

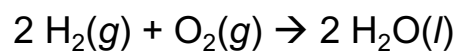
© 2017 Pearson Education, Inc.

Lecture Presentation

Chapter 19 Electrochemistry

Pulling the Plug on the Power Grid

- The power grid distributes centrally generated electricity throughout the country to homes and businesses.
- The average U.S. household currently consumes about 1000 kWh of electricity per month.
- Some companies are developing small, fuel-cell power plants, about the size of a refrigerator.
- Similar fuel cells can power cars.
- Fuel cells are based on oxidation–reduction reactions.



© 2017 Pearson Education, Inc.

Electricity from Chemistry

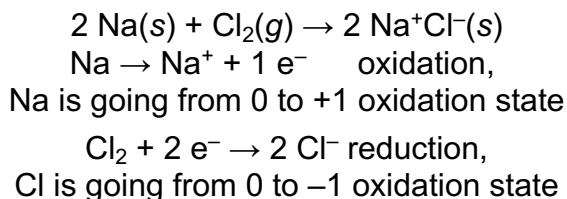
- In a hydrogen–oxygen fuel cell, the hydrogen and oxygen are separated, forcing electrons to travel through an external wire.
- The moving electrons constitute an electrical current.
- A fuel cell employs the electron-gaining tendency of oxygen and the electron-losing tendency of hydrogen to force electrons to move through a wire, creating electricity.



© 2017 Pearson Education, Inc.

Oxidation–Reduction

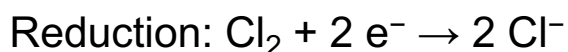
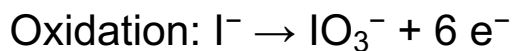
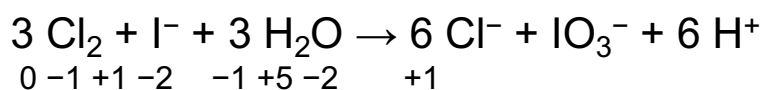
- Reactions where electrons are transferred from one atom to another are called oxidation–reduction reactions.
 - Redox reactions for short
- Atoms that lose electrons are being oxidized; atoms that gain electrons are being reduced.
- Increase in oxidation state is oxidation; decrease in oxidation state is reduction.



© 2017 Pearson Education, Inc.

Half-Reactions

- We generally split the redox reaction into two separate **half-reactions**—reactions involving just oxidation or reduction, as on the previous slide.
 - The oxidation half-reaction has electrons as products.
 - The reduction half-reaction has electrons as reactants.



© 2017 Pearson Education, Inc.

Balancing Redox Reactions by the Half-Reaction Method

- This method is a helpful way to balance complex redox reactions in solution.
- The reaction is broken down into two half-reactions, one for oxidation and another for reduction.
- Each half-reaction is balanced individually, for both mass and charge.
- The two half-reactions are added back together to get the overall balanced equation.

© 2017 Pearson Education, Inc.

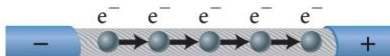
Balancing Redox Reactions

1. Assign oxidation states.
 - a) Determine the element oxidized and the element reduced.
2. Write oxidation and reduction half-reactions.
3. Balance the mass of half-reactions.
 - a) First balance elements other than H and O.
 - b) Balance O by adding H_2O where O is needed.
 - c) Balance H by adding H^+ where H is needed.
 - d) If the reaction is in a basic solution, neutralize H^+ with OH^- .
4. Balance charge of half-reactions by adding electrons.
5. Make the number of electrons in both half-reactions the same by multiplying one or both by a small whole number.
6. Add half-reactions, and cancel like terms.
7. Check by counting atoms and total charge.

© 2017 Pearson Education, Inc.

Electrical Current

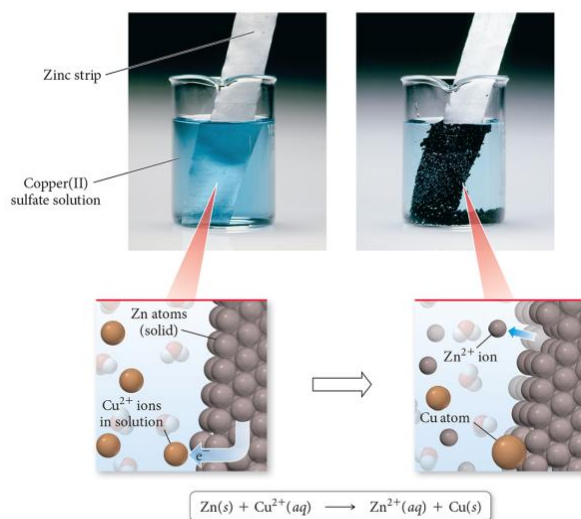
- Electrons flow through a conductor in response to an electrical potential difference similar to water flowing downhill in response to a difference in gravitational potential energy.
- Electric current—the amount of electric charge that passes a point in a given period of time
 - Whether as electrons flowing through a wire, or ions flowing through a solution



© 2017 Pearson Education, Inc.

Electric Current Flowing Directly between Atoms

A Spontaneous Redox Reaction: $\text{Zn} + \text{Cu}^{2+}$



© 2017 Pearson Education, Inc.

Electrical Current

- **Current** is the number of electrons that flow through the system per second.
 - Unit = ampere (or amp, A)
- 1 A of current = 1 coulomb of charge flowing each second
 - $1 \text{ A} = 6.242 \times 10^{18}$ electrons per second

© 2017 Pearson Education, Inc.

Potential Difference

- The difference in potential energy between the reactants and products is the **potential difference**.
 - Unit = volt
- $1\text{ V} = 1\text{ J}$ of energy per coulomb of charge
 - The voltage needed to drive electrons through the external circuit
- The amount of force pushing the electrons through the wire is called the **electromotive force, emf**.

© 2017 Pearson Education, Inc.

Cell Potential

- The difference in potential energy between the anode and the cathode in a voltaic cell is called the **cell potential**.
- The cell potential depends on the relative ease with which the oxidizing agent is reduced at the cathode and the reducing agent is oxidized at the anode.
- The cell potential under standard conditions is called the **standard emf, E°_{cell}** .
 - $25\text{ }^\circ\text{C}$, 1 atm for gases, 1 M concentration of solution
 - Sum of the cell potentials for the half-reactions

© 2017 Pearson Education, Inc.

Electrochemical Cells

- Oxidation and reduction half-reactions are kept separate in **half-cells**.
- Electron flow through a wire along with ion flow through a solution constitutes an electric circuit.
- It requires a conductive solid **electrode** to allow the transfer of electrons.
 - Through external circuit
 - Metal or graphite
- Requires ion exchange between the two half-cells of the system.
 - Electrolyte

© 2017 Pearson Education, Inc.

Electrodes and Salt Bridge

- **Anode**
 - Electrode where oxidation always occurs
 - More negatively charged electrode in voltaic cell
- **Cathode**
 - Electrode where reduction always occurs
 - More positively charged electrode in voltaic cell
- **Salt bridge** is an inverted, U-shaped tube containing a strong electrolyte and connecting the two half-cells.

© 2017 Pearson Education, Inc.

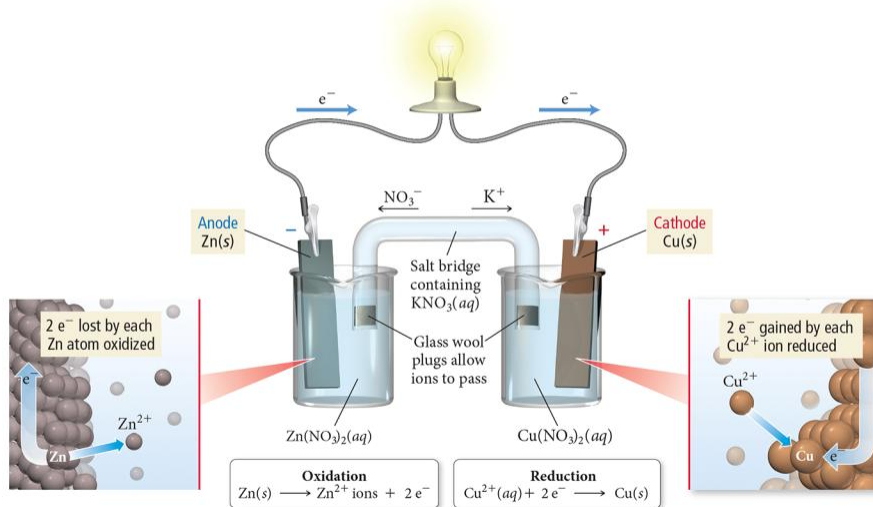
Electrodes

- Typically
 - The anode is made of the metal that is oxidized.
 - The cathode is made of the same metal as is produced by the reduction.
- If the redox reaction involves the oxidation or reduction of an ion to a different oxidation state, or the oxidation or reduction of a gas, we may use an inert electrode.
 - An **inert electrode** is one that not does participate in the reaction but just provides a surface on which the transfer of electrons can take place.

© 2017 Pearson Education, Inc.

Voltaic Cell

A Voltaic Cell



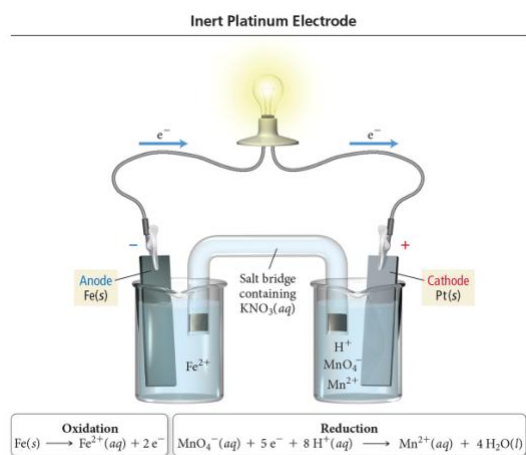
© 2017 Pearson Education, Inc.

Cell Notation

- Shorthand representation of an electrochemical cell
- Oxidation half-cell on the left, reduction half-cell on the right, separated by two vertical lines
- Substances in different phases are separated by a single vertical line, which represents the boundary between the phases.
- Single | = phase barrier
 - If multiple species are in same phase, a comma is used rather than |.
 - Often use an **inert electrode**
- Double line || = salt bridge
- Electrode | electrolyte || electrolyte | electrode

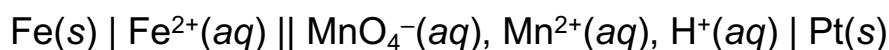
© 2017 Pearson Education, Inc.

Electrochemical Cell Notation



Because the half-reaction involves reducing the Mn oxidation state from +7 to +2, we use an electrode that will provide a surface for the electron transfer without reacting with the MnO_4^- .

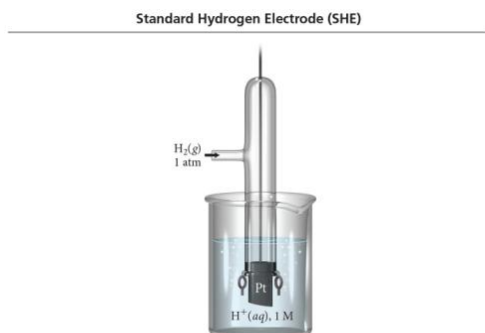
Platinum works well because it is extremely nonreactive and conducts electricity.



© 2017 Pearson Education, Inc.

Standard Reduction Potential

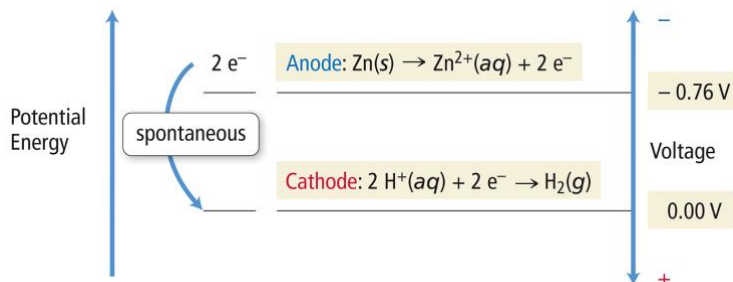
- We cannot measure the absolute tendency of a half-reaction; we can measure it only relative to another half-reaction.
- We select as a standard half-reaction the reduction of H^+ to H_2 under standard conditions, which we assign a potential difference = 0 v.
 - Standard hydrogen electrode, SHE**



© 2017 Pearson Education, Inc.

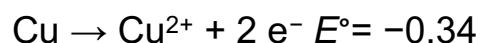
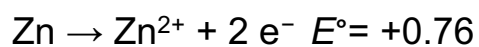
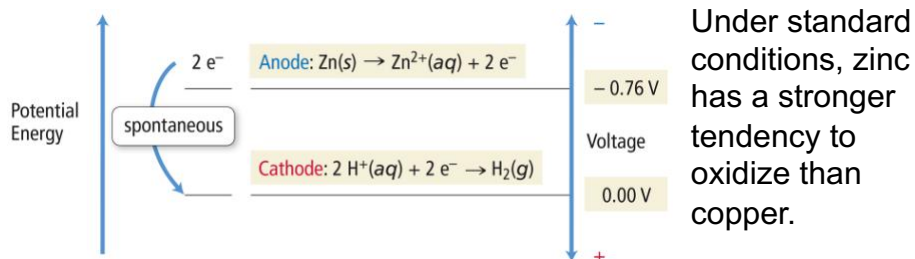
Cell Potential

- A half-reaction with a strong tendency to occur has a large positive half-cell potential.
- When two half-cells are connected, the electrons will flow so that the half-reaction with the stronger tendency will occur.



© 2017 Pearson Education, Inc.

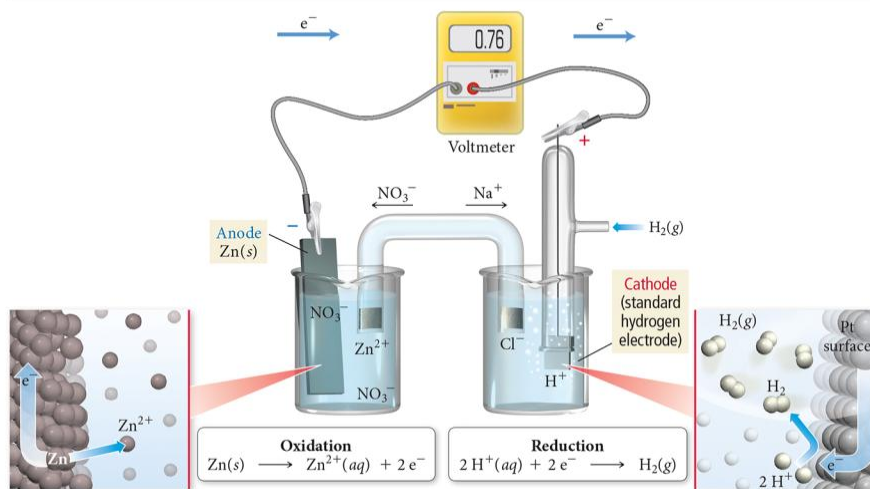
Which Way Will Electrons Flow?



© 2017 Pearson Education, Inc.

Measuring Electrode Potential

Measuring Half-Cell Potential with the SHE



© 2017 Pearson Education, Inc.

Half-Cell Potentials

- SHE reduction potential is defined to be exactly 0 V.
- Standard reduction potentials compare the tendency for a particular reduction half-reaction to occur relative to the reduction of H^+ to H_2 .
 - Under standard conditions
- Half-reactions with a stronger tendency toward reduction than the SHE have a positive value for E°_{red} .
- Half-reactions with a stronger tendency toward oxidation than the SHE have a negative value for E°_{red} .
- For an oxidation half-reaction, $E^\circ_{\text{oxidation}} = -E^\circ_{\text{reduction}}$.
- $E^\circ_{\text{cell}} = -E^\circ_{\text{reduction}} - E^\circ_{\text{oxidation}}$

© 2017 Pearson Education, Inc.

TABLE 19.1. Standard Electrode Potentials at 25 °C

Reduction Half-Reaction	$E^\circ(\text{V})$
$\text{F}_2(\text{g}) + 2 \text{e}^- \rightarrow 2 \text{F}^-(\text{aq})$	2.87
$\text{H}_2\text{O}_2(\text{aq}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow 2 \text{H}_2\text{O}(\text{l})$	1.78
$\text{PtO}_2(\text{s}) + 4 \text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 2 \text{e}^- \rightarrow \text{PtSO}_4(\text{s}) + 2 \text{H}_2\text{O}(\text{l})$	1.68
$\text{MnO}_2(\text{s}) + 4 \text{H}^+(\text{aq}) + 3 \text{e}^- \rightarrow \text{MnO}(\text{s}) + 2 \text{H}_2\text{O}(\text{l})$	1.68
$\text{MnO}_2(\text{s}) + 8 \text{H}^+(\text{aq}) + 5 \text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l})$	1.51
$\text{Au}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Au}(\text{s})$	1.50
$\text{PtO}_2(\text{s}) + 4 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{Pt}^{2+}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$	1.46
$\text{Cl}_2(\text{g}) + 2 \text{e}^- \rightarrow 2 \text{Cl}^-(\text{aq})$	1.36
$\text{O}_2/\text{H}^+(\text{aq}) + 14 \text{H}^+(\text{aq}) + 6 \text{e}^- \rightarrow 2 \text{O}^{2-}(\text{aq}) + 7 \text{H}_2\text{O}(\text{l})$	1.33
$\text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O}(\text{l})$	1.23
$\text{MnO}_2(\text{s}) + 4 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$	1.23
$\text{IO}_3^-(\text{aq}) + 6 \text{H}^+(\text{aq}) + 5 \text{e}^- \rightarrow \frac{1}{2} \text{I}_2(\text{aq}) + 3 \text{H}_2\text{O}(\text{l})$	1.20
$\text{Br}_2(\text{l}) + 2 \text{e}^- \rightarrow 2 \text{Br}^-(\text{aq})$	1.09
$\text{VO}_2^+(\text{aq}) + 2 \text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{VO}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	1.00
$\text{NO}_2^-(\text{aq}) + 4 \text{H}^+(\text{aq}) + 3 \text{e}^- \rightarrow \text{NO}(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$	0.96
$\text{ClO}_2(\text{g}) + \text{e}^- \rightarrow \text{ClO}_2^-(\text{aq})$	0.95
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	0.80
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	0.77
$\text{O}_2(\text{g}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2\text{O}_2(\text{aq})$	0.70
$\text{MnO}_4^-(\text{aq}) + \text{e}^- \rightarrow \text{MnO}_4^{2-}(\text{aq})$	0.56
$\text{I}_2(\text{s}) + 2 \text{e}^- \rightarrow 2 \text{I}^-(\text{aq})$	0.54
$\text{Cu}^+(\text{aq}) + \text{e}^- \rightarrow \text{Cu}(\text{s})$	0.52
$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^- \rightarrow 4 \text{OH}^-(\text{aq})$	0.40
$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cu}(\text{s})$	0.34
$\text{SO}_4^{2-}(\text{aq}) + 4 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2\text{SO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l})$	0.20
$\text{Cu}^+(\text{aq}) + \text{e}^- \rightarrow \text{Cu}(\text{s})$	0.16
$\text{Sn}^{4+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Sn}^{2+}(\text{aq})$	0.15
$2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g})$	0
$\text{Fe}^{2+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.036
$\text{Pb}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Pb}(\text{s})$	-0.13
$\text{Sn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Sn}(\text{s})$	-0.14
$\text{Ni}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.23
$\text{Co}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Co}(\text{s})$	-0.40
$\text{Fe}^{3+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.45
$\text{Cr}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Cr}^{2+}(\text{aq})$	-0.50
$\text{Cr}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Cr}(\text{s})$	-0.73
$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
$2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$	-0.83
$\text{Mn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Mn}(\text{s})$	-1.18
$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Al}(\text{s})$	-1.66
$\text{Mg}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Mg}(\text{s})$	-2.37
$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$	-2.71
$\text{Ca}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Ca}(\text{s})$	-2.76
$\text{Ba}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Ba}(\text{s})$	-2.90
$\text{K}^+(\text{aq}) + \text{e}^- \rightarrow \text{K}(\text{s})$	-2.92
$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.04

© 2017 Pearson Education, Inc.

Calculating Cell Potentials under Standard Conditions

- $E^\circ_{\text{cell}} = E^\circ_{\text{reduction}} - E^\circ_{\text{oxidation}}$
- When adding E° values for the half-cells, if you need to multiply the half-reactions to balance the equation, *do not multiply* the half-cell E° values.

© 2017 Pearson Education, Inc.

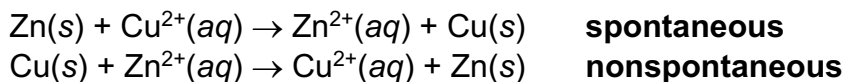
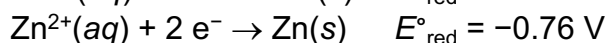
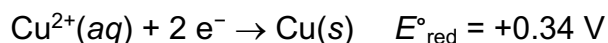
Tendencies from the Table of Standard Reduction Potentials

- Higher on the table of standard reduction potentials, the stronger tendency for the reactant to be reduced
- Lower on the table of standard reduction potentials, the stronger tendency for the product to be oxidized

© 2017 Pearson Education, Inc.

Predicting Spontaneity of Redox Reactions

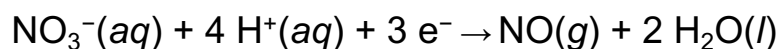
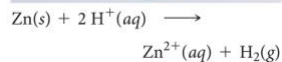
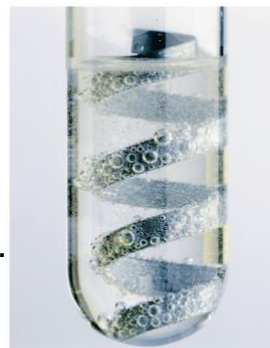
- Substances listed at the top of Table 19.1 tend to undergo reduction; they are good oxidizing agents.
- Substances listed near the bottom of Table 19.1 tend to undergo oxidation; they are good reducing agents.
- Any reduction reaction in Table 19.1 is spontaneous when paired with the reverse of any of the reactions listed below it on the table.



© 2017 Pearson Education, Inc.

Predicting Whether a Metal Will Dissolve in Acid

- Metals whose reduction half-reactions are listed below the reduction of H^{+} to H_2 in Table 19.1 dissolve in acids.
- Metals listed above H^{+} to H_2 in Table 19.1 do not dissolve in acids.
- Almost all metals will dissolve in HNO_3 .
 - Having N reduced rather than H
 - Au and Pt dissolve in $\text{HNO}_3 + \text{HCl}$

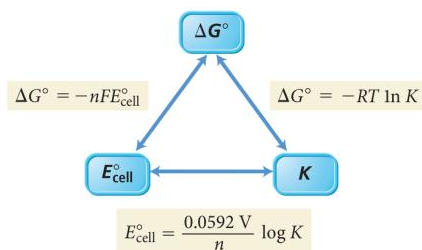


© 2017 Pearson Education, Inc.

E°_{cell} , ΔG° , and K

- For a spontaneous reaction, one that proceeds in the forward direction with the chemicals in their standard states

- $\Delta G^\circ < 0$ (negative)
- $E^\circ > 0$ (positive)
- $K > 1$



- $\Delta G^\circ = -nFE^\circ_{\text{cell}}$
 - n = the number of electrons
 - F = Faraday's constant = 96,485 C/mol e^-

© 2017 Pearson Education, Inc.

Relationship between E°_{cell} and K

- $\Delta G^\circ = -RT \ln K$
- $-nFE^\circ_{\text{cell}} = -RT \ln K$
- $E^\circ_{\text{cell}} = \frac{RT}{nF} \ln K$
- Substituting values for R , F , and 298.15K for T , and converting to log instead of ln, we get

- $E^\circ_{\text{cell}} = \frac{0.0592 \text{ V}}{n} \log K$

© 2017 Pearson Education, Inc.

Cell Potential under Nonstandard Conditions

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

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

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln Q$$

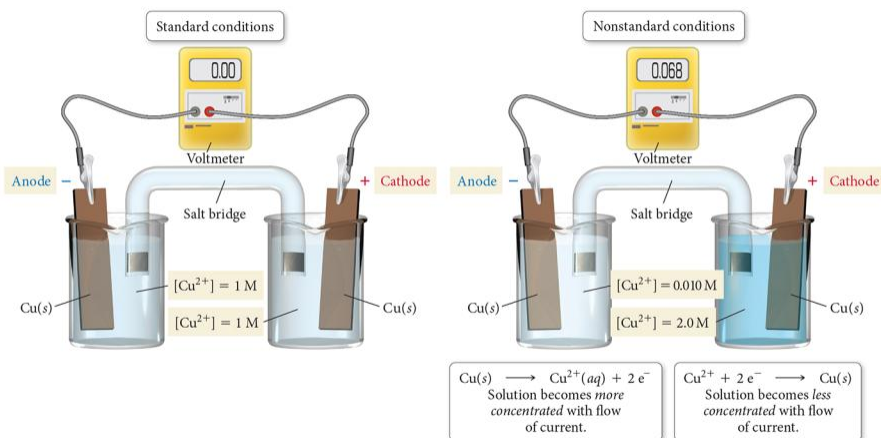
$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592 \text{ V}}{n} \log Q$$

This equation, known as the **Nernst equation**, helps us determine the cell potential at nonstandard conditions.

© 2017 Pearson Education, Inc.

Concentration Cells

A Concentration Cell



© 2017 Pearson Education, Inc.

Concentration Cells

- It is possible to get a spontaneous reaction when the oxidation and reduction reactions are the same, as long as the electrolyte concentrations are different.
- Calculating cell potential using the Nernst equation helps us determine the direction of spontaneity in the cell.
- Electrons will flow from the electrode in the less concentrated solution to the electrode in the more concentrated solution.
 - Oxidation of the electrode in the less concentrated solution will increase the ion concentration in the solution; the less concentrated solution has the anode.
 - Reduction of the solution ions at the electrode in the more concentrated solution reduces the ion concentration; the more concentrated solution has the cathode.

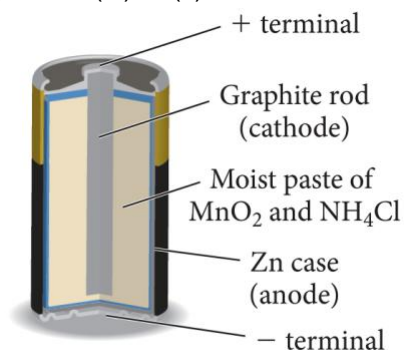
© 2017 Pearson Education, Inc.

Dry-Cell Batteries

- Anode = Zn (or Mg)

$$\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2 \text{e}^{-}$$
- Cathode = graphite rod
- MnO_2 is reduced.

$$2 \text{MnO}_2(\text{s}) + 2 \text{NH}_4^{+}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^{-} \rightarrow 2 \text{NH}_4\text{OH}(\text{aq}) + 2 \text{Mn}(\text{O})\text{OH}(\text{s})$$
- Cell voltage = 1.5 V



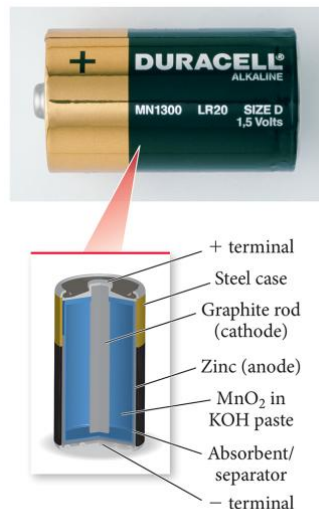
© 2017 Pearson Education, Inc.

Alkaline Dry-Cell Batteries

- Same basic cell as acidic dry cell, except electrolyte is alkaline KOH paste
- Anode = Zn (or Mg)

$$\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2 \text{e}^{-}$$
- Cathode = graphite or brass rod
- MnO_2 is reduced.

$$2 \text{MnO}_2(\text{s}) + 2 \text{NH}_4^{+}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^{-} \rightarrow 2 \text{NH}_4\text{OH}(\text{aq}) + 2 \text{Mn}(\text{O})\text{OH}(\text{s})$$
- Cell voltage = 1.54 V
- Longer shelf life than acidic dry cells, longer working time, and little corrosion of zinc

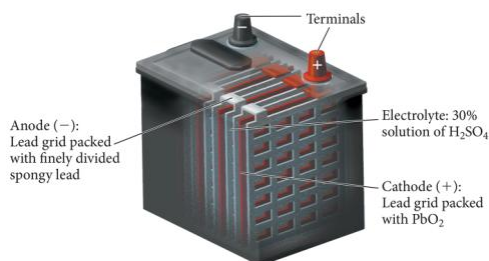


© 2017 Pearson Education, Inc.

Lead Storage Battery

- Six electrochemical cells in series, each producing 2 V for a total of 12 V
- Electrolyte = 30% H_2SO_4
- Anode: $\text{Pb(s)} + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + 2 \text{e}^{-}$
- Cathode: Pb coated with PbO_2
- PbO_2 is reduced.

$$\text{PbO}_2(\text{s}) + 4 \text{H}^{+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 2 \text{e}^{-} \rightarrow \text{PbSO}_4(\text{s}) + 2 \text{H}_2\text{O}(\text{l})$$



© 2017 Pearson Education, Inc.

NiCad Battery

- Electrolyte is concentrated KOH solution.
- Anode: Cd(s); cathode: NiO(OH)(s)
- Cd is oxidized; NiO₂ is reduced.
 - $\text{Cd(s)} + 2 \text{OH}^{\text{-}}(\text{aq}) \rightarrow \text{Cd(OH)}_2(\text{s}) + 2 \text{e}^{\text{-}} \quad E^{\circ} = 0.81 \text{ V}$
 - $\text{NiO}_2(\text{s}) + 2 \text{H}_2\text{O(l)} + 2 \text{e}^{\text{-}} \rightarrow \text{Ni(OH)}_2(\text{s}) + 2\text{OH}^{\text{-}} \quad E^{\circ} = 0.49 \text{ V}$
- Cell voltage = 1.30 V
- Rechargeable, long life, light; however, recharging incorrectly can lead to battery breakdown

© 2017 Pearson Education, Inc.

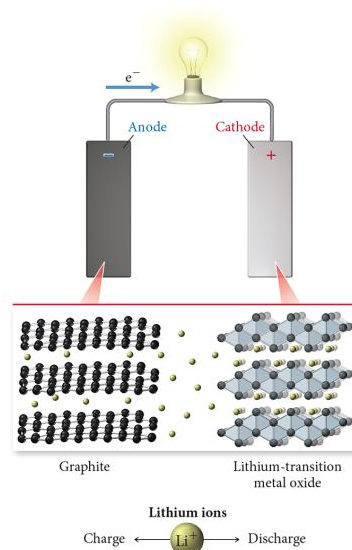
Ni-MH Battery

- Electrolyte is concentrated KOH solution.
- Anode: metal alloy with dissolved hydrogen
- Cathode: Ni coated with NiO₂
- Oxidation of H from H⁰ to H⁺; NiO₂ is reduced.
 - $\text{M} \cdot \text{H(s)} + \text{OH}^{\text{-}}(\text{aq}) \rightarrow \text{M(s)} + \text{H}_2\text{O(l)} + \text{e}^{\text{-}} \quad E^{\circ} = 0.89 \text{ V}$
 - $\text{NiO}_2(\text{s}) + 2 \text{H}_2\text{O(l)} + 2 \text{e}^{\text{-}} \rightarrow \text{Ni(OH)}_2(\text{s}) + 2\text{OH}^{\text{-}} \quad E^{\circ} = 0.49 \text{ V}$
- Cell voltage = 1.30 V
- Rechargeable, long life, light, more environmentally friendly than NiCad, greater energy density than NiCad

© 2017 Pearson Education, Inc.

Lithium-Ion Battery

- Electrolyte is concentrated KOH solution.
- Anode: graphite impregnated with Li ions
- Cathode: Li—transition metal oxide
 - Reduction of transition metal
- Works on Li ion migration from anode to cathode causing a corresponding migration of electrons from anode to cathode
- Rechargeable, long life, very light, more environmentally friendly, greater energy density



© 2017 Pearson Education, Inc.

TABLE 19.2 Energy Density and Overcharge Tolerance of Several Rechargeable Batteries

Battery Type	Energy Density (W · h/kg)	Overcharge Tolerance
NiCad	45–80	Moderate
NiMH	60–120	Low
Li ion	110–160	Low
Pb storage	30–50	High

© 2017 Pearson Education, Inc.

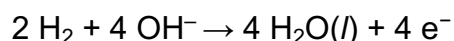
Fuel Cells

- Like batteries in which reactants are constantly being added
 - So it never runs down!

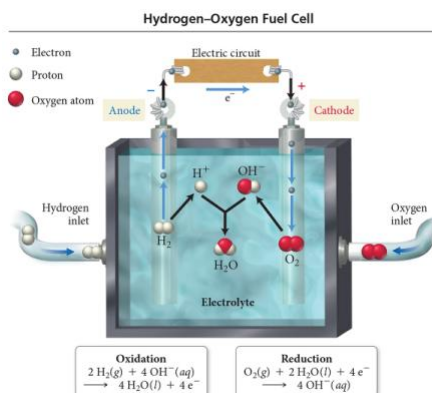
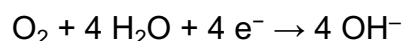
- Anode and cathode both Pt -coated metal

- Electrolyte is OH^- solution.

- Anode reaction



- Cathode reaction



© 2017 Pearson Education, Inc.

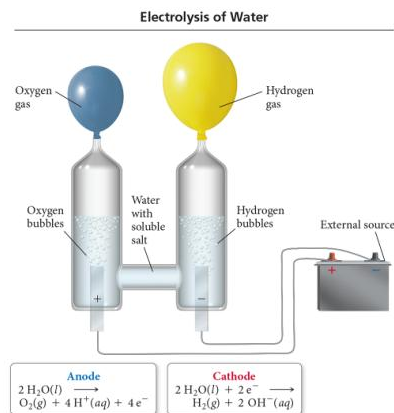
Driving Nonspontaneous Reactions

- In all cells, whether voltaic or electrolytic, oxidation occurs at the anode, and reduction occurs at the cathode.
- Voltaic cells—Spontaneous reaction generates electricity.
 - Anode is the source of electrons and has a (–) charge.
 - Cathode draws electrons and has a (+) charge.
- Electrolytic cells—nonspontaneous reaction driven by external electrical current

© 2017 Pearson Education, Inc.

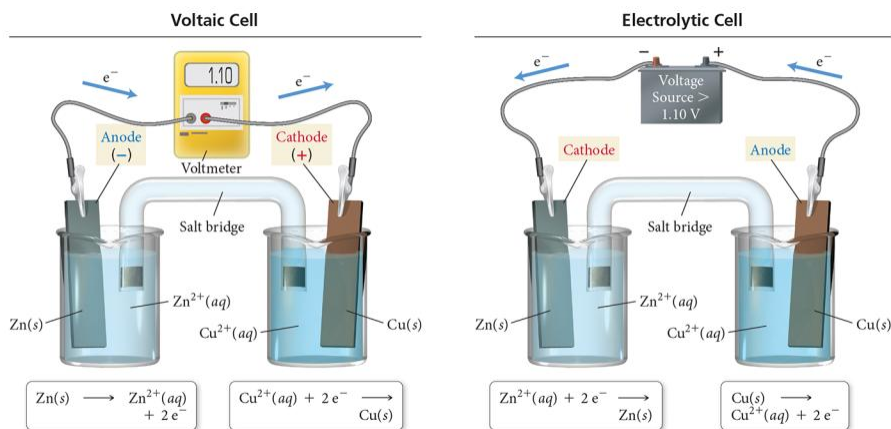
Electrolysis

- **Electrolysis** is the process of using electrical current to drive nonspontaneous reaction.
- Electrolysis is carried out in an electrolytic cell.
- Electrolytic cells can be used to separate compounds into their elements.



© 2017 Pearson Education, Inc.

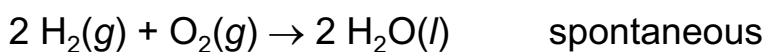
Voltaic versus Electrolytic Cells



© 2017 Pearson Education, Inc.

Electrolytic Cells

- Electrons are drawn away from the anode, which must be connected to the positive terminal of the external power source (anode +).
- Electrons are forced to the cathode, which must be connected to the negative terminal of the power source (cathode -).
- The reaction that takes place is the nonspontaneous process.



© 2017 Pearson Education, Inc.

Electrolytic Cells

- The electrical energy is supplied by a direct-current power supply, a battery or DC power supply.
- Some electrolysis reactions require more voltage than E_{cell} predicts. This is called the **overvoltage**.

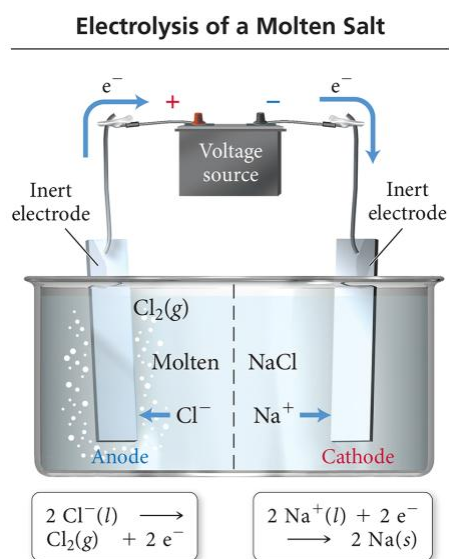
© 2017 Pearson Education, Inc.

Electrolysis of Pure Compounds

- The compound must be in a molten (liquid) state.
- Electrodes are normally graphite.
- Cations are reduced.
- Anions are oxidized.

© 2017 Pearson Education, Inc.

Electrolysis of NaCl(l)



© 2017 Pearson Education, Inc.

Mixtures of Ions

- When more than one cation is present, the cation that is easiest to reduce will be reduced first at the cathode.
 - Least negative or most positive E°_{red}
- When more than one anion is present, the anion that is easiest to oxidize will be oxidized first at the anode.
 - Least negative or most positive E°_{ox}

© 2017 Pearson Education, Inc.

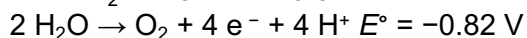
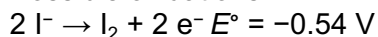
Electrolysis of Aqueous Solutions

- Possible cathode reactions
 - Reduction of cation to metal
 - Reduction of water to H_2
 - $2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2 + 2 \text{OH}^-$ $E^\circ = -0.83 \text{ V}$ at stand. cond.
 $E^\circ = -0.41 \text{ V}$ at pH 7
- Possible anode reactions
 - Oxidation of anion to element
 - Oxidation of H_2O to O_2
 - $2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4 \text{e}^- + 4 \text{H}^+$ $E^\circ = -1.23 \text{ V}$ at stand. cond.
 $E^\circ = -0.82 \text{ V}$ at pH 7
 - Oxidation of electrode
 - Particularly Cu
 - Graphite doesn't oxidize.
- Half-reactions that lead to least negative E_{cell} will occur.
 - Unless overvoltage changes the conditions

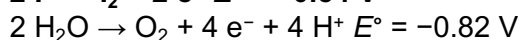
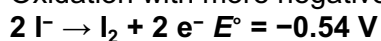
© 2017 Pearson Education, Inc.

Electrolysis of NaI(aq) with Inert Electrodes

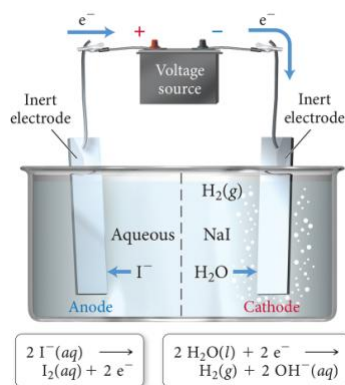
Possible oxidations



Oxidation with more negative E°



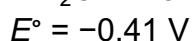
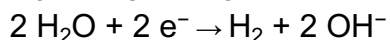
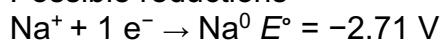
Electrolysis of an Aqueous Salt Solution



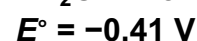
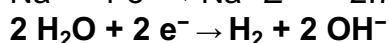
© 2017 Pearson Education, Inc.

Electrolysis of NaI(aq) with Inert Electrodes

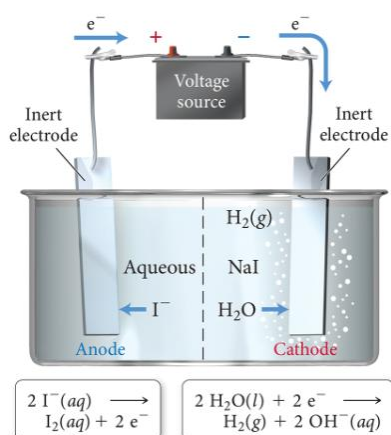
Possible reductions



Reduction with greatest E°



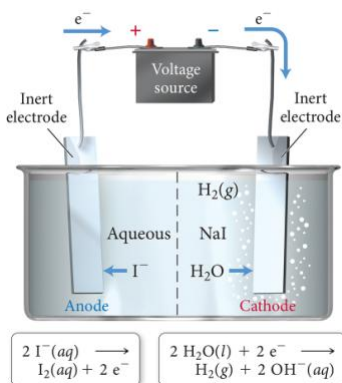
Electrolysis of an Aqueous Salt Solution



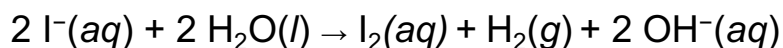
© 2017 Pearson Education, Inc.

Electrolysis of NaI(aq) with Inert Electrodes

Electrolysis of an Aqueous Salt Solution



Overall reaction



© 2017 Pearson Education, Inc.

Stoichiometry of Electrolysis

- In an electrolytic cell, the amount of product made is related to the number of electrons transferred.
 - Essentially, the electrons are a reactant.
- The number of moles of electrons that flow through the electrolytic cell depends on the current and length of time.
 - 1 amp = 1 coulomb of charge/second
 - 1 mole of e^- = 96,485 coulombs of charge
 - Faraday's constant

© 2017 Pearson Education, Inc.

Corrosion

- **Corrosion** is the undesirable, spontaneous, gradual oxidation of a metal by oxidizing agents in the environment.
 - Mainly O_2
- A metal must usually be reduced to extract it from its ore. In corrosion, the metal is oxidized back to its more natural state.

© 2017 Pearson Education, Inc.

Reduction of O_2

- O_2 is very easy to reduce in moist conditions.

$$O_2(g) + 2 H_2O(l) + 4 e^- \rightarrow 2 OH^-(aq) \quad E^\circ = 0.40 \text{ V}$$
- O_2 is even easier to reduce under acidic conditions.

$$O_2(g) + 4 H^+ + 4 e^- \rightarrow 2 H_2O(l) \quad E^\circ = 1.23 \text{ V}$$
- Because the reduction of most metal ions lies below O_2 on the table of standard reduction potentials, the oxidation of those metals by O_2 is spontaneous.

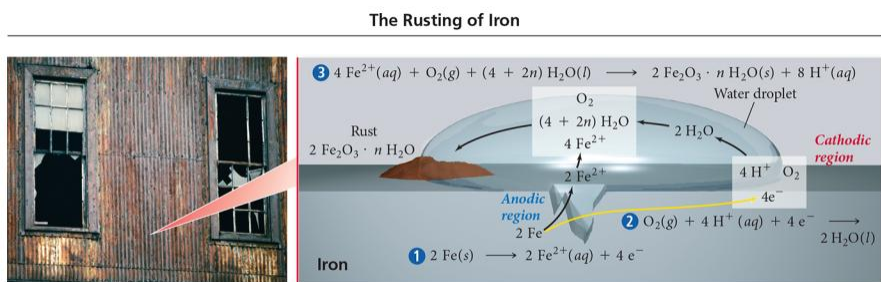
© 2017 Pearson Education, Inc.

Corrosion of Iron: Rusting

- At the anodic regions, Fe(s) is oxidized to Fe^{2+} .
- The electrons travel through the metal to a cathodic region where O_2 is reduced.
 - In acidic solution from gases dissolved in the moisture
- The Fe^{2+} ions migrate through the moisture to the cathodic region where they are further oxidized to Fe^{3+} , which combines with the oxygen and water to form **rust**.
 - Rust is hydrated iron(III) oxide, $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$.
 - Moisture must be present. Water is a reactant.
 - Ion flow is required between cathodic and anodic regions.
- Electrolytes promote rusting.
 - Enhance current flow
- Acids promote rusting.
 - Lowering pH will lower E°_{red} of O_2 .

© 2017 Pearson Education, Inc.

Corrosion of Iron: Rusting



© 2017 Pearson Education, Inc.

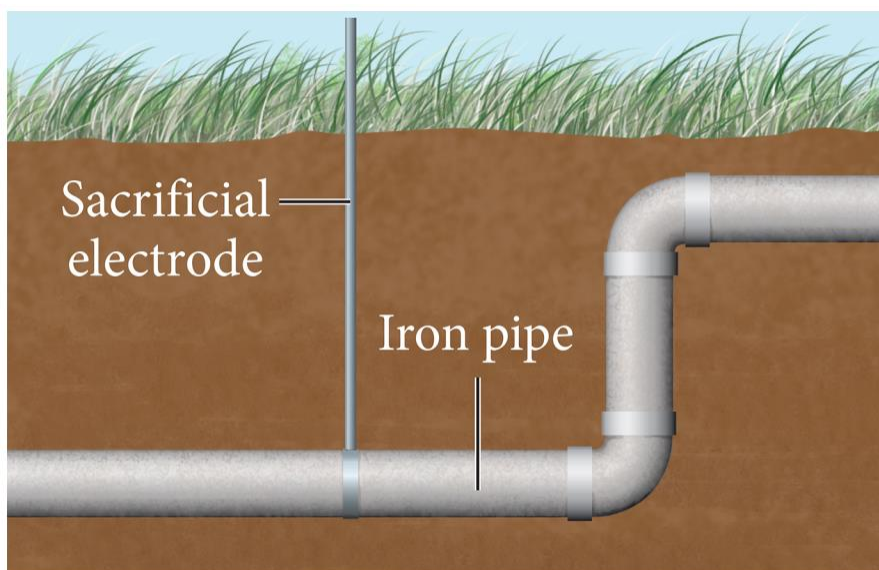
Preventing Corrosion

- One way to reduce or slow corrosion is to coat the metal surface to keep it from contacting corrosive chemicals in the environment.
 - Paint
 - Some metals, such as Al, form an oxide that strongly attaches to the metal surface, preventing the rest of the metal from corroding.
- Another method to protect a metal is to attach it to a more reactive metal that is cheap.
 - Sacrificial electrode
 - Galvanized nails



© 2017 Pearson Education, Inc.

Sacrificial Anode



© 2017 Pearson Education, Inc.