Oxidation Reduction Reactions

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Printed: August 11, 2016

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CHAPTER 1 Oxidation Reduction Reactions

CHAPTER OUTLINE

Have you ever seen someone breathe into a device like this? This person is breathing into a breathalyzer, a device used to detect the presence of ethanol (an alcohol) in a person's breath. One version of the breathalyzer works by measuring the color change of a solution of the dichromate ion. In the presence of ethanol, the solution changes from orange to green as the dichromate ion is converted to a chromium(III) ion. The extent of the color change is then related to actual blood-alcohol content. The device is very accurate, because the chemical reaction on which the device is based is very predictable. This is an example of an oxidation-reduction reaction.

Courtesy of Senior Airman Natasha Stannard, US Air Force. commons.wikimedia.org/wiki/File:Breathalyzer_study.jpg. Public Domain.

1.1 Nature of Oxidation and Reduction

Lesson Objectives

- List three ways in which oxidation has been defined.
- List three ways in which reduction has been defined.
- Identify oxidation-reduction (redox) reactions.
- Identify common oxidizing agents and reducing agents.

Lesson Vocabulary

- **oxidation-reduction reaction**: A chemical reaction in which one substance is being oxidized and another is being reduced.
- **oxidation**: Classified by gain of oxygen atoms, loss of hydrogen atoms, or loss of electrons.
- **reduction**: Classified by loss of oxygen atoms, gain of hydrogen atoms, or gain of electrons.
- **oxidizing agent**: The reduced species; causes the other reactant to become oxidized.
- **reducing agent**: The oxidized species; causes the other reactant to become reduced.

Check Your Understanding

What happens when metallic sodium is added to water?

Introduction

What do the rusting of a nail, the tarnishing of silverware, and the burning of propane gas all have in common? As you have seen, there are many types of chemical reactions that occur depending on the combination of reactants and the conditions under which the reactants are placed. The processes we have just mentioned are all classified as oxidation-reduction reactions. In this lesson you will learn some possible ways to classify oxidation-reduction reactions based on certain characteristics.

Identifying Oxidation and Reduction

If an iron nail is exposed to the elements for a long enough period of time, it will eventually rust. This process is due to the following reaction between metallic iron and molecular oxygen:

$$4\ Fe(s) + 3\ O_2(g) \rightarrow 2\ Fe_2O_3(s)$$

FIGURE 1.1
Rust on a car caused by the oxidation of iron.

The rusting process is often accelerated when the metal comes into contact with electrolytes, such as the salts used to melt ice on streets in the winter.

Similarly, silverware will tarnish when exposed to some sulfur-containing compounds. The layer of black tarnish (Ag_2S) can easily be removed by cleaning the silverware with a mixture of aluminum and baking soda:

$$3\ Ag_2S(s) + 2\ Al(s) \rightarrow 6\ Ag(s) + Al_2S_3(s)$$

FIGURE 1.2
Tarnished silver. The object on the left has tarnished. The plate on the right and the object being held have both been polished.

Many homes are heated by burning propane gas, which combusts in the presence of oxygen:

$$CH_3CH_2CH_3 + 5\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O$$

FIGURE 1.3
Some fireplaces use propane gas rather than wood as fuel.

All of these seemingly disparate processes are examples of **oxidation-reduction (redox) reactions**. In a redox reaction, one substance is undergoing an **oxidation** and another is undergoing a **reduction**. The ways in which these terms are defined have varied over the years. The broadest definitions of oxidation and reduction are related to oxidation numbers, which will be discussed in the following lesson. However, many redox reactions can be identified on the basis of earlier definitions. Three general types of oxidation processes are listed below:

1. Gain of oxygen –When one or more oxygen atoms are added to a compound over the course of a reaction, that compound is being oxidized. This is the oldest definition of the word and the origin of the name. For example, when carbon monoxide is used to extract iron from iron ore, the following reaction takes place:

$Fe_2O_3(s) + 3\ CO(g) \rightarrow 2\ Fe(s) + 3\ CO_2(g)$

The carbon monoxide molecule is being oxidized; it gains an oxygen atom to form carbon dioxide.

2. Loss of hydrogen –When one or more hydrogen atoms leave a compound during a chemical reaction, this is often a type of oxidation. For example, when ethanol reacts with potassium dichromate, the ethanol molecule loses two hydrogen atoms:

CH_3CH_2OH (ethanol) $\rightarrow$ CH_3CHO (acetaldehyde)

In this process, ethanol is being oxidized to form acetaldehyde. The other components of the reaction are not shown, in order to highlight the oxidation.

It should be noted that not all losses of hydrogen are oxidations. For example, in the previous chapter on *Acids and Bases*, we saw many reactions in which a hydrogen ion is transferred from an acid to a base. However, because H^+ is being transferred but all of the electrons remain with their original compounds, this is actually *not* an oxidation process. This distinction will become clearer in the next lesson when we introduce the concept of oxidation numbers.

3. Loss of electrons –If an atom, ion, or molecule loses one or more electrons during a reaction, it is being oxidized. For example, when a neutral metal is converted to a metal cation, the metal is being oxidized. An example would be the reaction of metallic sodium with water:

$$2\ Na(s) + 2\ H_2O(l) \rightarrow 2\ NaOH(aq) + H_2(g)$$

Over the course of this reaction, neutral sodium atoms are being converted to sodium cations (Na^+). This net loss of an electron is a common type of oxidation.

The opposite of each of these criteria generally indicates that a reduction is occurring.

1. Loss of oxygen –When one or more oxygen atoms are removed from a compound, it is generally being reduced. Look again at the reaction between ferric oxide and carbon monoxide:

$$Fe_2O_3(s) + 3\ CO(g) \rightarrow 2\ Fe(s) + 3\ CO_2(g)$$

Oxygen atoms are being removed from the iron oxide, so that component is being reduced. The term reduction originated from this type of process, where a metal oxide is "reduced" to its pure metal form by treating it with the appropriate chemicals.

2. Addition of hydrogen –The oxidation of ethanol (shown above) can be reversed by reacting acetaldehyde with hydrogen gas in the presence of an appropriate catalyst:

$$CH_3CHO(l) + H_2(g) \rightarrow CH_3CH_2OH(l)$$

In this reaction, acetaldehyde is being reduced.

3. Gain of electrons –When metallic sodium is treated with gaseous chlorine, a violent reaction occurs:

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

On the reactant side, we see two neutral chlorine atoms covalently bonded into a chlorine molecule. On the product side, each chlorine atom has gained an electron to become Cl^- ions. Chlorine is being reduced in this reaction.

Two things should be emphasized at this point. First, not all processes that involve the gain or loss of oxygen or hydrogen are redox reactions. Although those definitions often work well with organic (carbon-based) compounds, there are many situations in inorganic chemistry for which they are insufficient. Second, oxidation and reduction must always take place together. In order for one compound to be oxidized, another must be reduced, and vice versa. For example, based on the electron-transfer definition, one compound must lose electrons (be oxidized) in order for another compound to gain electrons (be reduced).

Oxidizing and Reducing Agents

If a species is oxidized, there must be something present to make that process happen. This "something" is known as an **oxidizing agent**. When something is reduced, a **reducing agent** is necessary to for the reaction to occur. In every oxidation-reduction reaction, there is an oxidizing agent and a reducing agent. You cannot have an oxidation-reduction reaction without both being present.

Look again at the following reaction:

$$Fe_2O_3 + 3\ CO \rightarrow 2\ Fe + 3\ CO_2$$

In this process, carbon monoxide is being oxidized (oxygen is added), and iron oxide is being reduced (oxygen is lost). Because the added oxygen is provided by the iron oxide, Fe_2O_3 is the oxidizing agent in this reaction. Similarly, because CO is required to "remove" oxygen from the iron oxide, carbon monoxide is the reducing agent.

We can also identify oxidizing and reducing agents in terms of which species are undergoing each type of transformation. In a redox reaction, the substance that is oxidized causes the other substance to be reduced; it is therefore the reducing agent. The substance that is reduced causes the other substance to be oxidized; it is therefore the oxidizing agent.

Lesson Summary

- Oxidation often involves the loss of hydrogen, the gain of oxygen, or the loss of electrons.
- Reduction often involves the gain of hydrogen, the loss of oxygen, or the gain of electrons.
- An oxidizing agent causes the oxidation of another species in the reaction.
- A reducing agent causes the reduction of another species in the reaction.
- Oxidations and reductions always take place together; you cannot have a complete reaction in which only one of the two processes is occurring.

Lesson Review Questions

1. Explain in your own words the following oxidation processes:
   a. Gain of oxygen
   b. Loss of hydrogen
   c. Loss of electrons
2. Explain in your own words the following reduction processes:
   a. Loss of oxygen
   b. Gain of hydrogen
   c. Gain of electrons
3. What is the purpose of the oxidizing agent?
4. What is the purpose of the reducing agent?
5. In each of the following reactions, indicate which substance is oxidized, which is reduced, which is the oxidizing agent, and which is the reducing agent:
   a. $Mg + 2\ HCl \rightarrow MgCl_2 + H_2$
   b. $2\ Fe + 3\ V_2O_3 \rightarrow Fe_2O_3 + 6\ VO$
   c. $2\ Na + FeCl_2 \rightarrow 2\ NaCl + Fe$
   d. $AgNO_3 + Cu \rightarrow CuNO_3 + Ag$

e. $2\ Na + 2\ H_2O \rightarrow 2\ NaOH + H_2$

Further Reading/Supplementary Links

- Oxidation-reduction basics: http://library.kcc.hawaii.edu/external/chemistry/basic_model.html
- Oxidation-reduction video: http://www.youtube.com/watch?v=a6RR4kPsnlE

Points to Consider

- How can we tell which species are oxidized and which are reduced in a complex reaction?
- What types of reactions are redox reactions?

1.2 Oxidation Numbers

Lesson Objectives

- Be able to assign an oxidation number to each atom in a compound based on the given set of guidelines.
- Determine whether an atom is oxidized or reduced based on changes in oxidation number over the course of a chemical reaction.
- Give examples of typical oxidation-reduction reactions.

Lesson Vocabulary

- **oxidation number**: The charge that an atom would have if all polar covalent and ionic bonds resulted in a complete transfer of electrons from the less electronegative atom to the more electronegative one. Also referred to as oxidation state.

Check Your Understanding

1. If a neutral iron atom were to lose one, two, or three electrons, what would the charge be on each of the resulting ions?
2. If a neutral chlorine atom were to gain an electron during a reaction with another chemical species, what would be the charge of the resulting chloride ion? Is it likely that a chlorine atom would gain more than one electron? Why or why not?
3. How many valence electrons would be assigned to aluminum and oxygen before and after the following reaction takes place?

$4\ Al + 3\ O_2 \rightarrow 2\ Al_2O_3$

Introduction

In the previous lesson, we looked at the rusting of iron as an example of an oxidation-reduction (redox) reaction.

The formation of rust is summarized by the following chemical equation:

$4\ Fe(s) + 3\ O_2(g) \rightarrow 2\ Fe_2O_3(s)$

Based on the definition of a redox reaction as an electron-transfer process, we can easily see that rusting is a redox reaction. Metallic iron is losing electrons (being oxidized), and nonmetallic oxygen is gaining electrons (being reduced). The result is an ionic compound composed of metal cations and nonmetal anions. There are many other examples of redox reactions between metals and nonmetals to make ionic compounds. However, not all redox reactions are so obvious. For example, consider the following reaction:

FIGURE 1.4
An ancient cannon covered in rust.

$3\ Cu_2 + 14\ HNO_3 \rightarrow 6\ Cu(NO_3)_2 + 2\ NO + 7\ H_2O$

Is this a redox reaction? If so, what is being oxidized, and what is being reduced? As it turns out, this is a redox reaction. In order to determine whether electron transfers are occurring, chemists have developed a system of assigning electrons to various atoms. By assigning each valence electron in a compound to a particular atom, each atom can be given an oxidation number. In this lesson, we will learn how to determine the oxidation numbers for atoms in various compounds and how to use that information to identify whether a given reaction is a redox process.

Rules for Assigning Oxidation Numbers

Overall, the **oxidation number** (or *oxidation state*) of an atom is the charge that the atom would have if all polar covalent and ionic bonds resulted in a complete transfer of electrons from the less electronegative atom to the more electronegative one. Oxidation numbers can be assigned by looking at the Lewis structure for a given substance, but for many simpler compounds, they can also be assigned using the set of rules outlined below.

First, the oxidation numbers for the atoms in any substance or compound must add up to the overall charge of that species. As a result:

1. The atoms in any neutral elemental substance each have an oxidation state of zero. This includes neutral metals (e.g., Na, Be, K), diatomic molecules of a single element (e.g., H_2, Br_2, O_2), and sometimes more complex structures (e.g., P_4, S_8).
2. Monatomic ions have an oxidation number equal to their charge. Li^+ has an oxidation state of +1, Ba^{2+} has an oxidation state of +2, I^- has an oxidation state of -1, and so on.
3. If we know the oxidation numbers for all but one of the atoms in a substance, we can deduce the oxidation state of the unknown atom by comparing the sum of the other oxidation states with the overall charge of the compound or ion (this will be illustrated with examples later).

Additionally, many elements take on the same oxidation number in most or all of their compounds.

1. Elements with very low electronegativity values tend to lose all of their valence electrons when present in a compound, so the resulting oxidation state is equal to the number of valence electrons in the neutral atom.

a. Alkali metals have an oxidation state of +1 in their compounds. Although neutral alkali metals still have an oxidation state of zero, as soon as they react with other elements, alkali metals tend to give up their single valence electron, resulting in a charge of +1.
b. Alkaline earth metals have an oxidation state of +2 in their compounds. The reasoning is the same as for the Group 1 metals.
c. Aluminum tends to have an oxidation state of +3 in its compounds. However, this is not always the case for some of the more electronegative members of Group 13.

2. Elements with very high electronegativity values often have an oxidation number equal to the charge of the ion that would be formed in order to attain a noble gas configuration.

a. Fluorine has an oxidation state of -1 in all of its compounds. Because fluorine is the most electronegative element, it is assigned any shared electrons. The only way for fluorine to have a stable octet without an oxidation state of -1 is for it to be bonded to another fluorine atom. (The oxidation state of fluorine in F_2 is zero.)
b. Oxygen has an oxidation state of -2 in most of its compounds. Oxygen is the second most electronegative element, so it also tends to be assigned all shared electrons. Exceptions include O_2 (oxidation state = 0), peroxides, in which two oxygen atoms are connected by a single bond (oxidation state usually = -1), and any compound in which oxygen is bonded to fluorine (pretty rare and reactive).
c. Other halides often have an oxidation state of -1, but this trend breaks down when they are bonded to more electronegative atoms, such as nitrogen, oxygen, or fluorine.

3. The oxidation state of hydrogen can also be predicted based on the atoms to which it is bonded.

a. As with other pure elements, hydrogen has an oxidation state of zero in H_2.
b. When bonded to other nonmetals, which are nearly all *more* electronegative than hydrogen, hydrogen has an oxidation state of +1.
c. When bonded to metals, which are nearly all *less* electronegative than hydrogen, hydrogen has an oxidation state of -1.

Other elements also have preferred oxidation numbers when forming compounds, but we must look at the additional elements in the compound to know which of these states is present. Some preferred oxidation states for various transition metals are shown in **Table** 1.1.

TABLE 1.1: Transition metal oxidation states

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
8																●										●				
7					●										●	○									●					
6				●	●	○								●	●	●	○							●	○	●	○			
5			●	○	●	●							●	●	○	○	○						●	●	●	○				
4		●	●		●	○	○					●	●	●	●	●	●	●				●	●	●	●	●	●	●		
3	●	●	●	●	●	●	●	●			●	●	●	●		●	●				●	○	●	●	●	○	●		●	
2		●	●	●	●	●	●	●	●	●		○	●	●		●	●	●	○	●			○	○	●	○	○	●		●
1									●										●										●	●

This table shows some of the possible oxidation states found in compounds of the transition metals. A solid circle represents a common oxidation state, and a ring represents a less common (energetically less favorable) oxidation state.

For many compounds, all of the atoms can be assigned an oxidation state based on the rules above. Sometimes, there will be one atom in a compound whose oxidation state is not as easy to predict as the others. When this is the case, we can make use of the fact that the sum of the oxidation states must equal the overall charge of the compound. Let's take a look at how this might work:

Example 22.1

Assign oxidation numbers to each atom in the compound $KMnO_4$.

Answer:

Potassium is an alkali metal, so we would expect it to have an oxidation state of +1, and we can assume that oxygen has an oxidation state of -2. Overall, this is a neutral compound, so the sum of all the oxidation states must equal zero. Therefore:

$$\begin{aligned} &K + Mn + 4(O) = 0 \\ &\quad +1 + Mn + 4(-2) = 0 \\ &\quad Mn - 7 = 0 \\ &\quad Mn = +7 \end{aligned}$$

In this compound, manganese has an oxidation state of +7. Note that we must include an oxidation state of -2 for *each* of the four oxygen atoms. Let's look at another example.

Example 22.2

What is the oxidation state of iron in Fe_2O_3? Does it have a different oxidation state in ${FeCl_4}^{2-}$?

Answer:

In the first compound, we can assume that oxygen has an oxidation state of -2, since it is bonded to a metal, which would be significantly less electronegative.

$$\begin{aligned} &2(Fe) + 3(O) = 0 \\ &\quad 2(Fe) + 3(-2) = 0 \\ &\quad 2(Fe) - 6 = 0 \\ &\quad 2(Fe) = +6 \\ &\quad Fe = +3 \end{aligned}$$

In iron(III) oxide, iron has an oxidation state of +3. Note that this is the same as its charge when we dissociate this compound into its ions. Because the polyatomic ion has an overall charge, the oxidation states in ${FeCl_4}^{2-}$ will add up to -2, not zero. We can assume that chlorine has an oxidation state of -1, because it is bonded to a metal and not a very electronegative nonmetal.

$$\begin{aligned} &Fe + 4(Cl) = -2 \\ &\quad Fe + 4(-1) = -2 \\ &\quad Fe - 4 = -2 \\ &\quad Fe = +2 \end{aligned}$$

In this ion, iron has an oxidation state of +2. Both of these are common oxidation states for iron, so we must look at the surrounding atoms to determine which is present in a given compound.

Identifying and Analyzing Redox Reactions

The system of assigning oxidation numbers allows for a more general definition of redox reactions. A redox process is one in which the oxidation numbers of one or more atoms change over the course of the reaction. Any atom whose oxidation number becomes more positive (or less negative) is being oxidized, and an atom whose oxidation number becomes more negative (or less positive) is being reduced. By assigning oxidation numbers to each atom in a reaction, we can determine whether or not it is a redox reaction.

In our previous chapter on *Chemical Reactions*, we talked about various different ways that reactions could be classified. Some of the reaction types we studied included combination (synthesis), decomposition, single and double replacement, and combustion. Any of these general reaction types may also be a redox reaction. In this section, we will look at examples of redox reactions that fall into each of these categories.

Combination Reactions

In combination or synthesis reactions, two chemical species combine to produce a new compound. The general expression for a combination reaction is:

$$A + B \rightarrow C$$

One example of this type of reaction is the rusting of iron, which we have already looked at extensively in this chapter:

$$4\ Fe(s) + 3\ O_2(g) \rightarrow 2\ Fe_2O_3(s)$$

Here is a short video showing the oxidation of iron.

MEDIA

Click image to the left or use the URL below.

URL: https://www.ck12.org/flx/render/embeddedobject/84883

We saw in example problem 22.2 that the oxidation states of the atoms in iron (III) oxide are +3 for iron and -2 for oxygen. The atoms in the reactants are all pure elemental substances, so they have oxidation numbers of zero. Over the course of this reaction, iron is being oxidized (from 0 to +3), and oxygen is being reduced (from 0 to -2).

There are many other examples of redox reactions in which two neutral elements combine to make a compound. These often take the form of a metal being oxidized and a nonmetal being reduced, resulting in an ionic compound. Two nonmetallic elements can also undergo a redox reaction of this type, in which the less electronegative element is oxidized and the more electronegative element is reduced.

Decomposition Reactions

A decomposition process is the exact opposite of a combination process; one reactant compound breaks down into two or more products:

$$C \rightarrow A + B$$

For example, hydrogen peroxide will decompose over time to produce water and oxygen gas. The equation is written below, along with the oxidation numbers for each atom:

$$2\overset{+1}{H}_2\overset{-1}{O}_2 \rightarrow 2\overset{+1}{H}_2\overset{-2}{O} + \overset{0}{O}_2$$

In this reaction, some atoms of oxygen are being reduced to water (from -1 to -2), while others are being oxidized to molecular oxygen (from -1 to 0). For a redox decomposition reaction, the single reactant must act as both the oxidizing agent and the reducing agent. This is one type of reaction that is very difficult to recognize as a redox reaction by any of the previous definitions of oxidation and reduction; oxidation numbers must be assigned in order to see that changes in oxidation state are occurring.

Single Replacement Reactions

Single replacement reactions are quite common and often include a pure metal reacting with an aqueous solution of an acid or a salt. They have the following generic form:

A + BC → AC + B

When a reactive enough pure metal is placed in an acidic solution, the following reaction often takes place:

Metal + acid → metal salt + hydrogen gas

For example, if a piece of solid zinc is added to a solution of HCl, hydrogen bubbles will immediately start to form on the surface of the zinc:

FIGURE 1.5
Zinc metal reacting with a solution of hydrochloric acid. Notice the hydrogen bubbles surrounding the zinc metal.

At the same time, some of the zinc atoms are released into the solution as Zn^{2+} cations. The balanced chemical equation for this single displacement reaction is shown below.

$$\overset{0}{Zn} + 2\overset{+1}{H}\overset{-1}{Cl} \rightarrow \overset{+2}{Zn}\overset{-1}{Cl_2} + \overset{0}{H_2}$$

Notice how the oxidation states change for the elements involved in this process. One pure element (with an oxidation state of 0) is being oxidized (in this case, to an oxidation state of +2), and a cationic species (H^+, which has an oxidation state of +1) is being reduced to a neutral element (H_2, which has an oxidation state of 0). In this reaction, the chloride anion is acting as a spectator ion, so its form (and its oxidation state) does not change.

Another example of a single displacement reaction is when a solid metal is placed in a solution containing cations of a less reactive metal. The metal in the solid phase will dissolve into solution as a cation, and the metal cations in solution will precipitate out of solution as a solid metal. For example, if we were to place a piece of zinc in a solution of an iron salt, the following process would take place:

$$\overset{0}{Zn} + \overset{+2}{Fe}\overset{+6}{S}\overset{-2}{O_4} \rightarrow \overset{0}{Fe} + \overset{+2}{Zn}\overset{+6}{S}\overset{-2}{O_4}$$

Notice that the oxidation states only change for the two metal species. Zinc is oxidized from 0 to +2 and Fe is reduced from +2 to 0. The oxidation states of the elements in the spectator ion (SO_4^{2-}) do not change.

Combustion Reactions

In a combustion reaction, a hydrocarbon reacts with molecular oxygen to produce carbon dioxide and water. The molecular oxygen (oxidation state = 0) is reduced (oxidation state = -2 in both CO_2 and H_2O), while the carbon atoms in the hydrocarbon are oxidized (to +4 in carbon dioxide). A familiar combustion reaction involves the burning of fossil fuels to produce heat or electricity, or to power a motor vehicle or other machine. The process of cellular respiration, in which our bodies break down sugar molecules into water and carbon dioxide in order to harness the resulting release of energy, can also be thought of as a form of combustion, albeit a relatively slow and complex one. Cellular respiration in our bodies is governed by a series of enzymatic steps, whereas burning a marshmallow in a hot fire is a fast and uncontrolled reaction. However, the gradual digestion and the fast combustion of sucrose both result in the same net reaction:

$$C_{12}H_{22}O_{11} \text{ (sucrose)} + 12\ O_2 \rightarrow 12\ CO_2 + 11\ H_2O$$

FIGURE 1.6
Combustion reaction of a marshmallow (sucrose) and wood (cellulose).

Lesson Summary

- Oxidation numbers can be defined for each atom in a compound based on a set of rules.
- Oxidation and reduction are currently defined according to changes in oxidation number over the course of a reaction.
- All elements have an oxidation number of zero in their pure form.
- Many elements have only one common oxidation state in chemical compounds. These can serve as guidelines for determining the oxidation states of more variable elements, using the fact that all oxidation states in a chemical species must add up to the overall charge of the atom, molecule, compound, or ion.
- Examples of redox reactions are found in various categories of chemical reactions, including combination, decomposition, single replacement, and combustion.

Lesson Review Questions

1. Determine the oxidation number for the indicated element.
   a. calcium metal
   b. F in NaF
   c. S in Na_2SO_4
   d. Cl in $KClO_3$
   e. Ca in CaO
2. State the type of reaction illustrated by each of the following equations.
   a. $ZnS + 2\ O_2 \rightarrow ZnSO_4$
   b. $Fe + CuSO_4 \rightarrow FeSO_4 + Cu$
   c. $2KClO_3 \rightarrow 2KCl + 3O_2$
   d. $2Hg + O_2 \rightarrow 2HgO$
3. For each reaction in problem 2, indicate which atom was oxidized and which was reduced. Show the changes in oxidation number in each case.
4. Running a strong enough electric current through water will cause it to decompose into hydrogen and oxygen gas. Write the balanced chemical equation for this process. What is being oxidized, and what is being reduced?
5. Write the balanced chemical equation for the following reaction, including all oxidation numbers: Magnesium metal is placed in a solution of hydrochloric acid.
6. Write the balanced chemical equation for the following combination reaction: Hydrogen and oxygen gas react explosively to produce water. Which substance is being oxidized, and which is being reduced?
7. Write the chemical equation for the following combustion reaction, including all oxidation numbers: Methanol (CH_3OH) combusts in the presence of oxygen to produce carbon dioxide and water.
8. Assign oxidation numbers to each of the atoms in the following compounds/ions:

Further Reading/Supplementary Links

- Determining oxidation numbers: http://www.occc.edu/kmbailey/chem1115tutorials/oxidation_numbers.htm
- Common types of oxidation-reduction reactions: http://www.wisc-online.com/objects/ViewObject.aspx?ID=GCH7904
- Combustion of magnesium metal: http://www.youtube.com/watch?v=m2i9jLPXprQ

Points to Consider

- Why do you suppose oxidation numbers are used to describe the mechanics of redox processes? Why can't the charge of a given chemical species suffice?

1.3 Balancing Redox Equations

Lesson Objectives

- Be able to write half-reactions for oxidation-reduction processes.
- Be able to distinguish the oxidation half-reaction from the reduction half-reaction.
- Be able to balance redox reactions.

Lesson Vocabulary

- **half-reaction**: Describes half of the redox reaction process.

Check Your Understanding

Study the following diagram, which depicts the mass change that occurs when steel wool burns in air.

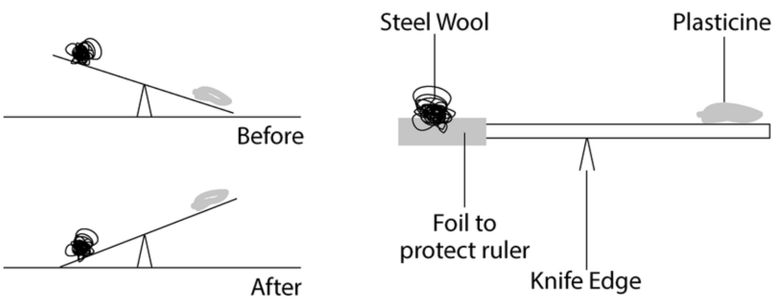

FIGURE 1.7
Mass changes for steel wool burning in air.

What happens to the mass of the steel wool as the reaction proceeds? Given that mass must be conserved in chemical reactions (it cannot come from nowhere), what is your explanation for the change in the mass of the steel wool?

Introduction

You have already learned the basic methods for balancing chemical equations to describe chemical reactions. Sometimes complicated reactions can be identified as redox reactions, in which case a special method of balancing chemical equations can be used to simplify the process and prevent unnecessary guessing and checking. In this lesson you will learn how to use this method.

Oxidation-Reduction Half-Reactions

In some cases, it can be helpful to analyze the oxidation and reduction processes separately for a complete redox reaction. A **half-reaction** contains only half of the entire redox process. One half-reaction illustrates the oxidation component and is the oxidation half-reaction; the other illustrates the reduction component and is the reduction half-reaction. For example, consider the following combination reaction:

$$ZnS(aq) + 2O_2(g) \rightarrow ZnSO_4(aq)$$

First, we need to assign oxidation states to each atom. Some of these compounds have multiple atoms for which the oxidation states are not easily predicted. However, if we convert this to an ionic equation, our task becomes simpler:

$$Zn^{2+}(aq) + S^{2-}(aq) + 2O_2(g) \rightarrow Zn^{2+}(aq) + SO_4^{2-}(aq)$$

On the reactant side, each component is a pure element, so the oxidation states are simply equal to the charge of the ion or molecule. Zinc has an oxidation state of +2, sulfur is -2, and oxygen is 0. Now look at the product side. Zinc is still a monatomic ion with a charge of +2, so nothing has changed. Zinc is a spectator ion. In the sulfate ion, we can assume that oxygen has its usual oxidation state of -2. The oxidation state of sulfur can then be calculated as follows:

S + 4(O) = -2
S + 4(-2) = -2
S - 8 = -2
S = +6

Based on the changes in oxidation number, we can identify the oxidation and reduction processes separately. The oxidized element, sulfur, is losing electrons, and the reduced element, oxygen, is gaining them. The superscript of zero on the reactant oxygen atom simply indicates that it begins with an oxidation state of 0.

$S^{2-} \rightarrow S^{6+} + 8e^-$ Oxidation Half-Reaction
$O^0 + 2e^- \rightarrow O^{2-}$ Reduction Half-Reaction

Note that these are purely theoretical processes. Sulfur does not physically become an ion with a charge of +6, because electrons are not fully transferred from the sulfur anion to the oxygen atoms. Additionally, the oxygen atoms don't exist as neutral, isolated species; they are always covalently bonded to at least one other atom. However, being able to break a reaction down into theoretical half-reactions is a useful tool, as we will see in the next section and in the following chapter on *Electrochemistry*.

Using Half-Reactions to Balance Equations

One use for half-reactions is to help balance very complex chemical equations. We will illustrate the overall process with a simple reaction first. Let's say that we were given the *unbalanced* version of the combination reaction from the previous section.

$$ZnS(aq) + O_2(g) \rightarrow ZnSO_4(aq)$$

Pretend for a moment that this was not a very easy equation to balance by trial and error. We determined that this could be broken down into the following half-reactions:

$S^{2-} \rightarrow S^{6+} + 8e^-$
$O^0 + 2e^- \rightarrow O^{2-}$

In the complete reaction, both of these processes occur simultaneously. However, free electrons are not actually a reactant or product of this reaction. In order for the electrons to cancel out, we would need the number of electrons lost by oxidation to be equal to the number gained during reduction. This can be accomplished by multiplying the entire second reaction by 4:

$S^{2-} \rightarrow S^{6+} + 8e^-$
$4O^0 + 8e^- \rightarrow 4O^{2-}$

For the electron flow in this reaction to be balanced, four oxygen atoms are reduced for each sulfur atom that is oxidized. Therefore, for each unit of ZnS (which contains one sulfur atom), we would need two molecules of O_2 (four oxygen atoms total). The ratio of reactants must be the following:

$$ZnS(aq) + 2O_2(g) \rightarrow$$

We can then find the coefficient of the product (in this case, 1) by inspection:

$$ZnS(aq) + 2O_2(g) \rightarrow ZnSO_4(aq)$$

Now that we have seen the basic procedure, let's try a more difficult problem.

Example 22.3

Balance the following equation using the half-reaction method:

$$KMnO_4(aq) + KNO_2(aq) + H_2SO_4(aq) \rightarrow MnSO_4(aq) + H_2O(l) + KNO_3(aq) + K_2SO_4(aq)$$

Answer:

First, determine which atoms are being oxidized and which are being reduced. In order to assign oxidation numbers, we should convert this molecular equation into an ionic one (no coefficients are used, since we are not starting with a balanced equation anyway):

$$K^+(aq) + MnO_4^-(aq) + NO_2^-(aq) + H^+(aq) + SO_4^{2-}(aq) \rightarrow Mn^{2+} + SO_4^{2-}(aq) + H_2O(l) + K^+(aq) + NO_3^-(aq)$$

There are 6 elements in this reaction. All of the monatomic ions have oxidation numbers equal to their charges. Additionally, we can assign an oxidation state of -2 to each oxygen atom and +1 to each hydrogen atom. Now, we just need to assign the oxidation states of manganese in $MnO_4{}^-$, nitrogen in the nitrite and nitrate ions, and sulfur in the sulfate ion. These can be determined by choosing a value for which all of the oxidation states in the ion add up to its overall charge. For example, in the nitrite ion:

N + 2(O) = -1
N + 2(-2) = -1
N - 4 = -1
N = +3

Nitrogen has an oxidation number of +3 in the nitrite ion. Similar reasoning shows us that manganese is +7 in $MnO_4{}^-$, nitrogen is +5 in $NO_3{}^-$, and sulfur is +6 in $SO_4{}^{2-}$. The only two elements that change oxidation numbers over the course of the reaction are Mn (from +7 in $MnO_4{}^-$ to +2 in Mn^{2+}) and N (from +3 in $NO_2{}^-$ to +5 in $NO_3{}^-$). Thus, we can write the two half-reactions as follows:

$N^{3+} \rightarrow N^{5+} + 2e^-$
$Mn^{7+} + 5e^- \rightarrow Mn^{2+}$

In order to equalize the number of electrons for these two half-reactions, we need to multiply the oxidation portion by 5 and the reduction portion by 2:

$5N^{3+} \rightarrow 5N^{5+} + 10e^-$
$2Mn^{7+} + 10e^- \rightarrow 2Mn^{2+}$

For every five nitrogen atoms that are oxidized, two manganese atoms are reduced. Now let's look back at the original equation:

$$KMnO_4(aq) + KNO_2(aq) + H_2SO_4(aq) \rightarrow MnSO_4(aq) + H_2O(l) + KNO_3(aq) + K_2SO_4(aq)$$

Nitrogen and manganese are each in only one compound on each side of the equation. Start by putting the coefficients from the balanced half-reactions on their corresponding compounds:

$$2KMnO_4(aq) + 5KNO_2(aq) + H_2SO_4(aq) \rightarrow 2MnSO_4(aq) + H_2O(l) + 5KNO_3(aq) + K_2SO_4(aq)$$

The coefficients for $KMnO_4$, KNO_2, $MnSO_4$, and KNO_3, are now set, but we can alter the coefficients on H_2SO_4, H_2O, and K_2SO_4 to finish balancing the equation. In order for potassium to be balanced, the coefficient on K_2SO_4 must be 1.

$$2KMnO_4(aq) + 5KNO_2(aq) + H_2SO_4(aq) \rightarrow 2MnSO_4(aq) + H_2O(l) + 5KNO_3(aq) + 1K_2SO_4(aq)$$

Then, H_2SO_4 is the last unbalanced compound that contains sulfur. In order for sulfur to be balanced (3 atoms on each side), H_2SO_4 must have a coefficient of 3.

$$2KMnO_4(aq) + 5KNO_2(aq) + 3H_2SO_4(aq) \rightarrow 2MnSO_4(aq) + H_2O(l) + 5KNO_3(aq) + 1K_2SO_4(aq)$$

Finally, hydrogen and oxygen can be balanced by changing the coefficient on H_2O. There are 6 hydrogen atoms on the left side, so water would need a coefficient of 3.

$$2KMnO_4(aq) + 5KNO_2(aq) + 3H_2SO_4(aq) \rightarrow 2MnSO_4(aq) + 3H_2O(l) + 5KNO_3(aq) + K_2SO_4(aq)$$

Double-checking our oxygen atoms, we see that there are 30 on each side. This is a fully balanced equation. Of course, most of the equations that you will be required to balance are not this difficult. However, it does demonstrate that using the half-reaction method gives you a good starting point for balancing especially complicated redox reactions.

Lesson Summary

- Oxidation-reduction half-reactions single out the changes in oxidation state of certain elements within a chemical equation.
- Balancing the electrons lost and gained in two simultaneously occurring half-reactions can be used to help balance complicated redox equations.

Lesson Review Questions

1. Write half-reactions for the following redox processes:
   a. $Fe + V_2O_3 \rightarrow Fe_2O_3 + VO$
   b. $K_2Cr_2O_7 + SnCl_2 + HCl \rightarrow CrCl_3 + SnCl_4 + KCl + H_2O$
   c. $K_2Cr_2O_7 + H_2O + S \rightarrow SO_2 + KOH + Cr_2O_3$
2. Write the balanced chemical equations for the following reactions:
   a. Magnesium carbonate is heated strongly to produce magnesium oxide and carbon dioxide gas.
   b. Hydrogen peroxide decomposes to produce water and oxygen gas.
   c. Solid potassium chlorate is heated in the presence of manganese dioxide as a catalyst to produce potassium chloride and oxygen gas.
   d. Lead sulfide reacts with molecular oxygen to form sulfur dioxide and lead(II) oxide.
3. Write oxidation and reduction half-reactions for the following single-replacement reaction: $Fe(s) + CuSO_4(aq) \rightarrow FeSO_4(aq) + Cu(s)$.
4. Use the half-reaction method to balance the following redox equation: $As_4 + NaOCl + H_2O \rightarrow NaCl + H_3AsO_4$.

Further Reading / Supplemental Links

Explanation and practice for balancing redox equations: http://www.mpcfaculty.net/mark_bishop/redox_balance_oxidation.htm

Points to Consider

- Although oxidation and reduction processes must occur simultaneously, they do not necessarily have to occur in the same space. How can this be used to generate electricity, which is essentially the flow of electrons through a wire?

1.4 References

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