Electricity from Chemical reactions

Electrochemistry is…

Oxidation–Reduction (it's all about the electrons)

- Reactions where electrons are transferred from one atom to another are called oxidation–reduction reactions.
  - Redox reactions for short
- Atoms that lose electrons are being oxidized (OIL); atoms that gain electrons are being reduced (RIG).

Half-Reactions

- 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.

$Cu^{2+} + 2e^- \rightarrow Cu$

$Zn \rightarrow Zn^{2+} + 2e^-$

Balancing Oxidation-Reduction reactions in acidic solution

- Separate into 2 half equations
- Balance all atoms except O and H
- Add water molecules and H^+ to the equation to balance O and H atoms
- Balance for charge (add up charges on both, sides add e- as needed)
- Write the redox equation by adding two half reactions (making sure the e- cancel out when adding the two half reactions

Balancing Oxidation-Reduction Reactions in Acidic Solution

$$H_2O_2 + Sn^{2+} \longrightarrow H_2O + Sn^{4+}$$

Balancing Oxidation-Reduction reactions in bas solution

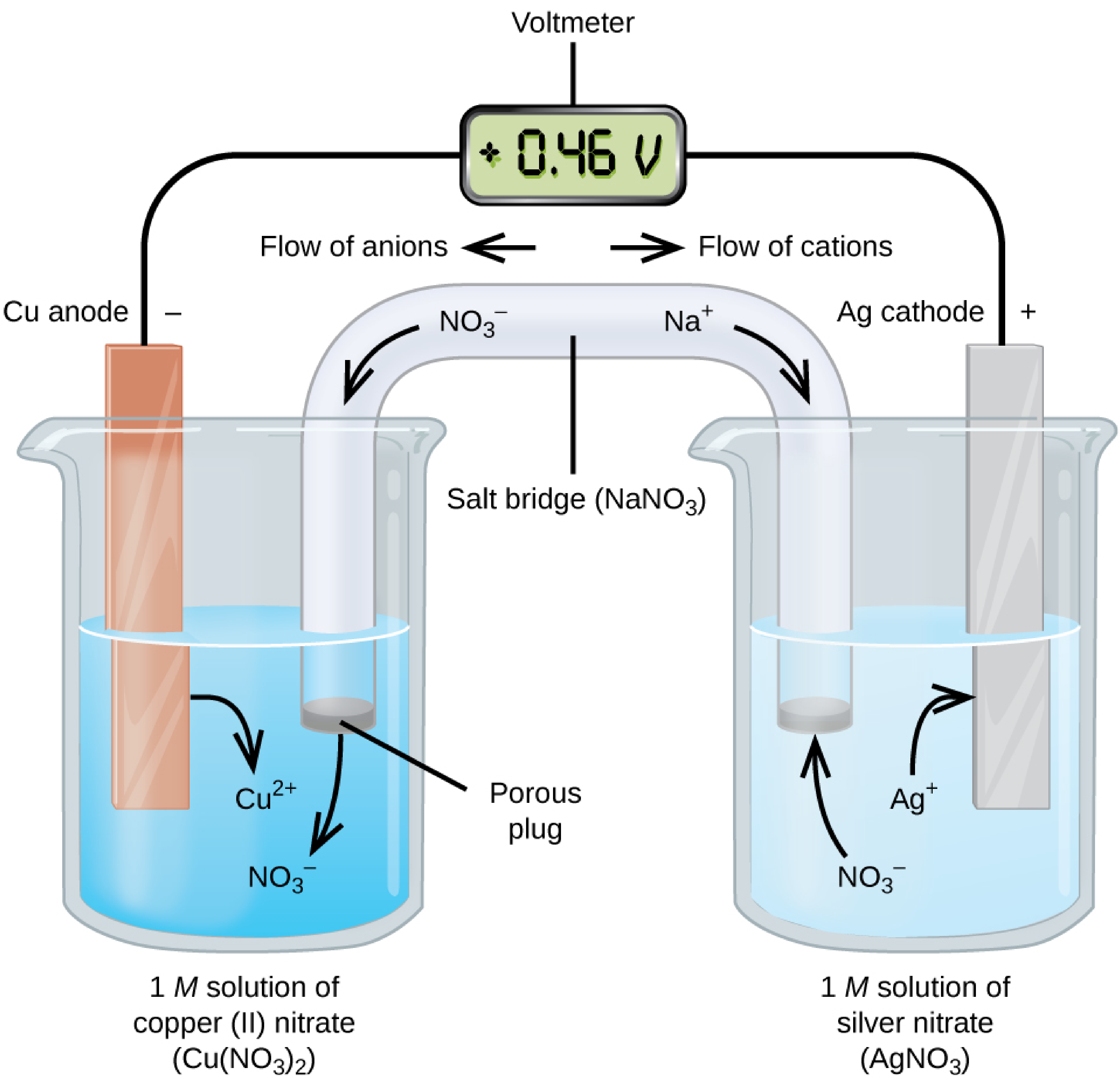
- Separate into two half reactions
- Balance atoms except O and H
- Balance O and H by adding water and/or H+
- Add OH- to neutralize H+
- If OH- and H+ on same side combine to form H_2O, simplify
- Balance for charge (add up charge on both sides, add e- as needed
- Add two half reactions to get redox reaction

Balancing Oxidation-Reduction Reactions in Basic Solution

- $SO_3^{2-}(aq)+Cu(OH)_2(s)\longrightarrow SO_4^{2-}(aq)+Cu(OH)(s)$

Voltaic cell (chemical energy→electrical)

$Cu + 2Ag^+ \rightarrow Ag + Cu^{2+}$ (redox reaction)



Spontaneous process has a + voltage (Ecell) because $\Delta G = -nFE$, where F is Faraday's constant

Cell Potential

- Measured in reference to a standard hydrogen electrode (SHE) that has an Ecell of 0

- The cell potential under standard conditions is called the **standard emf, $E°_{cell}$**.
  - 25 °C, 1 atm for gases, 1 M concentration of solution
  - Sum of the cell potentials for the half-reactions

Reduction reaction	**E^{θ} / V**
$Au^{+} + e^{-} \rightarrow Au$	+1.69
$Au^{3+} + 3e^{-} \rightarrow Au$	+1.40
$2Hg^{2+} + 2e^{-} \rightarrow Hg_2^{2+}$	+0,92
$Hg^{2+} + 2e^{-} \rightarrow Hg$	+0,86
$Ag^{+} + e^{-} \rightarrow Ag$	**+0,80**
$Hg_2^{2+} + 2e^{-} \rightarrow 2Hg$	+0.79
$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$	+0,77
$Cu^{2+} + e^{-} \rightarrow Cu+$	+0,16
$Cr^{3+} + 3e^{-} \rightarrow Cr$	-0.74
$Na^{+} + e^{-} \rightarrow Na$	-2,71

Calculating Cell Potentials under Standard Conditions

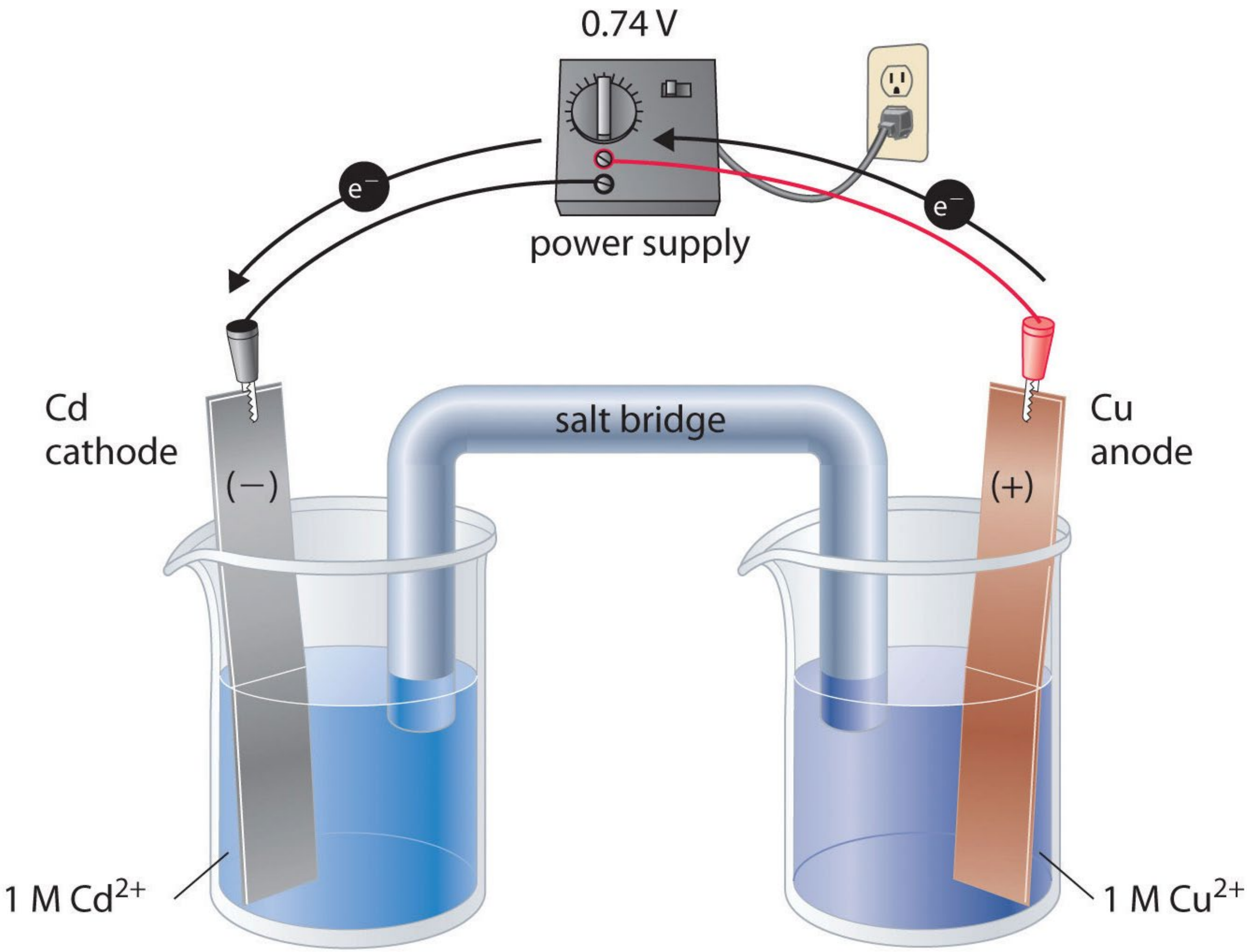
- $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

Cu(s) | 1MCu(NO3)2(aq) ‖ 1MAgNO3(aq) | Ag(s)

Voltaic (galvanic) cell E°cell is + (spontaneous redox rxn)

Electrolytic cell E°cell is – (non-spontaneous redox rxn)

Electrolytic Cells



cathode:
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$

anode:
$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

Overall reaction: $Cd^{2+}(aq) + Cu(s) \rightarrow Cd(s) + Cu^{2+}(aq)$

Electrolysis

- In electrolysis we use electrical energy to overcome the energy barrier of a nonspontaneous reaction, allowing it to occur.

- The reaction that takes place is the opposite of the spontaneous process.

  $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$ spontaneous

  $2\ H_2O(l) \rightarrow 2\ H_2(g) + O_2(g)$ electrolysis

- Some applications are (1) metal extraction from minerals and purification, (2) production of H_2 for fuel cells, and (3) metal plating.

Deposition

- Example 1 : In the electrolysis of a solution of Ni^{2+} (aq), metallic Ni(s) deposits on a cathode. Using a current of 0.150 A for 12.2 min, what mass of nickel will form?

The Nernst Equation

- For a cell under non-standard conditions
- $E = E^o - (RT/nF) \ln Q$,
  - Where R is the gas law constant 8.314472 J/K mol, n is the number of moles of electrons transferred , F is the Faraday constant (9.6485338×10^4 C/mol) , Q is the reaction quotient
  - RT/nFlnQ “corrects” the standard potential under non-standard conditions or concentrtations

E^o cell and the equilibrium constant (K)

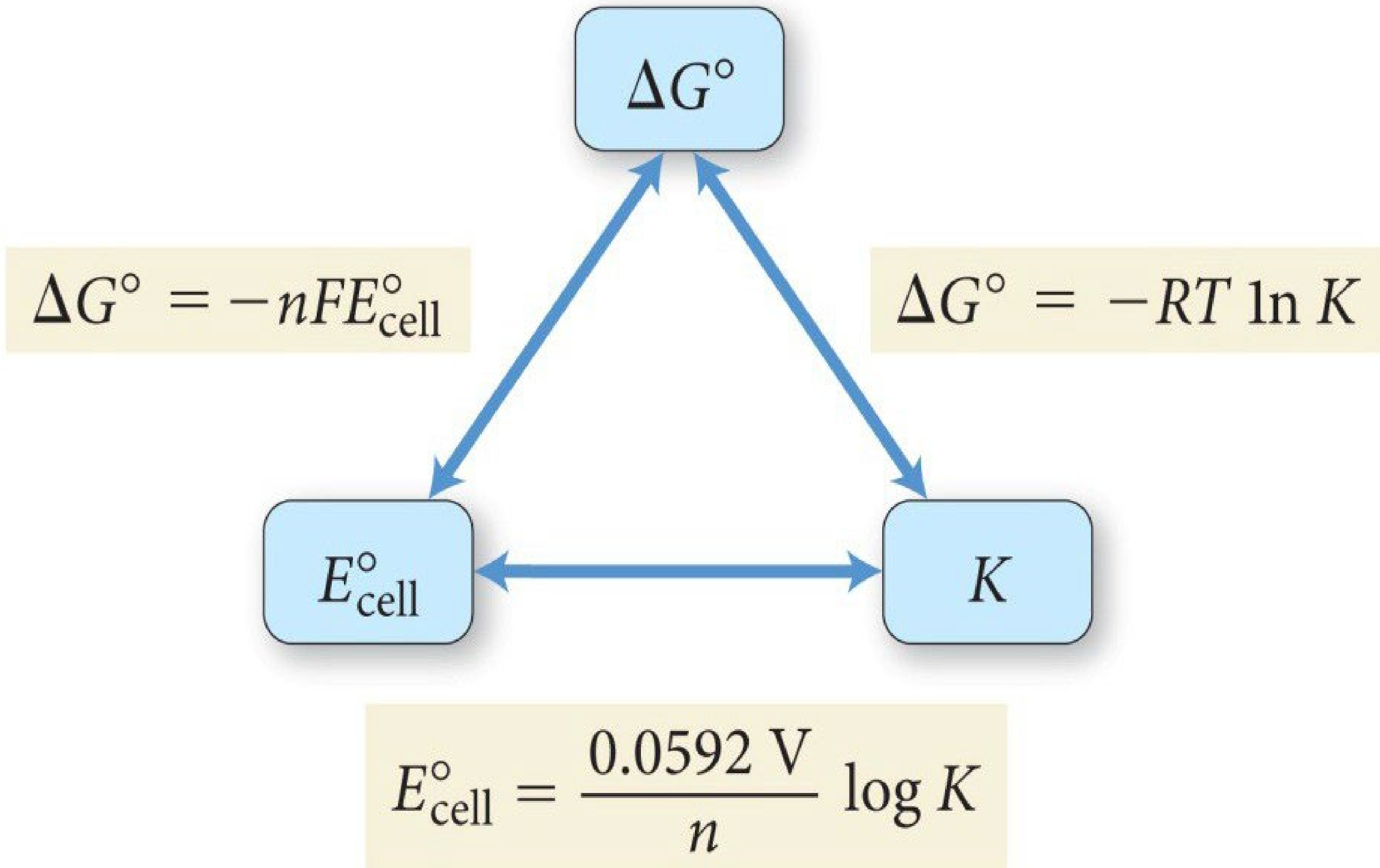
- When E cell = 0 , the reactants and products are at equilibrium , so Q = K
- Substituting the into the Nernst equation :

- $\ln K = nE^o/0.0257$ at 25ºC

ΔG and E°_{cell}

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

E°_{cell}, ΔG°, and K



Ecell = - (0.0257/n) ln K