General Chemistry:
An Integrated Approach
Hill, Petrucci, 4th Edition

Chapter 18
Electrochemistry

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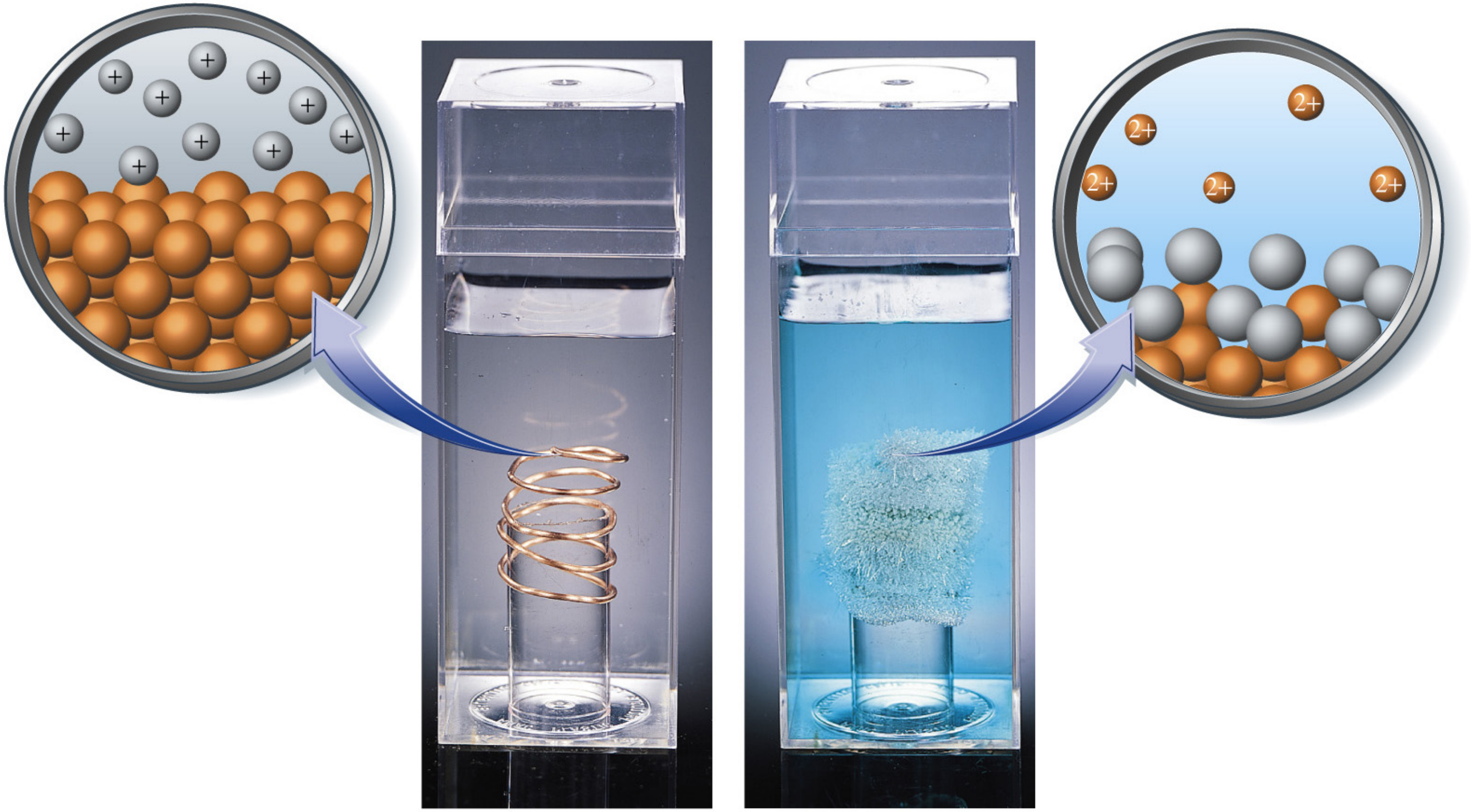
Oxidation–Reduction

Redox involves the transfer of electrons



Reactions Involving Oxidation and Reduction

- ***Oxidation***: Loss of electrons
- ***Reduction***: Gain of electrons
- Both oxidation and reduction must occur simultaneously.
  - A species that loses electrons must lose them ***to*** something else (something that gains them).
  - A species that gains electrons must gain them ***from*** something else (something that loses them).
- Historical: “oxidation” used to mean “combines with oxygen”; the modern definition is much more general.

Oxidation Numbers

- An ***oxidation number*** is the charge on an ion, or a *hypothetical* charge assigned to an atom in a molecule or polyatomic ion.
- Examples: in NaCl, the oxidation number of Na is +1, that of Cl is –1 (the actual charge).
- In CO_2 (a molecular compound, no ions) the oxidation number of oxygen is –2, because oxygen as an ion would be expected to have a 2– charge.
- The carbon in CO_2 has an oxidation number of +4 (Why?)

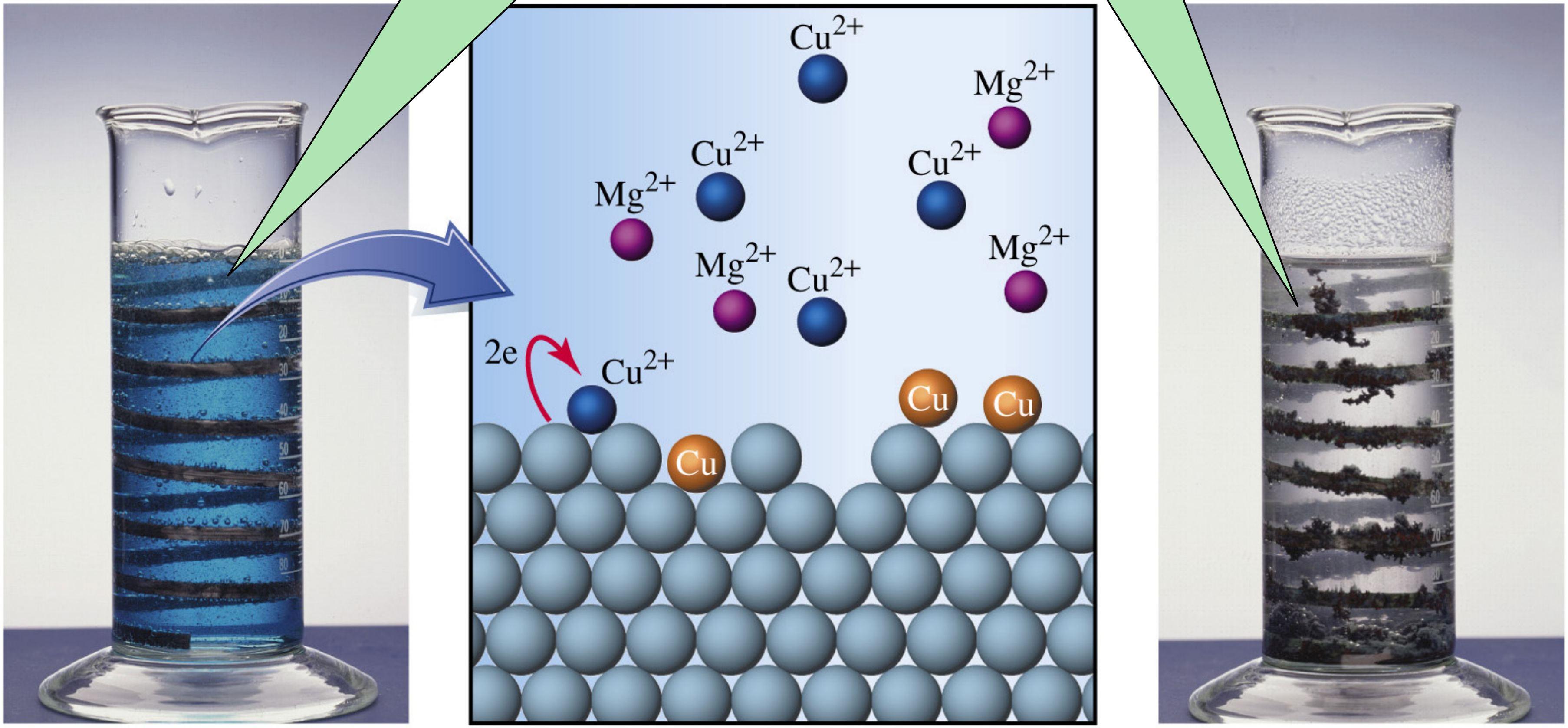
Identifying Oxidation–Reduction Reactions

- In a redox reaction, the oxidation number of a species *changes* during the reaction.
- ***Oxidation*** occurs when the oxidation number increases (species loses electrons).
- ***Reduction*** occurs when the oxidation number decreases (species gains electrons).
- If ***any*** species is oxidized or reduced in a reaction, that reaction is a redox reaction.
- Examples of redox reactions: displacement of an element by another element; combustion; incorporation of an element into a compound, etc.

A Redox Reaction: $Mg + Cu^{2+} \rightarrow Mg^{2+} + Cu$

Electrons are transferred from Mg metal to Cu^{2+} ions and …

… the products are Cu metal and Mg^{2+} ions.



(a) (b) (c)

Oxidizing and Reducing Agents

- An ***oxidizing agent*** causes another substance to be oxidized.
- The oxidizing agent is *reduced*.
- A ***reducing agent*** causes another substance to be reduced.
- The reducing agent is *oxidized*.

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

What is the oxidizing agent? What is the reducing agent?

Oxidation–Reduction Equations

- Redox equations must be balanced according to both *mass* and *electric charge*.

The Half-Reaction Method of Balancing Redox Equations

1. Separate a redox equation into two half-equations, one for oxidation and one for reduction.
2. Balance the number of *atoms* of each element in each half-equation. Usually we balance O and H atoms last.
3. Balance each half-reaction for *charge* by adding electrons to the *left* in the *reduction* half-equation and to the *right* in the *oxidation* half-equation.
4. Adjust the coefficients in the half-equations so that the same number of electrons appears in each half-equation.
5. Add together the two adjusted half-equations to obtain an overall redox equation.
6. Simplify the overall redox equation as necessary.

Half-Reactions

In any oxidation–reduction reaction, there are two **half-reactions**

Oxidation takes place when a species **loses electrons** to another species

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

Reduction takes place when a species **gains electrons** from another species

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

Redox Rxn

Half-Reaction Method of Balancing Redox Equations

Separate an oxidation–reduction equation into two half-equations, one for oxidation and one for reduction

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

$\mathrm{Ag^{+}(aq)} + e^{-} \rightarrow \mathrm{Ag(s)}$ reduction

As with all chemical equations, one must have ***mass*** **AND** ***charge*** balance

Half-Reaction Method of Balancing Redox Equations

Balance the atoms and the electric charge in each half-reaction

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

$2\ Ag^{+}(aq) + 2\,e^{-} \rightarrow 2\ Ag(s)$ reduction

Adjust the coefficients in the half-equations so that the same number of electrons appears in each half-equation

Half-Reaction Method of Balancing Redox Equations

Add together the two adjusted half-equations to obtain an overall oxidation–reduction equation

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

$2\ Ag^+(aq) + 2\ e^- \rightarrow 2\ Ag(s)$ reduction

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

Write the net balanced chemical equation …

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

Redox Reactions
in Acidic Solution

In these reactions, it will be necessary to **add molecules of water and protons (H^+)** to achieve a balanced equation

Balance all atoms ***other than*** **H** and **O**

After these equations have been “mass balanced,” they will need to be “charge balanced”

Use **e^- and H^+** to achieve charge balance and **water to offset added H^+**

The use of half-reactions provides a general way to balance redox reactions.

Example: The reaction between permanganate ion (MnO_4^-) and oxalate ion ($C_2O_4^{2-}$) in acidic solution: When these ions combine in an acidic solution, they react to produce manganese ion (Mn^{2+}) and CO_2 gas.

Here is the *unbalanced* equation that describes this reaction:

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

To balance this redox reaction using the method of half- reactions, begin by writing the incomplete oxidation and reduction half-reactions:

$$\mathbf{MnO_4^- \rightarrow Mn^{2+}(\mathit{aq})}$$

$$\mathbf{C_2O_4^{2-} \rightarrow CO_2(\mathit{g})}$$

Which compound is being reduced and which one is being oxidized?

In the above half-reactions, the Mn appears to be balanced on both sides of its half-reaction. However, the carbon is not balanced in the second half-reaction - we need another carbon in the products:

$$\mathbf{MnO_4^- \rightarrow Mn^{2+}(\mathit{aq})}$$

$$\mathbf{C_2O_4^{2-} \rightarrow 2CO_2(\mathit{g})}$$

Since the reaction is done under acidic aqueous solution, H^+ and H_2O can be added to reactants or products to balance H and O atoms.

In the manganese half-reaction we have 4 O atoms on the left and none on the right: We add 4 H_2O molecules on the right to take care of this:

$$\mathbf{MnO_4^- \rightarrow Mn^{2+}(\mathit{aq}) + 4H_2O(\mathit{l})}$$

We now have 8 H atoms on the right that need to be balanced. So we balance the H atoms by adding $H^+(aq)$ ions on the left:

$$\mathbf{MnO_4^- + 8H^+ \rightarrow Mn^{2+}(\mathit{aq}) + 4H_2O(\mathit{l})}$$

The atoms are now balanced, *but the charges are not*. We have a net charge of 7+ on the left, and 2+ on the right. We want to balance the charge without altering the number of atoms (they are balanced already).

We balance the charge by adding the appropriate number of electrons:

$$\mathbf{MnO_4^- + 8H^+ + 5e\text{-} \rightarrow Mn^{2+}(\mathit{aq}) + 4H_2O(\mathit{l})}$$

(balanced atoms, balanced charge)

How about the other half-reaction?

$$\mathbf{C_2O_4^{2-} \rightarrow 2CO_2(g)}$$

The atoms are balanced, but the charges are not. We have a net charge of 2- on the left and 0 on the right. We can balance this by adding the appropriate number of electrons:

$$\mathbf{C_2O_4^{2-} \rightarrow 2CO_2(g) + 2e\text{-}}$$

(balanced atoms, balanced charge)

In a redox reaction the overall electrons produced in the oxidation half-reaction **must equal** the number of electrons consumed in the reduction half-reaction. We have not yet identified which is the oxidation half-reaction and which is the reduction half-reaction, but it is clear that the electrons are not balancing (we have one half-reaction with 5e- and the other with 2e-). So, the half-reactions must be multiplied by some factor, such that the electrons present in the half-reactions balance each other

For the above half-reactions, ***the lowest common multiple is 10***.

Thus, ***the half-reaction with 5e- should be mulitiplied by 2, and the half-reaction with 2e- should be multiplied by 5***:

$$\mathbf{2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+}(aq) + 8H_2O(l)}$$

$$\mathbf{5C_2O_4^{2-} \rightarrow 10CO_2(g) + 10e^-}$$

The oxidation half-reaction is:

$$5C_2O_4^{2-} \rightarrow 10CO_2(g) + 10e-$$

The reduction half-reaction is:

$$2MnO_4^- + 16H^+ + 10e- \rightarrow 2Mn^{2+}(aq) + 8H_2O(l)$$

In other words, the oxalate ion is oxidized by the permananate ion (and the permanganate ion is reduced)

The *overall balanced redox reaction* is the combination of the two balanced half-reactions:

$$2MnO_4^- + 16H^+ + 10e- \rightarrow 2Mn^{2+}(\mathit{aq}) + 8H_2O(\mathit{l})$$

$$\underline{\qquad\qquad 5C_2O_4^{2-} \rightarrow 10CO_2(\mathit{g}) + 10e- \qquad\qquad}$$

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 10CO_2(\mathit{g}) + 2Mn^{2+}(\mathit{aq}) + 8H_2O(\mathit{l})$$

Summary of balancing half-reactions in *acidic solutions:*

1. Divide reaction into two incomplete half-reactions.

2. Balance each half-reaction by doing the following:

- *a. Balance all elements, except O and H*
- *b. Balance O by adding* H_2O
- *c. Balance H by adding* H^+
- *d. Balance charge by adding e-as needed*

3. If the electrons in one half-reaction do not balance those in the other, then multiply each half-reaction to get a common multiple.

4. The overall reaction is the sum of the half-reactions.

5. The oxidation half-reaction is the one that produces electrons as products, and the reduction half-reaction is the one that uses electrons as reactants.

Redox Reactions/Basic Solution

For a reaction in basic solution, **OH^- should appear instead of H^+** in the balanced equation

One method used to balance such equations is to balance the equation ***as if*** the reaction occurs in acidic solution

Then, to each side of the net equation, **add a number of OH^- ions *equal* to the number of H^+** appearing in the equation

One side of the equation will have **H^+ and OH^- ions in equal number**; those can be **combined into water**

Balancing Redox Reactions That Occur in Basic Solution

In a basic aqueous solution the half-reactions must be balanced using ***OH^- and H_2O (instead of H^+ and H_2O)***.

The procedure for balancing in this case is actually the same as for balancing in an acidic solution, with one small twist:

- ***Since we are under basic conditions, we have to neutralize any H+ ions in solution.***
    - ***We achieve this by adding the appropriate number of OH- ions.***
    - ***We keep things balanced by adding the same number of OH- ions to both sides of the half-reaction***

Here's an example of an ***unbalanced redox reaction that occurs under basic conditions:***

$$CN^-(aq) + MnO_4^-(aq) \rightarrow CNO^-(aq) + MnO_2(s)$$

Balancing Redox Reactions That Occur in Basic Solution

- Let's run through the steps to balance as if it were under acidic conditions. Here are the two incomplete half-reactions:

$$CN^-(aq) \rightarrow CNO^-(aq)$$

$$MnO_4^-(aq) \rightarrow MnO_2(s)$$

- Balance each individually as if in acid:

$$CN^-(aq) \rightarrow CNO^-(aq)$$

$$CN^-(aq) + H_2O(l) \rightarrow CNO^-(aq)$$

$$CN^-(aq) + H_2O(l) \rightarrow CNO^-(aq) + 2H^+(aq)$$

$$CN^-(aq) + H_2O(l) \rightarrow CNO^-(aq) + 2H^+(aq) + 2e-$$

Balancing Redox Reactions That Occur in Basic Solution

- Now the other half-reaction:

$$\mathbf{MnO_4^-(\mathit{aq}) \rightarrow MnO_2(s)}$$

$$\mathbf{MnO_4^-(\mathit{aq}) \rightarrow MnO_2(s) + 2H_2O(\mathit{l})}$$

$$\mathbf{MnO_4^-(\mathit{aq}) + 4H^+(\mathit{aq}) \rightarrow MnO_2(s) + 2H_2O(\mathit{l})}$$

$$\mathbf{MnO_4^-(\mathit{aq}) + 4H^+(\mathit{aq}) + 3e^- \rightarrow MnO_2(s) + 2H_2O(\mathit{l})}$$

- Now balance electrons by using a common multiple:

$$\mathbf{3CN^-(\mathit{aq}) + 3H_2O(\mathit{l}) \rightarrow 3CNO^-(\mathit{aq}) + 6H^+(\mathit{aq}) + 6e^-}$$

$$\mathbf{2MnO_4^-(\mathit{aq}) + 8H^+(\mathit{aq}) + 6e^- \rightarrow 2MnO_2(s) + 4H_2O(\mathit{l})}$$

Balancing Redox Reactions That Occur in Basic Solution

- Now, at this point, we will make the necessary modification for the basic nature of the solution. We will neutralize $H^+(aq)$ by adding and equal number of $OH^-(aq)$ ions. ***This will produce $H_2O(l)$***.

$$3CN^-(aq) + 3H_2O(l) \rightarrow 3CNO^-(aq) + 6H^+(aq) + 6e^-$$

(To balance the $6H^+$ we need to add 6 OH^-, to keep things balanced we add to both sides)

$$3CN^-(aq) + 3H_2O(l) + 6OH^-(aq) \rightarrow 3CNO^-(aq) + 6H^+(aq) + 6OH^-(aq) + 6e^-$$

(The six H+ and OH- ions on the right side will neutralize to form $6H_2O$)

$$3CN^-(aq) + 3H_2O(l) + 6OH^-(aq) \rightarrow 3CNO^-(aq) + 6H_2O(l) + 6e^-$$

(We have three H_2O on the left, and six on the right. We can simplify as:)

$$3CN^-(aq) + 6OH^-(aq) \rightarrow 3CNO^-(aq) + 3H_2O(l) + 6e^-$$

Balancing Redox Reactions That Occur in Basic Solution

- Now the other half-reaction:

$$2MnO_4^-(aq) + 8H^+(aq) + 6e- \rightarrow 2MnO_2(s) + 4H_2O(l)$$

$$2MnO_4^-(aq) +8H^+(aq) +8OH^-(aq) +6e- \rightarrow 2MnO_2(s) +4H_2O(l) + 8OH^-(aq)$$

$$2MnO_4^-(aq) + 8H_2O(l) + 6e- \rightarrow 2MnO_2(s) + 4H_2O(l) + 8OH^-(aq)$$

$$2MnO_4^-(aq) + 4H_2O(l) + 6e- \rightarrow 2MnO_2(s) + 8OH^-(aq)$$

- The balanced half-reactions, and the net overall redox reaction are:

$$3CN^-(aq) + 6OH^-(aq) \rightarrow 3CNO^-(aq) + 3H_2O(l) + 6e-$$

$$2MnO_4^-(aq) + 4H_2O(l) + 6e- \rightarrow 2MnO_2(s) + 8OH^-(aq)$$

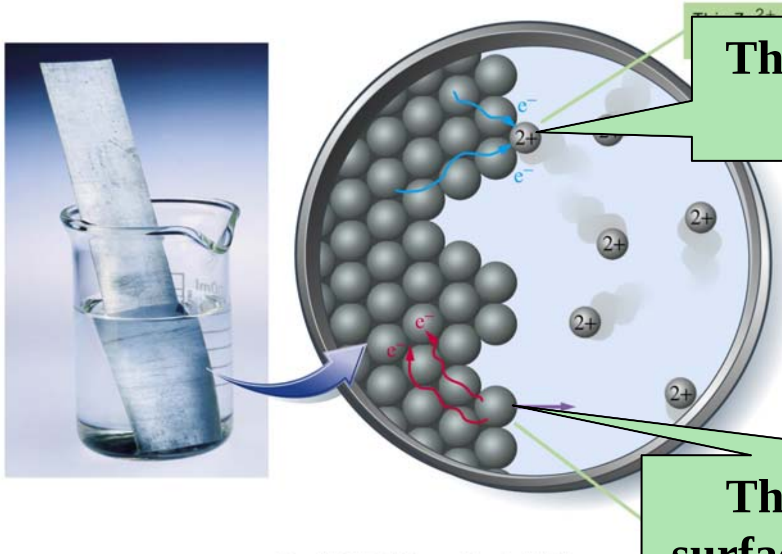
$$3CN^-(aq) +H_2O(l) +2MnO_4^-(aq) \rightarrow 3CNO^-(aq) +2MnO_2(s) +2OH^-(aq)$$

Redox Reactions in Acidic and in Basic Solution

- Redox reactions in acidic solution and in basic solution may be very different from one another.
- If ***acidic*** solution is specified, we must add H_2O and/or H^+ as needed when we balance the number of atoms.
- If ***basic*** solution is specified, the final equation may have $OH^–$ and/or water molecules in it.
- A simple way to balance an equation in basic solution:
  - Balance the equation as though it were in acidic solution.
  - Add as many $OH^–$ ions to *each* side as there are H^+ ions in the equation.
  - Combine the H^+ and $OH^–$ ions to give water molecules on one side, and simplify the equation as necessary.

A Qualitative Description of Voltaic Cells

- **A spontaneous redox reaction involves *the transfer of electrons.***
- **In principle, this transfer or movement of electrons can be used to do a type of work - specifically, electrical work.**
- **A type of device that makes use of redox reactions to produce electron flow, and to allow electrical work, is known as a *Voltaic Cell* (named after Count Alessandro Volta, 1745-1827, an Italian physicist)**
- **A half-cell consists of an electrode (strip of metal or other conductor) immersed in a solution of ions.**



This Zn^{2+} becomes a Zn atom.

This Zn atom leaves the surface to become a Zn^{2+} ion.

Both oxidation and reduction occur at the electrode surface, and equilibrium is reached.

Important Electrochemical Terms

- An ***electrochemical cell*** consists of two half-cells with the appropriate connections between electrodes and solutions.
- Two half-cells may be joined by a ***salt bridge*** that permits migration of ions, without completely mixing the solutions.
- The ***anode*** is the electrode at which oxidation occurs.
- The ***cathode*** is the electrode at which reduction occurs.
- In a ***voltaic cell***, a spontaneous redox reaction occurs and current is generated.
- ***Cell potential*** ($\boldsymbol{E_{\text{cell}}}$) is the potential difference in volts between anode and cathode.
- E_{cell} is the driving force that moves electrons and ions.

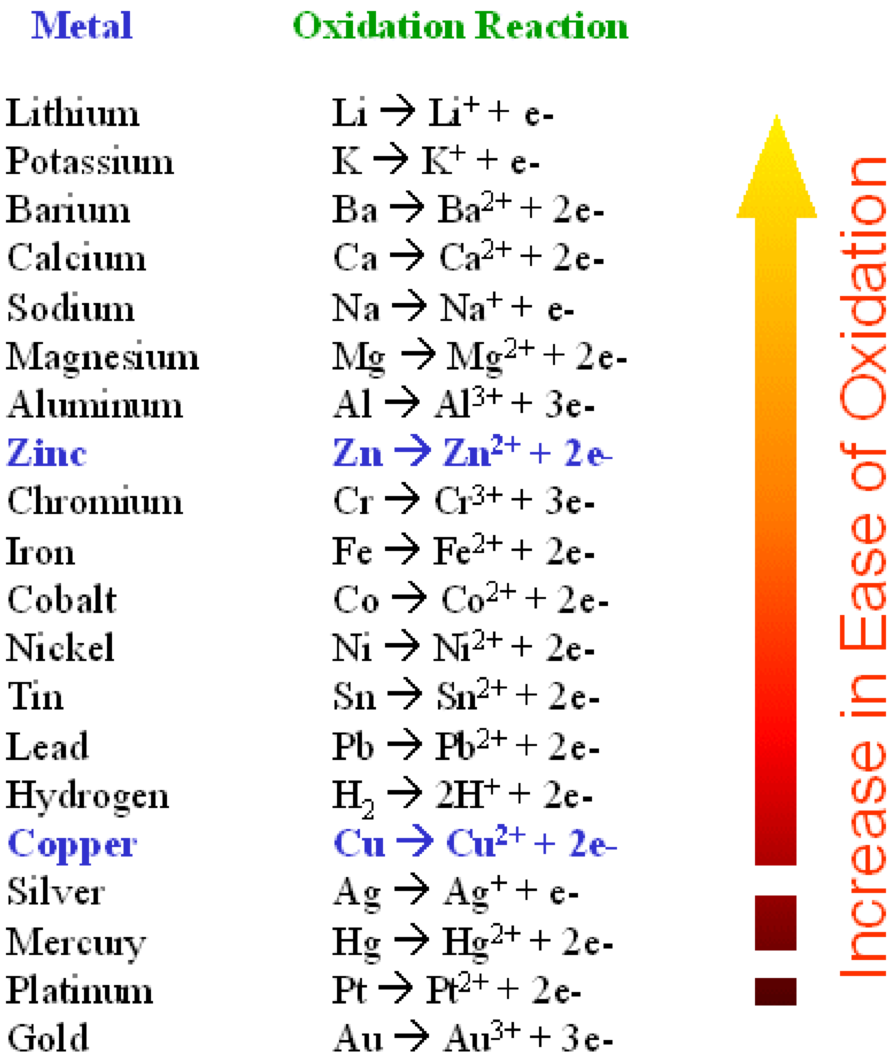
The development of the voltaic cell begins as follows... A spontaneous redox reaction involves the metals Zinc (Zn) and Copper (Cu)

The development of the voltaic cell begins as follows...
A spontaneous redox reaction involves the metals Zinc (Zn) and Copper (Cu). If you recall the *Activity Series for metals and hydrogen ion:*

When comparing Zinc with Copper in the activity series, ***Zinc should be easier to oxidize (i.e. should give up electrons easier) than Copper.***
The *spontaneity* of the reaction between zinc and copper ion reflects the Activity Series relationship:

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

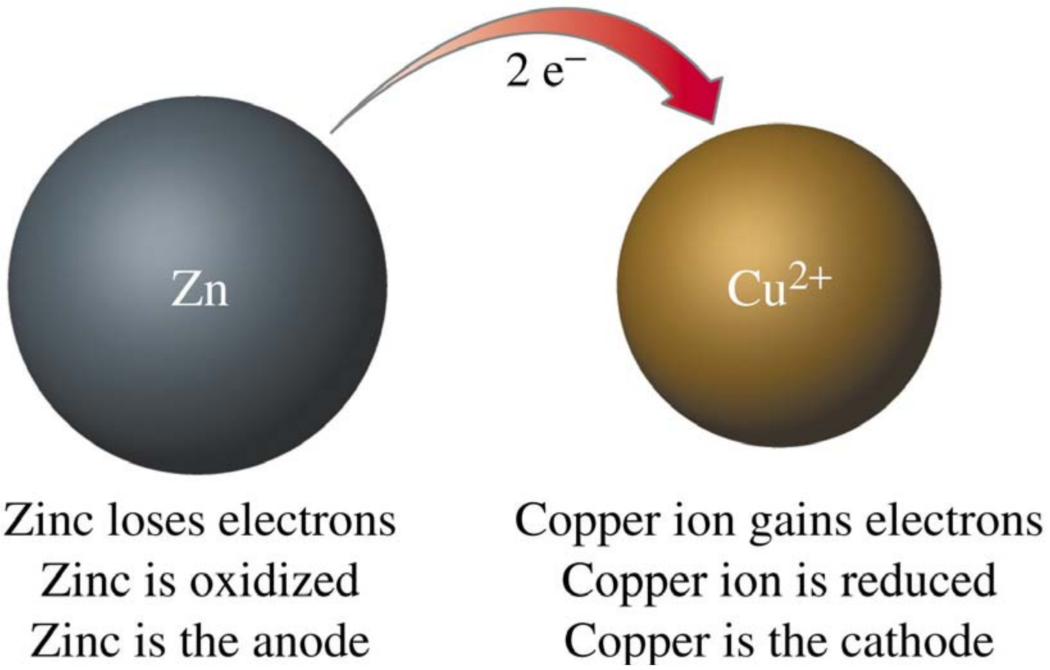
The reaction is spontaneous.



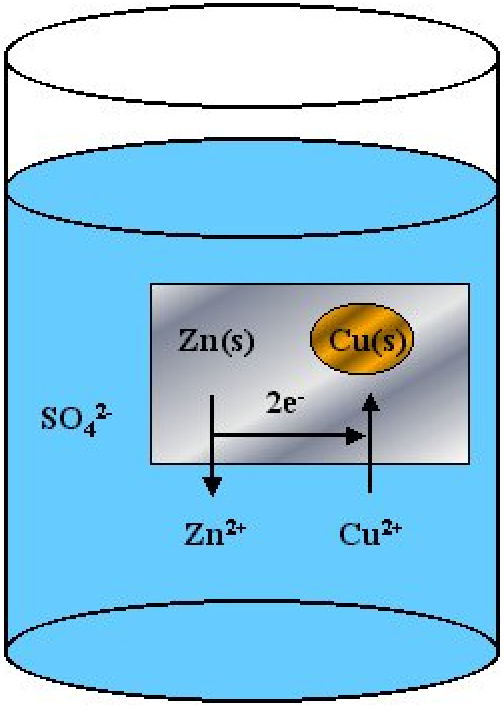
Metal	Oxidation Reaction
Lithium	$Li \rightarrow Li^{+} + e^{-}$
Potassium	$K \rightarrow K^{+} + e^{-}$
Barium	$Ba \rightarrow Ba^{2+} + 2e^{-}$
Calcium	$Ca \rightarrow Ca^{2+} + 2e^{-}$
Sodium	$Na \rightarrow Na^{+} + e^{-}$
Magnesium	$Mg \rightarrow Mg^{2+} + 2e^{-}$
Aluminum	$Al \rightarrow Al^{3+} + 3e^{-}$
Zinc	$Zn \rightarrow Zn^{2+} + 2e^{-}$
Chromium	$Cr \rightarrow Cr^{3+} + 3e^{-}$
Iron	$Fe \rightarrow Fe^{2+} + 2e^{-}$
Cobalt	$Co \rightarrow Co^{2+} + 2e^{-}$
Nickel	$Ni \rightarrow Ni^{2+} + 2e^{-}$
Tin	$Sn \rightarrow Sn^{2+} + 2e^{-}$
Lead	$Pb \rightarrow Pb^{2+} + 2e^{-}$
Hydrogen	$H_2 \rightarrow 2H^{+} + 2e^{-}$
Copper	$Cu \rightarrow Cu^{2+} + 2e^{-}$
Silver	$Ag \rightarrow Ag^{+} + e^{-}$
Mercury	$Hg \rightarrow Hg^{2+} + 2e^{-}$
Platinum	$Pt \rightarrow Pt^{2+} + 2e^{-}$
Gold	$Au \rightarrow Au^{3+} + 3e^{-}$

The Zinc metal is *oxidized*, and the Copper ion is *reduced*
The reverse reaction, the oxidation of Copper and the reduction of Zinc ion, *is not spontaneous*. The *redox half-reactions are:*
***Oxidation:* $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$**
***Reduction:* $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$**

The oxidation of a Zinc atom releases 2 electrons. The reduction of a Copper ion is achieved by the acceptance of 2 electrons. *Thus, there would appear to be a movement, or flow, of electrons from the Zinc metal to the Copper ions.*



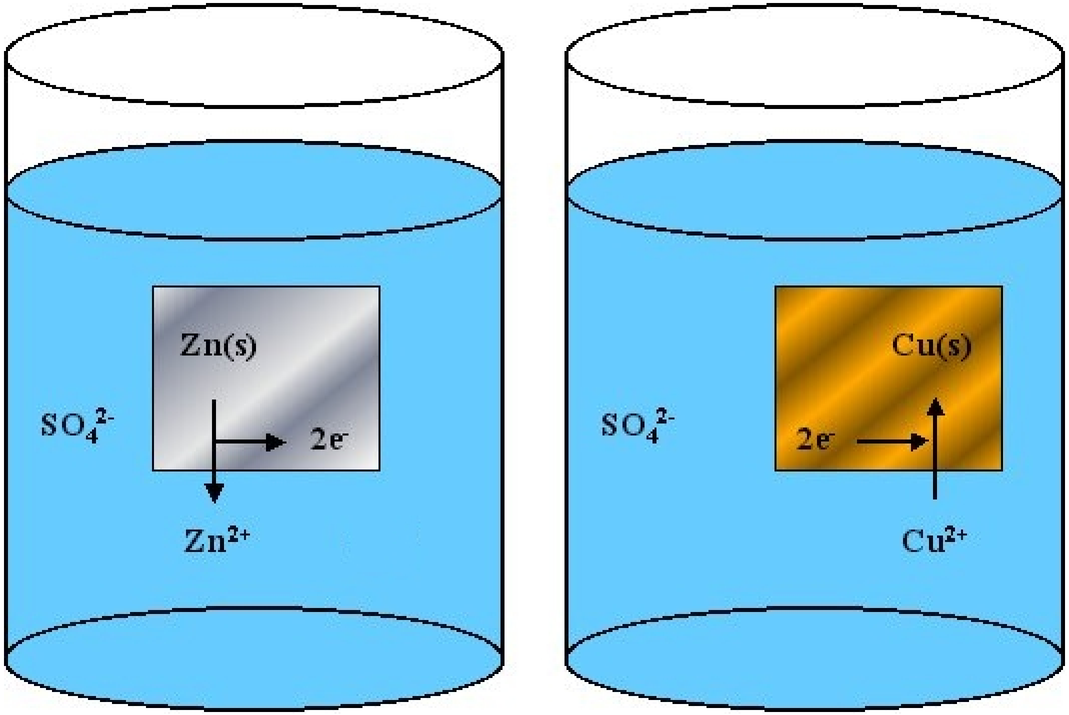
Accordingly, if Zinc metal is placed in an aqueous solution containing Cu^{2+} ions (e.g. a solution of $CuSO_4$ salt), the following will occur:



- At the surface of the Zn metal, the oxidation of Zn atoms will be coupled to the reduction of Cu^{2+} ions.
- Electrons from the oxidation of the Zn will reduce the Cu ions to elemental Cu on the surface of the Zn metal.
- Over time, the Zn metal will dissolve (as solid Zn is oxidized to Zn ion) and Zn ion will build up in the solution.
- Also over time, the solution will no longer contain Cu ions, an the copper will be present in elemental form.

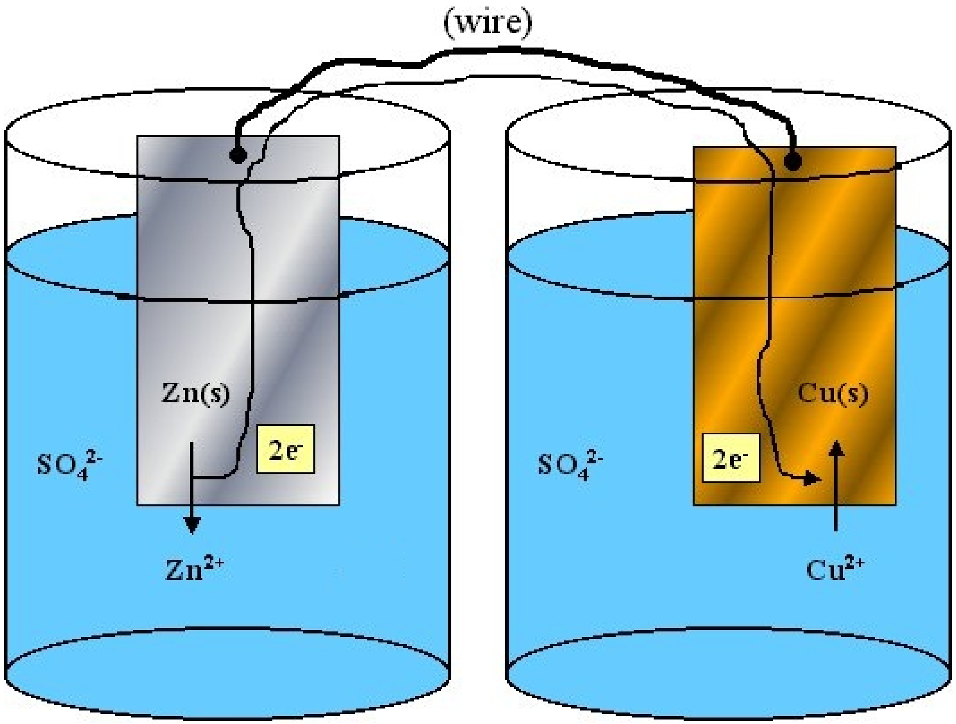
In the above case, Zn and Cu metal/ions ***are in direct contact with each other and that the reduced form of the copper (i.e. the metal) builds up on the surface of Zn.***

What if we separated the $Cu(s)/Cu^{2+}$ from the $Zn(s)/Zn^{2+}$?



- **The reaction <u>will not occur because</u> there is no way for the electrons released by the oxidation of Zinc metal to get over to the Copper ions and reduce them to Copper metal**

What if we provide a path of conductance for the electrons released by the oxidation of the zinc to get over to the copper?



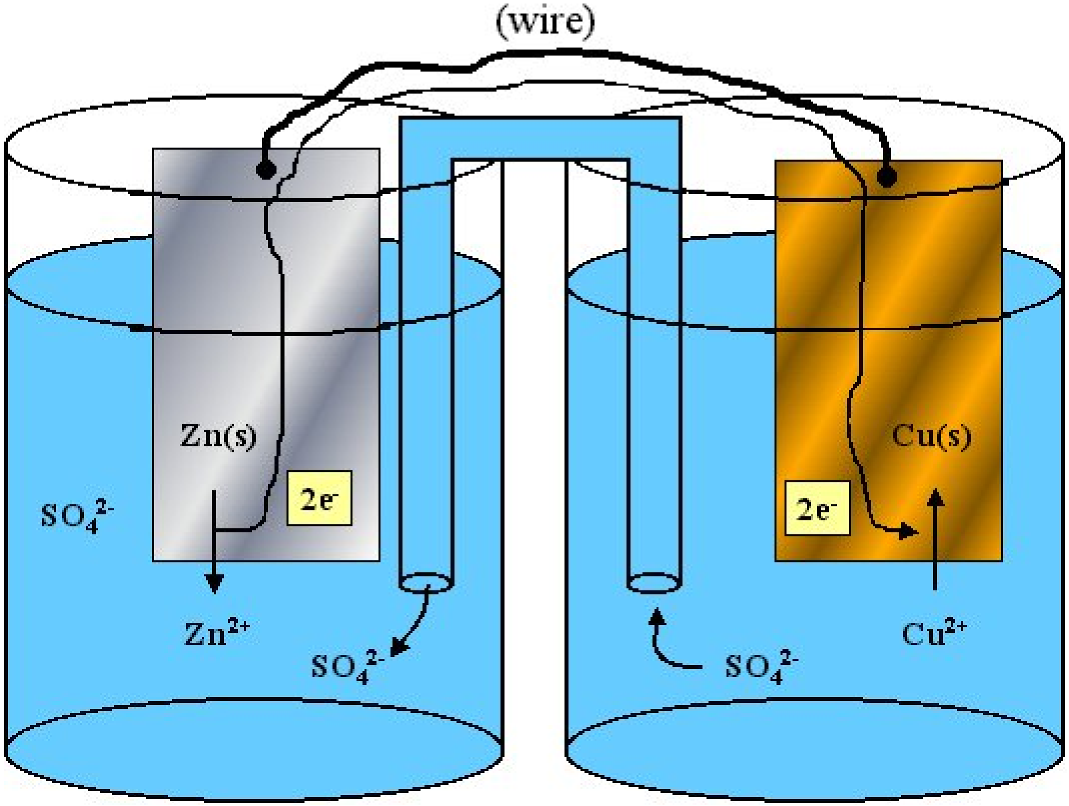
- **Now that the electrons have a path to the Cu/Cu^{2+} side it would appear that the reaction can proceed**

However, we now have <u>another problem</u> ...

- **As the redox reaction proceeds we build up Zn^{2+} ions in the solution where the Zinc is being oxidized. Conversely, we remove Cu^{2+} ions from solution where the Copper ion is being reduced.**
- **Yet, the anion concentration (sulfate ion in this case) does not change.**
- **Thus, we are building up a *net positive charge* in the zinc solution, and *a net negative charge* in the copper solution.**
- **These charges will oppose the flow of electrons. The positive charge in the zinc solution will make it harder for the negative electrons to leave. Likewise, the negative charge in the copper solution will repel the electrons that are trying to come over from the Zn side**

- *We need a way to neutralize the charge build-up in the solutions due to the change in soluble ion concentration*

What if we had a tube filled with aqueous solution that connected the two redox reactions?

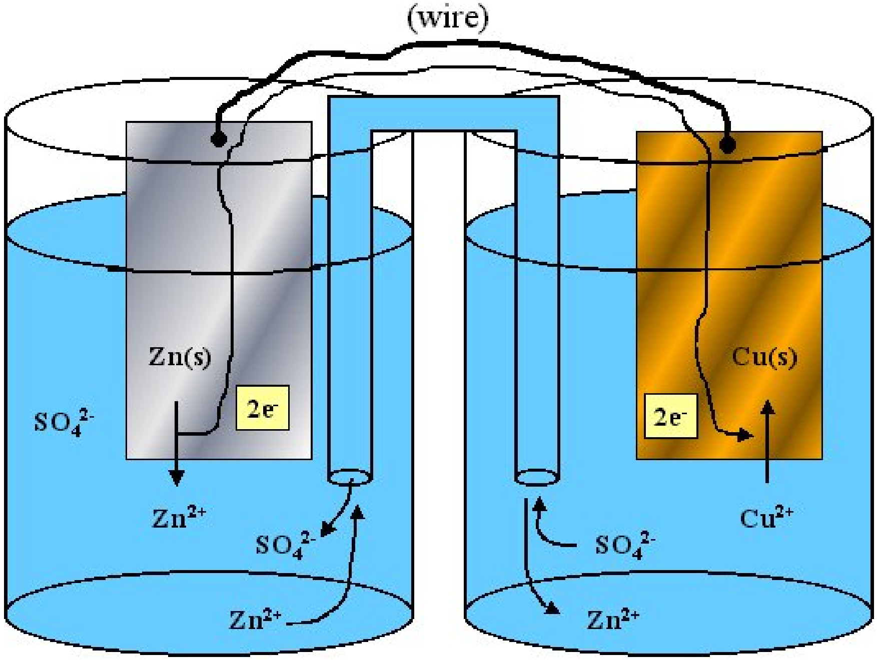


- **This would allow anion to move from the copper reduction side to the zinc oxidation side and keep the charges in solution neutral**
- **In turn, this would now allow the electrons to flow**
- **However, as the reaction proceeds...**

Although movement of anion allows the overall charges in solution to remain neutral, the net movement of anion produces a ***concentration gradient*** across the two solutions. In other words, after a while the net concentration of ions in the Zn oxidation side will be greater than in the Cu reduction side. This concentration gradient will oppose movement of anions.

What it means is that we have to realize that charge neutralization can occur by either anions moving to the left or *cations moving to the right.*

In consideration of keeping the overall concentration of ions in balance between the two sides, cations will also be moving to the right:

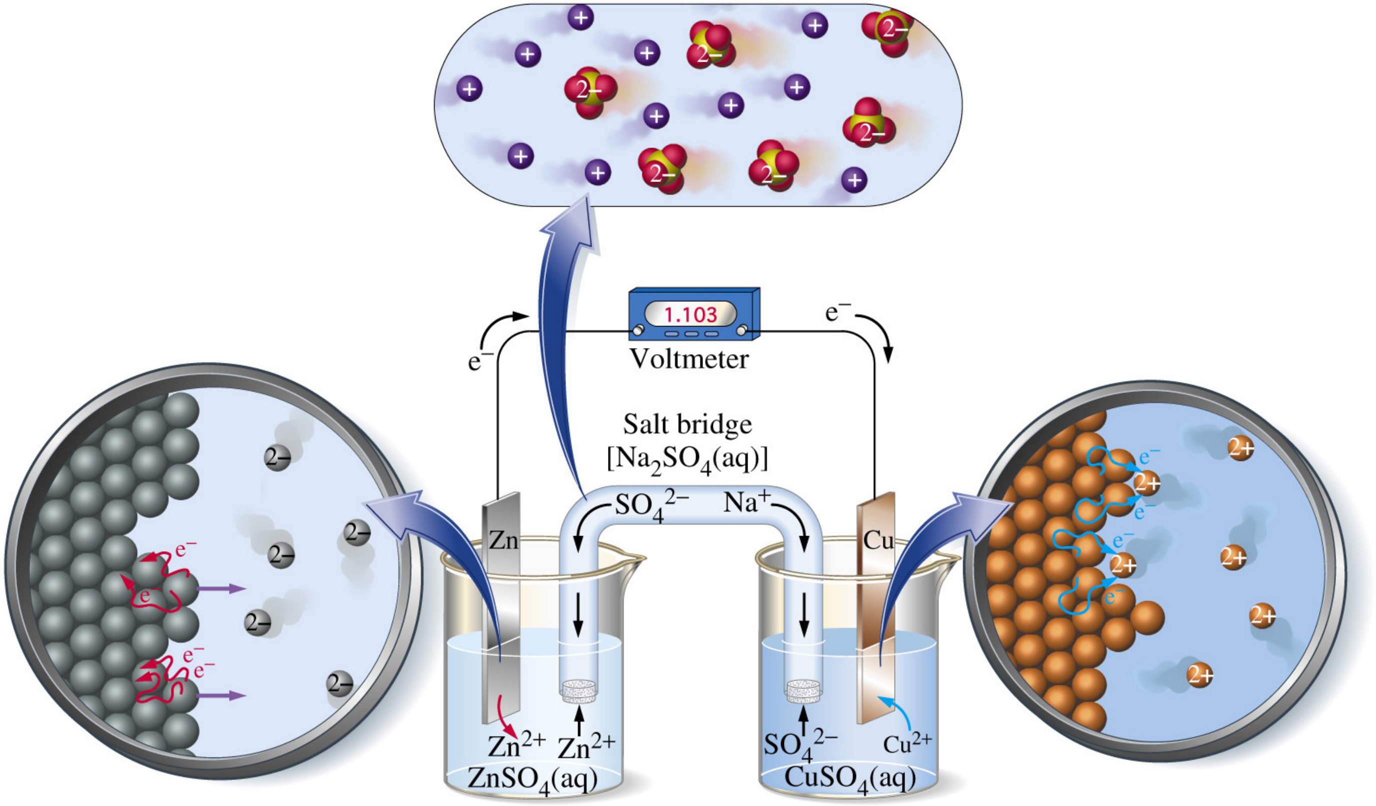


Thus, in the connecting tube of solution we have net movement of both types of ions:

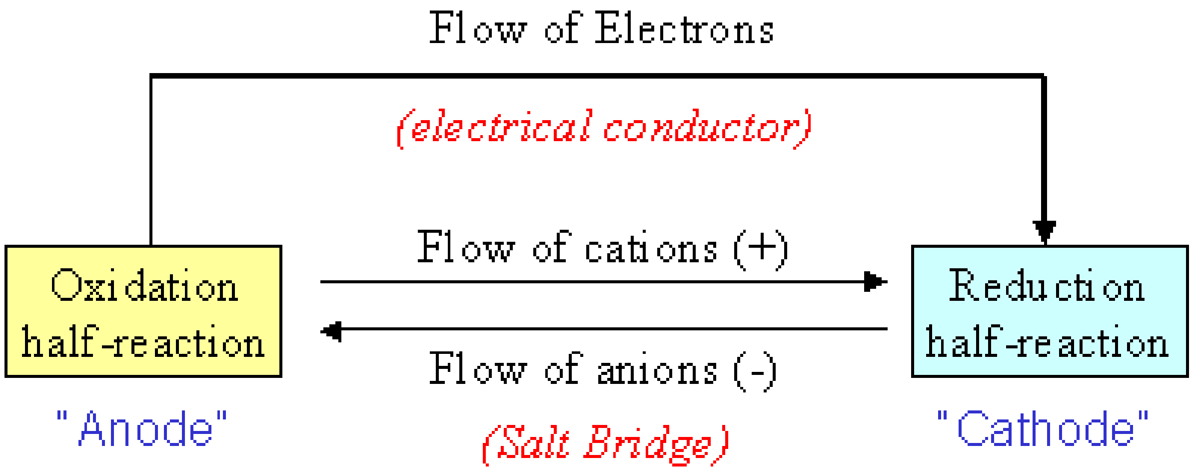
anions are going into the oxidation side

cations going into the reduction side

- **The connecting tube of solution is called a Salt Bridge**



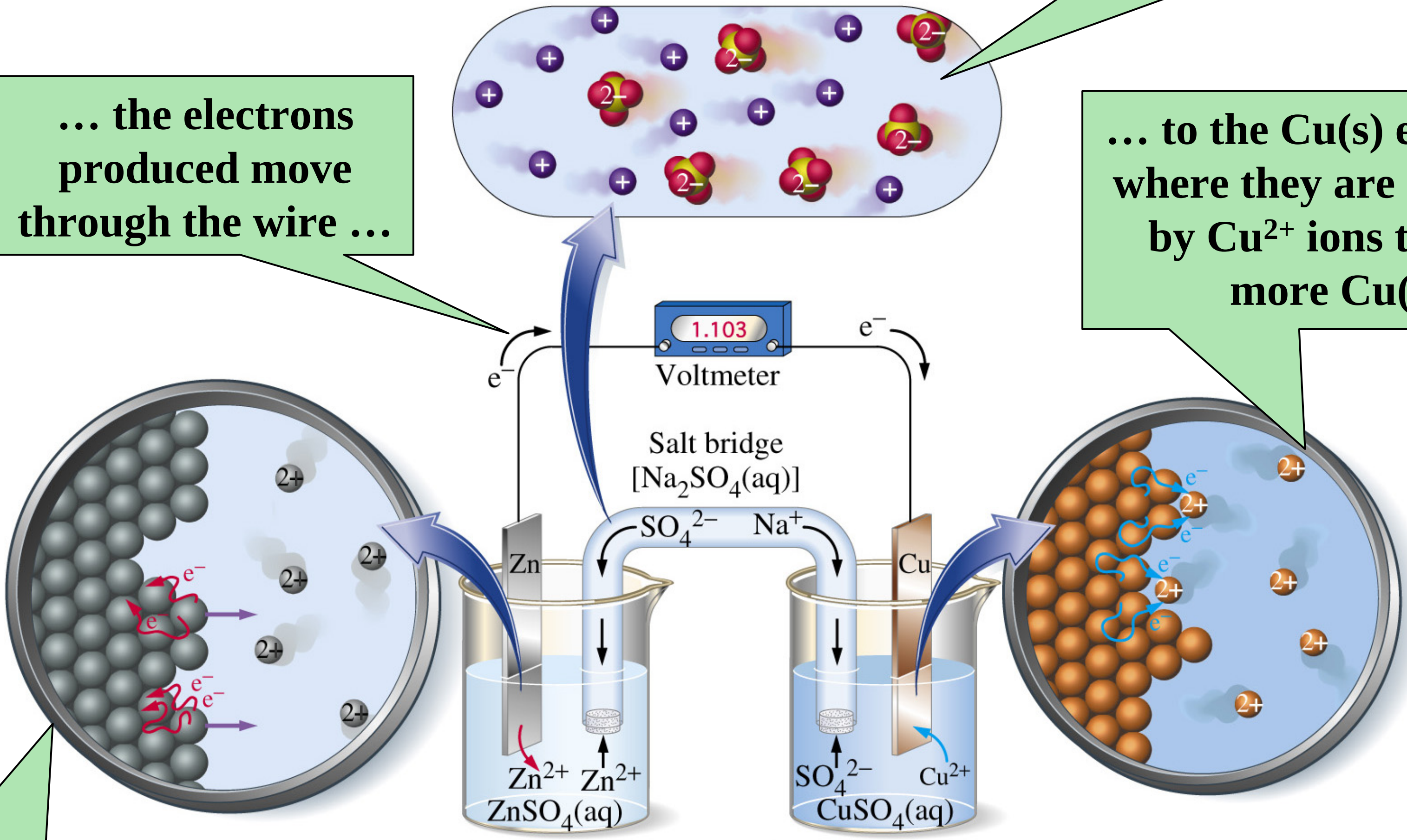
Summary of the movement of ions, electrons and the redox half-reactions in a *voltaic cell*:



The two solid metals in the different half-reactions are called *electrodes*.

- ***The metal in the half-reaction where oxidation is occurring is called the Anode***
- ***The metal in the half-reaction where reduction is occurring is called the Cathode***
- ***The cathode is often labeled with a "+"; "this electrode attracts electrons"***
- ***The anode is often labeled with a "-"; "this electrode repels electrons"***

A Zinc–Copper Voltaic Cell



Zn(s) is oxidized to Zn^{2+} ions, and …

… the electrons produced move through the wire …

… to the Cu(s) electrode, where they are accepted by Cu^{2+} ions to form more Cu(s).

Positive and negative ions move through the salt bridge to equalize the charge.

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

Cell Diagrams – Conventions

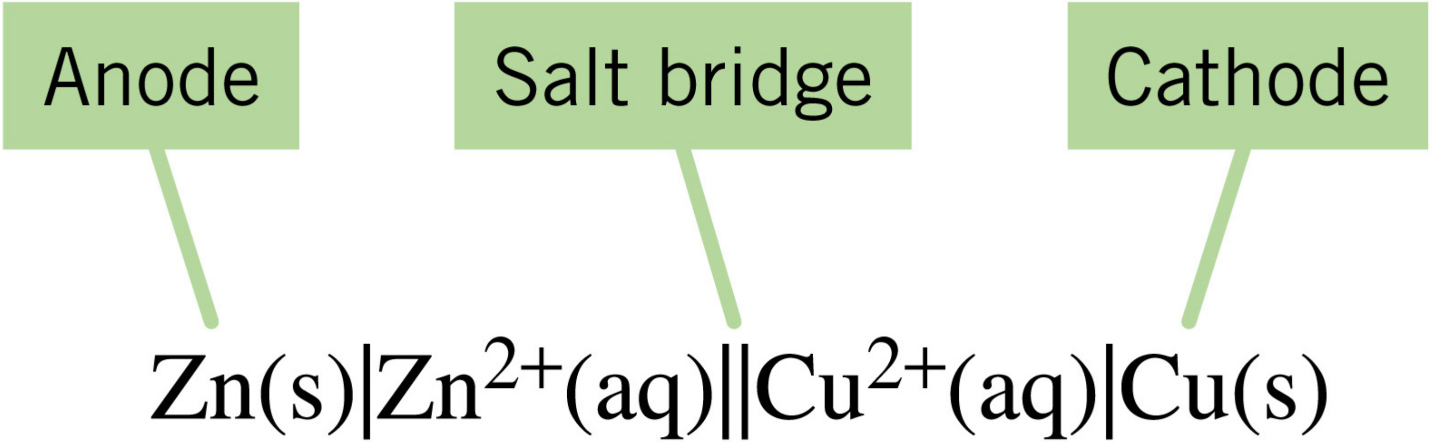
Place the ***anode*** on the ***left*** side of the diagram

Place the ***cathode*** on the ***right*** side of the diagram

Use a single vertical line (|) to represent the **boundary between different phases**, such as between an electrode and a solution

Use a double vertical line (||) to represent a **salt bridge or porous barrier** separating two half-cells

An Example Cell Diagram



Anode

Salt bridge

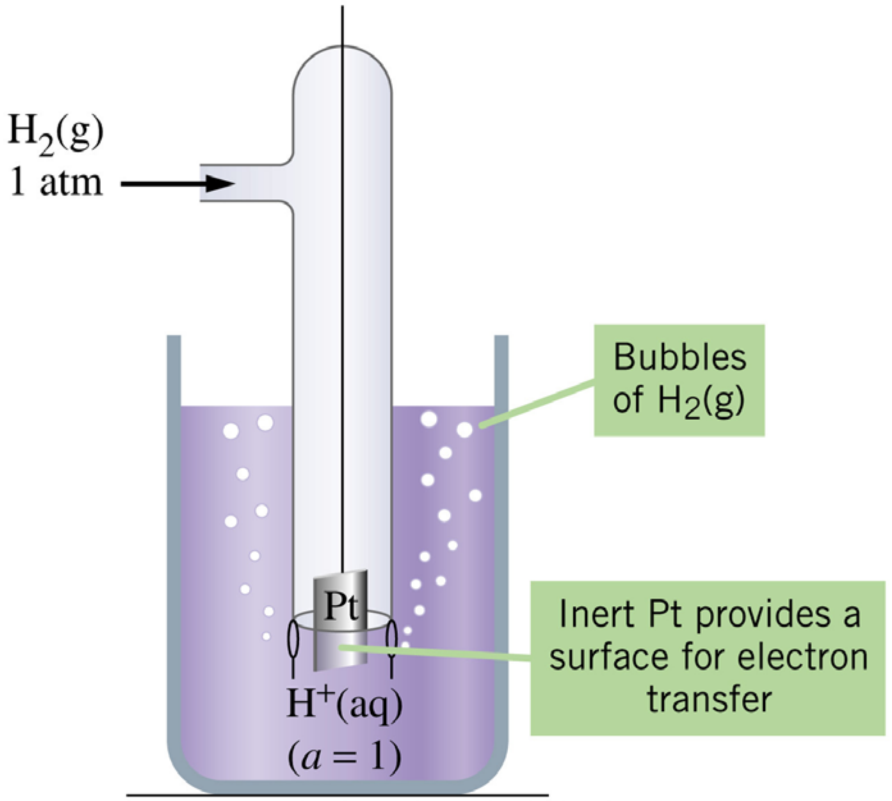
Cathode

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

Half-cell
(oxidation)

Half-cell
(reduction)

Standard Hydrogen Electrode



In the **standard hydrogen electrode**, ***hydrogen gas at exactly 1 bar pressure*** is bubbled over an **inert platinum electrode** and into an aqueous solution with the concentration adjusted so that the ***activity of H_3O^+ is exactly equal to one***

Standard Electrode Potentials

A **standard electrode potential**, ***E^o***, is based on the tendency for reduction to occur at the electrode

The cell voltage, called the **standard cell potential** **(E^o_{cell})**, is the ***difference between*** the standard potential of the ***cathode*** and that of the ***anode***

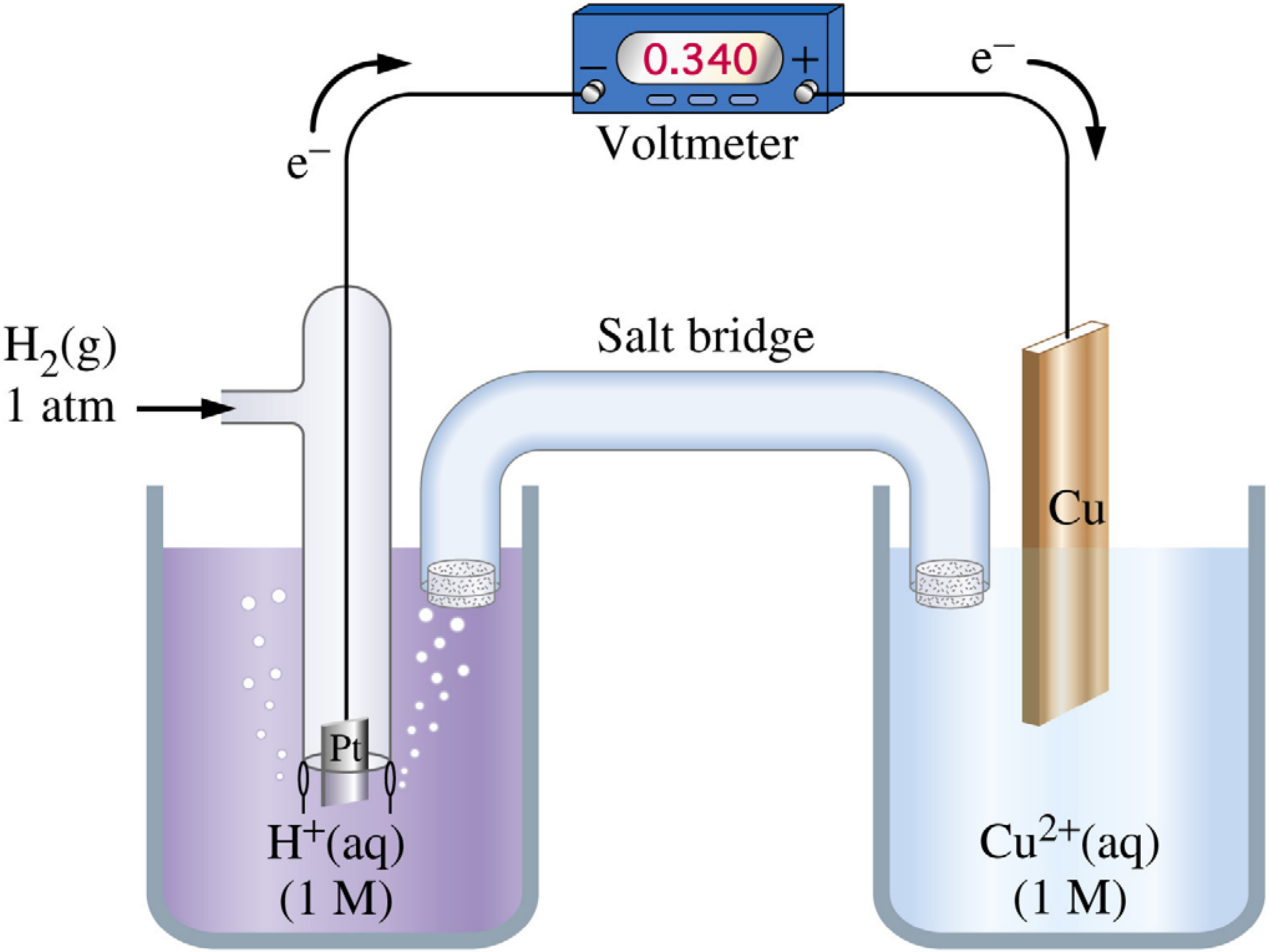
Voltaic cells can produce **electrical work**

$$w = -n\,F\,E_{\mathrm{cell}}$$

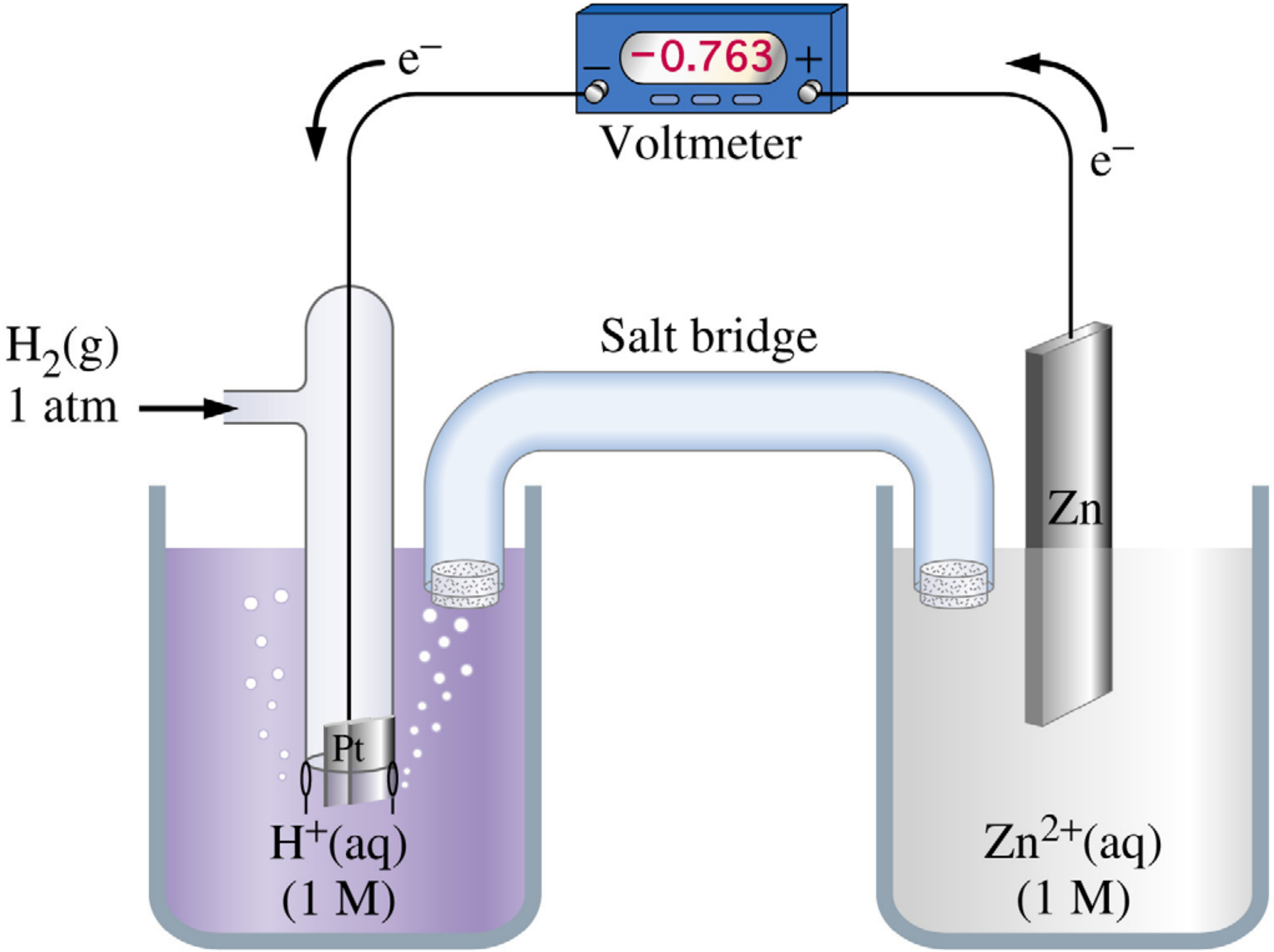
Two illustrations … Cu and Zn

VideoClip

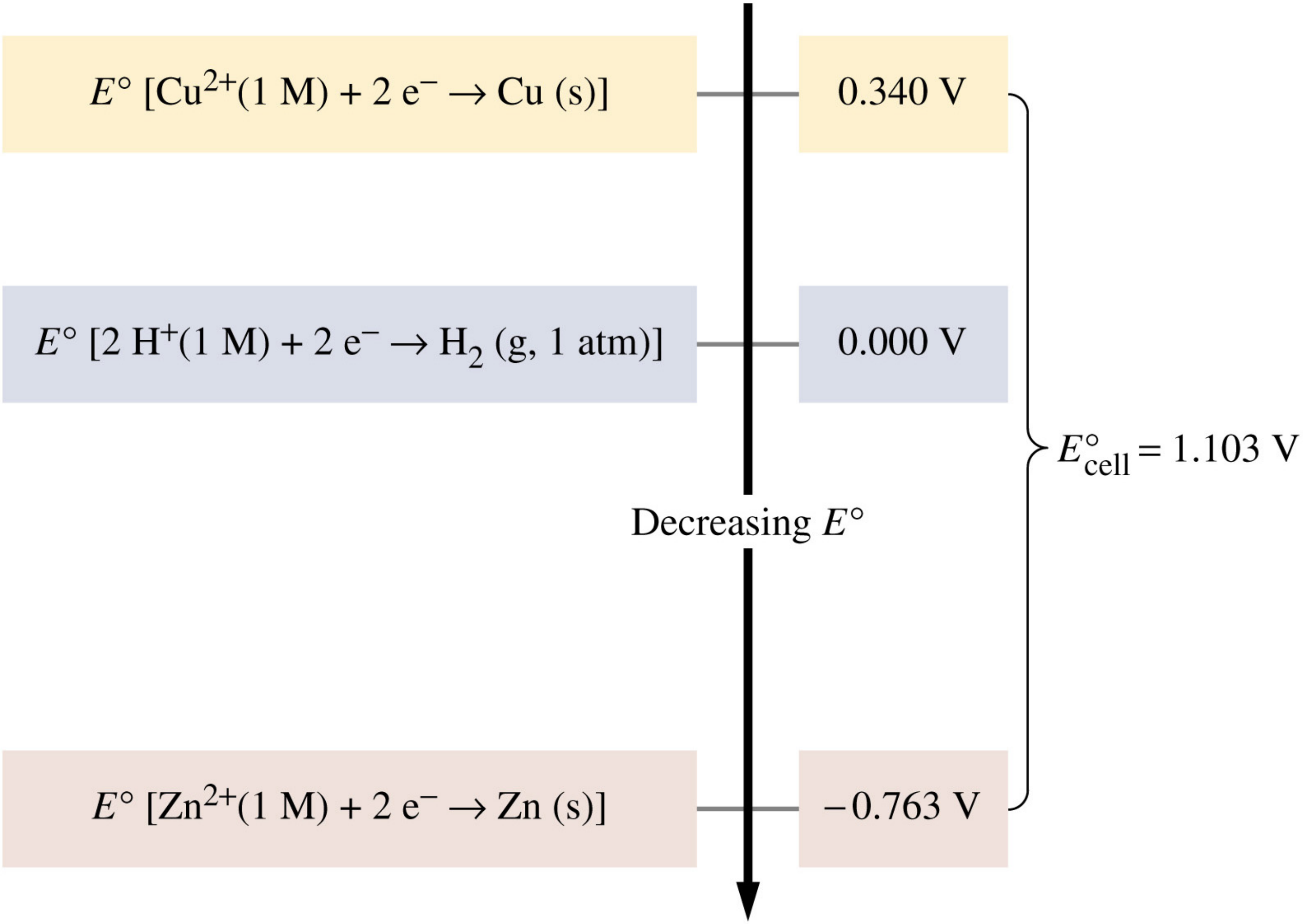
Cu^{2+}/Cu Electrode



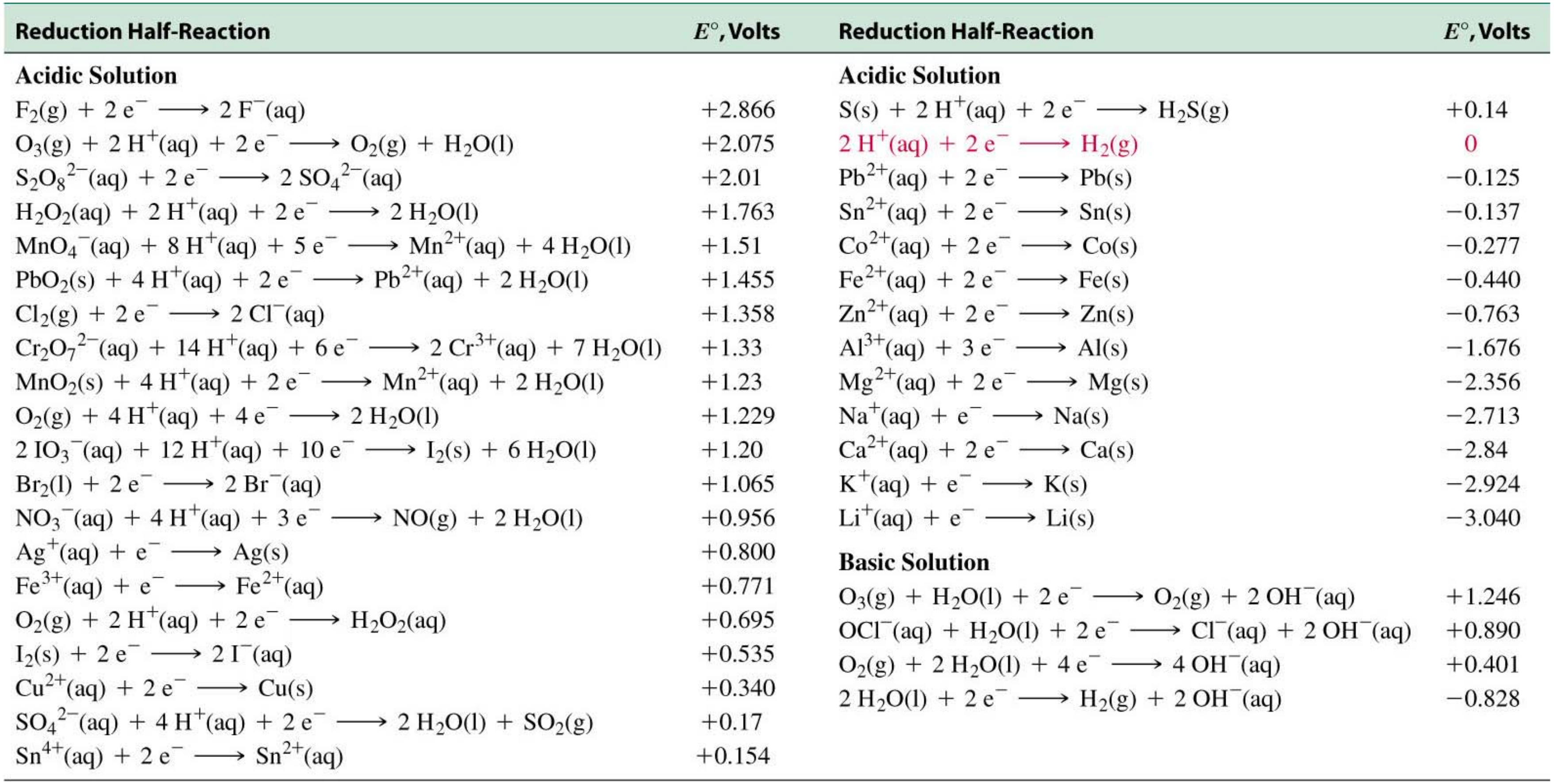
Zn^{2+}/Zn Electrode



Observed Voltages …



Selected Standard Electrode Potentials at 25 ^oC



Reduction Half-Reaction	**$E°$, Volts**	**Reduction Half-Reaction**	**$E°$, Volts**
Acidic Solution		**Acidic Solution**	
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.866	$S(s) + 2H^+(aq) + 2e^- \longrightarrow H_2S(g)$	+0.14
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O(l)$	+2.075	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0
$S_2O_8{}^{2-}(aq) + 2e^- \longrightarrow 2SO_4{}^{2-}(aq)$	+2.01	$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.125
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O(l)$	+1.763	$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.137
$MnO_4{}^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.51	$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.277
$PbO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Pb^{2+}(aq) + 2H_2O(l)$	+1.455	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.440
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.358	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.763
$Cr_2O_7{}^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.676
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O(l)$	+1.23	$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.356
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$	+1.229	$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.713
$2IO_3{}^-(aq) + 12H^+(aq) + 10e^- \longrightarrow I_2(s) + 6H_2O(l)$	+1.20	$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.84
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.065	$K^+(aq) + e^- \longrightarrow K(s)$	−2.924
$NO_3{}^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O(l)$	+0.956	$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.040
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.800	**Basic Solution**	
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.771	$O_3(g) + H_2O(l) + 2e^- \longrightarrow O_2(g) + 2OH^-(aq)$	+1.246
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.695	$OCl^-(aq) + H_2O(l) + 2e^- \longrightarrow Cl^-(aq) + 2OH^-(aq)$	+0.890
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.535	$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$	+0.401
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.340	$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.828
$SO_4{}^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow 2H_2O(l) + SO_2(g)$	+0.17		
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.154		

Important Points About Electrode and Cell Potentials

Electrode potentials and cell voltages are ***intensive*** properties – ***independent of the amount of matter***

Cell voltages can be ascribed to oxidation–reduction reactions without regard to voltaic cells

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

Criteria for Spontaneous Change

If E_{cell} is ***positive***, the reaction in the **forward direction** (from left to right) is **spontaneous**

If E_{cell} is ***negative***, the reaction is non***spontaneous***
If E_{cell} **= 0,** the system is at ***equilibrium***

When a cell reaction is ***reversed***, $\boldsymbol{E_{\text{cell}}}$ **and** $\boldsymbol{\Delta G}$ **change signs**

Equilibrium Constants for Redox Reactions

$\Delta G^{\text{o}} = -RT\ln K_{\text{eq}} = -n \times F \times E^{\text{o}}_{\text{cell}}$ $\boldsymbol{E^{\text{o}}_{\text{cell}} = \frac{RT}{nF}\ln K_{\text{eq}}}$

$E^{\text{o}}_{\text{cell}}$ = standard cell potential

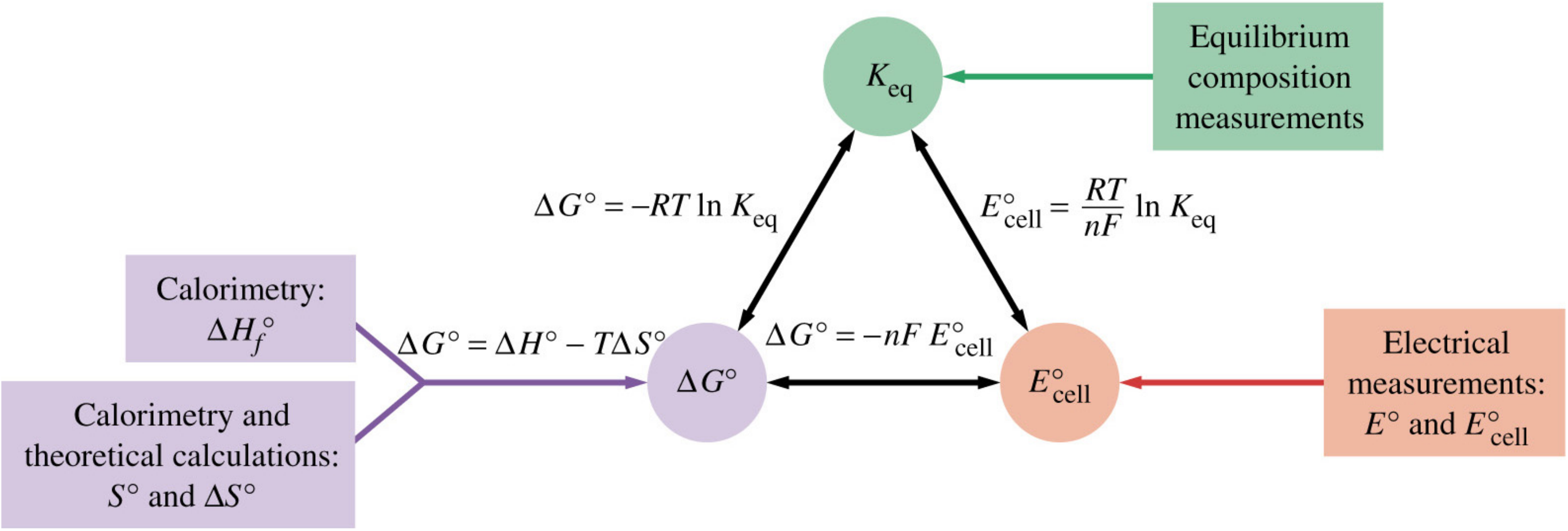
R is the gas constant (8.3145 J mol^{-1} K^{-1})

T is the Kelvin temperature

n is the number of moles of electrons involved in the reaction

F is the faraday constant

Summary of Important Relationships



K_{eq}

Equilibrium composition measurements

$\Delta G^\circ = -RT \ln K_{eq}$

$E^\circ_{cell} = \frac{RT}{nF} \ln K_{eq}$

Calorimetry: ΔH_f°

Calorimetry and theoretical calculations: S° and ΔS°

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

ΔG°

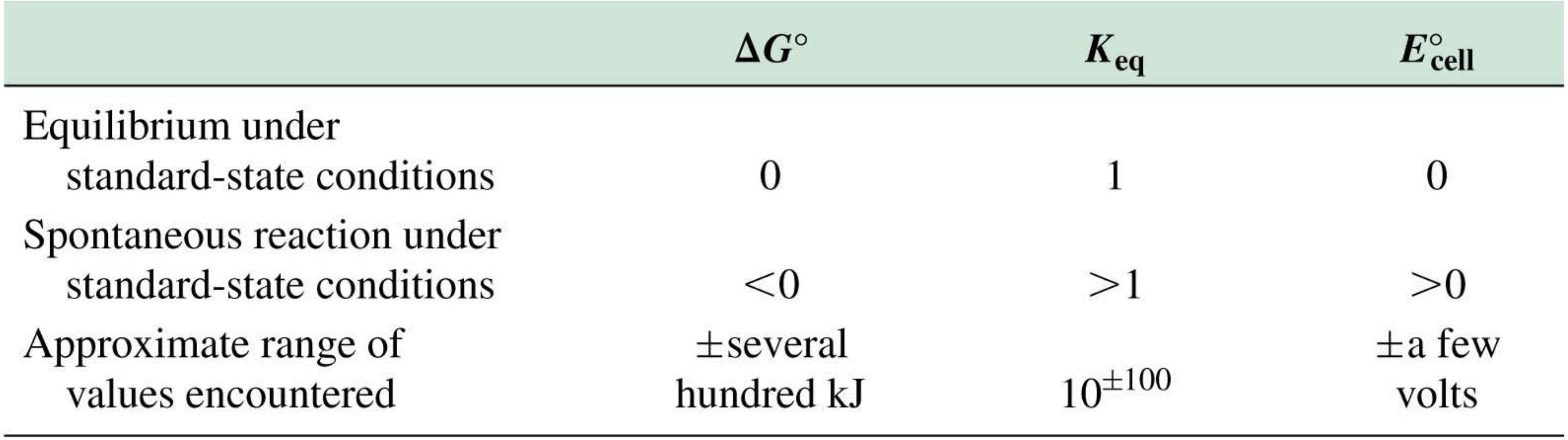
$\Delta G^\circ = -nF\,E^\circ_{cell}$

E°_{cell}

Electrical measurements: E° and E°_{cell}

General Values and Meanings

Reaction behavior can be predicted using the following information …



	ΔG°	K_{eq}	E°_{cell}
Equilibrium under standard-state conditions	0	1	0
Spontaneous reaction under standard-state conditions	<0	>1	>0
Approximate range of values encountered	±several hundred kJ	$10^{\pm 100}$	±a few volts

Concentration and Cell Voltage

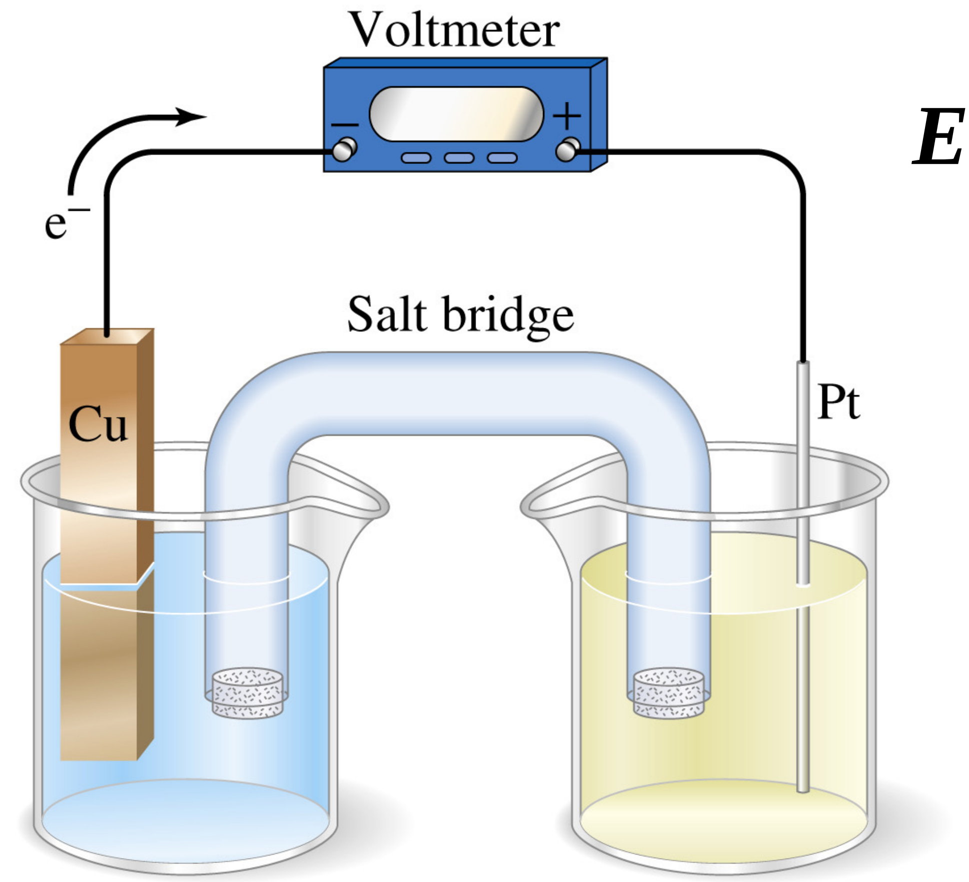
If the discussion is limited to 25 °C, the equation is

$$\boldsymbol{E}_{\text{cell}} = \boldsymbol{E}^{\text{o}}_{\text{cell}} - \frac{\boldsymbol{RT}}{\boldsymbol{nF}} \ln \boldsymbol{Q} = \boldsymbol{E}^{\text{o}}_{\text{cell}} - \frac{0.0592}{\boldsymbol{n}} \ln \boldsymbol{Q}$$

The **Nernst equation** relates a cell voltage for ***nonstandard conditions (E_{cell})*** to a standard cell voltage, $E^{\text{o}}_{\text{cell}}$, and the concentrations of reactants and products

The Nernst equation is useful for determining the concentration of a species in a voltaic cell through a measurement of E_{cell}

A Sample Problem



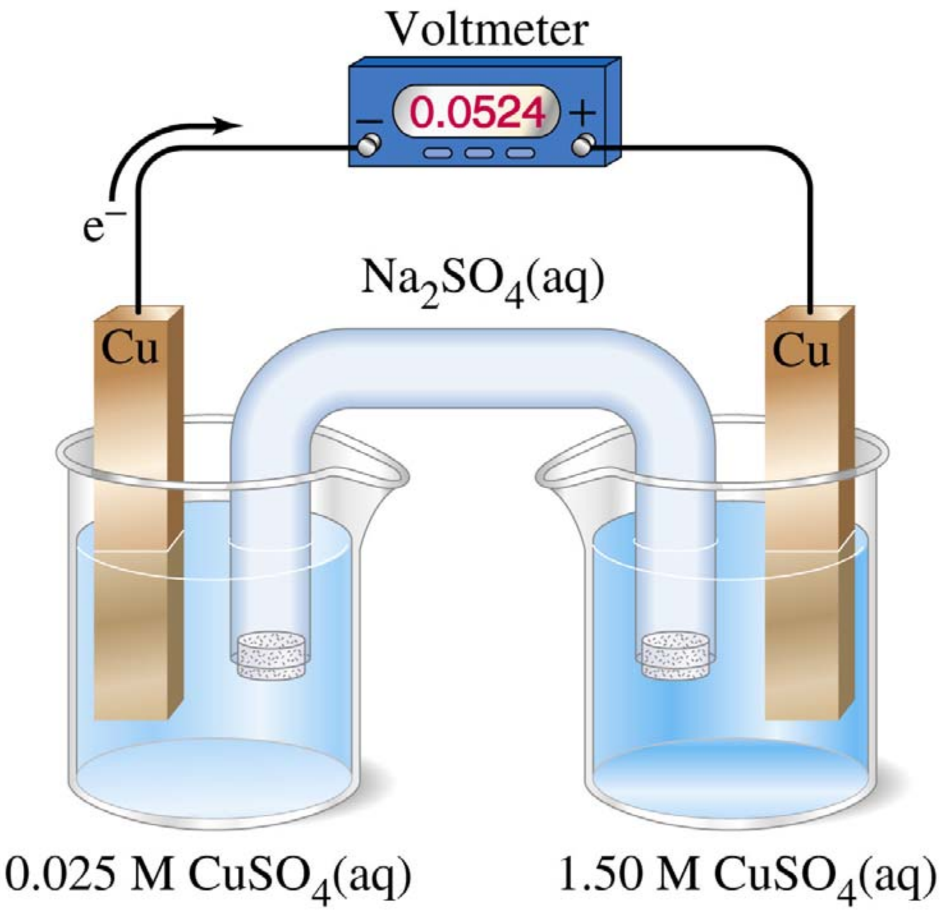
$[Cu^{2+}] = 0.50\ M$

$[Fe^{2+}] = 0.10\ M$

$[Fe^{3+}] = 0.20\ M$

$$\boldsymbol{E}_{\text{cell}} = \boldsymbol{E}^{\text{o}}_{\text{cell}} - \frac{0.0592}{\boldsymbol{n}} \ln \boldsymbol{Q}$$

Concentration Cells



If the cell potential is determined solely by a difference in the concentration of solutes in equilibrium with identical electrodes, that cell is called a ***concentration cell***

pH Measurement

One useful concentration cell is the hydrogen cell … it is directly related to pH

The Nernst equation can be rewritten in terms of concentration cells using hydrogen electrodes

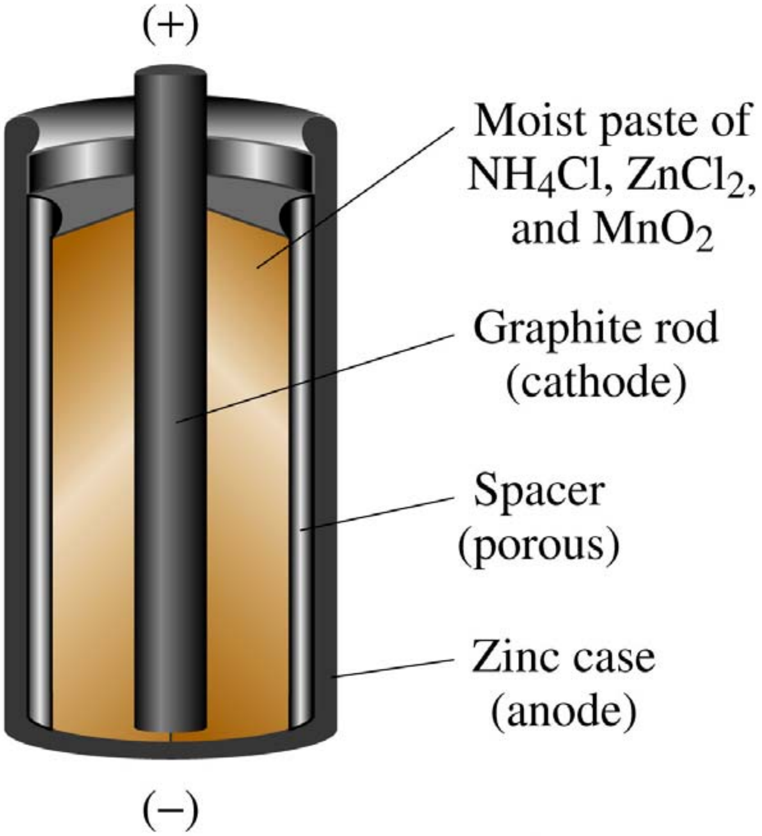
$$E_{\text{cell}} = (0.0592)(\text{pH})$$

The Dry Cell

Portable electronic devices use *primary cells* (also called *dry cells*)

The reactions in primary cells are irreversible

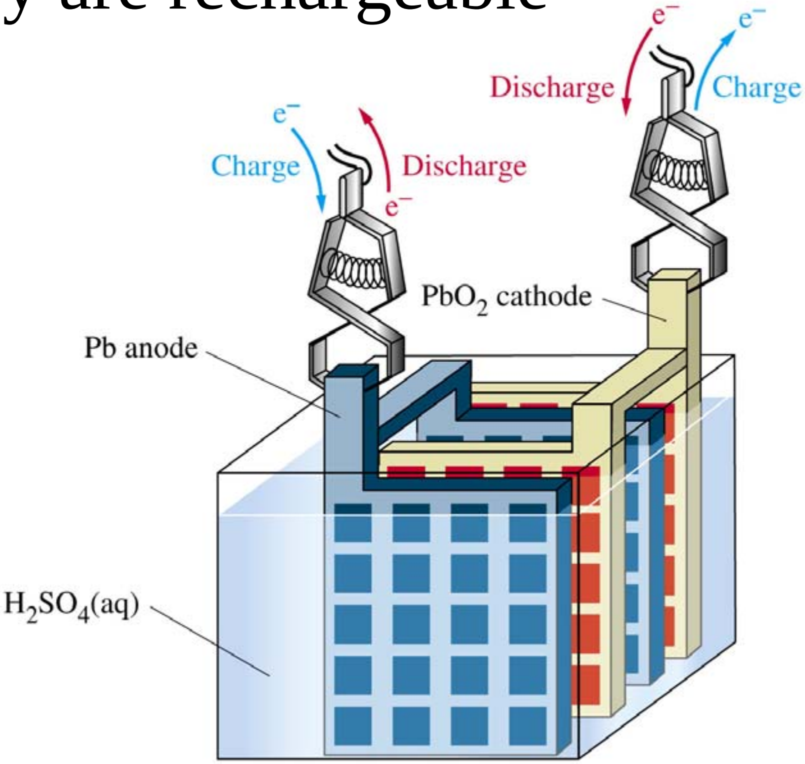
$Zn \rightarrow Zn^{2+}$, accumulates near anode, causing rapid drop in voltage vs. time



The Lead–Acid Storage Battery

The lead–acid storage battery used in automobiles uses *secondary cells*; they are rechargeable

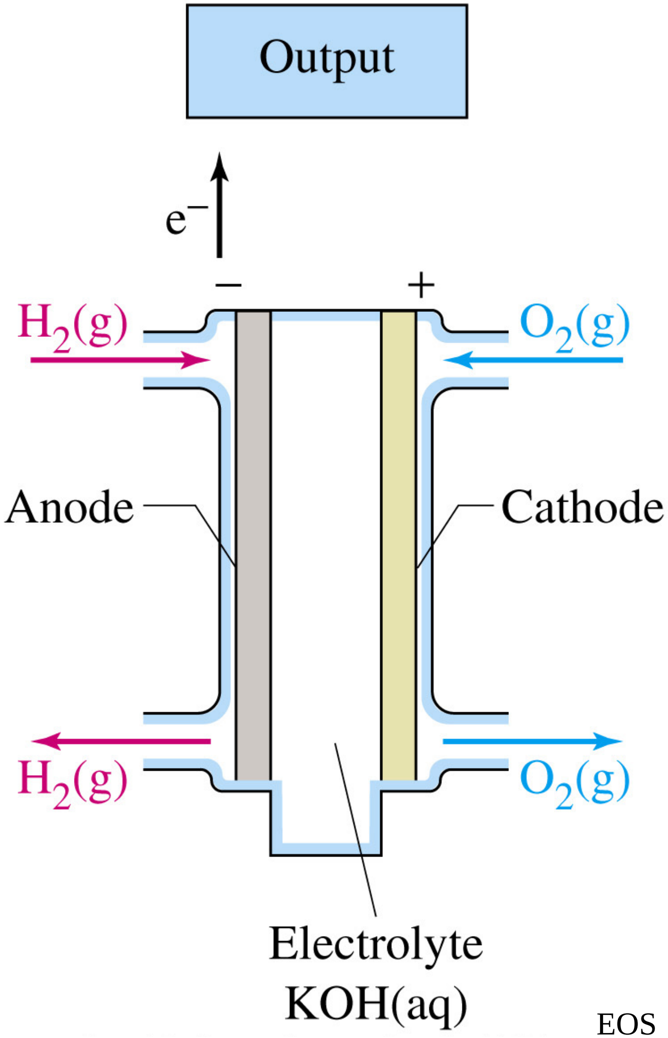
As the cell reaction proceeds, $PbSO_4(s)$ precipitates and partially coats both electrodes; the water formed dilutes the $H_2SO_4(aq)$. In this condition the cell is discharged



Fuel Cells

Fuel cells are voltaic cells in which the cell reaction is equivalent to a combustion reaction

Fuel cells are generally operated at nonstandard conditions and at temperatures often considerably higher than 25 °C



Corrosion: Metal Loss Through Voltaic Cells

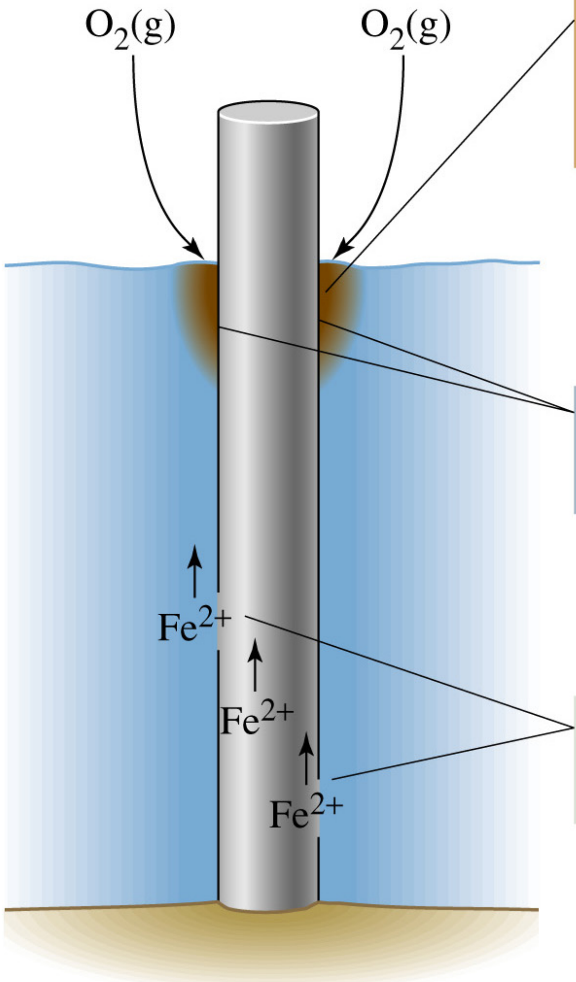
In moist air, exposed iron can be oxidized to Fe^{2+} … these areas are referred to as *anodic areas*

Other regions of the iron serve as *cathodic areas*

Electrons from the anodic areas reduce atmospheric oxygen to the OH^- ion

Iron (II) ions migrate from the anodic areas to the cathodic areas, where they combine with the hydroxide ions and are further oxidized to iron(III) hydroxide by atmospheric oxygen … ***$Fe_2O_3 \cdot xH_2O$ is common rust***

Corrosion Illustrated



Rust formation:

$Fe^{2+}(aq) + 2\ OH^-(aq) \longrightarrow Fe(OH)_2(s)$

$4\ Fe(OH)_2(s) + O_2(g) + 2\ H_2O(l) \longrightarrow 4\ Fe(OH)_3(s)$

Cathode:

$O_2(g) + 2\ H_2O(l) + 4\ e^- \longrightarrow 4\ OH^-(aq)$

Anode:

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

Protecting Iron from Corrosion

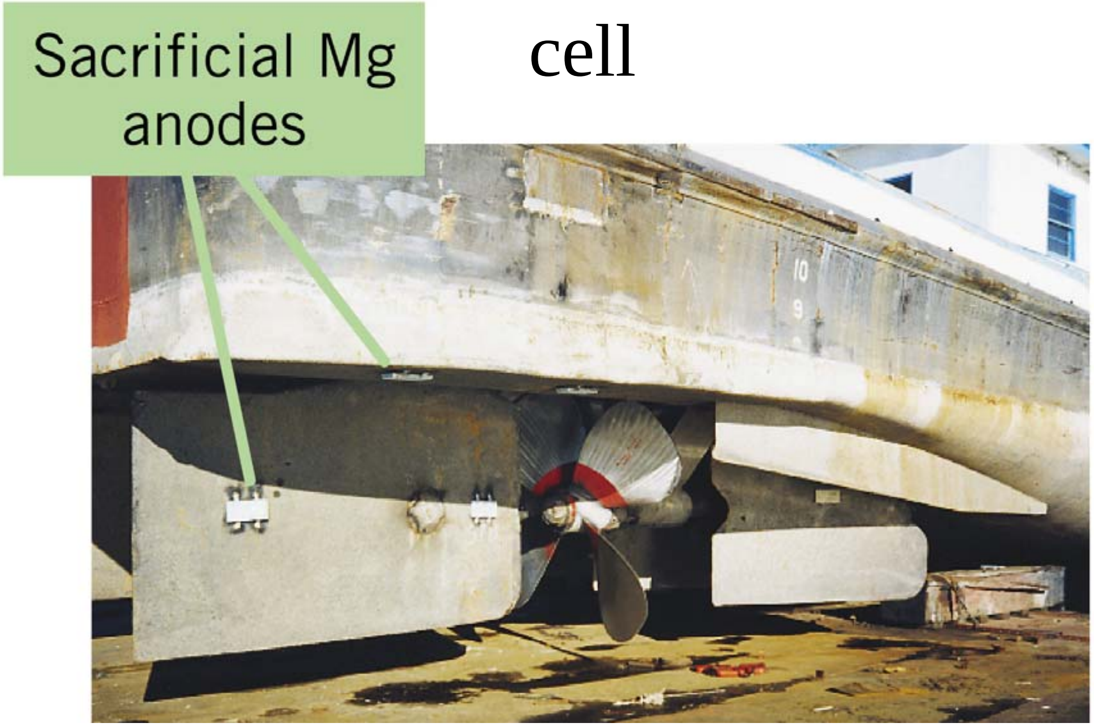
The simplest line of defense against the corrosion of iron is to paint it to exclude oxygen from the surface

Another approach is to coat the iron with a thin layer of a less active metal

An entirely different approach is to protect iron with a *more* active metal, as in the zinc-clad iron known as *galvanized iron*

Cathodic Protection

The iron object to be protected is connected to a chunk of an active metal and the iron serves as the reduction half-cell



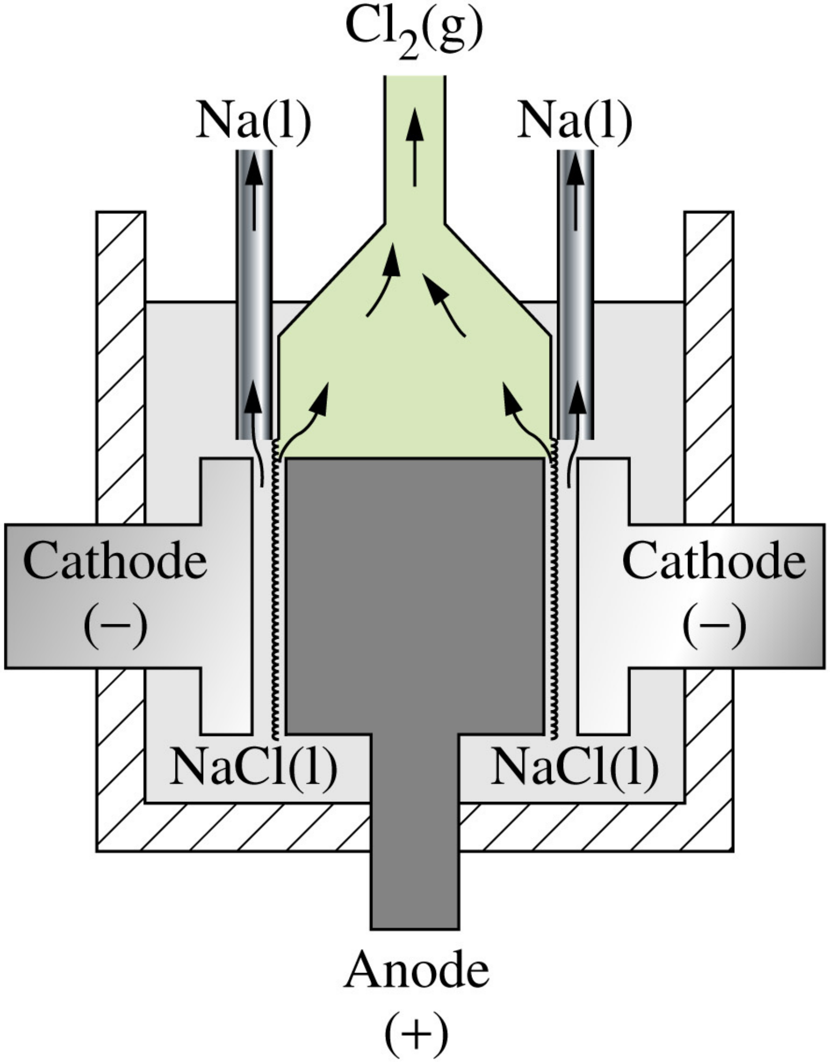
Electrolytic Cells

When ***electric current from an external source*** is passed through a cell, a nonspontaneous reaction called ***electrolysis*** occurs, and the cell is called an ***electrolytic cell***

The external source of electricity acts like an "electron pump." Electrons move from the *anode* toward the *cathode*, where reduction takes place

The ***polarities of the electrodes are reversed*** from those in the voltaic cell

Electrolysis Example



Predicting Electrolysis Reactions

All combinations of cathode and anode half-reactions will give *negative* values of E^{o}_{cell}

The reaction ***most likely*** to occur is the one with the ***least negative*** value of E^{o}_{cell}

Various interactions at electrode surfaces make the required voltage for electrolysis **higher** than the voltage calculated from E^{o} data

Overvoltage is the excess voltage above the voltage calculated from E^{o} values that is required in electrolysis

Quantitative Electrolysis

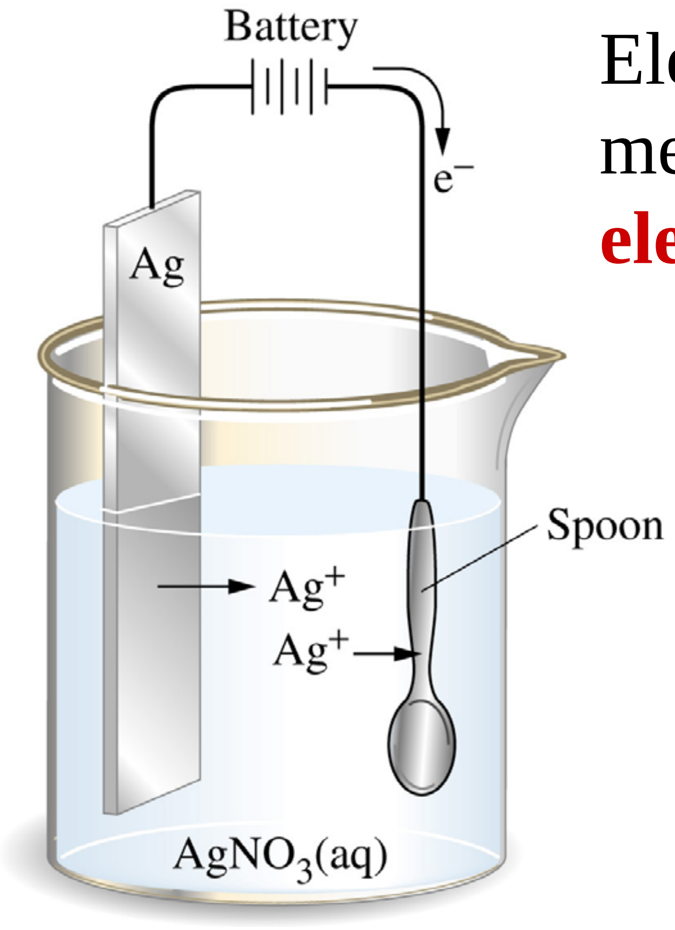
Quantity of reactant consumed or product formed depends on …

Molar mass*, *quantity of charge used,* *and* *number of electrons transferred

The unit of electric charge is the **coulomb** (**C**), and the charge on one electron is -1.6022×10^{-19} C

Electric current, expressed in **amperes** (**A**), is the rate of flow of electric charge

Producing Chemicals by Electrolysis



Electrolysis can be used to coat one metal onto another, a process called **electroplating**

Video

The object to be electroplated is cast of an inexpensive metal and then coated with a thin layer of a more attractive, corrosion-resistant, and expensive metal, such as silver or gold

Summary of Concepts

- An oxidation–reduction reaction can be separated into two half-reactions, one for oxidation and one for reduction
- Half-reactions can be conducted in half-cells
- A cell diagram for a voltaic cell is written with the anode on the left and the cathode on the right
- A standard hydrogen electrode has H^+ ion at unit activity in equilibrium with H_2 gas on an inert platinum electrode

Summary (cont'd)

- A redox reaction for which $E_{\text{cell}} > 0$ occurs spontaneously
- The Nernst equation relates a cell voltage under nonstandard conditions to E^{o}_{cell}, the number of electrons transferred, and the reaction quotient
- In concentration cells, the half-cells have identical electrodes and solutions of the same electrolyte but at different concentrations

Summary (cont’d)

- In primary voltaic cells, the electrode reaction is irreversible and in secondary cells, the electrode reaction is reversible
- A corroding metal consists of anodic areas, at which dissolution of the metal occurs, and cathodic areas, where atmospheric oxygen is reduced to hydroxide ion
- A metal can be protected against corrosion by plating it with a second metal that corrodes less readily
- In an electrolytic cell, direct electric current from an external source produces nonspontaneous changes