STRENGTHS OF OXIDIZING AND REDUCING AGENTS (section 20.4)

20.43 From each of the following pairs of substances, use data in Appendix E to choose the one that is the stronger reducing agent:
(**a**) $Fe(s)$ or $Mg(s)$
(**b**) $Ca(s)$ or $Al(s)$
(**c**) $H_2(g$, acidic solution$)$ or $H_2S(g)$
(**d**) $BrO_3^-(aq)$ or $IO_3^-(aq)$

20.44 From each of the following pairs of substances, use data in Appendix E to choose the one that is the stronger oxidizing agent:
(**a**) $Cl_2(g)$ or $Br_2(l)$
(**b**) $Zn^{2+}(aq)$ or $Cd^{2+}(aq)$
(**c**) $Cl^-(aq)$ or $ClO_3^-(aq)$
(**d**) $H_2O_2(aq)$ or $O_3(g)$

20.45 By using the data in Appendix E, determine whether each of the following substances is likely to serve as an oxidant or a reductant: (**a**) $Cl_2(g)$, (**b**) $MnO_4^-(aq$, acidic solution$)$, (**c**) $Ba(s)$, (**d**) $Zn(s)$.

20.46 Is each of the following substances likely to serve as an oxidant or a reductant: (**a**) $Ce^{3+}(aq)$, (**b**) $Ca(s)$, (**c**) $ClO_3^-(aq)$, (**d**) $N_2O_5(g)$?

20.47 (**a**) Assuming standard conditions, arrange the following in order of increasing strength as oxidizing agents in acidic solution: $Cr_2O_7^{2-}$, H_2O_2, Cu^{2+}, Cl_2, O_2. (**b**) Arrange the following in order of increasing strength as reducing agents in acidic solution: Zn, I^-, Sn^{2+}, H_2O_2, Al.

20.48 Based on the data in Appendix E, (**a**) which of the following is the strongest oxidizing agent and which is the weakest in acidic solution:, Br_2, H_2O_2, Zn, $Cr_2O_7^{2-}$? (**b**) Which of the following is the strongest reducing agent, and which is the weakest in acidic solution: F^-, Zn, $N_2H_5^+$, I_2, NO?

20.49 The standard reduction potential for the reduction of $Eu^{3+}(aq)$ to $Eu^{2+}(aq)$ is -0.43 V. Using Appendix E, which of the following substances is capable of reducing $Eu^{3+}(aq)$ to $Eu^{2+}(aq)$ under standard conditions: Al, Co, H_2O_2, $N_2H_5^+$, $H_2C_2O_4$?

20.50 The standard reduction potential for the reduction of $RuO_4^-(aq)$ to $RuO_4^{2-}(aq)$ is $+0.59$ V. By using Appendix E, which of the following substances can oxidize $RuO_4^{2-}(aq)$ to $RuO_4^-(aq)$ under standard conditions: $Br_2(l)$, $BrO_3^-(aq)$, $Mn^{2+}(aq)$, $O_2(g)$, $Sn^{2+}(aq)$?

FREE ENERGY AND REDOX REACTIONS (section 20.5)

20.51 Given the following reduction half-reactions:

$$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq) \qquad E^\circ_{red} = +0.77 \text{ V}$$

$$S_2O_6^{2-}(aq) + 4\,H^+(aq) + 2\,e^- \longrightarrow 2\,H_2SO_3(aq) \qquad E^\circ_{red} = +0.60 \text{ V}$$

$$N_2O(g) + 2\,H^+(aq) + 2\,e^- \longrightarrow N_2(g) + H_2O(l) \qquad E^\circ_{red} = -1.77 \text{ V}$$

$$VO_2^+(aq) + 2\,H^+(aq) + e^- \longrightarrow VO^{2+} + H_2O(l) \qquad E^\circ_{red} = +1.00 \text{ V}$$

(**a**) Write balanced chemical equations for the oxidation of $Fe^{2+}(aq)$ by $S_2O_6^{2-}(aq)$, by $N_2O(aq)$, and by $VO_2^+(aq)$. (**b**) Calculate ΔG° for each reaction at 298 K. (**c**) Calculate the equilibrium constant K for each reaction at 298 K.

20.52 For each of the following reactions, write a balanced equation, calculate the standard emf, calculate ΔG° at 298 K, and calculate the equilibrium constant K at 298 K. (**a**) Aqueous iodide ion is oxidized to $I_2(s)$ by $Hg_2^{2+}(aq)$. (**b**) In acidic solution, copper(I) ion is oxidized to copper(II) ion by nitrate ion. (**c**) In basic solution, $Cr(OH)_3(s)$ is oxidized to $CrO_4^{2-}(aq)$ by $ClO^-(aq)$.

20.53 If the equilibrium constant for a two-electron redox reaction at 298 K is 1.5×10^{-4}, calculate the corresponding ΔG° and E°_{red}.

20.54 If the equilibrium constant for a one-electron redox reaction at 298 K is 8.7×10^4, calculate the corresponding ΔG° and E°_{red}.

20.55 Using the standard reduction potentials listed in Appendix E, calculate the equilibrium constant for each of the following reactions at 298 K:
(**a**) $Fe(s) + Ni^{2+}(aq) \longrightarrow Fe^{2+}(aq) + Ni(s)$
(**b**) $Co(s) + 2\,H^+(aq) \longrightarrow Co^{2+}(aq) + H_2(g)$
(**c**) $10\,Br^-(aq) + 2\,MnO_4^-(aq) + 16\,H^+(aq) \longrightarrow 2\,Mn^{2+}(aq) + 8\,H_2O(l) + 5\,Br_2(l)$

20.56 Using the standard reduction potentials listed in Appendix E, calculate the equilibrium constant for each of the following reactions at 298 K:
(**a**) $Cu(s) + 2\,Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2\,Ag(s)$
(**b**) $3\,Ce^{4+}(aq) + Bi(s) + H_2O(l) \longrightarrow 3\,Ce^{3+}(aq) + BiO^+(aq) + 2\,H^+(aq)$
(**c**) $N_2H_5^+(aq) + 4\,Fe(CN)_6^{3-}(aq) \longrightarrow N_2(g) + 5\,H^+(aq) + 4\,Fe(CN)_6^{4-}(aq)$

20.57 A cell has a standard cell potential of $+0.177$ V at 298 K. What is the value of the equilibrium constant for the reaction (**a**) if $n = 1$? (**b**) if $n = 2$? (**c**) if $n = 3$?

20.58 At 298 K a cell reaction has a standard cell potential of $+0.17$ V. The equilibrium constant for the reaction is 5.5×10^5. What is the value of n for the reaction?

20.59 A voltaic cell is based on the reaction

$$Sn(s) + I_2(s) \longrightarrow Sn^{2+}(aq) + 2\,I^-(aq)$$

Under standard conditions, what is the maximum electrical work, in joules, that the cell can accomplish if 75.0 g of Sn is consumed?

20.60 Consider the voltaic cell illustrated in Figure 20.5, which is based on the cell reaction

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

Under standard conditions, what is the maximum electrical work, in joules, that the cell can accomplish if 50.0 g of copper is formed?

CELL EMF UNDER NONSTANDARD CONDITIONS (section 20.6)

20.61 (**a**) Under what circumstances is the Nernst equation applicable? (**b**) What is the numerical value of the reaction quotient, *Q*, under standard conditions? (**c**) What happens to the emf of a cell if the concentrations of the reactants are increased?

20.62 (**a**) A voltaic cell is constructed with all reactants and products in their standard states. Will this condition hold as the cell operates? Explain. (**b**) Can the Nernst equation be used at temperatures other than room temperature? Explain. (**c**) What happens to the emf of a cell if the concentrations of the products are increased?

20.63 What is the effect on the emf of the cell shown in Figure 20.9, which has the overall reaction $Zn(s) + 2\,H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$, for each of the following changes? (**a**) The pressure of the H_2 gas is increased in the cathode half-cell. (**b**) Zinc nitrate is added to the anode half-cell. (**c**) Sodium hydroxide is added to the cathode half-cell, decreasing $[H^+]$. (**d**) The surface area of the anode is doubled.

20.64 A voltaic cell utilizes the following reaction:

$$Al(s) + 3\,Ag^+(aq) \longrightarrow Al^{3+}(aq) + 3\,Ag(s)$$

What is the effect on the cell emf of each of the following changes? (**a**) Water is added to the anode half-cell, diluting the solution. (**b**) The size of the aluminum electrode is increased. (**c**) A solution of $AgNO_3$ is added to the cathode half-cell, increasing the quantity of Ag^+ but not changing its concentration. (**d**) HCl is added to the $AgNO_3$ solution, precipitating some of the Ag^+ as AgCl.

20.65 A voltaic cell is constructed that uses the following reaction and operates at 298 K:

$$Zn(s) + Ni^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Ni(s)$$

(**a**) What is the emf of this cell under standard conditions? (**b**) What is the emf of this cell when $[Ni^{2+}] = 3.00\,M$ and $[Zn^{2+}] = 0.100\,M$? (**c**) What is the emf of the cell when $[Ni^{2+}] = 0.200\,M$ and $[Zn^{2+}] = 0.900\,M$?

20.66 A voltaic cell utilizes the following reaction and operates at 298 K:

$$3\,Ce^{4+}(aq) + Cr(s) \longrightarrow 3\,Ce^{3+}(aq) + Cr^{3+}(aq)$$

(**a**) What is the emf of this cell under standard conditions? (**b**) What is the emf of this cell when $[Ce^{4+}] = 3.0\,M$, $[Ce^{3+}] = 0.10\,M$, and $[Cr^{3+}] = 0.010\,M$? (**c**) What is the emf of the cell when $[Ce^{4+}] = 0.010\,M$, $[Ce^{3+}] = 2.0\,M$, and $[Cr^{3+}] = 1.5\,M$?

20.67 A voltaic cell utilizes the following reaction:

$$4\,Fe^{2+}(aq) + O_2(g) + 4\,H^+(aq) \longrightarrow 4\,Fe^{3+}(aq) + 2\,H_2O(l)$$

(**a**) What is the emf of this cell under standard conditions? (**b**) What is the emf of this cell when $[Fe^{2+}] = 1.3\,M$, $[Fe^{3+}] = 0.010\,M$, $P_{O_2} = 0.50$ atm, and the pH of the solution in the cathode half-cell is 3.50?

20.68 A voltaic cell utilizes the following reaction:

$$2\,Fe^{3+}(aq) + H_2(g) \longrightarrow 2\,Fe^{2+}(aq) + 2\,H^+(aq)$$

(**a**) What is the emf of this cell under standard conditions? (**b**) What is the emf for this cell when $[Fe^{3+}] = 3.50\,M$, $P_{H_2} = 0.95$ atm, $[Fe^{2+}] = 0.0010\,M$, and the pH in both half-cells is 4.00?

20.69 A voltaic cell is constructed with two Zn^{2+}–Zn electrodes. The two half-cells have $[Zn^{2+}] = 1.8\,M$ and $[Zn^{2+}] = 1.00 \times 10^{-2}\,M$, respectively. (**a**) Which electrode is the anode of the cell? (**b**) What is the standard emf of the cell? (**c**) What is the cell emf for the concentrations given? (**d**) For each electrode, predict whether $[Zn^{2+}]$ will increase, decrease, or stay the same as the cell operates.

20.70 A voltaic cell is constructed with two silver–silver chloride electrodes, each of which is based on the following half-reaction:

$$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$$

The two half-cells have $[Cl^-] = 0.0150\,M$ and $[Cl^-] = 2.55\,M$, respectively. (**a**) Which electrode is the cathode of the cell? (**b**) What is the standard emf of the cell? (**c**) What is the cell emf for the concentrations given? (**d**) For each electrode, predict whether $[Cl^-]$ will increase, decrease, or stay the same as the cell operates.

20.71 The cell in Figure 20.9 could be used to provide a measure of the pH in the cathode half-cell. Calculate the pH of the cathode half-cell solution if the cell emf at 298 K is measured to be +0.684 V when $[Zn^{2+}] = 0.30\,M$ and $P_{H_2} = 0.90$ atm.

20.72 A voltaic cell is constructed that is based on the following reaction:

$$Sn^{2+}(aq) + Pb(s) \longrightarrow Sn(s) + Pb^{2+}(aq)$$

(**a**) If the concentration of Sn^{2+} in the cathode half-cell is 1.00 *M* and the cell generates an emf of +0.22 V, what is the concentration of Pb^{2+} in the anode half-cell? (**b**) If the anode half-cell contains $[SO_4^{2-}] = 1.00\,M$ in equilibrium with $PbSO_4(s)$, what is the K_{sp} of $PbSO_4$?

BATTERIES AND FUEL CELLS (section 20.7)

20.73 (**a**) What happens to the emf of a battery as it is used? Why does this happen? (**b**) The AA-size and D-size alkaline batteries are both 1.5-V batteries that are based on the same electrode reactions. What is the major difference between the two batteries? What performance feature is most affected by this difference?

20.74 (**a**) Suggest an explanation for why liquid water is needed in an alkaline battery. (**b**) What is the advantage of using highly concentrated or solid reactants in a voltaic cell?

20.75 During a period of discharge of a lead-acid battery, 402 g of Pb from the anode is converted into $PbSO_4(s)$. (**a**) What mass of $PbO_2(s)$ is reduced at the cathode during this same period? (**b**) How many coulombs of electrical charge are transferred from Pb to PbO_2?

20.76 During the discharge of an alkaline battery, 4.50 g of Zn is consumed at the anode of the battery. (**a**) What mass of MnO_2 is reduced at the cathode during this discharge? (**b**) How many coulombs of electrical charge are transferred from Zn to MnO_2?

20.77 Heart pacemakers are often powered by lithium–silver chromate "button" batteries. The overall cell reaction is

$$2\,Li(s) + Ag_2CrO_4(s) \longrightarrow Li_2CrO_4(s) + 2\,Ag(s)$$