> *"'Reduce' is derived from Latin words meaning 'to lead back' and if iron, for instance, is observed to turn to rust . . . it is natural to think of rust as being 'led back' to iron."*
>
> *Isaac Asimov*

Electrochemistry

Before you continue your study of electrochemistry, you might do well to consider two of the most common words used in this field: reduction and oxidation. These terms originated from early chemists who studied metal ores. According to Isaac Asimov, the term *reduced* is derived from Latin, meaning "to lead back." For instance, when iron ore (solid iron oxides) is combined with coke (a nearly pure form of carbon derived from coal) and heated, a chemical change takes place where the carbon atoms from the coke combine with the oxygen atoms in the ore, producing carbon dioxide, and pure iron is left behind. The iron ore is *reduced*. Since the carbon caused the iron ore to be reduced, it is called the *reducing agent*. Carbon has taken on oxygen atoms, so it is said to be *oxidized*.

As you have learned from your textbook, the modern definitions of the terms oxidation and reduction are no longer restricted to reactions involving oxygen. Oxidation is the loss of electrons. Reduction is the gain of electrons. One of the most fascinating aspects of oxidation–reduction reactions is the tendency of various substances to gain or lose electrons. If a substance with a powerful tendency to gain electrons is paired with a substance with a tendency to lose electrons, a *battery* or *fuel cell* is created in which the energy of the electron transfer can be tapped. Utilizing the energy of electron-transfer reactions has far-reaching consequences ranging from powering calculators and laptop computers to translating food to usable energy in living organisms.

Half Reactions

Consider two half reactions, the reduction of copper(II) ions and the oxidation of nickel metal:

$$\mathrm{Cu^{2+}(aq) + 2\,e^{-} \rightleftharpoons Cu(s)} \qquad \textbf{(1)}$$

$$\mathrm{Ni(s) \rightleftharpoons Ni^{2+}(aq) + 2\,e^{-}} \qquad \textbf{(2)}$$

Combining these two half reactions, we obtain the complete balanced redox reaction:

$$\mathrm{Cu^{2+}(aq) + Ni(s) \rightleftharpoons Cu(s) + Ni^{2+}(aq)} \qquad \textbf{(3)}$$

Let's consider how this reaction might be carried out in the laboratory. The simplest method is to place a piece of nickel into a solution that contains copper(II) ions, such as copper(II) chloride. This is illustrated in Figure 1. The solution originally is blue, which is the color of copper(II) ions in aqueous solution. As the reaction proceeds, nickel atoms transfer electrons to copper(II) ions, and the resulting nickel ions become hydrated, increasing the concentration of $Ni^{2+}(aq)$ in solution. As the copper(II) ion concentration decreases and the nickel ion concentration in solution increases, the solution color changes from blue to green, the color of $Ni^{2+}(aq)$. The energy associated with the electron transfer in this experiment is not used for useful work and is wasted as heat.

By separating the reactants and connecting them with a wire, the electron will do work as it moves from the nickel to the copper. Since the electron will have a different energy at one end of the connecting wire than the other, a potential energy difference or *voltage* exists. The units of voltage are volts. A potential energy difference of one volt exists when one coulomb of electron charge does one joule of work at it moves from one point to another.

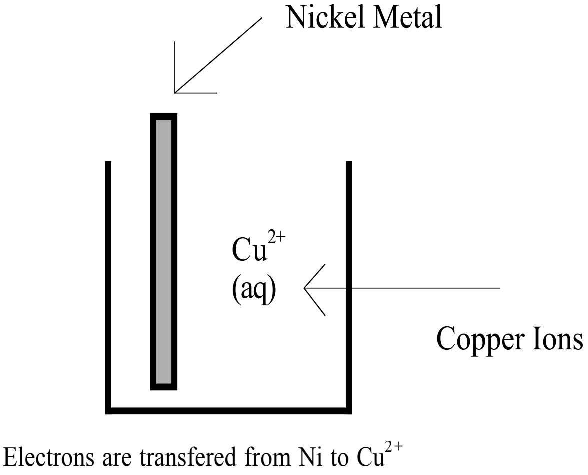

Figure 1. A piece of nickel metal is placed in a solution of copper(II) chloride. The solution is originally blue because of the copper(II) ions, but as the reaction proceeds, the solution turns green, as a result of the presence of nickel ions.

The definition of a volt makes the definition of a coulomb necessary. We can think of a coulomb as the charge on 6.24×10^{18} electrons. You may wonder why a mole of electrons was not chosen to define a coulomb, but to the chagrin of chemists (and chemistry students alike!), the coulomb was defined before the mole. Don't let the units make you lose sight of the main point, however: the voltage of an electrochemical cell can be measured, and the greater the voltage, the greater the potential energy difference for the movement of electrons from anode to cathode.

Consider the cell illustrated in Figure 2. When electrons transfer across the cell, a buildup of negative charge occurs on the copper strip, and there is a deficit of electrons on the nickel. This will prevent, after a brief moment, any further flow of electrons, as they will be repulsed by the highly negative electrode. To solve this problem of buildup of charge, a salt bridge is added to the cell to provide an alternate pathway so that ions are free to move from one side to the other.

In an electrochemical cell such as the one illustrated in Figure 2, the electrons flow spontaneously, with no external power source. Such a cell is known as a *voltaic* or *galvanic* cell. Electrons flow from the anode to the cathode. The salt bridge, filled with an aqueous solution of an ionic compound, such as NaCl(aq), allows ions to move to compensate for the buildup of electrons at the cathode. In this cell, the chloride anions would move from the cathode to the anode.

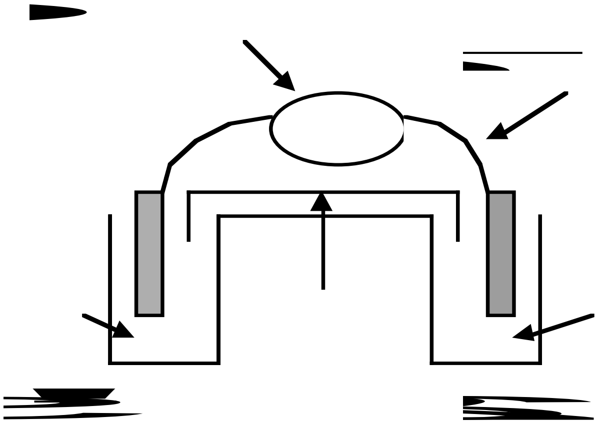

Figure 2. An electrochemical cell consisting of one compartment with copper metal submersed in a copper(II) ion-containing solution and the other compartment with nickel metal in a nickel in-containing solution. The metal strips are connected by a conducting wire, and the solutions are connected by a salt bridge.

If the nickel and copper(II) ion concentrations are 1.00 M in the cell in Figure 2, the potential is 0.57 volt. A useful reference point to use to think about cell potentials is a common alkaline battery, such as those used to power personal stereos and flashlights. Such batteries have a potential of 1.5 volts. The potential in a cell can be viewed as arising from the relative tendencies of the two half cells to give or take electrons. Each redox half reaction has a half-cell potential. If the potential is measured at standard conditions, it is called the standard half-cell potential, which is symbolized as E°.

For the cell in Figure 2:

Half-cell Reaction	Standard Reduction Potential, E° (V)
$Cu^{2+}(aq) + 2\ e^{-} \rightleftharpoons Cu(s)$	0.34
$Ni^{2+}(aq) + 2\ e^{-} \rightleftharpoons Ni(s)$	–0.23

Standard reduction potentials are determined by constructing a cell and measuring the potential of the half reaction versus the hydrogen half reaction with all solutes at 1.00 M and gases at 1.00 atm. The reaction $2\ H^{+}(aq) + 2\ e^{-} \rightarrow H_2(g)$ with 1.00 M $H^{+}(aq)$ and 1.00 atm $H_2(g)$ is assigned a potential of exactly zero. Therefore all standard reduction potentials are a measure of the tendency of that half reaction to gain or lose an electron relative to the standard hydrogen electrode.

The total potential for a cell is the sum of the potentials of the half cells. The half-cell reaction listed for the reduction of the copper(II) ion is exactly as listed above. However, the spontaneous half-cell reaction for Ni is the opposite of what is listed. In general,

$$E^{\circ}_{total} = E^{\circ}_{cathode} - E^{\circ}_{anode}{}^{*} \qquad \textbf{(4)}$$

The Nernst Equation

From a table of standard potentials you can calculate the cell voltage for a cell composed of any combination of half reactions, as long as the cell is at standard conditions. When the concentrations are nonstandard, the Nernst equation, named after the German chemist Walther Nernst (1864–1941), allows the voltage to be determined:

$$E = E^{\circ} - \frac{0.0592}{n} \log Q \qquad \textbf{(5)}$$

The equation is valid when potentials are measured in volts and the temperature is 25°C. Q in this equation is called the *reaction quotient* and is set up just like an equilibrium constant expression. When a solid or gas is present, its concentration term is set to one. Dissolved solute concentrations are expressed in moles per liter. The Nernst equation for the copper-nickel cell in Figure 2 is:

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*Some textbooks give this equation as its equivalent, $E^{\circ}_{cell} = E^{\circ}_{oxidation} + E^{\circ}_{reduction}$.

$$E = 0.34 - \frac{0.0592}{n} \log \left(\frac{[Ni^{2+}]}{[Cu^{2+}]}\right) \qquad \textbf{(6)}$$

Electrolytic Cells

To this point we have only considered voltaic (galvanic) cells where a chemical reaction is used to create a potential which can do work. The reverse situation in which a potential is used to cause a reaction to occur is also important. Such cells are called *electrolytic cells*. A common example is the recharging of a rechargeable battery, such as those found in cars. The spontaneous reaction that occurs in a lead automobile battery is

$$Pb(s) + PbO_2(s) + 2\,SO_4^{2-}(aq) + 4\,H^+(aq) \rightleftharpoons 2\,PbSO_4(s) + 2\,H_2O(\ell) \qquad \textbf{(7)}$$

When the battery is fully discharged, which means that the voltaic reaction has essentially gone to completion, the battery can be recharged by applying a voltage of 2 V and switching the anode and cathode reactions. Electrons naturally flow from plus to minus. The electrode marked plus is the cathode, and the electron marked minus is the anode. When the external voltage source is attached to the battery, the plus lead is attached to the cathode and the minus to the cathode. This causes the external voltage to be applied against the spontaneous flow of the current in the cell, which regenerates the original reactants.