# Appendix 1: Relation between Free Energy and Electrode Potential, and Derivation of the Nernst Equation

We can define a value $\Delta G^o$ for any chemical (or electrochemical) reaction. G is termed the Gibbs free energy, and $\Delta G^o$ for a reaction determines the difference between the free energies of the reactants and products when all of the components are present at standard-state conditions (room temperature, 298K; and unit activity of species, i.e. one molar concentrations for solutions or one atmosphere pressure for gaseous reactions).

If $\Delta G^o < 0$, the reaction is favourable (i.e. it shifts to the right) and occurs spontaneously (i.e. energy is given off)
If $\Delta G^o > 0$, the reaction is unfavourable (i.e. energy is required)
If $\Delta G^o = 0$, the reaction is in equilibrium.

$\Delta G^o$ can also be defined in terms of the equilibrium constant, K, for the reaction.
$\Delta G^o = -RT \ln K$.

When the chemical species are not in their standard states, we use the term $\Delta G$ to describe the energy change for the reaction.

$$\Delta G = \Delta G^o + RT \ln Q$$

Q is the reaction quotient. It is like K except it is computed using the current concentrations or pressures, and not the equilibrium ones.
(For a general reaction: $aA + bB = cC + dD$, $Q = [C]^c[D]^d / [A]^a[B]^b$, where [ ] denotes concentration).

Note when $Q=K$, $\Delta G = 0$ and then the driving force for the forward (or backward) reactions are zero: the system is in dynamic equilibrium.

A schematic plot of $\Delta G$ versus $\ln Q$ is shown below:
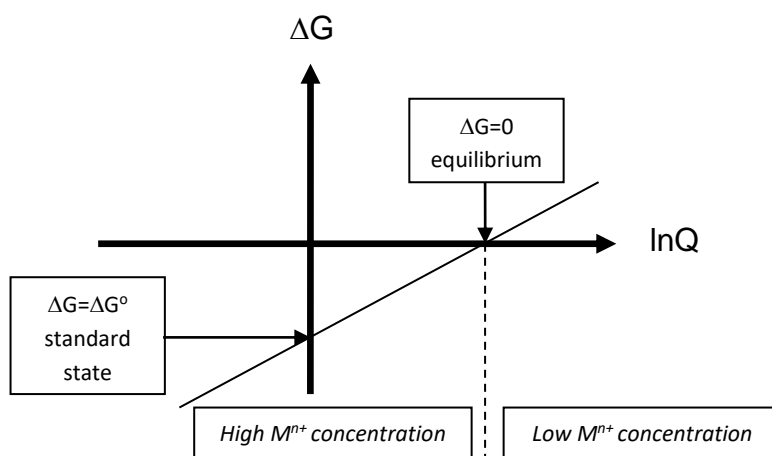
For an electrode in contact with its own ions: $M^{n+} + ne- \leftrightarrow M$ we can write:

$$\Delta G = \Delta G^O + RT \ln Q \quad (= -RT \ln K + RT \ln Q)$$

$$\Delta G = \Delta G^O + RT \ln \frac{[M]}{[M^{n+}]}$$

For ideal solutions, Henry's law applies, where [M] is equivalent to the *activity*, *a*, of M. We can then write:

$$\Delta G = \Delta G^o + RT \ln \frac{a_M}{a_M^{n+}}$$

Now, for a system which performs electrical energy reversibly (as a result of spontaneous reaction) the magnitude of the energy change is a function of the charge transported and the electrical potential difference. The standard free energy change for the reaction, $\Delta G^o$, is given by:

$$\Delta G^o = -zE^oF$$

$z$= number of electrons involved in reaction (per mol. of product)
$E^o$ = standard reversible electrode potential
$F$ = Faraday's constant

And so,

$$-zEF = -zE^oF + RT \ln \frac{a_M}{a_M^{n+}}$$

Dividing through by -nF yields:

$$E = E^o - \frac{RT}{zF} \ln \frac{a_M}{a_M^{n+}}$$

or, more generally:

$$E = E^o - \frac{RT}{zF} \ln \frac{a_{red}}{a_{oxid}} \qquad \textbf{NERNST EQUATION}$$