

## 20.4: Standard Reduction Potentials

### Learning Objectives

- To use redox potentials to predict whether a reaction is spontaneous.
- To balance redox reactions using half-reactions.

In a galvanic cell, current is produced when electrons flow externally through the circuit from the anode to the cathode because of a difference in potential energy between the two electrodes in the electrochemical cell. In the Zn/Cu system, the valence electrons in zinc have a substantially higher potential energy than the valence electrons in copper because of shielding of the s electrons of zinc by the electrons in filled d orbitals. Hence electrons flow spontaneously from zinc to copper(II) ions, forming zinc(II) ions and metallic copper. Just like water flowing spontaneously downhill, which can be made to do work by forcing a waterwheel, the flow of electrons from a higher potential energy to a lower one can also be harnessed to perform work.

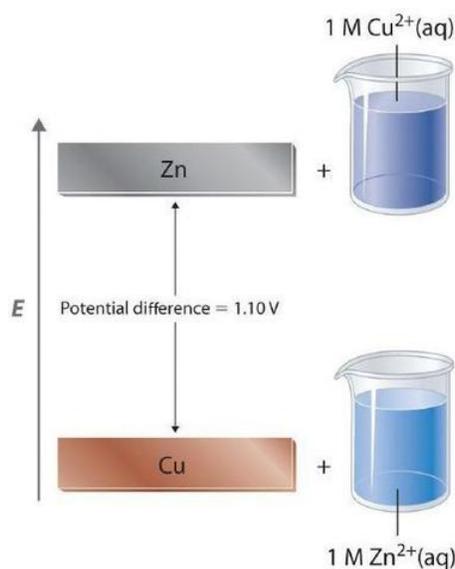


Figure 20.4.1: Potential Energy Difference in the Zn/Cu System. The potential energy of a system consisting of metallic Zn and aqueous  $\text{Cu}^{2+}$  ions is greater than the potential energy of a system consisting of metallic Cu and aqueous  $\text{Zn}^{2+}$  ions. Much of this potential energy difference is because the valence electrons of metallic Zn are higher in energy than the valence electrons of metallic Cu. Because the  $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq})$  system is higher in energy by 1.10 V than the  $\text{Cu(s)} + \text{Zn}^{2+}(\text{aq})$  system, energy is released when electrons are transferred from Zn to  $\text{Cu}^{2+}$  to form Cu and  $\text{Zn}^{2+}$ .

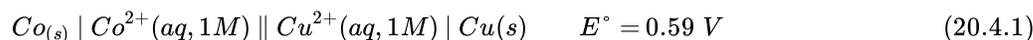
Because the potential energy of valence electrons differs greatly from one substance to another, the voltage of a galvanic cell depends partly on the identity of the reacting substances. If we construct a galvanic cell similar to the one in part (a) in Figure 20.4.1 but instead of copper use a strip of cobalt metal and 1 M  $\text{Co}^{2+}$  in the cathode compartment, the measured voltage is not 1.10 V but 0.51 V. Thus we can conclude that the difference in potential energy between the valence electrons of cobalt and zinc is less than the difference between the valence electrons of copper and zinc by 0.59 V.

The measured potential of a cell also depends strongly on the concentrations of the reacting species and the temperature of the system. To develop a scale of relative potentials that will allow us to predict the direction of an electrochemical reaction and the magnitude of the driving force for the reaction, the potentials for oxidations and reductions of different substances must be measured under comparable conditions. To do this, chemists use the **standard cell potential** ( $E^\circ_{\text{cell}}$ ), defined as the potential of a cell measured under standard conditions—that is, with all species in their standard states (1 M for solutions, concentrated solutions of salts (about 1 M) generally do not exhibit ideal behavior, and the actual standard state corresponds to an activity of 1 rather than a concentration of 1 M. Corrections for non ideal behavior are important for precise quantitative work but not for the more qualitative approach that we are taking here. 1 atm for gases, pure solids or pure liquids for other substances) and at a fixed temperature, usually 25°C.

*Measured redox potentials depend on the potential energy of valence electrons, the concentrations of the species in the reaction, and the temperature of the system.*

## Measuring Standard Electrode Potentials

It is physically impossible to measure the potential of a single electrode: only the difference between the potentials of two electrodes can be measured (this is analogous to measuring **absolute enthalpies** or **free energies**; recall that only differences in enthalpy and free energy can be measured.) We can, however, compare the standard cell potentials for two different galvanic cells that have one kind of electrode in common. This allows us to measure the potential difference between two dissimilar electrodes. For example, the measured standard cell potential ( $E^\circ$ ) for the Zn/Cu system is 1.10 V, whereas  $E^\circ$  for the corresponding Zn/Co system is 0.51 V. This implies that the potential difference between the Co and Cu electrodes is  $1.10\text{ V} - 0.51\text{ V} = 0.59\text{ V}$ . In fact, that is exactly the potential measured under standard conditions if a cell is constructed with the following cell diagram:



This cell diagram corresponds to the oxidation of a cobalt anode and the reduction of  $\text{Cu}^{2+}$  in solution at the copper cathode.

All tabulated values of standard electrode potentials by convention are listed for a reaction written as a reduction, not as an oxidation, to be able to compare standard potentials for different substances (Table P1). The standard cell potential ( $E^\circ_{\text{cell}}$ ) is therefore the difference between the tabulated reduction potentials of the two half-reactions, not their sum:

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \quad (20.4.2)$$

In contrast, recall that half-reactions are written to show the reduction and oxidation reactions that actually occur in the cell, so the overall cell reaction is written as the sum of the two half-reactions. According to Equation 20.4.2, when we know the standard potential for any single half-reaction, we can obtain the value of the standard potential of many other half-reactions by measuring the standard potential of the corresponding cell.

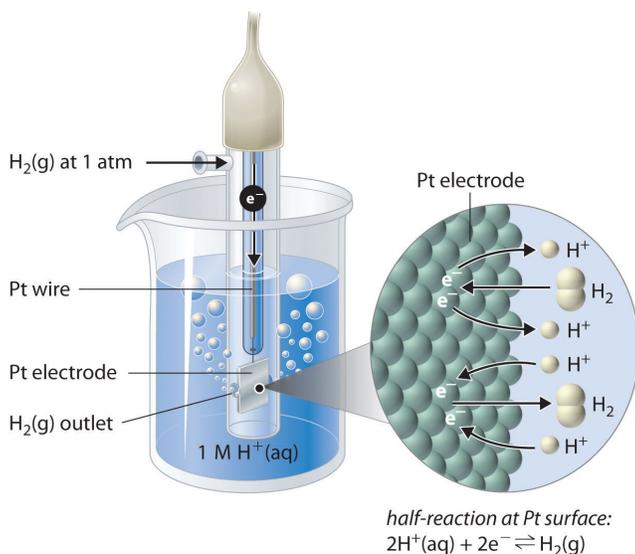


Figure 20.4.2: The Standard Hydrogen Electrode. The SHE consists of platinum wire that is connected to a Pt surface in contact with an aqueous solution containing 1 M  $\text{H}^+$  in equilibrium with  $\text{H}_2$  gas at a pressure of 1 atm. In the molecular view, the Pt surface catalyzes the oxidation of hydrogen molecules to protons or the reduction of protons to hydrogen gas. (Water is omitted for clarity.) The standard potential of the SHE is arbitrarily assigned a value of 0 V.

Although it is impossible to measure the potential of any electrode directly, we can choose a reference electrode whose potential is defined as 0 V under standard conditions. The **standard hydrogen electrode (SHE)** is universally used for this purpose and is assigned a standard potential of 0 V. It consists of a strip of platinum wire in contact with an aqueous solution containing 1 M  $\text{H}^+$ . The  $[\text{H}^+]$  in solution is in equilibrium with  $\text{H}_2$  gas at a pressure of 1 atm at the Pt-solution interface (Figure 20.4.2). Protons are reduced or hydrogen molecules are oxidized at the Pt surface according to the following equation:



One especially attractive feature of the SHE is that the Pt metal electrode is not consumed during the reaction.

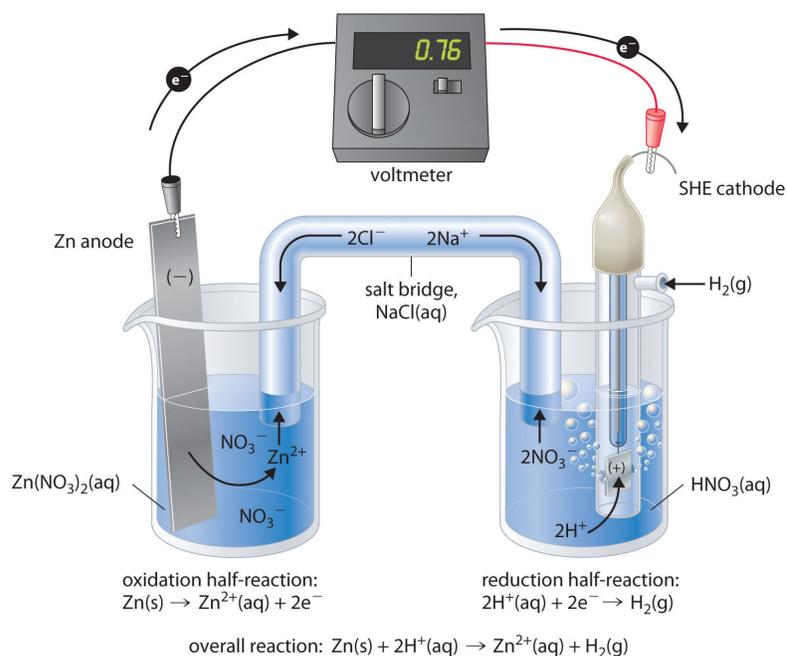
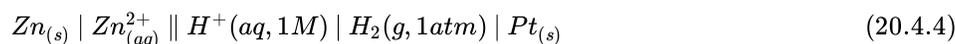


Figure 20.4.3: Determining a Standard Electrode Potential Using a Standard Hydrogen Electrode. The voltmeter shows that the standard cell potential of a galvanic cell consisting of a SHE and a Zn/Zn<sup>2+</sup> couple is  $E^{\circ}_{\text{cell}} = 0.76 \text{ V}$ . Because the zinc electrode in this cell dissolves spontaneously to form Zn<sup>2+</sup>(aq) ions while H<sup>+</sup>(aq) ions are reduced to H<sub>2</sub> at the platinum surface, the standard electrode potential of the Zn<sup>2+</sup>/Zn couple is  $-0.76 \text{ V}$ .

Figure 20.4.3 shows a galvanic cell that consists of a SHE in one beaker and a Zn strip in another beaker containing a solution of Zn<sup>2+</sup> ions. When the circuit is closed, the voltmeter indicates a potential of 0.76 V. The zinc electrode begins to dissolve to form Zn<sup>2+</sup>, and H<sup>+</sup> ions are reduced to H<sub>2</sub> in the other compartment. Thus the hydrogen electrode is the cathode, and the zinc electrode is the anode. The diagram for this galvanic cell is as follows:

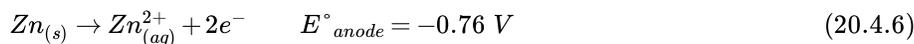


The half-reactions that actually occur in the cell and their corresponding electrode potentials are as follows:

- cathode:



- anode:



- overall:



We then use Equation 20.4.2 to calculate the cell potential

$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} \\ &= 0.76 \text{ V} \end{aligned}$$

Although the reaction at the anode is an oxidation, by convention its tabulated  $E^{\circ}$  value is reported as a reduction potential. The potential of a half-reaction measured against the SHE under standard conditions is called the **standard electrode potential** for that half-reaction. In this example, the standard reduction potential for  $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Zn(s)}$  is  $-0.76 \text{ V}$ , which means that the standard electrode potential for the reaction that occurs at the anode, the oxidation of Zn to Zn<sup>2+</sup>, often called the Zn/Zn<sup>2+</sup> redox couple, or the Zn/Zn<sup>2+</sup> couple, is  $-(-0.76 \text{ V}) = 0.76 \text{ V}$ . We must therefore subtract  $E^{\circ}_{\text{anode}}$  from  $E^{\circ}_{\text{cathode}}$  to obtain

$$E^{\circ}_{\text{cell}} : 0 \text{ V} - (-0.76 \text{ V}) = 0.76 \text{ V}$$

Because electrical potential is the energy needed to move a charged particle in an electric field, standard electrode potentials for half-reactions are intensive properties and do not depend on the amount of substance involved. Consequently,  $E^\circ$  values are independent of the stoichiometric coefficients for the half-reaction, and, most important, the coefficients used to produce a balanced overall reaction do not affect the value of the cell potential.

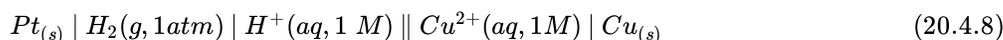
*$E^\circ$  values do NOT depend on the stoichiometric coefficients for a half-reaction, because it is an intensive property.*



The Standard Hydrogen Electrode (SHE): [The Standard Hydrogen Electrode \(SHE\)\(opens in new window\)](#) [youtu.be]

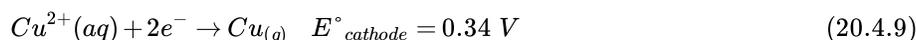
## Standard Electrode Potentials

To measure the potential of the  $\text{Cu}/\text{Cu}^{2+}$  couple, we can construct a galvanic cell analogous to the one shown in Figure 20.4.3 but containing a  $\text{Cu}/\text{Cu}^{2+}$  couple in the sample compartment instead of  $\text{Zn}/\text{Zn}^{2+}$ . When we close the circuit this time, the measured potential for the cell is negative ( $-0.34\text{ V}$ ) rather than positive. The negative value of  $E^\circ_{\text{cell}}$  indicates that the direction of spontaneous electron flow is the opposite of that for the  $\text{Zn}/\text{Zn}^{2+}$  couple. Hence the reactions that occur spontaneously, indicated by a positive  $E^\circ_{\text{cell}}$ , are the reduction of  $\text{Cu}^{2+}$  to  $\text{Cu}$  at the copper electrode. The copper electrode gains mass as the reaction proceeds, and  $\text{H}_2$  is oxidized to  $\text{H}^+$  at the platinum electrode. In this cell, the copper strip is the cathode, and the hydrogen electrode is the anode. The cell diagram therefore is written with the SHE on the left and the  $\text{Cu}^{2+}/\text{Cu}$  couple on the right:



The half-cell reactions and potentials of the spontaneous reaction are as follows:

- Cathode:



- Anode:



- Overall:



We then use Equation 20.4.2 to calculate the cell potential

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= 0.34\text{ V} \end{aligned}$$

Thus the standard electrode potential for the  $\text{Cu}^{2+}/\text{Cu}$  couple is  $0.34\text{ V}$ .



Electrode Potentials and ECell: [Electrode and Potentials and Ecell\(opens in new window\)](#) [youtu.be]

## Balancing Redox Reactions Using the Half-Reaction Method

In [Section 4.4](#), we described a method for balancing redox reactions using oxidation numbers. Oxidation numbers were assigned to each atom in a redox reaction to identify any changes in the oxidation states. Here we present an alternative approach to balancing redox reactions, the half-reaction method, in which the overall redox reaction is divided into an oxidation half-reaction and a reduction half-reaction, each balanced for mass and charge. This method more closely reflects the events that take place in an electrochemical cell, where the two half-reactions may be physically separated from each other.

We can illustrate how to balance a redox reaction using half-reactions with the reaction that occurs when Drano, a commercial solid drain cleaner, is poured into a clogged drain. Drano contains a mixture of sodium hydroxide and powdered aluminum, which in solution reacts to produce hydrogen gas:



In this reaction,  $\text{Al}_{(s)}$  is oxidized to  $\text{Al}^{3+}$ , and  $\text{H}^+$  in water is reduced to  $\text{H}_2$  gas, which bubbles through the solution, agitating it and breaking up the clogs.

The overall redox reaction is composed of a reduction half-reaction and an oxidation half-reaction. From the standard electrode potentials listed [Table P1](#), we find the corresponding half-reactions that describe the reduction of  $\text{H}^+$  ions in water to  $\text{H}_2$  and the oxidation of Al to  $\text{Al}^{3+}$  in basic solution:

- reduction:



- oxidation:



The half-reactions chosen must exactly reflect the reaction conditions, such as the basic conditions shown here. Moreover, the physical states of the reactants and the products must be identical to those given in the overall reaction, whether gaseous, liquid, solid, or in solution.

In [Equation 20.4.13](#) two  $\text{H}^+$  ions gain one electron each in the reduction; in [Equation 20.4.14](#) the aluminum atom loses three electrons in the oxidation. The charges are balanced by multiplying the reduction half-reaction ([Equation 20.4.13](#)) by 3 and the oxidation half-reaction ([Equation 20.4.14](#)) by 2 to give the same number of electrons in both half-reactions:

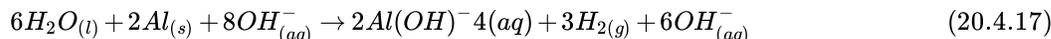
- reduction:



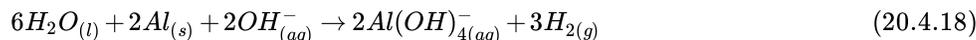
- oxidation:



Adding the two half-reactions,



Simplifying by canceling substances that appear on both sides of the equation,



We have a  $-2$  charge on the left side of the equation and a  $-2$  charge on the right side. Thus the charges are balanced, but we must also check that atoms are balanced:



The atoms also balance, so Equation 20.4.18 is a balanced chemical equation for the redox reaction depicted in Equation 20.4.12

*The half-reaction method requires that half-reactions exactly reflect reaction conditions, and the physical states of the reactants and the products must be identical to those in the overall reaction.*

We can also balance a redox reaction by first balancing the atoms in each half-reaction and then balancing the charges. With this alternative method, we do not need to use the half-reactions listed in Table P1, but instead focus on the atoms whose oxidation states change, as illustrated in the following steps:

**Step 1:** Write the reduction half-reaction and the oxidation half-reaction.

For the reaction shown in Equation 20.4.12 hydrogen is reduced from  $H^+$  in  $OH^-$  to  $H_2$ , and aluminum is oxidized from  $Al^0$  to  $Al^{3+}$ :

- reduction:



- oxidation:



**Step 2:** Balance the atoms by balancing elements other than O and H. Then balance O atoms by adding  $H_2O$  and balance H atoms by adding  $H^+$ .

Elements other than O and H in the previous two equations are balanced as written, so we proceed with balancing the O atoms. We can do this by adding water to the appropriate side of each half-reaction:

- reduction:



- oxidation:

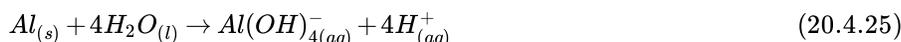


Balancing H atoms by adding  $H^+$ , we obtain the following:

- reduction:



- oxidation:

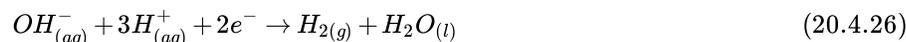


We have now balanced the atoms in each half-reaction, but the charges are not balanced.

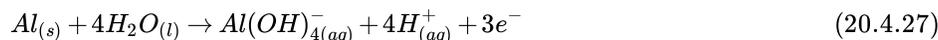
**Step 3:** Balance the charges in each half-reaction by adding electrons.

Two electrons are gained in the reduction of  $H^+$  ions to  $H_2$ , and three electrons are lost during the oxidation of  $Al^0$  to  $Al^{3+}$ :

- reduction:



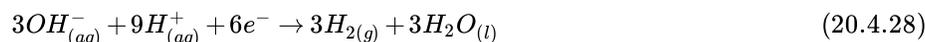
- oxidation:



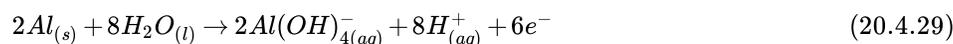
**Step 4:** Multiply the reductive and oxidative half-reactions by appropriate integers to obtain the same number of electrons in both half-reactions.

In this case, we multiply Equation 20.4.26 (the reductive half-reaction) by 3 and Equation 20.4.27 (the oxidative half-reaction) by 2 to obtain the same number of electrons in both half-reactions:

- reduction:



- oxidation:

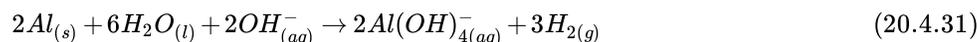


**Step 5:** Add the two half-reactions and cancel substances that appear on both sides of the equation.

Adding and, in this case, canceling  $8\text{H}^+$ ,  $3\text{H}_2\text{O}$ , and  $6e^-$ ,



We have three  $\text{OH}^-$  and one  $\text{H}^+$  on the left side. Neutralizing the  $\text{H}^+$  gives us a total of  $5\text{H}_2\text{O} + \text{H}_2\text{O} = 6\text{H}_2\text{O}$  and leaves  $2\text{OH}^-$  on the left side:

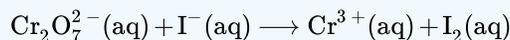


**Step 6:** Check to make sure that all atoms and charges are balanced.

Equation 20.4.31 is identical to Equation 20.4.18 obtained using the first method, so the charges and numbers of atoms on each side of the equation balance.

#### ✓ Example 20.4.1

In acidic solution, the redox reaction of dichromate ion ( $\text{Cr}_2\text{O}_7^{2-}$ ) and iodide ( $\text{I}^-$ ) can be monitored visually. The yellow dichromate solution reacts with the colorless iodide solution to produce a solution that is deep amber due to the presence of a green  $\text{Cr}^{3+}(\text{aq})$  complex and brown  $\text{I}_2(\text{aq})$  ions (Figure 20.4.4):



Balance this equation using half-reactions.

**Given:** redox reaction and Table P1

**Asked for:** balanced chemical equation using half-reactions

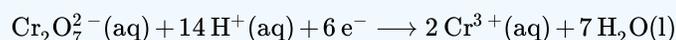
**Strategy:**

Follow the steps to balance the redox reaction using the half-reaction method.

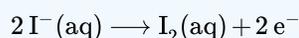
**Solution**

From the standard electrode potentials listed in Table P1, we find the half-reactions corresponding to the overall reaction:

- reduction:



- oxidation:

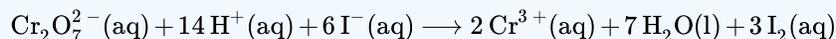


Balancing the number of electrons by multiplying the oxidation reaction by 3,

- oxidation:



Adding the two half-reactions and canceling electrons,



We must now check to make sure the charges and atoms on each side of the equation balance:

$$\begin{aligned} (-2) + 14 + (-6) &= +6 \\ +6 &\stackrel{\checkmark}{=} +6 \end{aligned}$$

and atoms

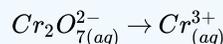


Both the charges and atoms balance, so our equation is balanced.

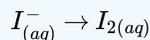
We can also use the alternative procedure, which does not require the half-reactions listed in [Table P1](#).

**Step 1:** Chromium is reduced from  $\text{Cr}^{6+}$  in  $\text{Cr}_2\text{O}_7^{2-}$  to  $\text{Cr}^{3+}$ , and  $\text{I}^{-}$  ions are oxidized to  $\text{I}_2$ . Dividing the reaction into two half-reactions,

- reduction:

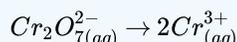


- oxidation:

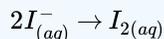


**Step 2:** Balancing the atoms other than oxygen and hydrogen,

- reduction:

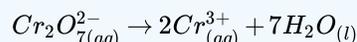


- oxidation:



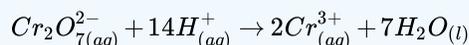
We now balance the O atoms by adding  $\text{H}_2\text{O}$ —in this case, to the right side of the reduction half-reaction. Because the oxidation half-reaction does not contain oxygen, it can be ignored in this step.

- reduction:



Next we balance the H atoms by adding  $\text{H}^{+}$  to the left side of the reduction half-reaction. Again, we can ignore the oxidation half-reaction.

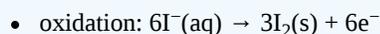
- reduction:



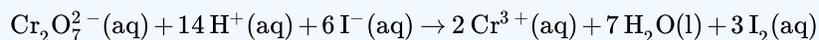
**Step 3:** We must now add electrons to balance the charges. The reduction half-reaction ( $2\text{Cr}^{6+}$  to  $2\text{Cr}^{3+}$ ) has a +12 charge on the left and a +6 charge on the right, so six electrons are needed to balance the charge. The oxidation half-reaction ( $2\text{I}^{-}$  to  $\text{I}_2$ ) has a -2 charge on the left side and a 0 charge on the right, so it needs two electrons to balance the charge:

- reduction:  $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^{+}(\text{aq}) + 6 \text{e}^{-} \rightarrow 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O}(\text{l})$
- oxidation:  $2 \text{I}^{-}(\text{aq}) \rightarrow \text{I}_2(\text{aq}) + 2 \text{e}^{-}$

**Step 4:** To have the same number of electrons in both half-reactions, we must multiply the oxidation half-reaction by 3:



**Step 5:** Adding the two half-reactions and canceling substances that appear in both reactions,



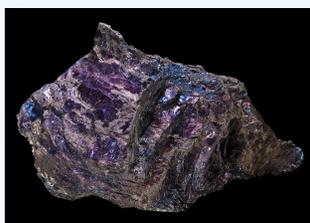
**Step 6:** This is the same equation we obtained using the first method. Thus the charges and atoms on each side of the equation balance.

### ? Exercise 20.4.1

Copper is found as the mineral covellite ( $\text{CuS}$ ). The first step in extracting the copper is to dissolve the mineral in nitric acid ( $\text{HNO}_3$ ), which oxidizes sulfide to sulfate and reduces nitric acid to  $\text{NO}$ :



Balance this equation using the half-reaction method.



Covellite (also known as covelline) is a rare copper sulfide mineral with an indigo blue color that is ubiquitous in copper ores. (CC SA-BY 3.0; Didier Descouens).

**Answer**



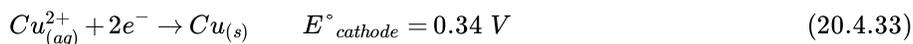
## Calculating Standard Cell Potentials

The standard cell potential for a redox reaction ( $E^\circ_{\text{cell}}$ ) is a measure of the tendency of reactants in their standard states to form products in their standard states; consequently, it is a measure of the driving force for the reaction, which earlier we called voltage. We can use the two standard electrode potentials we found earlier to calculate the standard potential for the Zn/Cu cell represented by the following cell diagram:

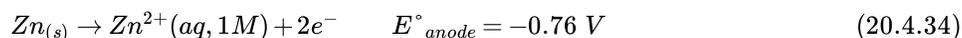


We know the values of  $E^\circ_{\text{anode}}$  for the reduction of  $\text{Zn}^{2+}$  and  $E^\circ_{\text{cathode}}$  for the reduction of  $\text{Cu}^{2+}$ , so we can calculate  $E^\circ_{\text{cell}}$ :

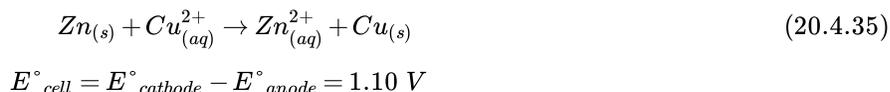
• cathode:



• anode:



• overall:



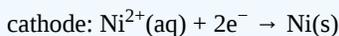
This is the same value that is observed experimentally. If the value of  $E^\circ_{\text{cell}}$  is positive, the reaction will occur spontaneously as written. If the value of  $E^\circ_{\text{cell}}$  is negative, then the reaction is not spontaneous, and it will not occur as written under standard conditions; it will, however, proceed spontaneously in the opposite direction. As we shall see in [Section 20.9](#), this does not mean

that the reaction cannot be made to occur at all under standard conditions. With a sufficient input of electrical energy, virtually any reaction can be forced to occur. Example 20.4.2 and its corresponding exercise illustrate how we can use measured cell potentials to calculate standard potentials for redox couples.

A positive  $E^\circ_{cell}$  means that the reaction will occur spontaneously as written. A negative  $E^\circ_{cell}$  means that the reaction will proceed spontaneously in the opposite direction.

#### ✓ Example 20.4.2

A galvanic cell with a measured standard cell potential of 0.27 V is constructed using two beakers connected by a salt bridge. One beaker contains a strip of gallium metal immersed in a 1 M solution of  $\text{GaCl}_3$ , and the other contains a piece of nickel immersed in a 1 M solution of  $\text{NiCl}_2$ . The half-reactions that occur when the compartments are connected are as follows:



If the potential for the oxidation of Ga to  $\text{Ga}^{3+}$  is 0.55 V under standard conditions, what is the potential for the oxidation of Ni to  $\text{Ni}^{2+}$ ?

**Given:** galvanic cell, half-reactions, standard cell potential, and potential for the oxidation half-reaction under standard conditions

**Asked for:** standard electrode potential of reaction occurring at the cathode

#### Strategy:

- Write the equation for the half-reaction that occurs at the anode along with the value of the standard electrode potential for the half-reaction.
- Use Equation 20.4.2 to calculate the standard electrode potential for the half-reaction that occurs at the cathode. Then reverse the sign to obtain the potential for the corresponding oxidation half-reaction under standard conditions.

#### Solution

**A** We have been given the potential for the oxidation of Ga to  $\text{Ga}^{3+}$  under standard conditions, but to report the standard electrode potential, we must reverse the sign. For the reduction reaction  $\text{Ga}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Ga}(\text{s})$ ,  $E^\circ_{\text{anode}} = -0.55 \text{ V}$ .

**B** Using the value given for  $E^\circ_{cell}$  and the calculated value of  $E^\circ_{\text{anode}}$ , we can calculate the standard potential for the reduction of  $\text{Ni}^{2+}$  to Ni from Equation 20.4.2

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ 0.27 \text{ V} &= E^\circ_{\text{cathode}} - (-0.55 \text{ V}) \\ E^\circ_{\text{cathode}} &= -0.28 \text{ V} \end{aligned}$$

This is the standard electrode potential for the reaction  $\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$ . Because we are asked for the potential for the oxidation of Ni to  $\text{Ni}^{2+}$  under standard conditions, we must reverse the sign of  $E^\circ_{\text{cathode}}$ . Thus  $E^\circ = -(-0.28 \text{ V}) = 0.28 \text{ V}$  for the oxidation. With three electrons consumed in the reduction and two produced in the oxidation, the overall reaction is not balanced. Recall, however, that standard potentials are independent of stoichiometry.

#### ? Exercise 20.4.2

A galvanic cell is constructed with one compartment that contains a mercury electrode immersed in a 1 M aqueous solution of mercuric acetate  $\text{Hg}(\text{CH}_3\text{CO}_2)_2$  and one compartment that contains a strip of magnesium immersed in a 1 M aqueous solution of  $\text{MgCl}_2$ . When the compartments are connected, a potential of 3.22 V is measured and the following half-reactions occur:

- cathode:  $\text{Hg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Hg}(\text{l})$
- anode:  $\text{Mg}(\text{s}) \rightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{e}^-$

If the potential for the oxidation of Mg to  $\text{Mg}^{2+}$  is 2.37 V under standard conditions, what is the standard electrode potential for the reaction that occurs at the cathode?

**Answer**

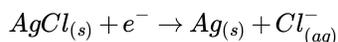
0.85 V

## Reference Electrodes and Measuring Concentrations

When using a galvanic cell to measure the concentration of a substance, we are generally interested in the potential of only one of the electrodes of the cell, the so-called **indicator electrode**, whose potential is related to the concentration of the substance being measured. To ensure that any change in the measured potential of the cell is due to only the substance being analyzed, the potential of the other electrode, the **reference electrode**, must be constant. You are already familiar with one example of a reference electrode: the SHE. The potential of a reference electrode must be unaffected by the properties of the solution, and if possible, it should be physically isolated from the solution of interest. To measure the potential of a solution, we select a reference electrode and an appropriate indicator electrode. Whether reduction or oxidation of the substance being analyzed occurs depends on the potential of the half-reaction for the substance of interest (the sample) and the potential of the reference electrode.

*The potential of any reference electrode should not be affected by the properties of the solution to be analyzed, and it should also be physically isolated.*

There are many possible choices of reference electrode other than the SHE. The SHE requires a constant flow of highly flammable hydrogen gas, which makes it inconvenient to use. Consequently, two other electrodes are commonly chosen as reference electrodes. One is the **silver–silver chloride electrode**, which consists of a silver wire coated with a very thin layer of AgCl that is dipped into a chloride ion solution with a fixed concentration. The cell diagram and reduction half-reaction are as follows:



If a saturated solution of KCl is used as the chloride solution, the potential of the silver–silver chloride electrode is 0.197 V versus the SHE. That is, 0.197 V must be subtracted from the measured value to obtain the standard electrode potential measured against the SHE.

A second common reference electrode is the **saturated calomel electrode (SCE)**, which has the same general form as the silver–silver chloride electrode. The SCE consists of a platinum wire inserted into a moist paste of liquid mercury ( $Hg_2Cl_2$ ; called calomel in the old chemical literature) and KCl. This interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution (part (a) in Figure 20.4.5. Although it sounds and looks complex, this cell is actually easy to prepare and maintain, and its potential is highly reproducible. The SCE cell diagram and corresponding half-reaction are as follows:



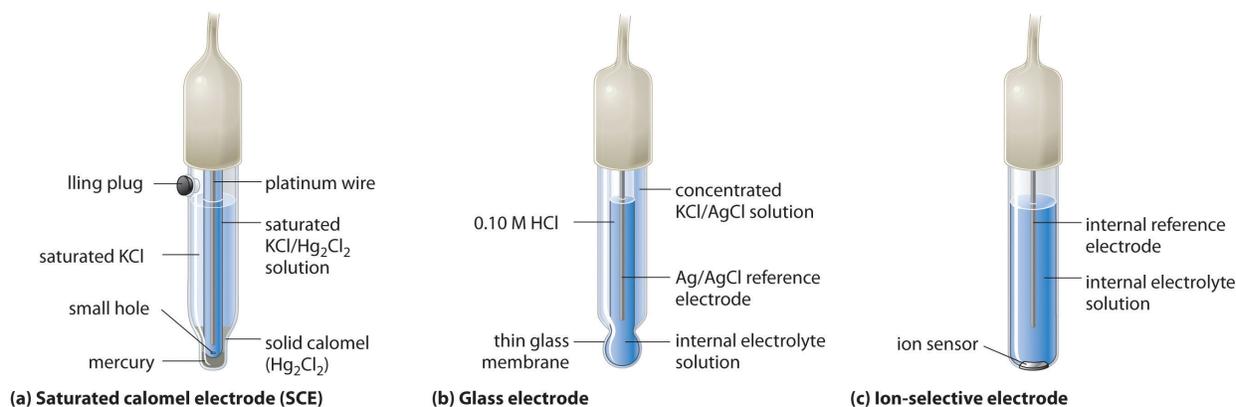


Figure 20.4.5: Three Common Types of Electrodes. (a) The SCE is a reference electrode that consists of a platinum wire inserted into a moist paste of liquid mercury (calomel;  $\text{Hg}_2\text{Cl}_2$ ) and KCl. The interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution. (b) In a glass electrode, an internal Ag/AgCl electrode is immersed in a 1 M HCl solution that is separated from the sample solution by a very thin glass membrane. The potential of the electrode depends on the  $\text{H}^+$  ion concentration of the sample. (c) The potential of an ion-selective electrode depends on the concentration of only a single ionic species in solution. (CC BY-SA-NC; anonymous)

At 25°C, the potential of the SCE is 0.2415 V versus the SHE, which means that 0.2415 V must be subtracted from the potential versus an SCE to obtain the standard electrode potential.

One of the most common uses of electrochemistry is to measure the  $\text{H}^+$  ion concentration of a solution. A **glass electrode** is generally used for this purpose, in which an internal Ag/AgCl electrode is immersed in a 0.10 M HCl solution that is separated from the solution by a very thin glass membrane (part (b) in Figure 20.4.5). The glass membrane absorbs protons, which affects the measured potential. The extent of the adsorption on the inner side is fixed because  $[\text{H}^+]$  is fixed inside the electrode, but the adsorption of protons on the outer surface depends on the pH of the solution. The potential of the glass electrode depends on  $[\text{H}^+]$  as follows (recall that  $\text{pH} = -\log[\text{H}^+]$ ):

$$E_{\text{glass}} = E' + (0.0591 \text{ V} \times \log[\text{H}^+]) = E' - 0.0591 \text{ V} \times \text{pH} \quad (20.4.39)$$

The voltage  $E'$  is a constant that depends on the exact construction of the electrode. Although it can be measured, in practice, a glass electrode is calibrated; that is, it is inserted into a solution of known pH, and the display on the pH meter is adjusted to the known value. Once the electrode is properly calibrated, it can be placed in a solution and used to determine an unknown pH.

**Ion-selective electrodes** are used to measure the concentration of a particular species in solution; they are designed so that their potential depends on only the concentration of the desired species (part (c) in Figure 20.4.5). These electrodes usually contain an internal reference electrode that is connected by a solution of an electrolyte to a crystalline inorganic material or a membrane, which acts as the sensor. For example, one type of ion-selective electrode uses a single crystal of Eu-doped  $\text{LaF}_3$  as the inorganic material. When fluoride ions in solution diffuse to the surface of the solid, the potential of the electrode changes, resulting in a so-called fluoride electrode. Similar electrodes are used to measure the concentrations of other species in solution. Some of the species whose concentrations can be determined in aqueous solution using ion-selective electrodes and similar devices are listed in Table 20.4.1.

Table 20.4.1: Some Species Whose Aqueous Concentrations Can Be Measured Using Electrochemical Methods

Species	Type of Sample
$\text{H}^+$	laboratory samples, blood, soil, and ground and surface water
$\text{NH}_3/\text{NH}_4^+$	wastewater and runoff water
$\text{K}^+$	blood, wine, and soil
$\text{CO}_2/\text{HCO}_3^-$	blood and groundwater
$\text{F}^-$	groundwater, drinking water, and soil
$\text{Br}^-$	grains and plant extracts
$\text{I}^-$	milk and pharmaceuticals

Species	Type of Sample
$\text{NO}_3^-$	groundwater, drinking water, soil, and fertilizer

## Summary

Redox reactions can be balanced using the half-reaction method. The standard cell potential is a measure of the driving force for the reaction.  $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$  The flow of electrons in an electrochemical cell depends on the identity of the reacting substances, the difference in the potential energy of their valence electrons, and their concentrations. The potential of the cell under standard conditions (1 M for solutions, 1 atm for gases, pure solids or liquids for other substances) and at a fixed temperature (25°C) is called the standard cell potential ( $E^\circ_{\text{cell}}$ ). Only the difference between the potentials of two electrodes can be measured. By convention, all tabulated values of standard electrode potentials are listed as standard reduction potentials. The overall cell potential is the reduction potential of the reductive half-reaction minus the reduction potential of the oxidative half-reaction ( $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$ ). The potential of the standard hydrogen electrode (SHE) is defined as 0 V under standard conditions. The potential of a half-reaction measured against the SHE under standard conditions is called its standard electrode potential. The standard cell potential is a measure of the driving force for a given redox reaction. All  $E^\circ$  values are independent of the stoichiometric coefficients for the half-reaction. Redox reactions can be balanced using the half-reaction method, in which the overall redox reaction is divided into an oxidation half-reaction and a reduction half-reaction, each balanced for mass and charge. The half-reactions selected from tabulated lists must exactly reflect reaction conditions. In an alternative method, the atoms in each half-reaction are balanced, and then the charges are balanced. Whenever a half-reaction is reversed, the sign of  $E^\circ$  corresponding to that reaction must also be reversed. If  $E^\circ_{\text{cell}}$  is positive, the reaction will occur spontaneously under standard conditions. If  $E^\circ_{\text{cell}}$  is negative, then the reaction is not spontaneous under standard conditions, although it will proceed spontaneously in the opposite direction. The potential of an indicator electrode is related to the concentration of the substance being measured, whereas the potential of the reference electrode is held constant. Whether reduction or oxidation occurs depends on the potential of the sample versus the potential of the reference electrode. In addition to the SHE, other reference electrodes are the silver–silver chloride electrode; the saturated calomel electrode (SCE); the glass electrode, which is commonly used to measure pH; and ion-selective electrodes, which depend on the concentration of a single ionic species in solution. Differences in potential between the SHE and other reference electrodes must be included when calculating values for  $E^\circ$ .

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