Nernst Equation, Equlibrium and Potential

Starting with the Nernst Equation for the equlibrium; Ox + *n* e^- <--> Red :

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

Typical form of Nernst Equation

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

Rearange

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

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

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

Reduced variables to ΔE, the difference between the equlibrium potential and the applied potential.

This function describes how the equlibrium 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 $C_{ox}/C_{red} = 1$. This is the conditions for the standard state.

If $\Delta E > 0$ Where the applied potential is positive of E^o. Now the exponent is greater than 0 so the ratio of $C_{ox}/C_{red} > 1$. 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^o pulls e^-'s off and causes oxidation.

If $\Delta E < 0$. Where the applied potential is negative of E^o. Now the exponent is less than 0 so the ratio of $C_{ox}/C_{red} < 1$. 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^o 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:

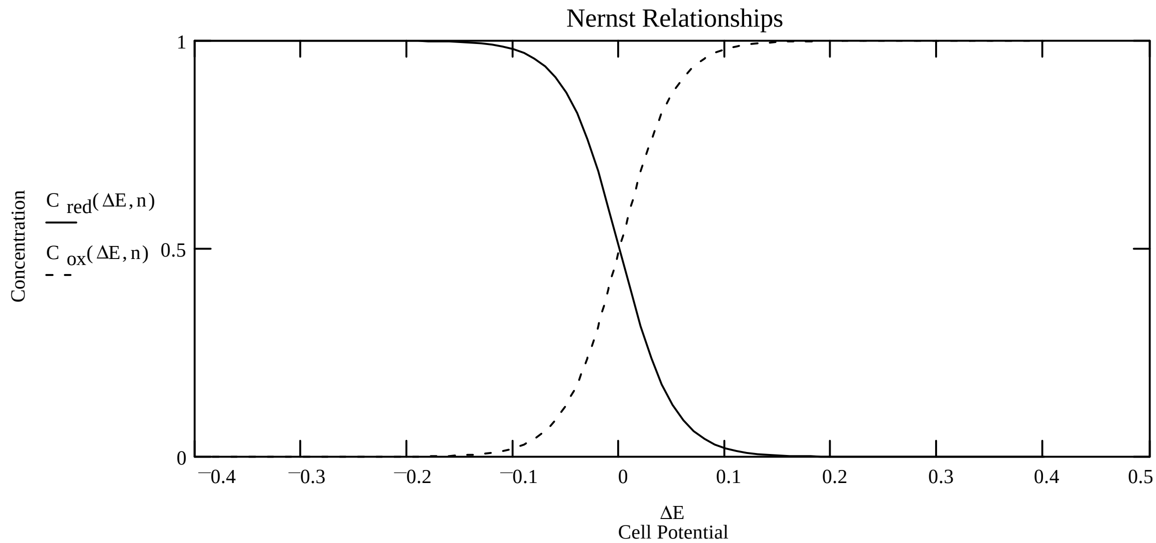
$\Delta E := -0.4\cdot volt, -0.39\cdot volt .. 0.4\cdot volt$ $\qquad$ $n := 1$

Some Constants for electrochemistry:

$R := 8.31441\cdot joule\cdot K^{-1}\cdot mole^{-1}$ $\qquad$ $T := 298\cdot K$ $\qquad$ $F := 96484.6\cdot coul\cdot mole^{-1}$

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

$$\alpha(\Delta E, n) := e^{\Delta E\cdot\left(\frac{n\cdot F}{R\cdot T}\right)} \qquad C_{red}(\Delta E, n) := \frac{1}{1+\alpha(\Delta E, n)} \qquad C_{ox}(\Delta E, n) := 1 - C_{red}(\Delta E, n)$$



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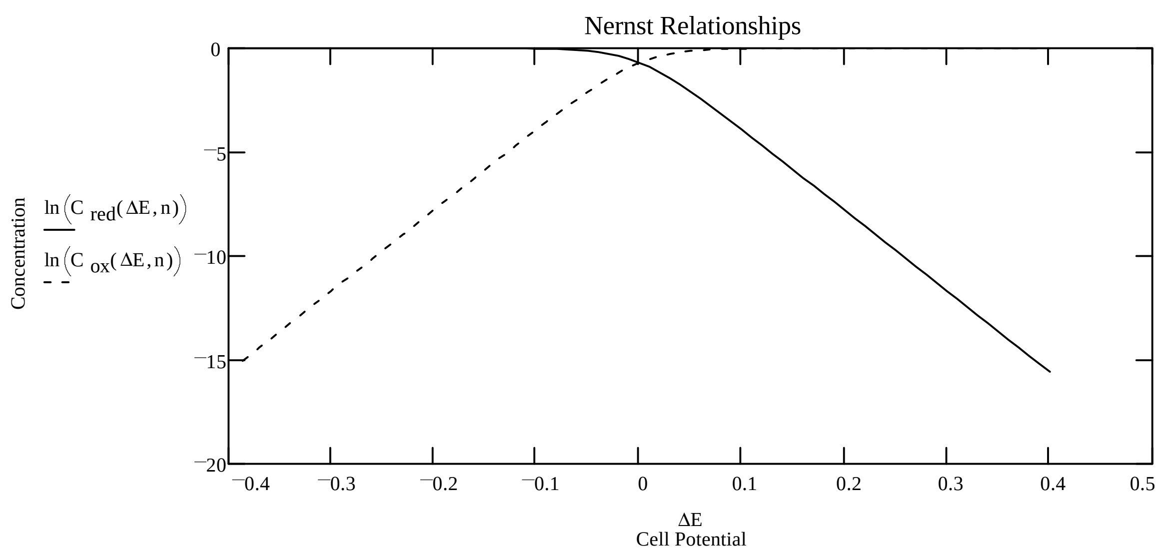
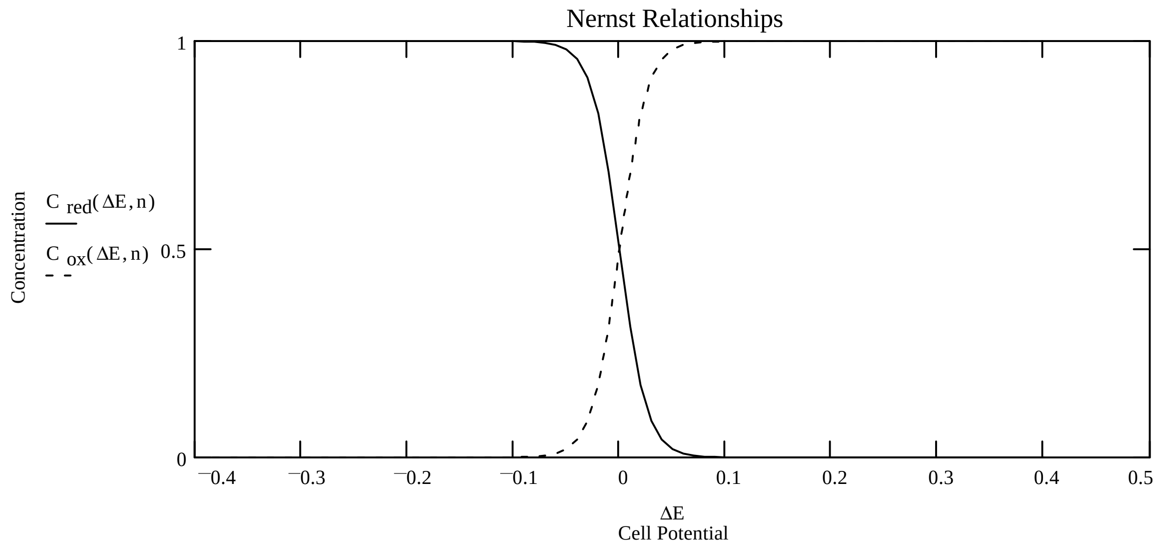


Now, let's see what happens if the number of electrons changes: $n := 2$



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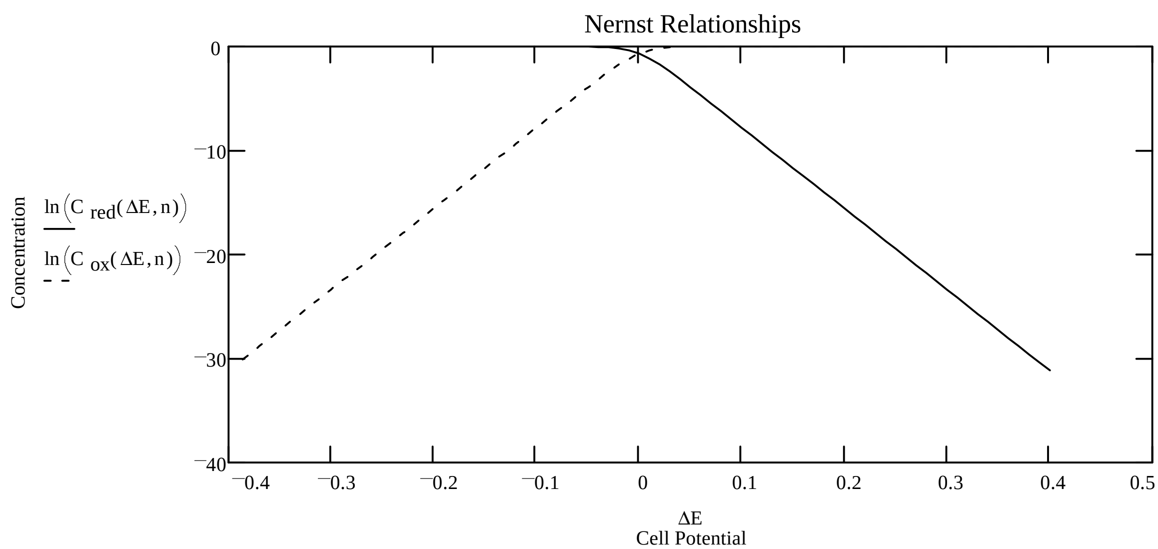

$n := 3$