

N45 - Electrochemistry

Variables Unite!

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Target: I can connect Thermodynamics, Equilibrium, and Electrochemistry. The big finale of the year!



$$\Delta G^\circ$$

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

$$\Delta G^\circ = -RT \ln K$$

$$E_{\text{cell}}^\circ$$

$$K$$

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

E°_{cell} , ΔG° , and K

For a spontaneous reaction

One that proceeds in the forward direction with the chemicals in their standard states

$$\Delta G^\circ < 0 \text{ (negative)}$$

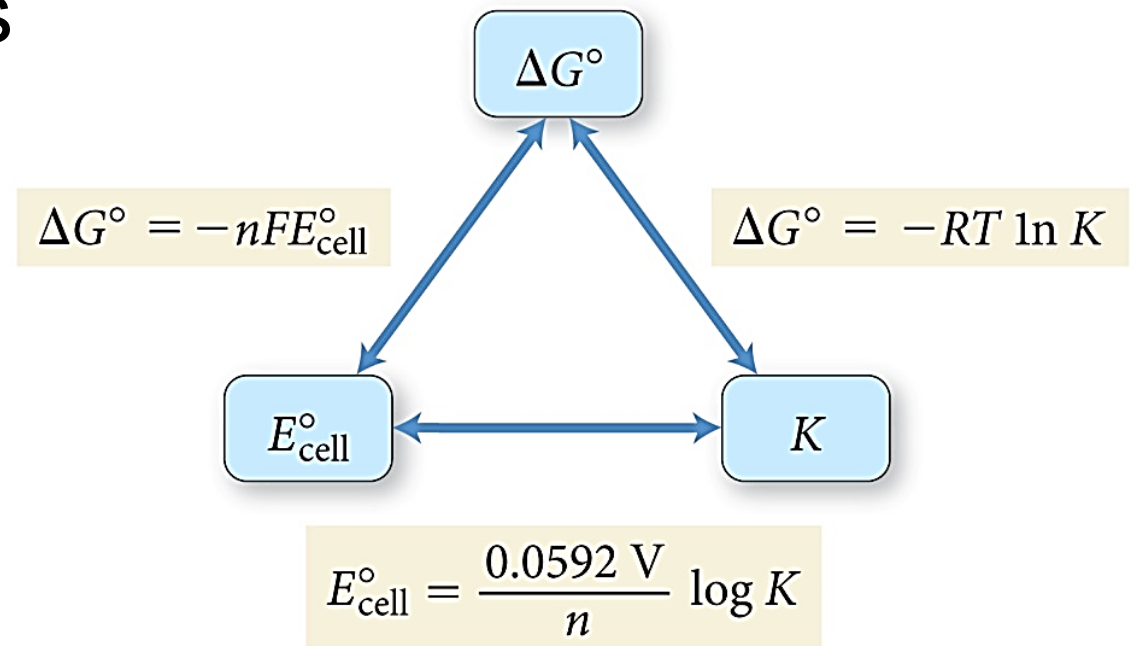
$$E^\circ > 0 \text{ (positive)}$$

$$K > 1$$

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

n = the number of electrons

F = Faraday's constant = 96,485 C/mol e^-
(often see it as 96,500 C/mol e^-)



Calculating ΔG^0 for a Cell

$$\Delta G^0 = -nFE^0$$

n = moles of electrons in balanced redox equation

F = Faraday constant = 96,485 coulombs/mol e^-



$$\Delta G^0 = -(2 \text{ mol } e^-) \left(96485 \frac{\text{coulombs}}{\text{mol } e^-} \right) \left(1.10 \frac{\text{Joules}}{\text{Coulomb}} \right)$$

$$\Delta G^0 = -212267 \text{ Joules} = -212 \text{ kJ}$$

The Nernst Equation

Standard potentials assume a concentration of 1 M. The Nernst equation allows us to calculate potential when the two cells are **not** 1.0 M.

$$E = E^0 - \frac{RT}{nF} \ln(Q)$$

R = 8.31 J/(mol·K)

T = Temperature in K

n = moles of electrons in balanced redox equation

F = Faraday constant = 96,485 coulombs/mol e⁻

Deriving the Nernst Equation

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

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$$-nF E_{\text{cell}} = -nF E_{\text{cell}}^\circ + RT \ln Q$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln Q$$

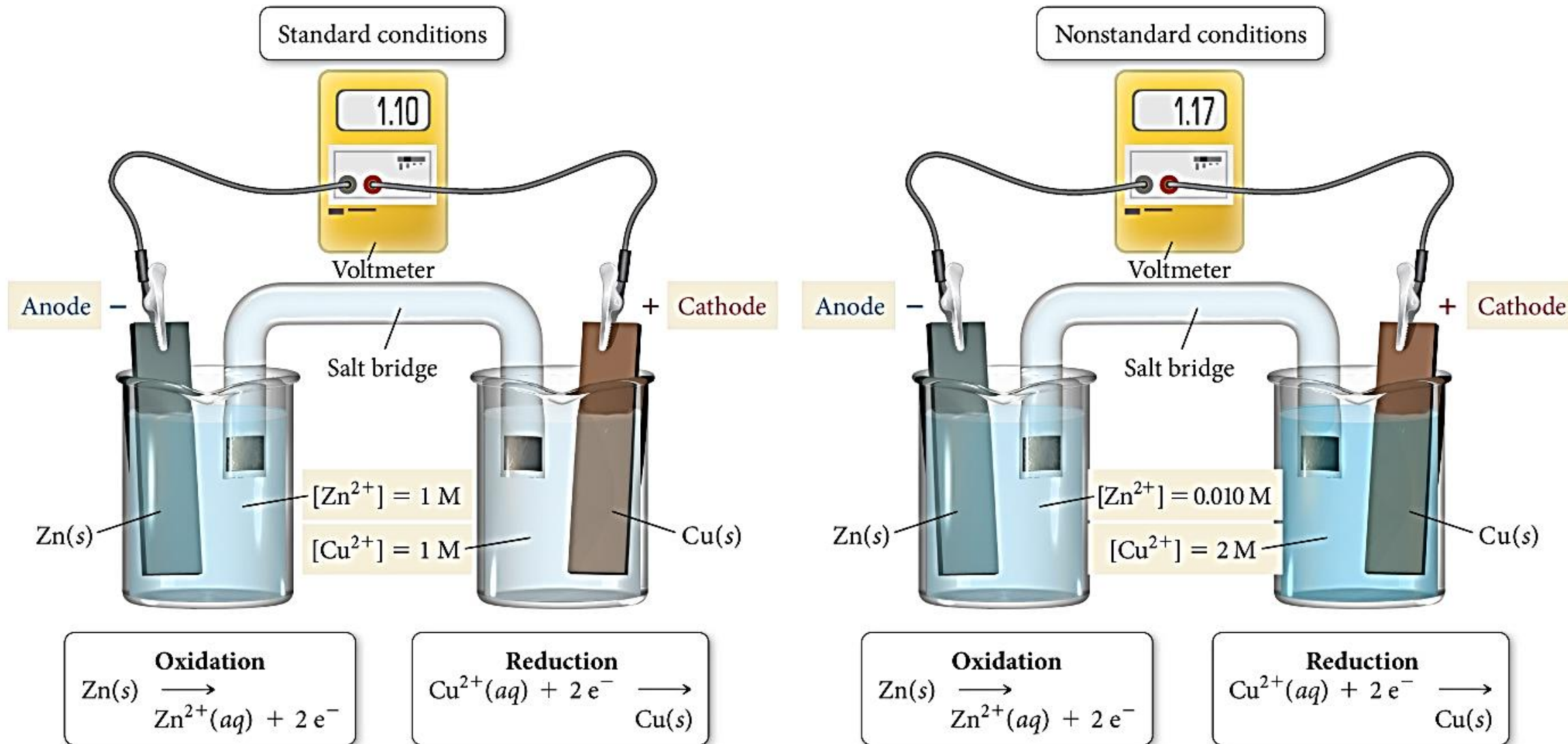
Nernst Equation Simplified

At 25 °C (298 K) the Nernst Equation is simplified this way:

$$E = E^0 - \frac{0.0592}{n} \log(Q)$$

Sometimes you may see 0.0591 on a key or online. It should be 0.0592

E_{cell} When Ion Concentrations Are Not 1 M



Equilibrium Constants and Cell Potential

At equilibrium, forward and reverse reactions occur at equal rates, therefore:

1. The battery is “dead” 😞
2. The cell potential, E , is zero volts

Modifying the Nernst Equation (at 25 °C):

$$0 \text{ volts} = E^\circ - \frac{0.0592}{n} \log(\mathbf{K})$$

Calculating an Equilibrium Constant from a Cell Potential



$$0 \text{ volts} = 1.10 - \frac{0.0592}{2} \log(K)$$

$$\frac{(1.10)(2)}{0.0592} = \log(K)$$

$$37.2 = \log(K)$$

$$10^{37.2} = K = 1.58 \times 10^{37}$$

Standard Conditions and Nonstandard Conditions for the Zn/Cu Galvanic Cell



Equation	E°	ΔG°	K
$\text{Zn}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s)$	+1.10 V	-212 kJ/mol	1.5×10^{37}

$$E = E^\circ - \frac{RT}{nF} \ln Q \quad Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

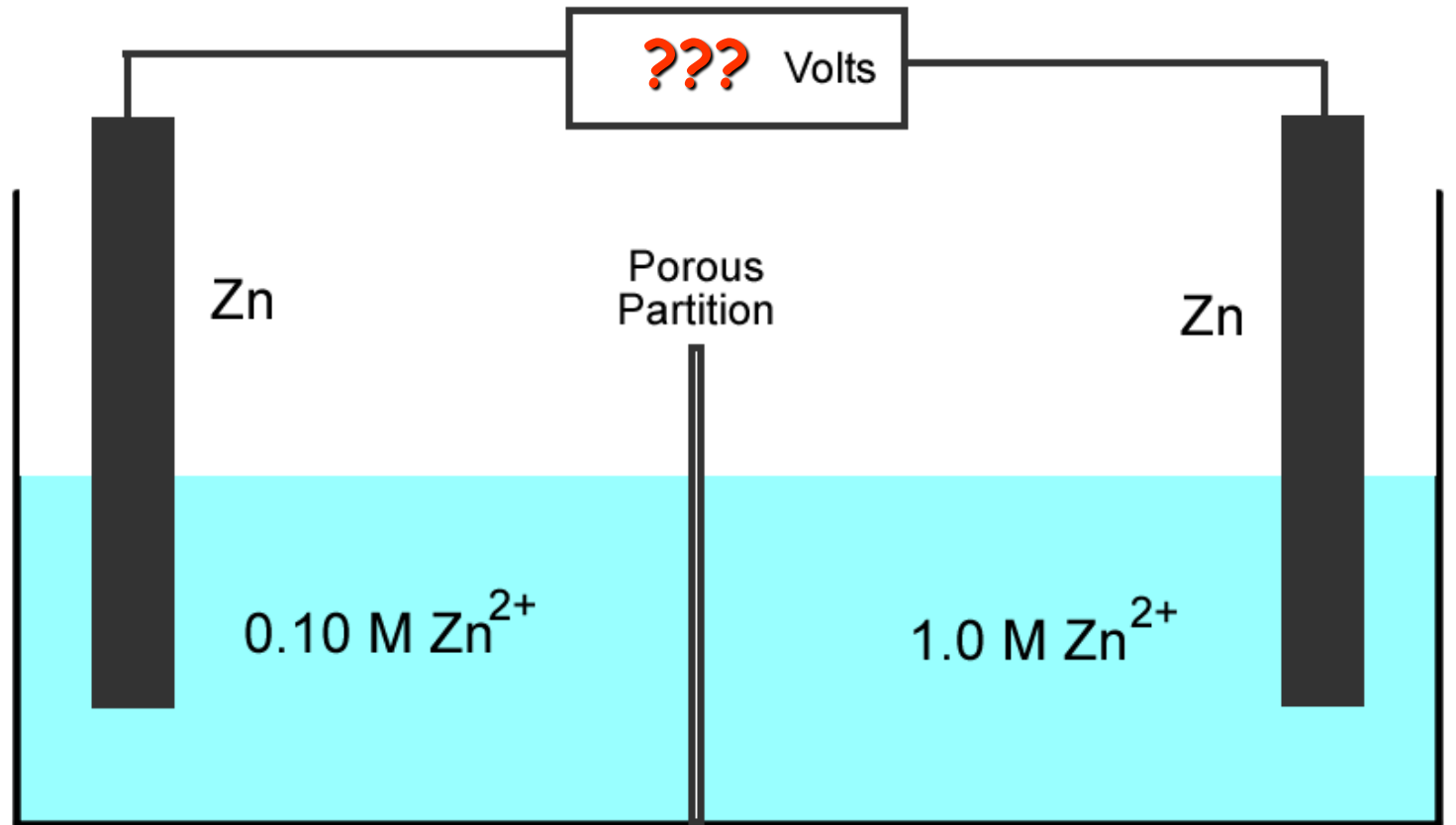
Farther Away From Equilibrium than Standard Conditions	Standard Conditions	Closer To Equilibrium than Standard Conditions	At Equilibrium The cell is "dead"
$Q < 1$	$Q = 1$	$Q > 1$	$Q = K = 1.5 \times 10^{37}$
$E > E^\circ$	$E = E^\circ$	$E < E^\circ$	$E = \text{zero}$
$[\text{Zn}^{2+}] < [\text{Cu}^{2+}]$	$[\text{Zn}^{2+}] = [\text{Cu}^{2+}]$	$[\text{Zn}^{2+}] > [\text{Cu}^{2+}]$	$[\text{Zn}^{2+}] \gg [\text{Cu}^{2+}]$
decreased [product] or increased [reactant] compared to standard conditions	[product] = [reactant]	increased [product] or decreased [reactant] compared to standard conditions	

Concentration Cell

Both sides of the cell have the same components but at different concentrations.

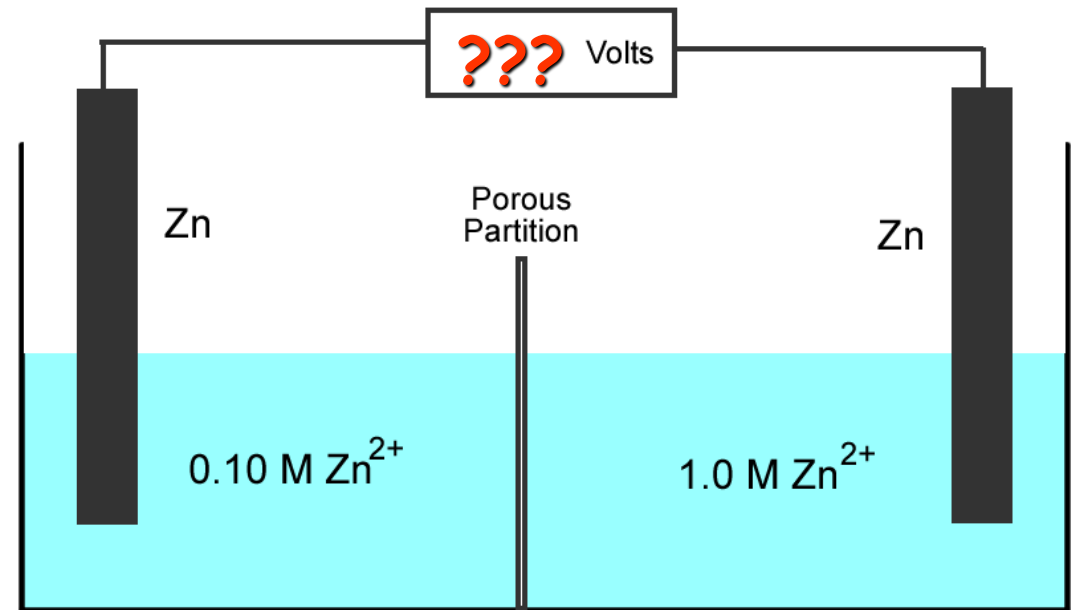
Step 1:

Determine which side undergoes oxidation, and which side undergoes reduction.



Concentration Cell

The **1.0 M Zn²⁺** must **decrease** in concentration, and the **0.10 M Zn²⁺** must **increase** in concentration



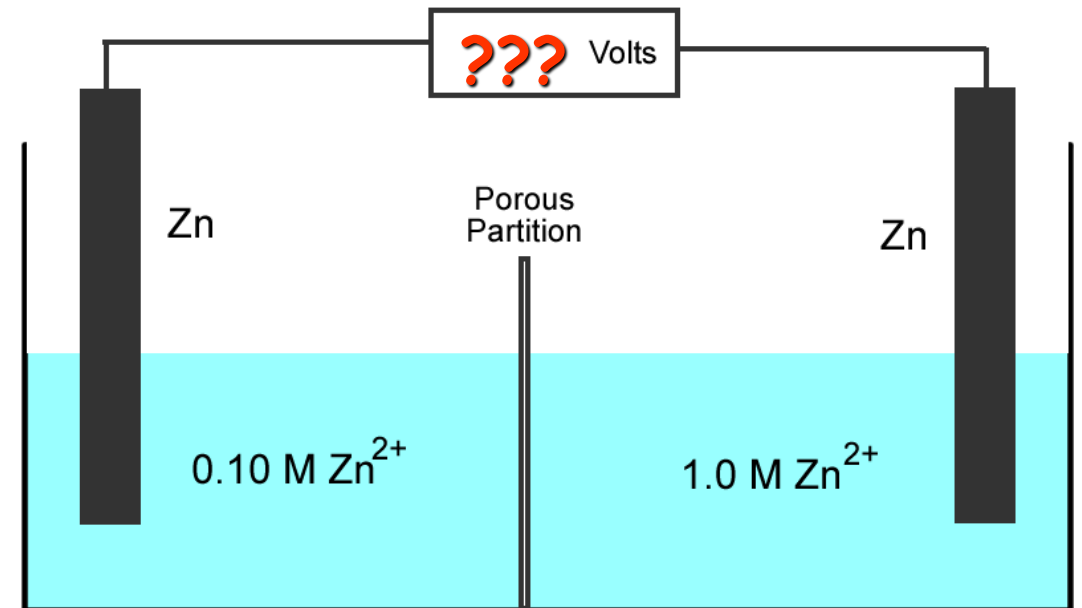
Concentration Cell

Step 2:

Calculate cell potential using the Nernst Equation (assuming 25 °C).



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



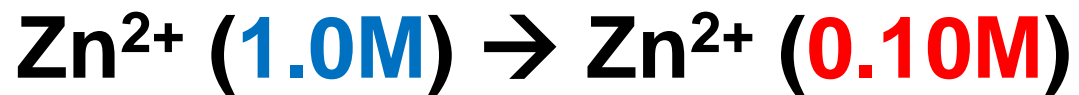
Concentration Cell

$$E^\circ = 0$$

$$Q = \frac{[\text{product}]}{[\text{reactant}]} = \frac{[\text{low}]}{[\text{high}]}$$

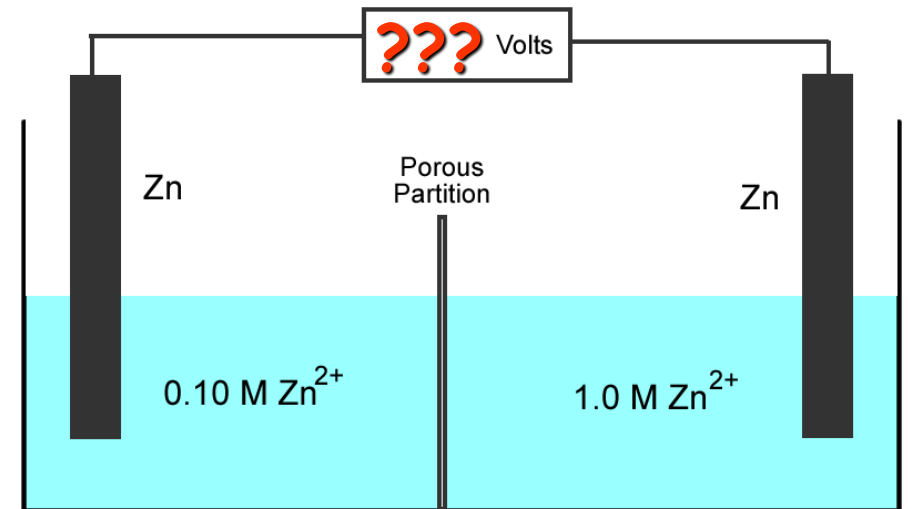
Step 2:

Calculate cell potential using the Nernst Equation (assuming 25 °C).



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

$$E = 0 - \frac{0.0592}{2} \log\left(\frac{0.10}{1.0}\right) = 0.030 \text{ volts}$$



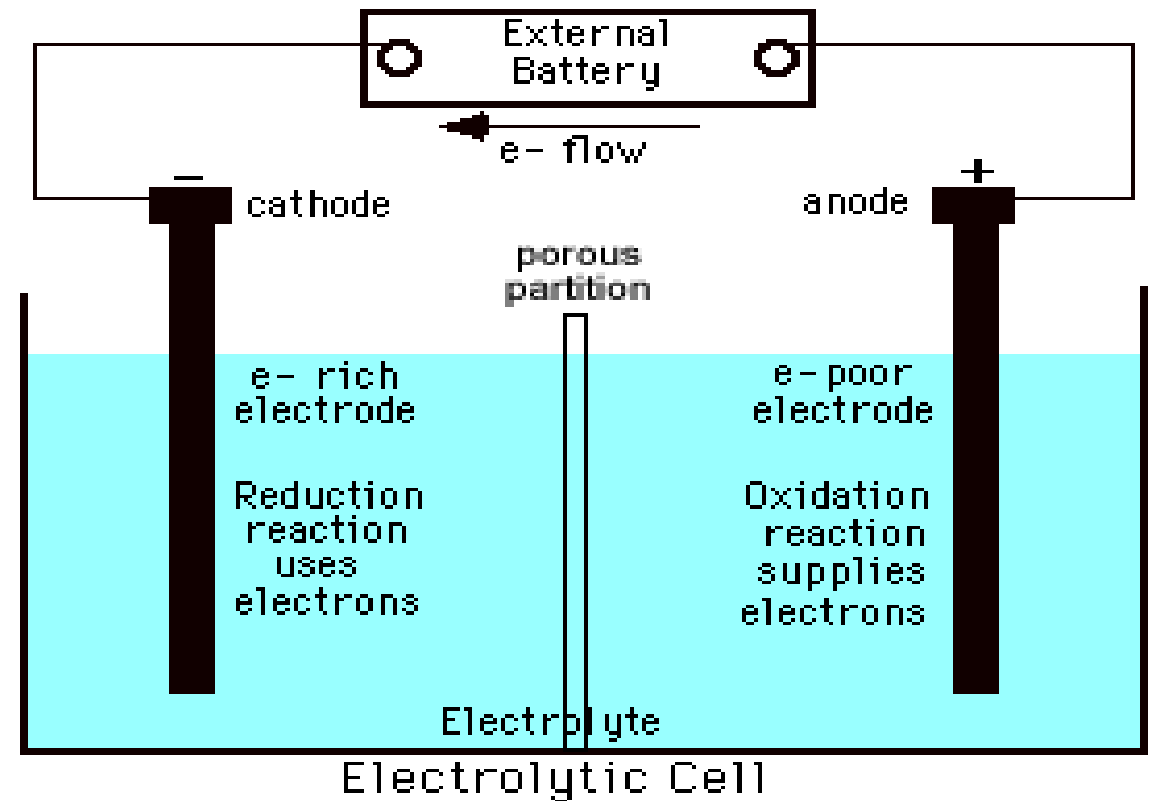
Reminder...Electrolytic Processes

Electrolytic processes are NOT spontaneous.

They have:

A negative cell potential, ($-E^\circ$)

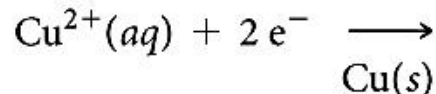
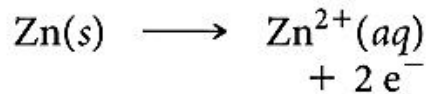
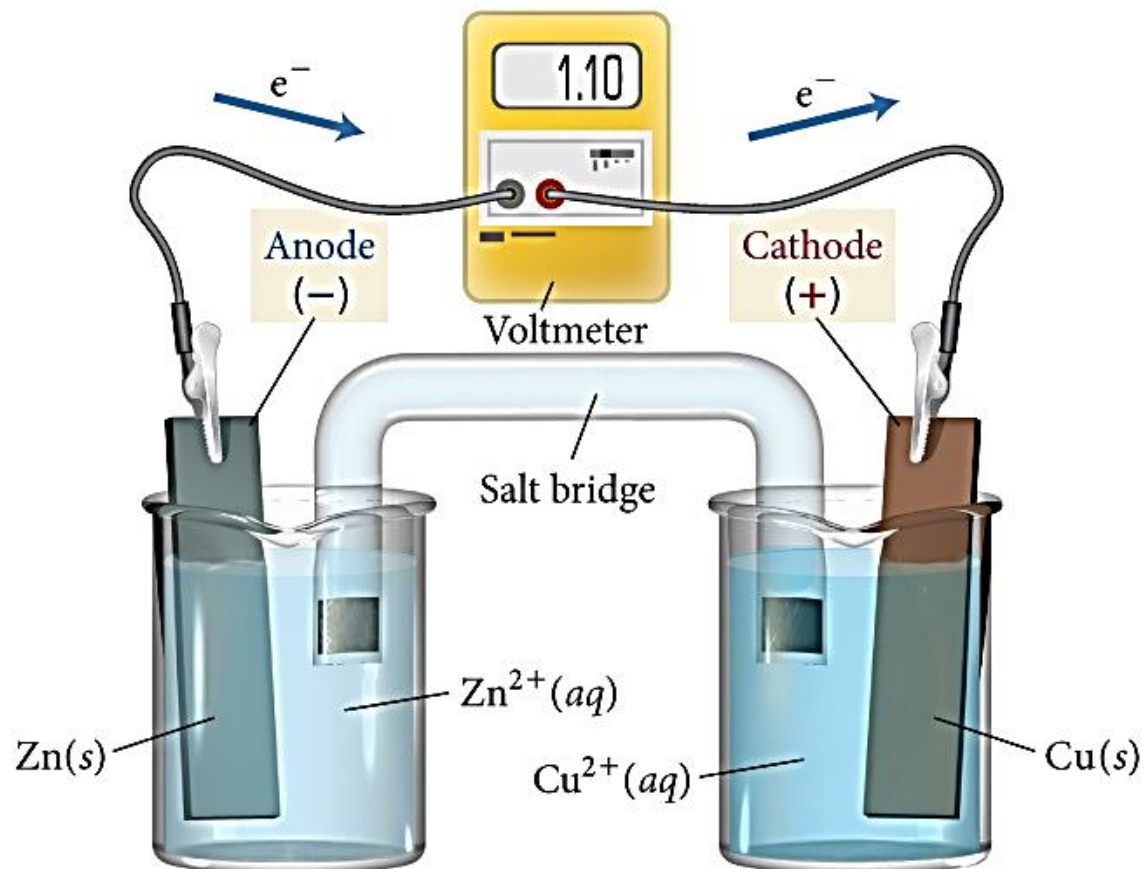
A positive free energy change, ($+\Delta G$)



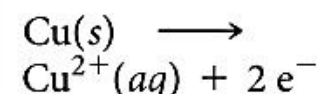
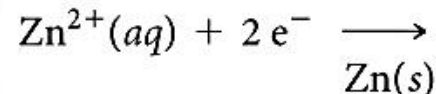
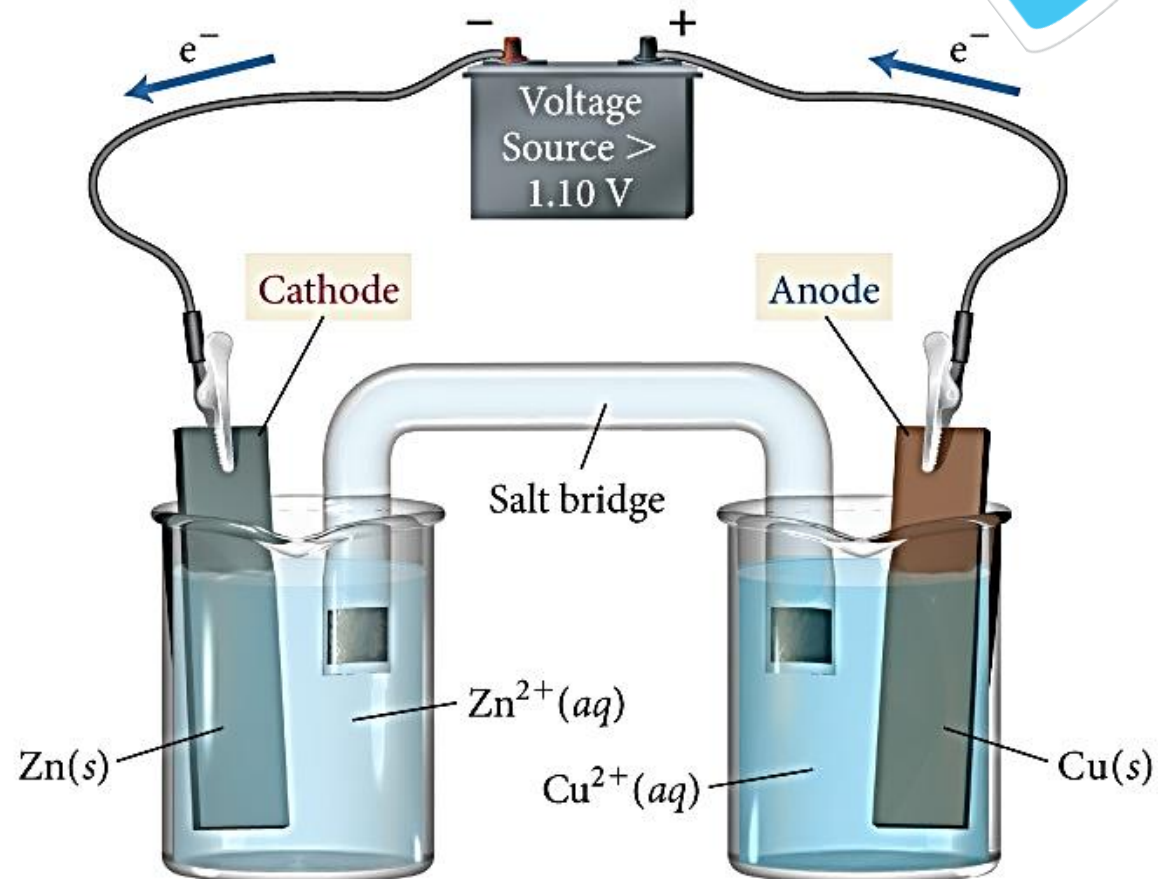
Voltaic versus Electrolytic Cells



Voltaic Cell



Electrolytic Cell



Why Would We Want an Electrolytic Cell?

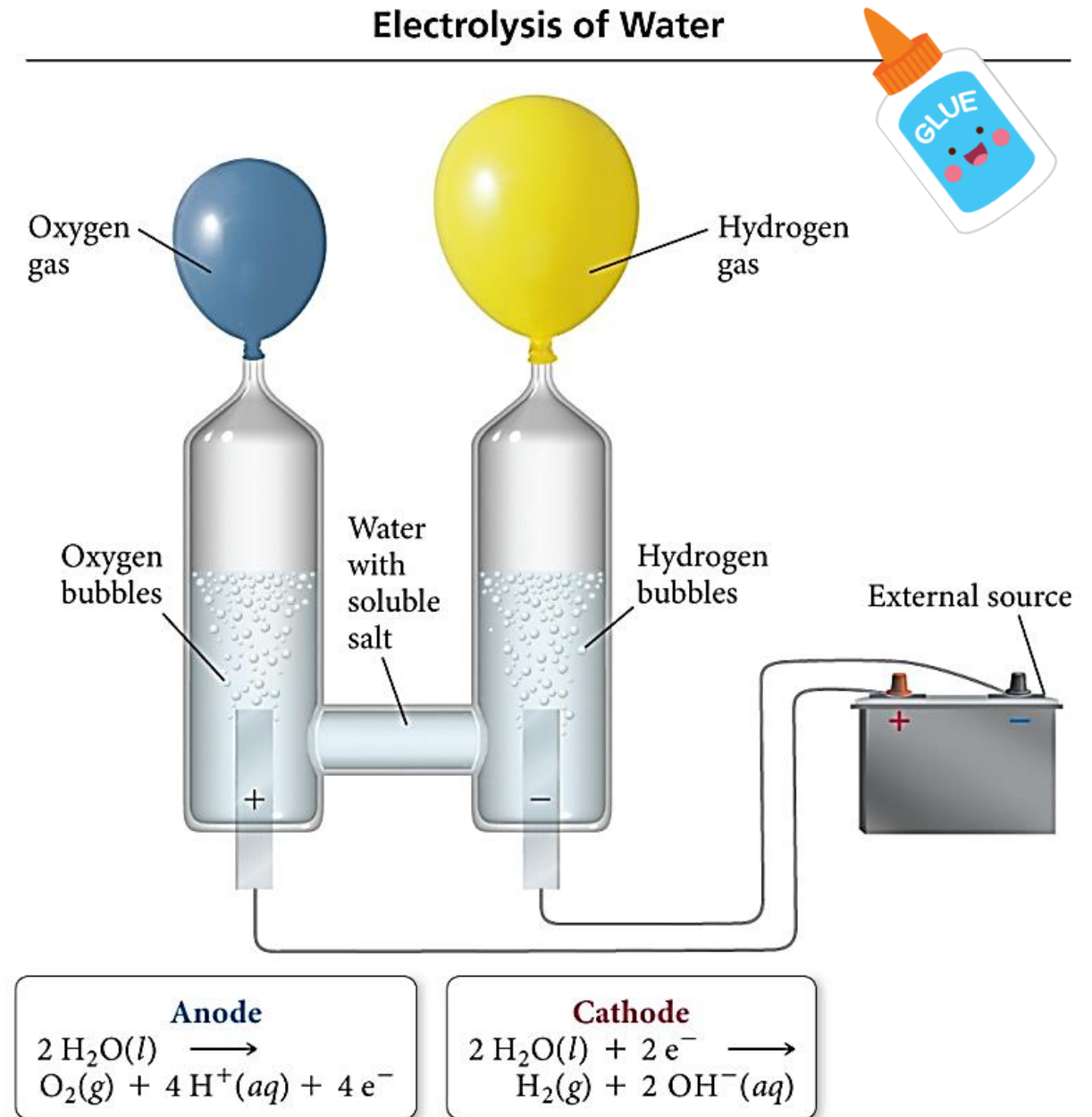
Can be useful!

Can make things happen that would not otherwise happen on their own.

Electrolysis

Electrolysis is the process of using electrical energy to break a compound apart.

- **Electrolysis is done in an electrolytic cell.**
- **Electrolytic cells can be used to separate elements from their compounds.**



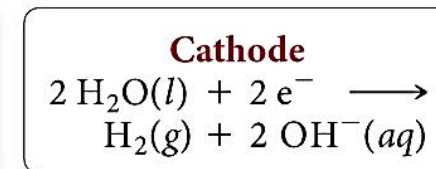
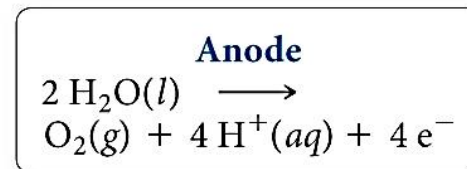
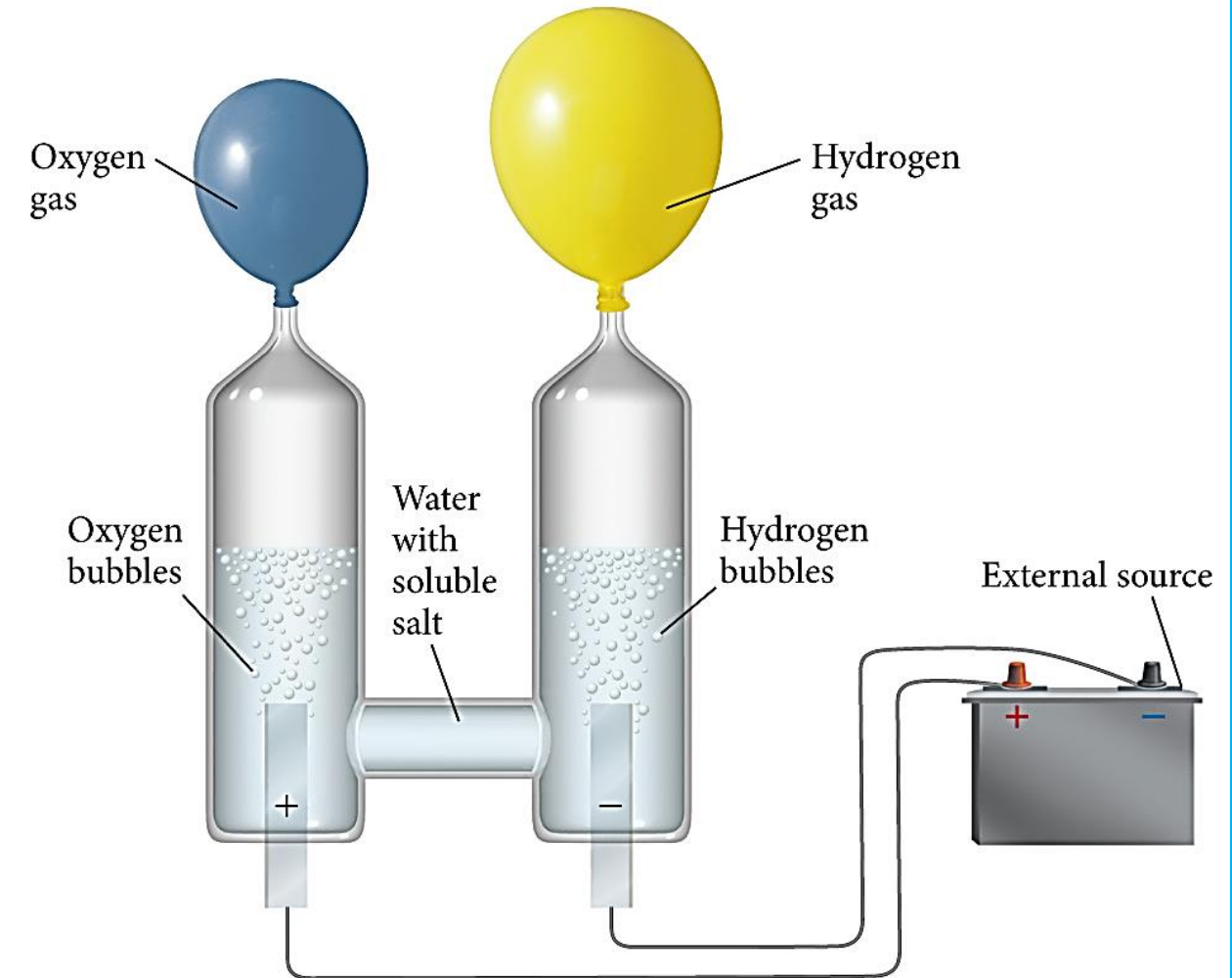
Electrolysis of Water

Anode – oxidation – loss e^-
 $2\text{H}_2\text{O}_{(l)} \rightarrow \text{O}_{2(g)} + 4\text{H}^+_{(aq)} + 4e^-$

Cathode – reduction – gain e^-
 $2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_{2(g)} + 2\text{OH}^-_{(aq)}$

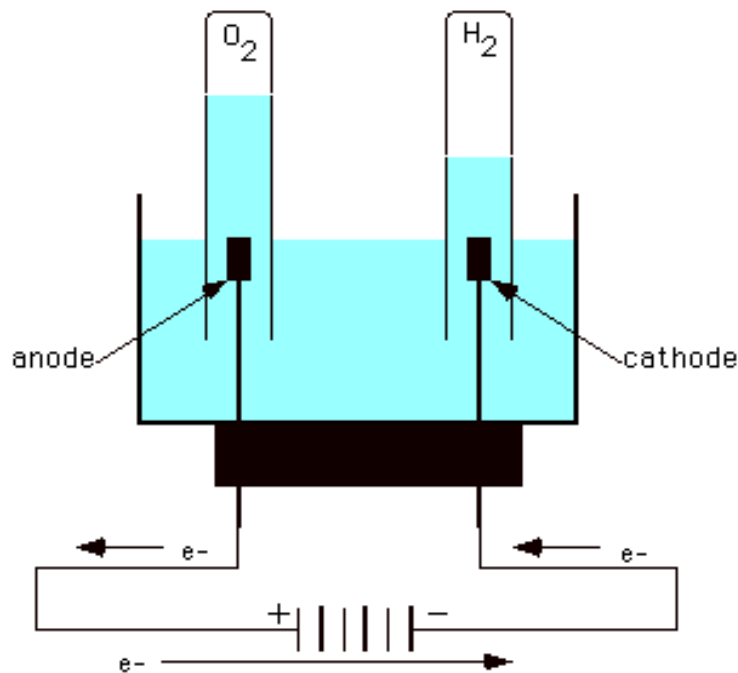
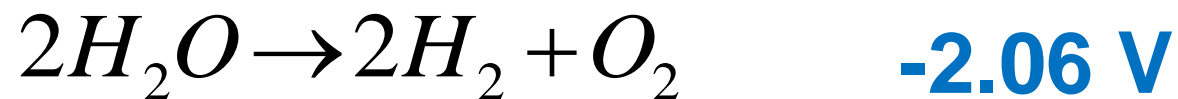
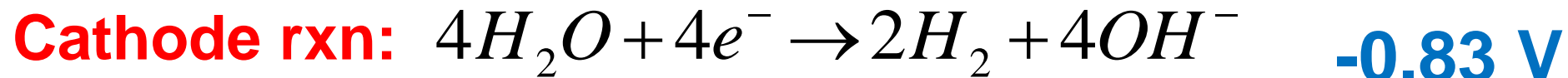
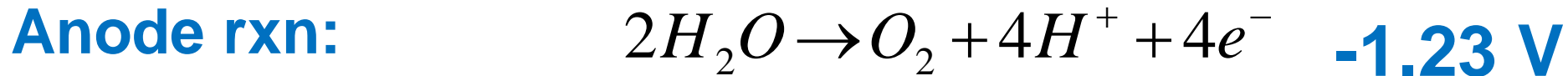
Memorize which equations!
Everyone always forgets it,
even though it is on the
standard reduction sheet.

Electrolysis of Water



Electrolysis of Water

In acidic solution



$E^\circ = \text{negative}$

Therefore $\Delta G = \text{positive}$

Nonspontaneous!

That's why you need to use electricity to make it happen!

Electroplating of Silver



Anode reaction:

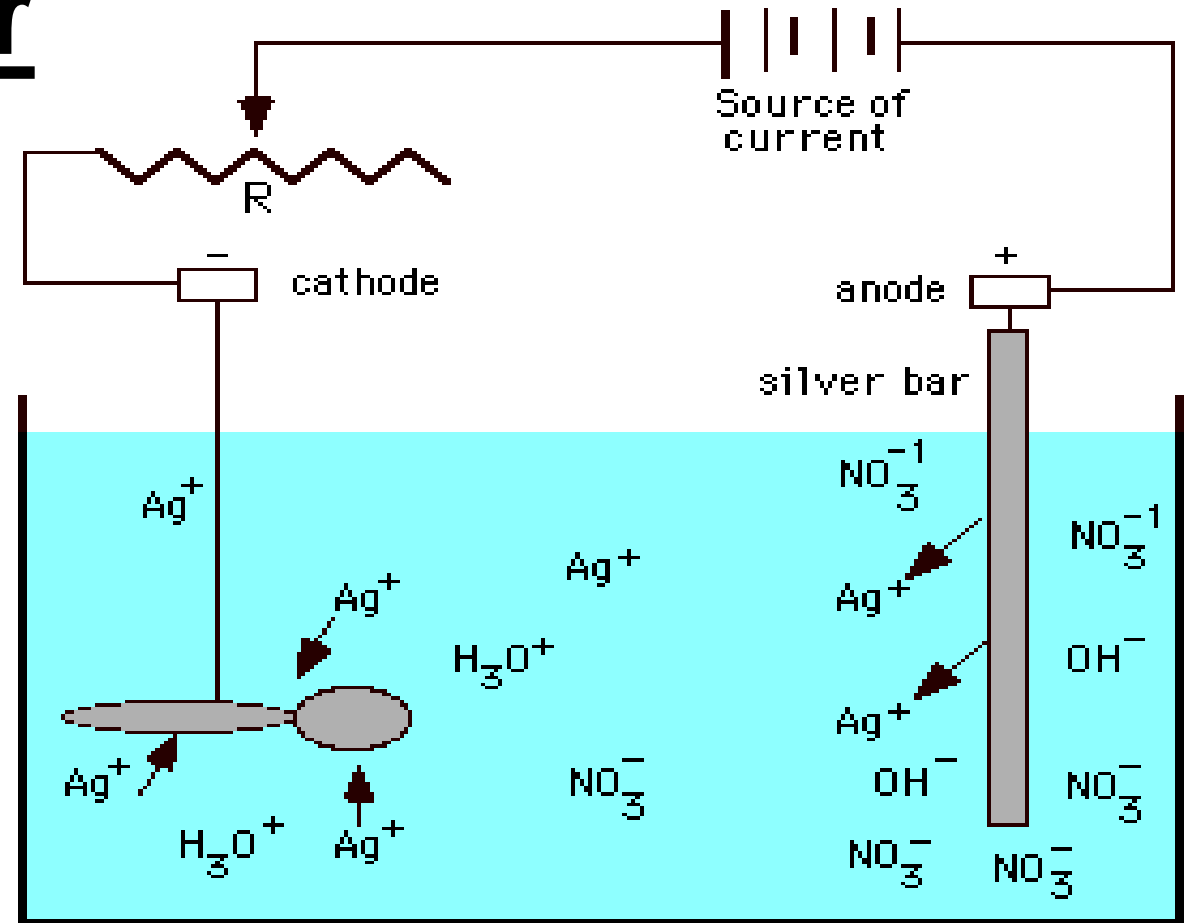


Cathode reaction:



Electroplating requirements:

1. Solution of the plating metal
2. Anode made of the plating metal
3. Cathode with the object to be plated
4. Source of current



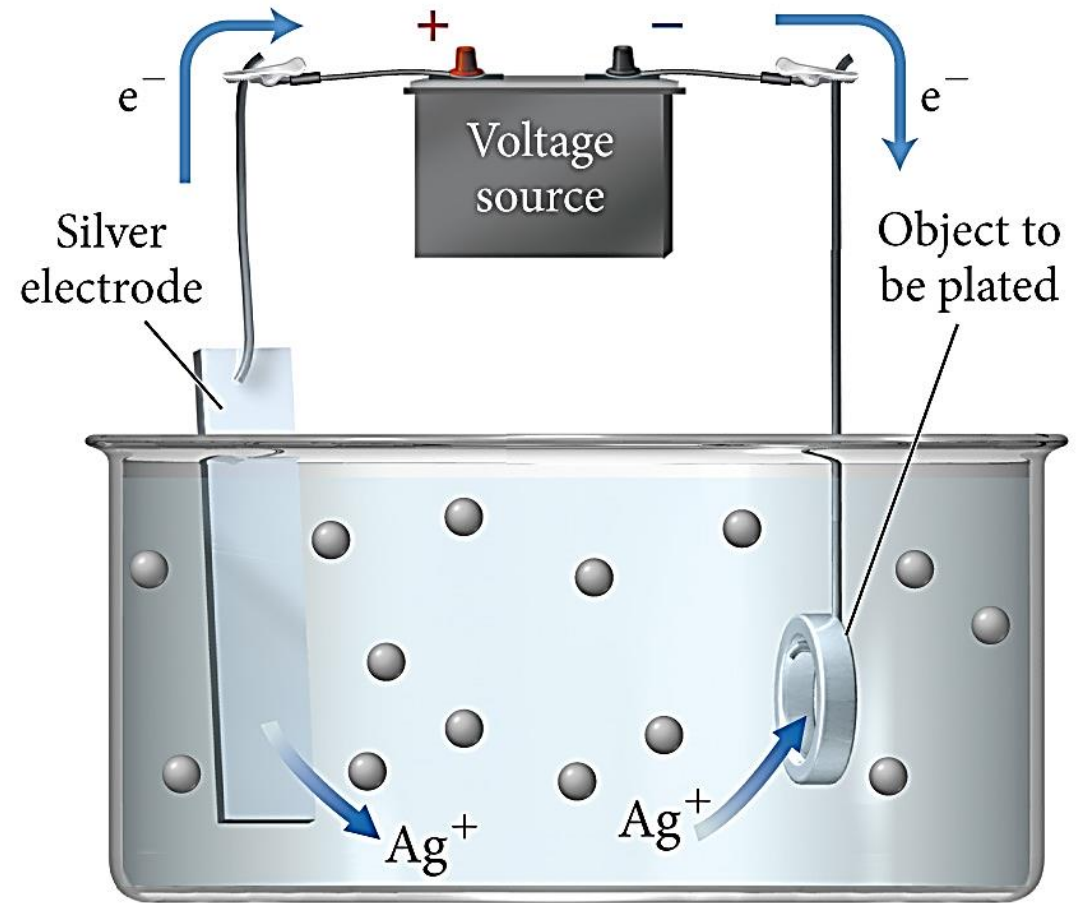
Electroplating

In electroplating, the **work piece** is the **cathode**.

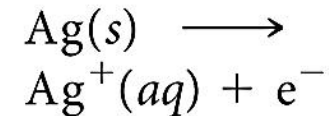
Cations are reduced at cathode, turned into neutral (s) metal, and **plate** on to the surface of work piece.

The **anode** is made of the **plate metal**. The anode oxidizes and replaces the metal cations in the solution. The anode will get smaller over time as it is turned into aqueous cations.

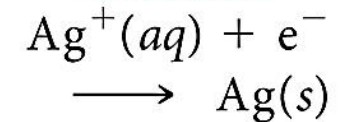
Electrolytic Cell for Silver Plating



Anode



Cathode



Solving an Electroplating Problem

Q: How many seconds will it take to plate out 5.0 grams of silver from a solution of AgNO_3 using a 20.0 Ampere current?



$$\frac{5.0 \text{ g}}{107.87 \text{ g}} \left| \frac{1 \text{ mol Ag}}{1 \text{ mol Ag}} \right| \frac{1 \text{ mol e}^-}{1 \text{ mol e}^-} \left| \frac{96\,485 \text{ C}}{1 \text{ mol e}^-} \right| \frac{1 \text{ s}}{20.0 \text{ C}} = 2.2 \times 10^2 \text{ s}$$

1 amp = 1 Coulomb/sec

96485 Coulombs = 1 mol e^-

YouTube Link to Presentation

<https://youtu.be/9JrIJUUGopY>