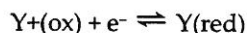
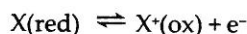
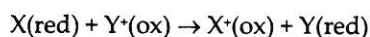
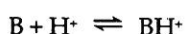
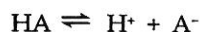


20 Electrochemistry

Visualizing Concepts

20.1 Consider the Brønsted-Lowry acid-base reaction and the redox reaction below.



Just as acid-base reactions can be viewed as proton-transfer reactions, redox reactions can be viewed as electron-transfer reactions. In the Brønsted-Lowry acid-base reaction, H^+ is transferred from HA to B. In the redox reaction, X(red) loses electrons and $\text{Y}^+(\text{ox})$ gains electrons; the number of electrons gained and lost must be equal. The concept of electron transfer from one reactant to the other is clearly applicable to redox reactions. (The path of the transfer may or may not be direct, but ultimately electrons are transferred during redox reactions.)

Furthermore, the species in redox reactions each have an oxidized and reduced form, like a conjugate acid-conjugate base pair. The reduced form has more electrons; the oxidized form has less. The greater the tendency of HA to donate H^+ (the stronger the acid), the lesser the tendency of A^- to gain them (the weaker the conjugate base). Similarly, the greater the tendency of X(red) to donate electrons (the stronger the reducing agent) the lesser the tendency of $\text{X}^+(\text{ox})$ to gain electrons (the weaker the oxidizing agent). Similar arguments exist for B, BH^+ and $\text{Y}^+(\text{ox})$, Y(red).

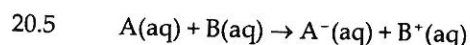
20.2 Unintended oxidation reactions in the body lead to unwanted health effects, just as unwanted oxidation of metals leads to corrosion. Antioxidants probably have modes of action similar to anti-corrosion agents. They can preferentially react with oxidizing agents (cathodic protection), create conditions that are unfavorable to the oxidation-reduction reaction, or physically coat or surround the molecule being oxidized to prevent the oxidant from attacking it. The first of these modes of action is likely to be safest in biological systems. Adjusting reaction conditions in our body can be dangerous, and physical protection is unlikely to provide lasting protection against oxidation. Anti-oxidants are likely to be reductants that preferentially react with oxidizing agents.

20.3 *Analyze/Plan.* Apply the definitions of oxidation, reduction, anode and cathode to the diagram. Recall relationship between atomic and ionic size from Chapter 7. *Solve.*

- (a) Oxidation. The gray spheres are uniformly sized and closely aligned; they represent an elemental solid. The diagram shows atoms from the surface of the solid going into solution. In a voltaic cell, this happens when metal atoms on an electrode surface are oxidized. They lose electrons, form cations and move into solution.
- (b) Anode. Oxidation occurs at the anode.
- (c) When a neutral atom loses a valence electron, Z_{eff} for the remaining electrons increases, and the radius of the resulting cation is smaller than the radius of the neutral atom. The neutral atoms in the electrode are represented by larger spheres than the cations moving into solution.

20.4 *Analyze/Plan.* Consider the voltaic cell pictured in Figure 20.5 as a model. The reaction in a voltaic cell is spontaneous. To generate a standard emf, substances must be present in their standard states.

- (a) A concentration of 1 M is the standard state for ions in solution. Ions, but not solution, must be able to flow between compartments in order to complete the circuit so that the cell can develop an emf. Add 1 M $A^{2+}(\text{aq})$ to the beaker with the A(s) electrode. Add 1 M $B^{2+}(\text{aq})$ to the beaker with the B(s) electrode. Add a salt bridge to enable the flow of ions from one compartment to the other.
- (b) Reduction occurs at the cathode. In order for the reaction to occur spontaneously (and thus generate an emf), the half-reaction with the greater E_{red}° will be the reduction half-reaction. In this cell, it is the half-reaction involving A(s) and $A^{2+}(\text{aq})$. The A electrode functions as the cathode.
- (c) According to Figure 20.5, electrons flow through the external circuit from the anode to the cathode. In this example, B is the anode and A is the cathode, so electrons flow from B to A through the external circuit.
- (d) $E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ}(\text{cathode}) - E_{\text{red}}^{\circ}(\text{anode})$
 $E_{\text{cell}}^{\circ} = -0.10 \text{ V} - (-1.10 \text{ V}) = 1.00 \text{ V}$



- (a) A gains electrons and is being reduced; it is the cathode. B loses electrons and is being oxidized; it is the anode.
- (a) Reduction occurs at the cathode; oxidation occurs at the anode.
 $A(\text{aq}) + 1e^{-} \rightarrow A^{-}(\text{aq})$ occurs at the cathode.
 $B(\text{aq}) \rightarrow B^{+}(\text{aq}) + 1e^{-}$ occurs at the anode.
- (b) In a voltaic cell, the anode is at higher potential energy than the cathode. The anode reaction, $B(\text{aq}) \rightarrow B^{+}(\text{aq}) + 1e^{-}$, is higher in potential energy.
- (d) $\Delta G^{\circ} = -nFE^{\circ}$; the signs of ΔG° and E° (or ΔG and E) are opposite. Since this is a spontaneous reaction, ΔG° is negative and E° is positive.

- 20.6 *Analyze.* Given a series of reduction half-reactions and their standard electrode potentials (E_{red}°), draw conclusions about their relative strengths as oxidizing and reducing agents. *Plan.* The reactant with the largest E_{red}° is the easiest to reduce and the strongest oxidizing agent. The reduced form of this substance, the product of the reduction half-reaction, is the most difficult to oxidize and the weakest reducing agent. Conversely, the reactant with the smallest E_{red}° is the hardest to reduce and the weakest oxidizing agent. The reduced form of this substance, the product of the reduction half-reaction, is the easiest to oxidize and the strongest reducing agent. *Solve.*
- $A^{+}(\text{aq})$ is the strongest oxidizing agent, and D^{3+} is the weakest oxidizing agent.
 - $D(\text{s})$ is the strongest reducing agent, and $A(\text{s})$ is the weakest reducing agent.
 - Reactants with more positive E_{red}° than $C^{3+}(\text{aq})$ will oxidize $C^{2+}(\text{aq})$. Both $A^{+}(\text{aq})$ and $B^{2+}(\text{aq})$ will oxidize $C^{2+}(\text{aq})$.
- 20.7 *Analyze.* Given a redox reaction with a negative E° , answer questions regarding ΔG° , the equilibrium constant (K), and work (w). *Plan.* $\Delta G^{\circ} = -nFE^{\circ}$; $\Delta G^{\circ} = -RT \ln K$; $w_{\text{max}} = -nFE$. *Solve.*
- The signs of ΔG° and E° are opposite. If E° is negative, ΔG° is positive. (The reaction is not spontaneous in the forward direction.)
 - If ΔG° is positive, $\ln K$ is negative and $K < 1$. Also, K is less than one for a nonspontaneous reaction.
 - No. If E° is negative, the sign of w is positive. A positive value for w means that work is done on the system by the surroundings. An electrochemical cell based on this reaction cannot accomplish work on its surroundings.
- 20.8 *Analyze.* Given the voltaic cell shown in the diagram, answer questions about the cell and the effect of solution concentration on cell potential, E . *Plan.* Use the definition of a voltaic cell and standard emf, along with the Nernst equation, $E = \Delta E^{\circ} - (0.0592 \text{ V}/n) \log Q$, to answer the questions. *Solve.*
- A voltaic cell involves a spontaneous redox reaction, one with positive E_{cell}° . In order to achieve a positive E_{cell}° , the half-reaction with the more positive E_{red}° occurs at the cathode. For this cell the two half reactions are

$$\text{Ag}^{+}(\text{aq}) + \text{e}^{-} \rightarrow \text{Ag}(\text{s}), E_{\text{red}}^{\circ} = 0.799 \text{ V}$$

$$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Fe}(\text{s}), E_{\text{red}}^{\circ} = -0.440 \text{ V}$$
 The $\text{Ag}(\text{s})$ electrode is the cathode.
 - The standard emf is just E_{cell}° .

$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ}(\text{cathode}) - E_{\text{red}}^{\circ}(\text{anode}) = 0.799 \text{ V} - (-0.440 \text{ V}) = 1.239 \text{ V}$$
 The cell in the diagram is at standard conditions, with solid metal electrodes and 1 M aqueous solutions, so the potential on the meter in the circuit is the standard emf.
 - $2\text{Ag}^{+}(\text{aq}) + \text{Fe}(\text{s}) \rightarrow 2\text{Ag}(\text{s}) + \text{Fe}^{2+}(\text{aq}); n = 2; E = E^{\circ} - \frac{0.0592}{2} \log \frac{[\text{Fe}^{2+}]}{[\text{Ag}^{+}]^2}$

The solution in the cathode half-cell is $\text{Ag}^+(\text{aq})$. If $[\text{Ag}^+(\text{aq})]$ increases by a factor of 10, the change in cell voltage is $E - E^\circ = -\frac{0.0592}{2} \log \frac{[1]}{[10]^2} = 0.0592 \text{ V}$.

- (d) The solution in the anode half-cell is $\text{Fe}^{2+}(\text{aq})$. If $[\text{Fe}^{2+}(\text{aq})]$ increases by a factor of 10, the change in cell voltage is $E - E^\circ = -\frac{0.0592}{2} \log \frac{[10]}{[1]^2} = -0.0296 \text{ V}$.

20.9 *Analyze/Plan.* Consider the Nernst equation, which describes the variation of potential (emf) with respect to changes in concentration.

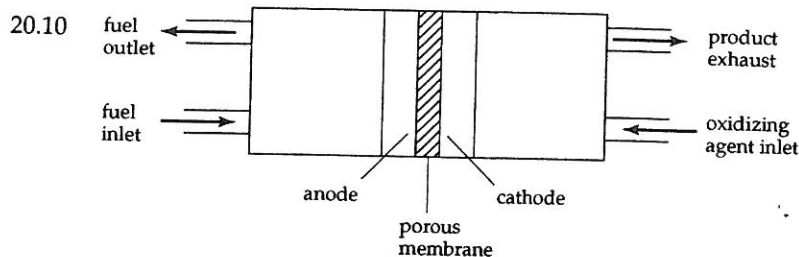
Solve. $E = E^\circ - \frac{0.0592}{n} \log Q$.

- (a) For this half-reaction, $E_{\text{red}}^\circ = 0.799 \text{ V}$; $Q = 1/[\text{Ag}^+]$

$$E = 0.80 - \frac{0.0592}{1} \log \frac{1}{[\text{Ag}^+]}; \quad E = 0.80 + \frac{0.0592}{1} \log [\text{Ag}^+]$$

The y-intercept of the graph is E° . The slope of the line is $+0.0592$. So, as $[\text{Ag}^+]$ and $\log[\text{Ag}^+]$ increase, E increases. The line that describes this behavior is line 1.

- (b) When $\log[\text{Ag}^+] = 0$, $[\text{Ag}^+] = 1 \text{ M}$; this is the standard state for $\text{Ag}^+(\text{aq})$, so $E_{\text{red}} = E_{\text{red}}^\circ = 0.799 \text{ V}$.



The main difference between a fuel cell and a battery is that a fuel cell is not self-contained. That is, there is a continuous supply of fuel (reductant) and oxidant to the cell, and continuous exhaust of products. The fuel cell produces electrical current as long as reactants are supplied. It never goes "dead."

20.11 Zinc, $E_{\text{red}}^\circ = -0.763 \text{ V}$, is more easily oxidized than iron, $E_{\text{red}}^\circ = -0.440 \text{ V}$. If conditions are favorable for oxidation, zinc will be preferentially oxidized, preventing iron from corroding. The protection lasts until all the Zn coating has reacted.

20.12 (a) $\text{MgCl}_2(\text{l})$

- (b) Oxidation occurs at the anode. Formation of $\text{Cl}_2(\text{g})$ from $2\text{Cl}^-(\text{l})$ is oxidation, so the carbon electrode is the anode.

Reduction occurs at the cathode. Formation of $\text{Mg}(\text{l})$ from $\text{Mg}^{2+}(\text{l})$ is reduction, so the steel electrode is the cathode.

Check. Note that this electrolysis cell does not comply with the convention of drawing anode on the left and cathode on the right.

- (c) $\text{MgCl}_2(\text{l}) \rightarrow \text{Mg}(\text{l}) + \text{Cl}_2(\text{g})$ overall
 $2\text{Cl}^- \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$ anode(oxidation)
 $\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}(\text{l})$ cathode(reduction)
- (d) Magnesium is an active metal. It must be separated from the $\text{Cl}_2(\text{g})$ that is also formed by electrolysis (see screen in diagram) or MgCl_2 will spontaneously reform. Also, the $\text{Mg}(\text{l})$ and $\text{Mg}(\text{g})$ should not come in contact with air (O_2) or moisture (H_2O).

Oxidation - Reduction Reactions (section 20.1)

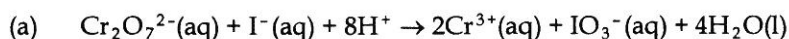
- 20.13 (a) *Oxidation* is the loss of electrons.
 (b) The electrons appear on the products side (right side) of an oxidation half-reaction.
 (c) The *oxidant* is the reactant that is reduced; it gains the electrons that are lost by the substance being oxidized.
 (d) An *oxidizing agent* is the substance that promotes oxidation. That is, it gains electrons that are lost by the substance being oxidized. It is the same as the oxidant.
- 20.14 (a) *Reduction* is the gain of electrons.
 (b) The electrons appear on the reactants side (left side) of a reduction half-reaction.
 (c) The *reductant* is the reactant that is oxidized; it provides the electrons that are gained by the substance being reduced.
 (d) A *reducing agent* is the substance that promotes reduction. It donates the electrons gained by the substance that is reduced. It is the same as the reductant.
- 20.15 (a) True.
 (b) False. Fe^{3+} is reduced to Fe^{2+} , so it is the oxidizing agent, and Co^{2+} is the reducing agent.
 (c) True.
- 20.16 (a) False. If something is reduced, it gains electrons.
 (b) True.
 (c) True. Oxidation can be thought of as a gain of oxygen atoms. Looking forward, this view will be useful for organic reactions, Chapter 24.
- 20.17 *Analyze/Plan.* Given a chemical equation, we are asked to indicate which elements undergo a change in oxidation number and the magnitude of the change. Assign oxidation numbers according to the rules given in Section 4.4. Note the changes and report the magnitudes. *Solve.*
- (a) I is reduced from +5 to 0; C is oxidized from +2 to +4.
 (b) Hg is reduced from +2 to 0; N is oxidized from -2 to 0.

- (c) N is reduced from +5 to +2; S is oxidized from -2 to 0.
 (d) Cl is reduced from +4 to +3; O is oxidized from -1 to 0.
- 20.18 (a) No oxidation-reduction
 (b) I is oxidized from -1 to +5; Cl is reduced from +1 to -1.
 (c) S is oxidized from +4 to +6; N is reduced from +5 to +2.
 (d) S is reduced from +6 to +4; Br is oxidized from -1 to 0.

Balancing Oxidation-Reduction Reactions (section 20.2)

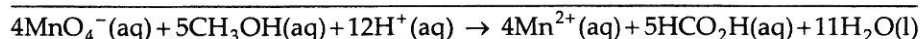
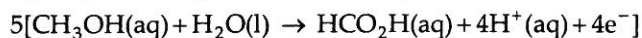
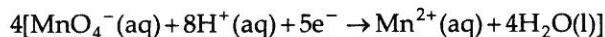
- 20.19 *Analyze/Plan.* Write the balanced chemical equation and assign oxidation numbers. The substance oxidized is the reductant and the substance reduced is the oxidant. *Solve.*
- (a) $\text{TiCl}_4(\text{g}) + 2\text{Mg}(\text{l}) \rightarrow \text{Ti}(\text{s}) + 2\text{MgCl}_2(\text{l})$
 (b) Mg(l) is oxidized; $\text{TiCl}_4(\text{g})$ is reduced.
 (c) Mg(l) is the reductant; $\text{TiCl}_4(\text{g})$ is the oxidant.
- 20.20 (a) $2\text{N}_2\text{H}_4(\text{g}) + \text{N}_2\text{O}_4(\text{g}) \rightarrow 3\text{N}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$
 (b) $\text{N}_2\text{H}_4(\text{g})$ is oxidized; $\text{N}_2\text{O}_4(\text{g})$ is reduced.
 (c) $\text{N}_2\text{H}_4(\text{g})$ serves as the reducing agent; it is itself oxidized. $\text{N}_2\text{O}_4(\text{g})$ serves as the oxidizing agent; it is itself reduced.
- 20.21 *Analyze/Plan.* Follow the logic in Sample Exercises 20.2 and 20.3. If the half-reaction occurs in basic solution, balance as in acid, then add OH^- to each side. *Solve.*
- (a) $\text{Sn}^{2+}(\text{aq}) \rightarrow \text{Sn}^{4+}(\text{aq}) + 2\text{e}^-$, oxidation
 (b) $\text{TiO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{Ti}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$, reduction
 (c) $\text{ClO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow \text{Cl}^-(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$, reduction
 (d) $\text{N}_2(\text{g}) + 8\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{NH}_4^+(\text{aq})$, reduction
 (e) $4\text{OH}^-(\text{aq}) \rightarrow \text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^-$, oxidation
 (f) $\text{SO}_3^{2-}(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{SO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^-$, oxidation
 (g) $\text{N}_2(\text{g}) + 6\text{H}_2\text{O} + 6\text{e}^- \rightarrow 2\text{NH}_3(\text{g}) + 6\text{OH}^-(\text{aq})$, reduction
- 20.22 (a) $\text{Mo}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Mo}(\text{s})$, reduction
 (b) $\text{H}_2\text{SO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^-$, oxidation
 (c) $\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \rightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$, reduction
 (d) $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$, reduction
 (e) $\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$, reduction
 (O_2 is reduced to OH^- , not H_2O , in basic solution)
 (f) $\text{Mn}^{2+}(\text{aq}) + 4\text{OH}^-(\text{aq}) \rightarrow \text{MnO}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^-$, oxidation
 (g) $\text{Cr}(\text{OH})_3(\text{s}) + 5\text{OH}^-(\text{aq}) \rightarrow \text{CrO}_4^{2-}(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) + 3\text{e}^-$, oxidation

20.23 *Analyze/Plan.* Follow the logic in Sample Exercises 20.2 and 20.3 to balance the given equations. Use the method in Sample Exercise 20.1 to identify oxidizing and reducing agents. *Solve.*

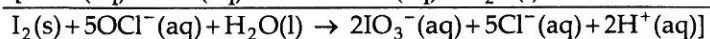
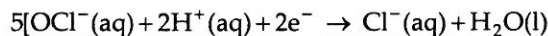
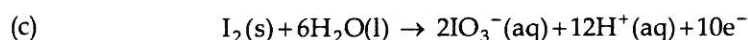


oxidizing agent, $\text{Cr}_2\text{O}_7^{2-}$; reducing agent, I^-

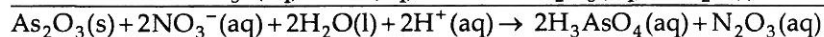
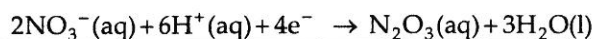
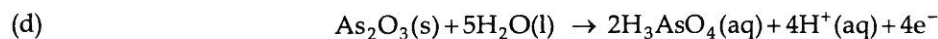
(b) The half-reactions are:



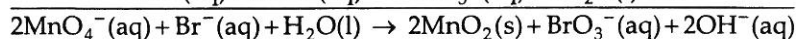
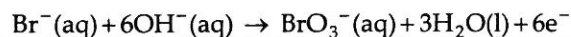
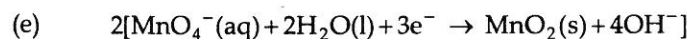
oxidizing agent, MnO_4^- ; reducing agent, CH_3OH



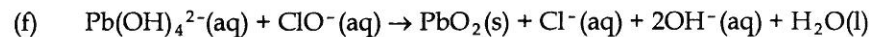
oxidizing agent, OCl^- ; reducing agent, I_2



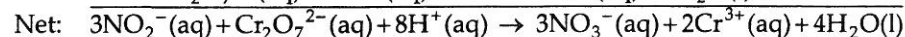
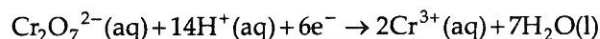
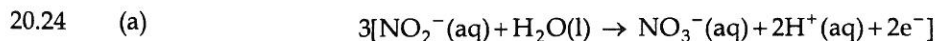
oxidizing agent, NO_3^- ; reducing agent, As_2O_3



oxidizing agent, MnO_4^- ; reducing agent, Br^-

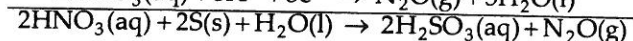
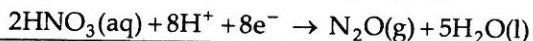
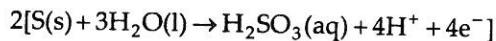
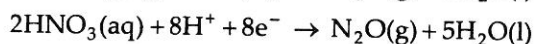
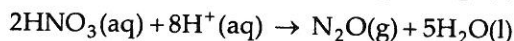
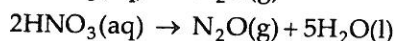
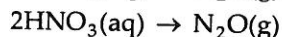
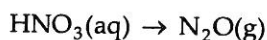


oxidizing agent, ClO^- ; reducing agent, $\text{Pb}(\text{OH})_4^{2-}$

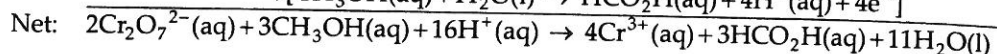
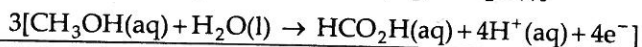
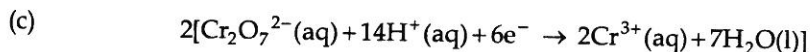


oxidizing agent, $\text{Cr}_2\text{O}_7^{2-}$; reducing agent, NO_2^-

(b) The oxidation half-reaction involves S, and is listed in Appendix E. The reduction half-reaction involves N, and must be written and balanced, according to the procedure in Section 20.2.

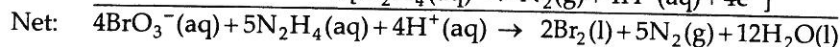
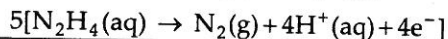
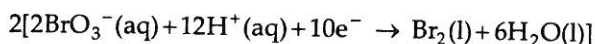


oxidizing agent, HNO_3 ; reducing agent, S.



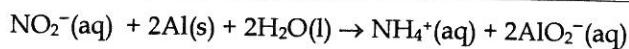
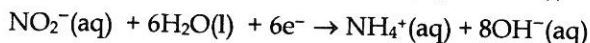
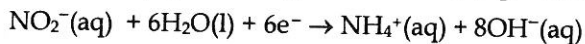
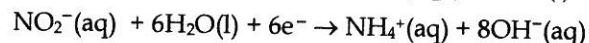
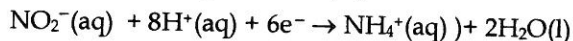
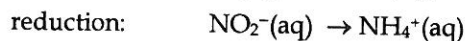
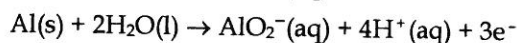
oxidizing agent, $\text{Cr}_2\text{O}_7^{2-}$; reducing agent, CH_3OH

- (d) The half-reaction involving N_2H_4 is given in Appendix E in base. We add $4\text{H}^+(\text{aq})$ to each side and reverse the reaction to obtain oxidation half-reaction shown below.

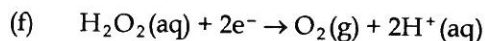


oxidizing agent, BrO_3^- ; reducing agent, N_2H_4

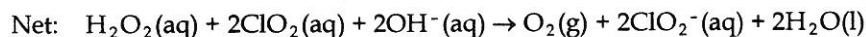
- (e) Write and balance each half-reaction, and then sum to get the overall reaction. Follow the procedure in Sample Exercise 20.3 for reactions in basic solution.



oxidizing agent, NO_2^- ; reducing agent, Al



Since the reaction is in base, the H^+ can be "neutralized" by adding 2OH^- to each side of the equation to give $\text{H}_2\text{O}_2(\text{aq}) + 2\text{OH}^-(\text{aq}) + 2\text{e}^- \rightarrow \text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$. The other half reaction is $2[\text{ClO}_2(\text{aq}) + \text{e}^- \rightarrow \text{ClO}_2^-(\text{aq})]$.

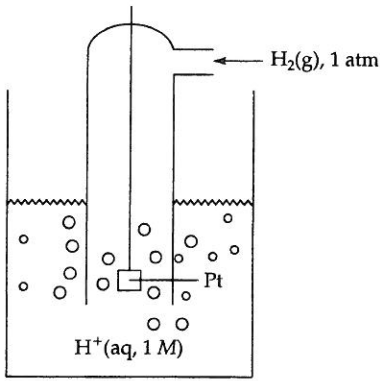


oxidizing agent, ClO_2 ; reducing agent, H_2O_2

Voltaic Cells (section 20.3)

- 20.25 (a) The reaction $\text{Cu}^{2+}(\text{aq}) + \text{Zn}(\text{s}) \rightarrow \text{Cu}(\text{s}) + \text{Zn}^{2+}(\text{aq})$ is occurring in both figures. In Figure 20.3, the reactants are in contact, and the concentrations of the ions in solution aren't specified. In Figure 20.4 the oxidation half-reaction and reduction half-reaction are occurring in separate compartments, joined by a porous connector. The concentrations of the two solutions are initially 1.0 M. In Figure 20.4, electrical current is isolated and flows through the voltmeter. In Figure 20.3, the flow of electrons cannot be isolated or utilized.
- (b) In the cathode compartment of the voltaic cell in Figure 20.5, Cu^{2+} cations are reduced to Cu atoms, decreasing the number of positively charged particles in the compartment. Na^+ cations are drawn into the compartment to maintain charge balance as Cu^{2+} ions are removed.
- 20.26 (a) The porous glass dish in Figure 20.4 provides a mechanism by which ions not directly involved in the redox reaction can migrate into the anode and cathode compartments to maintain charge neutrality of the solutions. Ionic conduction within the cell, through the glass disk, completes the cell circuit.
- (b) In the anode compartment of Figure 20.5, Zn atoms are oxidized to Zn^{2+} cations, increasing the number of positively charged particles in the compartment. NO_3^- anions migrate into the compartment to maintain charge balance as Zn^{2+} ions are produced.
- 20.27 *Analyze/Plan.* Follow the logic in Sample Exercise 20.4. *Solve.*
- (a) Fe(s) is oxidized, $\text{Ag}^+(\text{aq})$ is reduced.
- (b) $\text{Ag}^+(\text{aq}) + 1\text{e}^- \rightarrow \text{Ag}(\text{s}); \text{Fe}(\text{s}) \rightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{e}^-$
- (c) Fe(s) is the anode, Ag(s) is the cathode.
- (d) Fe(s) is negative; Ag(s) is positive.
- (e) Electrons flow from the Fe(-) electrode toward the Ag(+) electrode.
- (f) Cations migrate toward the Ag(s) cathode; anions migrate toward the Fe(s) anode.
- 20.28 (a) Al(s) is oxidized, $\text{Ni}^{2+}(\text{aq})$ is reduced.
- (b) $\text{Al}(\text{s}) \rightarrow \text{Al}^{3+}(\text{aq}) + 3\text{e}^-; \text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$
- (c) Al(s) is the anode; Ni(s) is the cathode.
- (d) Al(s) is negative (-); Ni(s) is positive (+).
- (e) Electrons flow from the Al(-) electrode toward the Ni(+) electrode.
- (f) Cations migrate toward the Ni(s) cathode; anions migrate toward the Al(s) anode.

Cell Potentials under Standard Conditions (section 20.4)

- 20.29 (a) *Electromotive force, emf*, is the driving force that causes electrons to flow through the external circuit of a voltaic cell. It is the potential energy difference between an electron at the anode and an electron at the cathode.
- (b) One *volt* is the potential energy difference required to impart 1 J of energy to a charge of 1 coulomb. $1 \text{ V} = 1 \text{ J/C}$.
- (c) *Cell potential, E_{cell}* , is the emf of an electrochemical cell.
- 20.30 (a) In a voltaic cell, the anode has the higher potential energy for electrons. To achieve a lower potential energy, electrons flow from the anode to the cathode.
- (b) The units of electrical potential are volts. A potential of one volt imparts one joule of energy to one coulomb of charge.
- (c) A *standard* cell potential describes the potential of an electrochemical cell where all components are present at standard conditions: elements in their standard states, gases at 1 atm pressure and 1 M aqueous solutions.
- 20.31 (a) $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$
- (b) A *standard* hydrogen electrode is a hydrogen electrode where the components are at standard conditions, 1 M $\text{H}^+(\text{aq})$ and $\text{H}_2(\text{g})$ at 1 atm.
- (c) The platinum foil in an SHE serves as an inert electron carrier and a solid reaction surface.
- 20.32 (a) $\text{H}_2(\text{g}) \rightarrow 2\text{H}^+(\text{aq}) + 2\text{e}^-$
- (b) The platinum electrode serves as a reaction surface; the greater the surface area, the more H_2 or H^+ that can be adsorbed onto the surface to facilitate the flow of electrons.
- (c)
- 
- 20.33 (a) A *standard reduction potential* is the relative potential of a reduction half-reaction measured at standard conditions, 1 M aqueous solution and 1 atm gas pressure.
- (b) $E_{\text{red}}^{\circ} = 0 \text{ V}$ for a standard hydrogen electrode.
- 20.34 (a) It is not possible to measure the standard reduction potential of a single half-reaction because each voltaic cell consists of two half-reactions and only the potential of a complete cell can be measured.

- (b) The standard reduction potential of a half-reaction is determined by combining it with a reference half-reaction of known potential and measuring the cell potential. Assuming the half-reaction of interest is the reduction half-reaction:

$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ}(\text{cathode}) - E_{\text{red}}^{\circ}(\text{anode}) = E_{\text{red}}^{\circ}(\text{unknown}) - E_{\text{red}}^{\circ}(\text{reference});$$

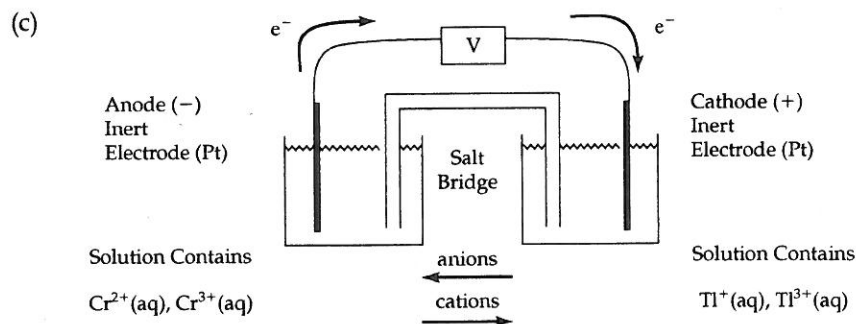
$$E_{\text{red}}^{\circ}(\text{unknown}) = E_{\text{cell}}^{\circ} + E_{\text{red}}^{\circ}(\text{reference}).$$

20.35 *Analyze/Plan.* Follow the logic in Sample Exercise 20.5. *Solve.*

- (a) The two half-reactions are:



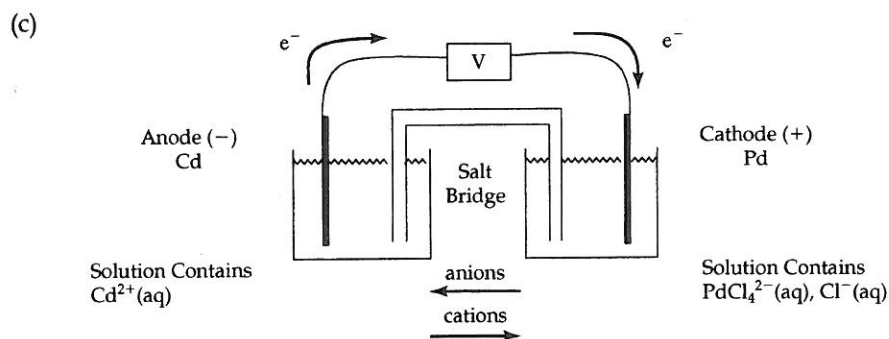
- (b) $E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ}(\text{cathode}) - E_{\text{red}}^{\circ}(\text{anode}); 1.19 \text{ V} = E_{\text{red}}^{\circ} - (-0.41 \text{ V});$
 $E_{\text{red}}^{\circ} = 1.19 \text{ V} - 0.41 \text{ V} = 0.78 \text{ V}$



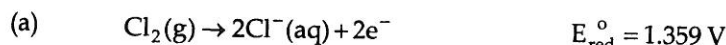
Note that because $\text{Cr}^{2+}(\text{aq})$ is readily oxidized, it would be necessary to keep oxygen out of the left-hand cell compartment.

- 20.36 (a) $\text{PdCl}_4^{2-}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Pd}(\text{s}) + 4\text{Cl}^{-}$ cathode $E_{\text{red}}^{\circ} = ?$
 $\text{Cd}(\text{s}) \rightarrow \text{Cd}^{2+}(\text{aq}) + 2\text{e}^{-}$ anode $E_{\text{red}}^{\circ} = -0.403 \text{ V}$

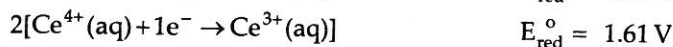
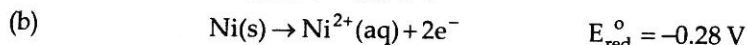
- (b) $E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ}(\text{cathode}) - E_{\text{red}}^{\circ}(\text{anode}); 1.03 \text{ V} = E_{\text{red}}^{\circ} - (-0.403 \text{ V});$
 $E_{\text{red}}^{\circ} = 1.03 \text{ V} - 0.403 = 0.63 \text{ V}$



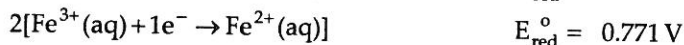
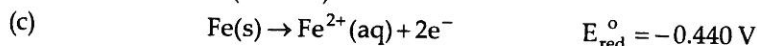
20.37 *Analyze/Plan.* Follow the logic in Sample Exercise 20.6. *Solve.*



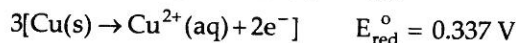
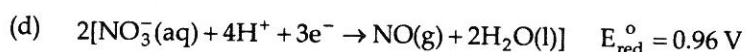
$$E^\circ = 1.359 \text{ V} - 0.536 \text{ V} = 0.823 \text{ V}$$



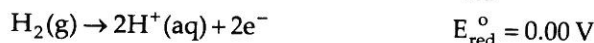
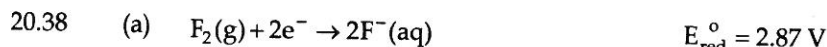
$$E^\circ = 1.61 \text{ V} - (-0.28 \text{ V}) = 1.89 \text{ V}$$



$$E^\circ = 0.771 \text{ V} - (-0.440 \text{ V}) = 1.211 \text{ V}$$



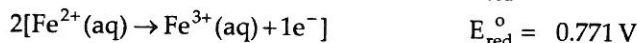
$$E^\circ = 0.96 \text{ V} - (0.337 \text{ V}) = 0.623 = 0.62 \text{ V}$$



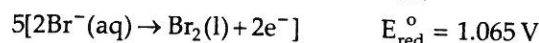
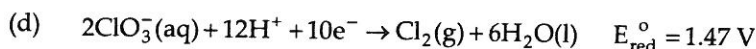
$$E^\circ = 2.87 \text{ V} - 0.00 \text{ V} = 2.87 \text{ V}$$



$$E^\circ = 0.337 \text{ V} - (-2.87 \text{ V}) = 3.21 \text{ V}$$

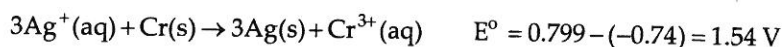
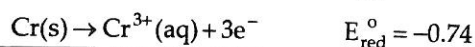
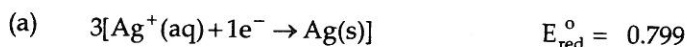


$$E^\circ = -0.440 \text{ V} - 0.771 \text{ V} = -1.211 \text{ V}$$

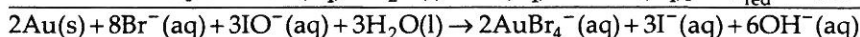
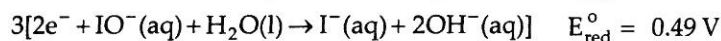
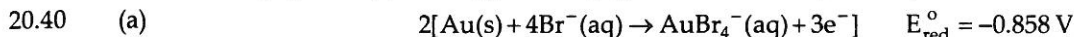
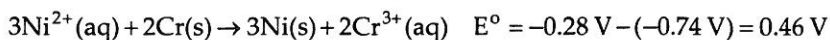
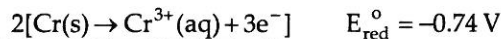
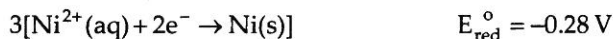
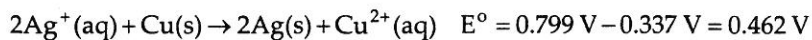
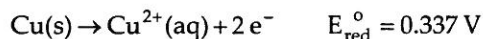
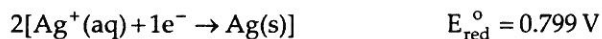


$$E^\circ = 1.47 \text{ V} - 1.065 \text{ V} = 0.405 = 0.41 \text{ V}$$

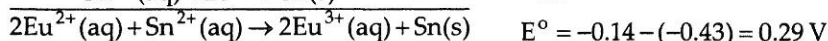
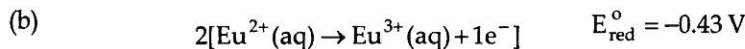
20.39 *Analyze/Plan.* Given four half-reactions, find E_{red}° from Appendix E and combine them to obtain a desired E_{cell}° . (a) The largest E_{cell}° will combine the half-reaction with the most positive E_{red}° as the cathode reaction and the one with the most negative E_{red}° as the anode reaction. (b) The smallest positive E_{cell}° will combine two half-reactions whose E_{red}° values are closest in magnitude and sign. *Solve.*



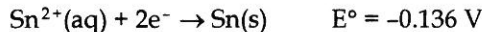
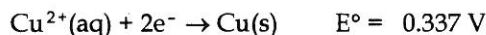
- (b) Two of the combinations have essentially equal
- E°
- values.



$$E^\circ = 0.49 - (-0.858) = 1.35 \text{ V}$$



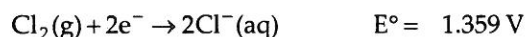
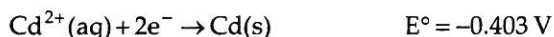
- 20.41 *Analyze/Plan.* Given the description of a voltaic cell, answer questions about this cell. Combine ideas in Sample Exercises 20.4 and 20.7. The reduction half-reactions are:



Solve.

- (a) It is evident that Cu^{2+} is more readily reduced. Therefore, Cu serves as the cathode, Sn as the anode.
- (b) The copper electrode gains mass as Cu is plated out, the Sn electrode loses mass as Sn is oxidized.
- (c) The overall cell reaction is $\text{Cu}^{2+}(\text{aq}) + \text{Sn}(\text{s}) \rightarrow \text{Cu}(\text{s}) + \text{Sn}^{2+}(\text{aq})$
- (d) $E^\circ = 0.337 \text{ V} - (-0.136 \text{ V}) = 0.473 \text{ V}$

- 20.42 (a) The two half-reactions are:



Because E° for the reduction of Cl_2 is greater, Cl_2 is reduced at the cathode, the Pt electrode. Cd(s) is oxidized at the anode, the Cd electrode.

- (b) The Cd anode loses mass as $\text{Cd}^{2+}(\text{aq})$ is produced.
- (c) $\text{Cl}_2(\text{g}) + \text{Cd}(\text{s}) \rightarrow \text{Cd}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq})$
- (d) $E^\circ = 1.359 \text{ V} - (-0.403 \text{ V}) = 1.762 \text{ V}$

Strengths of Oxidizing and Reducing Agents (section 20.4)

- 20.43 *Analyze/Plan.* The more readily a substance is oxidized, the stronger it is as a reducing agent. In each case choose the half-reaction with the more negative reduction potential and the given substance on the right. *Solve.*
- Mg(s) (-2.37 V vs. -0.440 V)
 - Ca(s) (-2.87 V vs. -1.66 V)
 - H₂(g, acidic) (0.000 V vs. 0.141 V)
 - IO₃⁻(aq) [Both IO₃⁻(aq) and BrO₃⁻(aq) are good oxidizing agents, but IO₃⁻(aq) has the smaller positive reduction potential. (1.195 V vs. 1.52 V)]
- 20.44 Follow the logic in Sample Exercise 20.8. In each case, choose the half-reaction with the more positive reduction potential and with the given substance on the left.
- Cl₂(g) (1.359 V vs. 1.065 V)
 - Cd²⁺(aq) (-0.403 V vs. -0.763 V)
 - ClO₃⁻(aq) (Cl⁻(aq) is in its minimum oxidation state and cannot act as an oxidizing agent)
 - O₃(g) (2.07 V vs. 1.776 V)
- 20.45 *Analyze/Plan.* If the substance is on the left of a reduction half-reaction, it will be an oxidant; if it is on the right, it will be a reductant. The sign and magnitude of the E_{red}° determines whether it is strong or weak. *Solve.*
- Cl₂(aq): strong oxidant (on the left, $E_{\text{red}}^{\circ} = 1.359 \text{ V}$)
 - MnO₄⁻(aq, acidic): strong oxidant (on the left, $E_{\text{red}}^{\circ} = 1.51 \text{ V}$)
 - Ba(s): strong reductant (on the right, $E_{\text{red}}^{\circ} = -2.90 \text{ V}$)
 - Zn(s): reductant (on the right, $E_{\text{red}}^{\circ} = -0.763 \text{ V}$)
- 20.46 If the substance is on the left of a reduction half-reaction, it will be an oxidant; if it is on the right, it will be a reductant. The sign and magnitude of the E_{red}° determine whether it is strong or weak.
- Ce³⁺(aq): very weak reductant (on the right, $E_{\text{red}}^{\circ} = 1.61 \text{ V}$)
 - Ca(s): strong reductant (on the right, $E_{\text{red}}^{\circ} = -2.87 \text{ V}$)
 - ClO₃⁻(aq): strong oxidant (on the left, $E_{\text{red}}^{\circ} = 1.47 \text{ V}$)
 - N₂O₅(g): oxidant (N has maximum oxidation number, +5; can only be reduced and act as oxidant.)
- 20.47 *Analyze/Plan.* Follow the logic in Sample Exercise 20.8. *Solve.*
- Arranged in order of increasing strength as oxidizing agents (and increasing reduction potential):
Cu²⁺(aq) < O₂(g) < Cr₂O₇²⁻(aq) < Cl₂(g) < H₂O₂(aq)
 - Arranged in order of increasing strength as reducing agents (and decreasing reduction potential):
H₂O₂(aq) < I⁻(aq) < Sn²⁺(aq) < Zn(s) < Al(s)

- 20.48 (a) The strongest oxidizing agent is the species most readily reduced, as evidenced by a large, positive reduction potential. That species is H_2O_2 . The weakest oxidizing agent is the species that least readily accepts an electron. We expect that it will be very difficult to reduce Zn(s) ; indeed, Zn(s) acts as a comparatively strong **reducing** agent. No potential is listed for reduction of Zn(s) , but we can safely assume that it is less readily reduced than any of the other species present.
- (b) The strongest reducing agent is the species most easily oxidized (the largest negative reduction potential). Zn , $E_{\text{red}}^{\circ} = -0.76 \text{ V}$, is the strongest reducing agent and F^- , $E_{\text{red}}^{\circ} = 2.87 \text{ V}$, is the weakest.
- 20.49 *Analyze/Plan.* In order to reduce Eu^{3+} to Eu^{2+} , we need an oxidizing agent, one of the reduced species from Appendix E. It must have a greater tendency to be oxidized than Eu^{3+} has to be reduced. That is, E_{red}° must be more negative than -0.43 V . *Solve.*
- Any of the **reduced** species in Appendix E from a half-reaction with a reduction potential more negative than -0.43 V will reduce Eu^{3+} to Eu^{2+} . From the list of possible reductants in the exercise, Al and $\text{H}_2\text{C}_2\text{O}_4$ will reduce Eu^{3+} to Eu^{2+} .
- 20.50 Any oxidized species from Appendix E with a reduction potential greater than 0.59 V will oxidize RuO_4^{2-} to RuO_4^- . From the list of possible oxidants in the exercise, $\text{Br}_2(\text{l})$ and $\text{BrO}_3^-(\text{aq})$ will definitely oxidize RuO_4^{2-} to RuO_4^- . $\text{Sn}^{2+}(\text{aq})$ will not, and $\text{O}_2(\text{g})$ depends on conditions. In base, it will not, but in strongly acidic solution, it will.

Free Energy and Redox Reactions (section 20.5)

- 20.51 *Analyze/Plan.* In each reaction, $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ will be the oxidation half-reaction and one of the other given half-reactions will be the reduction half-reaction. Follow the logic in Sample Exercise 20.10 to calculate E° and ΔG° for each reaction. *Solve.*
- (a) $2\text{Fe}^{2+}(\text{aq}) + \text{S}_2\text{O}_6^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) \rightarrow 2\text{Fe}^{3+}(\text{aq}) + 2\text{H}_2\text{SO}_3(\text{aq})$
 $E^{\circ} = 0.60 \text{ V} - 0.77 \text{ V} = -0.17 \text{ V}$
 $2\text{Fe}^{2+}(\text{aq}) + \text{N}_2\text{O}(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow 2\text{Fe}^{3+}(\text{aq}) + \text{N}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
 $E^{\circ} = -1.77 \text{ V} - 0.77 \text{ V} = -2.54 \text{ V}$
 $\text{Fe}^{2+}(\text{aq}) + \text{VO}_2^+(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{VO}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
 $E^{\circ} = 1.00 \text{ V} - 0.77 \text{ V} = +0.23 \text{ V}$
- (b) $\Delta G^{\circ} = -nFE^{\circ}$ For the first reaction,
 $\Delta G^{\circ} = -2 \text{ mol} \times \frac{96,485 \text{ J}}{1 \text{ V} \cdot \text{mol}} \times (-0.17 \text{ V}) = 3.280 \times 10^4 = 3.3 \times 10^4 \text{ J}$ or 33 kJ
 For the second reaction, $\Delta G^{\circ} = -2(96,485)(-2.54) = 4.901 \times 10^5 = 4.90 \times 10^2 \text{ kJ}$
 For the third reaction, $\Delta G^{\circ} = -1(96,485)(0.23) = -2.22 \times 10^4 \text{ J} = -22 \text{ kJ}$
- (c) $\Delta G^{\circ} = -RT \ln K$; $\ln K = -\Delta G^{\circ}/RT$; $K = e^{-\Delta G^{\circ}/RT}$
 For the first reaction,
 $\ln K = \frac{-3.281 \times 10^4 \text{ J}}{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})} = -13.243 = -13$; $K = e^{-13.2428} = 1.78 \times 10^{-6} = 2 \times 10^{-6}$
 [Convert \ln to \log ; the number of decimal places in the \log is the number of sig figs in the result.]

For the second reaction,

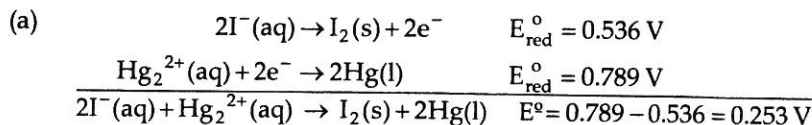
$$\ln K = \frac{-4.902 \times 10^5 \text{ J}}{8.314 \text{ J/mol} \cdot \text{K} \times 298 \text{ K}} = -197.86 = -198; K = e^{-198} = 1.23 \times 10^{-86} = 10^{-86}$$

For the third reaction,

$$\ln K = \frac{-(-2.22 \times 10^4 \text{ J})}{8.314 \text{ J/mol} \cdot \text{K} \times 298 \text{ K}} = 8.958 = 9.0; K = e^{9.0} = 7.77 \times 10^3 = 8 \times 10^3$$

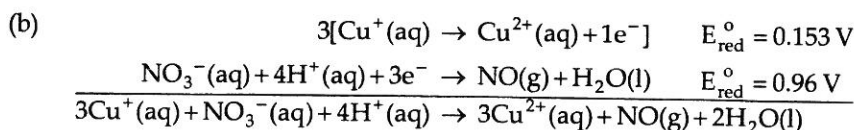
Check. The equilibrium constants calculated here are indicators of equilibrium position, but are not particularly precise numerical values.

20.52



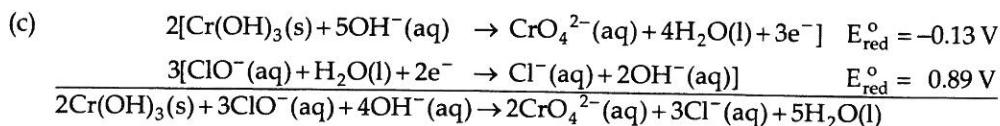
$$\Delta G^\circ = -nFE^\circ = -2 \text{ mol e}^- \times \frac{96.5 \text{ kJ}}{\text{V} \cdot \text{mol e}^-} \times 0.253 \text{ V} = -48.829 = -48.8 \text{ kJ}$$

$$\ln K = \frac{-(-4.8829 \times 10^4 \text{ J})}{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})} = 19.708 = 19.7; K = e^{19.7} = 3.61 \times 10^8 = 3.6 \times 10^8$$



$$E^\circ = 0.96 - 0.153 = 0.81 \text{ V}; \Delta G^\circ = -3(96.5)(0.81) = -2.345 \times 10^2 \text{ kJ} = -2.3 \times 10^5 \text{ J}$$

$$\ln K = \frac{-(-2.345 \times 10^5 \text{ J})}{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})} = 94.65 = 95; K = e^{95} = 1.3 \times 10^{41} = 10^{41}$$



$$E^\circ = 0.89 - (-0.13) = 1.02 \text{ V}; \Delta G^\circ = -6(96.5)(1.02) = -590.58 \text{ kJ} = -5.91 \times 10^5 \text{ J}$$

$$\ln K = \frac{-(-5.9058 \times 10^5 \text{ J})}{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})} = 238.37 = 238; K = 3.3 \times 10^{103} = 10^{103}$$

This is an unimaginably large number.

20.53

Analyze/Plan. Given K , calculate ΔG° and E° . Reverse the logic in Sample Exercise 20.10. According to Equation [19.20], $\Delta G^\circ = -RT \ln K$. According to Equation [20.12], $\Delta G^\circ = -nFE^\circ$, $E^\circ = -\Delta G^\circ/nF$. *Solve.*

$$K = 1.5 \times 10^{-4}$$

$$\Delta G^\circ = -RT \ln K = -(8.314 \text{ J/mol} \cdot \text{K})(298) \ln (1.5 \times 10^{-4}) = 2.181 \times 10^4 \text{ J} = 21.8 \text{ kJ}$$

$$E^\circ = -\Delta G^\circ/nF; n = 2; F = 96.5 \text{ kJ/mol e}^-$$

$$E^\circ = \frac{-21.81 \text{ kJ}}{2 \text{ mol e}^- \times 96.5 \text{ kJ/V} \cdot \text{mol e}^-} = -0.113 \text{ V}$$

Check. The unit of ΔG° is actually kJ/mol, which means kJ per 'mole of reaction', or for the reaction as written. Since we don't have a specific reaction, we interpret the unit as referring to the overall reaction.

20.54 $K = 8.7 \times 10^4$; $\Delta G^\circ = -RT \ln K$; $E^\circ = -\Delta G^\circ/nF$; $n = 1$; $T = 298 \text{ K}$

$$\Delta G^\circ = -8.314 \text{ J/mol-K} \times 298 \text{ K} \times \ln(8.7 \times 10^4) = -2.818 \times 10^4 \text{ J} = -28.2 \text{ kJ}$$

$$E^\circ = -\Delta G^\circ/nF = \frac{-(-28.18 \text{ kJ})}{1e^- \times 96.5 \text{ kJ/V-mol } e^-} = 0.292 \text{ V}$$

20.55 *Analyze.* Given E_{red}° values for half reactions, calculate the value of K for a given redox reaction.

Plan. Combine the relationships involving E° , ΔG° and K to get a direct relationship between E° and K . For each reaction, calculate E° from E_{red}° , then apply the relationship to calculate K .

Solve. $\Delta G^\circ = -nFE^\circ$, $\Delta G^\circ = -RT \ln K$; $\ln K = 2.303 \log K$

$$-nFE^\circ = -RT \ln K, E^\circ = \frac{RT}{nF} \ln K = \frac{2.303 RT}{nF} \log K$$

From Equation [20.17] and [20.18], $2.303 RT/F = 0.0592$.

$$E^\circ = \frac{0.0592}{n} \log K; \log K = \frac{nE^\circ}{0.0592}; K = 10^{\log K}$$

(a) $E^\circ = -0.28 - (-0.440) = 0.16 \text{ V}$, $n = 2$ ($\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$)

$$\log K = \frac{2(0.16)}{0.0592} = 5.4054 = 5.4; K = 2.54 \times 10^5 = 3 \times 10^5$$

(b) $E^\circ = 0 - (-0.277) = 0.277 \text{ V}$; $n = 2$ ($2\text{H}^+ + 2e^- \rightarrow \text{H}_2$)

$$\log K = \frac{2(0.277)}{0.0592} = 9.358 = 9.36; K = 2.3 \times 10^9$$

(c) $E^\circ = 1.51 - 1.065 = 0.445 = 0.45 \text{ V}$; $n = 10$ ($2\text{MnO}_4^- + 10e^- \rightarrow 2\text{Mn}^{+2}$)

$$\log K = \frac{10(0.445)}{0.0592} = 75.169 \approx 75; K = 1.5 \times 10^{75} = 10^{75}$$

Check. Note that small differences in E° values lead to large changes in the magnitude of K . Sig fig rules limit precision of K values; using log instead of ln leads to more sig figs in the K value. This result is strictly numerical and does not indicate any greater precision in the data.

20.56 $E^\circ = \frac{0.0592 \text{ V}}{n} \log K$; $\log K = \frac{nE^\circ}{0.0592 \text{ V}}$. See Solution 20.55 for a more complete explanation.

(a) $E^\circ = 0.799 \text{ V} - 0.337 \text{ V} = 0.462 \text{ V}$; $n = 2$ ($2\text{Ag}^+ + 2e^- \rightarrow 2\text{Ag}$)

$$\log K = \frac{2(0.462 \text{ V})}{0.0592 \text{ V}} = 15.6081 = 15.6; K = 4.056 \times 10^{15} = 4 \times 10^{15}$$

$$(b) \quad E^\circ = 1.61 \text{ V} - 0.32 \text{ V} = 1.29 \text{ V}; n = 3 (3\text{Ce}^{4+} + 3\text{e}^- \rightarrow 3\text{Ce}^{3+})$$

$$\log K = \frac{3(1.29)}{0.0592} = 65.372 = 65.4; K = 2.35 \times 10^{65} = 2 \times 10^{65}$$

$$(c) \quad E^\circ = 0.36 \text{ V} - (-0.23 \text{ V}) = 0.59 \text{ V}; n = 4 (4\text{Fe}(\text{CN})_6^{3-} + 4\text{e}^- \rightarrow 4\text{Fe}(\text{CN})_6^{4-})$$

$$\log K = \frac{4(0.59)}{0.0592} = 39.865 = 40; K = 7.3 \times 10^{39} = 10^{40}$$

20.57 *Analyze/Plan.* $E^\circ = \frac{0.0592 \text{ V}}{n} \log K$. See Solution 20.55 for a more complete development. $\log K = \frac{nE^\circ}{0.0592 \text{ V}}$. *Solve.*

$$(a) \quad \log K = \frac{1(0.177 \text{ V})}{0.0592 \text{ V}} = 2.9899 = 2.99; K = 9.8 \times 10^2$$

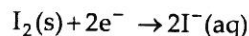
$$(b) \quad \log K = \frac{2(0.177 \text{ V})}{0.0592 \text{ V}} = 5.9797 = 5.98; K = 9.5 \times 10^5$$

$$(c) \quad \log K = \frac{3(0.177 \text{ V})}{0.0592 \text{ V}} = 8.9696 = 8.97; K = 9.32 \times 10^8 = 9.3 \times 10^8$$

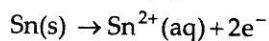
20.58 $E^\circ = \frac{0.0592 \text{ V}}{n} \log K$; $n = \frac{0.0592 \text{ V}}{E^\circ} \log K$. See Solution 20.55 for a more complete development.

$$n = \frac{0.0592 \text{ V}}{0.17 \text{ V}} \log (5.5 \times 10^5); n = 2$$

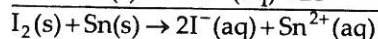
20.59 *Analyze/Plan.* Given a spontaneous chemical reaction, calculate the maximum possible work for a given amount of reactant at standard conditions. Separate the equation into half-reactions and calculate cell emf. Use Equation [20.14], $w_{\max} = -nFE$, to calculate maximum work. At standard conditions, $E = E^\circ$. *Solve.*



$$E_{\text{red}}^\circ = 0.536 \text{ V}$$



$$E_{\text{red}}^\circ = -0.136 \text{ V}$$



$$E^\circ = 0.536 - (-0.136) = 0.672 \text{ V}$$

$$w_{\max} = -2(96.5)(0.672) = -129.7 = -130 \text{ kJ/mol Sn}$$

$$\frac{-129.7 \text{ kJ}}{\text{mol Sn}(\text{s})} \times \frac{1 \text{ mol Sn}}{118.71 \text{ g Sn}} \times 75.0 \text{ g Sn} \times \frac{1000 \text{ J}}{\text{kJ}} = -8.19 \times 10^4 \text{ J}$$

Check. The (-) sign indicates that work is done by the cell.

20.60 For this cell at standard conditions, $E^\circ = 1.10 \text{ V}$.

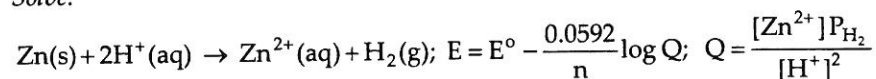
$$w_{\max} = \Delta G^\circ = -nFE^\circ = -2(96.5)(1.10) = -212.3 = -212 \text{ kJ/mol Cu}$$

$$50.0 \text{ g Cu} \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \times \frac{-212.3 \text{ kJ}}{\text{mol Cu}} = -167 \text{ kJ} = -1.67 \times 10^5 \text{ J}$$

Cell EMF under Nonstandard Conditions (section 20.6)

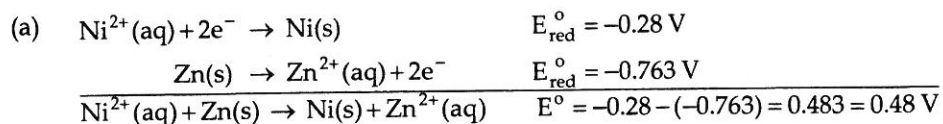
20.61 (a) The Nernst equation is applicable when the components of an electrochemical cell are at nonstandard conditions.

- (b) $Q = 1$ if all reactants and products are at standard conditions.
- (c) If concentration of reactants increases, Q decreases, and E increases.
- 20.62 (a) No. As the spontaneous chemical reaction of the voltaic cell proceeds, the concentrations of products increase and the concentrations of reactants decrease, so standard conditions are not maintained.
- (b) Yes. The Nernst equation is applicable to cell emf at nonstandard conditions, so it must be applicable at temperatures other than 298 K. There are two terms in the Nernst Equation. First, values of E° at temperatures other than 298 K are required. Then, in the form of Equation [20.16], there is a variable for T in the second term. In the short-hand form of Equation [20.18], the value 0.0592 assumes 298 K. A different coefficient would apply to cells at temperatures other than 298 K.
- (c) If concentration of products increases, Q increases, and E decreases.
- 20.63 *Analyze/Plan.* Given a circumstance, determine its effect on cell emf. Each circumstance changes the value of Q . An increase in Q reduces emf; a decrease in Q increases emf. *Solve.*



- (a) P_{H_2} increases, Q increases, E decreases
- (b) $[\text{Zn}^{2+}]$ increases, Q increases, E decreases
- (c) $[\text{H}^+]$ decreases, Q increases, E decreases
- (d) No effect; does not appear in the Nernst equation
- 20.64 $\text{Al(s)} + 3\text{Ag}^+(\text{aq}) \rightarrow \text{Al}^{3+}(\text{aq}) + 3\text{Ag(s)}; E = E^\circ - \frac{0.0592}{n} \log Q; Q = \frac{[\text{Al}^{3+}]}{[\text{Ag}^+]^3}$
- Any change that causes the reaction to be less spontaneous (that causes Q to increase and ultimately shifts the equilibrium to the left) will result in a less positive value for E .
- (a) Increases E by decreasing $[\text{Al}^{3+}]$ on the right side of the equation, which decreases Q .
- (b) No effect; the "concentrations" of pure solids and liquids do not influence the value of K for a heterogeneous equilibrium.
- (c) No effect; the concentration of Ag^+ and the value of Q are unchanged.
- (d) Decreases E ; forming AgCl(s) decreases the concentration of Ag^+ , which increases Q .

- 20.65 *Analyze/Plan.* Follow the logic in Sample Exercise 20.11. *Solve.*

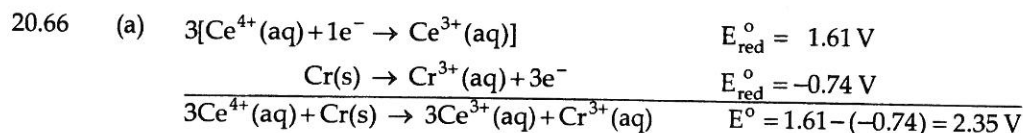


$$(b) \quad E = E^\circ - \frac{0.0592}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Ni}^{2+}]}; \quad n = 2$$

$$E = 0.483 - \frac{0.0592}{2} \log \frac{(0.100)}{(3.00)} = 0.483 - \frac{0.0592}{2} \log (0.0333)$$

$$E = 0.483 - \frac{0.0592(-1.477)}{2} = 0.483 + 0.0437 = 0.527 = 0.53 \text{ V}$$

$$(c) \quad E = 0.483 - \frac{0.0592}{2} \log \frac{(0.900)}{(0.200)} = 0.483 - 0.0193 = 0.464 = 0.46 \text{ V}$$



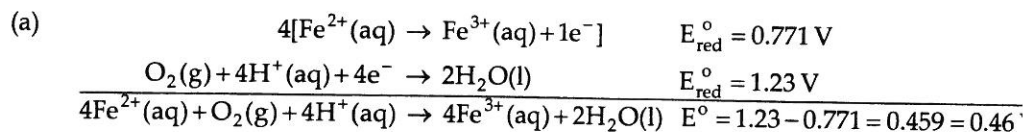
$$(b) \quad E = E^\circ - \frac{0.0592}{n} \log \frac{[\text{Ce}^{3+}]^3 [\text{Cr}^{3+}]}{[\text{Ce}^{4+}]^3}; \quad n = 3$$

$$E = 2.35 - \frac{0.0592}{3} \log \frac{(0.10)^3 (0.010)}{(3.0)^3} = 2.35 - \frac{0.0592}{3} \log (3.704 \times 10^{-7})$$

$$E = 2.35 - \frac{0.0592(-6.431)}{3} = 2.35 + 0.127 = 2.48 \text{ V}$$

$$(c) \quad E = 2.35 - \frac{0.0592}{3} \log \frac{(2.0)^3 (1.5)}{(0.010)^3} = 2.35 - 0.1397 = 2.21 \text{ V}$$

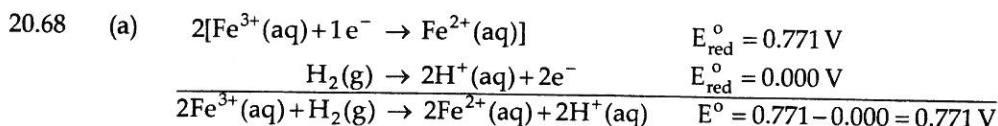
20.67 *Analyze/Plan.* Follow the logic in Sample Exercise 20.11. *Solve.*



$$(b) \quad E = E^\circ - \frac{0.0592}{n} \log \frac{[\text{Fe}^{3+}]^4}{[\text{Fe}^{2+}]^4 [\text{H}^+]^4 P_{\text{O}_2}}; \quad n = 4, [\text{H}^+] = 10^{-3.50} = 3.2 \times 10^{-4} \text{ M}$$

$$E = 0.459 \text{ V} - \frac{0.0592}{4} \log \frac{(0.010)^4}{(1.3)^4 (3.2 \times 10^{-4})^4 (0.50)} = 0.459 - \frac{0.0592}{4} \log (7.0 \times 10^5)$$

$$E = 0.459 - \frac{0.0592}{4} (5.845) = 0.459 - 0.0865 = 0.3725 = 0.37 \text{ V}$$



$$(b) \quad E = E^\circ - \frac{0.0592}{n} \log \frac{[\text{Fe}^{2+}]^2 [\text{H}^+]^2}{[\text{Fe}^{3+}]^2 P_{\text{H}_2}}; [\text{H}^+] = 10^{-\text{pH}} = 1.0 \times 10^{-4}, n = 2$$

$$E = 0.771 - \frac{0.0592}{2} \log \frac{(0.0010)^2 (1.0 \times 10^{-4})^2}{(3.50)^2 (0.95)} = 0.771 - \frac{0.0592}{2} \log (8.6 \times 10^{-16})$$

$$E = 0.771 - \frac{0.0592(-15.066)}{2} = 0.771 + 0.446 = 1.217 \text{ V}$$

20.69 *Analyze/Plan.* We are given a concentration cell with Zn electrodes. Use the definition of a concentration cell in Section 20.6 to answer the stated questions. Use Equation [20.18] to calculate the cell emf. For a concentration cell, $Q = [\text{dilute}]/[\text{concentrated}]$. *Solve.*

(a) The compartment with the more dilute solution will be the anode. That is, the compartment with $[\text{Zn}^{2+}] = 1.00 \times 10^{-2} \text{ M}$ is the anode.

(b) Since the oxidation half-reaction is the opposite of the reduction half-reaction, E° is zero.

$$(c) \quad E = E^\circ - \frac{0.0592}{n} \log Q; Q = [\text{Zn}^{2+}, \text{dilute}]/[\text{Zn}^{2+}, \text{conc.}]$$

$$E = 0 - \frac{0.0592}{2} \log \frac{(1.00 \times 10^{-2})}{(1.8)} = 0.0668 \text{ V}$$

(d) In the anode compartment, $\text{Zn}(s) \rightarrow \text{Zn}^{2+}(\text{aq})$, so $[\text{Zn}^{2+}]$ increases from $1.00 \times 10^{-2} \text{ M}$. In the cathode compartment, $\text{Zn}^{2+}(\text{aq}) \rightarrow \text{Zn}(s)$, so $[\text{Zn}^{2+}]$ decreases from 1.8 M.

20.70 (a) The compartment with 0.0150 M Cl^- (aq) is the cathode.

$$(b) \quad E^\circ = 0 \text{ V}$$

$$(c) \quad E = E^\circ - \frac{0.0592}{n} \log Q; Q = [\text{Cl}^-, \text{dilute}]/[\text{Cl}^-, \text{conc.}]$$

$$E = 0 - \frac{0.0592}{1} \log \frac{(0.0150)}{(2.55)} = -0.13204 = -0.1320 \text{ V}$$

(d) In the anode compartment, $[\text{Cl}^-]$ will decrease from 2.55 M. In the cathode, $[\text{Cl}^-]$ will increase from 0.0150 M.

20.71 *Analyze/Plan.* Follow the logic in Sample Exercise 20.12. *Solve.*

$$E = E^\circ - \frac{0.0592}{2} \log \frac{[P_{\text{H}_2}][\text{Zn}^{2+}]}{[\text{H}^+]^2}; E^\circ = 0.0 \text{ V} - (-0.763 \text{ V}) = 0.763 \text{ V}$$

$$0.684 = 0.763 - \frac{0.0592}{2} \times (\log [P_{\text{H}_2}][\text{Zn}^{2+}] - 2 \log [\text{H}^+])$$

$$= 0.763 - \frac{0.0592}{2} \times (-0.5686 - 2 \log [\text{H}^+])$$

$$0.684 = 0.763 + 0.0168 + 0.0592 \log [\text{H}^+]; \log [\text{H}^+] = \frac{0.684 - 0.0168 - 0.763}{0.0592}$$

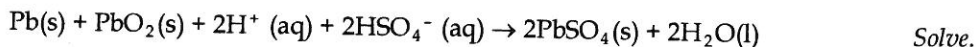
$$\log [\text{H}^+] = -1.6188 = -1.6; [\text{H}^+] = 0.0241 = 0.02 \text{ M}; \text{pH} = 1.6$$

- 20.72 (a) $E^\circ = -0.136 \text{ V} - (-0.126 \text{ V}) = -0.010 \text{ V}; n = 2$
- $$0.22 = -0.010 - \frac{0.0592}{2} \log \frac{[\text{Pb}^{2+}]}{[\text{Sn}^{2+}]} = -0.010 - \frac{0.0592}{2} \log \frac{[\text{Pb}^{2+}]}{1.00}$$
- $$\log [\text{Pb}^{2+}] = \frac{-0.23(2)}{0.0592} = -7.770 = -7.8; [\text{Pb}^{2+}] = 1.7 \times 10^{-8} = 2 \times 10^{-8} \text{ M}$$
- (b) For $\text{PbSO}_4(\text{s})$, $K_{\text{sp}} = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = (1.0)(1.7 \times 10^{-8}) = 1.7 \times 10^{-8}$

Batteries and Fuel Cells (section 20.7)

- 20.73 (a) The emf of a battery decreases as it is used. This happens because the concentrations of products increase and the concentrations of reactants decrease. According to the Nernst equation, these changes increase Q and decrease E_{cell} .
- (b) The major difference between AA- and D-size batteries is the amount of reactants present. The additional reactants in a D-size battery enable it to provide power for a longer time.
- 20.74 (a) First, H_2O is a reactant in the cathodic half-reaction, so it must be present in some form. Additionally, liquid water enhances mobility of the hydroxide ion in the alkaline battery. OH^- is produced in the cathode compartment and consumed in the anode compartment. It must be available at all points where $\text{Zn}(\text{s})$ is being oxidized. If the $\text{Zn}(\text{s})$ near the separator is mostly reacted, OH^- must diffuse through the gel until it reaches fresh $\text{Zn}(\text{s})$. A small amount of $\text{H}_2\text{O}(\text{l})$ mobilizes OH^- so that redox can continue until reactants throughout the battery are depleted.
- (b) Highly concentrated or solid reactants offer a large amount of reactant in a small sample volume. The more available reactant, the longer the cell produces a voltage. A voltaic cell with solid or highly concentrated reactants has the advantages of small size and long operational lifetime.
- 20.75 *Analyze/Plan.* Given mass of a reactant (Pb), calculate mass of product (PbO_2), and coulombs of charge transferred. This is a stoichiometry problem; we need the balanced equation for the chemical reaction that occurs in the lead-acid battery.

The overall cell reaction is:



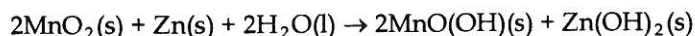
- (a) $\text{g Pb} \rightarrow \text{mol Pb} \rightarrow \text{mol PbO}_2 \rightarrow \text{g PbO}_2$

$$402 \text{ g Pb} \times \frac{1 \text{ mol Pb}}{207.2 \text{ g Pb}} \times \frac{1 \text{ mol PbO}_2}{1 \text{ mol Pb}} \times \frac{239.2 \text{ g PbO}_2}{1 \text{ mol PbO}_2} = 464 \text{ g PbO}_2$$

- (b) From the half-reactions for the lead-acid battery, 2 mol electrons are transferred for each mol of Pb reacted. From section 20.5, $96,485 \text{ C/mol e}^-$.

$$402 \text{ g Pb} \times \frac{1 \text{ mol Pb}}{207.2 \text{ g Pb}} \times \frac{2 \text{ mol e}^-}{1 \text{ mol Pb}} \times \frac{96,485 \text{ C}}{1 \text{ mol e}^-} = 374,392 = 3.74 \times 10^5 \text{ C}$$

20.76 (a) The overall cell reaction is:



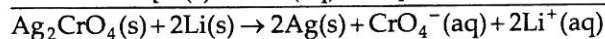
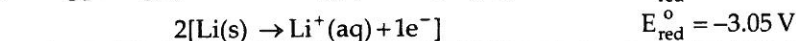
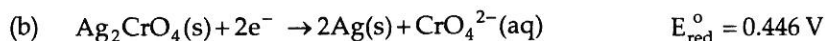
$$4.50 \text{ g Zn} \times \frac{1 \text{ mol Zn}}{65.39 \text{ g Zn}} \times \frac{2 \text{ mol MnO}_2}{1 \text{ mol Zn}} \times \frac{86.94 \text{ g MnO}_2}{1 \text{ mol MnO}_2} = 12.0 \text{ g MnO}_2$$

(b) Two mol e^- are transferred for every mol of Zn reacted. 96,485 C/mol e^-

$$4.50 \text{ g Zn} \times \frac{1 \text{ mol Zn}}{65.39 \text{ g Zn}} \times \frac{2 \text{ mol } e^-}{1 \text{ mol Zn}} \times \frac{96,485 \text{ C}}{1 \text{ mol } e^-} = 13,280 = 1.32 \times 10^4 \text{ C}$$

20.77 *Analyze/Plan.* We are given a redox reaction and asked to write half-reactions, calculate E° , and indicate whether Li(s) is the anode or cathode. Determine which reactant is oxidized and which is reduced. Separate into half-reactions, find E_{red}° for the half-reactions from Appendix E and calculate E° . *Solve.*

(a) Li(s) is oxidized at the anode.



$$E^\circ = 0.446 \text{ V} - (-3.05 \text{ V}) = 3.496 = 3.50 \text{ V}$$

(c) The emf of the battery, 3.5 V, is exactly the standard cell potential calculated in part (b).

(d) For this battery at ambient conditions, $E \approx E^\circ$, so $\log Q \approx 0$. This makes sense because all reactants and products in the battery are solids and thus present in their standard states. Assuming that E° is relatively constant with temperature, the value of the second term in the Nernst equation is ≈ 0 at 37°C, and $E \approx 3.5 \text{ V}$.

20.78 (a) $\text{HgO}(\text{s}) + \text{Zn}(\text{s}) \rightarrow \text{Hg}(\text{l}) + \text{ZnO}(\text{s})$

$$(b) E_{\text{cell}}^\circ = E_{\text{red}}^\circ(\text{cathode}) - E_{\text{red}}^\circ(\text{anode})$$

$$E_{\text{red}}^\circ(\text{anode}) = E_{\text{red}}^\circ - E_{\text{cell}}^\circ = 0.098 - 1.35 = -1.25 \text{ V}$$

(c) E_{red}° is different from $\text{Zn}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Zn}(\text{s})$ (-0.76 V) because in the battery the process happens in the presence of base and Zn^{2+} is stabilized as $\text{ZnO}(\text{s})$. Stabilization of a reactant in a half-reaction decreases the driving force, so E_{red}° is more negative.

20.79 *Analyze/Plan.* (a) Consider the function of Zn in an alkaline battery. What effect would it have on the redox reaction and cell emf if Cd replaces Zn? (b) Both batteries contain Ni. What is the difference in environmental impact between Cd and the metal hydride? *Solve.*

(a) E_{red}° for Cd (-0.40 V) is less negative than E_{red}° for Zn (-0.76 V), so E_{cell} will have a smaller (less positive) value.

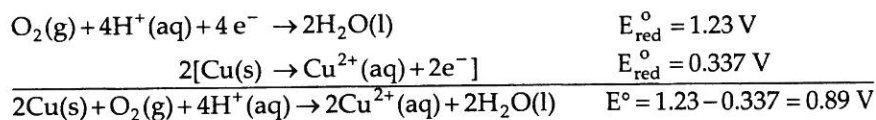
(b) NiMH batteries use an alloy such as ZrNi_2 as the anode material. This eliminates the use and concomitant disposal problems associated with Cd, a toxic heavy metal.

- 20.80 (a) The alkali metal Li has much greater metallic character than Zn, Cd, Pb or Ni. The reduction potential for Li is thus more negative, leading to greater overall cell emf for the battery. Also, Li is less dense than the other metals, so greater total energy for a battery can be achieved for a given total mass of material. One disadvantage is that Li is very reactive and the cell reactions are difficult to control.
- (b) Li has a much smaller molar mass (6.94 g/mol) than Ni (58.69 g/mol). A Li-ion battery can have many more charge-carrying particles than a Ni-based battery with the same mass. That is, Li-ion batteries have a greater *energy density* than Ni-based batteries.
- 20.81 The main advantage of a $\text{H}_2\text{-O}_2$ fuel cell over an alkaline battery is that the fuel cell is not a closed system. Fuel, H_2 , and oxidant, O_2 are continuously supplied to the fuel cell, so that it can produce electrical current for a time limited only by the amount of available fuel. An alkaline battery contains a finite amount of reactant and produces current only until the reactants are spent, or reach equilibrium.
- Alkaline batteries are much more convenient, because they are self-contained. Fuel cells require a means to acquire and store volatile and explosive $\text{H}_2(\text{g})$. Disposal of spent alkaline batteries, which contain zinc and manganese solids, is much more problematic. $\text{H}_2\text{-O}_2$ fuel cells produce only $\text{H}_2\text{O}(\text{l})$, which is not a disposal problem.
- 20.82 (a) Both batteries and fuel cells are electrochemical power sources. Both take advantage of spontaneous oxidation-reduction reactions to produce a certain voltage. The difference is that batteries are self-contained (all reactants and products are present inside the battery casing) while fuel cells require continuous supply of reactants and exhaust of products.
- (b) No. The fuel in a fuel cell must be fluid, either gas or liquid. Because fuel must be continuously supplied to the fuel cell, it must be capable of flow; the fuel cannot be solid.

Corrosion (section 20.8)

- 20.83 *Analyze/Plan.* (a) Decide which reactant is oxidized and which is reduced. Write the balanced half-reactions and assign the appropriate one as anode and cathode. (b) Write the balanced half-reaction for $\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. Use the reduction half-reaction from part (a) to obtain the overall reaction. *Solve.*
- (a) anode: $\text{Fe}(\text{s}) \rightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{e}^-$
 cathode: $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$
- (b) $2\text{Fe}^{2+}(\text{aq}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow \text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}(\text{s}) + 6\text{H}^+(\text{aq}) + 2\text{e}^-$
 $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$
- (Multiply the oxidation half-reaction by two to balance electrons and obtain the overall balanced reaction.)

- 20.84 (a) Calculate E_{cell}° for the given reactants at standard conditions.



At standard conditions with $\text{O}_2(\text{g})$ and $\text{H}^+(\text{aq})$ present, the oxidation of $\text{Cu}(\text{s})$ has a positive E° value and is spontaneous. $\text{Cu}(\text{s})$ will oxidize (corrode) in air in the presence of acid.

- (b) Fe^{2+} has a more negative reduction potential (-0.440 V) than Cu^{2+} ($+0.337 \text{ V}$), so $\text{Fe}(\text{s})$ is more readily oxidized than $\text{Cu}(\text{s})$. If the two metals are in contact, $\text{Fe}(\text{s})$ would act as a sacrificial anode and oxidize (corrode) in preference to $\text{Cu}(\text{s})$; this would weaken the iron support skeleton of the statue. The teflon spacers prevent contact between the two metals and insure that the iron skeleton doesn't corrode when the $\text{Cu}(\text{s})$ skin comes in contact with atmospheric $\text{O}_2(\text{g})$ and $\text{H}^+(\text{aq})$.
- 20.85 (a) A "sacrificial anode" is a metal that is oxidized in preference to another when the two metals are coupled in an electrochemical cell; the sacrificial anode has a more negative E_{red}° than the other metal. In this case, Mg acts as a sacrificial anode because it is oxidized in preference to the pipe metal; it is sacrificed to preserve the pipe.
- (b) E_{red}° for Mg^{2+} is -2.37 V , more negative than most metals present in pipes, including Fe ($E_{\text{red}}^{\circ} = -0.44 \text{ V}$) and Zn ($E_{\text{red}}^{\circ} = -0.763 \text{ V}$).

- 20.86 No. To afford cathodic protection, a metal must be more difficult to reduce (have a more negative reduction potential) than Fe^{2+} . $E_{\text{red}}^{\circ} \text{Co}^{2+} = -0.28 \text{ V}$, $E_{\text{red}}^{\circ} \text{Fe}^{2+} = -0.44 \text{ V}$.

- 20.87 *Analyze/Plan.* Given the materials brass, composed of Zn and Cu , and galvanized steel, determine the possible spontaneous redox reactions that could occur when the materials come in contact. Calculate E° values for these reactions.

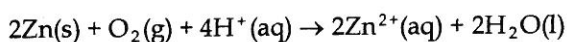
Solve. The main metallic component of steel is Fe . Galvanized steel is steel plated with Zn . The three metals in question are Fe , Zn , and Cu ; their E_{red}° values are shown below.

$$E_{\text{red}}^{\circ} \text{Fe}^{2+}(\text{aq}) = -0.440 \text{ V}$$

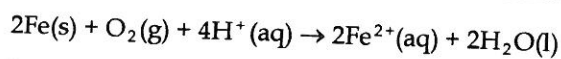
$$E_{\text{red}}^{\circ} \text{Zn}^{2+}(\text{aq}) = -0.763 \text{ V}$$

$$E_{\text{red}}^{\circ} \text{Cu}^{2+}(\text{aq}) = 0.337 \text{ V}$$

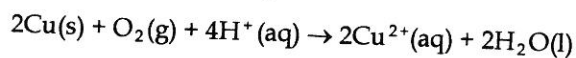
Zn , with the most negative E_{red}° value, can act as a sacrificial anode for either Fe or Cu . That is, $\text{Zn}(\text{s})$ will be preferentially oxidized when in contact with $\text{Fe}(\text{s})$ or $\text{Cu}(\text{s})$. For environmental corrosion, the oxidizing agent is usually $\text{O}_2(\text{g})$ in acidic solution, $E_{\text{red}}^{\circ} = 1.23 \text{ V}$. The pertinent reactions and their E° values are:



$$E^{\circ} = 1.23 \text{ V} - (-0.763 \text{ V}) = 1.99 \text{ V}$$



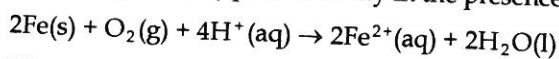
$$E^\circ = 1.23 \text{ V} - (-0.440 \text{ V}) = 1.67 \text{ V}$$



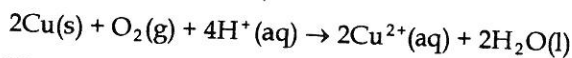
$$E^\circ = 1.23 \text{ V} - (0.337 \text{ V}) = 0.893 \text{ V}$$

Note, however, that Fe has a more negative E_{red}° than Cu so when the two are in contact Fe acts as the sacrificial anode, and corrosion (of Fe) occurs preferentially. This is verified by the larger E° value for the corrosion of Fe, 1.67 V, relative to the corrosion of Cu, 0.893 V. When the three metals Zn, Fe, and Cu are in contact, oxidation of Zn will happen first, followed by oxidation of Fe, and finally Cu.

- 20.88 The principal metallic component of steel is Fe. E_{red}° for Fe, -0.763 V , is more negative than that of Cu, 0.337 V . When the two are in contact, Fe acts as the sacrificial anode and corrodes (oxidizes) preferentially in the presence of $\text{O}_2\text{(g)}$.



$$E^\circ = 1.23 \text{ V} - (-0.440 \text{ V}) = 1.67 \text{ V}$$



$$E^\circ = 1.23 \text{ V} - (0.337 \text{ V}) = 0.893 \text{ V}$$

Both reactions are spontaneous, but the corrosion of Fe has the larger E° value and happens preferentially.

Electrolysis; Electrical Work (section 20.9)

- 20.89 (a) *Electrolysis* is an electrochemical process driven by an outside energy source.
 (b) Electrolysis reactions are, by definition, nonspontaneous.
 (c) $2\text{Cl}^-\text{(l)} \rightarrow \text{Cl}_2\text{(g)} + 2\text{e}^-$
 (d) When an aqueous solution of NaCl undergoes electrolysis, H_2O is preferentially reduced to form $\text{H}_2\text{(g)}$.
- 20.90 (a) An *electrolytic cell* is the vessel in which electrolysis occurs. It consists of a power source and two electrodes in a molten salt or aqueous solution.
 (b) It is the cathode. In an electrolysis cell, as in a voltaic cell, electrons are consumed (via reduction) at the cathode. Electrons flow from the negative terminal of the voltage source and then to the cathode.
 (c) A small amount of $\text{H}_2\text{SO}_4\text{(aq)}$ present during the electrolysis of water acts as a charge carrier, or supporting electrolyte. This facilitates transfer of electrons through the solution and at the electrodes, speeding up the reaction. (Considering $\text{H}^+\text{(aq)}$ as the substance reduced at the cathode changes the details of the half-reactions, but not the overall E° for the electrolysis. $\text{SO}_4^{2-}\text{(aq)}$ cannot be oxidized.)
 (d) If the active metal salt is present as an aqueous solution during electrolysis, water is reduced [to $\text{H}_2\text{(g)}$] rather than the metal ion being reduced to the metal. This is true for any active metal with an E_{red}° value more negative than -0.83 V .

20.91 *Analyze/Plan.* Follow the logic in Sample Exercise 20.14, paying close attention to units. Coulombs = **amps-s**; since this is a $3e^-$ reduction, each mole of Cr(s) requires 3 Faradays. *Solve.*

$$(a) \quad 7.60 \text{ A} \times 2.00 \text{ d} \times \frac{24 \text{ hr}}{1 \text{ d}} \times \frac{60 \text{ min}}{1 \text{ hr}} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{1 \text{ C}}{1 \text{ amp-s}} \times \frac{1 \text{ F}}{96,485 \text{ C}} \\ \times \frac{1 \text{ mol Cr}}{3 \text{ F}} \times \frac{52.00 \text{ g Cr}}{1 \text{ mol Cr}} = 236 \text{ g Cr(s)}$$

$$(b) \quad 0.250 \text{ mol Cr} \times \frac{3 \text{ F}}{1 \text{ mol Cr}} \times \frac{96,485 \text{ C}}{\text{F}} \times \frac{1 \text{ amp-s}}{1 \text{ C}} \times \frac{1}{8.00 \text{ hr}} \times \frac{1 \text{ hr}}{60 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}} \\ = 2.51 \text{ A}$$

20.92 Coulombs = **amps-s**; since this is a $2e^-$ reduction, each mole of Mg(s) requires 2 Faradays.

$$(a) \quad 4.55 \text{ A} \times 4.50 \text{ d} \times \frac{24 \text{ h}}{1 \text{ d}} \times \frac{60 \text{ min}}{1 \text{ h}} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{1 \text{ C}}{1 \text{ amp-s}} \times \frac{1 \text{ F}}{96,485 \text{ C}} \\ \times \frac{1 \text{ mol Mg}}{2 \text{ F}} \times \frac{24.31 \text{ g Mg}}{1 \text{ mol Mg}} = 223 \text{ g Mg}$$

$$(b) \quad 25.00 \text{ g Mg} \times \frac{1 \text{ mol Mg}}{24.31 \text{ g Mg}} \times \frac{2 \text{ F}}{1 \text{ mol Mg}} \times \frac{96,485 \text{ C}}{\text{F}} \times \frac{1 \text{ amp-s}}{\text{C}} \times \frac{1 \text{ min}}{60 \text{ s}} \times \frac{1}{3.50 \text{ A}} \\ = 945 \text{ min}$$

20.93 *Analyze/Plan.* Combine the ideas in Sample Exercises 20.14 and 20.15, paying close attention to units. Li^+ is reduced at the anode; Cl^- is oxidized at the anode. *Solve.*

$$(a) \quad \text{If the cell is 85\% efficient, } \frac{96,485 \text{ C}}{\text{F}} \times \frac{1 \text{ F}}{0.85 \text{ mol}} = 1.13512 \times 10^5 \\ = 1.1 \times 10^5 \text{ C/mol Li required}$$

$$7.5 \times 10^4 \text{ A} \times 24 \text{ h} \times \frac{3600 \text{ s}}{1 \text{ h}} \times \frac{1 \text{ C}}{1 \text{ amp-s}} \times \frac{1 \text{ mol Li}}{1.13512 \times 10^5 \text{ C}} \times \frac{6.94 \text{ g Li}}{1 \text{ mol Li}} \\ = 3.962 \times 10^5 = 4.0 \times 10^5 \text{ g Li}$$

$$(b) \quad E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ}(\text{cathode}) - E_{\text{red}}^{\circ}(\text{anode}) = -3.05 \text{ V} - (1.359 \text{ V}) = -4.409 = -4.41 \text{ V}$$

The minimum voltage required to drive the reaction is the magnitude of E_{cell}° , 4.41 V.

$$20.94 \quad (a) \quad 7.5 \times 10^3 \text{ A} \times 48 \text{ h} \times \frac{3600 \text{ s}}{1 \text{ h}} \times \frac{1 \text{ C}}{1 \text{ amp-s}} \times \frac{1 \text{ F}}{96,485 \text{ C}} \times \frac{1 \text{ mol Ca}}{2 \text{ F}} \times 0.68 \times \frac{40.0 \text{ g Ca}}{1 \text{ mol Ca}} \\ = 1.830 \times 10^5 = 1.8 \times 10^5 \text{ g Ca}$$

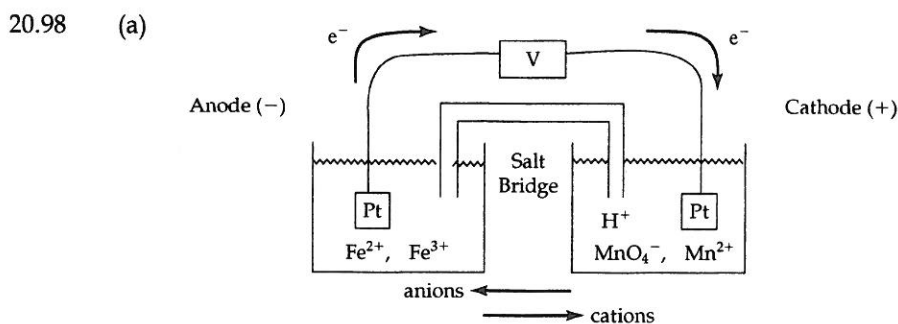
$$(b) \quad E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ}(\text{cathode}) - E_{\text{red}}^{\circ}(\text{anode}) = -2.87 \text{ V} - (1.359 \text{ V}) = -4.229 = -4.23 \text{ V}$$

The minimum voltage required to drive the reaction is the magnitude of E_{cell}° , 4.23 V.

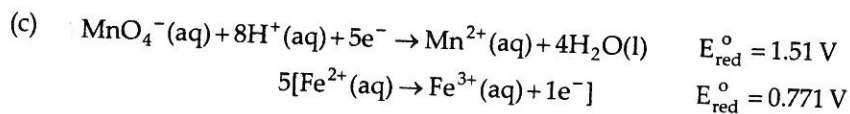
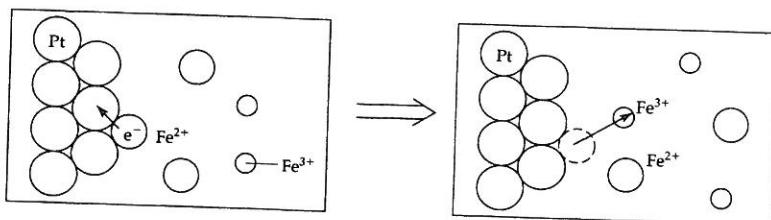
- 20.95 Table 4.5 is "The Activity Series of the Metals". Gold is the least active metal on this table, less active than copper. This means that gold is more difficult to oxidize than copper (and that E_{red}° for Au^{3+} is more positive than E_{red}° for Cu^{2+}). When crude copper is refined by electrolysis, Cu is oxidized from the crude anode, but any metallic gold present in the crude copper is not oxidized, so it accumulates near the anode, along with other impurities less active than copper.
- 20.96 The standard reduction potential for Te^{4+} , 0.57 V, is more positive than that of Cu^{2+} , 0.34 V. This means the Te^{4+} is "easier" to reduce than Cu^{2+} , but Te is harder to oxidize and less active than Cu. During electrorefining, while Cu is oxidized from the crude anode, Te will not be oxidized. It is likely to accumulate along with other impurities less active than Cu, in the so-called anode sludge.

Additional Exercises

- 20.97 (a) $\text{Ni}^{+}(\text{aq}) + 1\text{e}^{-} \rightarrow \text{Ni}(\text{s})$
 $\text{Ni}^{+}(\text{aq}) \rightarrow \text{Ni}^{2+}(\text{aq}) + 1\text{e}^{-}$
 $\hline 2\text{Ni}^{+}(\text{aq}) \rightarrow \text{Ni}(\text{s}) + \text{Ni}^{2+}(\text{aq})$
- (b) $\text{MnO}_4^{2-}(\text{aq}) + 4\text{H}^{+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{MnO}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l})$
 $2[\text{MnO}_4^{2-}(\text{aq}) \rightarrow \text{MnO}_4^{-}(\text{aq}) + 1\text{e}^{-}]$
 $\hline 3\text{MnO}_4^{2-}(\text{aq}) + 4\text{H}^{+}(\text{aq}) \rightarrow 2\text{MnO}_4^{-}(\text{aq}) + \text{MnO}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l})$
- (c) $\text{H}_2\text{SO}_3(\text{aq}) + 4\text{H}^{+}(\text{aq}) + 4\text{e}^{-} \rightarrow \text{S}(\text{s}) + 3\text{H}_2\text{O}(\text{l})$
 $2[\text{H}_2\text{SO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{HSO}_4^{-}(\text{aq}) + 3\text{H}^{+}(\text{aq}) + 2\text{e}^{-}]$
 $\hline 3\text{H}_2\text{SO}_3(\text{aq}) \rightarrow \text{S}(\text{s}) + 2\text{HSO}_4^{-}(\text{aq}) + 2\text{H}^{+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
- (d) $\text{Cl}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{ClO}^{-}(\text{aq}) + 4\text{H}^{+}(\text{aq}) + 2\text{e}^{-}$
 $4\text{OH}^{-}(\text{aq}) + 4\text{OH}^{-}(\text{aq})$
 $\hline \text{Cl}_2(\text{aq}) + 4\text{OH}^{-}(\text{aq}) \rightarrow 2\text{ClO}^{-}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^{-}$
 $\text{Cl}_2(\text{aq}) + 2\text{e}^{-} \rightarrow 2\text{Cl}^{-}(\text{aq})$
 $\hline 1/2[2\text{Cl}_2(\text{aq}) + 4\text{OH}^{-}(\text{aq}) \rightarrow 2\text{Cl}^{-}(\text{aq}) + 2\text{ClO}^{-}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})]$
 $\text{Cl}_2(\text{aq}) + 2\text{OH}^{-}(\text{aq}) \rightarrow \text{Cl}^{-}(\text{aq}) + \text{ClO}^{-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$



(b)



$$E^\circ = 1.51 \text{ V} - 0.771 \text{ V} = 0.74 \text{ V}$$

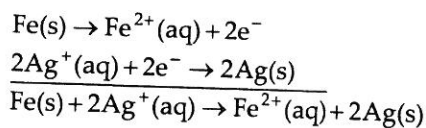
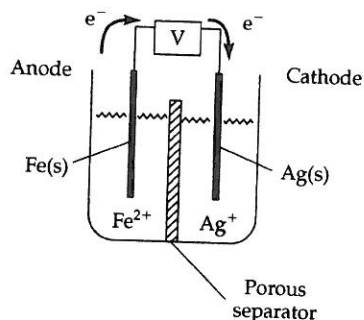
(d)

$$E = E^\circ - \frac{0.0592}{5} \log \frac{[\text{Fe}^{3+}]^5 [\text{Mn}^{2+}]}{[\text{Fe}^{2+}]^5 [\text{MnO}_4^-] [\text{H}^+]^8}; \text{pH} = 0.0, [\text{H}^+] = 1.0$$

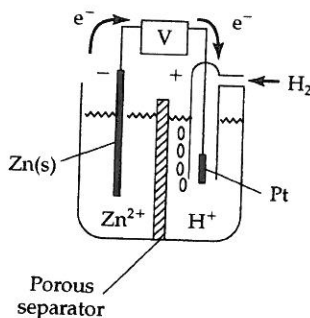
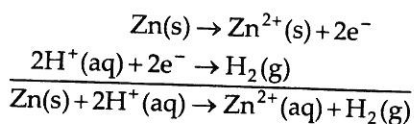
$$E = 0.74 \text{ V} - \frac{0.0592}{5} \log \frac{(2.5 \times 10^{-4})^5 (0.001)}{(0.10)^5 (1.50)(1.0)^8}; Q = 6.510 \times 10^{-17} = 6.5 \times 10^{-17}$$

$$E = 0.74 \text{ V} - \frac{0.0592(-16.1864)}{5} = 0.74 \text{ V} + 0.19 \text{ V} = 0.93 \text{ V}$$

20.99 (a)



(b)



(c) $\text{Cu} | \text{Cu}^{2+} || \text{ClO}_3^-, \text{Cl}^- | \text{Pt}$ Here, both the oxidized and reduced forms of the cathode solution are in the same phase, so we separate them by a comma, and then indicate an inert electrode.