Chemistry, The Central Science, 10th edition
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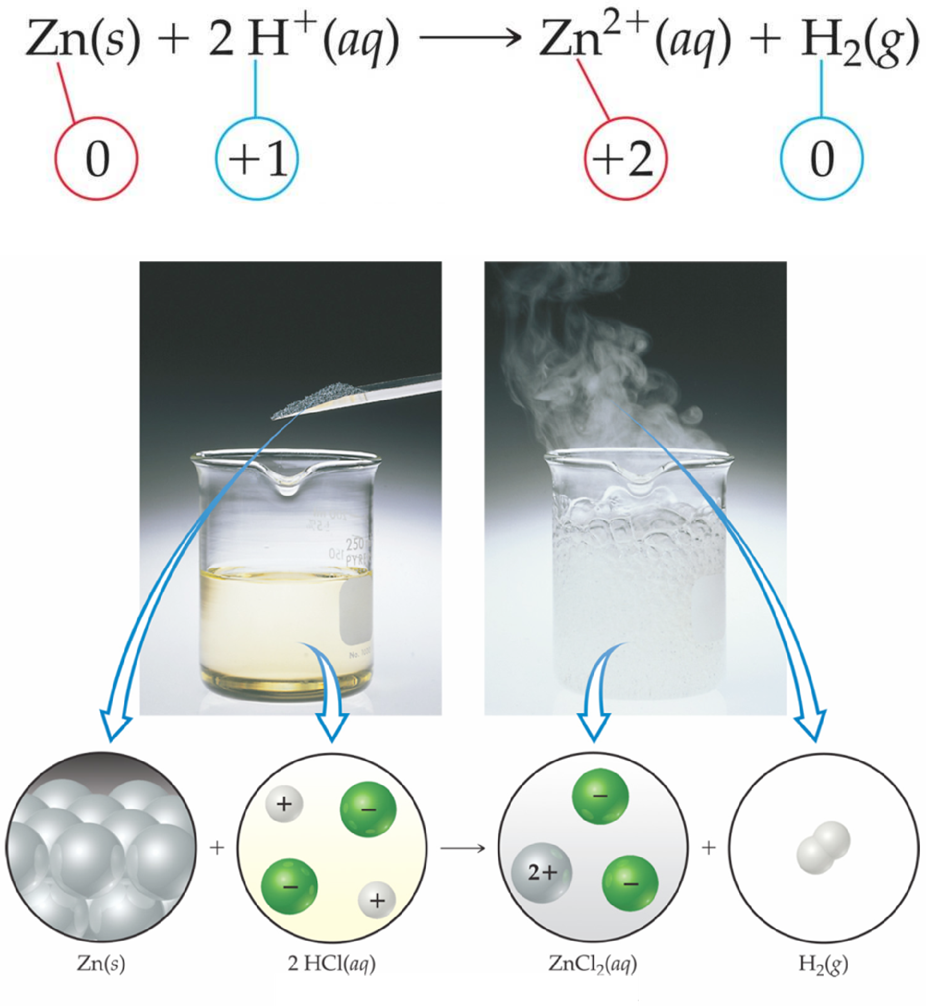
Chapter 20
Electrochemistry

Electrochemical Reactions

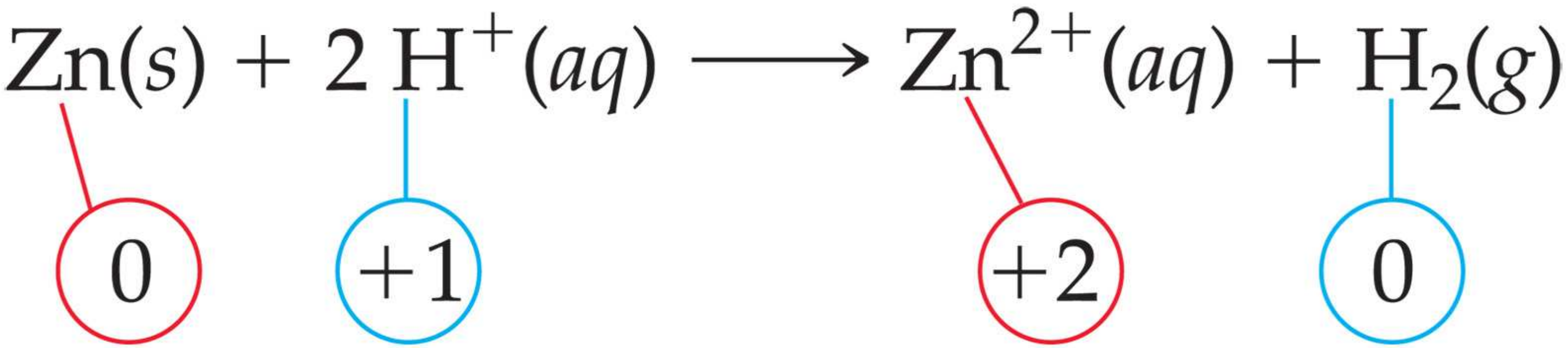
In electrochemical reactions, electrons are transferred from one species to another.

Oxidation Numbers


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

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

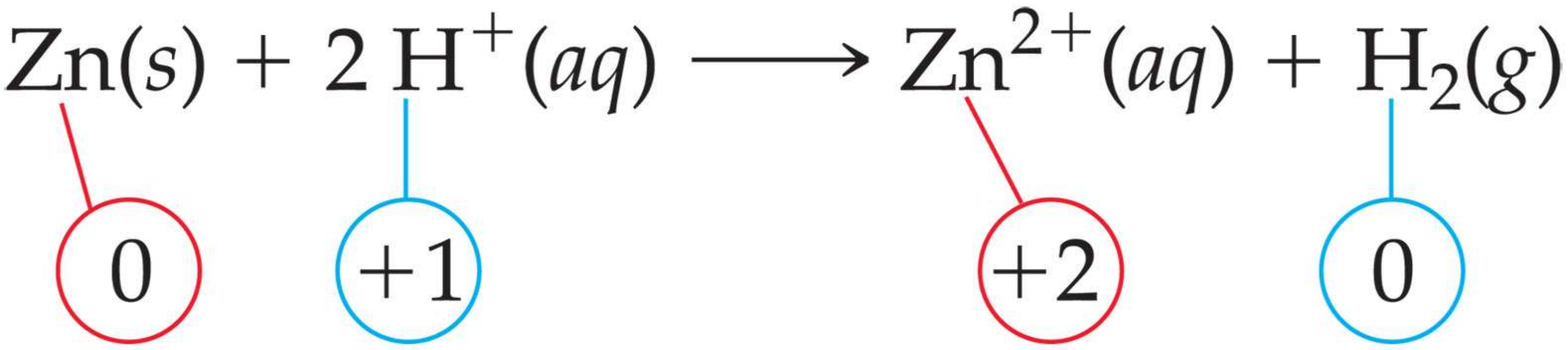
Oxidation and Reduction



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

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

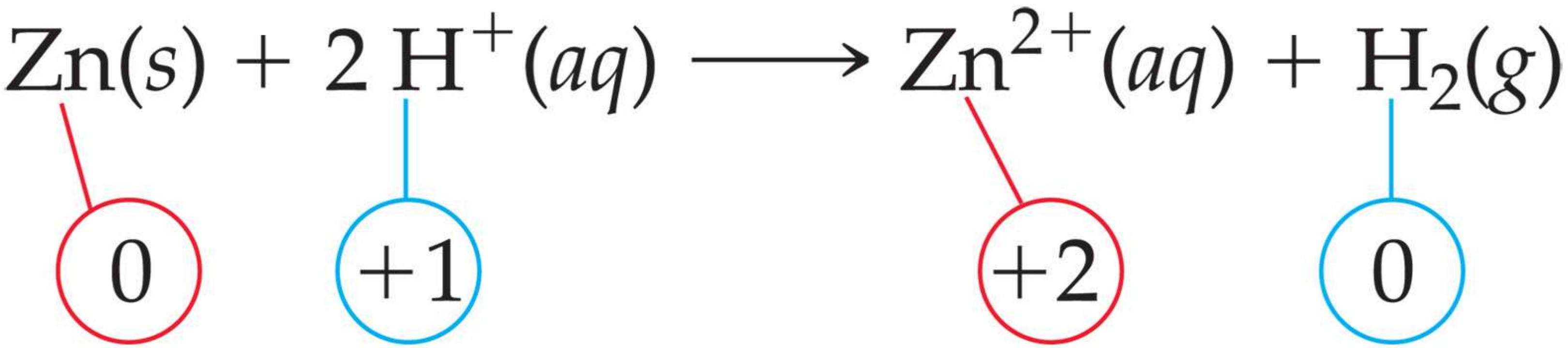
Oxidation and Reduction



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

- A species is reduced when it gains electrons.
  - Here, each of the H^+ gains an electron and they combine to form H_2.

Oxidation and Reduction



$$\underset{\boxed{0}}{\mathrm{Zn}}(s) + 2\,\underset{\boxed{+1}}{\mathrm{H}}{}^{+}(aq) \longrightarrow \underset{\boxed{+2}}{\mathrm{Zn}}{}^{2+}(aq) + \underset{\boxed{0}}{\mathrm{H}}{}_2(g)$$

- 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 in which it has an oxidation number of −1.
    - Hydrogen is −1 when bonded to a metal, +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 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.

Half-Reaction Method

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

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.
4. Multiply the half-reactions by integers so that the electrons gained and lost are the same.

Half-Reaction Method

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.

Half-Reaction Method

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

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

Half-Reaction Method

First, we assign oxidation numbers.

$$\overset{\overset{+7}{\downarrow}}{\mathrm{Mn}}\mathrm{O}_4^{-} + \overset{\overset{+3}{\downarrow}}{\mathrm{C}}_2\mathrm{O}_4^{2-} \longrightarrow \overset{\overset{+2}{\downarrow}}{\mathrm{Mn}}^{2+} + \overset{\overset{+4}{\downarrow}}{\mathrm{C}}\mathrm{O}_2$$

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:

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

Oxidation Half-Reaction

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

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

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

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.

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

Reduction Half-Reaction

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

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

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

Reduction Half-Reaction

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

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

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

Combining the Half-Reactions

Now we evaluate the two half-reactions together:

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

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

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

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

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

When we add these together, we get:

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

$$2\ Mn^{2+} + 8\ H_2O + 10\ CO_2 + 10\ e^-$$

Combining the Half-Reactions

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

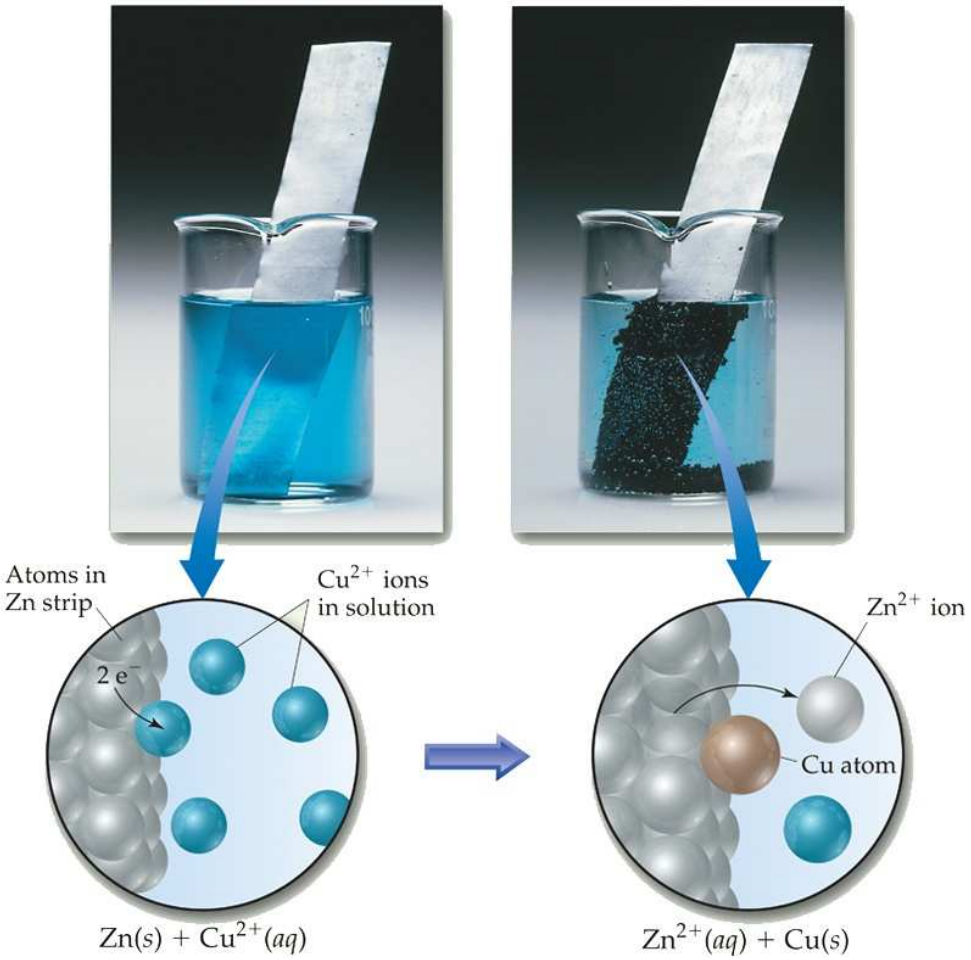
The only thing that appears on both sides are the electrons. Subtracting them, we are left with:

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

Balancing in Basic Solution

- If a reaction occurs in basic solution, one can balance it as if it occurred in acid.
- Once the equation is balanced, add OH^- to each side to “neutralize” the H^+ in the equation and create water in its place.
- If this produces water on both sides, you might have to subtract water from each side.

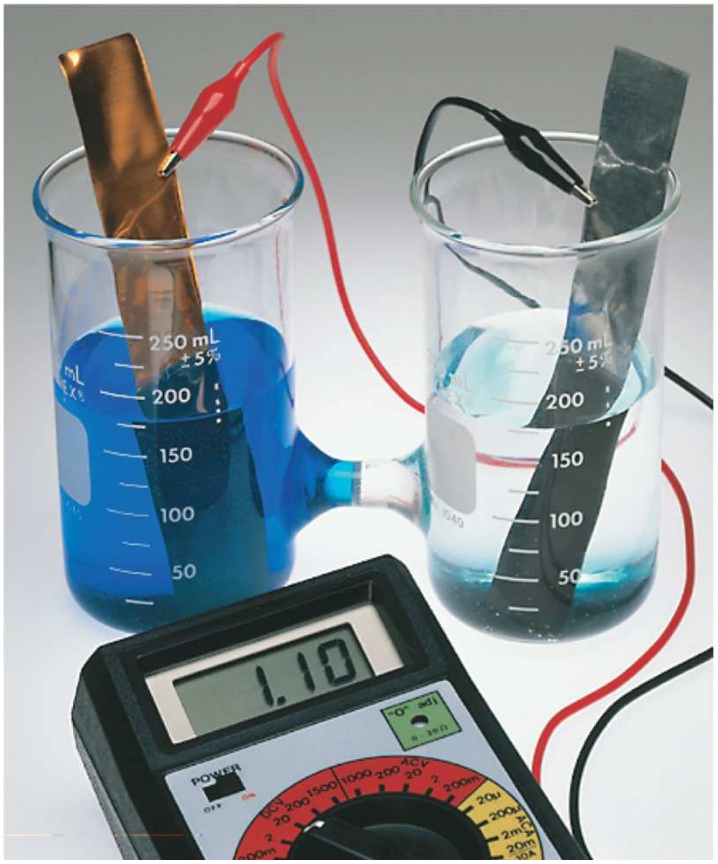
Voltaic Cells



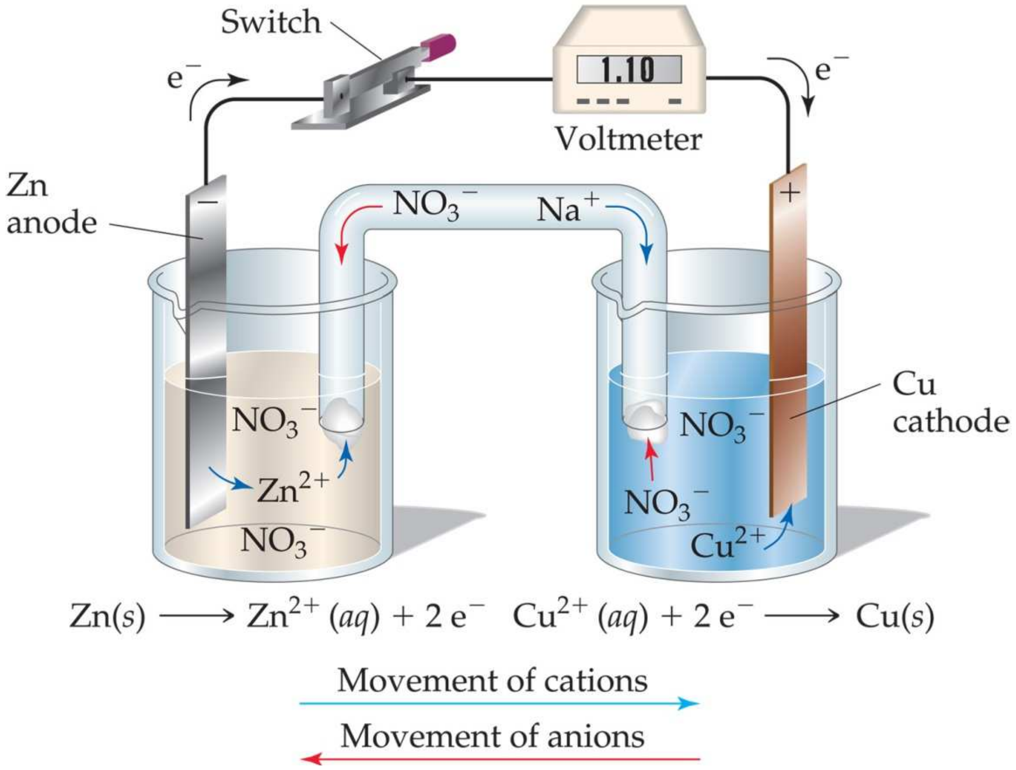
In spontaneous oxidation-reduction (redox) reactions, electrons are transferred and energy is released.

Voltaic Cells

- We can use that energy to do work if we make the electrons flow through an external device.
- We call such a setup a voltaic cell.

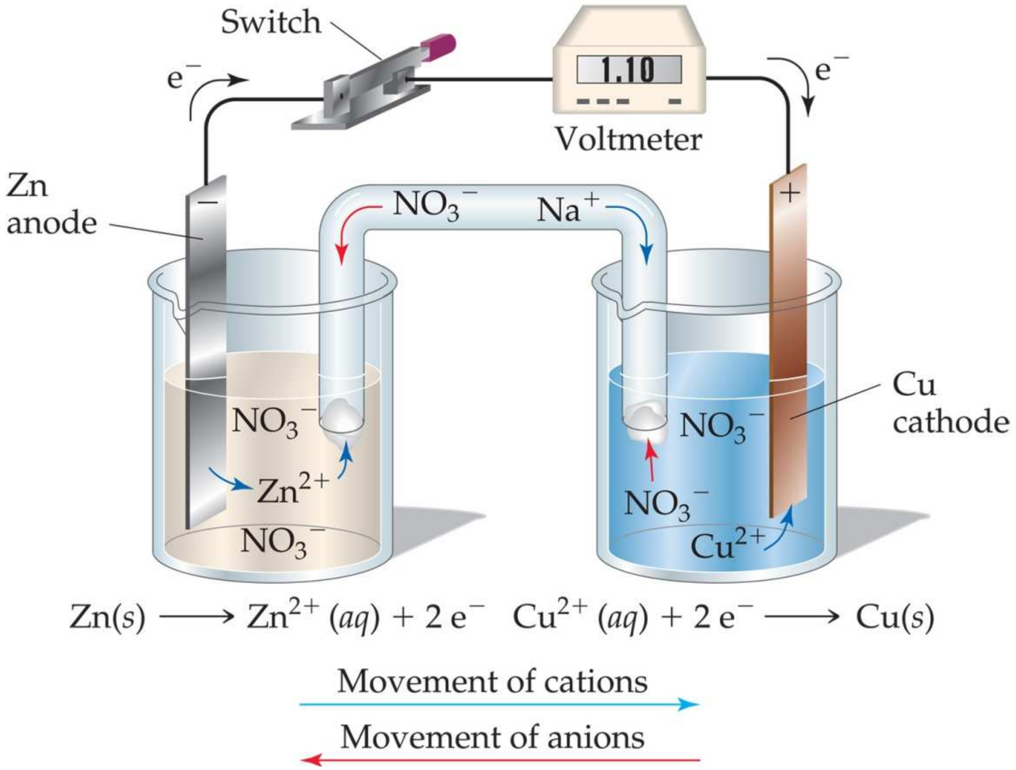


Voltaic Cells



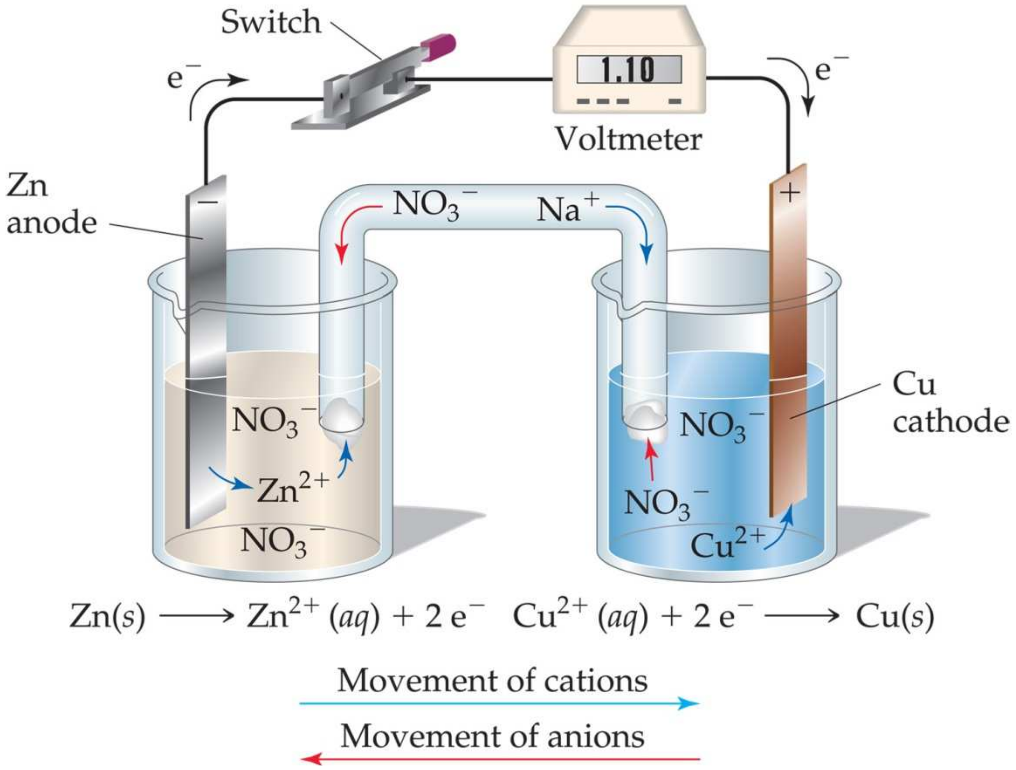
- A typical cell looks like this.
- The oxidation occurs at the anode.
- The reduction occurs at the cathode.

Voltaic Cells



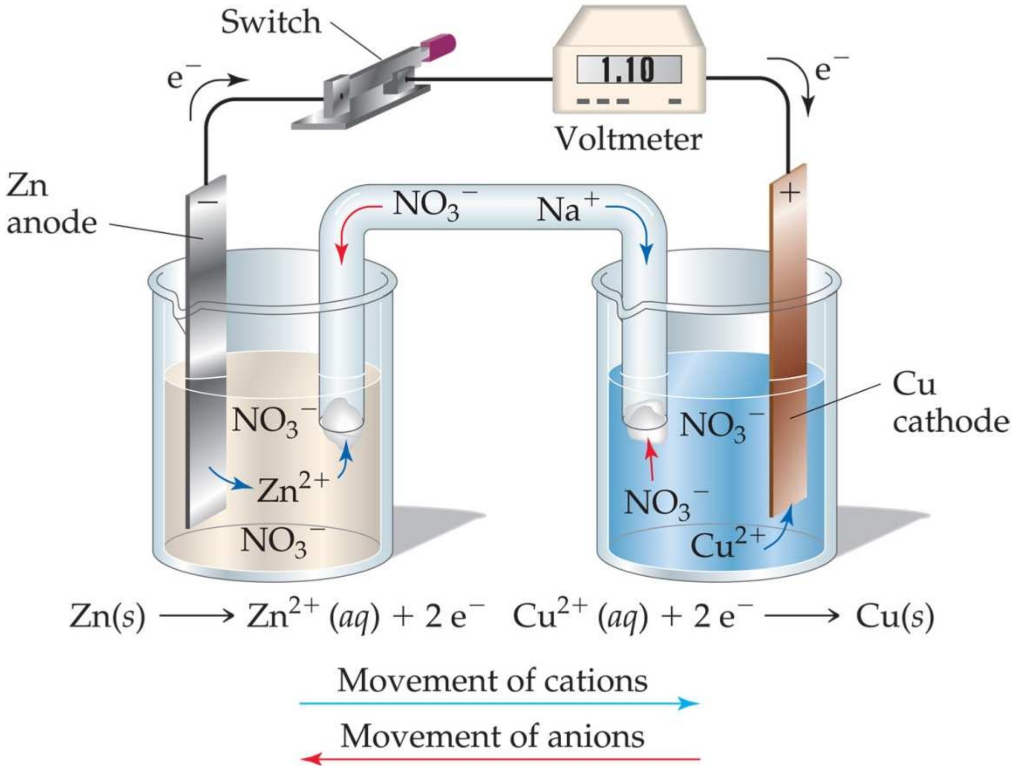
Once even one electron flows from the anode to the cathode, the charges in each beaker would not be balanced and the flow of electrons would stop.

Voltaic Cells



- Therefore, we use a salt bridge, usually a U-shaped tube that contains a salt solution, to keep the charges balanced.
  - ➢ Cations move toward the cathode.
  - ➢ Anions move toward the anode.

Voltaic Cells



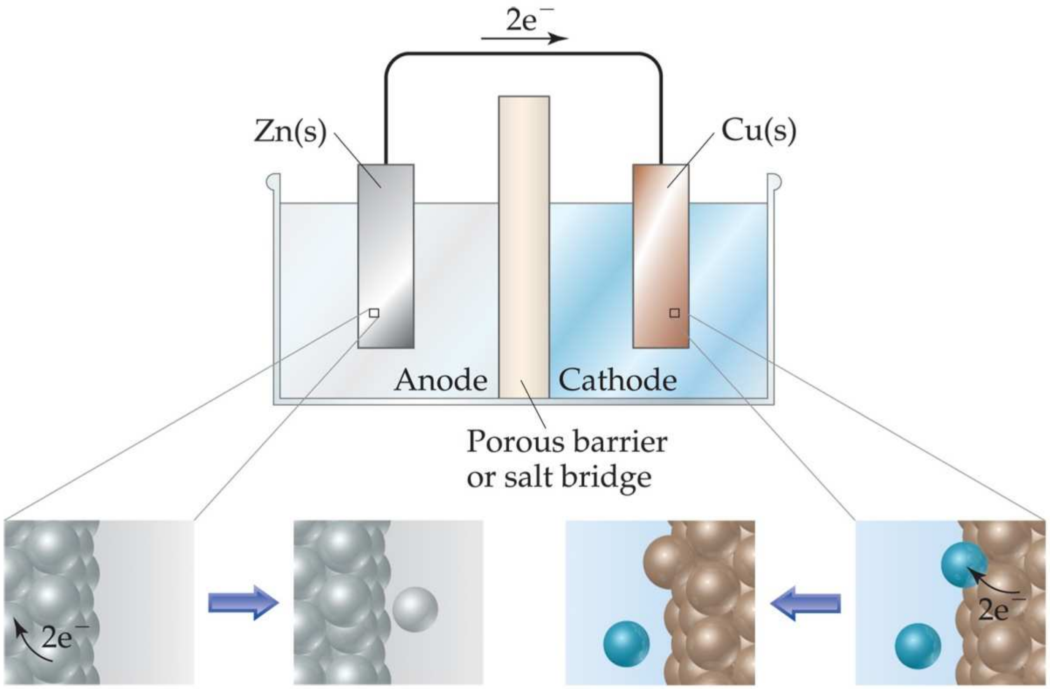
- Remember-

  Although anode and cathode are labeled with a – and + signs, this is not the charge on the electrode. The charges on electrodes are essentially zero.

  The – and + label tells us the electrode at which electrons are released to the external circuit.

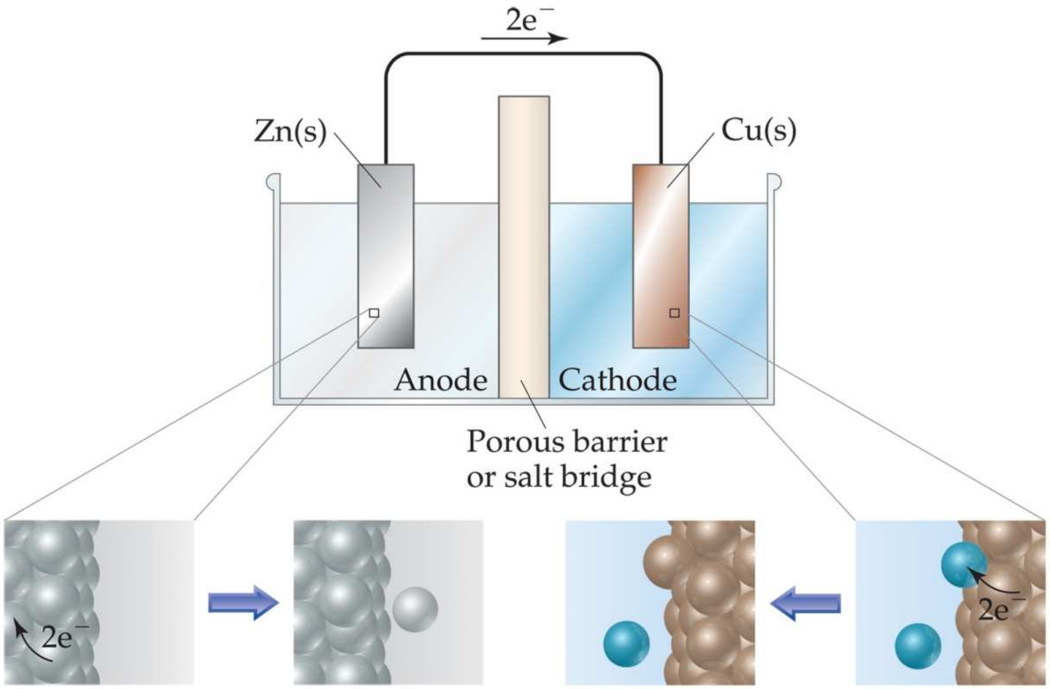
Voltaic Cells

- 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.



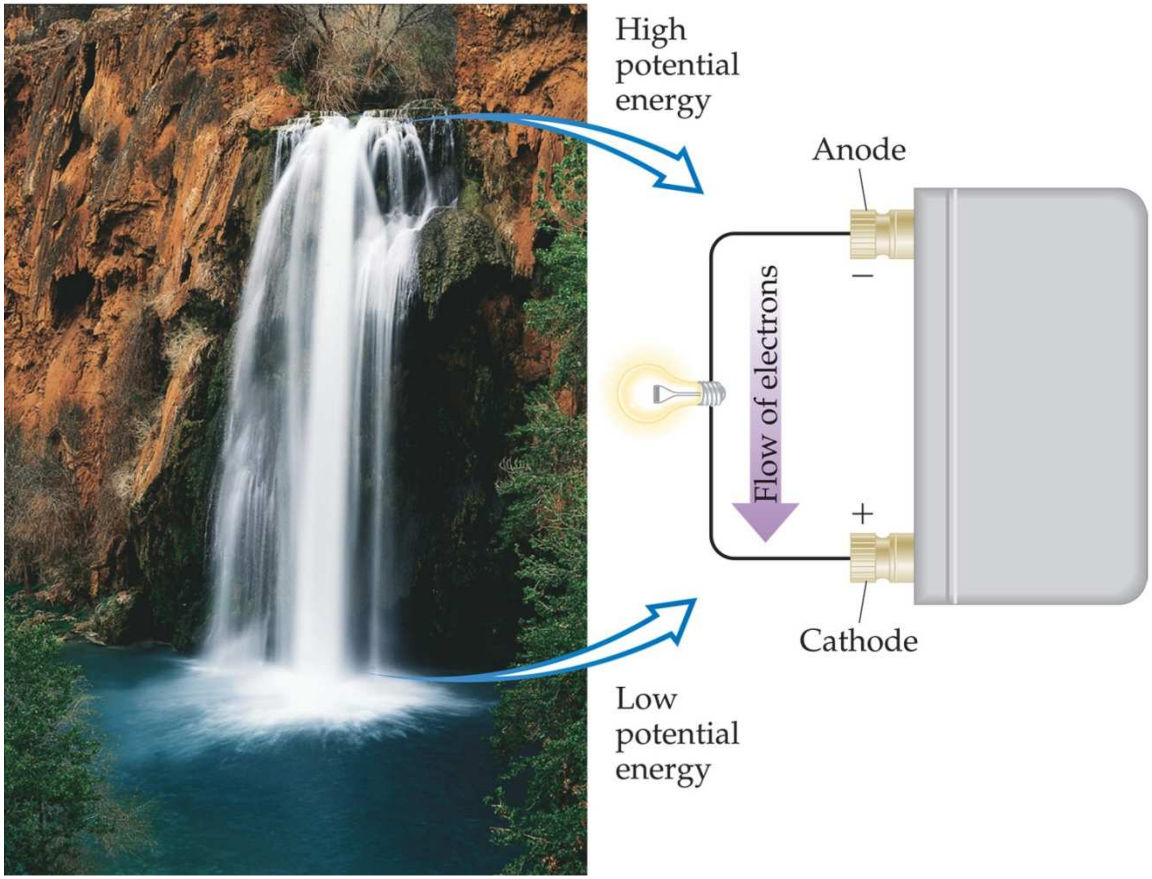
Voltaic Cells

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



Sample exercise

Practice exercise



- 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.

Potential Difference

- The energy that would be required to move a unit of electrical charge from one point to the other against the electrostatic field that is present. As potential difference increases, the current increases as well

Cell Difference

It is measured in volts (V).

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

Electromotive Force (emf)

- The potential difference between the anode and cathode in a cell is the driving force for the electrons to move across the external circuit hence it is called the electromotive force (emf).
- It is also called the cell potential, and is designated E_{cell}.

- Because E_{cell} is measured in volts it is also called the cell voltage.
- For any reaction in a cell that is spontaneous the cell potential will have to be positive.

The cell potential or emf or E_{cell} depends on:

- Specific reaction that occur at the cathode and anode,
- Concentrations of the reactants and products
- And the temperature, which we assume as $25^{o}C$ unless otherwise stated.

We are going to focus on cells that operate under standard conditions of-

- 25^{o}C
- 1M concentration of reactants and products and 1 atm pressure for those that are gases.

Under these conditions the emf is called the standard emf or the standard cell potential

So for the Zn/Cu voltaic cell

$Zn(s) + Cu^{2+}(aq,1M) \rightarrow Zn^{2+}(aq) + Cu(s)$ $E^{o}cell = +1.10V$

The superscript ^{o} indicates standard state conditions

Standard Reduction (Half Cell) Potential

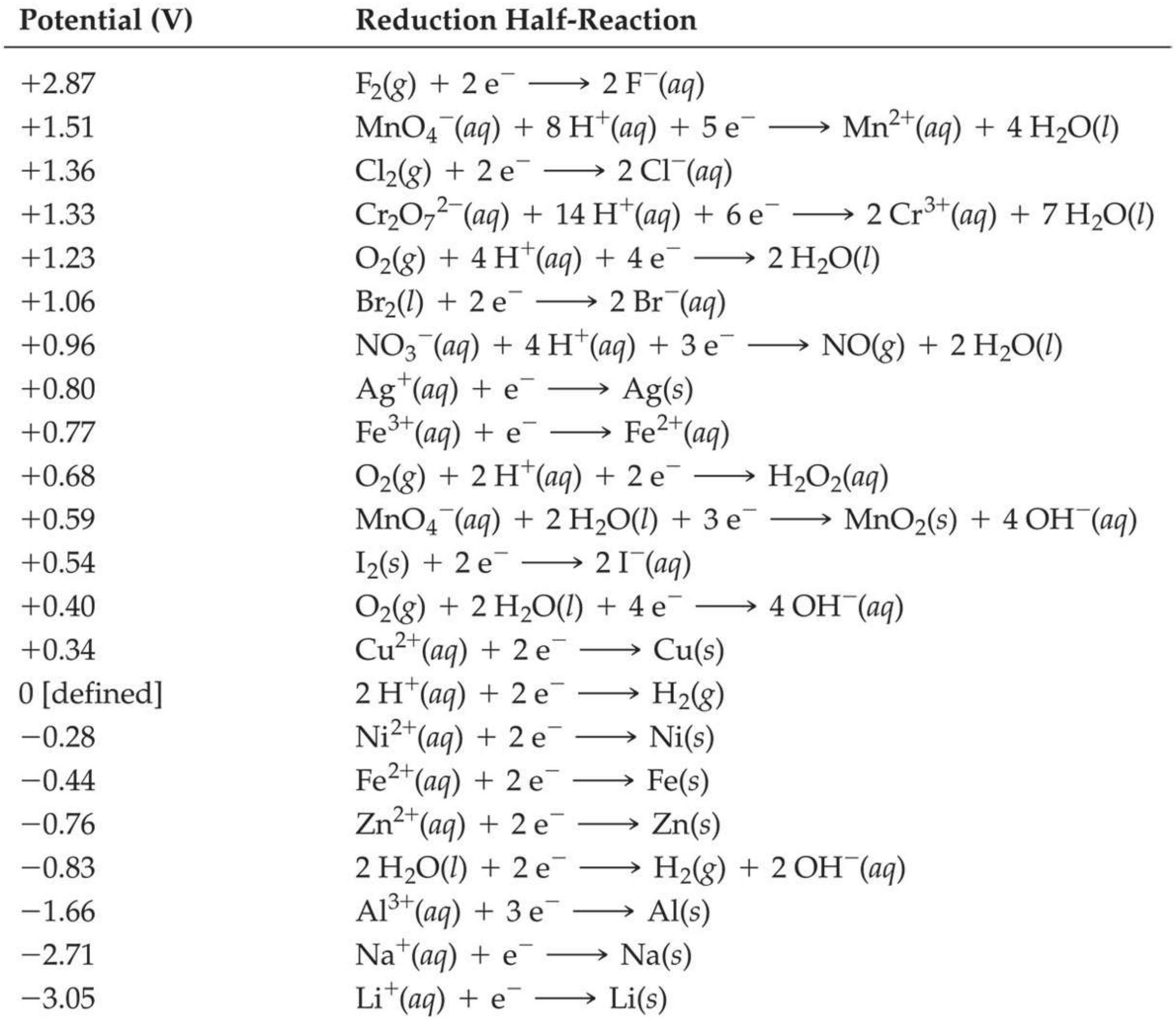
- We can tabulate the standard cell potential for al the possible cathode / anode combinations.
- But it is not really needed to do so.

- The cell potential is the difference between two electrode potentials
- By convention the potential associated with each electrode is the potential for reduction to occur at that electrode.
- Thus standard electrode potentials are the standard reduction potentials denoted E^{o}_{red}

- The cell potential is given by the standard reduction potential of the cathode reaction minus the standard reduction potential of the anode reaction

$$E^{o}_{Cell} = E^{o}_{red}\,(\text{cathode}) - E^{o}_{red}\,(\text{anode})$$

Standard Reduction Potentials



Potential (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	$Li^+(aq) + e^- \longrightarrow Li(s)$

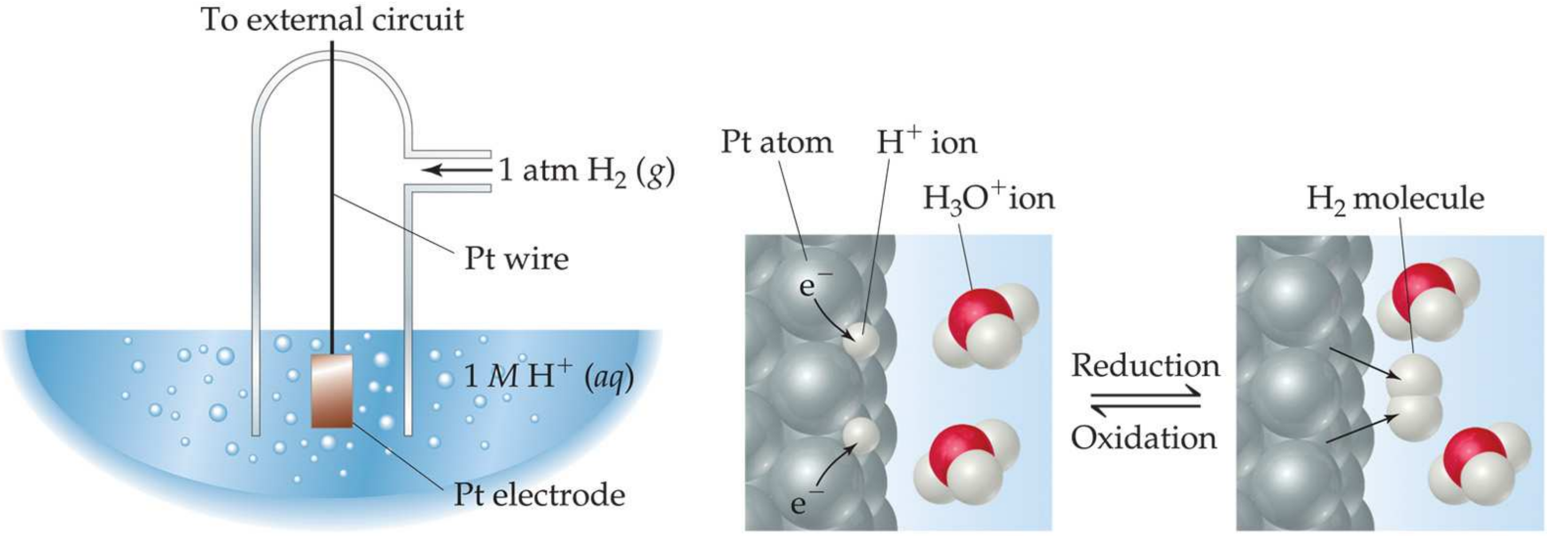
Reduction potentials for many electrodes have been measured and tabulated.

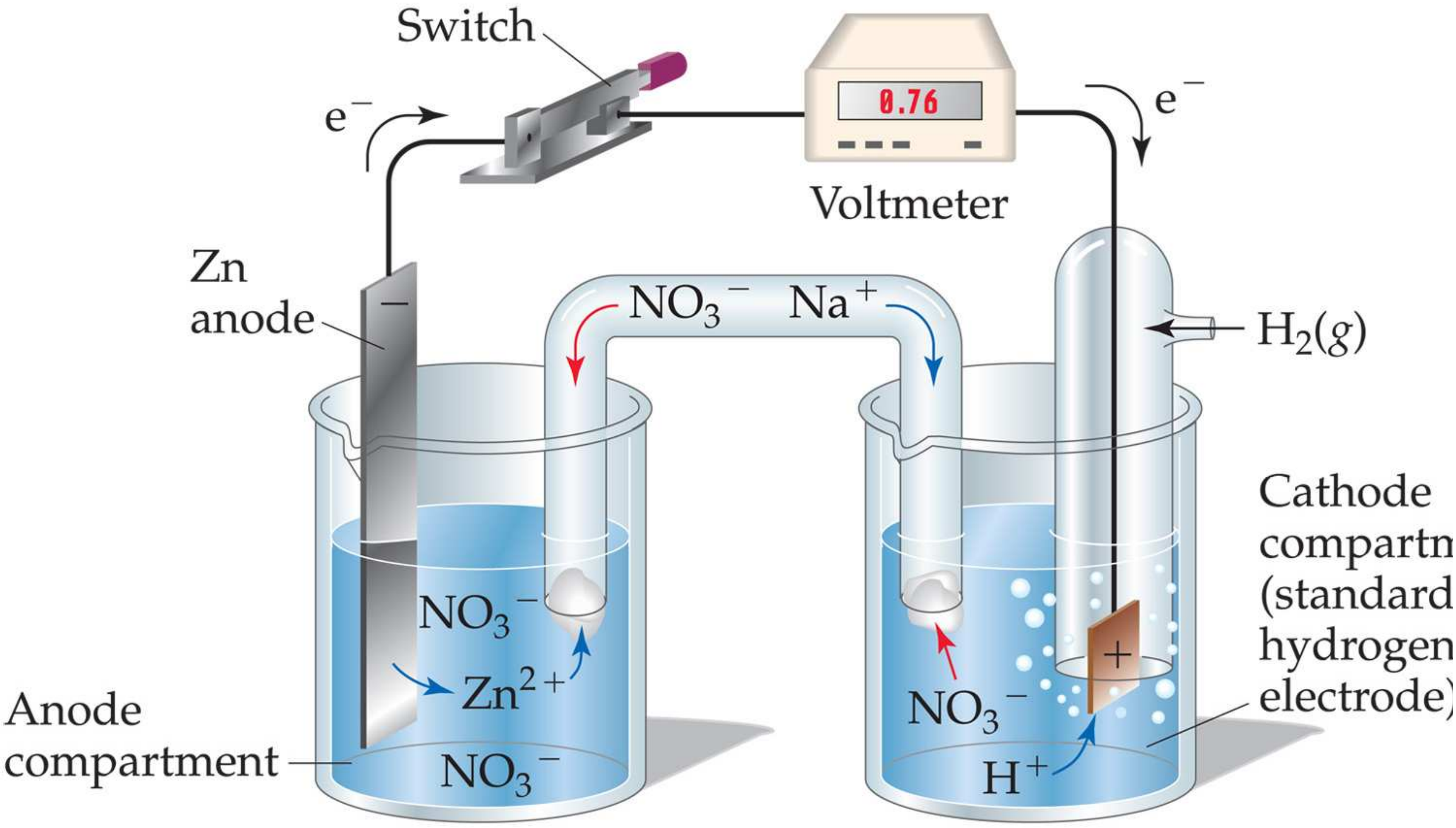
The standard Hydrogen electrode (SHE) has a potential of 0

Standard Hydrogen Electrode

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

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





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

PRACTICE EXERCISE

A voltaic cell is based on the half-reactions

$$In^{+}(aq) \longrightarrow In^{3+}(aq) + 2\,e^{-}$$

$$Br_2(l) + 2\,e^{-} \longrightarrow 2\,Br^{-}(aq)$$

The standard emf for this cell is 1.46 V. Using the data in Table 20.1, calculate E°_{red} for the reduction of In^{3+} to In^{+}.

PRACTICE EXERCISE

A voltaic cell is based on the half-reactions

$$In^{+}(aq) \longrightarrow In^{3+}(aq) + 2\,e^{-}$$

$$Br_2(l) + 2\,e^{-} \longrightarrow 2\,Br^{-}(aq)$$

The standard emf for this cell is 1.46 V. Using the data in Table 20.1, calculate E°_{red} for the reduction of In^{3+} to In^{+}.

For the Zn-Cu^{2+} voltaic cell shown in Figure 20.5, we have

$$\mathrm{Zn}(s) + \mathrm{Cu}^{2+}(aq, 1\ M) \longrightarrow \mathrm{Zn}^{2+}(aq, 1\ M) + \mathrm{Cu}(s) \qquad E^{\circ}_{\mathrm{cell}} = 1.10\ \mathrm{V}$$

Given that the standard reduction potential of Zn^{2+} to Zn(*s*) is –0.76 V, calculate the E°_{red} for the reduction of Cu^{2+} to Cu:

$$\mathrm{Cu}^{2+}(aq, 1\ M) + 2\ \mathrm{e}^{-} \longrightarrow \mathrm{Cu}(s)$$

For the Zn-Cu^{2+} voltaic cell shown in Figure 20.5, we have

$$\mathrm{Zn}(s) + \mathrm{Cu}^{2+}(aq, 1\,M) \longrightarrow \mathrm{Zn}^{2+}(aq, 1\,M) + \mathrm{Cu}(s) \qquad E^\circ_{\mathrm{cell}} = 1.10\ \mathrm{V}$$

Given that the standard reduction potential of Zn^{2+} to Zn(s) is –0.76 V, calculate the E°_{red} for the reduction of Cu^{2+} to Cu:

$$\mathrm{Cu}^{2+}(aq, 1\,M) + 2\,\mathrm{e}^- \longrightarrow \mathrm{Cu}(s)$$

Answer: –0.40 V

Using the standard reduction potentials listed in Table 20.1, calculate the standard emf for the voltaic cell described in Sample Exercise 20.4, which is based on the reaction

$$\mathrm{Cr_2O_7^{2-}}(aq) + 14\,\mathrm{H^+}(aq) + 6\,\mathrm{I^-}(aq) \longrightarrow 2\,\mathrm{Cr^{3+}}(aq) + 3\,\mathrm{I_2}(s) + 7\,\mathrm{H_2O}(l)$$

PRACTICE EXERCISE

Using data in Table 20.1, calculate the standard emf for a cell that employs the following overall cell reaction:

$$2\,\mathrm{Al}(s) + 3\,\mathrm{I_2}(s) \longrightarrow 2\,\mathrm{Al^{3+}}(aq) + 6\,\mathrm{I^-}(aq)$$

PRACTICE EXERCISE

Using data in Table 20.1, calculate the standard emf for a cell that employs the following overall cell reaction:

$$2\,\mathrm{Al}(s) + 3\,\mathrm{I_2}(s) \longrightarrow 2\,\mathrm{Al^{3+}}(aq) + 6\,\mathrm{I^-}(aq)$$

Answer: +2.20 V

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.

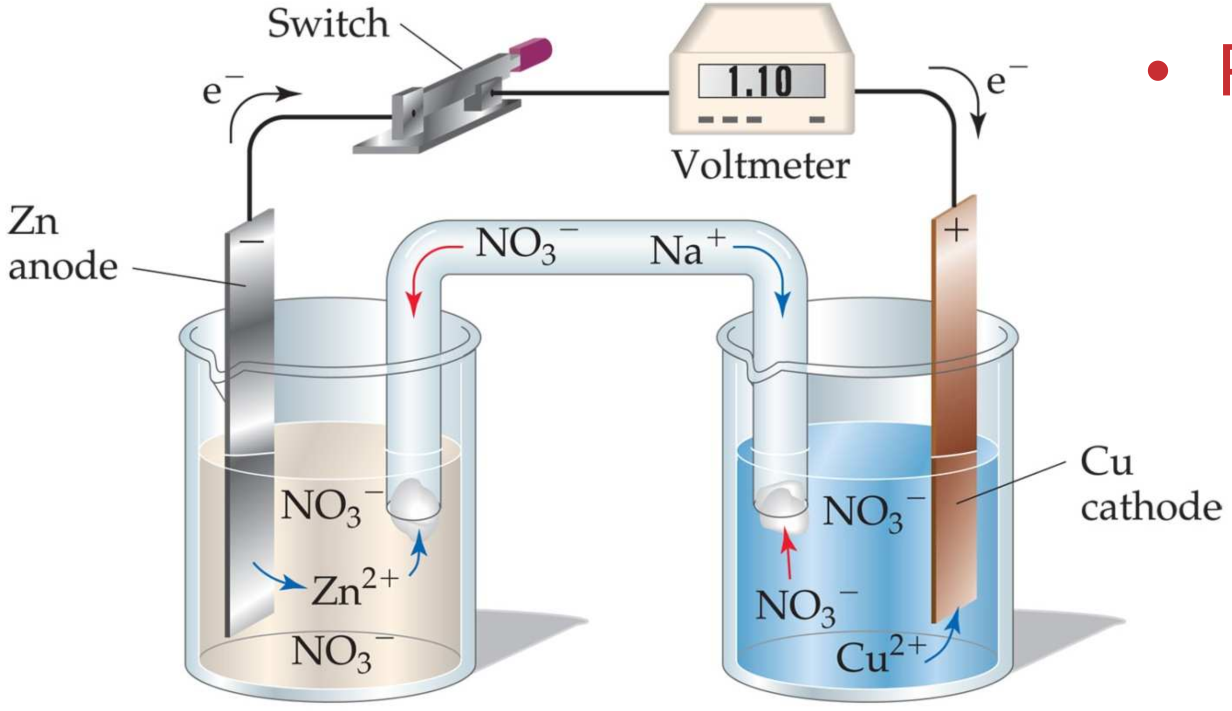
Cell Potentials

- For the oxidation in this cell,

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

- For the reduction,

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



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

Cell Potentials

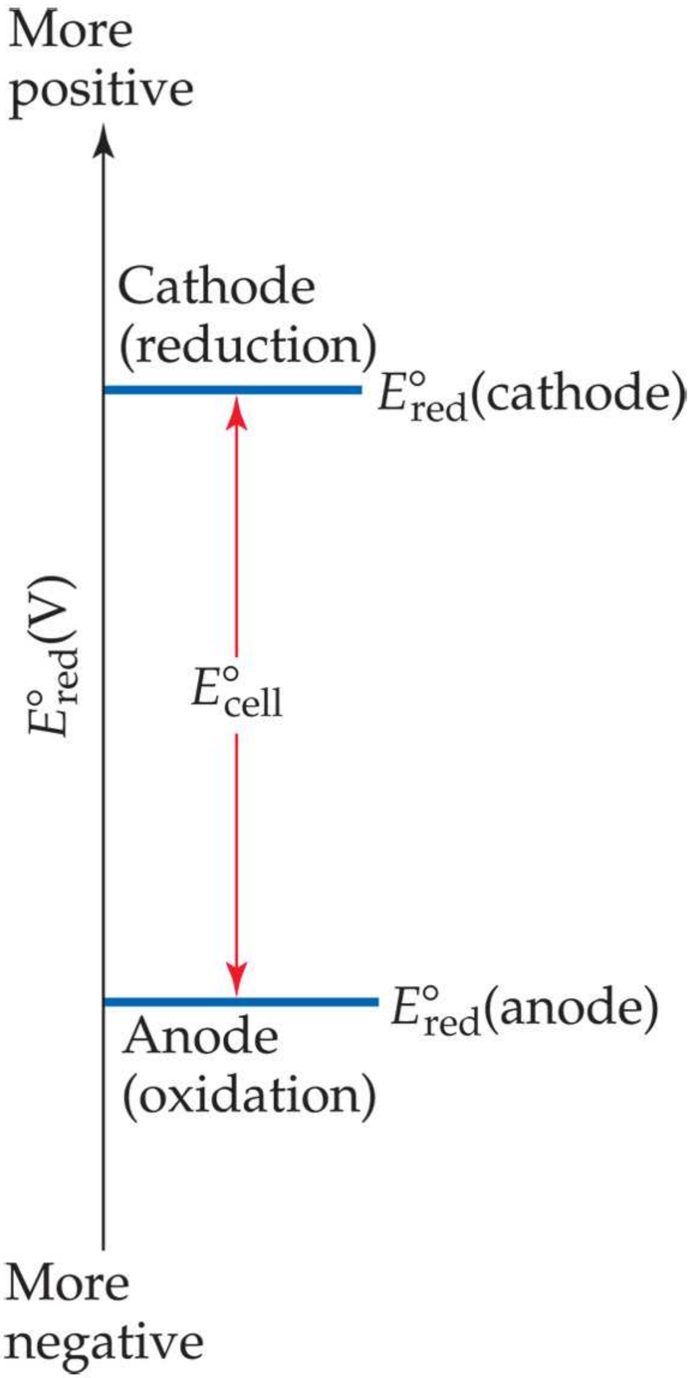
$$E^\circ_{\text{cell}} = E^\circ_{\text{red}}\ (\text{cathode}) - E^\circ_{\text{red}}\ (\text{anode})$$

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

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

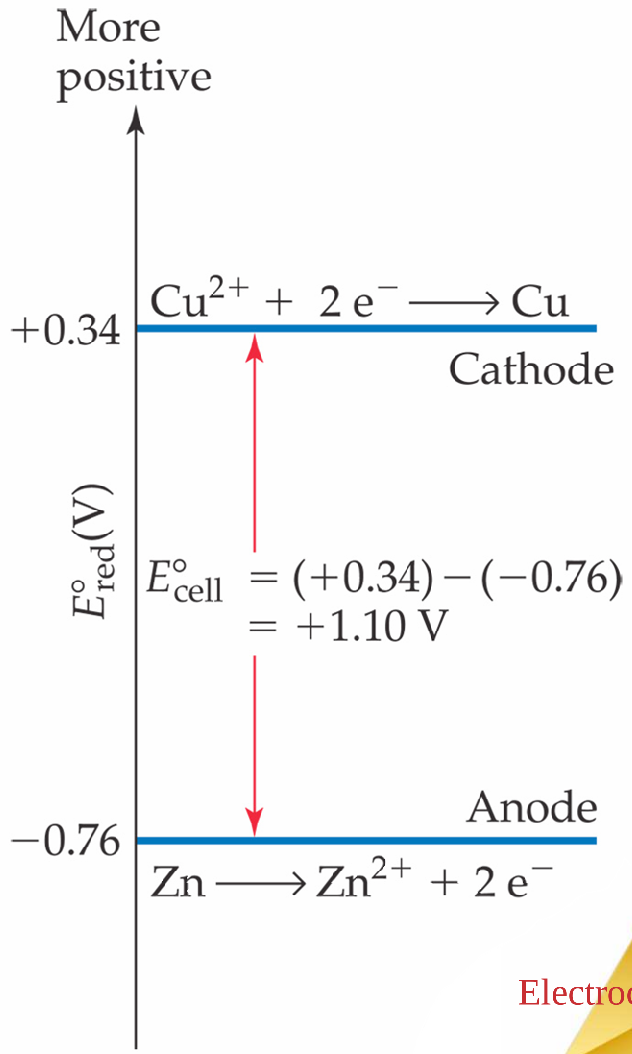
- If we use Hess’s Law

- In any voltaic cell the reaction at the cathode has more positive value of E^{o}_{red} than does the reaction at the anode.


More positive
Cathode (reduction)
E°_{red}(cathode)
E°_{red}(V)
E°_{cell}
E°_{red}(anode)
Anode (oxidation)
More negative

Oxidizing and Reducing Agents

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



A voltaic cell is based on the following two standard half-reactions:

$$\mathrm{Cd^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Cd}(s)$$
$$\mathrm{Sn^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Sn}(s)$$

By using the data in Appendix E, determine **(a)** the half-reactions that occur at the cathode and the anode, and **(b)** the standard cell potential

Strengths of Oxidizing and Reducing Agents

- The more positive the E^{o}_{red} value of the half reaction, the greater is the tendency of the reactant of the half reaction to be reduced and therefore to oxidize other species.

  $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

The E^{o}_{red} value for Cu^{2+} is 0.34 V and for Zn is -0.76V

Frequently used Oxidizing Agents

- Halogens
- O_2
- Oxianions whose central atoms have high oxidation states

MnO_4^{-}

$Cr_2O_7^{2-}$

NO_3^{-}

All these undergo reduction with

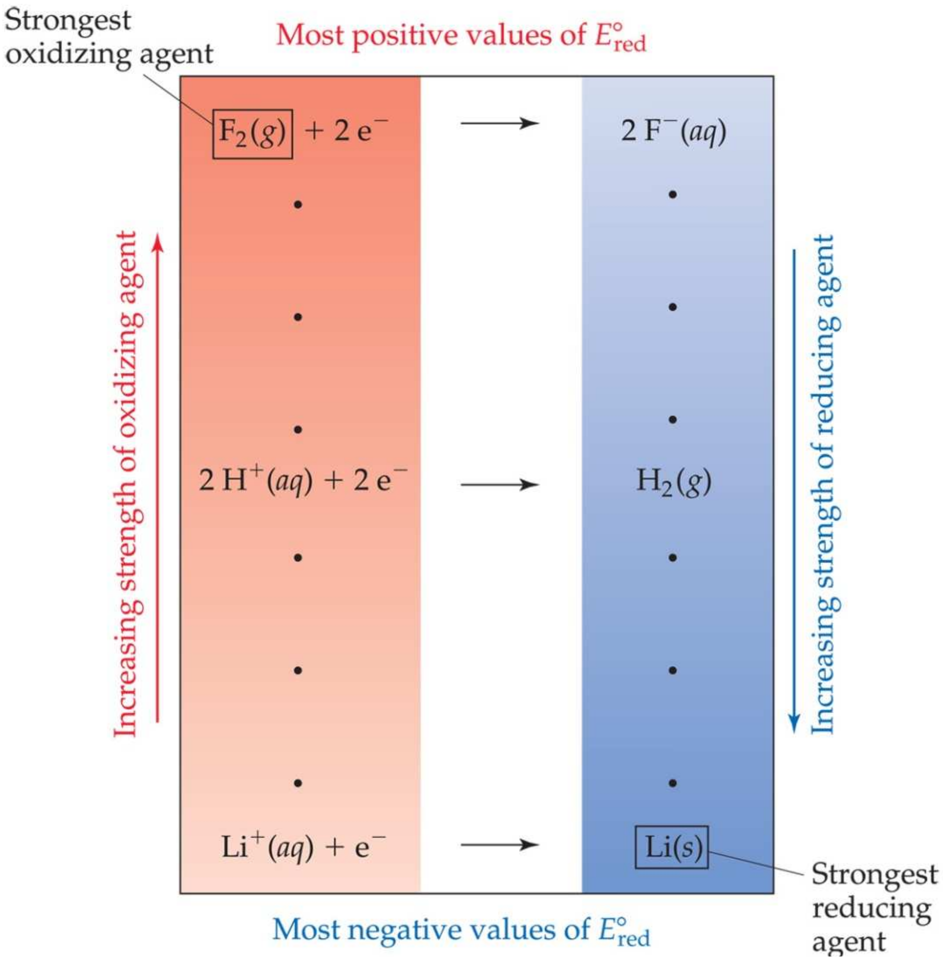
Large positive values of E^o_{red}

Frequently used Reducing Agents

- H_2
- Active metals

  Alkali and Alkaline earth metals
- Zn and Iron – the metals with negative E^o_{red} values.

Oxidizing and Reducing Agents



Strongest oxidizing agent

Most positive values of E°_{red}

$\boxed{F_2(g)} + 2e^- \longrightarrow 2F^-(aq)$

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

$Li^+(aq) + e^- \longrightarrow \boxed{Li(s)}$

Increasing strength of oxidizing agent

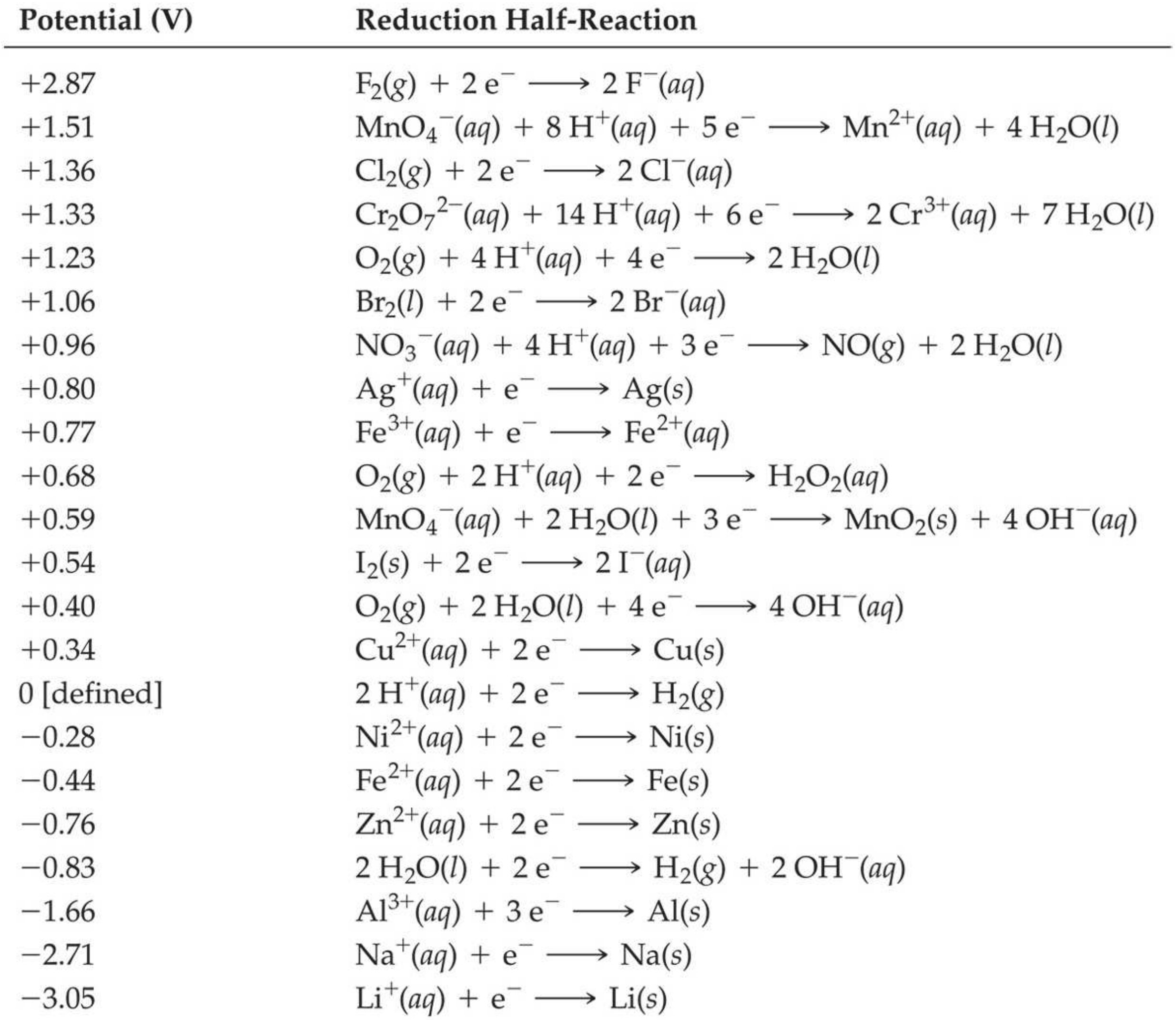
Increasing strength of reducing agent

Most negative values of E°_{red}

Strongest reducing agent

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

Standard Reduction Potentials



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

Reduction potentials for many electrodes have been measured and tabulated.

The standard Hydrogen electrode (SHE) has a potential of 0

Free Energy and Redox Reactions

- We know by now that Voltaic Cells use redox reactions that occur spontaneously
- How do we find out if a redox reaction will be spontaneous

- Do you remember the reaction:

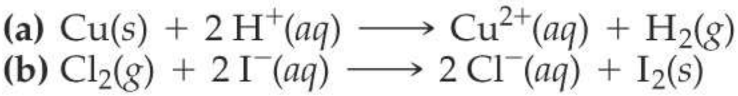
$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}}\ (\text{cathode}) - E^{\circ}_{\text{red}}\ (\text{anode})$$

- We can rewrite this equation more generally as:

$$E^{\circ} = E^{\circ}_{\text{red}}\ (\text{reduction process}) - E^{\circ}_{\text{red}}\ (\text{oxidation process})$$

A positive value of E indicates a spontaneous process and a negative value indicates a nonspontaneous process

Using standard reduction potentials (Table 20.1), determine whether the following reactions are spontaneous under standard conditions.



(a) $Cu(s) + 2\,H^+(aq) \longrightarrow Cu^{2+}(aq) + H_2(g)$
(b) $Cl_2(g) + 2\,I^-(aq) \longrightarrow 2\,Cl^-(aq) + I_2(s)$

a. Now find out which one is the oxidation and which one is the reduction reaction

b. Then find the E^o_{red} valus from a table

c. Now fill these values in the formula

$E^\circ = E^\circ_{red}$ (reduction process) $- E^\circ_{red}$ (oxidation process)

Now remember that a positive value means a spontaneous process.

If the value is negative the reverse reaction will be spotaneous.

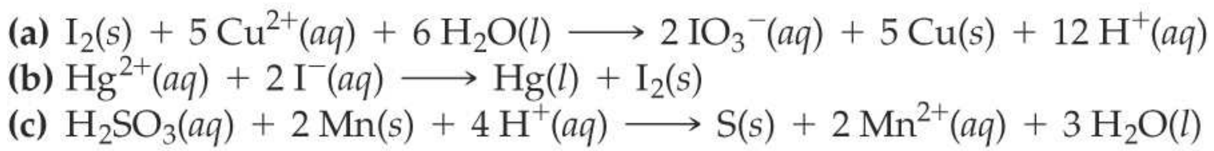
Using standard reduction potentials (Table 20.1), determine whether the following reactions are spontaneous under standard conditions.

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

(b) $Cl_2(g) + 2\,I^-(aq) \longrightarrow 2\,Cl^-(aq) + I_2(s)$

PRACTICE EXERCISE

Using the standard reduction potentials listed in Appendix E, determine which of the following reactions are spontaneous under standard conditions:



(a) $I_2(s) + 5\,Cu^{2+}(aq) + 6\,H_2O(l) \longrightarrow 2\,IO_3^{-}(aq) + 5\,Cu(s) + 12\,H^{+}(aq)$

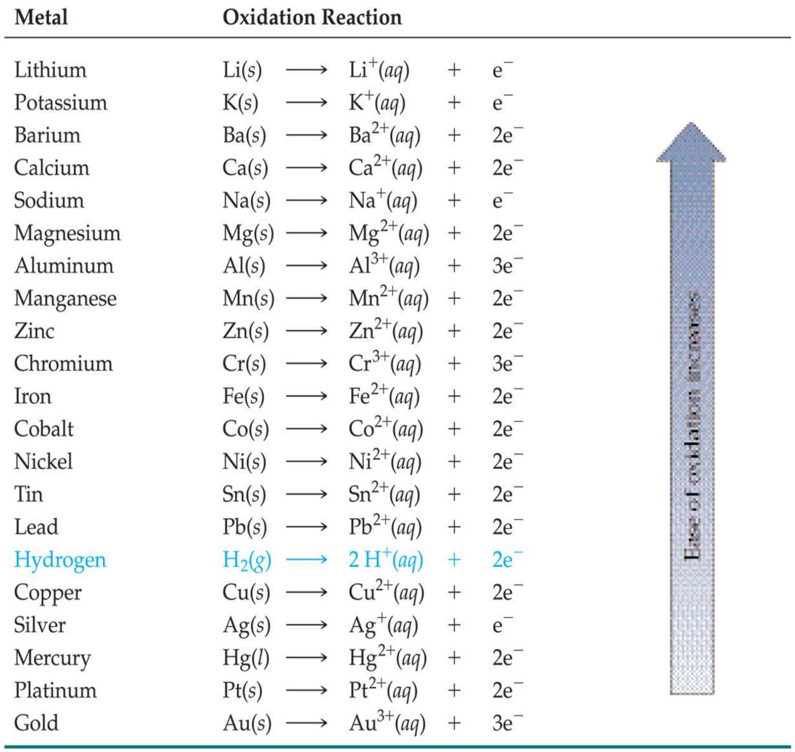
(b) $Hg^{2+}(aq) + 2\,I^{-}(aq) \longrightarrow Hg(l) + I_2(s)$

(c) $H_2SO_3(aq) + 2\,Mn(s) + 4\,H^{+}(aq) \longrightarrow S(s) + 2\,Mn^{2+}(aq) + 3\,H_2O(l)$

- Do you remember the activity series from chapter 4?

- Do you remember the activity series from chapter 4?
- You do not !!!!?????
- How could you

Activity Series



Metal	Oxidation Reaction
Lithium	$\mathrm{Li}(s) \longrightarrow \mathrm{Li}^{+}(aq) + e^{-}$
Potassium	$\mathrm{K}(s) \longrightarrow \mathrm{K}^{+}(aq) + e^{-}$
Barium	$\mathrm{Ba}(s) \longrightarrow \mathrm{Ba}^{2+}(aq) + 2e^{-}$
Calcium	$\mathrm{Ca}(s) \longrightarrow \mathrm{Ca}^{2+}(aq) + 2e^{-}$
Sodium	$\mathrm{Na}(s) \longrightarrow \mathrm{Na}^{+}(aq) + e^{-}$
Magnesium	$\mathrm{Mg}(s) \longrightarrow \mathrm{Mg}^{2+}(aq) + 2e^{-}$
Aluminum	$\mathrm{Al}(s) \longrightarrow \mathrm{Al}^{3+}(aq) + 3e^{-}$
Manganese	$\mathrm{Mn}(s) \longrightarrow \mathrm{Mn}^{2+}(aq) + 2e^{-}$
Zinc	$\mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq) + 2e^{-}$
Chromium	$\mathrm{Cr}(s) \longrightarrow \mathrm{Cr}^{3+}(aq) + 3e^{-}$
Iron	$\mathrm{Fe}(s) \longrightarrow \mathrm{Fe}^{2+}(aq) + 2e^{-}$
Cobalt	$\mathrm{Co}(s) \longrightarrow \mathrm{Co}^{2+}(aq) + 2e^{-}$
Nickel	$\mathrm{Ni}(s) \longrightarrow \mathrm{Ni}^{2+}(aq) + 2e^{-}$
Tin	$\mathrm{Sn}(s) \longrightarrow \mathrm{Sn}^{2+}(aq) + 2e^{-}$
Lead	$\mathrm{Pb}(s) \longrightarrow \mathrm{Pb}^{2+}(aq) + 2e^{-}$
Hydrogen	$\mathrm{H}_2(g) \longrightarrow 2\,\mathrm{H}^{+}(aq) + 2e^{-}$
Copper	$\mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2+}(aq) + 2e^{-}$
Silver	$\mathrm{Ag}(s) \longrightarrow \mathrm{Ag}^{+}(aq) + e^{-}$
Mercury	$\mathrm{Hg}(l) \longrightarrow \mathrm{Hg}^{2+}(aq) + 2e^{-}$
Platinum	$\mathrm{Pt}(s) \longrightarrow \mathrm{Pt}^{2+}(aq) + 2e^{-}$
Gold	$\mathrm{Au}(s) \longrightarrow \mathrm{Au}^{3+}(aq) + 3e^{-}$

- Decreasing ease of oxidation
- Active metals to noble metals
- Any metal on the list can be oxidized by the ions of elements below it
- $2\mathrm{Li} + \mathrm{Cu}^{2+} \rightarrow 2\mathrm{Li}^{+} + \mathrm{Cu}$

LEO GER

Electrochemistry

$2Li + Cu^{2+} \rightarrow 2Li^{+} + Cu$

LEO GER

$$E^{\circ} = E^{\circ}_{red}\ (\text{reduction process}) - E^{\circ}_{red}\ (\text{oxidation process})$$

$E^{o} = (+0.34V) – (-3.05V) = 0.34\ V + 3.05\ V = +3.39\ V$

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

So even if the ions are doubled in the reaction the reduction potential is not.

Gibbs Free Energy

- $\Delta G = \Delta H + T\Delta S$

Δ H= Change in enthalpy

Δ S= Change in entropy

The change in Gibbs Energy (free energy change) is a measure of the spontaneity of a process at constant temperature and pressure.

Because emf, E of a redox reaction is an indication of the spontaneity of the reaction there is a relationship between ΔG and E

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

As n and F are both positive values a positive value of E leads to a negative value of ΔG.

Therefore

A positive value of E and a negative value of ΔG both represent a spontaneous reaction

Under standard conditions,

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

This is an important equation which relates the standard emf E^o to the standard free energy change ΔG°

ΔG° is related to the equilibrium constant K

$$\Delta G^\circ = - RT\ \mathrm{In}\ K$$

the E^o can be related to the K too.

- Problem

Nernst Equation

- Remember that

$$\Delta G = \Delta G° + RT \ln Q$$

- This means

$$-nFE = -nFE° + RT \ln Q$$

Nernst Equation

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

$$E = E° - \frac{RT}{nF} \ln Q$$

or, using base-10 logarithms,

$$E = E° - \frac{2.303\ RT}{nF} \ln Q$$

Nernst Equation

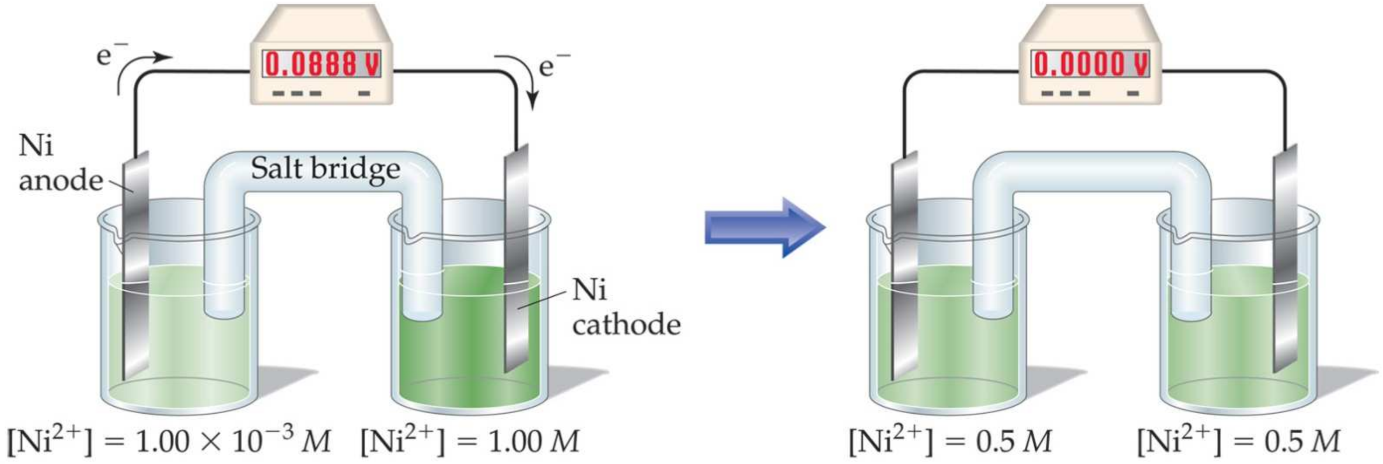
At room temperature (298 K),

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

Thus the equation becomes

$$E = E^\circ - \frac{0.0592}{n} \ln Q$$

Concentration Cells

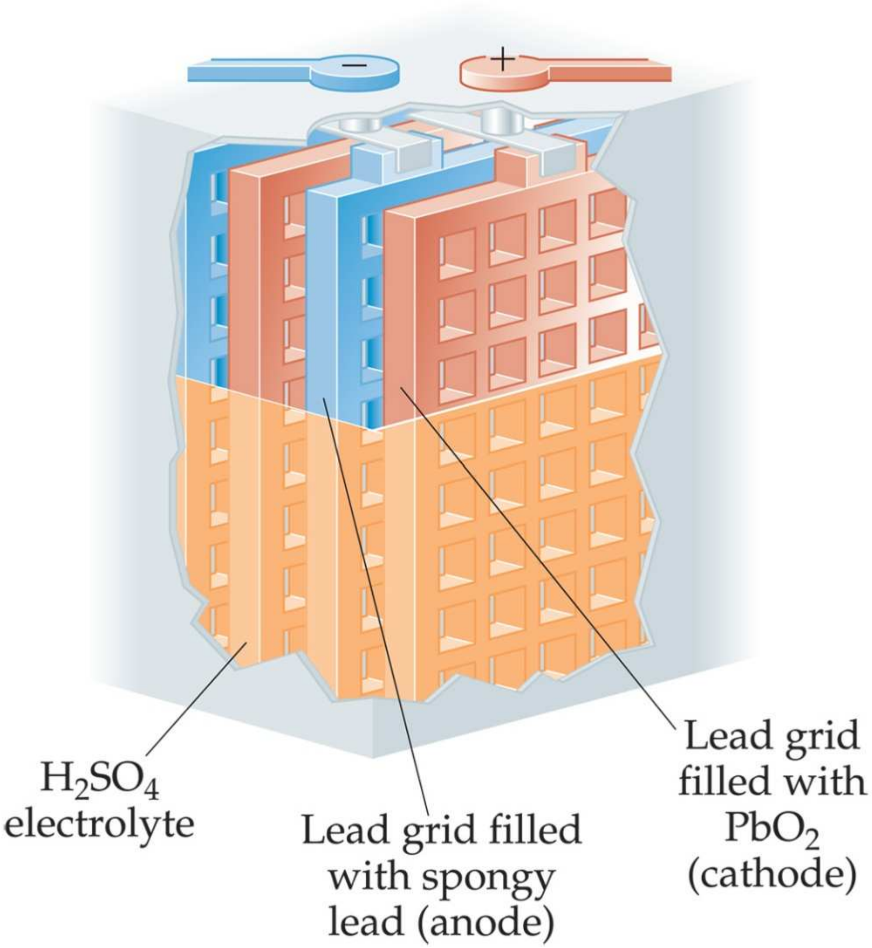


- Notice that the Nernst equation implies that a cell could be created that has the same substance at both electrodes.
- For such a cell, E°_{cell} would be 0, but *Q* would not.
- Therefore, as long as the concentrations are different, *E* will not be 0.

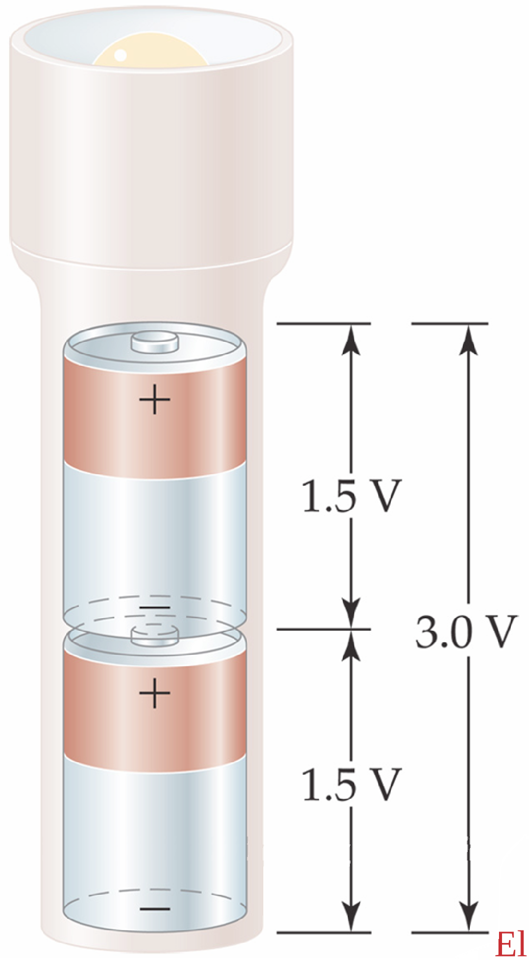
Applications of Oxidation-Reduction Reactions

Electrochemistry

Batteries

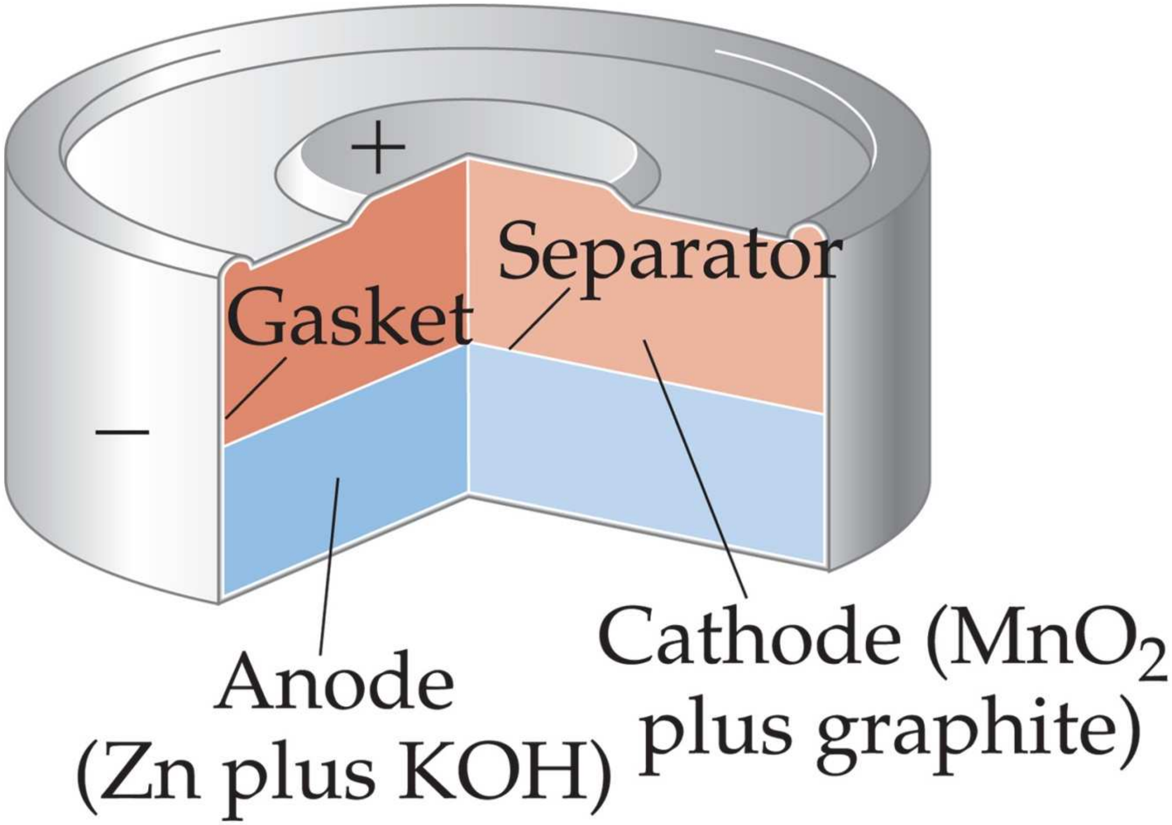


−
+
H_2SO_4 electrolyte
Lead grid filled with spongy lead (anode)
Lead grid filled with PbO_2 (cathode)

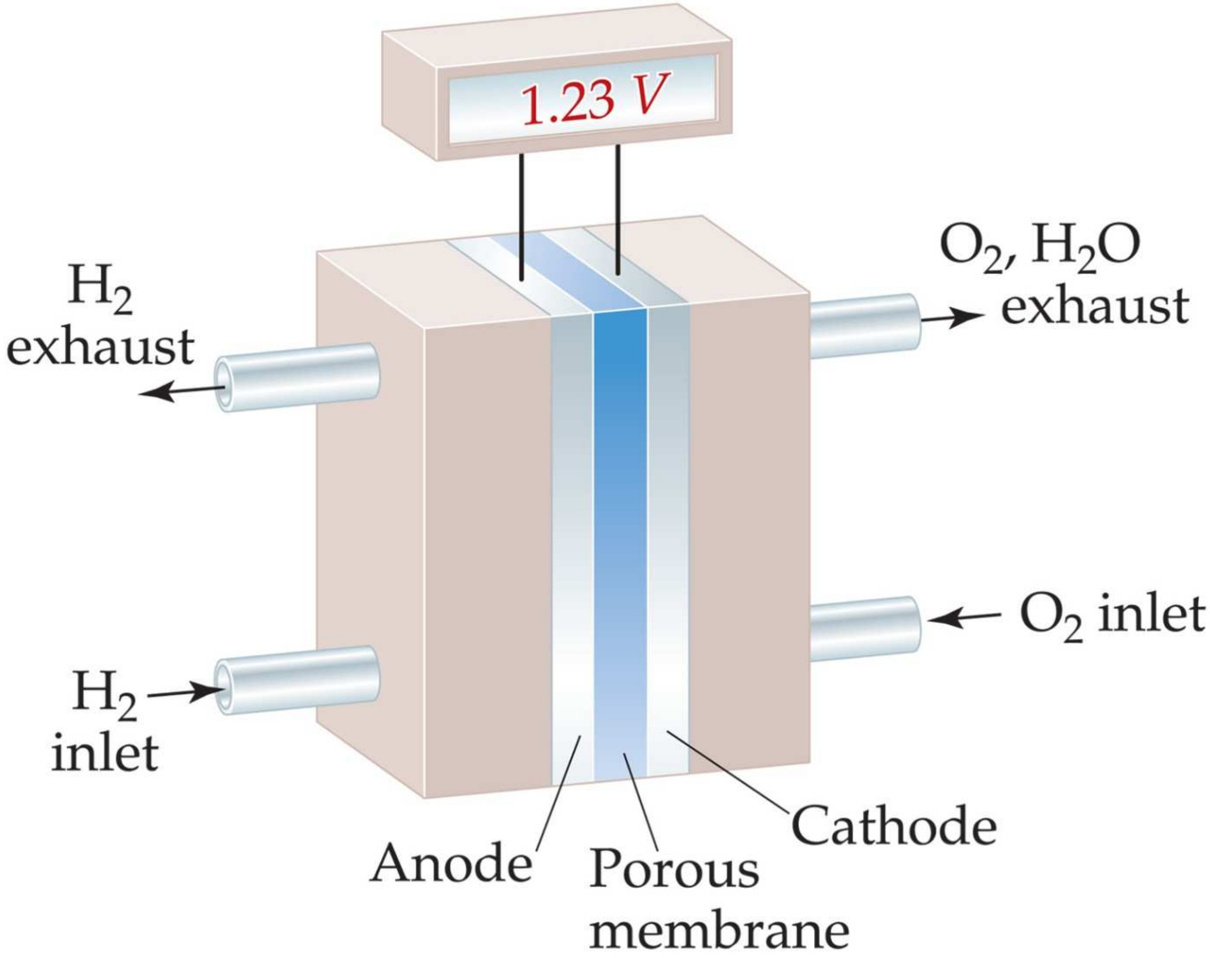


+
−
+
−
1.5 V
1.5 V
3.0 V

Alkaline Batteries

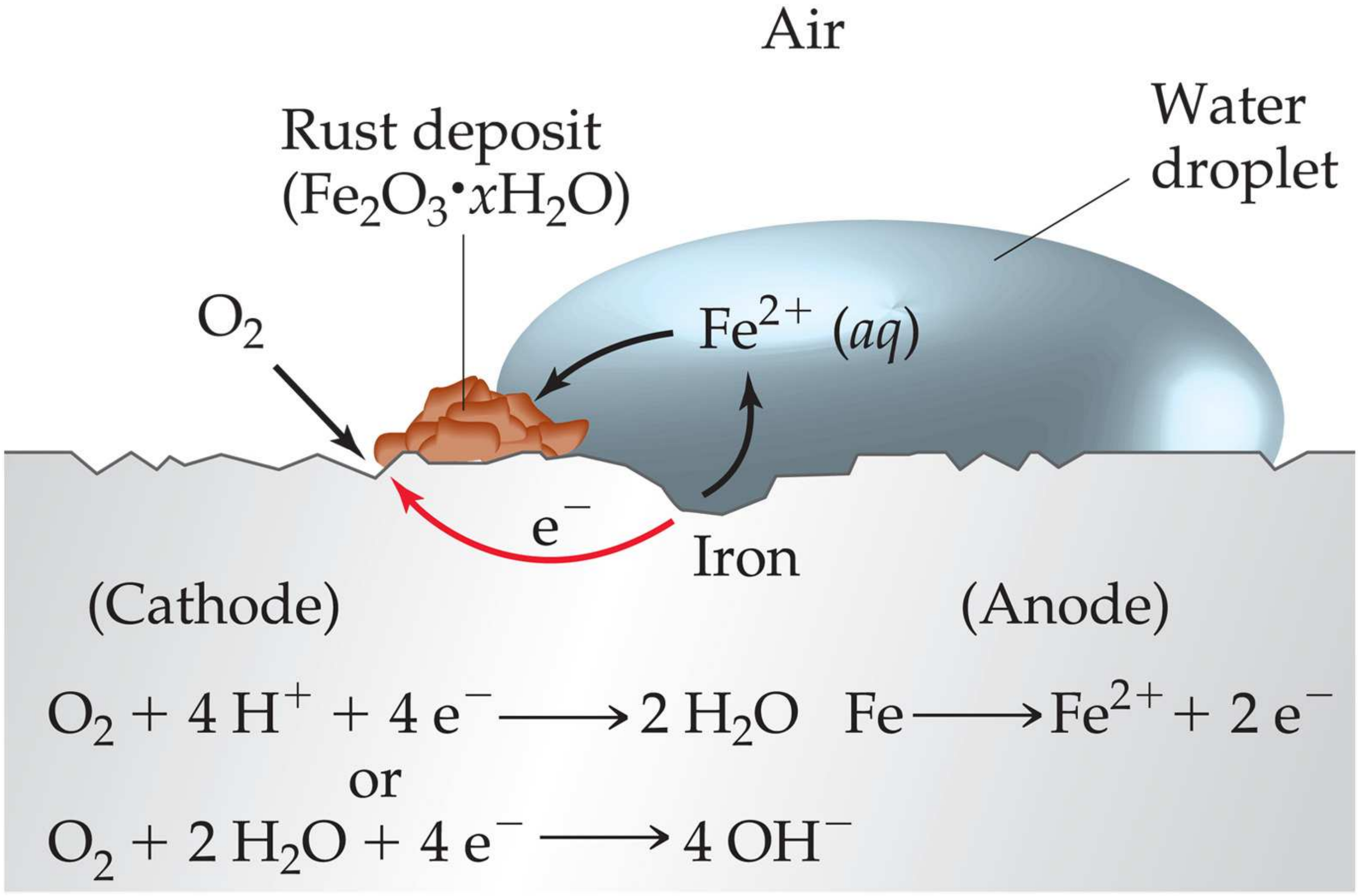


Hydrogen Fuel Cells



Electrochemistry

Corrosion and…



$$O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O \qquad Fe \longrightarrow Fe^{2+} + 2\,e^-$$

or

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

…Corrosion Prevention