13.2 PREDICTING REDOX REACTIONS

Investigation 13.2: Spontaneity of Redox Reactions

(Pages 569, 602)

Purpose
The purpose of this investigation is to test the assumption that all single replacement reactions are spontaneous.

Problem
Which combinations of copper, lead, silver, and zinc metals and their aqueous metal ion solutions produce spontaneous reactions?

Prediction
Based on previous assumptions made concerning chemical reactions, all combinations that result in products that are different from reactants are spontaneous. Therefore, all metals should react with compounds of other metal ions.

Procedure
1. Clean one side of each of the four metal strips using steel wool or sandpaper.
2. Add 1 drop of Cu(NO₃)₂(aq) to each of the four metals.
3. Repeat step 2 using Pb(NO₃)₂(aq), AgNO₃(aq), and Zn(NO₃)₂(aq) on different locations on the metal strips.
4. Rinse the lead and silver solutions into a labelled waste container and clean the metal strips for reuse.

Evidence
Table 1: Reactions of Metals and Metal Ions

<table>
<thead>
<tr>
<th></th>
<th>Cu(s)</th>
<th>Pb(s)</th>
<th>Ag(s)</th>
<th>Zn(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu²⁺(aq)</td>
<td>slightly cleaner metal surface</td>
<td>red-brown precipitate</td>
<td>no change</td>
<td>red-brown precipitate</td>
</tr>
<tr>
<td>Pb²⁺(aq)</td>
<td>no change</td>
<td>no change</td>
<td>no change</td>
<td>black precipitate</td>
</tr>
<tr>
<td>Ag⁺(aq)</td>
<td>silver-grey crystals</td>
<td>silver-grey crystals</td>
<td>no change</td>
<td>silver-grey crystals</td>
</tr>
<tr>
<td>Zn²⁺(aq)</td>
<td>no change</td>
<td>no change</td>
<td>no change</td>
<td>no change</td>
</tr>
</tbody>
</table>

Analysis
The evidence obtained is consistent with spontaneous, single replacement reactions for only the combinations of copper and silver ions, lead and copper(II) ions, lead and silver ions, and zinc and each of copper(II), silver, and lead(II) ions.

Evaluation
The experimental design of adding drops of metal ion solutions onto clean metal surfaces was adequate to answer the problem because only evidence for a reaction (not the identity of the product) was required. This design seems to be the best in terms of efficiency and minimizing quantities of chemicals used. The materials were adequate to answer the problem, but the addition of a microscope might be useful to ensure that a small, slow change could not be misinterpreted as no reaction. The procedure and technological skills were adequate, although the short observation time did create a little uncertainty for those combinations that did not appear to react. I would be more certain of the results if those mixtures were left for at least one day or viewed under magnification. Other sources of uncertainty include the purity of the solutions and metals. Overall, I am reasonably certain of the experimental evidence collected.

Overall, the prediction is judged to be falsified since six out of the twelve predicted spontaneous reactions did not give any evidence of a chemical change. The mixture of a metal and a solution of its own ion was predicted to be non-spontaneous and this was verified with the possible exception of the copper system, which would require further testing. The assumption of
spontaneous single replacement reactions is judged to be unacceptable since the prediction was clearly falsified. The assumption will need to be restricted, revised, or discarded.

The purpose of this investigation was clearly accomplished even with the uncertainties identified.

Web Quest—Piercings: A Rash Decision

(Page 570)
[Students’ presentations should include responses to the following questions, for which sample answers are provided.]

What is allergic contact dermatitis and what are its symptoms?
Allergic contact dermatitis (ACD) is an allergic reaction caused by exposure to a specific chemical agent. Some of these agents include perfumes, solvents, poison ivy, and certain metals—primarily nickel. The symptoms of ACD vary greatly, ranging from dry, swollen skin to blisters. Left untreated, the skin may darken and become leathery, cracked, and scaly. Although the rash is usually confined to the contact region, it may spread to other areas of the body like the eyelids and genitals, if the allergen is on the fingers.

Why is nickel allergic contact dermatitis becoming more common?
Nickel allergic contact dermatitis is becoming more prevalent because so many of the metallic objects we come into contact with on a daily basis are made of alloys containing nickel. Earrings and studs, rings, watches, and other jewellery, belt buckles, zippers, and even pennies all contain nickel. Because nickel is found in so many common objects, and because more people than ever before are having body piercings, the likelihood that someone will develop a nickel sensitivity and ultimately a nickel allergy is increasing. Unfortunately, there is no cure and no way to desensitize a sufferer. Once a person is sensitized to nickel, a subsequent exposure to even tiny quantities of nickel can trigger an allergic reaction.

What proportion of the population is nickel sensitive? Why is this condition more common among women than men?
It is estimated that up to 15% of women and 5% of men have a nickel allergy. Metal allergies are more common among women than men, presumably because women are more likely to wear jewellery. However, as the popularity of piercings catches on with men, the difference between the two sexes in terms of nickel allergies may disappear. Another factor to take into consideration with respect to gender related allergies to nickel, is the fact that some people may also develop metal allergies that occur as a result of frequent occupational contact with metals.

What factors contribute to the occurrence of nickel ACD?
The condition of the skin can be an important factor in the spread of nickel ACD. Dry, broken skin is a more likely place for nickel sensitivity to begin than smooth, healthy skin. Other contributing factors include temperature, amount of perspiration, humidity, and whether the affected area of skin is covered by tight-fitting clothing, such as a glove covering the hand.

What role does oxidation play in ACD?
The real culprit of nickel-caused ACD is not the element nickel, but the ion Ni²⁺(aq). Prolonged contact with the skin and perspiration promotes the oxidation of nickel atoms into ions. Migration of nickel ions into the skin triggers the allergic reaction. Dissolved electrolytes in perspiration increases the rate of oxidation.

Why are body piercings particularly associated with the development of nickel ACD?
Piercing any body part results in some bleeding. Blood contains electrolytes, which can oxidize nickel in the studs or hoops, which then releases nickel ions. Once the piercing occurs, the ions have easy access, through the new wound, into the body. Soft tissue, such as what is found in earlobes, heals quickly because it does not have a lot of blood flow. Tongue piercings are riskier than earlobe piercings because the tongue is thicker and contains far more blood vessels than the earlobe, making the healing period for the tongue much longer. Also, the tongue is constantly
bathed in saliva (and initially blood), which contains electrolytes, oxidizing any nickel in the
tongue stud. During a tongue piercing, nickel ions can then easily pass into the bloodstream and
trigger a nickel allergy.

**Which metals or metallic products cause a nickel ACD reaction?**

Many common metals and metallic products contain nickel. Stainless steel for example, is an
alloy of iron, nickel, and chromium, found in numerous household products ranging from cutlery
to eyeglass frames, jewellery, clasps, zippers, razors, braces, and even surgical implants. Inferior
grades of stainless steel will corrode when they come into contact with perspiration, to release
nickel ions. Better-quality stainless steel, such as surgical steel, is essentially corrosion-free and
poses no risk. In some cases, gold jewellery can trigger an allergic response. However, this is
usually caused by the nickel content of the jewellery and not the gold itself. Because pure gold is
too soft to be useful as jewellery, alloying gold with other metals, (such as nickel and silver),
gives it added hardness and colour variation. Many chrome-plated objects may also contain
sufficient nickel to induce an allergic reaction in people who are already sensitized to nickel.

**How can nickel ACD reactions be avoided?**
The obvious “fix” for a nickel allergy is to minimize contact with the metal, which includes the
following:

- Avoid wearing jewellery containing nickel, or at least remove jewellery overnight.
- Keep your hands dry as perspiration accelerates nickel corrosion.
- Switch to gold! Jewellery with a higher gold content, like 18-karat gold, is less likely to
  contain enough nickel to trigger a response.
- Coat your favourite jewellery with a relatively unreactive metal such as platinum or titanium.

**Practice**

*(Page 571)*

1. Oxidation and reduction are processes that work together in the transfer of electrons that
takes place in redox reactions. Oxidation is the process of losing electrons, while reduction is
the process of gaining electrons. Oxidizing agents and reducing agents are the substances
directly involved in the transfer of electrons in a redox reaction. Oxidizing agents remove
electrons from reducing agents, causing the reducing agent to be oxidized (a loss of electrons)
and the oxidizing agent to be reduced (a gain of electrons).

2. A substance that is a very strong oxidizing agent has a very strong attraction for electrons.

3. A substance that is a very strong reducing agent has a weak attraction for its electrons, which
are easily removed.

4. An agent is one who acts for another to secure a desired effect.
   Using this definition of an agent, a loans agent would be analogous to a reducing agent.
   While a loans agent helps someone get a loan (and in doing so, “loses” money), a reducing
   agent “helps” another substance get some electrons and in doing so, loses electrons itself.

5. Lead and zinc react spontaneously with a copper(II) ion solution.

6. Silver and copper did not appear to react with a copper(II) ion solution.

7. The metals, Pb(s) and Zn(s), react spontaneously with Cu²⁺ (aq), and both appear below the
   Cu²⁺(aq) line in a table of reduction half-reactions.

8. Only zinc metal reacts spontaneously with lead(II) ions; silver, copper, and lead metals did
   not react with lead(II) ions. The metal, Zn(s), appears below the Pb²⁺(aq) line in a table of
   reduction half-reactions.

9. My hypothesis is that metal ions react spontaneously with metals listed below them in a table
   of reduction half-reactions. Using this hypothesis and Table 3, silver ions should react
   spontaneously with copper, lead, and zinc metals, and zinc ions should not react
   spontaneously with any of the metals tested. On the basis of the evidence, these predictions
   are correct and the hypothesis is verified.
10. The following table of reduction half-reaction equations is based on the evidence presented in Table 4.

Relative Strengths of Oxidizing and Reducing Agents

<table>
<thead>
<tr>
<th>Decreasing Reactivity of Oxidizing Agents</th>
<th>SOA</th>
<th>Cl₂(aq) + 2 e⁻ ⇌ 2 Cl⁻(aq)</th>
<th>Decreasing Activity of Reducing Agents</th>
<th>SRA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SOA</td>
<td>Br₂(aq) + 2 e⁻ ⇌ 2 Br⁻(aq)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SOA</td>
<td>I₂(aq) + 2 e⁻ ⇌ 2 I⁻(aq)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Lab Exercise 13.A: Building a Redox Table

(Page 572)

Purpose
The purpose of this lab exercise is to create an extended table of relative strengths of oxidizing and reducing agents.

Problem
What is the table of relative strengths of oxidizing and reducing agents for the combined results from three experiments?

Analysis
According to the evidence collected,

(a) SOA

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Br₂(aq) + 2 e⁻ ⇌ 2 Br⁻(aq)</td>
<td></td>
</tr>
<tr>
<td>Ag⁺(aq) + e⁻ ⇌ Ag(s)</td>
<td></td>
</tr>
<tr>
<td>I₂(aq) + 2 e⁻ ⇌ 2 I⁻(aq)</td>
<td></td>
</tr>
<tr>
<td>Cu²⁺(aq) + 2 e⁻ ⇌ Cu(s)</td>
<td>SRA</td>
</tr>
</tbody>
</table>

(b) SOA

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₂(aq) + 2 e⁻ ⇌ 2 Cl⁻(aq)</td>
<td></td>
</tr>
<tr>
<td>Br₂(aq) + 2 e⁻ ⇌ 2 Br⁻(aq)</td>
<td></td>
</tr>
<tr>
<td>Ag⁺(aq) + e⁻ ⇌ Ag(s)</td>
<td></td>
</tr>
<tr>
<td>I₂(aq) + 2 e⁻ ⇌ 2 I⁻(aq)</td>
<td></td>
</tr>
<tr>
<td>Cu²⁺(aq) + 2 e⁻ ⇌ Cu(s)</td>
<td></td>
</tr>
<tr>
<td>Pb²⁺(aq) + 2 e⁻ ⇌ Pb(s)</td>
<td></td>
</tr>
<tr>
<td>Zn²⁺(aq) + 2 e⁻ ⇌ Zn(s)</td>
<td>SRA</td>
</tr>
</tbody>
</table>

Practice

(Page 573)

11. Co²⁺(aq) + 2 e⁻ ⇌ Co(s)
    Zn²⁺(aq) + 2 e⁻ ⇌ Zn(s)
    Mg²⁺(aq) + 2 e⁻ ⇌ Mg(s)
12. Cu²⁺(aq) + 2 e⁻ ⇌ Cu(s)
    2 H⁺(aq) + 2 e⁻ ⇌ H₂(g)
    Cd²⁺(aq) + 2 e⁻ ⇌ Cd(s)
    Be²⁺(aq) + 2 e⁻ ⇌ Be(s)
    Ca²⁺(aq) + 2 e⁻ ⇌ Ca(s)
13. The redox spontaneity rule is empirical because it is based directly on observations of redox reactions and provides no theoretical explanation.

14. \( \text{Cl}_2(g) + 2 \text{e}^- \rightleftharpoons 2 \text{Cl}^-(aq) \)
   \( \text{Br}_2(l) + 2 \text{e}^- \rightleftharpoons 2 \text{Br}^-(aq) \)
   \( \text{Ag}^+(aq) + \text{e}^- \rightleftharpoons \text{Ag(s)} \)
   \( \text{I}_2(s) + 2 \text{e}^- \rightleftharpoons 2 \text{I}^-(aq) \)
   \( \text{Cu}^{2+}(aq) + 2 \text{e}^- \rightleftharpoons \text{Cu(s)} \)

**Practice**

(Page 574)

15. \( \text{Ag}^+(aq), \text{Cu}^{2+}(aq), \text{Pb}^{2+}(aq), \text{Zn}^{2+}(aq) \). This order agrees with the evidence presented in Table 3 (page 570 of the textbook).

16. (a) Metal ions, nonmetals, and a variety of acidic solutions usually behave as oxidizing agents.
    (b) Nonmetal ions, metals, and basic solutions of various entities usually behave as reducing agents.

17. According to atomic theory, nonmetal atoms have almost-filled valence energy levels and tend to attract electrons to attain stable, filled energy levels of the nearest noble gas. Metal atoms, however, have few electrons in their valence energy levels, have weak attractions for the valence electrons, and tend to lose electrons to attain filled energy levels of their nearest noble gas. This is consistent with the empirically determined table, which shows that nonmetals tend to act as oxidizing agents (electron acceptors) and that metals tend to act as reducing agents (electron donors).

18. Since fluorine is the most reactive nonmetal, and nonmetals are generally oxidizing agents, fluorine is expected to be the strongest oxidizing agent. Fluorine is the most reactive nonmetal because it has the greatest attraction for electrons. This reason relates the observed reactivity to the theoretical definition of an oxidizing agent. 
   [Some further “why” questions are as follows. Why does fluorine have the greatest attraction for electrons? Why does fluorine have the highest electronegativity? Why do atoms with almost-filled energy levels have higher electronegativities than those without? It should soon become obvious that the theory presented, to this point, can provide only a limited explanation of the redox table.]

19. (a/b)

(c) These entities can gain or lose electrons. For example, tin(II) ions can either lose electrons to produce tin(IV) ions or gain electrons to produce tin atoms. The explanation for copper(I) and chromium(II) ions is similar, but there is no simple explanation for the behaviour of water molecules, which can also act as both oxidizing and reducing agents.

20. (a) spontaneous
(b) nonspontaneous  
(c) nonspontaneous  
(d) spontaneous  
(e) spontaneous  
(f) spontaneous  

21. **Purpose**  
The purpose of this investigation is to test the order of strengths of oxidizing and reducing agents given on the redox table (Appendix I).  

**Problem**  
What is the relative order of strengths of oxidizing and reducing agents for aluminium, nickel, lead, cobalt, and their respective aqueous ions?  

**Prediction**  
According to the empirical redox table in Appendix I, the relative order of strengths is:  
aluminium $\rightarrow$ cobalt $\rightarrow$ nickel $\rightarrow$ lead  
strongest reducing agent $\rightarrow$ weakest reducing agent  

Pb$^{2+}$(aq) $\rightarrow$ Ni$^{2+}$(aq) $\rightarrow$ Co$^{2+}$(aq) $\rightarrow$ Al$^{3+}$(aq)  
strongest oxidizing agent $\rightarrow$ weakest oxidizing agent  

**Design**  
Place small clean pieces of each of the four metals in each of the solutions in a well plate (spot plate), and observe for evidence of any reaction. The manipulated variable is the metal/metal ion; the responding variable is the visible evidence of reaction (precipitates); and some controlled variables include concentration of the solutions and temperature.  

**Materials**  
- eye protection  
- lab apron  
- four samples of each of aluminium, nickel, lead, and cobalt  
- sandpaper or steel wool  
- 10 mol/L solutions of aluminium nitrate, nickel(II) nitrate, lead(II) nitrate, and cobalt(II) nitrate  
- well plate (spot plate)  
- four small pipettes or medicine droppers  

CAUTION: Lead(II) nitrate is toxic; aluminium nitrate, nickel(II) nitrate, and cobalt(II) nitrate are irritants; all cobalt compounds are carcinogenic. Avoid eye and skin contact and inhalation and do not ingest. Seek immediate medical attention if the lead(II) or cobalt(II) compounds are ingested.  

22.  
(1) Mix all combinations of oxidizing and reducing agents from a list of elements and their ions. The oxidizing agent that reacts spontaneously with the greatest number of reducing agents is the strongest. The oxidizing agent that reacts with the next greatest number of reducing agents is the next strongest, etc. From this information, the order of reactivity and the half-reaction equations can be determined.  

(2) Study selected mixtures of oxidizing agents and reducing agents and use the spontaneity rule to order the oxidizing and reducing agents in each reactant mixture. Combine the individual results to form a final table of half-reactions.  

(If $n$ half-reaction equations are to be placed in a table, a minimum of $n - 1$ reactions must be studied.)  

23. Gold and silver (and platinum) are commonly found as metals, while sodium and potassium are never found in their elemental form. Gold and silver are listed near the top of the table of relative strengths of oxidizing and reducing agents, and are very weak reducing agents (relatively unreactive). Sodium and potassium are listed near the bottom of the table of
relative strengths of oxidizing and reducing agents and are very strong reducing agents (meaning they are very reactive).

24. The empirical way of knowing has been most useful to this point in predicting the spontaneity of redox reactions because the construction of tables of relative strengths of oxidizing and reducing agents is based on observations of reactions. The theory presented to this point can barely provide an initial explanation after the fact, and has little predictive power.

Practice
(Page 575)

25. (a) $\text{Cu}^{2+}(\text{aq}) \rightarrow \text{Pb(s)} \rightarrow \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{H}_2\text{O(l)}$

(b) $\text{Au(s)} \rightarrow \text{H}^+(\text{aq}) \rightarrow \text{NO}_3^-(\text{aq}) \rightarrow \text{H}_2\text{O(l)}$

(c) $\text{K}^+(\text{aq}) \rightarrow \text{Cr}_2\text{O}_7^{2-}(\text{aq}) \rightarrow \text{H}^+(\text{aq}) \rightarrow \text{NO}_3^-(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) \rightarrow \text{H}_2\text{O(l)}$

(d) $\text{Cl}_2(\text{aq}) \rightarrow \text{H}_2\text{SO}_3(\text{aq}) \rightarrow \text{H}_2\text{O(l)}$

(e) $\text{K}^+(\text{aq}) \rightarrow \text{MnO}_4^-(\text{aq}) \rightarrow \text{H}^+(\text{aq}) \rightarrow \text{Sn}^{2+}(\text{aq}) \rightarrow \text{Cl}^-(\text{aq}) \rightarrow \text{H}_2\text{O(l)}$

(f) $\text{OH}^-(\text{aq}) \rightarrow \text{MnO}_2(\text{s}) \rightarrow \text{I}_2(\text{aq}) \rightarrow \text{H}_2\text{O(l)}$

Investigation 13.3: Predicting the Reaction of Sodium Metal (Demonstration)
(Pages 578, 602)

Purpose
The purpose of this demonstration is to test the five-step method for predicting redox reactions.

Problem
What are the products of the reaction of sodium metal with water?

Prediction
According to the five-step method for predicting redox reactions, the products of the reaction are hydrogen gas and aqueous sodium hydroxide.

SOA
$\text{Na(s, H}_2\text{O(l)}$

SRA $\text{Ra}$
$2 \text{H}_2\text{O(l)} + 2 e^- \rightarrow \text{H}_2(\text{g}) + 2 \text{OH}^- (\text{aq})$

$2 [\text{Na(s)} \rightarrow \text{Na}^+ (\text{aq}) + e^- ]$

$2 \text{H}_2\text{O(l)} + 2 \text{Na(s)} \rightarrow \text{spontaneously} \rightarrow 2 \text{Na}^+ (\text{aq}) + \text{H}_2(\text{g}) + 2 \text{OH}^- (\text{aq})$

Design
A small piece of clean sodium metal is added to pure water. The following diagnostic tests are conducted first on pure water (as a control) and then on the final reaction mixture. If a flame is inserted into a sample of the gas above the water, and a squeal or popping sound is heard, then hydrogen is likely present. If red and blue litmus paper is immersed in the solution, and the red
paper turns blue, then hydroxide ions are likely present. If a flame test is conducted on the liquid, and the flame is bright yellow, then sodium ions are likely present.

**Evidence**

<table>
<thead>
<tr>
<th>Diagnostic test</th>
<th>Pure water control</th>
<th>Final reaction mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrogen test</td>
<td>no sound heard</td>
<td>High, squeaky sound heard</td>
</tr>
<tr>
<td>litmus test</td>
<td>no colour change</td>
<td>red litmus turned blue</td>
</tr>
<tr>
<td>flame test</td>
<td>pale yellow flame</td>
<td>bright yellow flame</td>
</tr>
</tbody>
</table>

**Analysis**

According to the evidence from the diagnostic tests, hydrogen gas, sodium ions, and hydroxide ions were likely produced in the reaction of sodium metal and water.

**Evaluation**

The experimental design is judged to be adequate because the problem was answered with no obvious flaws. The use of a control makes the results quite certain. *The materials, procedure, and skills were not evaluated because this is a demonstration.*

The prediction was verified because it clearly agrees with the evidence obtained. Therefore, the five-step method for predicting redox reactions is judged to be acceptable for this reaction.

The purpose was achieved only to a limited extent. One test is not sufficient to provide a reliable evaluation. Many other reactions should be predicted and then tested in further investigations.

**Practice**

(Page 579)

26. (a)  
\[
\begin{align*}
\text{Zn}(s) + \text{H}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{H}_2\text{O}(l) \\
\text{SRA} \quad \text{RA} \quad \text{RA} \quad \text{RA} \\
2 \text{H}^+(aq) + 2 \text{e}^- \rightarrow \text{H}_2(g) \\
\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2 \text{e}^- \\
2 \text{H}^+(aq) + \text{Zn}(s) \rightarrow \text{H}_2(g) + \text{Zn}^{2+}(aq)
\end{align*}
\]

If a flame is inserted into a sample of the gas produced and a “pop” sound is heard, then hydrogen gas is likely present. *Other diagnostic tests include pre- and post-tests for pH, mass measurement of zinc, and a flame test for Zn$^{2+}(aq)$.*

(b)  
\[
\begin{align*}
\text{Au}(s) + \text{H}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{H}_2\text{O}(l) \\
\text{RA} \quad \text{RA} \quad \text{RA} \quad \text{SRA} \\
2 [2 \text{H}^+(aq) + 2 \text{e}^- \rightarrow \text{H}_2(g)] \\
2 \text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4 \text{H}^+(aq) + 4 \text{e}^- \\
2 \text{H}_2\text{O}(l) \rightarrow 2 \text{H}_2(g) + \text{O}_2(g)
\end{align*}
\]

(c)  
\[
\begin{align*}
\text{H}^+(aq) + \text{NO}_3^-(aq) + \text{Cu}(s) \rightarrow \text{H}_2\text{O}(l) \\
\text{SRA} \quad \text{RA} \\
2 \text{NO}_3^-(aq) + 4 \text{H}^+(aq) + 2 \text{e}^- \rightarrow \text{N}_2\text{O}_4(g) + 2 \text{H}_2\text{O}(l) \\
\text{Cu}(s) \rightarrow \text{Cu}^{2+}(aq) + 2 \text{e}^- \\
2 \text{NO}_3^-(aq) + 4 \text{H}^+(aq) + \text{Cu}(s) \rightarrow \text{N}_2\text{O}_4(g) + 2 \text{H}_2\text{O}(l) + \text{Cu}^{2+}(aq)
\end{align*}
\]

If the colour of the final solution near the copper surface is blue, then it is likely that copper(II) ions are produced. *If a brown gas is produced during the course of the reaction, then nitrogen dioxide (from the decomposition of N$_2$O$_4$(g)) is likely produced.* Other diagnostic tests include pre- and post-tests for pH, mass measurement of copper, and a flame test for Cu$^{2+}(aq)$.
27. (a) \[2 \text{Fe(s)} + 3 \text{CuSO}_4(aq) \rightarrow 3 \text{Cu(s)} + 2 \text{Fe}^{2+}(aq)\] (assuming common ion, Fe\(^{3+}\)(aq))
\[2 \text{Fe(s)} + 3 \text{Cu}^{2+}(aq) \rightarrow \text{Cu(s)} + 2 \text{Fe}^{3+}(aq)\] (net ionic)
(b) \[
\begin{align*}
\text{SO} & \text{OA} \\
\text{Fe(s)} & \text{Cu}^{2+}(aq) & \text{SO}_4^{2-}(aq) & \text{H}_2\text{O(l)} \\
\text{SRA} & \text{RA} & \text{RA} & \text{RA}
\end{align*}
\]
\[\text{Cu}^{2+}(aq) + 2 e^- \rightarrow \text{Cu(s)}\]
\[\text{Fe(s)} \rightarrow \text{Fe}^{2+}(aq) + 2 e^-\]
\[\text{Fe(s)} + \text{Cu}^{2+}(aq) \text{ spont.} \rightarrow \text{Cu(s)} + \text{Fe}^{2+}(aq)\]
(c) Both predictions cannot be correct; either iron(III) ions are formed or iron(II). The redox table and rules are more likely to be correct because they are based on extensive observations of relative strengths of oxidizing and reducing agents supported by the idea of electron transfer. The single displacement rule is a generalization that has been useful in the past, but does not have the same empirical basis or any theoretical justification.
(d) Qualitatively, one could ensure complete reaction of the blue copper(II) solution and then observe the colour of the solution. If the iron(III) ion is produced, the solution should be light yellow, but if the iron(II) ion is produced, the solution should be light green.
Quantitatively, one could measure the mass of iron reacted and the mass of copper metal produced. Convert the masses to chemical amounts and calculate the ratio of the chemical amount of copper produced to the chemical amount of iron reacted. If the ratio is 3:2, then iron(III) is produced, but if the ratio is 1:1, then iron(II) is produced.

28. **Problem**
What are the products of the reaction of tin(II) chloride with an ammonium dichromate solution acidified with hydrochloric acid?

**Prediction**
According to redox concepts and the table of relative strengths of oxidizing and reducing agents, the products of the reaction are water, chromium(III) ions, and tin(IV) ions. The reasoning is as shown.
\[
\begin{align*}
\text{OA} & \text{OA} \\
\text{Sn}^{2+}(aq) & \text{Cl}^{-}(aq) & \text{H}_2\text{O(l)} & \text{NH}_4^{+}(aq) & \text{Cr}_2\text{O}_7^{2-}(aq) & \text{H}^{+}(aq) \\
\text{SRA} & \text{RA} & \text{RA} & \text{RA} & \text{RA} & \text{RA}
\end{align*}
\]
\[\text{Cr}_2\text{O}_7^{2-}(aq) + 14 \text{H}^{+}(aq) + 6 e^- \rightarrow 2 \text{Cr}^{3+}(aq) + 7 \text{H}_2\text{O(l)}\]
\[3 \text{[Sn}^{2+}(aq) \rightarrow \text{Sn}^{4+}(aq) + 2 e^-]\]
\[\text{Cr}_2\text{O}_7^{2-}(aq) + 14 \text{H}^{+}(aq) + 3 \text{Sn}^{2+}(aq) \rightarrow \text{spont.} 2 \text{Cr}^{3+}(aq) + 7 \text{H}_2\text{O(l)} + 3 \text{Sn}^{4+}(aq)\]

**Design**
An excess of tin(II) chloride is added to the acidic ammonium dichromate solution. If the colour of the mixture is observed before and after the reaction, and the colour changes from orange to green, then chromium(III) ions are likely produced.
Avoid contact and wear protective equipment. Tin(II) chloride is corrosive and harmful if swallowed. Ammonium dichromate is a strong oxidizer and a carcinogen. Both substances should be disposed of into labelled waste containers and not into the sink.

29. Although aluminium is a reactive metal it does not corrode readily. When aluminium is exposed to air, a microscopically thin, impermeable layer of aluminium oxide immediately forms on the surface, protecting it from further oxidation. The small pits that develop in aluminium cooking pots could be due to the reaction of aluminium with hydrogen ions, where the metal is exposed by scratching during stirring. The process is slow because the protective layer of aluminium oxide soon re-forms.
[Note: The presence of chloride ions (from salt) accelerates the pitting process, because chloride ions replace oxygen in the protective coating and reduce its protective integrity.]
30. Because an excess of acid is present, \( \text{O}_2(g) \) and \( \text{H}^+(aq) \) will remain as the strongest oxidizing agent throughout all of the reactions.

\[
\text{O}_2(g) + 4 \text{H}^+(aq) + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O(l)}
\]

Oxygen in an acidic solution will spontaneously oxidize (in order) iodide ions, iron(II) ions, and lastly iodine (a product of the iodide oxidation).

\[
\begin{align*}
2 \text{I}^-(aq) & \rightarrow \text{I}_2(s) + 2 \text{e}^- \\
\text{Fe}^{2+}(aq) & \rightarrow \text{Fe}^{3+}(aq) + \text{e}^- \\
\text{I}_2(s) + 6 \text{H}_2\text{O(l)} & \rightarrow 2 \text{IO}_3^-(aq) + 12 \text{H}^+(aq) + 10 \text{e}^- 
\end{align*}
\]

The spontaneous reactions are:

\[
\begin{align*}
\text{O}_2(g) + 4 \text{H}^+(aq) + 4 \text{I}^-(aq) & \rightarrow 2 \text{H}_2\text{O(l)} + 2 \text{I}_2(s) \\
\text{O}_2(g) + 4 \text{H}^+(aq) + 4 \text{Fe}^{2+}(aq) & \rightarrow 2 \text{H}_2\text{O(l)} + 4 \text{Fe}^{3+}(aq) \\
5 \text{O}_2(g) + 2 \text{I}_2(s) + 2 \text{H}_2\text{O(l)} & \rightarrow 4 \text{IO}_3^-(aq) + 4 \text{H}^+(aq)
\end{align*}
\]

### Practice

(Page 581)

31. (a) \[
4 \left[ \text{Zn(s)} \rightarrow \text{Zn}^{2+}(aq) + 2 \text{e}^- \right] \\
\text{NO}_3^-(aq) + 10 \text{H}^+(aq) + 8 \text{e}^- \rightarrow \text{NH}_4^+(aq) + 3 \text{H}_2\text{O(l)}
\]

\[
4 \text{Zn(s)} + \text{NO}_3^-(aq) + 10 \text{H}^+(aq) \rightarrow 4 \text{Zn}^{2+}(aq) + \text{NH}_4^+(aq) + 3 \text{H}_2\text{O(l)}
\]

(b) \[
\frac{\text{Cl}_2(aq) + 2 \text{e}^- \rightarrow 2 \text{Cl}^-(aq)}{\text{SO}_2(g) + 2 \text{H}_2\text{O(l)} \rightarrow \text{SO}_4^{2-}(aq) + 4 \text{H}^+(aq) + 2 \text{e}^-}
\]

\[
\text{Cl}_2(aq) + \text{SO}_2(g) + 2 \text{H}_2\text{O(l)} \rightarrow 2 \text{Cl}^-(aq) + \text{SO}_4^{2-}(aq) + 4 \text{H}^+(aq)
\]

32. (a) \[
2 \left[ \text{MnO}_4^-(aq) + 2 \text{H}_2\text{O(l)} + 3 \text{e}^- \rightarrow \text{MnO}_2(s) + 4 \text{OH}^-(aq) \right]
\]

\[
3 \left[ 2 \text{I}^-(aq) \rightarrow \text{I}_2(s) + 2 \text{e}^- \right]
\]

\[
2 \text{MnO}_4^-(aq) + 4 \text{H}_2\text{O(l)} + 6 \text{I}^-(aq) \rightarrow 2 \text{MnO}_2(s) + 8 \text{OH}^-(aq) + 3 \text{I}_2(s)
\]

(b) \[
\frac{3 \left[ \text{CN}^-(aq) + 2 \text{OH}^-(aq) \rightarrow \text{CNO}^-(aq) + \text{H}_2\text{O(l)} + 2 \text{e}^- \right]}{\text{IO}_3^-(aq) + 3 \text{H}_2\text{O(l)} + 6 \text{e}^- \rightarrow \text{I}^-(aq) + 6 \text{OH}^-(aq)}
\]

\[
3 \text{CN}^-(aq) + \text{IO}_3^-(aq) + 3 \text{H}_2\text{O(l)} \rightarrow 3 \text{CNO}^-(aq) + \text{I}^-(aq)
\]

(c) \[
\frac{2 \left[ \text{OCl}^-(aq) + \text{H}_2\text{O(l)} + 2 \text{e}^- \rightarrow \text{Cl}^-(aq) + 2 \text{OH}^-(aq) \right]}{3 \left[ \text{OCl}^-(aq) + 4 \text{OH}^-(aq) \rightarrow \text{ClO}_3^-(aq) + 2 \text{H}_2\text{O(l)} + 4 \text{e}^- \right]}
\]

\[
3 \text{OCl}^-(aq) + 2 \text{Cl}^-(aq) + \text{ClO}_3^-(aq)
\]

33. [Note that MnO_4^- changes to Mn^{2+}, H_2S changes to S, and the rest are spectator ions.]

\[
2 \left[ \text{MnO}_4^-(aq) + 8 \text{H}^+(aq) + 5 \text{e}^- \rightarrow \text{Mn}^{2+}(aq) + 4 \text{H}_2\text{O(l)} \right]
\]

\[
5 \left[ \text{H}_2\text{S(aq)} \rightarrow \text{S(s)} + 2 \text{H}^+(aq) + 2 \text{e}^- \right]
\]

\[
2 \text{MnO}_4^-(aq) + 6 \text{H}^+(aq) + 5 \text{H}_2\text{S(aq)} \rightarrow 2 \text{Mn}^{2+}(aq) + 5 \text{S(s)} + 8 \text{H}_2\text{O(l)}
\]

Adding spectator ions:

\[
2 \text{KMnO}_4(aq) + 5 \text{H}_2\text{S(aq)} + 3 \text{H}_2\text{SO}_4(aq) \rightarrow \text{K}_2\text{SO}_4(aq) + 2 \text{MnSO}_4(aq) + 5 \text{S(s)} + 8 \text{H}_2\text{O(l)}
\]

### Section 13.2 Questions

(Page 582)

1. The key idea used to explain a redox reaction is the transfer of electrons between chemical entities.
2. According to modern theory, oxidation refers to the process of losing electrons, while oxidizing agent refers to the chemical entity that causes the oxidation of another entity by removing electrons from it.

3. According to modern theory, reduction refers to the process of gaining electrons, while reducing agent refers to the chemical entity that causes the reduction of another entity by donating electrons to it.

4. (a) $\text{Cu}^{2+} (aq) + 2 \text{e}^- \rightarrow \text{Cu} (s)$ (reduction)  
   $\text{Co} (s) \rightarrow \text{Co}^{2+} (aq) + 2 \text{e}^- \quad \text{(oxidation)}$

   (b) $\text{Zn}^{2+} (aq) + 2 \text{e}^- \rightarrow \text{Zn} (s)$ (reduction)  
   $\text{Cd} (s) \rightarrow \text{Cd}^{2+} (aq) + 2 \text{e}^- \quad \text{(oxidation)}$

   (c) $\text{Br}_2 (l) + 2 \text{e}^- \rightarrow 2 \text{Br}^- (aq)$ (reduction)  
   $2 \text{I}^- (aq) \rightarrow \text{I}_2 (s) + 2 \text{e}^- \quad \text{(oxidation)}$

5. (a) spontaneous  
   (b) nonspontaneous  
   (c) spontaneous

6. $\text{SOA} \quad \text{TI}^+ (aq) + \text{e}^- \rightleftharpoons \text{TI} (s)$  
   $\text{In}^{3+} (aq) + 3 \text{e}^- \rightleftharpoons \text{In} (s)$  
   $\text{Ga}^{3+} (aq) + 3 \text{e}^- \rightleftharpoons \text{Ga} (s)$  
   $\text{Al}^{3+} (aq) + 3 \text{e}^- \rightleftharpoons \text{Al} (s)$  
   SRA

7. $\text{Pt}^{4+} (aq) + 4 \text{e}^- \rightleftharpoons \text{Pt} (s)$  
   $2 \text{H}^+ (aq) + 2 \text{e}^- \rightleftharpoons \text{H}_2 (g)$  
   $\text{Ni}^{2+} (aq) + 2 \text{e}^- \rightleftharpoons \text{Ni} (s)$  
   $\text{Ce}^{3+} (aq) + 3 \text{e}^- \rightleftharpoons \text{Ce} (s)$  
   $\text{Sr}^{2+} (aq) + 2 \text{e}^- \rightleftharpoons \text{Sr} (s)$

8. Design: Each of the three metals is placed separately in solutions of the other three metal ions. The reaction is allowed to proceed, and observations are made. While zinc ions can be safely disposed of down the drain with copious amounts of water, cadmium (in solid as well as ionic form) and mercury (solid and ionic form) must be deposited in appropriate containers for safe disposal.

9. (a) $\text{SOA} \quad \text{OA} \quad \text{OA}$
   \begin{align*}
   &\text{Ni}^{2+} (aq), \quad \text{NO}_3^-(aq), \quad \text{Fe}^{2+} (aq), \quad \text{Cl}^-(aq), \quad \text{H}_2\text{O}(l) \\
   &\text{SRA} \quad \text{RA} \quad \text{RA} \quad \text{RA}
   \end{align*}

   \[2 \text{Fe}^{2+} (aq) + \text{Ni}^{2+} (aq) \rightarrow 2 \text{Fe}^{3+} (aq) + \text{Ni} (s)\]

   If the solutions are mixed, and the colour does not change from blue-green to a pale yellowish, and no solid forms, then the reaction is nonspontaneous.

   (b) $\text{SOA} \quad \text{OA} \quad \text{OA}$
   \begin{align*}
   &\text{O}_2 (g), \quad \text{H}_2\text{O}(l), \quad \text{Ag}(s), \quad \text{Na}^+(aq), \quad \text{I}^-(aq), \\
   &\text{RA} \quad \text{RA} \quad \text{SRA} \quad \text{RA}
   \end{align*}

   \[4 \text{Ag(s) + 4 I}^-(aq) \rightarrow 4 \text{AgI(s)} + 4 \text{OH}^- (aq)\]

   If the final solution is tested with litmus paper, and the litmus paper turns blue, then the solution is basic and hydroxide ions have formed.
K\(^+\)(aq), Cr\(_2\)O\(_7\)^{2-}(aq), H\(^+\)(aq), Na\(^+\)(aq), I\(^-\)(aq), H\(_2\)O(l)

\[
\begin{array}{c}
\text{Cr}_2\text{O}_7^{2-}(aq) + 14 H^+(aq) + 6 e^- & \rightarrow 2 Cr^{3+}(aq) + 7 H_2O(l) \\
3 [2 I(aq) \rightarrow I_2(s) + 2 e^-] & \\
\text{Cr}_2\text{O}_7^{2-}(aq) + 14 H^+(aq) + 6 I^-(aq) & \rightarrow 2 Cr^{3+}(aq) + 7 H_2O(l) + 3 I_2(s)
\end{array}
\]

If a few millilitres of hexane are added to the final solution, and the colour of the solvent layer after shaking appears purple, then iodine is likely present.

10. (a) The solution will be stable because no spontaneous reaction occurs according to the table of relative strengths of oxidizing and reducing agents and the spontaneity rule.

(b) The solution will not be stable because a spontaneous reaction occurs according to the table of relative strengths of oxidizing and reducing agents and the spontaneity rule.

11. Cl\(_2\)(g) + 2 e\(^-\) \rightarrow 2 Cl\(^-\)(aq)

\[
\begin{array}{c}
\text{Cl}_2(g) + 2 I^-(aq) \rightarrow 2 Cl^-(aq) + I_2(s)
\end{array}
\]

12. O\(_2\)(g) + 4 H\(^+\)(aq) + 4 e\(^-\) \rightarrow 2 H\(_2\)O(l)

\[
\begin{array}{c}
O_2(g) + 4 H^+(aq) + 2 Fe(s) \rightarrow 2 H_2O(l) + 2 Fe^{2+}(aq)
\end{array}
\]

13. Disproportionation occurs when an entity is simultaneously oxidized and reduced.

\[
\begin{array}{c}
\text{Sn}^{2+}(aq) + 2 e^- \rightarrow \text{Sn}(s) \\
\text{Sn}^{2+}(aq) \rightarrow \text{Sn}^{4+}(aq) + 2 e^-
\end{array}
\]

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

The oxidizing agents that will spontaneously react, in order of decreasing strength, are:

Ag\(^+\)(aq), Fe\(^{3+}\)(aq), Cu\(^{2+}\)(aq).

Ag\(^+\)(aq) + e\(^-\) \rightarrow Ag(s)

Fe\(^{3+}\)(aq) + e\(^-\) \rightarrow Fe\(^{2+}\)(aq)

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

The balanced redox chemical equations that are spontaneous are as follows:

\[
\begin{array}{c}
Co(s) + 2 Ag^+(aq) \rightarrow Co^{2+}(aq) + 2 Ag (s) \\
Co(s) + 2 Fe^{3+}(aq) \rightarrow Co^{2+}(aq) + 2 Fe^{2+}(aq)
\end{array}
\]

\text{OA} \hspace{1cm} \text{SOA} \hspace{1cm} \text{OA} \hspace{1cm} \text{OA} \hspace{1cm} \text{OA}

\begin{array}{c}
\text{H}^+(aq) \quad \text{Sn}^{2+}(aq) \quad \text{Cl}^-(aq) \quad \text{H}_2\text{O}(l) \\
\text{SRA} \quad \text{RA} \quad \text{RA} \quad \text{RA}
\end{array}

\text{OA} \hspace{1cm} \text{OA} \hspace{1cm} \text{OA} \hspace{1cm} \text{OA} \hspace{1cm} \text{OA}

\begin{array}{c}
\text{Cu}^{2+}(aq) \quad \text{NO}_3^-(aq) \quad \text{H}_2\text{O}(l) \quad \text{Sn}(s) \\
\text{RA} \quad \text{SRA}
\end{array}
15.  \[2 \text{Mn}^{2+} + 4 \text{H}_2\text{O} \rightarrow 5 \text{MnO}_4^- + 8 \text{H}^+ + 5 \text{e}^-\]  
\[5 \text{HBI}_3 + 5 \text{H}^+ + 2 \text{e}^- \rightarrow 5 \text{Bi}^{3+} + 3 \text{H}_2\text{O} \]

\[2 \text{Mn}^{2+} + 5 \text{HBI}_3 + 9 \text{H}^+ \rightarrow 5 \text{Bi}^{3+} + 2 \text{MnO}_4^- + 7 \text{H}_2\text{O} \]

16. (a)  \[2 \text{Cr(OH)}_3 + 5 \text{OH}^- \rightarrow \text{CrO}_4^{2-} + 4 \text{H}_2\text{O} + 3 \text{e}^-\]  
\[2 \text{Cr(OH)}_3 + 6 \text{H}_2\text{O} + 6 \text{OH}^- \rightarrow 2 \text{CrO}_4^{2-} + 5 \text{H}_2\text{O} + \text{I}_2\]  

(b)  \[\text{Ag}_2\text{O} + \text{H}_2\text{O} + 2 \text{e}^- \rightarrow 2 \text{Ag} + 2 \text{OH}^-\]  
\[\text{CH}_2\text{O} + 3 \text{OH}^- \rightarrow 2 \text{CHO}_2^- + 2 \text{H}_2\text{O} + 2 \text{e}^-\]  
\[\text{Ag}_2\text{O} + \text{OH}^- + \text{CH}_2\text{O} \rightarrow 2 \text{Ag} + 2 \text{CHO}_2^- + \text{H}_2\text{O}\]  

17. (a)  \[2 \text{Al} + 4 \text{OH}^- \rightarrow \text{Al(OH)}_4^- + 3 \text{e}^-\]  
\[3 \text{H}_2\text{O} + 6 \text{e}^- \rightarrow 2 \text{H}_2 + 2 \text{OH}^-\]  
\[2 \text{Al} + 2 \text{OH}^- + 6 \text{H}_2\text{O} \rightarrow 2 \text{Al(OH)}_4^- + 3 \text{H}_2\]  

(b)  This technology provides heat and force (of the gas produced) to help displace blockages in drains. Therefore it is an inexpensive, efficient, effective and simple solution to a common problem.

(c)  Sodium hydroxide is very caustic and should be handled with gloves and eye protection. Flushing aluminium compounds down the drain has an impact on the environment because aluminium ions are toxic to fish and other aquatic organisms.

18. WHMIS Symbol Household Symbol

Extension

19. The term antioxidant suggests preventing oxidation. Antioxidants deactivate free radicals, which usually come in the form of oxygen molecules. Often, the products of oxidation can be carcinogenic. Examples of antioxidants are vitamins (A, C, and E), selenium, and carotenoids. The ability of antioxidants to prevent cancer and other diseases has not been established empirically, yet they continue to be marketed under this guise. Some synthetic antioxidant supplements have been found to increase free radical formation.
20. Researched Information on Chlorophyll

- the structure of the main form of chlorophyll

![Diagram of chlorophyll molecule]

- its general role in electron transfer reactions
  As chlorophyll absorbs light energy, one of its electrons moves from a lower to a higher energy state. A series of electron-transfer steps follows, ending in an electron being transferred to carbon dioxide. Once carbon dioxide has the extra electron, it can participate in further reactions, resulting in the formation of glucose.

- close relatives containing iron and cobalt
  The part of chlorophyll that surrounds the magnesium is called porphyrin. Other compounds containing porphyrin (but with different metal ions) are hemoglobin (containing iron) and vitamin B12 (containing cobalt).

- a technological application inspired by the chlorophyll molecule
  As many porphyrins are brightly coloured, they have been used as natural dyes. Similar synthetic dyes have been manufactured and can be used medically to kill certain undesirable cells when activated by light.

13.3 OXIDATION STATES

Practice

(Page 585)

1. (a) +4
   (b) +7
   (c) +6
   (d) +6
   (e) –1
   (f) –1

2. (a) +1
   (b) +2
   (c) +4
   (d) –3
   (e) –2
   (f) +5
   (g) 0
   (h) –3