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化学原理

——了解原子和分子的世界

（英文版）

Conceptual Chemistry

Understanding Our World of Atoms and Molecules

（美）约翰　A. 祖霍基　著
（John　A. Suchocki）

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2002 年 3 月

序

这是一本新版的普通化学教科书。全书共19章，前12章以化学基本原理为主，通过学科发展的简介和与现实生活的联系，使学生更容易了解和接受化学基本原理和概念。后7章是为了使学生在探索与化学相关的其它课题时获得阅读有关材料的经验。所以后7章是一些相对独立的应用领域，如生活中的化学物质、药物化学、粮食生产的优化、淡水资源、空气资源、材料资源、能源。本书取材生动活泼，插图精美，可读性强。

该书和现有的普通化学教材的最大差别，在于理论的深度和系统性的不同。书中几乎没有关于初等量子力学和化学热力学的内容，这在近年来我所见过的多种国内外普通化学教材中几乎是唯一的。对于该书作者的这种处理，我认为不失为解决普通化学教学出路的一种有价值的尝试。例如，内容繁杂而又极其重要的有机化学，在普通化学教材编写时，由于篇幅和学时的限制，一直是一个很难处理的问题。作者在该书中仅用了36页的篇幅就完成了关于有机粔学基础的介绍。该章共分4节，即：碳氢化合物只包含碳和氢；不饱和碳氢化合物含有多重键；按功能团分类的有机分子；有机分子可以连接成为高聚物。读后颇有耳目一新之感。

各章所设栏目如下：概念自查（附有问题，随之给出解答。有助于学生在学习新概念之前加深对已学概念的理解）；身边的化学（使学生不在化学实验室时，利用家里的器具和物品也能进行化学探究，以提高学生远程学习和课堂学习的积极性）；计算角（不是每章都有，以练习定量计算为主）。各章后均附有关键术语和有关定义，复习问题，身边化学现象的讨论，练习题，问题，讨论题（13～19章），建议的阅读材料和网址。

该书在文字叙述上，一改原有教材的传统风格，以贴近学生为主，语言生动活泼；内容涉及面较广，比喻生动有趣，可读性强，图文并茂；版面设计和栏目安排都很有特色。

该书作者在化学学科领域不大为人所知，但是他所编写的这本教科书却颇有特色，在体现化学教学新理念方面有比较大的进步，是一本值得向国内普通化学教学界推荐的教科书和参考书。

宋心琦

清华大学化学系

2002年3月

Chapter 11

Oxidation and Reduction

Transferring Electrons

In the previous chapter we discussed acid–base reactions, which are chemical reactions that involve the transfer of *protons* from one reactant to another. In this chapter, we explore reactions that involve the transfer of one or more *electrons* from one reactant to another. These are called **oxidation–reduction reactions**, and a common example is the burning of wood. Wood is mainly cellulose, a substance made up of carbon and hydrogen. As wood burns, its carbon–hydrogen bonds break and the carbon and hydrogen atoms form new bonds with oxygen molecules in the air to create carbon dioxide and water. The formation of these products involves the transfer of electrons from one atom to another and so is by definition an oxidation–reduction reaction.

We begin exploring oxidation–reduction reactions by defining necessary terms. With the background on chemical reactions given in Chapter 9, we are then ready to jump right into the various applications of oxidation–reduction reactions.

11.1 Oxidation Is the Loss of Electrons and Reduction Is the Gain of Electrons

Oxidation is the process whereby a reactant loses one or more electrons. **Reduction** is the opposite process whereby a reactant gains one or more electrons. Oxidation and reduction are complementary and simultaneous processes. They always occur together; you cannot have one without the other. The electrons lost by one chemical in an oxidation reaction don't simply disappear; they are gained by another chemical in a reduction reaction.

An oxidation–reduction reaction occurs when elemental sodium and chlorine react exothermically to form sodium chloride, as shown in Figure 11.1. The equation for this reaction is

$$2\ \mathrm{Na} + \mathrm{Cl_2} \longrightarrow 2\ \mathrm{NaCl}$$

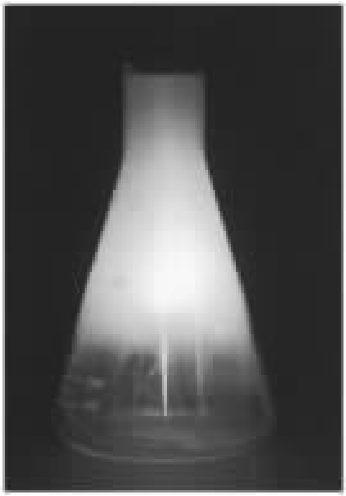


Figure 11.1
In the exothermic formation of sodium chloride, sodium metal is oxidized by chlorine gas, and chlorine gas is reduced by sodium metal.

To see how electrons are transferred in this reaction, we can look at each reactant individually. Each electrically neutral sodium atom changes to a positively charged ion—each atom loses an electron and is therefore oxidized:

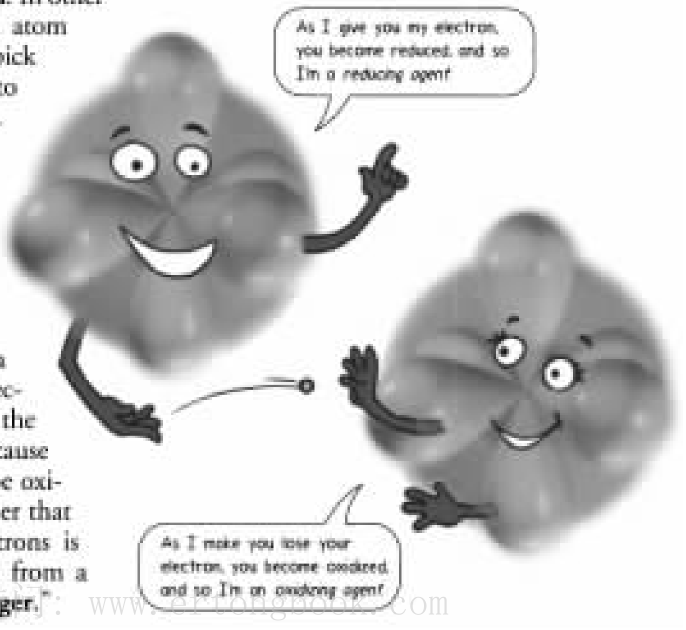
$$2\ \mathrm{Na} \longrightarrow 2\ \mathrm{Na^+} + 2\ \mathrm{e^-} \qquad \text{Oxidation}$$

Each electrically neutral chlorine molecule changes to two negatively charged ions—each atom gains an electron and is therefore reduced:

$$\mathrm{Cl_2} + 2\ \mathrm{e^-} \longrightarrow 2\ \mathrm{Cl^-} \qquad \text{Reduction}$$

The net result is that the two electrons lost by the sodium atoms are transferred to the chlorine atoms. Therefore, the two equations shown above actually represent one process, called a **half reaction**. In other words, an electron won't be lost from a sodium atom without there being a chlorine atom available to pick up that electron. Both half reactions are required to represent the *whole* oxidation–reduction process. Half reactions are useful for showing which reactant loses electrons and which reactant gains them, which is why half reactions are used throughout this chapter.

Because the sodium causes reduction of the chlorine, the sodium is acting as a *reducing agent*, which is any reactant that causes another reactant to be reduced. Note that in behaving as a reducing agent, the sodium is oxidized—it loses electrons. Conversely, the chlorine causes oxidation of the sodium and so is acting as an *oxidizing agent*. Because it gains electrons as it causes another reactant to be oxidized, an oxidizing agent is reduced. Just remember that **l**oss of **e**lectrons is **o**xidation, and **g**ain of **e**lectrons is **r**eduction. Here is a helpful mnemonic adapted from a once-popular children's story: **Leo** the lion went "**ger**."



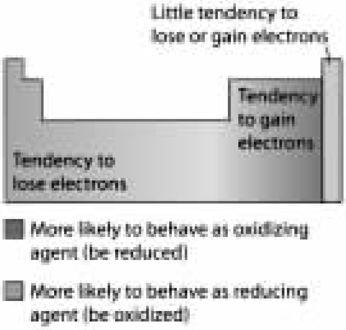


Figure 11.2
The ability of an atom to gain or lose electrons is a function of its position in the periodic table. Those at the upper right tend to gain electrons, and those at the lower left tend to lose them.

Different elements have different oxidation and reduction tendencies—some lose electrons more readily, while others gain electrons more readily, as Figure 11.2 illustrates. The tendency to do one or the other is a function of how strongly the atom's nucleus holds electrons. The greater the effective nuclear charge (Section 5.8), the greater the tendency of the atom to *gain* electrons. Because the atoms of elements at the upper right of the periodic table have the strongest effective nuclear charges (with the noble gases excluded), these atoms have the greatest tendency to gain electrons and hence behave as oxidizing agents. The atoms of elements at the lower left of the periodic table have the weakest effective nuclear charges and therefore the greatest tendency to *lose* electrons and behave as reducing agents.

Concept Check ✓

True or false:

1. Reducing agents are oxidized in oxidation–reduction reactions.
2. Oxidizing agents are reduced in oxidation–reduction reactions.

Were these your answers? Both statements are true.

11.2 Photography Works by Selective Oxidation and Reduction

Figure 11.3
A camera can be used to focus an image on wax paper as well as it does on photographic film.

Lay some wax paper on the back of an open unloaded camera as shown in Figure 11.3. Hold the shutter open, then focus. Voila! You have an image. Let the shutter close, however, and the image is gone. This is the same image that forms on the photographic film inside a loaded camera. The difference between the film and the wax paper is that the film is able to retain the image after the shutter has closed. How does it do that? The answer has to do with oxidation–reduction chemistry.

Follow the steps in Figure 11.4 as you read this simplified explanation of how a black-and-white photograph is produced.

1. Unexposed black-and-white photographic film is a transparent strip of plastic coated with a gel containing microcrystals of silver bromide, AgBr. Light reflected from the subject being photographed passes through the camera lens and is focused on these microcrystals. The light causes many of the bromide ions in the microcrystals to oxidize. The electrons set loose by this oxidation are transferred to the silver ions, which are thereby reduced to opaque silver atoms. The more light received by a microcrystal, the greater the number of opaque silver atoms formed. In this way, the photographic image is encoded, and the film is said to have been *exposed*.
2. The light reflected from the subject does not typically result in the formation of enough silver atoms to make a visible image. The more silver atoms a microcrystal contains, however, the more susceptible it is to further oxidation–reduction reactions. To make a visible image, the

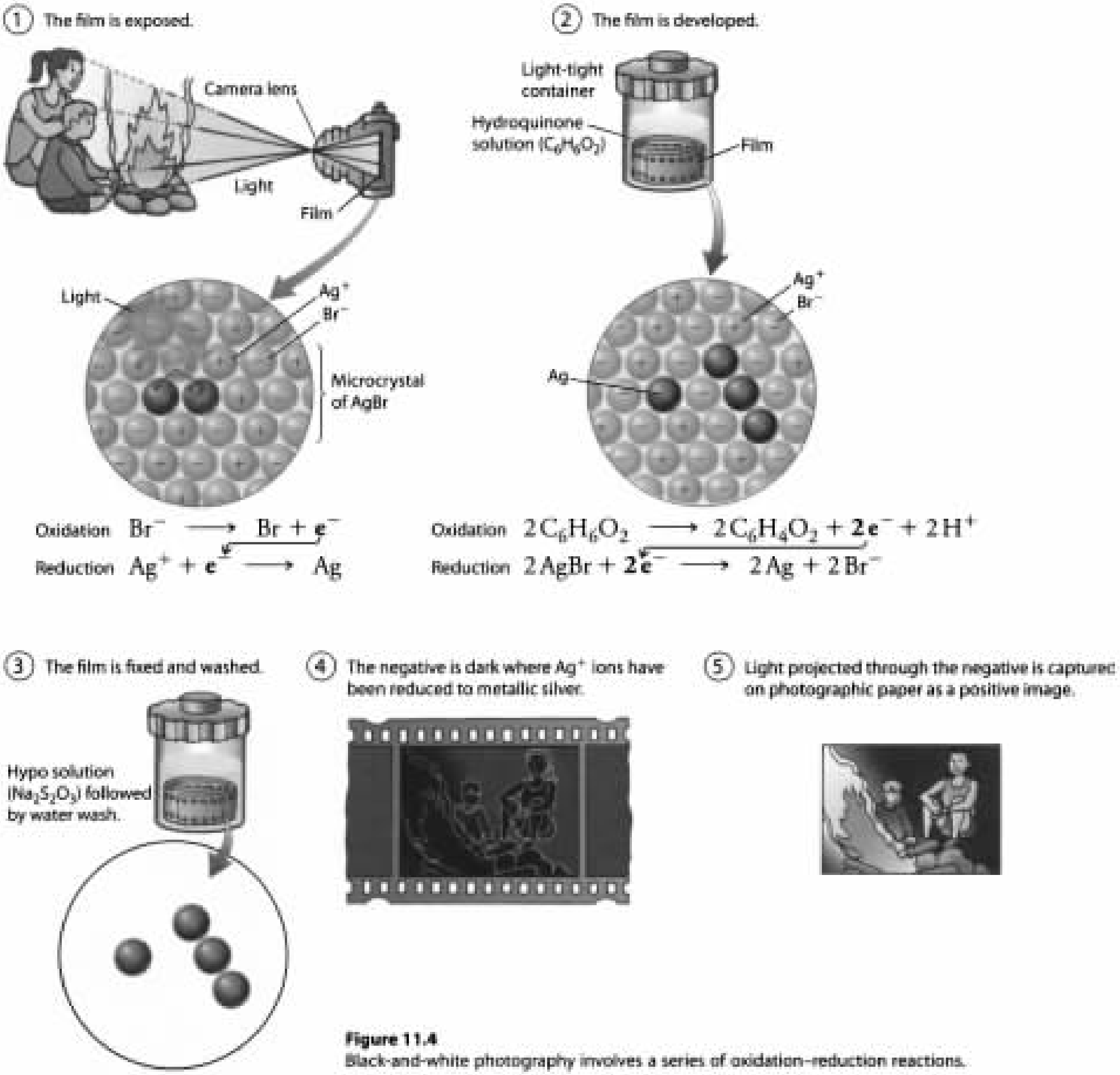


Figure 11.4
Black-and-white photography involves a series of oxidation–reduction reactions.

photographer puts the film in a light-tight container to prevent further exposure. Then the film is treated with a reducing agent, such as hydroquinone, $C_6H_6O_2$, which reveals the encoded image by causing the formation of many more opaque silver atoms. Through this step the image *develops.*

3. The reduction of silver ions by the hydroquinone developing solution is stopped by treating the film with a solution of sodium thiosulfate, $Na_2S_2O_3$, also called either *hypo* or *fixing solution.* The thiosulfate ion, $S_2O_3^{2-}$, binds with any unreduced silver ions to form a water-soluble salt. Subsequent washing with water removes everything

Hands-On Chemistry: Silver Lining

Tarnish on silverware is a coating of silver sulfide, Ag_2S, an ionic compound consisting of two silver ions, Ag^+, and one sulfide ion, S^{2-}. Tarnishing begins when silver atoms in the silverware come into contact with airborne hydrogen sulfide, H_2S, a smelly gas produced by the digestion of food in mammals and other organisms. The half reaction for the silver and hydrogen sulfide is

$$4\,Ag + 2\,H_2S \longrightarrow 4\,Ag^+ + 4\,H^+ + 2\,S^{2-} + 4\,e^- \quad \text{Oxidation}$$

The silver ions and sulfide ions combine to form blackish silver sulfide, while at the same time the hydrogen ions and electrons combine with atmospheric oxygen to form water:

$$4\,H^+ + 4\,e^- + O_2 \longrightarrow 2\,H_2O \quad \text{Reduction}$$

The balanced chemical equation for the tarnishing of silver is the combination of these two half reactions:

$$4\,Ag + 2\,H_2S + O_2 \longrightarrow 2\,Ag_2S + 2\,H_2O$$

From these equations we see that the hydrogen sulfide causes the silver to lose electrons to oxygen. To restore the silver to its shiny elemental state, we need to return the electrons it lost. The oxygen won't relinquish electrons back to silver, but with the proper connection, aluminum atoms will.

What You Need

Very clean aluminum pot (or non-aluminum pot and aluminum foil), water, baking soda, piece of tarnished silver

Procedure

① Put about a liter of water and several heaping tablespoons of baking soda in the aluminum pot or the non-aluminum pot containing aluminum foil.

② Bring the water to boiling and then remove the pot from the heat source.

③ Slowly immerse the tarnished silver; you'll see an immediate effect as the silver and aluminum make contact. (Add more baking soda if you don't.) Also, as the silver ions accept electrons from the aluminum and are thereby reduced to shiny silver atoms, the sulfide ions are free to re-form hydrogen sulfide gas, which is released back into the air. You may smell it!

The baking soda serves as a conductive ionic solution that permits electrons to move from the aluminum atoms to the silver ions. What is the advantage of this approach over polishing the silver with an abrasive paste?

except the silver atoms adhering to the film, which are most abundant where the greatest amount of light hit the film when the photograph was taken. The film is now *fixed*.

4. Because the silver atoms are opaque, the film appears as a *negative*, which is dark where the subject was light and light where the subject was dark.
5. Light is projected through the negative onto photographic paper, which is developed using the same reactions that produced the negative. The resulting developed image is a negative of the negative—in other words, a positive print.

Color photographic film is coated with a variety of chemicals that respond to light of different frequencies (colors). There are more oxidation–reduction reactions involved in the developing of a color photograph, but the basic principle is the same—the selective reduction of only those chemicals exposed to light. Digital photography, by contrast, is an outgrowth of photovoltaic cells, which are made of metalloids, such as silicon, that lose electrons upon exposure to light. We explore photovoltaic cells in Chapter 19 in our discussion of energy sources.

Concept Check ✓

Would a photographic negative be mostly transparent or mostly opaque if the camera shutter remained open too long and too much light fell on the film? What would the positive print from this negative look like?

Were these your answers? The more light that hits the film, the greater the number of silver ions reduced by the bromide ions or hydroquinone. The reduction of the silver ions results in opaque silver atoms that adhere to the film. Such an overexposed negative, therefore, would be mostly opaque because of all the opaque silver atoms.

The positive print would be very light because there would be very little light passing through the negative to sensitize the silver ions in the photographic paper.

11.3 The Energy of Flowing Electrons Can Be Harnessed

Electrochemistry is the study of the relationship between electrical energy and chemical change. It involves either the use of an oxidation–reduction reaction to produce an electric current or the use of an electric current to produce an oxidation–reduction reaction.

To understand how an oxidation–reduction reaction can generate an electric current, consider what happens when a reducing agent is placed in direct contact with an oxidizing agent: Electrons flow from the reducing agent to the oxidizing agent. This flow of electrons is an electric current, which is a form of kinetic energy that can be harnessed for useful purposes.

Iron, Fe, for example, is a better reducing agent than the copper ion Cu^{2+}. So when a piece of iron metal and a solution containing copper ions are placed in contact with each other, electrons flow from the iron to the copper ions, as Figure 11.5 on page 330 illustrates. The result is the oxidation of iron and the reduction of copper ions.

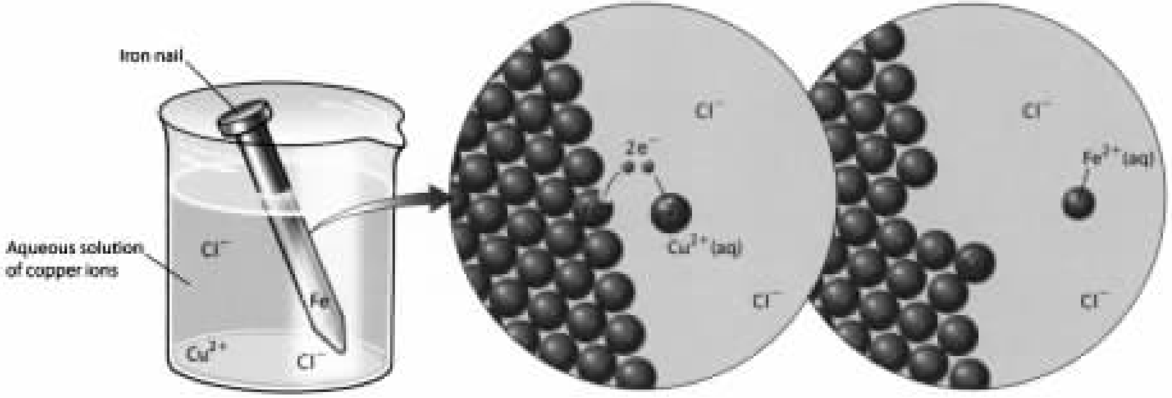
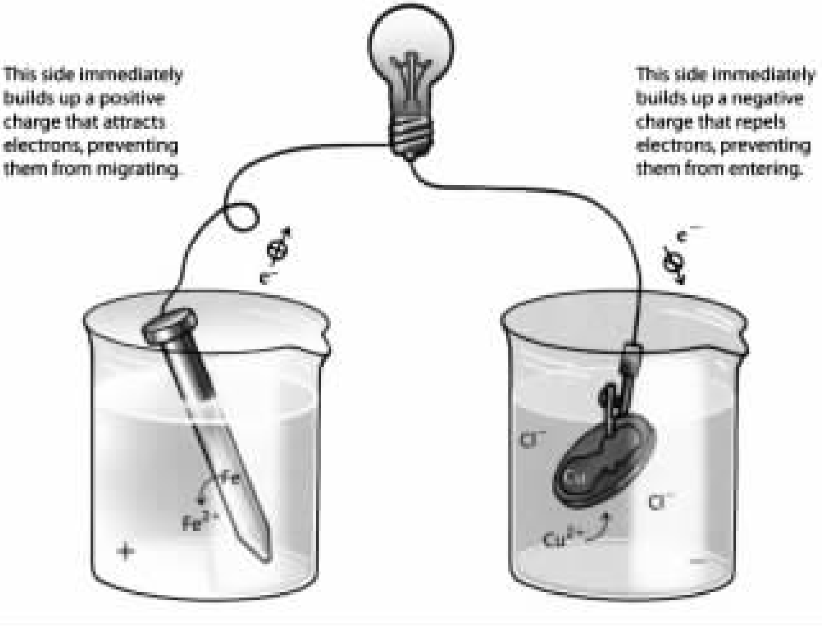


Figure 11.5
A nail made of iron placed in a solution of Cu^{2+} ions oxidizes to Fe^{2+} ions, which dissolve in the water. At the same time, copper ions are reduced to metallic copper, which coats the nail. (Negatively charged ions, such as chloride ions, Cl^-, must also be present to balance these positively charged ions in solution.)

$$\text{Oxidation} \quad Fe \longrightarrow Fe^{2+} + \mathbf{2}\,e^-$$
$$\text{Reduction} \quad Cu^{2+} + \mathbf{2}\,e^- \longrightarrow Cu$$

The elemental iron and copper ions need not be in physical contact in order for electrons to flow between them. If they are in separate containers but bridged by a conducting wire, the electrons can flow from the iron to the copper ions through the wire. The resulting electric current in the wire could be attached to some useful device, such as a light bulb. But alas, an electric current is not sustained by this arrangement.

The reason the electric current is not sustained is shown in Figure 11.6. An initial flow of electrons through the wire immediately results in a buildup of electric charge in both containers. The container on the left builds up positive charge as it accumulates Fe^{2+} ions from the nail. The container on the right builds up negative charge as electrons accumulate on

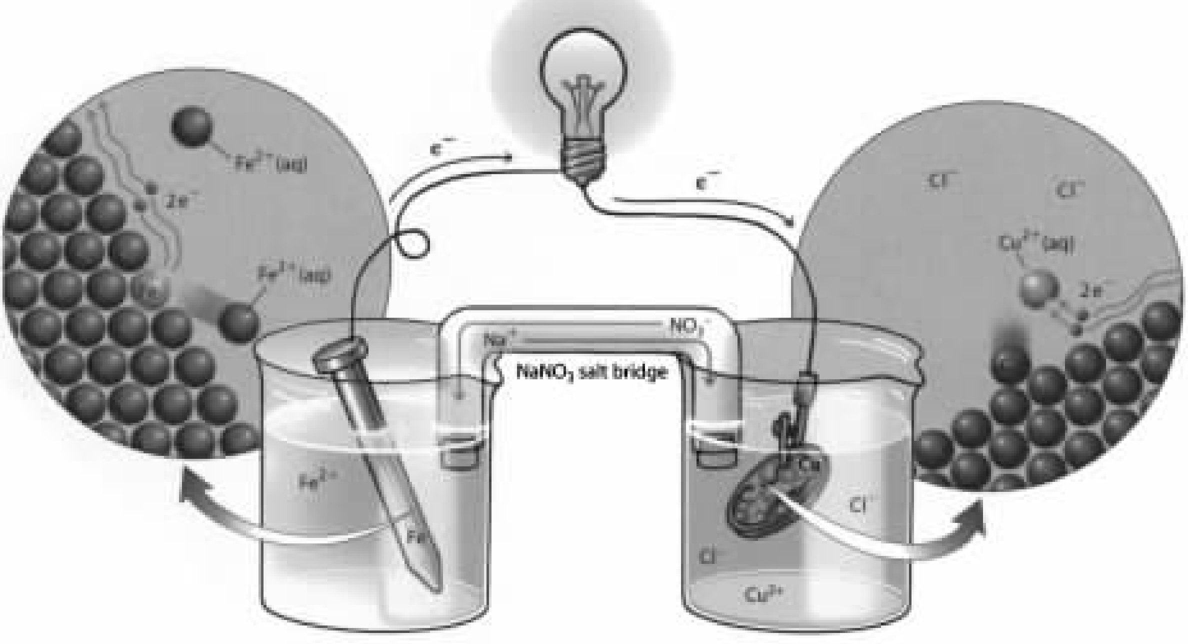

This side immediately builds up a positive charge that attracts electrons, preventing them from migrating.

This side immediately builds up a negative charge that repels electrons, preventing them from entering.

Figure 11.6
An iron nail is placed in water and connected by a conducting wire to a solution of copper ions. Nothing happens because this arrangement results in a buildup of charge that prevents the further flow of electrons.

this side. This situation prevents any further migration of electrons through the wire. Recall that electrons are negative, and so they are repelled by the negative charge in the right container and attracted to the positive charge in the left container. The net result is that the electrons do not flow through the wire, and the bulb remains unlit.

The solution to this problem is to allow ions to migrate into either container so that neither builds up any positive or negative charge. This is accomplished with a *salt bridge*, which may be a U-shaped tube filled with a salt, such as sodium nitrate, $NaNO_3$, and closed with semiporous plugs. Figure 11.7 shows how a salt bridge allows the ions it holds to enter either container, permitting the flow of electrons through the conducting wire and creating a complete electric circuit.



Oxidation $Fe \longrightarrow Fe^{2+} + 2\,e^-$

Reduction $Cu^{2+} + 2\,e^- \longrightarrow Cu$

Figure 11.7
The salt bridge completes the electric circuit. Electrons freed as the iron is oxidized pass through the wire to the container on the right. Nitrate ions, NO_3^-, from the salt bridge flow into the left container to balance the positive charges of the Fe^{2+} ions that form and prevent any buildup of positive charge. Meanwhile, Na^+ ions from the salt bridge enter the right container to balance the Cl^- ions "abandoned" by the Cu^{2+} ions as the Cu^{2+} ions pick up electrons to become metallic copper.

The Electricity of a Battery Comes from Oxidation–Reduction Reactions

So we see that with the proper setup it is possible to harness electrical energy from an oxidation–reduction reaction. The apparatus shown in Figure 11.7 is one example. Such devices are called *voltaic cells*. Instead of two containers, a voltaic cell can be an all-in-one, self-contained unit, in which case it is called a *battery*. Batteries are either disposable or rechargeable, and

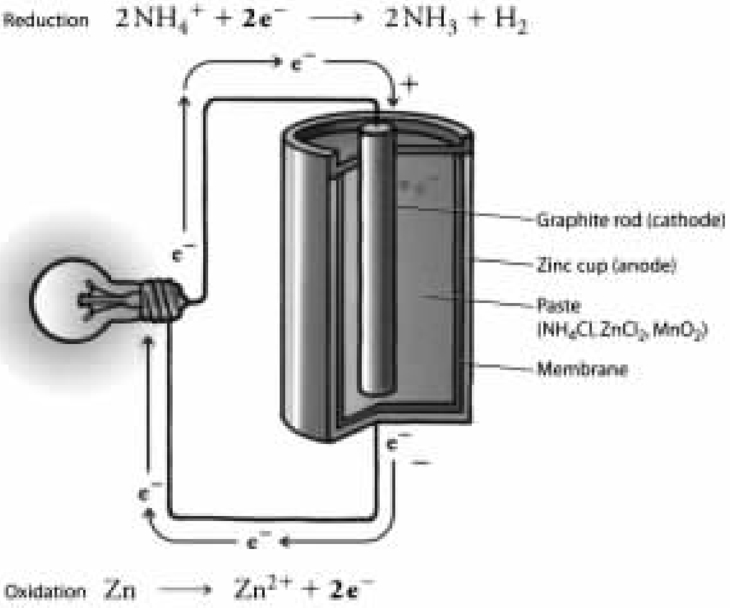


Figure 11.8
A common dry-cell battery with a graphite rod immersed in a paste of ammonium chloride, manganese dioxide, and zinc chloride.

here we explore some examples of each. Although the two types differ in design and composition, they function by the same principle: Two materials that oxidize and reduce each other are connected by a medium through which ions travel to balance an external flow of electrons.

Let's look at disposable batteries first. The common *dry-cell battery* was invented in the 1860s and is still used today as probably the cheapest disposable energy source for flashlights, toys, and the like. The basic design consists of a zinc cup filled with a thick paste of ammonium chloride, NH_4Cl, zinc chloride, $ZnCl_2$, and manganese dioxide, MnO_2. Immersed in this paste is a porous stick of graphite that projects to the top of the battery, as shown in Figure 11.8.

Graphite is a good conductor of electricity, and it is at the graphite stick that the chemicals in the paste receive electrons and so are reduced. The reaction for the ammonium ions, for instance, is

$$2\,NH_4^+(aq) + 2\,e^- \longrightarrow 2\,NH_3(g) + H_2(g) \qquad \text{Reduction}$$

An **electrode** is any material that conducts electrons into or out of a medium in which electrochemical reactions are occurring. The electrode where chemicals are reduced is called a **cathode**. For any battery, such as the one shown in Figure 11.8, the cathode is always positive (+), which indicates that electrons are naturally attracted to this location. The electrons gained by chemicals at the cathode originate at the **anode**, which is the electrode where chemicals are oxidized. For any battery, the anode is always negative (−), which indicates that electrons are streaming away from this location. The anode in Figure 11.8 is the zinc cup, where zinc atoms lose electrons to form zinc ions:

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^- \qquad \text{Oxidation}$$

The reduction of ammonium ions in a dry-cell battery produces two gases—ammonia, NH_3, and hydrogen, H_2—that need to be removed to avoid a pressure buildup and a potential explosion. Removal is accomplished by having the ammonia and hydrogen react with the zinc chloride and manganese dioxide:

$$ZnCl_2(aq) + 2\ NH_3(g) \longrightarrow Zn(NH_3)_2Cl_2(s)$$

$$2\ MnO_2(s) + H_2(g) \longrightarrow Mn_2O_3(s) + H_2O(\ell)$$

The life of a dry-cell battery is relatively short. Oxidation causes the zinc cup to deteriorate, and eventually the contents leak out. Even while the battery is not operating, the zinc corrodes as it reacts with ammonium ions. This zinc corrosion can be inhibited by storing the battery in a refrigerator. As discussed in Chapter 9, chemical reactions slow down with decreasing temperature. Chilling a battery therefore slows down the rate at which the zinc corrodes, which increases the life of the battery.

Another type of disposable battery, the more expensive *alkaline battery*, shown in Figure 11.9, avoids many of the problems of dry-cell batteries by operating in a strongly alkaline paste. In the presence of hydroxide ions, the zinc oxidizes to insoluble zinc oxide:

$$Zn(s) + 2\ OH^-(aq) \longrightarrow ZnO(s) + H_2O(\ell) + 2\ e^- \quad \text{Oxidation}$$

while at the same time manganese dioxide is reduced:

$$2\ MnO_2(s) + H_2O(\ell) + 2\ e^- \longrightarrow Mn_2O_3(s) + 2\ OH^-(aq) \quad \text{Reduction}$$

Figure 11.9
Alkaline batteries last a lot longer than dry-cell batteries and give a steadier voltage, but they are expensive.

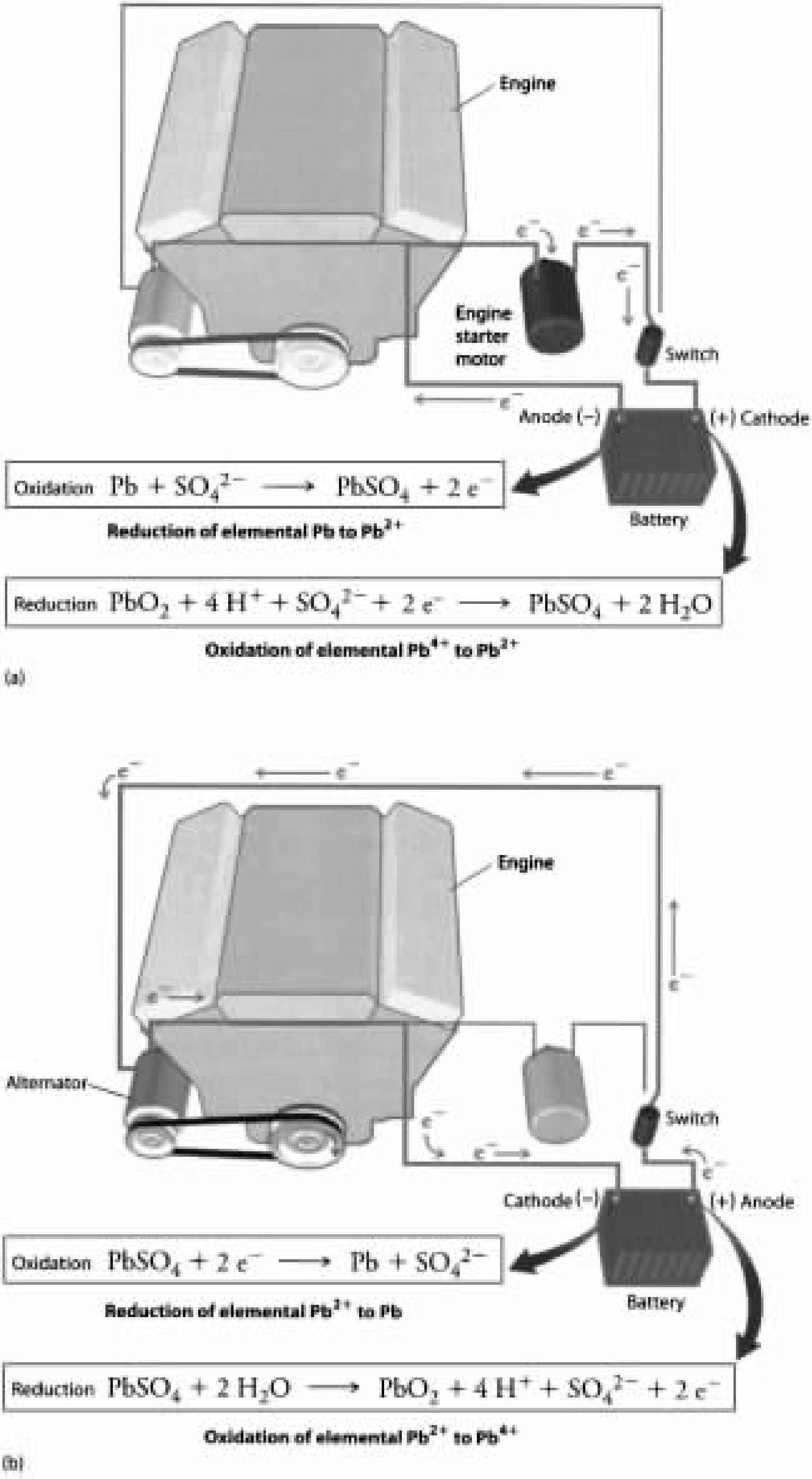
Note how these two reactions avoid the use of the zinc-corroding ammonium ion (which means alkaline batteries last a lot longer than dry-cell batteries) and the formation of any gaseous products. Furthermore, these reactions are better-suited to maintaining a given voltage during longer periods of operation.

The small mercury and lithium disposable batteries used for calculators and cameras are variations of the alkaline battery. In the mercury battery, mercuric oxide, HgO, is reduced rather than manganese dioxide. Manufacturers are phasing out these batteries because of the environmental hazard posed by mercury, which is poisonous. In the lithium battery, lithium metal is used as the source of electrons rather than zinc. Not only is lithium able to maintain a higher voltage than zinc, it is about 13 times less dense, which allows for a lighter battery.

Disposable batteries have relatively short lives because electron-producing chemicals are consumed. The main feature of rechargeable batteries is the reversibility of the oxidation and reduction reactions. In your car's rechargeable lead storage battery, for example, electrical energy is produced as lead dioxide, lead, and sulfuric acid are consumed to form lead sulfate and water. The elemental lead is oxidized to Pb^{2+}, and the oxygen in the lead dioxide is reduced from the O^- state to the O^{2-} state. Combining the two half reactions gives the complete oxidation–reduction reaction:

$$PbO_2 + Pb + 2\ H_2SO_4 \longrightarrow 2\ PbSO_4 + 2\ H_2O + \text{electrical energy}$$

Figure 11.10
(a) Electrical energy from the battery forces the starter motor to start the engine. (b) The combustion of fuel keeps the engine running and provides energy to spin the alternator, which recharges the battery. Note that the battery has a reversed cathode–anode orientation during recharging.



This reaction can be reversed by supplying electrical energy, as Figure 11.10 shows. This is the task of the car's alternator, which is powered by the engine:

$$\text{electrical energy} + 2\,PbSO_4 + 2\,H_2O \longrightarrow PbO_2 + Pb + 2\,H_2SO_4$$

So running the engine maintains concentrations of lead dioxide, lead, and sulfuric acid in the battery. With the engine turned off, these reactants stand ready to supply electric power as needed to start the engine, operate the emergency blinkers, or play the radio.

Concept Check ✓

What is recharged in a car battery?

Was this your answer? When the battery is being recharged, electrical energy from a source (the alternator) outside the battery is used to regenerate reactants that were earlier transformed to products during the oxidation–reduction reaction that produced the electrical energy needed to start the engine. The reactants being regenerated are lead dioxide, elemental lead, and sulfuric acid.

Many rechargeable batteries smaller than car batteries are made of compounds of nickel and cadmium (ni–cad batteries). As with the lead storage battery, ni–cad reactants are replenished by supplying electrical energy from some external source, such as an electrical wall outlet. Like mercury batteries, ni–cad batteries pose an environmental hazard because cadmium is toxic to humans and other organisms. For this reason, alkaline batteries designed to be rechargeable are rapidly gaining a place in the market.

Fuel Cells Are Highly Efficient Sources of Electrical Energy

A *fuel cell* is a device that changes the chemical energy of a fuel to electrical energy. Fuel cells are by far the most efficient means of generating electricity. A hydrogen–oxygen fuel cell is shown in Figure 11.11 on page 336. It has two compartments, one for entering hydrogen fuel and the other for entering oxygen fuel, separated by a set of porous electrodes. Hydrogen is oxidized upon contact with hydroxide ions at the hydrogen-facing electrode (the anode). The electrons from this oxidation flow through an external circuit and provide electric power before meeting up with oxygen at the oxygen-facing electrode (the cathode). The oxygen readily picks up the electrons (in other words, the oxygen is reduced) and reacts with water to form hydroxide ions. To complete the circuit, these hydroxide ions migrate across the porous electrodes and through an ionic paste of potassium hydroxide, KOH, to meet up with hydrogen at the hydrogen-facing electrode.

As the oxidation equation shown at the top of Figure 11.11 demonstrates, the hydrogen and hydroxide ions react to produce steam as well as electrons. This steam may be used for heating or to generate electricity in a steam turbine. Furthermore, the water that condenses from the steam is pure water, suitable for drinking!