9.3 Predicting Redox Reactions

Hydrogen sulfide is a toxic, colourless gas with a distinctive "rotten eggs" smell. Hydrogen sulfide is produced by naturally occurring bacteria that digest dissolved sulfate ions in the water. Redox reactions within these bacteria reduce sulfate into sulfur-containing compounds such as sulfites and hydrogen sulfide. These ions and compounds also dissolve in water. Many Canadian homes rely on groundwater as their source of drinking water. Normally, the concentrations of hydrogen sulfide in groundwater are too low to pose a health hazard. However, low levels of hydrogen sulfide are a nuisance because they give drinking water a foul odour and taste (**Figure 1**). CAREER LINK

Figure 1 The presence of hydrogen sulfide gas gives water an unpleasant odour. The dissolved gas evaporates quickly so tests should be carried out "on site."

One way to remove hydrogen sulfide from drinking water is to oxidize it into a less offensive substance. How do you choose the appropriate oxidizing agent? Conducting trial-and-error chemical tests is one option. The hydrogen ions in acids are known to oxidize certain metals. Yet, tests show that hydrogen ions do not oxidize hydrogen sulfide. Chlorine bleach, on the other hand, does react. Chlorine bleach is a solution of sodium hypochlorite, NaClO(aq). Bubbling hydrogen sulfide gas through chlorine bleach produces solid sulfur and chloride ions. Using this information and the skills you learned in Section 9.2, we can write the following half-reaction equations:

Reduction: $2\ H^+(aq) + ClO^-(aq) + 2\ e^- \rightarrow Cl^-(aq) + H_2O(l)$
Oxidation: $H_2S(g) \rightarrow S(s) + 2\ H^+(aq) + 2\ e^-$

Combining these equations gives the net ionic equation for the reaction:

$$H_2S(g) + ClO^-(aq) \rightarrow Cl^-(aq) + S(s) + H_2O(l)$$

The success of hypochlorite at oxidizing hydrogen sulfide indicates that the hypochlorite ion is a stronger oxidizing agent than hydrochloric acid. Could we have predicted the results without actually mixing the reactants? Can we predict if a redox reaction will occur and what products will arise? The answer is yes. Patterns in experimental data from many different redox reactions allow us to make generalizations that can be used to make such predictions.

Relative Strengths of Oxidizing and Reducing Agents

Suppose we place samples of silver, lead, nickel, and magnesium metal in solutions of silver, lead(II), nickel(II), and magnesium ions. Some of the metal–ion combinations react immediately, but others do not react at all. All the reactions that occur are redox reactions in which the metal ion oxidizes the metal. The general pattern for these reactions is

$$\underset{\text{(oxidizing agent)}}{A^{2+}(aq)} + \underset{\text{(reducing agent)}}{M(s)} \rightarrow M^{2+}(aq) + A(s)$$

Table 1 ranks the results of these combinations according to the reactivity of each metal with each aqueous metal ion tested. This ranking may look familiar: it reflects the reactivity series of metals that you learned about in earlier Chemistry courses.

Table 1 Reactivity of Metals with Aqueous Metal Ions

Metal	Mg(s)	Ni(s)	Pb(s)	Ag(s)
Reacted with	$Ag^+(aq)$, $Ni^{2+}(aq)$, $Pb^{2+}(aq)$	$Ag^+(aq)$, $Pb^{2+}(aq)$	$Ag^+(aq)$	none
Reactivity order	most reactive metal →			least reactive metal

Magnesium metal reacts with all the other metal ions. This evidence suggests that magnesium has the greatest tendency to lose electrons, which implies that its nucleus has the weakest hold on its electrons. Recall that a reducing agent is a substance that loses electrons in a redox reaction. Therefore, magnesium metal is the strongest reducing agent—the element that is most readily oxidized—in this set of metals.

Silver metal does not react with any of the metal ions, so it has the least tendency to lose electrons. Silver metal is the weakest reducing agent in this set. If we write the half-reaction equations for these metals in order from strongest to weakest reducing agents, we get the following list:

Strongest reducing agent (SRA): $Mg(s) \rightarrow Mg^{2+}(aq) + 2\,e^-$

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

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

Weakest reducing agent: $Ag(s) \rightarrow Ag^{+}(aq) + e^-$

In Table 1, we observed the reaction from the perspective of the reducing agent (the metal). We can also view the reaction from the perspective of the oxidizing agent (the ion). In **Table 2**, we use the results from our set of reactions to rank the reactivities of the aqueous metal ions with the different metals.

Table 2 Reactivity of Aqueous Metal Ions with Different Metals

Ion in solution	$Ag^{+}(aq)$	$Pb^{2+}(aq)$	$Ni^{2+}(aq)$	$Mg^{2+}(aq)$
Reacted with	Mg(s), Ni(s), Pb(s)	Mg(s), Ni(s)	Mg(s)	none
Reactivity order	most reactive			least reactive

Recall that the oxidizing agent in a redox reaction gains electrons. According to the evidence in Table 2, silver ions had the greatest tendency to gain electrons in this set of reactions. Therefore, the silver ion is the strongest oxidizing agent in this group. Since the magnesium ion did not react with any metal in this set, it is the weakest oxidizing agent. If we now write the half-reaction equations for the metal ions in order from strongest to weakest oxidizing agent, we get

Strongest oxidizing agent (SOA): $Ag^{+}(aq) + e^- \rightarrow Ag(s)$

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

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

Weakest oxidizing agent: $Mg^{2+}(aq) + 2\,e^- \rightarrow Mg(s)$

Since our two sets of reactions are opposites of each other, we can combine them to produce **Table 3**. The double arrows in these equations indicate that these equations can be read from left to right (as reductions) or from right to left (as oxidations). By convention, tables of half-reactions are written from left to right as reductions, with the electrons on the left. The strongest oxidizing agent (SOA) is found on the top left side of Table 3 and the strongest reducing agent (SRA) appears on the bottom right side.

Table 3 Relative Strength of Oxidizing and Reducing Agents

	SOA $Ag^{+}(aq) + e^- \rightleftharpoons Ag(s)$	
Decreasing strength of oxidizing agents	$Pb^{2+}(aq) + 2\,e^- \rightleftharpoons Pb(s)$	Decreasing strength of reducing agents
	$Ni^{2+}(aq) + 2\,e^- \rightleftharpoons Ni(s)$	
	$Mg^{2+}(aq) + 2\,e^- \rightleftharpoons Mg(s)$ **SRA**	

Based on a great deal of empirical evidence (observations) of redox reactions, scientists have organized the metals into an ordered list. You have encountered this list as the reactivity series of metals. When the reduction half-reactions are included, the arrangement is called a redox (or standard reduction potentials) table. Reactions

LEARNING **TIP**

Metals and Metal Ions

Elemental metals always lose electrons in redox reactions to form cations (positively charged ions). As a result, metals are reducing agents. Conversely, metal cations usually gain electrons to form metal atoms. Hence, metal ions are usually oxidizing agents. There are some exceptions. For example, the iron(II) ion can be both oxidized and reduced:

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

Reduction: $Fe^{2+}(aq) + 2\,e^- \rightarrow Fe(s)$

UNIT TASK BOOKMARK

How could you use information about predicting the spontaneity of a redox reaction as you work on the Unit Task on page 684?

occur spontaneously only when the oxidizing agent is combined with a reducing agent that is below it on the redox table (**Figure 2**). For example, for the half-reactions shown in Table 3, silver ions were observed to react spontaneously with magnesium metal. Notice how a line from the oxidizing agent, $Ag^+(aq)$, to the reducing agent, Mg(s), forms a downward diagonal (left to right) on the redox table in Figure 2. Any combination of an oxidizing agent with a reducing agent that is above it in Table 3 does not react spontaneously. For example, when $Mg^{2+}(aq)$ is the oxidizing agent and Ag(s) is the reducing agent, the line joining them would form an upward diagonal (left to right) on the redox table. We can therefore predict that no reaction occurs.

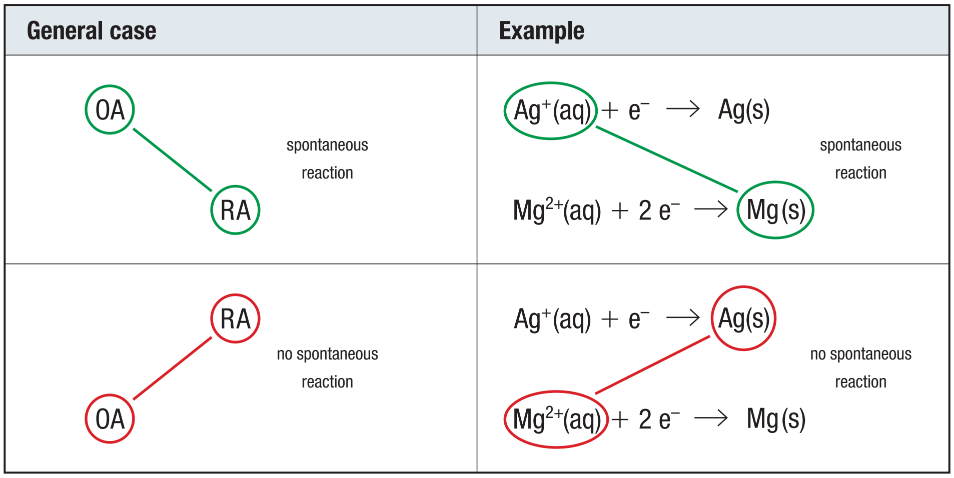

Figure 2 When an oxidizing agent (OA) is above the reducing agent (RA) on the redox table, a spontaneous reaction occurs. But when an oxidizing agent is below the reducing agent, no spontaneous reaction occurs. As an example, when $Ag^+(aq)$ is the oxidizing agent and Mg(s) is the reducing agent, a reaction occurs.

An Expanded Table of Oxidizing and Reducing Agents

redox table a table listing standard reduction potentials of common oxidizing agents and reducing agents in order from strongest to weakest; standard reduction potentials table

The collection of empirical evidence on various combinations of oxidizing and reducing agents has led to the development of an expanded redox table (Table 1 in Appendix B7). This **redox table**, also called a standard reduction potentials table, lists some of the most common oxidizing and reducing agents. In all the redox tables in this book, the oxidizing agents are listed on the left-hand side of the table with the strongest oxidizing agent at the top. Consequently, the reducing agents are on the right side with the strongest reducing agent at the bottom.

We can use a redox table to predict whether a reaction will occur spontaneously between an oxidizing agent and a reducing agent, using the method illustrated in Figure 2. However, such predictions do not guarantee that a reaction will occur. Other factors, such as the nature of the reactants, temperature, or the presence of a catalyst, also affect whether a reaction will occur. Tutorial 1 outlines how to use a redox table to predict which combinations of oxidizing and reducing agents react spontaneously.

Tutorial 1 Predicting Redox Reactions Using a Redox Table

In this tutorial, you will use Table 1 in Appendix B7 to predict redox reactions and write chemical equations for those that are likely to occur. Since many redox reactions occur in solution, hydrogen ions, hydroxide ions, and water may also participate in the reaction.

The following steps outline a general problem-solving approach:

1. List all of the entities present.
2. Use Table 1 to identify the strongest oxidizing agent in the reaction mixture. Oxidizing agents (OA) are located on the left side of the table.

3. Use Table 1 to identify the strongest reducing agent in the reaction mixture. Reducing agents are located on the right side and the strongest reducing agents are toward the bottom of the table.
4. Predict whether the reaction will occur spontaneously.
5. Write the half-reaction equations.
6. Balance the electrons in each equation, if necessary.
7. Combine the half-reaction equations to give the overall reaction equation.

Sample Problem 1 Predicting the Occurrence of a Redox Reaction

Does a redox reaction occur when copper metal is placed into a solution of nitric acid? If it does, write a balanced equation for the reaction.

Solution

Step 1. List all of the entities present.

Since nitric acid is a strong acid, it completely ionizes. You must therefore list hydrogen ions and nitrate ions instead of $HNO_3(aq)$. Therefore, the reaction mixture contains

$H^+(aq)$, $NO_3^-(aq)$, $H_2O(l)$, and $Cu(s)$.

Step 2. Use Table 1 to identify the strongest oxidizing agent in the reaction mixture.

The only equations relating to chemicals in the reaction mixture as oxidizing agents are

$NO_3^-(aq) + 2\,H^+(aq) + e^- \rightarrow NO_2(g) + H_2O(l) \quad E°_r = +0.80\text{ V}$

$2\,H^+(aq) + 2\,e^- \rightarrow H_2(g) \quad E°_r = 0.00\text{ V}$

$2\,H_2O(l) + 2\,e^- \rightarrow H_2(g) + 2\,OH^-(aq) \quad E°_r = -0.83\text{ V}$

Since $NO_3^-(aq)$ occurs highest on the table, $NO_3^-(aq)$ is the strongest oxidizing agent.

Step 3. Use Table 1 to identify the strongest reducing agent in the reaction mixture.

The only equations relating to chemicals in the reaction mixture as reducing agents are

$O_2(g) + 2\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2O(l) \quad E°_r = +0.70\text{ V}$

$Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s) \quad E°_r = +0.34\text{ V}$

Since copper occurs lower on the table, copper is the stronger reducing agent.

Step 4. Predict whether the reaction will occur spontaneously.

The relative positions of NO_3^- and Cu do form a downward diagonal to the right on Table 1. Therefore, you can predict that the reaction will occur spontaneously.

Step 5. Write the half-reaction equations.

Remember to reverse the direction of the oxidation reaction.

Reduction: $NO_3^-(aq) + 2\,H^+(aq) + e^- \rightarrow NO_2(g) + H_2O(l)$

Oxidation: $Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^-$

Step 6. Balance the electrons.

The number of electrons gained and lost must be equal. You can accomplish this by multiplying one or both equations by an integer. In this case, you must multiply the reduction half-reaction by 2.

Reduction: $NO_3^-(aq) + 2\,H^+(aq) + e^- \rightarrow NO_2(g) + H_2O(l)$

$2\,NO_3^-(aq) + 4\,H^+(aq) + 2\,e^- \rightarrow 2\,NO_2(g) + 2\,H_2O(l)$

Oxidation: $Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^-$

LEARNING TIP

Half-Reactions Involving Water

There are several half-reaction equations that include water listed in Table 1 in Appendix B7.

For example,

$SO_4^{2-}(aq) + H_2O(l) + 2\,e^- \rightarrow SO_3^{2-}(aq) + 2\,OH^-(aq) \quad E°_r = -0.93\text{ V}$

The only equation in which only water is reduced is

$2\,H_2O(l) + 2\,e^- \rightarrow H_2(g) + 2\,OH^-(aq) \quad E°_r = -0.83\text{ V}$

The only equation in which only water is oxidized is

$O_2(g) + 2\,H^+(aq) + 4e^- \rightarrow 2\,H_2O(l) \quad E°_r = +0.70\text{ V}$

Investigation 9.3.1

Spontaneity of Redox Reactions (page 625)

In this investigation, you will determine experimentally whether a redox table accurately predicts the spontaneity of a redox reaction.

Step 7. Combine the half-reaction equations to give the overall reaction equation.

Reduction: $2\ NO_3^-(aq) + 4\ H^+(aq) + 2\ e^- \rightarrow 2\ NO_2(g) + 2\ H_2O(l)$

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

$$Cu(s) + 2\ NO_3^-(aq) + 4\ H^+(aq) + \cancel{2\ e^-} \rightarrow Cu^{2+}(aq) + \cancel{2\ e^-} + 2\ NO_2(g) + 2\ H_2O(l)$$

The reaction is spontaneous and the balanced equation is

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

Practice

1. Identify the half-reactions in each of the following equations, and use them to determine if the reaction is spontaneous: T/I
   (a) $Co(s) + Cu(NO_3)_2(aq) \rightarrow Cu(s) + Co(NO_3)_2(aq)$
   (b) $Br_2(l) + 2\ KI(aq) \rightarrow I_2(s) + 2\ KBr(aq)$
   (c) $Ni(s) + Zn(NO_3)_2(aq) \rightarrow Zn(s) + Ni(NO_3)_2(aq)$
2. Determine whether copper pipe would react spontaneously with hydrochloric acid. If it would, determine the balanced equation for the reaction. T/I A
3. Does a redox reaction occur when solid calcium is placed into water? If it does, write the half-reaction equations, state whether the calcium is oxidized or reduced, and write a balanced chemical equation for the reaction. T/I
4. Does a redox reaction occur when a solution of potassium permanganate, $KMnO_4(aq)$, is poured into a solution of chromium(II) sulfate, $CrSO_4(aq)$, under acidic conditions? If it does, write the half-reaction equations and a balanced equation for the reaction. T/I

Research This

Which Bleach Is Best?

Skills: Questioning, Researching, Evaluating, Communicating, Identifying Alternatives, Defending a Decision — SKILLS HANDBOOK A5

Chlorine bleach (a solution of sodium hypochlorite, NaClO(aq)) has many applications as an oxidizing agent (**Figure 3**). As you saw in the opening of this section, chlorine is used to remove hydrogen sulfide from groundwater. It also removes stains by oxidizing coloured substances to substances without colour. However, because of its reactivity with acids and bases, many workplaces have banned the use of chlorine bleach. CAREER LINK

1. Research the hazards of accidentally mixing chlorine bleach with acids or bases.
2. Research at least five uses of chlorine bleach.
3. Many workplaces now have replaced chlorine bleach with hydrogen peroxide as their primary bleach. Research the use of hydrogen peroxide as a replacement for chlorine bleach.

A. Create a table to compare the pros and cons of chlorine bleach and hydrogen peroxide bleach. C

B. What else should also be considered, besides safety, when approving a product for use in the workplace? K/U A

C. For which uses is chlorine bleach the better choice and for which is hydrogen peroxide better? Give reasons. K/U A

Figure 3 Containers of chlorine bleach that are sold to consumers have HHPS on their labels, which warn of the danger of mixing the contents with other chemicals.

WEB LINK

9.3 Review

Summary

- A relative ranking of the strength of oxidizing and reducing agents has been developed from empirical evidence.
- Redox tables list the strongest oxidizing agent in the top left corner of the table and the strongest reducing agent in the bottom right corner of the table.
- Redox tables can be used to predict whether a redox reaction occurs spontaneously.

Questions

1. Rank the strength of the following as oxidizing agents, going from strongest to weakest: $Hg^{2+}(aq)$, $Au^{3+}(aq)$, $Cu^{2+}(aq)$, $Sn^{2+}(aq)$ K/U
2. Identify a substance that would react spontaneously with chromium ions, $Cr^{2+}(aq)$, to form solid chromium metal. T/I
3. Identify which of the following equations represent(s) spontaneous reactions: T/I
   (a) $Cu(s) + Br_2(l) \rightarrow Cu^{2+}(aq) + 2\,Br^-(aq)$
   (b) $2\,Al(s) + 3\,Pb^{2+}(aq) \rightarrow 2\,Al^{3+}(aq) + 3\,Pb(s)$
   (c) $Na^+(aq) + Cr^{2+}(aq) \rightarrow Cr^{3+}(aq) + Na(s)$
4. A student places a piece of solid iron into a solution containing copper(II) ions. T/I
   (a) Write the chemical equation for the reaction that produces iron(II) ions and solid copper.
   (b) Predict whether the reaction is spontaneous.
5. A geology lab technician mixes a solution of potassium permanganate with a solution of iron(II) sulfate, under acidic conditions. T/I
   (a) List all the possible oxidizing agents in the mixture and identify which is the strongest.
   (b) List all the possible reducing agents in the mixture and identify which is the strongest.
6. A chemist's pure gold ring accidentally falls into a solution of nitric acid, $HNO_3(aq)$. T/I
   (a) Write the two half-reaction equations for the reaction of nitric acid and gold forming a solution of $Au^{3+}(aq)$.
   (b) Use the data in a redox table to predict whether nitric acid will damage the ring.
7. Use Table 1 in Appendix B7 to answer the following questions: T/I
   (a) Predict which combinations of the following metals and metal ions react spontaneously:
   Metals: Cu(s), Au(s), Zn(s), Co(s)
   Metal ions: $Cu^+(aq)$, $Au^{3+}(aq)$, $Zn^{2+}(aq)$, $Co^{2+}(aq)$
   (b) Identify the strongest reducing agent and oxidizing agent in (a). Justify your answer.
8. Based on an investigation of four metals and solutions of four metal ions, a student summarized the observations in **Table 4**. T/I

Table 4 Observations

Ion solution	$Ba^{2+}(aq)$	$Fe^{2+}(aq)$	$Pb^{2+}(aq)$	$Cu^{2+}(aq)$
Reacts with the following metals:	none	Ba(s)	Ba(s), Fe(s)	Ba(s), Fe(s), Pb(s)

   (a) List the metal ions from strongest to weakest oxidizing agent.
   (b) Write the balanced equation for the redox reaction of copper(II) ions with solid lead.
   (c) From these observations, what can you determine about the strongest reducing agent?
   (d) Gold is a weaker reducing agent than copper. Predict how gold metal would react with each of the ion solutions in Table 4.
9. **Figure 4** shows what happens when copper is added to different concentrations of hydrochloric acid and nitric acid. T/I A

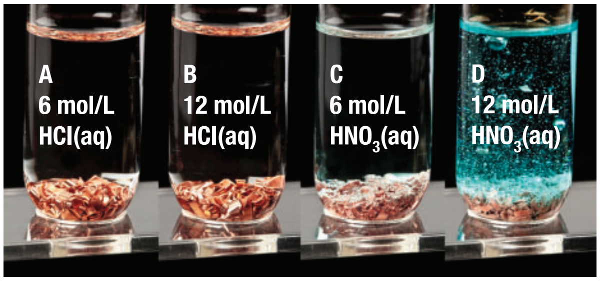

Figure 4 Identical pieces of copper metal are placed in hydrochloric acid and nitric acid. A reaction is only observed in test tube D. After a few minutes the solution in this test tube turns blue, the characteristic colour of the copper(II) ion.

   (a) Use the Table 1 in Appendix B7 to justify the difference between the reactivity of copper in hydrochloric acid and its reactivity in nitric acid.
   (b) Suggest an explanation for the difference in reactivity in the two nitric acid solutions.