multiply reduction rx. by 3:
\[ 3[\text{ClO}_4^-] + 8\text{H}^+ + 8\text{e}^- \rightarrow 3\text{Cl}^- + 4\text{H}_2\text{O} \]
\[ 3\text{ClO}_4^- + 24\text{H}^+ + 24\text{e}^- \rightarrow 3\text{Cl}^- + 12\text{H}_2\text{O} \]
combine:
\[ 4\text{Br}^- + 12\text{H}_2\text{O} + 3\text{ClO}_4^- + 24\text{H}^+ + 24\text{e}^- \rightarrow 4\text{BrO}_3^- + 24\text{H}^+ + 3\text{Cl}^- + 12\text{H}_2\text{O} \]
balance:
\[ 3\text{ClO}_4^- + 4\text{Br}^- \rightarrow 3\text{Cl}^- + 4\text{BrO}_3^- \]

b. oxidation:
\[ \text{N}_2\text{O}_5(g) \rightarrow \text{NO}_3^- + \text{aq} \]
\[ \text{N}_2\text{O}_5(g) \rightarrow 2\text{NO}_3^- + \text{aq} \]
\[ \text{N}_2\text{O}_5(g) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{NO}_3^- + \text{aq} + 4\text{H}^+ + \text{aq} \]
\[ \text{N}_2\text{O}_5(g) + 2\text{H}_2\text{O}(l) + 4\text{OH}^- + \text{aq} \rightarrow 2\text{NO}^- + \text{aq} + 4\text{OH}^- + \text{aq} \]
\[ \text{N}_2\text{O}_5(g) + 2\text{H}_2\text{O}(l) + 4\text{OH}^- + \text{aq} \rightarrow 2\text{NO}_3^- + \text{aq} + 4\text{H}_2\text{O}(l) + 2\text{e}^- \]

reduction:
\[ \text{TeO}_3^{2-} + \text{aq} \rightarrow \text{Te}(s) \]
\[ \text{TeO}_3^{2-} + \text{aq} \rightarrow \text{Te}(s) + 3\text{H}_2\text{O}(l) \]
\[ \text{TeO}_3^{2-} + \text{aq} + 6\text{H}^+ + 6\text{OH}^- + \text{aq} \rightarrow \text{Te}(s) + 3\text{H}_2\text{O}(l) + 6\text{OH}^- \]
\[ \text{TeO}_3^{2-} + 6\text{H}_2\text{O}(l) \rightarrow \text{Te}(s) + 3\text{H}_2\text{O}(l) + 6\text{OH}^- \]
\[ \text{TeO}_3^{2-} + 3\text{H}_2\text{O}(l) \rightarrow \text{Te}(s) + 6\text{OH}^- \]
\[ \text{TeO}_3^{2-} + 3\text{H}_2\text{O}(l) + 4\text{e}^- \rightarrow \text{Te}(s) + 6\text{OH}^- \]
multiply oxidation rx. by 2:
\[ 2[\text{N}_2\text{O}_5(g) + 2\text{H}_2\text{O}(l) + 4\text{OH}^- + \text{aq} \rightarrow 2\text{NO}_3^- + 4\text{H}_2\text{O}(l) + 2\text{e}^- + 4\text{OH}^- + \text{aq} \]
\[ 2\text{N}_2\text{O}_5(g) + 4\text{H}_2\text{O}(l) + 8\text{OH}^- + \text{aq} \rightarrow 4\text{NO}_3^- + 8\text{H}_2\text{O}(l) + 4\text{e}^- + 8\text{OH}^- + \text{aq} \]
multiply reduction rx. by 1:
\[ \text{TeO}_3^{2-} + 6\text{H}_2\text{O}(l) + 4\text{e}^- \rightarrow \text{Te}(s) + 3\text{H}_2\text{O}(l) + 6\text{OH}^- \]
combine:
\[ 2\text{N}_2\text{O}_5(g) + 4\text{H}_2\text{O}(l) + 8\text{OH}^- + \text{aq} + \text{TeO}_3^{2-} + 3\text{H}_2\text{O}(l) + 4\text{e}^- \rightarrow 4\text{NO}_3^- + 8\text{H}_2\text{O}(l) + 4\text{e}^- \]
balance:
\[ 2\text{N}_2\text{O}_5(g) + \text{TeO}_3^{2-} + 2\text{OH}^- + \text{aq} \rightarrow \text{Te}(s) + 4\text{NO}_3^- + \text{aq} + \text{H}_2\text{O}(l) \]
c. oxidation:
\[ \text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{O}_2(\text{g}) \]
\[ \text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{O}_2(\text{g}) + 2\text{H}^+ + \text{aq} \]
\[ \text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{O}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- + \text{aq} \]

reduce:
\[ \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \]
\[ \text{Cr}_2\text{O}_7^{2-} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \]

multiply oxidation rx. by 3:
\[ 3[\text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{O}_2(\text{g}) + 2\text{H}^+ + \text{aq} + 2\text{e}^- \]
\[ 3\text{H}_2\text{O}_2(\text{aq}) \rightarrow 3\text{O}_2(\text{g}) + 6\text{H}^+ + \text{aq} + 6\text{e}^- \]
multiply reduction rx. by 1:
\[ \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \]

14. It is a redox reaction because sulfur is both oxidized from an oxidation number of 2 to an oxidation number of 0 in S(s) and reduced from an oxidation number of +4 in SO_2(g) to an oxidation number of 0 in S(s).

Answers to Section 9.3 Review Questions
(Student textbook page 617)

1. Fluorine is the most electronegative element in the periodic table. Therefore, it does not “lose” electrons in chemical bonds. It has seven valence electrons, and thus forms bonds in which it gains one valence electron, satisfying the octet rule. Because it is in the second row of the periodic table, its outer occupied energy level cannot accommodate more than eight electrons (as bromine, iodine, or chlorine can). Therefore, it does not form bonds in which it gains more than one electron, and its oxidation number is always –1.

2. a. MnO_2 + 4
   b. +7
   c. +6
   d. KMnO_4 + 7

3. Zero in the diatomic molecule, O_2(g); –1 in peroxides, H_2O_2(g); –2 in most anions, CO_3^{2-}(aq); +2 in an oxygen difluoride, OF_2(g)

4. a. yes
   b. no
   c. no
   d. yes
5. Students may suggest definitions similar to the following:
   - A redox reaction is a chemical reaction in which there is a change in the oxidation number of some or all of the atoms of the reactants.
   - A redox reaction is a chemical reaction in which atoms of one element are oxidized and atoms of another element are reduced.
   - A redox reaction is a chemical reaction in which electrons are transferred among reactants. Thus, the total increase in oxidation numbers corresponds to the number of electrons lost by oxidation. The total decrease in oxidation numbers corresponds to the number of electrons gained by reduction. In a reaction, the atoms in uncombined elements have an oxidation number of 0. However, different elements have different electronegativities. Therefore, when they combine in a compound, atoms of the less electronegative element are oxidized and atoms of the more electronegative element are reduced.

6. When one element combines with another element in a chemical reaction, the reaction is always a redox reaction. The atoms in uncombined elements have an oxidation number of 0. However, different elements have different electronegativities. Therefore, when they combine in a compound, atoms of the less electronegative element are oxidized and atoms of the more electronegative element are reduced.

7. The total increase in oxidation numbers corresponds to the number of electrons lost by oxidation. The total decrease in oxidation numbers corresponds to the number of electrons gained by reduction. In a reaction, net gain of electrons must be equal to net loss of electrons. Thus, the total increase in oxidation numbers must equal the total decrease in oxidation numbers.

8. \(4\text{NH}_3(g) + 7\text{O}_2(g) \rightarrow 4\text{NO}_2(g) + 6\text{H}_2\text{O}(\ell)\)

9. a. +2
   b. Using a Lewis structure, students may arrive at two different oxidation numbers for sulfur using the following reasoning. The central sulfur atom usually has 6 electrons in its valence shell. The three oxygen atoms, however, have a greater electronegativity than sulfur. Therefore, they can be considered to have taken these electrons, leaving the central sulfur with a +6 oxidation number. The sulfur atom bonded to the central sulfur atom may be considered to share its electrons with the central sulfur. Therefore, it will have an oxidation number of −1. Since the central sulfur (+6) can now be considered to have one shared electron it will have a total oxidation number of +6 + (−1) = +5.
   c. Using the first method, the oxidation number for both sulfur atoms is +2. Using the second method, the oxidation number for one sulfur atom is −1, and for the other is +5. (Notice the average of the second result gives the first result).
   d. Using Lewis structures allows for the fact that atoms of the same element in a molecule or polyatomic ion may have different oxidation numbers, depending on the bonding arrangement. The disadvantage to this method is that it is more difficult and time-consuming than using the rules.
   e. The advantage to using the oxidation number rules is that they apply to most cases and are quick and easy to use. The disadvantage to using these rules is that they do not allow for the possibility of different oxidation numbers for the same atoms in a molecule or polyatomic ion.

10. a. \(\text{CH}_3\text{COOH(aq)} + \text{O}_2(g) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O(\ell)}\)
    Oxidation number method:
    (Note: The zero oxidation numbers for the carbon atoms in ethanoic acid represent an average value.)
    The coefficient 1 goes in front of the ethanoic acid and the coefficient 2 goes in front of the oxygen.
    \(\text{CH}_3\text{COOH(aq)} + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O(\ell)}\)
    Balance the right side of the equation by inspection, ensuring that the ratios of the carbon and oxygen atoms remain as above:
    \(\text{CH}_3\text{COOH(aq)} + 2\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 2\text{H}_2\text{O(\ell)}\)

b. \(\text{O}_2(g) + \text{H}_2\text{SO}_3(aq) \rightarrow \text{HSO}_4^-(aq)\)
   Because the reaction takes place in acidic conditions, add \(\text{H}^+\) to balance the charge. Then balance by inspection.
   \(\text{O}_2(g) + 2\text{H}_2\text{SO}_3(aq) \rightarrow 2\text{HSO}_4^-(aq) + 2\text{H}^+(aq)\)

11. a. \(\text{NH}_3(g) + \text{Cl}_2(g) \rightarrow \text{NH}_4\text{Cl(aq)} + \text{N}_2(g)\)
    Assign oxidation numbers.
    (Notice among the products, that there are two nitrogen atoms with different oxidation numbers, −3 and 0. Some of the nitrogen atoms in the reactants will not change oxidation numbers, while others will change from −3 to 0. Therefore, to keep things clear, create two sets of ammonia molecules on the reactant side.)
    \(\text{NH}_3(g) + \text{NH}_3(g) + \text{Cl}_2(g) \rightarrow \text{NH}_4\text{Cl(aq)} + \text{N}_2(g)\)
    Now track the gain and loss of electrons. There is only one nitrogen atom in \(\text{NH}_3\), but two chlorine
atoms in Cl₂. When the ratio of the number of atoms undergoing oxidation and reduction differs, you must account for all of the electrons gained or lost by the molecule. So, when each atom in Cl₂ gains 1 electron, the molecule gains 2 electrons.

\[
\text{NH}_3(g) + \text{N}_2(g) + \text{Cl}_2(g) \rightarrow \text{NH}_4\text{Cl}(aq) + \text{N}_2(g)
\]

Place a coefficient of 2 in front of the first ammonia symbol and a coefficient of 3 in front of the chlorine symbol.

\[
2\text{NH}_3(g) + \text{NH}_3(g) + 3\text{Cl}_2(g) \rightarrow \text{NH}_4\text{Cl}(aq) + \text{N}_2(g)
\]

The ratio of these coefficients cannot change. Balance the equation by adding coefficients in front of the other compounds where needed.

\[
2\text{NH}_3(g) + 6\text{NH}_3(g) + 3\text{Cl}_2(g) \rightarrow 6\text{NH}_4\text{Cl}(aq) + \text{N}_2(g)
\]

Now that the equation is balanced, combine the two ammonia compounds among the reactants.

\[
8\text{NH}_3(g) + 3\text{Cl}_2(g) \rightarrow 6\text{NH}_4\text{Cl}(aq) + \text{N}_2(g)
\]

b. \(\text{Mn}_3\text{O}_4(aq) + \text{Al}(s) \rightarrow \text{Al}_2\text{O}_3(aq) + \text{Mn}(s)\)

Assign oxidation numbers.

\[
\text{Mn}_3\text{O}_4(aq) + \text{Al}(g) \rightarrow \text{Al}_2\text{O}_3(aq) + \text{Mn}(s)
\]

The oxidation number of +8/3 is an average of the three manganese atoms. When comparing the number of atoms gained and lost, you must consider the ratio of atoms. In the reactants there are three manganese atoms and one aluminum atom. Therefore you must consider the total number of electrons gained or lost for all of the atoms in the compound. So, when the three manganese atoms are reduced from an oxidation number of +8/3, there are a total of 8 electrons gained. When one aluminum atom is oxidized form an oxidation number of +3 to 0, it loses 3 electrons.

\[
\text{Mn}_3\text{O}_4(aq) + \text{Al}(g) \rightarrow \text{Al}_2\text{O}_3(aq) + \text{Mn}(s)
\]

Place the coefficient 8 in front of the Al and the coefficient 3 in front of the \(\text{Mn}_3\text{O}_4\).

\[
3\text{Mn}_3\text{O}_4(aq) + 8\text{Al}(s) \rightarrow \text{Al}_2\text{O}_3(aq) + 3\text{Mn}(s)
\]

Balance the rest of the equation by inspection.

\[
3\text{Mn}_3\text{O}_4(aq) + 8\text{Al}(s) \rightarrow 4\text{Al}_2\text{O}_3(aq) + 9\text{Mn}(s)
\]

12. Oxidation numbers are values assigned to elements in a redox reaction to keep track of changes in charge. This system of book keeping is developed on a base of assumptions, that may seem arbitrary at times, but in fact do allow for the tracking of changes in charge.

**Answers to Practice Problems**

For full solutions to Practice Problems, see Part B of this Solutions Manual.

(Student textbook page 598)

1. \(\text{MnO}_4^{-}(aq) + 5\text{Ag}(s) + 8\text{H}^{+}(aq) \rightarrow \text{Mn}^{2+}(aq) + 5\text{Ag}^{+}(aq) + 4\text{H}_2\text{O}(\ell)\)
   
   Oxidizing agent: \(\text{MnO}_4^{-}(aq)\); reducing agent: \(\text{Ag}(s)\)

2. \(\text{Hg}(\ell) + 2\text{NO}_3^{-}(aq) + 4\text{Cl}^{-}(aq) + 4\text{H}^{+}(aq) \rightarrow \text{HgCl}_2^{2-}(s) + 2\text{NO}_2(g) + 2\text{H}_2\text{O}(\ell)\)
   
   Oxidizing agent: \(\text{NO}_3^{-}(aq)\); reducing agent: \(\text{Hg}(\ell)\)

3. \(4\text{H}_2\text{O}(\ell) + \text{AsH}_3(s) + 4\text{Zn}^{2+}(aq) \rightarrow \text{H}_3\text{AsO}_4(aq) + 4\text{Zn}(s) + 8\text{H}^{+}(aq)\)
   
   Oxidizing agent: \(\text{Zn}^{2+}(aq)\); reducing agent: \(\text{AsH}_3(s)\)

4. \(\text{I}_2(s) + 5\text{ClO}^{-}(aq) + \text{H}_2\text{O}(\ell) \rightarrow 2\text{IO}_3^{-}(aq) + 5\text{Cl}^{-}(aq) + 2\text{H}^{+}(aq)\)
   
   Oxidizing agent: \(\text{ClO}^{-}(aq)\); reducing agent: \(\text{I}_2(s)\)

5. \(6\text{MnO}_4^{-}(aq) + \Gamma^{-}(aq) + 6\text{OH}^{-}(aq) \rightarrow 6\text{MnO}_2^{2-}(aq) + \text{IO}_3^{-}(aq) + 3\text{H}_2\text{O}(\ell)\)
   
   Oxidizing agent: \(\text{MnO}_4^{-}(aq)\); reducing agent: \(\Gamma^{-}(aq)\)

6. \(3\text{H}_2\text{O}_2(aq) + 2\text{ClO}_2^{-}(aq) + 2\text{H}^{+}(aq) \rightarrow 2\text{ClO}^{-}(aq) + 3\text{O}_2(g) + 4\text{H}_2\text{O}(\ell)\)
   
   Oxidizing agent: \(\text{ClO}_2^{-}(aq)\); reducing agent: \(\text{H}_2\text{O}_2(aq)\)

7. \(6\text{ClO}^{-}(aq) + 2\text{Cr}_2\text{O}_7^{2-}(aq) + 2\text{H}^{+}(aq) \rightarrow 2\text{CrO}_4^{2-}(aq) + 3\text{Cl}_2(g) + 4\text{OH}^{-}(aq)\)
   
   Oxidizing agent: \(\text{ClO}^{-}(aq)\); reducing agent: \(\text{Cr}_2\text{O}_7^{2-}(aq)\)

8. \(4\text{Al}(s) + 3\text{NO}_3^{-}(aq) + 4\text{H}_2\text{O}(\ell) + \text{OH}^{-}(aq) \rightarrow 3\text{NH}_3(g) + 4\text{AlO}_2^{-}(aq)\)
   
   Oxidizing agent: \(\text{NO}_3^{-}(aq)\); reducing agent: \(\text{Al}(s)\)

9. \(\text{ClO}_3^{-}(aq) + 2\text{MnO}_4(s) + 2\text{OH}^{-}(aq) \rightarrow \text{Cl}^{-}(aq) + 2\text{MnO}_4^{-}(aq) + \text{H}_2\text{O}(\ell)\)
   
   Oxidizing agent: \(\text{ClO}_3^{-}(aq)\); reducing agent: \(\text{MnO}_4(s)\)

10. \(5\text{PbO}_2(s) + \text{I}_2(s) + 8\text{H}^{+}(aq) \rightarrow 5\text{Pb}^{2+}(aq) + 2\text{IO}_3^{-}(aq) + 4\text{H}_2\text{O}(\ell)\)
    
    Oxidizing agent: \(\text{PbO}_2(s)\); reducing agent: \(\text{I}_2(s)\)

(Student textbook page 606)

11. +3
12. 0
13. +6
14. +5
15. 0