# Electrochemistry, Free Energy & Equilibrium

**Unit:** Electrochemistry

### Knowledge/Understanding Goals:

* how standard voltage relates to free energy, spontaneity of reaction, and the activity series

### Skills:

* calculate standard voltage E° for cells at standard conditions
* calculate relationships between E°, ΔG° and K
* calculate E° at different concentrations or gas pressures

### Notes:

## Electrochemistry and Free Energy

As with all chemical reactions, the Gibbs Free Energy is the driving force. If ΔG is negative, the reaction is spontaneous, and proceeds. This means a positive E° corresponds with a negative ΔG. The relationship between the two is:



where:

ΔG° = Gibbs free energy (J per mole of reaction)

*n* = moles of electrons transferred per mole of reaction as written

= Faraday’s constant 

E° = standard voltage

## Effect of Concentration

Recall from thermodynamics that the free energy of a reaction that is not at equilibrium is given by the equation:

ΔG = ΔG° + RT ln Q

A similar calculation is necessary in voltaic cells when the concentrations are different from 1 M and/or the gas pressures are different from 1 atm:



This relationship is called the Nernst Equation, after its discoverer, Walther Nernst.

Note that as the reactions proceed in a voltaic cell, the concentrations of ions at the cathode decrease steadily, causing the voltage to decrease steadily. When the concentration (and voltage) reach zero, the voltaic cell is “dead” (produces no voltage).