Chapter 17 Review Questions and Text Homework Solutions

Review Questions

2. Before we answer the question, here are four important terms relating to redox reactions and galvanic cells.

   a. Cathode: The electrode at which reduction occurs.

   b. Anode: The electrode at which oxidation occurs.

   c. Oxidation half-reaction: The half-reaction in which electrons are products. In a galvanic cell, the oxidation half-reaction always occurs at the anode.

   d. Reduction half-reaction: The half-reaction in which electrons are reactants. In a galvanic cell, the reduction half-reaction always occurs at the cathode.

   See Figures 17.2 and 17.3 for designs of galvanic cells. The electrode compartment in which reduction occurs is called the cathode and the electrode compartment in which oxidation occurs is called the anode. These compartments have electrodes (a solid surface) immersed in a solution. For a standard cell, the solution contains the reactant and product solutes and gases that are in the balanced half-reactions. The solute concentrations are all 1 *M* and gas partial pressures are all 1 atm for a standard cell. The electrodes are connected via a wire and a salt-bridge connects the two solutions.

   The purpose of the electrodes is to provide a solid surface for electron transfer to occur in the two compartments. Electrons always flow from the anode (where they are produced) to the cathode (where they are reactants). The salt bridge allows counter ions to flow into the two cell compartments to maintain electrical neutrality. Without a salt bridge, no sustained electron flow can occur. In the salt bridge, anions flow into the anode to replenish the loss of negative charge as electrons are lost; cations flow into the cathode to balance the negative charge as electrons are transferred into the cathode. The "pull" or driving force on the electrons is called the cell potential ($\mathcal{E}_{cell}$) or the electromotive force. The unit of electrical potential is the volt (V) which is defined as 1 joule of work per coulomb of charge transferred. It is the cell potential that can be used to do useful work. We harness the spontaneous redox reaction to produce a cell potential which can do useful work.

3. The zero point for standard reduction potentials ($\mathcal{E}°$) is the standard hydrogen electrode. The half-reaction is: $2\ H^+ + 2\ e^- \rightarrow H_2$. This half-reaction is assigned a standard potential of zero, and all other reduction half-reactions are measured relative to this zero point. Sub-stances less easily reduced than H^+ have negative standard reduction potentials ($\mathcal{E}° < 0$), while substances more easily reduced than H^+ have positive standard reduction potentials ($\mathcal{E}° > 0$). The species most easily reduced has the most positive $\mathcal{E}°$ value; this is F_2. The least easily reduced species is Li^+ with the most negative $\mathcal{E}°$ value.

When a reduction half-reaction is reversed to obtain an oxidation half-reaction, the sign of the reduction potential is reversed to give the potential for the oxidation half-reaction ($\mathcal{E}^{\circ}_{\text{ox}} = -\mathcal{E}^{\circ}_{\text{red}}$). The species oxidized are on the product side of the reduction half-reactions listed in Table 17.1. Li will have the most positive oxidation potential [$\mathcal{E}^{\circ}_{\text{ox}} = -\mathcal{E}^{\circ}_{\text{red}} = -(-3.05\text{ V}) = 3.05\text{ V}$], so Li is the most easily oxidized of the species. The species most easily oxidized is the best reducing agent. The worst reducing agent is F^- because it has the most negative oxidation potential ($\mathcal{E}^{\circ}_{\text{ox}} = -2.87\text{ V}$).

For a spontaneous reaction at standard conditions, $\mathcal{E}^{\circ}_{\text{cell}}$ must be positive ($\mathcal{E}^{\circ}_{\text{cell}} = \mathcal{E}^{\circ}_{\text{red}} + \mathcal{E}^{\circ}_{\text{ox}} > 0$). For any two half-reactions, there is only one way to manipulate them to come up with a positive $\mathcal{E}^{\circ}_{\text{cell}}$ (a spontaneous reaction). Because the half-reactions do not depend on how many times the reaction occurs, half-reactions are an intensive property. This means that the value of $\mathcal{E}^{\circ}_{\text{red}}$ or $\mathcal{E}^{\circ}_{\text{ox}}$ is not changed when the half-reactions are multiplied by integers to get the electrons to cross off.

The line notation of the standard galvanic cell illustrated in Figure 17.5 of the text would be:

$Zn(s) \mid Zn^{2+}(aq) \parallel H_2(g) \mid H^+(aq) \mid Pt$ or

$Zn(s) \mid Zn^{2+}(1.0\ M) \parallel H_2(1.0\text{ atm}) \mid H^+(1.0\ M) \mid Pt$

The double line represents the salt-bridge separating the anode and cathode compartments. To the left of the double line are the pertinent anode compartment contents, and to the right are the pertinent cathode compartment contents. At each end, the electrodes are listed; to the inside, the solution contents are listed. A single line is used to separate the contents of each compartment whenever there is a phase change. Here in the cathode compartment, a single line is used to separate $H_2(g)$ from $H^+(aq)$ and to separate $H^+(aq)$ from Pt (the electrode). When concentrations and partial pressures are not listed, they are assumed to be standard (1.0 *M* for solutes and 1.0 atm for gases). For cells having nonstandard concentrations and pressures, we always include the actual concentrations and pressures in the line notation instead of the phases.

4. $\Delta G^{\circ} = -nF\mathcal{E}^{\circ}$; ΔG° is the standard free energy change for the overall balanced reaction, n is the number of electrons transferred in the overall balanced reaction, F is called the Faraday constant (1 F = 96,485 coulombs of charge transferred per mole of electrons), and $\mathcal{E}^{\circ}$ is the standard cell potential for the reaction. For a spontaneous redox reaction, $\mathcal{E}^{\circ}_{\text{cell}}$ is positive while $\Delta G^{\circ}_{\text{rxn}}$ is negative. The negative sign is necessary to convert the positive $\mathcal{E}^{\circ}_{\text{cell}}$ value for a spontaneous reaction into a negative $\Delta G^{\circ}_{\text{rxn}}$. The superscript ° indicates standard conditions. These are $T = 25^{\circ}C$, solute concentrations of 1.0 *M*, and gas partial pressures of 1.0 atm. Note that n is necessary in order to convert the intensive property $\mathcal{E}^{\circ}$ into the extensive property ΔG°.

5. $\mathcal{E} = \mathcal{E}^{\circ} - \dfrac{RT}{nF}\ln Q$; at 25°C, the Nernst equation is: $\mathcal{E} = \mathcal{E}^{\circ} - \dfrac{0.0591}{n}\log Q$

Nonstandard conditions are when solutes are not all 1.0 *M* and/or partial pressures of gases are not all 1.0 atm. Nonstandard conditions also occur when $T \neq 25°C$, For most problem solving, $T = 25°C$ is usually assumed, hence the second version of the Nernst equation is most often used.

$\mathcal{E}$ = cell potential at the conditions of the cell; $\mathcal{E}°$ = standard cell potential; n = number of electrons transferred in the overall reaction, and Q is the reaction quotient determined at the concentrations and partial pressures of the cell contents.

At equilibrium, $\mathcal{E} = 0$ and $Q = K$. At 25˚C, $\mathcal{E}° = (0.0591/n)\log K$. The standard cell potential allows calculation of the equilibrium constant for a reaction. When $K < 1$, the log K term is negative, so $\mathcal{E}^{o}_{\text{cell}}$ is negative and $\Delta G°$ is positive. When $K > 1$, the log K term is positive, so $\mathcal{E}^{o}_{\text{cell}}$ is positive and $\Delta G°$ is negative.

From the equation $\mathcal{E}° = (0.0591/n)\log K$, the value of $\mathcal{E}°$ allows calculation of the equilibrium constant K. We say that $\mathcal{E}°$ gives the equilibrium position for a reaction. $\mathcal{E}$ is the actual cell potential at the conditions of the cell reaction. The sign of $\mathcal{E}$ determines the spontaneity of the cell reaction. If $\mathcal{E}$ is positive, then the cell reaction is spontaneous as written (the forward reaction can be used to make a galvanic cell to produce a voltage). If $\mathcal{E}$ is negative, the forward reaction is not spontaneous at the conditions of cell, but the reverse reaction is spontaneous. The reverse reaction can be used to form a galvanic cell. $\mathcal{E}°°$ can only be used to determine spontaneity when all reactants and products are at standard conditions ($T = 25˚C$, [ ] = 1.0 *M*, $P = 1.0$ atm).

6. Concentration cell: A galvanic cell in which both compartments contain the same components, but at different concentrations. All concentration cells have $\mathcal{E}^{o}_{\text{cell}} = 0$ because both compartments contain the same contents. The driving force for the cell is the different ion concentrations between the anode and cathode. The cell produces a voltage as long as the ion concentrations are different. Equilibrium for a concentration cell is reached ($\mathcal{E} = 0$) when the ion concentrations in the two compartments are equal.
The net reaction in a concentration cell is:

$$M^{a+}(\text{cathode}, x\,M) \rightarrow M^{a+}(\text{anode}, y\,M) \quad \mathcal{E}^{o}_{\text{cell}} = 0$$

and the Nernst equation is:

$$\mathcal{E} = \mathcal{E}° - \frac{0.0591}{n}\log Q = -\frac{0.0591}{a}\log\frac{[M^{a+}(\text{anode})]}{[M^{a+}(\text{cathode})]}$$

where a is the number of electrons transferred.

To register a potential ($\mathcal{E} > 0$), the log Q term must be a negative value. This occurs when M^{a+}(cathode) > M^{a+}(anode). The higher ion concentration is always at the cathode and the lower ion concentration is always at the anode. The magnitude of the cell potential depends on the magnitude of the differences in ion concentrations between the anode and cathode. The larger the difference in ion concentrations, the more negative the log Q term and the more positive the cell potential. Thus, as the difference in ion concentrations between the anode and cathode compartments increase, the cell potential increases. This can be accomplished by decreasing the ion concentration at the anode and/or by increasing the ion concentration at the cathode.

When NaCl is added to the anode compartment, Ag^+ reacts with Cl^- to form AgCl(*s*). Add-ing Cl^- lowers the Ag^+ concentration which causes an increase in the cell potential. To determine K_{sp} for AgCl ($K_{sp} = [Ag^+][Cl^-]$), we must know the equilibrium Ag^+ and Cl^- concentrations. Here, $[Cl^-]$ is given and we use the Nernst equation to calculate the $[Ag^+]$ at the anode.

7. As a battery discharges, $\mathcal{E}_{cell}$ decreases, eventually reaching zero. A charged battery is not at equilibrium. At equilibrium, $\mathcal{E}_{cell} = 0$ and $\Delta G = 0$. We get no work out of an equilibrium system. A battery is useful to us because it can do work as it approaches equilibrium.

Both fuel cells and batteries are galvanic cells that produce cell potentials to do useful work. However, fuel cells, unlike batteries, have the reactants continuously supplied and can produce a current indefinitely.

The overall reaction in the hydrogen-oxygen fuel cell is $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$. The half-reactions are:

$4\ e^- + O_2 + 2\ H_2O \rightarrow 4\ OH^-$ cathode

$2\ H_2 + 4\ OH^- \rightarrow 4\ H_2O + 4\ e^-$ anode

Utilizing the standard potentials in Table 17.1, $\mathcal{E}^{o}_{cell} = 0.40\ V + 0.83\ V = 1.23\ V$ for the hydrogen-oxygen fuel cell. As with all fuel cells, the $H_2(g)$ and $O_2(g)$ reactants are con-tinuously supplied. See Figure 17.16 of the text for a schematic of this fuel cell.

8. The corrosion of a metal can be viewed as the process of returning metals to their natural state. The natural state of metals is to have positive oxidation numbers. This corrosion is the oxidation of a pure metal (oxidation number = 0) into its ions. For corrosion of iron to take place, you must have:

a. exposed iron surface – a reactant

b. $O_2(g)$ – a reactant

c. $H_2O(l)$ – a reactant, but also provides a medium for ion flow (it provides the salt bridge)

d. ions – to complete the salt bridge

Because water is a reactant and acts as a salt bridge for corrosion, cars do not rust in dry air climates, while corrosion is a big problem in humid climates. Salting roads in the winter also increases the severity of corrosion. The dissolution of the salt into ions on the surface of a metal increases the conductivity of the aqueous solution and accelerates the corrosion process.

Some of the ways metals (iron) are protected from corrosion are listed below.

a. Paint: Covers the metal surface so no contact occurs between the metal and air. This only works as long as the painted surface is not scratched.

b. Durable oxide coatings: Covers the metal surface so no contact occurs between the metal and air.

c. Galvanizing: Coating steel with zinc; Zn forms an effective oxide coating over steel; also, zinc is more easily oxidized than the iron in the steel.

d. Sacrificial metal: Attaching a more easily oxidized metal to an iron surface; the more active metal is preferentially oxidized instead of iron.

e. Alloying: Adding chromium and nickel to steel; the added Cr and Ni form oxide coatings on the steel surface.

f. Cathodic protection: A more easily oxidized metal is placed in electrical contact with the metal we are trying to protect. It is oxidized in preference to the protected metal. The protected metal becomes the cathode electrode, thus, cathodic protection.

9. An electrolytic cell uses electrical energy to produce a chemical change. The process of electrolysis involves forcing a current through a cell to produce a chemical change for which the cell potential is negative. Electrical work is used to force a nonspontaneous reaction to occur.

The units for current are amperes (A) which equal 1 coulomb of charge per second.

current (A) × time (s) = coulombs of charge passed

We use Faraday's constant (F = 96,485 coulombs of charge per mole) to convert coulombs of charge passed into moles of electrons passed. The half-reaction gives the mole ratio between moles of electrons and moles of metal produced (or plated out). Plating means depositing the neutral metal on the electrode by reducing the metal ions in solution.

In electrolysis, as with any redox reaction, the reaction that occurs first is the one most favored thermodynamically. The reduction reaction most favored thermodynamically has the largest, most positive $\mathcal{E}^{o}_{red}$ value. The oxidation reaction most likely to occur is the one with the largest, most positive $\mathcal{E}^{o}_{ox}$ value. Note that for electrolytic cells, $\mathcal{E}^{o}_{cell} < 0$, so the $\mathcal{E}^{o}_{red}$ and $\mathcal{E}^{o}_{ox}$ values are commonly negative. The half-reactions that occur first as a current is applied are the ones with the least negative potentials (which are the most positive potentials). To predict the cathode half-reaction, write down the half-reaction and $\mathcal{E}^{o}_{red}$ value for all species present that can be reduced. The cathode reaction that occurs has the least negative (most positive) $\mathcal{E}^{o}_{red}$ value. The same thing is done for the anode; write down everything present that can be oxidized; the species oxidized has the least negative (most positive) $\mathcal{E}^{o}_{ox}$ value. Note that we commonly assume standard conditions when predicting which half-reactions occur, so we can use the standard potentials in Table 17.1.

When molten salts are electrolyzed, there is only one species present that can be oxidized (the anion in simple salts) and there is only one species that can be reduced (the cation in simple salts). When H_2O is present as is the case when aqueous solutions are electrolyzed, we must consider the oxidation and reduction of water as potential reactions that can occur. When water is present, more reactions can take place, making predictions more difficult.

When the voltage required to force a chemical reaction to occur is larger than expected, this is called overvoltage. The amount of overvoltage necessary to force a reaction to occur varies with the type of substance present. Because of this, $\mathcal{E}°$ values must be used cautiously when predicting the half-reactions that occur.

10. Electrolysis is used to produce many pure metals and pure elements for commercial use. It also is used to purify metals as well as to plate out thin coatings on substances to provide protection from corrosion and to beautify objects. Another application of electrolysis is the charging of batteries.

When aqueous NaCl is electrolyzed, water, with its less negative reduction potential is preferentially reduced over Na^+ ions. Thus, the presence of water doesn't allow Na^+ ions to be reduced to Na. In molten NaCl, water is not present, so Na^+ can be reduced to Na.

Purification by electrolysis is called electrorefining. See the text for a discussion of the electrorefining of copper. Electrorefining is possible because of the selectivity of electrode reactions. The anode is made up of the impure metal. A potential is applied so just the metal of interest and all more easily oxidized metals are oxidized at the anode. The metal of interest is the only metal plated at the cathode due to the careful control of the potential applied. The metal ions that could plate out at the cathode in preference to the metal we are purifying will not be in solution, because these metals were not oxidized at the anode.

Text Homework

15. Oxidation: increase in oxidation number; loss of electrons
Reduction: decrease in oxidation number; gain of electrons

17. The species oxidized shows an increase in oxidation numbers and is called the reducing agent. The species reduced shows a decrease in oxidation numbers and is called the oxidizing agent. The pertinent oxidation numbers are listed by the substance oxidized and the substance reduced.

	Redox?	Ox. Agent	Red. Agent	Substance Oxidized	Substance Reduced
a.	Yes	H_2O	CH_4	CH_4 (C, $-4 \rightarrow +2$)	H_2O (H, $+1 \rightarrow 0$)
b.	Yes	$AgNO_3$	Cu	Cu ($0 \rightarrow +2$)	$AgNO_3$ (Ag, $+1 \rightarrow 0$)
c.	Yes	HCl	Zn	Zn ($0 \rightarrow +2$)	HCl (H, $+1 \rightarrow 0$)
d.	No; there is no change in any of the oxidation numbers.				

19. Electrochemistry is the study of the interchange of chemical and electrical energy. A redox (oxidation-reduction) reaction is a reaction in which one or more electrons are transferred. In a galvanic cell, a spontaneous redox reaction occurs that produces an electric current. In an electrolytic cell, electricity is used to force a nonspontaneous redox reaction to occur.

21. Magnesium is an alkaline earth metal; Mg will oxidize to Mg^{2+}. The oxidation state of hydrogen in HCl is +1. To be reduced, the oxidation state of H must decrease. The obvious choice for the hydrogen product is $H_2(g)$, where hydrogen has a zero oxidation state. The balanced reaction is

$Mg(s) + 2\ HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$. Mg goes from the 0 to the +2 oxidation state by losing two electrons. Each H atom goes from the +1 to the 0 oxidation state by gaining one electron. Since there are two H atoms in the balanced equation, then a total of two electrons are gained by the H atoms. Hence two electrons are transferred in the balanced reaction. When the electrons are transferred directly from Mg to H^+, no work is obtained. To harness this reaction to do useful work, we must control the flow of electrons through a wire. This is accomplished by making a galvanic cell that separates the reduction reaction from the oxidation reaction to control the flow of electrons through a wire to produce a voltage.

22. Galvanic cells use spontaneous redox reactions to produce a voltage. For a spontaneous redox reaction, the key is to have an overall positive E^{o}_{cell} value when manipulating the half-reactions. For any two half-reactions, the half-reaction with the most positive reduction potential will always be the cathode reaction. The remaining half-reaction (the one with the most negative E^{o}_{red}) will be reversed and become the anode half-reaction. This combination will always yield an overall reaction having a positive standard cell potential that can be used to run a galvanic cell.

23. An extensive property is one that depends directly on the amount of substance. The free-energy change for a reaction depends on whether 1 mole of product is produced or 2 moles of product is produced or 1 million moles of product is produced. This is not the case for cell potentials, which do not depend on the amount of substance. The equation that relates ΔG to E is $\Delta G = -nFE$. It is the n term that converts the intensive property E into the extensive property ΔG. n is the number of moles of electrons transferred in the balanced reaction that ΔG is associated with.

24. $E = E^{o}_{cell} - \frac{0.0591}{n}\log Q$

A concentration cell has the same anode and cathode contents; thus $E^{o}_{cell} = 0$ for a con-centration cell. No matter which half-reaction you choose, the opposite half-reaction is occurring in the other cell. The driving force to produce a voltage is the $-\log Q$ term in the Nernst equation. Q is determined by the concentration of ions in the anode and cathode compartments. The larger the difference in concentrations, the larger is the $-\log Q$ term, and the larger is the voltage produced. Therefore, the driving force for concentration cells is the difference in ion concentrations between the cathode and anode compartments. When the ion concentrations are equal, $Q = 1$ and $\log Q = 0$, and no voltage is produced.

27. $Zn \rightarrow Zn^{2+} + 2\ e^-\quad -E° = 0.76\ V$; $Fe \rightarrow Fe^{2+} + 2\ e^-\quad -E° = 0.44\ V$

It is easier to oxidize Zn than Fe, so the Zn would be preferentially oxidized, protecting the iron of the *Monitor's* hull.

28. Aluminum has the ability to form a durable oxide coating over its surface. Once the HCl dissolves this oxide coating, Al is exposed to H^+ and is easily oxidized to Al^{3+}, i.e., the Al foil disappears after the oxide coating is dissolved.

29. You need to know the identity of the metal so that you know which molar mass to use. You need to know the oxidation state of the metal ion in the salt so that the moles of electrons transferred can be determined. And finally, you need to know the amount of current and the time the current

was passed through the electrolytic cell. If you know these four quantities, then the mass of metal plated out can be calculated.

38. A galvanic cell at standard conditions must have a positive overall standard cell potential ($E^\circ_{cell} > 0$). The only combination of the half-reactions that gives a positive cell potential is:

$$\begin{array}{ll}
Cu^{2+} + 2e^- \rightarrow Cu & E^\circ(\text{cathode}) = 0.34\text{ V} \\
Zn \rightarrow Zn^{2+} + 2e^- & -E^\circ(\text{anode}) = 0.76\text{ V} \\
\hline
Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq) & E^\circ_{cell} = 1.10\text{ V}
\end{array}$$

a. The reducing agent causes reduction to occur since it always contains the species which is oxidized. Zn is oxidized in the galvanic cell, so Zn is the reducing agent. The oxidizing agent causes oxidation to occur since it always contains the species which is reduced. Cu^{2+} is reduced in the galvanic cell, so Cu^{2+} is the oxidizing agent. Electrons will flow from the zinc compartment (the anode) to the copper compartment (the cathode).

b. From the work above, $E^\circ_{cell} = 1.10$ V.

c. The pure metal that is a product in the spontaneous reaction is copper. So the copper electrode will increase in mass as $Cu^{2+}(aq)$ is reduced to Cu(s). The zinc electrode will decrease in mass for this galvanic cell as Zn(s) is oxidized to $Zn^{2+}(aq)$.

43. Reference the answer to Exercise 39 for a typical galvanic cell design. The contents of each half-cell compartment are identified below with all solute concentrations at 1.0 *M* and all gases at 1.0 atm. For each pair of half-reactions, the half-reaction with the largest (most positive) standard reduction potential will be the cathode reaction, and the half-reaction with the smallest (most negative) reduction potential will be reversed to become the anode reaction. Only this combination gives a spontaneous overall reaction, i.e., a reaction with a positive overall standard cell potential. Note that in a galvanic cell as illustrated in Exercise 39 the cations in the salt bridge migrate to the cathode, and the anions migrate to the anode.

a.

$$\begin{array}{ll}
Cl_2 + 2\,e^- \rightarrow 2\,Cl^- & E^\circ = 1.36\text{ V} \\
2\,Br^- \rightarrow Br_2 + 2\,e^- & -E^\circ = -1.09\text{ V} \\
\hline
Cl_2(g) + 2\,Br^-(aq) \rightarrow Br_2(aq) + 2\,Cl^-(aq) & E^\circ_{cell} = 0.27\text{ V}
\end{array}$$

The contents of each compartment are:

Cathode: Pt electrode; $Cl_2(g)$ bubbled in, Cl^- in solution

Anode: Pt electrode; Br_2 and Br^- in solution

b.

$$\begin{array}{ll}
(2\,e^- + 2\,H^+ + IO_4^- \rightarrow IO_3^- + H_2O) \times 5 & E^\circ = 1.60\text{ V} \\
(4\,H_2O + Mn^{2+} \rightarrow MnO_4^- + 8\,H^+ + 5\,e^-) \times 2 & -E^\circ = -1.51\text{ V} \\
\hline
10\,H^+ + 5\,IO_4^- + 8\,H_2O + 2\,Mn^{2+} \rightarrow 5\,IO_3^- + 5\,H_2O + 2\,MnO_4^- + 16\,H^+ & E^\circ_{cell} = 0.09\text{ V}
\end{array}$$

This simplifies to:

$$3\,H_2O(l) + 5\,IO_4^-(aq) + 2\,Mn^{2+}(aq) \rightarrow 5\,IO_3^-(aq) + 2\,MnO_4^-(aq) + 6\,H^+(aq) \qquad E^\circ_{cell} = 0.09\text{ V}$$

The contents of each compartment are:

Cathode: Pt electrode; IO_4^-, IO_3^-, and H_2SO_4 (as a source of H^+) in solution

Anode: Pt electrode; Mn^{2+}, MnO_4^-, and H_2SO_4 in solution

45. In standard line notation, the anode is listed first, and the cathode is listed last. A double line separates the two compartments. By convention, the electrodes are on the ends with all solutes and gases toward the middle. A single line is used to indicate a phase change. We also included all concentrations.

39a. $Pt \mid Cr^{3+}$ (1.0 M), $Cr_2O_7^{2-}$ (1.0 M), H^+ (1.0 M) $\|$ Cl_2 (1.0 atm) $\mid$ Cl^- (1.0 M) $\mid Pt$

39b. $Mg \mid Mg^{2+}$ (1.0 M) $\|$ Cu^{2+} (1.0 M) $\mid Cu$

43a. $Pt \mid Br^-$ (1.0 M), Br_2 (1.0 M) $\|$ Cl_2 (1.0 atm) $\mid$ Cl^- (1.0 M) $\mid Pt$

43b. $Pt \mid Mn^{2+}$ (1.0 M), MnO_4^- (1.0 M), H^+ (1.0 M) $\|$ IO_4^- (1.0 M), H^+ (1.0 M), IO_3^- (1.0 M) $\mid Pt$

48. a.

$$\begin{array}{lr} (H_2O_2 + 2\,H^+ + 2\,e^- \rightarrow 2\,H_2O) \times 3 & E^\circ = 1.78\text{ V} \\ 2\,Cr^{3+} + 7\,H_2O \rightarrow Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- & -E^\circ = -1.33\text{ V} \\ \hline 3\,H_2O_2(aq) + 2\,Cr^{3+}(aq) + H_2O(l) \rightarrow Cr_2O_7^{2-}(aq) + 8\,H^+(aq) & E^\circ_{cell} = 0.45\text{ V} \end{array}$$

b.

$$\begin{array}{lr} (2\,H^+ + 2\,e^- \rightarrow H_2) \times 3 & E^\circ = 0.00\text{ V} \\ (Al \rightarrow Al^{3+} + 3\,e^-) \times 2 & -E^\circ = 1.66\text{ V} \\ \hline 6\,H^+(aq) + 2\,Al(s) \rightarrow 3\,H_2(g) + 2\,Al^{3+}(aq) & E^\circ_{cell} = 1.66\text{ V} \end{array}$$

54. Because the cells are at standard conditions, $w_{max} = \Delta G = \Delta G^\circ = -nFE^\circ_{cell}$. See Exercise 48 for the balanced overall equations and for E°_{cell}.

48a. $w_{max} = -(6\text{ mol }e^-)(96{,}485\text{ C/mol }e^-)(0.45\text{ J/C}) = -2.6 \times 10^5\text{ J} = -260\text{ kJ}$

48b. $w_{max} = -(6\text{ mol }e^-)(96{,}485\text{ C/mol }e^-)(1.66\text{ J/C}) = -9.61 \times 10^5\text{ J} = -961\text{ kJ}$

58. $CH_3OH(l) + 3/2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l)$ $\quad \Delta G^\circ = 2(-237) + (-394) - [-166] = -702\text{ kJ}$

The balanced half-reactions are:

$H_2O + CH_3OH \rightarrow CO_2 + 6\,H^+ + 6\,e^-$ and $O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$

For 3/2 mol O_2, 6 mol of electrons will be transferred (n = 6).

$$\Delta G^\circ = -nFE^\circ,\ E^\circ = \frac{-\Delta G^\circ}{nF} = \frac{-(-702{,}000\text{ J})}{(6\text{ mol }e^-)(96{,}485\text{ C/mol }e^-)} = 1.21\text{ J/C} = 1.21\text{ V}$$

59. Good oxidizing agents are easily reduced. Oxidizing agents are on the left side of the reduc-tion half-reactions listed in Table 17.1. We look for the largest, most positive standard reduction potentials to correspond to the best oxidizing agents. The ordering from worst to best oxidizing agents is:

	K^+	<	H_2O	<	Cd^{2+}	<	I_2	<	$AuCl_4^-$	<	IO_3^-
E° (V)	−2.92		−0.83		−0.40		0.54		0.99		1.20

60. Good reducing agents are easily oxidized. The reducing agents are on the right side of the reduction half-reactions listed in Table 17.1. The best reducing agents have the most negative standard reduction potentials (E°) or the most positive standard oxidation potentials E°_{ox} (= −E°). The ordering from worst to best reducing agents is:

	F^-	<	H_2O	<	I_2	<	Cu^+	<	H^-	<	K
−E° (V)	−2.87		−1.23		−1.20		−0.16		2.23		2.92

63. $Cl_2 + 2\,e^- \rightarrow 2\,Cl^-$ E° = 1.36 V $Ag^+ + e^- \rightarrow Ag$ E° = 0.80 V
$Pb^{2+} + 2\,e^- \rightarrow Pb$ E° = −0.13 V $Zn^{2+} + 2\,e^- \rightarrow Zn$ E° = −0.76 V
$Na^+ + e^- \rightarrow Na$ E° = −2.71 V

a. Oxidizing agents (species reduced) are on the left side of the preceding reduction half-reactions. Of the species available, Ag^+ would be the best oxidizing agent since it has the largest E° value. Note that Cl_2 is a better oxidizing agent than Ag^+, but it is not one of the choices listed.

b. Reducing agents (species oxidized) are on the right side of the reduction half-reactions. Of the species available, Zn would be the best reducing agent since it has the largest −E° value.

c. $SO_4^{2-} + 4\,H^+ + 2\,e^- \longrightarrow H_2SO_3 + H_2O$ E° = 0.20 V; SO_4^{2-} can oxidize Pb and Zn at standard conditions. When SO_4^{2-} is coupled with these reagents, E°_{cell} is positive.

d. $Al \longrightarrow Al^{3+} + 3\,e^-$ −E° = 1.66 V; Al can reduce Ag^+ and Zn^{2+} at standard conditions because $E^\circ_{cell} > 0$.

65. a. $2\,Br^- \longrightarrow Br_2 + 2\,e^-$ −E° = −1.09 V; $2\,Cl^- \longrightarrow Cl_2 + 2\,e^-$ −E° = −1.36 V; E° > 1.09 V to oxidize Br^-; E° < 1.36 V to not oxidize Cl^-; $Cr_2O_7^{2-}$, O_2, MnO_2, and IO_3^- are all possible since when all of these oxidizing agents are coupled with Br^-, $E^\circ_{cell} > 0$, and when coupled with Cl^-, $E^\circ_{cell} < 0$ (assuming standard conditions).

b. $Mn \rightarrow Mn^{2+} + 2\,e^-$ −E° = 1.18; $Ni \rightarrow Ni^{2+} + 2\,e^-$ −E° = 0.23 V; any oxidizing agent with −0.23 V > E° > −1.18 V will work. $PbSO_4$, Cd^{2+}, Fe^{2+}, Cr^{3+}, Zn^{2+}, and H_2O will be able to oxidize Mn but not Ni (assuming standard conditions).

69.

$$\begin{array}{lr} H_2O_2 + 2\,H^+ + 2\,e^- \rightarrow 2\,H_2O & E° = 1.78\text{ V} \\ (Ag \rightarrow Ag^+ + e^-) \times 2 & -E° = -0.80\text{ V} \\ \hline H_2O_2(aq) + 2\,H^+(aq) + 2\,Ag(s) \rightarrow 2\,H_2O(l) + 2\,Ag^+(aq) & E^o_{cell} = 0.98\text{ V} \end{array}$$

a. A galvanic cell is based on spontaneous redox reactions. At standard conditions, this reaction produces a voltage of 0.98 V. Any change in concentration that increases the tendency of the forward reaction to occur will increase the cell potential. Conversely, any change in concentration that decreases the tendency of the forward reaction to occur (increases the tendency of the reverse reaction to occur) will decrease the cell potential. Using Le Chatelier's principle, increasing the reactant concentrations of H_2O_2 and H^+ from 1.0 to 2.0 *M* will drive the forward reaction further to right (will further increase the tendency of the forward reaction to occur). Therefore, E_{cell} will be greater than E^o_{cell}.

b. Here, we decreased the reactant concentration of H^+ and increased the product concentration of Ag^+ from the standard conditions. This decreases the tendency of the forward reaction to occur, which will decrease E_{cell} as compared to E^o_{cell} ($E_{cell} < E^o_{cell}$).

72. As is the case for all concentration cells, $E^o_{cell} = 0$, and the smaller ion concentration is always in the anode compartment. The general Nernst equation for the Ni | Ni^{2+}(*x M*) || Ni^{2+}(*y M*) | Ni concentration cell is:

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log Q = \frac{-0.0591}{2}\log\frac{[Ni^{2+}]_{anode}}{[Ni^{2+}]_{cathode}}$$

a. Both compartments are at standard conditions ($[Ni^{2+}]$ = 1.0 *M*), and $E_{cell} = E^o_{cell} = 0$ V. No electron flow occurs.

b. Cathode = 2.0 *M* Ni^{2+}; anode = 1.0 *M* Ni^{2+}; electron flow is always from the anode to the cathode, so electrons flow to the right in the diagram.

$$E_{cell} = \frac{-0.0591}{2}\log\frac{[Ni^{2+}]_{anode}}{[Ni^{2+}]_{cathode}} = \frac{-0.0591}{2}\log\frac{1.0}{2.0} = 8.9 \times 10^{-3}\text{ V}$$

c. Cathode = 1.0 *M* Ni^{2+}; anode = 0.10 *M* Ni^{2+}; electrons flow to the left in the diagram.

$$E_{cell} = \frac{-0.0591}{2}\log\frac{0.10}{1.0} = 0.030\text{ V}$$

d. Cathode = 1.0 *M* Ni^{2+}; anode = 4.0×10^{-5} *M* Ni^{2+}; electrons flow to the left in the diagram.

$$E_{cell} = \frac{-0.0591}{2}\log\frac{4.0\times10^{-5}}{1.0} = 0.13\text{ V}$$

e. Because both concentrations are equal, log(2.5/2.5) = log 1.0 = 0, and E_{cell} = 0. No electron flow occurs.

80. a.

$$\begin{array}{lr} Au^{3+} + 3\,e^- \rightarrow Au & E° = 1.50\text{ V} \\ (Tl \rightarrow Tl^+ + e^-) \times 3 & -E° = 0.34\text{ V} \\ \hline Au^{3+}(aq) + 3\,Tl(s) \rightarrow Au(s) + 3\,Tl^+(aq) & E^o_{cell} = 1.84\text{ V} \end{array}$$

b. $\Delta G° = -nFE°_{cell} = -(3\text{ mol e}^-)(96{,}485\text{ C/mol e}^-)(1.84\text{ J/C}) = -5.33 \times 10^5\text{ J} = -533\text{ kJ}$

$$\log K = \frac{nE°}{0.0591} = \frac{3(1.84)}{0.0591} = 93.401,\ \ K = 10^{93.401} = 2.52 \times 10^{93}$$

c. At 25°C, $E_{cell} = E°_{cell} - \frac{0.0591}{n}\log Q$, where $Q = \frac{[Tl^+]^3}{[Au^{3+}]}$.

$$E_{cell} = 1.84\text{ V} - \frac{0.0591}{3}\log\frac{[Tl^+]^3}{[Au^{3+}]} = 1.84 - \frac{0.0591}{3}\log\frac{(1.0 \times 10^{-4})^3}{1.0 \times 10^{-2}}$$

$E_{cell} = 1.84 - (-0.20) = 2.04$ V

83. $Cu^{2+}(aq) + H_2(g) \rightarrow 2\ H^+(aq) + Cu(s)$ $E°_{cell} = 0.34\text{ V} - 0.00\text{ V} = 0.34\text{ V}$; $n = 2$

$P_{H_2} = 1.0$ atm and $[H^+] = 1.0\ M$: $E_{cell} = E°_{cell} - \frac{0.0591}{2}\log\frac{1}{[Cu^{2+}]}$

Use the K_{sp} expression to calculate the Cu^{2+} concentration in the cell.

$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2\ OH^-(aq)$ $K_{sp} = 1.6 \times 10^{-19} = [Cu^{2+}][OH^-]^2$

From problem, $[OH^-] = 0.10\ M$, so: $[Cu^{2+}] = \frac{1.6 \times 10^{-19}}{(0.10)^2} = 1.6 \times 10^{-17}\ M$

$$E_{cell} = E°_{cell} - \frac{0.0591}{2}\log\frac{1}{[Cu^{2+}]} = 0.34\text{ V} - \frac{0.0591}{2}\log\frac{1}{1.6 \times 10^{-17}}$$

$E_{cell} = 0.34 - 0.50 = -0.16$ V

Because $E_{cell} < 0$, the forward reaction is not spontaneous, but the reverse reaction is spontaneous. The Cu electrode becomes the anode and $E_{cell} = 0.16$ V for the reverse reaction. The cell reaction is $2\ H^+(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + H_2(g)$.

84. $3\ Ni^{2+}(aq) + 2\ Al(s) \rightarrow 2\ Al^{3+}(aq) + 3\ Ni(s)$ $E°_{cell} = -0.23\text{ V} + 1.66\text{ V} = 1.43\text{ V}$; $n = 6$

$$E_{cell} = E°_{cell} - \frac{0.0591}{n}\log\frac{[Al^{3+}]^2}{[Ni^{2+}]^3},\ \ 1.82\text{ V} = 1.43\text{ V} - \frac{0.0591}{6}\log\frac{[Al^{3+}]^2}{(1.0)^3}$$

$\log [Al^{3+}]^2 = -39.59$, $[Al^{3+}]^2 = 10^{-39.59}$, $[Al^{3+}] = 1.6 \times 10^{-20}\ M$

$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3\ OH^-(aq)$ $K_{sp} = [Al^{3+}][OH^-]^3$; from the problem, $[OH^-] = 1.0 \times 10^{-4}\ M$.

$K_{sp} = (1.6 \times 10^{-20})(1.0 \times 10^{-4})^3 = 1.6 \times 10^{-32}$

89.

$$\begin{array}{l} (Cr^{2+} \rightarrow Cr^{3+} + e^-) \times 2 \\ \underline{Co^{2+} + 2\ e^- \rightarrow Co} \\ 2\ Cr^{2+}(aq) + Co^{2+}(aq) \rightarrow 2\ Cr^{3+}(aq) + Co(s) \end{array}$$

$$E^{o}_{cell} = \frac{0.0591}{n}\log K = \frac{0.0591}{2}\log(2.79 \times 10^{7}) = 0.220\ \text{V}$$

$$E = E° - \frac{0.0591}{n}\log\frac{[Cr^{3+}]^{2}}{[Cr^{2+}]^{2}[Co^{2+}]} = 0.220\ \text{V} - \frac{0.0591}{2}\log\frac{(2.0)^{2}}{(0.30)^{2}(0.20)} = 0.151\ \text{V}$$

$\Delta G = -nFE = -$ (2 mol e^{-})(96,485 C/mol e^{-})(0.151 J/C) $= -2.91 \times 10^{4}$ J $= -29.1$ kJ

91. The K_{sp} reaction is $FeS(s) \rightleftharpoons Fe^{2+}(aq) + S^{2-}(aq)$ $K = K_{sp}$. Manipulate the given equations so that when added together we get the K_{sp} reaction. Then we can use the value of E^{o}_{cell} for the reaction to determine K_{sp} (by using the equation log K = nE°/0.0591).

$$\begin{array}{rl} FeS + 2\,e^{-} \rightarrow Fe + S^{2} & E° = -1.01\ \text{V} \\ Fe \rightarrow Fe^{2+} + 2\,e^{-} & -E° = 0.44\ \text{V} \\ \hline Fe(s) \rightarrow Fe^{2+}(aq) + S^{2-}(aq) & E^{o}_{cell} = -0.57\ \text{V} \end{array}$$

$$\log K_{sp} = \frac{nE^{o}}{0.0591} = \frac{2(-0.57)}{0.0591} = -19.29,\ K_{sp} = 10^{-19.29} = 5.1 \times 10^{-20}$$

94.

$$\begin{array}{ll} CuI + e^{-} \rightarrow Cu + I^{-} & E^{o}_{CuI} = ? \\ Cu \rightarrow Cu^{+} + e^{-} & -E° = -0.52\ \text{V} \\ \hline CuI(s) \rightarrow Cu^{+}(aq) + I^{-}(aq) & E^{o}_{cell} = E^{o}_{CuI} - 0.52\ \text{V} \end{array}$$

For this overall reaction, $K = K_{sp} = 1.1 \times 10^{-12}$:

$$E^{o}_{cell} = \frac{0.0591}{n}\log K_{sp} = \frac{0.0591}{1}\log(1.1\times10^{-12}) = -0.71\ \text{V}$$

$E^{o}_{cell} = -0.71$ V $= E^{o}_{CuI} - 0.52$, $E^{o}_{CuI} = -0.19$ V

95. a. $Al^{3+} + 3\,e^{-} \rightarrow Al$; 3 mol e^{-} are needed to produce 1 mol Al from Al^{3+}.

$$1.0 \times 10^{3}\ \text{g Al} \times \frac{1\ \text{mol Al}}{26.98\ \text{g Al}} \times \frac{3\ \text{mol } e^{-}}{\text{mol Al}} \times \frac{96{,}485\ \text{C}}{\text{mol } e^{-}} \times \frac{1\ \text{s}}{100.0\ \text{C}} = 1.07 \times 10^{5}\ \text{s} \quad 30.\ \text{hours}$$

b. $$1.0\ \text{g Ni} \times \frac{1\ \text{mol Ni}}{58.69\ \text{g Ni}} \times \frac{2\ \text{mol } e^{-}}{\text{mol Ni}} \times \frac{96{,}485\ \text{C}}{\text{mol } e^{-}} \times \frac{1\ \text{s}}{100.0\ \text{C}} = 33\ \text{s}$$

c. $$5.0\ \text{mol Ag} \times \frac{1\ \text{mol } e^{-}}{\text{mol Ag}} \times \frac{96{,}485\ \text{C}}{\text{mol } e^{-}} \times \frac{1\ \text{s}}{100.0\ \text{C}} = 4.8 \times 10^{3}\ \text{s} = 1.3\ \text{hours}$$

98. Al is in the +3 oxidation in Al_2O_3, so 3 mol e^{-} are needed to convert Al^{3+} into Al(s).

$$2.00\ \text{h} \times \frac{60\ \text{min}}{\text{h}} \times \frac{60\ \text{s}}{\text{min}} \times \frac{1.00\times10^{6}\ \text{C}}{\text{s}} \times \frac{1\ \text{mol } e^{-}}{96{,}485\ \text{C}} \times \frac{1\ \text{mol Al}}{3\ \text{mol } e^{-}} \times \frac{26.98\ \text{g Al}}{\text{mol Al}} = 6.71 \times 10^{5}\ \text{g}$$

99. $74.1\text{ s} \times \frac{2.00\text{ C}}{\text{s}} \times \frac{1\text{ mol e}^-}{96{,}485\text{ C}} \times \frac{1\text{ mol M}}{3\text{ mol e}^-} = 5.12 \times 10^{-4}$ mol M, where M = unknown metal

Molar mass = $\frac{0.107\text{ g M}}{5.12 \times 10^{-4}\text{ mol M}} = \frac{209\text{ g}}{\text{mol}}$; the element is bismuth.

105. $2.30\text{ min} \times \frac{60\text{ s}}{\text{min}} = 138\text{ s}$; $138\text{ s} \times \frac{2.00\text{ C}}{\text{s}} \times \frac{1\text{ mol e}^-}{96{,}485\text{ C}} \times \frac{1\text{ mol Ag}}{\text{mol e}^-} = 2.86 \times 10^{-3}$ mol Ag

$[Ag^+] = 2.86 \times 10^{-3}$ mol Ag^+/0.250 L = 1.14×10^{-2} *M*

107. $Au^{3+} + 3\,e^- \rightarrow Au$ E° = 1.50 V $Ni^{2+} + 2\,e^- \rightarrow Ni$ E° = −0.23 V

$Ag^+ + e^- \rightarrow Ag$ E° = 0.80 V $Cd^{2+} + 2\,e^- \rightarrow Cd$ E° = −0.40 V

$2\,H_2O + 2e^- \rightarrow H_2 + 2\,OH^-$ E° = −0.83 V (Water can also be reduced.)

Au(s) will plate out first since it has the most positive reduction potential, followed by Ag(s), which is followed by Ni(s), and finally Cd(s) will plate out last since it has the most negative reduction potential of the metals listed. Water will not interfere with the plating process.

109. Species present: Na^+, SO_4^{2-}, and H_2O. H_2O and Na^+ can be reduced and H_2O and SO_4^{2-} can be oxidized. From the potentials, H_2O is the most easily reduced and the most easily oxidized species present. This is the case because water, of the species present, has the most positive reduction potential as well as the most positive oxidation potential. The reactions are:

Cathode: $2\,H_2O + 2\,e^- \rightarrow H_2(g) + 2\,OH^-$; anode: $2\,H_2O \rightarrow O_2(g) + 4\,H^+ + 4\,e^-$

112. Reduction occurs at the cathode, and oxidation occurs at the anode. First, determine all the species present; then look up pertinent reduction and/or oxidation potentials in Table 17-1 for all these species. The cathode reaction will be the reaction with the most positive reduction potential, and the anode reaction will be the reaction with the most positive oxidation potential.

a. Species present: K^+ and F^-; K^+ can be reduced to K, and F^- can be oxidized to F_2 (from Table 17.1). The reactions are:

Cathode: $K^+ + e^- \rightarrow K$ E° = −2.92 V
Anode: $2\,F^- \rightarrow F_2 + 2\,e^-$ −E° = −2.87 V

b. Species present: Cu^{2+} and Cl^-; Cu^{2+} can be reduced, and Cl^- can be oxidized. The reactions are:

Cathode: $Cu^{2+} + 2\,e^- \rightarrow Cu$ E° = 0.34 V
Anode: $2\,Cl^- \rightarrow Cl_2 + 2\,e^-$ −E° = −1.36 V

c. Species present: Mg^{2+} and I^-; Mg^{2+} can be reduced, and I^- can be oxidized. The reactions are:

Cathode: $Mg^{2+} + 2\,e^- \rightarrow Mg$ E° = −2.37 V
Anode: $2\,I^- \rightarrow I_2 + 2\,e^-$ −E° = −0.54 V

114. These are all in aqueous solutions, so we must also consider the reduction and oxidation of H_2O in addition to the potential redox reactions of the ions present. For the cathode reaction, the species with the most positive reduction potential will be reduced, and for the anode reaction, the species with the most positive oxidation potential will be oxidized.

a. Species present: K^+, F^-, and H_2O. Possible cathode reactions are:

$K^+ + e^- \rightarrow K$ $\qquad E° = -2.92\ V$

$2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$ $\qquad E° = -0.83\ V$

Because it is easier to reduce H_2O than K^+ (assuming standard conditions), H_2O will be reduced by the preceding cathode reaction.

Possible anode reactions are:

$2\ F^- \rightarrow F_2 + 2\ e^-$ $\qquad -E° = -2.87\ V$

$2\ H_2O \rightarrow 4\ H^+ + O_2 + 4\ e^-$ $\qquad -E° = -1.23\ V$

Because H_2O is easier to oxidize than F^- (assuming standard conditions), H_2O will be oxidized by the preceding anode reaction.

b. Species present: Cu^{2+}, Cl^-, and H_2O; Cu^{2+} and H_2O can be reduced. The reduction potentials are $E° = 0.34\ V$ for Cu^{2+} and $E° = -0.83\ V$ for H_2O (assuming standard conditions). Cu^{2+} will be reduced to Cu at the cathode ($Cu^{2+} + 2\ e^- \rightarrow Cu$).

Cl^- and H_2O can be oxidized. The oxidation potentials are $-E° = -1.36\ V$ for Cl^- and $-E° = -1.23\ V$ for H_2O (assuming standard conditions). From the potentials, we would predict H_2O to be oxidized at the anode ($2\ H_2O \rightarrow 4\ H^+ + O_2 + 4\ e^-$). *Note*: In real life, Cl^- is oxidized to Cl_2 when water is present due to a phenomenon called overvoltage (see Section 17.8 of the text). Because overvoltage is difficult to predict, we will generally ignore it.

c. Species present: Mg^{2+}, I^-, and H_2O: The only possible cathode reactions are:

$2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$ $\qquad E° = -0.83\ V$

$Mg^{2+} + 2\ e^- \rightarrow Mg$ $\qquad E° = -2.37\ V$

Reduction of H_2O will occur at the cathode since $E^{o}_{H_2O}$ is more positive.

The only possible anode reactions are:

$2\ I^- \rightarrow I_2 + 2\ e^-$ $\qquad -E° = -0.54\ V$

$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$ $\qquad -E° = -1.23\ V$

Oxidation of I^- will occur at the anode because $-E^{o}_{H_2O}$ is more positive.

120. $Ag^+(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + 2\ Ag(s)$ $E^\circ_{cell} = 0.80 - 0.34\ V = 0.46\ V$; a galvanic cell produces a voltage as the forward reaction occurs. Any stress that increases the tendency of the forward reaction to occur will increase the cell potential, whereas a stress that decreases the tendency of the forward reaction to occur will decrease the cell potential.

a. Added Cu^{2+} (a product ion) will decrease the tendency of the forward reaction to occur, which will decrease the cell potential.

b. Added NH_3 removes Cu^{2+} in the form of $Cu(NH_3)_4^{2+}$. Because a product ion is removed, this will increase the tendency of the forward reaction to occur, which will increase the cell potential.

c. Added Cl^- removes Ag^+ in the form of AgCl(s). Because a reactant ion is removed, this will decrease the tendency of the forward reaction to occur, which will decrease the cell potential.

d. $Q_1 = \dfrac{[Cu^{2+}]_0}{[Ag^+]_0^2}$; as the volume of solution is doubled, each concentration is halved.

$$Q_2 = \frac{1/2\ [Cu^{2+}]_0}{(1/2\ [Ag^+]_0)^2} = \frac{2[Cu^{2+}]_0}{[Ag^+]_0^2} = 2Q_1$$

The reaction quotient is doubled because the concentrations are halved. Because reactions are spontaneous when $Q < K$, and because Q increases when the solution volume doubles, the reaction is closer to equilibrium, which will decrease the cell potential.

e. Because Ag(s) is not a reactant in this spontaneous reaction, and because solids do not appear in the reaction quotient expressions, replacing the silver electrode with a platinum electrode will have no effect on the cell potential.

125. a.

$$\begin{array}{rr}
(Au^{3+} + 3\ e^- \rightarrow Au) \times 2 & E^\circ = 1.50\ V \\
(Mg \rightarrow Mg^{2+} + 2\ e^-) \times 3 & -E^\circ = 2.37\ V \\
\hline
2\ Au^{3+}(aq) + 3\ Mg(s) \rightarrow 2\ Au(s) + 3\ Mg^{2+}(aq) & E^\circ_{cell} = 3.87\ V
\end{array}$$

b. $E_{cell} = 3.87\ V - \dfrac{0.0591}{6} \log \dfrac{[Mg^{2+}]^3}{[Au^{3+}]^2}$, $4.01 = 3.87 - \dfrac{0.0591}{6} \log \dfrac{(1.0 \times 10^{-5})^3}{[Au^{3+}]^2}$

$\dfrac{(1.0 \times 10^{-5})^3}{[Au^{3+}]^2} = 10^{-14.21}$, $[Au^{3+}] = 0.40\ M$

129. Only statement e is true. The attached metals that are more easily oxidized than iron are called sacrificial metals. For statement a, corrosion is a spontaneous process, like the ones harnessed to make galvanic cells. For statement b, corrosion of steel is the oxidation of iron coupled with the reduction of oxygen. For statement c, cars rust more easily in high-moisture areas (the humid areas) because water is a reactant in the reduction half-reaction as well as providing a medium for ion migration (a salt bridge of sorts). For statement d, salting roads adds ions to the corrosion process, which increases the conductivity of the aqueous solution and, in turn, accelerates corrosion.

130. For C_2H_5OH, H has a +1 oxidation state, and O has a −2 oxidation state. This dictates a −2 oxidation state for C. For CO_2, O has a −2 oxidation state, so carbon has a +4 oxidation state. Six moles of electrons are transferred per mole of carbon oxidized (C goes from $-2 \rightarrow +4$). Two moles of carbon are in the balanced reaction, so n = 12.

$w_{max} = -1320\ \text{kJ} = \Delta G = -nFE$, $-1320 \times 10^3\ \text{J} = -nFE = -(12\ \text{mol e}^-)(96{,}485\ \text{C/mol e}^-)E$

$E = 1.14\ \text{J/C} = 1.14\ \text{V}$

131. $2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l)$; oxygen goes from the zero oxidation state to the −2 oxidation state in H_2O. Because 2 mol of O are in the balanced reaction, n = 4 moles of electrons transferred.

a. $E^\circ_{cell} = \dfrac{0.0591}{n}\log K = \dfrac{0.0591}{4}\log(1.28 \times 10^{83})$, $E^\circ_{cell} = 1.23\ \text{V}$

$\Delta G^\circ = -nFE^\circ_{cell} = -(4\ \text{mol e}^-)(96{,}485\ \text{C/mol e}^-)(1.23\ \text{J/C}) = -4.75 \times 10^5\ \text{J} = -475\ \text{kJ}$

b. .Because the moles of gas decrease as reactants are converted into products, ΔS° will be negative (unfavorable). Because the value of ΔG° is negative, ΔH° must be negative to override the unfavorable ΔS° ($\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$).

c. $\Delta G = w_{max} = \Delta H - T\Delta S$. Because ΔS is negative, as T increases, ΔG becomes more positive (closer to zero). Therefore, w_{max} will decrease as T increases.

142. Moles of e^- = $50.0\ \text{min} \times \dfrac{60\ \text{s}}{\text{min}} \times \dfrac{2.50\ \text{C}}{\text{s}} \times \dfrac{1\ \text{mol e}^-}{96{,}485\ \text{C}} = 7.77 \times 10^{-2}\ \text{mol e}^-$

Moles of Ru = $2.618\ \text{g Ru} \times \dfrac{1\ \text{mol Ru}}{101.1\ \text{g Ru}} = 2.590 \times 10^{-2}\ \text{mol Ru}$; $Ru^{3+} + 3\,e^- \rightarrow Ru$

$\dfrac{\text{Moles of e}^-}{\text{Moles of Ru}} = \dfrac{7.77 \times 10^{-2}\ \text{mol e}^-}{2.590 \times 10^{-2}\ \text{mol Ru}} = 3.00$; the charge on the ruthenium ions is +3.

147.

$$\begin{array}{rll}
(Ag^+ + e^- \rightarrow Ag) \times 2 & & E^\circ = 0.80\ \text{V} \\
Pb \rightarrow Pb^{2+} + 2\,e^- & & -E^\circ = -(-0.13) \\
\hline
2\,Ag^+(aq) + Pb(s) \rightarrow 2\,Ag(s) + Pb^{2+}(aq) & & E^\circ_{cell} = 0.93\ \text{V}
\end{array}$$

$$E = E^\circ - \frac{0.0591}{n}\log\frac{[Pb^{2+}]}{[Ag^+]^2},\quad 0.83\ \text{V} = 0.93\ \text{V} - \frac{0.0591}{n}\log\frac{(1.8)}{[Ag^+]^2}$$

$$\log\frac{(1.8)}{[Ag^+]^2} = \frac{0.10(2)}{0.0591} = 3.4,\quad \frac{(1.8)}{[Ag^+]^2} = 10^{3.4},\quad [Ag^+] = 0.027\ M$$

	$Ag_2SO_4(s)$	⇌	$2\,Ag^+(aq)$	+	$SO_4^{2-}(aq)$	$K_{sp} = [Ag^+]^2[SO_4^{2-}]$
Initial	s = solubility (mol/L)		0		0	
Equil.			$2s$		s	

From problem: $2s = 0.027\ M$, $s = 0.027/2$

$K_{sp} = (2s)^2(s) = (0.027)^2(0.027/2) = 9.8 \times 10^{-6}$