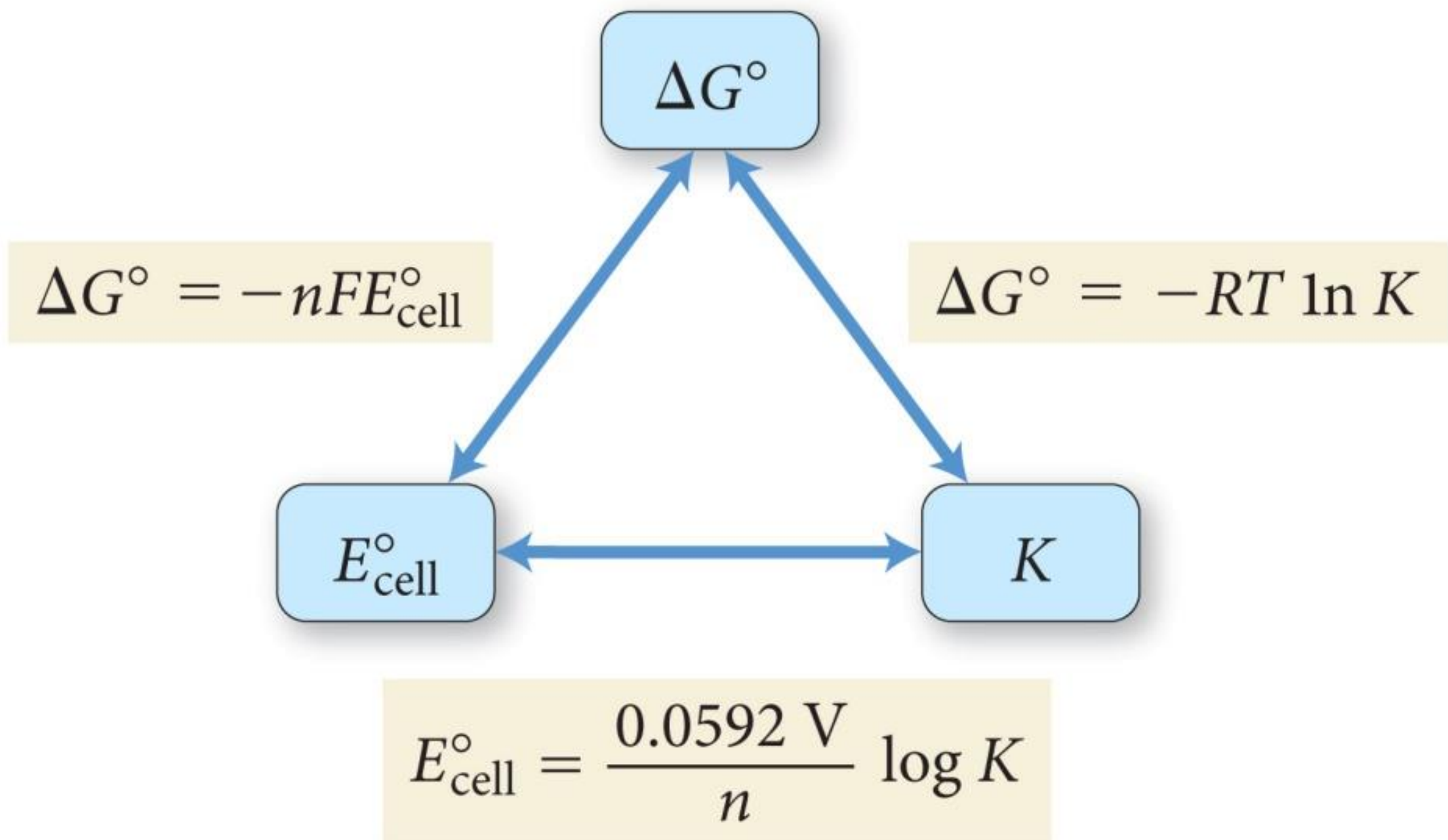


# **N45 - Electrochemistry**

**Variables Unite**



# $E^\circ_{\text{cell}}$ , $\Delta G^\circ$ , and $K$

## For a spontaneous reaction

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

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

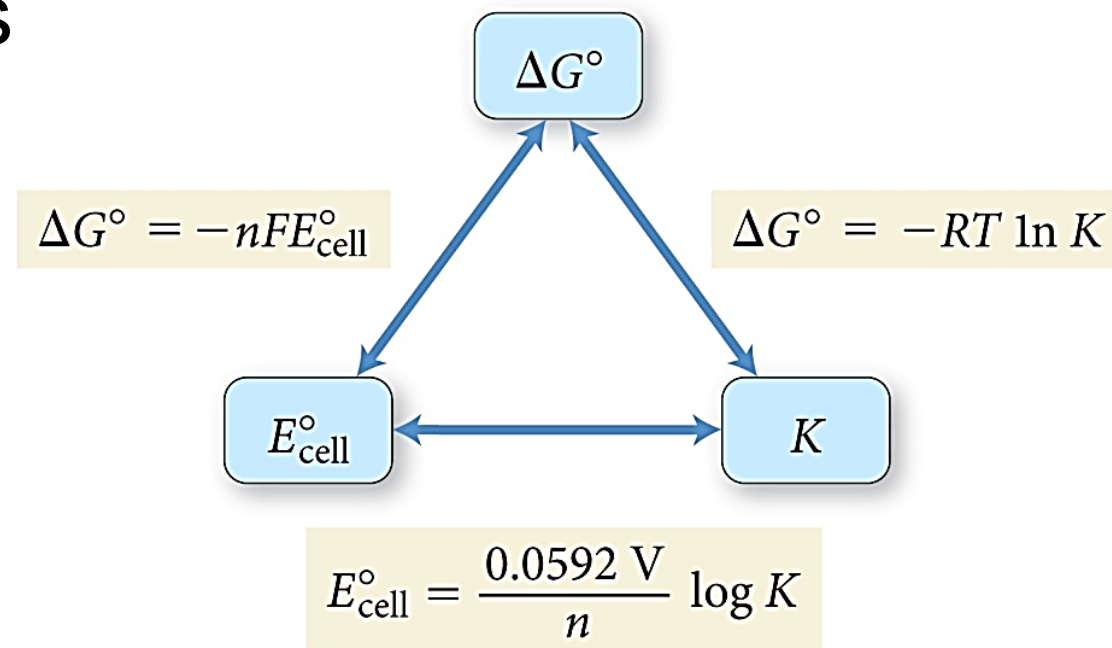
$$E^\circ > 0 \text{ (positive)}$$

$$K > 1$$

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

$n$  = the number of electrons

$F$  = Faraday's constant = 96,485 C/mol  $e^-$   
(often see it as 96,5000 C/mol  $e^-$ )



# Calculating $\Delta G^0$ for a Cell

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

**n** = moles of electrons in balanced redox equation

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



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

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

# 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<sup>-</sup>

# Deriving the Nernst Equation

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

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

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

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

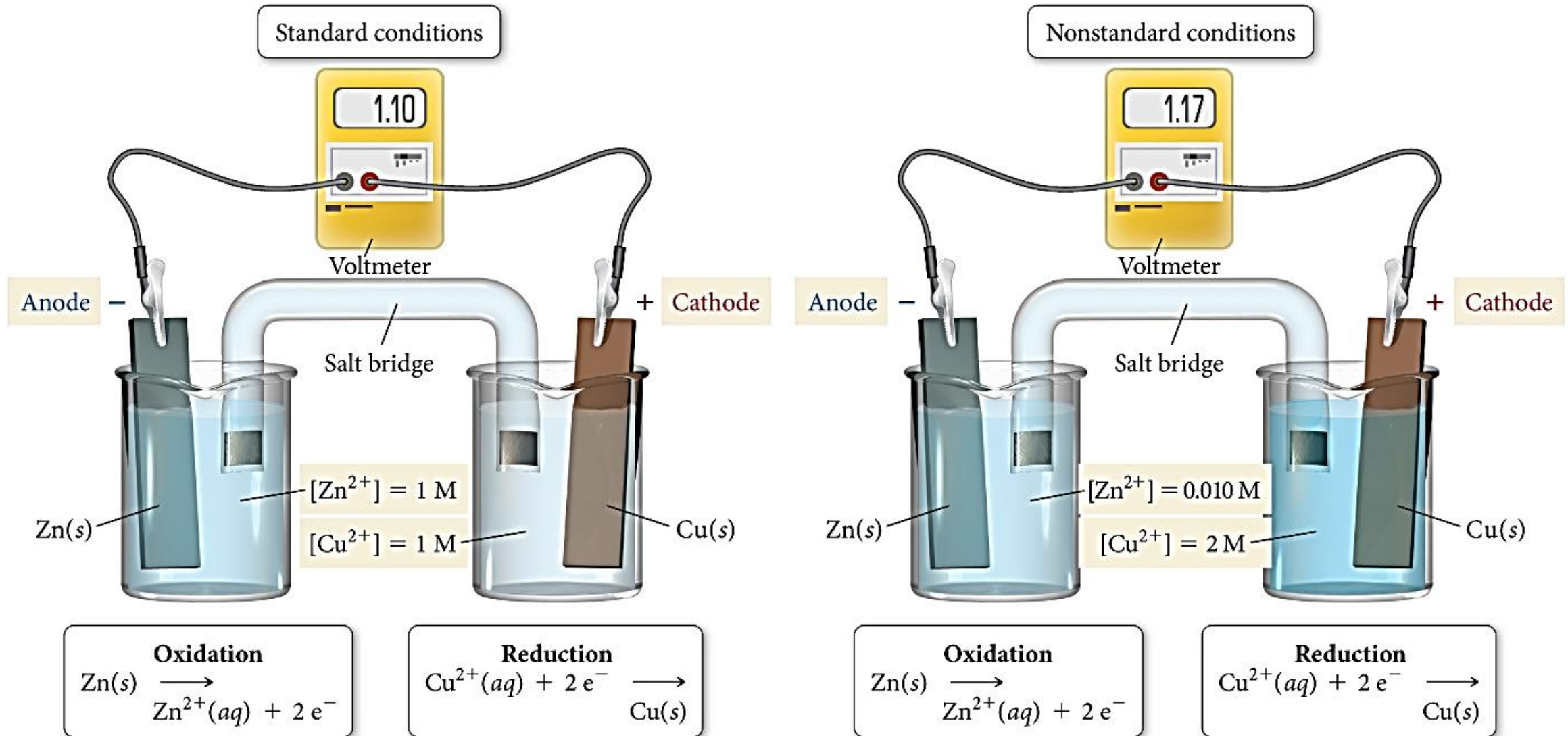
# Nernst Equation Simplified

**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

# $E_{\text{cell}}$ 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):

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

# Calculating an Equilibrium Constant from a Cell Potential



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

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

$$37.2 = \log(K)$$

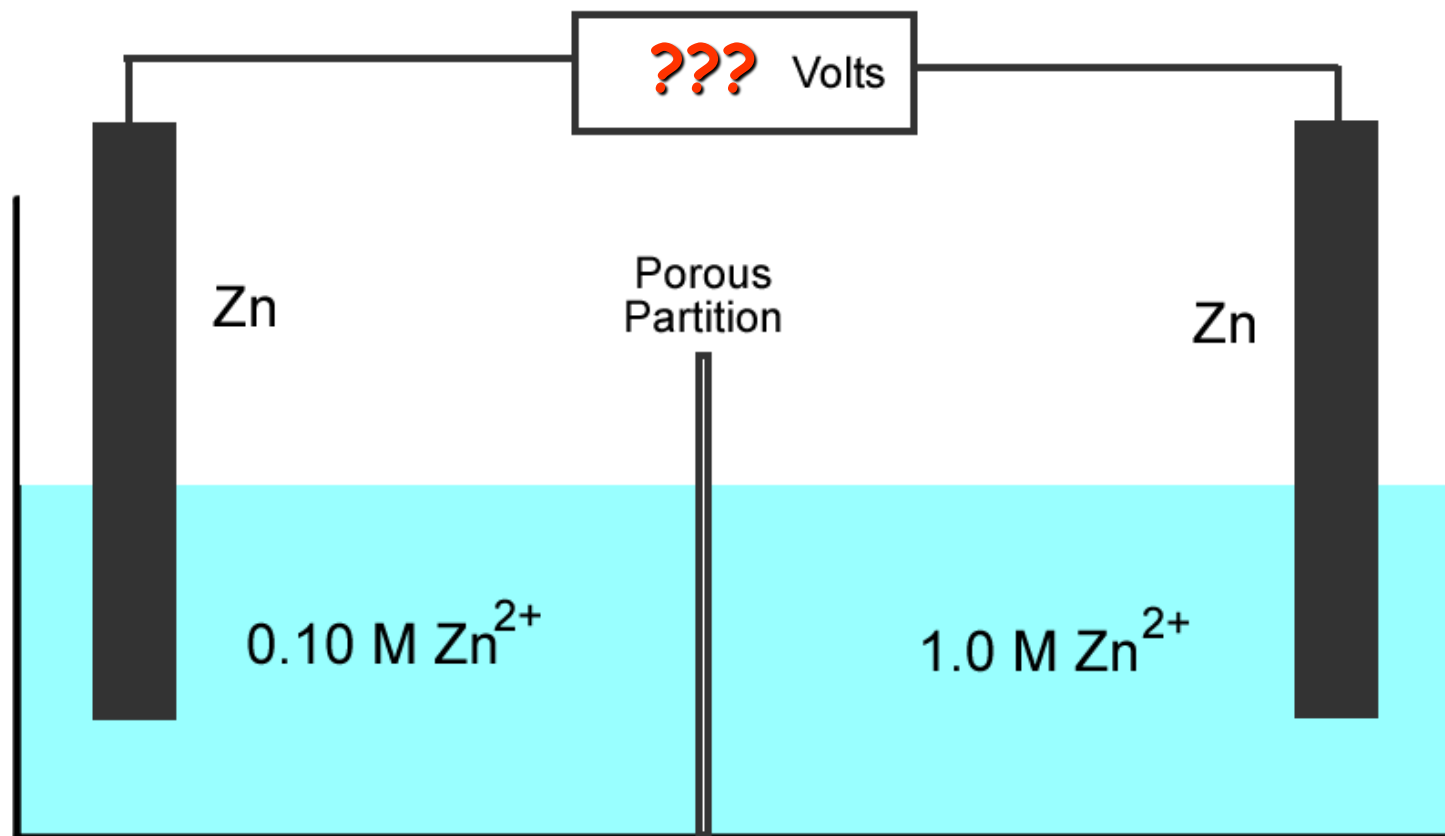
$$10^{37.2} = K = 1.58 \times 10^{37}$$

# Concentration Cell

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

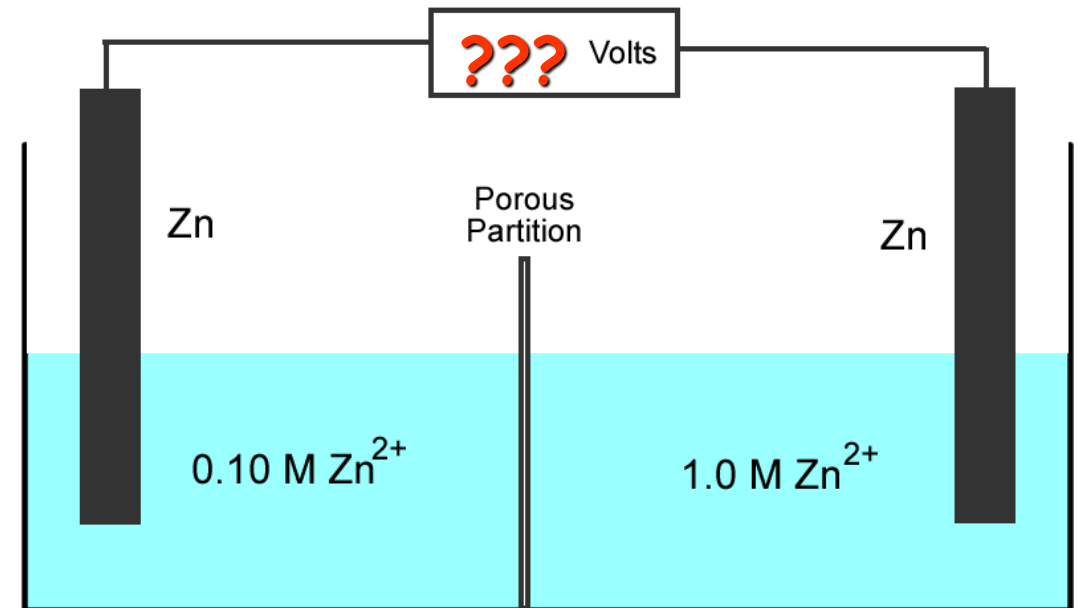
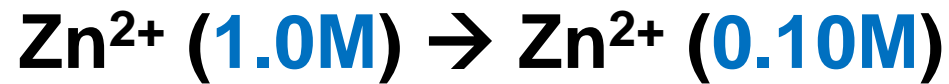
## Step 1:

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



# Concentration Cell

The 1.0 M  $\text{Zn}^{2+}$  must decrease in concentration, and the 0.10 M  $\text{Zn}^{2+}$  must increase in concentration



# Concentration Cell

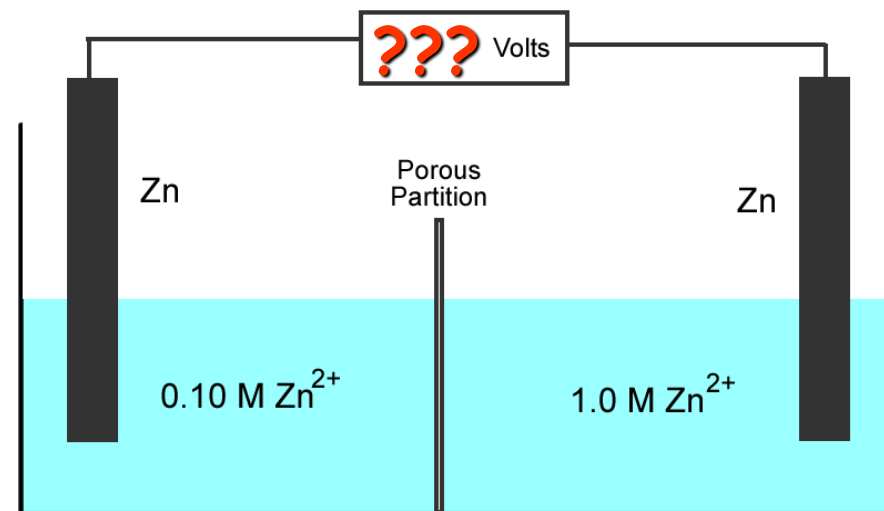
## Step 2:

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



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

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



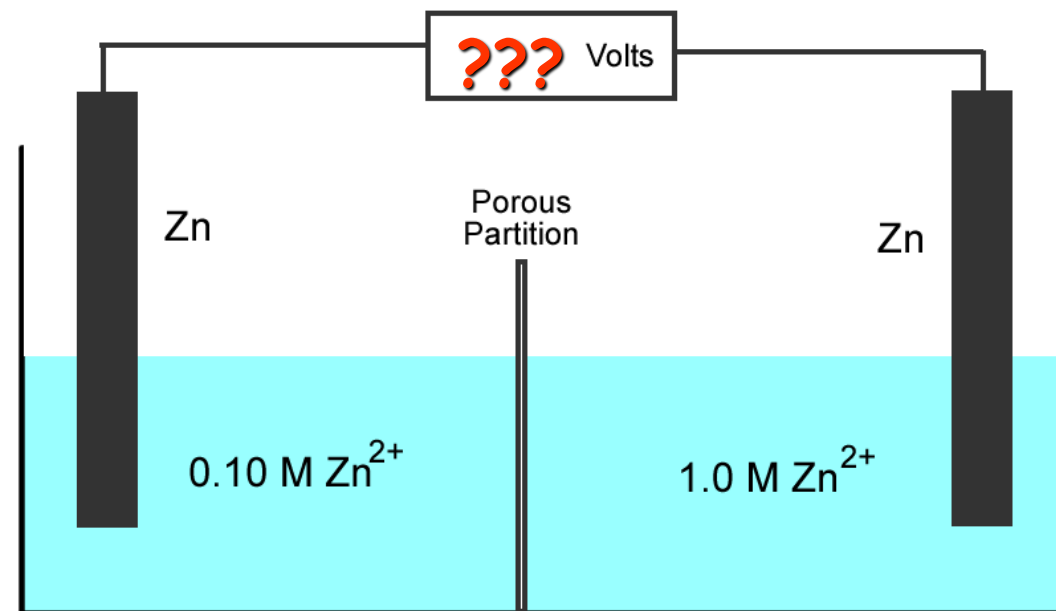
# Concentration Cell

## Step 2:

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



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



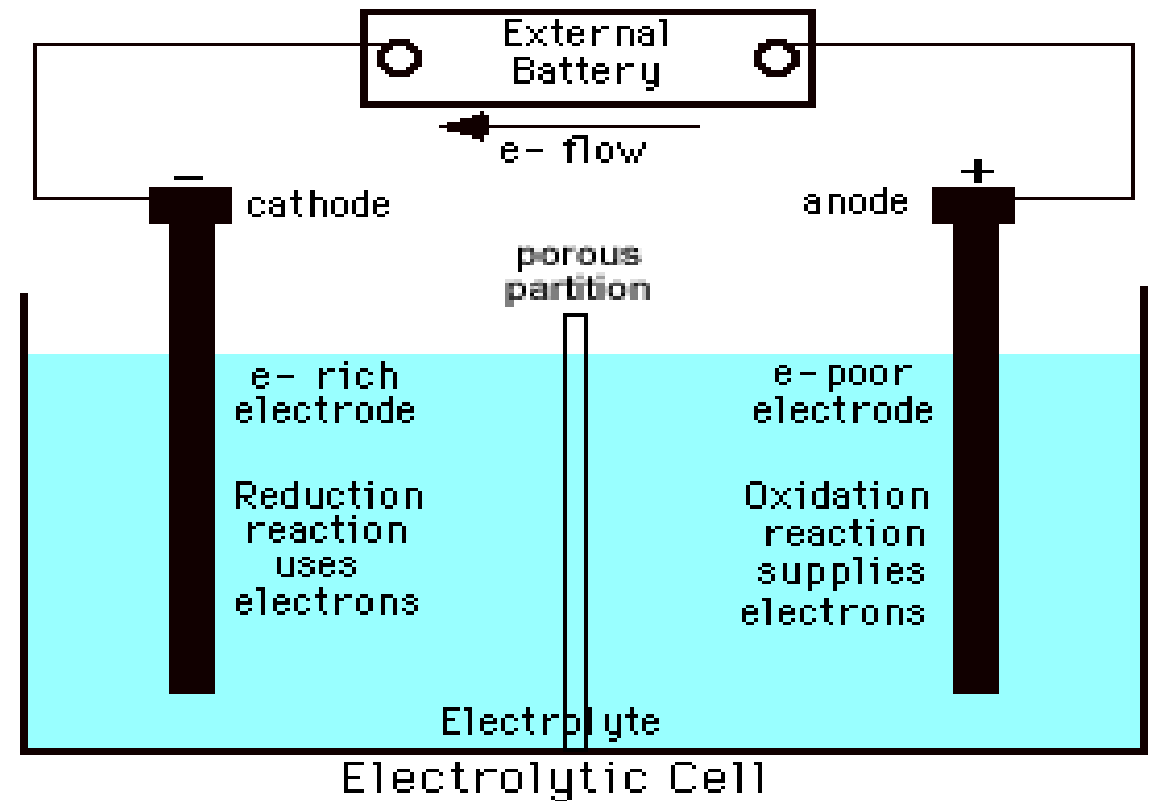
# Electrolytic Processes

Electrolytic processes are NOT spontaneous.

They have:

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

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



# Electrochemical Cells

**In all electrochemical cells, oxidation occurs at the anode, reduction occurs at the cathode.**

## **In voltaic cells**

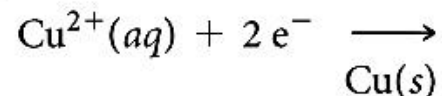
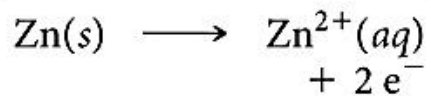
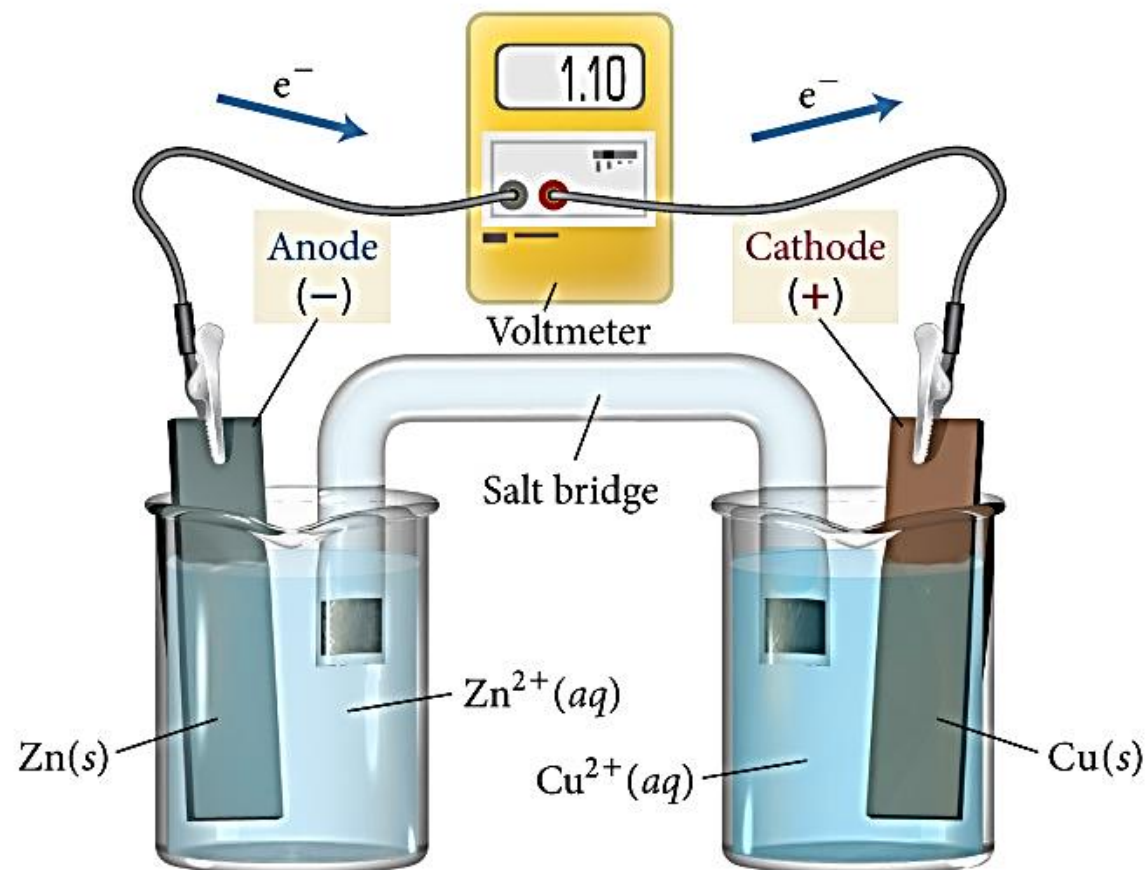
- Anode is the source of electrons and has a (–) charge.
- Cathode draws electrons and has a (+) charge.

## **In electrolytic cells**

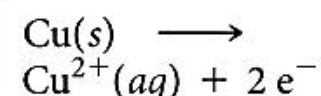
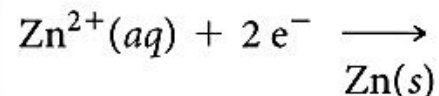
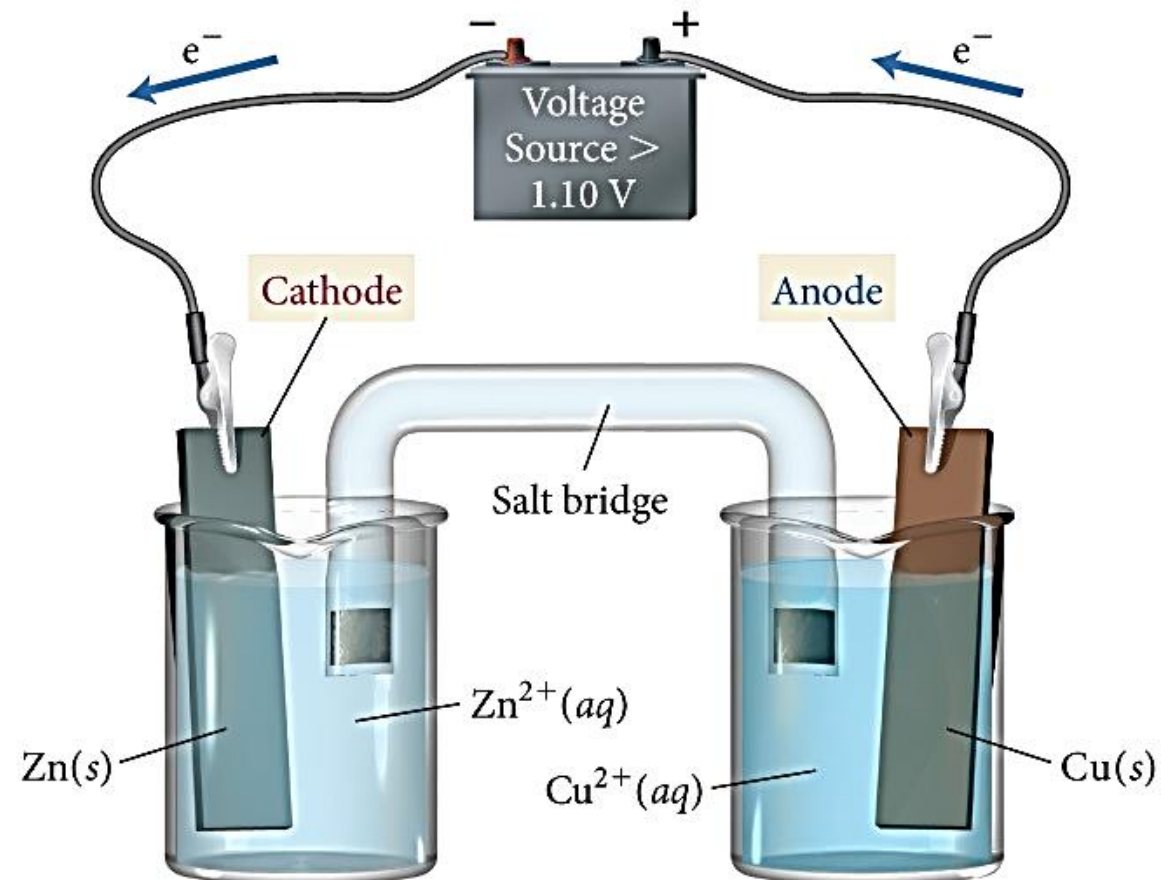
- Electrons are drawn off the anode, so it must have a place to release the electrons—the positive terminal of the battery.
- Electrons are forced toward the anode, so it must have a source of electrons—the negative terminal of the battery.

# Voltaic versus Electrolytic Cells

Voltaic Cell



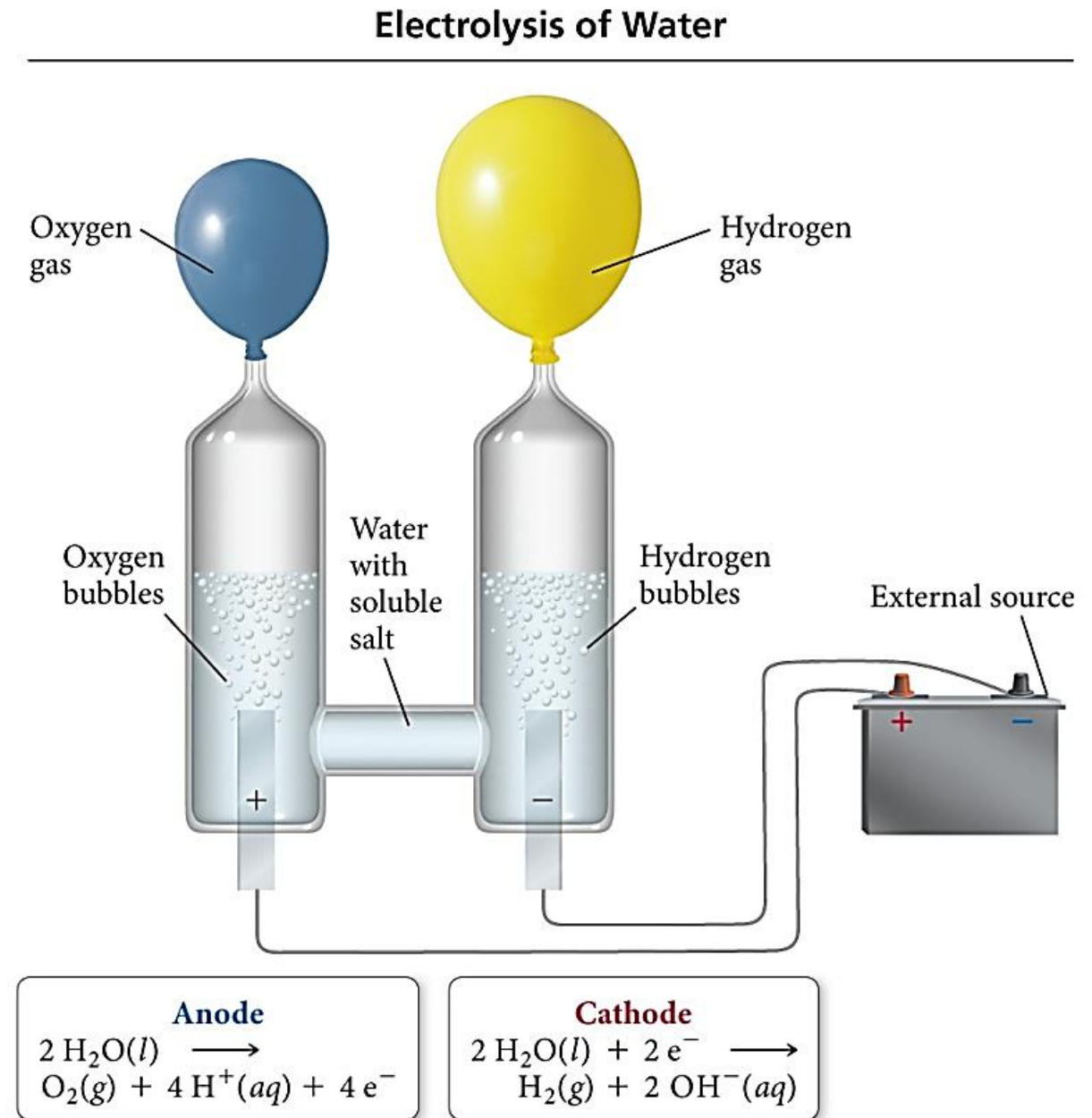
Electrolytic Cell



# Electrolysis

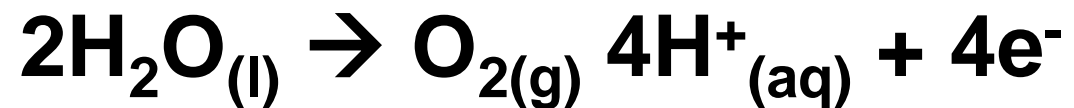
**Electrolysis** is the process of using electrical energy to break a compound apart.

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

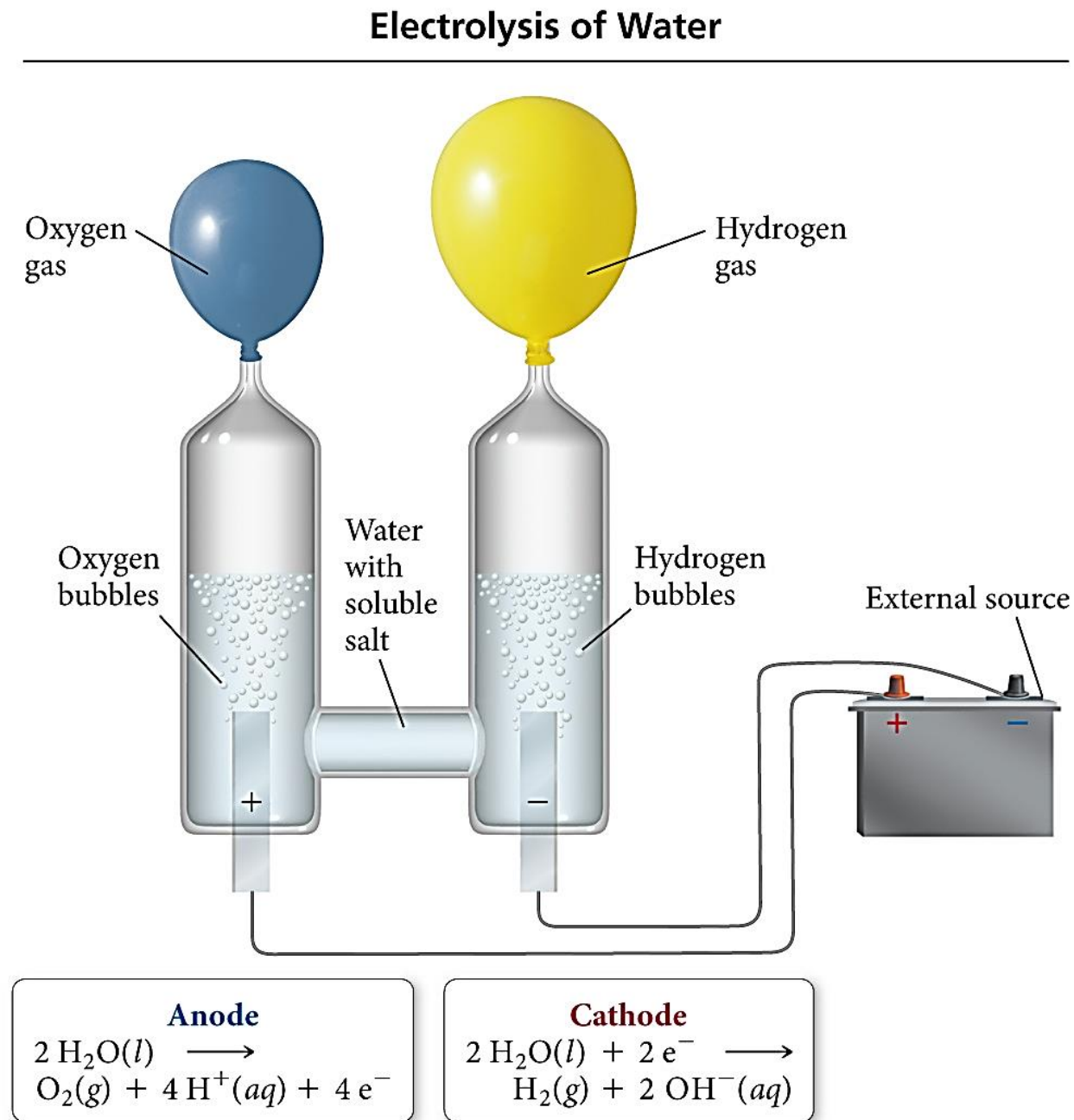
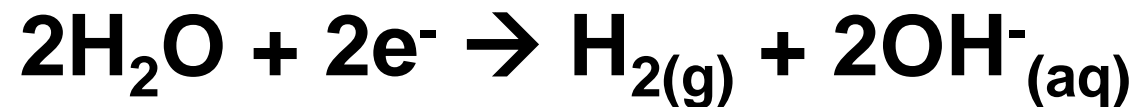


# Electrolysis of Water

**Anode** – oxidation – loss  $e^-$

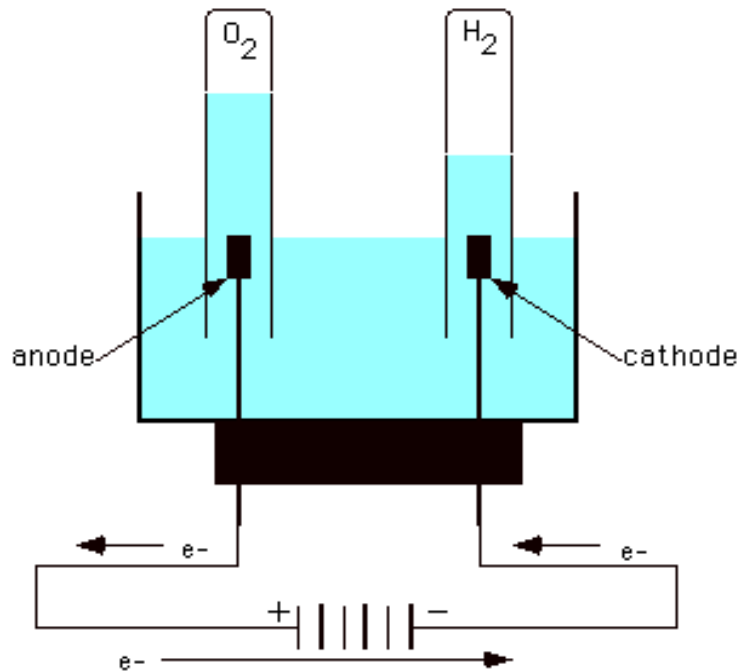
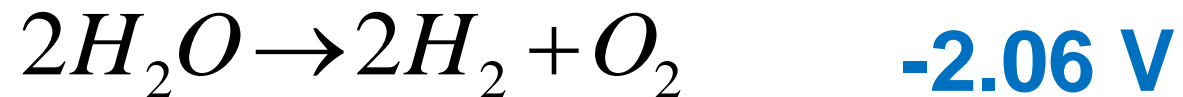
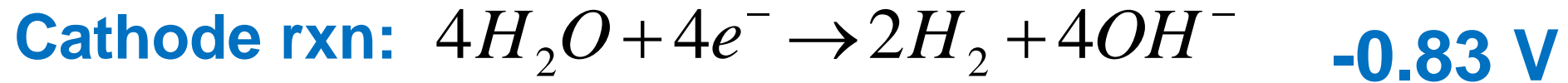
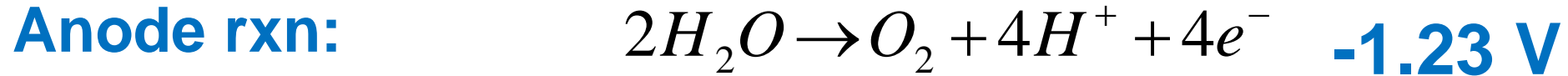


**Cathode** – reduction – gain  $e^-$



# Electrolysis of Water

In acidic solution



**$E^\circ$  = negative**

**Therefore  $\Delta G$  = positive**

**Nonspontaneous!**

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

# Electroplating of Silver

**Anode reaction:**

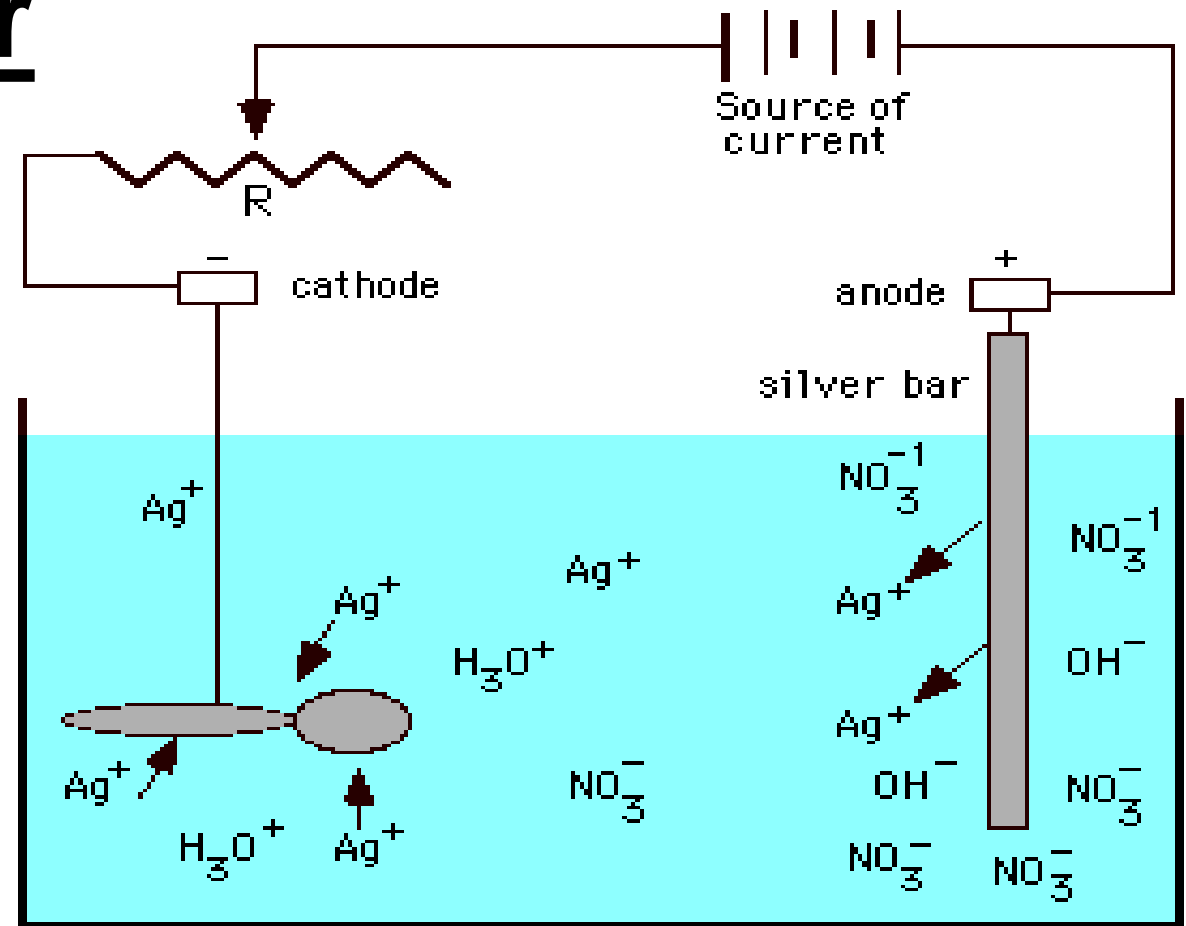


**Cathode reaction:**



**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



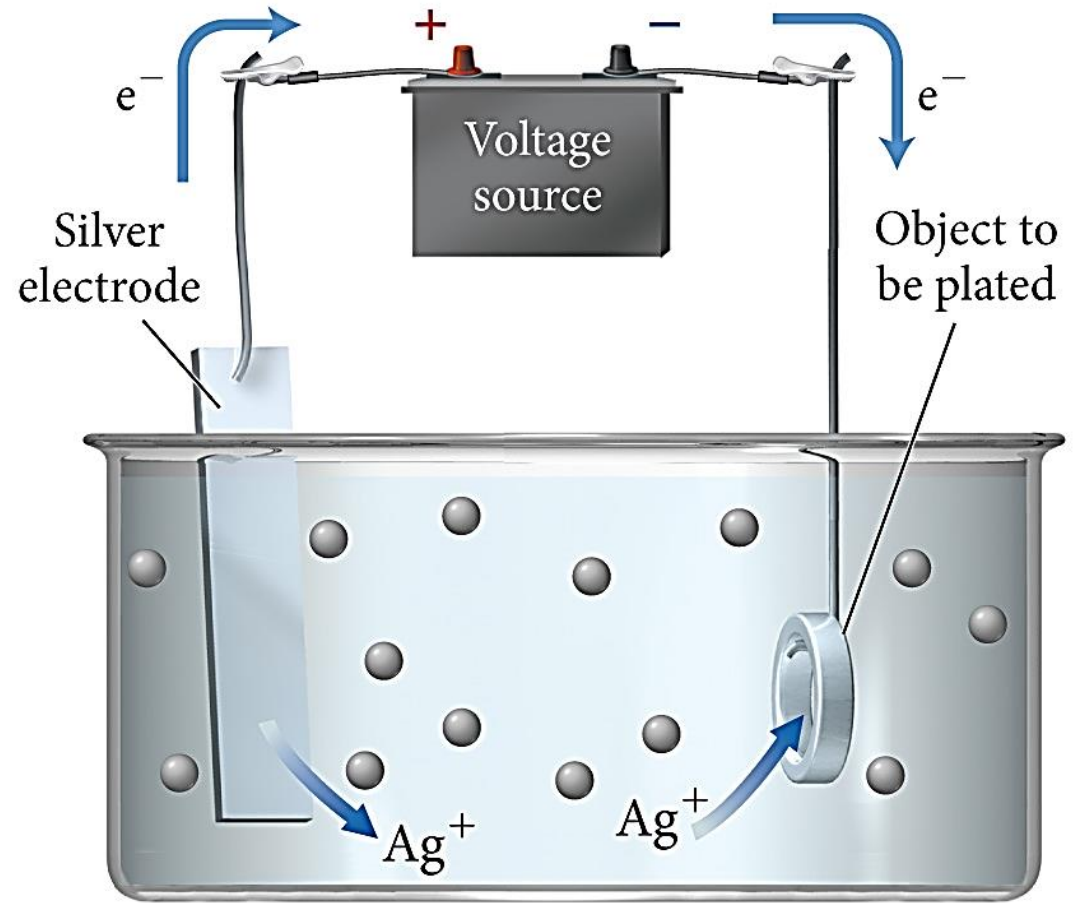
# Electroplating

In electroplating, the work piece is the cathode.

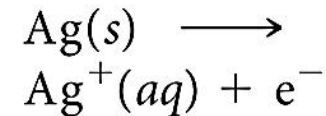
Cations are reduced at cathode and plate to the surface of the work piece.

The anode is made of the plate metal. The anode oxidizes and replaces the metal cations in the solution.

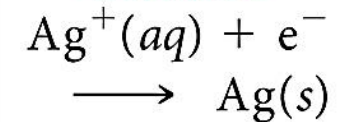
## Electrolytic Cell for Silver Plating



### 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  $\text{AgNO}_3$  using a 20.0 Ampere current?



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