Unit 9
Electrochemistry

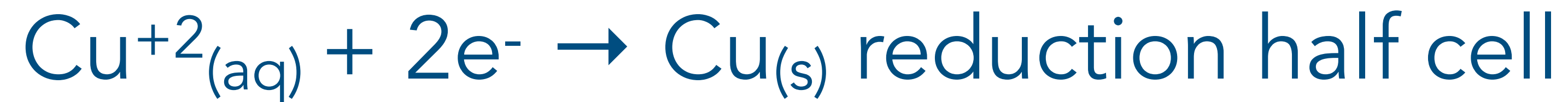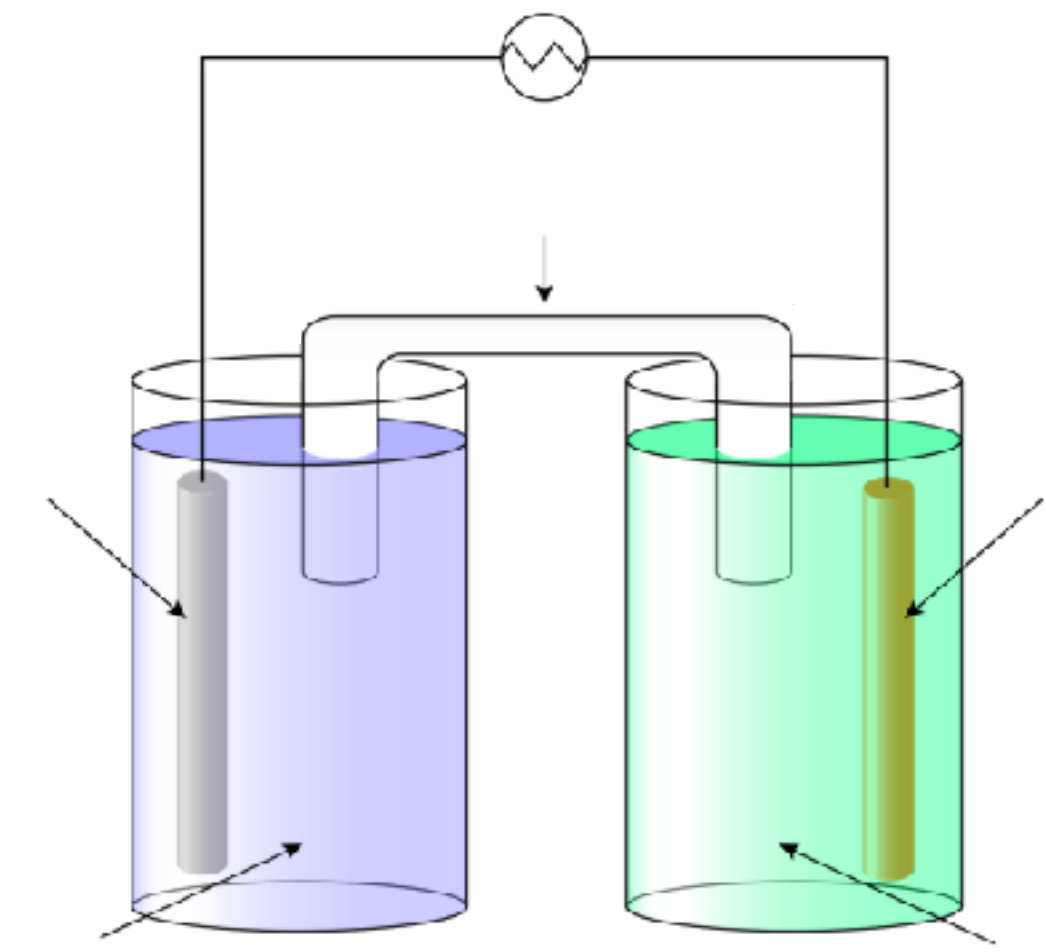# 9.7 - 9.10 Electrochemistry

- Galvanic (Voltaic) & Electrolytic Cells

- Cell Potential & Free Energy

- Electrolysis & Faraday's Law

Voltaic (Galvanic) Cells

- Converts <u>chemical</u> energy to <u>electrical</u> energy.

- Reaction is spontaneous

- Contains 2 half cells and a salt bridge

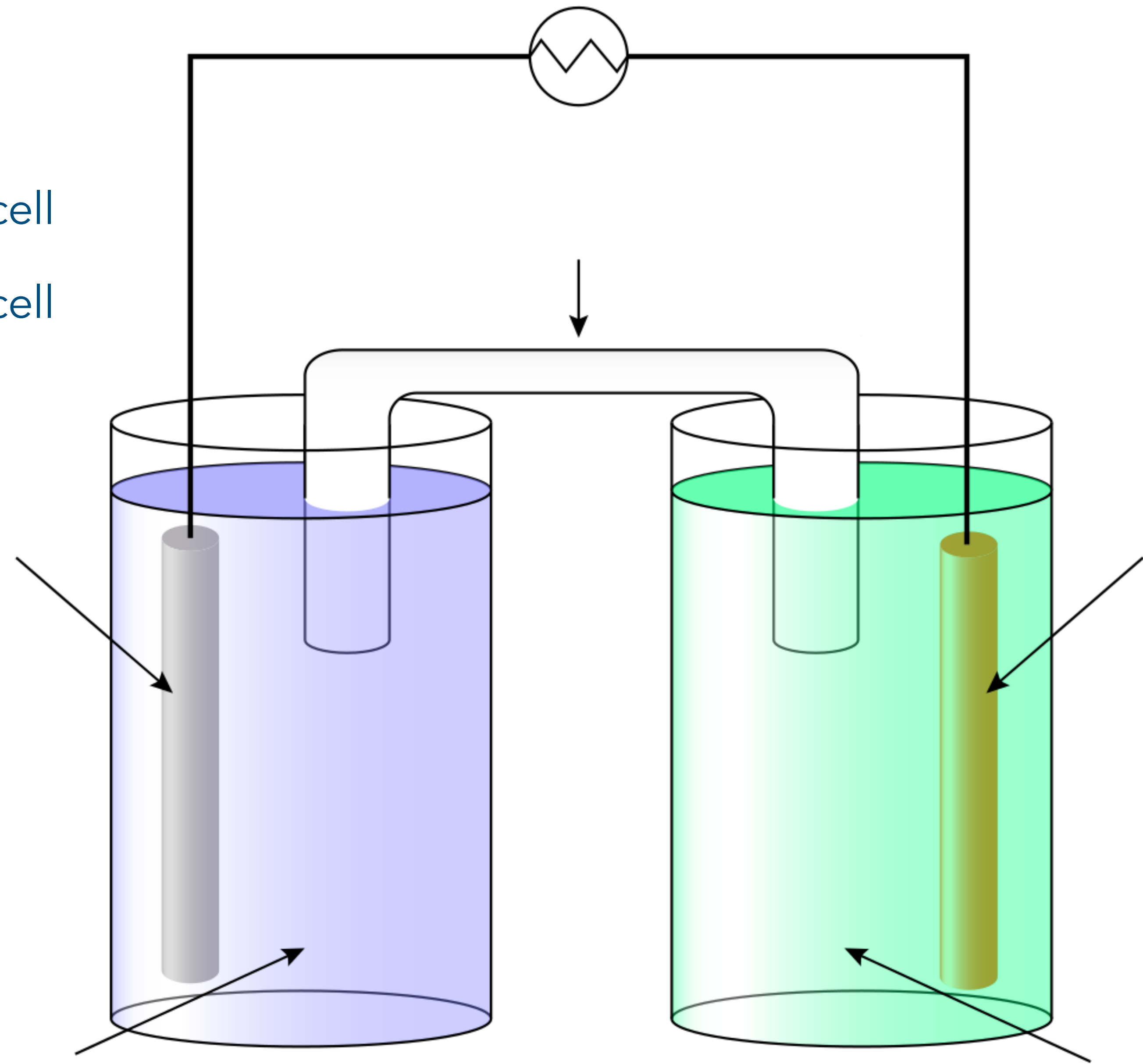- A battery is an example of this type of electrochemical cell

Voltaic (Galvanic) Cells

Copper & Zinc

$$Zn_{(s)} \rightarrow Zn^{+2}_{(aq)} + 2e^- \quad \text{oxidation half cell}$$

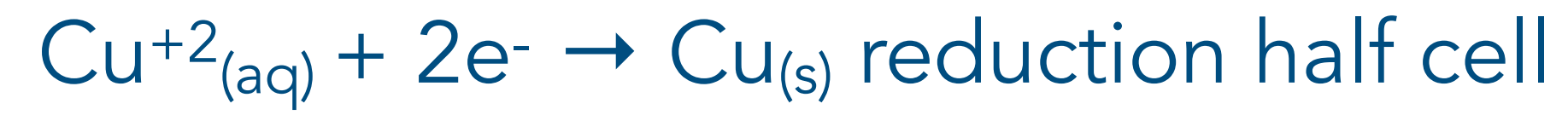$$Cu^{+2}_{(aq)} + 2e^- \rightarrow Cu_{(s)} \quad \text{reduction half cell}$$

- These half cells will generate electrical potentials
  - *Chemical Energy converted to Electrical Energy (from the previous slide)*

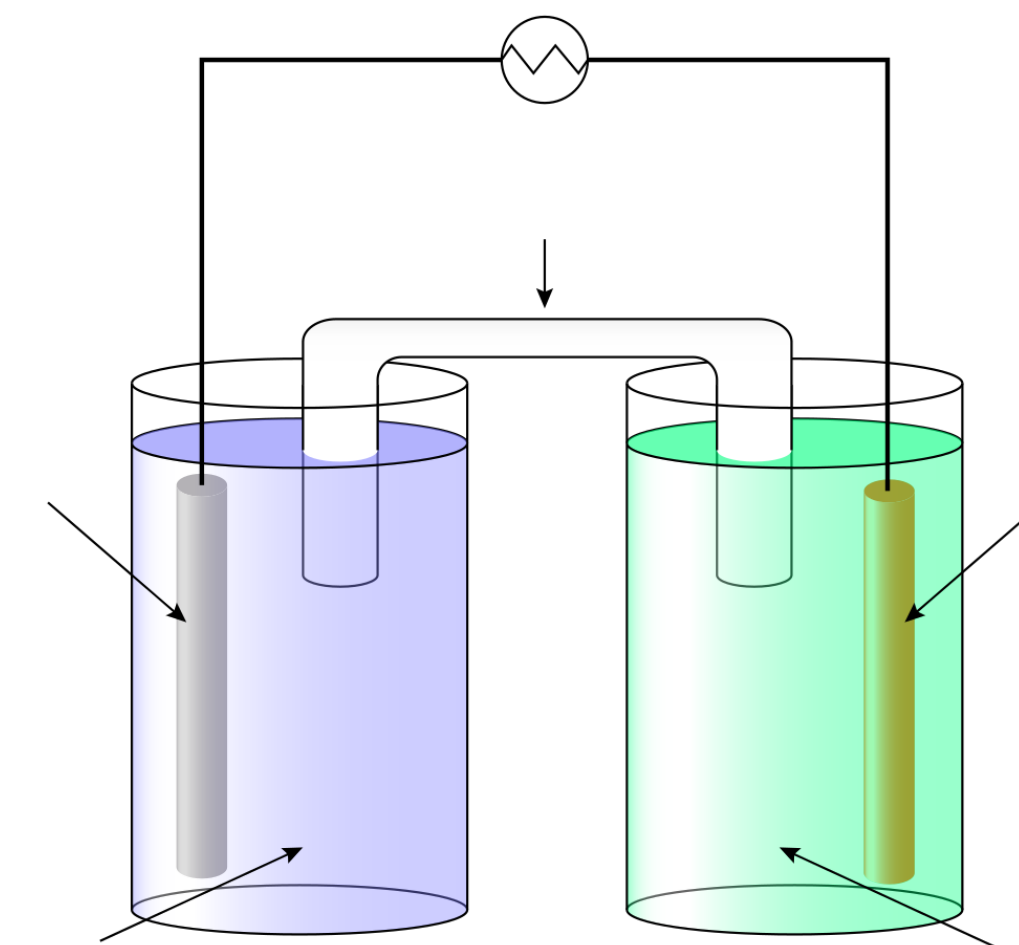# Voltaic (Galvanic) Cells

Copper & Zinc

$Zn_{(s)} \rightarrow Zn^{+2}_{(aq)} + 2e^-$ oxidation half cell

$Cu^{+2}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ reduction half cell

Standard Electrode Potentials

You will be given this data!

- Since half-reactions can either be oxidation or reduction, we need to standardize which electrode the potential (voltage) represents.

- The *standard electrode potential* is always given for the **reduction** reaction.

- Therefore, E° (standard electrode potential) is often called the *standard reduction potential.*

- *This results in a calculation of the **emf** (electromotive force) and is reported in volts (V).*

Example:

You will be given this data!

$$E^0_{cell} = E^0_{half\text{-}cell\ where\ reduction\ occurs} - E^0_{half\text{-}cell\ where\ oxidation\ occurs}$$
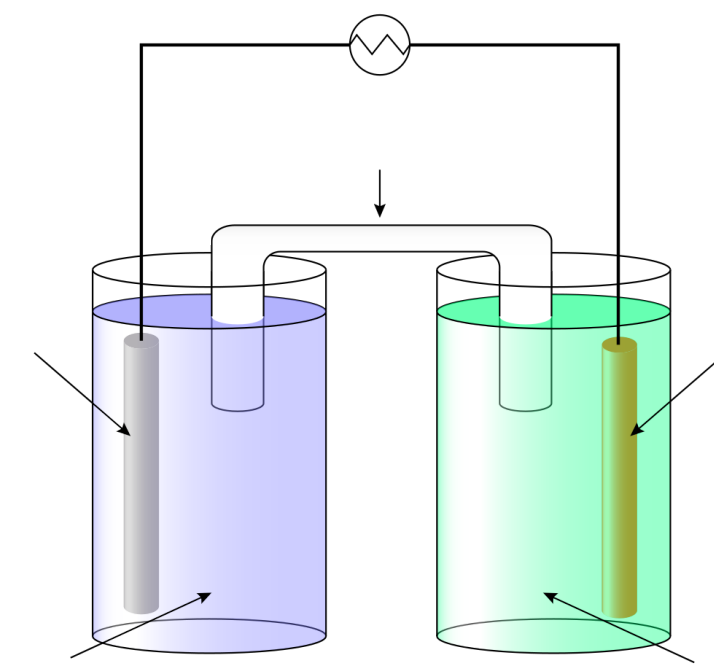
Metal	Reaction	Electrode Potential (V)
Gold	$Au^+ + e^- = Au$	+ 1.692
Silver	$Ag^+ + e^- = Ag$	+0.7996
Copper	$Cu^{2+} + 2e^- = Cu$	+0.342
Iron	$Fe^{3+} + 3e^- = Fe$	-0.037
Lead	$Pb^{2+} + 2e^- = Pb$	-0.126
Nickel	$Ni^{2+} + 2e^- = Ni$	-0.257
Cadmium	$Cd^{2+} + 2e^- = Cd$	-0.403
Iron	$Fe^{2+} + 2e^- = Fe$	-0.447
Zinc	$Zn^{2+} + 2e^- = Zn$	-0.762
Aluminum	$Al^{3+} + 3e^- = Al$	-1.662

Calculate the emf for a voltaic cell constructed from a **zinc** half-cell and a **copper** half-cell. Identify the anode and cathode.

(HINT! - figure out who is more likely to oxidize, find the half reactions and calculate)

▷ All for the reduction reaction
▷ E° → reduction potential
▷ If you switch the sign on the value --> Oxidation
▷ Do not need to be scaled for stoichiometry (# of e-)
▷ The more positive the value, the more readily it is reduced
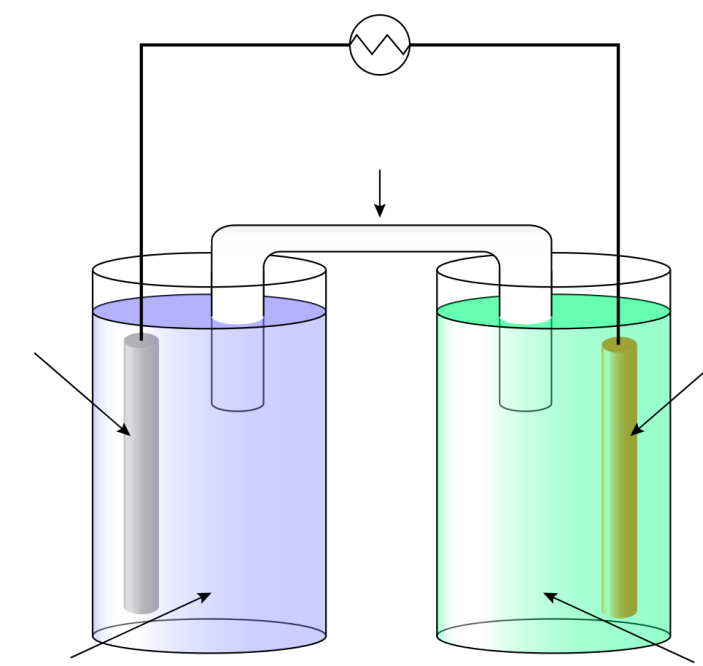
Determining Spontaneity
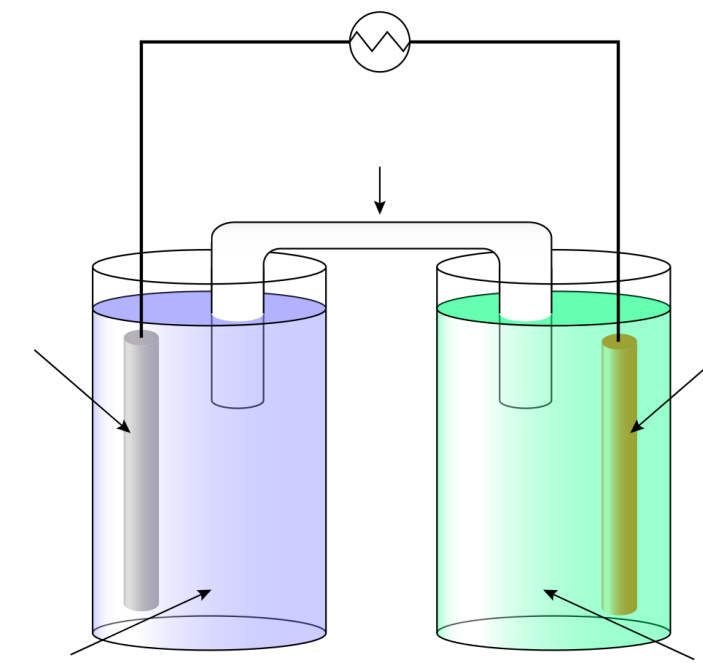
- $E°_{cell}$: positive - the reaction will occur spontaneously

- $E°_{cell}$: negative - the reaction will not occur

- If $E°_{cell}$ is negative, the reverse reaction will be spontaneous

Example: Use E° values to determine whether the reaction is spontaneous under standard conditions:

$$Ni_{(s)} + Mn^{+2}_{(aq)} \rightarrow Ni^{+2}_{(aq)} + Mn_{(s)}$$

Electrode Potential & Free Energy

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

- n = # of moles of electrons transferred in the reaction
- F = the charge carried by 1 mole of electrons, known as the Faraday constant.

- When E_{cell} is positive, ΔG is negative => spontaneous
- When E_{cell} is negative, ΔG is positive => non-spontaneous

Calculate the free energy change at 298 K for the zinc - copper voltaic cell, which has a standard cell potential of +1.10 V.
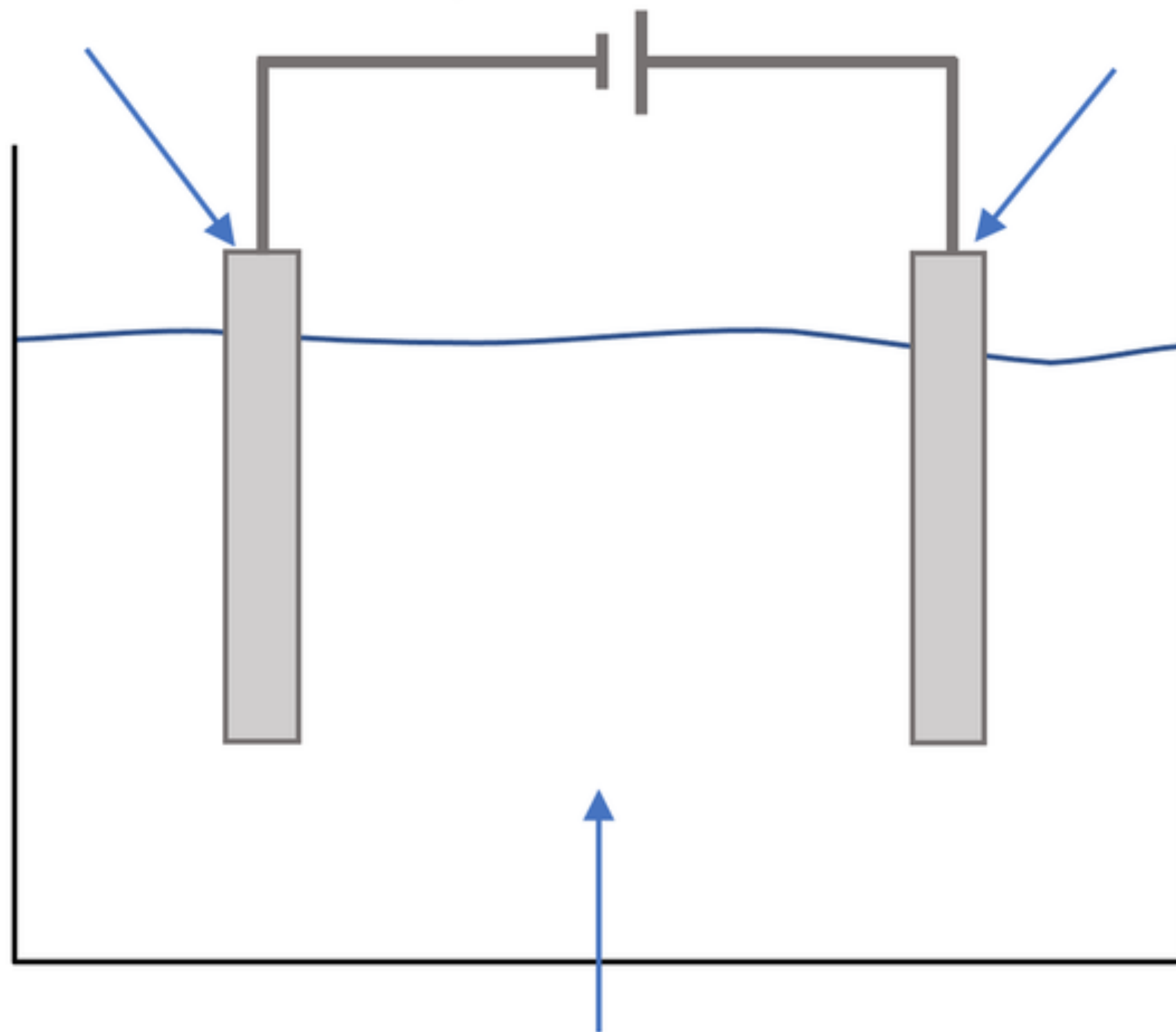
Electrolytic Cells

- Converts electrical energy to chemical energy

- Reaction NOT spontaneous (refer to Table J)

- Needs a power source, such as a battery or plug, to get it going.

- Only needs one container, NO salt bridge needed.

- Use this type of cell for electroplating metals.

Electrolytic Cells

negative electrode

power source

positive electrode

electrolyte

Comparisons

Voltaic Cell	Electrolytic Cell
Energy is released (exothermic) from spontaneous redox reaction	Energy is absorbed (endothermic) to drive non-spontaneous redox reaction
System does work on surroundings	Surroundings (power supply) do work on system (cell)

Factors Affecting the Amount of Product in Electrolysis

- The charge depends on the current (how much electricity is flowing) and the amount of time the current flows for.
- charge = current x time (seconds)
  - So: Charge, Q, measured in coulombs (C), depends on the current, I, measured in amperes (A) and the time, t, measured in seconds (s).
- The charge carried by one mole of electrons, known as a Faraday (F), is 96,485 C.

- We can now relate laboratory measurements to the amounts of products as follows.
  - $Q = I \times t$
  - $F = Q/96,485$
  - number of faradays (F) = moles of electrons
  - Let's do an example…

Example: CuCl$_2$ Electrolytic Cell

- How many grams of Cu are deposited on the cathode of an electrolytic cell containing CuCl$_{2(aq)}$ if a current of 2.00 A is run for 15 min?
- How would the amount differ if the same conditions were applied using CuCl$_{(aq)}$?

Example: AgNO$_3$ Electrolytic Cell

- If a current of 2.00 A is passed through a solution of AgNO$_3$ for 10 minutes it is found that 0.0124 moles of Ag are formed.

  a) How many moles would form if a current of 1.00 A is passed through the same solution for 30 minutes?

  b) What amount of moles of Cu would form if the quantity of electricity in (a) was passed through a solution of CuSO$_4$?

Cell EMF under Nonstandard Conditions

- **The Nernst equation calculates electrochemical cell potential at any known temperature, pressure, and concentration. The equation relates the reduction potential of the cell at a non-standard condition to that of the standard conditions (298 K, 1 atm, and 1 *M* concentration).**

- E_{Cell} = cell potential
- $E°$ = Cell potential under standard conditions
- R = Universal gas constant (8.314 J/(mol•K))
- T = Temperature (K)
- n = Number of electrons transferred in the reaction
- F = Faraday constant (96,485 C/mol)
- Q = Reaction Quotient

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

Example: Nernst Equation

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

- First find the cell potential for the following under **_standard_** conditions:

$$Al(s)\,|\,Al^{3+}(1M)\,||\,Fe^{2+}(1M)\,|\,Fe(s)$$

$Al^{3+} + 3e^- \rightarrow Al$ $E_{red} = -1.706\ V$

$Fe^{2+} + 2e^- \rightarrow Fe$ $E_{red} = -0.409\ V$

Example: Nernst Equation

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

- Find the cell potential for the following under **_nonstandard_** conditions:

$$Al(s) \mid Al^{3+}(0.1M) \mid\mid Fe^{2+}(0.01M) \mid Fe(s)$$

- Since the cell is not in its standard state, we need to pay attention to the concentrations. This requires the use of the balanced redox equation AND the Nernst equation. The n used for the Nernst equation is from the number of electrons in the balanced redox reaction.

- How many electrons are involved in this reaction? (n = ?)

- T = 298 K

- F = 96,485 C/mol

- R = 8.314 J/mol•K

- Calculate the cell potential under nonstandard conditions.

- Which way would the equilibrium shift according to Le Chatelier's Principle?