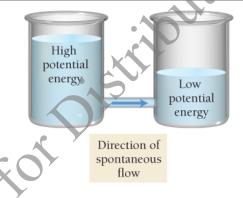
# 19.4: Standard Electrode Potentials

# Key Concept Video Standard Electrode Potentials

As we have just seen, the standard cell potential  $\left(E_{\text{cell}}^{\circ}\right)$  for an electrochemical cell depends on the specific halfreactions occurring in the half-cells and is a measure of the potential energy difference (per unit charge) between the two electrodes. We can think of the electrode in each half-cell as having its own individual potential, called the **standard electrode potential**  $^{\circ}$ . The overall standard cell potential  $\left(E_{\text{cell}}^{\circ}\right)$  is the difference between the two standard electrode potentials.

We can better understand this idea with an analogy. Consider two water tanks with different water levels connected by a common pipe, as shown in Figure 19.5. The water in each tank has its own level and corresponding potential energy. When the tanks are connected, water flows from the tank with the higher water level (higher potential energy) to the tank with a lower water level (lower potential energy). Similarly, each halfcell in an electrochemical cell has its own charge and corresponding electrode potential. When the cells are connected, electrons flow from the electrode with greater potential energy (more negatively charged) to the electrode with less potential energy (more positively charged).

Figure 19.5 An Analogy for Electrode Potential



One limitation to this analogy is that, unlike the water level in a tank, we cannot measure the electrode potential in a half-cell directly—we can only measure the overall potential that occurs when two half-cells are combined in a whole cell. However, we can arbitrarily assign a potential of zero to the electrode in a particular type of halfcell and then measure all other electrode potentials relative to that zero.

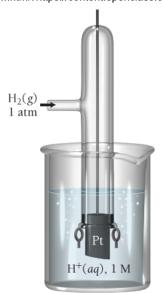
The half-cell electrode that is normally chosen to have a potential of zero is the standard hydrogen electrode (SHE). This half-cell consists of an inert platinum electrode immersed in 1 M HCl with hydrogen gas at 1 atm bubbling through the solution, as shown in Figure 19.6 . When the standard hydrogen electrode acts as the cathode, the following half-reaction occurs:

$$2 \text{ H}^+(aq) + 2 \text{ e}^- \rightarrow \text{H}_2(g) \quad E_{\text{cathode}}^\circ = 0.00 \text{ V}$$

## Figure 19.6 The Standard Hydrogen Electrode

All other electrode potentials are then measured relative to the SHE.

# Standard Hydrogen Electrode (SHE)



The standard hydrogen electrode (SHE) is arbitrarily assigned an electrode potential of zero.

If we connect the standard hydrogen electrode to an electrode in another half-cell of interest, we can measure the potential difference (or voltage) between the two electrodes. Since we assigned the standard hydrogen electrode zero voltage, we can determine the electrode potential of the other half-cell.

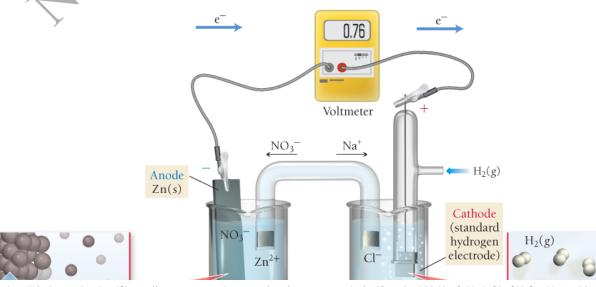
Consider the electrochemical cell shown in Figure 19.7. In this electrochemical cell, Zn is oxidized to  $Zn^{2+}$  and  $H^+$  is reduced to  $H_2$  under standard conditions (all solutions are 1 M in concentration and all gases are 1 atm in pressure) and at 25 °C. Electrons travel from the anode (where oxidation occurs) to the cathode (where reduction occurs), so we define  $E_{cell}^{\circ}$  as the difference in voltage between the cathode (final state) and the anode (initial state).

$$E_{\text{cell}}$$
  $=$   $E_{\text{final}}^{\circ} - E_{\text{initial}}^{\circ}$   
 $=$   $E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$ 

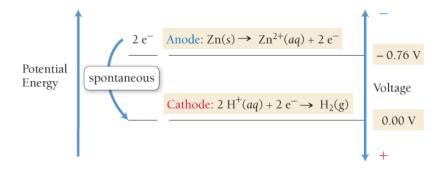
Figure 19.7 Measuring Electrode Potential

Because the electrode potential of the SHE is zero, the electrode potential for the oxidation of Zn is equal to the cell potential.

# Measuring Half-Cell Potential with the SHE



The measured cell potential for this cell is +0.76 V. The anode (in this case,  $Zn/Zn^{2+}$ ) is at a more negative voltage (higher potential energy) than the cathode (in this case, the SHE). Therefore, electrons spontaneously flow from the anode to the cathode. We can diagram the potential energy and the voltage as follows:



Referring back to our water tank analogy, the zinc half-cell is like the water tank with the higher water level. Electrons therefore flow from the zinc electrode to the standard hydrogen electrode.

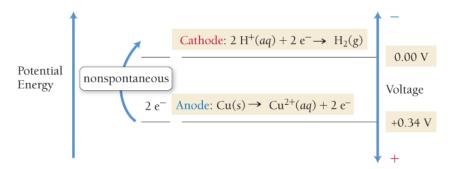
Because we assigned the SHE a potential of zero (0.00 V), we can determine the electrode potential for the  $Zn/Zn^{2+}$  half-cell (the anode) from the measured cell potential  $\left(E_{cell}^{\circ}\right)$ .

$$E_{\text{cell}}^{\circ}$$
 =  $E_{\text{cathode}}^{\circ}$   $E_{\text{anode}}^{\circ}$   
 $0.76 \text{ V}$  =  $0.00 \text{ V} - E_{\text{anode}}^{\circ}$   
 $E_{\text{anode}}^{\circ}$  =  $0.70 \text{ V}$ 

The potential for the  $Zn/Zn^{2+}$  electrode is *negative*. The negative potential indicates that an electron at the  $Zn/Zn^{2+}$  electrode has greater potential energy than it does at the SHE. *Remember that the more negative the electrode* potential is, the greater the potential energy of an electron at that electrode.

What would happen if we connected an electrode in which the electron has *more positive* potential (than the standard hydrogen electrode) to the standard hydrogen electrode? That electrode would then have a more *positive* voltage (lower potential energy for an electron).

For example, suppose we connect the standard hydrogen electrode to a Cu electrode immersed in a 1 M  $\text{Cu}^{2+}$  solution. The measured cell potential for this cell is -0.34 V. The anode  $\left(\text{Cu/Cu}^{2+}\right)$  is at a more positive voltage (lower potential energy) than the cathode (the SHE). Therefore, electrons do *not* spontaneously flow from the anode to the cathode. We diagram the potential energy and the voltage of this cell as follows:



The copper half-cell is like the water tank with the lower water level, and electrons do not spontaneously flow

from the copper electrode to the standard hydrogen electrode.

We can determine the electrode potential for the Cu/Cu<sup>2+</sup> half-cell (the anode) from the measured cell potential as we did for the  $Zn/Zn^{2+}$  half-cell.

$$E_{\text{cell}}^{\circ}$$
 =  $E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$   
 $-0.34 \text{ V}$  =  $0.00 \text{ V} - E_{\text{anode}}^{\circ}$   
 $E_{\text{anode}}^{\circ}$  =  $+0.34 \text{ V}$ 

The potential for the  $Cu/Cu^{2+}$  electrode is *positive*. The positive potential indicates that an electron at the  $Cu/Cu^{2+}$ electrode has lower potential energy than it does at the SHE. The more positive the electrode potential, the lower the potential energy of an electron at that electrode.

By convention, standard electrode potentials are written for reduction half-reactions. We write the standard electrode potentials for the two half-reactions just discussed as:

$$\text{Cu}^{2+}(aq) + 2 e^{-} \rightarrow \text{Cu}(s) \quad E^{\circ} = +0.34 \text{ V}$$
  
 $\text{Zn}^{2+}(aq) + 2 e^{-} \rightarrow \text{Zn}(s) \quad E^{\circ} = -0.76 \text{ V}$ 

We can see that the  $Cu/Cu^{2+}$  electrode is positive relative to the SHE (and will therefore tend to draw electrons away from the SHE) and that the  $Zn/Zn^{2+}$  electrode is negative relative to the SHE (and will therefore tend to repel electrons toward the SHE). The standard electrode potentials for a number of common half-reactions are listed in Table 19.1<sup>□</sup>.

Table 19.1 Standard Electrode Potentials at 25 °C

| Reduction Half-Re           | eaction   |   |
|-----------------------------|---|---|
| Stronger                    | F <sub>2</sub> (g) + 2 e <sup>-</sup>                           |   |
| oxidizing agent             | $H_2O_2(aq) + 2 H^+(aq) + 2 e$                                  | → 2 H <sub>2</sub> O(I)   |
| <b>1</b>                    | $PbO_2(s) + 4 H^+(aq) + SO_4^{2-}(aq) + 2 e^-$                  | $\longrightarrow PbSO_4(s) + 2 H_2O(I)$                           |
|                             | $MnO_4^-(aq) + 4 H^+(aq) + 3 e^-$                               | $\longrightarrow MnO_2(s) + 2 H_2O(I)$                            |
| <u> </u>                    | $MnO_4^{-}(aq) + 8 H^{+}(aq) + 5 e^{-}$                         | $\longrightarrow$ Mn <sup>2+</sup> (aq) + 4 H <sub>2</sub> O(I)   |
|                             | Au <sup>3+</sup> (aq) + 3 e <sup>-</sup>                        | —→ Au( <i>s</i> )   |
|                             | PbO <sub>2</sub> (s) + 4 H <sup>+</sup> (aq) + 2 e <sup>-</sup> | $\longrightarrow Pb^{2+}(aq) + 2 H_2O(I)$                         |
|                             | Cl <sub>2</sub> (g) + 2 e <sup>-</sup>                          | —→ 2 CI <sup>-</sup> ( <i>aq</i> )                                |
|                             | $Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e^-$                         | $\longrightarrow$ 2 Cr <sup>3+</sup> (aq) + 7 H <sub>2</sub> O(I) |
| X                           | $O_2(g) + 4 H^+(aq) + 4 e^-$                                    | → 2 H <sub>2</sub> O( <i>I</i> )                                  |
|                             | $MnO_2(s) + 4 H^+(aq) + 2 e^-$                                  | $\longrightarrow$ Mn <sup>2+</sup> (aq) + 2 H <sub>2</sub> O(I)   |
|                             | $IO_3^-(aq) + 6 H^+(aq) + 5 e^-$                                | $\longrightarrow \frac{1}{2}I_2(aq) + 3H_2O(I)$                   |
|                             | Br <sub>2</sub> (/) + 2 e <sup>-</sup>                          | > 2 Br <sup>-</sup> ( <i>aq</i> )                                 |
|                             | $VO_2^+(aq) + 2 H^+(aq) + e^-$                                  | $\longrightarrow VO^{2+}(aq) + H_2O(I)$                           |
|                             | $NO_3^-(aq) + 4 H^+(aq) + 3 e^-$                                | $\longrightarrow NO(g) + 2 H_2O(I)$                               |
|                             | $CIO_2(g) + e^-$  | $\longrightarrow CIO_2^-(aq)$                                     |
|                             | $Ag^+(aq) + e^-$  | $\longrightarrow$ Ag(s)   |
|                             | Fe <sup>3+</sup> ( <i>aq</i> ) + e <sup>-</sup>                 | $\longrightarrow$ Fe <sup>2+</sup> (aq)                           |
|                             | $O_2(g) + 2 H^+(aq) + 2 e^-$                                    | $\longrightarrow H_2O_2(aq)$                                      |
|                             | $MnO_4^-(aq) + e^-$   | $\longrightarrow MnO_4^{2-}(aq)$                                  |
|                             | I <sub>2</sub> (s) + 2 e <sup>-</sup>                           |   |
|                             | Cu <sup>+</sup> ( <i>aq</i> ) + e <sup>-</sup>                  | > Cu( <i>s</i> )  |
|                             | $O_2(g) + 2 H_2O(I) + 4 e^-$                                    | > 4 OH⁻( <i>aq</i> )  |
|                             | Cu <sup>2+</sup> ( <i>aq</i> ) + 2 e <sup>-</sup>               | > Cu(s)   |
|                             | $SO_4^{2-}(aq) + 4 H^+(aq) + 2 e^-$                             | $\longrightarrow H_2SO_3(aq) + H_2O(I)$                           |
|                             | Cu <sup>2+</sup> ( <i>aq</i> ) + e <sup>-</sup>                 | $\longrightarrow$ Cu <sup>+</sup> ( <i>aq</i> )                   |
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| _        |     |   |   |  |
|----------|-----|---|---|--|
|          |     | $Sn^{4+}(aq) + 2 e^{-}$                           |   | $\longrightarrow \operatorname{Sn}^{2+}(aq)$ |
|          |     | 2 H <sup>+</sup> (aq) + 2 e <sup>-</sup>          |   | $\longrightarrow H_2(g)$                     |
|          |     | $Fe^{3+}(aq) + 3e^{-}$                            |   | —→ Fe( <i>s</i> )                            |
|          |     | $Pb^{2+}(aq) + 2 e^{-}$                           |   | $\longrightarrow Pb(s)$                      |
|          |     | $Sn^{2+}(aq) + 2 e^{-}$                           |   | > Sn( <i>s</i> )                             |
|          | ·   | Ni <sup>2+</sup> (aq) + 2 e <sup>-</sup>          |   | —→ Ni( <i>s</i> )                            |
|          | · · | Cd <sup>2+</sup> (aq) + 2 e <sup>-</sup>          |   | —→ Cd(s)                                     |
|          | · · | Fe <sup>2+</sup> ( <i>aq</i> ) + 2 e <sup>-</sup> |   | —→ Fe( <i>s</i> )                            |
|          | · · | $Cr^{3+}(aq) + e^{-}$                             |   | $\longrightarrow$ Cr <sup>2+</sup> (aq)      |
|          |     | Cr <sup>3+</sup> (aq) + 3 e <sup>-</sup>          |   | —→ Cr( <i>s</i> )                            |
|          |     | Zn <sup>2+</sup> ( <i>aq</i> ) + 2 e <sup>-</sup> |   | —→ Zn( <i>s</i> )                            |
|          |     | 2 H <sub>2</sub> O(I) + 2 e <sup>-</sup>          |   | $\longrightarrow H_2(g) + 2 OH^-(aq)$        |
|          |     | $Mn^{2+}(aq) + 2 e^{-}$                           |   | —→ Mn( <i>s</i> )                            |
|          |     | Al <sup>3+</sup> (aq) + 3 e <sup>-</sup>          |   | $\longrightarrow$ AI(s)                      |
|          |     | Mg <sup>2+</sup> ( <i>aq</i> ) + 2 e <sup>-</sup> |   | —→ Mg( <i>s</i> )                            |
|          |     | Na <sup>+</sup> ( <i>aq</i> ) + e <sup>-</sup>    |   | —→ Na(s)                                     |
|          |     | Ca <sup>2+</sup> (aq) + 2 e <sup>-</sup>          |   | —→ Ca(s)                                     |
| Wea      | ker | Ba <sup>2+</sup> ( <i>aq</i> ) + 2 e <sup>-</sup> |   | —→ Ba( <i>s</i> )                            |
| oxidizin |     | $K^{+}(aq) + e^{-}$                               |   | —→ K(s)                                      |
|          |     | Li <sup>+</sup> ( <i>aq</i> ) + e <sup>-</sup>    | ^ | —→ Li( <i>s</i> )                            |

**Summarizing Standard Electrode Potentials:** 

- The electrode potential of the standard hydrogen electrode (SHE) is exactly zero.
- The electrode in any half-cell with a greater tendency to undergo reduction is positively charged relative to the SHE and therefore has a positive E°.
- The electrode in any half-cell with a lesser tendency to undergo reduction (or greater tendency to undergo oxidation) is negatively charged relative to the SHE and therefore has a negative *E*°.
- The cell potential of any electrochemical cell  $(E_{\text{cell}}^{\circ})$  is the difference between the electrode potentials of the cathode and the anode  $(E_{\text{cell}}^{\circ} = E_{\text{cat}}^{\circ} E_{\text{an}}^{\circ})$ .
- $E_{\rm cell}^{\circ}$  is positive for spontaneous reactions and negative for nonspontaneous reactions.

Multiplying a half-reaction by some constant does *not* affect the value of  $E^{\circ}$  for the half-reaction.

$$\text{Cu}^{2+}(aq) + 2 \text{ e}^{-} \rightarrow \text{Cu}(s)$$
  $E^{\circ} = 0.34 \text{ V}$   
2  $\text{Cu}^{2+}(aq) + 4 \text{ e}^{-} \rightarrow 2 \text{ Cu}(s)$   $E^{\circ} = 0.34 \text{ V}$ 

Example 19.4 illustrates how to calculate the standard potential of an electrochemical cell from the standard electrode potentials of the half-reactions.

# **Example 19.4** Calculating Standard Potentials for Electrochemical Cells from Standard Electrode Potentials of the Half-Reactions

Use tabulated standard electrode potentials to calculate the standard cell potential for this reaction occurring in an electrochemical cell at 25  $^{\circ}$ C (The equation is balanced.)

$$Al(s) + NO_3^-(aq) + 4 H^+(aq) \rightarrow Al^{3+}(aq) + NO(g) + 2 H_2O(l)$$

**SOLUTION** Begin by separating the reaction into oxidation and reduction half-reactions. (In this case, you can readily see that Al(s) is oxidized. In cases where it is not so apparent, you may want to assign oxidation states to determine the correct half-reactions.)

**OXIMITION:** Al(s)  $\rightarrow$  Al (aq) + 3 = 0

**Reduction:**  $NO_3^-(aq) + 4 H^+(aq) + 3 e^- \rightarrow NO(g) + 2 H_2O(l)$ 

Look up the standard electrode potentials for each half-reaction in Table 19.1. Add the half-cell reactions together to obtain the overall redox equation. Calculate the standard cell potential by subtracting the electrode potential of the anode from the electrode potential of the cathode.

### Oxidation

(Anode): Al(s)  $\to$  Al<sup>3+</sup>(aq) + 3 e<sup>-</sup> E° = -1.66 V

#### Reduction

(Cathode):  $\frac{\text{NO}_3^-(aq) + 4 \text{ H}^+(aq) + 3 \text{ e}^- \rightarrow \text{NO}(g) + 2 \text{ H}_2\text{O}(l)}{\text{Al}(s) + \text{NO}_3^-(aq) + 4 \text{ H}^+(aq) \rightarrow \text{Al}^{3+}(aq) + \text{NO}(g) + 2 \text{ H}_2\text{O}(l)}$ 

$$E_{\text{cell}}^{\circ} = E_{\text{cat}}^{\circ} - E_{\text{an}}^{\circ}$$
  
= 0.96 V - ( - 1.66 V)  
= 2.62 V

**FOR PRACTICE 19.4** Use tabulated standard electrode potentials to calculate the standard cell potential for this reaction occurring in an electrochemical cell at 25 °C. (The equation is balanced.)

$$3 \text{ Pb}^{2+}(aq) + 2 \text{ Cr}(s) \rightarrow 3 \text{ Pb}(s) + 2 \text{ Cr}^{3+}(aq)$$

Interactive Worked Example 19.4 Calculating Standard Potentials for Electrochemical Cells from Standard Electrode Potentials of the Half-Reactions

Conceptual Connection 19.2 Standard Electrode Potentials

# Fredicting the Spontaneous Direction of an Oxidation–Reduction Reaction

The following mnemonics (NIO and PIR) can help you predict the spontaneous direction of redox reactions: N.I.O.-More Negative Is Oxidation P.I.R.-More Positive Is Reduction

To determine the spontaneous direction of an oxidation–reduction reaction, we examine the electrode potentials of the two relevant half-reactions in Table 19.1. The half-reaction with the more *negative* electrode potential tends to lose electrons and therefore undergo oxidation. (Remember that negative charge repels electrons.) The half-reaction having the more *positive* electrode potential tends to gain electrons and therefore undergo reduction. (Remember that positive charge attracts electrons.)

Consider the two reduction half-reactions:

$$Ni^{2+}(aq) + 2 e^{-} \rightarrow Ni(s)$$
  $E^{\circ} = -0.23 \text{ V}$   
 $Mn^{2+}(aq) + 2 e^{-} \rightarrow Mn(s)$   $E^{\circ} = -1.18 \text{ V}$ 

Because the manganese half-reaction has a more negative electrode potential, it repels electrons and proceeds in the reverse direction (oxidation). Because the nickel half-reaction has the more positive (or less negative) electrode potential, it attracts electrons and proceeds in the forward direction.

We can confirm this by calculating the standard electrode potential for manganese acting as the anode (oxidation) and nickel acting as the cathode (reduction).

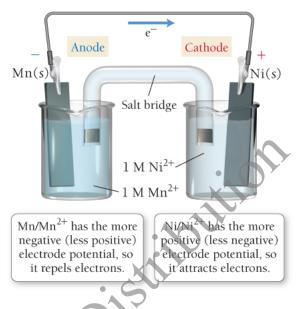
Oxidation (Anode): 
$$Mn(s) \longrightarrow Mn^{2+}(aq) + 2e^{s}$$
  $E^{\circ} = -1.18 \text{ V}$ 

Reduction (Cathode):  $Ni^{2+}(aq) + 2e^{s} \longrightarrow Ni(s)$   $E^{\circ} = -0.23 \text{ V}$ 
 $Ni^{2+}(aq) + Mn(s) \longrightarrow Ni(s) + Mn^{2+}(aq)$   $E^{\circ}_{cell} = E^{\circ}_{cat} - E^{\circ}_{an}$ 
 $= -0.23 \text{ V} - (-1.18 \text{ V})$ 
 $= 0.95 \text{ V}$ 

The overall cell potential is positive, indicating a spontaneous reaction. Consider the electrochemical cell as the anode and the nickel half-cell on the right as the cathode. Electrons flow from the anode to the cathode.

## Figure 19.8 Mn/Ni<sup>2+</sup> Electrochemical Cell

Since the reduction of  $Mn^{2+}$  is listed below the reduction of  $Ni^{2+}$  in Table 19.1 , the reduction of  $Ni^{2+}$  is spontaneous when paired with the oxidation of Mn.



Another way to predict the spontaneity of a redox reaction is to note the relative positions of the two halfreactions in Table 19.1 . The table lists half-reactions in order of decreasing electrode potential, so the halfreactions near the top of the table—those having large positive electrode potentials—attract electrons and therefore tend to occur in the forward direction. Half-reactions near the bottom of the table-those having large negative electrode potentials—repel electrons and therefore tend to occur in the reverse direction. In other words, as we move down Table 19.1 , the half-reactions become less likely to occur in the forward direction and more likely to occur in the reverse direction. As a result, any reduction half-reaction listed is spontaneous when paired with the reverse of a half-reaction that appears below it in Table 19.1.

For example, if we return to our two previous half-reactions involving manganese and nickel, we see that the manganese half-reaction is listed below the nickel half-reaction in Table 19.1 ...

$$Ni^{2+}(aq) + 2 e^{-} \rightarrow Ni(s)$$
  $E^{\circ} = -0.23 \text{ V}$   
 $Mn^{2+}(aq) + 2 e^{-} \rightarrow Mn(s)$   $E^{\circ} = -1.18 \text{ V}$ 

Therefore, the nickel reaction occurs in the forward direction (reduction) and the manganese reaction occurs in the reverse direction (oxidation).

Recall from Section 8.9 that an oxidizing agent causes the oxidation of another substance (and is itself reduced) and that a reducing agent causes the reduction of another substance (and is itself oxidized).

Summarizing the Prediction of Spontaneous Direction for Redox Reactions:

• The half-reaction with the more *positive* electrode potential attracts electrons more strongly and undergoes reduction. (Substances listed at the ton of Table 19.1 🗗 tend to undergo reduction: they are good oxidizing

non, (ourstances useed at the top of fare 17.1- tend to undergo reduction, they are good oxidizing agents.)

- · The half-reaction with the more negative electrode potential repels electrons more strongly and undergoes oxidation. (Substances listed near the bottom of Table 19.1 tend to undergo oxidation; they are good reducing agents.)
- Any reduction reaction in Table 19.1 □ is spontaneous when paired with the reverse of any of the reactions listed below it on the table.

# **Example 19.5** Predicting Spontaneous Redox Reactions and Sketching **Electrochemical Cells**

Without calculating  $E_{\mathrm{cell'}}^{\circ}$  predict whether each of these redox reactions is spontaneous (when the reactants and products are in their standard states). If the reaction is spontaneous as written, make a sketch of the electrochemical cell in which the reaction could occur. If the reaction is not spontaneous as written, write an equation for the direction in which the spontaneous reaction occurs and sketch the corresponding electrochemical cell. In your sketches, make sure to label the anode (which should be drawn on the left), the cathode, and the direction of electron flow.

**a.** 
$$\operatorname{Fe}(s) + \operatorname{Mg}^{2+}(aq) \to \operatorname{Fe}^{2+}(aq) + \operatorname{Mg}(s)$$

**b.** 
$$Fe(s) + Pb^{2+}(aq) \rightarrow Fe^{2+}(aq) + Pb(s)$$

### **SOLUTION**

**a.**  $Fe(s) + Mg^{2+}(aq) \rightarrow Fe^{2+}(aq) + Mg(s)$ 

This reaction involves the reduction of Mg<sup>2+</sup>:

$$Mg^{2+}(aq) + 2e^{-} \rightarrow Mg(s)$$
  $E^{\circ} = -2.37 \text{ V}$ 

and the oxidation of Fe:

$$Fe(s) \to Fe^{2+}(aq) + 2e^{-}$$
  $E^{\circ} = -0.45 \text{ V}$ 

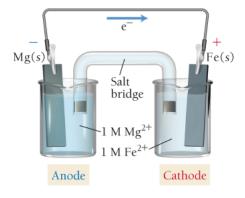
The magnesium half-reaction has the more negative electrode potential and therefore repels electrons more strongly and undergoes oxidation. The iron half-reaction has the more positive electrode potential and therefore attracts electrons more strongly and undergoes reduction. So the reaction as written is not spontaneous. (The reaction pairs the reduction of  ${\rm Mg}^{2+}$  with the reverse of a half-reaction above it in Table 19.1 ☐—such pairings are not spontaneous.)

However, the reverse reaction is spontaneous:

$$\mathrm{Fe^{2+}}(aq) + \mathrm{Mg}(s) \rightarrow \mathrm{Fe}(s) + \mathrm{Mg^{2+}}(aq)$$

The corresponding electrochemical cell is shown in Figure 19.9<sup>□</sup>.

Figure 19.9 Mg/Fe<sup>2+</sup> Electrochemical Cell



**b.**  $Fe(s) + Pb^{2+}(aq) \rightarrow Fe^{2+}(aq) + Pb(s)$ 

This reaction involves the reduction of Pb<sup>2+</sup>:

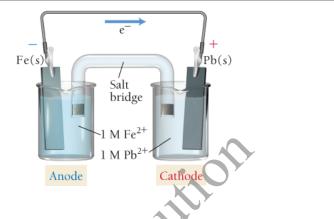
$$Pb^{2+}(aq) + 2e^{-} \rightarrow Pb(s)$$
  $E^{\circ} = -0.13 \text{ V}$ 

and the oxidation of iron:

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-} E^{\circ} = -0.45 \text{ V}$$

The iron half-reaction has the more negative electrode potential and therefore repels electrons and undergoes oxidation. The lead half-reaction has the more positive electrode potential and therefore attracts electrons and undergoes reduction. The reaction *is* spontaneous as written. (The reaction pairs the reduction of  $Pb^{2+}$  with the reverse of a half-reaction *below it* in Table 19.1 — such pairings are always spontaneous.) The corresponding electrochemical cell is shown in Figure 19.10 —.

 $Figure~19.10~~Fe/Pb^{2+}~\textbf{Electrochemical Cell}$ 



FOR PRACTICE 19.5 Are these redox reactions spontaneous under standard conditions?

**a.** 
$$\operatorname{Zn}(s) + \operatorname{Ni}^{2+}(aq) \to \operatorname{Zn}^{2+}(aq) + \operatorname{Ni}(s)$$

**b.** 
$$\operatorname{Zn}(s) + \operatorname{Ca}^{2+}(aq) \to \operatorname{Zn}^{2+}(aq) + \operatorname{Ca}(s)$$

# Conceptual Connection 19,3 Selective Oxidation

# Ifredicting Whether a Metal Will Dissolve in Acid

Recall from Chapter 16 to that acids dissolve some metals. Most acids dissolve metals by the reduction of H<sup>+</sup> ions to hydrogen gas and the corresponding oxidation of the metal to its ion. For example, if solid Zn is submersed into hydrochloric acid, the following reaction occurs:

We observe the reaction as the dissolving of the zinc and the bubbling of hydrogen gas. The zinc is oxidized and the  $H^+$  ions are reduced. Notice that this reaction involves the pairing of a reduction half-reaction (the reduction of  $H^+$ ) with the reverse of a half-reaction that is listed below it in Table 19.1. Therefore, this reaction is spontaneous.

What happens, in contrast, if we pair the reduction of  $H^+$  with the oxidation of Cu? The reaction is not spontaneous because it involves pairing the reduction of  $H^+$  with the reverse of a half-reaction that is listed *above it* in the table. Consequently, copper does not react with  $H^+$  and does not dissolve in acids such as HCl. In

general, metals with reduction half-reactions listed below the reduction of  $H^+$  to  $H_2$  in Table 19.1  $\square$  dissolve in acids, while metals listed above it do not.

An important exception to this rule is nitric acid (HNO3), which can oxidize metals through the reduction halfreaction:

$$NO_3^-(aq) + 4 H^+(aq) + 3 e^- \rightarrow NO(g) + 2 H_2O(l)$$
  $E^\circ = 0.96 V$ 

Since this half-reaction is above the reduction of H<sup>+</sup> in Table 19.1 , HNO<sub>3</sub> can oxidize metals (such as copper) that can't be oxidized by HCl.



When zinc is immersed in hydrochloric acid, the zinc is oxidized, forming ions that become solvated in the solution. Hydrogen ions are reduced, forming bubbles of hydrogen gas.

### Conceptual Connection 19.4 Metals Dissolving in Acids

Aot for Distribution

Aot for Distribution