Recap

- ❑ pH curve for strong base/weak acid titration
- ❑ Stoichiometric points for polyprotic acids
- ❑ K_{sp} and solubility
- ❑ Common-ion effect and complex formation

The first battery

Long time ago…

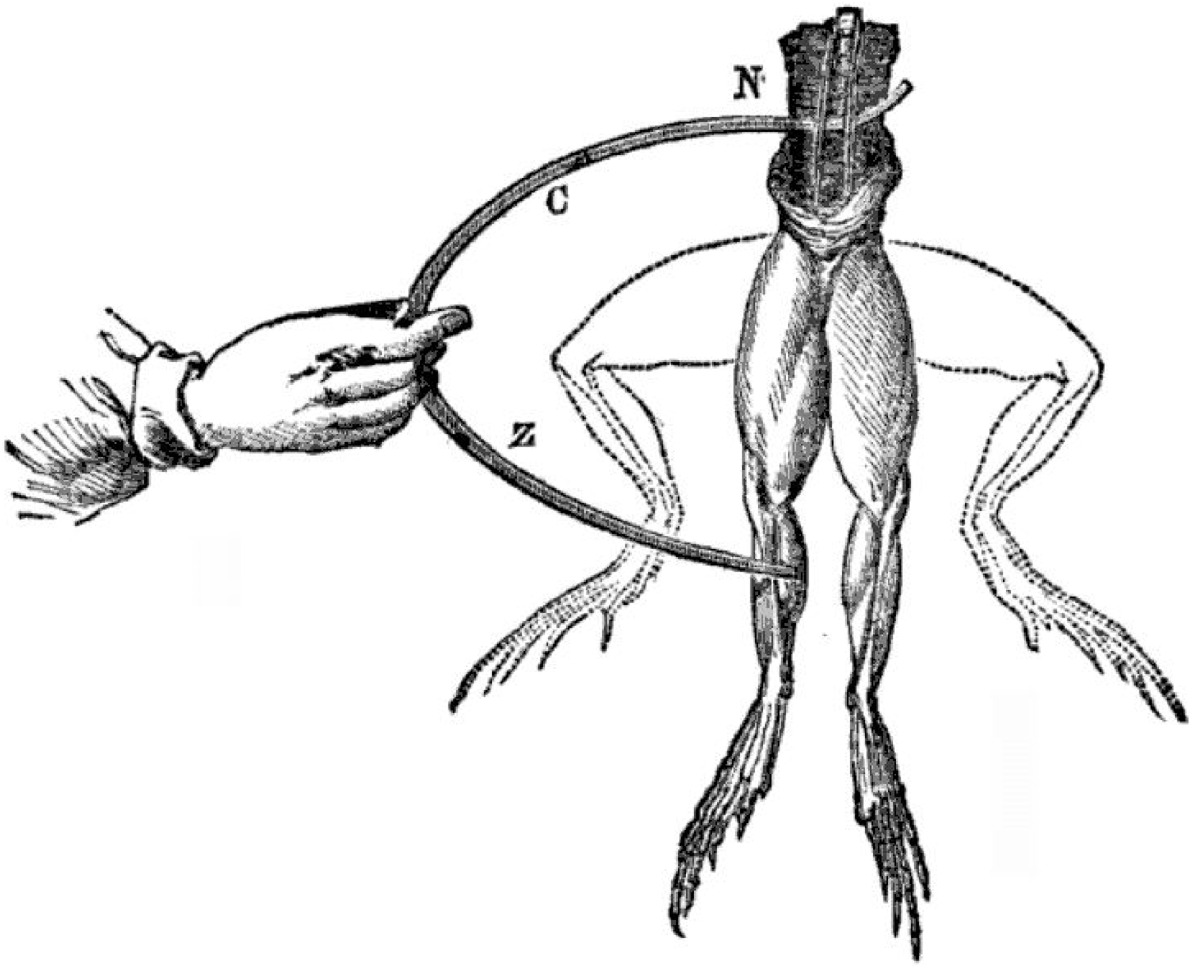
~200 years ago

Luigi Galvani
1734-1798

Physician, Physicist, Biologist, Philosopher

University of Bologna, Italy

- Overturned Balloonist theory
- Father of “animal electricity”



- Muscle movement is driven by electricity
  - **Electricity is generated by animals**

Alessandro Volta
1745-1827

Physicist, Chemist

Chair of experimental physics,
University of Pavia, Italy

1794, Copley Medal

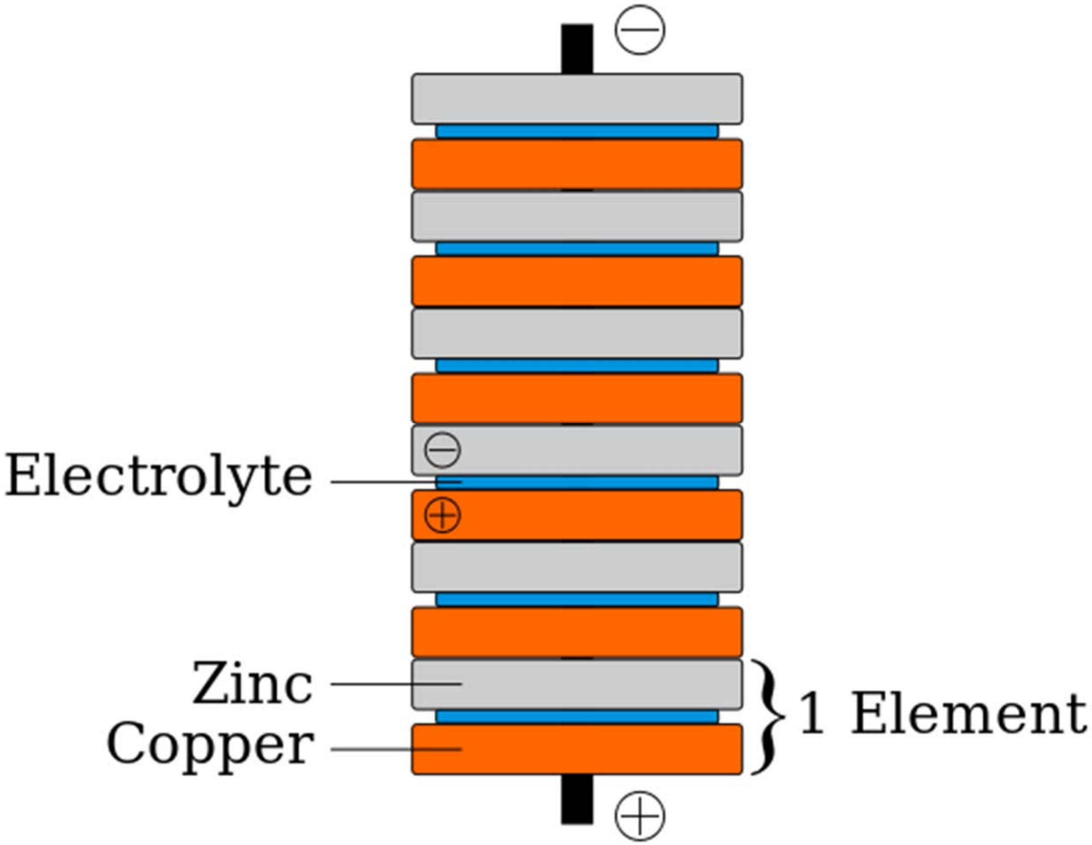
Toyota Alessandro Volta
2004

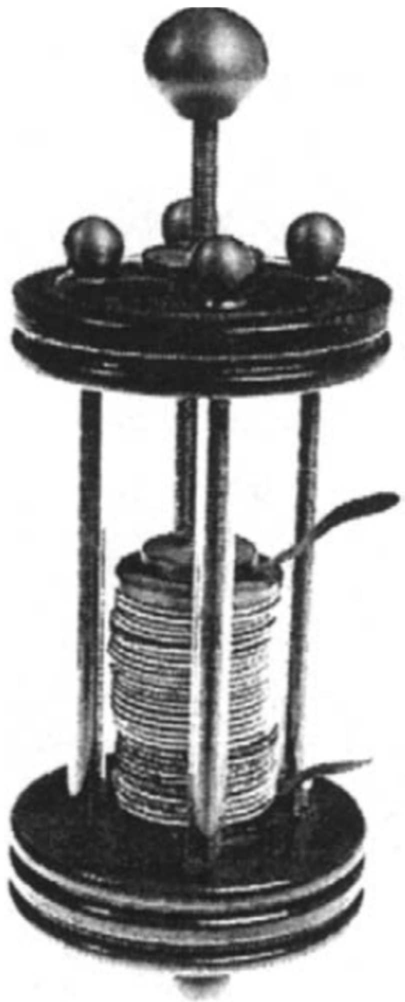
- Voltaic pile
- Electrochemistry
- Volt, SI unit

Two experiments disapprove “animal electricity”

1. Try different metallic rods
2. Build a cell which does not contain biologic materials

Voltaic Pile
(built in 1799, reported to Royal Society in 1800)





Energy spectrum

0.5 Wh

15 Wh

75 Wh

30-100 Wh

90 Wh

200 Wh

24,000 Wh

> 1,000,000 Wh

Reduction Oxidation (Redox) Reactions

Redox reaction (Section K) is combination of two separate reactions called **half-reactions**.

***Electrons* removed**—called an **oxidation reaction**

***Electron* taken**—called a **reduction reaction**

The reactants used in Volta's 1800's battery

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

$Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^{-}$ **oxidation half-reaction**

$Cu^{2+}(aq) + 2\,e^{-} \rightarrow Cu(s)$ **reduction half-reaction**

Practice: Identify as either an oxidation or a reduction reaction, and identify the oxidizing and reducing agents.

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

Reduction, Mn^{7+} is an oxidizing agent.

$Au(s) \rightarrow Au^{3+} + 3\,e^-$

Oxidation, Au(s) is the reducing agent.

$Cl_2(g) + 2\,e^- \rightarrow 2\,Cl^-$

Reduction, Cl_2(g) is the oxidizing agent.

$Tl^{3+} + 2\,e^- \rightarrow Tl^+$

Reduction, Tl^{3+} is the oxidizing agent.

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

Oxidation, Pt(s) is the reducing agent.

Practice: Find the oxidation numbers of the underlined element $\underline{S}O_3$, $\underline{N}_2O$ and $\underline{Cr}_2O_7^{2-}$.

+6	-2		+1	-2		+6	-2	
S	O_3		N_2	O		Cr_2	O_7^{2-}	
+6	-6	= 0	+2	-2	= 0	+12	-14	= -2

The "-" side is -6, so what combines with a -6 = 0?
"+6" (+6 -6 = 0) or S^{6+}.

The "-" side is -2, so what combines with a -2 = 0 ? "+2"
Since there are two N atoms, their total charge is +2, so each N^+.

The "-" side is -14, so what combines with a -14 = -2 ? "+12"
Since there are two Cr atoms, their total charge is +12, so each Cr^{+6}.

Redox Couple

$Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-$ **oxidation half-reaction** (loss of an e^-)

$2\,Ag^+(aq) + 2\,e^- \rightarrow 2\,Ag(s)$ **reduction half-reaction** (gain of an e^-)

$Zn(s)$ and $Zn^{2+}(aq)$ are jointly formed, so we refer to these as **couples**, and they are written as Zn^{2+}/Zn.

A note on *formalism*: Couples are written as **reductions**, so Zn^{2+}/Zn implies $Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$.

The silver couple is written at Ag^+/Ag.

Redox Couple: Practice

Write the couple for the following half-reaction:

$MnO_4^- + 8\,H^+ + 5\,e^- \rightarrow Mn^{2+} + 4\,H_2O$ $\qquad$ MnO_4^-/Mn^{2+}

$Au(s) \rightarrow Au^{3+} + 3\,e^-$ $\qquad$ Au^{3+}/Au

Given the couples, how would you write their half-reactions?

Cl_2/Cl^- (gain or reduction) $\qquad$ $Cl_2(g) + 2\,e^- \rightarrow 2\,Cl^-$

Tl^{3+}/Tl^+ $\qquad$ $Tl^{3+} + 2\,e^- \rightarrow Tl^+$

Balancing Redox Equations

Balancing chemical equations by inspection is common.

Now we run across redox chemical equations which we *cannot balance by inspection*.

In aqueous redox reactions, **water** is not an innocent bystander.

Often, **H^+ (aq)** and **OH^- (aq)** participate, so the number of electrons gained or lost is not obvious.

We now learn balancing a redox reaction in either an acidic or basic solution. This is a multistep process.

Balancing Redox Equations

Method for balancing oxidation-reduction reactions in an acidic solution:

A. Write the equations for the oxidation and reduction half-reactions.

B. For each half-reaction:
   1. Balance all of the elements except hydrogen and oxygen;
   2. Balance oxygen using H_2O;
   3. Balance hydrogen using H^+;
   4. Balance the charge using electrons;
   5. Cancel like-species and combine remaining species.

Example (**Acidic solution**):

$$MnO_4^-(aq) + Os^{4+}(aq) \rightarrow OsO_4(s) + MnO_2(s)$$

A. Write each half-reaction.

$$MnO_4^- \rightarrow MnO_2$$

$$Os^{4+} \rightarrow OsO_4$$

Step 1. Balance all the elements except H and O.

$MnO_4^- \rightarrow MnO_2$

$Os^{4+} \rightarrow OsO_4$

Since there are the same number of Mn and Os on each side of the reaction, we skip this step.

Step 2. Balance oxygen using H_2O. *These reactions are done in water, and water can be part of the reaction in the form of either* H^+ *or* OH^-.

$$MnO_4^- \rightarrow MnO_2$$

We add 2 H_2O molecules to the product side, so we balance a total of 4 O atoms on each side of the reactions.

$$4\ H_2O + Os^{4+} \rightarrow OsO_4$$

We do the same for the other half-reaction, and it also happens to be four oxygen atoms.

Step 3. Balance hydrogen by using H^+.

$$MnO_4^- \rightarrow MnO_2 + 2\,H_2O$$

We add 4 H^+ ions to the reactant side to give 4 H atoms on each side.

$$4\,H_2O + Os^{4+} \rightarrow OsO_4$$

Add 8 H^+ ions to the reactant side of the Os half-reaction.

At this point ALL atoms are balanced.

Step 4. Balance the charge using electrons

We balance the charges of each side of the reaction using electrons. To get an idea of how many electrons we need, we consider the charge on each side of the half-reaction.

$$\underbrace{4\,H^+ + MnO_4^-}_{\substack{4+ \quad + \quad 1- \\ = 3+}} \rightarrow \underbrace{MnO_2 + 2\,H_2O}_{\substack{0 \quad + \quad 0 \\ = 0}}$$

To make the 3+ = 0, we add 3 -e to the 3+ side.

$$\underbrace{3\,e^- + 4H^+ + MnO_4^-}_{\substack{3- \quad + \quad 4+ \quad + \quad 1- \\ = 0}} \rightarrow \underbrace{MnO_2 + 2\,H_2O}_{\substack{0 \quad + \quad 0 \\ = 0}}$$

Now the charge is balanced on both sides of the reaction.

The charge is balanced on both sides of the reaction. We now look at the other half-reaction.

$$\underbrace{4\,H_2O \quad + \quad Os^{4+}}_{\substack{0 \quad + \quad 4+ \\ = \ 4+}} \quad \rightarrow \quad \underbrace{OsO_4 \quad + \quad 8\,H^+}_{\substack{0 \quad + \quad 8+ \\ = \ 8+}}$$

Balance the charges using electrons.

$$\underbrace{4\,H_2O \quad + \quad Os^{4+}}_{\substack{0 \quad + \quad 4+ \\ = \ 4+}} \quad \rightarrow \quad \underbrace{OsO_4 \quad + \quad 8\,H^+ \ + \ 4\,e^-}_{\substack{0 \quad + \quad 8+ \ + \ 4- \\ = 4+}}$$

We need the same number of electrons for each oxidation and reduction reaction;

$$4\,[3\,e^- + 4\,H^+ + MnO_4^- \rightarrow MnO_2 + 2\,H_2O]$$

$$3\,[4\,H_2O + Os^{4+} \rightarrow OsO_4 + 8\,H^+ + 4\,e^-]$$

Expand :

$$12\,e^- + 16\,H^+ + 4\,MnO_4^- \rightarrow 4\,MnO_2 + 8\,H_2O$$

$$12\,H_2O + 3\,Os^{4+} \rightarrow 3\,OsO_4 + 24\,H^+ + 12\,e^-$$

We now have the same number of electrons leaving and going into this redox reaction.

Previous step:

$12\ e^- + 16\ H^+ + 4\ MnO_4^- \rightarrow 4\ MnO_2 + 8\ H_2O$

$12\ H_2O + 3\ Os^{4+} \rightarrow 3\ OsO_4 + 24\ H^+ + 12\ e^-$

Step 5. Cancel like-species, and add the two half-reactions.

$12e^-$ cancel on each side
Combine the H^+ and H_2O

$$\cancel{12\ e^-} + \cancel{16\ H^+} + 4\ MnO_4^- \rightarrow 4\ MnO_2 + \cancel{8\ H_2O}$$

$$\overset{4\ H_2O}{\cancel{12}\ H_2O} + 3\ Os^{4+} \rightarrow 3\ OsO_4 + \overset{8\ H^+}{\cancel{24}\ H^+} + \cancel{12}\ e^-$$

$$4\ H_2O + 3\ Os^{4+} + 4\ MnO_4^- \rightarrow 4\ MnO_2 + 3\ OsO_4 + 8\ H^+$$

Check to make sure all elements balance on each side of the reaction.

The Half-Reaction Method for Balancing Equations in a **Basic Solution**

Example:

$$Fe(OH)_2 \quad + \quad CrO_4^{2-} \quad \rightarrow \quad Fe_2O_3 \quad + \quad Cr(OH)_4^-$$

Write out the half-reactions.

$$Fe(OH)_2 \rightarrow Fe_2O_3$$

$$CrO_4^{-2} \rightarrow Cr(OH)_4^-$$

Step 1. Balance the atoms, except for O and H.

$$2\ Fe(OH)_2 \rightarrow Fe_2O_3$$
$$CrO_4^{-2} \rightarrow Cr(OH)_4^-$$

Step 2. Balance the O atoms with H_2O.

$$2\ Fe(OH)_2 \rightarrow Fe_2O_3$$
$$CrO_4^{-2} \rightarrow Cr(OH)_4^-$$

Step 3. Balance the H atoms with H^+.

$$2\ Fe(OH)_2 \rightarrow Fe_2O_3 + H_2O$$
$$CrO_4^{-2} \rightarrow Cr(OH)_4^-$$

Step 4. Balance charges with electrons.

$$\underbrace{2\ Fe(OH)_2}_{0} \rightarrow \underbrace{Fe_2O_3 + H_2O + 2\ H^+}_{0 \quad + \quad 0 \quad + \ 2+}$$

$= 0$ $\qquad\qquad = +2$

Add e^-

$$\underbrace{2\ Fe(OH)_2}_{= 0} \rightarrow Fe_2\underbrace{O_3 + H_2O + 2\ H^+ + 2\ e^-}_{= 0}$$

$$\underbrace{4\,H^{+} \quad + \quad CrO_4^{-2}}_{\substack{4+ \quad + \quad 2- \\ = 2+}} \quad \rightarrow \quad \underbrace{Cr(OH)_4^{-}}_{\substack{1- \\ = 1-}}$$

$$3\,e^{-} \; + \underbrace{4\,H^{+} \quad + \quad CrO_4^{-2}}_{\substack{3- \quad + \quad 4+ \quad + \quad 2- \\ = 1-}} \quad \rightarrow \quad \underbrace{Cr(OH)_4^{-}}_{\substack{1- \\ = 1-}}$$

$$3\,[2\ Fe(OH)_2 \rightarrow Fe_2O_3 + H_2O + 2\ H^+ + 2\ e^-]$$

$$2\,[3\ e^- + 4\ H^+ + CrO_4^{-2} \rightarrow Cr(OH)_4^-]$$

which equals

$$6\ Fe(OH)_2 \rightarrow 3\ Fe_2O_3 + 3\ H_2O + 6\ H^+ + 6\ e^-$$

$$6\ e^- + 8\ H^+ + 2\ CrO_4^{-2} \rightarrow 2\ Cr(OH)_4^-$$

Step 5. Cancel like-species and add the two half-reactions:

$$6\,Fe(OH)_2 \rightarrow 3\,Fe_2O_3 + 3H_2O + \cancel{6\,H^+} + \cancel{6\,e^-}$$

$$\cancel{6\,e^-} + \overset{2\,H^+}{\cancel{8}\,H^+} + 2\,CrO_4^{-2} \rightarrow 2\,Cr(OH)_4^-$$

$$2\,H^+ + 6\,Fe(OH)_2 + 2\,CrO_4^{-2} \rightarrow 3\,Fe_2O_3 + 3\,H_2O + 2\,Cr(OH)_4^-$$

Step 6 (new for balancing in a basic solution):

"Basic" means replace H^+ with OH^-, by adding the same number of OH^- ions on each side of the reaction.

$$\cancel{2\ H^+} + 6\ Fe(OH)_2 + 2\ CrO_4^{-2} \rightarrow 3\ Fe_2O_3 + 3\ H_2O + 2\ Cr(OH)_4^-$$
$$+ \cancel{2\ OH^-} \qquad\qquad\qquad\qquad + 2\ OH^-$$

Recall: $2\ H^+ + 2\ OH^- = 2\ H_2O$, so replace and rewrite.

$$2\ H_2O + 6\ Fe(OH)_2 + 2\ CrO_4^{-2} \rightarrow 3\ Fe_2O_3 + 3\ H_2O + 2Cr(OH)_4^- + 2\ OH^-$$

Cancel the water molecules appearing on both sides.

Then, write the finished reaction.

$6\ Fe(OH)_2 + 2\ CrO_4^{-2} \rightarrow 3\ Fe_2O_3 + H_2O + 2\ Cr(OH)_4^- + 2\ OH^-$

Check that you have the same number of atoms on each side.

Sample exercise: Balancing a redox equation in **acidic solution** (also shown as a basic reaction at the end).

$$MnO_4^- (aq) \quad + \quad H_2C_2O_4 (aq) \rightarrow \quad Mn^{2+} (aq) \quad + \quad CO_2 (g)$$

Step 1. Balance the atoms, except for O and H.

$$MnO_4^- \quad \rightarrow \quad Mn^{2+}$$

$$H_2C_2O_4 \rightarrow \quad 2CO_2$$

Step 2. Balance the O atoms with H_2O.

$$MnO_4^- \rightarrow \quad Mn^{2+} \quad + \; 4\,H_2O$$

$$H_2C_2O_4 \rightarrow \quad 2CO_2$$

Step 3. Balance H with H^+.

$$8\,H^+ \; + \quad MnO_4^- \rightarrow \quad Mn^{2+} \quad + \; 4\,H_2O$$

$$H_2C_2O_4 \rightarrow \quad 2CO_2 \quad + \; 2H^+$$

Step 4. Balance charges with electrons.

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

7+ 2+

$+ \ 5\,e^-$

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

$$H_2C_2O_4 \rightarrow \ 2CO_2 \ + \ 2\,H^+$$

0 2+

$+2\,e^-$

$$H_2C_2O_4 \rightarrow \ 2\,CO_2 \ + \ 2H^+ + \ 2\,e^-$$

Step 5. Cancel like-species and add the two half-reactions.

$$2\,[5\,e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4\,H_2O]$$

$$5\,[H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + 2\,e^-]$$

which equals

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

$$5\,H_2C_2O_4 \rightarrow 10\,CO_2 + \cancel{10}H^+ + \cancel{10\,e^-}$$

Cancel like-species.

$$6\,H^+ + 2\,MnO_4^- + 5\,H_2C_2O_4 \rightarrow 10\,CO_2 + 2\,Mn^{2+} + 8\,H_2O$$

Next slide shows this in a basic solution.

Balanced in a basic solution:

$$6\,H^+ + 2\,MnO_4^- + 5\,H_2C_2O_4 \rightarrow 10\,CO_2 + 2\,Mn^{2+} + 8\,H_2O$$

$$6OH^- \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad 6OH^-$$

$$2\,MnO_4^- + 5\,H_2C_2O_4 \rightarrow 10\,CO_2 + 2\,Mn^{2+} + 2\,H_2O + 6\,OH^-$$

Galvanic Cells

Galvanic cells are *spontaneous* reactions generating electric current.

Batteries are a collection of galvanic cells joined in series, where the total voltage is the sum of each cell.

Voltage is the **ability** to push an electric current through a circuit.

The formal term for "voltage" is potential difference, measured in volts: $1\ V = J \cdot C^{-1}$ (more on this later).

Galvanic cells are also known as voltaic cells.

Telsla Model S

> 7000 18650 Li battery

Slightly larger than AA
(or #5) battery

The first true battery
Voltaic pile (1800)

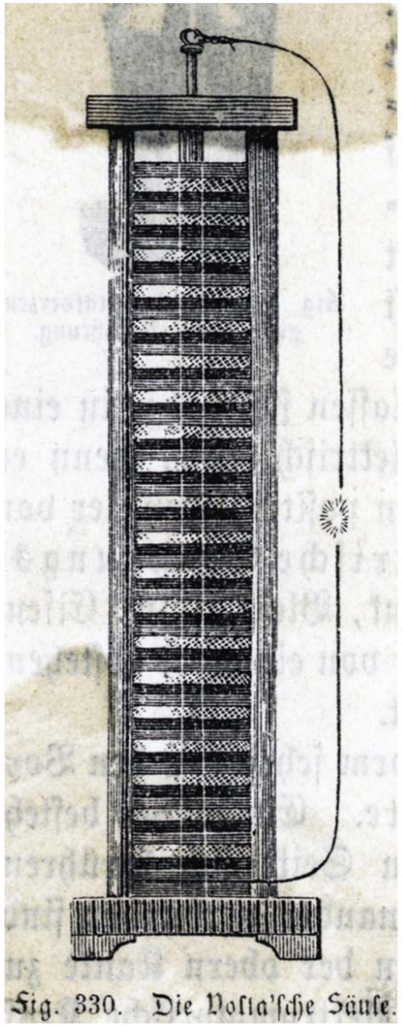
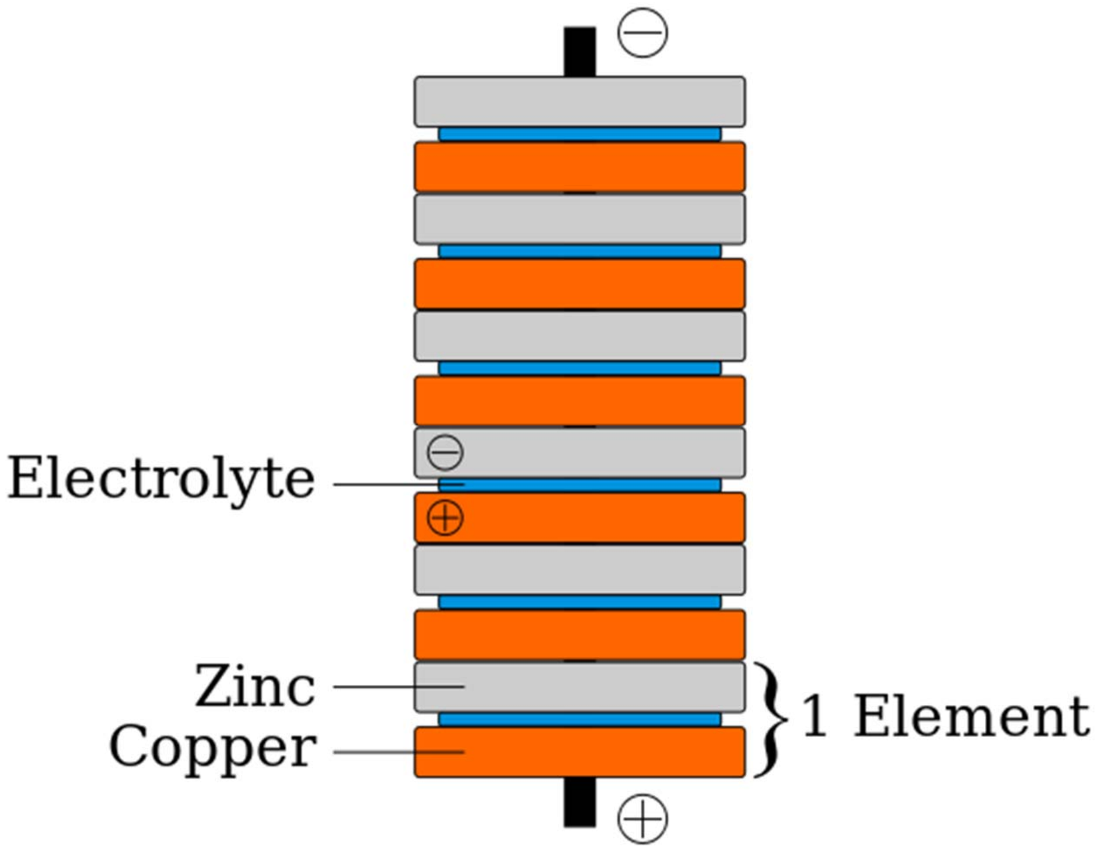


Figure 6L.1
Atkins, *Chemical Principles: The Quest for Insight*, 7e



Last for only one hour max.!

- Prone to short circuiting
- Bubble evolution on Cu increases resistance
- Contact tension theory

Current understanding of Galvanic Cells

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

The **anode** is where **oxidation** takes place.

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

The "-" charge is because *electrons are being generated in the oxidation reaction*.

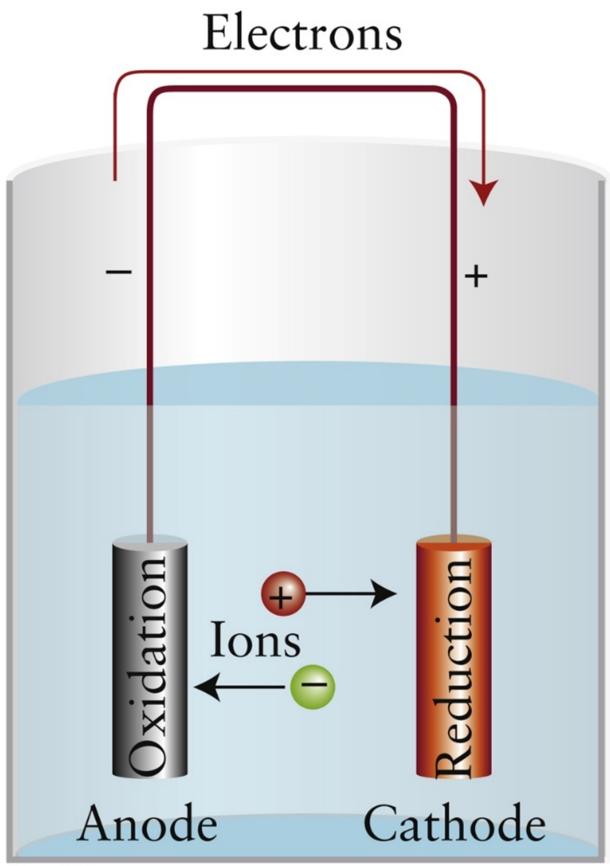


Figure 6L.2
Atkins, *Chemical Principles: The Quest for Insight*, 7e

Current understanding of Galvanic Cells

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

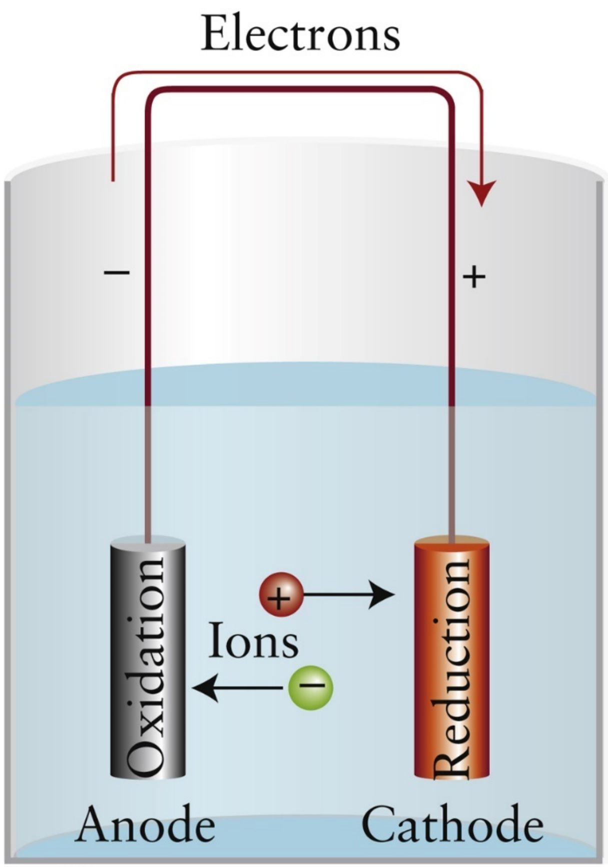


Figure 6L.2
Atkins, *Chemical Principles: The Quest for Insight*, 7e

The **cathode** is where **reduction** occurs

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

The “+” potential means electrons are being ***attracted*** (pulled) here.

The Structure of Daniell Cells

A battery *prevents **direct** contact* of the anode and cathode reactions.

Electrons are funneled through a wire from one cell to another.

Daniell cells contain a ***porous pot***, which is a barrier through which ions travel.

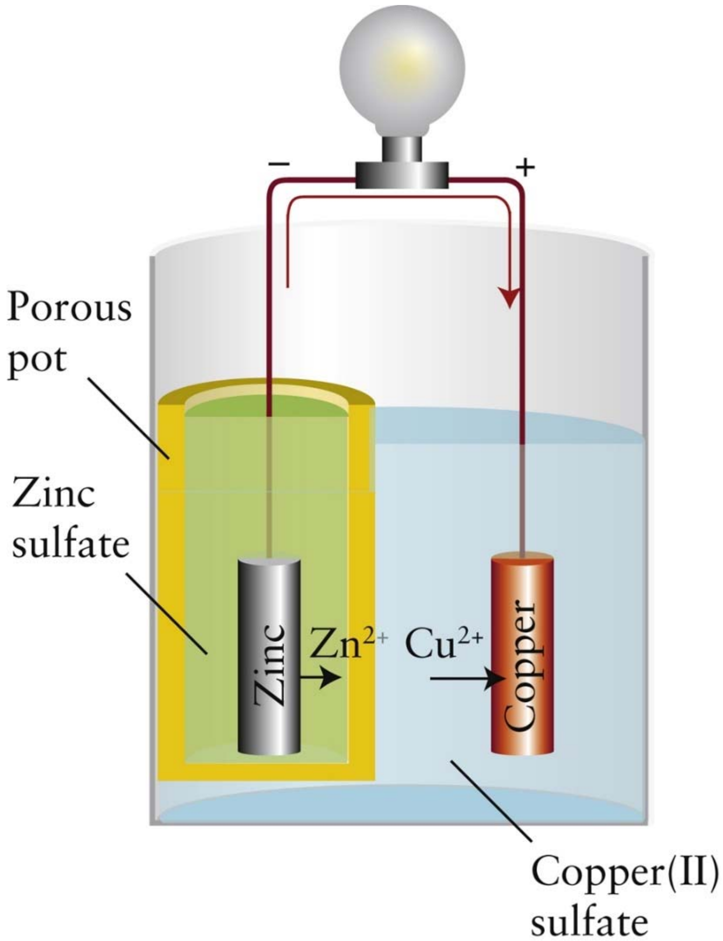


Figure 6L.3
Atkins, *Chemical Principles: The Quest for Insight*, 7e

The Structure of a Daniell Cell: **Ion Transport**

$Zn \rightarrow Zn^{2+}$ loss of electrons, so this will build up a "+" charge (excess Zn^{2+}).

$Cu^{2+} \rightarrow Cu$ gain of electrons, so this will build up a "-" charge (fewer Cu^{2+}).

The ***porous pot*** allows *ion exchange,* thereby electrically neutralizing the anode and cathode.

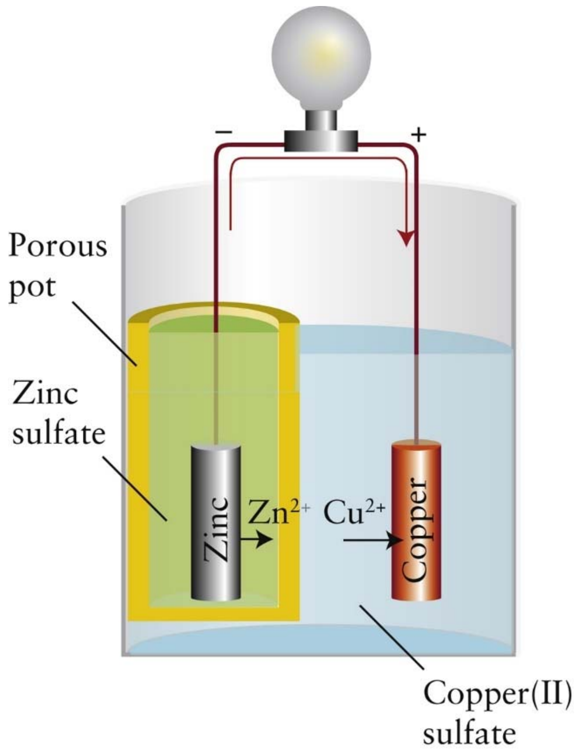


Figure 6L.3
Atkins, *Chemical Principles: The Quest for Insight*, 7e
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Cell Potential

A cell's electrical force is measured by its cell potential, *E*.

E is the *ability* of a cell to *force* electrons through a circuit.

If **both** the anode and cathode have **a lot** of pushing-and-pulling power, this will generate a *high cell potential* (colloquially, a high voltage).

Cell Potential

Exhausted batteries at equilibrium have no pushing or pulling power, and the cell potential is zero.

The SI unit of potential is the volt (V) defined as the charge of one coulomb (1 C) falling through a potential difference of one volt (1 V) releasing one joule (1 J) of energy:

Volts: $1\ V = J{\cdot}C^{-1}$

One coulomb is the magnitude of charge delivered one ampere flowing for one second: $1\ C = 1\ A{\cdot}s$

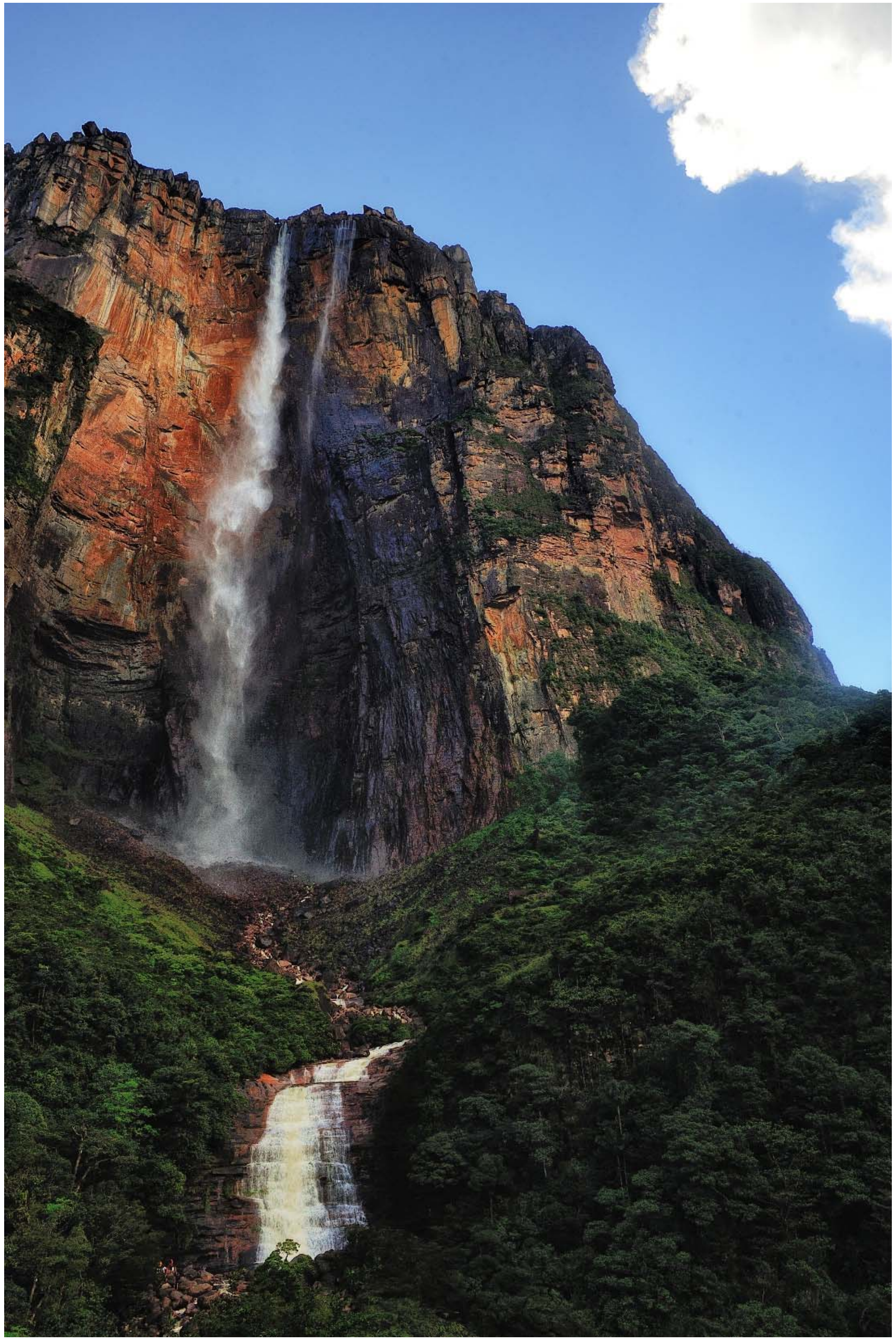
Cell Potential

A **high cell potential** difference or high **voltage** can be represented by the height of a waterfall.

Each water drop is like an electron.

A **Coulomb** is the **magnitude** of charge delivered per second, (C = Amp·sec). The larger waterfall represents a higher **volume of electrons delivered per second**.

Niagara Falls ("large coulomb")



Angel Falls
(“Highest Voltage”)

Cell Potential and Reaction Gibbs Free Energy

Electrical **work** is neither a change in pressure nor volume.

Electrical work is **nonexpansion work**.

Gibbs free energy is the measure of the maximum nonexpansion work that a reaction can do at constant pressure and temperature: $\Delta G = w_e$

Cell Potential and Reaction Gibbs Free Energy

Electrical **work** is an electron moving through a potential difference (height of a waterfall) called ***E*** (measured in voltage, V): $\Delta G = w_e$

The *electrical charge* of one electron is $-e$.

Therefore, the amount of charge for one mole of electrons (Avogadro's constant) is $-eN_A$

And for one mole of electrical charge, "n" electrons (number of moles, an integer) traveling is $-neN_A$.

So, the total *electrical* **work** done is $w_e = -neN_AE$.

Cell Potential and Reaction Gibbs Free Energy

Faraday's constant, F, is the *magnitude* of the charge *per mole* of electrons (the product of the elementary charge $-e$ and Avogadro's constant N_A):

$F = eN_A = (1.602177 \times 10^{-19}\text{C})\ \{6.0223 \times 10^{23}(\text{mol } e^-)^{-1}\} = 96{,}485\ \text{C}\cdot\text{mol}^{-1}$

We can substitute $w_e = -n\boldsymbol{eN_A}E$

with Faraday's constant: $w_e = -nFE$ or

$\Delta G = -nFE$

Cell Potential and Reaction Gibbs Free Energy

$\Delta G = w_e = -nFE$

The maximum amount of work is the maximum cell potential produced in the reaction and is called the electromotive force, **emf**, of a cell.

From now on, *E* will always be taken to represent this emf.

[Note: The definition of **reversibility**, Section 8.3, requires the pushing force balance against an *equal* and opposite force. Under these conditions the **maximum work** occurs for a reversible process.]

Example 6L.1 The emf of the Daniell cell for certain concentrations of copper and zinc ions is 1.04 V. What is the reaction Gibbs free energy under those conditions?

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

Use $\Delta G = -nFE$ to determine a reaction Gibbs free energy.

$$\Delta G = -nFE, = -(2\text{ mol}) \times (96{,}485\text{ C·mol}^{-1}) \times (1.04\text{ V}) = -2.01 \times 10^{5}\text{ C·V}$$

Because $1\ C{\cdot}V = 1\ J$, we can conclude that the Gibbs free energy of this reaction is -201 kJ (spontaneous).

Standard Reaction

For standard $E°$ or standard emf, we can write $\Delta G° = -nFE°$.

1 bar of pressure, 1 M solutions

The Meaning of *E*

The value of *E* is the same, regardless of how we write the equation, but the value of $\Delta G°$ depends on the stoichiometric coefficients in the chemical equation.

	$\Delta G°$	$E°$
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$	<u>-212 kJ</u>	**+ 1.10V**
$10\ Zn(s) + 10\ Cu^{2+}(aq) \rightarrow 10\ Zn^{2+}(aq) + 10\ Cu(s)$	<u>-2,120 kJ</u>	**+ 1.10V**

You would get the same voltage if you had a battery that could fit in your hand or was the size of an Olympic-sized swimming pool (only amperage would change).

The Notation for Cells: IUPAC, for a Daniell Cell

Anode electrode | anode electrolyte | |cathode electrolyte |cathode electrode

"|" means phase change like an electrode and solution.
"| |" means a salt bridge.

The anode is also called the <u>anodic compartment</u>, and <u>cathodic compartment</u> is used for the cathode.

The salt bridge allows ions to move back and forth.

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

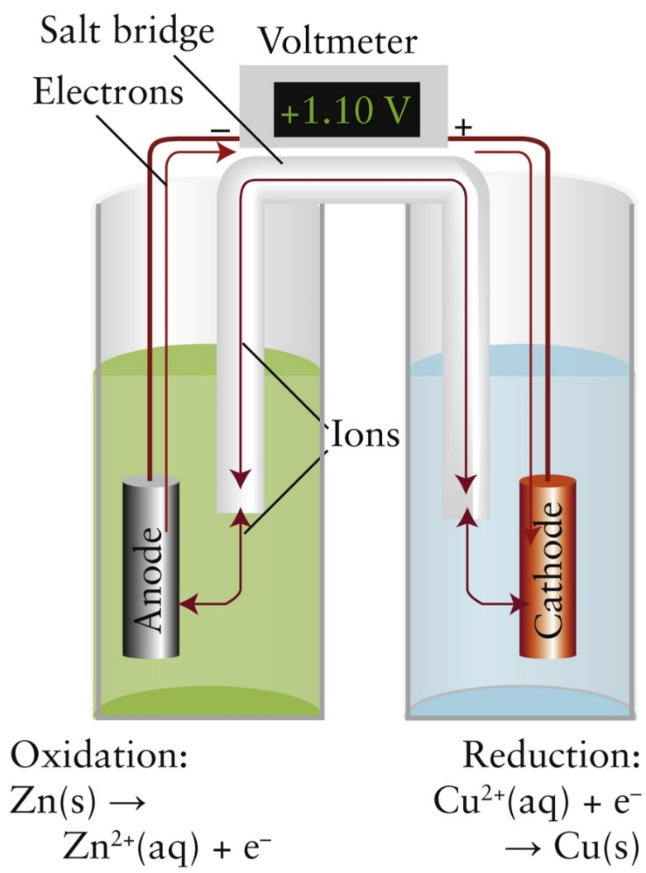


Figure 6L.4
Atkins, *Chemical Principles: The Quest for Insight*, 7e
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Inert Electrode

The field of electrochemistry would be very small if we only had metallic electrodes. How about gases?

Inert electrodes allow electrons to pass, yet will not react with platinum, gold, and carbon.

For instance, measuring the potential of two aqueous ions:

$$||Fe^{3+}\,(aq),\, Fe^{2+}\,(aq)|Pt\,(s)$$

or a gas: $||H^{+}\,(aq)|H_2(g)|Pt(s)$

only the species and not the electrode undergo redox.

Electronic Voltmeter: $\Delta G° = -nFE°$

Voltmeters (aka potentiometer) measure voltage.

Figure 6L.5
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman photo by Ken Karp.

Voltage for $Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$ is E = + 1.10 V. Zn is the anode, (-), and Cu is the cathode (+).

Here ***E* > 0**, so *G* < 0 and this is a **spontaneous** cell.

Switching the leads around would read electrons flowing in the opposite direction, $Cu(s)|Cu^{2+}(aq)||Zn^{2+}(aq)|Zn(s)$ then *E* = -1.10 V

Here ***E* < 0**, so G > 0 and this is a **nonspontaneous** cell.

Example 6L.2 Write the cell reaction for the cell

$Pt(s)|H_2(g)|HCl(aq)|Hg_2Cl_2(s)|Hg(l)$.

We note there is **no salt bridge**, so this is done in a single beaker. The anode is where oxidation takes place, and this is the hydrogen electrode

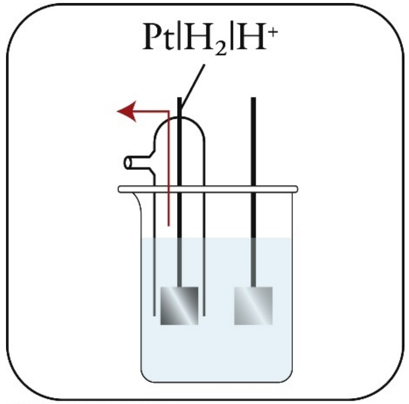
$$H_2(g) \rightarrow 2H^+(aq) + 2\,e^-$$

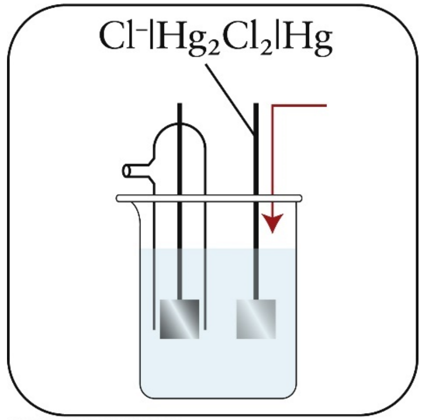
The cathode is where reduction takes place, and this is the Hg.

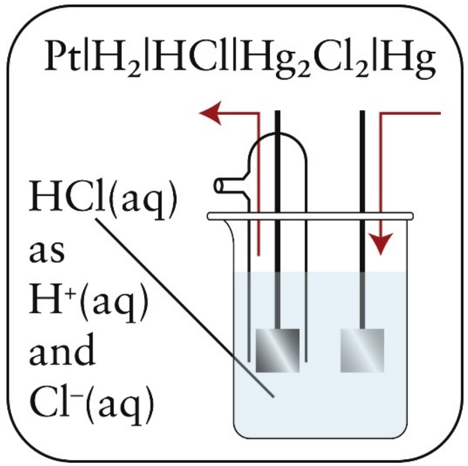
$$Hg_2Cl_2(s) + 2\,e^- \rightarrow 2Hg(l) + 2Cl^-(aq)$$

Combine the two half-reactions.

$$H_2(g) + Hg_2Cl_2(s) \rightarrow 2Hg(l) + 2Cl^-(aq) + 2H^+(aq)$$







Standard Potentials

Each electrode makes its own characteristic contribution to the cell potential, called its standard potential, $\boldsymbol{E°}$, a measure of its electron-pulling power.

Galvanic cells measure the overall pulling power of the cell, called the **cell's standard emf**; a **difference** of the **standard potentials of the two electrodes**.

The difference is written as: $E° = E°(\text{cathode}) - E°(\text{anode})$

or sometimes $E° = E_{cat}° - E_{anode}°$

Standard Potentials: SHE

The standard potential, $E°$, is only measuring a **difference**.

Instead, an electrode is chosen to be the standard against which all other electrodes are measured—the hydrogen electrode.

$$2\ H^+(aq) + 2\ e^- \rightarrow H_2(g)\quad E° = 0.0\ V$$

This is called the **Standard Hydrogen Electrode** (SHE).

Standard Potentials: SHE

For example, for the cell written below, the cell potential is:

$Pt(s)|H_2(g)|H^+(aq)||Cu^{2+}(aq)|Cu(s)$, and the standard emf is +0.34 V.

Since the hydrogen electrode is zero, the emf is **attributed entirely to the copper** electrode, and we write

$Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$ $\qquad E°(Cu^{2+}/Cu) = +0.34$ V

Additionally, the hydrogen electrode is *always* the anode.

Standard Potentials: **Their Meaning**

Pt(s)|H_2(g)|H^+ (aq)||Cu^{2+} (aq)|Cu(s)
(anode) (cathode)

Since the standard emf is +0.34 V, the reaction is **spontaneous** $E > 0$ ($\Delta G° = -nFE°$).

$E° = E_{cat}° - E_{anode}° = +.34V - 0.0V$

The *more positive the potential is:*

1. *the greater the electron-pulling power of the reduction half-reaction;*
2. it is a stronger oxidizing agent.

Standard Potentials

For Pt(s)|H_2(g)|H^+ (aq)||Zn^{2+} (aq)|Zn(s): emf is -0.76 V

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

The reaction is **nonspontaneous** $E < 0$ ($\Delta G° = -nFE°$). Zinc ion has a poor electron-pulling ability, therefore it is a poor oxidizing agent when compared to H^+.

The reverse of the cell reaction,

Zn(s) + H^+ (aq) $\rightarrow$ Zn^{2+} (aq) + H_2(g) the emf is +0.76 V.

This is **spontaneous,** so zinc metal has a strong electron-pulling ability. Therefore, zinc is a better reducing agent when compared to hydrogen (H_2).