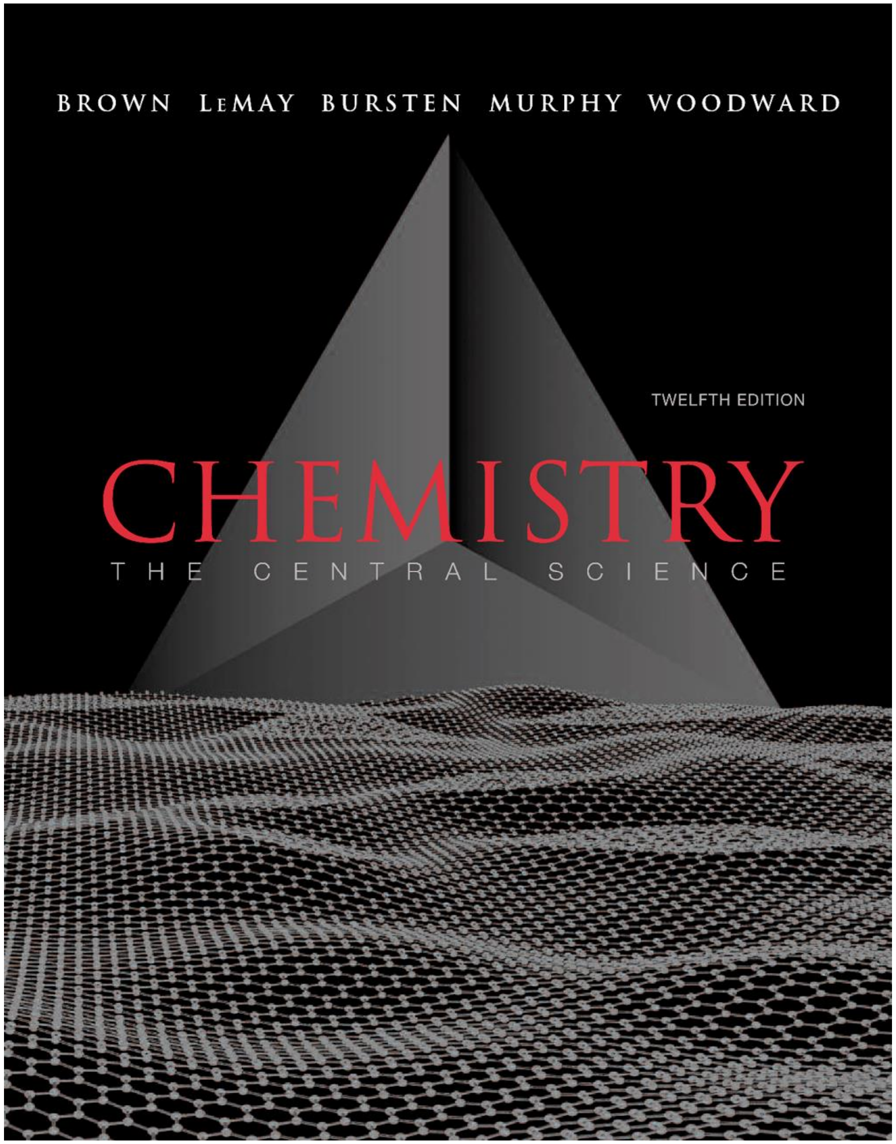


Lecture Presentation

Chapter 20

Electrochemistry

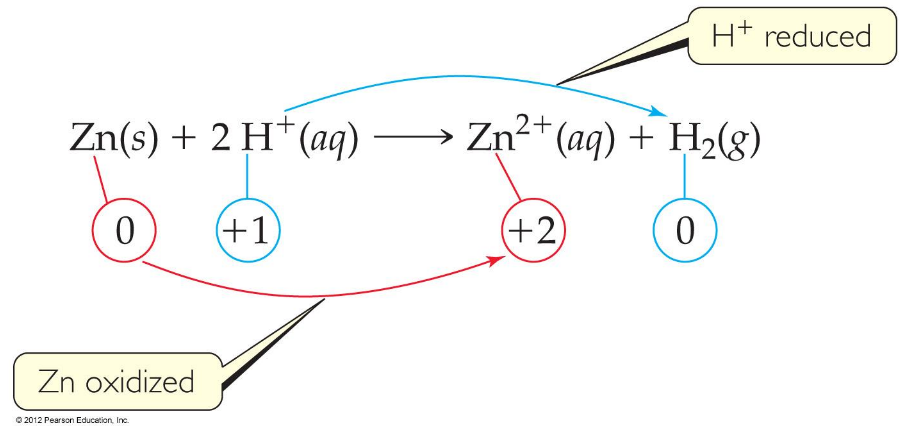
John D. Bookstaver
St. Charles Community College
Cottleville, MO

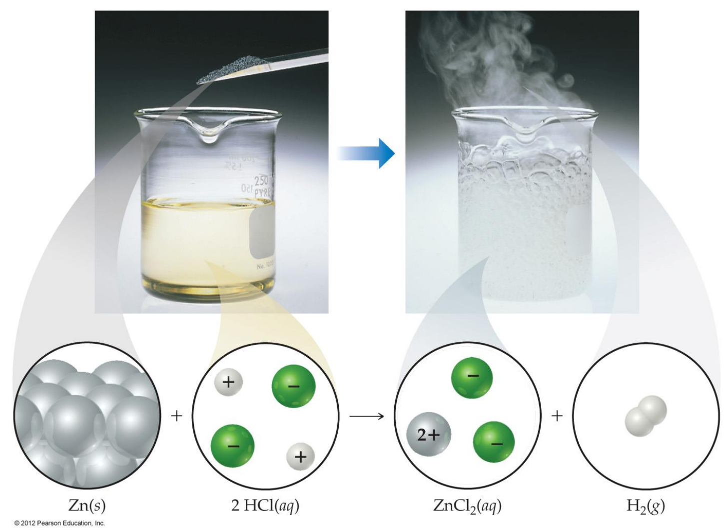
Electrochemical Reactions

In **electrochemical reactions,** electrons are transferred from one species to another.

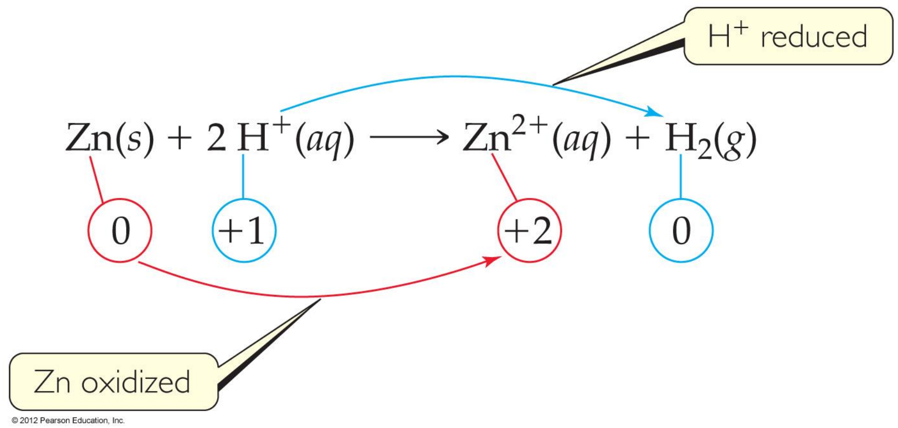
Oxidation Numbers

In order to keep track of what loses electrons and what gains them, we assign **oxidation numbers**.



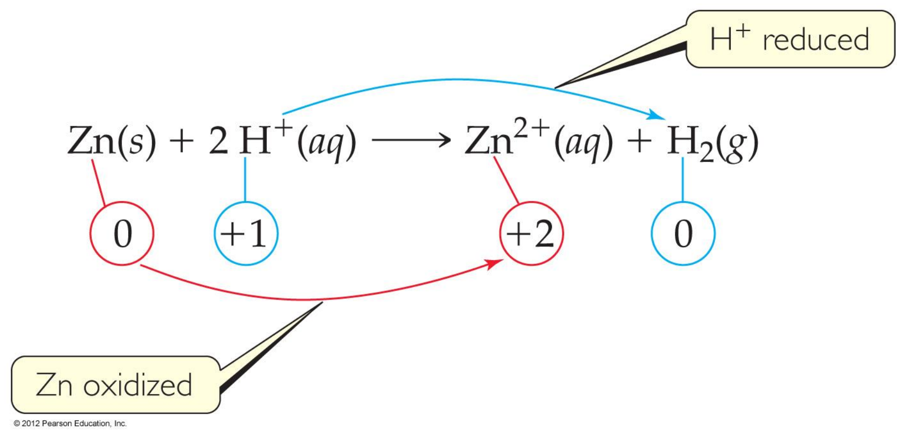


Oxidation and Reduction



- A species is **oxidized** when it loses electrons.
  - Here, zinc loses two electrons to go from neutral zinc metal to the Zn^{2+} ion.

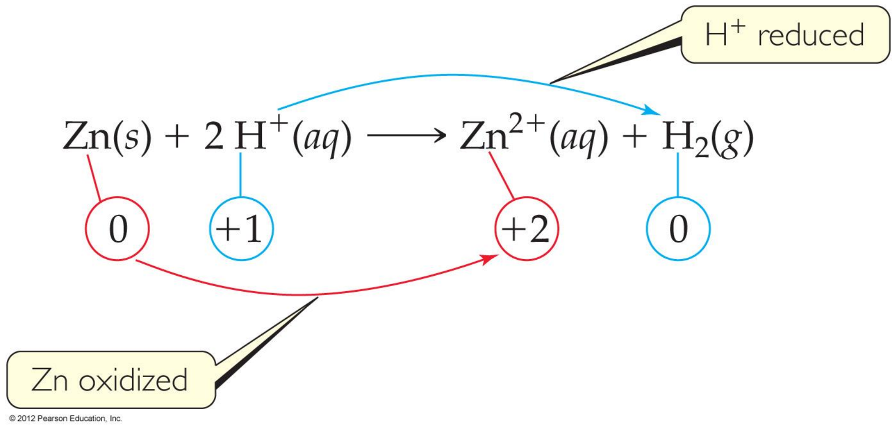
Oxidation and Reduction



Å A species is **reduced** when it gains electrons.

ï Here, each of the H^+ gains an electron, and they combine to form H_2.

Oxidation and Reduction



- What is reduced is the **oxidizing agent**.
  - H^+ oxidizes Zn by taking electrons from it.
- What is oxidized is the **reducing agent.**
  - Zn reduces H^+ by giving it electrons.

Assigning Oxidation Numbers

1. Elements in their elemental form have an oxidation number of 0.
2. The oxidation number of a monatomic ion is the same as its charge.

Assigning Oxidation Numbers

3. Nonmetals tend to have negative oxidation numbers, although some are positive in certain compounds or ions.
   - Oxygen has an oxidation number of –2, except in the peroxide ion, which has an oxidation number of –1.
   - Hydrogen is –1 when bonded to a metal, and +1 when bonded to a nonmetal.

Assigning Oxidation Numbers

3. Nonmetals tend to have negative oxidation numbers, although some are positive in certain compounds or ions.
   - Fluorine always has an oxidation number of –1.
   - The other halogens have an oxidation number of –1 when they are negative. They can have positive oxidation numbers, however; most notably in oxyanions.

Assigning Oxidation Numbers

4. The sum of the oxidation numbers in a neutral compound is 0.
5. The sum of the oxidation numbers in a polyatomic ion is the charge on the ion.

Balancing Oxidation-Reduction Equations

Perhaps the easiest way to balance the equation of an oxidation-reduction reaction is via the **half-reaction method**.

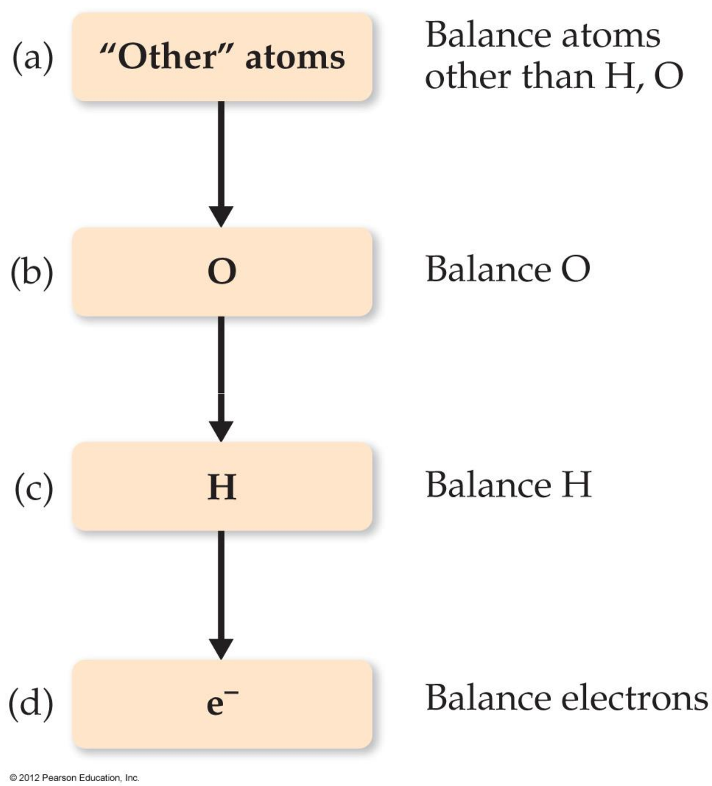
Balancing Oxidation-Reduction Equations

This method involves treating (on paper only) the oxidation and reduction as two separate processes, balancing these half-reactions, and then combining them to attain the balanced equation for the overall reaction.

The Half-Reaction Method

1. Assign oxidation numbers to determine what is oxidized and what is reduced.
2. Write the oxidation and reduction half-reactions.

The Half-Reaction Method

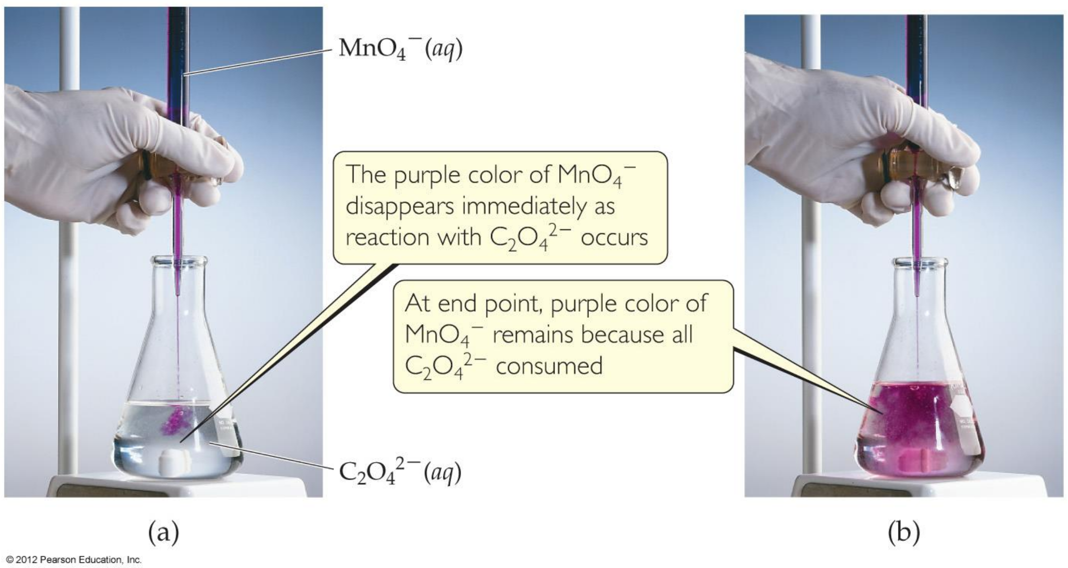


3. Balance each half-reaction.
    a. Balance elements other than H and O.
    b. Balance O by adding H_2O.
    c. Balance H by adding H^+.
    d. Balance charge by adding electrons.

The Half-Reaction Method

4. Multiply the half-reactions by integers so that the electrons gained and lost are the same.
5. Add the half-reactions, subtracting things that appear on both sides.
6. Make sure the equation is balanced according to mass.
7. Make sure the equation is balanced according to charge.

The Half-Reaction Method



Consider the reaction between MnO_4^- and $C_2O_4^{2-}$:

$$MnO_4^-(aq) + C_2O_4^{2-}(aq) \longrightarrow Mn^{2+}(aq) + CO_2(aq)$$

The Half-Reaction Method

First, we assign oxidation numbers:

$$\overset{+7}{Mn}O_4^- + \overset{+3}{C_2}O_4^{2-} \longrightarrow \overset{+2}{Mn^{2+}} + \overset{+4}{C}O_2$$

Since the manganese goes from +7 to +2, it is reduced.

Since the carbon goes from +3 to +4, it is oxidized.

Oxidation Half-Reaction

$$C_2O_4^{2-} \longrightarrow CO_2$$

To balance the carbon, we add a coefficient of 2:

$$C_2O_4^{2-} \longrightarrow 2CO_2$$

Oxidation Half-Reaction

$$C_2O_4^{2-} \longrightarrow 2CO_2$$

The oxygen is now balanced as well. To balance the charge, we must add 2 electrons to the right side:

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

Reduction Half-Reaction

$$MnO_4^- \longrightarrow Mn^{2+}$$

The manganese is balanced; to balance the oxygen, we must add 4 waters to the right side:

$$MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$$

Reduction Half-Reaction

$$MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$$

To balance the hydrogen, we add $8H^+$ to the left side:

$$8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$$

Reduction Half-Reaction

$$8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$$

To balance the charge, we add $5e^-$ to the left side:

$$5e^- + 8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$$

Combining the Half-Reactions

Now we evaluate the two half-reactions together:

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$
$$5e^- + 8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$$

To attain the same number of electrons on each side, we will multiply the first reaction by 5 and the second by 2:

Combining the Half-Reactions

$$5C_2O_4^{2-} \longrightarrow 10CO_2 + 10e^-$$

$$10e^- + 16H^+ + 2MnO_4^- \longrightarrow 2Mn^{2+} + 8H_2O$$

When we add these together, we get:

$$10e^- + 16H^+ + 2MnO_4^- + 5C_2O_4^{2-} \longrightarrow$$
$$2Mn^{2+} + 8H_2O + 10CO_2 + 10e^-$$

Combining the Half-Reactions

$$10e^{-} + 16H^{+} + 2MnO_4^{-} + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2 + 10e^{-}$$

The only thing that appears on both sides are the electrons. Subtracting them, we are left with:

$$16H^{+} + 2MnO_4^{-} + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

Balancing in Basic Solution

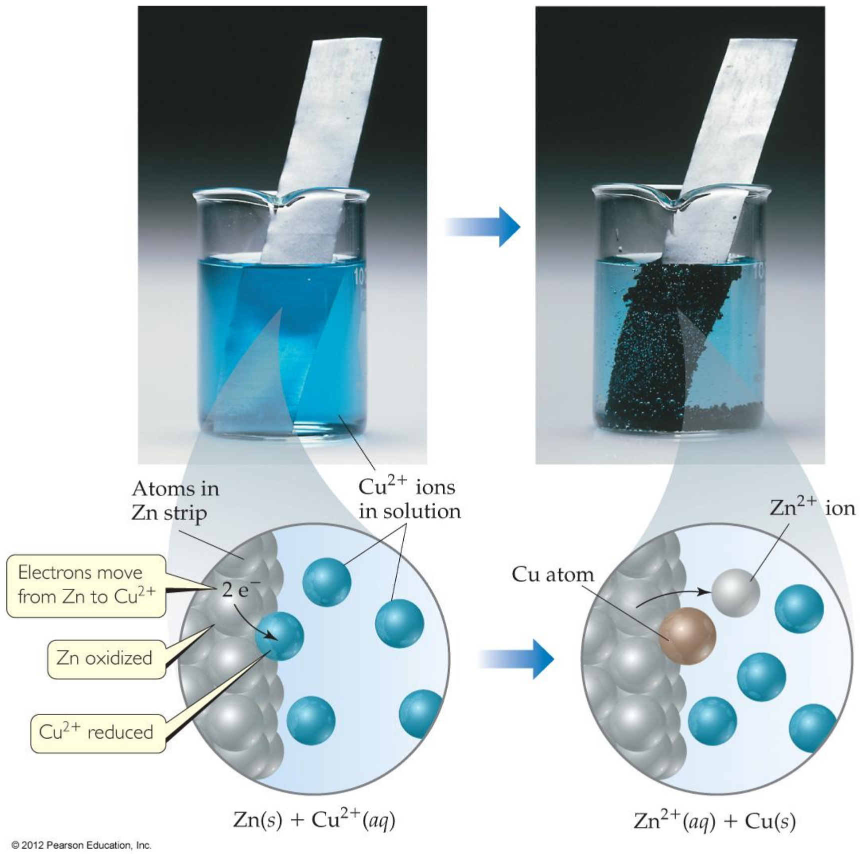
Å If a reaction occurs in a basic solution, one can balance it as if it occurred in acid.

Å Once the equation is balanced, add OH^- to each side to ñneutralizeò the H^+ in the equation and create water in its place.

Å If this produces water on both sides, you might have to subtract water from each side.

Voltaic Cells

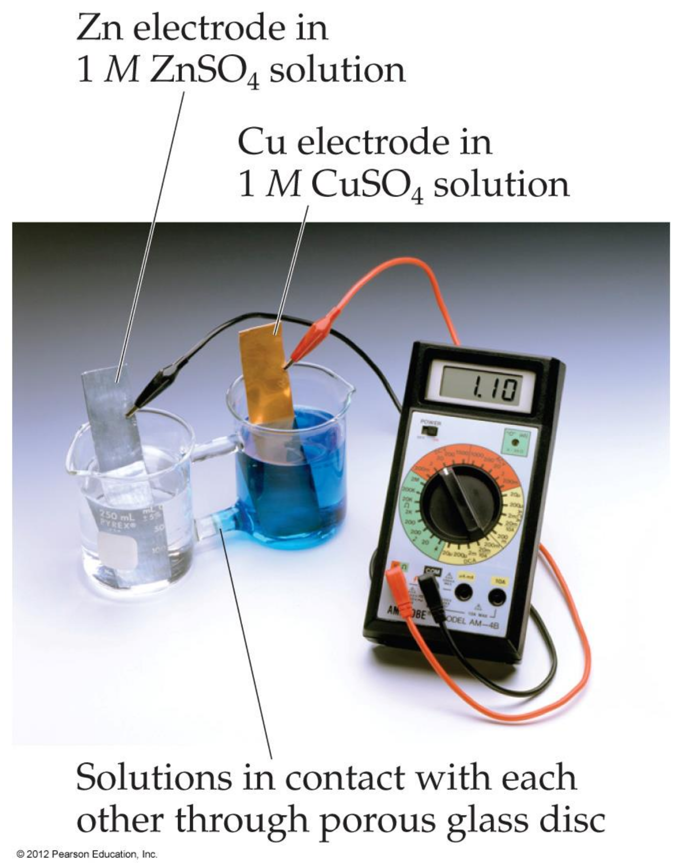
In spontaneous oxidation-reduction (redox) reactions, electrons are transferred and energy is released.



Voltaic Cells

Å We can use that energy to do work if we make the electrons flow through an external device.

Å We call such a setup a **voltaic cell**.

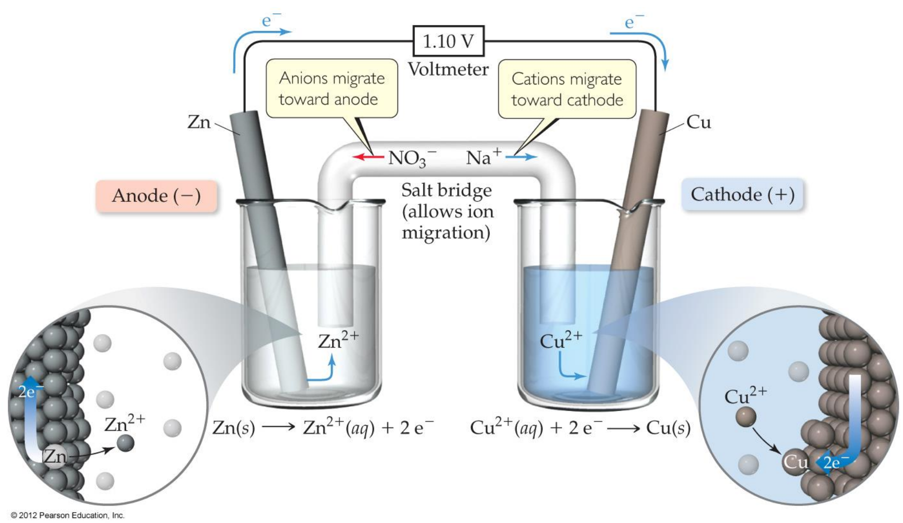


Voltaic Cells

Å A typical cell looks like this.

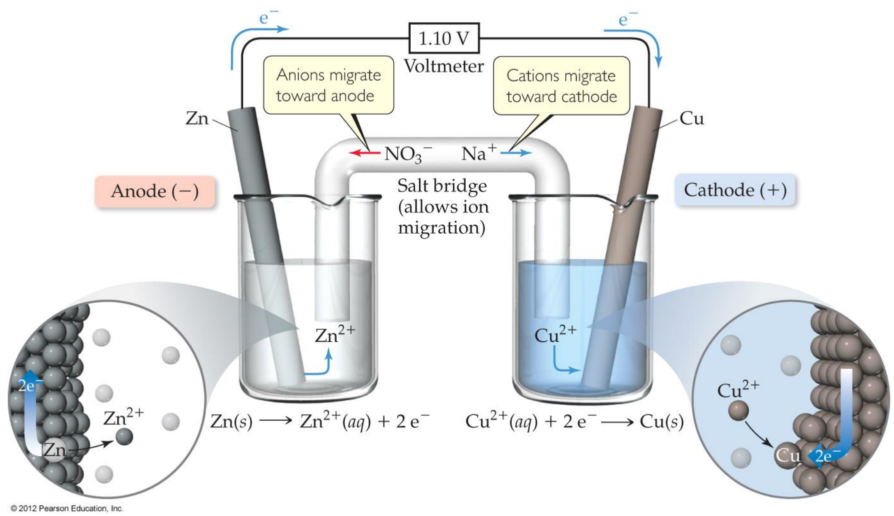
Å The oxidation occurs at the **anode**.

Å The reduction occurs at the **cathode**.



Voltaic Cells

Once even one electron flows from the anode to the cathode, the charges in each beaker would not be balanced and the flow of electrons would stop.

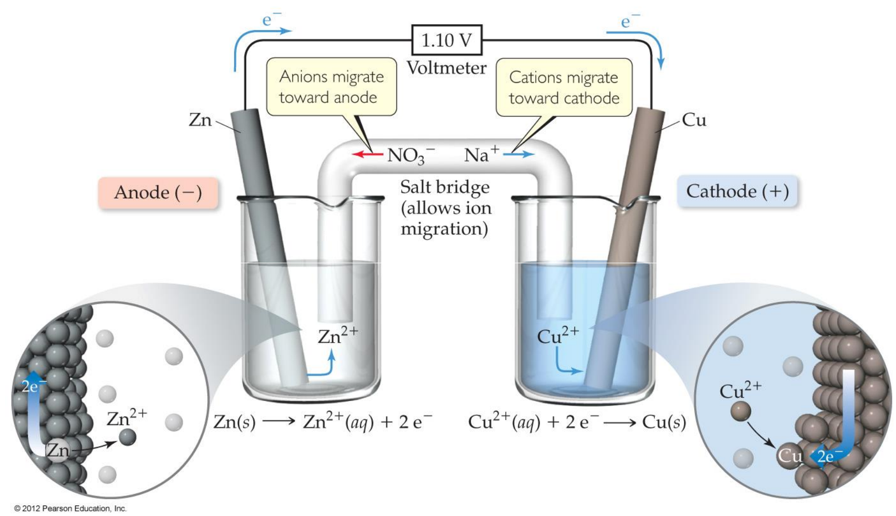


Voltaic Cells

Å Therefore, we use a salt bridge, usually a U-shaped tube that contains a salt solution, to keep the charges balanced.

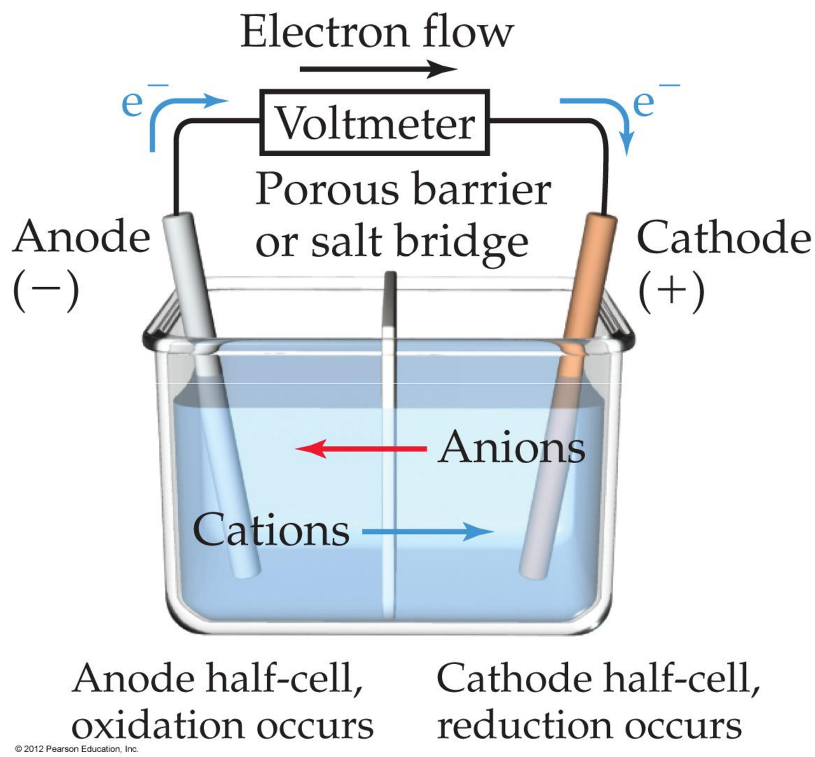
ï Cations move toward the cathode.

ï Anions move toward the anode.



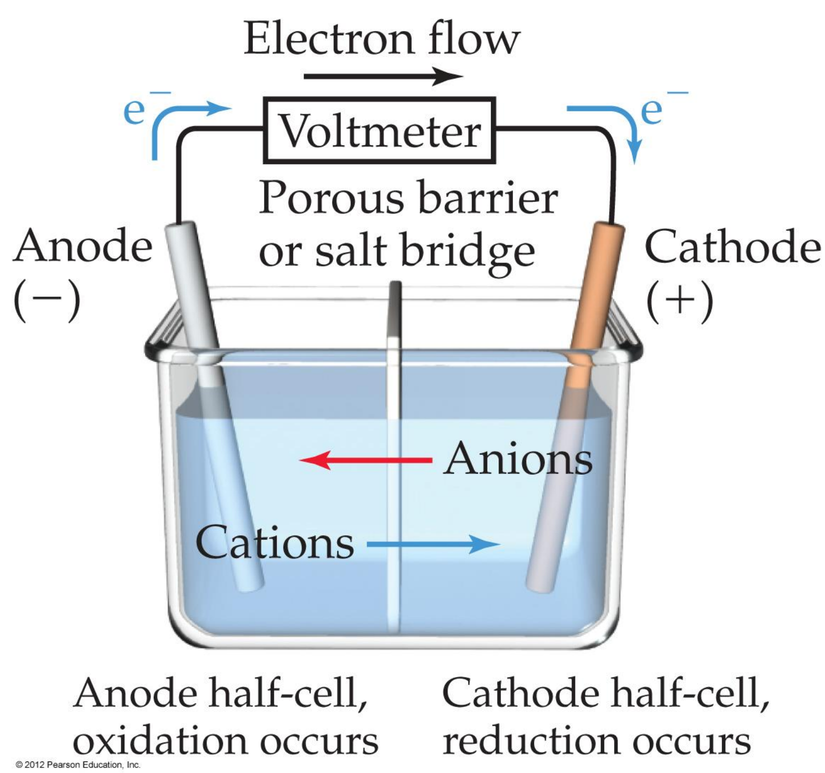
Voltaic Cells

- In the cell, then, electrons leave the anode and flow through the wire to the cathode.
- As the electrons leave the anode, the cations formed dissolve into the solution in the anode compartment.



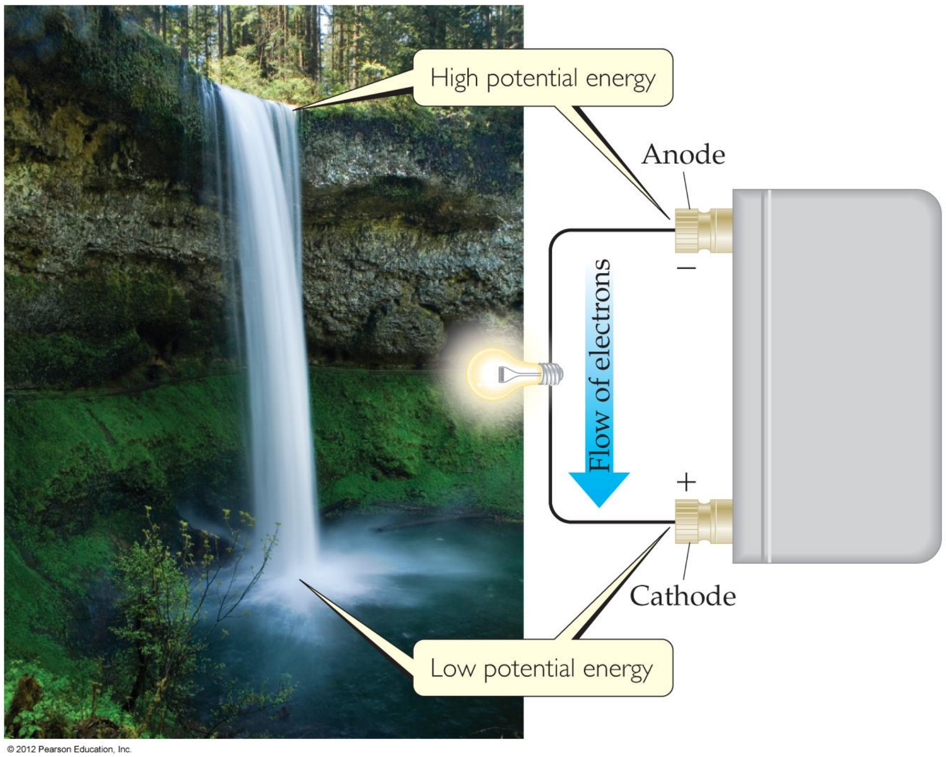
Voltaic Cells

- Å As the electrons reach the cathode, cations in the cathode are attracted to the now negative cathode.
- Å The electrons are taken by the cation, and the neutral metal is deposited on the cathode.



Electromotive Force (emf)

- Water only spontaneously flows one way in a waterfall.
- Likewise, electrons only spontaneously flow one way in a redox reaction—from higher to lower potential energy.



Electromotive Force (emf)

Å The potential difference between the anode and cathode in a cell is called the **electromotive force (emf)**.

Å It is also called the **cell potential** and is designated E_{cell}.

Cell Potential

Cell potential is measured in volts (V).

$$1\ \text{V} = 1\,\frac{\text{J}}{\text{C}}$$

Standard Reduction Potentials

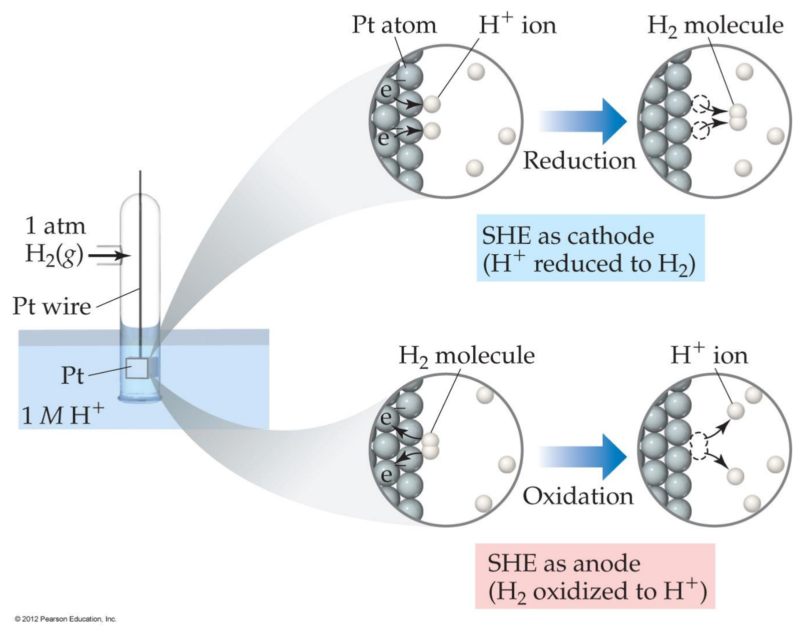
Reduction potentials for many electrodes have been measured and tabulated.

TABLE 20.1 • Standard Reduction Potentials in Water at 25 °C

E°_{red} (V)	Reduction Half-Reaction
+2.87	$F_2(g) + 2\,e^- \longrightarrow 2\,F^-(aq)$
+1.51	$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$
+1.36	$Cl_2(g) + 2\,e^- \longrightarrow 2\,Cl^-(aq)$
+1.33	$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$
+1.23	$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$
+1.06	$Br_2(l) + 2\,e^- \longrightarrow 2\,Br^-(aq)$
+0.96	$NO_3^-(aq) + 4\,H^+(aq) + 3\,e^- \longrightarrow NO(g) + 2\,H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
+0.68	$O_2(g) + 2\,H^+(aq) + 2\,e^- \longrightarrow H_2O_2(aq)$
+0.59	$MnO_4^-(aq) + 2\,H_2O(l) + 3\,e^- \longrightarrow MnO_2(s) + 4\,OH^-(aq)$
+0.54	$I_2(s) + 2\,e^- \longrightarrow 2\,I^-(aq)$
+0.40	$O_2(g) + 2\,H_2O(l) + 4\,e^- \longrightarrow 4\,OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$
0 [defined]	$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$
−0.28	$Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s)$
−0.44	$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$
−0.76	$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$
−0.83	$2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq)$
−1.66	$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$
−2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
−3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

Standard Hydrogen Electrode

- Their values are referenced to a standard hydrogen electrode (SHE).
- By definition, the reduction potential for hydrogen is 0 V:



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

Standard Cell Potentials

The cell potential at standard conditions can be found through this equation:

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}}\,(\text{cathode}) - E^\circ_{\text{red}}\,(\text{anode})$$

Because cell potential is based on the potential energy per unit of charge, it is an intensive property.

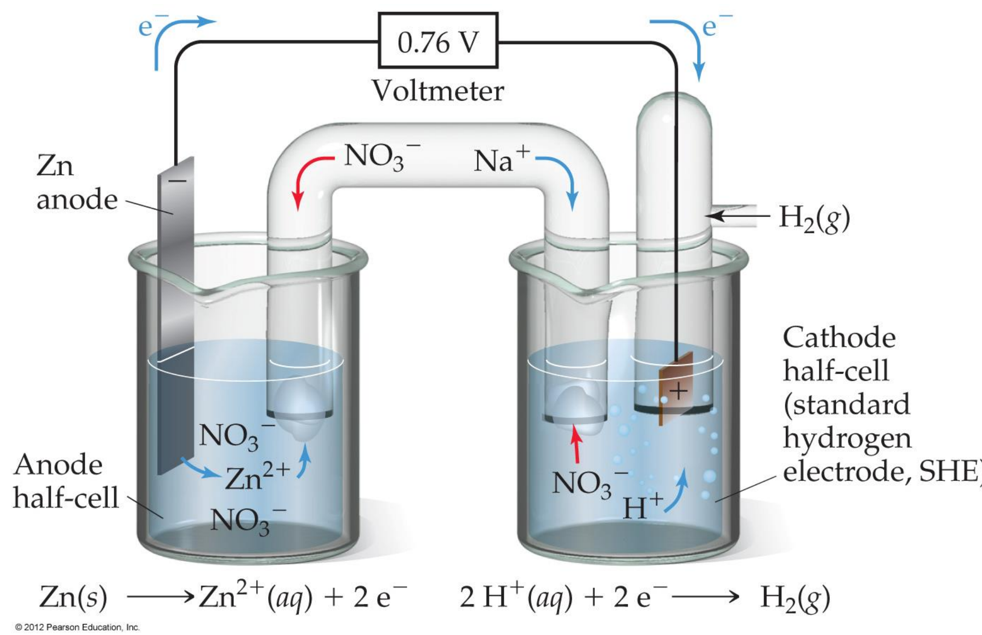
Cell Potentials

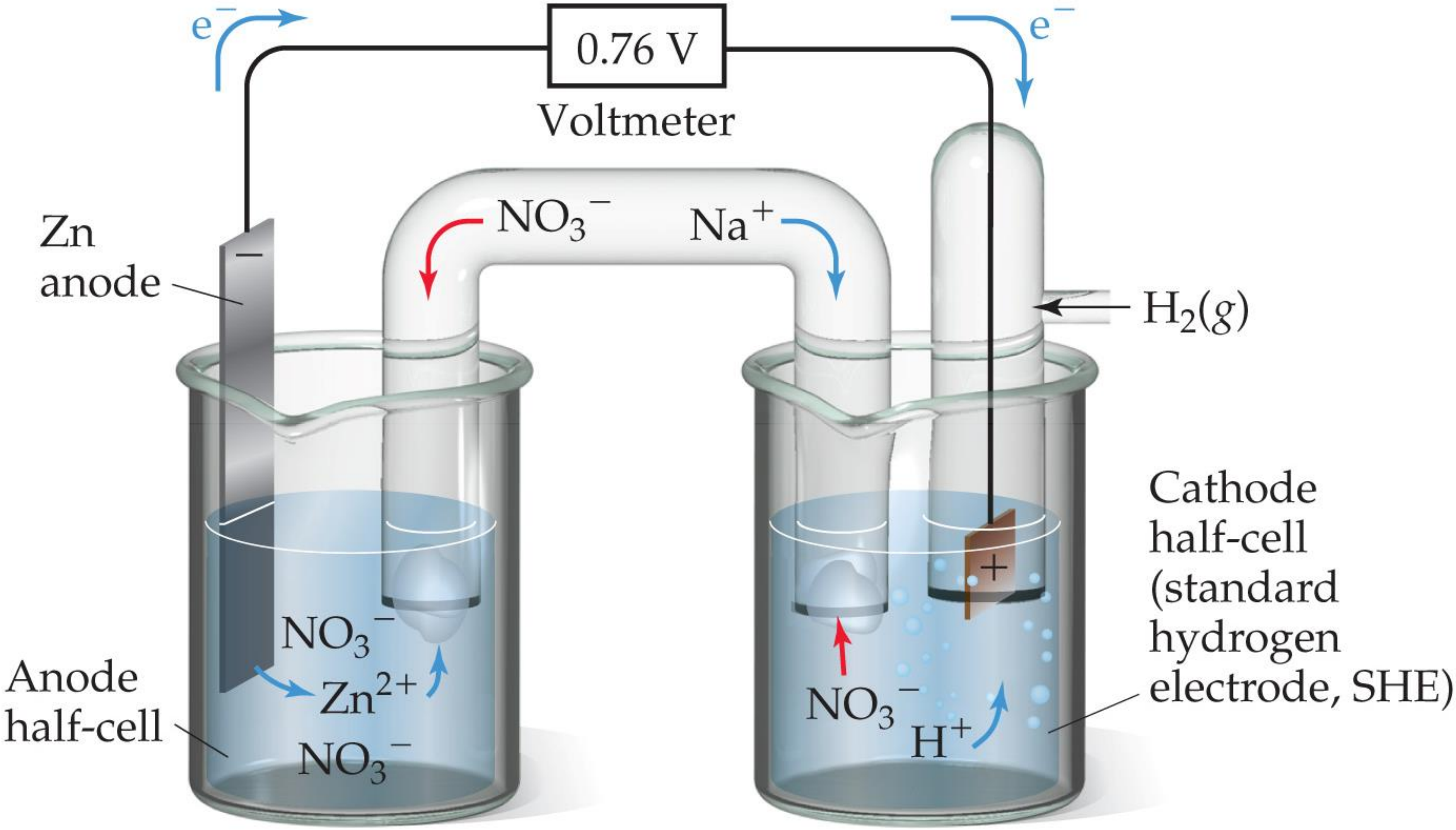
Å For the oxidation in this cell,

$$E^{\circ}_{red} = -0.76\ \text{V}$$

Å For the reduction,

$$E^{\circ}_{red} = +0.34\ \text{V}$$





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

Cell Potentials

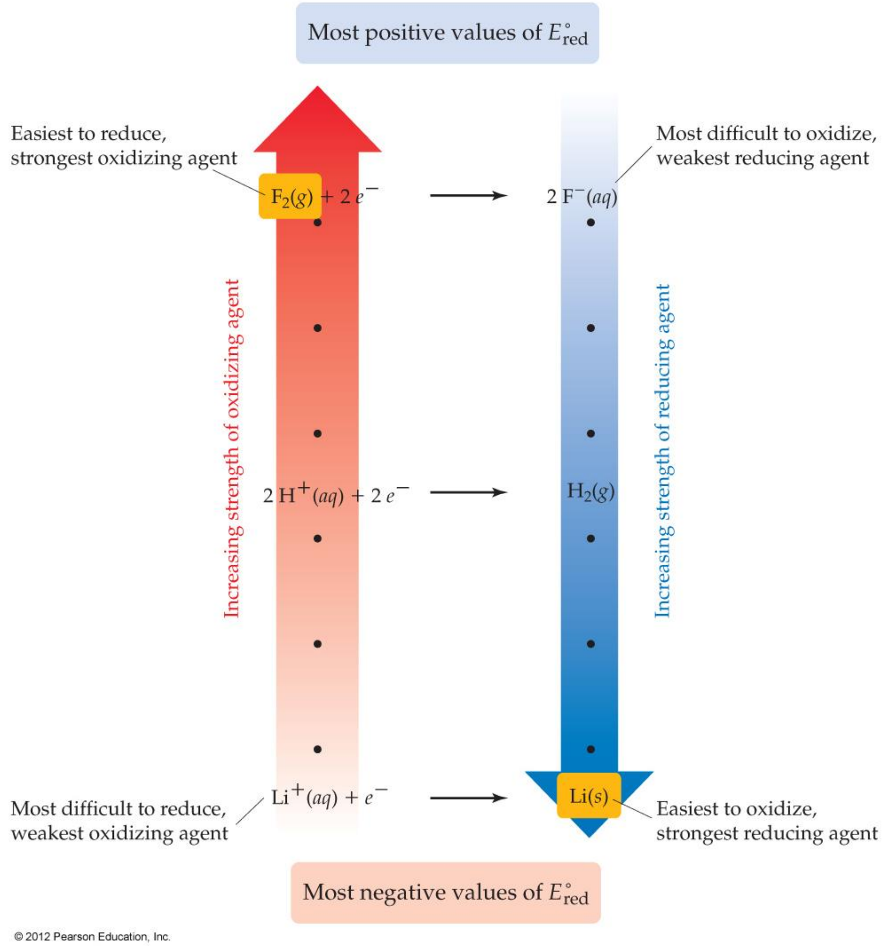
$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}}\ \text{(cathode)} - E^{\circ}_{\text{red}}\ \text{(anode)}$$

$$= +0.34\ \text{V} - (-0.76\ \text{V})$$

$$= +1.10\ \text{V}$$

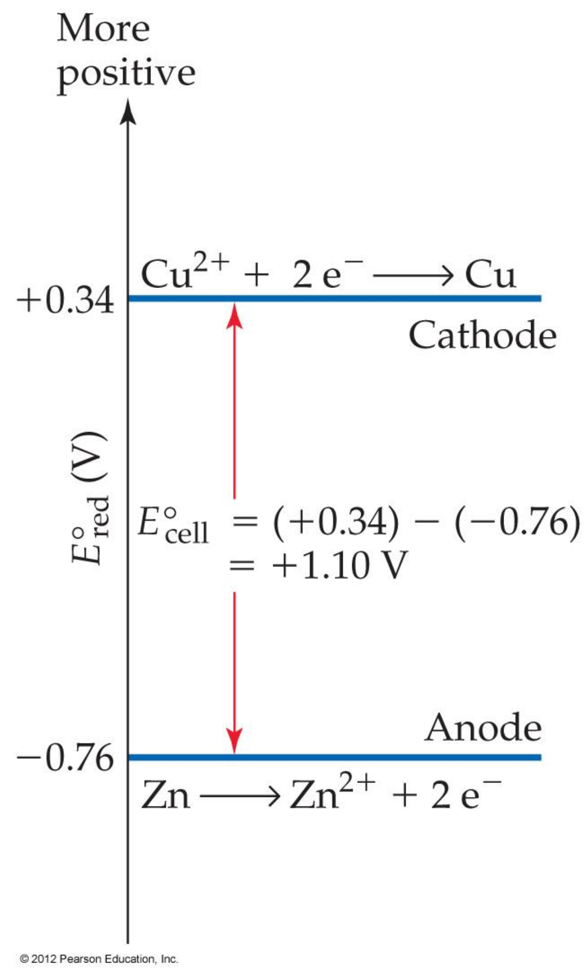
Oxidizing and Reducing Agents

- The strongest oxidizers have the most positive reduction potentials.
- The strongest reducers have the most negative reduction potentials.



Oxidizing and Reducing Agents

The greater the difference between the two, the greater the voltage of the cell.



Free Energy

ΔG for a redox reaction can be found by using the equation

$$\Delta G = -nFE$$

where n is the number of moles of electrons transferred, and F is a constant, the Faraday:

$1\ F = 96{,}485$ C/mol $= 96{,}485$ J/V-mol

Free Energy

Under standard conditions,

$$\Delta G^\circ = -nFE^\circ$$

Nernst Equation

- Remember that

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

- This means

$$-nFE = -nFE^\circ + RT \ln Q$$

Nernst Equation

Dividing both sides by $-nF$, we get the **Nernst equation**:

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

or, using base-10 logarithms,

$$E = E^\circ - \frac{2.303RT}{nF} \log Q$$

Nernst Equation

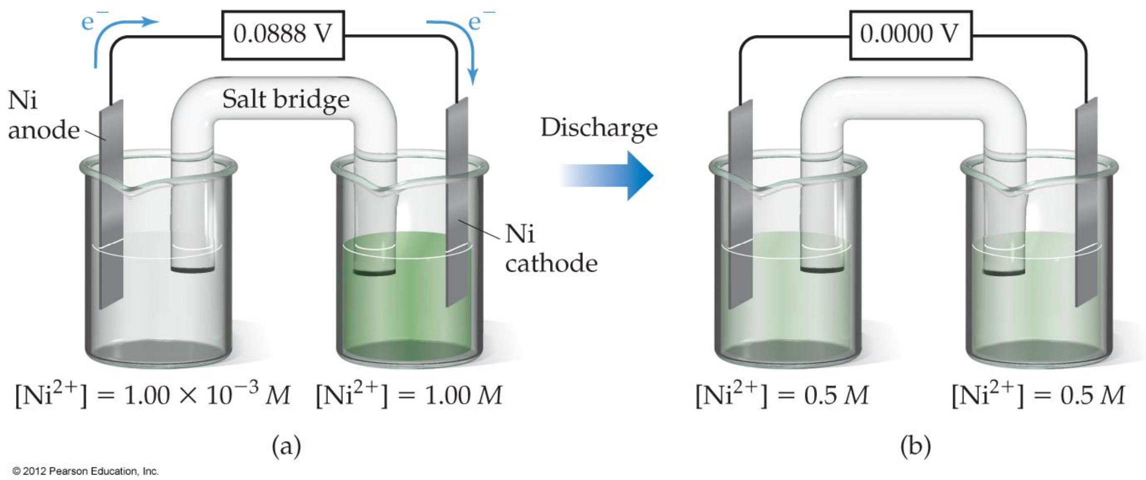
At room temperature (298 K),

$$\frac{2.303RT}{F} = 0.0592 \text{ V}$$

Thus, the equation becomes

$$E = E° - \frac{0.0592}{n} \log Q$$

Concentration Cells



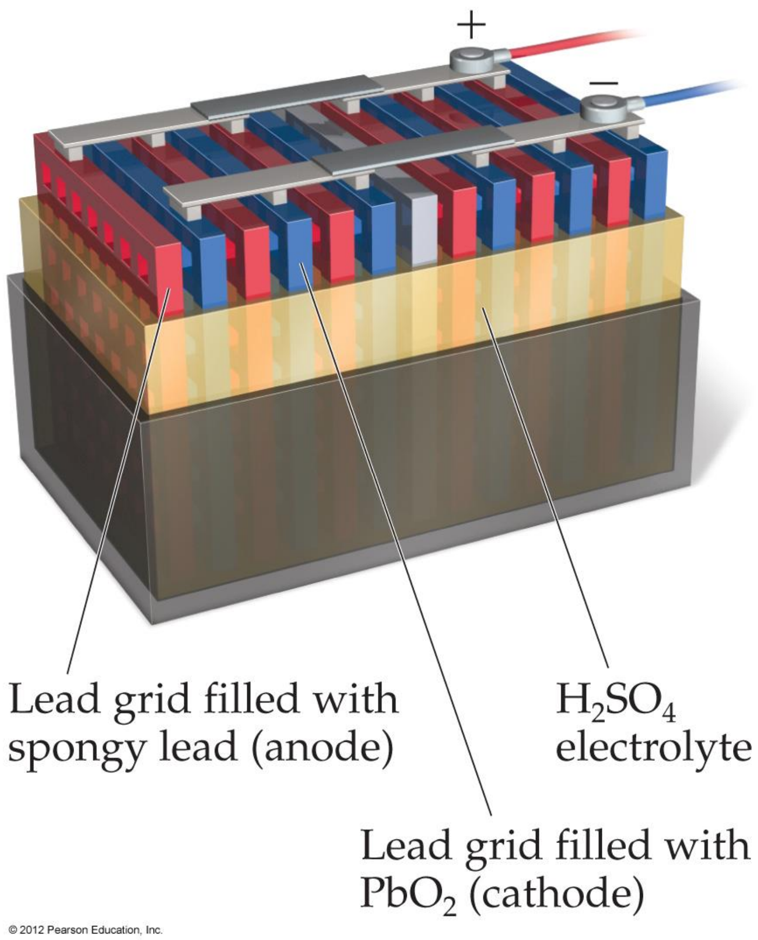
Å Notice that the Nernst equation implies that a cell could be created that has the same substance at both electrodes.

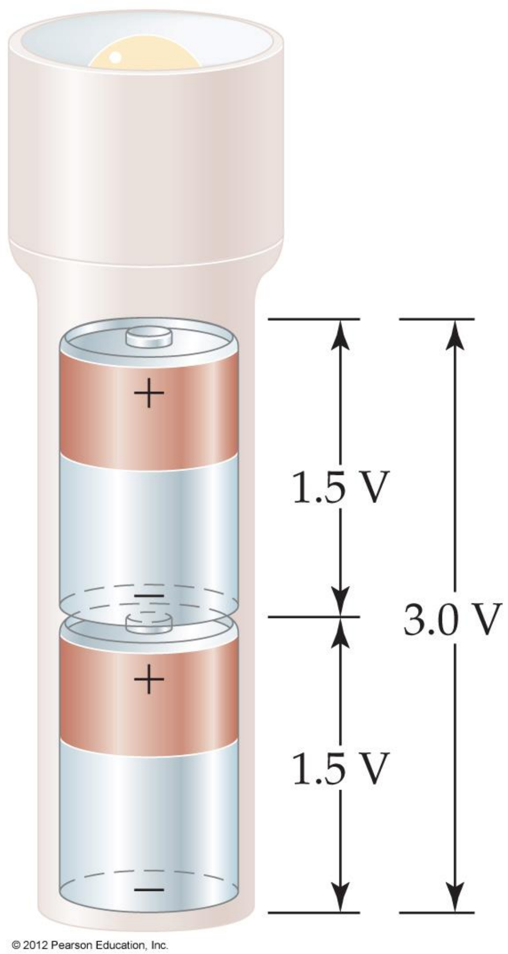
Å For such a cell, E°_{cell} would be 0, but *Q* would not.

Å Therefore, as long as the concentrations are different, *E* will not be 0.

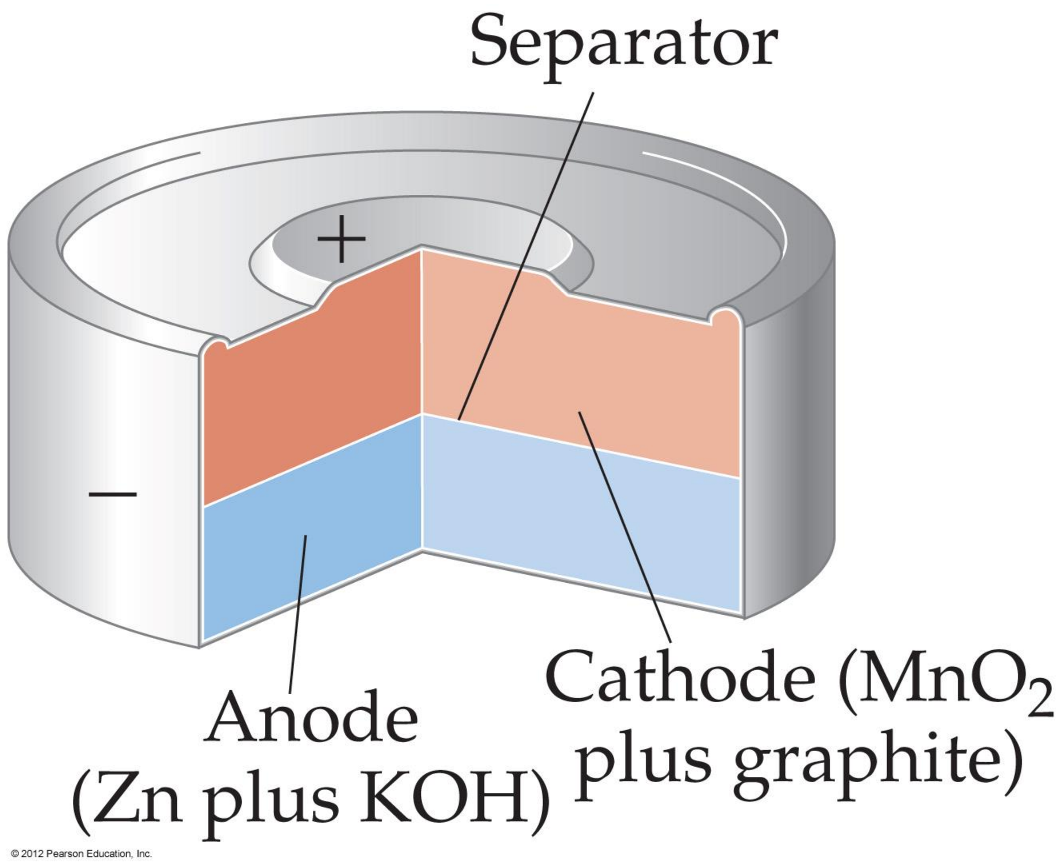
Applications of Oxidation-Reduction Reactions

Batteries

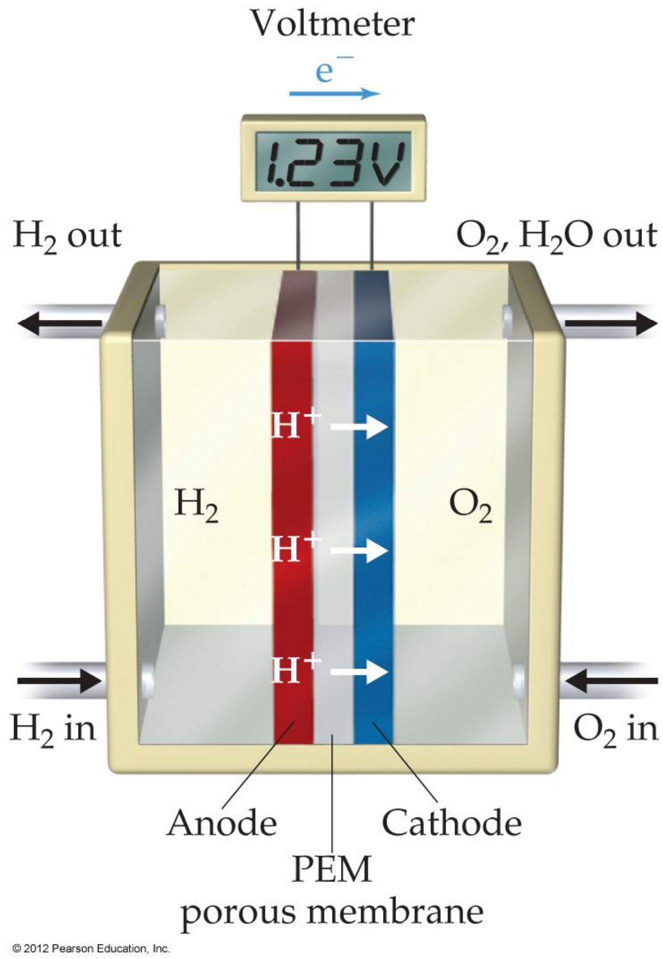

+
−
Lead grid filled with spongy lead (anode)
H_2SO_4 electrolyte
Lead grid filled with PbO_2 (cathode)
© 2012 Pearson Education, Inc.


+
−
+
−
1.5 V
1.5 V
3.0 V
© 2012 Pearson Education, Inc.

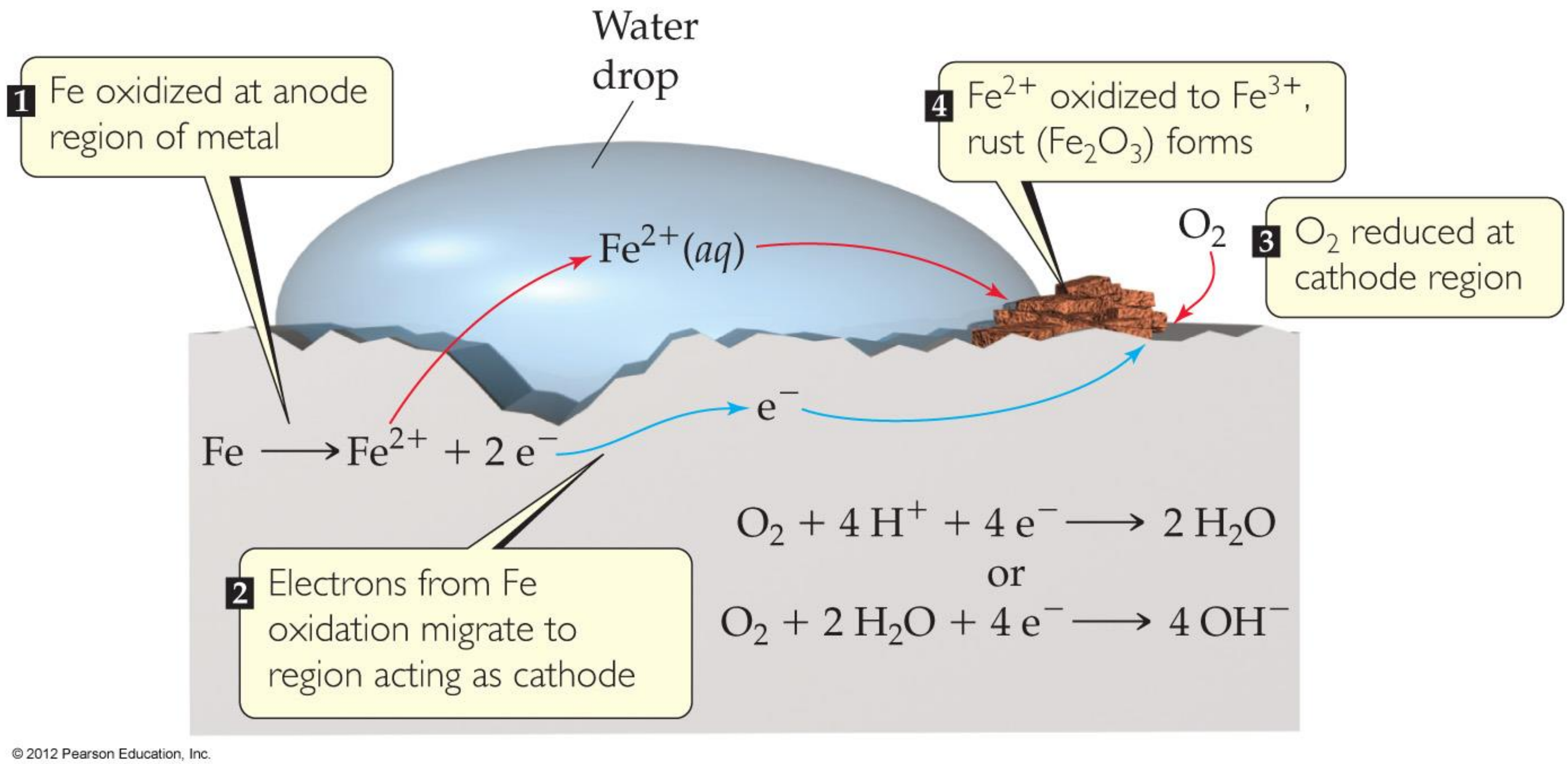
Alkaline Batteries



Hydrogen Fuel Cells



Corrosion andé



é Corrosion Prevention