Recap

❑ Balancing redox reactions (e^-, charge, mass)
❑ Potentials of half-reactions
❑ Gibbs free energy and emf

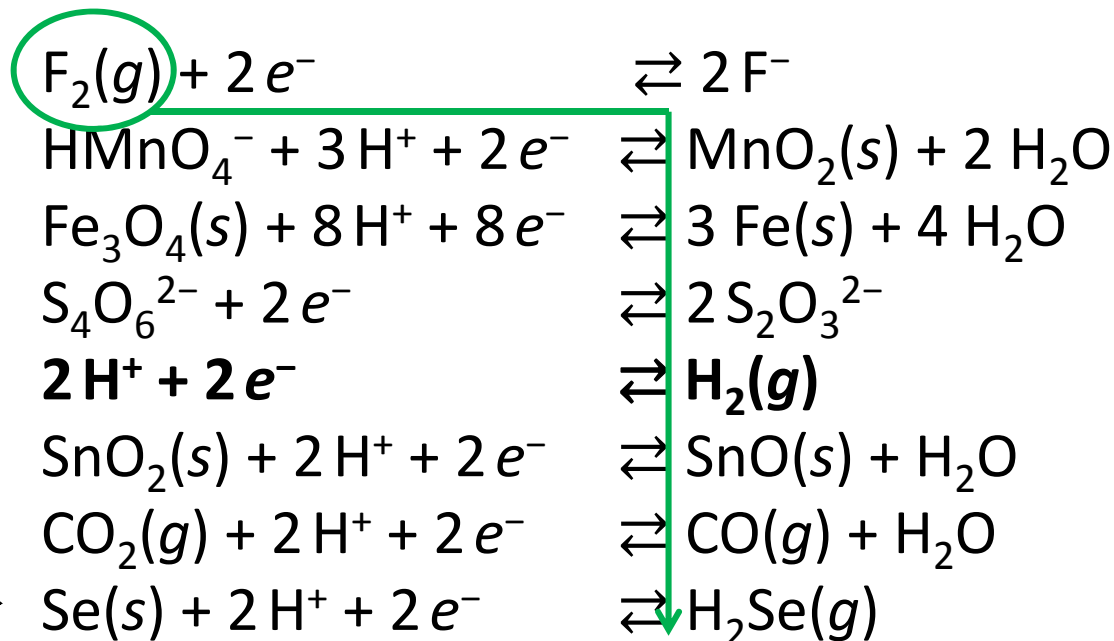## 6M.1 Table of **Standard Electrode Potentials** at 25 °C

$$F_2(g) + 2\,e^- \rightleftharpoons 2\,F^- \qquad\qquad\qquad +2.87$$
$$HMnO_4^- + 3\,H^+ + 2\,e^- \rightleftharpoons MnO_2(s) + 2\,H_2O \qquad +2.09$$
$$O_3(g) + 2\,H^+ + 2\,e^- \rightleftharpoons O_2(g) + H_2O \qquad +2.075$$
$$Fe_3O_4(s) + 8\,H^+ + 8\,e^- \rightleftharpoons 3\,Fe(s) + 4\,H_2O \qquad +0.085$$
$$S_4O_6^{2-} + 2\,e^- \rightleftharpoons 2\,S_2O_3^{2-} \qquad\qquad \text{SHE} \quad +0.08$$
$$\mathbf{2\,H^+ + 2\,e^- \rightleftharpoons H_2(g)} \qquad\qquad\qquad \mathbf{0.0000}$$
$$SnO_2(s) + 2\,H^+ + 2\,e^- \rightleftharpoons SnO(s) + H_2O \qquad -0.09$$
$$SnO(s) + 2\,H^+ + 2\,e^- \rightleftharpoons Sn(s) + H_2O \qquad -0.10$$
$$CO_2(g) + 2\,H^+ + 2\,e^- \rightleftharpoons CO(g) + H_2O \qquad -0.11$$
$$Se(s) + 2\,H^+ + 2\,e^- \rightleftharpoons H_2Se(g) \qquad\qquad -0.11$$

Oxidizing Potential (oxidizing agents-more **pushing**)

Strongest Reducing Potential (reducing agents-more **pulling**)

1. Written as reductions
2. Ranked from highest to lowest oxidizing potential

F$_2$ has the strongest oxidizing potential.

Se has the strongest reducing potential.

$$F_2(g) + 2\,e^- \rightleftarrows 2\,F^-$$
$$HMnO_4^- + 3\,H^+ + 2\,e^- \rightleftarrows MnO_2(s) + 2\,H_2O$$
$$Fe_3O_4(s) + 8\,H^+ + 8\,e^- \rightleftarrows 3\,Fe(s) + 4\,H_2O$$
$$S_4O_6^{2-} + 2\,e^- \rightleftarrows 2\,S_2O_3^{2-}$$
$$\mathbf{2\,H^+ + 2\,e^- \rightleftarrows H_2(g)}$$
$$SnO_2(s) + 2\,H^+ + 2\,e^- \rightleftarrows SnO(s) + H_2O$$
$$CO_2(g) + 2\,H^+ + 2\,e^- \rightleftarrows CO(g) + H_2O$$
$$Se(s) + 2\,H^+ + 2\,e^- \rightleftarrows H_2Se(g)$$

At the top are the strongest oxidizing (e$^-$ pushing) agents, and the bottom lists the strongest reducing (e$^-$ pulling) agents.

F$_2$(g) pulls electrons strongly, so it is a strong oxidizing element. It can oxidize any other species below it in the table.

246

$$F_2(g) + 2\,e^- \quad\quad\quad\quad \rightleftarrows 2\,F^-$$
$$HMnO_4^- + 3\,H^+ + 2\,e^- \quad \rightleftarrows MnO_2(s) + 2\,H_2O$$
$$Fe_3O_4(s) + 8\,H^+ + 8\,e^- \quad \rightleftarrows 3\,Fe(s) + 4\,H_2O$$
$$S_4O_6^{2-} + 2\,e^- \quad\quad\quad \rightleftarrows 2\,S_2O_3^{2-}$$
$$\mathbf{2\,H^+ + 2\,e^-} \quad\quad\quad\quad \rightleftarrows \mathbf{H_2(g)}$$
$$SnO_2(s) + 2\,H^+ + 2\,e^- \quad \rightleftarrows SnO(s) + H_2O$$
$$CO_2(g) + 2\,H^+ + 2\,e^- \;\;\textcolor{red}{X}\;\; \rightleftarrows CO(g) + H_2O$$
$$Se(s) + 2\,H^+ + 2\,e^- \quad\quad \rightleftarrows H_2Se(g)$$
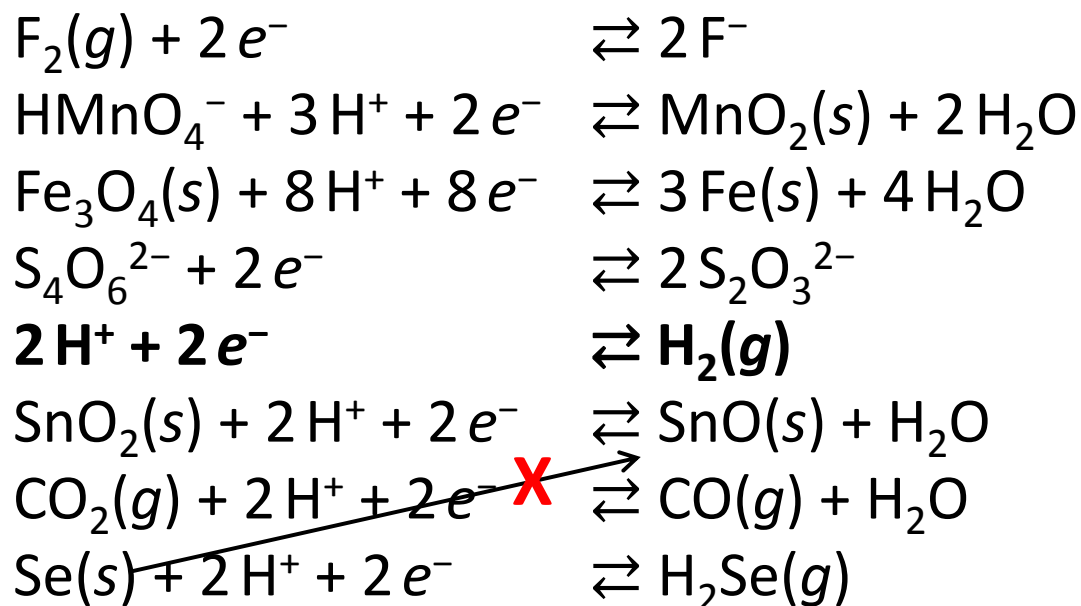
Se(s), is not a strong pusher of electrons (it is easily oxidized).

Se(s) cannot oxidize any species above it (it would be like pushing electrons up a waterfall).

[On the other hand, $H_2Se(g)$ is a stronger electron puller so it could react with any species (diagonal) above it.]

Can you make iron metal by reacting iron(III) with zinc metal to produce aqueous zinc ions under standard conditions?

$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$	0, by definition
$Fe^{3+}(aq) + 3\,e^- \longrightarrow Fe(s)$	-0.04
$O_2(g) + H_2O(l) + 2\,e^- \longrightarrow HO_2^-(aq) + OH^-(aq)$	-0.08
$Pb^{2+}(aq) + 2\,e^- \longrightarrow Pb(s)$	-0.13
$Sn^{2+}(aq) + 2\,e^- \longrightarrow Sn(s)$	-0.14
$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$	-0.44
$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$	-0.76
$2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq)$	$-0.83; -0.42$ at $pH = 7$
$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$	-1.66

$$Fe^{3+}(aq) + Zn(s) \rightarrow Fe(s) + Zn^{2+}(aq)$$
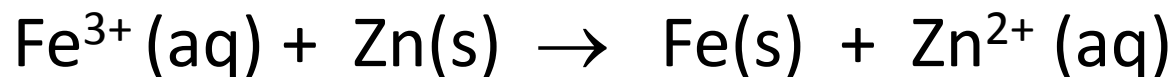
Yes, Fe^{3+} is a stronger oxidizing agent than Zn^{2+}.

Using the Standard Reduction Potential Table

Example 6M.1 For $Zn(s)|Zn^{+2}(aq)||Sn^{4+}(aq),Sn^{2+}(aq)|Pt(s)$ the emf, $E°$, is +0.91 V.

The standard potential of a zinc electrode is -0.76 V. What is the standard potential of the Sn^{4+}/Sn^{2+} electrode?

Written as anode||cathode, so Zn is the anode getting oxidized, and Sn is getting reduced.

We know $E° = E_{cat}°- E_{anode}°$

And $E° = +0.91V$, and E_{anode} (Zn) = -0.76V

$E° = E° = E_{cat}°- E_{anode}°$, $+0.91V = E_{cat}° - (-0.76V)$,

$E_{cat}° = +0.91V - 0.76V = +0.15$ V

Main Group Standard Potentials

Hardest to oxidize are strongest oxidizing agents.

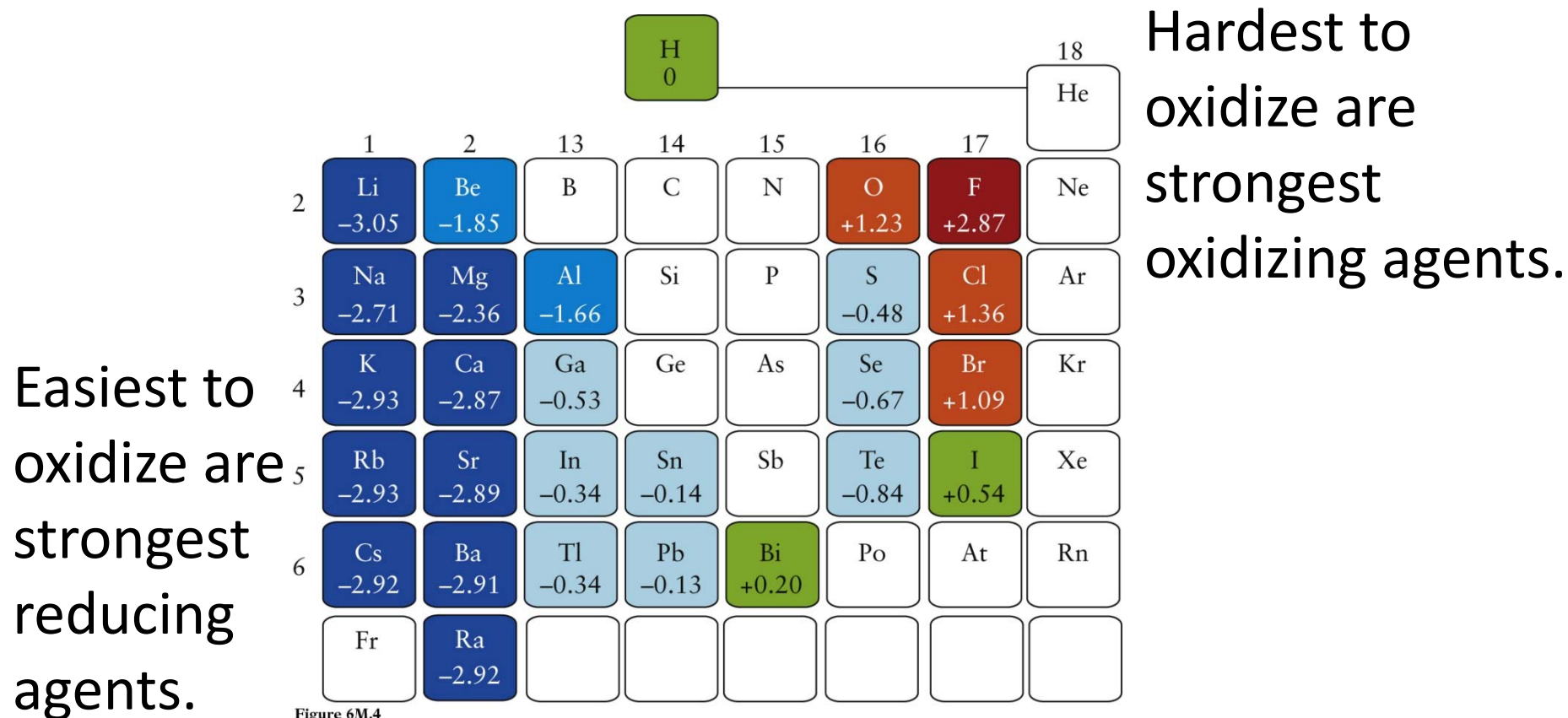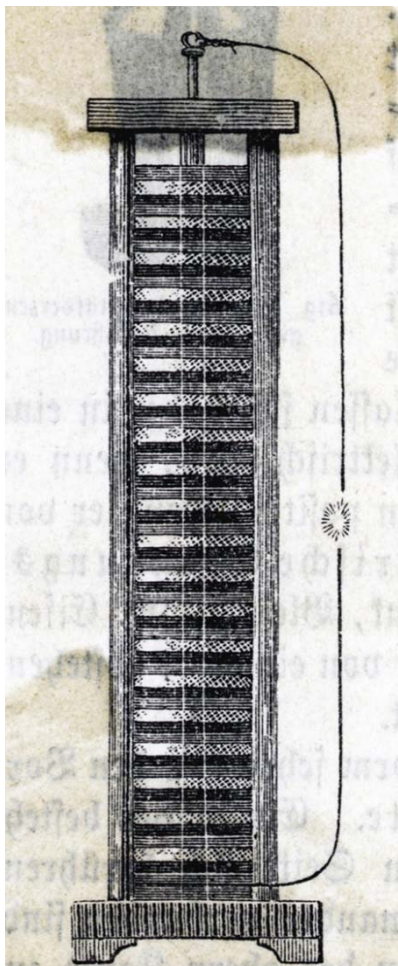Easiest to oxidize are strongest reducing agents.

Figure 6M.4
Atkins, *Chemical Principles: The Quest for Insight*, 7e
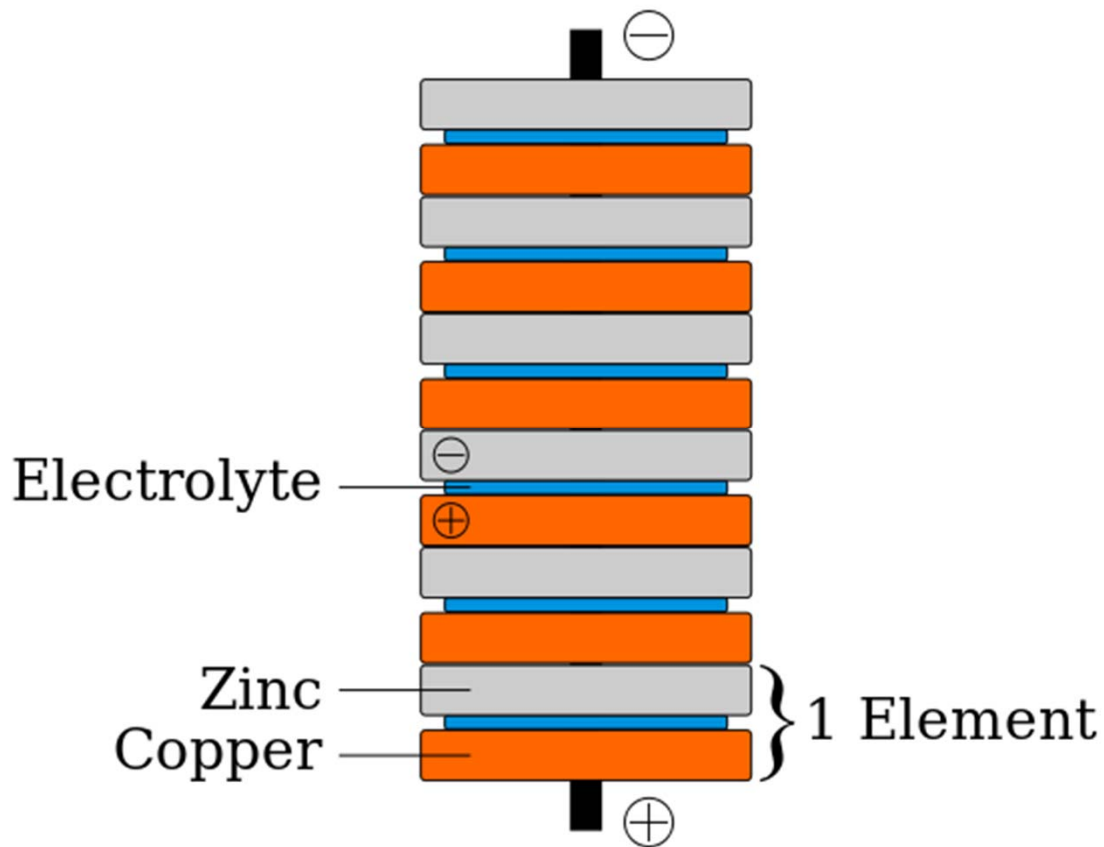W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

Note that the most negative values are in the *s*-block and that the most positive values are close to fluorine.

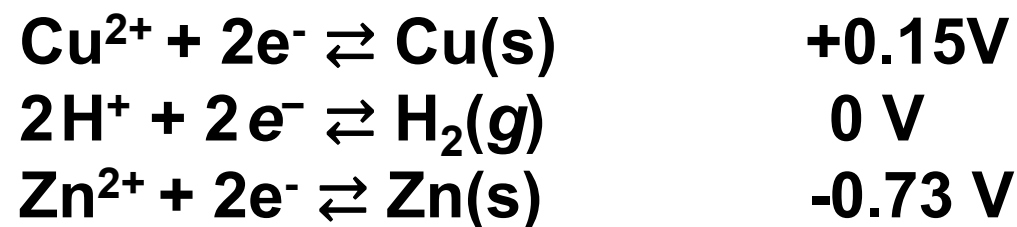# The first true battery
Voltaic pile (1800)

Figure 6L.1
Atkins, *Chemical Principles: The Quest for Insight*, 7e
© Bettmann/CORBIS.

Electrolyte

Zinc

Copper

1 Element

❑ Bio-materials are not necessary, but different metals
❑ Bubble evolution on Cu

$$Cu^{2+} + 2e^- \rightleftarrows Cu(s) \qquad +0.15V$$
$$2H^+ + 2e^- \rightleftarrows H_2(g) \qquad 0\ V$$
$$Zn^{2+} + 2e^- \rightleftarrows Zn(s) \qquad -0.73\ V$$

Example 6M.2 Use the information in Appendix 2B to determine the **NEW** standard potential for the redox couple Ce^{4+}/Ce, for which the reduction half-reaction is: $Ce^{4+}(aq) + 4\,e^- \rightarrow Ce(s)$.

In Appendix 2B we find the following

$Ce^{3+}(aq) + 3\,e^- \rightarrow Ce(s)$ $E° = -2.48V$

$Ce^{4+}(aq) + 1\,e^- \rightarrow Ce^{3+}(aq)$ $E° = +1.61V$

Since [$\Delta G = \Sigma nG$ (products) - ΣnG (reactants)], we don't add the values. Instead, use $\Delta G° = -nFE°$ or $\Delta G°$(total) = $\Delta G°(Ce^{3+}) + \Delta G°(Ce^{4+})$.
(note n)   4 $\Delta G°$(total) = 3 $\Delta G°(Ce^{3+}) + \Delta G°(Ce^{4+})$

or 4 $E°$(total) = 3 $E°(Ce^{3+}) + E°(Ce^{4+})$, $\dfrac{3(-2.48V) + 1.61V}{4}$ = -1.46V

Predicting the Spontaneous Direction of a Redox Reaction Under Standard Conditions
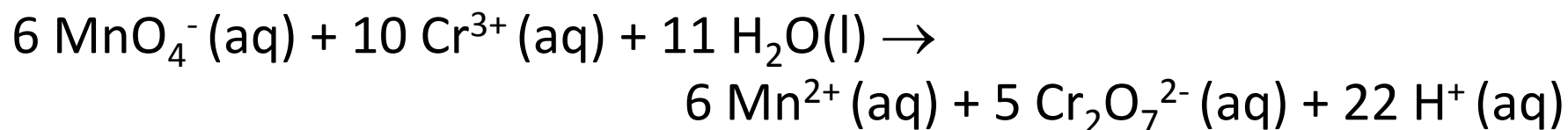
Which is the more powerful oxidizing agent under standard conditions, an acidified aqueous permanganate solution or an acidified aqueous dichromate solution? Specify the cell for the spontaneous reaction of the two couples by writing a cell diagram that under standard conditions has a positive emf. Determine the standard emf of the cell.

We look the reactions up and find their potential.

$MnO_4^-(aq) + 8 H^+(aq) + 5 e^- \rightarrow Mn^{2+}(aq) + 4 H_2O(l)$ $E° = +1.51$ V

$Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e^- \rightarrow 2 Cr^{3+}(aq) + 7 H_2O(l)$ $E° = +1.33$ V
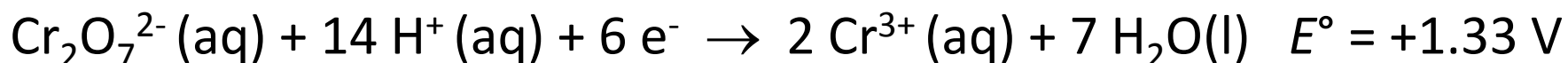
From $\Delta G° = -nFE°$, if $\Delta G°$ is negative, the cell is spontaneous, so $E > 0$. Therefore, to get the highest $E°$, we rewrite as a reduction oxidation cell, where MnO_4^- is a stronger oxidizing agent.

For $E° = E_{cat}° - E_{anode}°$ or +1.51 V - (+1.33 V) = +0.18V

(spontaneous)

$6\ MnO_4^-\ (aq) + 10\ Cr^{3+}\ (aq) + 11\ H_2O(l) \rightarrow$

$6\ Mn^{2+}\ (aq) + 5\ Cr_2O_7^{2-}\ (aq) + 22\ H^+\ (aq)$

$Pt\ |\ Cr^{3+}\ (aq),\ Cr_2O_7^{2-}\ (aq)\ ||\ MnO_4^-\ (aq),\ Mn^{2+}\ (aq)\ |\ Pt$
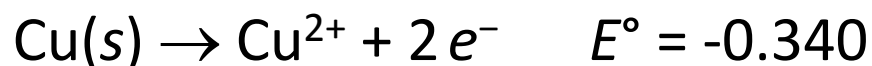
Which is the stronger oxidizing agent, Cu^{2+} or Ag^+, in aqueous solution under standard conditions? Evaluate the standard emf of the appropriate cell, specify the cell with a cell diagram, and write the net ionic equation for the corresponding cell reaction.
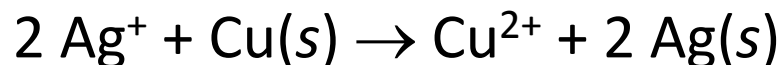
$$Ag^+ + e^- \rightarrow Ag(s) \qquad E° = +0.7996 \text{ V}$$
$$Cu^{2+} + 2\,e^- \rightarrow Cu(s) \qquad E° = +0.340 \text{ V}$$
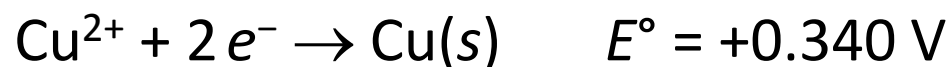
For a spontaneous cell, $E° > 0$. Ag^+ is a stronger oxidizing agent than Cu^{2+}, therefore Cu^{2+} will become reduced.

We can rewrite the cell:
$$Ag^+ + e^- \rightarrow Ag(s) \qquad E° = +0.7996$$
$$Cu(s) \rightarrow Cu^{2+} + 2\,e^- \qquad E° = -0.340$$

$E° = E°_{anode} + E°_{cathode}, \quad +0.7996 - 0.340 = +0.460V$

$$2\,Ag^+ + Cu(s) \rightarrow Cu^{2+} + 2\,Ag(s)$$
anode||cathode, $Cu(s)|Cu^{2+}(aq)||Ag^+(aq)|Ag(s)$

Standard Potentials and Equilibrium Constants

The standard reaction Gibbs free energy, $\Delta G_r°$, is related to the *equilibrium constant* $\Delta G_r° = -RT \ln K$.

In this chapter, the standard reaction Gibbs free energy is related to the *standard emf* $\Delta G° = -nFE°$.
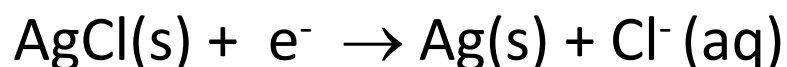
We can rearrange to the following:

$$\ln K = \frac{nFE°}{RT} \quad \text{For} \quad \frac{RT}{F} = 0.025693 \text{ V} \quad \text{so} \quad \ln K = \frac{nE°}{0.025693 \text{V}}$$

K increases exponentially with $E°$. A large $E°$ means $K >>> 1$ (product favored).

Example 6N.1 Calculate the equilibrium constant at 25.00 °C for the reaction $AgCl(s) \rightarrow Ag^+ (aq) + Cl^- (aq)$.
The equilibrium constant is the solubility product, K_{sp} $[Ag^+][Cl^-]$.

$\ln K = \dfrac{nE°}{0.025693V}$. To find K, we need $E°$.

$AgCl(s) + e^- \rightarrow Ag(s) + Cl^- (aq)$ $\qquad\qquad$ $E° = +0.22V$
$Ag^+ (aq) + e^- \rightarrow Ag(s)$ $\qquad\qquad$ $E° = +0.80V$ (this is the stronger oxidizing agent)

So $\qquad AgCl(s) + e^- \rightarrow Ag(s) + Cl^- (aq)$ $\qquad\qquad$ $E° = +0.22V$
$\qquad\qquad Ag(s)   \rightarrow \qquad\qquad Ag^+ (aq) + e^-$ $\qquad\qquad$ $E° = -0.80V$
$AgCl(s) \rightarrow Ag^+ (aq) + Cl^- (aq)$ $\qquad$ $E° = +0.22V - 0.80V = -0.58V$

$\ln K = \dfrac{nE°}{0.025693V}, \dfrac{(1) \times (-0.58V)}{0.025693V}$, $K = e^{\frac{(1) \times (-0.58V)}{0.025693V}} = 1.6 \times 10^{-10}$

The Nernst Equation

As a reaction proceeds, reactants are consumed, the concentrations change and eventually the battery becomes "dead." This happens when ΔG approaches zero, or at equilibrium zero potential is generated.

The Nernst equation is a quantitative measure of a cell potential at different concentrations.

We know $\Delta G_r = \Delta G_r° + RT \ln Q$ (Q is the reaction quotient).

Since $\Delta G_r = -nFE$ and $\Delta G_r° = -nFE°$, we can substitute these two into the above equation.

The Nernst Equation

$-nFE = -nFE° + RT \ln Q$ or $E = E° - \dfrac{RT}{nF} \ln Q$

Previously, we showed RT/F = 0.025693 V, and using log calculations, we arrive at

$E = E° - \dfrac{0.025693V}{n} \ln Q$

The Nernst equation is widely used to estimate the emf of cells under nonstandard conditions.

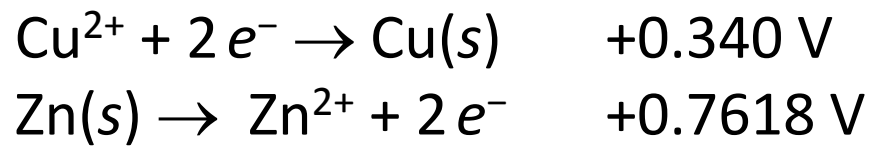Example 6N.2 Calculate the emf at 25 °C of a Daniell cell in which the concentration of Zn^{2+} ions is 0.10 mol·L^{-1} and that of the Cu^{2+} ions is 0.0010 mol·L^{-1}.

$Cu^{2+} + 2\,e^- \rightarrow Cu(s)$ +0.340

$Zn^{2+} + 2\,e^- \rightarrow Zn(s)$ -0.7618
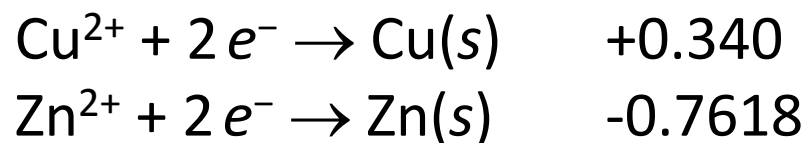
$$E = E° - \frac{0.025693V}{n}\ln Q$$

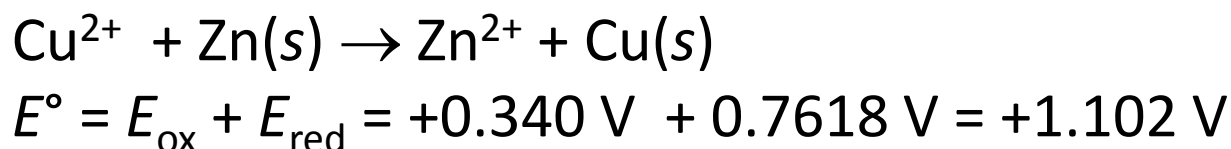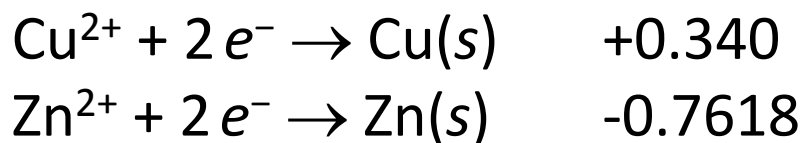We solve for E, so we need to find $E°$ and Q, $n = 2$.

For a Daniell cell, E is positive. Since Cu^{2+} is a stronger oxidizing agent, Zn will get oxidized.

$Cu^{2+} + 2\,e^- \rightarrow Cu(s)$ +0.340 V

$Zn(s) \rightarrow Zn^{2+} + 2\,e^-$ +0.7618 V
_____

(Note reaction and sign are reversed.)

Example 6N.2 Calculate the emf at 25 °C of a Daniell cell in which the concentration of Zn^{2+} ions is 0.10 mol·L^{-1} and that of the Cu^{2+} ions is 0.0010 mol·L^{-1}.

$Cu^{2+} + 2\,e^- \rightarrow Cu(s)$ +0.340
$Zn^{2+} + 2\,e^- \rightarrow Zn(s)$ -0.7618

$Cu^{2+} + Zn(s) \rightarrow Zn^{2+} + Cu(s)$
$E° = E_{ox} + E_{red}$ = +0.340 V + 0.7618 V = +1.102 V

$$Q = \frac{products}{reactants} = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{0.10\ mol·L^{-1}}{0.0010\ mol·L^{-1}}$$

$$E = E° - \frac{0.025693V}{n}\ \ln Q\ ,$$

$$E = 1.102\ V - \frac{0.025693V}{2}\ \ln \frac{0.10\ mol·L^{-1}}{0.0010\ mol·L^{-1}}$$

= +1.04 V

Example 6N.3 Each electrode compartment of a galvanic cell contains a silver electrode and 10.0 mL of 0.10 M $AgNO_3$(aq); they are connected by a salt bridge. You now add 10.0 mL of 0.10 M NaCl(aq) to the *left-hand electrode compartment*. Almost all the silver ion precipitates as silver chloride, but a little remains in solution as a saturated solution of AgCl. The measured emf is E = +0.42 V. What is the concentration of Ag^+ in the saturated solution?
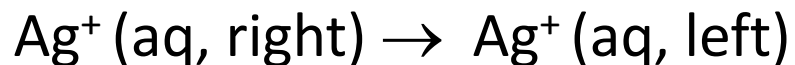
$$Ag^+ (aq, right) \rightarrow Ag^+ (aq, left)$$
Strongest oxidizing agent $\rightarrow$ Strongest reducing agent

$$Ag(s)|Ag^+ (aq, left) || Ag^+ (aq, right)|Ag(s)$$
Anode (oxidation/RA) || Cathode (reduction/OA)

The Nernst Equation: Finding Concentration in a Precipitation Reaction

Ag(s)|Ag$^+$ (aq, left) || Ag$^+$ (aq, right)|Ag(s)

Anode (oxidation/RA) || Cathode (reduction/OA)

$$Q = \frac{products}{reactants} = \frac{[Ag^+ \text{ (aq, left)}]}{[Ag^+ \text{ (aq, right)}]} = \frac{[Ag^+ \text{ (aq, left)}]}{0.10 \text{ M}}$$

$E = E° - \dfrac{RT}{nF} \ln Q$, here $E° = 0$, so $\ln Q = \dfrac{-EnF}{RT} = \dfrac{-0.42 \text{ V}}{0.025693V} = -16.34$

Take e to both sides $\dfrac{[Ag^+ \text{ (aq, left)}]}{0.10 \text{ M}} = e^{-16.34}$, $[Ag^+ \text{ (aq, left)}] =$

$e^{-16.34} \times 0.10 \text{ M} =$

8.0×10^{-9} M

Ion-Selective Electrodes

The pH of a solution can be measured electrochemically with a **pH meter**.

To measure H_3O^+ ions, we select an electrode sensitive to the H_3O^+ concentration.

Each different ion is measured with its own ion-selective electrode.

Figure 6B.1
Atkins, *Chemical Principles: The Quest for Insight*, 7e
Charles D. Winters/Science Source

Ion-Selective Electrodes

We only measure ΔE. A typical **reference** electrode is hydrogen $2\,H^+ + 2\,e^- \rightarrow H_2(g)$ 0.0 V.

For its stability, we use a reference electrode called a **calomel electrode**, which contains mercury (I) chloride, Hg_2Cl_2.

Often, the calomel electrode is built directly into a probe.

Probes are typically glass electrodes—thin-walled bulbs containing a calomel electrode. Common probes include Na^+, Ca^{2+}, NH_4^+, CN^-, or S^{2-}.

Figure 6B.1
Atkins, *Chemical Principles: The Quest for Insight*, 7e
Charles D. Winters/Science Source

thin-walled bulbs

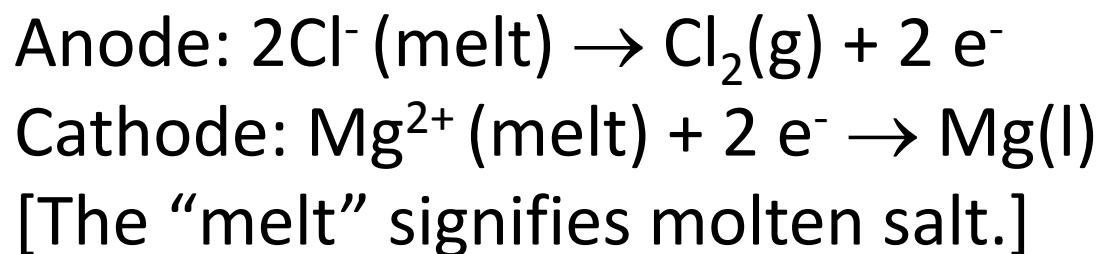## Electrolytic Cells: The **Opposite** of a Galvanic or Voltaic Cell

Electrolytic cells are nonspontaneous cells, where a current is forced in the opposite direction to drive the reaction.

This process is called electrolysis, and is the opposite of a Galvanic cell.

Whereas electrons flow spontaneously in a **Galvanic cell** from the anode to cathode, **electrolytic cells** apply an emf at the cathode, making the **cathode "-"** and the **anode "+."**

The following is an example of a nonspontaneous reaction, driven by an external power supply.

Anode: $2Cl^-$ (melt) $\rightarrow$ $Cl_2(g)$ + 2 e^-

Cathode: Mg^{2+} (melt) + 2 e^- $\rightarrow$ Mg(l)

[The "melt" signifies molten salt.]

Note that only the sign **changes**.

Electrons are forced into the cathode and are drawn toward a higher potential anode.
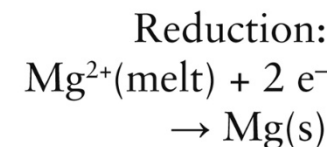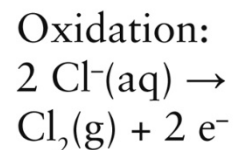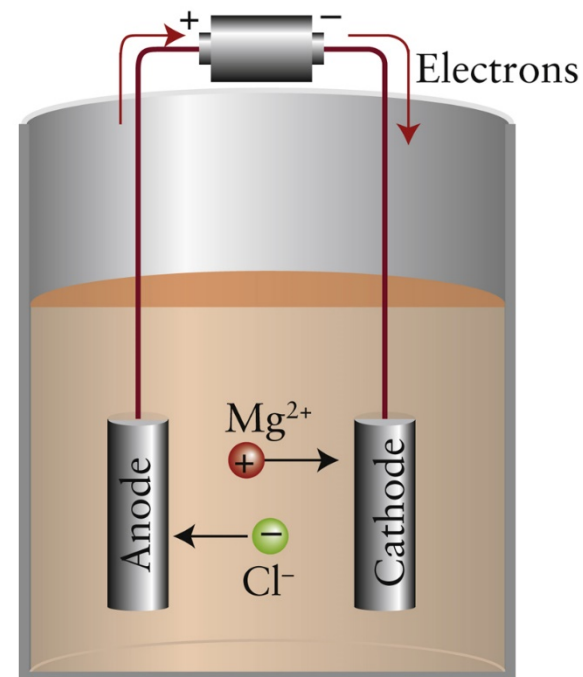
Notice the *lack of a salt bridge*.

The Dow Process

Electrons

Mg^{2+}

Anode

Cathode

Cl$^-$

Oxidation:
2 Cl$^-$(aq) $\rightarrow$
Cl$_2$(g) + 2 e$^-$

Reduction:
Mg^{2+}(melt) + 2 e$^-$
$\rightarrow$ Mg(s)

Figure 60.1
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

Overpotential is having to apply a higher voltage than the potential sited in a table.

In practice, the applied potential must be substantially greater than the cell emf. The **additional potential** is called the **overpotential**. This is common for many reactions.

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l) \qquad E = +1.23\ V\ \text{at pH} = 7$$
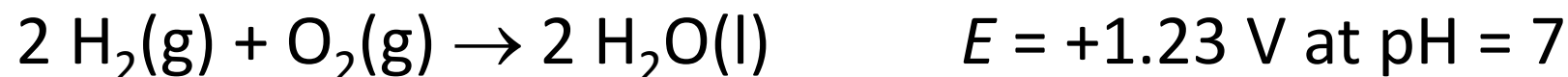
Frequently, water is a problem. For platinum electrodes, the overpotential for the **production of water** from hydrogen and oxygen is **0.6 V** more, or about 1.8 V (0.6 + 1.23) V.

Other Electrolytic Considerations

Pure water will not conduct electricity, but add a solute and the ionic solution will.

$O_2(g) + 4 H^+ + 4 e^- \rightarrow 2 H_2O(l)$ E = +0.82 V, typical seawater
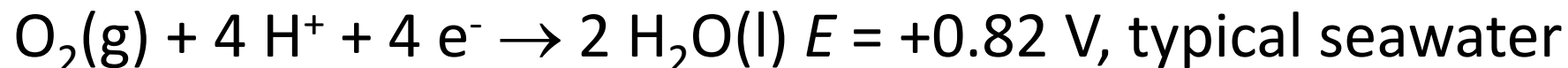
The problem is seawater also has chloride, and from our tables we find $Cl_2(g) + 2 e^- \rightarrow 2 Cl^-$ (aq) E = 1.36 V.

At first glance, these values appear far enough apart, however taking into consideration the overpotential of water (0.6 + 0.82 = 1.4), the production of $Cl_2(g)$ will begin before the production of oxygen can.

Other Electrolytic Considerations

Seawater also has a considerable amount of Na^+. It would be optimal to produce sodium metal, $Na(s)$, from seawater.

Compare the reduction potentials for water and sodium.

$2\,H_2O + 2\,e^- \rightleftarrows H_2(g) + 2\,OH^-$ -0.8277

$Na^+ + e^- \rightleftarrows Na(s)$ -2.71
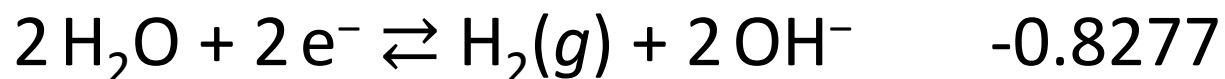
Even taking into account the overpotential of water, water still has a lower reduction potential than sodium. Therefore, in the reduction of seawater, hydrogen gas is produced before sodium metal.

Example 6O.1 Suppose that an aqueous solution with pH = 7 and containing I^- ions at 1 mol·L^{-1} is being electrolyzed. Will O_2 or I_2 be produced at the anode?

$$2\ I^-\ (aq) \rightarrow I_2(s) + 2\ e^- \qquad E° = 0.54\ V$$
$$2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+ + 4\ e^- \qquad E = 0.82\ V$$
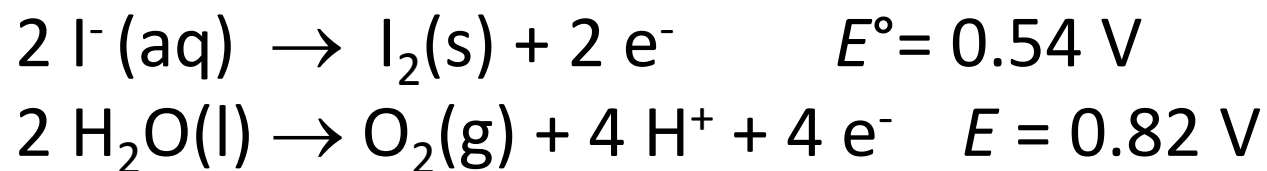
Since the I^- (aq) potential is lower (more positive), we expect it to be oxidzied at the anode first.

The Products of Electrolysis
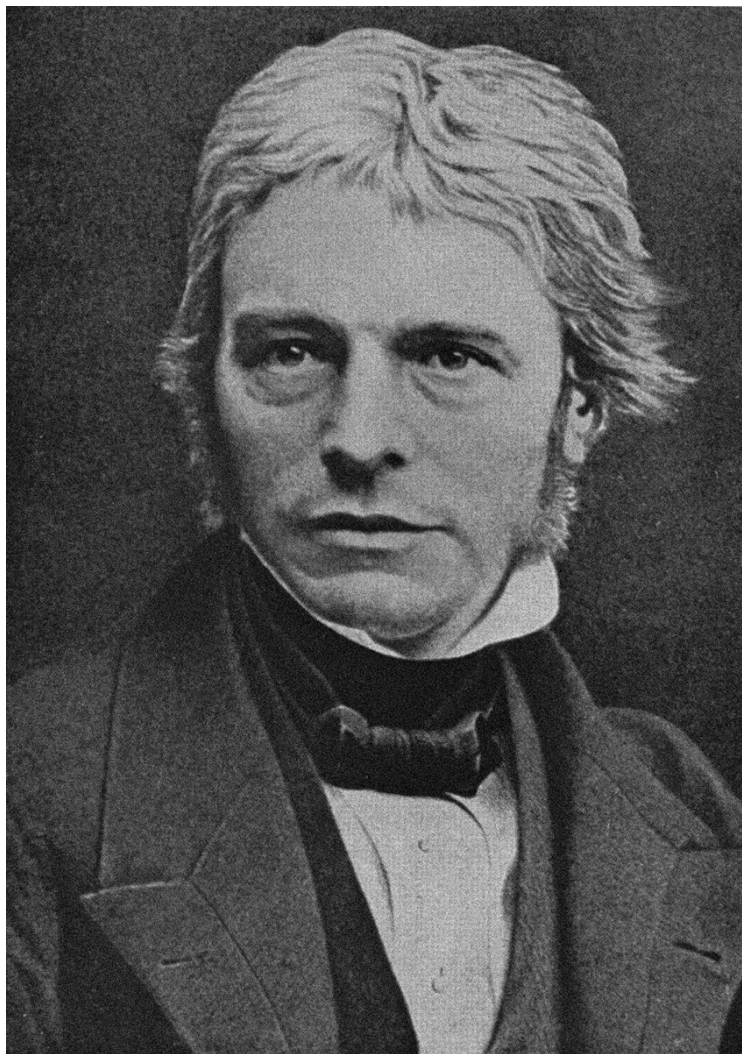
Michael Faraday was the first to calculate quantities from electrolysis experiments.

Two key observations were the (1) connection between moles and coulombs and (2) coulombs and amps.
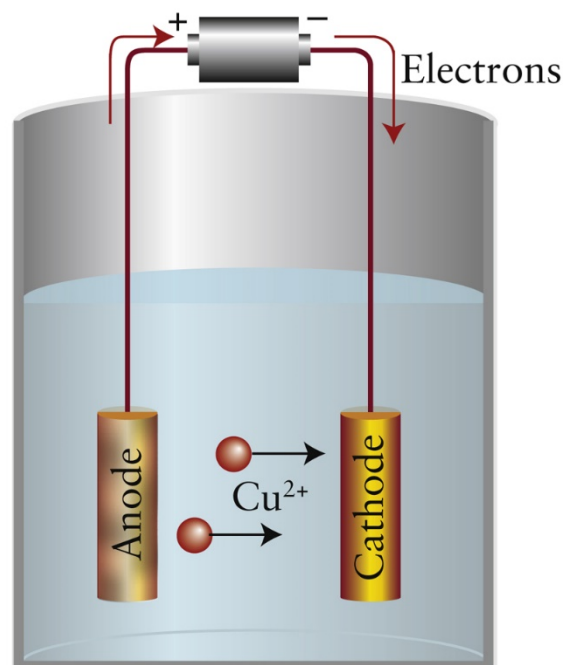
$F = 96,485 \ C \cdot mol^{-1}$

1 coulomb = ampere·second

Copper is refined electrolytically by using an impure form of copper metal called **blister copper** as the anode in an electrolytic cell. Supplied current drives the oxidation of the blister copper to copper(II) ions, Cu^{2+}, which are then reduced to pure copper metal at the cathode.

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

Impure copper

Copper is 100% recyclable.

99.99% pure, aqueous!

+ − Electrons

Anode

Cu^{2+}

Cathode

Oxidation:
$Cu(s) \rightarrow$
$Cu^{2+}(aq) + 2 e^-$

Reduction:
$Cu^{2+}(aq) + 2 e^-$
$\rightarrow Cu(s)$

Figure 6O.3
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman