Pearson

19.3: Voltaic (or Galvanic) Cells: Generating Electricity from Spontaneous Chemical Reactions

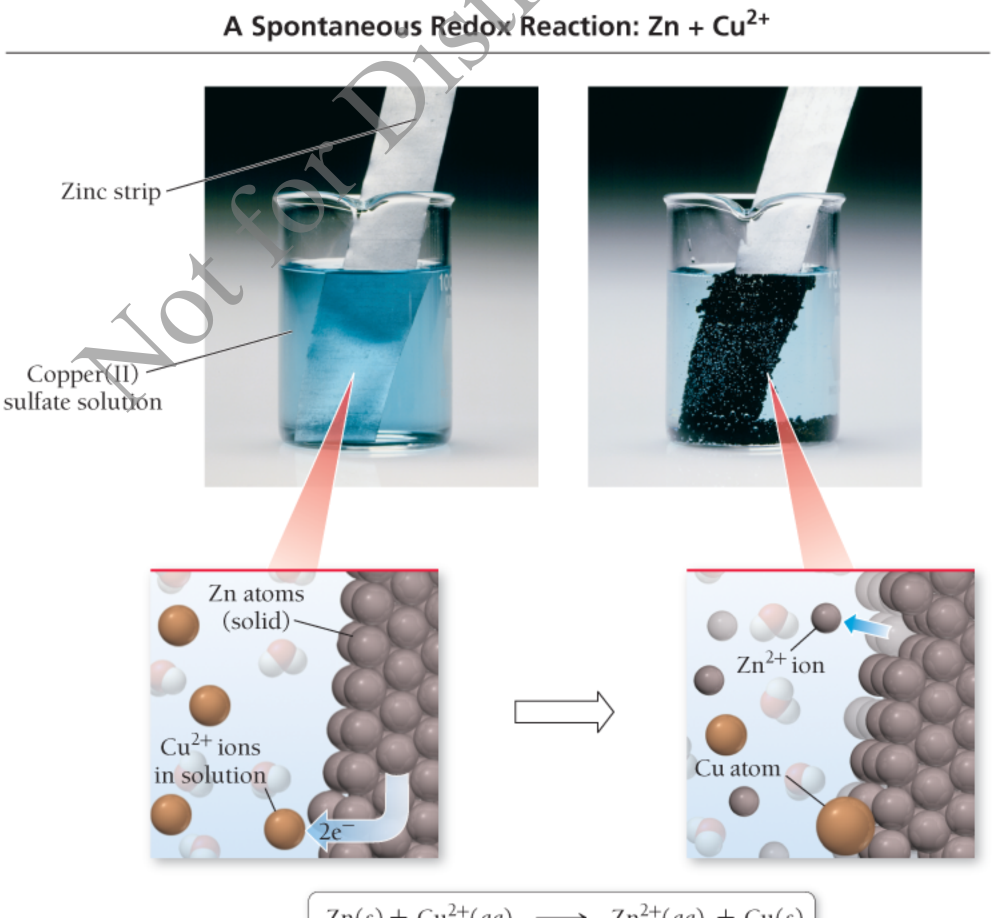
Electrical current is the flow of electric charge. Electrons flowing through a wire or ions flowing through a solution both constitute electrical current. Because redox reactions involve the transfer of electrons from one substance to another, they have the potential to generate electrical current as we discussed in Section 19.1. For example, consider the spontaneous redox reaction:

$$\mathrm{Zn}\,(s) + \mathrm{Cu}^{2+}\,(aq) \rightarrow \mathrm{Zn}^{2+}\,(aq) + \mathrm{Cu}\,(s)$$

When Zn metal is placed in a Cu^{2+} solution, the greater tendency of zinc to lose electrons results in Zn being oxidized and Cu^{2+} being reduced. Electrons are transferred directly from the Zn to the Cu^{2+} (Figure 19.1). Although the actual process is more complicated, we can imagine that—on the atomic scale—a zinc atom within the zinc metal transfers two electrons to a copper ion in solution. The zinc atom then becomes a zinc ion dissolved in the solution. The copper(II) ion accepts the two electrons and is deposited on the zinc as solid copper.

Figure 19.1 **A Spontaneous Oxidation–Reduction Reaction**

When zinc is immersed in a solution containing copper(II) ions, the zinc atoms transfer electrons to the copper(II) ions. The zinc atoms are oxidized and dissolve in the solution. The copper(II) ions are reduced and are deposited on the electrode.


A Spontaneous Redox Reaction: Zn + Cu2+
Zinc strip
Copper(II) sulfate solution
Zn atoms (solid)
Cu2+ ions in solution
2e−
Zn2+ ion
Cu atom

$$\mathrm{Zn}(s) + \mathrm{Cu}\ (aq) \longrightarrow \mathrm{Zn}\ (aq) + \mathrm{Cu}(s)$$

We can separate the zinc atoms and copper(II) ions and force the electron transfer to occur another way—not directly from the zinc atom to the copper(II) ion, but through a wire connecting the two half-reactions. The flowing electrons constitute an electrical current and can be used to do electrical work.

The Voltaic Cell

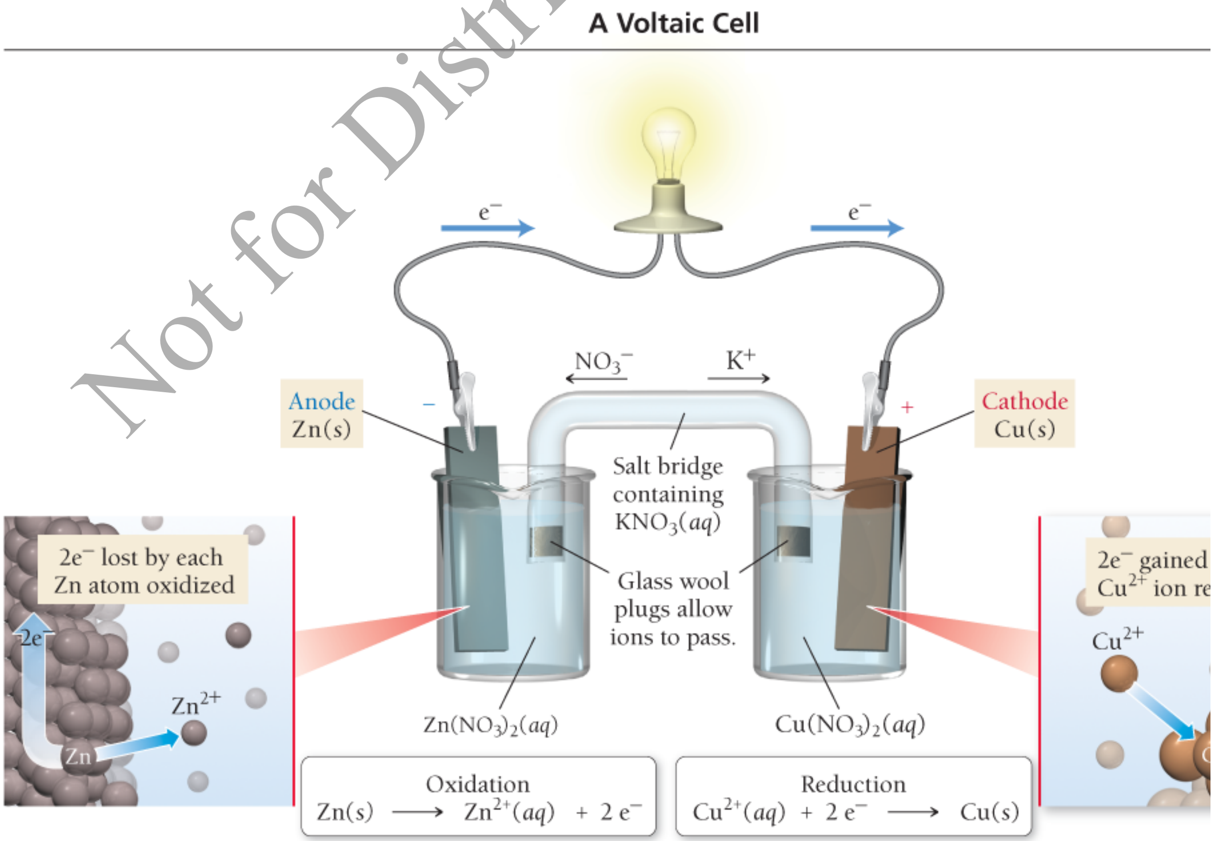
The generation of electricity through redox reactions is normally carried out in a device called an **electrochemical cell**. A **voltaic (or galvanic) cell** is an electrochemical cell that *produces* electrical current from a *spontaneous* chemical reaction. A second type of electrochemical cell, called an **electrolytic cell**, *consumes* electrical current to drive a *nonspontaneous* chemical reaction. We discuss voltaic cells in this section and electrolytic cells in Section 19.8.

In the voltaic cell in Figure 19.2, a solid strip of zinc is placed in a $\mathrm{Zn(NO_3)_2}$ solution to form a **half-cell**. A solid strip of copper placed in a $\mathrm{Cu(NO_3)_2}$ solution forms a second half-cell. The strips act as electrodes, conductive surfaces through which electrons can enter or leave the half-cells. Each metal strip reaches equilibrium with its ions in solution according to these half-reactions:

$$\mathrm{Zn}\,(s) \rightleftharpoons \mathrm{Zn}^{2+}\,(aq) + 2\,\mathrm{e}^-$$
$$\mathrm{Cu}\,(s) \rightleftharpoons \mathrm{Cu}^{2+}\,(aq) + 2\,\mathrm{e}^-$$

Figure 19.2 A Voltaic Cell

The tendency of zinc to transfer electrons to copper results in a flow of electrons through the wire that lights the bulb. The movement of electrons from the zinc anode to the copper cathode creates a positive charge buildup at the zinc half-cell and a negative charge buildup at the copper half-cell. The flow of ions within the salt bridge (which we describe later in this section) neutralizes this charge buildup, allowing the reaction to continue.



However, the position of these equilibria—which depends on the potential energy of the electrons in each metal

—is not the same for both metals. The electrons in zinc have a higher potential energy, and therefore zinc has a greater tendency to ionize than copper, so that the zinc half-reaction lies further to the right. As a result, the zinc electrode becomes negatively charged relative to the copper electrode.

> The *continual* flow of electrical current in a voltaic cell requires a pathway by which counterions can flow to neutralize charge buildup; we discuss this later in the chapter.

If the two half-cells are connected by a wire running from the zinc—through a light bulb or other electrical device—to the copper, electrons spontaneously flow from the zinc electrode (where they have higher potential energy) to the copper electrode (where they have lower potential energy). As the electrons flow away from the zinc electrode, the $\mathrm{Zn/Zn^{2+}}$ equilibrium shifts to the right (according to Le Châtelier's principle) and oxidation occurs. As electrons flow to the copper electrode, the $\mathrm{Cu/Cu^{2+}}$ equilibrium shifts to the left, and reduction occurs. The flowing electrons constitute an electrical current that lights the bulb.

> The idea that one electrode in a voltaic cell becomes more negatively charged relative to the other electrode due to differences in ionization tendencies is central to understanding how a voltaic cell works.

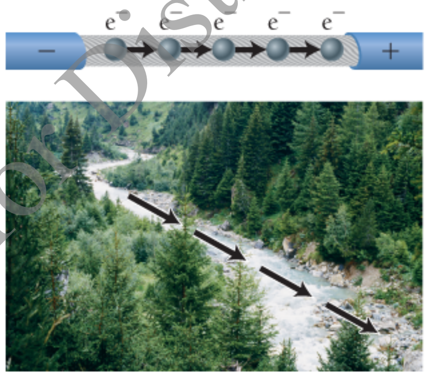
Electrical Current and Potential Difference

We can understand electrical current and why it flows by analogy with water current in a stream (Figure 19.3). The *rate of electrons flowing* through a wire is analogous to the *rate of water moving* through a stream. We measure electrical current in units of **amperes (A)** also called *amps*. One ampere represents the flow of one coulomb (a measure of electrical charge) per second.

$$1\ \mathrm{A} = 1\ \mathrm{C/s}$$

Figure 19.3 An Analogy for Electrical Current

Just as water flows downhill in response to a difference in gravitational potential energy, electrons flow through a conductor in response to an electrical potential difference, creating an electrical current.



Water flowing in a stream is analogous to electrons flowing in a wire.

Because an electron has a charge of 1.602×10^{-19} C, 1 A corresponds to the flow of 6.242×10^{18} electrons per second.

The *driving force* for electrical current is analogous to the driving force for water current. Water current is driven by a difference in gravitational potential energy. Streams flow downhill, from higher to lower potential energy. Electrical current is also driven by a difference in potential energy. Electrons flow from the electrode in which they have higher potential energy to the electrode in which they have lower potential energy. The difference in potential energy between the two electrodes is called **potential difference**. *Potential difference is a measure of the difference in potential energy (usually in joules) per unit of charge (coulombs).* The SI unit of potential difference is the **volt (V)**, which is equal to one joule per coulomb.

$$1\ \mathrm{V} = 1\ \mathrm{J/C}$$

In other words, a potential difference of one volt indicates that a charge of one coulomb experiences an energy difference of one joule between the two electrodes.

A large potential difference corresponds to a large difference in potential energy between the two electrodes and therefore a strong tendency for electron flow (analogous to a steeply descending streambed). Potential difference, because it gives rise to the force that results in the motion of electrons, is also referred to as **electromotive force (emf)**. In a voltaic cell, the potential difference between the two electrodes is the **cell potential (E_{cell})** or **cell emf**. The cell potential depends on the relative tendencies of the reactants to undergo oxidation and reduction. Combining the oxidation of a substance with a strong tendency to undergo oxidation and the reduction of a substance with a strong tendency to undergo reduction produces a large difference in charge between the two electrodes and therefore a high positive cell potential.

In general, the cell potential also depends on the concentrations of the reactants and products in the cell and the temperature (which we assume to be 25 °C unless otherwise noted). When the reactants and products are in their standard states (1 M concentration for substances in solution and 1 atm pressure for gaseous substances), the cell potential is called the **standard cell potential (E°_{cell})** or **standard emf**. For example, the standard cell potential in the zinc and copper cell described previously is 1.10 volts:

$$\mathrm{Zn}\,(s) + \mathrm{Cu}^{2+}\,(aq) \rightarrow \mathrm{Zn}^{2+}\,(aq) + \mathrm{Cu}\,(s) \quad E^{\circ}_{\text{cell}} = +1.10\ \mathrm{V}$$

> Standard states, indicated by the symbol °, represent a very specific reaction mixture. For a reaction mixture with reactants and products in their standard states, $Q = 1$.

If the zinc is replaced with nickel (which has a lower tendency to be oxidized) the standard cell potential is lower:

$$\mathrm{Ni}\,(s) + \mathrm{Cu}^{2+}\,(aq) \rightarrow \mathrm{Ni}^{2+}\,(aq) + \mathrm{Cu}\,(s) \quad E^{\circ}_{\text{cell}} = +0.62\ \mathrm{V}$$

The cell potential is a measure of the overall tendency of the redox reaction to occur spontaneously—the lower the cell potential, the lower the tendency to occur. A negative cell potential indicates that the forward reaction is not spontaneous.

Anode, Cathode, and Salt Bridge

In all electrochemical cells, the electrode where oxidation occurs is the **anode**, and the electrode where reduction occurs is the **cathode**. In a voltaic cell, the anode is the more negatively charged electrode, and we label it with a negative (−) sign. The cathode of a voltaic cell is the more positively charged electrode, and we label it with a (+) sign. Electrons flow from the anode to the cathode (from negative to positive) through the wires connecting the electrodes.

> Note that the anode and cathode need not actually be negatively and positively charged, respectively. The anode is the electrode with the relatively *more* negative (or less positive) charge.

As electrons flow out of the anode, positive ions (Zn^{2+} in the preceding example) form in the oxidation half-cell, resulting in a buildup of *positive charge* in the *solution*. As electrons flow into the cathode, positive ions (Cu^{2+} in the preceding example) are reduced at the reduction half-cell, resulting in a buildup of *negative charge* in the *solution.*

If the movement of electrons from anode to cathode were the only flow of charge, the buildup of the opposite charge in the solution would stop electron flow almost immediately. The cell needs a pathway by which counterions can flow between the half-cells without the solutions in the half-cells totally mixing. One such pathway is a **salt bridge**, an inverted, U-shaped tube that contains a strong electrolyte such as $\mathrm{KNO_3}$ and connects the two half-cells (see Figure 19.2). The electrolyte is usually suspended in a gel and held within the tube by permeable stoppers. The salt bridge allows a flow of ions that neutralizes the charge buildup in the solution. *The negative ions within the salt bridge flow to neutralize the accumulation of positive charge at the anode, and* solution. *The negative ions within the salt bridge flow to neutralize the accumulation of positive charge at the anode, and the positive ions flow to neutralize the accumulation of negative charge at the cathode*. In other words, the salt bridge completes the circuit, allowing electrical current to flow.

Conceptual Connection 19.1 Voltaic Cells

Electrochemical Cell Notation

We represent electrochemical cells with a compact notation called a *cell diagram* or *line notation*. For example, we can represent the electrochemical cell in which Zn is oxidized to Zn^{2+} and Cu^{2+} is reduced to Cu as follows:

$$\mathrm{Zn}\,(s)\,|\mathrm{Zn}^{2+}\,(aq)||\mathrm{Cu}^{2+}\,(aq)|\,\mathrm{Cu}\,(s)$$

In this representation,

- we write the oxidation half-reaction on the left and the reduction on the right. A double vertical line, indicating the salt bridge, separates the two half-reactions.
- substances in different phases are separated by a single vertical line, which represents the boundary between the phases.
- for some redox reactions, the reactants and products of one or both of the half-reactions may be in the same phase. In these cases (which we explain further next), we separate the reactants and products from each other with a comma in the line diagram. Such cells use an inert electrode, such as platinum (Pt) or graphite, as the anode or cathode (or both).

Consider the redox reaction in which Fe(s) is oxidized and $MnO_4{}^-\,(aq)$ is reduced:

$$5\,\mathrm{Fe}\,(s) + 2\,\mathrm{MnO_4}^-\,(aq) + 16\,\mathrm{H}^+\,(aq) \rightarrow 5\,\mathrm{Fe}^{2+}\,(aq) + 2\,\mathrm{Mn}^{2+}\,(aq) + 8\,\mathrm{H_2O}\,(l)$$

The half-reactions for this overall reaction are:

> ***Oxidation:*** $\mathrm{Fe}\,(s) \rightarrow \mathrm{Fe}^{2+}\,(aq) + 2\,\mathrm{e}^-$
>
> ***Reduction:*** $\mathrm{MnO_4}^-\,(aq) + 5\,\mathrm{e}^- + 8\,\mathrm{H}^+\,(aq) \rightarrow \mathrm{Mn}^{2+}\,(aq) + 4\,\mathrm{H_2O}\,(l)$

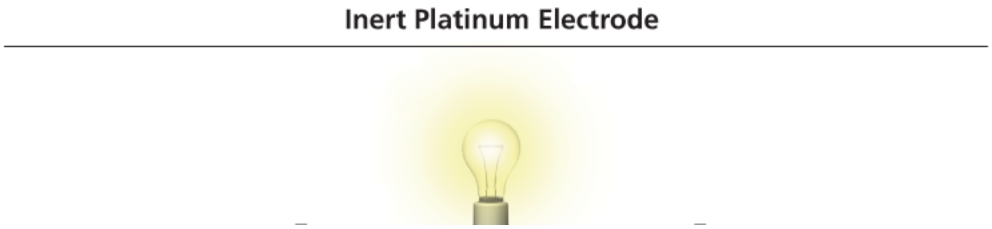
Notice that in the reduction half-reaction the principal species are all in the aqueous phase. In this case, the electron transfer needs an electrode on which to occur. An inert platinum electrode is employed, and the electron transfer takes place at its surface. Using line notation, we represent the electrochemical cell corresponding to the above reaction as:

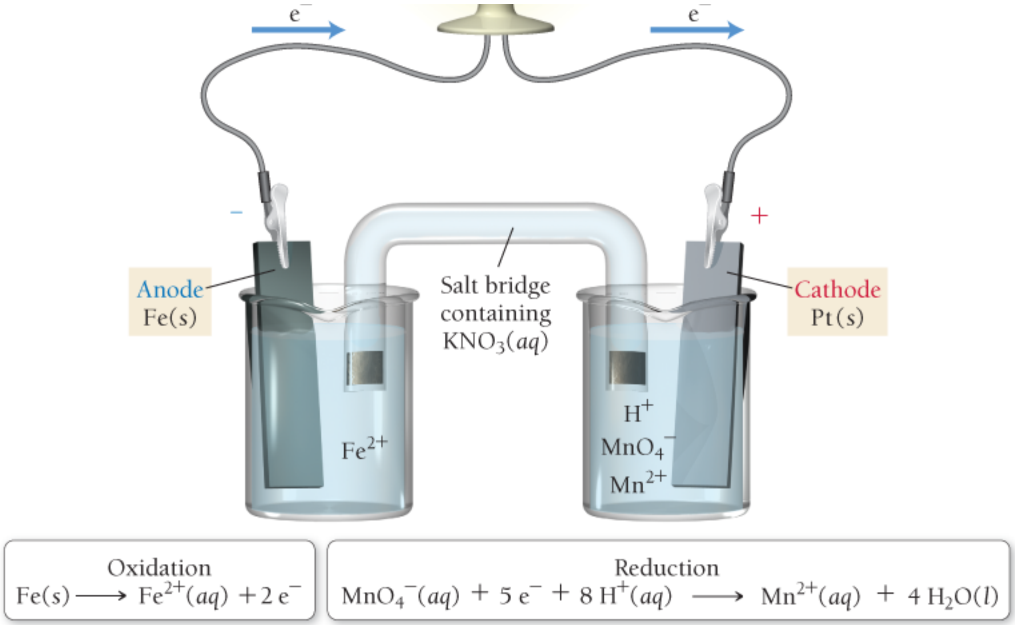
$$\mathrm{Fe}\,(s)\,|\mathrm{Fe}^{2+}\,(aq)||\mathrm{MnO_4}^-\,(aq)\,,\mathrm{H}^+\,(aq)\,,\mathrm{Mn}^{2+}\,(aq)|\,\mathrm{Pt}\,(s)$$

The Pt(s) on the far right indicates that an inert platinum electrode acts as the cathode in this reaction, as depicted in Figure 19.4.

Figure 19.4 Inert Platinum Electrode

When the participants in a half-reaction are all in the aqueous phase, a conductive surface is needed for electron transfer to take place. In such cases, an inert electrode of graphite or platinum is often used. In this electrochemical cell, an iron strip acts as the anode and a platinum strip acts as the cathode. Iron is oxidized at the anode, and $MnO_4{}^-$ is reduced at the cathode.




e^-
e^-
−
+
Anode
Fe(s)
Salt bridge containing $KNO_3(aq)$
Cathode
Pt(s)
Fe^{2+}
H^+
MnO_4^-
Mn^{2+}
Oxidation
$Fe(s) \longrightarrow Fe^{2+}(aq) + 2\,e^-$
Reduction
$MnO_4^-(aq) + 5\,e^- + 8\,H^+(aq) \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$