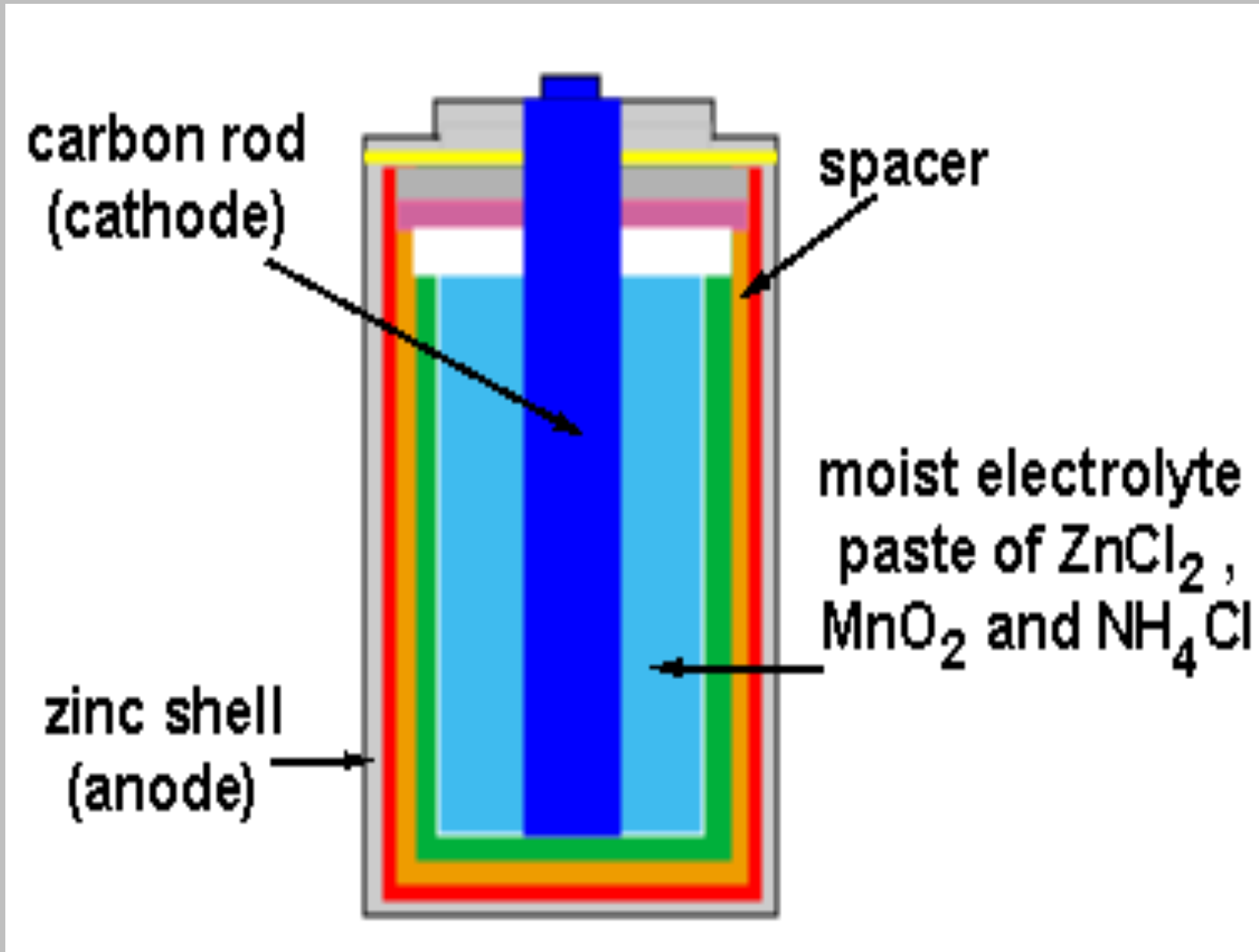
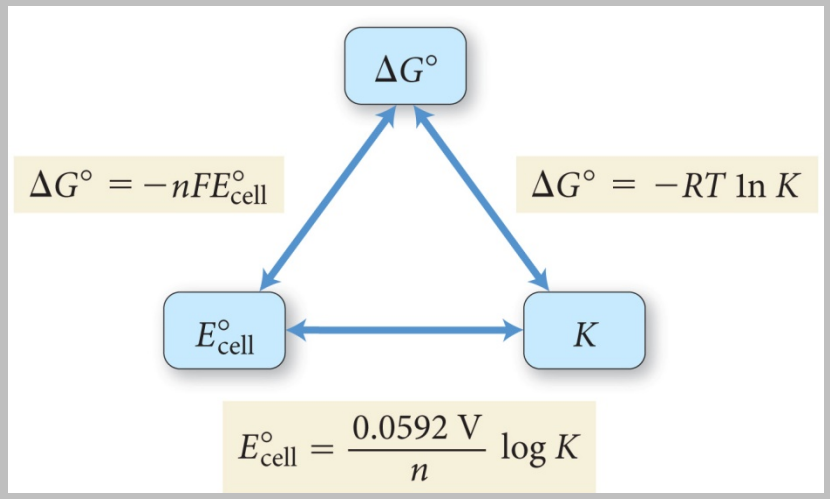
Electrochemistry – Variables Unite



$E°_{cell}$, $\Delta G°$, and K

- For a spontaneous reaction
  - one that proceeds in the forward direction with the chemicals in their standard states

    $\Delta G° < 0$ (negative)
  - $E° > 0$ (positive)
  - $K > 1$



- $\Delta G° = -RT\ln(K) = -nFE°_{cell}$
  - n = the number of electrons
  - F = Faraday's constant = 96,485 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^-

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$ $\qquad E^0 = +1.10$ V

$$\Delta G^0 = -(2\,mol\,e^-)(96\,485\,\frac{coulombs}{mol\,e^-})(1.10\,\frac{Joules}{Coulomb})$$

$$\Delta G^0 = -212267\,Joules = -212\,kJ$$

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

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

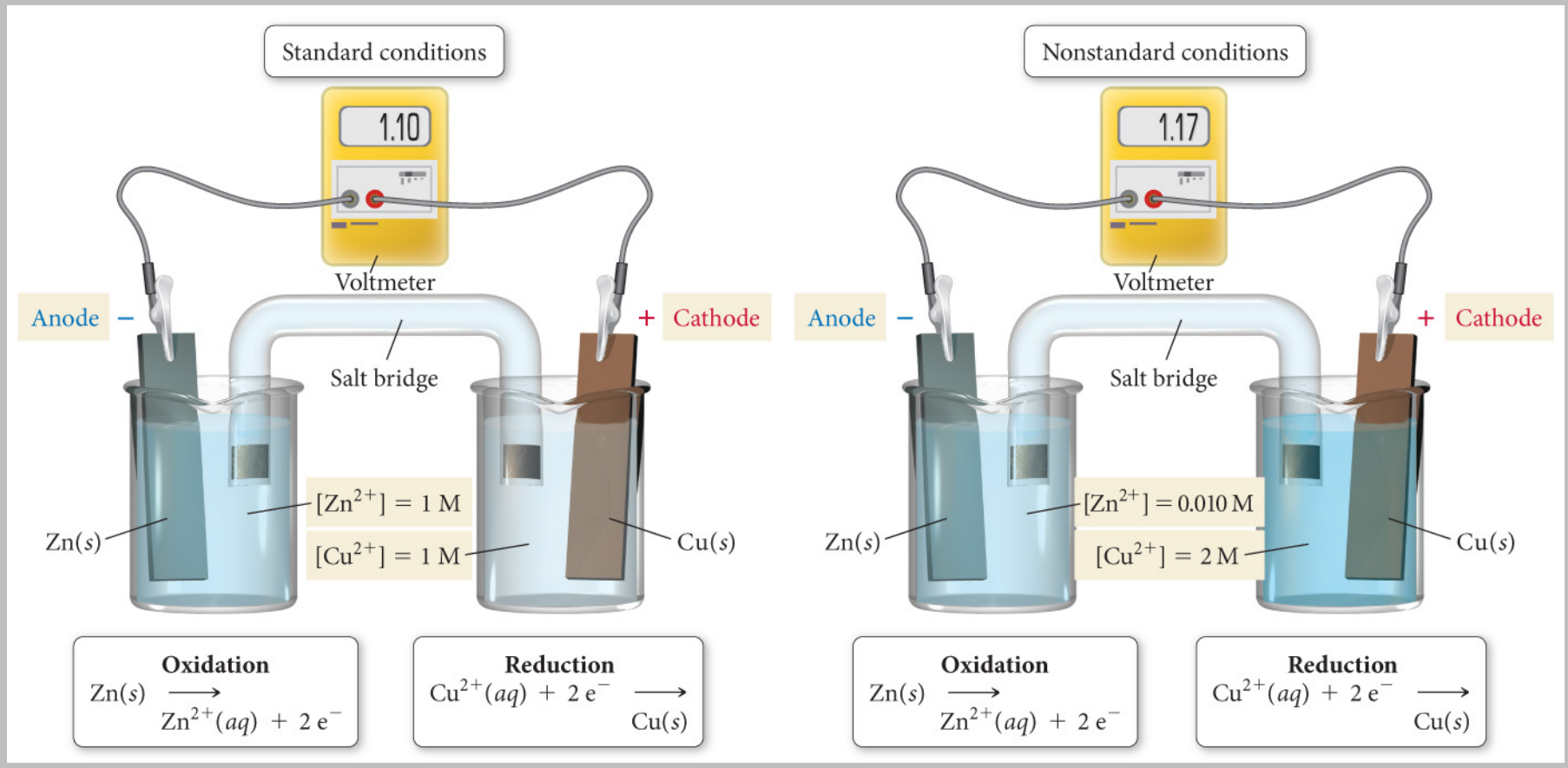
$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592\,\text{V}}{n} \log Q$$

Nernst Equation Simplified

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

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

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):

$$0\,volts = E^0 - \frac{0.0591}{n}\log(K)$$

Calculating an Equilibrium Constant from a Cell Potential

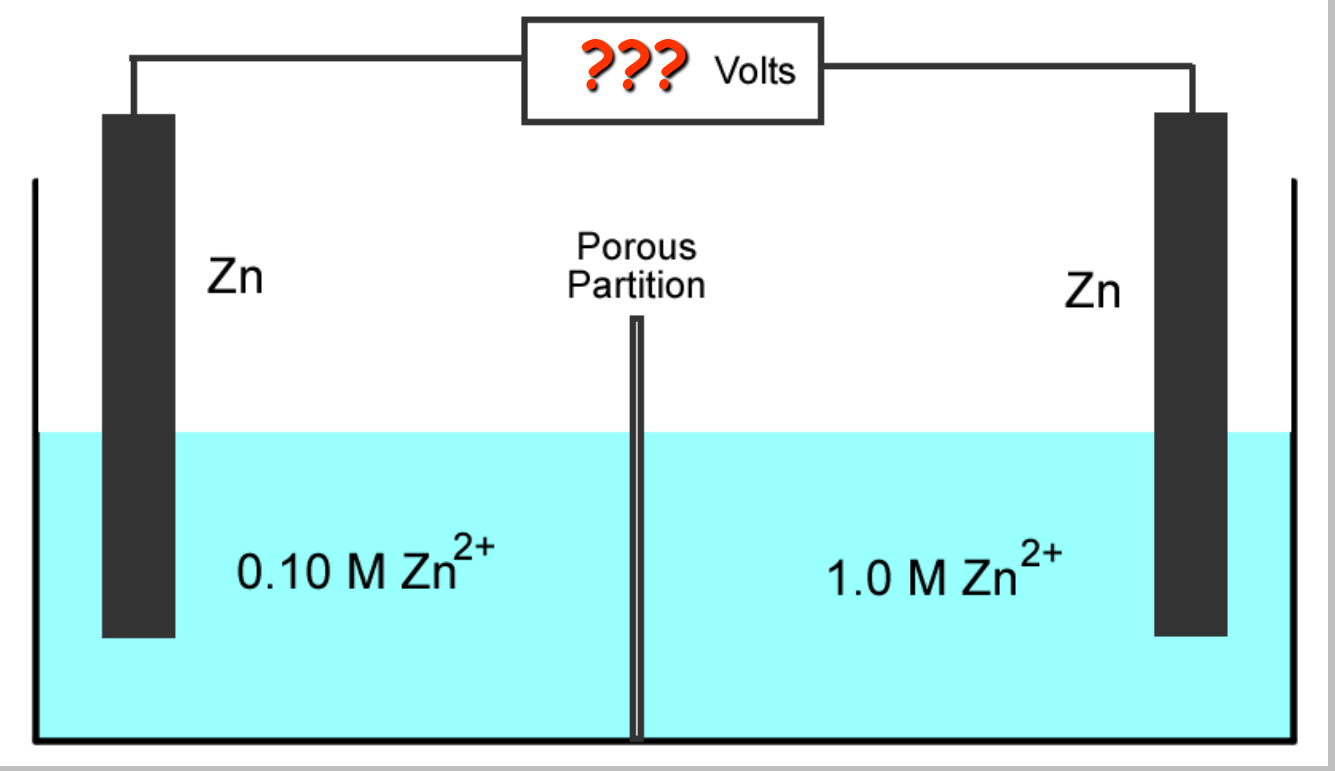
$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$ $\quad E^0 = +1.10\ V$

$$0\,volts = 1.10 - \frac{0.0591}{2}\log(K)$$

$$\frac{(1.10)(2)}{0.0591} = \log(K)$$

$$37.2 = \log(K)$$

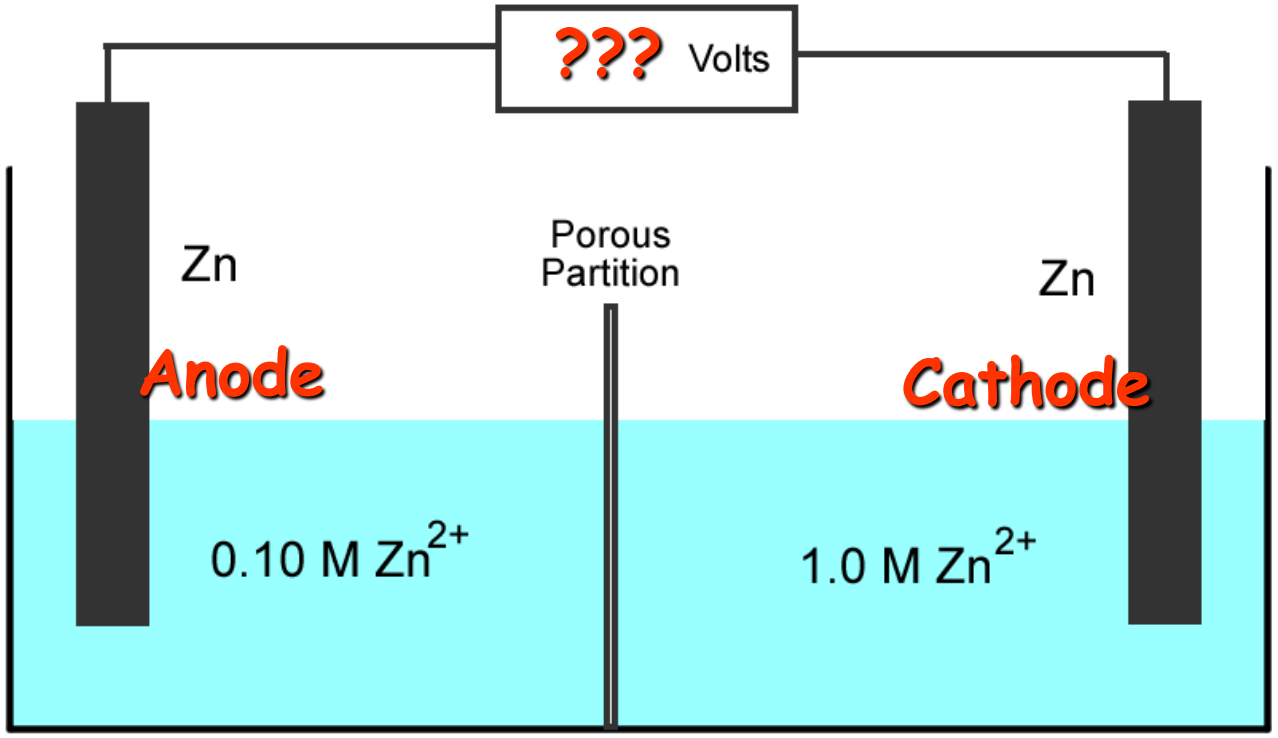
$$10^{37.2} = K = 1.58\,x10^{37}$$



Concentration Cell

Both sides have the same components but at different concentrations.

Step 1: Determine which side undergoes oxidation, and which side undergoes reduction.



Concentration Cell

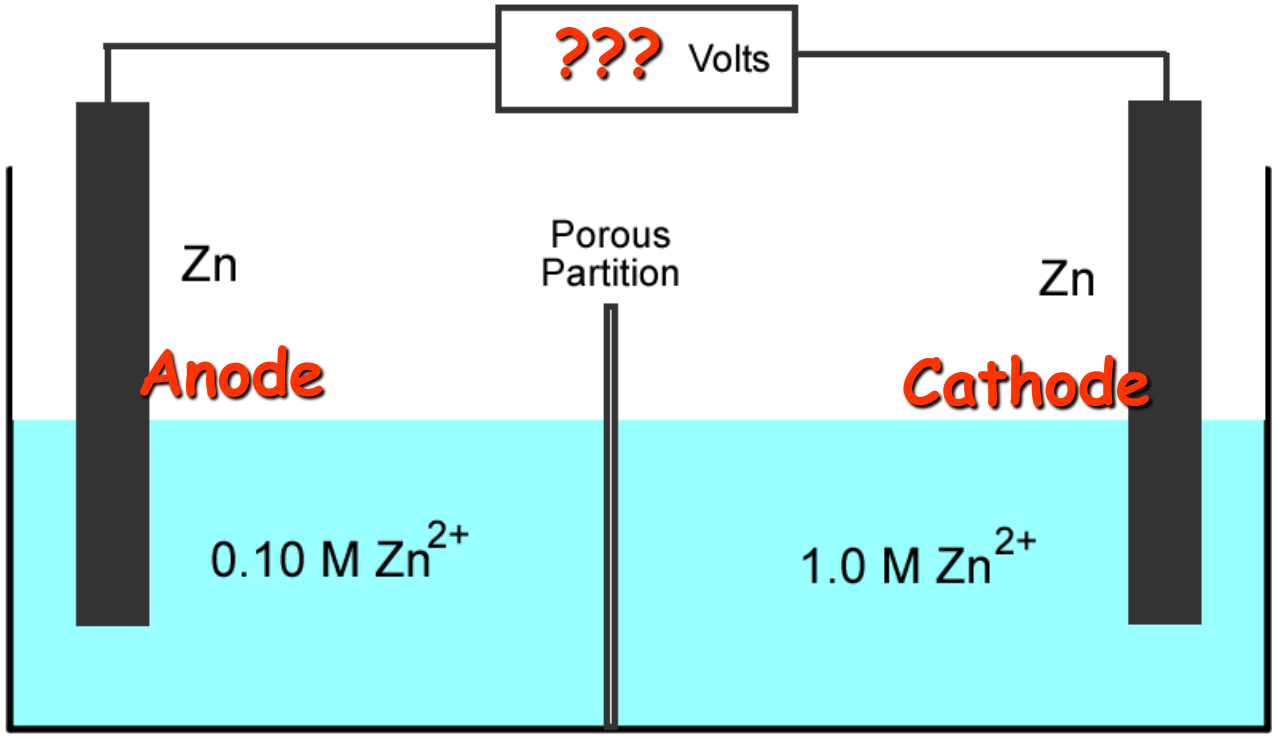
Both sides have the same components but at different concentrations.

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

Zn^{2+} (1.0M) + $2e^-$ → Zn (reduction)

Zn → Zn^{2+} (0.10M) + $2e^-$ (oxidation)

Zn^{2+} (1.0M) → Zn^{2+} (0.10M)



Concentration Cell

Both sides have the same components but at different concentrations.

Step 2: Calculate cell potential using the Nernst Equation (assuming 25 °C).

Zn^{2+} (1.0M) → Zn^{2+} (0.10M)

$$E = E^0 - \frac{0.0591}{n}\log(Q)$$

Nernst Calculations

Zn^{2+} (1.0M) → Zn^{2+} (0.10M)

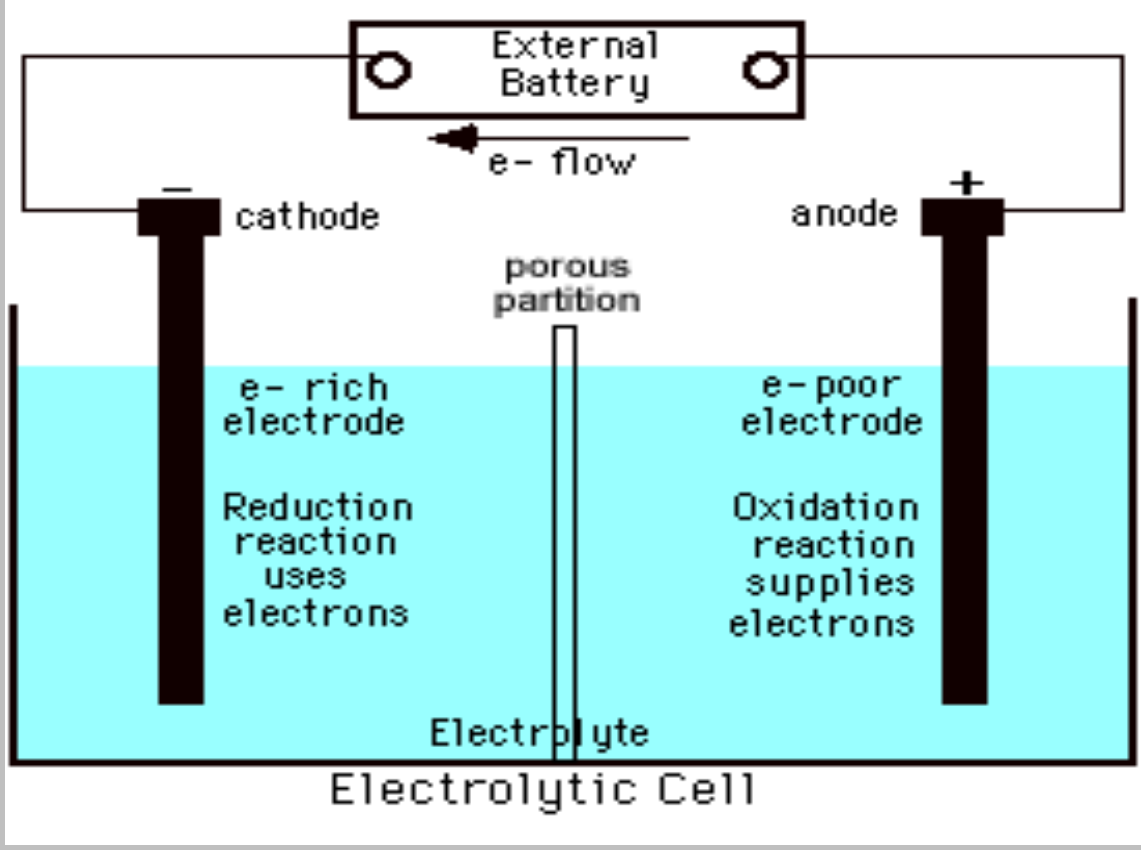
$$E = E^0 - \frac{0.0591}{n}\log(Q)$$

$$E^0 = 0.0\ Volts \qquad n = 2 \qquad Q = \frac{(0.10)}{(1.0)}$$

$$E = 0.0 - \frac{0.0591}{2}\log\left(\frac{0.10}{1.0}\right) = 0.030\ Volts$$

Electrolytic Processes

Electrolytic processes are NOT spontaneous. They have:



Electrolytic Cell

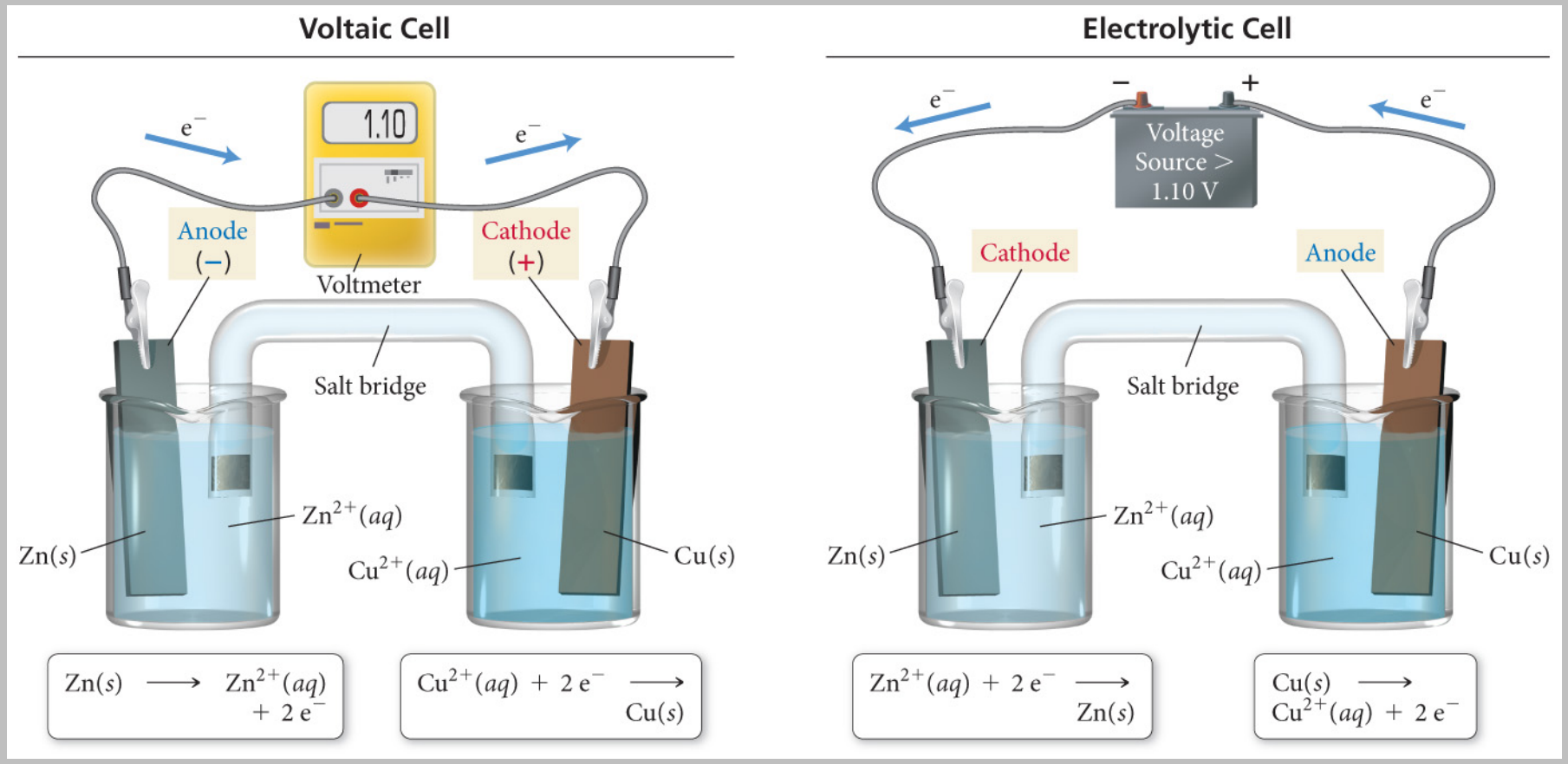
A negative cell potential, ($-E^0$)

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

Electrochemical Cells

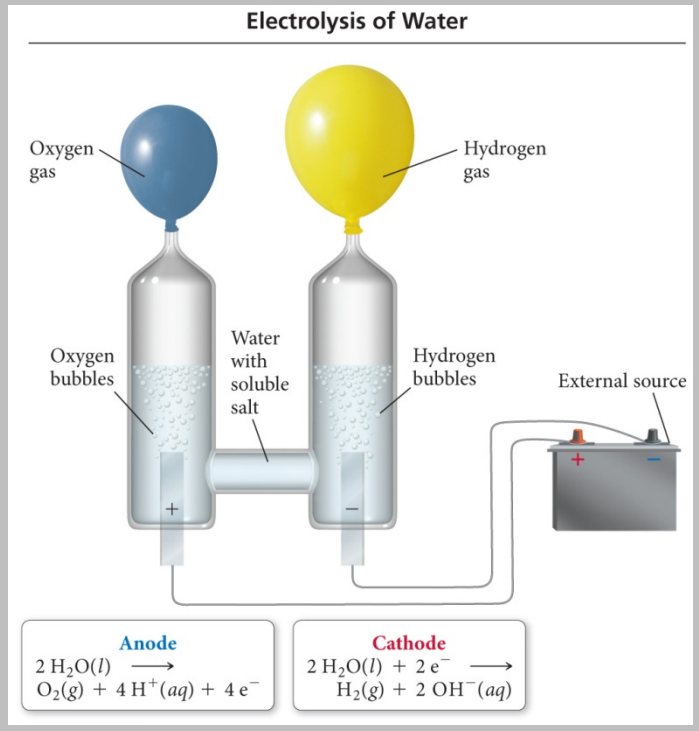
- In all electrochemical cells, oxidation occurs at the anode, reduction occurs at the cathode.
- In voltaic cells
  - Anode is the source of electrons and has a (−) charge.
  - Cathode draws electrons and has a (+) charge.
- In electrolytic cells
  - Electrons are drawn off the anode, so it must have 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

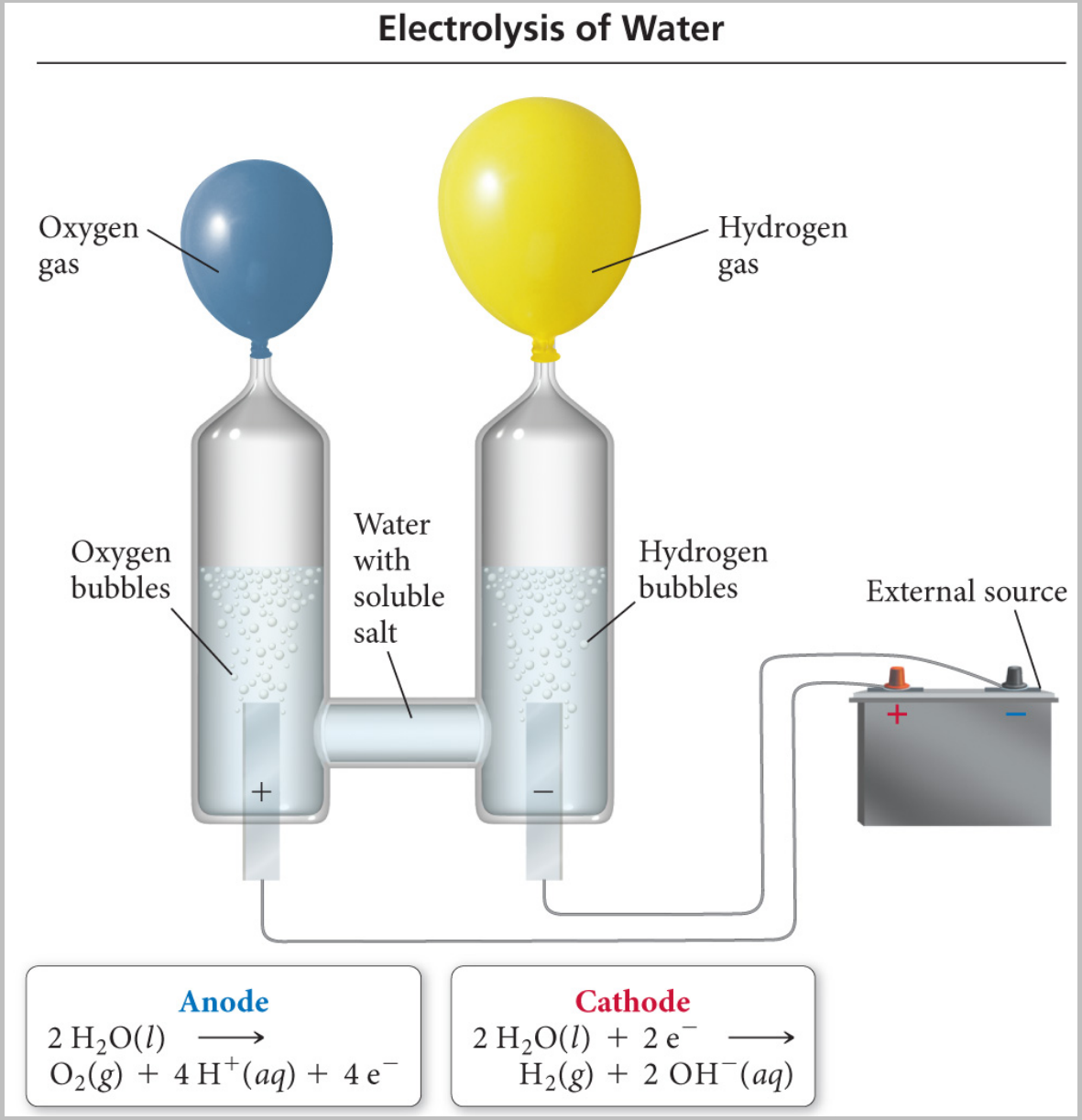


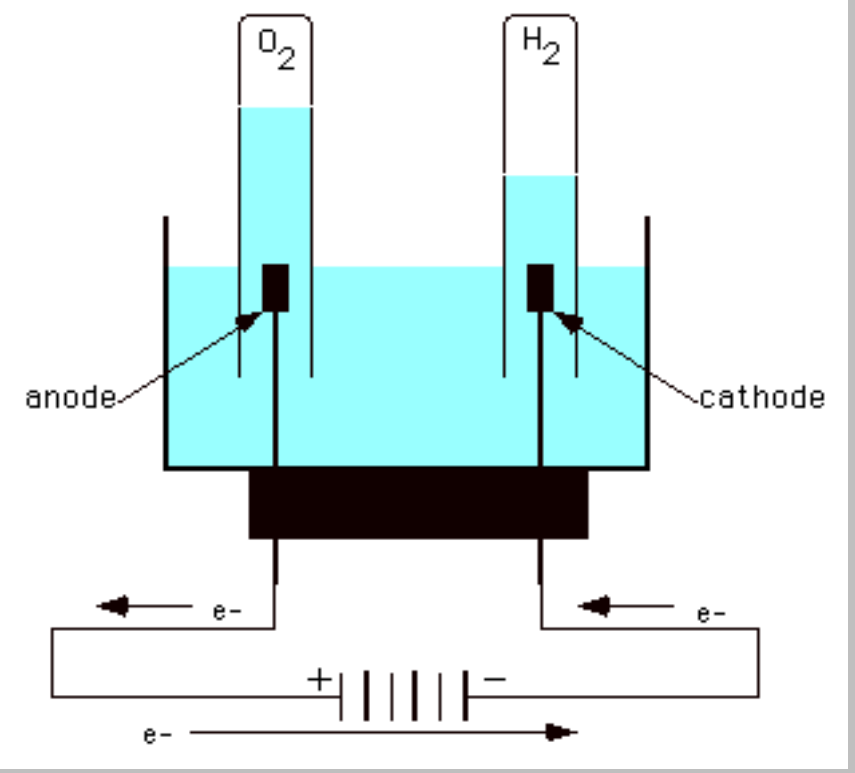
Electrolysis

- **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





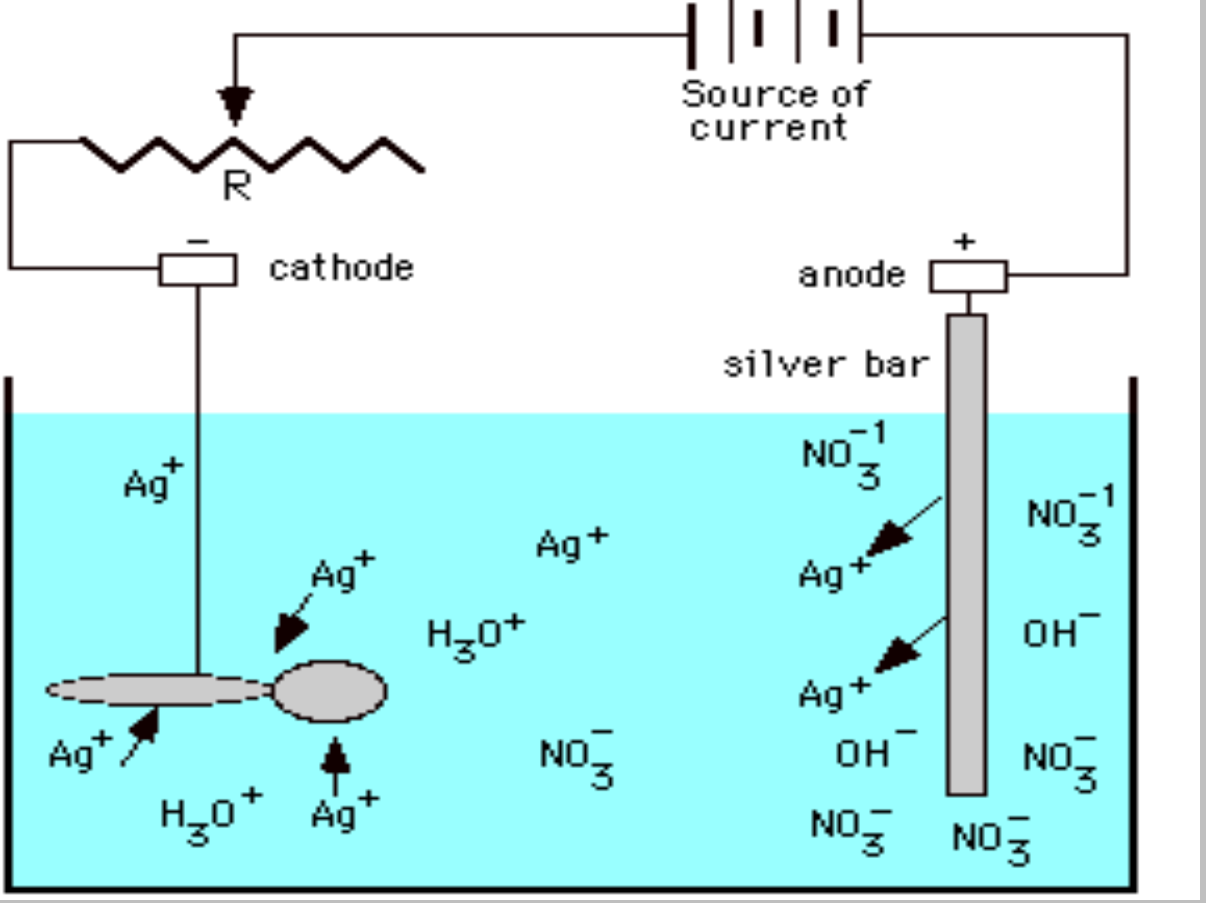
Electrolysis of Water

In acidic solution

Anode rxn: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ -1.23 V

Cathode rxn: $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$ -0.83 V

$2H_2O \rightarrow 2H_2 + O_2$ -2.06 V



Electroplating of Silver

Anode reaction:

$Ag \rightarrow Ag^+ + e^-$

Cathode reaction:

$Ag^+ + e^- \rightarrow Ag$

Electroplating requirements:

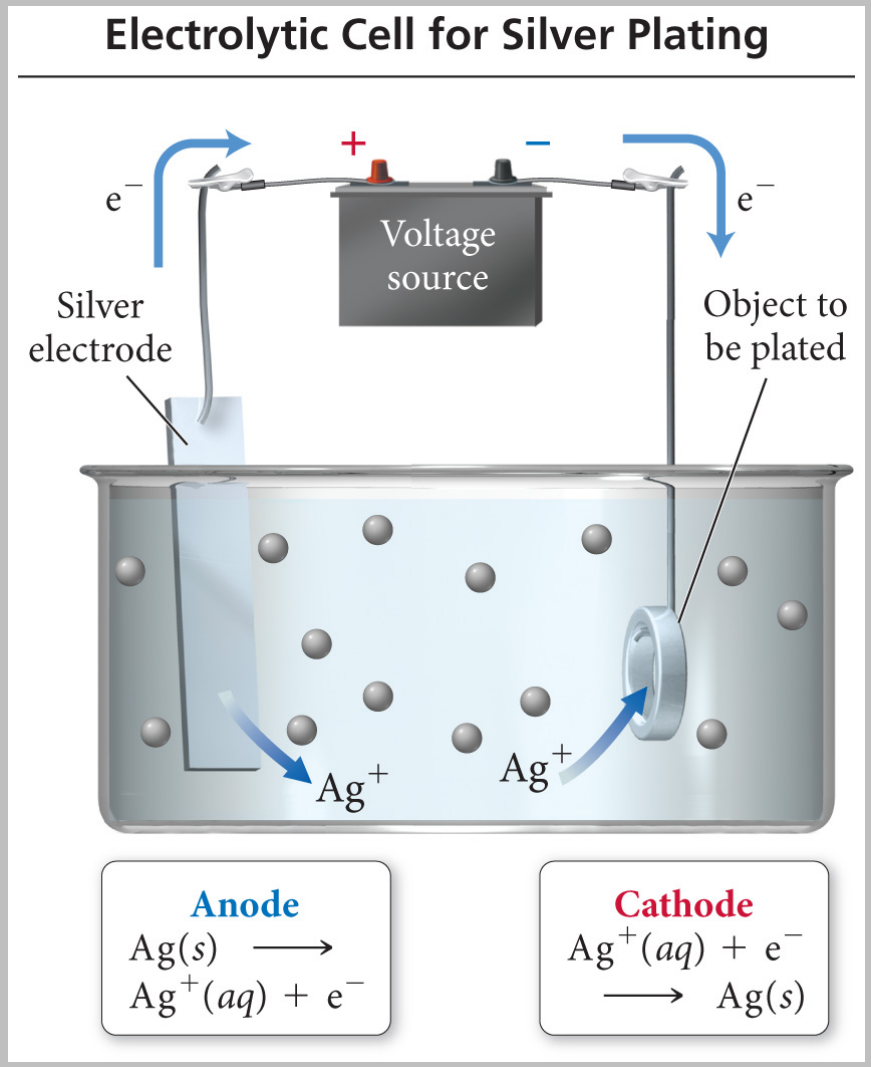
1. Solution of the plating metal
2. Anode made of the plating metal
3. Cathode with the object to be plated
4. Source of current

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.



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?

$$Ag^+ + e^- \rightarrow Ag$$

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

$$= 2.2 \times 10^2\ \text{s}$$

Half-Reactions

- We generally split the redox reaction into two separate **half-reactions**—a reaction just involving oxidation or reduction.
  - The oxidation half-reaction has electrons as products.
  - The reduction half-reaction has electrons as reactants.

$$\underset{0}{3\,Cl_2} + \underset{-1}{I^-} + \underset{+1\ -2}{3H_2O} \rightarrow \underset{-1}{6\,Cl^-} + \underset{+5\ -2}{IO_3^-} + \underset{+1}{6\,H^+}$$

Oxidation: $I^- \rightarrow IO_3^- + 6\,e^-$

Reduction: $Cl_2 + 2\,e^- \rightarrow 2\,Cl^-$

Balancing Redox Reactions by the Half-Reaction Method

- In this method, the reaction is broken down into two half-reactions, one for oxidation and another for reduction.
- Each half-reaction includes electrons.
  - Electrons go on the product side of the oxidation half-reaction—loss of electrons.
  - Electrons go on the reactant side of the reduction half-reaction—gain of electrons.
- Each half-reaction is balanced for its atoms.
- Then the two half-reactions are adjusted so that the electrons lost and gained will be equal when combined.