Electrochemistry

Lecture (14)

Stage 3

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that contains hydrogen ions. This arrangement is called a *hydrogen electrode*. The entire compartment with metal conductor and electrolyte solution is commonly referred to as "the electrode" or more formally as a half-cell.

In a galvanic cell, a spontaneous chemical reaction draws electrons into the cell through the cathode, the site of reduction, and releases them at the anode, the site of oxidation.

13.4 Cell Potential and Reaction Gibbs Free Energy

A reaction with a lot of pushing-and-pulling power generates a high potential difference (colloquially, a high voltage). A reaction with little pushing-and-pulling power generates only a small potential difference (a low voltage). An exhausted battery is a cell in which the reaction is at equilibrium; it has lost its power to move electrons and has a potential difference of zero. The SI unit of potential (and potential difference) is the volt (V). A volt is defined so that a charge of one coulomb (1 C) falling through a potential difference of one volt (1 V) releases one joule (1 J) of energy:

$$1 \text{ V·C} = 1 \text{ J}$$

One coulomb is the magnitude of the charge delivered by a current of one ampere flowing for one second: $1 \text{ C} = 1 \text{ A·s}$.

To express these ideas quantitatively it is helpful to note that electrical potential is analogous to gravitational potential. The maximum work that a falling weight can do is equal to its mass times the difference in gravitational potential. Similarly, the maximum work that an electron can do is equal to its charge times the difference in electrical potential through which it falls. Electrical work is a type of nonexpansion work because it involves moving electrons rather than changing the volume of the system. In Section 8.14 we established that at constant temperature and pressure, the maximum nonexpansion work that a system can do is equal to the change in the Gibbs free energy. We need to bring these two concepts together by finding the relation between the Gibbs free energy of a reaction (a thermodynamic property) and the potential difference (an electrochemical property) produced by that reaction.

HOW DO WE DO THAT? ▌

We established in Section 8.14 (Eq. 21) that the change in Gibbs free energy is the maximum nonexpansion work that a reaction can do at constant pressure and temperature:

$$\Delta G = w_e$$

The work done when an amount n of electrons (in moles) travels through a potential difference E is their total charge times the potential difference. The charge of one electron is $-e$; the charge per mole of electrons is $-eN_A$, where N_A is Avogadro's constant. Therefore, the total charge is $-neN_A$ and the work done is

$$w_e = \text{total charge} \times \text{potential difference} = (-neN_A) \times E$$

Faraday's constant, F, is the magnitude of the charge per mole of electrons (the product of the elementary charge e and Avogadro's constant N_A):

$$F = eN_A = (1.602\ 177 \times 10^{-19} \text{ C}) \times \{6.0223 \times 10^{23} \text{ (mol e}^-)^{-1}\}$$
$$= 9.6485 \times 10^4 \text{ C·(mol e}^-)^{-1}$$

Faraday's constant is normally abbreviated to $F = 9.6485 \times 10^4 \text{ C·mol}^{-1}$ (or $96.485 \text{ kC·mol}^{-1}$). We can now write the preceding expression for work as

$$w_e = -nFE$$

When this equation is combined with the thermodynamic equation relating Gibbs free energy and nonexpansion work, we obtain

$$\Delta G = -nFE$$

The units of ΔG are joules (or kilojoules), with a value that depends not only on E, but also on the amount n (in moles) of electrons transferred in the reaction. Thus, in reaction A, $n = 2$ mol. As in the discussion of the relation between Gibbs free energy and equilibrium

SOLVE

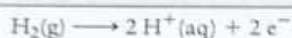**Step 1** Write the equation for the reduction at the right-hand electrode.
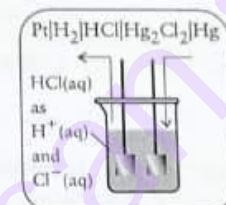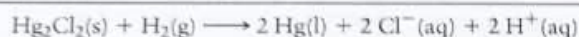
$$Hg_2Cl_2(s) + 2\,e^- \longrightarrow 2\,Hg(l) + 2\,Cl^-(aq)$$

$Cl^-|Hg_2Cl_2|Hg$
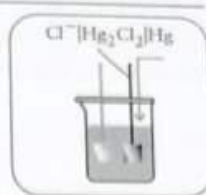
Step 2 Write the equation for the oxidation at the left-hand electrode.

$$\tfrac{1}{2}\,H_2(g) \longrightarrow H^+(aq) + e^-$$

$Pt|H_2|H^+$
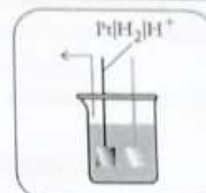
Step 3 To balance electrons, multiply the oxidation half-reaction by 2.

$$H_2(g) \longrightarrow 2\,H^+(aq) + 2\,e^-$$

Add the half-reactions together.

$$Hg_2Cl_2(s) + H_2(g) \longrightarrow 2\,Hg(l) + 2\,Cl^-(aq) + 2\,H^+(aq)$$

$Pt|H_2|HCl\|Hg_2Cl_2|Hg$

HCl(aq)
as
$H^+(aq)$
and
$Cl^-(aq)$

If the concentrations in the cell are such that it is reported as having a positive potential (that is, the mercury/mercury(I) chloride electrode is found to be positive), then mercury(I) ions are being reduced and the reaction is spontaneous as written. If the concentrations are such that the potential is found to be negative (that is, the hydrogen electrode is found to be positive), then the reverse of the reaction that we have derived would be spontaneous.

Self-Test 13.5A (a) Write the chemical equation for the reaction corresponding to the cell $Pt(s)|H_2(g)|H^+(aq)\|Co^{3+}(aq),Co^{2+}(aq)|Pt(s)$. (b) Given that the cell potential is positive, is the cell reaction spontaneous as written?

[*Answer:* (a) $H_2(g) + 2\,Co^{3+}(aq) \longrightarrow 2\,H^+(aq) + 2\,Co^{2+}(aq)$; (b) yes]
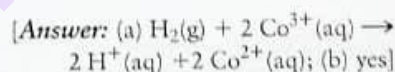
Self-Test 13.5B (a) Write the chemical equation for the reaction corresponding to the cell $Hg(l)|Hg_2Cl_2(s)|HCl(aq)\|Hg_2(NO_3)_2(aq)|Hg(l)$. (b) Given that the cell potential is positive, is the cell reaction spontaneous as written?

An electrode is designated by representing the interfaces between phases by a vertical line. A cell diagram depicts the physical arrangement of species and interfaces, with any salt bridge denoted by a double vertical line. The sign with which the cell potential is reported is the same as the measured sign of the right-hand electrode in the cell diagram. A positive cell potential indicates that the cell reaction is spontaneous as written.

13.6 Standard Potentials

There are thousands of possible galvanic cells that can be studied. However, instead of having to learn about all these different cells, it is much simpler to learn about the smaller number of electrodes that are combined to form the cells. Under standard conditions (all solutes present at $1\ mol \cdot L^{-1}$; all gases at 1 bar), we can think of each electrode as making a characteristic contribution to the cell potential called its standard potential, $E°$. Each standard potential is a measure of the electron-pulling power of a single electrode. In a galvanic cell, the electrodes pull in opposite directions, so the

Standard potentials are also called *standard electrode potentials.* Because they are always written for reduction half-reactions, they are also sometimes called *standard reduction potentials.*
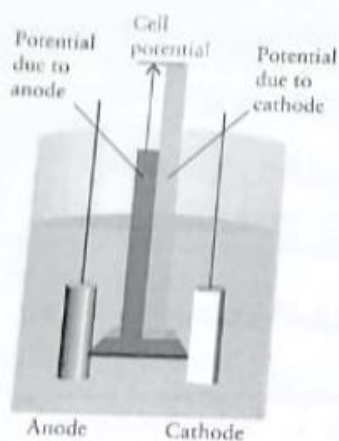
FIGURE 13.6 The cell potential can be thought of as the difference of the two potentials produced by the two electrodes.

overall pulling power of the cell, the cell's standard potential, is the *difference* of the standard potentials of the two electrodes (Fig. 13.6). That difference is always written as

$$E_{cell}° = E°(\text{electrode on right of cell diagram}) -$$
$$E°(\text{electrode on left of cell diagram})$$
(3a)

or, more succinctly,

$$E_{cell}° = E_R° - E_L°$$
(3b)

If $E_{cell}° > 0$, then the corresponding cell reaction is spontaneous under standard conditions (that is, as explained in Section 10.3, $K > 1$ for the reaction) and the electrode on the right of the cell diagram serves as the cathode. For example, for the cell

$$Fe(s)|Fe^{2+}(aq)\|Ag^+(aq)|Ag(s),$$

corresponding to $2\,Ag^+(aq) + Fe(s) \longrightarrow 2\,Ag(s) + Fe^{2+}(aq)$
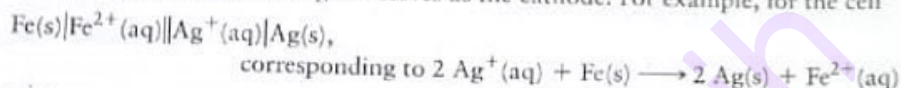
we write

$$E_{cell}° = E°(Ag^+/Ag) - E°(Fe^{2+}/Fe)$$

and find $E_{cell}° = +1.24$ V at 25°C. Because $E_{cell}° > 0$, the cell reaction has $K > 1$, with products dominant at equilibrium, and iron metal can reduce silver ions. If we had written the cell in the opposite order,

$$Ag(s)|Ag^+(aq)\|Fe^{2+}(aq)|Fe(s),$$

corresponding to $2\,Ag(s) + Fe^{2+}(aq) \longrightarrow Ag^+(aq) + Fe(s)$
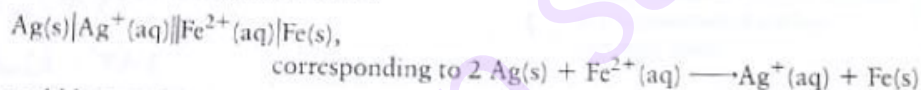
we would have written

$$E_{cell}° = E°(Fe^{2+}/Fe) - E°(Ag^+/Ag)$$

and would have found $E_{cell}° = -1.24$ V. We would report that for this reaction $K < 1$, with reactants dominant at equilibrium. However, the conclusion is the same: iron has a tendency to reduce silver.

A note on good practice: Although $E_{cell}° > 0$ is often said to signify a spontaneous reaction, it actually signifies that the reaction is spontaneous only when the reactants and products all have their standard values. At other compositions, the reverse reaction might be spontaneous. It is much better to regard $E_{cell}° > 0$ as signifying that $K > 1$ for the reaction and $E_{cell}° < 0$ as signifying that $K < 1$, because the equilibrium constant is a fixed characteristic of the reaction. Whether or not the forward reaction is positive then depends on the relative sizes of Q and K, as explained in Chapter 10.

A problem with compiling a list of standard potentials is that we know only the *overall* cell potential, not the contribution of a single electrode. A voltmeter placed between the two electrodes of a galvanic cell measures the *difference* of their potentials, not the individual values. To provide numerical values for individual standard potentials, we arbitrarily set the standard potential of one particular electrode, the hydrogen electrode, equal to zero at all temperatures:

$$2\,H^+(g) + 2\,e^- \longrightarrow H_2(g) \qquad E° = 0$$

In redox couple notation, $E°(H^+/H_2) = 0$ at all temperatures. A hydrogen electrode in its standard state, with hydrogen gas at 1 bar and the hydrogen ions present at 1 mol·L^{-1} (strictly, unit activity), is called a standard hydrogen electrode (SHE). The standard hydrogen electrode is then used to define the standard potentials of all other electrodes:

The standard potential of a couple is the standard potential of a cell (including the sign) in which the couple forms the right-hand electrode in the cell diagram and a hydrogen electrode forms the left-hand electrode in the cell diagram.

For example, for the cell

$$Pt(s)|H_2(g)|H^+(aq)\|Cu^{2+}(aq)|Cu(s)$$
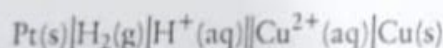
we find that the standard cell potential is 0.34 V with the copper electrode the cathode, and so $E_{cell}^\circ = +0.34$ V. Because the hydrogen electrode contributes zero to the standard cell potential, the cell potential is attributed entirely to the copper electrode, and we write

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

The standard potential of an electrode is a measure of the tendency of the associated half-reaction to occur relative to the reduction of H^+ ions. For example, because the cell reaction

$$Cu^{2+}(aq) + H_2(g) \longrightarrow Cu(s) + 2 H^+(aq)$$

has $K > 1$ (because $E_{cell}^\circ > 0$), we can consider the oxidizing ability of $Cu^{2+}(aq)$, as represented by the reduction half-reaction $Cu^{2+}(aq) + 2 e^- \longrightarrow Cu(s)$, to be greater than the oxidizing ability of $H^+(aq)$, as represented by $2 H^+(aq) + 2 e^- \longrightarrow H_2(g)$. Consequently, Cu^{2+} ions can be reduced to metallic copper by hydrogen gas, in the sense that $K > 1$ for the reaction. In general (Fig. 13.7):

The more *positive* the potential, the greater the electron-pulling power of the reduction half-reaction and, therefore, the more strongly *oxidizing* the redox couple (the stronger the tendency for the half-reaction to occur as a reduction).

Now consider the cell

$$Pt(s)|H_2(g)|H^+(aq)\|Zn^{2+}(aq)|Zn(s)$$

and the corresponding cell reaction

$$Zn^{2+}(aq) + H_2(g) \longrightarrow Zn(s) + 2 H^+(aq)$$

The magnitude of the standard cell potential is 0.76 V, but in this case the hydrogen electrode is found to be the cathode: therefore, the standard cell potential is reported as -0.76 V. Because the entire potential is attributed to the zinc electrode, we write

$$Zn^{2+}(aq) + 2 e^- \longrightarrow Zn(s) \qquad E^\circ(Zn^{2+}/Zn) = -0.76 \text{ V}$$
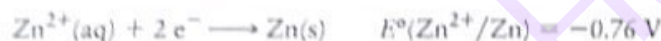
The negative standard potential means that the Zn^{2+}/Zn electrode is the anode in a cell with H^+/H_2 as the other electrode and, therefore, that the *reverse* of the cell reaction, specifically

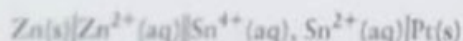$$Zn(s) + 2 H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

has $E_{cell}^\circ > 0$ and therefore $K > 1$. We can conclude that the reducing ability of $Zn(s)$ in the half-reaction $Zn(s) \rightarrow Zn^{2+}(aq) + 2 e^-$ is greater than the reducing ability of $H_2(g)$ in the half-reaction $H_2(g) \rightarrow 2 H^+(aq) + 2 e^-$. Consequently, zinc metal can reduce H^+ ions in acidic solution to hydrogen gas under standard conditions. In general (Fig. 13.8):

The more *negative* the potential, the greater the electron-donating power of the oxidation half-reaction and therefore the more strongly *reducing* the redox couple (that is, the stronger the tendency for the half-reaction to occur as an oxidation).

Table 13.1 lists a number of standard electrode potentials measured at 25°C (the only temperature we consider here); a longer list can be found in Appendix 2B. The standard potentials of elements vary in a complicated way through the periodic table (Fig. 13.9). However, the most negative—the most strongly reducing—are usually found toward the left of the periodic table, and the most positive—the most strongly oxidizing—are found toward the upper right.
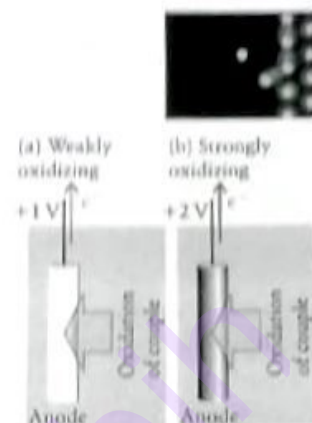

FIGURE 13.7 (a) A couple that has a small positive potential has only a small tendency to be reduced and so has a weak electron-pulling power (is a weak acceptor of electrons) relative to hydrogen ions; hence it is a weak oxidizing agent. (b) A couple with a high positive potential has strong pulling power (is a strong acceptor of electrons) and is a strong oxidizing agent.
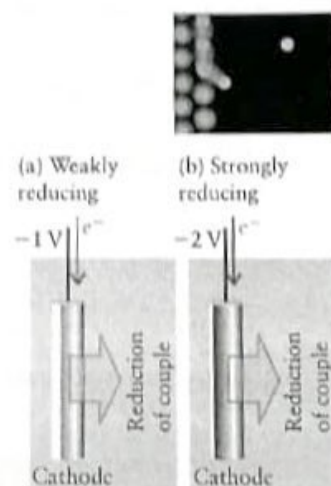
Animation 13.7

FIGURE 13.8 (a) A couple that has a small negative potential has only a small tendency to be oxidized and so has a poor pushing power (is a weak donor of electrons) relative to hydrogen; hence it is a weak reducing agent. (b) A couple with a large negative potential has strong pushing power (is a strong donor of electrons) and is a strong reducing agent.

Animation 13.8

In Appendix 2B, standard potentials are listed both by numerical value and alphabetically, to make it easy to find the one you want.

EXAMPLE 13.5 Determining the standard potential of an electrode

The standard potential of a zinc electrode is -0.76 V, and the standard potential of the cell

$$Zn(s)|Zn^{2+}(aq)\|Sn^{4+}(aq), Sn^{2+}(aq)|Pt(s)$$

is $+0.91$ V. What is the standard potential of the Sn^{4+}/Sn^{2+} electrode?

Find the standard potential from $E^\circ = E^\circ$(for reduction) − E°(for oxidation).
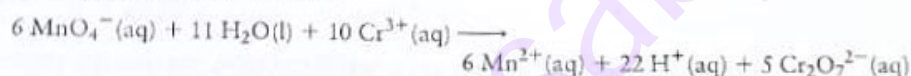
$E^\circ = 1.51 \text{ V} - 1.33 \text{ V}$

$= +0.18 \text{ V}$
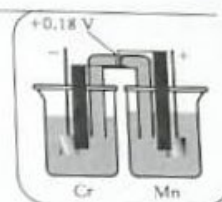
(b) To construct the cell reaction, combine the two half-reactions, leaving the permanganate half-reaction as a reduction and reversing the dichromate half-reaction. To match numbers of electrons, multiply the manganese half-reaction by 6 and the chromium half-reaction by 5:

$10 \text{ Cr}^{3+}(aq) + 35 \text{ H}_2\text{O}(l) \longrightarrow 5 \text{ Cr}_2\text{O}_7^{2-}(aq) + 70 \text{ H}^+(aq) + 30 \text{ e}^-$

$6 \text{ MnO}_4^-(aq) + 48 \text{ H}^+(aq) + 30 \text{ e}^- \longrightarrow 6 \text{ Mn}^{2+}(aq) + 24 \text{ H}_2\text{O}(l)$
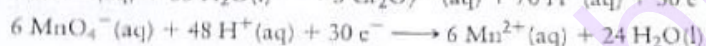
Their net sum gives the cell reaction:

$6 \text{ MnO}_4^-(aq) + 11 \text{ H}_2\text{O}(l) + 10 \text{ Cr}^{3+}(aq) \longrightarrow$
$6 \text{ Mn}^{2+}(aq) + 22 \text{ H}^+(aq) + 5 \text{ Cr}_2\text{O}_7^{2-}(aq)$

(c) Write the cell diagram with the cathode on the right-hand side:

$\text{Pt}(s)|\text{Cr}_2\text{O}_7^{2-}(aq),\text{Cr}^{3+}(aq),\text{H}^+(aq)\|\text{H}^+(aq),\text{MnO}_4^-(aq),\text{Mn}^{2+}(aq)|\text{Pt}(s)$

Evaluate As expected, the permanganate ion is the oxidizing agent in the cell reaction and the dichromate ion the reducing agent.

Self-Test 13.9A Which metal, zinc or nickel, is the stronger reducing agent in aqueous solution under standard conditions? (a) Evaluate the standard potential of the appropriate cell; (b) specify the cell with a cell diagram; (c) write the net ionic equation for the spontaneous reaction; (d) state your answer to the question.
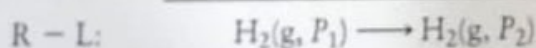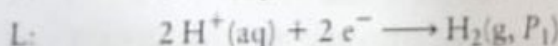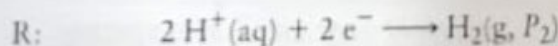
[*Answer:* (a) +0.53 V; (b) $\text{Zn}(s)|\text{Zn}^{2+}(aq)\|\text{Ni}^{2+}(aq)|\text{Ni}(s)$;
(c) $\text{Zn}(s) + \text{Ni}^{2+}(aq) \longrightarrow \text{Zn}^{2+}(aq) + \text{Ni}(s)$; (d) zinc]

Self-Test 13.9B Which is the stronger oxidizing agent, Cu^{2+} or Ag^+, in aqueous solution under standard conditions? Evaluate the standard potential of the appropriate cell, specify the cell with a cell diagram, and write the net ionic equation for the corresponding cell reaction.

The oxidizing and reducing power of a redox couple determines its position in the electrochemical series. The strongest oxidizing agents are at the top left of the table; the strongest reducing agents are at the bottom right of the table.

13.8 Standard Potentials and Equilibrium Constants

One of the most useful applications of standard potentials is in the calculation of equilibrium constants from electrochemical data. Perhaps surprisingly, the reactions need not be redox reactions: the techniques that we develop here can be applied to any kind of reaction, including neutralization and precipitation reactions, provided that they can be expressed as the difference of two reduction half-reactions. For example, even a "reaction" as simple as the expansion of a gas can be expressed as the difference of two reduction half-reactions:

R: $2 \text{ H}^+(aq) + 2 \text{ e}^- \longrightarrow \text{H}_2(g, P_2)$

L: $2 \text{ H}^+(aq) + 2 \text{ e}^- \longrightarrow \text{H}_2(g, P_1)$

R − L: $\text{H}_2(g, P_1) \longrightarrow \text{H}_2(g, P_2)$

We saw in Section 10.3 that the standard reaction Gibbs free energy, ΔG_r° (remember that the r signifies the molar convention) is related to the equilibrium constant of the

reaction by $\Delta G_r^\circ = -RT \ln K$. In this chapter, we have seen that the standard reaction Gibbs free energy is related to the standard potential of a galvanic cell by $\Delta G_r^\circ = -nFE_{cell}^\circ$, with n a pure number. When we combine the two equations, we get

$$nFE_{cell}^\circ = RT \ln K \tag{4}$$

This expression can be rearranged to allow us to calculate the equilibrium constant from the standard cell potential:

$$\ln K = \frac{nFE^\circ}{RT} \tag{5}^*$$

A note on good practice: Equation 5 was derived on the basis of the "molar" convention for writing the reaction Gibbs free energy; that means that the n must be interpreted as a pure number. That convention keeps the units straight: FE_{cell}° has the units joules per mole, so does RT, so the ratio FE_{cell}°/RT is a pure number and, with n a pure number, the right hand side is a pure number too (as it must be, if it is to be equal to a logarithm).

Because the magnitude of K increases exponentially with E_{cell}°, a reaction with a large positive E_{cell}° has $K \gg 1$. A reaction with a large negative E_{cell}° has $K \ll 1$.

Thinking point: What is the value of K for a reaction that has $E_{cell}^\circ = 0$?

The fact that we can calculate E_{cell}° from standard potentials allows us to calculate equilibrium constants for any reaction that can be expressed as two half-reactions. The reaction does not need to be spontaneous nor does it have to be a redox reaction. Toolbox 13.3 summarizes the steps and Example 13.8 shows the steps in action.

TOOLBOX 13.3   HOW TO CALCULATE EQUILIBRIUM CONSTANTS FROM ELECTROCHEMICAL DATA

CONCEPTUAL BASIS

The logarithm of the equilibrium constant of a reaction is proportional to the standard potential of the corresponding cell. We can expect a cell reaction with a large positive potential to have a strong tendency to take place, and therefore to produce a high proportion of products at equilibrium. Therefore, we expect $K > 1$ when $E^\circ > 0$ (and often $K \gg 1$). The opposite is true for a cell reaction with a negative standard potential.

PROCEDURE

The procedure for calculating an equilibrium constant from electrochemical data is as follows.

Step 1 Write the balanced equation for the reaction. Then find two reduction half-reactions in Appendix 2B that combine to give that equation. Reverse one of the half-reactions and add them together.

Step 2 Identify the numerical (unitless) value of n from the change in oxidation numbers or by examining the half-

reactions (after multiplication by appropriate factors) for the number of electrons transferred in the balanced equation.

Step 3 To obtain E_{cell}°, subtract the standard potential of the half-reaction that was reversed (oxidation) from the standard potential of the half-reaction that was left as a reduction: $E^\circ = E^\circ(\text{for reduction}) - E^\circ(\text{for oxidation})$. Alternatively, write a cell diagram for the reaction; in that case, $E_{cell}^\circ = E_R^\circ - E_L^\circ$.

Step 4 Use the relation $\ln K = nFE_{cell}^\circ/RT$ to calculate the value of K (with n a pure number).

At 25.00°C (298.15 K), $RT/F = 0.025\ 693$ V; so, at this temperature,

$$\ln K = \frac{nE_{cell}^\circ}{0.025\ 693\ \text{V}}$$

This procedure is illustrated in Example 13.8.

The Nernst Equation

zero. A "dead" battery is one in which the cell reaction has reached equilibrium. At equilibrium, a cell generates zero potential difference across its electrodes and the reaction can no longer do work. To describe this behavior quantitatively, we need to find how the cell potential varies with the concentrations of species in the cell.

HOW DO WE DO THAT? ▌

To establish how the cell potential depends on concentration, we first note that the potential is proportional to the reaction Gibbs free energy (Eq. 2). We already know how ΔG_r varies with composition:

$$\Delta G_r = \Delta G_r^\circ + RT \ln Q$$

where Q is the reaction quotient for the cell reaction (Eq. 5 of Section 10.3). Because $\Delta G_r = -nFE_{cell}$ and $\Delta G_r^\circ = -nFE_{cell}^\circ$, it follows at once that

$$-nFE_{cell} = -nFE_{cell}^\circ + RT \ln Q$$

At this point, we divide through by $-nF$ to get an expression for E_{cell} in terms of Q, which is given below.

The equation for the concentration dependence of the cell potential that we have derived,

$$E_{cell} = E_{cell}^\circ - \frac{RT}{nF} \ln Q \qquad (6a)^*$$

(with n a pure number) is called the **Nernst equation** for the German electrochemist Walther Nernst, who first derived it. At 298.15 K, $RT/F = 0.025\,693$ V; so at that temperature the Nernst equation takes the form

$$E_{cell} = E_{cell}^\circ - \frac{0.025\,693\,\text{V}}{n} \ln Q \qquad (6b)^*$$

It is sometimes convenient to use this equation with common logarithms, in which case we make use of the relation $\ln x = \ln 10 \times \log x = 2.303 \log x$. At 298.15 K,

$$E_{cell} = E_{cell}^\circ - \frac{RT \ln 10}{nF} \log Q = E_{cell}^\circ - \frac{0.059\,17\,\text{V}}{n} \log Q \qquad (6c)^*$$

The Nernst equation is widely used to estimate the potentials of cells under nonstandard conditions. In biology it is used, among other things, to estimate the potential difference across biological cell membranes, such as those of neurons.

EXAMPLE 13.9 Using the Nernst equation to predict a cell potential

Calculate the potential of a Daniell cell at 25°C in which the concentration of Zn^{2+} ions is 0.10 mol·L^{-1} and that of the Cu^{2+} ions is 0.0010 mol·L^{-1}.

PLAN Write the balanced equation for the cell reaction and the corresponding expression for Q, and note the value of n. Then determine E_{cell}° from the standard potentials in Table 13.1 or Appendix 2B. Determine the value of Q for the stated conditions. Calculate the cell potential by substituting these values into the Nernst equation, Eq. 6b.

SOLVE The Daniell cell and the corresponding cell reaction are

$$Zn(s)|Zn^{2+}(aq)\|Cu^{2+}(aq)|Cu(s) \qquad Cu^{2+}(aq) + Zn(s) \longrightarrow Zn^{2+}(aq) + Cu(s)$$
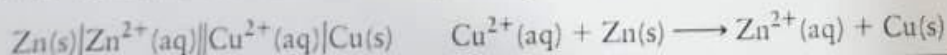
Set up the reaction quotient.

$$Q = \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}} = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{0.10}{0.0010}$$