

Chapter 4

Electrochemistry

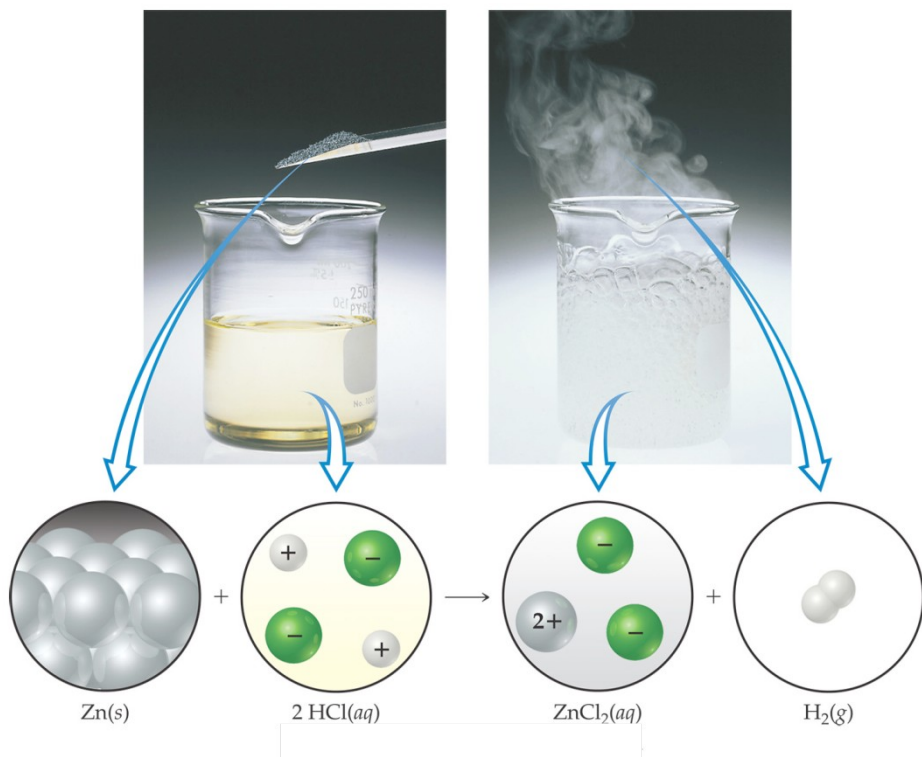
Electrochemical Reactions

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

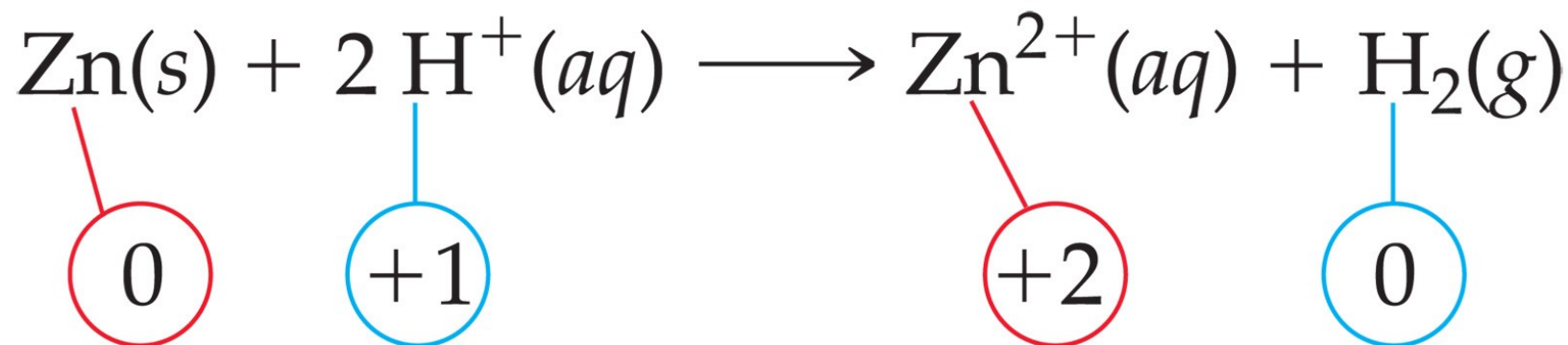
Oxidation Numbers



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

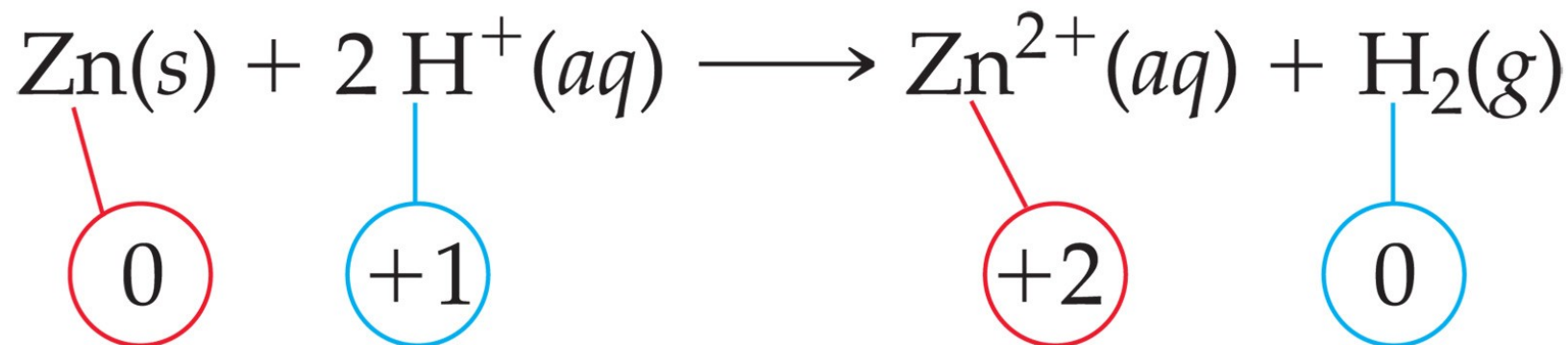


Oxidation and Reduction



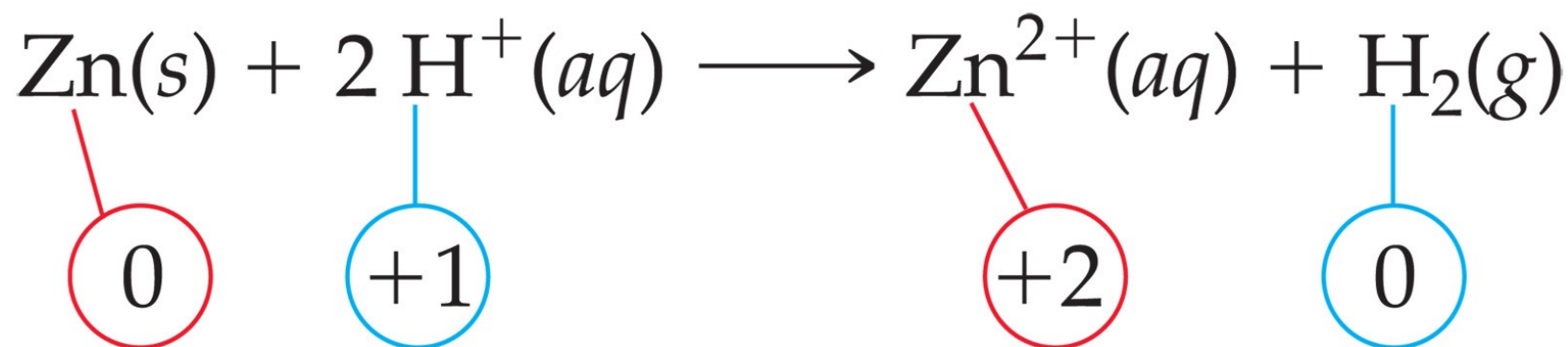
- A species is **oxidized** when it loses electrons.
 - Here, zinc loses two electrons to go from neutral zinc metal to the Zn²⁺ ion.

Oxidation and Reduction



- 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



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

Assigning Oxidation Numbers

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

Assigning Oxidation Numbers

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

Assigning Oxidation Numbers

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

Assigning Oxidation Numbers

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

Balancing Oxidation-Reduction Equations

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

Balancing Oxidation-Reduction Equations

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

The Half-Reaction Method

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

The Half-Reaction Method

3. Balance each half-reaction.
 - a. Balance elements other than H and O.
 - b. Balance O by adding H_2O .
 - c. Balance H by adding H^+ .
 - d. Balance charge by adding electrons.
4. Multiply the half-reactions by integers so that the electrons gained and lost are the same.

The 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.

Redox reactions that take place in aqueous solutions are commonly encountered in electrochemistry, and many involve water or its characteristic ions, $\text{H}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$, as reactants or products. In these cases, equations representing the redox reaction can be very challenging to balance by inspection, and the use of a systematic approach called the *half-reaction method* is helpful. This approach involves the following steps:

1. Write skeletal equations for the oxidation and reduction half-reactions.
2. Balance each half-reaction for all elements except H and O.
3. Balance each half-reaction for O by adding H_2O .
4. Balance each half-reaction for H by adding H^+ .
5. Balance each half-reaction for charge by adding electrons.
6. If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.
7. Add the two half-reactions and simplify.
8. If the reaction takes place in a basic medium, add OH^- ions the equation obtained in step 7 to neutralize the H^+ ions (add in equal numbers to both sides of the equation) and simplify.

The Half-Reaction Method

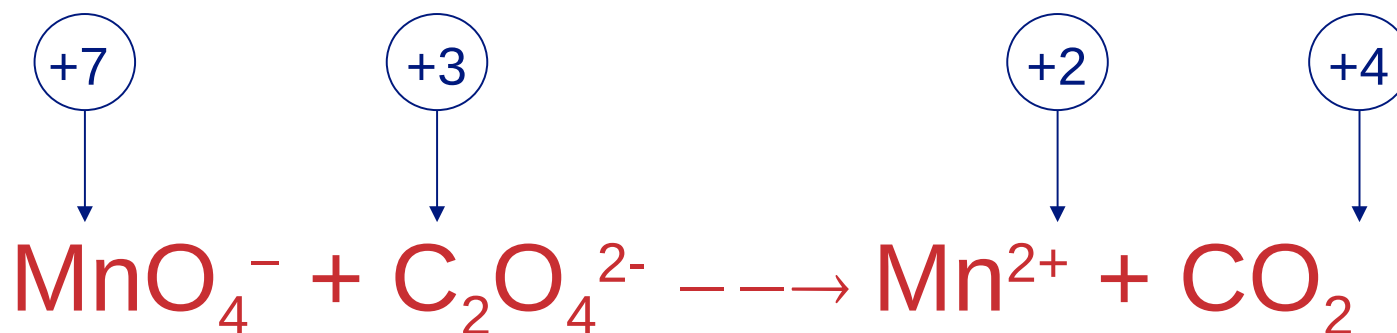


Consider the reaction between MnO_4^- and $\text{C}_2\text{O}_4^{2-}$:



The Half-Reaction Method

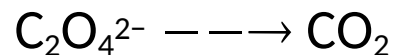
First, we assign oxidation numbers.



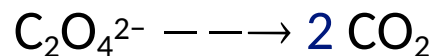
Since the manganese goes from +7 to +2, it is reduced.

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

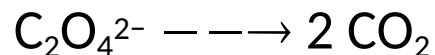
Oxidation Half-Reaction



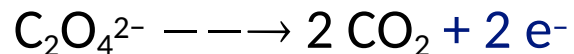
To balance the carbon, we add a coefficient of 2:



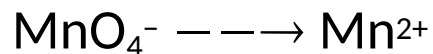
Oxidation Half-Reaction



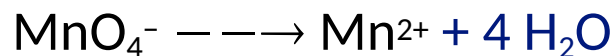
The oxygen is now balanced as well. To balance the charge, we must add 2 electrons to the right side.



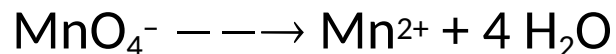
Reduction Half-Reaction



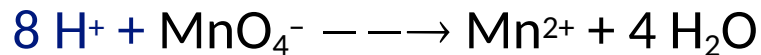
The manganese is balanced; to balance the oxygen, we must add 4 waters to the right side.



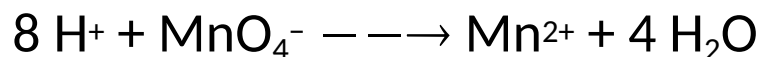
Reduction Half-Reaction



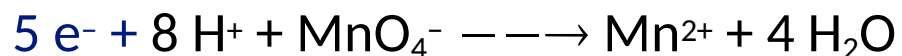
To balance the hydrogen, we add 8 H⁺ to the left side.



Reduction Half-Reaction

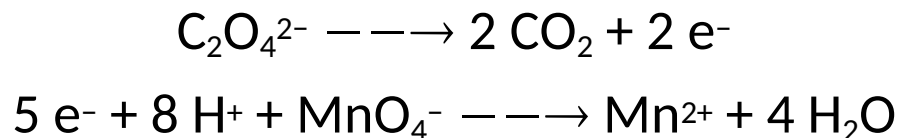


To balance the charge, we add 5 e⁻ to the left side.



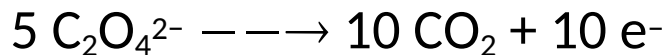
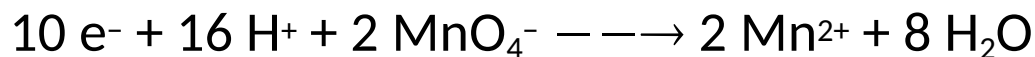
Combining the Half-Reactions

Now we evaluate the two half-reactions together:

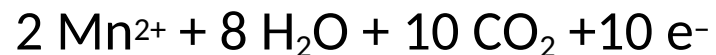


To attain the same number of electrons on each side, we will multiply the first reaction by 5 and the second by 2.

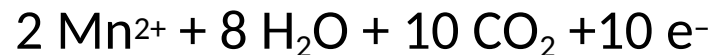
Combining the Half-Reactions



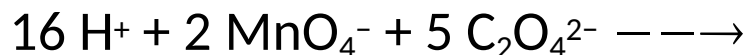
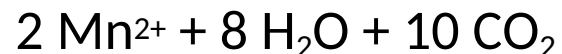
When we add these together, we get:



Combining the Half-Reactions



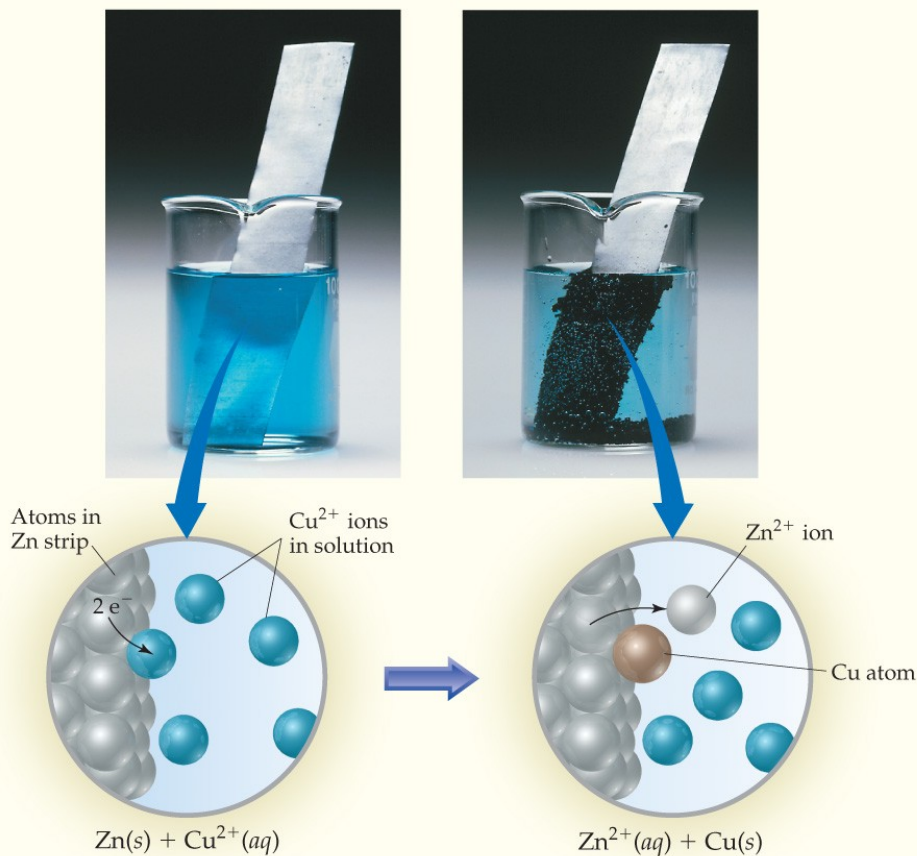
The only thing that appears on both sides are the electrons. Subtracting them, we are left with:



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



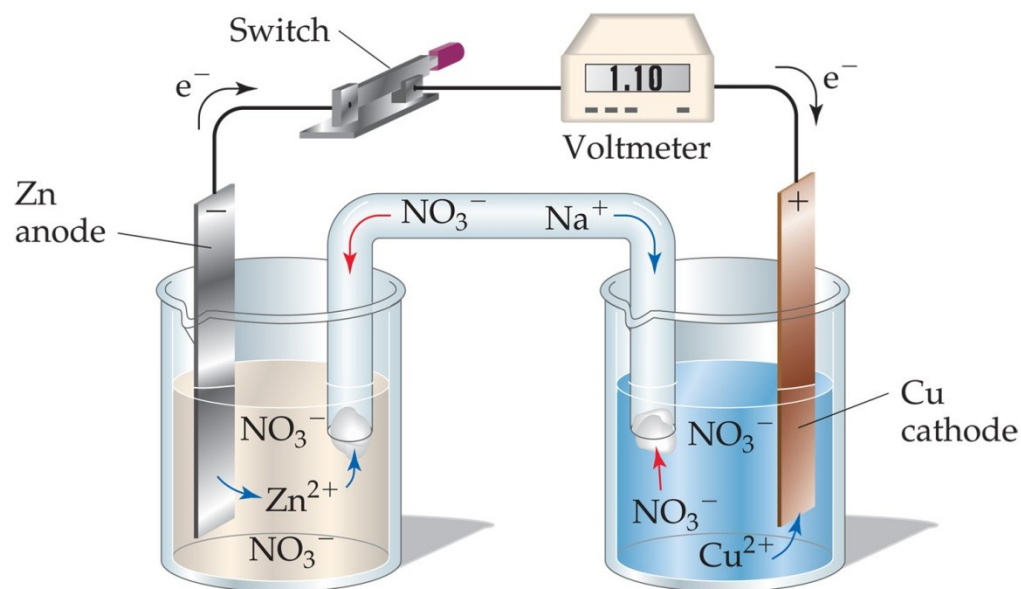
In spontaneous oxidation-reduction (redox) reactions, electrons are transferred and energy is released.

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**.



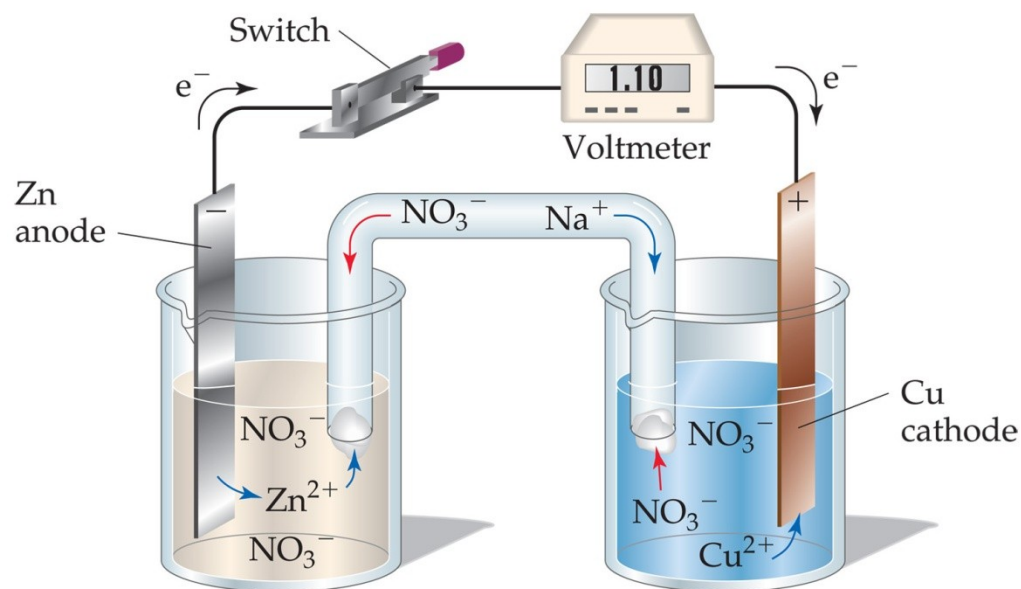
Voltaic Cells



Movement of cations →
 Movement of anions ←

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

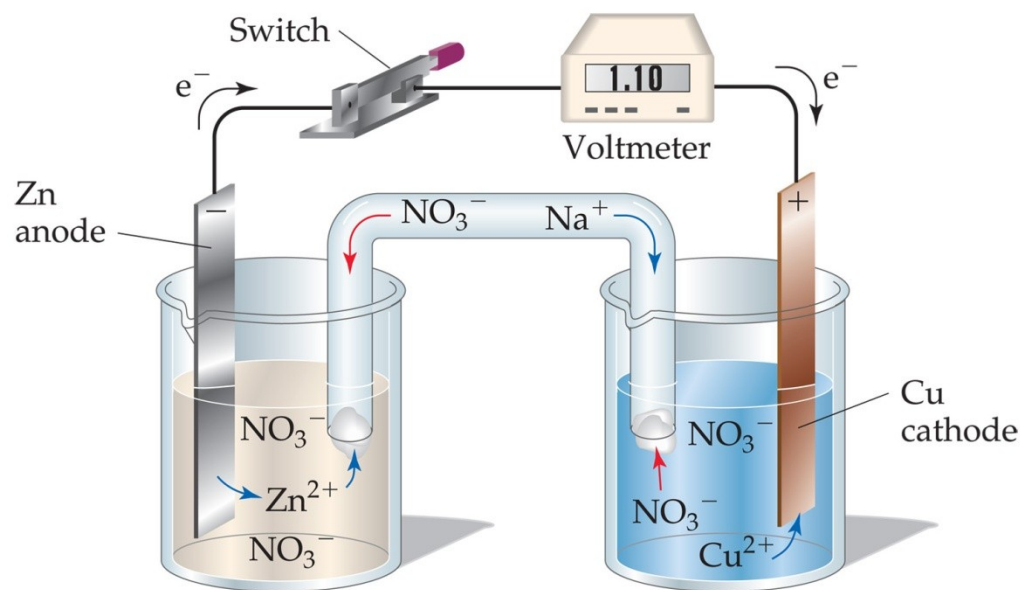
Voltaic Cells



Movement of cations $\longrightarrow$
 Movement of anions $\longleftarrow$

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

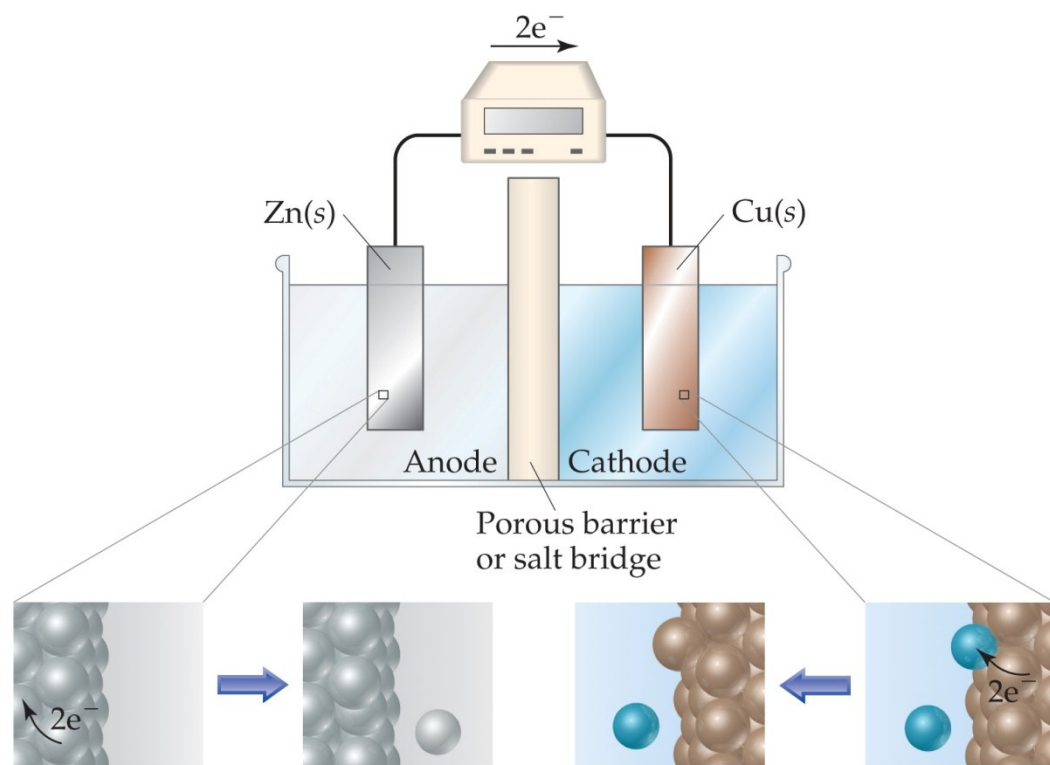


Movement of cations $\longrightarrow$
 Movement of anions $\longleftarrow$

- 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.

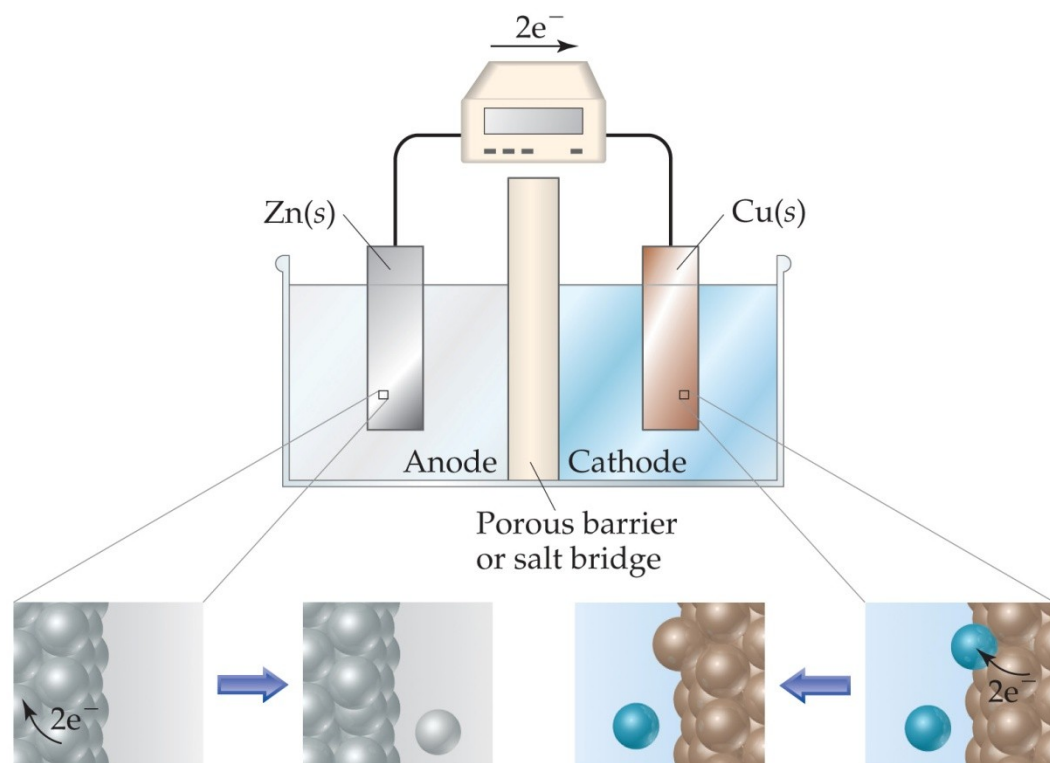
Voltaic Cells

- 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.



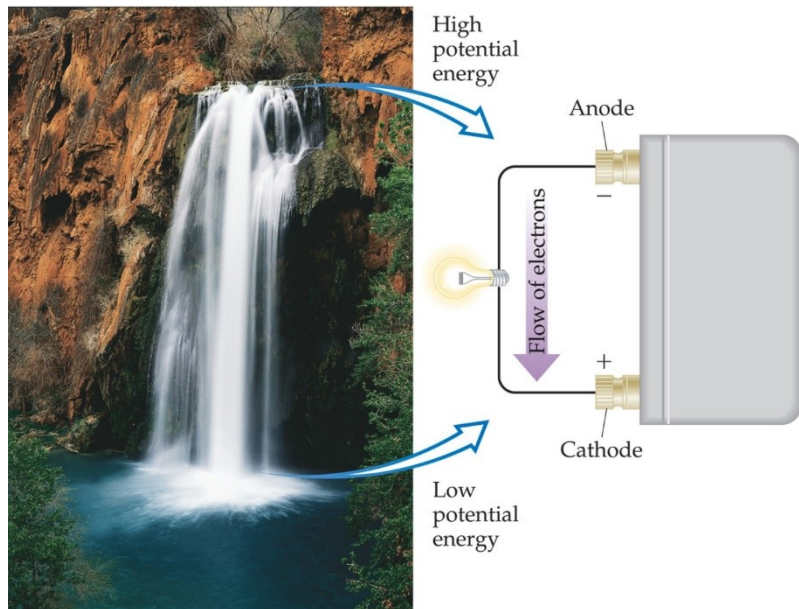
Voltaic Cells

- 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.



Electromotive Force (emf)

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



Electromotive Force (emf)

- The potential difference between the anode and cathode in a cell is called the **electromotive force (emf)**.
- It is also called the **cell potential** and is designated E_{cell} .

Cell Potential

Cell potential is measured in volts (V).

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

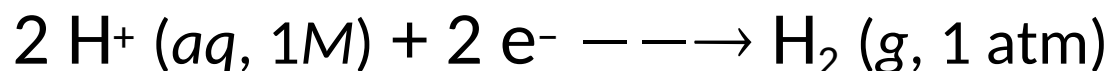
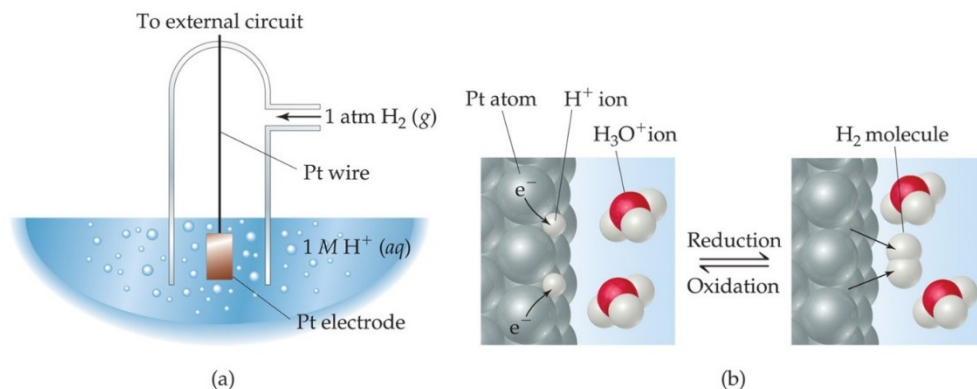
Standard Reduction Potentials

Potential (V)	Reduction Half-Reaction
+2.87	$\text{F}_2(\text{g}) + 2 \text{e}^- \longrightarrow 2 \text{F}^-(\text{aq})$
+1.51	$\text{MnO}_4^-(\text{aq}) + 8 \text{H}^+(\text{aq}) + 5 \text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l})$
+1.36	$\text{Cl}_2(\text{g}) + 2 \text{e}^- \longrightarrow 2 \text{Cl}^-(\text{aq})$
+1.33	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^+(\text{aq}) + 6 \text{e}^- \longrightarrow 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O}(\text{l})$
+1.23	$\text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 4 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(\text{l})$
+1.06	$\text{Br}_2(\text{l}) + 2 \text{e}^- \longrightarrow 2 \text{Br}^-(\text{aq})$
+0.96	$\text{NO}_3^-(\text{aq}) + 4 \text{H}^+(\text{aq}) + 3 \text{e}^- \longrightarrow \text{NO}(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$
+0.80	$\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$
+0.77	$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$
+0.68	$\text{O}_2(\text{g}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2\text{O}_2(\text{aq})$
+0.59	$\text{MnO}_4^-(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) + 3 \text{e}^- \longrightarrow \text{MnO}_2(\text{s}) + 4 \text{OH}^-(\text{aq})$
+0.54	$\text{I}_2(\text{s}) + 2 \text{e}^- \longrightarrow 2 \text{I}^-(\text{aq})$
+0.40	$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^- \longrightarrow 4 \text{OH}^-(\text{aq})$
+0.34	$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Cu}(\text{s})$
0 [defined]	$2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2(\text{g})$
-0.28	$\text{Ni}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Ni}(\text{s})$
-0.44	$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Fe}(\text{s})$
-0.76	$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Zn}(\text{s})$
-0.83	$2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \longrightarrow \text{H}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$
-1.66	$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \longrightarrow \text{Al}(\text{s})$
-2.71	$\text{Na}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Na}(\text{s})$
-3.05	$\text{Li}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Li}(\text{s})$

Reduction potentials for many electrodes have been measured and tabulated.

Standard Hydrogen Electrode

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



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Standard Cell Potentials

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

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

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

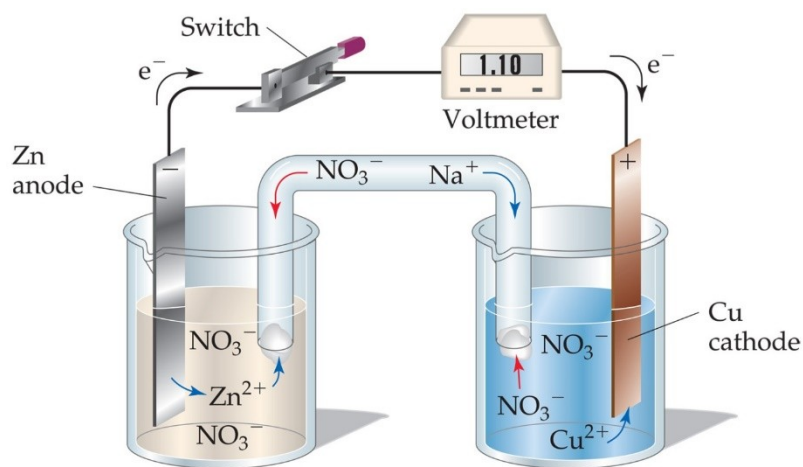
Cell Potentials

- For the oxidation in this cell,

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

- For the reduction,

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



Movement of cations

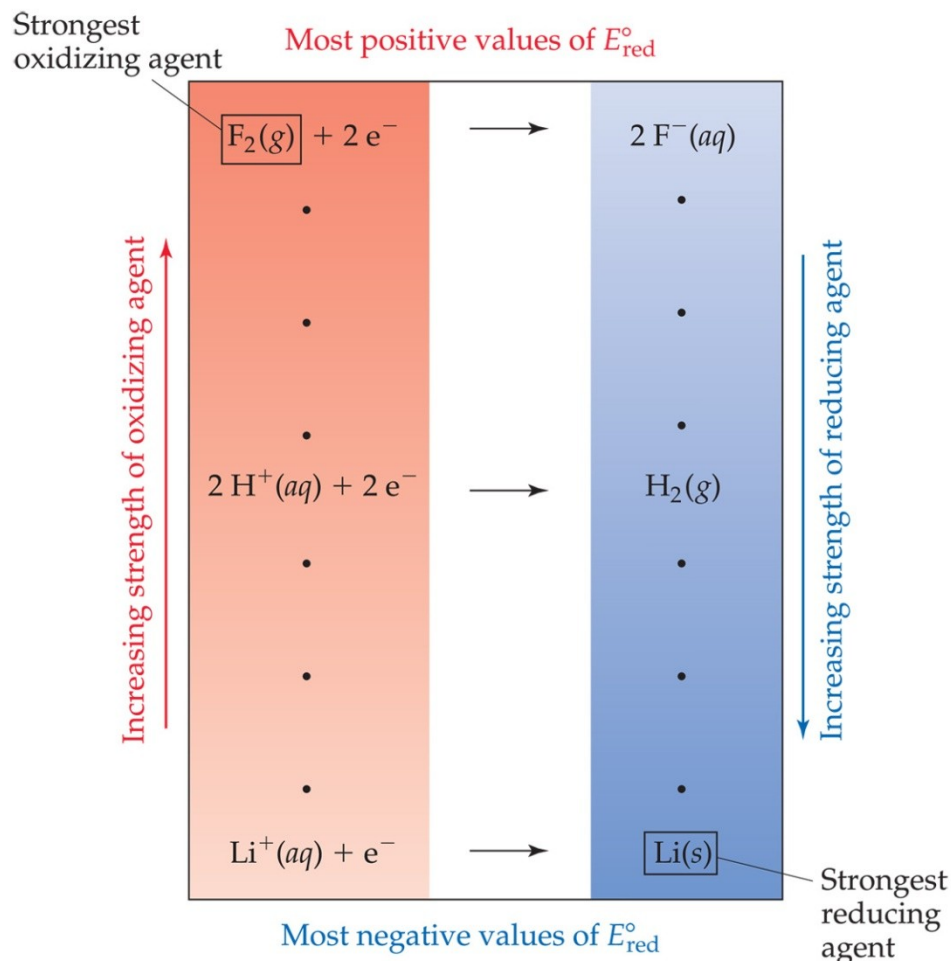
Movement of anions

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Cell Potentials

$$\begin{aligned}E_{\text{cell}}^{\circ} &= E_{\text{red}}^{\circ} (\text{cathode}) - E_{\text{red}}^{\circ} (\text{anode}) \\&= +0.34 \text{ V} - (-0.76 \text{ V}) \\&= +1.10 \text{ V}\end{aligned}$$

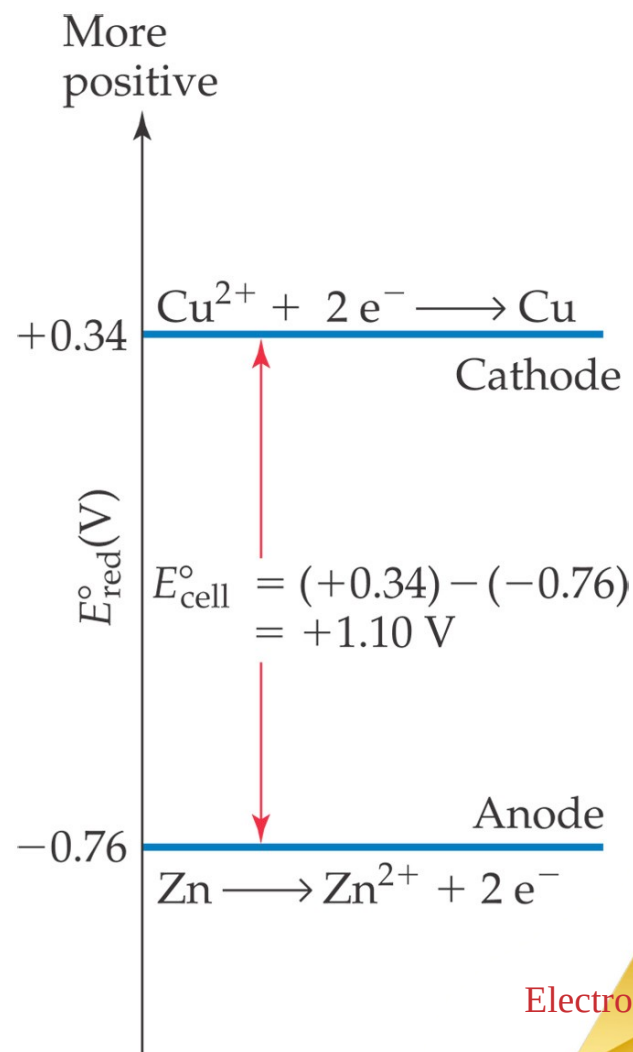
Oxidizing and Reducing Agents



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

Oxidizing and Reducing Agents

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



Free Energy

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

$$\Delta G = -nFE$$

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

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

Free Energy

Under standard conditions,

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

Nernst Equation

- Remember that

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

- This means

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

Nernst Equation

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

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

or, using base-10 logarithms,

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

Nernst Equation

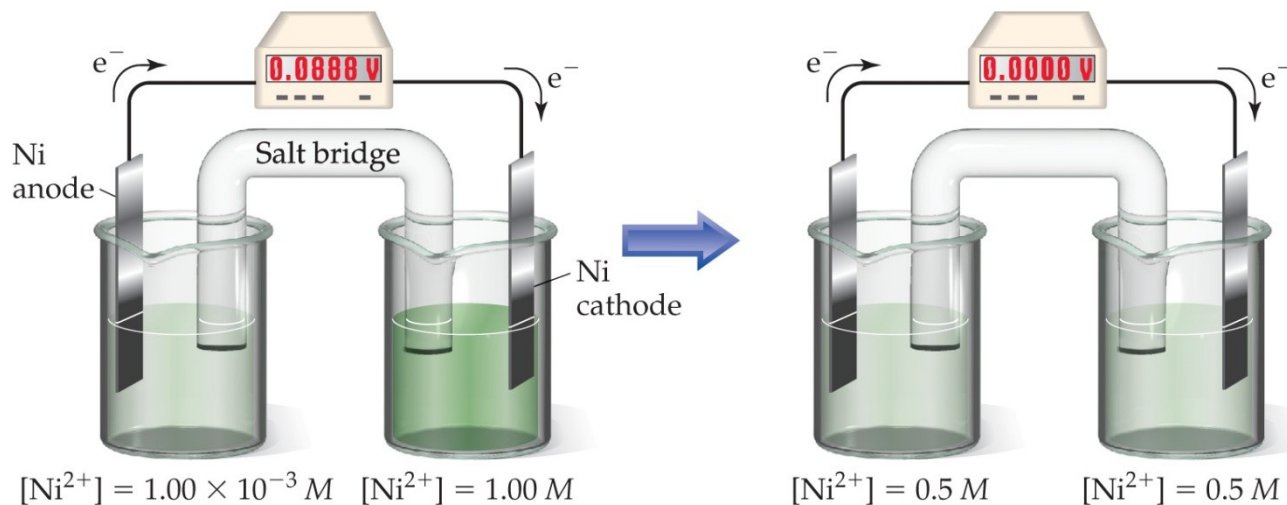
At room temperature (298 K),

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

Thus the equation becomes

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

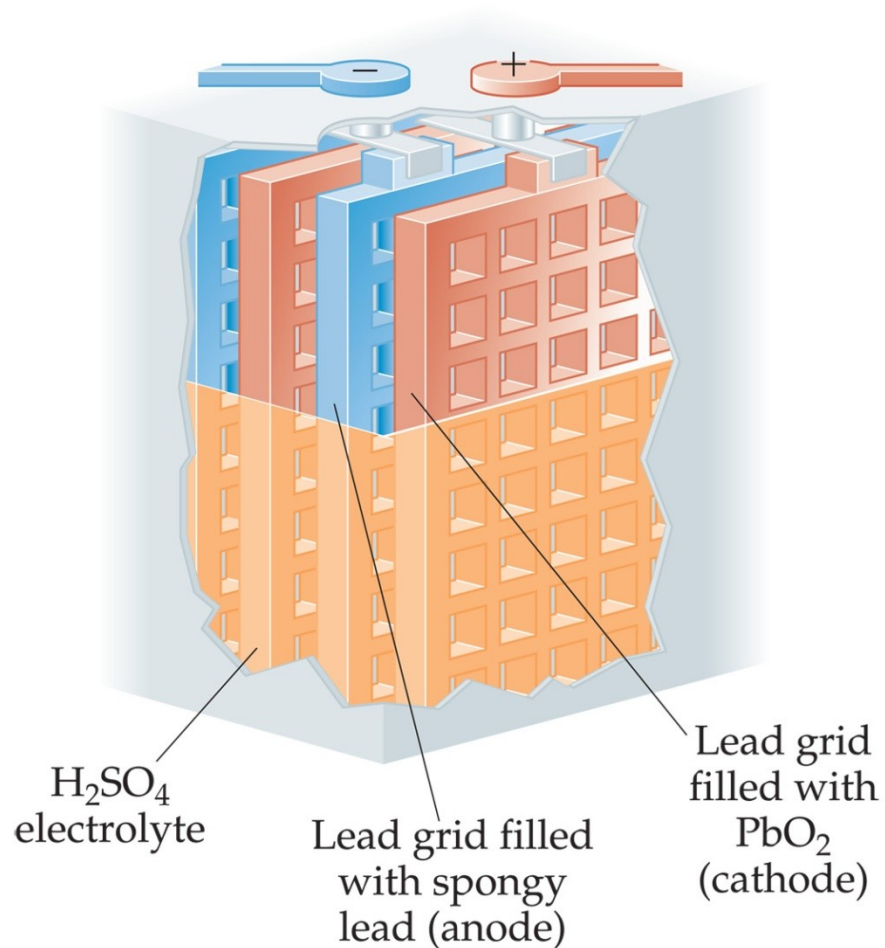
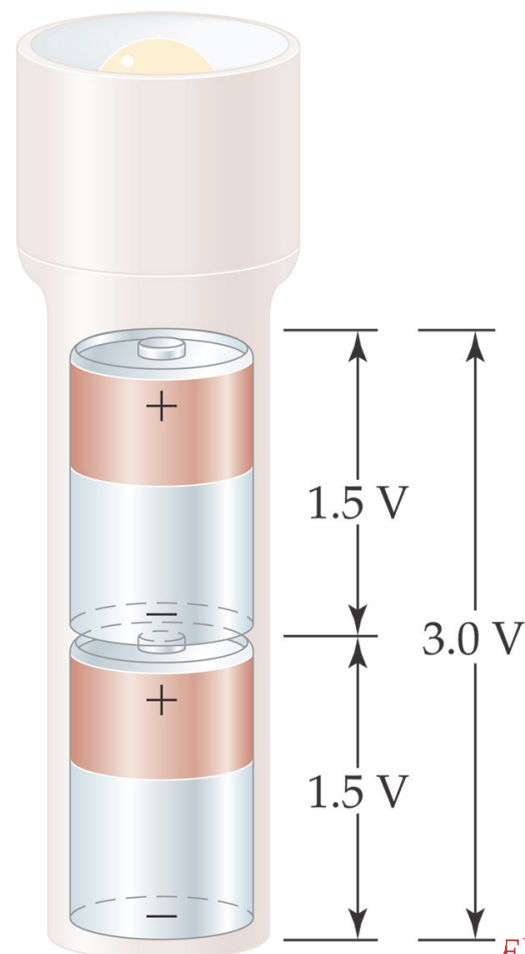
Concentration Cells



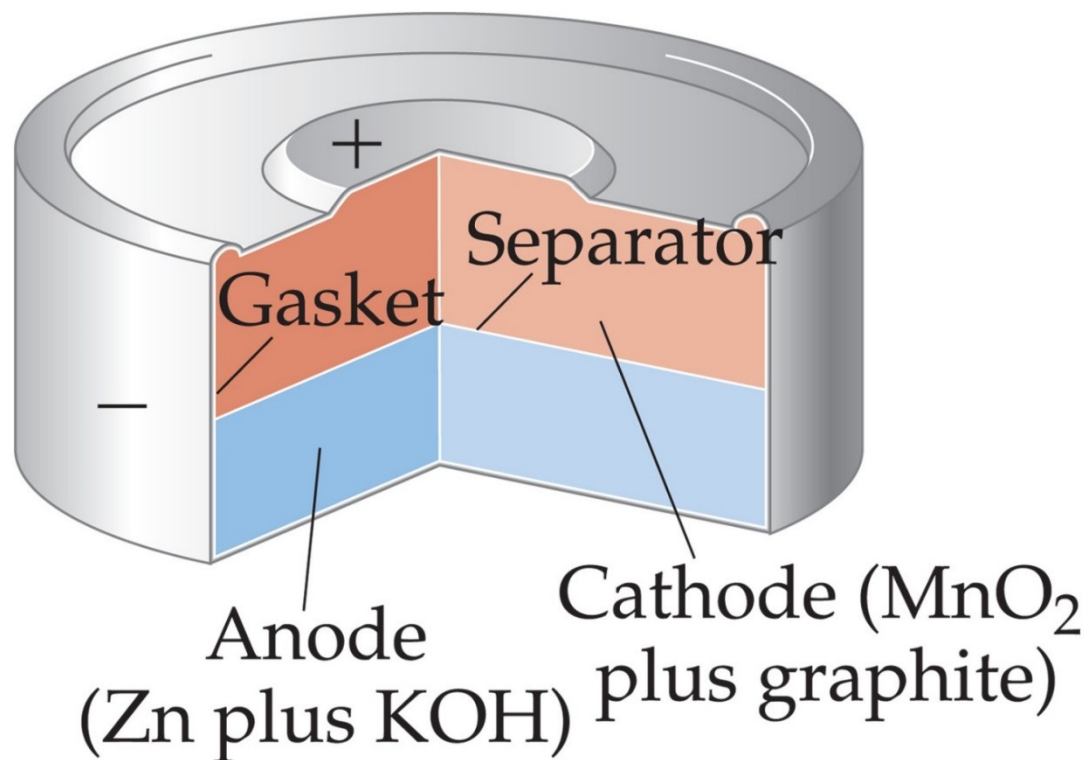
- Notice that the Nernst equation implies that a cell could be created that has the same substance at both electrodes.
- For such a cell, E_{cell} would be 0, but Q would not.
- Therefore, as long as the concentrations are different, E will not be 0.

Applications of Oxidation-Reduction Reactions

Batteries

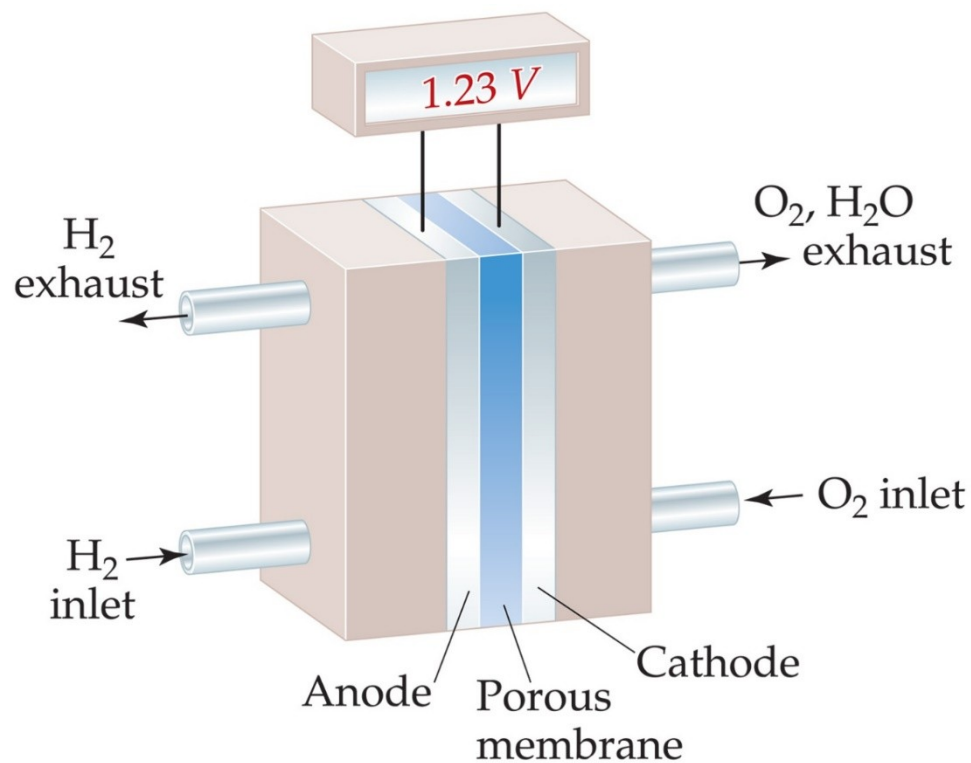


Alkaline Batteries



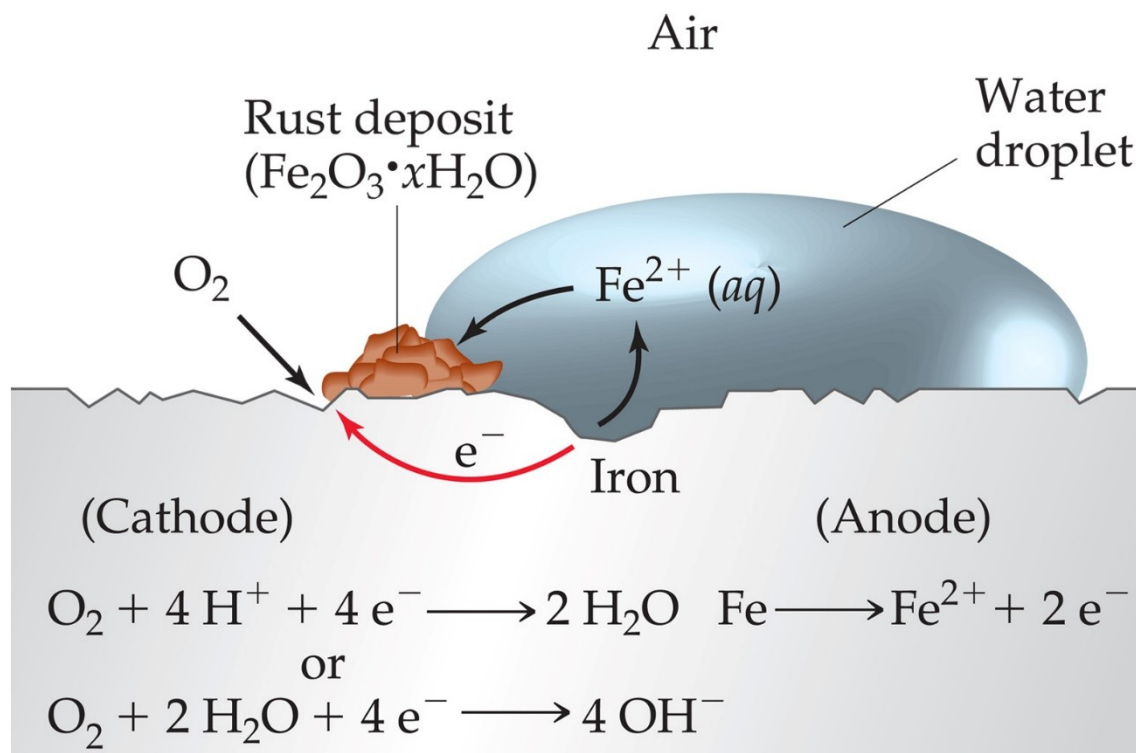
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Hydrogen Fuel Cells



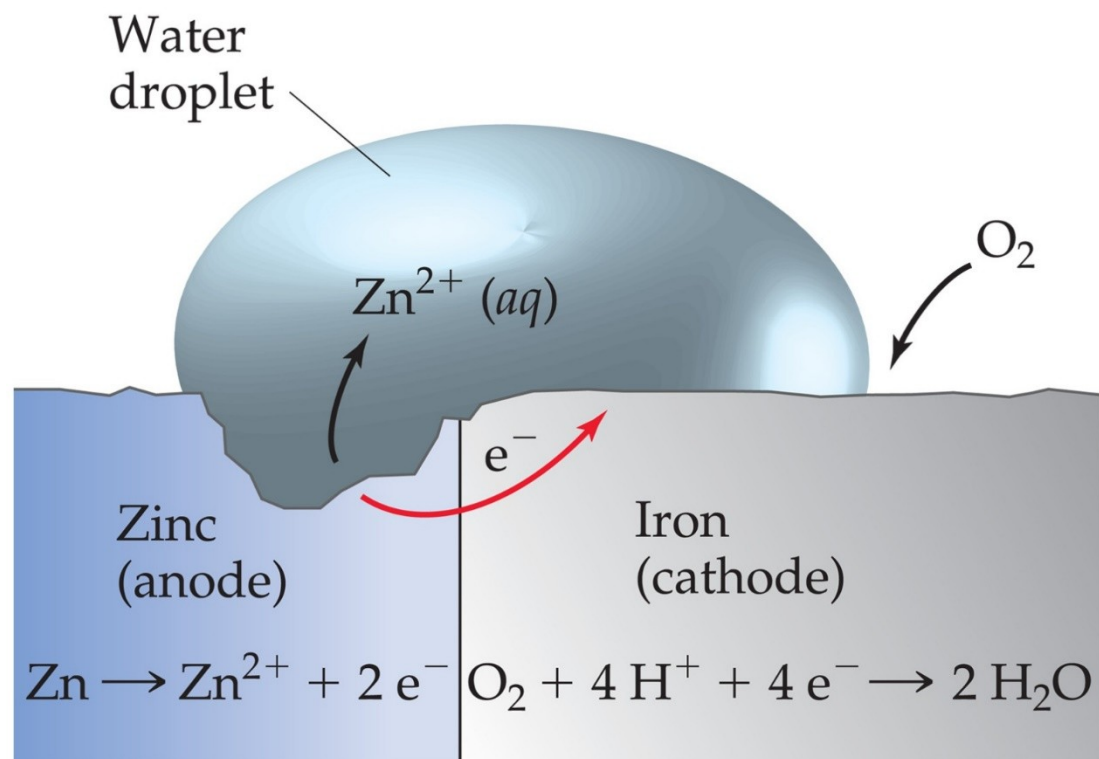
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Corrosion and...



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...Corrosion Prevention



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