

Sample Problem 22-4

Identify the oxidizing agent and the reducing agent in each equation in Sample Problem 22-3.

1. **ANALYZE** Plan a problem-solving strategy.

a.-c. Use the following facts to solve the problem: The substance oxidized in a reaction is the reducing agent, and the substance reduced is the oxidizing agent.

2. **SOLVE** Apply the problem-solving strategy.

- a. Chlorine is reduced, so Cl_2 is the oxidizing agent. Bromide (in HBr) is oxidized, so Br^- is the reducing agent.
- b. Carbon is oxidized, so C is the reducing agent. Oxygen is reduced, so O_2 is the oxidizing agent.
- c. Zinc is oxidized, so Zn is the reducing agent. Manganese (in MnO_2) is reduced, so Mn^{4+} is the oxidizing agent.

3. **EVALUATE** Do the results make sense?

It makes sense that what is oxidized in a chemical reaction is the reducing agent because it loses electrons—it becomes the agent by which the atom that is reduced gains electrons. Conversely, it makes sense that what is reduced in a chemical reaction is the oxidizing agent because it gains electrons—it is the agent by which the atom that is oxidized loses electrons. These facts were correctly applied in solving the problem.

Practice Problem

12. Identify the oxidizing agent and the reducing agent in each equation in Practice Problem 11.

section review 22.2

- 13. a. What is the oxidation number of nitrogen in nitrogen gas (N_2)? Explain.
- b. How would you determine the oxidation numbers of the elements in a compound?
- c. How is charge used to assign oxidation numbers to the elements in a polyatomic ion?
- 14. How are oxidation numbers determined and used?
- 15. Use the changes in oxidation numbers to identify which atoms are oxidized and which are reduced in each reaction.
 - a. $2\text{Na}(s) + \text{Cl}_2(g) \longrightarrow 2\text{NaCl}(s)$
 - b. $2\text{HNO}_3(aq) + 6\text{HI}(aq) \longrightarrow 2\text{NO}(g) + 3\text{I}_2(s) + 4\text{H}_2\text{O}(l)$
 - c. $3\text{H}_2\text{S}(aq) + 2\text{HNO}_3(aq) \longrightarrow 3\text{S}(s) + 2\text{NO}(g) + 4\text{H}_2\text{O}(l)$
 - d. $2\text{PbSO}_4(s) + 2\text{H}_2\text{O}(l) \longrightarrow \text{Pb}(s) + \text{PbO}_2(s) + 2\text{H}_2\text{SO}_4(aq)$
- 16. Identify the oxidizing agent and the reducing agent in each reaction in Problem 15.



Chem ASAP! Assessment 22.2 Check your understanding of the important ideas and concepts in Section 22.2.

BALANCING REDOX EQUATIONS

**objectives**

- Use the oxidation-number-change method to balance redox equations
- Break a redox equation into oxidation and reduction half-reactions, and then use the half-reaction method to balance the equation

key terms

- oxidation-number-change method
- half-reactions
- half-reaction method

The unattainable, but long pursued, goal of alchemists was to change common metals, such as lead or copper, into gold. One tool that the alchemists employed in their quest was aqua regia, which means "royal water." Aqua regia is a mixture of concentrated hydrochloric (HCl) and nitric (HNO₃) acids that is capable of dissolving gold. When gold is added to aqua regia, oxidation and reduction reactions produce gaseous nitrogen monoxide (NO) and stable AuCl₄⁻ ions. How can a balanced chemical equation for this redox reaction be written?

Identifying Redox Reactions

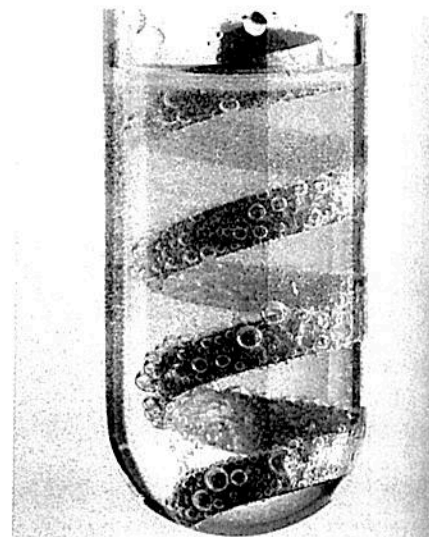
In general, all chemical reactions can be assigned to one of two classes. In oxidation-reduction (redox) reactions, electrons are transferred from one reacting species to another. In all other reactions, no electron transfer occurs. For example, double-replacement reactions and acid-base reactions are not redox reactions. Many single-replacement reactions, combination reactions, decomposition reactions, and combustion reactions, however, are redox reactions. Can you write a balanced equation for each reaction shown in Figure 22.15?

Figure 22.15

(a) Potassium metal reacts violently with water to produce hydrogen gas (which ignites) and potassium hydroxide. Is this a redox reaction? Explain. **(b)** Zinc metal reacts vigorously with hydrochloric acid to produce hydrogen gas and zinc chloride. Is this a redox reaction? Explain.

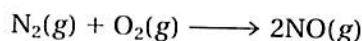


(a)



(b)

You can determine whether a reaction is a redox reaction by using oxidation numbers to keep track of electrons. If the oxidation number of an element in a reacting species changes, then that element has undergone either oxidation or reduction. Therefore the reaction as a whole must be a redox reaction. Consider this example: During an electrical storm, oxygen molecules and nitrogen molecules in the air react to form nitrogen(II) oxide. The equation for the reaction is



Is this a redox reaction? How can you tell? Does the oxidation number of either reacting species change? If so, what is that change?

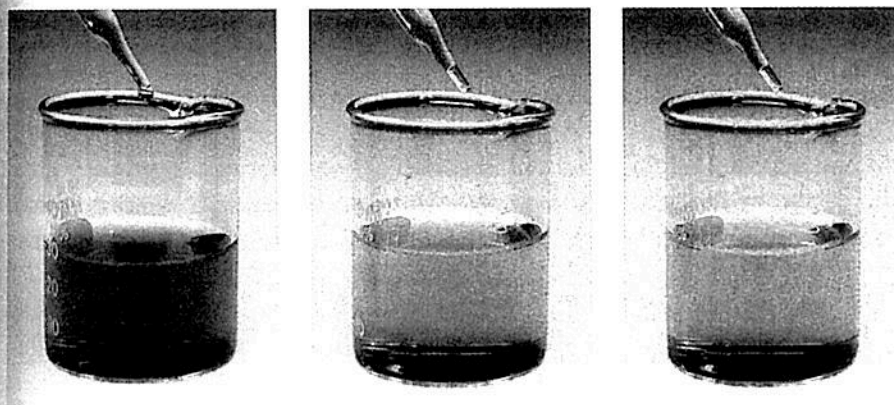
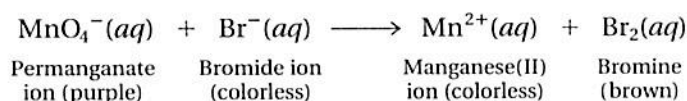


Figure 22.16

A color change can signal a redox reaction. When a colorless solution containing bromide ions is added to a solution containing permanganate ions, the distinctive purple color of the permanganate ion (MnO_4^-) is replaced by the pale brown color of bromine. What is the oxidation-number change in manganese and bromine?

Various other changes often signal that an oxidation–reduction reaction has taken place. One such change is a change in color. For example, look at Figure 22.16. When a colorless aqueous solution of bromide ions (Br^-) is added to a purple aqueous solution of permanganate ions (MnO_4^-), the solution changes from purple to pale brown. As the following unbalanced equation shows, bromide ions are oxidized to bromine, and permanganate ions are reduced to manganese(II) ions.



Color changes can do more than signal that a redox reaction has taken place. They can help obtain quantitative information about concentrations in redox reactions. The titration of reducing agents and oxidizing agents is similar to the titration of acids and bases, which you learned about in Section 21.1. For example, the titration of the reducing agent oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) with a solution of unknown concentration of the oxidizing agent potassium permanganate (KMnO_4) is illustrated in Figure 22.17. To obtain a quantitative result in such a titration, a balanced equation of the redox reaction is required. A known mass of colorless oxalic acid, the reducing

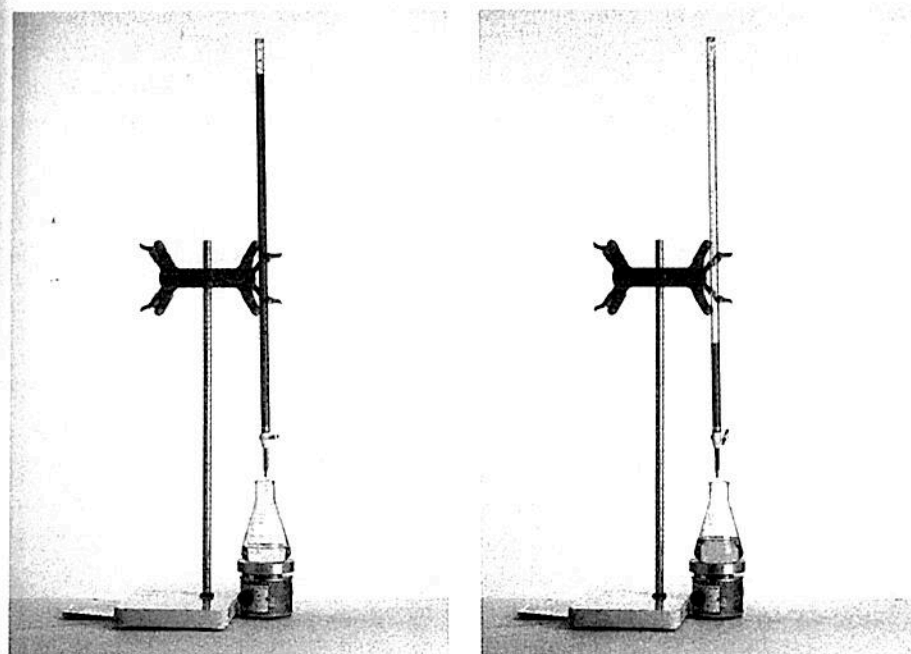
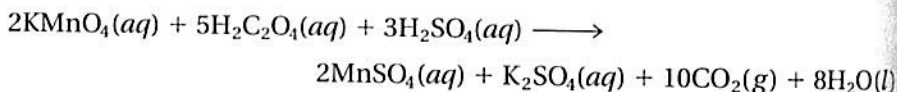


Figure 22.17

In this redox titration, the oxidizing agent in the buret (purple aqueous potassium permanganate) serves as the indicator. A known mass of the reducing agent, colorless oxalic acid, is dissolved in dilute sulfuric acid in the flask. As permanganate is added slowly to the contents of the flask, it immediately loses its purple color (left). When all the oxalic acid in the flask is oxidized, the next drop of permanganate remains unreacted, and the solution in the flask turns light purple (right). That is the end point of the redox titration.

agent, is dissolved in dilute sulfuric acid in the reaction flask. The concentration of the purple potassium permanganate solution can be calculated from the volume added to reach the end point, which is reached when all the oxalic acid is oxidized and the next drop of purple KMnO_4 remains unreacted. The net ionic equation for the reaction can be written. From this equation, the oxidation-number changes for the oxidized and reduced species can be determined. The full balanced equation for the reaction is



Sample Problem 22-5

Use the change in oxidation number to identify whether each reaction is a redox reaction or a reaction of some other type. If a reaction is a redox reaction, identify the element reduced, the element oxidized, the reducing agent, and the oxidizing agent.

- $\text{N}_2\text{O}_4(g) \longrightarrow 2\text{NO}_2(g)$
- $\text{Cl}_2(g) + 2\text{NaBr}(aq) \longrightarrow 2\text{NaCl}(aq) + \text{Br}_2(l)$
- $\text{PbCl}_2(aq) + \text{K}_2\text{SO}_4(aq) \longrightarrow 2\text{KCl}(aq) + \text{PbSO}_4(s)$
- $2\text{NaOH}(aq) + \text{H}_2\text{SO}_4(aq) \longrightarrow \text{Na}_2\text{SO}_4(aq) + 2\text{H}_2\text{O}(l)$

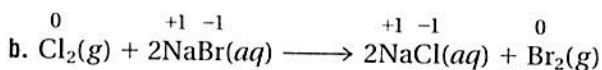
1. ANALYZE Plan a problem-solving strategy.

a.–d. Use the rules to assign oxidation numbers to each element. Note whether there are any changes in oxidation number. If there are, the reaction is a redox reaction. The element with an oxidation number that increases is oxidized and is the reducing agent. The element with an oxidation number that decreases is reduced and is the oxidizing agent.

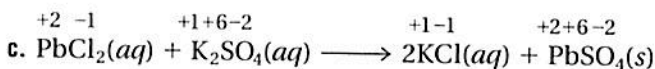
2. SOLVE Apply the problem-solving strategy.



This is a decomposition reaction. Neither oxygen nor nitrogen changes in oxidation number. Therefore the reaction is not a redox reaction.



This is a single-replacement reaction. The chlorine is reduced. The bromide ion is oxidized. This is a redox reaction. Chlorine is the oxidizing agent; bromide ion is the reducing agent.



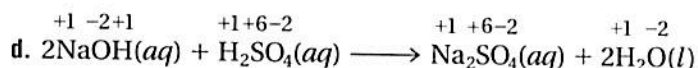
This is a double-replacement reaction. None of the elements changes in oxidation number. This is not a redox reaction.

Practice Problems

17. Identify which of the following are oxidation–reduction reactions. If a reaction is a redox reaction, name the element oxidized and the element reduced.

- $\text{BaCl}_2(aq) + 2\text{KIO}_3(aq) \longrightarrow \text{Ba}(\text{IO}_3)_2(s) + 2\text{KCl}(aq)$
- $\text{H}_2\text{CO}_3(aq) \longrightarrow \text{H}_2\text{O}(l) + \text{CO}_2(g)$
- $\text{Mg}(s) + \text{Br}_2(l) \longrightarrow \text{MgBr}_2(s)$
- $\text{NH}_4\text{NO}_2(s) \longrightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(l)$
- $2\text{KClO}_3(s) \longrightarrow 2\text{KCl}(s) + 3\text{O}_2(g)$

Sample Problem 22-5 (cont.)



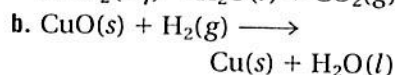
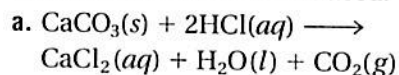
This is an acid–base (neutralization) reaction. None of the elements changes in oxidation number. This is not a redox reaction.

3. **EVALUATE** Do the results make sense?

Only in redox reactions do the oxidation numbers of reactants change as products form. Only reaction **b.** represents a redox reaction. In **b.**, each chlorine atom (Cl) accepts an electron from a bromide ion (Br^-). The chlorine molecule is reduced to two chloride ions (Cl^-); therefore, it is the oxidizing agent in the reaction. That makes sense because chlorine is more electronegative than bromine (see Table 14.2) and thus more apt to gain electrons. Because the bromide ions are oxidized to molecular bromine (Br_2), the bromide ions are the reducing agent.

Practice Problems (cont.)

18. Identify which of the following are oxidation–reduction reactions. If a reaction is a redox reaction, name the element oxidized and the element reduced.



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Problem-Solving 18

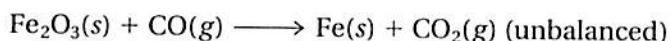
Solve Problem 18 with the help of an interactive guided tutorial.



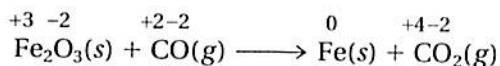
As you know, the ability to write a correctly balanced equation that accurately represents what happens in a chemical reaction is essential to chemists and chemical engineers. Many oxidation–reduction reactions are too complex to be balanced by trial and error. Fortunately, two systematic methods are available. These methods, described below, are based on the fact that the total number of electrons gained in reduction must equal the total number of electrons lost in oxidation. One method uses oxidation-number changes, and the other uses half-reactions.

Using Oxidation-Number Changes

In the **oxidation-number-change method**, a redox equation is balanced by comparing the increases and decreases in oxidation numbers. To use this method, start with a skeleton equation for the redox reaction. The reduction of iron ore is used here as an example.



Step 1. Assign oxidation numbers to all the atoms in the equation. Write the numbers above the atoms.



Note that the oxidation number is stated as the charge per atom. So although the total positive charge of Fe ions in Fe_2O_3 is 6+, the oxidation number of each Fe ion is +3.

Step 2. Identify which atoms are oxidized and which are reduced. In this reaction, iron decreases in oxidation number from +3 to 0, a change of –3. Therefore iron is reduced. Carbon increases in oxidation number from +2 to +4, a change of +2. Thus carbon is oxidized. Oxygen does not change in oxidation number.

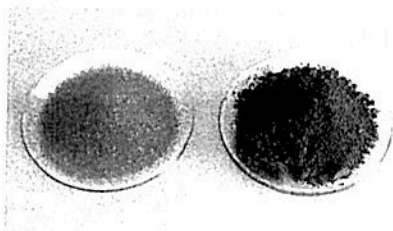
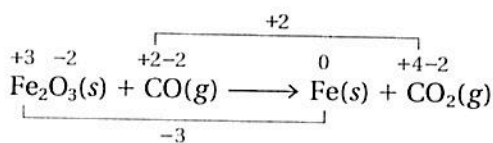


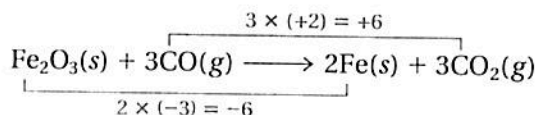
Figure 22.18

Potassium dichromate, shown on the left, is an orange crystalline substance. It reacts with water and sulfur to form chromium(III) oxide, the green compound shown on the right. What are the other products?

Step 3. Use one bracketing line to connect the atoms that undergo oxidation and another such line to connect those that undergo reduction. Write the oxidation-number change at the midpoint of each line.



Step 4. Make the total increase in oxidation number equal to the total decrease in oxidation number by using appropriate coefficients. In this example, the oxidation-number increase should be multiplied by 3 and the oxidation-number decrease should be multiplied by 2, which gives an increase of +6 and a decrease of -6. This can be done in the equation by placing the coefficient 2 in front of Fe on the right side and the coefficient 3 in front of both CO and CO₂. The formula Fe₂O₃ does not need a coefficient because the formula already indicates 2 Fe.

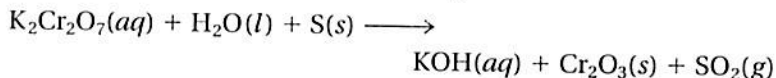


Step 5. Finally, make sure that the equation is balanced for both atoms and charge. If necessary, the remainder of the equation can be balanced by inspection.



Sample Problem 22-6

Balance this redox equation by using the oxidation-number-change method. Samples of the initial and final chromium-containing compounds for this reaction are shown in **Figure 22.18**.

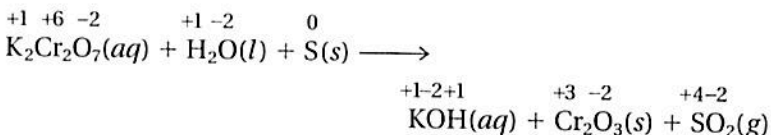


1. **ANALYZE** Plan a problem-solving strategy.

Apply the five steps of the oxidation-number-change method to balance the equation.

2. **SOLVE** Apply the problem-solving strategy.

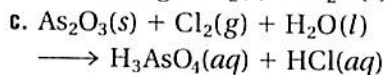
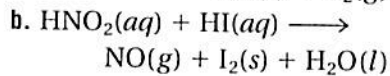
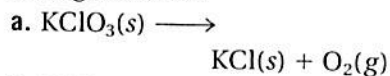
Step 1. Assign oxidation numbers.



Step 2. Identify which atoms are oxidized and which atoms are reduced. Cr is reduced because its oxidation number decreases, while S is oxidized because its oxidation number increases.

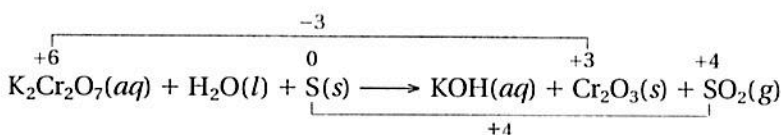
Practice Problems

19. Balance each redox equation using the oxidation-number-change method.

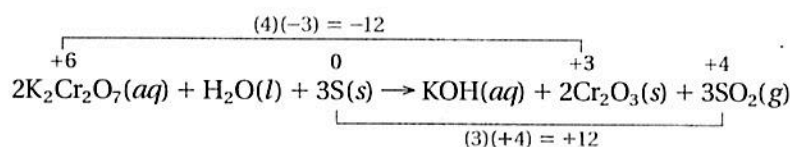


Sample Problem 22-6 (cont.)

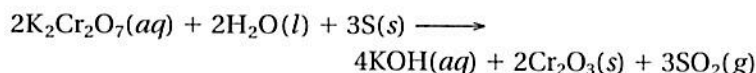
Step 3. Connect the atoms that change in oxidation number. Indicate the signs and magnitudes of the changes.



Step 4. Balance the increase and decrease in oxidation numbers. Four chromium atoms must be reduced ($4 \times (-3) = -12$ decrease) for each three sulfur atoms that are oxidized ($3 \times (+4) = +12$ increase). Put the coefficient 3 in front of S and SO₂ and the coefficient 2 in front of K₂Cr₂O₇ and Cr₂O₃.



Step 5. Check the equation and finish balancing by inspection if necessary. The coefficient 4 in front of KOH balances potassium. The coefficient 2 in front of H₂O balances hydrogen and oxygen. The final equation is

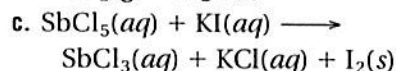
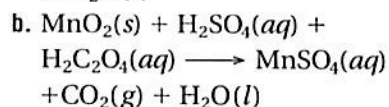
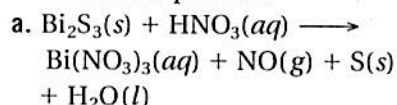


3. EVALUATE Does the result make sense?

Inspection reveals that the equation is correctly balanced.

Practice Problems (cont.)

20. Use the oxidation-number-change method to balance each redox equation.



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Problem-Solving 20

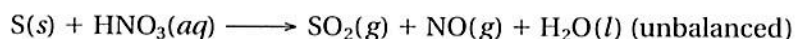
Solve Problem 20 with the help of an interactive guided tutorial.



Using Half-Reactions

You have just learned about the oxidation-number-change method, one of two methods often used to balance redox equations. A second method involves the use of **half-reactions**, or equations showing either the reduction or the oxidation of a species in an oxidation-reduction reaction. The **half-reaction method** is used to balance redox equations by balancing the oxidation and reduction half-reactions. The procedure is different, but the outcome is the same as with the oxidation-number-change method. The half-reaction method is particularly useful in balancing equations for ionic reactions.

The oxidation of sulfur by nitric acid in aqueous solution is one example of a redox reaction that can be balanced by the half-reaction method.



The following steps show how to balance this equation using the half-reaction method.

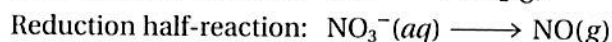
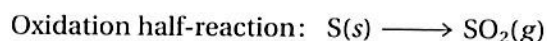
Step 1. Write the unbalanced equation in ionic form. In this case, only HNO₃ is ionized. The products are covalent compounds.



Table 22.2

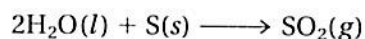
Oxidation Numbers of Sulfur in Different Compounds	
Compound	Oxidation Number
H ₂ SO ₄	+6
SO ₃	+6
H ₂ SO ₃	+4
SO ₂	+4
Na ₂ S ₂ O ₃	+2
SCl ₂	+2
S ₂ Cl ₂	+1
S	0
H ₂ S	-2

Step 2. Write separate half-reactions for the oxidation and reduction processes. As you can see from Table 22.2, which shows the oxidation numbers of sulfur in various compounds, sulfur is oxidized in this reaction because its oxidation number increases from 0 to 4. Nitrogen is reduced because its oxidation number decreases from +5 to +2.

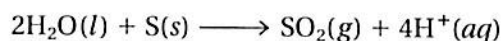


Step 3. Balance the atoms in the half-reactions.

- a. *Balance the oxidation half-reaction.* This reaction takes place in acid solution. In such cases, H₂O and H⁺ can be used to balance oxygen and hydrogen as needed. Sulfur is already balanced in the half-reaction. Add two molecules of H₂O on the left to balance the oxygen in the half-reaction.

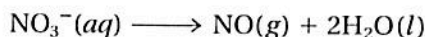


Oxygen is now balanced, but four hydrogen ions (4H⁺) must be added to the right to balance the hydrogen on the left.



This half-reaction is now balanced in terms of atoms. Note that it is not balanced for charge. The charges will be balanced in Step 4.

- b. *Balance the reduction half-reaction.* Nitrogen is already balanced. Add two molecules of H₂O on the right to balance the oxygen.



Oxygen is balanced, but four hydrogen ions (4H⁺) must be added to the left to balance hydrogen.

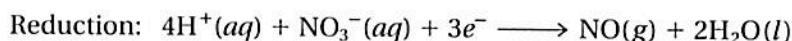


This half-reaction is now balanced in terms of atoms, but not for charge.

Step 4. Add sufficient electrons to one side of each half-reaction to balance the charges. Four electrons are needed on the right side in the oxidation half-reaction.

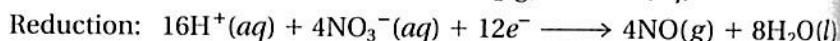


Three electrons are needed on the left side in the reduction half-reaction.

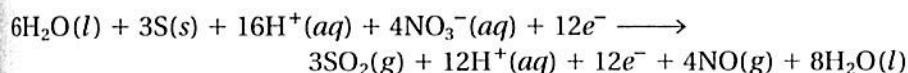


Each half-reaction is now balanced with respect to both atoms and charge.

Step 5. Multiply each half-reaction by an appropriate number to make the numbers of electrons equal in both. In any redox reaction, the number of electrons lost in oxidation must equal the number of electrons gained in reduction. In this case, the oxidation half-reaction is multiplied by 3 and the reduction half-reaction is multiplied by 4. Therefore the number of electrons lost in oxidation and the number of electrons gained in reduction both equal 12.



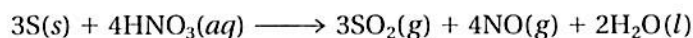
Step 6. Add the half-reactions to show an overall equation. Then subtract terms that appear on both sides of the equation. The equation is



Subtracting terms that are on both the left and right produces

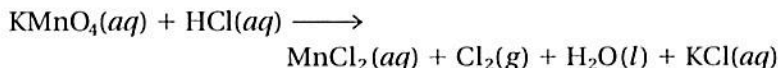


Step 7. Add the spectator ions and balance the equation. Recall from Chapter 8 that like the spectators at an athletic event, spectator ions are present but do not participate in or change during a reaction. Because none of the ions in the reactants appear in the products, there are no spectator ions in this particular example. The balanced equation above is thus correct. However, it can be written to show the HNO_3 as un-ionized.



Sample Problem 22-7

Use the half-reaction method to balance the equation for the following redox reaction.

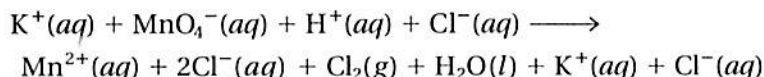


1. ANALYZE Plan a problem-solving strategy.

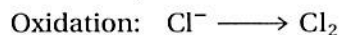
Follow the seven steps of the half-reaction method to balance the equation.

2. SOLVE Apply the problem-solving strategy.

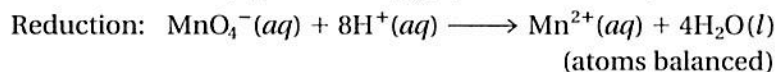
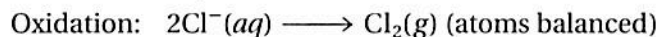
Step 1. Write the unbalanced equation in ionic form.



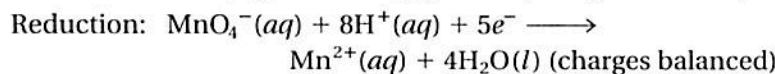
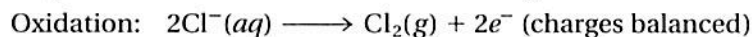
Step 2. Write separate half-reactions for the oxidation and reduction processes. Use oxidation numbers to determine the oxidation process and the reduction process.



Step 3. Balance the atoms in the half-reactions. Because the solution is acidic, use H_2O and H^+ to balance the oxygen and hydrogen if necessary. (If the solution were basic, H_2O and OH^- would be used.)



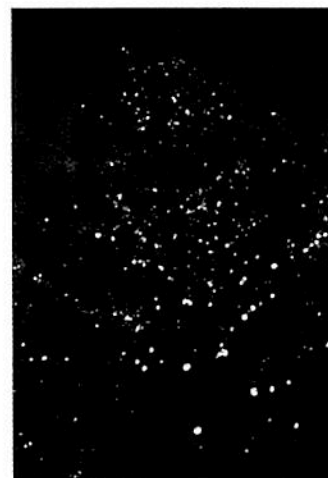
Step 4. Add electrons to balance the charges.



Link TO BIOLOGY

Bioluminescence

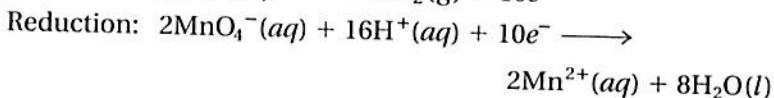
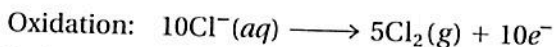
Some organisms produce light by means of oxidation–reduction reactions in a process known as bioluminescence. Light is given off when one of a class of



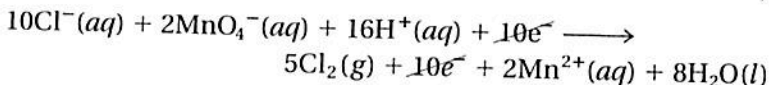
compounds called luciferins is oxidized by combination with oxygen. A product of these reactions is energy in the form of light. Bioluminescence serves different functions in different organisms. For example, fireflies use bioluminescence to attract mates, while some squids release a glowing cloud of “ink” to confuse and escape from their predators.

Sample Problem 22-7 (cont.)

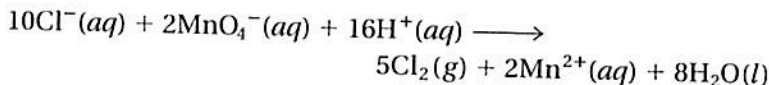
Step 5. Make the numbers of electrons equal. Multiply the oxidation half-reaction by 5 and the reduction half-reaction by 2, so that 10 electrons are lost in oxidation and 10 electrons are gained in reduction.



Step 6. Add the half-reactions and subtract terms that appear on both sides of the equation.

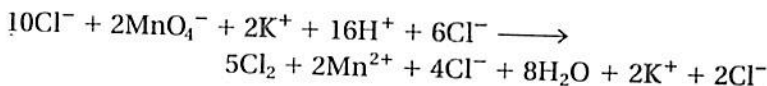


The equation, after subtracting terms that appear on both sides, is

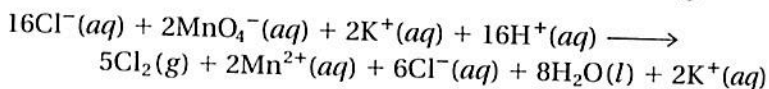


Step 7. Add the spectator ions and balance the equation. In the example, the permanganate ions come from KMnO_4 . The chloride ions come from HCl . K^+ ions, which appear on both sides of the unbalanced ionic equation in Step 1, come from KMnO_4 and must equal the number of MnO_4^- ions (given the formula, KMnO_4). The K^+ ions are spectator ions as are some of the Cl^- ions from the HCl —namely, those that are still present as products combined with Mn^{2+} and K^+ .

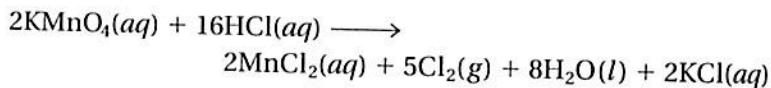
The number of spectator Cl^- ions combined with Mn^{2+} must be twice the number of Mn^{2+} ions (given the formula, MnCl_2). The number of spectator Cl^- ions combined with K^+ must equal the number of K^+ ions (given the formula, KCl). The spectator ions are now added to the equation and balanced. Spectator ions are shown in blue.



Summing spectator and nonspectator Cl^- on each side gives



The equation is balanced for atoms and charge. To show it balanced for the substances given in the question (rather than for ions), rewrite it as

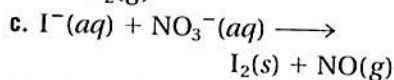
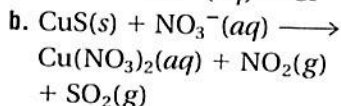
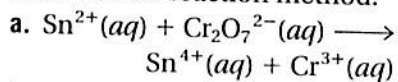


3. EVALUATE Does the result make sense?

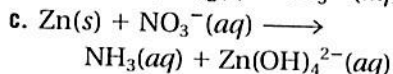
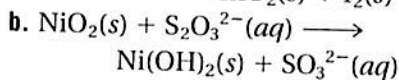
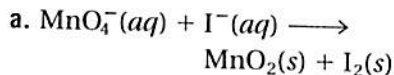
The equation is correctly balanced for atoms and charge.

Practice Problems

21. Write balanced ionic equations for the following reactions, which occur in acid solution. Use the half-reaction method.



22. The following reactions take place in basic solution. Use the half-reaction method to write a balanced ionic equation for each.



Chem ASAP!

Problem-Solving 22

Solve Problem 22 with the help of an interactive guided tutorial.



MINI LAB



Bleach It! Oxidize the Color Away

PURPOSE

To test the effect of oxidizing agents on stains and dyes.

MATERIALS

- spot plate
- medicine dropper
- water
- colorimeter (optional)

Oxidizing agents

- liquid chlorine bleach (5% (m/v) sodium hypochlorite)
- powder bleach
- oxalic acid solution (1% (m/v))
- sodium thiosulfate solution (hypo) (0.2M $\text{Na}_2\text{S}_2\text{O}_3$)

- hydrogen peroxide (3% (v/v) H_2O_2)

Samples

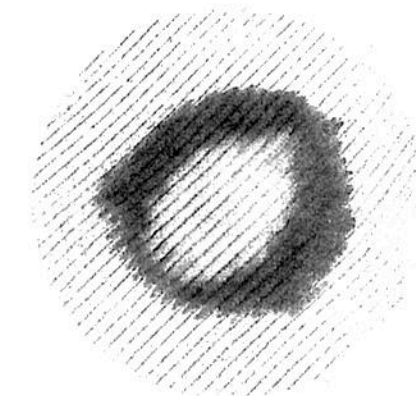
- iodine solution (1% I_2 in 2% (m/v) KI)
- potassium permanganate solution (0.05M KMnO_4)
- grape juice
- rusty water
- piece of colored fabric
- colored flower petals
- grass stain on piece of white fabric

PROCEDURE



Sensor version available in the Probeware Lab Manual.

1. Place samples on a spot plate. Use 4 drops of each liquid or a small piece of each solid.
2. Describe the color and appearance of each sample in Step 1.
3. Add a few drops of the first oxidizing agent to each sample.



4. Describe any immediate change in appearance and any further change after 15 minutes.
5. Repeat Steps 2–4 with each oxidizing agent.

ANALYSIS AND CONCLUSIONS

1. Make a grid and record your observations.
2. Compare the oxidizing power of the oxidizing agents.
3. How do you know that chemical changes have occurred?

section review 22.3

23. Balance each redox equation, using the oxidation-number-change method.
 - a. $\text{ClO}_3^-(aq) + \text{I}^-(aq) \longrightarrow \text{Cl}^-(aq) + \text{I}_2(aq)$ [acid solution]
 - b. $\text{C}_2\text{O}_4^{2-}(aq) + \text{MnO}_4^-(aq) \longrightarrow \text{Mn}^{2+}(aq) + \text{CO}_2(g)$ [acid solution]
 - c. $\text{Br}_2(l) + \text{SO}_2(g) \longrightarrow \text{Br}^-(aq) + \text{SO}_4^{2-}(aq)$ [acid solution]
24. Use the half-reaction method to write a balanced ionic equation for each reaction.
 - a. $\text{MnO}_4^-(aq) + \text{ClO}_2^-(aq) \longrightarrow \text{MnO}_2(s) + \text{ClO}_4^-(aq)$ [basic solution]
 - b. $\text{Cr}^{3+}(aq) + \text{ClO}^-(aq) \longrightarrow \text{CrO}_4^{2-}(aq) + \text{Cl}^-(aq)$ [basic solution]
 - c. $\text{Mn}^{3+}(aq) + \text{I}^-(aq) \longrightarrow \text{Mn}^{2+}(aq) + \text{IO}_3^-(aq)$ [basic solution]



Chem ASAP! Assessment 22.3 Check your understanding of the important ideas and concepts in Section 22.3.