates the tin from the normally acidic contents, which would react with the tin and add an unwanted "metallic" taste.

21.129 a) Aluminum half-reaction: $Al^{3+}(aq) + 3\ e^- \rightarrow Al(s)$, so n = 3. Remember that 1 A = 1 C / s.

$$\text{Time} = (1000\ \text{kg Al})\left(\frac{10^3\ \text{g}}{1\ \text{kg}}\right)\left(\frac{1\ \text{mol Al}}{26.98\ \text{g Al}}\right)\left(\frac{3\ \text{mol e}^-}{1\ \text{mol Al}}\right)\left(\frac{96485\ \text{C}}{1\ \text{mol e}^-}\right)\left(\frac{\text{A}}{\text{C}/\text{s}}\right)\left(\frac{1}{100{,}000\ \text{A}}\right)$$

$= 1.0728502 \times 10^5 = \mathbf{1.073 \times 10^5\ s}$

The molar mass of aluminum limits the significant figures.

b) 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.

$$\left(1.0728502 \times 10^5\ \text{s}\right)\left(\frac{100{,}000\ \text{C}}{\text{s}}\right)\left(\frac{5.0\ \text{J}}{\text{C}}\right)\left(\frac{1\ \text{kJ}}{10^3\ \text{J}}\right)\left(\frac{1\ \text{kW}\bullet\text{h}}{3.6 \times 10^3\ \text{kJ}}\right) = 1.4900698 \times 10^4 = \mathbf{1.5 \times 10^4\ kW\bullet h}$$

c) From part (b), the 1.5×10^4 kW•h calculated is per 1000 kg of aluminum. Use the ratio of kW•h to mass to find kW•h / lb and then use efficiency and cost per kW•h to find cost per pound.

$$\text{Cost} = \left(\frac{1.4900698 \times 10^4\ \text{kW}\bullet\text{h}}{1000\ \text{kg Al}}\right)\left(\frac{1\ \text{kg}}{2.205\ \text{lb}}\right)\left(\frac{0.90\ \text{cents}}{1\ \text{kW}\bullet\text{h}}\right)\left(\frac{100\%}{90.\%}\right) = 6.757686 = \mathbf{6.8¢\ /\ lb\ Al}$$

21.130 a) Electrons flow **from magnesium bar to the iron pipe** since magnesium is more easily oxidized than iron.

b) The magnesium half-reaction is: $Mg(s) \rightarrow Mg^{2+}(aq) + 2\ e^-$

Current is charge per time. The mass of magnesium can give the total charge. Convert the mass of magnesium to moles of magnesium and multiplying by 2 moles of electrons produced for each mole of magnesium and by Faradays constant to convert the moles of electrons to coulombs of charge. For units of amps time must be in seconds, so convert the 8.5 years to seconds.

$$\text{Current} = \frac{\text{Charge}}{\text{Time}}$$

$$= \frac{(12\ \text{kg Mg})\left(\frac{10^3\ \text{g}}{1\ \text{kg}}\right)\left(\frac{1\ \text{mol Mg}}{24.31\ \text{g Mg}}\right)\left(\frac{2\ \text{mol e}^-}{1\ \text{mol Mg}}\right)\left(\frac{96485\ \text{C}}{\text{mol e}^-}\right)}{(8.5\ \text{yr})\left(\frac{365.25\ \text{days}}{1\ \text{yr}}\right)\left(\frac{24\ \text{h}}{1\ \text{days}}\right)\left(\frac{3600\ \text{s}}{1\ \text{h}}\right)}\left(\frac{\text{A}}{\text{C}/\text{s}}\right) = 0.35511 = \mathbf{0.36\ A}$$

21.131 Statement: metal D + hot water → reaction Conclusion: D reduces water.

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 would is 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**.

21.132 The half-reaction is: $Ca^{2+} + 2\ e^- \rightarrow Ca$

$$\text{Coulombs} = (10.0\ \text{g Ca})\left(\frac{1\ \text{mol Ca}}{40.08\ \text{g Ca}}\right)\left(\frac{2\ \text{mol e}^-}{1\ \text{mol Ca}}\right)\left(\frac{96485\ \text{C}}{1\ \text{mol e}^-}\right) = 4.8146207 \times 10^4 = \mathbf{4.81 \times 10^4\ coulombs}$$

$$\text{Time} = (10.0\ \text{g Ca})\left(\frac{1\ \text{mol Ca}}{40.08\ \text{g Ca}}\right)\left(\frac{2\ \text{mol e}^-}{1\ \text{mol Ca}}\right)\left(\frac{96485\ \text{C}}{1\ \text{mol e}^-}\right)\left(\frac{\text{A}}{\text{C}/\text{s}}\right)\left(\frac{1}{15\ \text{A}}\right)\left(\frac{1\ \text{min}}{60\ \text{s}}\right) = 53.495786 = \mathbf{53\ min}$$

21.133 $3\ Pt(s) + 16\ H^+(aq) + 4\ NO_3^-(aq) + 18\ Cl^-(aq) \rightarrow 3\ PtCl_6^{2-}(aq) + 4\ NO(g) + 8\ H_2O(l)$

21.134 Substitute J / C for V.

a) Cell I: Oxidation number (O.N.) of H from 0 to +1, so 1 electron lost from each of 4 hydrogens for a total of 4 electrons. Oxygen O.N. goes from 0 to -2, indicating that 2 electrons are gained by each of the two oxygens for a total of 4 electrons. There is a transfer of **four electrons** in the reaction. The potential given in the problem allows the calculation of ΔG:

$$\Delta G° = -nFE° = -(4\ \text{mol e}^-)(96485\ \text{C / mol e}^-)(1.23\ \text{J / C}) = -4.747062 \times 10^5 = \mathbf{-4.75 \times 10^5\ J}$$

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

$$\Delta G° = -nFE° = -(2\ \text{mol e}^-)(96485\ \text{C / mol e}^-)(2.04\ \text{J / C}) = -3.936588 \times 10^5 = \mathbf{-3.94 \times 10^5\ J}$$

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 electrons** in the reaction.

$$\Delta G° = -nFE° = -(2\ \text{mol e}^-)(96485\ \text{C / mol e}^-)(2.35\ \text{J / C}) = -4.534795 \times 10^5 = \mathbf{-4.53 \times 10^5\ J}$$

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

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

Cell II: Mass of reactants =

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

= 642.58 g (unrounded)

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

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

= 172.73 g (unrounded)

$$\frac{w_{max}}{\text{Reactant Mass}} = \left(\frac{-4.534795 \times 10^5\ \text{J}}{172.73\ \text{g}}\right)\left(\frac{1\ \text{kJ}}{10^3\ \text{J}}\right) = -2.625366 = \mathbf{-2.62\ kJ/g}$$

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.

21.135 The current traveling through both cells is the same, so the amount of silver is proportional to the amount of zinc based on their reduction half-reactions:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ and $Ag^+(aq) + e^- \rightarrow Ag(s)$

$$\text{Mass Ag} = (1.2\ \text{g Zn})\left(\frac{1\ \text{mol Zn}}{65.41\ \text{g Zn}}\right)\left(\frac{2\ \text{mol e}^-}{1\ \text{mol Zn}}\right)\left(\frac{1\ \text{mol Ag}}{1\ \text{mol e}^-}\right)\left(\frac{107.9\ \text{g Ag}}{1\ \text{mol Ag}}\right) = 3.9590 = \mathbf{4.0\ g\ Ag}$$

21.136 A standard thermodynamic table would allow the calculation of the equilibrium constant by the equation $\Delta G° = -RT \ln K$. $\Delta G°$ could be calculated from ΔG_f^o values, or ΔH_f^o and $S°$ values. A table of standard electrode potentials would allow the calculation of the equilibrium constant by the following equation:

$$E° = (0.0592 \text{ V} / \text{n}) \log K$$

21.137 $2\ \text{Fe}(s) + \text{O}_2(g) + 4\ \text{H}^+(aq) \rightarrow 2\ \text{H}_2\text{O}(l) + 2\ \text{Fe}^{2+}(aq)$

An increase in temperature increases the cell potential for the above reaction. An increase in the temperature will cause the reaction rate to increase. Finally, K_w for water increases with temperature, thus at a higher temperature there will be a higher hydrogen ion concentration.

21.138 The cell reaction is: $\text{Cu}^{2+}(aq) + \text{Sn}(s) \rightarrow \text{Cu}(s) + \text{Sn}^{2+}(aq)$

a) Use the current and time to calculate total charge. Remember that the unit 1 A is 1C / 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 charge per mole of electrons. Each mole of copper deposited requires 2 moles of electrons, so divide moles of electrons by 2 to get moles of copper. Then convert to grams of copper.

$$\text{Mass Cu} = (0.15\ \text{A})\left(\frac{\text{C}/\text{s}}{\text{A}}\right)\left(\frac{3600\ \text{s}}{1\ \text{h}}\right)(54.0\ \text{h})\left(\frac{1\ \text{mol e}^-}{96485\ \text{C}}\right)\left(\frac{1\ \text{mol Cu}}{2\ \text{mol e}^-}\right)\left(\frac{63.55\ \text{g Cu}}{1\ \text{mol Cu}}\right) = 9.60314 = \mathbf{9.6\ g\ Cu}$$

b) The initial concentration of Cu^{2+} is 1.00 *M* (standard) and initial volume is 245 mL. Use this to calculate the initial moles of copper ions, then subtract the number of moles of copper ions converted to copper metal.

$$M\ \text{Cu}^{2+} = \frac{\left[\left(1.00 \frac{\text{mol Cu}^{2+}}{\text{L}}\right)(245\ \text{mL})\left(\frac{10^{-3}\ \text{L}}{1\ \text{mL}}\right)\right] - \left[(9.60314\ \text{g Cu})\left(\frac{1\ \text{mol Cu}}{63.55\ \text{g Cu}}\right)\right]}{(245\ \text{mL})\left(\frac{10^{-3}\ \text{L}}{1\ \text{mL}}\right)}$$

$$= 0.383218 = \mathbf{0.38}\ \boldsymbol{M}\ \mathbf{Cu^{2+}}$$

21.139 $2\ \text{H}_2\text{O}(l) + 2\ \text{e}^- \rightarrow \text{H}_2(g) + 2\ \text{OH}^-(aq)$

$$E = E° - \frac{0.0592\ \text{V}}{2} \log Q$$

$$\text{E}_{\text{H}_2\text{O}} = \text{E}°_{\text{H}_2\text{O}} - \frac{0.0592\ \text{V}}{2} \log\left(\text{P}_{\text{H}_2}[\text{OH}^-]^2\right)$$

$$= -0.83\ \text{V} - \frac{0.0592\ \text{V}}{2} \log\left[1(1.0 \times 10^{-7})^2\right]$$

$$= -0.83\ \text{V} + 0.4144 = -0.4156 = \mathbf{-0.42\ V}$$

21.140 Examine each reaction to determine which reactant is the oxidizing agent by which reactant gains electrons in the reaction.

From reaction between $\text{U}^{3+} + \text{Cr}^{3+} \rightarrow \text{Cr}^{2+} + \text{U}^{4+}$, find that Cr^{3+} oxidizes U^{3+}.
From reaction between $\text{Fe} + \text{Sn}^{2+} \rightarrow \text{Sn} + \text{Fe}^{2+}$, 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 $\text{Cr}^{3+} + \text{Fe} \rightarrow \text{Cr}^{2+} + \text{Fe}^{2+}$, find that Cr^{3+} oxidizes Fe.
From reaction between $\text{Cr}^{2+} + \text{Sn}^{2+} \rightarrow \text{Sn} + \text{Cr}^{3+}$, 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:

$\text{Sn}^{2+}(aq) + 2\ \text{e}^- \rightarrow \text{Sn}(s)$
$\text{Cr}^{3+}(aq) + \text{e}^- \rightarrow \text{Cr}^{2+}(aq)$
$\text{Fe}^{2+}(aq) + 2\ \text{e}^- \rightarrow \text{Fe}(s)$
$\text{U}^{4+}(aq) + \text{e}^- \rightarrow \text{U}^{3+}(aq)$

21.141 The given half-reactions are:

(1) $Fe^{3+}(aq) + e^- \leftrightarrows Fe^{2+}(aq)$
(2) $Fe^{2+}(aq) + 2\ e^- \leftrightarrows Fe(s)$
(3) $Fe^{3+}(aq) + 3\ e^- \leftrightarrows Fe(s)$

(a) $E°_1 = +0.77$ V $\quad E°_2 = -0.44$ V

Adding half-reaction (1) and (2) gives half-reaction (3), thus

$E°_3 = E°_1 + E°_2 = +0.77$ V -0.44 V = **0.33 V**

(b) $\Delta G° = -nFE°$

Reaction 1: $\Delta G° = -(1\ \text{mol}\ e^-)\ (96485\ \text{C / mol}\ e^-)\ (0.77\ \text{J / C}) = -7.429345 \times 10^4$ = **-7.4×10^4 J**

Reaction 2: $\Delta G° = -(2\ \text{mol}\ e^-)\ (96485\ \text{C / mol}\ e^-)\ (-0.44\ \text{J / C}) = 8.49068 \times 10^4$ = **8.5×10^4 J**

c) $\Delta G_3° = \Delta G_1° + \Delta G_2° = -7.429345 \times 10^4\ \text{J} + 8.49068 \times 10^4\ \text{J} = 1.061335 \times 10^4$ = **1.1×10^4 J**

d) $E° = -\Delta G° / nF = -(1.061335 \times 10^4\ \text{J}) / (3\ \text{mol}\ e^-)\ (96485\ \text{C / mol}\ e^-)[\text{V} / (\text{J / C})] = -0.036667$ = **-0.037 V**

e) The half-cells (1) and (2) add to (3) so their voltages should add to $E°_3$.

21.142 $6\ e^- + 14\ H^+ + Cr_2O_7^{2-} \rightarrow 2\ Cr^{3+} + 7\ H_2O$ (red half-reaction)
$CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 4\ H^+ + 4\ e^-$ (ox half-reaction)
$12\ e^- + 28\ H^+ + 2\ Cr_2O_7^{2-} \rightarrow 4\ Cr^{3+} + 14\ H_2O$
$3\ CH_3CH_2OH + 3\ H_2O \rightarrow 3\ CH_3COOH + 12\ H^+ + 12\ e^-$
Overall: $3\ CH_3CH_2OH + 2\ Cr_2O_7^{2-} + 16\ H^+ \rightarrow 3\ CH_3COOH + 4\ Cr^{3+} + 11\ H_2O$

21.143 At STP hydrogen gas occupies 22.4 L/mol. The reduction of zinc and of hydrogen both required 2 moles of electrons per mole of product, thus, the current percentages are equal to the mole percentages produced.

$$\text{Volume } H_2(g) = \left(\frac{22.4\ \text{L}\ H_2}{1\ \text{mol}\ H_2}\right)\left(\frac{8.50\ \text{mol}\ H_2}{91.50\ \text{mol Zn}}\right)\left(\frac{1\ \text{mol Zn}}{65.41\ \text{g Zn}}\right)\left(\frac{10^3\ \text{g}}{1\ \text{kg}}\right) = 31.81278577 = \mathbf{31.8\ L\ H_2/kg\ Zn}$$

21.144 a) The calomel half-cell is the anode and the silver half-cell is the cathode. The overall reaction is

$$2\ Ag^+(aq) + 2\ Hg(l) + 2\ Cl^-(aq) \rightarrow 2\ Ag(s) + Hg_2Cl_2(s)$$

The cell potential is 0.80 V - 0.24 V = 0.56 V with n = 2.

Use the Nernst equation to find $[Ag^+]$ when $E_{\text{cell}} = 0.60$ V.

$$E = E° - \frac{0.0592\ \text{V}}{\text{n}} \log Q$$

$$E = E° - \frac{0.0592\ \text{V}}{2} \log \frac{1}{\left[Ag^+\right]^2\left[Cl^-\right]^2}$$

$$0.060\ \text{V} = 0.56\ \text{V} - \frac{0.0592\text{V}}{2} \log \frac{1}{\left[Ag^+\right]^2\left[Cl^-\right]^2}$$

The problem suggests assuming that $[Cl^-]$ is constant. Assume it is 1.00 *M*.

$$(0.060\ \text{V} - 0.56\ \text{V})\ (-2 / 0.0592\ \text{V}) = \log \frac{1}{\left[Ag^+\right]^2[1.00]^2}$$

$\log [Ag^+]^2 = -16.89189$ (unrounded) {math note: log (1 / x) = -log (x)}
$[Ag^+]^2 = 10^{-16.89189}$
$[Ag^+]^2 = 1.2826554 \times 10^{-17}$
$[Ag^+] = 3.5814179 \times 10^{-9}$ = **3.6×10^{-9} *M***

Two significant figures come from subtracting 0.56 from 0.060 that gives 0.50 with only two significant figures.

b) Again use the Nernst equation and assume $[\mathrm{Cl}^-] = 1.00\ M$.

$$E = E° - \frac{0.0592\ \mathrm{V}}{2}\ \log\ \frac{1}{\left[\mathrm{Ag}^+\right]^2\left[\mathrm{Cl}^-\right]^2}$$

$$0.57\ \mathrm{V} = 0.56\ \mathrm{V} - \frac{0.0592\ \mathrm{V}}{2}\ \log\ \frac{1}{\left[\mathrm{Ag}^+\right]^2\left[\mathrm{Cl}^-\right]^2}$$

$$(0.57\ \mathrm{V} - 0.56\ \mathrm{V})\ (-2 / 0.0592\ \mathrm{V}) = \log\ \frac{1}{\left[\mathrm{Ag}^+\right]^2\left[1.00\right]^2}$$

$\log\ [\mathrm{Ag}^+]^2 = 0.337837837$ (unrounded)

$[\mathrm{Ag}^+]^2 = 10^{0.337837837}$

$[\mathrm{Ag}^+]^2 = 2.176896784$

$[\mathrm{Ag}^+] = 1.47543105 = \mathbf{1}\ \boldsymbol{M}$

One significant figure comes from subtracting 0.56 from 0.57 that gives 0.01 with only one significant figure.

21.145 $\mathrm{Ag}(s) \rightarrow \mathrm{Ag}^+(aq) + e^-$ $\quad E^o_{ox} = -0.80\mathrm{V}$

$\mathrm{AgCl}(s) + e^- \rightarrow \mathrm{Ag}(s) + \mathrm{Cl}^-(aq)$ $\quad E^o_{red} = +\ 0.22\mathrm{V}$

Overall: $\mathrm{AgCl}(s) \rightarrow \mathrm{Ag}^+(aq) + \mathrm{Cl}^-(aq)$ $\quad E^o_{cell} = -0.80\mathrm{V} + 0.22\mathrm{V} = -0.58\mathrm{V}$

$$\log K_{\mathrm{sp}} = \frac{\mathrm{nE_{cell}}°}{0.0592\ \mathrm{V}} = \frac{1(-0.58\ \mathrm{V})}{0.0592\ \mathrm{V}} = -9.797297\ \ \text{(unrounded)}$$

$K = 1.5947881 \times 10^{-10} = \mathbf{1.6 \times 10^{-10}}$

21.146 a) Nonstandard cell: $E_{\mathrm{waste}} = E^o_{cell} - (0.0592\ \mathrm{V} / 1)\ \log\ [\mathrm{Ag}^+]_{\mathrm{waste}}$

Standard cell: $E_{\mathrm{standard}} = E^o_{cell} - (0.0592\ \mathrm{V} / 1)\ \log\ [\mathrm{Ag}^+]_{\mathrm{standard}}$

b) To find $[\mathrm{Ag}^+]_{\mathrm{waste}}$: $\quad E^o_{cell} = E_{\mathrm{standard}} + (0.0592\ \mathrm{V} / 1)\ \log\ [\mathrm{Ag}^+]_{\mathrm{standard}} = E_{\mathrm{waste}} + (0.0592\ \mathrm{V} / 1)\ \log\ [\mathrm{Ag}^+]_{\mathrm{waste}}$

$E_{\mathrm{waste}} - E_{\mathrm{standard}} = (-0.0592\ \mathrm{V} / 1)\ \log\ ([\mathrm{Ag}^+]_{\mathrm{waste}} / [\mathrm{Ag}^+]_{\mathrm{standard}})$

$E_{\mathrm{standard}} - E_{\mathrm{waste}} = (0.0592\ \mathrm{V})\ (\log\ [\mathrm{Ag}^+]_{\mathrm{waste}} - \log\ [\mathrm{Ag}^+]_{\mathrm{standard}})$

$$\frac{\mathrm{E_{standard}} - \mathrm{E_{waste}}}{0.0592\ \mathrm{V}} = (\log\ [\mathrm{Ag}^+]_{\mathrm{waste}} - \log\ [\mathrm{Ag}^+]_{\mathrm{standard}})$$

$$\log\ [\mathrm{Ag}^+]_{\mathrm{waste}} = \frac{\mathrm{E_{standard}} - \mathrm{E_{waste}}}{0.0592} + \log\ [\mathrm{Ag}^+]_{\mathrm{standard}})$$

$$[\mathrm{Ag}^+]_{\mathrm{waste}} = [\mathrm{antilog}\ (\frac{\mathrm{E_{standard}} - \mathrm{E_{waste}}}{0.0592\ \mathrm{V}}\ )]([\mathrm{Ag}^+]_{\mathrm{standard}})$$

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

$E_{\mathrm{waste}} - E_{\mathrm{standard}} = (-0.0592\ \mathrm{V} / 1)\ \log\ ([\mathrm{Ag}^+]_{\mathrm{waste}} / [\mathrm{Ag}^+]_{\mathrm{standard}})$

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.

$$\mathrm{C}\ (\mathrm{Ag}^+)_{\mathrm{waste}} = \left[\mathrm{antilog}\left(\frac{\mathrm{E_{standard}} - \mathrm{E_{waste}}}{0.0592\ \mathrm{V}}\right)\right]\left(\mathrm{C}\left(\mathrm{Ag}^+\right)_{\mathrm{standard}}\right)$$

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

$$[\mathrm{Ag}^+]_{\mathrm{waste}} = \left[\mathrm{antilog}\left(\frac{-0.003}{0.0592\ \mathrm{V}}\right)\right]\left(1000.\mathrm{ng/L}\right) = 889.8654 = \mathbf{900\ ng\ /\ L}$$

e) Temperature is included in the RT / nF term, which equals 0.0592 V / n at 25°C. To account for different temperatures, insert the RT / nF term in place of 0.0592 V / n.

$E_{\text{standard}} + (2.303\ \mathrm{RT}_{\text{standard}} / \mathrm{nF}) \log [\mathrm{Ag}^+]_{\text{standard}} = E_{\text{waste}} + (2.303\ \mathrm{RT}_{\text{waste}} / \mathrm{nF}) \log [\mathrm{Ag}^+]_{\text{waste}}$

$E_{\text{standard}} - E_{\text{waste}} = (2.303\ \mathrm{R} / \mathrm{nF})\ (\mathrm{T}_{\text{waste}} \log [\mathrm{Ag}^+]_{\text{waste}} - \mathrm{T}_{\text{standard}} \log [\mathrm{Ag}^+]_{\text{standard}})$

$(E_{\text{standard}} - E_{\text{waste}})\ (\mathrm{nF} / 2.303\ \mathrm{R}) = \mathrm{T}_{\text{waste}} \log [\mathrm{Ag}^+]_{\text{waste}} - \mathrm{T}_{\text{standard}} \log [\mathrm{Ag}^+]_{\text{standard}}$

$(E_{\text{standard}} - E_{\text{waste}})\ (\mathrm{nF} / 2.303\ \mathrm{R}) + \mathrm{T}_{\text{standard}} \log [\mathrm{Ag}^+]_{\text{standard}} = \mathrm{T}_{\text{waste}} \log [\mathrm{Ag}^+]_{\text{waste}}$

$$\log\,[\mathrm{Ag}^+]_{\text{waste}} = \left(\frac{\left(\mathrm{E}_{\text{standard}} - \mathrm{E}_{\text{waste}}\right)\left(\mathrm{nF} / 2.303\,\mathrm{R}\right) + \mathrm{T}_{\text{standard}} \log\left[\mathrm{Ag}^+\right]_{\text{standard}}}{\mathrm{T}_{\text{waste}}}\right)$$

$$[\mathrm{Ag}^+]_{\text{waste}} = \text{antilog}\left(\frac{\left(\mathrm{E}_{\text{standard}} - \mathrm{E}_{\text{waste}}\right)\left(\mathrm{nF} / 2.303\,\mathrm{R}\right) + \mathrm{T}_{\text{standard}} \log\left[\mathrm{Ag}^+\right]_{\text{standard}}}{\mathrm{T}_{\text{waste}}}\right)$$

21.147 $\mathrm{Ag}^+(aq) + \mathrm{e}^- \rightarrow \mathrm{Ag}(s)$ $E^o_{red} = 0.80\mathrm{V}$

$\mathrm{Ag}(s) + 2\mathrm{NH}_3(aq) \rightarrow \mathrm{Ag(NH_3)_2}^+(aq) + \mathrm{e}^-$ $E^o_{ox} = -0.37\mathrm{V}$

Overall: $\mathrm{Ag}^+(aq) + 2\mathrm{NH}_3(aq) \rightarrow \mathrm{Ag(NH_3)_2}^+(aq)$ $E^o_{cell} = 0.80\mathrm{V} + (-0.37\mathrm{V}) = 0.43\mathrm{V}$

$$\log K_{\text{sp}} = \frac{\mathrm{nE_{cell}}^\circ}{0.0592\ \mathrm{V}} = \frac{1\left(0.43\ \mathrm{V}\right)}{0.0592\ \mathrm{V}} = 7.26351 \text{ (unrounded)}$$

$K = 1.834467 \times 10^7 = \mathbf{1.8 \times 10^7}$

21.148 a) Determine the total charge the cell can produce.

Capacity = (300. mA•h) (10^{-3} A / 1 mA) (3600 s / h) (1 C / 1 A•s) = **1.08×10^3 C**

b) The half-reactions are:

$\mathrm{Cd}^0 \rightarrow \mathrm{Cd}^{+2} + 2\ \mathrm{e}^-$ and $2\ (\mathrm{NiO(OH)} + \mathrm{H_2O}(l) + \mathrm{e}^- \rightarrow \mathrm{Ni(OH)_2} + \mathrm{OH}^-)$

2 mol e^- flow per mole of reaction.

Assume 100% conversion of reactants.

Mass Cd = (1080 C) (1 mol e^- / 96485 C) (1 mol Cd / 2 mol e^-) (112.4 g Cd / 1 mol Cd) = 0.62907 = **0.629 g Cd**

Mass NiO(OH) = (1080 C)(1 mol e^- / 96485 C) (1 mol NiO(OH) / 1 mol e^-) (91.70 g NiO(OH) / 1 mol NiO(OH))
= 1.026439 = **1.03 g NiO(OH)**

Mass $\mathrm{H_2O}$ = (1080 C) (1 mol e^- / 96485 C) (1 mol $\mathrm{H_2O}$ / 1 mol e^-) (18.02 g $\mathrm{H_2O}$ / 1 mol $\mathrm{H_2O}$)
= 0.20170596 = **0.202 g $\mathrm{H_2O}$**

Total mass of reactants = 0.62907 g Cd + 1.026439 g NiO(OH) + 0.20170596 g $\mathrm{H_2O}$
= 1.85721 = **1.86 g reactants**

c) Mass % reactants = $\left(\dfrac{1.85721\ \mathrm{g}}{13.3\ \mathrm{g}}\right)$ x 100% = 13.96398 = **14.0%**

21.149 a) $2\ \mathrm{Zn} \rightarrow 2\ \mathrm{Zn}^{2+} + 4\ \mathrm{e}^-$ and $4\ \mathrm{e}^- + \mathrm{O_2} \rightarrow 2\ \mathrm{O}^{2-}$ 4 mol e^- flow per mole of reaction.

Mass Zn = (1 / 10) (0.275 g battery) = 0.0275 g Zn (assuming the 1 / 10 is exact.)

Coulombs = (0.0275 g Zn) (1 mol Zn / 65.41 g Zn) (4 mol e^- / 2 mol Zn) (96485 C / 1 mol e^-)
= 81.1294 = **81.1 C**

b) Free energy (J) = (volts) (coulombs) = (1.3 V) (81.1294 C) = 105.46822 = **1.1×10^2 J**

21.150 Place the elements in order of increasing $E°$.

Reducing agent strength: Li > Ba > Na > Al > Mn > Zn > Cr > Fe > Ni > Sn > Pb > Cu > Ag > Hg > Au

Metals with potentials lower than that of water (-0.83 V) can displace hydrogen from water.

These can displace $\mathrm{H_2}$ from water: Li, Ba, Na, Al, and Mn

Metals with potentials lower than that of hydrogen (0.00 V) can displace hydrogen from acids.

These can displace $\mathrm{H_2}$ from acid: Li, Ba, Na, Al, Mn, Zn, Cr, Fe, Ni, Sn, and Pb

Metals with potentials above that of hydrogen (0.00 V) cannot displace hydrogen.

These cannot displace $\mathrm{H_2}$: Cu, Ag, Hg, and Au

21.151 Determine the $E°$ for the reaction given from the free energy:

$\Delta G° = -nFE°$

$E^{o}_{cell} = -\Delta G° / nF = -[(-298 \text{ kJ/mol})(10^{3} \text{ J} / 1 \text{ kJ})] / (2 \text{ mol e}^{-})(96485 \text{ C} / \text{mol e}^{-})[\text{V} / (\text{J} / \text{C})]$

$= 1.54428 \text{ V}$ (unrounded)

Using $E°$ for $Cu^{2+} + 2e^{-} \rightarrow Cu$ (cathode) from the Appendix, and the E^{o}_{cell} just found:

$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = 1.54428 \text{ V}$

$1.54428 \text{ V} = 0.34 \text{ V} - E^{o}_{anode}$

$E^{o}_{anode} = 0.34 \text{ V} - 1.54428 \text{ V} = -1.20428 = -1.20 \text{ V}$

The standard reduction potential of V^{2+} is **-1.20 V**.

For the Ti / V cell, $E^{o}_{cell} = 0.43 \text{ V}$ Vanadium is the anode.

$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = 0.43 \text{ V}$

$E^{o}_{cathode} - (-1.20428 \text{ V}) = 0.43 \text{ V}$

$E^{o}_{cathode} = 0.43 \text{ V} - 1.20428 \text{ V} = -0.77428 = -0.77 \text{ V}$

The standard reduction potential of Ti is **-077 V**.

21.152 a) The iodine goes from -1 to 0, so it was oxidized.

Iodine was oxidized, so **$S_4O_6^{2-}$ is the oxidizing agent**.

Iodine was oxidized, so **I^{-} is the reducing agent**.

b) $\Delta G° = -nFE°$ n = 2

$E^{o}_{cell} = -\Delta G° / nF = -[(87.8 \text{ kJ/mol})(10^{3} \text{ J} / 1 \text{ kJ})] / (2 \text{ mol e}^{-})(96485 \text{ C} / \text{mol e}^{-})[\text{V} / (\text{J} / \text{C})]$

$= -0.454993 =$ **-0.455 V**

c) $S_4O_6^{2-}(aq) + 2e^{-} \rightarrow 2 S_2O_3^{2-}(aq)$

Oxygen remains -2 throughout.

Sulfur is +2.5 in $S_4O_6^{2-}$ (2.5 is an average)

Sulfur is +2 in $S_2O_3^{2-}$

The potential for the iodine half-reaction comes from the Appendix. Since the iodine was oxidized, it is the anode.

$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = -0.454993 \text{ V}$

$E^{o}_{cathode} - (0.53 \text{ V}) = -0.454993 \text{ V}$

$E^{o}_{cathode} = 0.53 \text{ V} - 0.454993 \text{ V} = 0.075007 =$ **0.08 V**

21.153 a) The reference half-reaction is: $Cu^{2+}(aq) + 2\ e^{-} \rightarrow Cu(s)$ $E° = 0.34$ 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.

$$E = E° - \frac{0.0592\ V}{n}\ \log Q$$

$$0.129\ V = 0.00\ V - \frac{0.0592\ V}{2}\ \log \frac{\left[Cu^{2+}\right]_{ammonia}}{\left[Cu^{2+}\right]_{original}}$$

$$0.129\ V = - \frac{0.0592\ V}{2}\ \log \frac{\left[Cu^{2+}\right]_{ammonia}}{\left[0.0100\right]_{original}}$$

$$(0.129\ V)\ (-2\ /\ 0.0592) = \log \frac{\left[Cu^{2+}\right]_{ammonia}}{\left[0.0100\right]_{original}}$$

$$-4.358108108 = \log \frac{\left[Cu^{2+}\right]_{ammonia}}{\left[0.0100\right]_{original}}$$

$$4.3842154 \times 10^{-5} = \frac{\left[Cu^{2+}\right]_{ammonia}}{\left[0.0100\right]_{original}}$$

$[Cu^{2+}]_{ammonia} = 4.3842154 \times 10^{-7}\ M$ (unrounded)

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 number of moles of copper and the original number of moles of ammonia are found from the original volumes and molarities:

$$\text{Original moles of copper} = \left(\frac{0.0100\ mol\ Cu(NO_3)_2}{L}\right)\left(\frac{1\ mol\ Cu^{2+}}{1\ mol\ Cu(NO_3)_2}\right)\left(\frac{10^{-3}\ L}{1\ mL}\right)\left(90.0\ mL\right)$$

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

$$\text{Original moles of ammonia} = \left(\frac{0.500\ mol\ NH_3}{L}\right)\left(\frac{10^{-3}\ L}{1\ mL}\right)\left(10.0\ mL\right) = 5.00 \times 10^{-3}\ mol\ NH_3$$

Determine the moles of copper still remaining uncomplexed.

$$\text{Remaining moles of copper} = \left(\frac{4.3842154 \times 10^{-7}\ mol\ Cu^{2+}}{L}\right)\left(\frac{10^{-3}\ L}{1\ mL}\right)\left(100.0\ mL\right)$$

$= 4.3842154 \times 10^{-8}$ mol Cu

The difference between the original moles of copper and the copper ion remaining in solution is the copper in the complex (= moles of complex). The molarity of the complex may now be found.

Moles copper in complex = $(9.00 \times 10^{-4} - 4.3842154 \times 10^{-8})$ mol Cu^{2+}

$= 8.9995615 \times 10^{-4}$ mol Cu^{2+} (unrounded)

$$\text{Molarity of complex} = \left(\frac{8.9995615 \times 10^{-4}\ mol\ Cu^{2+}}{100.0\ mL}\right)\left(\frac{1\ mol\ Cu(NH_3)_4^{2+}}{1\ mol\ Cu^{2+}}\right)\left(\frac{1\ mL}{10^{-3}\ L}\right)$$

$= 8.9995615 \times 10^{-3}\ M\ Cu(NH_3)_4^{2+}$ (unrounded)

The concentration of the remaining ammonia is found as follows:

$$\text{Molarity of ammonia} = \left(\frac{\left(5.00 \text{ x } 10^{-3} \text{ mol NH}_3\right)-\left(8.9995615 \text{ x } 10^{-4} \text{ mol Cu}^{2+}\right)\left(\frac{4 \text{ mol NH}_3}{1 \text{ mol Cu}^{2+}}\right)}{100.0 \text{ mL}}\right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)$$

= 0.014001753 *M* ammonia (unrounded)

The K_f equilibrium is:

$Cu^{2+}(aq) + 4\ NH_3(aq) \leftrightarrows Cu(NH_3)_4^{2+}(aq)$

$$K_f = \frac{\left[Cu(NH_3)_4^{2+}\right]}{\left[Cu^{2+}\right]\left[NH_3\right]^4} = \frac{\left[8.9995615 \text{ x } 10^{-3}\right]}{\left[4.3842154 \text{ x } 10^{-7}\right]\left[0.014001753\right]^4} = 5.34072 \text{ x } 10^{11} = \mathbf{5.3 \text{ x } 10^{-11}}$$

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

Moles uncomplexed ammonia before the addition of new ammonia =

(0.014001753 mol NH_3 / L) (10^{-3} L / 1 mL) (100.0 mL) = 0.001400175 mol NH_3

Moles ammonia added = 5.00 x 10^{-3} mol NH_3 (same as original moles of ammonia)

From the stoichiometry:

	$Cu^{2+}(aq)$	+	$4\ NH_3(aq)$	→	$Cu(NH_3)_4^{2+}(aq)$
Initial moles:	4.3842154 x 10^{-8} mol		0.001400175 mol		8.9995615 x 10^{-4} mol
Added moles:			5.00 x 10^{-3} mol		
Cu^{2+} is limiting:	-(4.3842154 x 10^{-8} mol)		-4(4.3842154 x 10^{-8} mol)		+(4.3842154 x 10^{-8} mol)
After the reaction:	0		0.006400 mol		9.00000 x 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 *M* NH_3

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

= 0.008181818 *M* $Cu(NH_3)_4^{2+}$

Now allow the system to come to equilibrium:

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

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

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

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

$x = [Cu^{2+}] = 1.3369 \text{ x } 10^{-9}\ M\ Cu^{2+}$

Use the Nernst equation to determine the new cell potential:

$$E = 0.00 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \frac{\left[Cu^{2+}\right]_{\text{ammonia}}}{\left[Cu^{2+}\right]_{\text{original}}}$$

$$E = -\frac{0.0592 \text{ V}}{2} \log \frac{\left[1.3369 \text{ x } 10^{-9}\right]}{\left[0.0100\right]}$$

$E = 0.203467 = \mathbf{0.20\ V}$

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

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

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

The reaction:

	$Cu^{2+}(aq)$	+	$2\ OH^-(aq)$	→	$Cu(OH)_2(s)$
Initial moles:	9.00 x 10^{-4} mol		5.00 x 10^{-3} mol		
Cu^{2+} is limiting:	-(9.00 x 10^{-4} mol)		-2(9.00 x 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 M OH^-

Now allow the system to come to equilibrium:

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

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

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

Assume 2x is negligible compared to 0.032 M.

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

$x = [Cu^{2+}] = 2.1487375 \text{ x } 10^{-17} = 2.1 \text{ x } 10^{-17}\ M$

Use the Nernst equation to determine the new cell potential:

$$E = 0.00\ \text{V} - \frac{0.0592\ \text{V}}{2}\ \log\frac{\left[Cu^{2+}\right]_{\text{hydroxide}}}{\left[Cu^{2+}\right]_{\text{original}}}$$

$$E = -\ \frac{0.0592\ \text{V}}{2}\ \log\frac{\left[2.1487375 \text{ x } 10^{-17}\right]}{\left[0.0100\right]}$$

E = 0.434169 = **0.43 V**

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

$$E = 0.00\ \text{V} - \frac{0.0592\ \text{V}}{2}\ \log\frac{\left[Cu^{2+}\right]_{\text{hydroxide}}}{\left[Cu^{2+}\right]_{\text{original}}}$$

$$0.340 = -\ \frac{0.0592\ \text{V}}{2}\ \log\frac{\left[Cu^{2+}\right]_{\text{hydroxide}}}{\left[0.0100\right]}$$

$$(0.340\ \text{V})\ (-2\ /\ 0.0592) = \log\frac{\left[Cu^{2+}\right]_{\text{hydroxide}}}{\left[0.0100\right]}$$

$$-11.486486 = \log\frac{\left[Cu^{2+}\right]_{\text{hydroxide}}}{\left[0.0100\right]}$$

$$3.2622256 \text{ x } 10^{-12} = \frac{\left[Cu^{2+}\right]_{\text{hydroxide}}}{\left[0.0100\right]}$$

$[Cu^{2+}]_{\text{hydroxide}} = 3.2622256 \text{ x } 10^{-14}\ M$ (unrounded)

Now use the K_{sp} relationship:

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

$K_{sp} = [3.2622256 \text{ x } 10^{-14}][OH^-]^2 = 2.2 \text{ x } 10^{-20}$

$[OH^-]^2 = 6.743862 \text{ x } 10^{-7}$

$[OH^-] = 8.2121 \text{ x } 10^{-4} = 8.2 \text{ x } 10^{-4}\ M\ OH^- = \mathbf{8.2 \text{ x } 10^{-4}\ \mathit{M}\ NaOH}$

21.154 a) The half-reactions found in the Appendix are:

$Au^{3+}(aq) + 3\ e^- \leftrightarrows Au(s) \quad E° = 1.50\ V$

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

$Co^{2+}(aq) + 2\ e^- \leftrightarrows Co(s) \quad E° = -0.28\ V$

$Zn^{2+}(aq) + 2\ e^- \leftrightarrows Zn(s) \quad E° = -0.76\ V$

Calculate $E_{cell} = E^o_{cathode} - E^o_{anode}$

Au / Cr $E^o_{cell} = 1.50\ V - (-0.74\ V) = \mathbf{2.24\ V}$

Co / Zn $E^o_{cell} = -0.28\ V - (-0.76\ V) = \mathbf{0.48\ V}$

b) Connecting the cells as two voltaic cells in series will add the voltages.

$E_{series} = E_{Au / Cr} + E_{Co / Zn} = 2.24\ V + 0.48\ V = \mathbf{2.72\ V}$

c) Connecting the cells as one voltaic cell (Au / Cr) and one electrolytic (Co / Zn) in series will result in the difference in the voltages.

$E_{series} = E_{Au / Cr} - E_{Co / Zn} = 2.24\ V - 0.48\ V = \mathbf{1.76\ V}$

d) In parts a-c, Au^{3+} is reduced in the Au / Cr cell.

In parts a-b, Co^{2+} is reduced in the Co / Zn cell.

The connection in part c forces the Co / Zn cell to operate in reverse, thus, Zn^{2+} is reduced.

e) $$\left(2.00\text{ g Au}\right)\left(\frac{1\text{ mol Au}}{197.0\text{ g Au}}\right)\left(\frac{3\text{ mol e}^-}{1\text{ mol Au}}\right)\left(\frac{1\text{ mol Zn}}{2\text{ mol e}^-}\right)\left(\frac{65.41\text{ g Zn}}{1\text{ mol Zn}}\right) = 0.99609 = \mathbf{0.996\text{ g Zn}}$$

21.155 a) The half-reactions found in the Appendix are:

$Cd^{2+}(aq) + 2\ e^- \leftrightarrows Cd(s) \quad E° = -0.40\ V$

$Cu^{2+}(aq) + 2\ e^- \leftrightarrows Cu(s) \quad E° = 0.34\ V$

Calculate $E_{cell} = E^o_{cathode} - E^o_{anode}$

Cu / Cd $E^o_{cell} = 0.34\ V - (-0.40\ V) = \mathbf{0.74\ V}$

$\Delta G° = -nFE°$

$\Delta G° = -(2\text{ mol e}^-)(96485\text{ C / mol e}^-)(0.74\text{ J / C}) = -1.427978 \text{ x } 10^5 = \mathbf{-1.4 \text{ x } 10^5\ J}$

$$\log K = \frac{nE_{cell}°}{0.0592}$$

$$\log K = \frac{2(0.74)}{0.0592} = 25$$

$K = \mathbf{10^{25}}$

b) The cell reaction is: $Cu^{2+}(aq) + Cd(s) \leftrightarrows Cu(s) + Cd^{2+}(aq)$

Next, use the Nernst equation:

$$E = E° - \frac{0.0592\ V}{n}\log Q$$

$$E = 0.74\ V - \frac{0.0592\ V}{2}\log\frac{\left[Cd^{2+}\right]}{\left[Cu^{2+}\right]}$$

An increase in the cadmium concentration by 0.95 *M* requires an equal decrease in the copper concentration since the mole ratios are 1 : 1. Thus, when $[Cd^{2+}] = 1.95\ M$,

$[Cu^{2+}] = (1.00 - 0.95)\ M = 0.05\ M$.

$$E = 0.74\ V - \frac{0.0592\ V}{2}\log\frac{[1.95]}{[0.05]}$$

$E = 0.69290 = \mathbf{0.69\ V}$

c) At equilibrium, $\boldsymbol{E_{\text{cell}} = 0}$, and $\boldsymbol{\Delta G = 0}$

The Nernst equation is necessary to determine the [Cu^{2+}].

Let the copper ion completely react to give [Cu^{2+}] = 0.00 *M* and [Cd^{2+}] = 2.00 *M*. The system can now go to equilibrium giving [Cu^{2+}] = +x *M* and [Cd^{2+}] = (2.00 - x) *M*.

$$0.00 \text{ V} = 0.74 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \frac{[2.00 - \text{x}]}{[\text{x}]}$$

Assume x is negligible compared to 2.00.

$$(-0.74 \text{ V})\ (-2\ /\ 0.0592 \text{ V}) = \log \frac{[2.00]}{[\text{x}]}$$

$$25.0 = \log \frac{[2.00]}{[\text{x}]}$$

$$\text{x} = \mathbf{2.0 \times 10^{-25}}\ \boldsymbol{M}\ \mathbf{Cu^{2+}}$$

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

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

The heat of reaction may be determined from heats of formation in the Appendix or in the problem.

$$\Delta H° = \Sigma n\Delta H_f° - \Sigma m\Delta H_f°$$

$$\Delta H° = [(16 \text{ mol})\ (\Delta H_f°(CO_2(g)) + (18 \text{ mol})\ (\Delta H_f°(H_2O(g))] - [(2 \text{ mol})\ (\Delta H_f°(C_8H_{18}(l)) + (25 \text{ mol})\ (\Delta H_f°(O_2(g))]$$

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

$$\Delta H° = [-10648.868 \text{ kJ}] - [-500.2 \text{ kJ}] = -10148.668 = -10148.7 \text{ kJ}$$

The energy from 1.00 gallon of gasoline is:

$$(1.00 \text{ gal})\left(\frac{4 \text{ qt}}{1 \text{ gal}}\right)\left(\frac{1 \text{ L}}{1.057 \text{ qt}}\right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)\left(\frac{0.7028 \text{ g}}{\text{mL}}\right)\left(\frac{1 \text{ mol } C_8H_{18}}{114.22 \text{ g } C_8H_{18}}\right)\left(\frac{-10148.7 \text{ kJ}}{2 \text{ mol } C_8H_{18}}\right)$$

$$= -1.1815165 \times 10^5 = \mathbf{-1.18 \times 10^5\ kJ}$$

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

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

With the reaction written this way, the heat of reaction is simply the heat of formation of water vapor, and no additional calculations are necessary.

$$\Delta H° = -241.826 \text{ kJ}$$

The moles of hydrogen needed to produce the energy from part (a) are:

$$\text{Moles } H_2 = \left(-1.1815165 \times 10^5 \text{ kJ}\right)\left(\frac{1 \text{ mol } H_2}{-241.826 \text{ kJ}}\right) = 488.5812755 \text{ mol (unrounded)}$$

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

$$V = nRT\ /\ P = \frac{\left(488.5812755 \text{ mol } H_2\right)\left(0.0821 \frac{\text{L} \bullet \text{atm}}{\text{mol} \bullet \text{K}}\right)\left((273 + 25)\text{K}\right)}{(1.00 \text{ atm})} = 1.195353 \times 10^4 = \mathbf{1.20 \times 10^4\ L}$$

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

$$2\ H_2O(l) + 2\ e^- \rightarrow H_2(g) + 2\ OH^-(aq)$$

Use 1 A = 1 C / s

$$\text{Time} = \left(1.195353 \times 10^4 \text{ mol } H_2\right)\left(\frac{2 \text{ mol } e^-}{1 \text{ mol } H_2}\right)\left(\frac{96485 \text{ C}}{1 \text{ mol } e^-}\right)\left(\frac{\text{s}}{1.00 \times 10^3 \text{C}}\right) = 2.306673 \times 10^6 = \mathbf{2.31 \times 10^6\ seconds}$$

d) This is a straight factor-label problem.

$$\text{Power} = \left(\frac{1.00 \times 10^3 \text{C}}{\text{s}}\right)(5.00 \text{ V})\left(\frac{1 \text{ J}}{1\text{C} \bullet \text{V}}\right)\left(2.306673 \times 10^6 \text{ s}\right)\left(\frac{1 \text{ kW} \bullet \text{h}}{3.6 \times 10^6 \text{ J}}\right) = 3.2037125 \times 10^3 = \mathbf{3.20 \times 10^3\ kW{\bullet}h}$$

e) The process is only 90.0% efficient, additional electricity is necessary to produce sufficient hydrogen. This is the purpose of the (100% / 90.0%) factor.

Cost = (3.2037125×10^3 kW•h) (0.950 cents / kW•h) (100% / 90.0%) = 3381.6965 = **3.38×10^3 cents**

21.157 a) $6\ H^+ + XeO_3 + 9\ I^- \rightarrow Xe + 3\ I_3^- + 3\ H_2O$

b) $2\ HXeO_4^- + 2\ OH^- \rightarrow Xe + XeO_6^{4-} + 2\ H_2O + O_2$

c) $7\ H_2O + 5\ BiO_3^- + 2\ Mn^{2+} \rightarrow 5\ Bi^{3+} + 2\ MnO_4^- + 14\ OH^-$

d) $4\ OH^- + 2\ OF_2 \rightarrow 4\ F^- + 2\ O_2 + 2\ H_2O$

e) $4\ H^+ + MnO_2 + 2\ SO_3^{2-} \rightarrow Mn^{2+} + S_2O_6^{2-} + 2\ H_2O$

f) $At^- + 3\ Cl_2 + 3\ H_2O \rightarrow AtO_3^- + 6\ Cl^- + 6\ H^+$

21.158 The half-reactions are (from the Appendix):

$H_2(g) \rightarrow 2\ H^+(aq) + 2\ e^-$ $E = 0.00$ V

$2(Ag^+(aq) + 1\ e^- \rightarrow Ag(s))$ $E = 0.80$ V

$2\ Ag^+(aq) + H_2(g) \rightarrow 2\ Ag(s) + 2\ H^+(aq)$ $E_{cell} = 0.80$ V

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

$$E = E° - \frac{0.0592\ V}{2} \log Q$$

$$0.915\ V = 0.80\ V - \frac{0.0592\ V}{2} \log \frac{\left[H^+\right]^2}{\left[Ag^+\right]^2 P_{H_2}}$$

$$0.915\ V - 0.80\ V = -\frac{0.0592\ V}{2} \log \frac{\left[H^+\right]^2}{[0.100]^2(1.00)}$$

$$(0.915\ V - 0.80\ V)(-2 / 0.0592\ V) = \log \frac{\left[H^+\right]^2}{[0.100]^2(1.00)}$$

$$-3.885135 = \log \frac{\left[H^+\right]^2}{[0.0100]}$$

$$1.30276 \times 10^{-4} = \frac{\left[H^+\right]^2}{[0.0100]}$$

$[H^+] = 1.1413851 \times 10^{-3}$ *M* (unrounded)

pH = -log $[H^+]$ = -log (1.1413851×10^{-3}) = 2.94256779 = **2.94**