

Chapter 18: Electrochemistry

In an oxidation-reduction (redox) reaction,
_____ are transferred.



Oxidation: _____ of electrons

Reduction: _____ of electrons

Oxidizing agent:

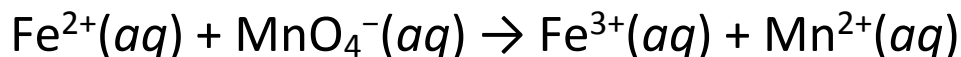
Reducing agent:

Oxidation numbers:

- Elements: # = 0
- Ions: # = charge
- O: usually -2
- H: usually +1
- Halogens: usually -1

Balancing redox reactions

Balance this net ionic equation (spectator ions omitted)



1. Divide net ionic equation into 2 half-reactions

2. Balance each half-reaction

- Elements (not O or H)
- O (add H₂O)
- H (add H⁺)
- Charge (add e⁻)

3. Multiply half-reactions by integers so # e⁻ is equal

4. Add two half-reactions and cancel electrons fully.

Balancing in basic solution

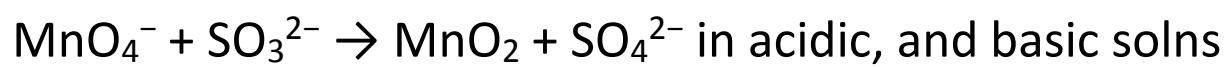
5. If you're told the reaction is in basic solution:

a. Add OH^- to both sides to cancel H^+

b. Combine $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$

c. Cancel excess H_2O

Practice balancing



Voltaic cells

Electrochemical cells involve the use of electrical energy in the transfer of electrons between substances

1. **Voltaic cells** (galvanic cells) contain a **spontaneous** reaction that produces electrical energy (like a battery)
2. **Electrolytic cells** use electrical energy to drive a **nonspontaneous** reaction

Most cells have two **electrodes** (conductive metal strips) in an **electrolyte** solution (soluble ionic compound)

One **half-reaction** takes place at each electrode:

1. **Anode**: electrode where oxidation occurs (electrons are **lost** from the cell at the anode)
2. **Cathode**: electrode where reduction occurs (electrons **enter** the cell at the cathode)

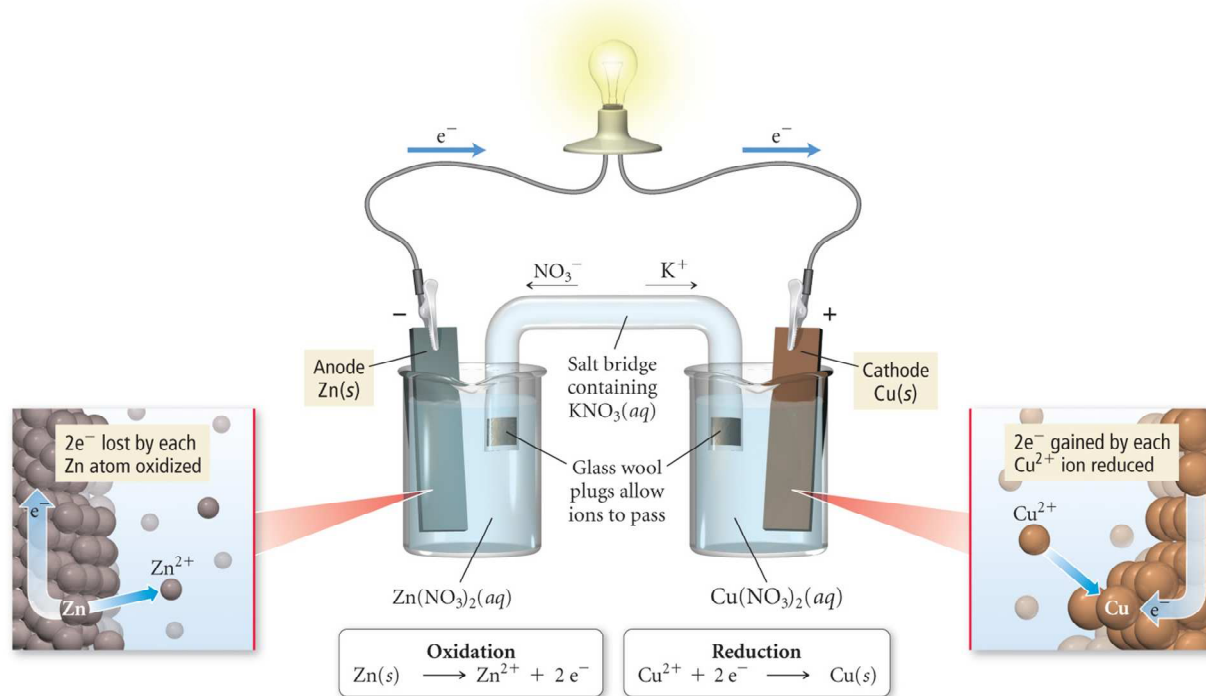


Oxidation half-reaction:

Reduction half-reaction:

Voltaic cells

A Voltaic Cell



The **anode** is the electrode of the oxidation half-rxn

The **cathode** is the electrode of the reduction half-rxn

Salt bridge: completes circuit by keeping charges constant in each container

Active electrode: metal is part of redox reaction

Inactive electrode: metal conducts electricity but does not participate in redox reaction (graphite or Pt)

Cell notation: shows two half reactions with phases separated by | and half reactions separated by ||

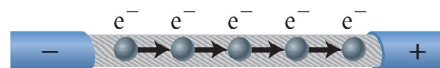
Reduction potentials

Electrical current: rate of electron flow (amperes, A)
related to stoichiometry of redox reactions - not covered
in this course

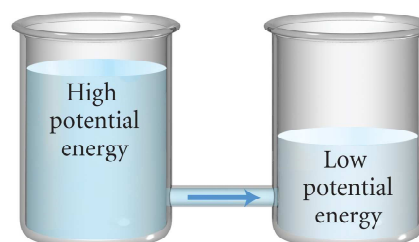
Electrical potential difference:

the driving force for flow of
electrons (volts, V)

- $1 \text{ V} = 1 \text{ J/C}$ (coulomb: unit of electrical charge)
- An energetic term, directly related to spontaneity and free energy
- **Cell potential** (E_{cell}): potential (in V) between two electrodes
- $E_{\text{cell}} > 0$ for a spontaneous process



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Direction of
spontaneous
flow





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Standard reduction potential (E°) potential for a
reduction, relative to the standard hydrogen electrode
 $2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g}) \quad E^\circ_{\text{red}} = 0.00 \text{ V}$ (by definition)

Reductions more spontaneous than this are **positive**,
reductions less spontaneous than this are **negative**.

Standard reduction potentials

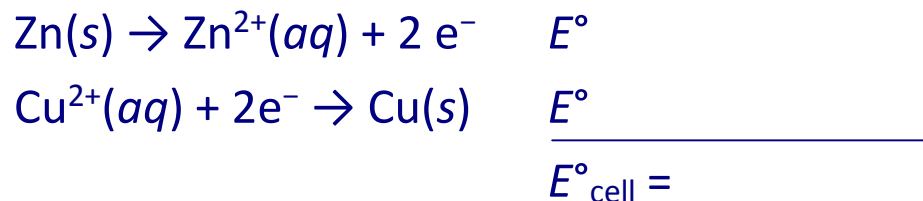
TABLE 18.1 Standard Reduction Potentials at 25 °C

	Reduction Half-Reaction	E° (V)		
Stronger oxidizing agent 	$F_2(g) + 2 e^-$	$\longrightarrow 2 F^-(aq)$	2.87	Weaker reducing agent 
	$H_2O_2(aq) + 2 H^+(aq) + 2 e^-$	$\longrightarrow 2 H_2O(l)$	1.78	
	$PbO_2(s) + 4 H^+(aq) + SO_4^{2-}(aq) + 2 e^-$	$\longrightarrow PbSO_4(s) + 2 H_2O(l)$	1.69	
	$MnO_4^-(aq) + 4 H^+(aq) + 3 e^-$	$\longrightarrow MnO_2(s) + 2 H_2O(l)$	1.68	
	$MnO_4^-(aq) + 8 H^+(aq) + 5 e^-$	$\longrightarrow Mn^{2+}(aq) + 4 H_2O(l)$	1.51	
	$Au^{3+}(aq) + 3 e^-$	$\longrightarrow Au(s)$	1.50	
	$PbO_2(s) + 4 H^+(aq) + 2 e^-$	$\longrightarrow Pb^{2+}(aq) + 2 H_2O(l)$	1.46	
	$Cl_2(g) + 2 e^-$	$\longrightarrow 2 Cl^-(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e^-$	$\longrightarrow 2 Cr^{3+}(aq) + 7 H_2O(l)$	1.33	
	$O_2(g) + 4 H^+(aq) + 4 e^-$	$\longrightarrow 2 H_2O(l)$	1.23	
	$MnO_2(s) + 4 H^+(aq) + 2 e^-$	$\longrightarrow Mn^{2+}(aq) + 2 H_2O(l)$	1.21	
	$IO_3^-(aq) + 6 H^+(aq) + 5 e^-$	$\longrightarrow \frac{1}{2} I_2(aq) + 3 H_2O(l)$	1.20	
	$Br_2(l) + 2 e^-$	$\longrightarrow 2 Br^-(aq)$	1.09	
	$VO_2^+(aq) + 2 H^+(aq) + e^-$	$\longrightarrow VO^{2+}(aq) + H_2O(l)$	1.00	
	$NO_3^-(aq) + 4 H^+(aq) + 3 e^-$	$\longrightarrow NO(s) + 2 H_2O(l)$	0.96	
	$ClO_2(g) + e^-$	$\longrightarrow ClO_2^-(aq)$	0.95	
	$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	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	
	$MnO_4^-(aq) + e^-$	$\longrightarrow MnO_4^{2-}(aq)$	0.56	
$I_2(s) + 2 e^-$	$\longrightarrow 2 I^-(aq)$	0.54		
$Cu^+(aq) + e^-$	$\longrightarrow Cu(s)$	0.52		
$O_2(g) + 2 H_2O(l) + 4 e^-$	$\longrightarrow 4 OH^-(aq)$	0.40		
$Cu^{2+}(aq) + 2 e^-$	$\longrightarrow Cu(s)$	0.34		
$SO_4^{2-}(aq) + 4 H^+(aq) + 2 e^-$	$\longrightarrow H_2SO_3(aq) + H_2O(l)$	0.20		
$Cu^{2+}(aq) + e^-$	$\longrightarrow Cu^+(aq)$	0.16		
$Sn^{4+}(aq) + 2 e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15		
<hr/>				
	$2 H^+(aq) + 2 e^-$	$\longrightarrow H_2(g)$	0	
	$Fe^{3+}(aq) + 3 e^-$	$\longrightarrow Fe(s)$	-0.036	
	$Pb^{2+}(aq) + 2 e^-$	$\longrightarrow Pb(s)$	-0.13	
	$Sn^{2+}(aq) + 2 e^-$	$\longrightarrow Sn(s)$	-0.14	
	$Ni^{2+}(aq) + 2 e^-$	$\longrightarrow Ni(s)$	-0.23	
	$Cd^{2+}(aq) + 2 e^-$	$\longrightarrow Cd(s)$	-0.40	
	$Fe^{2+}(aq) + 2 e^-$	$\longrightarrow Fe(s)$	-0.45	
	$Cr^{3+}(aq) + e^-$	$\longrightarrow Cr^{2+}(aq)$	-0.50	
	$Cr^{3+}(aq) + 3 e^-$	$\longrightarrow Cr(s)$	-0.73	
	$Zn^{2+}(aq) + 2 e^-$	$\longrightarrow Zn(s)$	-0.76	
	$2 H_2O(l) + 2 e^-$	$\longrightarrow H_2(g) + 2 OH^-(aq)$	-0.83	
	$Mn^{2+}(aq) + 2 e^-$	$\longrightarrow Mn(s)$	-1.18	
	$Al^{3+}(aq) + 3 e^-$	$\longrightarrow Al(s)$	-1.66	
	$Mg^{2+}(aq) + 2 e^-$	$\longrightarrow Mg(s)$	-2.37	
	$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	-2.71	
	$Ca^{2+}(aq) + 2 e^-$	$\longrightarrow Ca(s)$	-2.76	
	$Ba^{2+}(aq) + 2 e^-$	$\longrightarrow Ba(s)$	-2.90	
	$K^+(aq) + e^-$	$\longrightarrow K(s)$	-2.92	
Weaker oxidizing agent 	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	-3.04	Stronger reducing agent 

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Calculating standard cell potentials

For the zinc-copper cell,



From the table of **reduction** potentials:

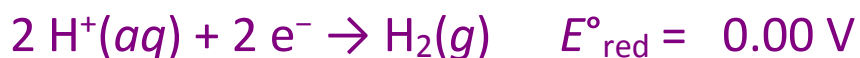


Simply add the oxidation potential and the reduction potential. Don't forget to switch the sign of the oxidation.

Since cell potentials are **intensive** properties, you only need to add the values - they **do not** depend on number of electrons or any coefficients.

Write the balanced equation and calculate the standard cell potential (E°_{cell}) for $\text{Cr}(s) \mid \text{Cr}^{3+}(aq) \parallel \text{Cl}_2(g) \mid \text{Cl}^{-}(aq)$.

Predicting the direction of spontaneous change



Which of the reactions above has the strongest tendency to occur in the forward direction as written?

That is the most favorable _____ reaction.

So, _____ is the strongest _____ agent.

The reaction with the **weakest** tendency to occur as written is the **most favorable** _____ reaction.

So, _____ is the strongest _____ agent.

What is the spontaneous reaction that will occur when a cell is constructed from $\text{Cd}(\text{s})$, $\text{Cd}^{2+}(\text{aq})$, $\text{Pb}(\text{s})$, and $\text{Pb}^{2+}(\text{aq})$

Cell potential, free energy, and the equilibrium constant

A spontaneous redox reaction has:

E_{cell}

ΔG_{rxn}

K

$$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$$

n = moles of electrons transferred in balanced eqn

$F = 96,485 \text{ C / mol e}^{-}$

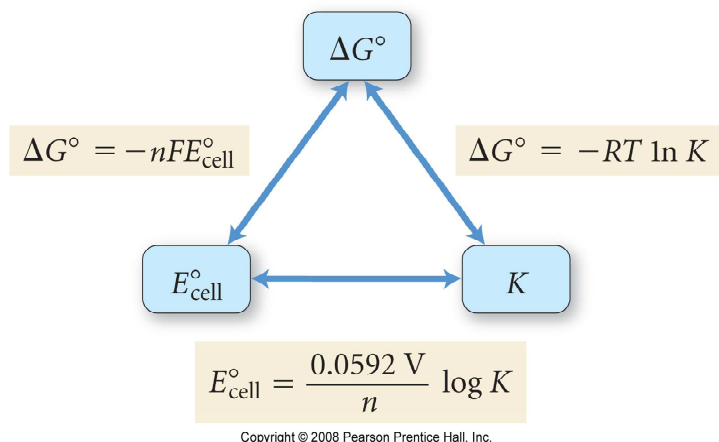
Calculate ΔG° (in kJ) for $2 \text{ Ag}^{+} + \text{Mg} \rightarrow \text{Mg}^{2+} + 2 \text{ Ag}$.

Is the reaction spontaneous? What 2 ways can you tell?

Cell potential, free energy, and equilibrium constant

$$\Delta G^\circ = -nFE^\circ_{\text{cell}} = -RT \ln K$$

$$E^\circ_{\text{cell}} = \frac{RT}{nF} \ln K = \frac{0.0592 \text{ V}}{n} \log K$$



If $E^\circ_{\text{cell}} = 3.18 \text{ V}$ and $n = 2 \text{ mol e}^-$, what is K under standard conditions?

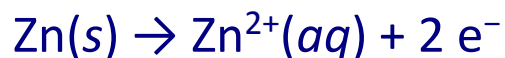
Nonstandard states in voltaic cells

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

Nernst equation: $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592 \text{ V}}{n} \log Q$

The standard zinc-copper cell has a potential of 1.10 V.

Standard conditions are:

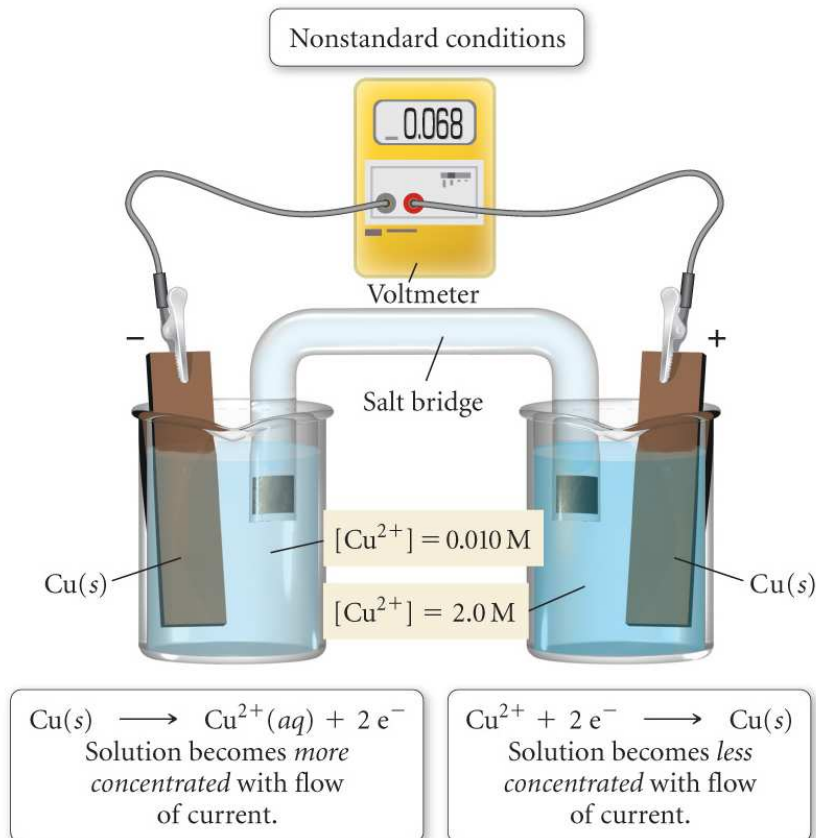
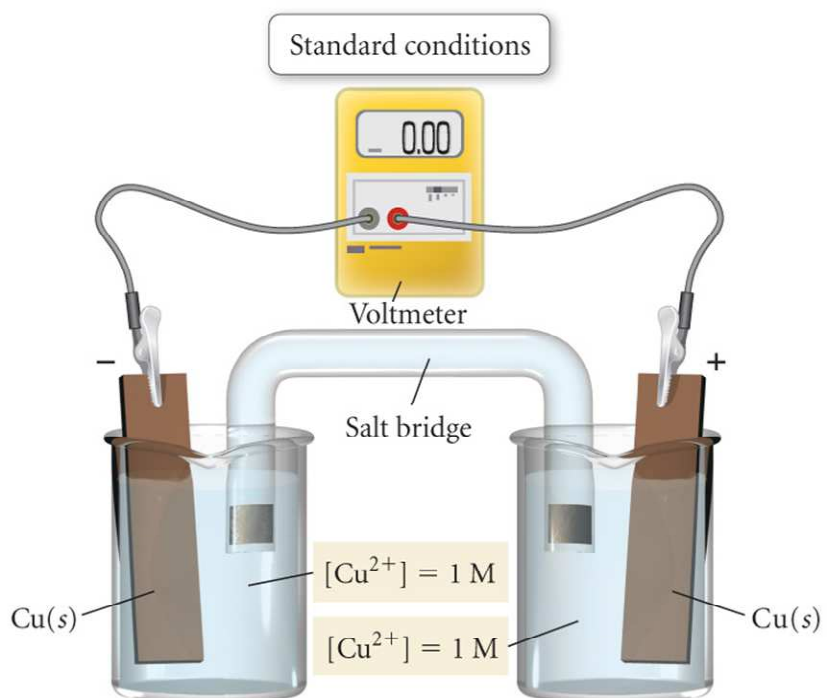


How will the cell potential change if we double the concentration of $\text{Zn}^{2+}(aq)$?

What if we double the concentration of $\text{Cu}^{2+}(aq)$?

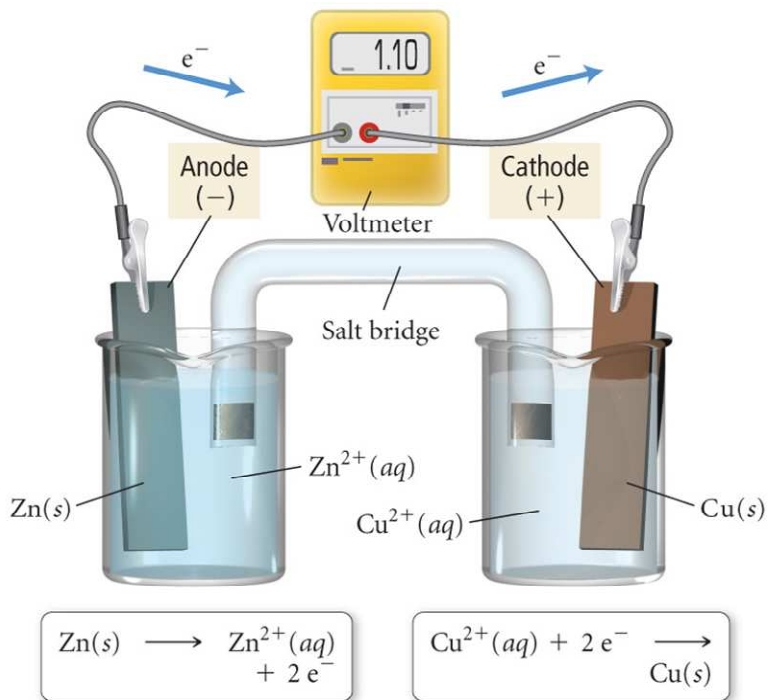
Concentration cells

A voltaic cell can be driven a difference in concentration between two otherwise identical half-cells.

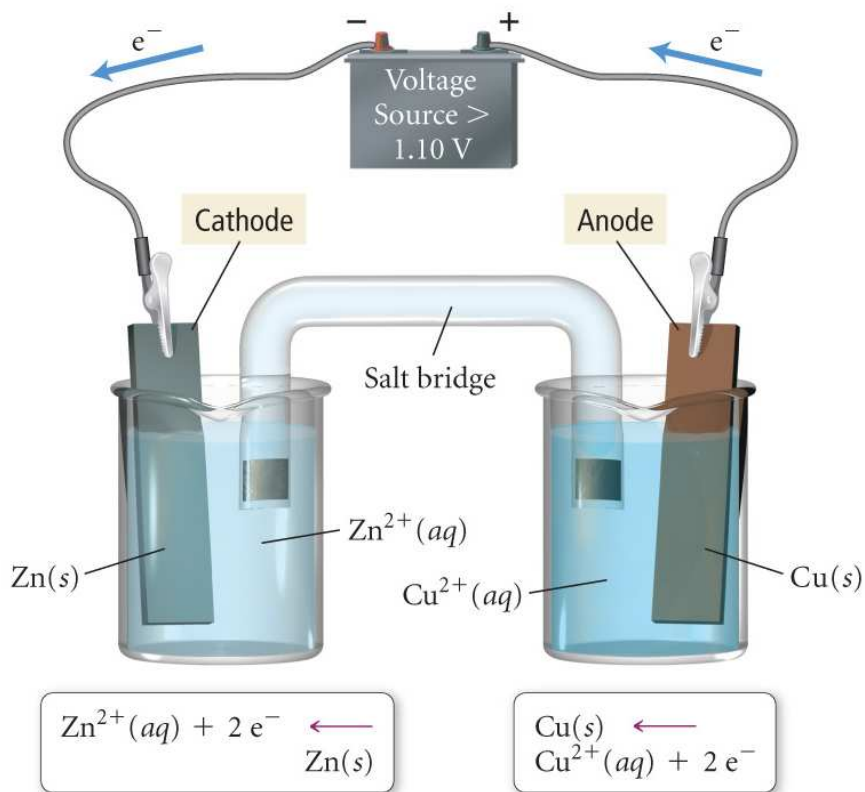


Voltaic vs electrolytic cells

Voltaic Cell



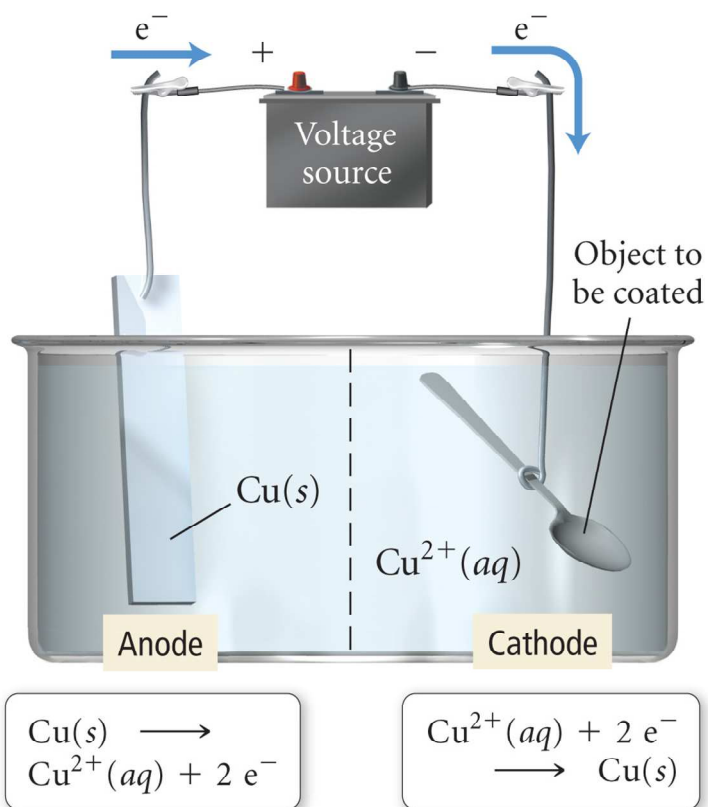
Electrolytic Cell



Electrolysis and electroplating



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