10.1



Figure 1 Dental braces that come in contact with aluminum, such as the aluminum in candy wrappers, can produce a strange tingling sensation.



Figure 3 The oxidizing and reducing agents of a redox reaction can be separated by placing them in different containers.

half-cell an electrode and an electrolyte that form half of a complete cell

electrode a solid electrical conductor

cell a system in which two connected electrodes are in contact with an electrolyte

Galvanic Cells

Have you ever bitten down on aluminum foil accidentally and experienced an unpleasant tingling feeling? Touching aluminum metal against dental work can cause this feeling (**Figure 1**). Touching a gold chain against metal dental braces can produce a similar feeling. The tingling is the result of a small electric current that is generated by an oxidation–reduction or redox reaction. The reaction involves two different metals and electrolytes in your saliva. The batteries that we use to provide energy for portable electrical devices work in a similar way.

Transforming Chemical Energy into Electrical Energy

During a redox reaction, one substance loses electrons while another substance gains electrons. As this occurs, electrons are transferred from the substance that is oxidized to the substance that is reduced. You are likely familiar with the chemical reaction of a strip of zinc metal, Zn(s), with a solution of copper(II) sulfate, $CuSO_4(aq)$ (**Figure 2**):

 $Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$



Figure 2 (a) A strip of zinc metal is placed in a solution of copper(II) sulfate. (b) After several hours, the characteristic blue colour of the copper(II) ion, $Cu^{2+}(aq)$, has disappeared, indicating that copper(II) ions are no longer present. Instead, solid copper metal remains in the beaker.

During this chemical reaction, electrons are transferred from the zinc metal to the aqueous copper(II) ions. As a result, the zinc metal is oxidized and the copper(II) ions are reduced. The half-reaction equations for these reactions can be written as follows:

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

Reduction: $Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s)$

The balanced chemical equation for the redox reaction is the sum of the two half-reaction equations:

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

Electrons are transferred directly from the zinc atoms to the copper(II) ions when the copper(II) ions collide with the zinc surface. This reaction occurs spontaneously, releasing a small quantity of energy. When the zinc metal and the copper(II) ions are in direct contact, the chemical energy of these transferred electrons cannot be harnessed directly. Instead, it is released to the environment as thermal energy. The key to harnessing the energy is to separate the oxidizing agent from the reducing agent in a way that forces electron transfer to occur through a wire. When electrons flow through a wire, electric current is produced. The current can then be directed through a device, such as an electric motor, a clock, or a music player.

The system illustrated in **Figure 3** is composed of two half-cells connected by a wire. Each **half-cell** consists of an electrode that is in contact with a solution of ions. An **electrode** is a solid electrical conductor. The metal strips in Figure 3 are the electrode. The system in Figure 3 can be called a **cell**, which is a system comprising of two electrodes in contact with appropriate electrolytes.

We might predict that the copper(II) ions in Figure 3 (in the beaker on the right) would attract electrons from the zinc electrode. This would result in a flow of electrons through the wire from the zinc strip to the copper strip. However, careful observation of the cell shows that current flows for an instant and then stops. Why? The current stops flowing because charges build up in the two half-cells. The oxidation of the zinc results in an increase in the concentration of zinc(II) ions in the zinc half-cell. This results in a buildup of positive charge. Similarly, the reduction of copper(II) ions in the copper half-cell reduces the concentration of copper(II) ions in the solution. This results in a buildup of negative charge in the copper half-cell due to the sulfate ions that remain. The buildup of charge in each half-cell prevents further electron transfer from occurring. As a result, the redox reaction stops. This problem can be solved very simply by connecting the solutions so that ions can flow between them to keep the net charge in each half-cell at zero.

Transforming Chemical Energy into Electrical Energy

The two half-cells could be connected with a salt bridge. A salt bridge is a U-shaped tube that is filled with a non-reactive electrolyte (Figure 4). The ends of the tube are plugged with cotton balls. The cotton plugs prevent the solution from falling out of the tube, but they are porous enough to permit some fluid and ions to flow in and out of the tube.





THE ROLE OF THE SALT BRIDGE

The salt bridge in Figure 4 consists of a U-shaped tube filled with a sodium sulfate solution. Sodium sulfate is an ideal electrolyte for this salt bridge because it is very soluble and its ions do not react with the electrodes or the electrolyte solutions. The cotton plugs at the ends of the tube are porous enough to allow ions to flow in and out of the tube, but they prevent the solution from pouring out.

As this cell operates, sulfate ions, $SO_4^{2-}(aq)$, spontaneously migrate into the zinc half-cell to offset any buildup of zinc(II) ions. Similarly, sodium ions spontaneously migrate into the copper half-cell to offset the loss of copper (II) ions. As a result of ion migration through the salt bridge, the solutions in each half-cell remain electrically neutral. 🏶 CAREER LINK

UNIT TASK BOOKMARK

Consider what kinds of electrodes and electrolytes you will need to construct a galvanic cell for the Unit Task outlined on page 684.



Characteristics of a Galvanic Cell

galvanic cell an arrangement of two connected half-cells that spontaneously produces electric current

anode the electrode where oxidation occurs

cathode the electrode where reduction occurs

If you explored the effect of inserting electrodes into fruits and vegetables at the beginning of this chapter, you made an electric cell. In honour of Luigi Galvani, this cell is called a **galvanic cell**: a device consisting of two connected half-cells that produce current electrical energy spontaneously. The reactions in a galvanic cell occur at the interface between the electrodes and the solutions where the electron transfer occurs. The electrode where oxidation occurs is called the **anode**. The electrode where reduction occurs is called the **cathode** (**Figure 5**). As the cell operates, electrons flow spontaneously from the anode to the cathode through an external path—the conducting wire. In the salt bridge, negatively charged ions, or anions, flow to the anode while positively charged ions, or cations, flow to the cathode.





What changes might we observe in the galvanic cell in Figure 5? What would we notice if we replaced the voltmeter with an ammeter? **Table 1** shows some typical observations and a theoretical interpretation of these observations.

Table 1	Evidence	and I	Interpretation	of the	Zinc-	Copper	Cel
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Evidence	Interpretation	
The zinc electrode decreases in mass.	Oxidation of the zinc metal is occurring at the zinc anode: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$	
The copper electrode increases in mass as copper is deposited on it. The blue colour of the copper(II) solution decreases in intensity.	Copper(II) ions in solution are reduced to copper metal at the copper cathode: $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	
A voltmeter indicates that the zinc electrode has a negative charge and the copper electrode has a positive charge.	Electrons move from the zinc electrode to the copper electrode.	
An ammeter indicates that electric current flows from the zinc electrode to the copper electrode.	Electrons leave the zinc half-cell and enter the copper half-cell.	

Predicting Cell Reactions and Equations

The direction of electron flow can be explained in terms of a competition for electrons, much like a "tug of war." Both zinc ions and copper(II) ions are capable of accepting electrons from another substance. In other words, both ions can act as oxidizing agents. According to the table of Standard Reduction Potentials (Table 1 in Appendix B7), $Cu^{2+}(aq)$ ions are a stronger oxidizing agent (SOA) than $Zn^{2+}(aq)$ ions. As a result, we would predict that the copper(II) ions should win the "tug of war" for electrons when the two half-cells in Figure 5 are connected. The source of these electrons is the stronger reducing agent (SRA) in the cell: zinc metal. Our prediction is supported by the evidence: electrons flow spontaneously from the zinc anode to the copper cathode as this cell operates.

The net ionic equation of the reaction in this cell can be determined using the same procedure that was used in Section 9.3 when predicting redox reactions:

Anode (oxidation) half-reaction equation:	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{>}$		
Cathode (reduction) half-reaction equation:	$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$		
Net ionic equation:	$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$		
	(SOA) (SRA)		

Galvanic Cells with Inert Electrodes

Chemists are continually exploring the various combinations of oxidizing and reducing agents, electrodes, and electrolytes that could be used to construct an electric cell. In a cell with a metal electrode and metal ions, the metal electrode usually participates in the cell reaction. However, not all galvanic cells are constructed this way. Many of the cells in batteries use an inert solid conductor, such as carbon (graphite), as an electrode. An inert electrode provides a surface on which the oxidation and reduction reactions may occur, but it does not participate in these reactions. An inert electrode is required in cells where the cell reaction involves only entities in the solution, not the electrode itself.

To understand the role of an inert electrode in a galvanic cell, consider the reaction between aqueous permanganate ions, $MnO_4^{-}(aq)$, and aqueous iron(II) ions, $Fe^{2+}(aq)$:

 $8 \text{ H}^{+}(\text{aq}) + \text{MnO}_{4}^{-}(\text{aq}) + 5 \text{ Fe}^{2+}(\text{aq}) \rightarrow \text{Mn}^{2+}(\text{aq}) + 5 \text{ Fe}^{3+}(\text{aq}) + 4 \text{ H}_{2}\text{O}(\text{l})$

During the reduction half-reaction, the manganese atoms of the permanganate ions are reduced from manganese with an oxidation number of +7 to manganese with an oxidation number of +2:

 $8 \text{ H}^+(\text{aq}) + \text{MnO}_4^-(\text{aq}) + 5 \text{ e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{ H}_2\text{O}(\text{l})$

During the oxidation half-reaction equation, iron(II) ions are oxidized to iron(III) ions:

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

To balance the two half-reaction equations, first multiply the oxidation reaction by 5:

$$5(\mathrm{Fe}^{2+}(\mathrm{aq}) \rightarrow \mathrm{Fe}^{3+}(\mathrm{aq}) + \mathrm{e}^{-})$$

 $5 \text{ Fe}^{2+}(aq) \rightarrow 5 \text{ Fe}^{3+}(aq) + 5 \text{ e}^{-1}$

Then, add the two half-reaction equations to get the balanced net ionic equation for the overall reaction:

$$8 \text{ H}^{+}(aq) + \text{MnO}_{4}^{-}(aq) + 5 \text{ Fe}^{2+}(aq) \rightarrow \text{Mn}^{2+}(aq) + 5 \text{ Fe}^{3+}(aq) + 4 \text{ H}_{2}\text{O}(l)$$
(SOA) (SRA)

In this reaction, permanganate, $MnO_4^{-}(aq)$, is the stronger oxidizing agent and iron(II) is the stronger reducing agent. The manganese(II) ion, $Mn^{2+}(aq)$, is the reduction product, and iron(III) is the oxidation product. The reduction half-reaction equation represents the reactions occurring at the cathode and the oxidation half-reaction equation represents the reactions occurring at the anode. The inert electrodes provide a place to connect the wire and a surface for the half-reactions to occur.

Line Notation and Galvanic Cells

Line notation is an abbreviated way to describe cells. In line notation, the anode components are listed on the left and the cathode components are listed on the right. They are separated by double vertical lines to indicate a salt bridge. A single vertical line indicates a boundary between two states of matter, such as the interface of an electrode and an electrolyte in a half-cell (**Figure 6**).



Figure 6 This example shows the general pattern for writing line notation.

Starting with the net ionic equation, we can produce the following line notation for the zinc–copper cell in Figure 5:

Net ionic equation:	$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
Line notation:	$Zn(s) Zn^{2+}(aq) Cu^{2+}(aq) Cu(s)$

Platinum, Pt(s), is the inert electrode that is generally used in the iron(II)–permanganate cell. The net ionic equation and line notation for this cell are written as follows:

Net ionic equation:

 $8 H^{+}(aq) + MnO_{4}^{-}(aq) + 5 Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 5 Fe^{3+}(aq) + 4 H_{2}O(l)$ Line notation: $Pt(s)|Fe^{2+}(aq)||MnO_{4}^{-}(aq)|Pt(s)$

Investigation 10.1.1

Investigating Galvanic Cells (page 671) In this investigation, you will build three different galvanic cells to

determine which cell produces the highest voltage.



Summary

- A galvanic cell consists of two separated half-cells. The electrodes are connected by a wire. The solutions are connected by a salt bridge.
- In a galvanic cell, reduction occurs at the cathode (the positive electrode) and oxidation occurs at the anode (the negative electrode).
- The stronger oxidizing agent is reduced at the cathode. The stronger reducing agent is oxidized at the anode.
- As the cell operates, electrons travel from the anode to the cathode via the external circuit (the wire). Ions flow through the salt bridge to keep the solutions electrically neutral (anions to the anode, cations to the cathode).

Questions

- 1. Why is it necessary to separate the oxidizing agent from the reducing agent in a galvanic cell?
- 2. Identify the two "connections" that are required before a galvanic cell can function.
- 3. What characteristics should the solution in a salt bridge have? **KU T**
- 4. A galvanic cell is constructed using the following materials: strip of nickel metal; strip of magnesium metal; nickel(II) sulfate, NiSO₄(s); magnesium sulfate, MgSO₄(s); sodium sulfate, Na₂SO₄(s), for the salt bridge; distilled water; connecting wires; U-shaped tube; cotton; 2 beakers; voltmeter. KU TTI C
 - (a) Draw and label a diagram of the cell.
 - (b) Identify the anode and the cathode in the cell.
 - (c) Label the directions of electron and ion flow.
 - (d) Identify the oxidizing and reducing agents.
 - (e) Write the equations for the half-reactions that occur in the cell.
 - (f) Write the net ionic equation for the cell reaction.
 - (g) Predict how the mass of the electrodes will change as the cell operates.
- 5. Consider the galvanic cells that are represented by the given line notations. For each cell,
 - (i) identify the stronger oxidizing agent and stronger reducing agent,
 - (ii) write chemical equations to represent the half-reactions at the cathode and anode, and
 - (iii) write the net ionic equation.
 - (a) $Mg(s)|Mg^{2+}(aq)||Cu^{+}(aq)|Cu(s)$
 - (b) $Fe(s)|Fe^{2+}(aq)||Ag^{+}(aq)|Ag(s)$
- A galvanic cell has a magnesium electrode in a 1.0 mol/L magnesium nitrate solution and an iron electrode in a 1.0 mol/L iron(II) nitrate solution.
 - (a) Draw a diagram of the cell. Include the following labels: anode, cathode, salt bridge, electron flow, ion flow.

- (b) Predict the half-reactions that will occur, and write their equations.
- (c) Write a net ionic equation for the cell reaction.
- (d) What visible evidence would you expect to see, indicating that the cell is functioning?
- Figure 7 shows a galvanic cell that consists of magnesium and copper electrodes in tap water. This cell generates enough electrical energy to operate a small digital clock. KU TI C
 - (a) Compare the design of this cell with the zinccopper cell in Figure 5.
 - (b) The anode half-reaction in this cell is the oxidation of magnesium. The cathode halfreaction involves the reduction of water. Use the redox table to write equations for both halfreactions and the net ionic equation for the cell reaction.
 - (c) What is the function of the copper electrode in this cell?
 - (d) The cell in Figure 7 works well with tap water but not with distilled water. Why do you think the type of water that is used makes a difference?

