CHAPTER 20 Electrochemistry

Section 1 Voltaic Cells

Practice Problems

For each of these pairs of half-reactions, write the balanced equation for the overall cell reaction and calculate the standard cell potential. Express the reaction using cell notation. Refer to the chapter on redox reactions to review writing and balancing redox equations.

1. $Pt^{2+}(aq) + 2e^- \rightarrow Pt(s)$ and
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$

$Pt^{2+}(aq) + Sn(s) \rightarrow Pt(s) + Sn^{2+}(aq)$

$E^0_{cell} = +1.18\ V - (-0.1375\ V)$

$E^0_{cell} = +1.32\ V$

$Sn|Sn^{2+}||Pt^{2+}|Pt$

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

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

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

$E^0_{cell} = -0.28\ V - (-0.744\ V)$

$E^0_{cell} = +0.46\ V$

$Cr|Cr^{3+}||Co^{2+}|Co$

3. $Hg^{2+}(aq) + 2e^- \rightarrow Hg(l)$

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

$Hg^{2+}(aq) + Cr(s) \rightarrow Hg(l) + Cr^{2+}(aq)$

$E^0_{cell} = +0.851\ V - (-0.913\ V)$

$E^0_{cell} = +1.764\ V$

$Cr|Cr^{2+}||Hg^{2+}|Hg$

4. Challenge Write the balanced equation for the cell reaction and calculate the standard cell potential for the reaction that occurs when these half-cells are connected. Describe the reaction using cell notation.

$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$

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

$4NO_3^-(aq) + 12OH^-(aq) + 16H^+(aq) \rightarrow 3O_2(g) + 4NO(g) + 14H_2O(l)$

$E^0_{cell} = +0.957\ V - (+0.401\ V)$

$E^0_{cell} = +0.556\ V$

$OH^-|O_2||NO_3^-|NO$

Calculate the cell potential to determine if each of the following balanced redox reactions is -spontaneous as written. Use Table 1 to help you determine the correct half-reactions.

5. $Sn(s) + Cu^{2+}(aq) \rightarrow Sn^{2+}(aq) + Cu(s)$

$E^0_{cell} = +0.3419\ V - (-0.1375\ V)$

$E^0_{cell} = +0.4794\ V$

$E^0_{cell} > 0$; spontaneous

6. $Mg(s) + Pb^{2+}(aq) \rightarrow Pb(s) + Mg^{2+}(aq)$

$E^0_{cell} = -0.1262\ V - (-2.372\ V)$

$E^0_{cell} = +2.246\ V$

$E^0_{cell} > 0$; spontaneous

7. $2Mn^{2+}(aq) + 8H_2O(l) + 10Hg^{2+}(aq) \rightarrow 2MnO_4^-(aq) + 16H^+(aq) + 5Hg_2^{2+}(aq)$

$E^0_{cell} = 0.920\ V - (+1.507\ V)$

$E^0_{cell} = -0.587\ V$

$E^0_{cell} < 0$; not spontaneous

8. $2SO_4^{2-}(aq) + Co^{2+}(aq) \rightarrow Co(s) + S_2O_8^{2-}(aq)$

$E^0_{cell} = -0.28\ V - (+2.010\ V)$

$E^0_{cell} = -2.29\ V$

$E^0_{cell} < 0$; not spontaneous

9. Challenge Using **Table 1,** write the equation and determine the cell voltage (E^0) for the following cell. Is the reaction spontaneous?

$Al|Al^{3+}||Hg^{2+}|Hg_2^{2+}$

$\mathbf{2Al(s) + 6Hg^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Hg_2^{2+}(aq)}$

$\mathbf{E^0_{cell} = 0.920\ V - (-1.662\ V) = +2.582\ V}$

The reaction is spontaneous.

Problem-Solving Strategy

Apply the Strategy

Determine for the spontaneous redox reaction that occurs between magnesium and nickel.

$\mathbf{Mg^{2+} + 2e^- \rightarrow Mg}$ $\mathbf{E^0 = -2.372\ V}$ **(Oxidation)**

$\mathbf{Ni^{2+} + 2e^- \rightarrow Ni}$ $\mathbf{E^0 = -0.257\ V}$ **(Reduction)**

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

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

Overall equation: $\mathbf{Mg + Ni^{2+} \rightarrow Mg^{2+} + Ni}$

$\mathbf{E^0_{cell} = -0.257\ V - (-2.372\ V) = +2.115\ V}$

Section 1 Review

10. Describe the conditions under which a redox reaction causes an electric current to flow through a wire.

An electrochemical cell in which an oxidation half-reaction and a reduction half-reaction are connected by a salt bridge and a conducting wire results in a flow of electrons (electric current) through the conducting wire.

11. Identify the components of a voltaic cell. Explain the role of each component in the operation of the cell.

A voltaic cell consists of an anode, a cathode, a salt bridge, and a connecting wire between the two electrodes. Oxidation takes place at the anode, reduction takes place at the cathode, the salt bridge allows movement of ions from one solution to the other, and the wire allows the passage of electrons from the anode to the cathode.

12. Write the balanced equation for the spontaneous reaction that occurs in a cell with these reduction half-reactions.

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

$\mathbf{2Ag^+ + Ni \rightarrow 2Ag + Ni^{2+}}$

b. $Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$ and $2H^+(aq) + 2e^- \rightarrow H_2(g)$

$\mathbf{Mg + 2H^+ \rightarrow Mg^{2+} + H_2}$

c. $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$ and $Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$

$\mathbf{2Fe^{3+}(aq) + 3Sn(s) \rightarrow 2Fe(s) + 3Sn^{2+}(aq)}$

d. $PbI_2(s) + 2e\ \mathbf{E^0_{cell}}\ ^- \rightarrow Pb(s) + 2I^-(aq)$ and $Pt^{2+}(aq) + 2e^- \rightarrow Pt(s)$

$\mathbf{Pb(s) + 2I^-(aq) + Pt^{2+}(aq) \rightarrow PbI_2(s) + Pt(s)}$

13. Determine the standard potential for electrochemical cells in which each equations represents the overall cell reaction. Identify the reactions as spontaneous or nonspontaneous as written.

a. $2Al^{3+}(aq) + 3Cu(s) \rightarrow 3Cu^{2+}(aq) + 2Al(s)$

$\mathbf{E^0_{cell} = -1.662\ V - (+0.3419\ V) = -2.004\ V}$

nonspontaneous

b. $Hg^{2+}(aq) + 2Cu^+(aq) \rightarrow 2Cu^{2+}(aq) + Hg(l)$

$\mathbf{E^0_{cell} = +0.851\ V - (+0.153\ V) = +0.698\ V}$

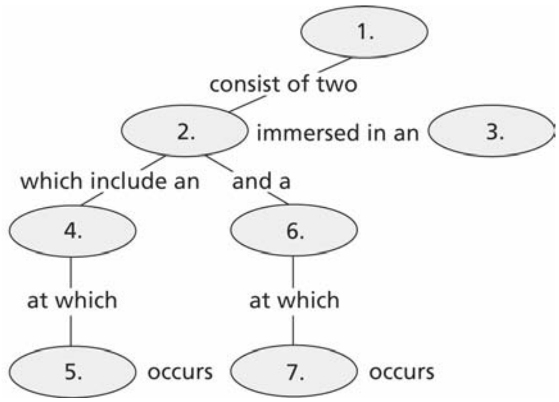
spontaneous

c. $Cd(s) + 2NO_3^-(aq) + 4H^+(aq) \rightarrow Cd^{2+}(aq) + 2NO_2(g) + 2H_2O(l)$

$\mathbf{E^0_{cell} = +0.775\ V - (-0.4030\ V) = +1.178\ V}$

spontaneous

14. **Design** a concept map for Section 1 starting with the word *electrochemical cell.* Incorporate all the new vocabulary words in your map.



Concept Maps should show that an electrochemical cell is a voltaic cell that consists of an anode and a cathode at which two half-cell reactions take place. Each half cell has a reduction potential that is measured against the standard hydrogen electrode. The half cells are connected by a conducting wire and a salt bridge.

Section 2 Batteries

Section 2 Review

15. **Identify** what is reduced and what is oxidized in the zinc-carbon dry-cell battery. What features make the alkaline dry cell an improvement over the earlier type of dry-cell battery?

Zinc is oxidized; manganese(IV) oxide is reduced in the electrolytic paste. Alkaline cells use zinc in a powdered form, which provides more surface area for reaction, thus more power in the package. Alkaline cells also eliminate the inactive carbon rod cathode.

16. **Explain** what happens when a battery is recharged.

A power source added to the system forces the cell to operate in the nonspontaneous direction. The original materials of the cell, which had become depleted, are restored.

17. **Describe** the half-reactions that occur in a hydrogen fuel cell and write the equation for the overall reaction.

At the anode, hydrogen gas is oxidized, in the presence of hydroxide ions, to water molecules. At the cathode, oxygen, in the presence of water molecules, is reduced to hydroxide ions. The overall reaction is $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$**.**

18. **Describe** the function of a sacrificial anode. How is the function of a sacrificial anode similar to galvanization?

A sacrificial anode has a lower reduction potential than the metal it is used to preserve. The sacrificial anode preferentially corrodes leaving the other metal untouched. Galvanization functions in the same way when the galvanized layer of zinc cracks or breaks. The zinc preferentially corrodes, leaving the metal underneath free of corrosion.

19. **Explain** why lithium is a good choice for the anode of a battery.

Lithium is light and has the lowest reduction potential of all the metals. When paired with the same reduction half-reaction, it produces more voltage than would a zinc half-cell.

20. **Calculate** Use data from **Table 1** to calculate the cell potential of the hydrogen-oxygen fuel cell.

$4H_2O(l) + 4e^- \rightarrow 2H_2(g) + 4OH^-(aq)$

$E^0 = -0.8277$ V

$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

$E^0 = +0.401$ V

$E^0_{cell} = +0.401 \text{ V} - (-0.8277 \text{ V}) = 1.229 \text{ V}$

21. **Design an Experiment** Use your knowledge of acids to devise a method for determining whether a lead-acid battery can deliver full charge or is beginning to run down.

A sample of the sulfuric acid electrolyte from the battery could be titrated with base and its molarity compared with the molarity of a sample of electrolyte taken from a new battery.

Section 3 Electrolysis

Section 3 Review

22. Define electrolysis and relate the definition to the spontaneity of redox reactions.

Electrolysis is the process of using electrical energy to produce a chemical reaction. The chemical reactions in an electrolytic process are not spontaneous.

23. Explain why the products of the electrolysis of brine and the electrolysis of molten sodium chloride are different.

brine: hydrogen gas, chlorine gas, and sodium hydroxide; molten NaCl: sodium metal and chlorine gas. Electrolysis of brine involves an aqueous solution, which affects the products.

24. Describe how impure copper obtained from the smelting of ore is purified by electrolysis.

Electrolysis of the product of copper smelting involves copper atoms being oxidized to Cu^{2+}, which are subsequently reduced to pure Cu atoms, with the impurities falling away.

25. Explain, by referring to the Hall-Héroult process, why recycling aluminum is very important.

The Hall-Héroult process requires high temperatures and a large amount of electricity to separate aluminum from its ore. Recyling requires only the heat needed to melt the metal.

26. Describe the anode and cathode of an electrolytic cell in which gold is to be plated on an object.

The anode is a bar of gold; the cathode is the object to be plated.

27. Explain why producing a kilogram of silver from its ions by electrolysis requires much less electric energy than producing a kilogram of aluminum from its ions.

First, a kilogram of silver contains many fewer atoms than a kilogram of aluminum because silver has a larger molar mass. Second, silver is easier to reduce. The reduction potential for silver is +0.7996 V. whereas the reduction potential for aluminum is –1.662 V.

28. Calculate Use **Table 1** to calculate the voltage of the Down's cell. Should the potential be positive or negative?

The Down's cell is a nonspontaneous reaction, so the potential should be negative.

Oxidation: $2Cl^- \rightarrow Cl_2 + 2e^-$ $E^0 = +1.35827$ V

Reduction: $Na^+ + e^- \rightarrow Na$ $E^0 = -2.71$ V

$E^0_{cell} = -2.71\text{ V} - (+1.35827\text{ V}) = -4.07\text{ V}$

29. Summarize Write a short paragraph summarizing each of the three objectives for Section 3 in your own words.

Student paragraphs should summarize the important ideas in the section. The paragraph for the first objective should state that spontaneous reactions in electrochemical cells can be reversed by applying an outside electric potential. For the second objective, students should show that in both processes, the reduction of Na^+ and the oxidation of Cl^- take place at the cathode and anode respectively. However, in the electrolysis of brine, other competing reactions also take place. At the cathode, water is reduced to H_2 and OH^-. At the anode, water is oxidized to H^+ and O_2. For the third objective, students should note that electrolysis is a means of separating metals from their ores and purifying them.

ChemLab

Analyze and Conclude

1. **Apply** In the data table, write the equations for the half-reactions occurring at the anode and cathode in each of the voltaic cells. Find the half-reaction potentials in **Table 1** and record them in the table.

   $\mathbf{Al \rightarrow Al^{3+} + 3e^{-}(-1.662\ V)}$
   $\mathbf{Cu^{2+} + 2e^{-} \rightarrow Cu(+0.3419\ V)}$

   $\mathbf{Al \rightarrow Al^{3+} + 3e^{-}(-1.662\ V)}$
   $\mathbf{Zn^{2+} + 2e \rightarrow Zn(-0.7618\ V)}$

   $\mathbf{Mg \rightarrow Mg^{2+} + 2e^{-}(-2.372\ V)}$
   $\mathbf{Al^{3+} + 3e^{-} \rightarrow Al(-1.662\ V)}$

   $\mathbf{Zn \rightarrow Zn^{2+} + 2e^{-}(-0.7618\ V)}$
   $\mathbf{Cu^{2+} + 2e^{-} \rightarrow Cu(+0.3419\ V)}$

   $\mathbf{Mg \rightarrow Mg^{2+} + 2e^{-}(-2.372\ V)}$
   $\mathbf{Cu^{2+} + 2e^{-} \rightarrow Cu(+0.3419\ V)}$

   $\mathbf{Mg \rightarrow Mg^{2+} + 2e^{-}(-2.372\ V)}$
   $\mathbf{Zn^{2+} + 2e^{-} \rightarrow Zn(-0.7618\ V)}$

2. **Calculate** and record the theoretical potential for each voltaic cell.

   Al/Cu
   $E^0_{cell} = +0.3419\ V - (-1.662\ V) = +2.004\ V$

   Al/Zn
   $E^0_{cell} = -0.7618\ V - (-1.662\ V) = +0.900\ V$

   Mg/Al
   $E^0_{cell} = -1.662\ V - (-2.372\ V) = +0.710\ V$

   Zn/Cu
   $E^0_{cell} = +0.3419\ V - (-0.7618\ V) = +1.104\ V$

   Mg/Cu
   $E^0_{cell} = +0.3419\ V - (-2.372\ V) = +2.714\ V$

   Mg/Zn
   $E^0_{cell} = -0.7618\ V - (-2.372\ V) = +1.610\ V$

3. **Predict** Using your data, rank the metals in order of most active to least active.

   Mg, Al, Zn, Cu

4. **Error Analysis** Calculate the percent error of the voltaic cell potential. Why is the percent error large for some voltaic cells and small for others?

   It is hard to get ideal conditions for each cell; some cells will get better results than others.

Chapter 20 Assessment

Section 1

Mastering Concepts

30. What feature of an oxidation–reduction reaction allows it to be used to generate an electric current?

    the transfer of electrons between reactants

31. Describe the process that releases electrons in a zinc–copper voltaic cell.

    oxidation of Zn(s) to Zn^{2+} releasing 2 electrons

32. What is the function of a salt bridge in a voltaic cell?

    The salt bridge completes the electrical circuit and prevents the accumulation of positive or negative charge in the half-cells.

33. What information do you need in order to determine the standard voltage of a voltaic cell?

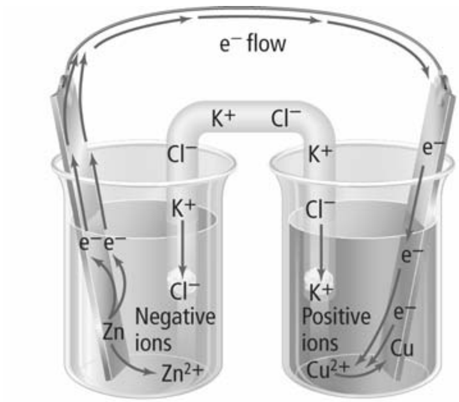
    standard reduction potentials for each half-reaction

34. In a voltaic cell represented by $Al|Al^{3+}||Cu^{2+}|Cu$, what is oxidized and what is reduced as the cell delivers current?

    Al is oxidized and Cu^{2+} is reduced.

35. Under what conditions are standard reduction potentials measured?

25°C, 1 atm, 1*M* ion solution



36. In **Figure 24,** identify the metal that is being oxidized. Identify the cathode.

Zinc is being oxidized; copper is the cathode

37. A salt bridge is filled with KNO_3. Explain why it is necessary that the potassium ions move through the salt bridge to the cathode.

The movement of the ions in the salt bridge allows the current to flow even though reactants are not in direct contact. Ions carry the electric current and prevent the build up of positive change at the anode and negative charge at the cathode.

38. Recall that a reducing agent is the substance being oxidized and an oxidizing agent is the substance being reduced. Use **Table 1** to select an oxidizing agent that will convert Au to Au^{3+} but will not convert Co^{2+} to Co^{3+}.

MnO_4^-, Au^+, H_2O_2

Mastering Problems

39. Using **Table 1,** write the standard cell notation for each cell in which each of the following half-cells is connected to the standard hydrogen electrode.

a. $Zn^{2+}|Zn$

$\mathbf{Zn|Zn^{2+}||H^+|H_2}$

b. $Hg^{2+}|Hg$

$\mathbf{H_2|H^+||Hg^{2+}|Hg}$

c. $Cu^{2+}|Cu$

$\mathbf{H_2|H^+||Cu^{2+}|Cu}$

d. $Al^{3+}|Al$

$\mathbf{Al|Al^{3+}||H^+|H_2}$

40. Write the balanced chemical equation for the standard cell notations listed below.

a. $I^-|I_2||Fe^{3+}|Fe^{2+}$

$\mathbf{2I^- + 2Fe^{3+} \rightarrow I_2 + 2Fe^{2+}}$

b. $Sn|Sn^{2+}||Ag^+|Ag$

$\mathbf{Sn + 2Ag^+ \rightarrow Sn^{2+} + 2Ag}$

c. $Zn|Zn^{2+}||Cd^{2+}|Cd$

$\mathbf{Zn + Cd^{2+} \rightarrow Zn^{2+} + Cd}$

41. Calculate the cell potentials for the following reactions.

a. $2Ag^+(aq) + Pb(s) \rightarrow Pb^{2+}(aq) + 2Ag(s)$

$\mathbf{Ag^+ + e^- \rightarrow Ag}$ **(reduced)** $\mathbf{E^0 = +0.7996\ V}$

$\mathbf{Pb \rightarrow Pb^{2+} + 2e^-}$ **(oxidized)** $\mathbf{E^0\ -0.1262\ V}$

$\mathbf{E^0_{cell} = +0.7996 - (-0.1262) = +0.9258\ V}$

b. $Mn(s) + Ni^{2+}(aq) \rightarrow Mn^{2+}(aq) + Ni(s)$

$\mathbf{Mn \rightarrow Mn^{2+} + 2e^-}$ **(oxidized)** $\mathbf{E^0 = -1.185}$

$\mathbf{Ni^{2+} + 2e^- \rightarrow Ni}$ **(reduced)** $\mathbf{E^0 = -0.257}$

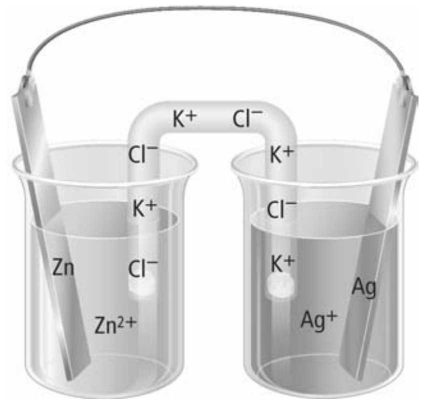
$\mathbf{E^0_{cell} = -0.257 - (-1.185) = +0.928\ V}$

c. $I_2(aq) + Sn(s) \rightarrow 2I^-(aq) + Sn^{2+}(aq)$

$I_2 + 2e^- \rightarrow 2I^-$(reduced) $E^0 = +0.5355$ V

$Sn \rightarrow Sn^{2+} + 2e^-$(oxidized) $E^0 = -0.1375$ V

$E^0_{cell} = +0.5355 \text{ V} - (-0.1375) = +0.673$ V



42. Figure 25 illustrates a voltaic cell consisting of a strip of zinc in a 1.0*M* solution of zinc nitrate and a strip of silver in a 1.0*M* solution of silver nitrate. Use the diagram and **Table 1** to answer these questions.

a. Identify the anode.

The anode is zinc.

b. Identify the cathode.

The cathode is silver.

c. Where does oxidation occur?

Oxidation occurs at the zinc electrode

d. Where does reduction occur?

Reduction occurs at the silver electrode.

e. In which direction is the current flowing through the connecting wire?

The current flows from the zinc electrode to the silver electrode.

f. In which direction are positive ions flowing through the salt bridge?

Positive ions flow from the anode half-cell to the cathode half-cell.

g. What is the cell potential?

$E^0 = +0.7996 \text{ V} - (-0.7618 \text{ V}) = +1.5614$ V

Section 2

Mastering Concepts

43. What part of a zinc–carbon dry cell is the anode? Describe the reaction that takes place there.

The anode is the zinc shell. Oxidation of Zn atoms to Zn^{2+} ions takes place.

44. How do primary and secondary batteries differ?

Primary batteries are “throw away”; the reaction is not easily reversed. Secondary batteries are rechargeable; the redox reaction is reversible.

45. Lead-Acid Battery What substance is reduced in a lead-acid storage battery? What substance is oxidized? What substances are produced in each reaction?

PbO_2(s) reduced; Pb(s) oxidized; $PbSO_4$(s) and water are produced.

46. Biofuel Cell At the cathode of a biofuel cell, Fe^{3+} in potassium hexacyanoferrate(III) ($K_3[Fe(CN)_6]$) is reduced to Fe^{2+} in potassium hexacyanoferrate (II) ($K_4[Fe(CN)_6]$). At the anode, reduced nicotinamide-adenine-dinucleotide (NADH) is oxidized to NAD^+. Use the following standard reduction potential to determine the potential of the cell.

$NAD^+ + H^+ + 2e^- \rightarrow NADH$
$E^0 = -0.320$ V

$[Fe(CN)_6]^{3-} + 1e^- \rightarrow [Fe(CN)_6]^{4-}$
$E^0 = +0.36$ V

$E^0_{cell} = +0.36 \text{ V} - (-0.320 \text{ V}) = +0.68$ V

47. Fuel Cells List two ways in which a fuel cell differs from an ordinary battery.

In a fuel cell, the oxidation of a fuel is used to produce electricity. Batteries must be recharged or replaced. Current can be produced and sustained in a fuel cell as long as a fuel source is present.

48. Galvanization What is galvanization? How does galvanizing iron protect it from corrosion?

Galvanization is the coating of corrosion-susceptible metals with self-protecting metals to prevent corrosion. Galvanization preserves the metal underneath by preventing air and moisture from coming in contact with it. When the galvanic coating breaks, it still protects the metal by acting as a sacrificial anode, becoming oxidized instead of the metal.

49. Batteries Explain why a lead storage battery does not produce a current when the level of H_2SO_4 is low.

Sulfuric acid participates in the reaction. When the concentration is low, the reaction cannot take place.

50. Steel wool is a bundle of filaments made of steel, an alloy of iron and carbon. Which would be the best way to store steel wool?

a. Store it in water.

b. Store it in open air.

c. Store it with a desiccant.

c. Water is a reactant in the rusting process. Desiccants absorb water from the air.

51. Corrosion Protection List three ways metals are protected from corrosion.

galvanizing, painting, sacrificial anodes

Mastering Problems

52. The half-reactions for the lead-acid storage battery are as follows.

$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l) \quad E^0 = +1.685\ V$

$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq) \quad E^0 = -0.3588\ V$

What is the standard cell potential for a car battery?

Cell potential = (+1.685 V) − (−0.3588 V) = +2.044 V

53. The setup in **Figure 26** acts as a battery.

a. Determine the reaction that takes place at the copper strip.

Cu^{2++} ions are reduced.

$Cu^{2+} + 2e^- \rightarrow Cu^0$

b. Determine the reaction that takes place at the magnesium strip.

The magnesium is oxidized.

$Mg^0 \rightarrow Mg^{2+} + 2e^-$

c. Identify the anode.

the magnesium wire

d. Identify the cathode.

the copper strip

e. Calculate the standard cell potential for this battery.

$E^0_{cell} = 0.3419\ V - (-2.372\ V) = +2.714\ V$

54. You design a battery that uses a half-cell containing Sn and Sn^{2+} and another half-cell containing Cu and Cu^{2+}. The copper electrode is the cathode, and the tin electrode is the anode. Draw the battery and write the half-reactions that occur in each half-cell. What is the maximum voltage this battery can produce?

Anode: $Sn^0 \rightarrow Sn^{2+} + 2e^-$

Cathode: $Cu^{2+} + 2e^- \rightarrow Cu^0$

Cell potential $= +0.3419$ V $- (-0.1375$ V$)$ $= +0.4794$ V

Section 3

Mastering Concepts

55. How can the spontaneous redox reaction of a voltaic cell be reversed?

by passing a current through it in the opposite direction

56. Where does oxidation take place in an electrolytic cell?

at the anode

57. Down's Cell What reaction takes place at the cathode when molten sodium chloride is electrolyzed?

Na^+ ions are reduced to Na atoms.

58. Industry Explain why the electrolysis of brine is done on a large scale at many sites around the world.

The electrolysis products of brine, hydrogen gas, chlorine gas, and sodium hydroxide, are important commercial products.

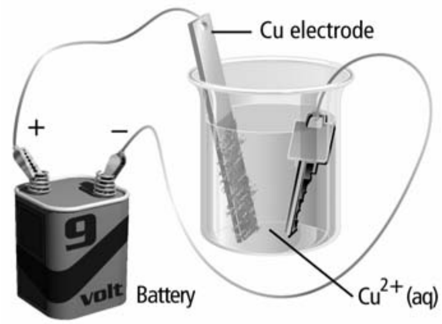
59. Recycling Explain how recycling aluminum conserves energy.

The aluminum in cans has already been separated from its ore, which is an energy-intensive process.

60. Describe what happens at the anode and the cathode in the electrolysis of KI(aq).

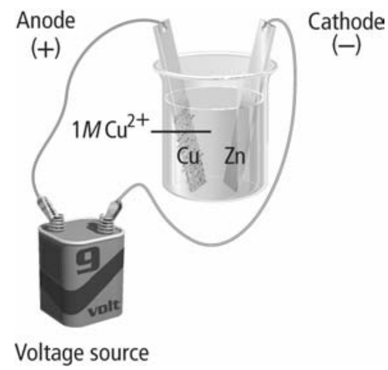
At the cathode, potassium ions are reduced to atoms of potassium; at the anode, iodide ions are oxidized to molecules of I_2.

Mastering Problems



61. Electroplating Figure 27 shows a key being electroplated with copper in an electrolytic cell. Where does oxidation occur? Explain your answer.

Oxidation occurs at the anode, which is the Cu electrode. Electrons move from it to the positive pole of the battery.



62. Answer the following questions based on **Figure 28.**

a. Which electrode grows? Write the reaction at this electrode.

The zinc electrode grows; $Cu^{2+} + 2e^- \rightarrow Cu$

b. Which electrode disappears? Write the reaction at this electrode.

The copper electrode disappears; $Cu \rightarrow Cu^{2+} + 2e^-$

63. Using **Figure 28,** explain what happens to the copper ions in solution.

The copper ions migrate to the cathode and plate out on it.

Mixed Review

64. Why do electrons flow from one electrode to the other in a voltaic cell?

In a voltaic cell, ions in solution at the cathode accept electrons more readily than the ions at the anode. When a salt bridge and wire are in place, redox occurs spontaneously and electrons flow from the anode to the cathode because there is a potential difference between the two electrodes.

65. Aluminum Production What substance is electrolyzed in the industrial process to produce aluminum metal?

oxide, O^{2-}

66. Write the oxidation and reduction half-reactions for a silver-chromium voltaic cell. Identify the anode, cathode, and electron flow.

oxidation: $Cr(s) \rightarrow Cr^{3+}(aq) + 3e^-$

reduction: $Ag^+(aq) + e^- \rightarrow Ag(s)$

Electrons flow from anode (Cr) to cathode (Ag).

67. Determine whether each of the following redox reactions is spontaneous or nonspontaneous as written.

a. $Mn^{2+}(aq) + 2Br^-(aq) \rightarrow Br_2(l) + Mn(s)$

$E^0_{cell} = -1.185\text{ V} - 1.066\text{ V} = -2.251\text{ V}$

nonspontaneous

b. $2Fe^{2+}(aq) + Sn^{2+}(aq) \rightarrow 2Fe^{3+}(aq) + Sn(s)$

$E^0_{cell} = -0.1375\text{ V} - 0.771\text{ V} = -0.908\text{ V}$

nonspontaneous

c. $Ni^{2+}(aq) + Mg(s) \rightarrow Mg^{2+}(aq) + Ni(s)$

$E^0_{cell} = -0.257\text{ V} - (-2.372\text{ V}) = +2.115\text{ V}$

spontaneous

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

$E^0_{cell} = -0.1262\text{ V} - 0.153\text{ V} = -0.279\text{ V}$

nonspontaneous

68. Determine the voltage of the cell in which each of the following half-cells is connected to a $Ag^+|Ag$ half-cell.

a. $Be^{2+}|Be$

$E^0_{cell} = +0.7996\text{ V} - (-1.847\text{ V}) = +2.647\text{ V}$

b. $S|S^{2-}$

$E^0_{cell} = +0.7996\text{ V} - (-0.47627\text{ V}) = +1.2759\text{ V}$

c. $Au^+|Au$

$E^0_{cell} = 1.692\text{ V} - (+0.7996\text{ V}) = +0.892\text{ V}$

d. $I_2|I^-$

$E^0_{cell} = +0.7996\text{ V} - (+0.5355\text{ V}) = +0.2641\text{ V}$

69. Corrosion Explain why water is necessary for the corrosion of iron.

Fe atoms oxidize to aqueous Fe^{2+} ions. then, part of the rust-forming process involves Fe^{2+} ions dispersing through water and reacting with O_2.

70. Space Travel The space shuttle uses a H_2/O_2 fuel cell to produce electricity.

a. What is the reaction at the anode? At the cathode?

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

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

b. What is the standard cell potential for the fuel cell?

Cell potential = +0.401 V – (–0.8277 V) = +1.229 V

71. Fuel Cells Explain how the oxidation of hydrogen in a fuel cell differs from the oxidation of hydrogen when it burns in air.

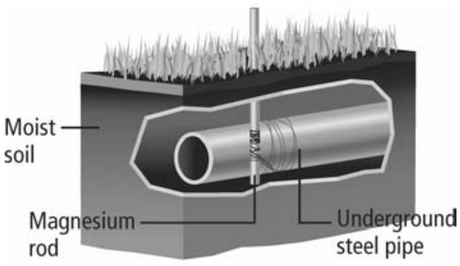
In a fuel cell, the oxidation of hydrogen is controlled so that most of the chemical energy is converted to electrical energy instead of heat.

72. **Copper Refining** In the electrolytic refining of copper, what factor determines which piece of copper is the anode and which is the cathode?

The direction that the current is directed through the cell determines that the impure copper will be the anode.

73. **Storage Batteries** Lead–acid batteries and other rechargeable batteries are sometimes called *storage batteries*. Precisely what is being stored in these batteries?

chemical potential energy



74. **Corrosion Prevention** **Figure 29** shows how buried steel pipeline can be protected against corrosion. The steel pipe is connected to a more active metal that corrodes instead of the steel.

a. What is the cathode? What is the anode?

cathode is steel; anode is Mg

b. Describe how the magnesium metal protects the steel.

Mg is more active and therefore more susceptible to redox. Thus, the magnesium corrodes before the steel.

Think Critically

75. **Predict** Suppose scientists had chosen the $Cu^{2+}|Cu$ half-cell as a standard instead of the $H^+|H_2$ half-cell? What would the potential of the hydrogen electrode be if the copper electrode were the standard? How would the relationships among the standard reduction potentials change?

Values in the standard reduction potential table would be reduced by 0.3419 V. Hydrogen electrode would be –0.3419 V. Relationships would not change but voltage values would change.

76. **Apply Concepts** Suppose that you have a voltaic cell in which one half-cell is made up of a strip of tin immersed in a solution of tin(II) ions.

a. How could you tell by measuring voltage whether the tin strip was acting as a cathode or an anode in the cell?

A voltmeter indicates the flow of electrons to or from the tin strip, which shows whether the strip acts as a cathode or an anode. If the voltage is positive, tin is being oxidized.

b. How could you tell by simple observation whether the tin strip was acting as a cathode or an anode?

A visible deposit at the cathode would indicate reduction of Sn^{2+}. As Sn is oxidized at the anode, the size of the strip would decrease. A decrease in strip size would indicate oxidation of Sn at the anode.

77. **Hypothesize** The potential of a half-cell varies with concentration of reactants and products. For this reason, standard potentials are measured at 1*M* concentration. Maintaining a pressure of 1 atm is especially important in half-cells that involve gases as reactants or products. Suggest a reason that gas pressure is especially critical in these cells.

Pressure is an indication of concentration; therefore, pressure is a concentration factor in half-cells involving gases.

78. Analyze An earthen vessel was discovered in 1938 near Baghdad. This ancient vessel contained an iron bar surrounded by a copper cylinder, as shown in **Figure 30.** When filled with an electrolyte such as vinegar, this vessel might have acted as a battery.

a. Identify the cathode.

the copper cylinder, $E^0 = +0.3419$ V

b. Identify the anode.

the iron bar, $E^0 = -0.447$ V

c. Calculate the standard cell potential of this battery.

$Cu^{2+} + 2e^- \rightarrow Cu$

$Fe^{2+} + 2e^- \rightarrow Fe$

Cell potential = +0.3419 V − (−0.447 V) = +0.789 V

79. Apply During electrolysis, an electrolytic cell gives off bromine vapor and hydrogen gas. After electrolysis, the cell is found to contain a concentrated solution of potassium hydroxide. What was the composition of the cell before electrolysis began?

potassium bromide and water

80. Hypothesize Suppose in galvanization, copper was plated on iron instead of zinc. Would copper continue to protect the iron from corrosion, as zinc does, if the copper coating became broken or cracked? Explain.

If the copper cracked, sites for corrosion would be exposed. No, iron is more readily oxidized than copper, so protection is diminished.

Challenge Problem

81. A battery is assembled using tin and mercury, which have the following reduction half-reactions:

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

$Hg^{2+}(aq) + 2e^- \rightarrow Hg(l)$

a. Write a balanced equation for the cell's reaction.

$Hg^{2+}(aq) + Sn(s) \rightarrow Hg(l) + Sn^{2+}(aq)$

b. What is oxidized and what is reduced? Identify the oxidizing agent and the reducing agent.

Mercury is reduced and tin is oxidized. The oxidizing agent is the mercury ions. The reducing agent is the tin electrode.

c. Which reaction occurs at the anode? At the cathode?

$Hg^{2+} + 2e^- \rightarrow Hg$ occurs at the cathode
$Sn \rightarrow Sn^{2+} + 2e^-$ occurs at the anode

d. What is the cell potential?

Cell potential = +0.851 V − (−0.1375 V) = +0.989 V

e. If sodium sulfate solution is in the salt bridge, in which direction do the sulfate ions move?

The sulfate ions move toward the tin half-cell.

Cumulative Review

82. If the volume of a sample of chlorine gas is 8.2 L at 1.2 atm and 306 K, what volume will the gas occupy at STP?

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$V_2 = \frac{P_1V_1T_2}{T_1P_2} = \frac{(1.2\ \cancel{atm})(8.2\ L)(273\ \cancel{K})}{(306\ \cancel{K})(1.0\ \cancel{atm})} = 8.8\ L$$

83. What is meant by solvation? Explain how this process is important for the dissolving of ionic salts in water.

Solvation is the process in which solute particles are surrounded by solvent particles to form a solution. Polar water molecules are attracted to either positive or negative ions in an ionic solid. This attraction is greater than the attraction of the ions for each other in the solid. Water molecules surround the ions and prevent them from recombining.

84. Explain how the molarity of a solution is different from its molality.

Molarity is the number of moles of solute in a liter of solution; molality is the moles of solute in a kilogram of solvent.

85. Define the calorie. State how the calorie is related to the Calorie and the joule.

The calorie is the amount of energy needed to raise the temperature of one gram of pure water by one degree Celsius. 1000 calories equals one Calorie. 1 calorie equals 4.184 J.

86. Explain why you would find an aluminum chair to be hotter to sit on than a wooden bench after each had been standing in the sunlight for the same amount of time.

The aluminum chair has a lower specific heat than wood.

87. What does a negative sign for the free energy of a reaction tell you about the reaction? ($\Delta G_{system} = \Delta H_{system} - T\Delta S_{system}$)

that the reaction is spontaneous as written

88. According to the collision model of chemical reactions, how is it possible that two molecules may collide but not react?

The molecules may not collide with the correct orientation, or the collision may lack the energy required to form the activated complex.

89. List five factors that can affect the rate of a reaction.

the nature of the reactants, temperature, concentration, surface area, and whether a catalyst is used

90. The decomposition reaction $A_2B \rightarrow 2A + B$ proceeds to equilibrium at 499°C. Analysis of the reaction mixture shows $[A_2B] = 0.855$ mol/L, $[A] = 2.045$ mol/L, and $[B] = 1.026$ mol/L. What is K_{eq}?

$$\mathbf{K_{eq} = \frac{[A]^2[B]}{[A_2B]} = \frac{(2.045)^2(1.026)}{(0.855)} = 5.02\ mol^2/L^2}$$

91. What is the solubility in mol/L of silver iodide, AgI. K_{sp} for AgI is 3.5×10^{-17}.

$\mathbf{s = [Ag^+] = [I^-];\ K_{sp} = [Ag^+][I^-] = 3.5 \times 10^{-17}}$

$\mathbf{s^2 = 3.5 \times 10^{-17};\ s = 5.9 \times 10^{-9}\ mol/L}$

92. If you have a solution of a strong acid, is that the same as having a concentrated solution of the acid? Explain your answer.

Not necessarily. A strong acid is one that ionizes completely in aqueous solution. A solution of a strong acid can be either concentrated or dilute. Whether it is concentrated or dilute depends upon the number of moles of acid in the solution.

93. What are the oxidation numbers for the elements in the ion PO_4^{3-}?

Each oxygen is –2 for a total of –8 for the oxygen atoms. To balance, phosphorus must be (+8) + (–3) = +5

Additional Assessment

Writing in Chemistry

94. Sunken Ships Study of the sunken ocean liner *Titanic* has opened the possibility that deterioration of the steel hull might be partly due to the biological activity of rusticle communities. Research how the biological activity of rusticle communities results in the oxidation of iron. Write an essay that describes the role of rusticle communities in the destruction of the *Titanic*.

Student papers might state that rusticles are biological communities that consist of up to 35% iron compounds. They are often found under water on wrought iron and use the iron as food. Their excretions form an inorganic structure that binds the microbial community together. Because rusticles form on iron surfaces such as the hull of the Titanic, it is likely that they are an important factor in the deterioration of Titanic's steel hull factor in the rusting process.

95. Statue of Liberty Several years ago, the supporting structure of the Statue of Liberty became so corroded that it had to be replaced entirely. Find out what the structure was and why it corroded so badly. Write a report that explains the chemical processes involved and include a timeline of the statue, starting in France before 1886.

The most critical corrosion resulted from a naturally occurring electrochemical cell involving the iron inner structure that supports the outer copper skin. The electrolyte in the system was salt water, which was readily available considering the statue's proximity to the Atlantic Ocean. Students should mention that because the iron inner structure was all interconnected, once begun, corrosion proceeded to affect the entire statue. As part of the restoration, the iron structure and the connecting rivets and hardware were replaced with stainless steel components. Student timelines should include the following important information. Frédéric-Auguste Bartholdi completes the statue design, inner structure designed by Alexandre-Gustave Eiffel; (October, 1881) statue assembly begins in France; (1885) Statue disassembled in France and shipped to U.S.; (October 28, 1886) Completed statue unveiled and dedicated in New York; (1901) First round of maintenance and repairs to the statue and island; (1903) Bronze tablet engraved with the poem The New Colossus attached; (October 15, 1924) Statue declared a national monument; (1984) Extensive restoration begins; (October 28, 1986) Centennial celebration.

Document-Based Questions

Electrochemical Biological Reactions *Standard reduction potentials for some important biological reactions are given in Table 2. The strongest oxidizing agent generally available in biological systems is molecular oxygen. Consider the oxidation of reduced nicotinamide-adenine-dinucleotide (NADH) by molecular oxygen. The reaction is the following:* $2NADH + 2H^+ + O_2 \rightarrow 2NAD^+ + 2H_2O$.

Data obtained from: Fromm. James Richard. 1997. Biochemical Electrochemistry.

Aqueous Standard Reduction Potentials at 25°C and pH 7.00	
Electrode Couple	**E^0(V)**
$2H^+ + 2e^- \rightarrow H_2(g)$	–0.4141
$NAD^+ + H^+ + 2e^- \rightarrow NADH$	–0.320
$HOOCCOCH_3{}^* + 2H^+ + 2e^- \rightarrow HOOCCHOHCH_3{}^{**}$	+0.19
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.769
$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O$	+0.8147

*$HOOCCOCH_3$ is pyruvic acid

**$HOOCCHOHCH_3$ is l-lactic acid

96. Write the two half-reactions that take place in this reaction.

$\mathbf{NADH \rightarrow NAD^+ + 2e^- + H^+}$

$\mathbf{O_2 + 4H^+ + 4e^- \rightarrow 2H_2O}$

97. Calculate the cell potential of this reaction using **Table 2.**

cell potential = +0.814 V – (–0.320 V) = +1.135 V

98. Will NAD^+ oxidize Fe^{2+} to Fe^{3+}? Explain your answer.

No, the NAD^+ has a reduction potential of –0.320 V.

The cell potential = –0.320 V – (+0.771 V) = –1.091 V, a nonspontaneous reaction.

Standardized Test Practice

Multiple Choice

Use the table below to answer Questions 1 to 4.

Selected Standard Reduction Potentials at 25°C, 1 atm and 1M Ion Concentration	
Half-Reaction	**E^0(V)**
$Mg^{2+} + 2e^- \rightarrow Mg$	–2.372
$Al^{3-} + 3e^- \rightarrow Al$	–1.662
$Pb^{2+} + 2e^- \rightarrow Pb$	–0.1262
$Ag^+ + e^- \rightarrow Ag$	0.7996
$Hg^{2+} + 2e^- \rightarrow Hg$	0.851

1. Which metal ion is most easily reduced?

a. Mg^{2+}
(b.) Hg^{2+}
c. Ag^+
d. Al^{3+}

2. On the basis of the standard reduction potentials shown above, which standard cell notation correctly represents its voltaic cell?

a. $Ag|Ag^+||Al^{3+}|A1$
(b.) $Mg|Mg^{2+}||H^+|H_2$
c. $H_2|H^+||Pb^{2+}|Pb$
d. $Pb|Pb^{2+}||Al^{3+}|Al$

3. A voltaic cell consists of a magnesium bar dipping into a 1*M* Mg^{2+} solution and a silver bar dipping into a 1*M* Ag^+ solution. What is the standard potential of this cell?

a. 1.572 V
(b.) 3.172 V
c. 0.773 V
d. 3.971 V

4. Assuming standard conditions, which cell will produce a potential of 2.513 V?

(a.) $Al|Al^{3+}||Hg^{2+}|Hg$
b. $H_2|H^+||Hg^{2+}|Hg$
c. $Mg|Mg^{2+}||Al^{3+}|Al$
d. $Pb|Pb^{2+}||Ag|Ag^+$

$Al|Al^{3+}||Hg^{2+}|Hg$ **(+0.851 V – (–1.662 V) = +2.513 V)**

$H_2|H^+||Hg^{2+}|Hg$ **(+0.851 V –0 V = –0.851 V)**

$Mg|Mg^{2+}||Al^{3+}|Al$ **(–1.662 V –. (–2.372 V) = +0.710 V)**

$Pb|Pb^{2+}||Ag|Ag^+$ = **(+0.7996 V – (–0.1262 V) +0.9258 V)**

5. Which statement is NOT true of batteries?

a. Batteries are compact forms of voltaic cells.
b. Secondary batteries are storage batteries.
c. A battery can consist of a single cell.
(d.) The redox reaction in a rechargeable battery is not reversible.

6. Which is NOT a characteristic of a basic solution?

a. tastes bitter
b. conducts electricity
(c.) contains more H^+ ions than OH^- ions
d. feels slippery

7. A carbonated soft drink has a pH of 2.5. What is the concentration of H+ ions in the soft drink?

a. $3 \times 10^{-12} M$
(b.) $3 \times 10^{-3} M$
c. $4 \times 10^{-1} M$
d. $1 \times 10^{1} M$

Solution:

$pH = -\log [H^+]$

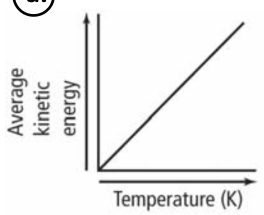
$-pH = \log [H^+]$

$\text{antilog}(-pH) = [H^+]$

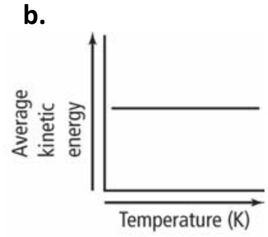
$\text{antilog}(-2.5) = [H^+] = 3 \times 10^{-3} M$

8. Which graph correctly shows the relationship between average kinetic energy of particles and the temperature of a sample?

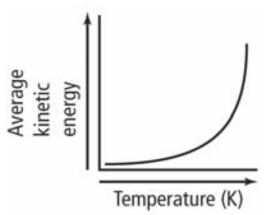
(a.)



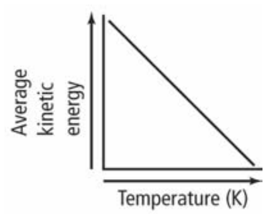
b.



c.



d.



Short Answer

Use the description below to answer Questions 9 to 11.

In an experimental setup, chlorine gas and nitrogen gas are in separate containers separated by a closed stopcock. One hour after the stopcock is opened, the gases have completely mixed.

9. Five minutes after the stopcock is opened, which gas will have traveled farther, the nitrogen or the chlorine?

The nitrogen will have traveled farther because it is made of smaller, lighter particles.

10. Give the ratio of the speed of nitrogen gas to the speed of chlorine gas.

$$\textbf{Rate of } N_2 \textbf{ compared to } Cl_2 = \sqrt{\frac{\textbf{molar mass } Cl_2}{\textbf{molar mass } N_2}}$$

$= \sqrt{\frac{70.906}{28.014}} = 1.59$**; nitrogen diffuses 1.59 times as fast as chlorine.**

11. Evaluate this statement: After one hour, the gas particles stop moving because they have completely mixed.

This is not a correct statement. At equilibrium, the rates of the forward and backward processes remain constant, but they still occur.

Extended Response

Use the table below to answer Question 12.

Standard Reduction Potentials at 25°C, 1 atm, and 1M Solution	
$Ag^{+} + e^{-} \rightarrow Ag$	0.7996
$Cr^{3+} + 3e^{-} \rightarrow Cr$	–0.744

12. Based on the standard reduction potentials given above, if a silver electrode and a chromium electrode are connected in a voltaic cell, which electrode will undergo oxidation and which will undergo reduction? Explain how you can tell.

The reaction for silver has a more positive standard reduction potential, while chromium has a more negative standard reduction potential. Of any two electrodes, the one with the lower standard reduction potential will operate in the reverse direction as shown in the table; in this case, it is the chromium. Since it would now be losing electrons, it will be oxidized. The electrode with the more positive standard reduction potential will be reduced; in this case, it will be the silver electrode.

13. Use Le Châtelier's principle to explain why the instructions for a chemical experiment sometimes instruct the chemist to cool the reaction in an ice bath.

If the forward reaction is exothermic, lowering the temperature will shift the equilibrium to the right. This will, in turn, favor the forward reaction. Cooling the reaction will in this case cause more product to be formed.

SAT Subject Test: Chemistry

14. The hydrogen sulfide produced as a by-product of petroleum refinement can be used to produce elemental sulfur: $2H_2S(g) + SO_2(g) \rightarrow 3S(l) + 2H_2O(g)$. What is the equilibrium constant expression for this reaction?

a. $K_{eq} = \dfrac{[H_2O]}{[H_2S][SO_2]}$

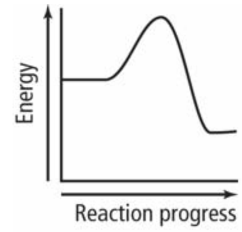
b. $K_{eq} = \dfrac{[H_2S]^2[SO_2]}{[H_2O]^2}$

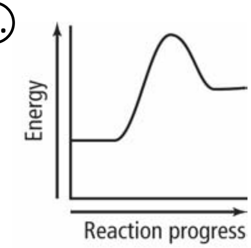
(c.) $K_{eq} = \dfrac{[H_2O]^2}{[H_2S]^2[SO_2]}$

d. $K_{eq} = \dfrac{[S]^3[H_2O]^2}{[H_2S]^2[SO_2]}$

e. $K_{eq} = \dfrac{[2H_2O]^2}{[2H_2S]^2[SO_2]}$

15. Which shows the correct graph of the activation energy needed for an endothermic reaction?

a.


(b.)


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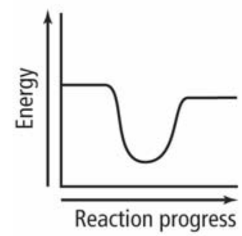

d.