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 **No**, one half-reaction cannot take place independently of the other because there is always a transfer of electrons from one substance to another. If one substance loses electrons (oxidation half-reaction), another substance must gain those electrons (reduction half-reaction).

21.3 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 ($\Delta G_{sys} > 0$).

21.4 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.

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

21.6 $2\ CrO_2^-(aq) + 2\ H_2O(l) + 6\ ClO^-(aq) \rightarrow 2\ CrO_4^{2-}(aq) + 3\ Cl_2(g) + 4\ OH^-(aq)$
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) $2\ NaCrO_2(aq) + 6\ NaClO(aq) + 2\ H_2O(l) \rightarrow 2\ Na_2CrO_4(aq) + 3\ Cl_2(g) + 4\ NaOH(aq)$

21.7 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 for a –1 charge on each side

$2\,I^-(aq) \rightarrow I_2(s) + 2\,e^-$ add 2 e^- to products for a –2 charge on each side

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

$ClO_3^-(aq) + 6\,H^+(aq) + 6\,e^- \rightarrow Cl^-(aq) + 3\,H_2O(l)$ 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 for a 0 charge on each side

$SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2\,H^+(aq) + 2\,e^-$ add 2 e^- to products for a –2 charge on each side

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

$2\{MnO_4^-(aq) + 4\,H^+(aq) + 3\,e^- \rightarrow MnO_2(s) + 2\,H_2O(l)\}$ 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^+

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

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

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

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

c) Divide into half-reactions:

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

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

Balance elements other than O and H

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

$H_2O_2(aq) \rightarrow O_2(g)$ No other elements to balance

Balance O by adding H_2O

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

$H_2O_2(aq) \rightarrow O_2(g)$ O is balanced

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 for +2 on each side

$H_2O_2(aq) \rightarrow O_2(g) + 2\ H^+(aq) + 2\ e^-$ add 2 e^- to products for 0 charge on each side

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

$2\{MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^- \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)\}$ 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:		Products:	
	2 Mn		2 Mn
	18 O		18 O
	16 H		16 H
	+4 charge		+4 charge

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

21.8 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^-

21.9 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

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

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

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

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 to give +3 on each side

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 charge to give +2 on each side

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

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

Add half-reactions. 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 to give 0 on each side

Balance the oxidation half-reaction

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

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

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

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

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

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

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

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

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

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.

21.11 $5\ Fe^{2+}(aq) + MnO_4^-(aq) + 8\ H^+(aq) \rightarrow Mn^{2+}(aq) + 5\ Fe^{3+}(aq) + 4\ H_2O(l)$

21.12 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 to give 0 on each side

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 to –4 on each side

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

$3\{NO_3^-(aq) + 2\ H^+(aq) + e^- \rightarrow NO_2(g) + H_2O(l)\}$ Multiply by 3 to give 3 e^-

$1\{Au(s) + 4\ Cl^-(aq) \rightarrow AuCl_4^-(aq) + 3\ e^-\}$ Multiply by 1 to give 3 e^-

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, $AuCl_4^-$.

21.13 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 solid metal.

21.14 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.

21.15 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.

21.16 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.

21.17 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.

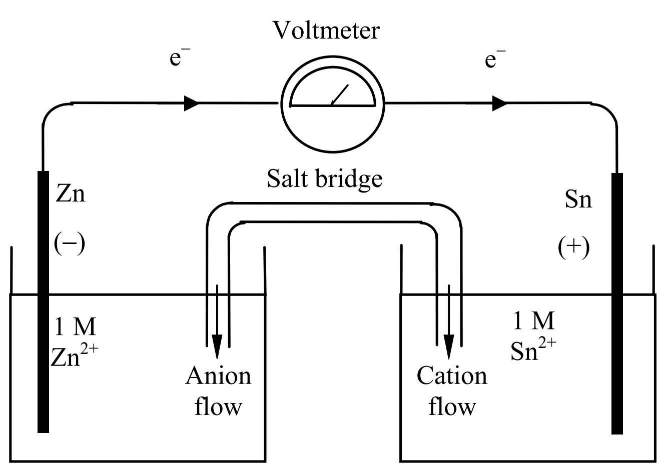
21.18 a) If the zinc electrode is negative, oxidation takes place at the zinc electrode:

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

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

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

b)

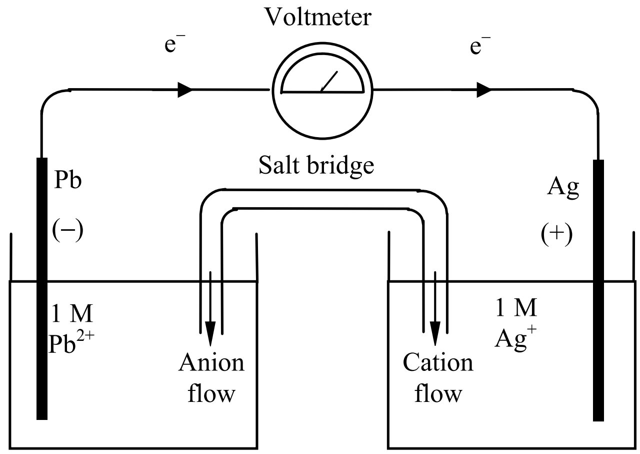


21.19 a) (red half-rxn) $Ag^+(aq) + 1\ e^- \rightarrow Ag(s)$

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

(overall rxn) $2\ Ag^+(aq) + Pb(s) \rightarrow 2\ Ag(s) + Pb^{2+}(aq)$

b)



21.20 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 towards the half-cell in which positive ions are being produced. The oxidation half-cell produces Fe^{2+}, so salt bridge anions move **from right** (nickel half-cell) **to left** (iron half-cell).

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

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

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

21.21 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: $Zn(s) + Co^{2+}(aq) \rightarrow Co(s) + Zn^{2+}(aq)$

21.22 In cell notation, the oxidation components of the anode compartment are written on the left of the salt bridge and the reduction components of the cathode compartment are written to the right of the salt bridge. A double vertical line separates the anode from the cathode and represents the salt bridge. A single vertical line separates species of different phases.

Anode || Cathode

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.

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

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

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

21.24 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.

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

21.26 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.

21.27 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) $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

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

21.28 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) $E^\circ_{cell} = E°_{ozone} - E°_{manganese}$

$E°_{manganese} = E°_{ozone} - E^\circ_{cell}$

$= 2.07\ V - 0.84\ V$

$= \mathbf{1.23\ V}$

21.29 The greater (more positive) the reduction potential, the greater the strength as an oxidizing agent.

a) From Appendix D:

$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ $E° = 0.77\ V$

$Br_2(l) + 2\ e^- \rightarrow 2\ Br^-(aq)$ $E° = 1.07\ V$

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

When placed in order of decreasing strength as oxidizing agents: $\mathbf{Br_2 > Fe^{3+} > Cu^{2+}}$.

b) From Appendix D:

$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$ $E° = –2.87$ V

$Cr_2O_7^{2–}(aq) + 14 H^+(aq)$ $6e^- \rightarrow 2 Cr^{3+}(aq) + 7 H_2O(l)$ $E° = 1.33$ V

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

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

21.30 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**

21.31 $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$ $E°$ values are found in Appendix D. Spontaneous reactions have $E^\circ_{cell} > 0$.

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

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

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

$E^\circ_{cell} = 0.00 \text{ V} - (–0.28 \text{ V}) = \mathbf{0.28\ V}$

Reaction is **spontaneous** under standard state conditions because E°_{cell} is positive.

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

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

Overall: $2 Mn^{2+}(aq) + 5 Br_2(l) + 8 H_2O(l) \rightarrow 2 MnO_4^-(aq) + 10 Br^-(aq) + 16 H^+(aq)$

$E^\circ_{cell} = 1.07 \text{ V} – 1.51 \text{ V} = \mathbf{–0.44\ V}$

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

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

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

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

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

$E^\circ_{cell} = 0.85 \text{ V} - 0.92 \text{ V} = \mathbf{–0.07\ V}$

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

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

$E^\circ_{cell} = E°_{Cl_2} – E°_{Fe^{3+}}$

$= 1.36 \text{ V} – (0.77 \text{ V})$

$= 0.59$ V

The reaction is **spontaneous**.

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

$E^\circ_{cell} = E°_{Co^{3+}} – E°_{MnO_2}$

$= 1.82 \text{ V} – (1.23 \text{ V})$

$= 0.59$ V

The reaction is **spontaneous**.

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

$E^\circ_{cell} = E°_{AgCl} – E°_{NO_3^-}$

$= 0.22 \text{ V} – (0.96 \text{ V})$

$= –0.74$ V

The reaction is **nonspontaneous**.

21.33 $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$ E° values are found in Appendix D. Spontaneous reactions have $E^\circ_{cell} > 0$.

a) Oxidation: $2\{Ag(s) \rightarrow Ag^+(aq) + e^-\}$ $E° = 0.80$ V
Reduction: $Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$ $E° = +0.34$ V
Overall: $2\ Ag(s) + Cu^{2+}(aq) \rightarrow 2\ Ag^+(aq) + Cu(s)$

E°_{cell} = +0.34 V – 0.80 V = **–0.46 V**

The reaction is **not spontaneous**.

b) Oxidation: $3\{Cd(s) \rightarrow Cd^{2+}(aq) + 2\ e^-\}$ $E° = -0.40$ V
Reduction: $Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ e^- \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)$ $E° = +1.33$ V
Overall: $Cr_2O_7^{2-}(aq) + 3\ Cd(s) + 14\ H^+(aq) \rightarrow 2\ Cr^{3+}(aq) + 3\ Cd^{2+}(aq) + 7\ H_2O(l)$

E°_{cell} = +1.33 V – (–0.40 V) = **+1.73**

The reaction is **spontaneous**.

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

E°_{cell} = –0.25 V – (–0.13 V) = **–0.12 V**

The reaction is **not spontaneous**.

21.34 a) $2\ Cu^+(aq) + PbO_2(s) + 4\ H^+(aq) + SO_4^{2-}(aq) \rightarrow 2\ Cu^{2+}(aq) + PbSO_4(s) + 2\ H_2O(l)$

$E^\circ_{cell} = E°_{PbO_2} - E°_{Cu^{2+}}$
= 1.70 V – (0.15 V)
= 1.55 V

The reaction is **spontaneous**.

b) $H_2O_2(aq) + Ni^{2+}(aq) \rightarrow 2\ H^+(aq) + O_2(g) + Ni(s)$

$E^\circ_{cell} = E°_{Ni^{2+}} - E°_{O_2}$
= –0.25 V – (0.68 V)
= –0.93 V

The reaction is **nonspontaneous**.

c) $3\ Ag^+(aq) + MnO_2(s) + 4\ OH^-(aq) \rightarrow 3Ag(s) + MnO_4^-(aq) + 2\ H_2O(l)$

$E^\circ_{cell} = E°_{Ag^+} - E°_{MnO_4^-}$
= 0.80 V – (0.59 V)
= 0.21 V

The reaction is **spontaneous**.

21.35 Spontaneous reactions have $E^\circ_{cell} > 0$. All three reactions are written as reductions. When two half-reactions are paired, one half-reaction must be reversed and written as an oxidation. Reverse the half-reaction that will result in a positive value of E°_{cell}.

Adding (1) and (2) to give a spontaneous reaction involves converting (1) to oxidation:
Oxidation: $2\{Al(s) \rightarrow Al^{3+}(aq) + 3\ e^-\}$ $E° = -1.66$ V
Reduction: $3\{N_2O_4(g) + 2\ e^- \rightarrow 2\ NO_2^-(aq)\}$ $E° = 0.867$ V
$3\ N_2O_4(g) + 2\ Al(s) \rightarrow 6\ NO_2^-(aq) + 2\ Al^{3+}(aq)$

E°_{cell} = 0.867 V – (–1.66 V) = **2.53 V**

Adding (1) and (3) to give a spontaneous reaction involves converting (1) to oxidation:
Oxidation: $2\{Al(s) \rightarrow Al^{3+}(aq) + 3\ e^-\}$ $E° = -1.66$ V
Reduction: $3\{SO_4^{2-}(aq) + H_2O(l) + 2\ e^- \rightarrow SO_3^{2-}(aq) + 2\ OH^-(aq)\}$ $E° = 0.93$ V
$2\ Al(s) + 3\ SO_4^{2-}(aq) + 3\ H_2O(l) \rightarrow 2\ Al^{3+}(aq) + 3\ SO_3^{2-}(aq) + 6\ OH^-(aq)$

E°_{cell} = 0.93 V – (–1.66 V) = **2.59 V**

Adding (2) and (3) to give a spontaneous reaction involves converting 2 to oxidation:
Oxidation: $2\ NO_2^{-}(aq) \rightarrow N_2O_4(g) + 2\ e^{-}$ $E° = 0.867$ V
Reduction: $SO_4^{2-}(aq) + H_2O(l) + 2\ e^{-} \rightarrow SO_3^{2-}(aq) + 2\ OH^{-}(aq)$ $E° = 0.93$ V

$SO_4^{2-}(aq) + 2\ NO_2^{-}(aq) + H_2O(l) \rightarrow SO_3^{2-}(aq) + N_2O_4(g) + 2\ OH^{-}(aq)$

$E^{\circ}_{cell} = 0.93\text{ V} - 0.867\text{ V} = \mathbf{0.06\ V}$

21.36 $3\ N_2O(g) + 6\ H^{+}(aq) + 2\ Cr(s) \rightarrow 3\ N_2(g) + 3\ H_2O(l) + 2\ Cr^{3+}(aq)$

$E^{\circ}_{cell} = 1.77\text{ V} - (-0.74\text{ V}) = 2.51$ V

$3\ Au^{+}(aq) + Cr(s) \rightarrow 3\ Au(s) + Cr^{3+}(aq)$

$E^{\circ}_{cell} = 1.69\text{ V} - (-0.74\text{ V}) = 2.43$ V

$N_2O(g) + 2\ H^{+}(aq) + 2\ Au(s) \rightarrow N_2(g) + H_2O(l) + 2\ Au^{+}(aq)$

$E^{\circ}_{cell} = 1.77\text{ V} - (1.69\text{ V}) = 0.08$ V

21.37 Spontaneous reactions have $E^{\circ}_{cell} > 0$. All three reactions are written as reductions. When two half-reactions are paired, one half-reaction must be reversed and written as an oxidation. Reverse the half-reaction that will result in a positive value of E°_{cell}.

Adding (1) and (2) to give a spontaneous reaction involves converting (2) to oxidation:
Oxidation: $Pt(s) \rightarrow Pt^{2+}(aq) + 2\ e^{-}$ $E° = 1.20$ V
Reduction: $2\ HClO(aq) + 2\ H^{+}(aq) + 2\ e^{-} \rightarrow Cl_2(g) + 2\ H_2O(l)$ $E° = 1.63$ V

$2\ HClO(aq) + Pt(s) + 2\ H^{+}(aq) \rightarrow Cl_2(g) + Pt^{2+}(aq) + 2\ H_2O(l)$

$E^{\circ}_{cell} = 1.63\text{ V} - 1.20\text{ V} = \mathbf{0.43\ V}$

Adding (1) and (3) to give a spontaneous reaction involves converting (3) to oxidation:
Oxidation: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2\ e^{-}$ $E° = -0.31$ V
Reduction: $2\ HClO(aq) + 2\ H^{+}(aq) + 2\ e^{-} \rightarrow Cl_2(g) + 2\ H_2O(l)$ $E° = 1.63$ V

$2\ HClO(aq) + Pb(s) + SO_4^{2-}(aq) + 2\ H^{+}(aq) \rightarrow Cl_2(g) + PbSO_4(s) + 2\ H_2O(l)$

$E^{\circ}_{cell} = 1.63\text{ V} - (-0.31\text{ V}) = \mathbf{1.94\ V}$

Adding (2) and (3) to give a spontaneous reaction involves converting (3) to oxidation:
Oxidation: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2\ e^{-}$ $E° = -0.31$ V
Reduction: $Pt^{2+}(aq) + 2\ e^{-} \rightarrow Pt(s)$ $E° = 1.20$ V

$Pt^{2+}(aq) + Pb(s) + SO_4^{2-}(aq) \rightarrow Pt(s) + PbSO_4(s)$

$E^{\circ}_{cell} = 1.20\text{ V} - (-0.31\text{ V}) = \mathbf{1.51\ V}$

21.38 $S_2O_8^{2-}(aq) + 2\ I^{-}(aq) \rightarrow 2\ SO_4^{2-}(aq) + I_2(s)$

$E^{\circ}_{cell} = 2.01\text{ V} - (0.53\text{ V}) = 1.48$ V

$Cr_2O_7^{2-}(aq) + 14\ H^{+}(aq) + 6\ I^{-}(aq) \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l) + 3\ I_2(s)$

$E^{\circ}_{cell} = 1.33\text{ V} - (0.53\text{ V}) = 0.80$ V

$3\ S_2O_8^{2-}(aq) + 2\ Cr^{3+}(aq) + 7\ H_2O(l) \rightarrow 6\ SO_4^{2-}(aq) + Cr_2O_7^{2-}(aq) + 14\ H^{+}(aq)$

$E^{\circ}_{cell} = 2.01\text{ V} - (1.33\text{ V}) = 0.68$ V

21.39 Metal A + Metal B salt → solid colored product on metal A

Conclusion: Product is solid metal B. B is undergoing reduction and plating out on A. 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 $\rightarrow$ no reaction

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

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

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

21.40 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) $E^\circ_{\text{cell}} = E^\circ_{\text{Cu}^{2+}} - E^\circ_{\text{Fe}^{2+}}$

$= 0.34 \text{ V} - (-0.44 \text{ V})$

$= 0.78 \text{ V}$

21.41 $E_{\text{cell}} = -\dfrac{0.0592 \text{ V}}{n}\log\left(\dfrac{Q}{K}\right)$ and $\Delta G = -nFE_{\text{cell}}$

a)When $Q/K < 1$, the reaction is preceding to the right; $E_{\text{cell}} > 0$ and $\Delta G < 0$ and the reaction is spontaneous.

When $Q/K = 1$, the reaction is at equilibrium; $E_{\text{cell}} = 0$ and $\Delta G = 0$.

When $Q/K > 1$, the reaction is preceding to the left; $E_{\text{cell}} < 0$ and $\Delta G > 0$ and the reaction is not spontaneous.

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

21.42 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°_{cell} are related by the Nernst equation: $E_{\text{cell}} = E^\circ_{\text{cell}} - (RT/nF)\ln([A^+]/[B^+])$.

$E_{\text{cell}} = E^\circ_{\text{cell}}$ 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°_{cell}.

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

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

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

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

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

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.

21.44 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.

21.45 The equilibrium constant can be found by using $\ln K = \frac{nFE°}{RT}$ or $\log K = \frac{nE°}{0.0592}$. Use $E°$ values from Appendix D to calculate $E°_{cell}$ and then calculate K.

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

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

$Ni(s) + 2Ag^+(aq) \rightarrow Ni^{2+}(aq) + 2Ag(s)$

$E°_{cell} = E°_{cathode} - E°_{anode}$ = 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) Oxidation: $3\{Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-\}$ $\quad E° = –0.44$ V

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

$E°_{cell} = E°_{cathode} - E°_{anode}$ = –0.74 V – (–0.44 V) = –0.30 V; 6 electrons are transferred.

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

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

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

$E°_{cell} = E°_{Cd^{2+}} - E°_{Al^{3+}}$

= –0.40 V – (–1.66 V)

= 1.26 V

$$\log K = \frac{nE°}{0.0592} = \frac{6(1.26\text{ V})}{0.0592\text{ V}} = 127.7027 \text{ (unrounded)}$$

$K = 5.04316 \times 10^{127} = \mathbf{5 \times 10^{127}}$

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

$E°_{cell} = E°_{I_2} - E°_{Br_2}$

= 0.53 V – (1.07 V)

= –0.54 V

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

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

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

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

21.49 Find $\Delta G°$ from the fact that $\Delta G° = -RT \ln K$. Then use $\Delta G°$ value to find $E°_{cell}$ from $\Delta G° = -nFE°$.

T = (273 + 25)K = 298 K

$\Delta G° = -RT \ln K = -(8.314\text{ J/mol•K})(298\text{ K}) \ln(5.0 \times 10^4) = -2.68067797 \times 10^4 = \mathbf{-2.7 \times 10^4\ J}$

$$E° = -\frac{\Delta G}{nF} = -\frac{-2.68067797 \times 10^4\text{ J}}{(1\text{ mol } e^-)(96485\text{ C/mol } e^-)}\left(\frac{1\text{ V}}{1\text{ J/C}}\right) = 0.27783365 = \mathbf{0.28\ V}$$

21.50 Use $\log K = \dfrac{nE^\circ_{\text{cell}}}{0.0592}$ and $\Delta G^\circ = -RT \ln K$. $T = (273 + 25)\text{K} = 298\text{ K}$

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

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

21.51 Since this is a voltaic cell, a spontaneous reaction is occurring. For a spontaneous reaction between H_2/H^+ and Cu/Cu^{2+}, Cu^{2+} must be reduced and H_2 must be oxidized:

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

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

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

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$
$$= 0.34\text{ V} - 0.00\text{ V}$$
$$= 0.34\text{ V}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{n} \log Q$$

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

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

$$0.22\text{ V} = 0.34\text{ V} - \frac{0.0592}{2} \log \frac{1.0}{\left[Cu^{2+}\right]1.0}$$

$$0.22\text{ V} - 0.34\text{ V} = -\frac{0.0592}{2} \log \frac{1.0}{\left[Cu^{2+}\right]1.0}$$

$$-0.12\text{ V} = -\frac{0.0592}{2} \log \frac{1.0}{\left[Cu^{2+}\right]1.0}$$

$$4.054054 = \log \frac{1.0}{\left[Cu^{2+}\right]1.0} \qquad \text{Raise each side to } 10^x.$$

$$1.132541 \times 10^4 = \frac{1}{[Cu^{2+}]}$$

$[Cu^{2+}] = 8.8296999 \times 10^{-5} = \mathbf{8.8 \times 10^{-5}}\ \boldsymbol{M}$

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

$$E^\circ_{\text{cell}} = E^\circ_{Pb^{2+}} - E^\circ_{Mn^{2+}}$$
$$= -0.13\text{ V} - (-1.18\text{ V})$$
$$= 1.05\text{ V}$$

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

$$0.44\text{ V} = 1.05\text{ V} - \frac{0.0592}{2} \log \frac{[1.4]}{\left[Pb^{2+}\right]}$$

$$(0.44\text{ V} - 1.05\text{ V}) (-2 / 0.0592) = \log \frac{[1.4]}{\left[Pb^{2+}\right]} = 20.608108 \text{ (unrounded)}$$

$$\frac{[1.4]}{\left[Pb^{2+}\right]} = 4.056095$$

$[Pb^{2+}] = 3.45160 \text{ x } 10^{-21} = \mathbf{3.5 \text{ x } 10^{-21}} \boldsymbol{M}$

21.53 The spontaneous reaction (voltaic cell) involves the oxidation of Co and the reduction of Ni^{2+}.

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

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

$Ni^{2+}(aq) + Co(s) \rightarrow Ni(s) + Co^{2+}(aq)$

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = -0.25 \text{ V} - (-0.28 \text{ V}) = 0.03 \text{ V}$$

a) Use the Nernst equation: $E_{\text{cell}} = E^{\circ}_{\text{cell}} - \dfrac{0.0592}{n}\log\dfrac{\left[Co^{2+}\right]}{\left[Ni^{2+}\right]}$ $\qquad n = 2\ e^-$

$$E_{\text{cell}} = 0.03 \text{ V} - \frac{0.0592}{2}\log\frac{[0.20]}{[0.80]} = 0.047820975 \text{ V} = \mathbf{0.05\ V}$$

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 $[Ni^{2+}] = 0.80\ M - x$ (There is a 1:1 mole ratio.)

$$0.03 \text{ V} = 0.03 \text{ V} - \frac{0.0592}{2}\log\frac{[0.20 + x]}{[0.80 - x]}$$

$$0 = -\frac{0.0592}{2}\log\frac{[0.20 + x]}{[0.80 - x]}$$

$$0 = \log\frac{[0.20 + x]}{[0.80 - x]} \qquad \text{Raise each side to } 10^x.$$

$$1 = \frac{[0.20 + x]}{[0.80 - x]}$$

$0.20 + x = 0.80 - x$

$x = 0.30\ M$

$[Ni^{2+}] = 0.80 - 0.30 = \mathbf{0.50}\ \boldsymbol{M}$

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

$$0.00 \text{ V} = 0.03 \text{ V} - \frac{0.0592}{2}\log\frac{[0.20 + x]}{[0.80 - x]}$$

$$-0.03 \text{ V} = -0.0296 \log\frac{[0.20 + x]}{[0.80 - x]}$$

$$1.0135135 = \log\frac{[0.20 + x]}{[0.80 - x]}$$

$$10.316052 = \frac{[0.20 + x]}{[0.80 - x]}$$

$x = 0.7116332$ (unrounded)

$[Co^{2+}] = 0.20 + 0.7116332 = 0.9116332 = \mathbf{0.91}\ \boldsymbol{M}$

$[Ni^{2+}] = 0.80 - 0.7116332 = 0.08837 = \mathbf{0.09}\ \boldsymbol{M}$

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

$E^\circ_{cell} = -0.40\ V - (-1.18\ V) = 0.78\ V.$

a) Use the Nernst equation: $E_{cell} = E^\circ_{cell} - \frac{0.0592}{n}\log\frac{[Mn^{2+}]}{[Cd^{2+}]}$ $\qquad n = 2\ e^-$

$$E_{cell} = 0.78 - \frac{0.0592}{2}\log\frac{[0.090]}{[0.060]}$$

$$= 0.774787698\ V = \mathbf{0.77\ V}$$

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

$$E_{cell} = 0.78 - \frac{0.0592}{2}\log\frac{[0.10]}{[0.050]}$$

$$= 0.771089512\ V = \mathbf{0.77\ V}$$

c) Increase the manganese and decrease the cadmium by equal amounts. Total = 0.150 *M*

$$0.055 = 0.78 - \frac{0.0592}{2}\log\frac{[Mn^{2+}]}{[Cd^{2+}]}$$

$([Mn^{2+}]/[Cd^{2+}]) = 3.1134596 \times 10^{24}$ (unrounded)
$[Mn^{2+}] + [Cd^{2+}] = 0.150\ M$
$[Cd^{2+}] = 4.81779 \times 10^{-26}\ M$ (unrounded)
$[Mn^{2+}] = 0.150\ M - [Cd^{2+}] = \mathbf{0.150\ M}$

d) At equilibrium $E_{cell} = 0.00$.

$$0.00 = 0.78 - \frac{0.0592}{2}\log\frac{[Mn^{2+}]}{[Cd^{2+}]}$$

$([Mn^{2+}]/[Cd^{2+}]) = 2.2456979 \times 10^{26}$ (unrounded)
$[Mn^{2+}] + [Cd^{2+}] = 0.150\ M$
$[Cd^{2+}] = 6.6794377 \times 10^{-28} = \mathbf{7 \times 10^{-28}\ M}$
$[Mn^{2+}] = 0.150\ M - [Cd^{2+}] = \mathbf{0.150\ M}$

21.55 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.

Oxidation: $H_2(g{:}0.90\ atm) \rightarrow 2H^+(aq{:}\ 0.10\ M) + 2\ e^-$ $\qquad E^\circ = 0.00\ V$
Reduction: $2H^+(aq{:}\ 2.0\ M) + 2\ e^- \rightarrow H_2(g{:}\ 0.50\ atm)$ $\qquad E^\circ = 0.00\ V$

$$2H^+(aq{:}\ 2.0\ M) + H_2(g{:}0.90\ atm) \rightarrow 2H^+(aq{:}\ 0.10\ M) + H_2(g{:}\ 0.50\ atm)$$

$$E^\circ_{cell} = 0.00\ V \qquad n = 2\ e^-$$

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

$E_{cell} = 0.00\ V - \dfrac{0.0592}{2}\log(0.001388889) = 0.084577 = \mathbf{0.085\ V}$

21.56 $Sn^{2+}(0.87\ M) \rightarrow Sn^{2+}(0.13\ M)$
Half-cell **B is the cathode**.
$E_{cell} = 0.00V - (0.0592\ V/)\log(0.13/0.87) = 0.024437 = \mathbf{0.024\ V}$

21.57 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.

21.58 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.

21.59 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**

21.60 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.

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

21.62 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.

21.63 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.

21.64 $3\ Cd^{2+}(aq) + 2\ Cr(s) \rightarrow 3\ Cd(s) + 2\ Cr^{3+}(aq)$

$$E^{\circ}_{\text{cell}} = -0.40\ \text{V} - (-0.74\ \text{V}) = 0.34\ \text{V}$$

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

21.65 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.

21.66 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.

21.67 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.

21.68 Iron and nickel are more easily oxidized than copper, so they are separated from the copper in the roasting step and conversion to slag. In the electrorefining process, all three metals are oxidized into solution, but only Cu^{2+} ions are reduced at the cathode to form $Cu(s)$.

21.69 Molten cryolite is a good solvent for Al_2O_3.

21.70 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**).

21.71 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**).

21.72 Possible reductions:

$Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$ $\quad E° = +0.34$ V
$Ba^{2+}(aq) + 2\,e^- \rightarrow Ba(s)$ $\quad E° = –2.90$ V
$Al^{3+}(aq) + 3\,e^- \rightarrow Al(s)$ $\quad E° = –1.66$ V
$2\,H_2O(l) + 2\,e^- \rightarrow H_2(g) + 2\,OH^-(aq)$ $\quad E = –1$ V with overvoltage

Copper can be prepared by electrolysis of its aqueous salt since its reduction half-cell potential is more positive than the potential for the reduction of water. The reduction of copper is more spontaneous than the reduction of water. Since the reduction potentials of Ba^{2+} and Al^{3+} are more negative and therefore less spontaneous than the reduction of water, these ions cannot be reduced in the presence of water since the water is reduced instead.

Possible oxidations:

$2Br^-(aq) \rightarrow Br_2(l) + 2\,e^-$ $\quad E° = +1.07$ V
$2\,H_2O(l) \rightarrow O_2(g) + 4\,H^+(aq) + 4\,e^-$ $\quad E = 1.4$ V with overvoltage

Bromine can be prepared by electrolysis of its aqueous salt because its reduction half-cell potential is more negative than the potential for the oxidation of water with overvoltage. The more negative reduction potential for Br^- indicates that its oxidation is more spontaneous than the oxidation of water.

21.73 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**.

21.74 a) Possible oxidations:

$2\,H_2O(l) \rightarrow O_2(g) + 4\,H^+(aq) + 4\,e^-$ $\quad E = 1.4$ V with overvoltage
$2\,F^- \rightarrow F_2(g) + 2\,e^-$ $\quad E° = 2.87$ V

Since the reduction potential of water is more negative than the reduction potential for F^-, the oxidation of water is more spontaneous than that of F^-. The oxidation of water produces oxygen gas (**O_2**), and hydronium ions (**H_3O^+**) at the anode.

Possible reductions:

$2\,H_2O(l) + 2\,e^- \rightarrow H_2(g) + 2\,OH^-(aq)$ $\quad E = –1$ V with overvoltage
$Li^+(aq) + e^- \rightarrow Li(s)$ $\quad E° = –3.05$ V

Since the reduction potential of water is more positive than that of Li^+, the reduction of water is more spontaneous than the reduction of Li^+. The reduction of water produces **H_2** gas and **OH^-** at the cathode.

b) Possible oxidations:

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

The oxidation of water produces oxygen gas (**O_2**), and hydronium ions (**H_3O^+**) at the anode.
The SO_4^{2-} ion cannot oxidize as S is already in its highest oxidation state in SO_4^{2-}.

Possible reductions:

$2\,H_2O(l) + 2\,e^- \rightarrow H_2(g) + 2\,OH^-(aq)$ $\quad E = –1$ V with overvoltage
$Sn^{2+}(aq) + 2\,e^- \rightarrow Sn(s)$ $\quad E° = –0.14$ V
$SO_4^{2-}(aq) + 4\,H^+(aq) + 2\,e^- \rightarrow SO_2(g) + 2\,H_2O(l)$ $\quad E = –0.63$ 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*.

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

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

21.75 a) Possible oxidations:

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

The oxidation of water produces oxygen gas (**O_2**), and hydronium ions (**H_3O^+**) at the anode.
NO_3– cannot oxidize since N is in its highest oxidation state in NO_3^-.

Possible reductions:

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

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

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

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

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

b) Possible oxidations:

$2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4\ e^-$ $\quad E = 1.4$ 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. Cl^- has a more negative reduction potential showing that it is more easily oxidized than water.

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. The reduction potential of Mn^{2+} is more negative than that of water showing that its reduction is less spontaneous than that of water.

21.76 $Mg^{2+} + 2\ e^- \rightarrow Mg$

a) $$(45.6\ \text{g Mg})\left(\frac{1\ \text{mol Mg}}{24.31\ \text{g Mg}}\right)\left(\frac{2\ \text{mol e}^-}{1\ \text{mol Mg}}\right) = 3.75154257 = \mathbf{3.75\ mol\ e^-}$$

b) $$(3.75154257\ \text{mol e}^-)\left(\frac{96485\ \text{C}}{\text{mol e}^-}\right) = 3.619676 \times 10^5 = \mathbf{3.62 \times 10^5\ coulombs}$$

c) $$\left(\frac{3.619676 \times 10^5\ \text{C}}{3.50\ \text{h}}\right)\left(\frac{1\ \text{h}}{3600\ \text{s}}\right)\left(\frac{\text{A}}{\text{C/s}}\right) = 28.727586 = \mathbf{28.7\ A}$$

21.77 $Na^+ + 1\ e^- \rightarrow Na$

a) $$(215\ \text{g Na})\left(\frac{1\ \text{mol Na}}{22.99\ \text{g Na}}\right)\left(\frac{1\ \text{mol e}^-}{1\ \text{mol Na}}\right) = 9.351892127 = \mathbf{9.35\ mol\ e^-}$$

b) $(9.351892127\ \text{mol e}^-)(96485\ \text{C / mol e}^-) = 9.0231731 \times 10^5 = \mathbf{9.02 \times 10^5\ coulombs}$

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

21.78 $Ra^{2+} + 2\ e^- \rightarrow Ra$

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

$$(235\ \text{C})\left(\frac{1\ \text{mol e}^-}{96485\ \text{C}}\right)\left(\frac{1\ \text{mol Ra}}{2\ \text{mol e}^-}\right)\left(\frac{226\ \text{g Ra}}{1\ \text{mol Ra}}\right) = 0.275224 = \mathbf{0.275\ g\ Ra}$$

21.79 $Al^{3+} + 3\ e^- \rightarrow Al$

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

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

21.80 $Zn^{2+} + 2\ e^- \rightarrow Zn$

$$\text{Time} = (65.5\ g\ Zn)\left(\frac{1\ mol\ Zn}{65.41\ g\ Zn}\right)\left(\frac{2\ mol\ e^-}{1\ mol\ Zn}\right)\left(\frac{96485\ C}{1\ mol\ e^-}\right)\left(\frac{1}{21.0\ A}\right)\left(\frac{1\ A}{C/s}\right) = 9.20169 \times 10^3 = \mathbf{9.20 \times 10^3\ seconds}$$

21.81 $Ni^{2+} + 2\ e^- \rightarrow Ni$

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

21.82 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 (–1 V) than the reduction of Na^+ (–2.71 V); the more spontaneous reduction of water will occur instead of the less spontaneous reduction of sodium ion. The oxidation of H_2O is the only oxidation possible because SO_4^{2-} cannot be oxidized under these conditions. In other words, it is easier to reduce H_2O than Na^+ and easier to oxidize H_2O than SO_4^{2-}.

21.83 a) Calculate amount of chlorine gas from stoichiometry, then use ideal gas law to find volume of chlorine gas.

$2\ NaCl(l) \rightarrow 2\ Na(l) + Cl_2(g)$ 2:1 Na:Cl_2 mole ratio

$$\text{Moles } Cl_2 = (30.0\ kg\ Na)\left(\frac{10^3\ g}{1\ kg}\right)\left(\frac{1\ mol\ Na}{22.99\ g\ Na}\right)\left(\frac{1\ mol\ Cl_2}{2\ mol\ Na}\right) = 652.45759\ mol\ Cl_2\ \text{(unrounded)}$$

$$V = \frac{nRT}{V} = \frac{(652.45759\ mol\ Cl_2)\left(0.0821\frac{L \bullet atm}{mol \bullet K}\right)((273 + 580.)K)}{(1.0\ atm)}$$

$= 4.5692 \times 10^4 = \mathbf{4.6 \times 10^4\ L}$

b) $2\ Cl^- \rightarrow Cl_2 + 2\ e^-$

Two moles of electrons are passed through the cell for each mole of Cl_2 produced.

$$\text{Coulombs} = (652.45759\ mol\ Cl_2)\left(\frac{2\ mol\ e^-}{1\ mol\ Cl_2}\right)\left(\frac{96485\ C}{1\ mol\ e^-}\right)$$

$= 1.259047 \times 10^8 = \mathbf{1.26 \times 10^8\ Coulombs}$

c) Current is charge per time with the amp unit equal to C/s.

$$(125904741\ C)\left(\frac{1\ s}{75\ C}\right) = 1.6787 \times 10^6 = \mathbf{1.68 \times 10^6\ seconds}$$

21.84 $Zn^{2+} + 2\ e^- \rightarrow Zn$

$$\text{Mass} = (0.855\ A)\left(\frac{C/s}{A}\right)\left(\frac{3600\ s}{1\ h}\right)\left(\frac{24\ h}{1\ day}\right)(2.50\ day)\left(\frac{1\ mol\ e^-}{96485\ C}\right)\left(\frac{1\ mol\ Zn}{2\ mol\ e^-}\right)\left(\frac{65.41\ g\ Zn}{1\ mol\ Zn}\right)$$

$= 62.599998 = \mathbf{62.6\ g\ Zn}$

21.85 $Mn^{2+}(aq) + 2\ H_2O(l) \rightarrow MnO_2(s) + 4\ H^+(aq) + 2\ e^-$

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

= 24.66196 = **24.7 hours**

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

21.86 a) The half-reactions are:

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

$2\ H^+(aq) + MnO_2(s) + 2\ e^- \rightarrow Mn(OH)_2(s)$.

2 moles of electrons flow per mole of reaction.

b) $$\text{Mass of MnO}_2 = (4.50\ \text{g Zn})\left(\frac{1\ \text{mol Zn}}{65.41\ \text{g Zn}}\right)\left(\frac{1\ \text{mol MnO}_2}{1\ \text{mol Zn}}\right)\left(\frac{86.94\ \text{g MnO}_2}{1\ \text{mol MnO}_2}\right) = 5.981196 = \mathbf{5.98\ g\ MnO_2}$$

$$\text{Mass of H}_2\text{O} = (4.50\ \text{g Zn})\left(\frac{1\ \text{mol Zn}}{65.41\ \text{g Zn}}\right)\left(\frac{1\ \text{mol H}_2\text{O}}{1\ \text{mol Zn}}\right)\left(\frac{18.02\ \text{g H}_2\text{O}}{1\ \text{mol H}_2\text{O}}\right) = 1.23972 = \mathbf{1.24\ g\ H_2O}$$

c) Total mass of reactants = 4.50 g Zn + 5.981196 g MnO_2 + 1.23972 g H_2O = 11.720916 = **11.72 g**

d) $$\text{Charge} = (4.50\ \text{g Zn})\left(\frac{1\ \text{mol Zn}}{65.41\ \text{g Zn}}\right)\left(\frac{2\ \text{mol e}^-}{1\ \text{mol Zn}}\right)\left(\frac{96485\ \text{coulombs}}{1\ \text{mol e}^-}\right) = 1.32757 \times 10^4 = \mathbf{1.33 \times 10^4\ C}$$

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.

21.87 From the current 65.0% of the moles of product will be copper and 35.0% zinc. Assume a current of exactly 100 coulombs. The amount of current used to generate copper would be (65.0%/100%) (100 C) = 65.0 C, and the amount of current used to generate zinc would be (35.0%/100%) (100 C) = 35.0 C.

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

$$\text{Mass copper} = (65.0\ \text{C})\left(\frac{1\ \text{mol e}^-}{96485\ \text{C}}\right)\left(\frac{1\ \text{mol Cu}}{2\ \text{mol e}^-}\right)\left(\frac{63.55\ \text{g Cu}}{1\ \text{mol Cu}}\right) = 0.021406177\ \text{g Cu (unrounded)}$$

$$\text{Mass zinc} = (35.0\ \text{C})\left(\frac{1\ \text{mol e}^-}{96485\ \text{C}}\right)\left(\frac{1\ \text{mol Zn}}{2\ \text{mol e}^-}\right)\left(\frac{65.41\ \text{g Zn}}{1\ \text{mol Zn}}\right) = 0.01186376\ \text{g Zn (unrounded)}$$

$$\text{Mass \% copper} = \left(\frac{0.021406177\ \text{g Cu}}{(0.021406177 + 0.01186376)\ \text{g Sample}}\right) \times 100\% = 64.340900 = \mathbf{64.3\%\ Cu}$$

21.88

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

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

a) Find the volume of gold needed to plate the earring and then use density to find the mass and moles of gold needed. The volume of the gold is the volume of a cylinder.

$V = \pi r^2 h$

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

$$(0.314159265\ \text{cm}^3)\left(\frac{19.3\ \text{g Au}}{1\ \text{cm}^3}\right)\left(\frac{1\ \text{mol Au}}{197.0\ \text{g Au}}\right) = 0.03077803\ \text{mol Au (unrounded)}$$

$$\text{Time} = (0.03077803\ \text{mol Au})\left(\frac{3\ \text{mol e}^-}{1\ \text{mol Au}}\right)\left(\frac{96485\ \text{C}}{1\ \text{mol e}^-}\right)\left(\frac{\text{A}}{\text{C/s}}\right)\left(\frac{1}{0.013\ \text{A}}\right)\left(\frac{1\ \text{h}}{3600\ \text{s}}\right)\left(\frac{1\ \text{day}}{24\ \text{h}}\right)$$

= 7.931675 = **8 days**

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

Time = (4) (7.931675 days) = 31.7267 = **32 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.

$$\text{Cost} = (4)(0.03077803\ \text{mol Au})\left(\frac{197.0\ \text{g Au}}{1\ \text{mol Au}}\right)\left(\frac{1\ \text{Troy Ounce}}{31.10\ \text{g}}\right)\left(\frac{\$920}{\text{Troy Ounce}}\right) = 717.455 = \mathbf{\$717}$$

21.90 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.

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

= 0.398569696 mol O_2 (unrounded)

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

= 1.97210×10^3 = **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

21.91 The half-reactions and the cell reaction are:

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

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

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

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.

$$\text{Moles Zn} = (0.75\ \text{g Zn})\left(\frac{80\%}{100\%}\right)\left(\frac{1\ \text{mol Zn}}{65.41\ \text{g Zn}}\right) = 0.00917291\ \text{mol Zn (unrounded)}$$

The 80% is assumed to have two significant figures.

$$\text{a) Time} = (0.00917291\ \text{mol Zn})\left(\frac{2\ \text{mol e}^-}{1\ \text{mol Zn}}\right)\left(\frac{96485\text{C}}{1\ \text{mol e}^-}\right)\left(\frac{\text{A}}{\text{C/s}}\right)\left(\frac{1\ \mu\text{A}}{10^{-6}\ \text{A}}\right)\left(\frac{1}{0.85\ \mu\text{A}}\right)\left(\frac{1\ \text{h}}{3600\ \text{s}}\right)\left(\frac{1\ \text{day}}{24\ \text{h}}\right)$$

= 2.410262×10^4 = **2.4×10^4 days**

$$\text{b) Mass Ag} = (0.00917291\ \text{mol Zn})\left(\frac{1\ \text{mol}\ Ag_2O}{1\ \text{mol Zn}}\right)\left(\frac{100\%}{95\%}\right)\left(\frac{2\ \text{mol Ag}}{1\ \text{mol}\ Ag_2O}\right)\left(\frac{107.9\ \text{g Ag}}{1\ \text{mol Ag}}\right)$$

= 2.0836989 = **2.1 g Ag**

$$\text{c) Cost} = (2.0836989\ \text{g Ag})\left(\frac{95\%}{100\%}\right)\left(\frac{1\ \text{troy oz}}{31.10\ \text{g Ag}}\right)\left(\frac{\$13.00}{\text{troy oz}}\right)\left(\frac{}{2.410262 \times 10^4\ \text{days}}\right)$$

= 3.433027×10^{-5} = **\$ 3.4×10^{-5}/day**

21.92 This problem deals with the stoichiometry of electrolysis. The balanced oxidation half-reaction for the chlor-alkali process is given in the chapter:

$$2\ Cl^-(aq) \rightarrow Cl_2(g) + 2\ e^-$$

Use the Faraday constant, F, ($1\ F = 96485$ C/mol e^-) and the fact that 1 mol of Cl_2 produces 2 mol e^- or 2 F, to convert coulombs to moles of Cl_2.

$$\text{Mass } Cl_2 = \left(3 \text{ x } 10^4 \text{ A}\right)\left(\frac{\text{C/s}}{\text{A}}\right)\left(\frac{3600 \text{ s}}{1 \text{ h}}\right)(8 \text{ h})\left(\frac{1 \text{ mol e}^-}{96485 \text{ C}}\right)\left(\frac{1 \text{ mol Cl}_2}{2 \text{ mol e}^-}\right)\left(\frac{70.90 \text{ g Cl}_2}{1 \text{ mol Cl}_2}\right)\left(\frac{1 \text{ kg}}{10^3 \text{ g}}\right)\left(\frac{2.205 \text{ lb}}{1 \text{ kg}}\right)$$

$= 699.9689 =$ **$7 \text{ x } 10^2$ pounds Cl_2**

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

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

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

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

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

$= 1.0728502 \text{ x } 10^5 =$ **$1.073 \text{ x } 10^5$ 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.

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

c) From part (b), the 1.5 x 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.

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

21.95 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.

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

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

21.96 Statement: metal D + hot water $\rightarrow$ reaction — Conclusion: D reduces water.

Statement: D + E salt $\rightarrow$ 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 $\rightarrow$ reaction — Conclusion: D reduces F salt. D is better reducing agent than F.

If E metal and F salt are mixed, the salt 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**.

21.97 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:

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

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.

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

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.

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

b) Cell I: $\text{Mass of reactants} = (2 \text{ mol } H_2)\left(\frac{2.016 \text{ g } H_2}{1 \text{ mol } H_2}\right) + (1 \text{ mol } O_2)\left(\frac{32.00 \text{ g } O_2}{1 \text{ mol } O_2}\right) = 36.032 \text{ g (unrounded)}$

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

Cell II: Mass of reactants =

$$(1 \text{ mol Pb})\left(\frac{207.2 \text{ g Pb}}{1 \text{ mol Pb}}\right) + (1 \text{ mol } PbO_2)\left(\frac{239.2 \text{ g } PbO_2}{1 \text{ mol } PbO_2}\right) + (2 \text{ mol } H_2SO_4)\left(\frac{98.09 \text{ g } H_2SO_4}{1 \text{ mol } H_2SO_4}\right)$$

= 642.58 g (unrounded)

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

Cell III: $\text{Mass of reactants} = (2 \text{ mol Na})\left(\frac{22.99 \text{ g Na}}{1 \text{ mol Na}}\right) + (1 \text{ mol } FeCl_2)\left(\frac{126.75 \text{ g } FeCl_2}{1 \text{ mol } FeCl_2}\right)$

= 172.73 g (unrounded)

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

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

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

From reaction between $U^{3+} + Cr^{3+} \rightarrow Cr^{2+} + U^{4+}$, find that Cr^{3+} oxidizes U^{3+}.
From reaction between $Fe + Sn^{2+} \rightarrow Sn + Fe^{2+}$, find that Sn^{2+} oxidizes Fe.
From the fact that there is no reaction that occurs between Fe and U^{4+}, find that Fe^{2+} oxidizes U^{3+}.
From reaction between $Cr^{3+} + Fe \rightarrow Cr^{2+} + Fe^{2+}$, find that Cr^{3+} oxidizes Fe.
From reaction between $Cr^{2+} + Sn^{2+} \rightarrow Sn + Cr^{3+}$, find that Sn^{2+} oxidizes Cr^{2+}.

Notice that nothing oxidizes Sn, so Sn^{2+} must be the strongest oxidizing agent. Both Cr^{3+} and Fe^{2+} oxidize U^{3+}, so U^{4+} must be the weakest oxidizing agent. Cr^{3+} oxidizes iron so Cr^{3+} is a stronger oxidizing agent than Fe^{2+}.

The half-reactions in order from strongest to weakest oxidizing agent:

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

21.99 Oxidation: $\cancel{Ag(s)} \rightarrow Ag^+(aq) + \cancel{e^-}$ $E^\circ_{red} = 0.80V$

Reduction: $AgCl(s) + \cancel{e^-} \rightarrow \cancel{Ag(s)} + Cl^-(aq)$ $E^\circ_{red} = +0.22V$

Overall: $AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq)$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.22\ V - 0.80\ V = -0.58V$

$$\log K_{sp} = \frac{nE^\circ_{cell}}{0.0592\ V} = \frac{1(-0.58\ V)}{0.0592\ V} = -9.797297 \text{ (unrounded)}$$

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

21.100 Reduction: $Ag^+(aq) + \cancel{e^-} \rightarrow \cancel{Ag(s)}$ $E^\circ_{red} = 0.80V$

Oxidation: $\cancel{Ag(s)} + 2NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq) + \cancel{e^-}$ $E^\circ_{red} = 0.37V$

Overall: $Ag^+(aq) + 2NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq)$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.80V - 0.37V = 0.43V$

$$\log K_{sp} = \frac{nE^\circ_{cell}}{0.0592\ V} = \frac{1(0.43\ V)}{0.0592\ V} = 7.26351 \text{ (unrounded)}$$

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

21.101 Place the elements in order of increasing (more positive) $E°$.
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 by reducing the hydrogen in water. These can displace 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 by reducing the H^+ in acid. These can displace 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 (reduce) hydrogen.
These cannot displace H_2: **Cu, Ag, Hg, and Au**

21.102 a) Use the stoichiometric relationships found in the balanced chemical equation to find mass of Al_2O_3. Assume that 1 metric ton Al is an exact number.

$2\ Al_2O_3$ (in Na_3AlF_6) $+ 3\ C(gr) \rightarrow 4\ Al(l) + 3\ CO_2(g)$

$$\text{mass } Al_2O_3 = (1\ t\ Al)\left(\frac{10^3\ kg}{1\ t}\right)\left(\frac{10^3\ g}{1\ kg}\right)\left(\frac{1\ mol\ Al}{26.98\ g\ Al}\right)\left(\frac{2\ mol\ Al_2O_3}{4\ mol\ Al}\right)\left(\frac{101.96\ g\ Al_2O_3}{1\ mol\ Al_2O_3}\right)\left(\frac{1\ kg}{10^3\ g}\right)\left(\frac{1\ t}{10^3\ kg}\right)$$

$= 1.8895478 = \mathbf{1.890}$ metric tons Al_2O_3

Therefore, **1.890 tons of Al_2O_3** are consumed in the production of 1 ton of pure Al.

b) Use a ratio of 3 mol C: 4 mol Al to find mass of graphite consumed.

$$\text{mass C} = (1\ t\ Al)\left(\frac{10^3\ kg}{1\ t}\right)\left(\frac{10^3\ g}{1\ kg}\right)\left(\frac{1\ mol\ Al}{26.98\ g\ Al}\right)\left(\frac{3\ mol\ C}{4\ mol\ Al}\right)\left(\frac{12.01\ g\ C}{1\ mol\ C}\right)\left(\frac{1\ kg}{10^3\ g}\right)\left(\frac{1\ t}{10^3\ kg}\right)$$

$= 0.3338584 = $ **0.3339 tons C**

Therefore, **0.3339 tons of C** are consumed in the production of 1 ton of pure Al, assuming 100% efficiency.

c) The percent yield with respect to Al_2O_3 is **100%** because the actual plant requirement of 1.89 tons Al_2O_3 equals the theoretical amount calculated in part (a).

d) The amount of graphite used in reality to produce 1 ton of Al is greater than the amount calculated in (b). In other words, a 100% efficient reaction takes only 0.3339 tons of graphite to produce a ton of Al, whereas real production requires more graphite and is less than 100% efficient. Calculate the efficiency using a simple ratio:

(0.45 t) (x) = (0.3338584 t) (100%)

x = 74.19076 = **74%**

e) For every 4 moles of Al produced, 3 moles of CO_2 are produced.

$$\text{moles C} = (1\ t\ Al)\left(\frac{10^3\ kg}{1\ t}\right)\left(\frac{10^3\ g}{1\ kg}\right)\left(\frac{1\ mol\ Al}{26.98\ g\ Al}\right)\left(\frac{3\ mol\ CO_2}{4\ mol\ Al}\right) = 2.7798 \times 10^4 \text{ mol } CO_2 \text{ (unrounded)}$$

The problem states that 1 atm is exact. Use the ideal gas law to calculate volume, given moles, temperature, and pressure.

$$V = nRT/P = \left(\frac{\left(2.7798 \text{ x } 10^4 \text{ mol } CO_2\right)\left(0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K}\right)\left((273 + 960.)\text{K}\right)}{1 \text{ atm}}\right)\left(\frac{10^{-3} \text{ m}^3}{1 \text{ L}}\right)$$

$= 2.812601 \text{ x } 10^3 =$ **$2.813 \text{ x } 10^3 \text{ m}^3$**

21.103 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.

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

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

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

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

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

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

$[Cu^{2+}]_{ammonia} = 4.3842154 \text{ x } 10^{-7}$ 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:

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

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

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

Determine the moles of copper still remaining uncomplexed.

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

$= 4.3842154 \text{ x } 10^{-8}$ 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 $= (9.00 \text{ x } 10^{-4} - 4.3842154 \text{ x } 10^{-8}) \text{ mol } Cu^{2+}$
$= 8.9995615 \text{ x } 10^{-4} \text{ mol } Cu^{2+}$ (unrounded)

$$\text{Molarity of complex} = \left(\frac{8.9995615 \text{ x } 10^{-4} \text{ mol Cu}^{2+}}{100.0 \text{ mL}}\right)\left(\frac{1 \text{ mol Cu(NH}_3)_4{}^{2+}}{1 \text{ mol Cu}^{2+}}\right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)$$

$= 8.9995615 \text{ x } 10^{-3}$ 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:

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

$$K_f = \frac{\left[\text{Cu(NH}_3)_4{}^{2+}\right]}{\left[\text{Cu}^{2+}\right]\left[\text{NH}_3\right]^4} = \frac{\left[8.9995615 \text{ x } 10^{-3}\right]}{\left[4.3842154 \text{ x } 10^{-7}\right]\left[0.014001753\right]^4} = 5.34072 \text{ x } 10^{11} = \mathbf{5.3 \text{ x } 10^{-11}}$$

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 = $5.00 \text{ x } 10^{-3}$ mol NH_3 (same as original moles of ammonia)

From the stoichiometry:

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

$[Cu(NH_3)_4{}^{2+}]$ = ($9.00000 \text{ x } 10^{-4}$ 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:	$+x$		$+4x$		$-x$
Equilibrium:	x		$0.0581818 + 4x$		$0.008181818 - x$

$$K_f = \frac{\left[\text{Cu(NH}_3)_4{}^{2+}\right]}{\left[\text{Cu}^{2+}\right]\left[\text{NH}_3\right]^4} = \frac{\left[0.008181818 - x\right]}{\left[x\right]\left[0.0581818 + 4x\right]^4} = 5.34072 \text{ x } 10^{11}$$

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:

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

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

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

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

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

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

The reaction:

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

Determine concentrations before equilibrium:

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

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

Now allow the system to come to equilibrium:

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

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

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

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:

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

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

$E = 0.434169 = \mathbf{0.43\ V}$

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

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

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

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

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

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

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

Now use the K_{sp} relationship:

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

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

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

$[OH^-] = 8.2121 \times 10^{-4} = 8.2 \times 10^{-4}$ *M* OH^- = **8.2×10^{-4} *M* NaOH**

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

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

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

Overall: $Cd(s) + Cu^{2+}(aq) \rightarrow Cd^{2+}(aq) + Cu(s)$

Calculate $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

Cu/Cd E°_{cell} = 0.34 V – (–0.40 V) = **0.74 V**

Note: Cd is a better reducing agent than Cu so Cu^{2+} reduces while Cd oxidizes.

$\Delta G° = –nFE°$

$\Delta G°$ = –(2 mol e^-) (96485 C/mol e^-) (0.74 J/C) = $–1.427978 \times 10^5$ = **$–1.4 \times 10^5$ J**

$$\log K = \frac{nE^\circ_{cell}}{0.0592}$$

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

K = **1×10^{25}**

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

Next, use the Nernst equation:

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

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

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 = **0.69 V**

c) At equilibrium, **E_{cell} = 0**, and **ΔG = 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*.

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

Assume *x* is negligible compared to 2.00.

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

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

x = **2.0×10^{-25} *M* Cu^{2+}**

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

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

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

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

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

$$0.915\ V - 0.80\ V = -\frac{0.0592\ V}{2}\ \log \frac{\left[H^+\right]^2}{\left[0.100\right]^2 (1.00)}$$

$$(0.915\ V - 0.80\ V)\ (-2/0.0592\ V) = \log \frac{\left[H^+\right]^2}{\left[0.100\right]^2 (1.00)}$$

$$-3.885135 = \log \frac{\left[H^+\right]^2}{\left[0.0100\right]}$$

$$1.30276 \times 10^{-4} = \frac{\left[H^+\right]^2}{\left[0.0100\right]}$$

$[H^+] = 1.1413851 \times 10^{-3}\ M$ (unrounded)

pH = $-\log [H^+] = -\log (1.1413851 \times 10^{-3}) = 2.94256779 =$ **2.94**