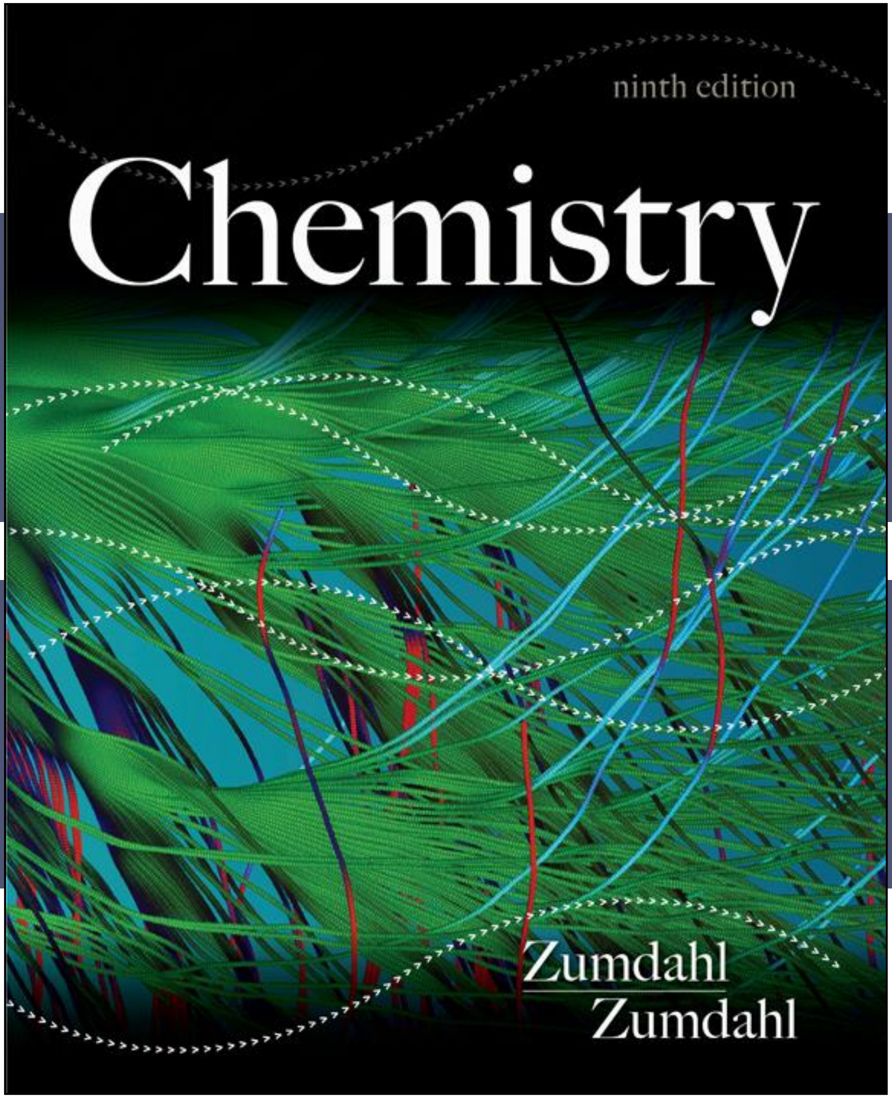


Chapter 18

Electrochemistry

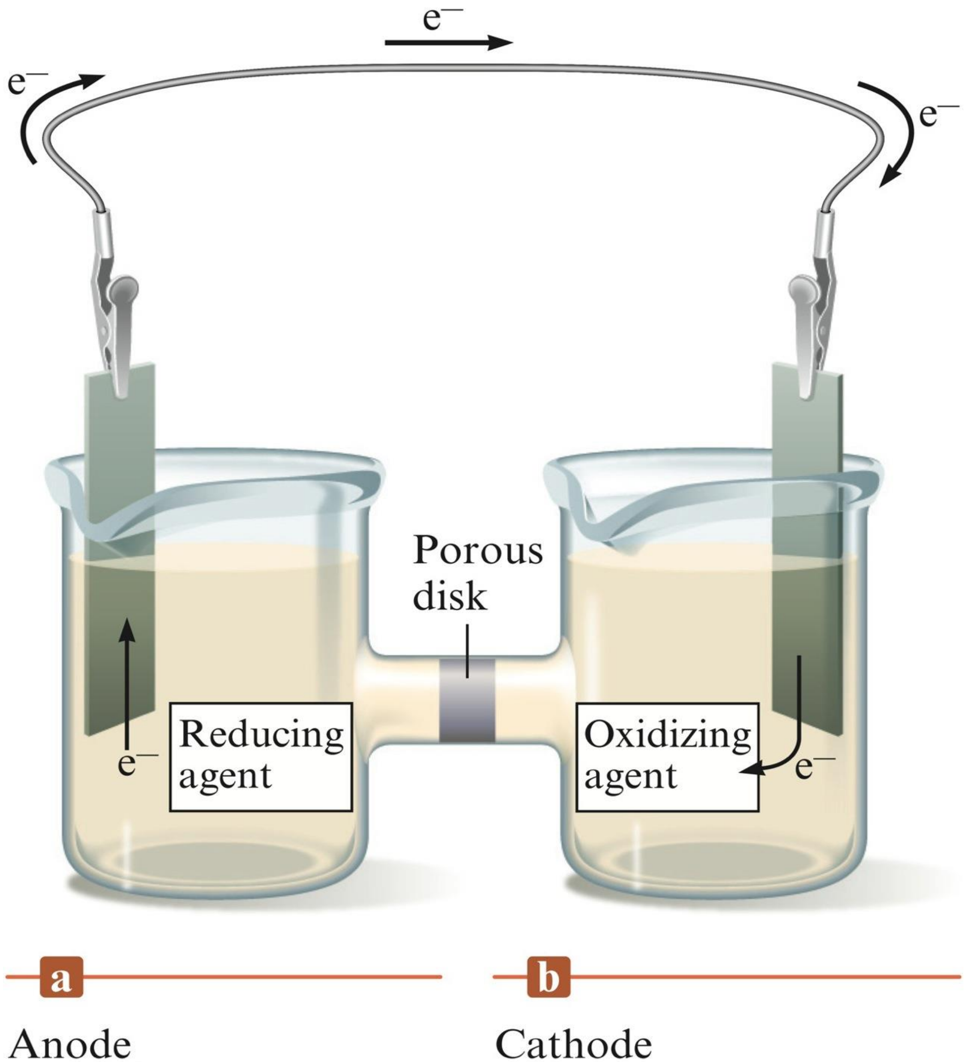
Electrochemistry

- is best defined as *the study of the interchange of chemical and electrical energy*
- constitutes one of the most important interfaces between chemistry and everyday life

Galvanic Cell

- Device in which chemical energy is changed to electrical energy.
- The reaction in an electrochemical cell occurs at the interface between the electrode and the solution where the electron transfer occurs.
- Uses a spontaneous redox reaction to produce a current that can be used to do work.

A Galvanic Cell



Galvanic Cell

- The electrode compartment in which *oxidation* occurs is called the **anode;**
- The electrode compartment in which *reduction* occurs is called the **cathode**
    - Oxidation occurs at the anode.
    - Reduction occurs at the cathode.
- Salt bridge or porous disk – devices that allow ions to flow without extensive mixing of the solutions.
    - Salt bridge – contains a strong electrolyte held in a Agar Jelly.
    - Porous disk – contains tiny passages that allow hindered flow of ions.

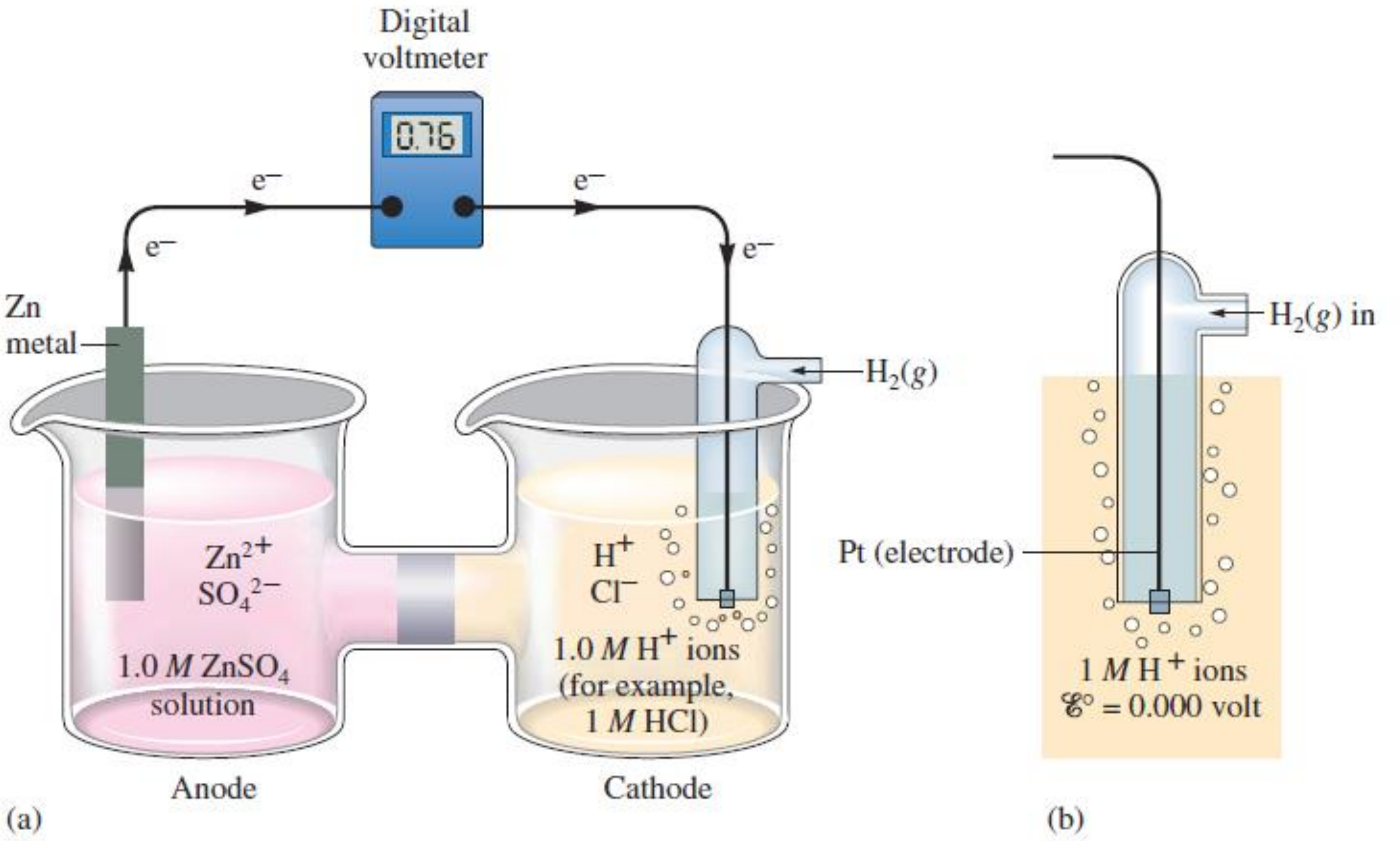
Cell Potential

- A galvanic cell consists of an oxidizing agent in one compartment that pulls electrons through a wire from a reducing agent in the other compartment.
- The “pull”, or driving force, on the electrons is called the cell potential ($\mathscr{E}_{\text{cell}}$), or the electromotive force (emf) of the cell.
  - Unit of electrical potential is the volt (V).
    - 1 joule of work per coulomb of charge transferred.

Galvanic Cell

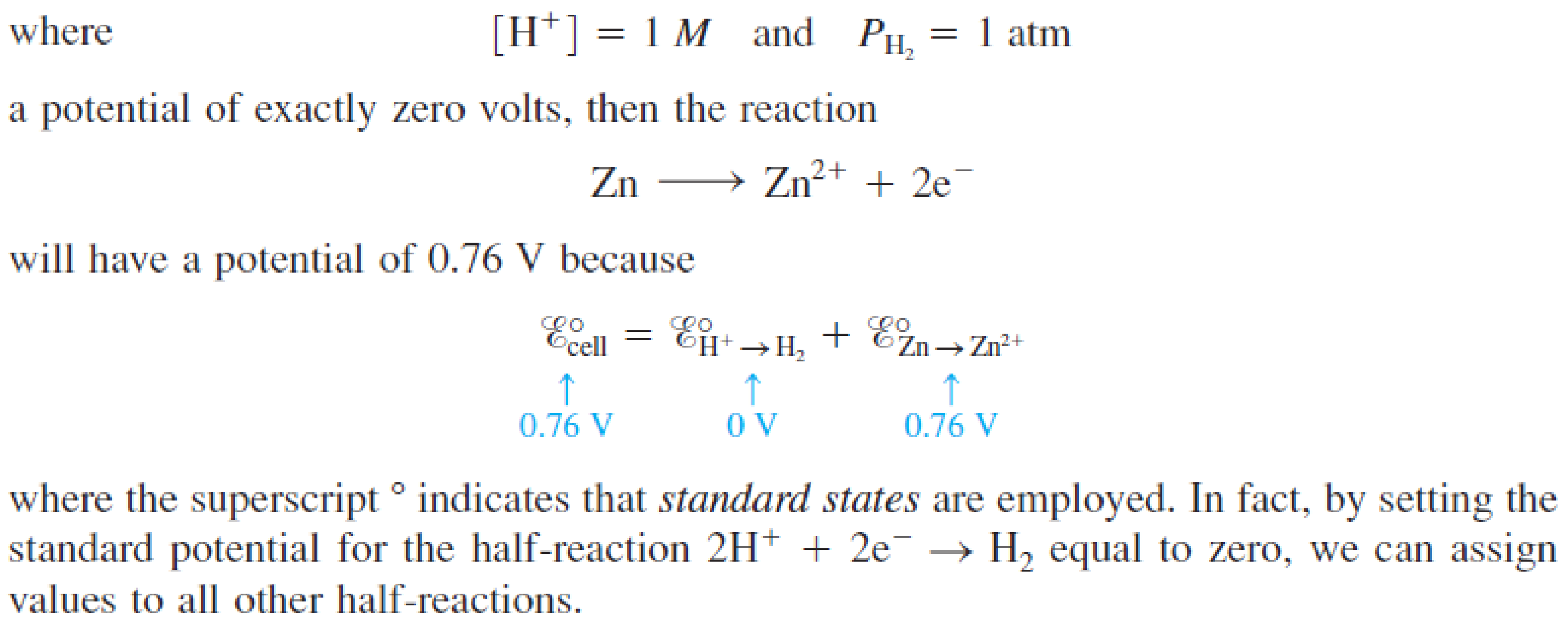
- All half-reactions are given as reduction processes in standard tables.
  - Table 18.1 in the Textbook
  - 1 *M*, 1atm, 25° C
- A galvanic cell runs spontaneously in the direction that gives a positive value for E°_{cell}.
- The values corresponding to reduction half-reactions with all solutes at 1 *M* and all gases at 1 atm are called **standard reduction potentials**

Section 18.3
Standard Reduction Potentials



Section 18.3

Standard Reduction Potentials



where $[H^+] = 1\ M$ and $P_{H_2} = 1$ atm

a potential of exactly zero volts, then the reaction

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

will have a potential of 0.76 V because

$$\underset{\substack{\uparrow \\ 0.76\text{ V}}}{\mathscr{E}^\circ_{\text{cell}}} = \underset{\substack{\uparrow \\ 0\text{ V}}}{\mathscr{E}^\circ_{H^+ \rightarrow H_2}} + \underset{\substack{\uparrow \\ 0.76\text{ V}}}{\mathscr{E}^\circ_{Zn \rightarrow Zn^{2+}}}$$

where the superscript ° indicates that *standard states* are employed. In fact, by setting the standard potential for the half-reaction $2H^+ + 2e^- \rightarrow H_2$ equal to zero, we can assign values to all other half-reactions.

- The cathode consists of a platinum electrode (used because it is a chemically inert conductor) in contact with 1 *M* H ions and bathed by hydrogen gas at 1 atm.
- Such an electrode, called the **standard hydrogen electrode**

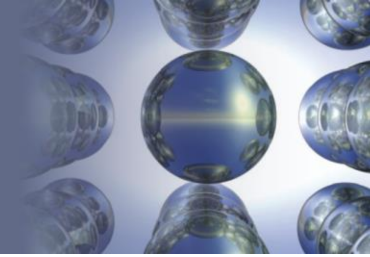
Combining two half-reactions to obtain a balanced oxidation–reduction reaction often requires two manipulations

1. One of the reduction half-reactions must be reversed
   - The half-reaction with the largest positive potential will run as written (as a reduction), and the other half-reaction will be forced to run in reverse (will be the oxidation reaction).
   - The net potential of the cell will be the difference between the two.

$$\mathscr{E}^{\circ}_{\text{cell}} = \mathscr{E}^{\circ}\,(\text{cathode}) - \mathscr{E}^{\circ}\,(\text{anode})$$

Section 18.3
Standard Reduction Potentials

1. Since the number of electrons lost must equal the number gained, the half-reactions must be multiplied by integers as necessary to achieve the balanced equation. However, the value of is not changed when a half-reaction is multiplied by an integer. Since a standard reduction potential is an intensive property (it does not depend on how many times the reaction occurs), the potential is not multiplied by the integer required to balance the cell reaction.



Example: $Fe^{3+}(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + Fe^{2+}(aq)$

- Half-Reactions:
  - $Fe^{3+} + e^{-} \rightarrow Fe^{2+}$ $E° = 0.77\ V$
  - $Cu^{2+} + 2e^{-} \rightarrow Cu$ $E° = 0.34\ V$
- To balance the cell reaction and calculate the cell potential, we must reverse reaction 2.
  - $Cu \rightarrow Cu^{2+} + 2e^{-}$ $-E° = -0.34\ V$
- Each Cu atom produces two electrons but each Fe^{3+} ion accepts only one electron, therefore reaction 1 must be multiplied by 2.
  - $2Fe^{3+} + 2e^{-} \rightarrow 2Fe^{2+}$ $E° = 0.77\ V$

Overall Balanced Cell Reaction

$2Fe^{3+} + 2e^{-} \rightarrow 2Fe^{2+}$ $\quad E^\circ = 0.77\ V$ (cathode)

$Cu \rightarrow Cu^{2+} + 2e^{-}$ $\quad -E^\circ = -0.34\ V$ (anode)

- Balanced Cell Reaction:

$Cu + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+}$

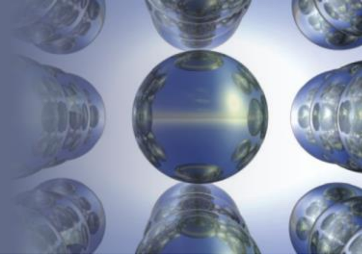
- Cell Potential:

$E^\circ_{cell} = E^\circ$ (cathode) – E° (anode)

$E^\circ_{cell} = 0.77\ V - 0.34\ V = 0.43\ V$

Line Notation

- Used to describe electrochemical cells.
- Anode components are listed on the left.
- Cathode components are listed on the right.
- Separated by double vertical lines which indicated salt bridge or porous disk.
- The concentration of aqueous solutions should be specified in the notation when known.
- Example: $Mg(s)|Mg^{2+}(aq)||Al^{3+}(aq)|Al(s)$
  - $Mg \rightarrow Mg^{2+} + 2e^{-}$ (anode)
  - $Al^{3+} + 3e^{-} \rightarrow Al$ (cathode)



Example

A galvanic cell is based on the reaction

$$MnO_4^-(aq) + H^+(aq) + ClO_3^-(aq) \longrightarrow ClO_4^-(aq) + Mn^{2+}(aq) + H_2O(l)$$

a) Give the balanced cell reaction and calculate E° for the cell
b) Write the line notation for this cell

Solution

The half-reactions are

$$MnO_4^- + 5e^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O \qquad \mathscr{E}^\circ = 1.51\ V \qquad (1)$$
$$ClO_4^- + 2H^+ + 2e^- \longrightarrow ClO_3^- + H_2O \qquad \mathscr{E}^\circ = 1.19\ V \qquad (2)$$

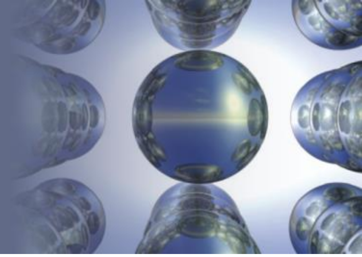
Section 18.3
Standard Reduction Potentials

- Half-reaction (2) must be reversed (it is the anode), and both half-reactions must be multiplied by integers to make the number of electrons equal:

$$
\begin{array}{rlr}
2(\mathrm{MnO_4^-} + 5\mathrm{e^-} + 8\mathrm{H^+} \longrightarrow \mathrm{Mn^{2+}} + 4\mathrm{H_2O}) & & \mathscr{E}^\circ\,(\text{cathode}) = \quad 1.51\ \mathrm{V} \\
5(\mathrm{ClO_3^-} + \mathrm{H_2O} \longrightarrow \mathrm{ClO_4^-} + 2\mathrm{H^+} + 2\mathrm{e^-}) & & -\mathscr{E}^\circ\,(\text{anode}) = -1.19\ \mathrm{V} \\
\hline
2\mathrm{MnO_4^-}(aq) + 6\mathrm{H^+}(aq) + 5\mathrm{ClO_3^-}(aq) \longrightarrow & & \mathscr{E}^\circ_{\text{cell}} = \mathscr{E}^\circ\,(\text{cathode}) - \mathscr{E}^\circ\,(\text{anode}) \\
\quad 2\mathrm{Mn^{2+}}(aq) + 3\mathrm{H_2O}(l) + 5\mathrm{ClO_4^-}(aq) & & = 1.51\ \mathrm{V} - 1.19\ \mathrm{V} = 0.32\ \mathrm{V}
\end{array}
$$

- all the components involved in the oxidation–reduction reaction are ions. Since none of these dissolved ions can serve as an electrode, a nonreacting (inert) conductor must be used. The usual choice is platinum.
- Thus, for the cell the line notation is

$$\mathrm{Pt}(s)\,|\,\mathrm{ClO_3^-}(aq), \mathrm{ClO_4^-}(aq), \mathrm{H^+}(aq)\,||\,\mathrm{H^+}(aq), \mathrm{MnO_4^-}(aq), \mathrm{Mn^{2+}}(aq)\,|\,\mathrm{Pt}(s)$$



Description of a Galvanic Cell

- The cell potential (always positive for a galvanic cell where $E^\circ_{cell} = E^\circ(\text{cathode}) - E^\circ(\text{anode})$) and the balanced cell reaction.
- The direction of electron flow, obtained by inspecting the half–reactions and using the direction that gives a positive E°_{cell}.

Description of a Galvanic Cell

- Designation of the anode and cathode.
- The nature of each electrode and the ions present in each compartment. A chemically inert conductor is required if none of the substances participating in the half–reaction is a conducting solid.

Example

- Describe completely the galvanic cell based on the following half-reactions under standard conditions:

$$\mathrm{Ag^{+} + e^{-} \longrightarrow Ag} \qquad \mathscr{E}^{\circ} = 0.80\ \mathrm{V} \qquad (1)$$

$$\mathrm{Fe^{3+} + e^{-} \longrightarrow Fe^{2+}} \qquad \mathscr{E}^{\circ} = 0.77\ \mathrm{V} \qquad (2)$$

Section 18.3
Standard Reduction Potentials

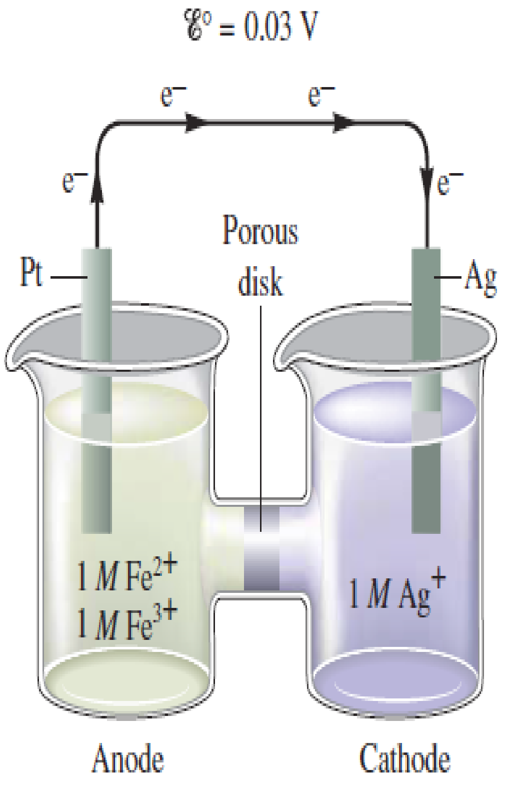


FIGURE 17.8

Schematic diagram for the galvanic cell based on the half-reactions

$$Ag^+ + e^- \longrightarrow Ag$$
$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

Solution

Item 1 Since a positive $\mathscr{E}°_{cell}$ value is required, reaction (2) must run in reverse:

$$\begin{array}{rlr} Ag^+ + e^- \longrightarrow Ag & & \mathscr{E}° \text{ (cathode)} = 0.80 \text{ V} \\ Fe^{2+} \longrightarrow Fe^{3+} + e^- & & -\mathscr{E}° \text{ (anode)} = -0.77 \text{ V} \\ \hline \text{Cell reaction:} \quad Ag^+(aq) + Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + Ag(s) & & \mathscr{E}°_{cell} = 0.03 \text{ V} \end{array}$$

Item 2 Since Ag^+ receives electrons and Fe^{2+} loses electrons in the cell reaction, the electrons will flow from the compartment containing Fe^{2+} to the compartment containing Ag^+.

Item 3 Oxidation occurs in the compartment containing Fe^{2+} (electrons flow from Fe^{2+} to Ag^+). Hence this compartment functions as the anode. Reduction occurs in the compartment containing Ag^+, so this compartment functions as the cathode.

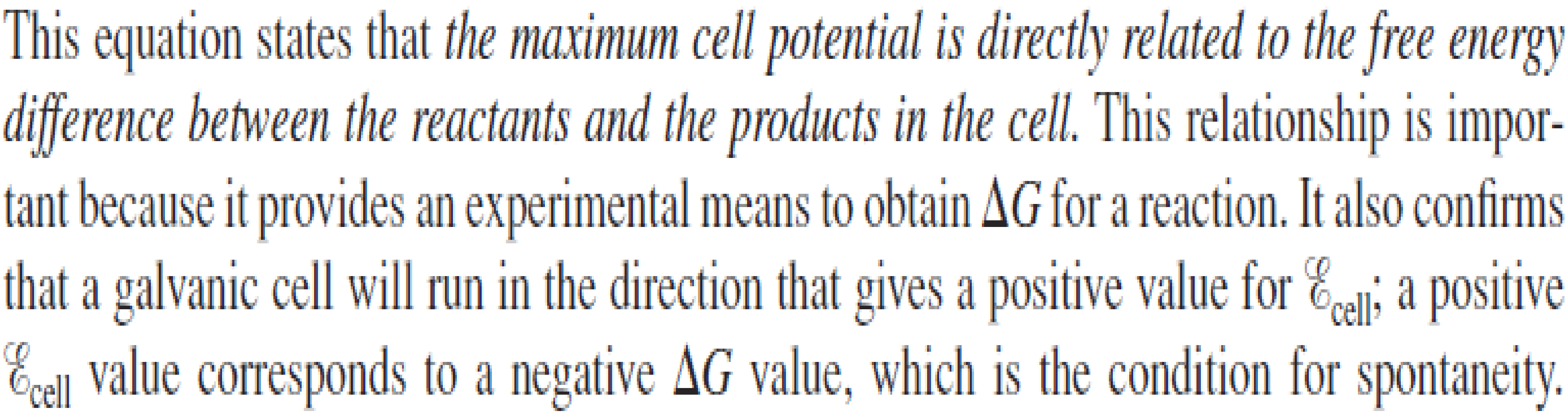
Item 4 The electrode in the Ag/Ag^+ compartment is silver metal, and an inert conductor, such as platinum, must be used in the Fe^{2+}/Fe^{3+} compartment. Appropriate counterions are assumed to be present. The diagram for this cell is shown in Fig. 17.8. The line notation for this cell is

Work

- Work is never the maximum possible if any current is flowing.
- In any real, spontaneous process some energy is always wasted – the actual work realized is always less than the calculated maximum.

Maximum Cell Potential

- Directly related to the free energy difference between the reactants and the products in the cell.
    - $\Delta G^\circ = -nF\text{E}^\circ$
        - F = 96,485 C/mol e^-



This equation states that *the maximum cell potential is directly related to the free energy difference between the reactants and the products in the cell.* This relationship is important because it provides an experimental means to obtain ΔG for a reaction. It also confirms that a galvanic cell will run in the direction that gives a positive value for $\mathcal{E}_{\text{cell}}$; a positive $\mathcal{E}_{\text{cell}}$ value corresponds to a negative ΔG value, which is the condition for spontaneity.

Example

calculate *G* for the reaction and state if the reaction is spontaneous.

$$Cu^{2+}(aq) + Fe(s) \longrightarrow Cu(s) + Fe^{2+}(aq)$$

Solution

The half-reactions are

$$\begin{array}{rcll}
Cu^{2+} + 2e^- & \longrightarrow & Cu & \mathscr{E}^\circ\ (\text{cathode}) = 0.34\ \text{V} \\
Fe & \longrightarrow & Fe^{2+} + 2e^- & -\mathscr{E}^\circ\ (\text{anode}) = 0.44\ \text{V} \\
\hline
Cu^{2+} + Fe & \longrightarrow & Fe^{2+} + Cu & \mathscr{E}^\circ_{\text{cell}} = 0.78\ \text{V}
\end{array}$$

We can calculate ΔG° from the equation

$$\Delta G^\circ = -nF\mathscr{E}^\circ$$

Since two electrons are transferred per atom in the reaction, 2 moles of electrons are required per mole of reactants and products. Thus $n = 2$ mol e$^-$, $F = 96{,}485$ C/mol e$^-$, and $\mathscr{E}^\circ = 0.78\ \text{V} = 0.78\ \text{J/C}$. Therefore,

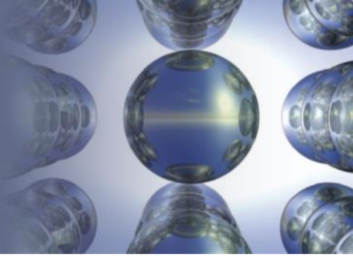
$$\begin{aligned}
\Delta G^\circ &= -(2\ \text{mol e}^-)\left(96{,}485\ \frac{\text{C}}{\text{mol e}^-}\right)\left(0.78\ \frac{\text{J}}{\text{C}}\right) \\
&= -1.5 \times 10^5\ \text{J}
\end{aligned}$$

The process is spontaneous, as indicated by both the negative sign of ΔG° and the positive sign of $\mathscr{E}^\circ_{\text{cell}}$.

This reaction is used industrially to deposit copper metal from solutions resulting from the dissolving of copper ores.

Dependence of Cell Potential on Concentration

- This can be answered qualitatively in terms of Le Châtelier's principle.
- An increase in the concentration will favor the forward reaction and thus increase the driving force on the electrons. The cell potential will increase.
- On the other hand, an increase in the concentration of a product will oppose the forward reaction, thus decreasing the cell potential.



Example

For the cell reaction

$$2\text{Al}(s) + 3\text{Mn}^{2+}(aq) \longrightarrow 2\text{Al}^{3+}(aq) + 3\text{Mn}(s) \qquad \mathscr{E}^\circ_{\text{cell}} = 0.48\ \text{V}$$

predict whether $\mathscr{E}_{\text{cell}}$ is larger or smaller than $\mathscr{E}^\circ_{\text{cell}}$ for the following cases.

a. $[\text{Al}^{3+}] = 2.0\ M$, $[\text{Mn}^{2+}] = 1.0\ M$
b. $[\text{Al}^{3+}] = 1.0\ M$, $[\text{Mn}^{2+}] = 3.0\ M$

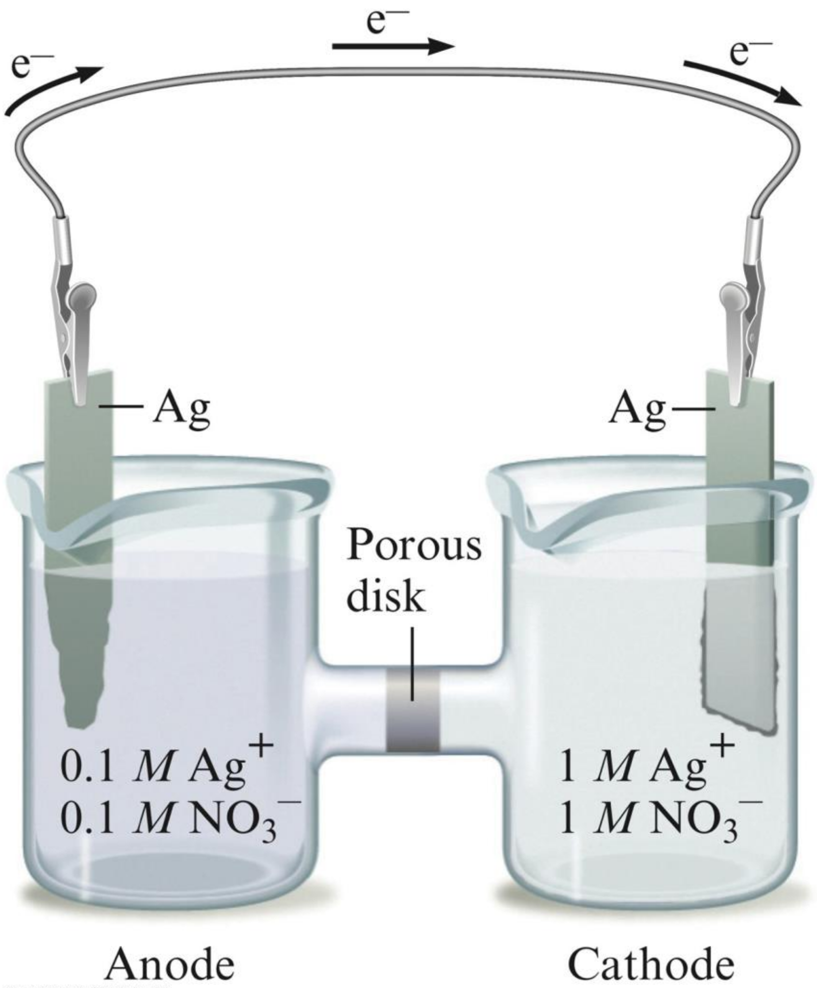
Solution

a. A product concentration has been raised above 1.0 *M*. This will oppose the cell reaction and will cause $\mathscr{E}_{\text{cell}}$ to be less than $\mathscr{E}^\circ_{\text{cell}}$ ($\mathscr{E}_{\text{cell}} < 0.48$ V).
b. A reactant concentration has been increased above 1.0 *M*, and $\mathscr{E}_{\text{cell}}$ will be greater than $\mathscr{E}^\circ_{\text{cell}}$ ($\mathscr{E}_{\text{cell}} > 0.48$ V).

A Concentration Cell

- Because cell potentials depend on concentration, we can construct galvanic cells where both compartments contain the same components but at different concentrations
- A cell in which both compartments have the same components but at different concentrations is called a **concentration cell.**
- The difference in concentration is the only factor that produces a cell potential in this case, and the voltages are typically small

A Concentration Cell



Nernst Equation

- The relationship between cell potential and concentrations of cell components

$$\mathscr{E} = \mathscr{E}^\circ - \frac{RT}{nF}\ln(Q)$$

- At 25° C: $\mathscr{E} = \mathscr{E}^\circ - \frac{0.0591}{n}\log(Q)$

Reaction Quotient, *Q*

- Used when all of the initial concentrations are nonzero.
- Apply the law of mass action using initial concentrations instead of equilibrium concentrations.

Reaction Quotient, *Q*

- $Q = K$; The system is at equilibrium. No shift will occur.

$$\mathscr{E}^\circ = \frac{0.0591}{n}\log(K)$$

- $Q > K$; The system shifts to the left.
  - Consuming products and forming reactants, until equilibrium is achieved.
- $Q < K$; The system shifts to the right.
  - Consuming reactants and forming products, to attain equilibrium.

Consider the following reaction at equilibrium:

$$jA + kB \rightleftharpoons lC + mD$$

$$K = \frac{[C]^l\,[D]^m}{[A]^j\,[B]^k}$$

- A, B, C, and D = chemical species.
- Square brackets = concentrations of species at equilibrium.
- j, k, l, and m = coefficients in the balanced equation.
- K = equilibrium constant (given without units).

EXAMPLE

Using this relationship, we can calculate the potential of a cell in which some or all of the components are not in their standard states.

For example, $\mathscr{E}^\circ_{\text{cell}}$ is 0.48 V for the galvanic cell based on the reaction

$$2\text{Al}(s) + 3\text{Mn}^{2+}(aq) \longrightarrow 2\text{Al}^{3+}(aq) + 3\text{Mn}(s)$$

Consider a cell in which

$$[\text{Mn}^{2+}] = 0.50\,M \quad \text{and} \quad [\text{Al}^{3+}] = 1.50\,M$$

The cell potential at 25°C for these concentrations can be calculated using the Nernst equation:

$$\mathscr{E}_{\text{cell}} = \mathscr{E}^\circ_{\text{cell}} - \frac{0.0591}{n}\log(Q)$$

Section 18.5
Dependence of Cell Potential on Concentration

We know that

$$\mathscr{E}^\circ_{\text{cell}} = 0.48 \text{ V}$$

and

$$Q = \frac{[\text{Al}^{3+}]^2}{[\text{Mn}^{2+}]^3} = \frac{(1.50)^2}{(0.50)^3} = 18$$

Since the half-reactions are

$$\begin{aligned} &\text{Oxidation:} \quad && 2\text{Al} \longrightarrow 2\text{Al}^{3+} + 6\text{e}^- \\ &\text{Reduction:} \quad && 3\text{Mn}^{2+} + 6\text{e}^- \longrightarrow 3\text{Mn} \end{aligned}$$

we know that

$$n = 6$$

Thus

$$\begin{aligned} \mathscr{E}_{\text{cell}} &= 0.48 - \frac{0.0591}{6}\log(18) \\ &= 0.48 - \frac{0.0591}{6}(1.26) = 0.48 - 0.01 = 0.47 \text{ V} \end{aligned}$$

Section 18.5

Dependence of Cell Potential on Concentration

- *the cell will spontaneously discharge until it reaches equilibrium,* at which point:

$$Q = K\,(\text{the equilibrium constant}) \quad \text{and} \quad \mathscr{E}_{\text{cell}} = 0$$

- A "dead" battery is one in which the cell reaction has reached equilibrium,
- there is no longer any chemical driving force to push electrons through the wire.
- for the cell reaction at the equilibrium concentrations
    - $\Delta G^{\circ} = 0$

EXAMPLE

Describe the cell based on the following half-reactions:

$$VO_2^+ + 2H^+ + e^- \longrightarrow VO^{2+} + H_2O \qquad \mathscr{E}^\circ = 1.00\text{ V} \qquad (1)$$

$$Zn^{2+} + 2e^- \longrightarrow Zn \qquad \mathscr{E}^\circ = -0.76\text{ V} \qquad (2)$$

where $T = 25°\text{C}$

$[VO_2^+] = 2.0\ M$

$[H^+] = 0.50\ M$

$[VO^{2+}] = 1.0 \times 10^{-2}\ M$

$[Zn^{2+}] = 1.0 \times 10^{-1}\ M$

SOLUTION

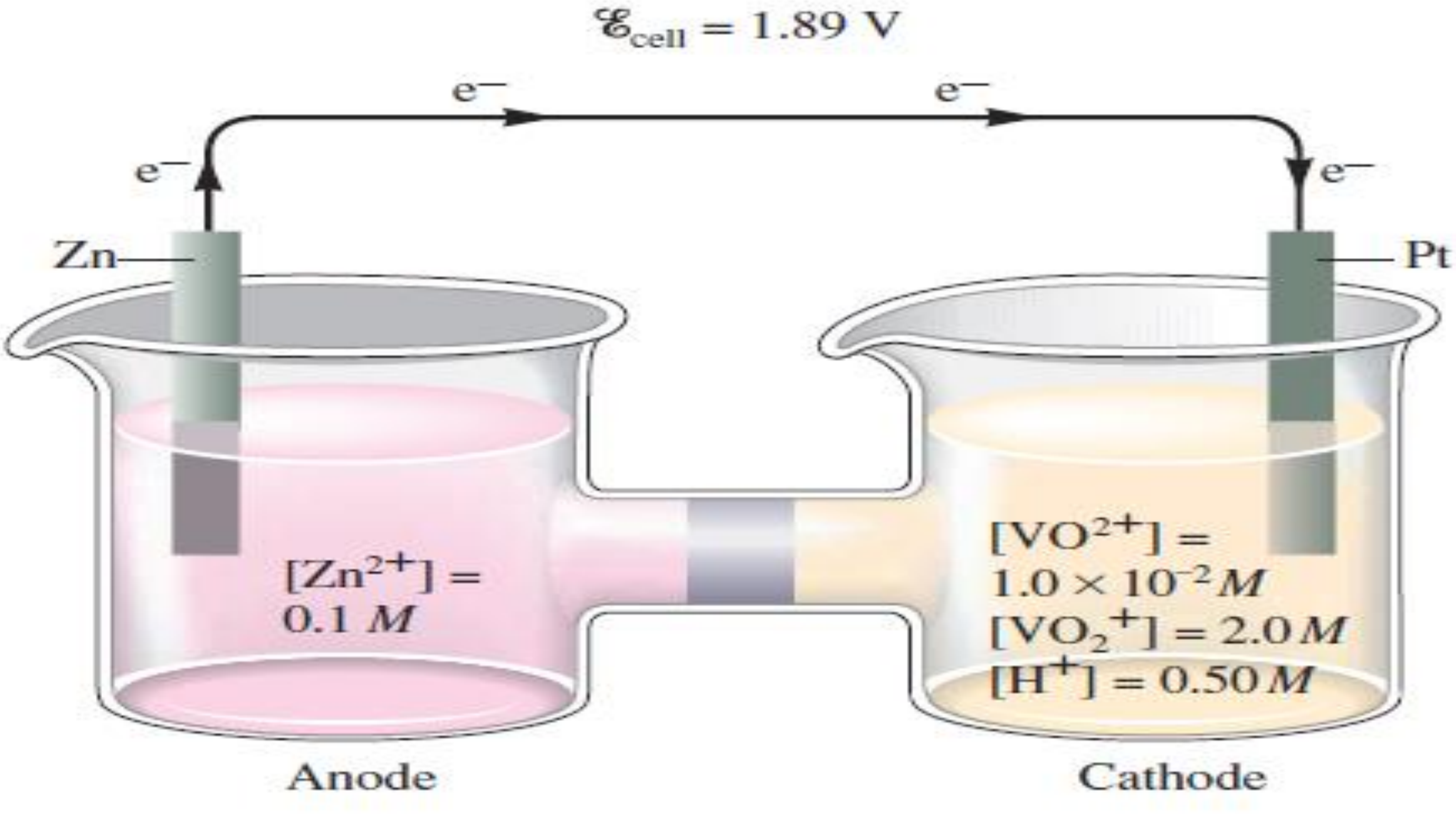
The balanced cell reaction is obtained by reversing reaction (2) and multiplying reaction (1) by 2:

2 × reaction (1)	$2VO_2^+ + 4H^+ + 2e^- \longrightarrow 2VO^{2+} + 2H_2O$	$\mathscr{E}^\circ$ (cathode) = 1.00 V
Reaction (2) reversed	$Zn \longrightarrow Zn^{2+} + 2e^-$	$-\mathscr{E}^\circ$ (anode) = 0.76 V
Cell reaction:	$2VO_2^+(aq) + 4H^+(aq) + Zn(s) \longrightarrow 2VO^{2+}(aq) + 2H_2O(l) + Zn^{2+}(aq)$	$\mathscr{E}^\circ_{\text{cell}} = 1.76\ \text{V}$

Since the cell contains components at concentrations other than 1 *M*, we must use the Nernst equation, where $n = 2$ (since two electrons are transferred), to calculate the cell potential. At 25°C we can use the equation

$$\begin{aligned}
\mathscr{E} &= \mathscr{E}^\circ_{\text{cell}} - \frac{0.0591}{n}\log(Q) \\
&= 1.76 - \frac{0.0591}{2}\log\left(\frac{[Zn^{2+}][VO^{2+}]^2}{[VO_2^+]^2[H^+]^4}\right) \\
&= 1.76 - \frac{0.0591}{2}\log\left(\frac{(1.0 \times 10^{-1})(1.0 \times 10^{-2})^2}{(2.0)^2(0.50)^4}\right) \\
&= 1.76 - \frac{0.0591}{2}\log(4 \times 10^{-5}) = 1.76 + 0.13 = 1.89\ \text{V}
\end{aligned}$$

The cell diagram is given



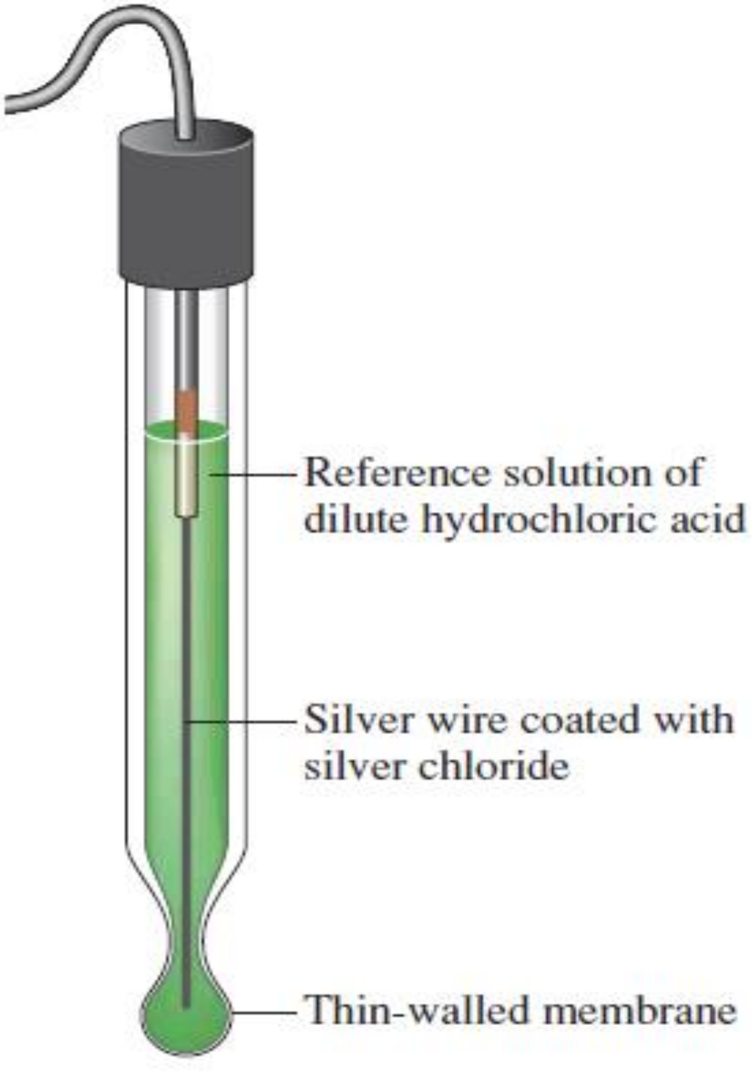
Ion-Selective Electrodes

- Electrodes that are sensitive to the concentration of a particular ion are called **ion-selective electrodes**

- cell potential is sensitive to the concentrations of the reactants and products involved in the cell reaction, measured potentials can be used to determine the concentration of an ion
- The ***pH meter*** has a special **glass electrode** that changes potential depending on the concentration of **H^+** ions

Section 18.5

Dependence of Cell Potential on Concentration



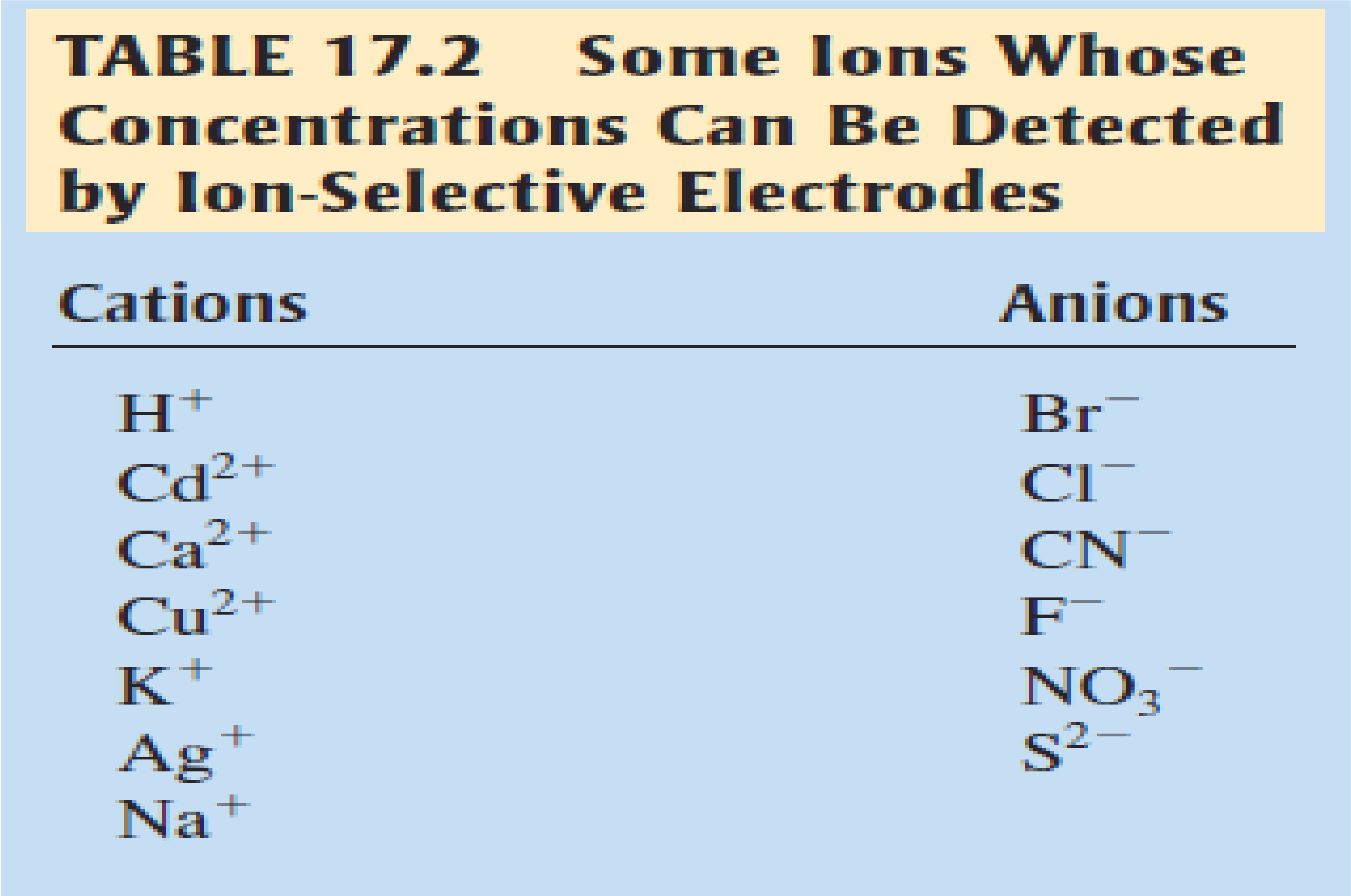


TABLE 17.2 Some Ions Whose Concentrations Can Be Detected by Ion-Selective Electrodes

Cations	Anions
H^+	Br^-
Cd^{2+}	Cl^-
Ca^{2+}	CN^-
Cu^{2+}	F^-
K^+	NO_3^-
Ag^+	S^{2-}
Na^+	

Calculation of Equilibrium Constants for Redox Reactions

- For a cell at equilibrium:

$$\mathscr{E}_{\text{cell}} = 0 \quad \text{and} \quad Q = K$$

Applying these conditions to the Nernst equation valid at 25°C,

$$\mathscr{E} = \mathscr{E}^{\circ} - \frac{0.0591}{n} \log(Q)$$

$$0 = \mathscr{E}^{\circ} - \frac{0.0591}{n} \log(K)$$

$$\log(K) = \frac{n\mathscr{E}^{\circ}}{0.0591} \qquad \text{at } 25^{\circ}\text{C}$$

Example

For the oxidation–reduction reaction

$$S_4O_6^{2-}(aq) + Cr^{2+}(aq) \longrightarrow Cr^{3+}(aq) + S_2O_3^{2-}(aq)$$

the appropriate half-reactions are

$$S_4O_6^{2-} + 2e^- \longrightarrow 2S_2O_3^{2-} \qquad \mathscr{E}^\circ = 0.17\text{ V} \qquad (1)$$

$$Cr^{3+} + e^- \longrightarrow Cr^{2+} \qquad \mathscr{E}^\circ = -0.50\text{ V} \qquad (2)$$

Balance the redox reaction, and calculate $\mathscr{E}^\circ$ and K (at 25°C).

SOLUTION

To obtain the balanced reaction, we must reverse reaction (2), multiply it by 2, and add it to reaction (1):

$$\begin{array}{llr}
 & S_4O_6^{2-} + 2e^- \longrightarrow 2S_2O_3^{2-} & \mathscr{E}^\circ\ (\text{cathode}) = 0.17\ \text{V} \\
\text{reversed} & 2(Cr^{2+} \longrightarrow Cr^{3+} + e^-) & -\mathscr{E}^\circ\ (\text{anode}) = -(-0.50)\ \text{V} \\
\hline
 & 2Cr^{2+}(aq) + S_4O_6^{2-}(aq) \longrightarrow 2Cr^{3+}(aq) + 2S_2O_3^{2-}(aq) & \mathscr{E}^\circ = 0.67\ \text{V}
\end{array}$$

In this reaction, 2 moles of electrons are transferred for every unit of reaction, that is, for every 2 mol Cr^{2+} reacting with 1 mol $S_4O_6^{2-}$ to form 2 mol Cr^{3+} and 2 mol $S_2O_3^{2-}$. Thus $n = 2$. Then

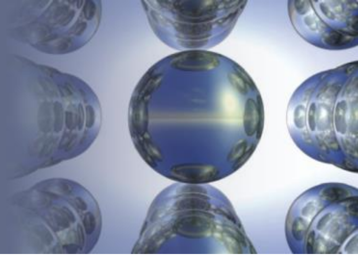
$$\log(K) = \frac{n\mathscr{E}^\circ}{0.0591} = \frac{2(0.67)}{0.0591} = 22.6$$

The value of K is found by taking the antilog of 22.6:

$$K = 10^{22.6} = 4 \times 10^{22}$$

This very large equilibrium constant is not unusual for a redox reaction.

Section 18.6
Batteries



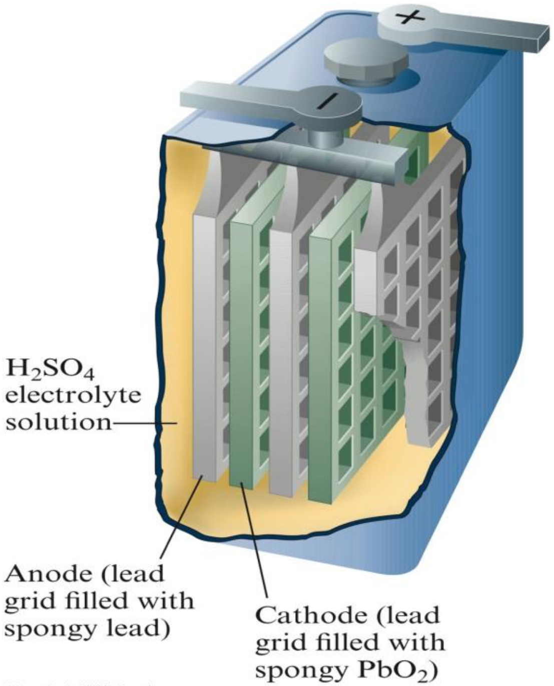
- Group of galvanic cells connected in series, where the potentials of the individual cells add to give the total battery potential.

  Batteries are a source of direct current and have become an essential source of portable power in our society.

Lead Storage Battery

One of the Six Cells in a 12–V

$$\begin{array}{lr}
\text{Anode reaction:} & \mathrm{Pb} + \mathrm{HSO_4^-} \longrightarrow \mathrm{PbSO_4} + \mathrm{H^+} + 2e^- \\
\text{Cathode reaction:} & \mathrm{PbO_2} + \mathrm{HSO_4^-} + 3\mathrm{H^+} + 2e^- \longrightarrow \mathrm{PbSO_4} + 2\mathrm{H_2O} \\
\hline
\text{Cell reaction:} & \mathrm{Pb}(s) + \mathrm{PbO_2}(s) + 2\mathrm{H^+}(aq) + 2\mathrm{HSO_4^-}(aq) \longrightarrow 2\mathrm{PbSO_4}(s) + 2\mathrm{H_2O}(l)
\end{array}$$



A Common Dry Cell Battery

Acid version

$$\text{Anode reaction:}\quad \mathrm{Zn} \longrightarrow \mathrm{Zn}^{2+} + 2e^-$$

$$\text{Cathode reaction:}\quad 2\mathrm{NH_4}^+ + 2\mathrm{MnO_2} + 2e^- \longrightarrow \mathrm{Mn_2O_3} + 2\mathrm{NH_3} + \mathrm{H_2O}$$

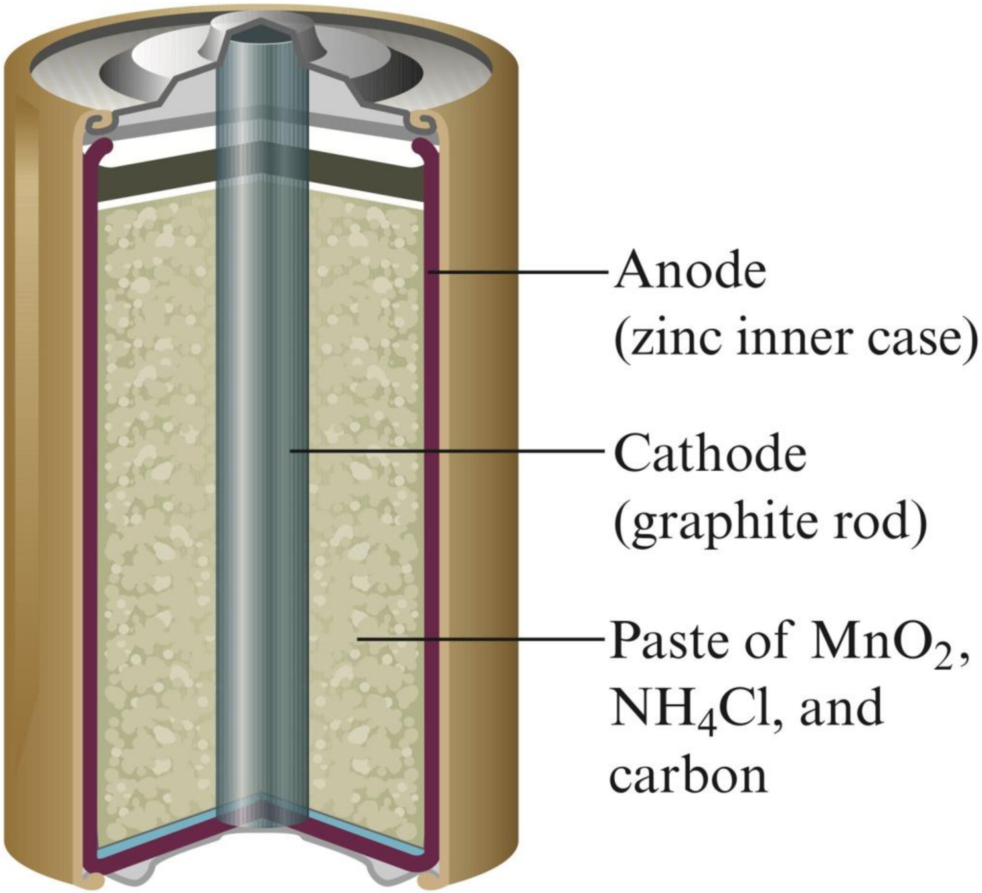
This cell produces a potential of about 1.5 V.

Alkaline Version

$$\text{Anode reaction:}\quad \mathrm{Zn} + 2\mathrm{OH}^- \longrightarrow \mathrm{ZnO} + \mathrm{H_2O} + 2e^-$$

$$\text{Cathode reaction:}\quad 2\mathrm{MnO_2} + \mathrm{H_2O} + 2e^- \longrightarrow \mathrm{Mn_2O_3} + 2\mathrm{OH}^-$$

A Common Dry Cell Battery



Other types of useful batteries

silver cell,

- Which has a Zn anode and a cathode that employs Ag2O as the oxidizing agent in a basic environment.

Mercury cells,

- Often used in calculators, have a Zn anode and a cathode involving HgO as the oxidizing agent in a basic medium

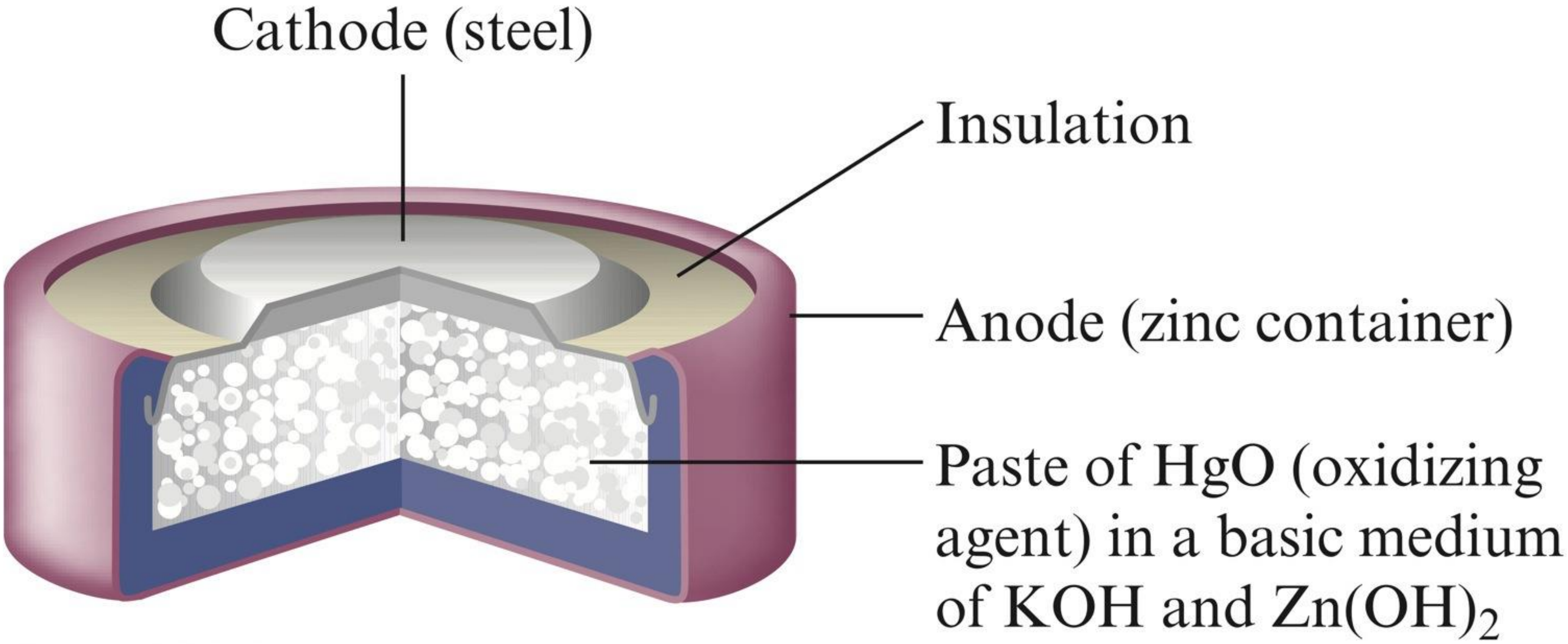
nickel–cadmium battery

- can be recharged an indefinite number of times.

Anode reaction: $Cd + 2OH^- \longrightarrow Cd(OH)_2 + 2e^-$

Cathode reaction: $NiO_2 + 2H_2O + 2e^- \longrightarrow Ni(OH)_2 + 2OH^-$

A Mercury Battery



Fuel Cells

- This is a galvanic cell for which the reactants are continuously supplied
- To illustrate the principles of fuel cells, let’s consider the exothermic redox reaction of methane with oxygen:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g) + \text{energy}$$

- fuel cell designed to use this reaction, the energy is used to produce an electric current: The electrons flow from the reducing agent (**CH_4**) to the oxidizing agent (**O_2**) through a conductor

Hydrogen-Oxygen Fuel Cell

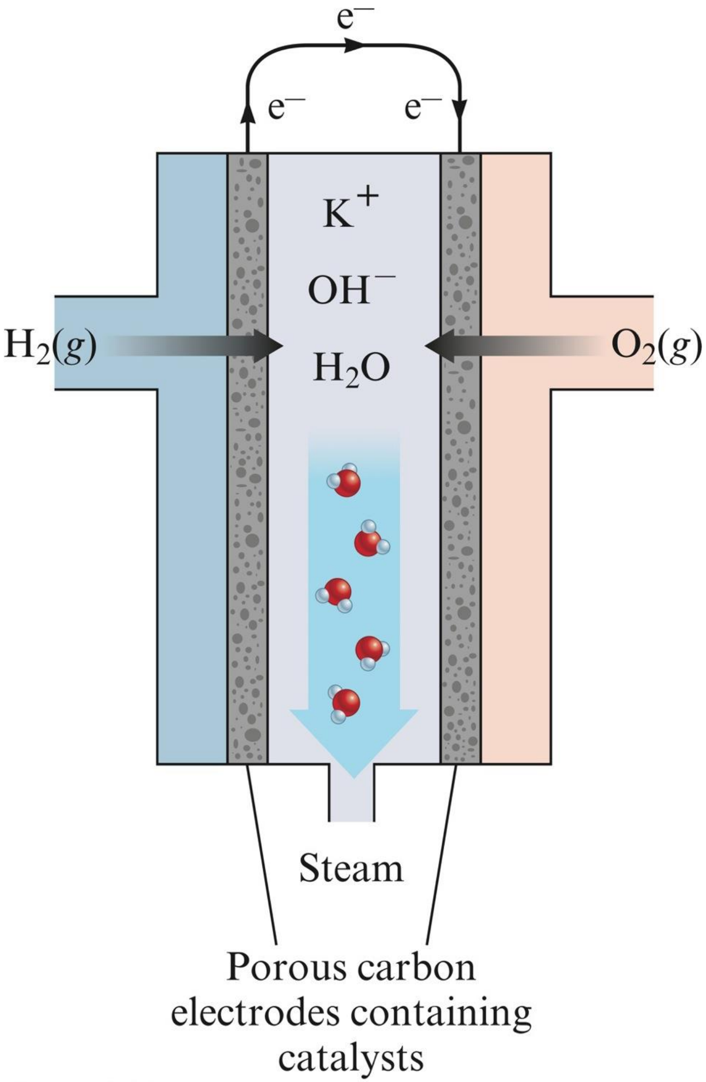
- The space shuttle uses a fuel cell based on the reaction of hydrogen and oxygen to form water:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

- Half reactions are:

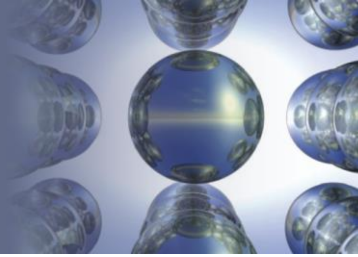
$$\begin{aligned} &\text{Anode reaction:} & 2H_2 + 4OH^- &\longrightarrow 4H_2O + 4e^- \\ &\text{Cathode reaction:} & 4e^- + O_2 + 2H_2O &\longrightarrow 4OH^- \end{aligned}$$

Schematic of the Hydrogen-Oxygen Fuel Cell



Section 18.7

Corrosion



- Process of returning metals to their natural state – the ores from which they were originally obtained.
- Involves oxidation of the metal.
- Since corroded metal often loses its structural integrity and attractiveness, this spontaneous process has great economic impact
- Metals commonly used for structural and decorative purposes all have standard reduction potentials less positive than that of oxygen gas.
- When any of these half-reactions is reversed (to show oxidation of the metal) and combined with the reduction half-reaction for oxygen, the result is a positive value.
- Thus the oxidation of most metals by oxygen is spontaneous
- Some metals, such as copper, gold, silver, and platinum, are relatively difficult to oxidize. These are often called *noble metals.*

Corrosion of Iron

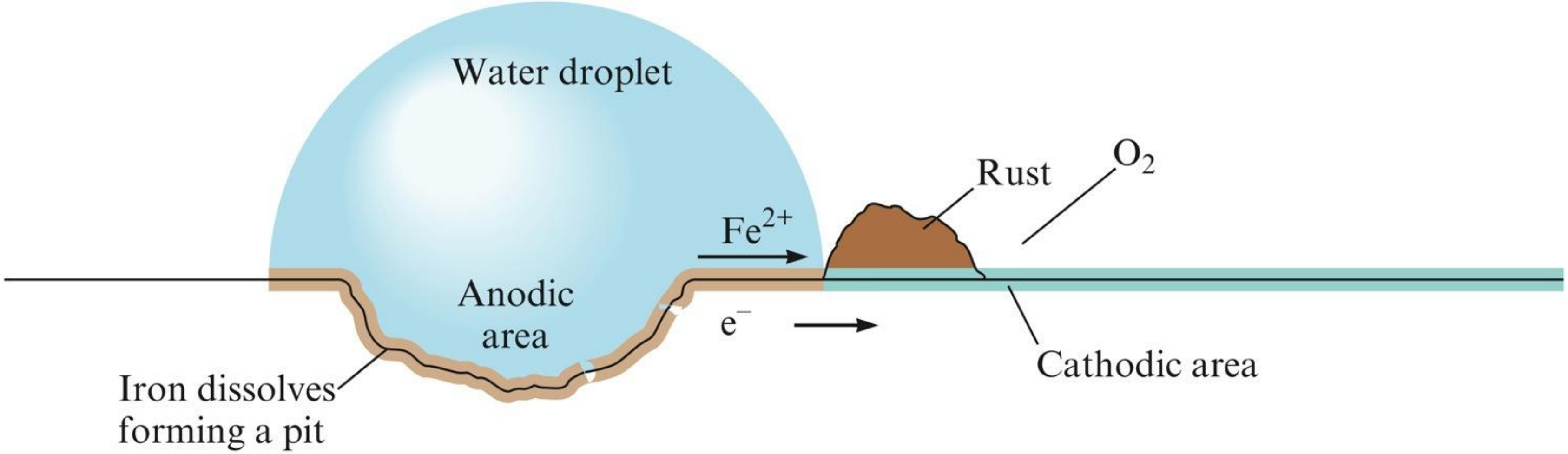
- Corrosion of iron is an electrochemical reaction
- Steel has a non-uniform surface which cause areas where the iron is more easily oxidized (*anodic regions*) than it is at others (*cathodic regions*).
- In the anodic regions $\mathrm{Fe} \longrightarrow \mathrm{Fe}^{2+} + 2e^{-}$
- The electrons that are released flow through the steel, as they do through the wire of a galvanic cell, to a cathodic region, where they react with oxygen:

$$O_2 + 2H_2O + 4e^{-} \longrightarrow 4OH^{-}$$

- The ions formed in the anodic regions travel to the cathodic regions through the moisture on the surface of the steel, Where it react with oxygen to form rust, which is hydrated iron(III) oxide of variable composition:

$$4Fe^{2+}(aq) + O_2(g) + (4 + 2n)H_2O(l) \longrightarrow \underset{\text{Rust}}{2Fe_2O_3 \cdot nH_2O(s)} + 8H^{+}(aq)$$

The Electrochemical Corrosion of Iron



(Anode reaction: $Fe \longrightarrow Fe^{2+} + 2e^-$) (Cathode reaction: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$)

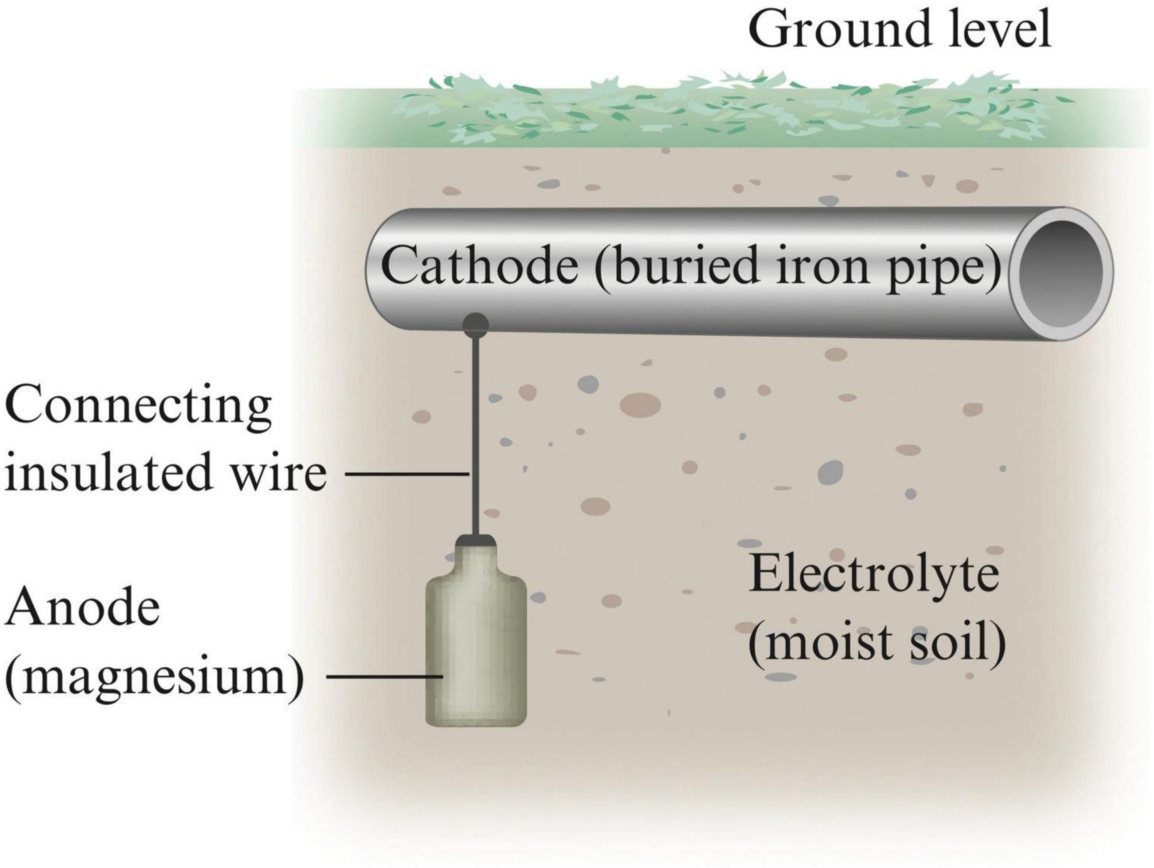
Corrosion Prevention

- Application of a coating (like paint or metal plating)
  - Galvanizing: Zinc acts as a “sacrificial” coating on steel.

$$\begin{aligned} \mathrm{Fe} &\longrightarrow \mathrm{Fe}^{2+} + 2e^- & -\mathcal{E}^\circ &= 0.44\ \mathrm{V} \\ \mathrm{Zn} &\longrightarrow \mathrm{Zn}^{2+} + 2e^- & -\mathcal{E}^\circ &= 0.76\ \mathrm{V} \end{aligned}$$

- Alloying: *Stainless steel* contains chromium and nickel, both of which form oxide coatings that change steel’s reduction potential to one characteristic of the noble metals
- **Cathodic Protection**
  - Protects steel in buried fuel tanks and pipelines.
  - An active metal, such as magnesium, is connected by a wire to the pipeline or tank to be protected

Cathodic Protection



- Forcing a current through a cell to produce a chemical change for which the cell potential is negative.
- Electrical work causes an otherwise non-spontaneous chemical reaction to occur.
- Great practical importance
    - charging a battery,
    - producing aluminum metal
    - chrome plating

Difference between a Galvanic and an Electrolytic cell

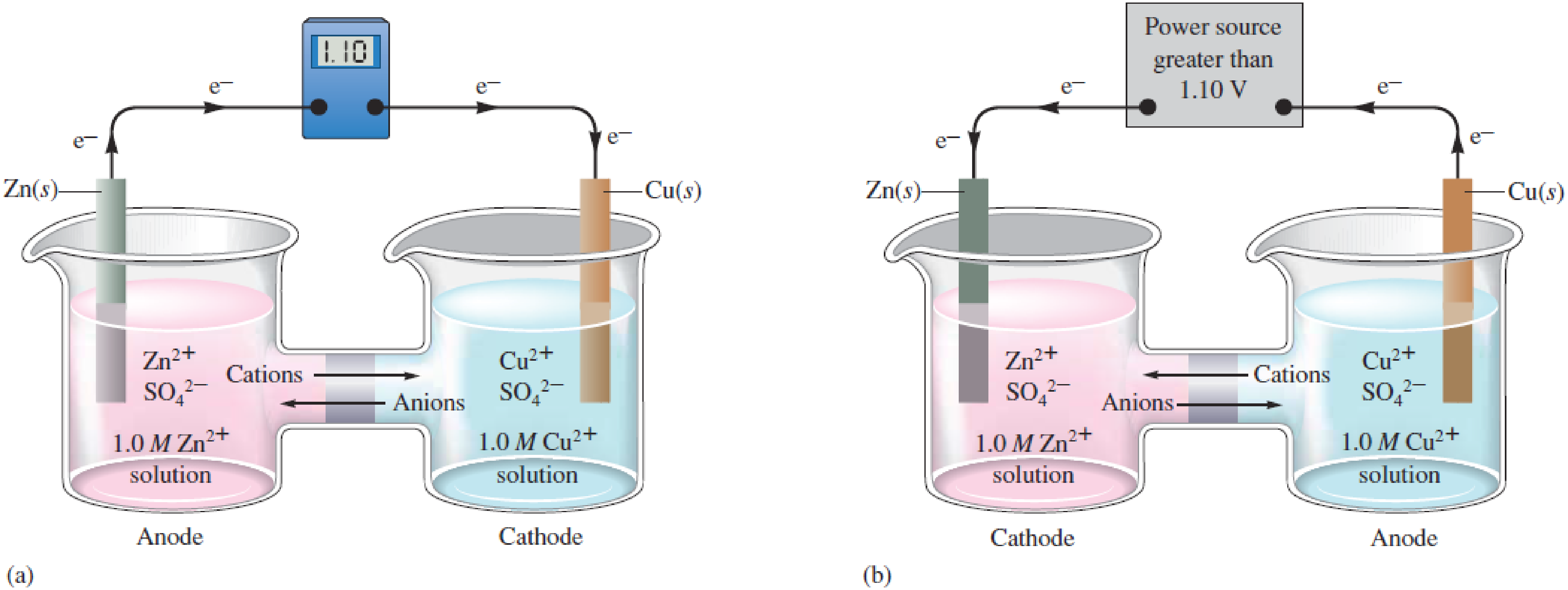


FIGURE 17.19
(a) A standard galvanic cell based on the spontaneous reaction

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

(b) A standard electrolytic cell. A power source forces the opposite reaction

$$Cu + Zn^{2+} \longrightarrow Cu^{2+} + Zn$$

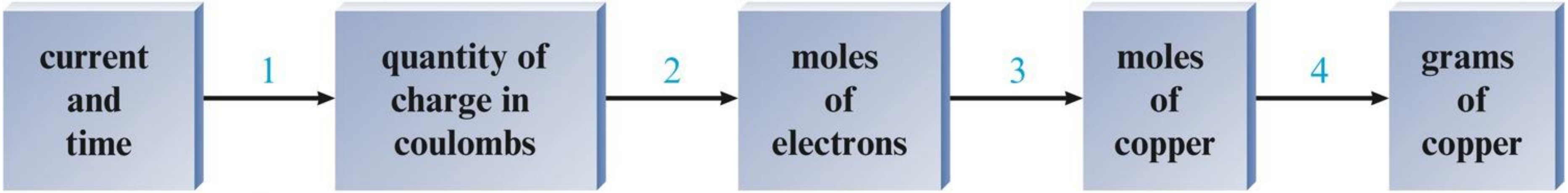
Stoichiometry of Electrolysis

- Determining how much chemical change occurs with the flow of a given current for a specified time.
- Suppose we wish to determine the mass of copper that is plated out when a current of 10.0 A is passed for 30.0 minutes through a solution containing $\mathbf{Cu^{2+}}$. (*Plating* means depositing the neutral metal on the electrode by reducing the metal ions in solution)

- **Cu^{2+}**ion requires two electrons to become an atom of copper metal:

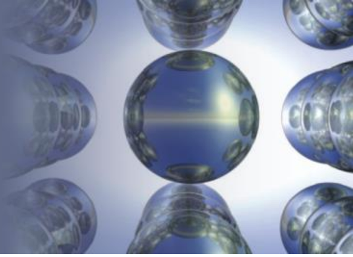
$$Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s)$$

- This reduction process will occur at the cathode of the electrolytic cell.
- To solve this stoichiometry problem, we need the following steps:


current and time $\xrightarrow{1}$ quantity of charge in coulombs $\xrightarrow{2}$ moles of electrons $\xrightarrow{3}$ moles of copper $\xrightarrow{4}$ grams of copper

Section 18.8

Electrolysis



➡ 1 Since an amp is a coulomb of charge per second, we multiply the current by the time in seconds to obtain the total coulombs of charge passed into the Cu^{2+} solution at the cathode:

$$\text{Coulombs of charge} = \text{amps} \times \text{seconds} = \frac{\text{C}}{\text{s}} \times \text{s}$$

$$= 10.0\,\frac{\text{C}}{\text{s}} \times 30.0\text{ min} \times 60.0\,\frac{\text{s}}{\text{min}}$$

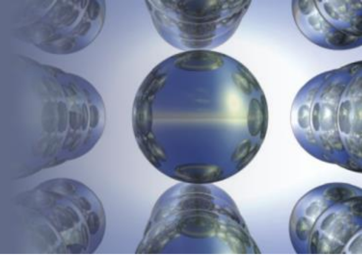
$$= 1.80 \times 10^{4}\text{ C}$$

➡ 2 Since 1 mole of electrons carries a charge of 1 faraday, or 96,485 coulombs, we can calculate the number of moles of electrons required to carry 1.80×10^{4} coulombs of charge:

$$1.80 \times 10^{4}\text{ C} \times \frac{1\text{ mol e}^{-}}{96{,}485\text{ C}} = 1.87 \times 10^{-1}\text{ mol e}^{-}$$

This means that 0.187 mole of electrons flowed into the Cu^{2+} solution.

Section 18.8
Electrolysis



➡ 3 Each Cu^{2+} ion requires two electrons to become a copper atom. Thus each mole of electrons produces $\frac{1}{2}$ mole of copper metal:

$$1.87 \times 10^{-1} \text{ mol e}^- \times \frac{1 \text{ mol Cu}}{2 \text{ mol e}^-} = 9.35 \times 10^{-2} \text{ mol Cu}$$

➡ 4 We now know the moles of copper metal plated onto the cathode, and we can calculate the mass of copper formed:

$$9.35 \times 10^{-2} \text{ mol Cu} \times \frac{63.546 \text{ g}}{\text{mol Cu}} = 5.94 \text{ g Cu}$$

Concept Check

- How long must a current of 5.00 A be applied to a solution of **Ag^{2+}** to produce 10.5 g silver metal?

- Ans: 31.3 min

Electrolysis of Water

- Hydrogen and oxygen combine spontaneously to form water and that theb accompanying decrease in free energy can be used to run a fuel cell to produce electricity.
- The reverse process, which is of course nonspontaneous, can be forced by electrolysis:

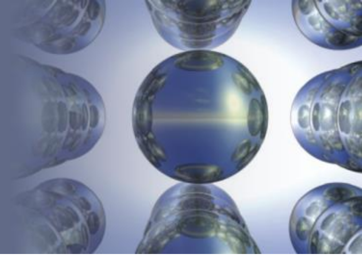
$$
\begin{array}{llcll}
\text{Anode reaction:} & 2H_2O & \longrightarrow & O_2 + 4H^+ + 4e^- & -\mathscr{E}^\circ = -1.23\ \text{V} \\
\text{Cathode reaction:} & 4H_2O + 4e^- & \longrightarrow & 2H_2 + 4OH^- & \mathscr{E}^\circ = -0.83\ \text{V} \\
\hline
\text{Net reaction:} & 6H_2O & \longrightarrow & 2H_2 + O_2 + \underbrace{4(H^+ + OH^-)}_{4H_2O} & \mathscr{E}^\circ = -2.06\ \text{V}
\end{array}
$$

or

$$2H_2O \longrightarrow 2H_2 + O_2$$

Electrolysis of Water

- if platinum electrodes connected to a 6-V battery are dipped into pure water, no reaction is observed because pure water contains so few ions that only a negligible current can flow.
- However, addition of even a small amount of a soluble salt causes an immediate evolution of bubbles of hydrogen and oxygen,



Electrolysis of Mixtures of Ions

- **Relative Oxidizing Abilities**
- The more *positive* the value, the more the reaction has a tendency to proceed in the direction indicated
- Suppose a solution in an electrolytic cell contains the ions **Ag^+ Cu^{2+}** and **Zn^{2+}** If the voltage is initially very low and is gradually turned up, in which order will the metals be plated out onto the cathode?

Section 18.8
Electrolysis

$$
\begin{aligned}
\mathrm{Ag^+ + e^- \longrightarrow Ag} &\qquad \mathscr{E}^\circ = 0.80\ \mathrm{V} \\
\mathrm{Cu^{2+} + 2e^- \longrightarrow Cu} &\qquad \mathscr{E}^\circ = 0.34\ \mathrm{V} \\
\mathrm{Zn^{2+} + 2e^- \longrightarrow Zn} &\qquad \mathscr{E}^\circ = -0.76\ \mathrm{V}
\end{aligned}
$$

Remember that the more *positive* the $\mathscr{E}^\circ$ value, the more the reaction has a tendency to proceed in the direction indicated. Of the three reactions listed, the reduction of Ag^+ occurs most easily, and the order of oxidizing ability is

$$\mathrm{Ag^+ > Cu^{2+} > Zn^{2+}}$$

This means that silver will plate out first as the potential is increased, followed by copper, and finally zinc.

Section 18.9

Commercial Electrolytic Processes

- Production of aluminum
- Purification of metals
- Metal plating
- Electrolysis of sodium chloride
- Production of chlorine and sodium hydroxide

These are summarized notes Please read more from the book for better understanding