

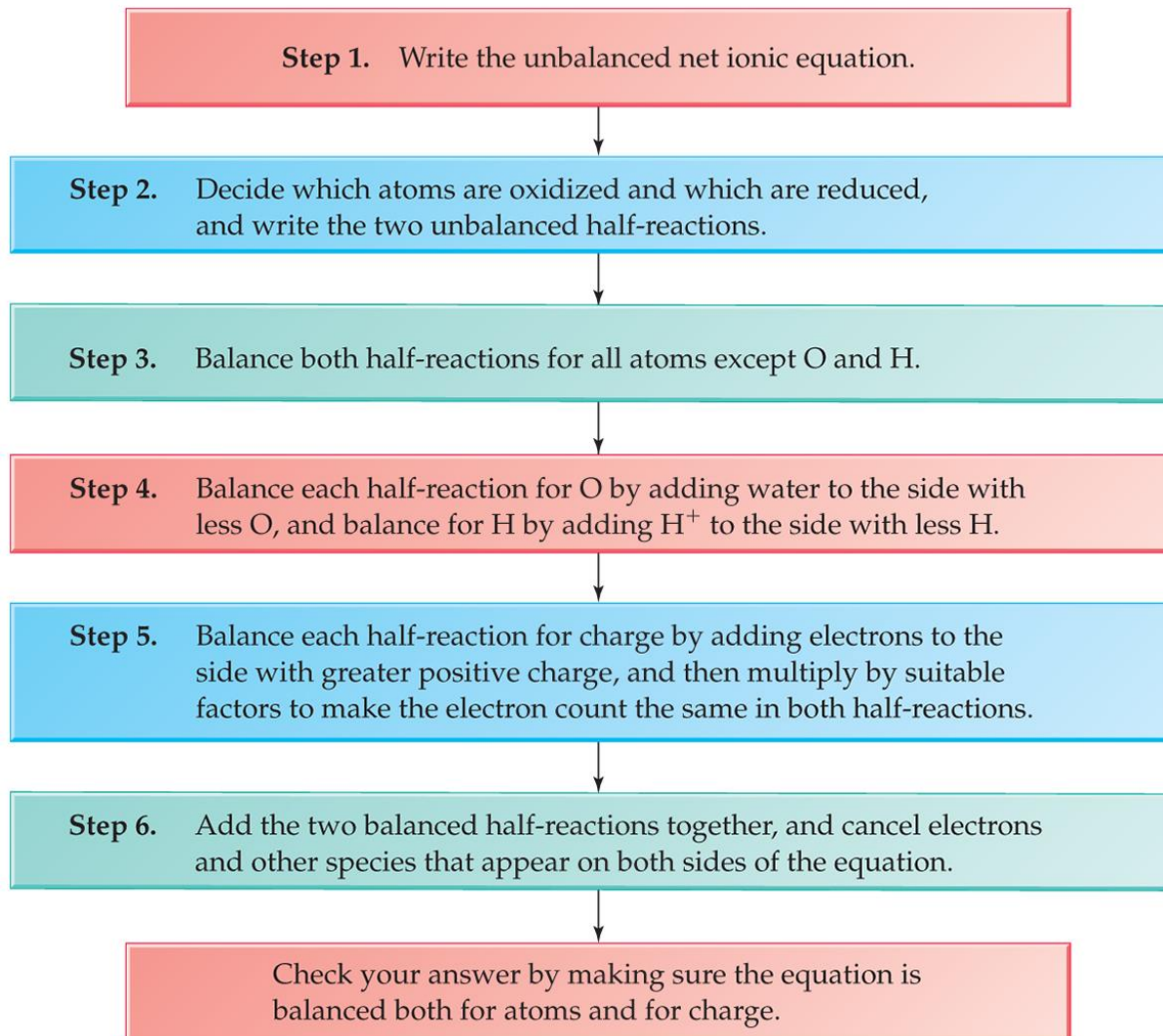
Lecture Presentation

## Chapter 18

# Electrochemistry

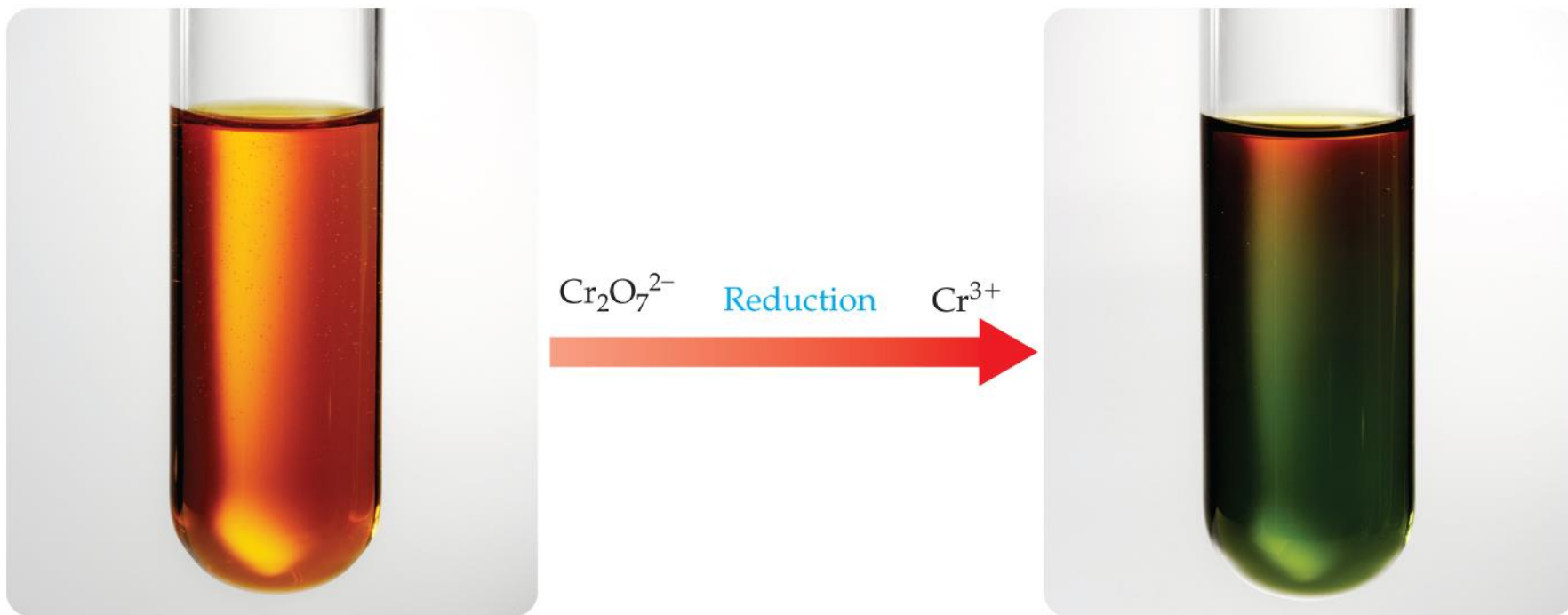
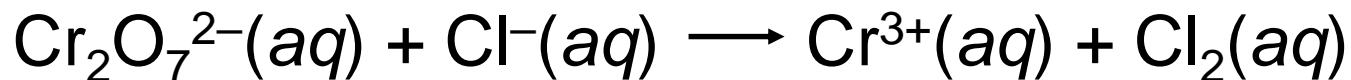
John E. McMurry  
Robert C. Fay

# Balancing Redox Reactions by the Half-Reaction Method



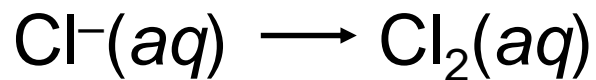
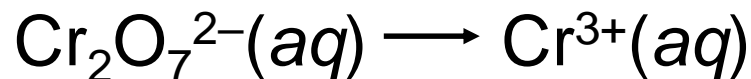
# Balancing Redox Reactions by the Half-Reaction Method

Balance the following net ionic equation in acidic solution:



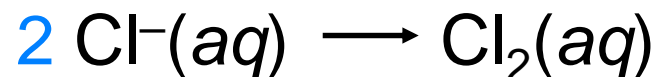
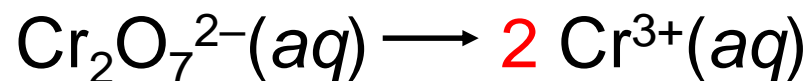
# Balancing Redox Reactions: The Half-Reaction Method

- Write the two unbalanced half-reactions.



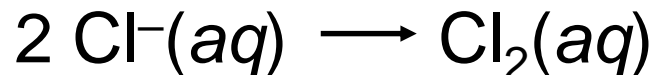
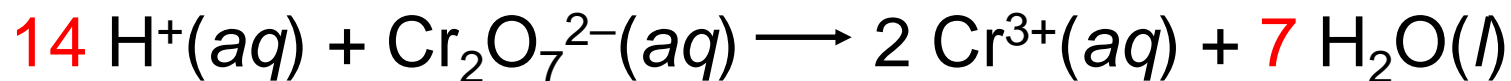
# Balancing Redox Reactions: The Half-Reaction Method

- Balance both half-reactions for all atoms except O and H.



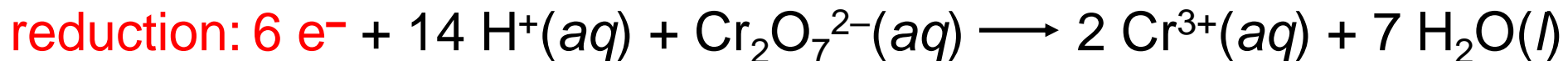
# Balancing Redox Reactions: The Half-Reaction Method

- Balance each half-reaction for O by adding H<sub>2</sub>O, and then balance for H by adding H<sup>+</sup>.

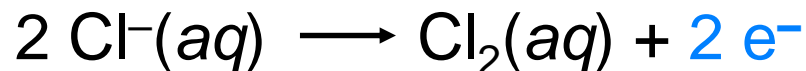


# Balancing Redox Reactions: The Half-Reaction Method

- Balance each half-reaction for charge by adding electrons to the side with greater positive charge.



oxidation:



# Balancing Redox Reactions: The Half-Reaction Method

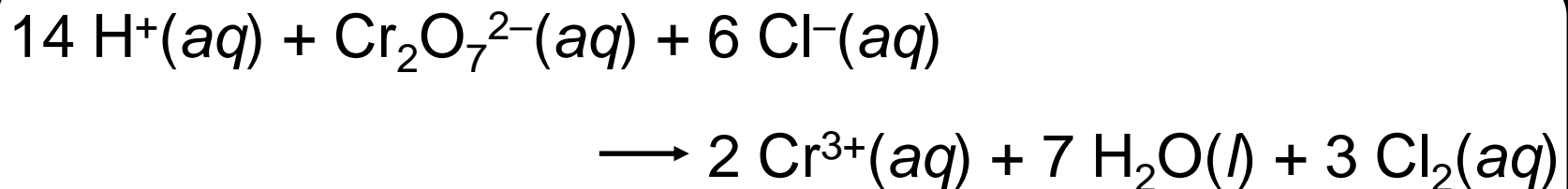
- Multiply each half-reaction by a factor to make the electron count the same in both half-reactions.





# Balancing Redox Reactions: The Half-Reaction Method

- Add the two balanced half-reactions together and cancel species that appear on both sides of the equation.



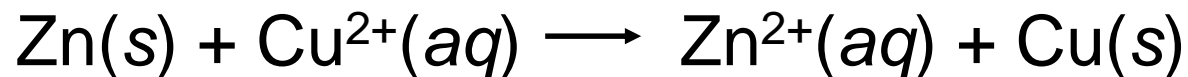
# Galvanic Cells

**Electrochemistry:** The area of chemistry concerned with the interconversion of chemical and electrical energy

**Galvanic (Voltaic) Cell:** A *spontaneous* chemical reaction that generates an electric current

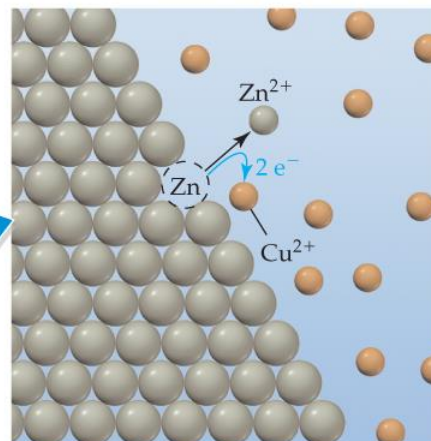
**Electrolytic Cell:** An electric current that drives a *nonspontaneous* reaction

# Galvanic Cells





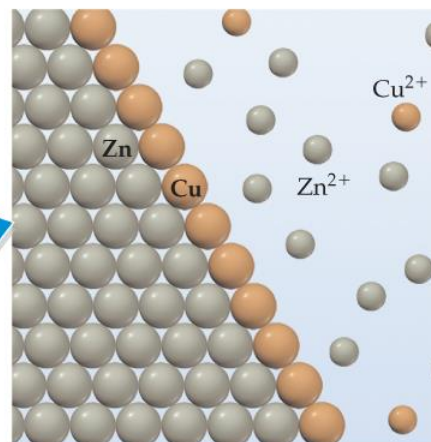
A strip of zinc metal is immersed in an aqueous copper sulfate solution.



At the metal-solution interface, Zn atoms transfer two electrons to  $\text{Cu}^{2+}$  ions, yielding  $\text{Zn}^{2+}$  ions and copper atoms.

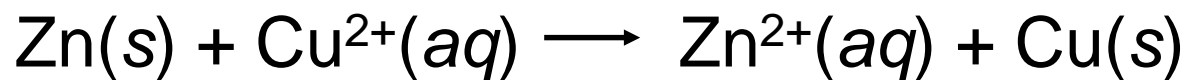


As time passes, a dark deposit of copper metal appears on the zinc, and the blue color of  $\text{Cu}^{2+}(aq)$  fades from the solution.



The surface of the zinc becomes covered with copper atoms, and  $\text{Zn}^{2+}$  ions replace  $\text{Cu}^{2+}$  ions in the solution.

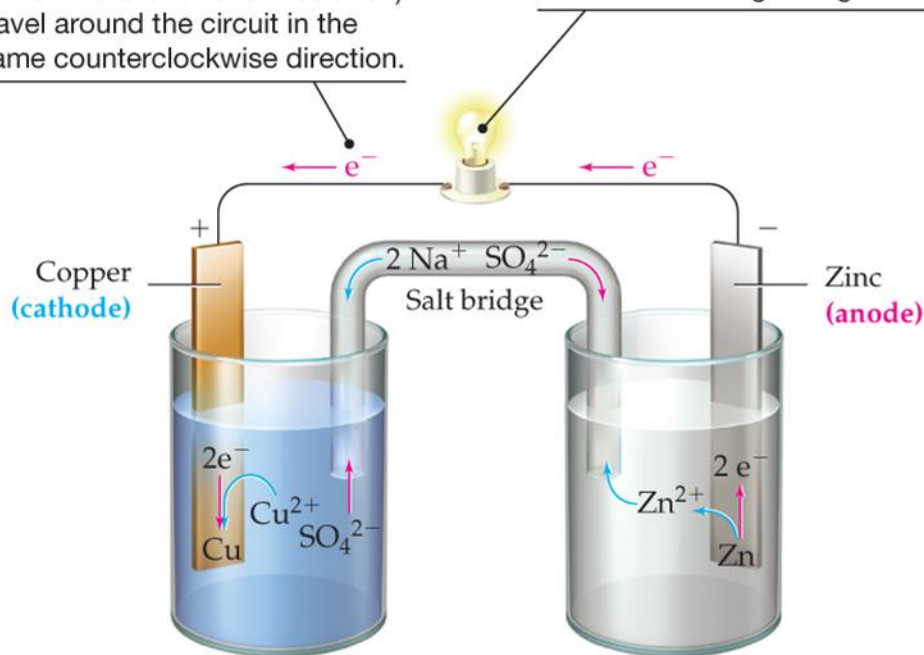
# Galvanic Cells



(a) A galvanic cell

The negative particles (electrons in the wire and anions in solution) travel around the circuit in the same counterclockwise direction.

The resulting electric current can be used to light a light bulb.



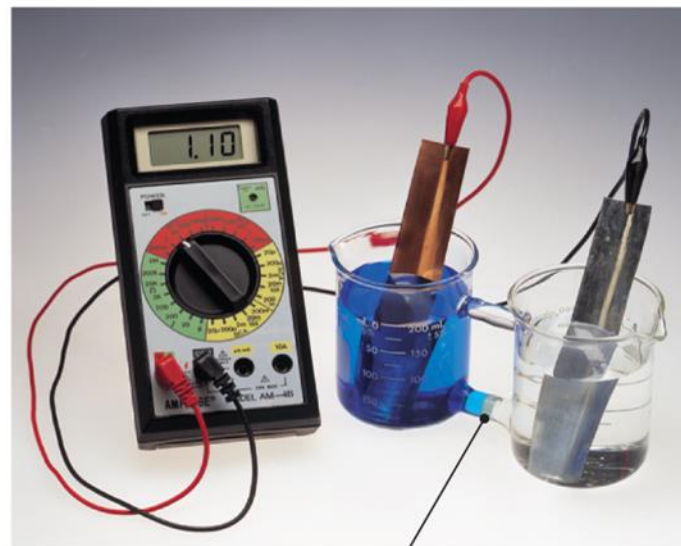
Movement of cations

←

Movement of anions

→

(b) An operating Daniell cell



The salt bridge in part (a) is replaced by a porous glass disk that allows ions to flow between the anode and cathode compartments but prevents bulk mixing. If  $\text{Cu}^{2+}$  crossed the membrane and came into direct contact with zinc, then electrons would be transferred directly and would not flow through the wire.

# Galvanic Cells

- **Anode:**
  - The electrode where oxidation occurs
  - The electrode where electrons are produced
  - Is what anions migrate toward
  - Has a negative sign

**Anode:** {  
Is where oxidation occurs  
Is where electrons are produced  
Is what anions migrate toward  
Has a negative sign

**Cathode:** {  
Is where reduction occurs  
Is where electrons are consumed  
Is what cations migrate toward  
Has a positive sign



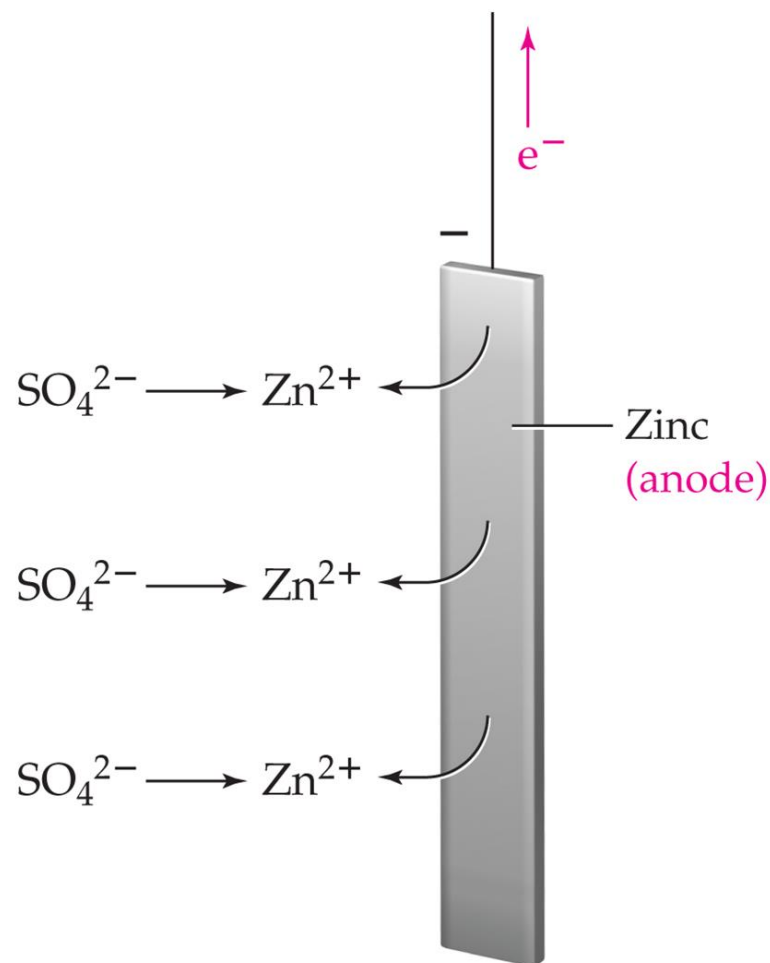
# Galvanic Cells



- **Cathode:**
  - The electrode where reduction occurs
  - The electrode where electrons are consumed
  - Is what cations migrate toward
  - Has a positive sign

# Galvanic Cells

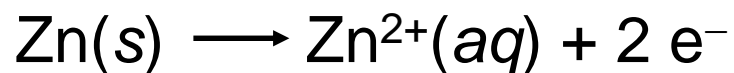
Why do negative ions (anions) move toward the negative electrode (anode)?



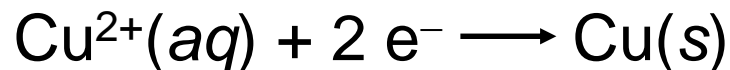


# Galvanic Cells

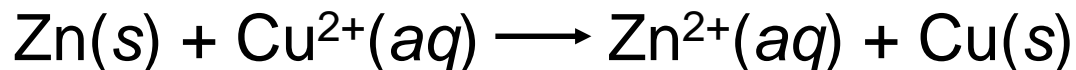
Anode half-reaction:



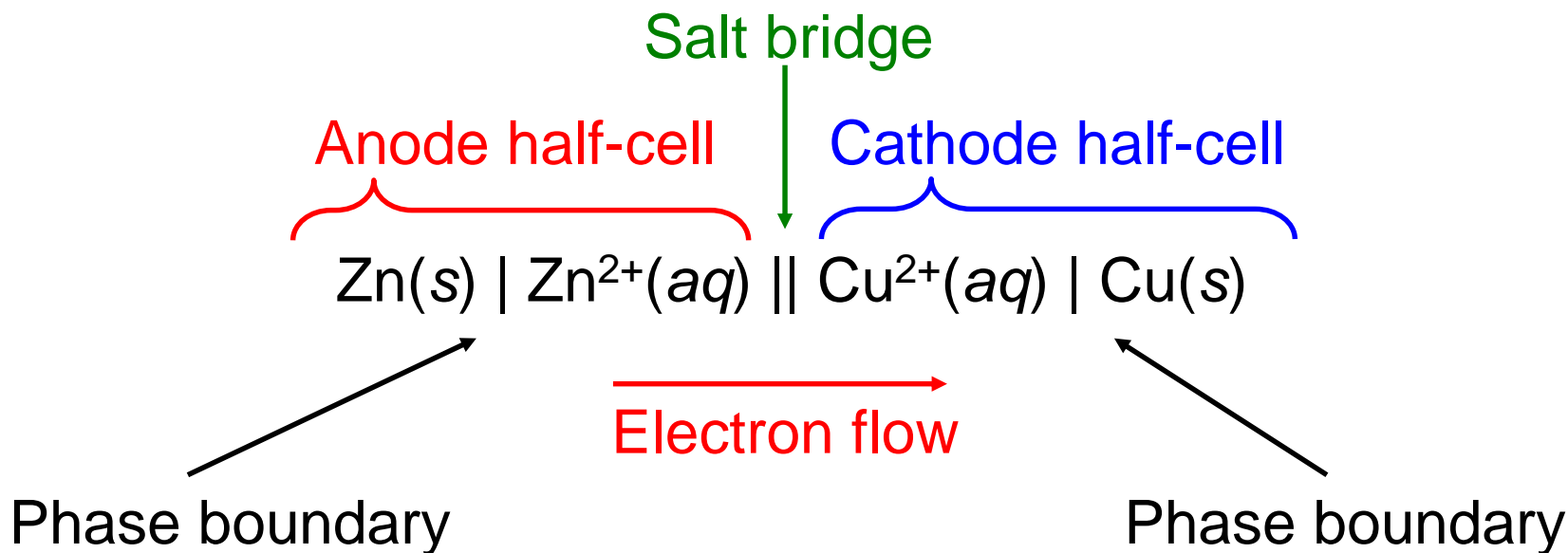
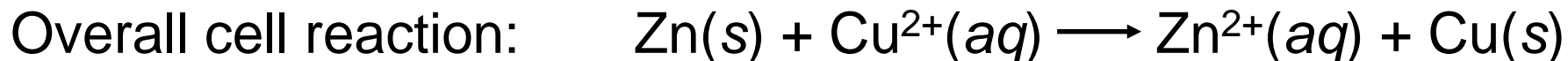
Cathode half-reaction:



Overall cell reaction:



# Shorthand Notation for Galvanic Cells

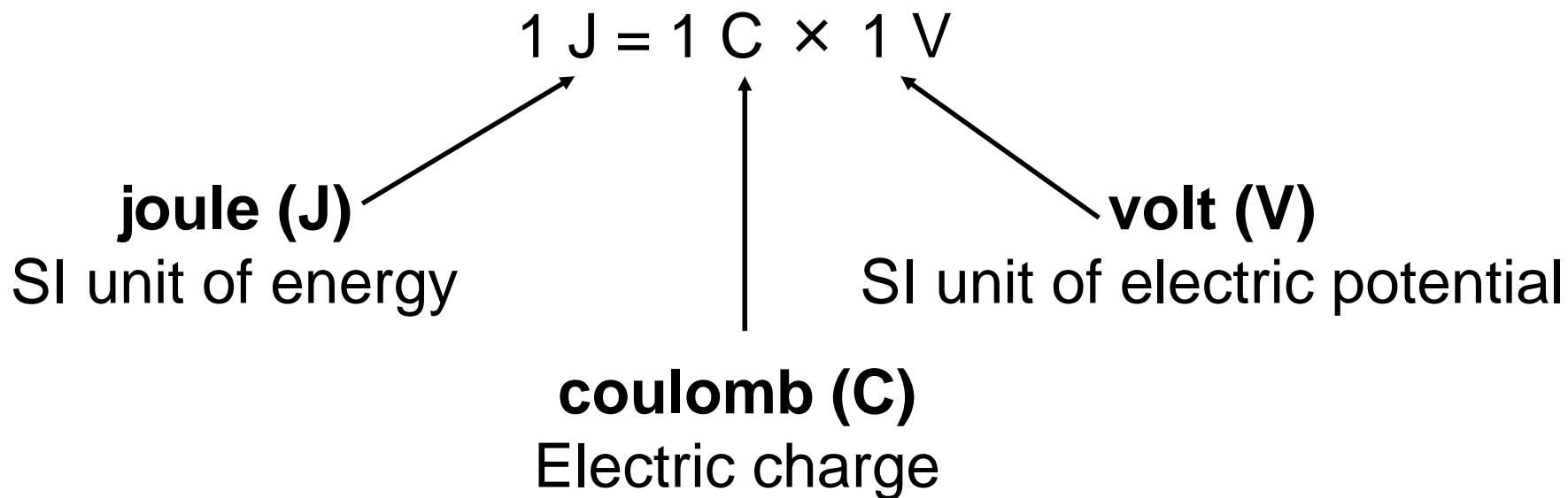


# Cell Potentials and Free-Energy Changes for Cell Reactions

**Electromotive Force (emf):** The force or electrical potential that pushes the negatively charged electrons away from the anode (– electrode) and pulls them toward the cathode (+ electrode)

It is also called the **cell potential ( $E$ )** or the **cell voltage**.

# Cell Potentials and Free-Energy Changes for Cell Reactions



1 coulomb is the amount of charge transferred when a current of 1 ampere (A) flows for 1 second.

# Cell Potentials and Free-Energy Changes for Cell Reactions

## faraday or Faraday constant

The electric charge on 1 mol of electrons and is equal to 96,500 C/mol e<sup>-</sup>

$$\Delta G = -nFE \quad \text{or} \quad \Delta G^\circ = -nFE^\circ$$

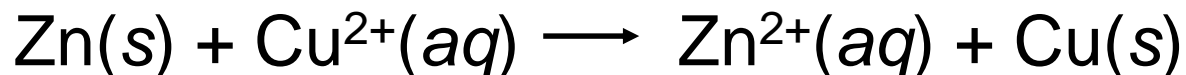
Free-energy change

Cell potential

Number of moles of electrons transferred in the reaction

# Cell Potentials and Free-Energy Changes for Cell Reactions

The standard cell potential at 25 °C is 1.10 V for the reaction:



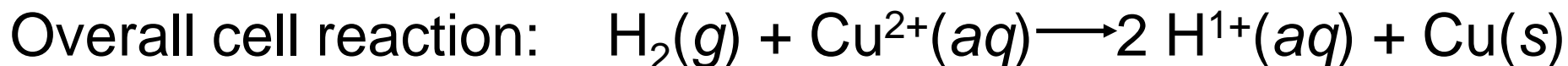
Calculate the standard free-energy change for this reaction at 25 °C.

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

$$= -(2 \text{ mol } e^-) \left( \frac{96,500 \text{ C}}{\text{mol } e^-} \right) (1.10 \text{ V}) \left( \frac{1 \text{ J}}{1 \text{ C V}} \right) \left( \frac{1 \text{ kJ}}{1000 \text{ J}} \right)$$

$$\Delta G^\circ = \boxed{-212 \text{ kJ}}$$

# Standard Reduction Potentials



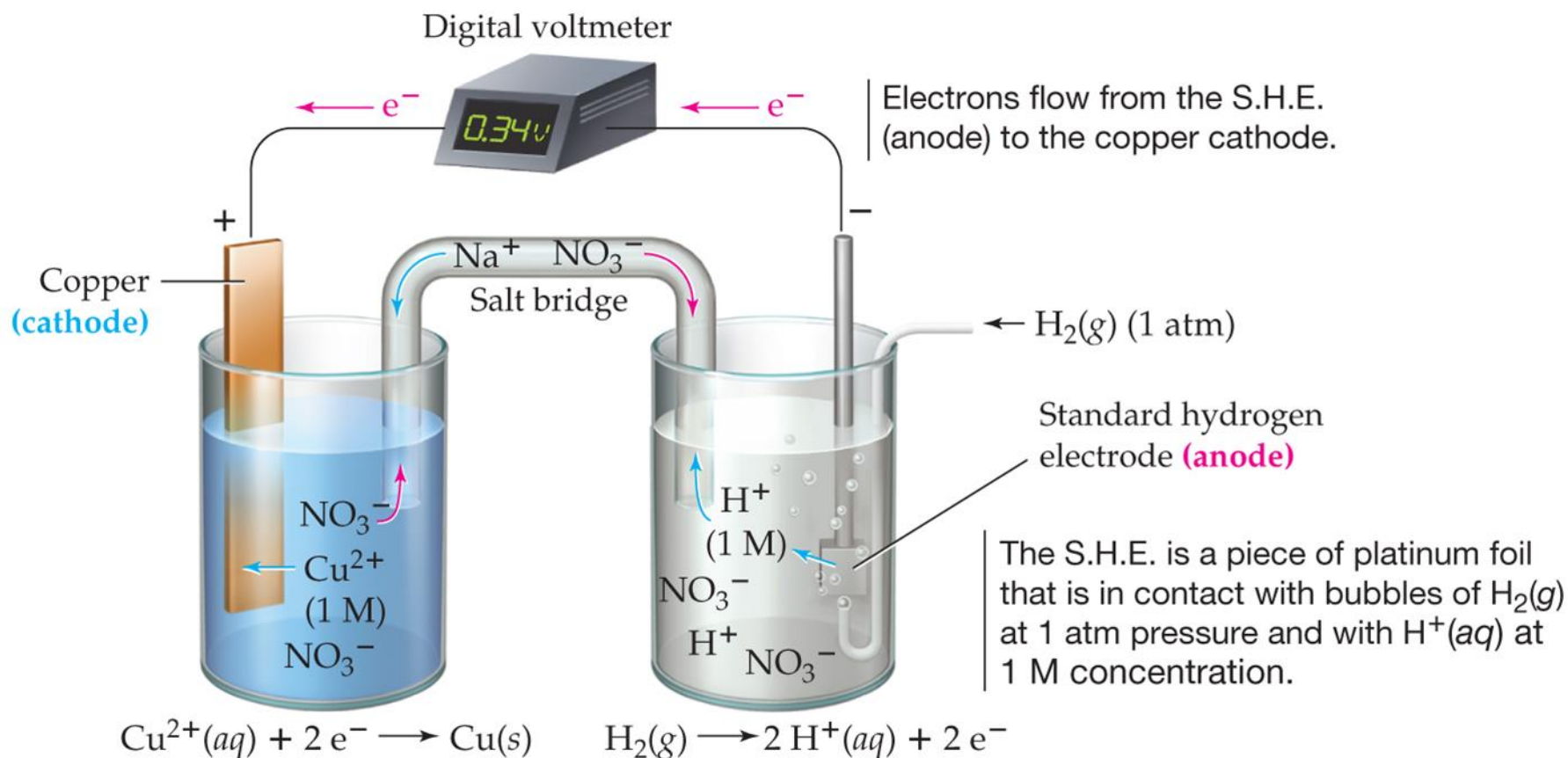
The standard potential of a cell is the sum of the standard half-cell potentials for oxidation at the anode and reduction at the cathode:

$$E^\circ_{\text{cell}} = E^\circ_{\text{ox}} + E^\circ_{\text{red}}$$

The measured potential for this cell:  $E^\circ_{\text{cell}} = 0.34 \text{ V}$

# Standard Reduction Potentials

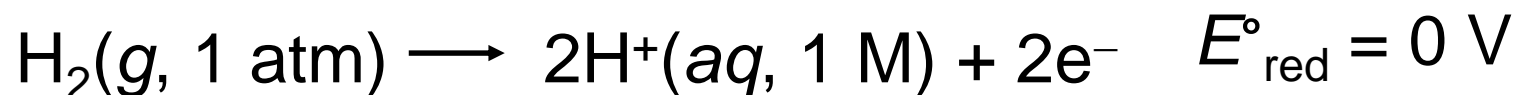
The **standard hydrogen electrode (S.H.E.)** has been chosen to be the reference electrode.





# Standard Reduction Potentials

The **standard hydrogen electrode (S.H.E.)** has been chosen to be the reference electrode.



# Standard Reduction Potentials



$$E^\circ_{\text{cell}} = E^\circ_{\text{ox}} + E^\circ_{\text{red}}$$

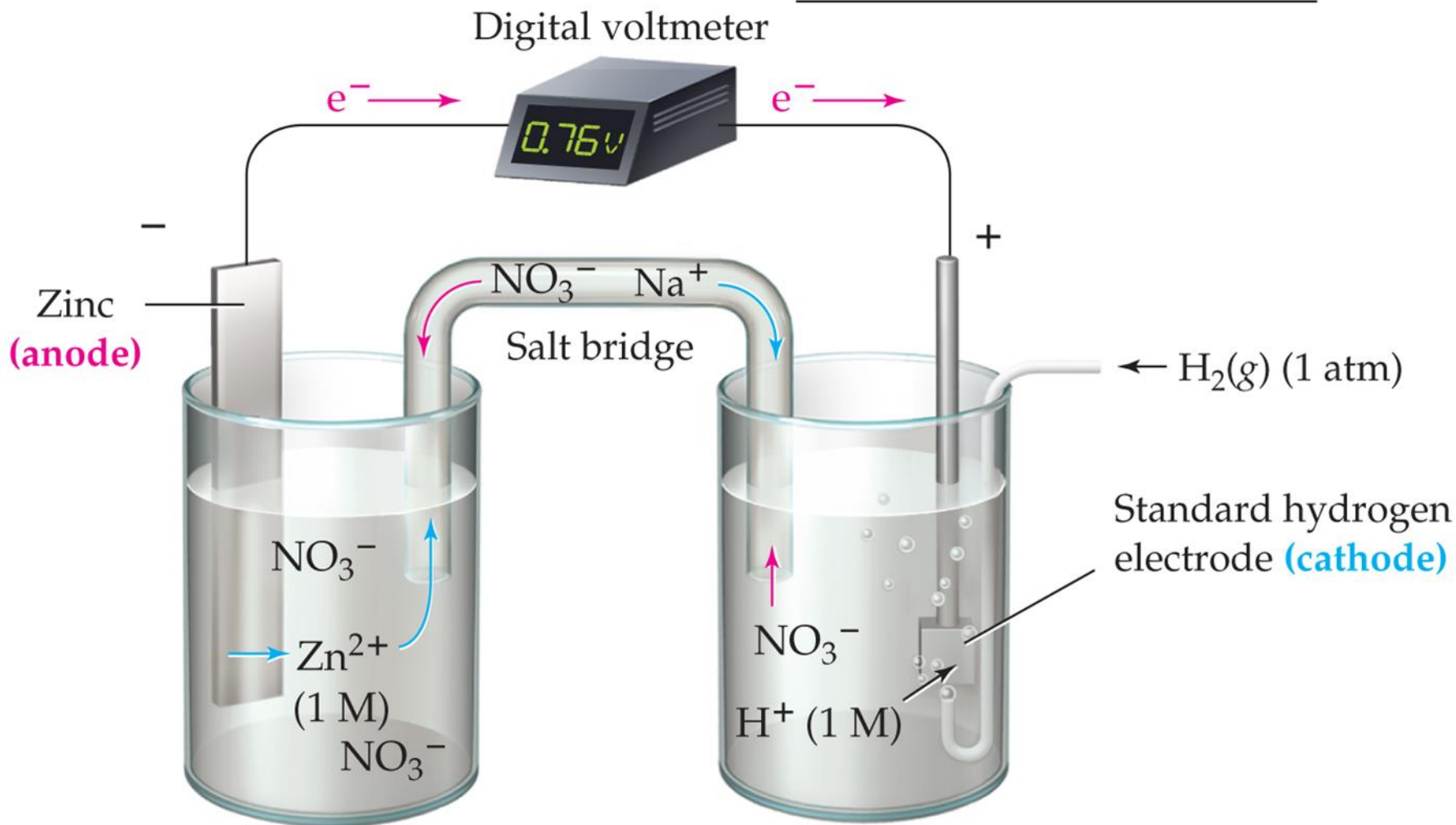
$$0.34 \text{ V} = 0 \text{ V} + E^\circ_{\text{red}}$$

A standard reduction potential can be defined:

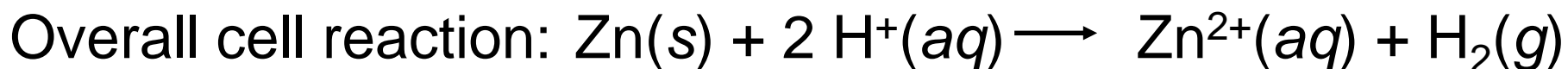
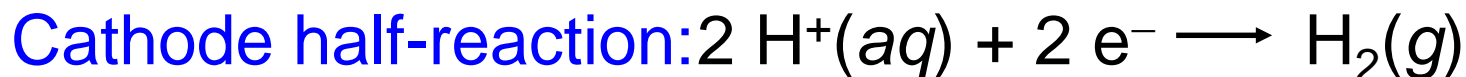


# Standard Reduction Potentials

Electrons flow from the zinc anode to the S.H.E. (cathode).

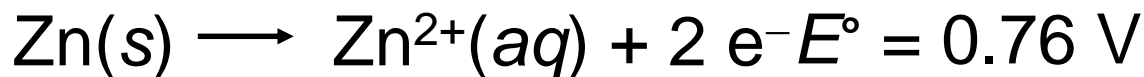


# Standard Reduction Potentials

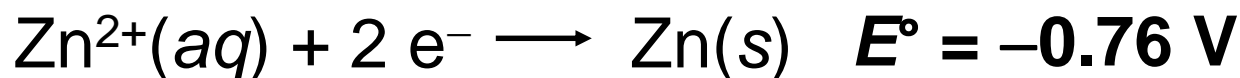


$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{ox}} + E^{\circ}_{\text{red}}$$

$$0.76 \text{ V} = E^{\circ}_{\text{ox}} + 0 \text{ V}$$





As a standard reduction potential:

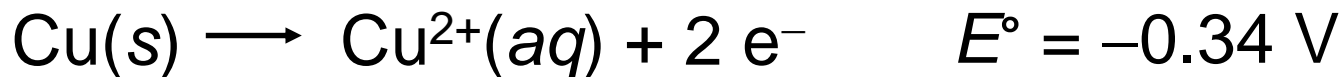
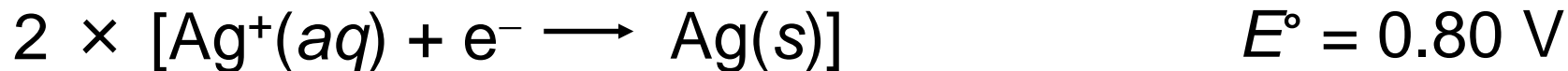
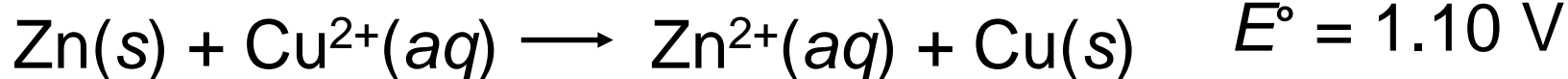
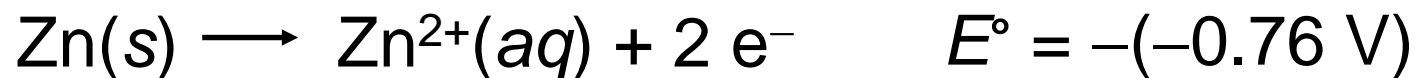


# Standard Reduction Potentials

**TABLE 18.1** Standard Reduction Potentials at 25 °C

	Reduction Half-Reaction	$E^\circ$ (V)		
 <p>Stronger oxidizing agent</p>	$F_2(g) + 2 e^- \longrightarrow 2 F^-(aq)$	2.87	 <p>Weaker reducing agent</p>	
	$H_2O_2(aq) + 2 H^+(aq) + 2 e^- \longrightarrow 2 H_2O(l)$	1.78		
	$MnO_4^-(aq) + 8 H^+(aq) + 5 e^- \longrightarrow Mn^{2+}(aq) + 4 H_2O(l)$	1.51		
	$Cl_2(g) + 2 e^- \longrightarrow 2 Cl^-(aq)$	1.36		
	$Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e^- \longrightarrow 2 Cr^{3+}(aq) + 7 H_2O(l)$	1.36		
	$O_2(g) + 4 H^+(aq) + 4 e^- \longrightarrow 2 H_2O(l)$	1.23		
	$Br_2(aq) + 2 e^- \longrightarrow 2 Br^-(aq)$	1.09		
	$Ag^+(aq) + e^- \longrightarrow Ag(s)$	0.80		
	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	0.77		
	$O_2(g) + 2 H^+(aq) + 2 e^- \longrightarrow H_2O_2(aq)$	0.70		
	$I_2(s) + 2 e^- \longrightarrow 2 I^-(aq)$	0.54		
	$O_2(g) + 2 H_2O(l) + 4 e^- \longrightarrow 4 OH^-(aq)$	0.40		
	$Cu^{2+}(aq) + 2 e^- \longrightarrow Cu(s)$	0.34		
	$Sn^{4+}(aq) + 2 e^- \longrightarrow Sn^{2+}(aq)$	0.15		
		<b><math>2 H^+(aq) + 2 e^- \longrightarrow H_2(g)</math></b>		<b>0</b>
		$Pb^{2+}(aq) + 2 e^- \longrightarrow Pb(s)$		-0.13
	$Ni^{2+}(aq) + 2 e^- \longrightarrow Ni(s)$	-0.26		
	$Cd^{2+}(aq) + 2 e^- \longrightarrow Cd(s)$	-0.40		
	$Fe^{2+}(aq) + 2 e^- \longrightarrow Fe(s)$	-0.45		
	$Zn^{2+}(aq) + 2 e^- \longrightarrow Zn(s)$	-0.76		
	$2 H_2O(l) + 2 e^- \longrightarrow H_2(g) + 2 OH^-(aq)$	-0.83		
	$Al^{3+}(aq) + 3 e^- \longrightarrow Al(s)$	-1.66		
	$Mg^{2+}(aq) + 2 e^- \longrightarrow Mg(s)$	-2.37		
	$Na^+(aq) + e^- \longrightarrow Na(s)$	-2.71		
<p>Weaker oxidizing agent</p>	$Li^+(aq) + e^- \longrightarrow Li(s)$	-3.04	<p>Stronger reducing agent</p>	

# Using Standard Reduction Potentials



Half-cell potentials are **intensive** properties.

# The Nernst Equation

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

Using:  $\Delta G = -nFE$  and  $\Delta G^\circ = -nFE^\circ$

**Nernst Equation:**  $E = E^\circ - \frac{RT}{nF} \ln Q$

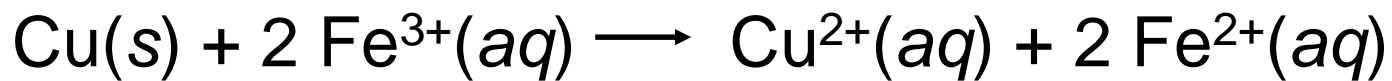
or

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

$$E = E^\circ - \frac{0.0592 \text{ V}}{n} \log Q \quad \text{in volts, at } 25 \text{ }^\circ\text{C}$$

# The Nernst Equation

Consider a galvanic cell that uses the reaction:



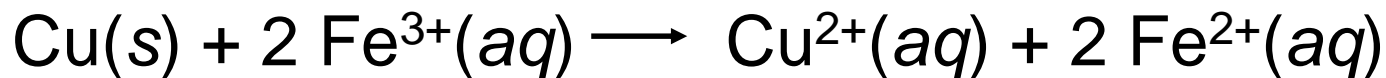
What is the potential of a cell at 25 °C that has the following ion concentrations?

$$[\text{Fe}^{3+}] = 1.0 \times 10^{-4} \text{ M} \quad [\text{Cu}^{2+}] = 0.25 \text{ M} \quad [\text{Fe}^{2+}] = 0.20 \text{ M}$$

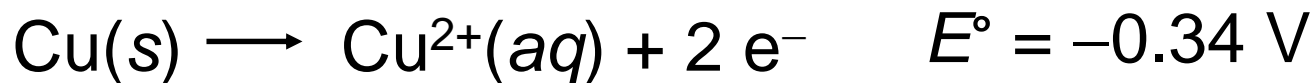


# The Nernst Equation

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



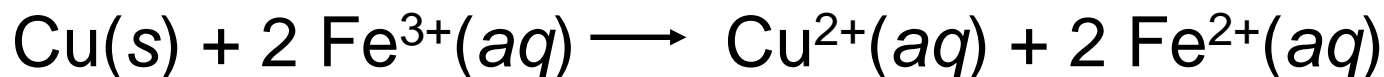
**Calculate  $E^{\circ}$ :**



$$E^{\circ}_{\text{cell}} = -0.34 \text{ V} + 0.77 \text{ V} = 0.43 \text{ V}$$

# The Nernst Equation

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



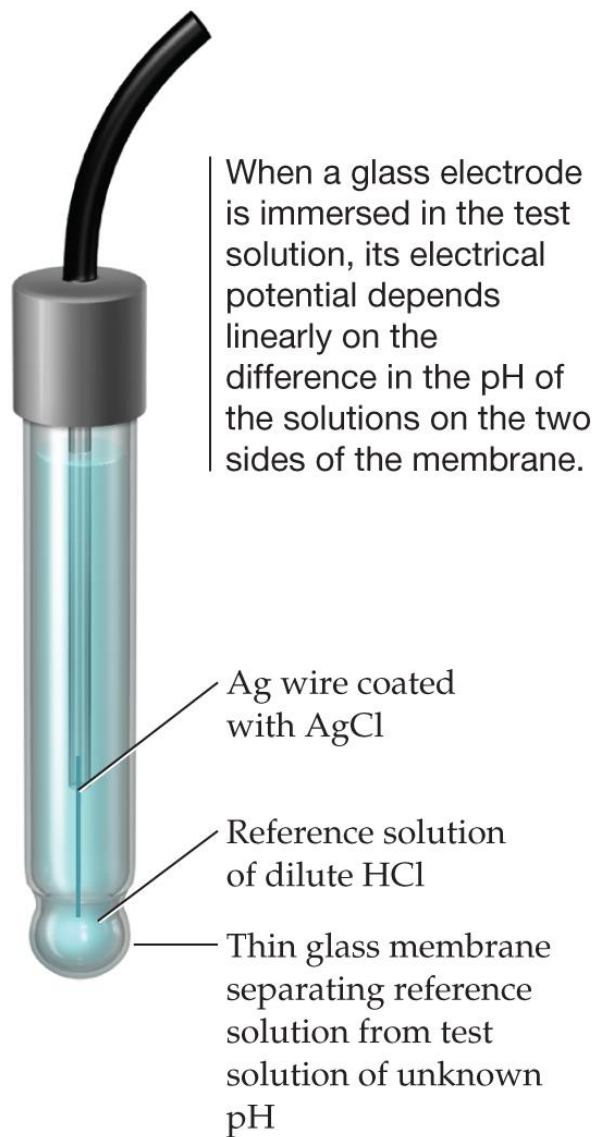
**Calculate  $E$ :**

$$E = E^\circ - \left( \frac{0.0592 \text{ V}}{n} \right) \log \frac{[\text{Cu}^{2+}][\text{Fe}^{2+}]^2}{[\text{Fe}^{3+}]^2}$$

$$= 0.43 \text{ V} - \left( \frac{0.0592 \text{ V}}{2} \right) \log \left( \frac{(0.25)(0.20)^2}{(1.0 \times 10^{-4})^2} \right)$$

$$E = \boxed{0.25 \text{ V}}$$

# Electrochemical Determination of pH



# Standard Cell Potentials and Equilibrium Constants

Using  $\Delta G^\circ = -nFE^\circ$  and  $\Delta G^\circ = -RT \ln K$

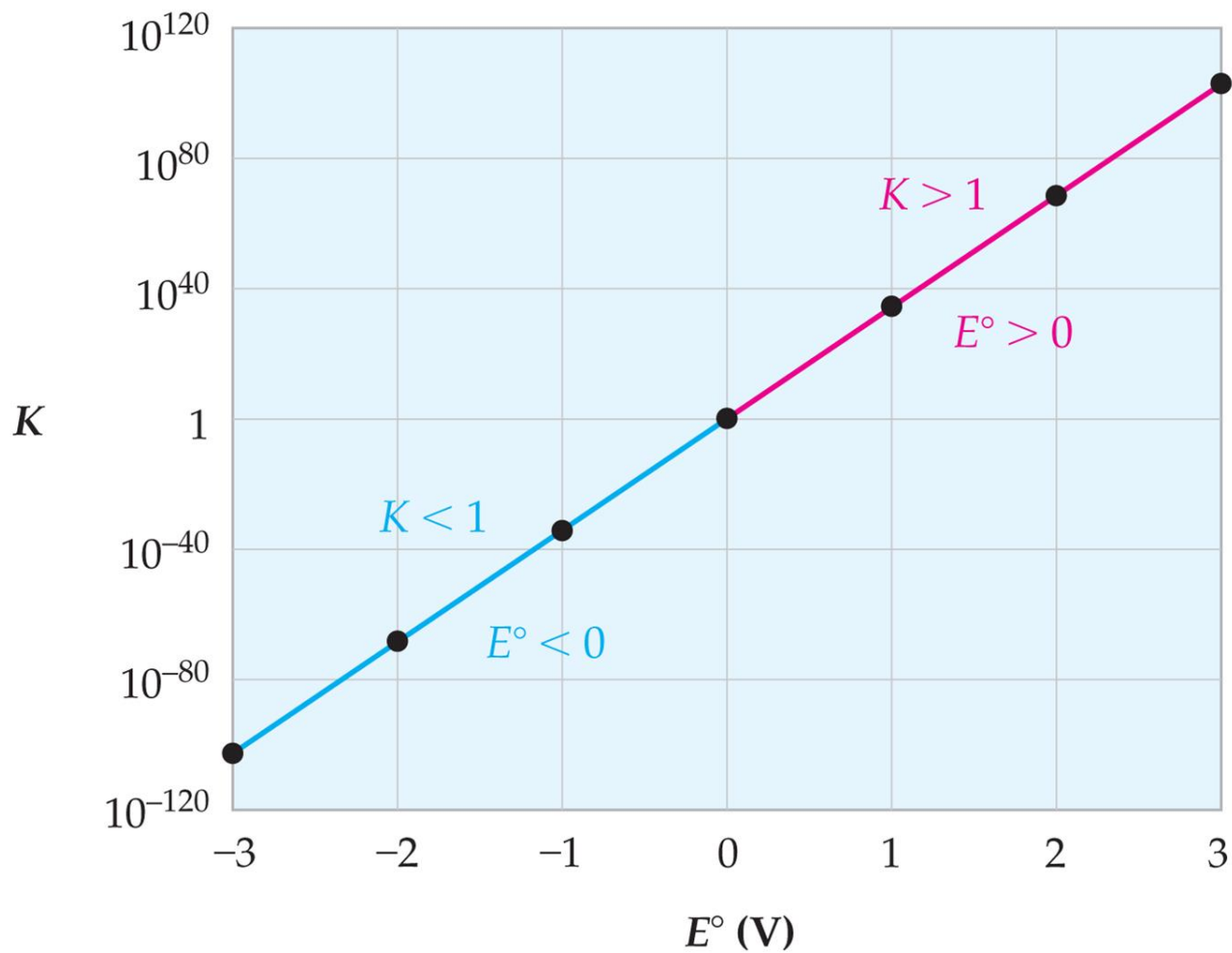
$$-nFE^\circ = -RT \ln K$$

$$E^\circ = \frac{RT}{nF} \ln K = \frac{2.303 RT}{nF} \log K$$

$$E^\circ = \frac{0.0592 \text{ V}}{n} \log K$$

in volts, at 25 °C

# Standard Cell Potentials and Equilibrium Constants



# Standard Cell Potentials and Equilibrium Constants

Three methods to determine equilibrium constants:

1.  $K$  from concentration data: 
$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

2.  $K$  from thermochemical data: 
$$\ln K = \frac{-\Delta G^\circ}{RT}$$

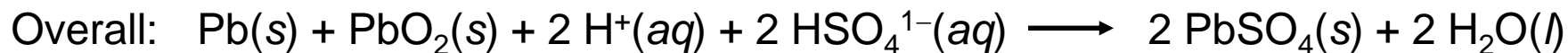
3.  $K$  from electrochemical data: 
$$E^\circ = \frac{RT}{nF} \ln K$$

or

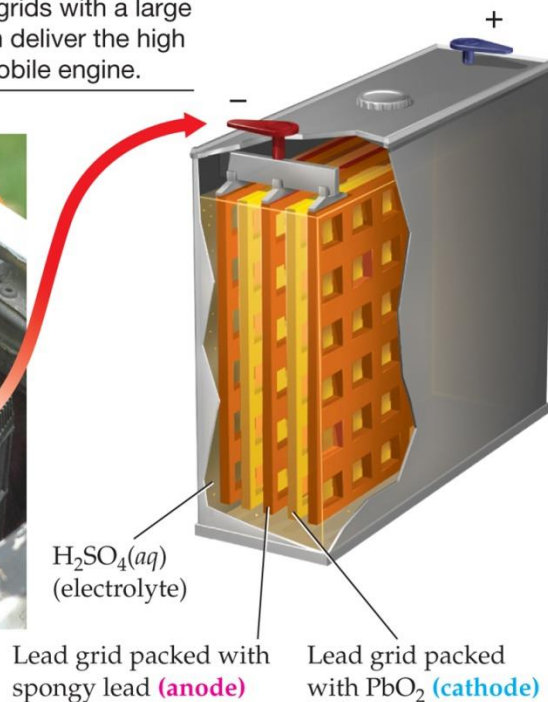
$$\ln K = \frac{nFE^\circ}{RT}$$

# Batteries

## Lead Storage Battery



Each electrode consists of several grids with a large surface area so that the battery can deliver the high currents required to start an automobile engine.

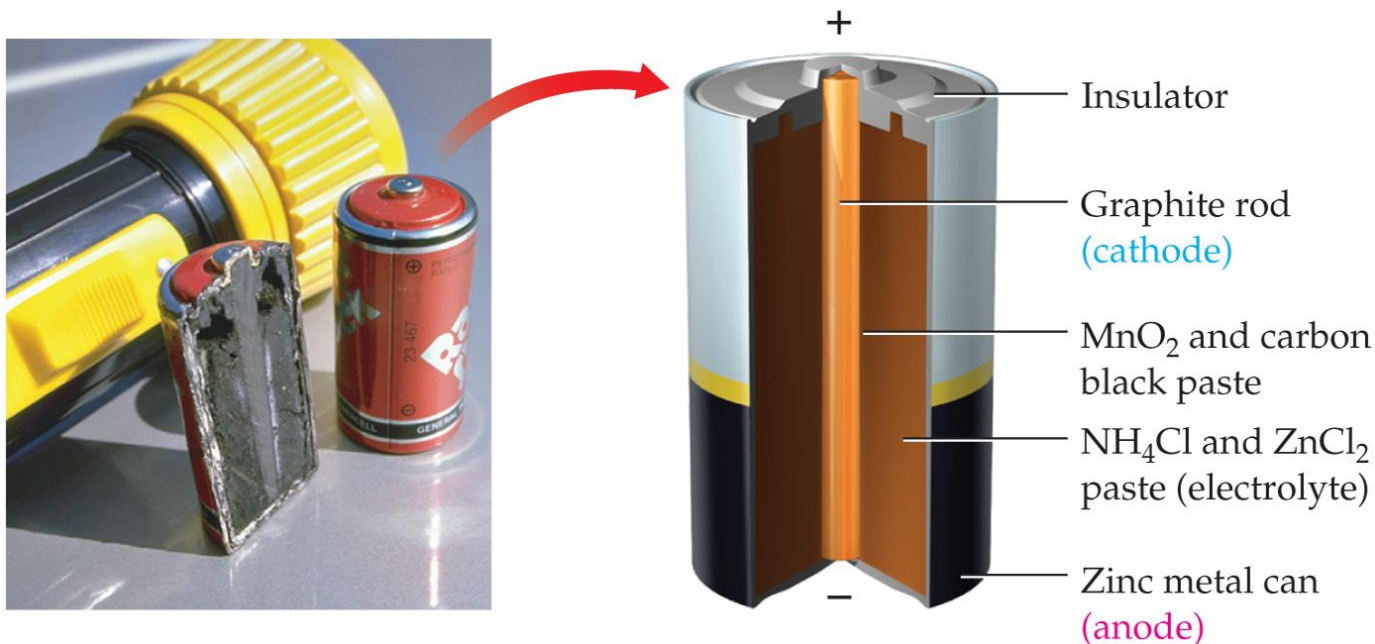
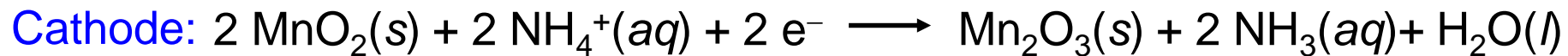


# Batteries

## Dry-Cell Batteries

### Leclanché cell

Anode:

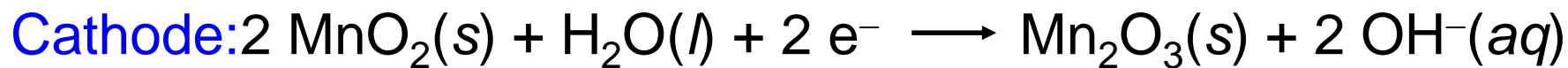
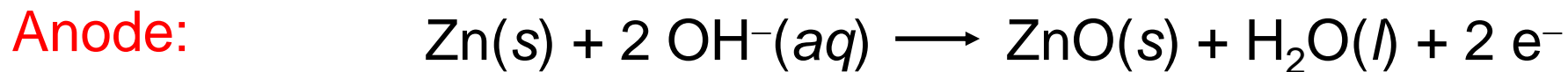




# Batteries

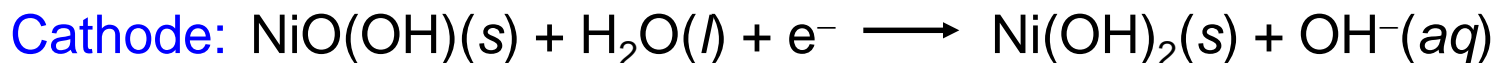
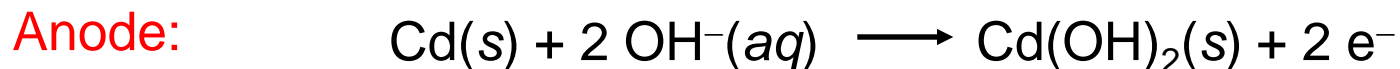
## Dry-Cell Batteries

Alkaline cell

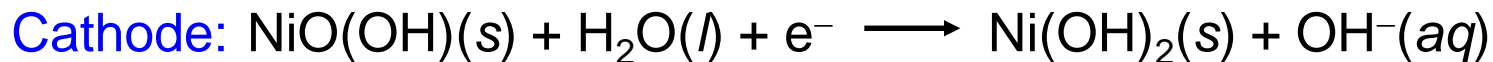
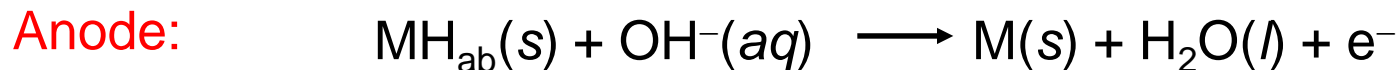


# Batteries

## Nickel-Cadmium (“*ni-cad*”) Batteries



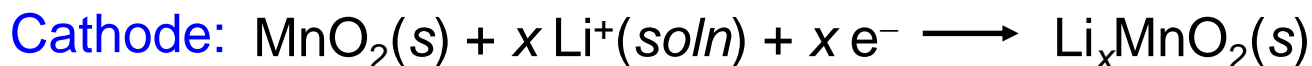
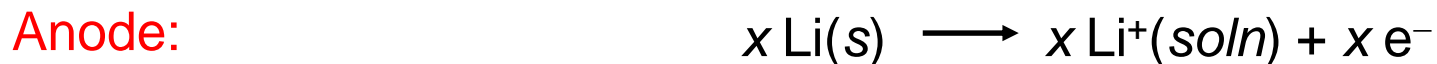
## Nickel-Metal Hydride (“*NiMH*”) Batteries



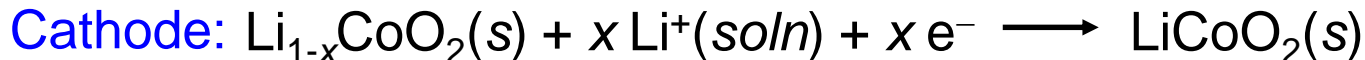
# Batteries

## Lithium and Lithium Ion Batteries

### Lithium



### Lithium Ion

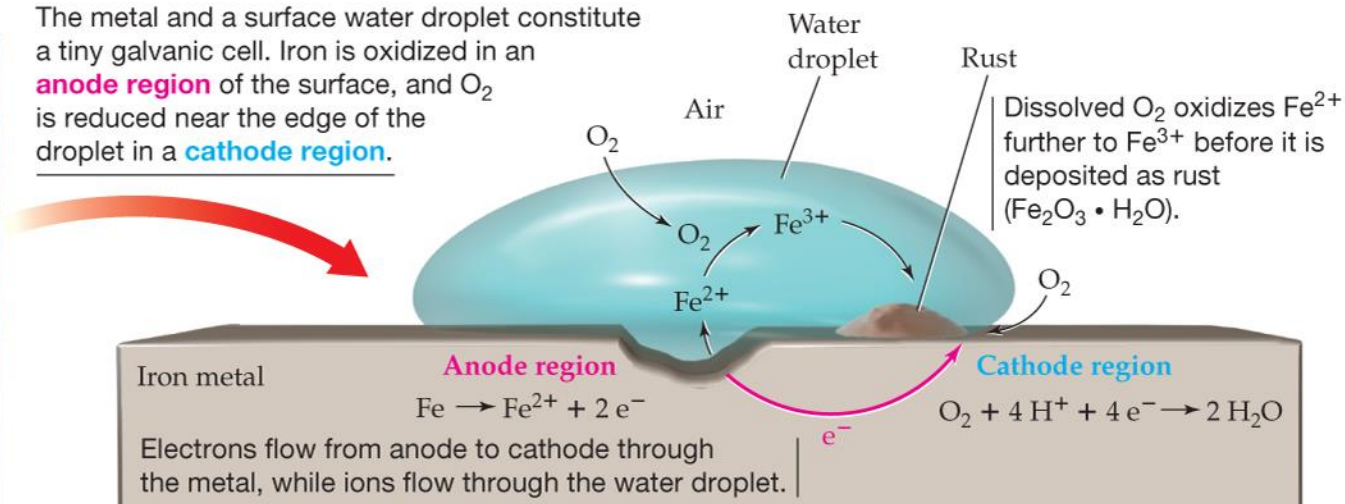


# Corrosion

## Corrosion: The oxidative deterioration of a metal



The metal and a surface water droplet constitute a tiny galvanic cell. Iron is oxidized in an **anode region** of the surface, and  $O_2$  is reduced near the edge of the droplet in a **cathode region**.



# Corrosion

## Prevention of Corrosion

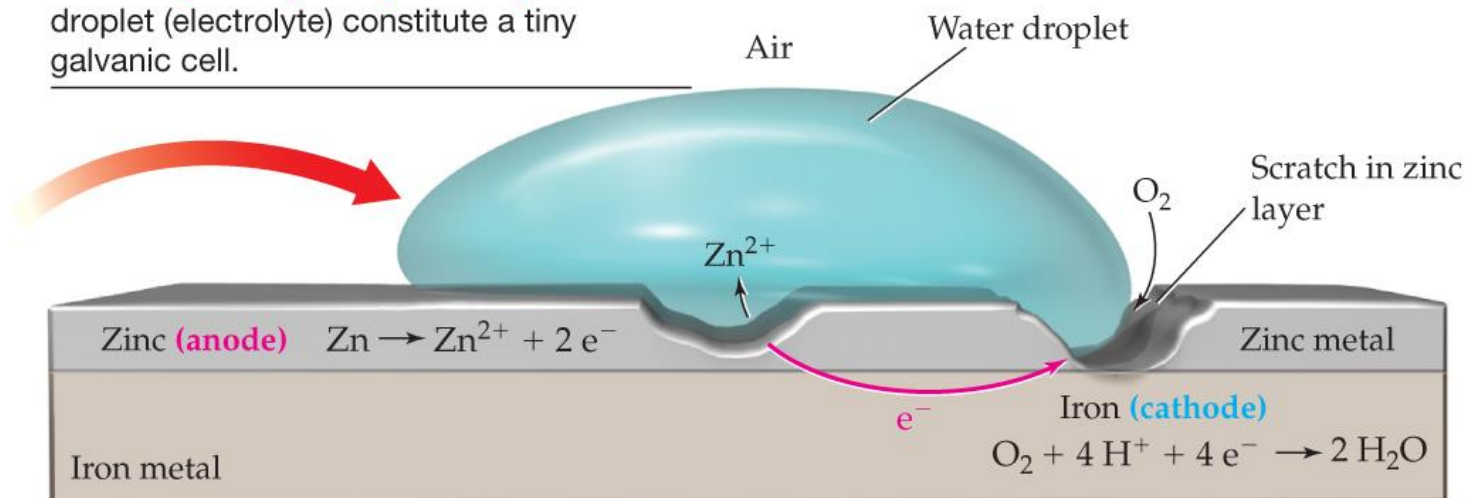
For some metals, oxidation protects the metal (aluminum, chromium, magnesium, titanium, zinc, and others). For other metals, there are two main techniques.

# Corrosion

## Prevention of Corrosion

### 1. Galvanization: The coating of iron with zinc

The zinc (**anode**), iron (**cathode**), and water droplet (electrolyte) constitute a tiny galvanic cell.



Oxygen is reduced at the cathode, and zinc is oxidized at the anode, thus protecting the iron from oxidation.

# Corrosion

## Prevention of Corrosion

### 1. Galvanization: The coating of iron with zinc

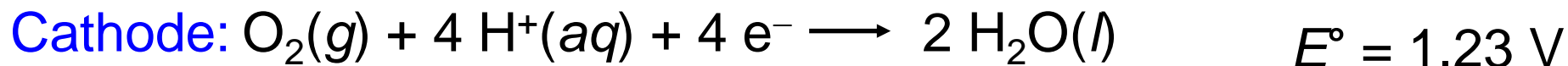
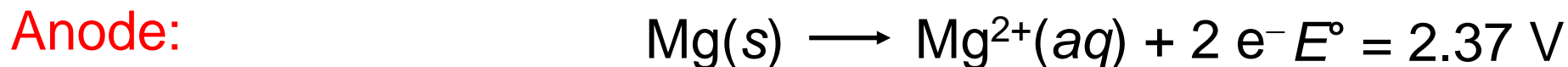
When some of the iron is oxidized (rust), the process is reversed since zinc will reduce  $\text{Fe}^{2+}$  to Fe:



# Corrosion

## Prevention of Corrosion

2. **Cathodic Protection:** Instead of coating the entire surface of the first metal with a second metal, the second metal is placed in electrical contact with the first metal:



Attaching a magnesium stake to iron will corrode the magnesium instead of the iron. Magnesium acts as a *sacrificial anode*.



# Electrolysis and Electrolytic Cells

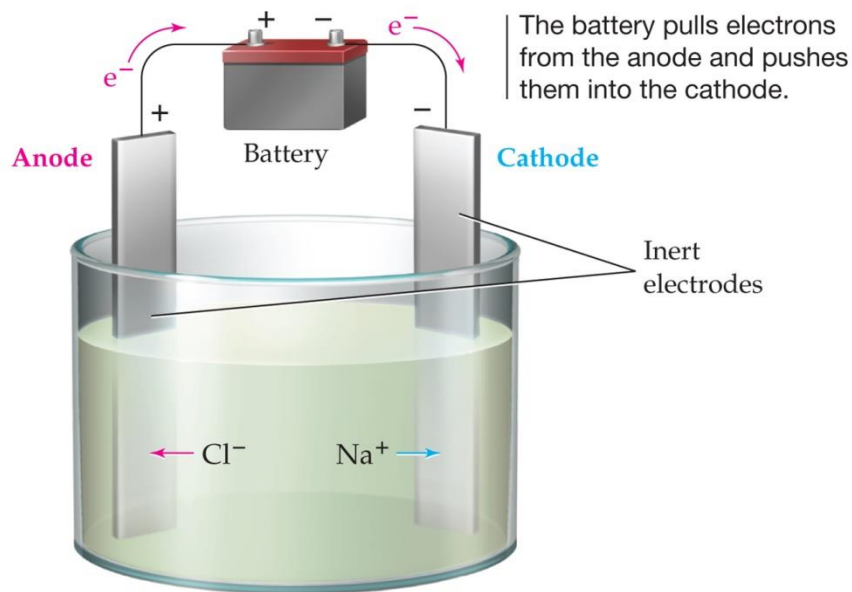
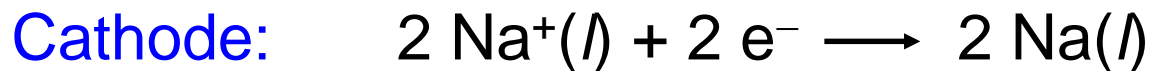
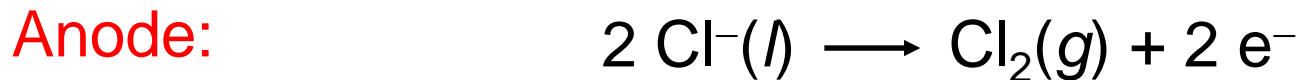
**Electrolysis:** The process of using an electric current to bring about chemical change

**TABLE 18.2** Relationship between Cell Potentials  $E$  and Free-Energy Changes  $\Delta G$

Reaction Type	$E$	$\Delta G$	Cell Type
Spontaneous	+	−	Galvanic (battery)
Nonspontaneous	−	+	Electrolytic
Equilibrium	0	0	Dead battery

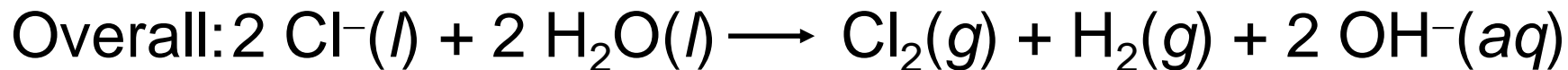
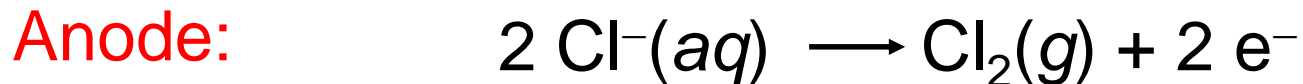
# Electrolysis and Electrolytic Cells

## Electrolysis of Molten Sodium Chloride



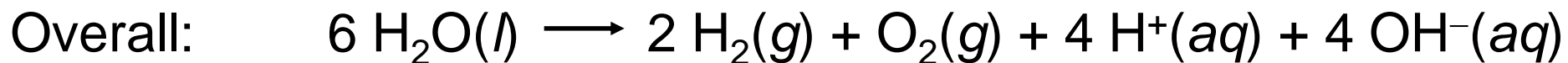
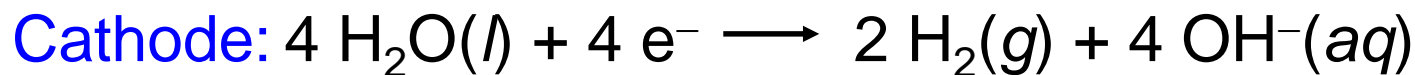
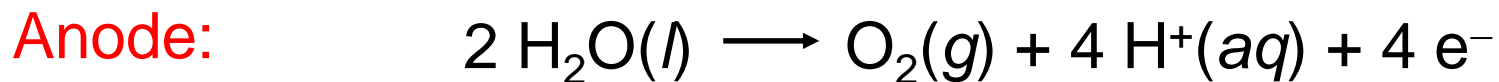
# Electrolysis and Electrolytic Cells

## Electrolysis of Aqueous Sodium Chloride



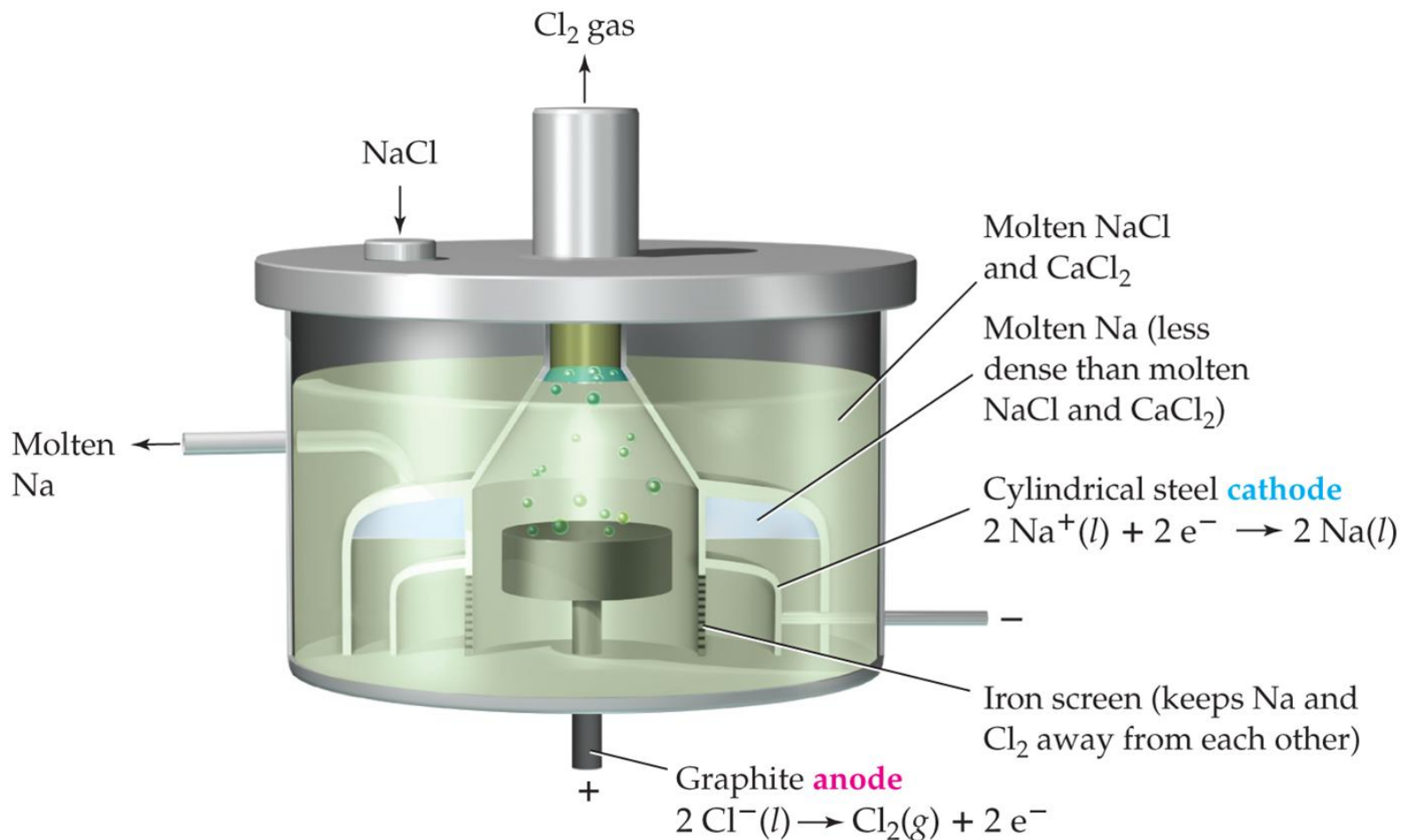
# Electrolysis and Electrolytic Cells

## Electrolysis of Water



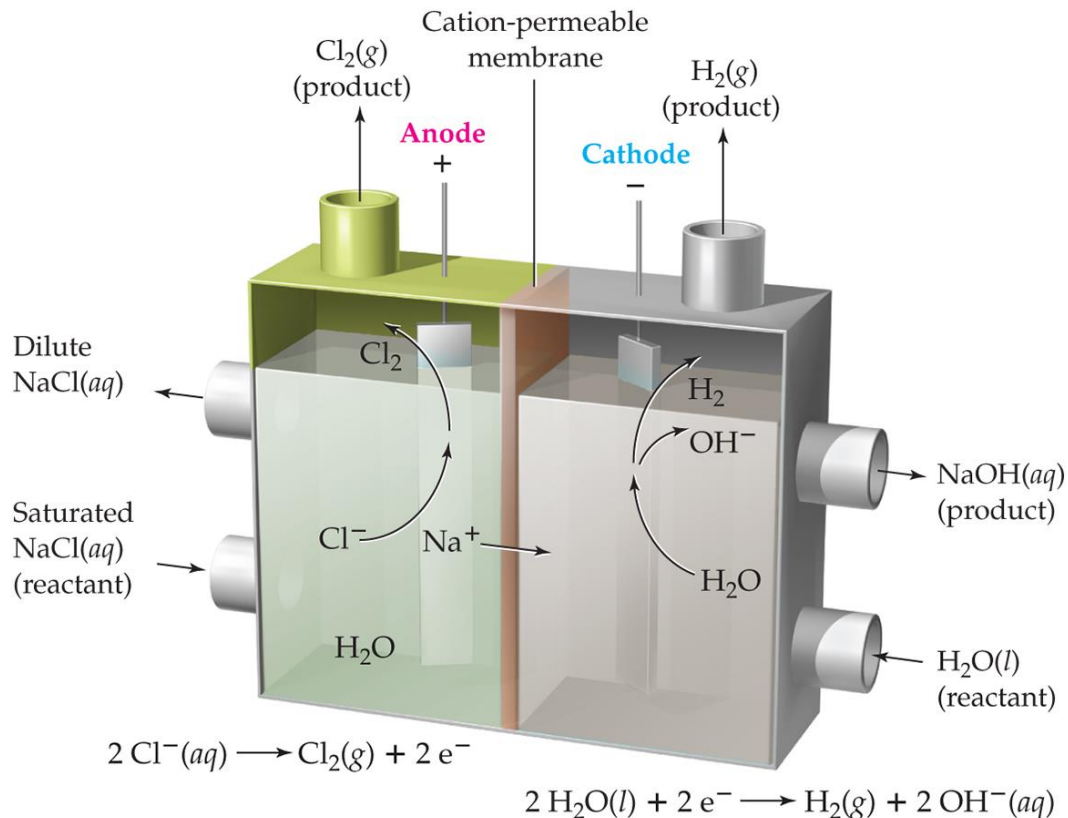
# Commercial Applications of Electrolysis

## Down's Cell for the Production of Sodium Metal



# Commercial Applications of Electrolysis

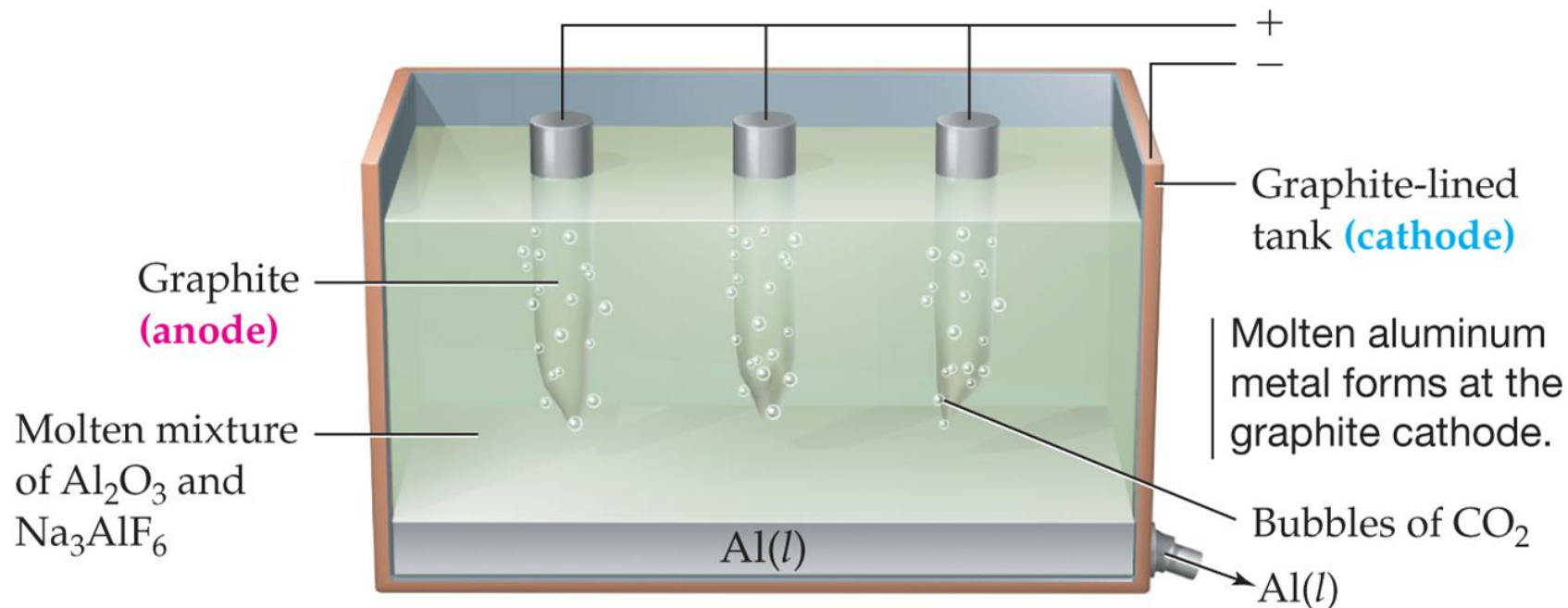
## A Membrane Cell for Electrolytic Production of $\text{Cl}_2$ and $\text{NaOH}$



Sodium ions move from the anode compartment to the cathode compartment through a cation-permeable membrane and then flow out of the cell as an aqueous solution of  $\text{NaOH}$ .

# Commercial Applications of Electrolysis

## Hall–Heroult Process for the Production of Aluminum



Because molten aluminum is denser than the  $\text{Al}_2\text{O}_3$ – $\text{Na}_3\text{AlF}_6$  mixture, it collects at the bottom of the cell and is drawn off periodically.

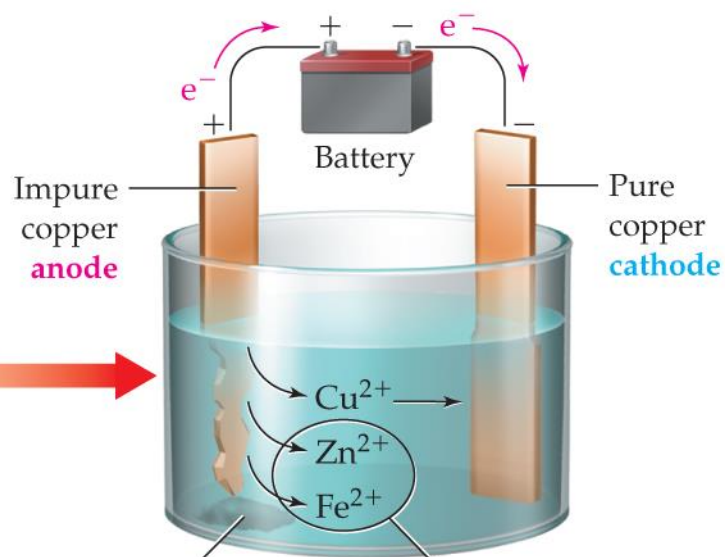
# Commercial Applications of Electrolysis

## Electrorefining of Copper Metal



Alternating slabs of impure copper and pure copper serve as the electrodes in electrolytic cells for the refining of copper.

Copper is transferred through the  $\text{CuSO}_4$  solution from the impure Cu anode to the pure Cu cathode.



Noble metal impurities (Ag, Au, Pt) are not oxidized and collect as anode mud.

More easily oxidized impurities (Zn, Fe) remain in solution as cations.



# Quantitative Aspects of Electrolysis

## GIVEN

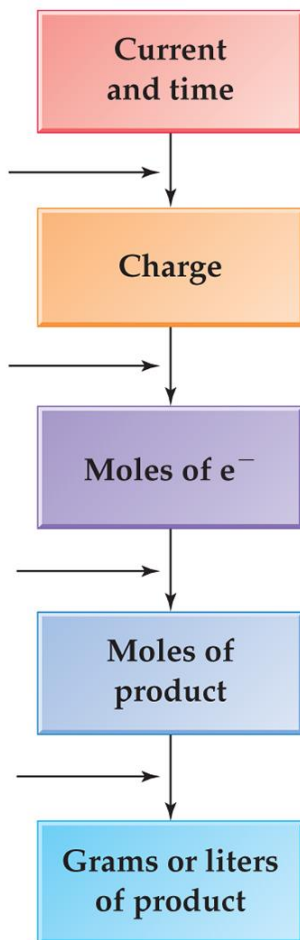
Find the product of current and time.

Use the faraday as a conversion factor.

Use coefficients in the balanced equation to find mole ratios.

Use molar mass or standard molar volume as a conversion factor.

## FIND



$$\text{Charge(C)} = \text{Current(A)} \times \text{Time(s)}$$

$$\text{Moles of e}^- = \text{Charge(C)} \times \frac{1 \text{ mol e}^-}{96,500 \text{ C}}$$

**Faraday constant**