Electrolyte Solutions:

oxidation/reduction

Lose e- = oxidation (LEO)

Gain e- = reduction (GER)

Ex: $Cu^{0} + Ag^{+1}NO_3 \rightarrow Ag^{0} + Cu^{+2}(NO_3)_2$

$Ag^{+1} \rightarrow Ag^{0}$ reduced ~ gained e-

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

$NaCl_{(aq)} \rightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}$

Na^{+} ↑ can accept e-

Cl^{-} ← can lose e-

$Na^{+} + e- \rightarrow Na$

Gain e- = Cathode
reduction

$Cl^{-} \rightarrow Cl_2 + e-$

lose e- = Anode
oxidation

How an electrolyte soln. sustains a current

Modern Chem, 2017

FIGURE 1.2

Oxidation States of Chromium Compounds Chromium provides a very visual example of oxidation numbers. Different oxidation states of chromium have dramatically different colors. Solutions with the same oxidation state show less dramatic differences.

CRITICAL THINKING

Relate Examine the tables of ions and their oxidation numbers, **Figures 1.1** and **1.3**, in the chapter "Chemical Formulas and Chemical Compounds." Compare the elements that have multiple ions or oxidation states with the placement of those elements on the periodic table. What relationship is there between the ability to form multiple ions and where those elements are generally found on the periodic table?

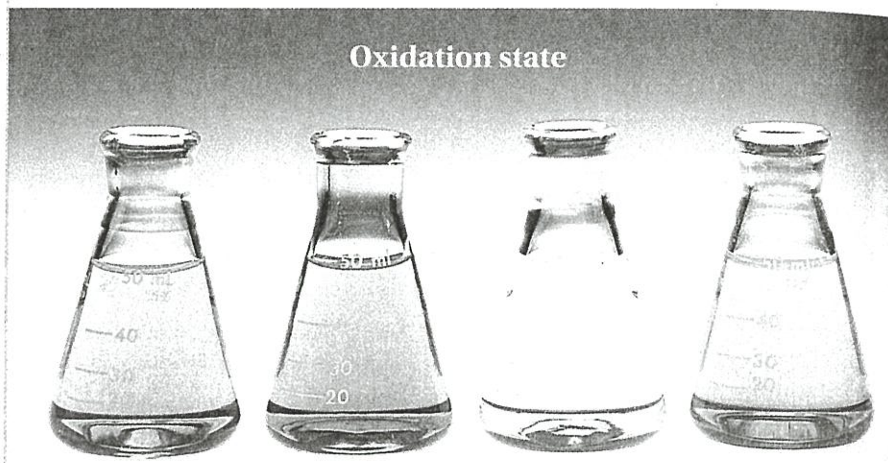
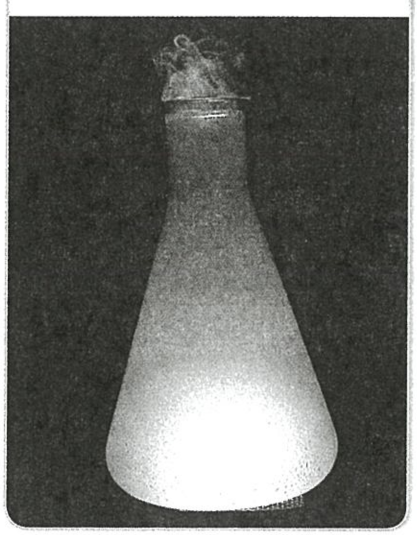


FIGURE 1.3

Oxidation in NaCl Synthesis

Sodium and chlorine react violently to form NaCl. The synthesis of NaCl from its elements illustrates the oxidation-reduction process.



MAIN IDEA

Oxidation occurs when valence electrons are lost.

Processes in which the atoms or ions of an element experience an increase in oxidation state are oxidation processes. The combustion of metallic sodium in an atmosphere of chlorine gas is shown in **Figure 1.3.** The sodium ions and chloride ions produced during this strongly exothermic reaction form a cubic crystal lattice in which sodium cations form ionic bonds to chloride anions. The chemical equation for this reaction is written as follows.

$$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$$

The formation of sodium ions illustrates an oxidation process because each sodium atom loses an electron to become a sodium ion. The oxidation state is represented by placing an oxidation number above the symbol of the atom and the ion.

$$\overset{0}{Na} \longrightarrow \overset{+1}{Na^+} + e^-$$

The oxidation state of sodium has changed from 0 to the +1 state of the ion (Rules 1 and 7, **Figure 1.1**). **A species whose oxidation number increases is oxidized.** The sodium atom is *oxidized* to a sodium ion.

MAIN IDEA

Reduction occurs when valence electrons are gained.

Processes in which the oxidation state of an element decreases are reduction processes. Consider the behavior of chlorine in its reaction with sodium. Each chlorine atom accepts an electron and becomes a chloride ion. The oxidation state of chlorine decreases from 0 to −1 for the chloride ion (Rules 1 and 2, **Figure 1.1**).

$$\overset{0}{Cl_2} + 2e^- \longrightarrow 2\overset{-1}{Cl^-}$$

A species that undergoes a decrease in oxidation state is reduced. The chlorine atom is reduced to the chloride ion.

MAIN IDEA

Oxidation and reduction are paired reactions.

Electrons are released in oxidation and acquired in reduction. Therefore, for oxidation to occur during a chemical reaction, reduction must also occur. Furthermore, the number of electrons produced in oxidation must equal the number of electrons acquired in reduction. Recall that electrons are negatively charged and that for charge to be conserved, the number of electrons lost must equal the number of electrons gained. Mass is conserved in any chemical reaction. Therefore, like mass, the electrons exchanged during oxidation and reduction are conserved.

But why do we say a substance is *reduced* when it *gains* electrons? Remember that when electrons are gained, their negative electrical charge will cause the overall oxidation number to drop, that is, be reduced.

A transfer of electrons causes changes in the oxidation states of one or more elements. **Any chemical process in which elements undergo changes in oxidation number is an oxidation-reduction reaction. This name is often shortened to redox reaction.** An example of a redox reaction can be seen in **Figure 1.4**, in which copper is being oxidized and NO_3^- from nitric acid is being reduced. **The part of the reaction involving oxidation or reduction alone can be written as a half-reaction.** The overall equation for a redox reaction is the sum of two half-reactions. Because the number of electrons involved is the same for oxidation and reduction, they cancel each other out and do not appear in the overall chemical equation.

Equations for the reaction between nitric acid and copper illustrate the relationship between half-reactions and the overall redox reaction.

$$\overset{0}{Cu} \longrightarrow \overset{+2}{Cu^{2+}} + 2e^- \quad \text{(oxidation half-reaction)}$$

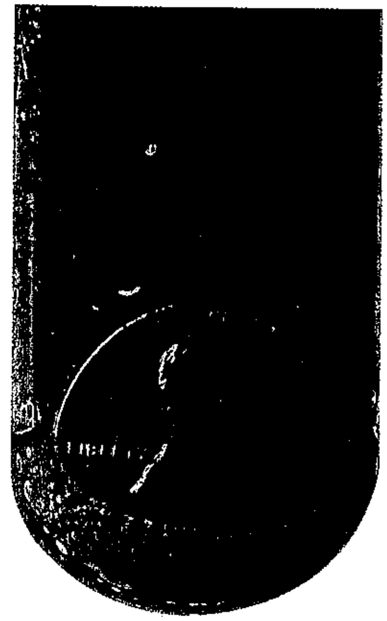
$$2\overset{+5\,-2}{NO_3^-} + 2e^- + 4\overset{+1}{H^+} \longrightarrow 2\overset{+4\,-2}{NO_2} + 2\overset{+1\,-2}{H_2O} \quad \text{(reduction half-reaction)}$$

$$\overset{0}{Cu} + 2\overset{+5}{NO_3^-} + 4H^+ \longrightarrow \overset{+2}{Cu^{2+}} + 2\overset{+4}{NO_2} + 2H_2O \quad \text{(redox reaction)}$$

Notice that electrons lost in oxidation appear on the product side of the oxidation half-reaction. Electrons are gained in reduction and appear as reactants in the reduction half-reaction.

FIGURE 1.4

Oxidation of Copper Copper is oxidized and nitrogen dioxide is produced when this penny is placed in a concentrated nitric acid solution.



WHY IT MATTERS

Photochromic Lenses S.T.E.M.

Photochromic eyeglasses darken when exposed to ultraviolet light and become transparent again in the absence of ultraviolet light. This process is the result of oxidation-reduction reactions. Silver chloride and copper(I) chloride are embedded in the lenses. The chloride ions absorb photons, and the silver chloride dissociates and forms chlorine atoms and silver atoms. The elemental silver darkens the lenses. Note that the chlorine ions are oxidized and the silver atoms are reduced. Then, the copper(I) ions reduce the chlorine atoms and form copper(II) ions. In the reverse process, the copper(II) ions oxidize the silver atoms back to the transparent silver ions.

CHAPTER 19

Oxidation-Reduction Reactions

SECTION REVIEW

1. How are oxidation numbers assigned?

2. Label each of the following half-reactions as either an oxidation or a reduction half-reaction:

   a. $\overset{0}{Br_2} + 2e^- \longrightarrow 2\overset{-1}{Br^-}$

   b. $\overset{0}{Na} \longrightarrow \overset{+1}{Na^+} + e^-$

   c. $2\overset{-1}{Cl^-} \longrightarrow \overset{0}{Cl_2} + 2e^-$

   d. $\overset{0}{Cl_2} + 2e^- \longrightarrow 2\overset{-1}{Cl^-}$

   e. $\overset{+1}{Na^+} + e^- \longrightarrow \overset{0}{Na}$

   f. $\overset{0}{Fe} \longrightarrow \overset{+2}{Fe^{2+}} + 2e^-$

   g. $\overset{+2}{Cu^{2+}} + 2e^- \longrightarrow \overset{0}{Cu}$

   h. $\overset{+3}{Fe^{3+}} + e^- \longrightarrow \overset{+2}{Fe^{2+}}$

3. Which of the following equations represent redox reactions?

   a. $2KNO_3(s) \longrightarrow 2KNO_2(s) + O_2(g)$

   b. $H_2(g) + CuO(s) \longrightarrow Cu(s) + H_2O(l)$

   c. $NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$

   d. $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

   e. $SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$

4. For each redox equation identified in the previous question, determine which element is oxidized and which is reduced.

5. Use the equations below for the redox reaction between aluminum metal and sodium metal to answer the following.

$$3\overset{0}{Na} \longrightarrow 3\overset{+1}{Na^+} + 3e^- \qquad \text{(oxidation)}$$

$$\overset{+3}{Al^{3+}} + 3e^- \longrightarrow \overset{0}{Al} \qquad \text{(reduction)}$$

$$3\overset{0}{Na} + \overset{+3}{Al^{3+}} \longrightarrow 3\overset{+1}{Na^+} + \overset{0}{Al} \qquad \text{(redox reaction)}$$

   a. Explain how this reaction illustrates that charge is conserved in a redox reaction.

   b. Explain how this reaction illustrates that mass is conserved in a redox reaction.

   c. Explain why electrons do not appear as reactants or products in the combined equation.

REVIEWING CONCEPTS

1. a. Distinguish between the processes of oxidation and reduction.
   b. Write an equation to illustrate each. (19-1)
2. Which of the following are redox reactions?
   a. $2Na + Cl_2 \longrightarrow 2NaCl$
   b. $C + O_2 \longrightarrow CO_2$
   c. $2H_2O \longrightarrow 2H_2 + O_2$
   d. $NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$
   e. $NH_3 + HCl \longrightarrow NH_4^+ + Cl^-$
   f. $2KClO_3 \longrightarrow 2KCl + 3O_2$
   g. $H_2 + Cl_2 \longrightarrow 2HCl$
   h. $H_2SO_4 + 2KOH \longrightarrow K_2SO_4 + 2H_2O$
   i. $Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$ (19-1)
3. For each oxidation-reduction reaction in the previous question, identify what is oxidized and what is reduced. (19-1)
4. a. Identify the most active reducing agent among all common elements.
   b. Why are all of the elements in its group in the periodic table very active reducing agents?
   c. Identify the most active oxidizing agent among the common elements. (19-3)
5. Based on Table 19-3, identify the strongest and weakest reducing agents among the substances listed within each of the following groupings:
   a. Ca, Ag, Sn, Cl^-
   b. Fe, Hg, Al, Br^-
   c. F^-, Pb, Mn^{2+}, Na
   d. Cr^{3+}, Cu^{2+}, NO_3^-, K^+
   e. Cl_2, S, Zn^{2+}, Ag^+
   f. Li^+, F_2, Ni^{2+}, Fe^{3+} (19-3)
6. Use Table 19-3 to respond to each of the following:
   a. Would Al be oxidized by Ni^{2+}?
   b. Would Cu be oxidized by Ag^+?
   c. Would Pb be oxidized by Na^+?
   d. Would F_2 be reduced by Cl^-?
   e. Would Br_2 be reduced by Cl^-? (19-3)
7. Distinguish between a voltaic cell and an electrolytic cell in terms of the nature of the reaction involved. (19-4)
8. a. What is electroplating?
   b. Distinguish between the nature of the anode and cathode in such a process. (19-4)
9. a. Explain what is meant by the potential difference between the two electrodes in an electrochemical cell.
   b. How, and in what units, is this potential difference measured? (19-4)
10. The standard hydrogen electrode is assigned an electrode potential of 0.00 V. Explain why this voltage is assigned. (19-4)
11. a. What information is provided by the electrode potential of a given half-cell?
    b. What does the relative value of the potential of a given half-reaction indicate about its oxidation-reduction tendency? (19-4)

PROBLEMS

Redox Equations

12. Each of the following atom/ion pairs undergoes the oxidation number change indicated below. For each pair, determine whether oxidation or reduction has occurred, and then write the electronic equation indicating the corresponding number of electrons lost or gained.
    a. $K \longrightarrow K^+$
    b. $S \longrightarrow S^{2-}$
    c. $Mg \longrightarrow Mg^{2+}$
    d. $F^- \longrightarrow F_2$
    e. $H_2 \longrightarrow H^+$
    f. $O_2 \longrightarrow O^{2-}$
    g. $Fe^{3+} \longrightarrow Fe^{2+}$
    h. $Mn^{2+} \longrightarrow MnO_4^-$
13. Identify the following reactions as redox or nonredox:
    a. $2NH_4Cl(aq) + Ca(OH)_2(aq) \longrightarrow 2NH_3(aq) + 2H_2O(l) + CaCl_2(aq)$
    b. $2HNO_3(aq) + 3H_2S(g) \longrightarrow 2NO(g) + 4H_2O(l) + 3S(s)$
    c. $[Be(H_2O)_4]^{2+}(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + [Be(H_2O)_3OH]^+(aq)$
14. Arrange the following in order of increasing oxidation number of the xenon atom: $CsXeF_8$, Xe, XeF_2, $XeOF_2$, XeO_3, XeF

Oxidation-Reduction Reactions

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b. $\overset{0}{Na} \longrightarrow \overset{+1}{Na^+} + e^-$ *oxidation*

c. $2\overset{-1}{Cl^-} \longrightarrow \overset{0}{Cl_2} + 2e^-$ *oxidation*

d. $\overset{0}{Cl_2} + 2e^- \longrightarrow 2\overset{-1}{Cl^-}$ *reduction*

e. $\overset{+1}{Na^+} + e^- \longrightarrow \overset{0}{Na}$ *reduction*

f. $\overset{0}{Fe} \longrightarrow \overset{+2}{Fe^{2+}} + 2e^-$ *oxidation*

g. $\overset{+2}{Cu^{2+}} + 2e^- \longrightarrow \overset{0}{Cu}$ *reduction*

h. $\overset{+3}{Fe^{3+}} + e^- \longrightarrow \overset{+2}{Fe^{2+}}$ *reduction*

3. Which of the following equations represent redox reactions?

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$\overset{+3}{Al^{3+}} + 3e^- \longrightarrow \overset{0}{Al}$	(reduction)
$3\overset{0}{Na} + \overset{+3}{Al^{3+}} \longrightarrow 3\overset{+1}{Na^+} + \overset{0}{Al}$	(redox reaction)

a. Explain how this reaction illustrates that charge is conserved in a redox reaction.

b. Explain how this reaction illustrates that mass is conserved in a redox reaction.

c. Explain why electrons do not appear as reactants or products in the combined equation.

$2\overset{+1}{K}\overset{+5}{N}\overset{-2}{O_3}(s) \longrightarrow 2\overset{+1}{K}\overset{-3}{N}\overset{-2}{O_2} + \overset{0}{O_2}$

O^{-2} oxidized
N^{+5} reduced

$\overset{+1}{Na}\overset{-2}{O}\overset{+1}{H} + \overset{+1}{H}\overset{-1}{Cl} \longrightarrow \overset{+1}{Na}\overset{-1}{Cl} + \overset{+1}{H_2}\overset{-2}{O}$

Nothing changes charge ∴
Not oxid-red.