Nernst Equation, Equilibrium and Potential

By S.E. Van Bramer, 2/22/98

Starting with the Nernst Equation for the equilibrium; Ox + n e⁻ <--> Red :

\[ E_{\text{cell}} = E_{\text{std\_cell}} + \frac{R \cdot T}{n \cdot F} \ln \left( \frac{C_{\text{ox}}}{C_{\text{red}}} \right) \]

Typical form of Nernst Equation

\left( E_{\text{cell}} - E_{\text{std\_cell}} \right) = \frac{n \cdot F}{R \cdot T} \ln \left( \frac{C_{\text{ox}}}{C_{\text{red}}} \right)

Rearrange

\[ \frac{C_{\text{ox}}}{C_{\text{red}}} = e^{\left( E_{\text{cell}} - E_{\text{std\_cell}} \right) \frac{n \cdot F}{R \cdot T}} \]

Gives the ratio of oxidized to reduced form of redox pair.

\[ \frac{C_{\text{ox}}}{C_{\text{red}}} = e^{\left( \Delta E \right) \frac{n \cdot F}{R \cdot T}} \]

Reduced variables to \( \Delta E \), the difference between the equilibrium potential and the applied potential.

This function describes how the equilibrium ration of oxidized and reduced form depend upon the applied potential. Notice that

if \( \Delta E = 0 \) Where the applied potential is the same as the standard cell potential. Then the exponent is 0, so the ratio of \( C_{\text{ox}}/C_{\text{red}} = 1 \). This is the conditions for the standard state.

If \( \Delta E > 0 \) Where the applied potential is positive of \( E^0 \). Now the exponent is greater than 0 so the ratio of \( C_{\text{ox}}/C_{\text{red}} > 1 \). The concentration of the oxidized form is greater than the concentration of the reduced form. This is consistent with the half reaction because an applied potential positive of \( E^0 \) pulls e⁻’s off and causes oxidation.

If \( \Delta E < 0 \). Where the applied potential is negative of \( E^0 \). Now the exponent is less than 0 so the ratio of \( C_{\text{ox}}/C_{\text{red}} < 1 \). The concentration of the oxidized form is less than the concentration of the reduced form. This is consistent with the half reaction because an applied potential negative of \( E^0 \) pushes e⁻’s on and causes reduction.
Now let’s take a graphical look at this function.

Look at a range of applied potentials for a reaction with 1 electron exchanged:
\[ \Delta E := -0.4\text{-volt}, -0.39\text{-volt}, 0.4\text{-volt} \]
\[ n := 1 \]

Some Constants for electrochemistry:
\[ R := 8.31441\text{ joule}\cdot\text{K}^{-1}\cdot\text{mole}^{-1} \]
\[ T := 298\text{ K} \]
\[ F := 96484.6\text{ coul}\cdot\text{mole}^{-1} \]

The functions to describe \( \alpha \) (the ratio of oxidized over reduced) and the concentration of each species (assuming a total concentration of 1).

\[ \alpha(\Delta E, n) := e^{\frac{\Delta E (nF)}{RT}} \]
\[ C_{\text{red}}(\Delta E, n) := \frac{1}{1 + \alpha(\Delta E, n)} \]
\[ C_{\text{ox}}(\Delta E, n) := 1 - C_{\text{red}}(\Delta E, n) \]
Now, let's see what happens if the number of electrons changes: \( n = 2 \)

\[
\begin{align*}
\Delta E & = n \ln \left( \frac{C_{\text{red}}}{C_{\text{ox}}} \right)
\end{align*}
\]

\( \Delta E \) is plotted against concentration for two different values of \( n \).

\( n = 3 \)
Now, let's see what happens if the number of electrons changes: \( n := 3 \)