11.3 Electrolytic Cells

For a galvanic cell, you have learned that the overall reaction is spontaneous, and that the cell potential has a positive value. A galvanic cell converts chemical energy to electrical energy. Electrons flow from a higher potential energy to a lower potential energy. As described earlier, the flow of electrons in the external circuit of a galvanic cell can be compared to water flowing downhill.

Although water flows downhill spontaneously, you can also pump water uphill. This process requires energy because it moves water from a position of lower potential energy to a position of higher potential energy. You will now learn about a type of cell that uses energy to move electrons from lower potential energy to higher potential energy. This type of cell, called an **electrolytic cell**, is a device that converts electrical energy to chemical energy. The process that takes place in an electrolytic cell is called **electrolysis**. The overall reaction in an electrolytic cell is non-spontaneous, and requires energy to occur. This type of reaction is the reverse of a spontaneous reaction, which generates energy when it occurs.

Like a galvanic cell, an electrolytic cell includes electrodes, at least one electrolyte, and an external circuit. Unlike galvanic cells, electrolytic cells require an external source of electricity, sometimes called the *external voltage*. This is included in the external circuit. Except for the external source of electricity, an electrolytic cell may look just like a galvanic cell. Some electrolytic cells include a porous barrier or salt bridge. In other electrolytic cells, the two half-reactions are not separated, and take place in the same container.

Electrolysis of Molten Salts

The electrolytic cell shown in Figure 11.14 decomposes sodium chloride into its elements. The cell consists of a single container with two inert electrodes dipping into liquid sodium chloride. To melt the sodium chloride, the temperature must be above its melting point of about 800°C. As in an aqueous solution of sodium chloride, the ions in molten sodium chloride have some freedom of movement. In other words, molten sodium chloride is the electrolyte of this cell.
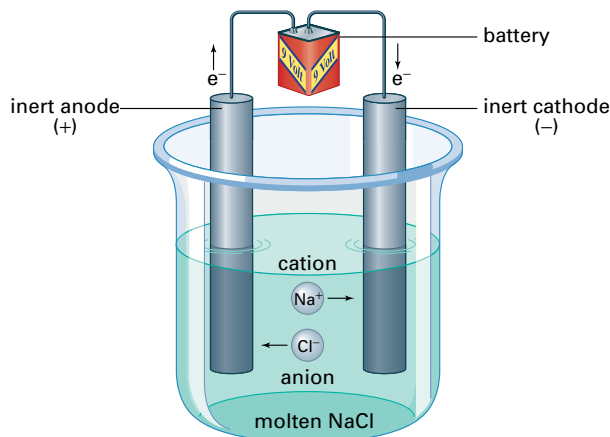

Figure 11.14 Molten sodium chloride decomposes into sodium and chlorine in this electrolytic cell. The sodium chloride is said to undergo electrolysis, or to be *electrolyzed*.
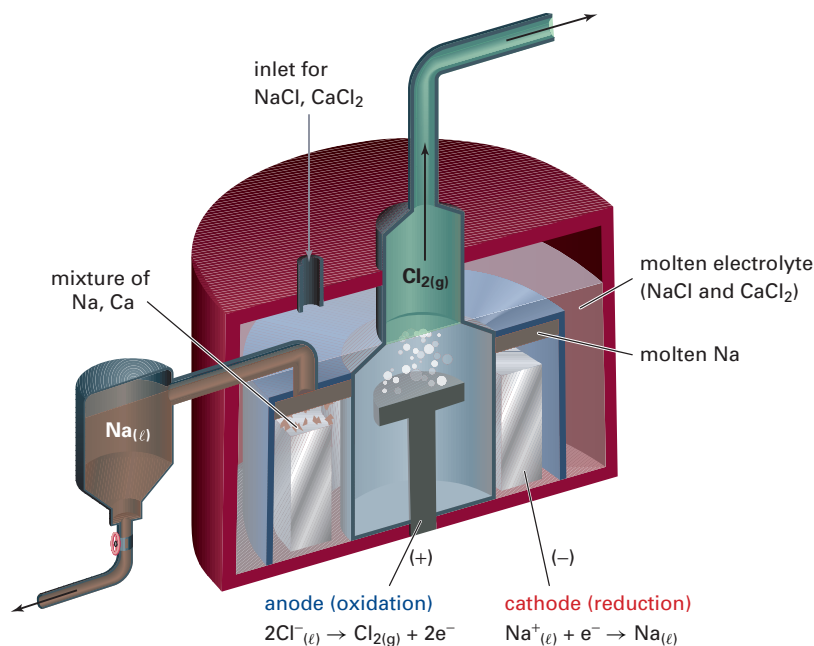
The external source of electricity forces electrons onto one electrode. As a result, this electrode becomes negative relative to the other electrode. The positive sodium ions move toward the negative electrode, where they gain electrons and are reduced to the element sodium. At this temperature, sodium metal is produced as a liquid. The negative chloride ions move toward the positive electrode, where they lose electrons and are oxidized to the element chlorine, a gas. *As in a galvanic cell, reduction occurs at the cathode, and oxidation occurs at the anode of an electrolytic cell.* The half-reactions for this electrolytic cell are as follows.

Reduction half-reaction (occurs at the cathode): $Na^+_{(\ell)} + e^- \rightarrow Na_{(\ell)}$

Oxidation half-reaction (occurs at the anode): $2Cl^-_{(\ell)} \rightarrow Cl_{2(g)} + 2e^-$

Because of the external voltage of the electrolytic cell, the electrodes do not have the same polarities in electrolytic and galvanic cells. In a galvanic cell, the cathode is positive and the anode is negative. In an electrolytic cell, the anode is positive and the cathode is negative.

The electrolysis of molten sodium chloride is an important industrial reaction. Figure 11.15 shows the large electrolytic cell used in the industrial production of sodium and chlorine. You will meet other industrial electrolytic processes later in this chapter.

inlet for NaCl, CaCl2
mixture of Na, Ca
$Cl_{2(g)}$
molten electrolyte (NaCl and CaCl2)
molten Na
$Na_{(\ell)}$
(+)
(−)
anode (oxidation)
$2Cl^-_{(\ell)} \rightarrow Cl_{2(g)} + 2e^-$
cathode (reduction)
$Na^+_{(\ell)} + e^- \rightarrow Na_{(\ell)}$

Figure 11.15 The large cell used for the electrolysis of sodium chloride in industry is known as a *Downs cell*. To decrease heating costs, calcium chloride is added to lower the melting point of sodium chloride from about 800°C to about 600°C. The reaction produces sodium and calcium by reduction at the cathode, and chlorine by oxidation at the anode.

Check your understanding of the introduction to electrolytic cells by completing the following practice problems.

Practice Problems

9. The electrolysis of molten calcium chloride produces calcium and chlorine. Write

(a) the half-reaction that occurs at the anode

(b) the half-reaction that occurs at the cathode

(c) the chemical equation for the overall cell reaction

10. For the electrolysis of molten lithium bromide, write

   (a) the half-reaction that occurs at the negative electrode

   (b) the half-reaction that occurs at the positive electrode

   (c) the net ionic equation for the overall cell reaction

11. A galvanic cell produces direct current, which flows in one direction. The mains supply at your home is a source of alternating current, which changes direction every fraction of a second. Explain why the external electrical supply for an electrolytic cell must be a source of direct current, rather than alternating current.

12. Suppose a battery is used as the external electrical supply for an electrolytic cell. Explain why the negative terminal of the battery must be connected to the cathode of the cell.

Electrolysis of Water

The electrolysis of aqueous solutions may not yield the desired products. Sir Humphry Davy (1778–1829) discovered the elements sodium and potassium by electrolyzing their molten salts. Before this discovery, Davy had electrolyzed aqueous solutions of sodium and potassium salts. He had not succeeded in reducing the metal ions to the pure metals at the cathode. Instead, his first experiments had produced hydrogen gas. Where did the hydrogen gas come from?

When electrolyzing an aqueous solution, there are two compounds present: water, and the dissolved electrolyte. Water may be electrolyzed as well as, or instead of, the electrolyte. The electrolysis of water produces oxygen gas and hydrogen gas, as shown in Figure 11.16.
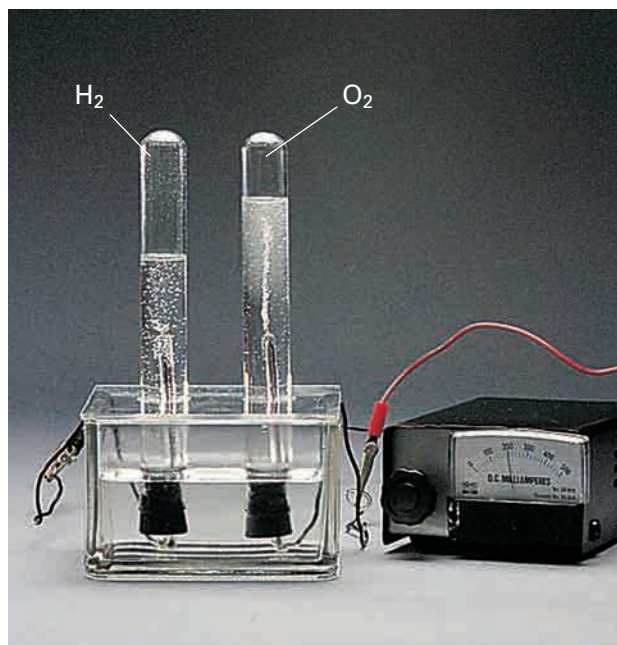

Figure 11.16 The electrolysis of water produces hydrogen gas at the cathode and oxygen gas at the anode. Explain why the volume of hydrogen gas is twice the volume of oxygen gas.

The half-reactions for the electrolysis of water are given below.

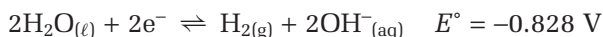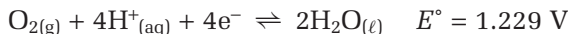Oxidation half-reaction (occurs at the anode):

$2H_2O_{(\ell)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$

Reduction half-reaction (occurs at the cathode):

$2H_2O_{(\ell)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$
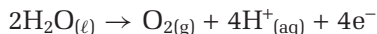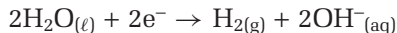
Because the number of electrons lost and gained must be equal, multiply the reduction half-reaction by 2. Then add and simplify to obtain the overall cell reaction.
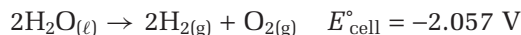
Overall cell reaction: $2H_2O_{(\ell)} \rightarrow 2H_{2(g)} + O_{2(g)}$
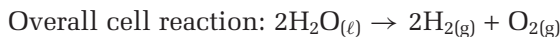
The standard reduction potentials are as follows.

$O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightleftharpoons 2H_2O_{(\ell)} \quad E° = 1.229 \text{ V}$

$2H_2O_{(\ell)} + 2e^- \rightleftharpoons H_{2(g)} + 2OH^-_{(aq)} \quad E° = -0.828 \text{ V}$

You can use these values to calculate the $E°_{cell}$ value for the decomposition of water.

$$E°_{cell} = E°_{cathode} - E°_{anode}$$
$$= -0.828 \text{ V} - 1.229 \text{ V}$$
$$= -2.057 \text{ V}$$

Therefore,

$$2H_2O_{(\ell)} \rightarrow 2H_{2(g)} + O_{2(g)} \quad E°_{cell} = -2.057 \text{ V}$$

The negative cell potential shows that the reaction is not spontaneous. Electrolytic cells are used for non-spontaneous redox reactions, so *all electrolytic cells have negative cell potentials*.

The standard reduction potentials used to calculate $E°_{cell}$ for the decomposition of water apply only to reactants and products in their standard states. However, in pure water at 25°C, the hydrogen ions and hydroxide ions each have concentrations of 1×10^{-7} mol/L. This is not the standard state value of 1 mol/L. The reduction potential values for the non-standard conditions in pure water are given below. The superscript zero is now omitted from the E symbol, because the values are no longer standard.

$O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightleftharpoons 2H_2O_{(\ell)} \quad E = 0.815 \text{ V}$

$2H_2O_{(\ell)} + 2e^- \rightleftharpoons H_{2(g)} + 2OH^-_{(aq)} \quad E = -0.414 \text{ V}$
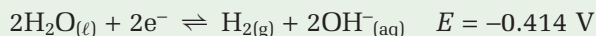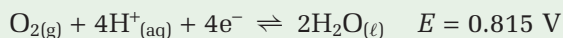
Using these new half-cell potentials, E_{cell} for the decomposition of pure water at 25°C by electrolysis has a calculated value of -1.229 V. Therefore, the calculated value of the external voltage needed is 1.229.

In practice, the external voltage needed for an electrolytic cell is always greater than the calculated value, especially for reactions involving gases. Therefore, the actual voltage needed to electrolyze pure water is *greater than* 1.229 V. The excess voltage required above the calculated value is called the **overvoltage**. Overvoltages depend on the gases involved and on the materials in the electrodes.

When electrolyzing water, there is another practical difficulty to consider. Pure water is a very poor electrical conductor. To increase the conductivity, an electrolyte that does not interfere in the reaction is added to the water.

Electrolysis of Aqueous Solutions

As stated previously, an electrolytic cell may have the same design as a galvanic cell, except for the external source of electricity. Consider, for example, the familiar Daniell cell. (This cell was described in section 11.1 and shown in Figure 11.5.) By adding an external electrical supply, with a voltage greater than the voltage of the Daniell cell, you can push electrons in the opposite direction. By pushing electrons in the opposite direction, you reverse the chemical reaction. Figure 11.17 shows both cells, while their properties are compared in Table 11.2.
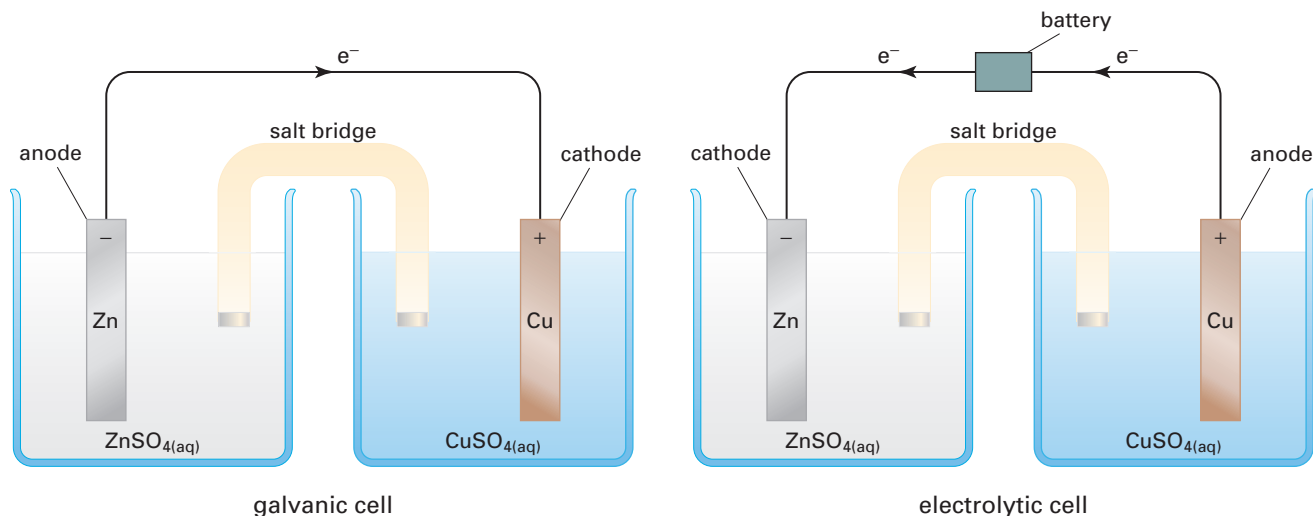

Figure 11.17 Adding an external voltage to reverse the electron flow converts a Daniell cell from a galvanic cell into an electrolytic cell. The result is to switch the anode and cathode.

Table 11.2 Cell Comparison

Galvanic Cell	Electrolytic Cell
Spontaneous reaction	Non-spontaneous reaction
Converts chemical energy to electrical energy	Converts electrical energy to chemical energy
Anode (negative): Zinc	Anode (positive): Copper
Cathode (positive): Copper	Cathode (negative): Zinc
Oxidation (at anode): $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$	Oxidation (at anode): $Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$
Reduction (at cathode): $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$	Reduction (at cathode): $Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$
Cell reaction: $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$	Cell reaction: $Cu_{(s)} + Zn^{2+}_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Zn_{(s)}$

In the galvanic cell, the zinc anode gradually dissolves. The copper cathode grows as more copper is deposited onto it. In the electrolytic cell, the copper anode gradually dissolves. The zinc cathode grows as more zinc is deposited onto it. The process in which a metal is deposited, or plated, onto the cathode in an electrolytic cell is known as **electroplating**. Electroplating is very important in industry, as you will learn later in this chapter.

Predicting the Products of Electrolysis for an Aqueous Solution

The comparison of the Daniell cell with the electrolytic version of the cell appears straightforward. One reaction is the reverse of the other. However, you have just learned that the electrolysis of an aqueous solution may involve the electrolysis of water. How can you predict the actual products for this type of electrolysis reaction?

To predict the products of an electrolysis involving an aqueous solution, you must examine all possible half-reactions and their reduction potentials. Then, you must find the overall reaction that requires the *lowest* external voltage. That is, you must find the overall cell reaction with a negative cell potential that is closest to zero. The next Sample Problem shows you how to predict the products of the electrolysis of an aqueous solution.

In practice, reaction products are sometimes different from the products predicted, using the method described here. Predictions are least reliable when the reduction potentials are close together, especially when gaseous products are expected. However, there are many cases in which the predictions are correct.

Sample Problem

Electrolysis of an Aqueous Solution

Problem

Predict the products of the electrolysis of 1 mol/L $LiBr_{(aq)}$.

What Is Required?

You need to predict the products of the electrolysis of 1 mol/L $LiBr_{(aq)}$.

What Is Given?

This is an aqueous solution. You are given the formula and concentration of the electrolyte. You have a table of standard reduction potentials, and you know the non-standard reduction potentials for water.
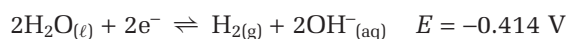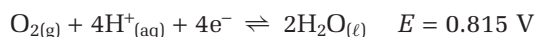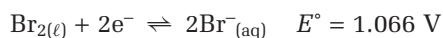
Plan Your Strategy

Step 1 List the four relevant half-reactions and their reduction potentials.

Step 2 Predict the products by finding the cell reaction that requires the lowest external voltage.

Act on Your Strategy

Step 1 The Li^+ and Br^- concentrations are 1 mol/L, so use the standard reduction potentials for the half-reactions that involve these ions. Use the non-standard values for water.

$$Br_{2(\ell)} + 2e^- \rightleftharpoons 2Br^-_{(aq)} \quad E° = 1.066 \text{ V}$$

$$O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightleftharpoons 2H_2O_{(\ell)} \quad E = 0.815 \text{ V}$$

$$2H_2O_{(\ell)} + 2e^- \rightleftharpoons H_{2(g)} + 2OH^-_{(aq)} \quad E = -0.414 \text{ V}$$

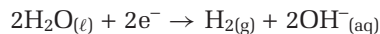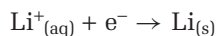$$Li^+_{(aq)} + e^- \rightleftharpoons Li_{(s)} \quad E° = -3.040 \text{ V}$$

There are two possible oxidation half-reactions at the anode: the oxidation of bromide ion in the electrolyte, or the oxidation of water.

$$2Br^-_{(aq)} \rightarrow Br_{2(\ell)} + 2e^-$$

$$2H_2O_{(\ell)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$$
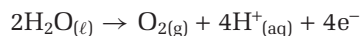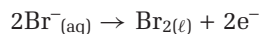
There are two possible reduction half-reactions at the cathode: the reduction of lithium ions in the electrolyte, or the reduction of water.

$$Li^+_{(aq)} + e^- \rightarrow Li_{(s)}$$

$$2H_2O_{(\ell)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$$
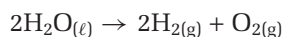
Step 2 Combine pairs of half-reactions to produce four possible overall reactions. (You learned how to do this in Chapter 10.)

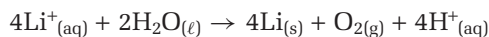Reaction 1: the production of lithium and bromine

$$2Li^+_{(aq)} + 2Br^-_{(aq)} \rightarrow 2Li_{(s)} + Br_{2(\ell)}$$
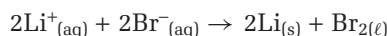
$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$
$$= -3.040 \text{ V} - 1.066 \text{ V}$$
$$= -4.106 \text{ V}$$
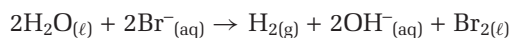
Reaction 2: the production of hydrogen and oxygen

$$2H_2O_{(\ell)} \rightarrow 2H_{2(g)} + O_{2(g)}$$

$$E_{cell} = E_{cathode} - E_{anode}$$
$$= -0.414 \text{ V} - 0.815 \text{ V}$$
$$= -1.229 \text{ V}$$

Reaction 3: the production of lithium and oxygen

$$4Li^+_{(aq)} + 2H_2O_{(\ell)} \rightarrow 4Li_{(s)} + O_{2(g)} + 4H^+_{(aq)}$$

$$E_{cell} = E^\circ_{cathode} - E_{anode}$$
$$= -3.040 \text{ V} - 0.815 \text{ V}$$
$$= -3.855 \text{ V}$$

Reaction 4: the production of hydrogen and bromine

$$2H_2O_{(\ell)} + 2Br^-_{(aq)} \rightarrow H_{2(g)} + 2OH^-_{(aq)} + Br_{2(\ell)}$$

$$E_{cell} = E_{cathode} - E^\circ_{anode}$$
$$= -0.414 \text{ V} - 1.066 \text{ V}$$
$$= -1.480 \text{ V}$$

The electrolysis of water requires the lowest external voltage. Therefore, the predicted products of this electrolysis are hydrogen and oxygen.

Check Your Solution

Use a potential ladder diagram, such as the one on the next page, part A, to visualize the cell potentials. For an electrolytic cell, the half-reaction at the anode is always on the upper rung, and the subtraction $E^\circ_{cathode} - E^\circ_{anode}$ always gives a negative cell potential, as shown in part B.

PROBLEM TIP

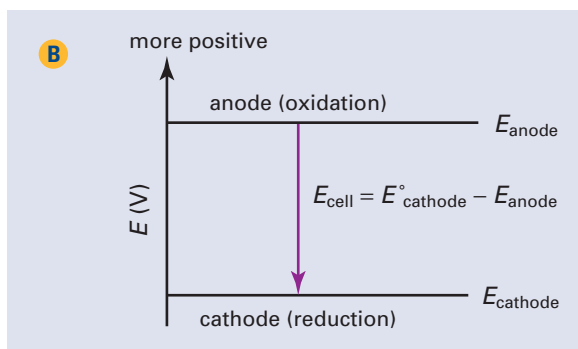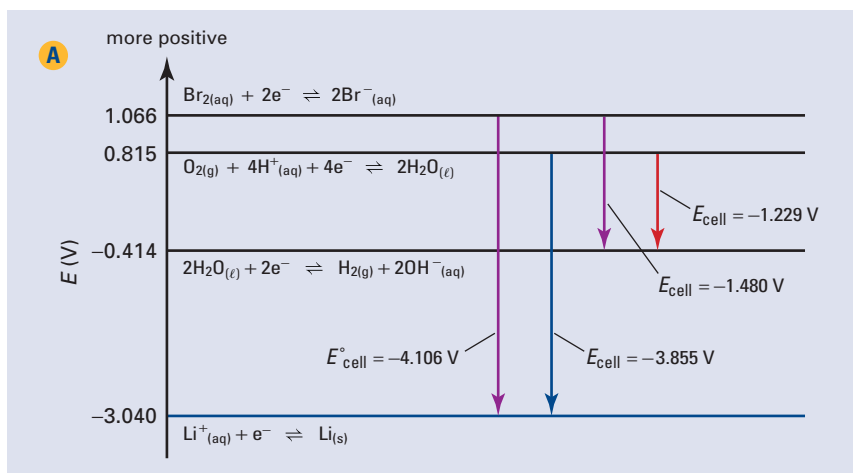- Remember that spectator ions do not appear in net ionic equations. In Reaction 3, the bromide ions are spectator ions. In Reaction 4, lithium ions are spectator ions.

- As for a galvanic cell, the cell potential for an electrolytic cell is the sum of a reduction potential and an oxidation potential. Using $E_{cell} = E_{red} + E_{ox}$
gives the same predicted products as using
$E_{cell} = E_{cathode} - E_{anode}$

A

more positive

E (V)

1.066 — $Br_{2(aq)} + 2e^- \rightleftharpoons 2Br^-_{(aq)}$

0.815 — $O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightleftharpoons 2H_2O_{(\ell)}$

$E_{cell} = -1.229$ V

$E_{cell} = -1.480$ V

−0.414 — $2H_2O_{(\ell)} + 2e^- \rightleftharpoons H_{2(g)} + 2OH^-_{(aq)}$

$E°_{cell} = -4.106$ V

$E_{cell} = -3.855$ V

−3.040 — $Li^+_{(aq)} + e^- \rightleftharpoons Li_{(s)}$

B

more positive

E (V)

anode (oxidation) — E_{anode}

$E_{cell} = E°_{cathode} - E_{anode}$

cathode (reduction) — $E_{cathode}$

Practice Problems

13. Predict the products of the electrolysis of a 1 mol/L solution of sodium chloride.

14. Explain why calcium can be produced by the electrolysis of molten calcium chloride, but not by the electrolysis of aqueous calcium chloride.

15. One half-cell of a galvanic cell has a nickel electrode in a 1 mol/L nickel(II) chloride solution. The other half-cell has a cadmium electrode in a 1 mol/L cadmium chloride solution.

   (a) Find the cell potential.

   (b) Identify the anode and the cathode.

   (c) Write the oxidation half-reaction, the reduction half-reaction, and the overall cell reaction.

16. An external voltage is applied to change the galvanic cell in question 15 into an electrolytic cell. Repeat parts (a) to (c) for the electrolytic cell.

In Investigation 11-B, you will build an electrolytic cell for the electrolysis of an aqueous solution of potassium iodide. You will predict the products of the electrolysis, and compare the observed products with your predictions.