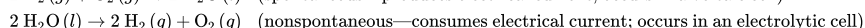
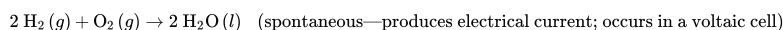


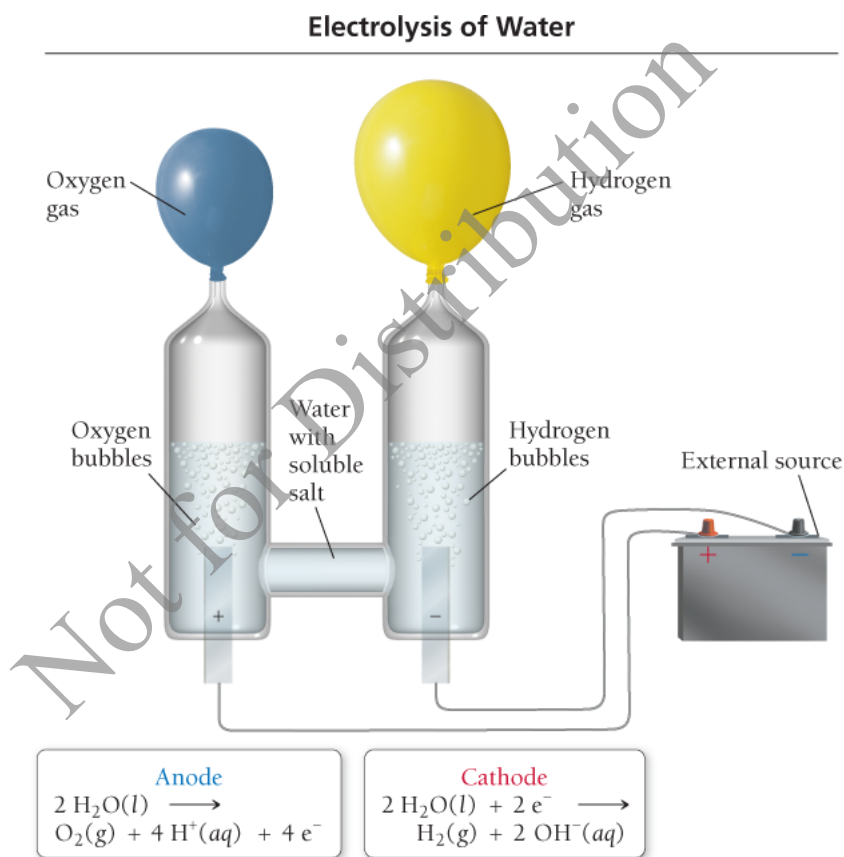
## 19.8: Electrolysis: Driving Nonspontaneous Chemical Reactions with Electricity

In a voltaic cell, a spontaneous redox reaction produces electrical current. In an *electrolytic cell*, electrical current drives an otherwise nonspontaneous redox reaction through a process called **electrolysis**. We have seen that the reaction of hydrogen with oxygen to form water is spontaneous and can be used to produce an electrical current in a fuel cell. Conversely, by *supplying* electrical current, we can cause the reverse reaction to occur, separating water into hydrogen and oxygen (Figure 19.16).



**Figure 19.16 Electrolysis of Water**

Electrical current can decompose water into hydrogen and oxygen gas.



Recall from the previous section that one of the problems prohibiting the widespread adoption of hydrogen fuel cells is the scarcity of hydrogen. Where will the hydrogen to power these fuel cells come from? One possible answer is to obtain hydrogen from water through solar-powered electrolysis. A solar-powered electrolytic cell can produce hydrogen from water when the sun is shining. The hydrogen made in this way could be converted back to water to generate electricity and could also be used to power fuel-cell vehicles.

Electrolysis also has numerous other applications. For example, most metals are found in Earth's crust as metal oxides. Converting an oxide to a pure metal requires that the metal be reduced, a nonspontaneous process.

Electrolysis can be used to produce these metals. Thus, sodium is produced by the electrolysis of molten sodium

Electrolysis can be used to produce more metal than that which is produced by the electrolysis of molten sodium chloride (discussed in the following subsection). Electrolysis is also used to plate metals onto other metals. For example, silver can be plated onto a less expensive metal using the electrolytic cell shown in Figure 19.17. In this cell, a silver electrode is placed in a solution containing silver ions. An electrical current causes the oxidation of silver at the anode (replenishing the silver ions in solution) and the reduction of silver ions at the cathode (coating the less expensive metal with solid silver).

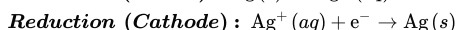
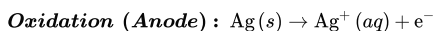
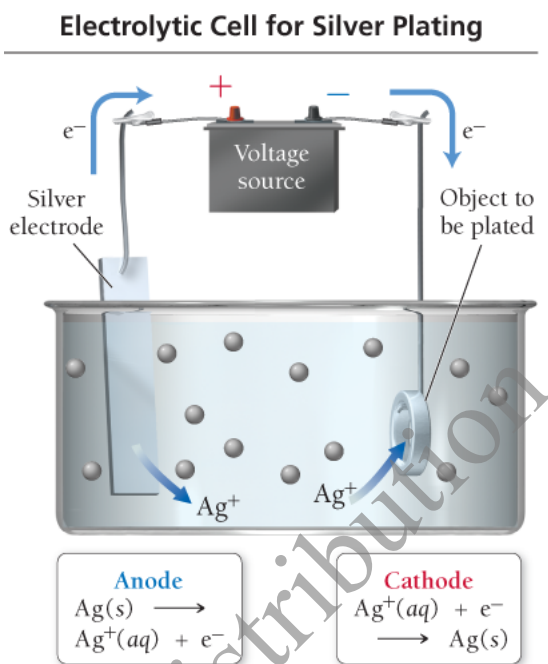


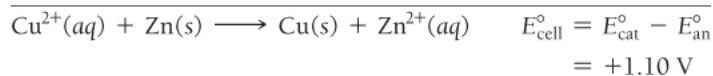
Figure 19.17 Silver Plating

Silver from a solution of silver ions can be plated onto metallic objects in an electrolytic cell.



Since the standard cell potential of the reaction is zero, the reaction is not spontaneous under standard conditions. An external power source drives current flow and causes the reaction to occur.

The voltage required to cause electrolysis depends on the specific half-reactions. For example, we have seen that the oxidation of zinc and the reduction of  $\text{Cu}^{2+}$  produces a voltage of 1.10 V under standard conditions.



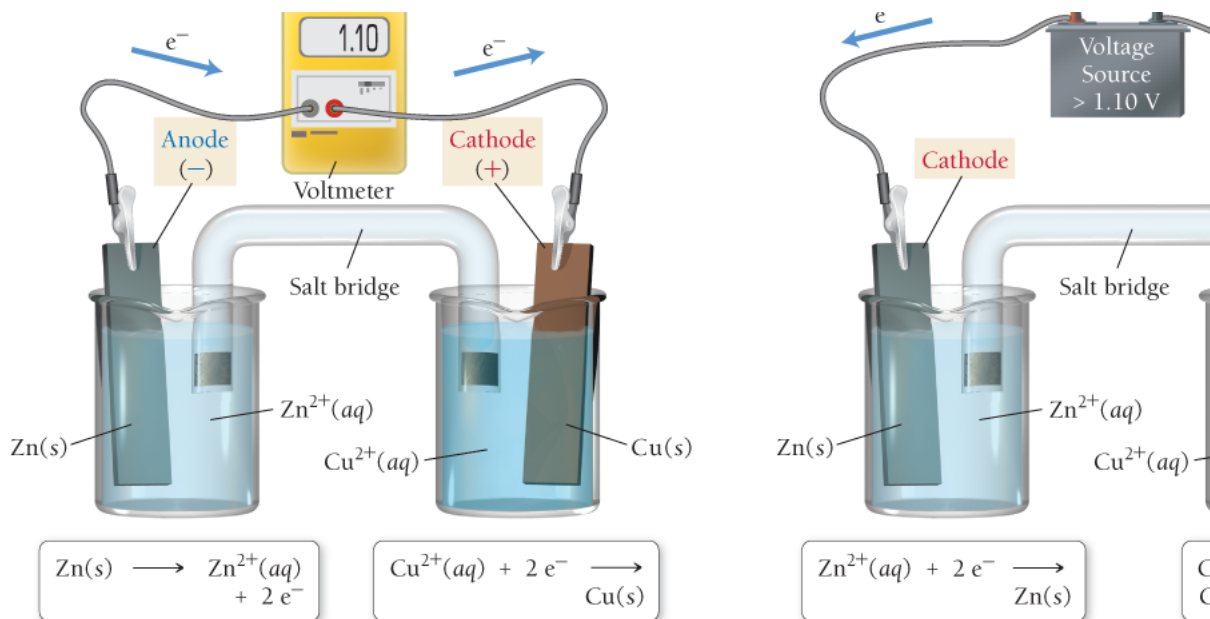
If a power source producing *more than 1.10 V* is inserted into the  $\text{Zn}/\text{Cu}^{2+}$  voltaic cell, electrons can be forced to flow in the opposite direction, causing the reduction of  $\text{Zn}^{2+}$  and the oxidation of Cu, as shown in Figure 19.18. Notice that in the electrolytic cell, the anode has become the cathode (oxidation always occurs at the anode) and the cathode has become the anode.

Figure 19.18 Voltaic versus Electrolytic Cells

In a  $\text{Zn}/\text{Cu}^{2+}$  voltaic cell, the reaction proceeds in the spontaneous direction. In a  $\text{Zn}^{2+}/\text{Cu}$  electrolytic cell, electrical current drives the reaction in the nonspontaneous direction.

### Voltaic Cell

### Electrolytic Cell



In a *voltaic cell*, the anode is the source of electrons and is therefore labeled with a negative charge. The cathode draws electrons and is therefore labeled with a positive charge. In an *electrolytic cell*, however, the source of the electrons is the external power source. The external power source must *draw electrons away* from the anode; thus, the anode must be connected to the positive terminal of the battery (as shown in Figure 19.18). Similarly, the power source drives electrons toward the cathode (where they will be used in reduction), so the cathode must be connected to the *negative* terminal of the battery. The charge labels (+ and -) on an electrolytic cell are the opposite of what they are in a voltaic cell.

#### Summarizing Characteristics of Electrochemical Cell Types:

##### In all electrochemical cells:

- Oxidation occurs at the anode.
- Reduction occurs at the cathode.

##### In voltaic cells:

- The anode is the source of electrons and has a negative charge (anode -).
- The cathode draws electrons and has a positive charge (cathode +).

##### In electrolytic cells:

- Electrons are drawn away from the anode, which must be connected to the positive terminal of the external power source (anode +).
- Electrons are driven to the cathode, which must be connected to the negative terminal of the power source (cathode -).

## Predicting the Products of Electrolysis

Predicting the products of an electrolysis reaction is in some cases relatively straightforward and in other cases more complex. We cover the simpler cases first and then discuss the more complex ones.

### Pure Molten Salts

Consider the electrolysis of a molten salt such as sodium chloride, shown in Figure 19.19.  $\text{Na}^+$  and  $\text{Cl}^-$  are the only species present in the cell. The chloride ion cannot be further reduced (-1 is its lowest oxidation state), so it must be oxidized. The sodium ion cannot be further oxidized (+1 is its highest oxidation state), so it must be

reduced. Thus, we can write the half-reactions:

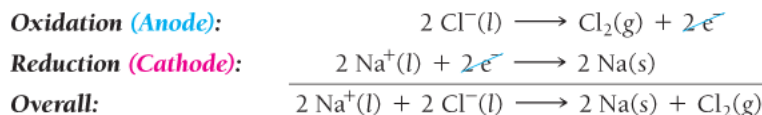
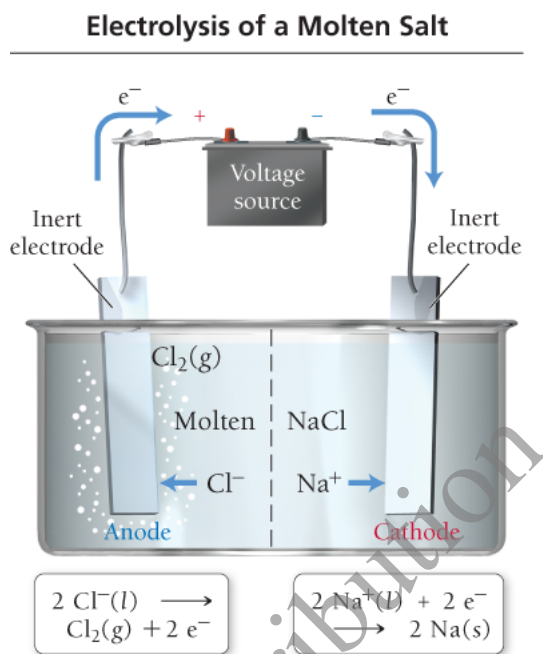


Figure 19.19 Electrolysis of Molten NaCl

In the electrolysis of a pure molten salt, the anion (in this case  $\text{Cl}^-$ ) is oxidized and the cation (in this case  $\text{Na}^+$ ) is reduced.



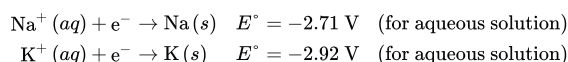
Although the reaction as written is not spontaneous, it can be driven to occur in an electrolytic cell by an external power source. We can generalize as follows:

- In the electrolysis of a pure molten salt, the anion is oxidized and the cation is reduced.

## Mixtures of Cations or Anions

What if a molten salt contains more than one anion or cation? For example, suppose the electrolysis cell we just introduced contains both NaCl and KCl. Which of the two cations is reduced at the cathode? To answer this question, we must determine which of the two cations is more easily reduced.

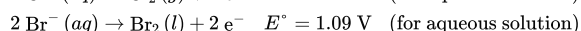
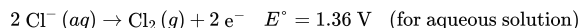
Although the values of electrode potentials for aqueous solutions given in Table 19.1 do not apply to molten salts, the relative ordering of the electrode potentials does reflect the relative ease with which the metal cations are reduced. We can see from the table that the reduction of  $\text{Na}^+$  is above the reduction of  $\text{K}^+$ ; that is,  $\text{Na}^+$  has a more positive electrode potential.



Throughout this discussion, “more positive” means the same thing as “less negative.”

Therefore,  $\text{Na}^+$  is easier to reduce than  $\text{K}^+$ . Consequently, in a mixture of NaCl and KCl,  $\text{Na}^+$  has a greater tendency to be reduced at the cathode.

Similarly, what if a mixture of molten salts contained more than one anion? For example, in a mixture of NaBr and NaCl, which of the two anions is oxidized at the cathode? The answer is similar: the anion that is more easily oxidized (the one with the more negative electrode potential).



Throughout this discussion, “more negative” means the same thing as “less positive.”

Since the electrode potential for the bromine half-reaction is more negative, electrons are more easily extracted from it. The bromide ion is therefore oxidized at the anode.

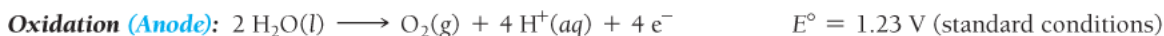
We can generalize as follows:

- The cation that is most easily reduced (the one with the more positive electrode potential) is reduced first.
- The anion that is most easily oxidized (the one with the more negative electrode potential) is oxidized first.

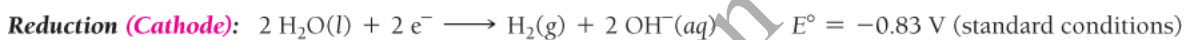
Remember NIO and PIR: N.I.O.–More Negative Is Oxidation P.I.R.–More Positive Is Reduction

## Aqueous Solutions

Electrolysis in an aqueous solution is complicated by the possibility of the electrolysis of water itself. Recall that water can be either oxidized or reduced according to the following half-reactions:



$$E = 0.82 \text{ V} \quad ([\text{H}^{+}] = 10^{-7} \text{ M})$$

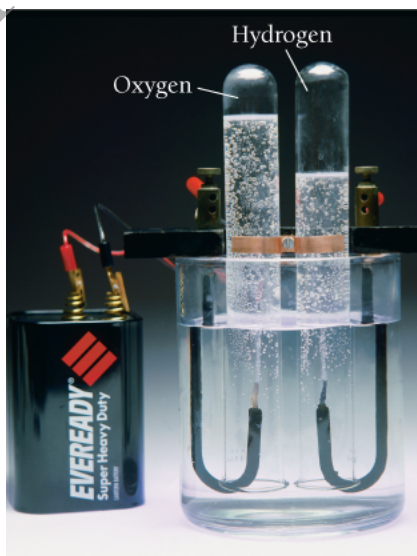


$$E = -0.41 \text{ V} \quad ([\text{OH}^{-}] = 10^{-7} \text{ M})$$

The electrode potentials under standard conditions are shown to the right of each half-reaction. However, in pure water at room temperature, the concentrations of  $\text{H}^{+}$  and  $\text{OH}^{-}$  are not standard. The electrode potentials for  $[\text{H}^{+}] = 10^{-7} \text{ M}$  and  $[\text{OH}^{-}] = 10^{-7} \text{ M}$  are shown in blue. Using those electrode potentials, we can calculate  $E_{\text{cell}}$  for the electrolysis of water as follows:

$$E_{\text{cell}} = E_{\text{cat}} - E_{\text{an}} = -0.41 \text{ V} - 0.82 \text{ V} = -1.23 \text{ V}$$

When a battery with a potential of several volts is connected to an electrolysis cell containing pure water, no reaction occurs because the concentration of ions in pure water is too low to conduct any significant electrical current. When an electrolyte such as  $\text{Na}_2\text{SO}_4$  is added to the water, however, electrolysis occurs readily.



Pure water is a poor conductor of electrical current, but the addition of an electrolyte allows electrolysis to take place, producing hydrogen and oxygen gas in a stoichiometric ratio.

In any aqueous solution in which electrolysis is to take place, the electrolysis of water is also possible. For example, consider the electrolysis of a sodium iodide solution, shown in Figure 19.20. For the electrolysis of molten NaI, we can readily predict that  $\text{I}^-$  is oxidized at the anode and that  $\text{Na}^+$  is reduced at the cathode. In an aqueous solution, however, two different oxidation half-reactions are possible at the anode: the oxidation of  $\text{I}^-$  and the oxidation of water.

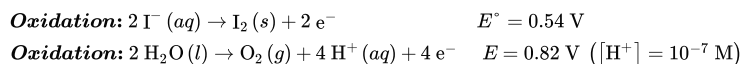
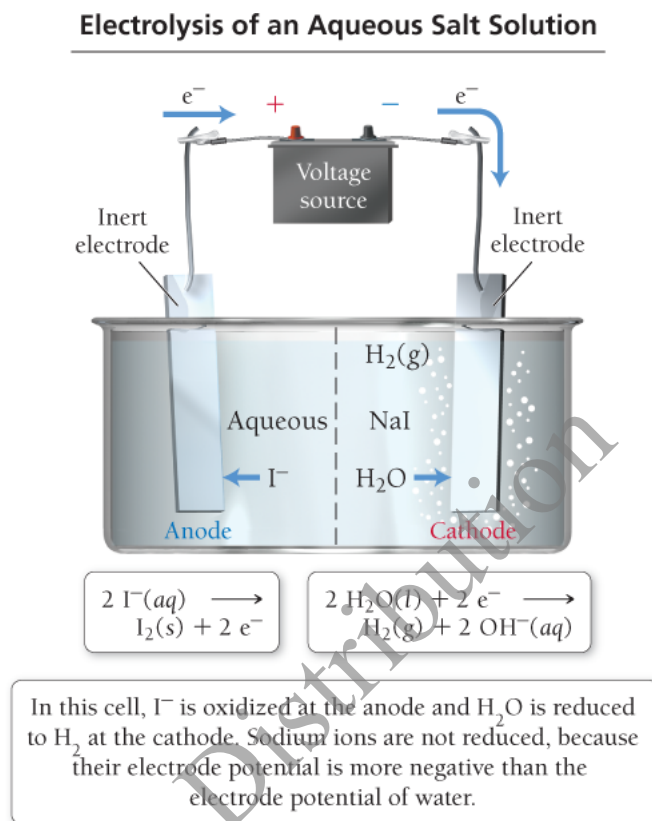
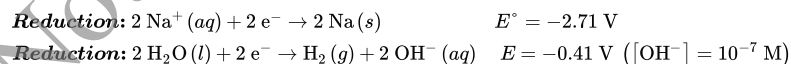


Figure 19.20 Electrolysis of Aqueous NaI



Similarly, two different reduction half-reactions are possible at the cathode: the reduction of  $\text{Na}^+$  and the reduction of water.



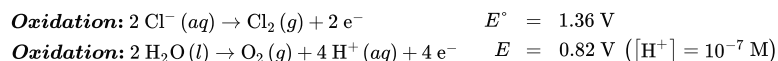
How do we know which reactions actually occur? In both cases, the answer is the same: *the half-reaction that occurs more easily*. For oxidation, the half-reaction with the more negative electrode potential is the easier one from which to extract electrons. In this case, therefore, the iodide ion is oxidized at the anode. For reduction, the half-reaction with the more positive electrode potential is the easier one to get to accept electrons. In this case, therefore, water is reduced at the cathode. Notice that  $\text{Na}^+$  cannot be reduced in an aqueous solution—water is reduced before  $\text{Na}^+$ . We can make the following generalization:

- The cations of active metals—those that are not easily reduced, such as  $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Al}^{3+}$ —cannot be reduced from aqueous solutions by electrolysis because water is reduced at a lower voltage.

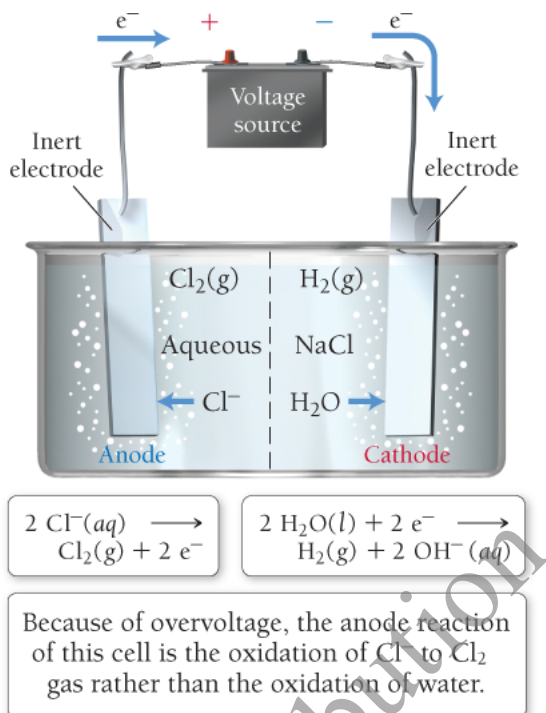
## The Electrolysis of Aqueous Sodium Chloride and Overvoltage

An additional complication that we must consider when predicting the products of electrolysis is *overvoltage*—an additional voltage that must be applied in order to get some nonspontaneous reactions to occur.

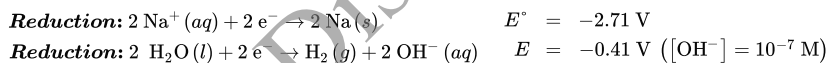
We can demonstrate this concept by considering the electrolysis of a sodium chloride solution, shown in **Figure 19.21**. In order to predict the product of the electrolysis, we consider the two possible oxidation half-reactions:



**Figure 19.21 Electrolysis of Aqueous NaCl: The Effect of Overvoltage**



and the two possible reduction half-reactions:



Since the oxidation of water has a more negative electrode potential than the oxidation of  $\text{Cl}^{-}$ , we would initially predict that it would be easier to remove electrons from water, and thus water should be oxidized at the anode. Similarly, since the reduction of water has a more positive electrode potential than the reduction of  $\text{Na}^{+}$ , we would expect that it would be easier to get water to accept electrons, so water should be reduced at the cathode. In other words, we initially predict that a sodium chloride solution would result in the electrolysis of water, producing oxygen gas at the anode and hydrogen gas at the cathode. If we construct such a cell, however, we find that, although hydrogen gas is indeed formed at the cathode (as predicted), oxygen gas is *not* formed at the anode—chlorine gas is formed instead. Why?

The answer is that even though the electrode potential for the oxidation of water is 0.82 V, the reaction actually requires a voltage greater than 0.82 V in order to occur. (The reasons for this behavior are related to kinetic factors that are beyond the scope of our current discussion.) This additional voltage, the *overvoltage*, increases the voltage required for the oxidation of water to about 1.4 V. The result is that the chloride ion oxidizes more easily than water and  $\text{Cl}_2(\text{g})$  forms at the anode.

### Example 19.9 Predicting the Products of Electrolysis Reactions

Predict the half-reaction occurring at the anode and the cathode for electrolysis for each reaction.

- a mixture of molten  $\text{AlBr}_3$  and  $\text{MgBr}_2$
- an aqueous solution of  $\text{LiI}$

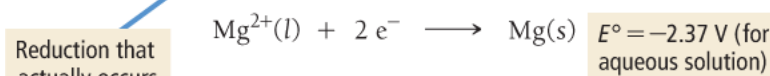
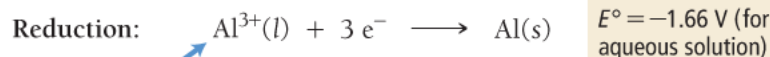
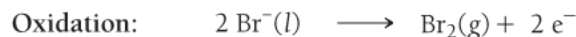


**SOLUTION**

a. In the electrolysis of a molten salt, the anion is oxidized and the cation is reduced. However, this mixture contains two cations. Start by writing the possible oxidation and reduction half-reactions that might occur.

Since  $\text{Br}^-$  is the only anion, write the equation for its oxidation, which occurs at the anode.

At the cathode, both the reduction of  $\text{Al}^{3+}$  and the reduction of  $\text{Mg}^{2+}$  are possible. The one that actually occurs is the one that occurs more easily. Since the reduction of  $\text{Al}^{3+}$  has a more positive electrode potential in aqueous solution, this ion is more easily reduced. Therefore, the reduction of  $\text{Al}^{3+}$  occurs at the cathode.

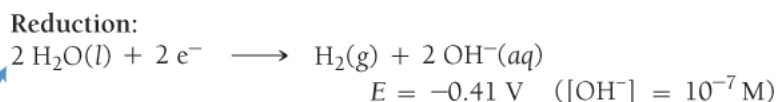
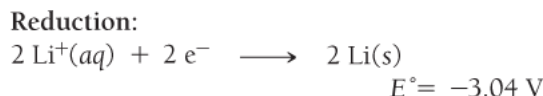
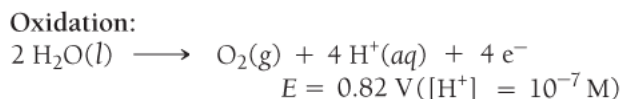
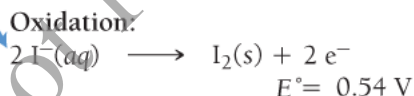


Reduction that actually occurs (more positive potential)

b. Because  $\text{LiI}$  is in an aqueous solution, two different oxidation half-reactions are possible at the anode, the oxidation of  $\text{I}^-$  and the oxidation of water. Write half-reactions for each, including the electrode potential. Remember to use the electrode potential of water under conditions in which  $[\text{H}^+] = 10^{-7} \text{ M}$ . Since the oxidation of  $\text{I}^-$  has the more negative electrode potential, it will be the half-reaction to occur at the anode.

Similarly, write half-reactions for the two possible reduction half-reactions that might occur at the cathode: the reduction of  $\text{Li}^+$  and the reduction of water. Since the reduction of water has the more positive electrode potential (even when considering overvoltage, which would raise the necessary voltage by about  $0.4 - 0.6 \text{ V}$ ), it is the half-reaction that occurs at the cathode.

Oxidation that actually occurs (more negative potential)



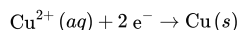
Reduction that actually occurs (more positive potential)



**FOR PRACTICE 19.9** Predict the half-reactions occurring at the anode and the cathode for the electrolysis of aqueous  $\text{Na}_2\text{SO}_4$ .

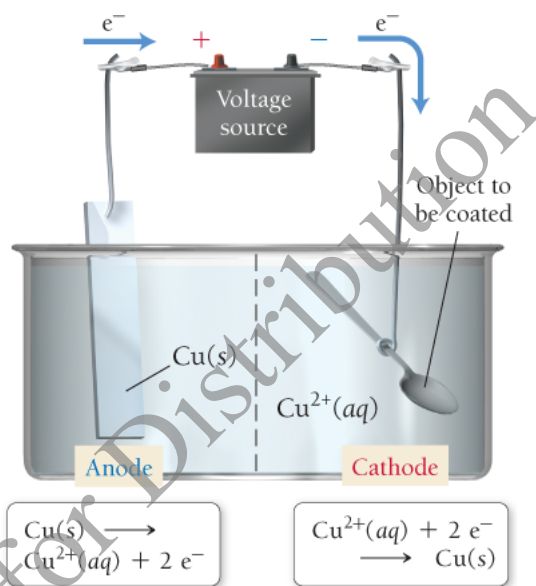
## Stoichiometry of Electrolysis

In an electrolytic cell, electrical current drives a particular chemical reaction. In a sense, the electrons act as a reactant and therefore have a stoichiometric relationship with the other reactants and products. Unlike ordinary reactants, for which we usually measure quantity as mass, for electrons we measure quantity as charge. For example, consider an electrolytic cell used to coat copper onto metals, as shown in Figure 19.22. The half-reaction by which copper is deposited onto the metal is:

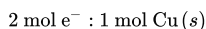


**Figure 19.22 Electrolytic Cell for Copper Plating**

In this cell, copper ions are plated onto other metals. It takes two moles of electrons to plate one mole of copper atoms.



For every 2 mol of electrons that flow through the cell, 1 mol of solid copper is plated. We can write the stoichiometric relationship:



We can determine the number of moles of electrons that flow in a given electrolytic cell by measuring the total charge that flows through the cell, which in turn depends on the *magnitude* of the current and on the *time* that the current runs. Recall from Section 19.3 that the unit of current is the ampere.

$$1 \text{ A} = 1 \frac{\text{C}}{\text{s}}$$

If we multiply the amount of current (in A) flowing through the cell by the time (in s) that the current flowed, we find the total charge that passed through the cell in that time:

$$\text{Current} \left( \frac{\text{C}}{\text{s}} \right) \times \text{time} (\text{s}) = \text{charge} (\text{C})$$

The relationship between charge and the number of moles of electrons is given by Faraday's constant, which, as

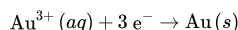
we saw previously, corresponds to the charge in coulombs of 1 mol of electrons.

$$F = \frac{96,485 \text{ C}}{\text{mol e}^-}$$

We can use these relationships to solve problems involving the stoichiometry of electrolytic cells, as demonstrated in **Example 19.10**.

### Example 19.10 Stoichiometry of Electrolysis

Gold can be plated out of a solution containing  $\text{Au}^{3+}$  according to the half-reaction:



What mass of gold (in grams) is plated by a 25-minute flow of 5.5 A current?

**SORT** You are given the half-reaction for the plating of gold, which shows the stoichiometric relationship between moles of electrons and moles of gold. You are also given the current and duration. You must find the mass of gold that is deposited in that time.

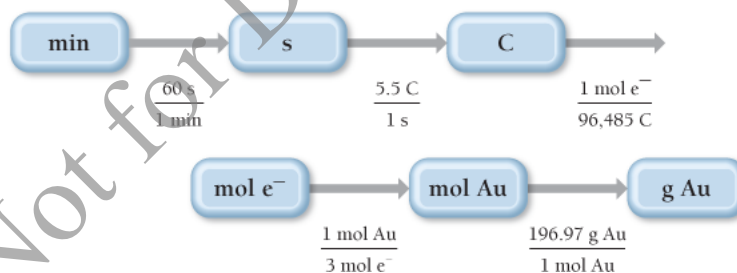
3 mol  $\text{e}^-$  : 1 mol Au

**GIVEN:** 5.5 amps  
25 min

**FIND:** g Au

**STRATEGIZE** You need to find the amount of gold, which is related stoichiometrically to the number of electrons that have flowed through the cell. Begin with time in minutes and convert to seconds. Then, since current is a measure of charge per unit time, use the given current and the time to find the number of coulombs. You can use Faraday's constant to calculate the number of moles of electrons and the stoichiometry of the reaction to find the number of moles of gold. Finally, use the molar mass of gold to convert to mass of gold.

#### CONCEPTUAL PLAN



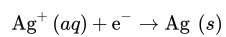
**SOLVE** Follow the conceptual plan to solve the problem, canceling units to arrive at the mass of gold.

#### SOLUTION

$$25 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{5.5 \text{ C}}{1 \text{ s}} \times \frac{1 \text{ mol e}^-}{96,485 \text{ C}} \times \frac{1 \text{ mol Au}}{3 \text{ mol e}^-} \times \frac{196.97 \text{ g Au}}{1 \text{ mol Au}} = 5.6 \text{ g Au}$$

**CHECK** The answer has the correct units (g Au). The magnitude of the answer is reasonable if you consider that 10 amps of current for 1 hour is the equivalent of about 1/3 mol of electrons (check for yourself), which would produce 1/9 mol (or about 20 g) of gold.

**FOR PRACTICE 19.10** Silver can be plated out of a solution containing  $\text{Ag}^+$  according to the half-reaction:



How much time (in minutes) does it take to plate 12 g of silver using a current of 3.0 A?

Not for Distribution

*Not for Distribution*

*Not for Distribution*