

# Nernst Equation, Equilibrium and Potential

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Starting with the Nernst Equation for the equilibrium;  $Ox + n e^- \rightleftharpoons Red$  :

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

Typical form of Nernst Equation

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

Rearrange

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

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  $\Delta E$ , 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  $C_{ox}/C_{red} = 1$ . This is the conditions for the standard state.

If  $\Delta E > 0$  Where the applied potential is positive of  $E^\circ$ . 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  $E^\circ$  pulls  $e^-$ 's off and causes oxidation.

If  $\Delta E < 0$ . Where the applied potential is negative of  $E^\circ$ . 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  $E^\circ$  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:

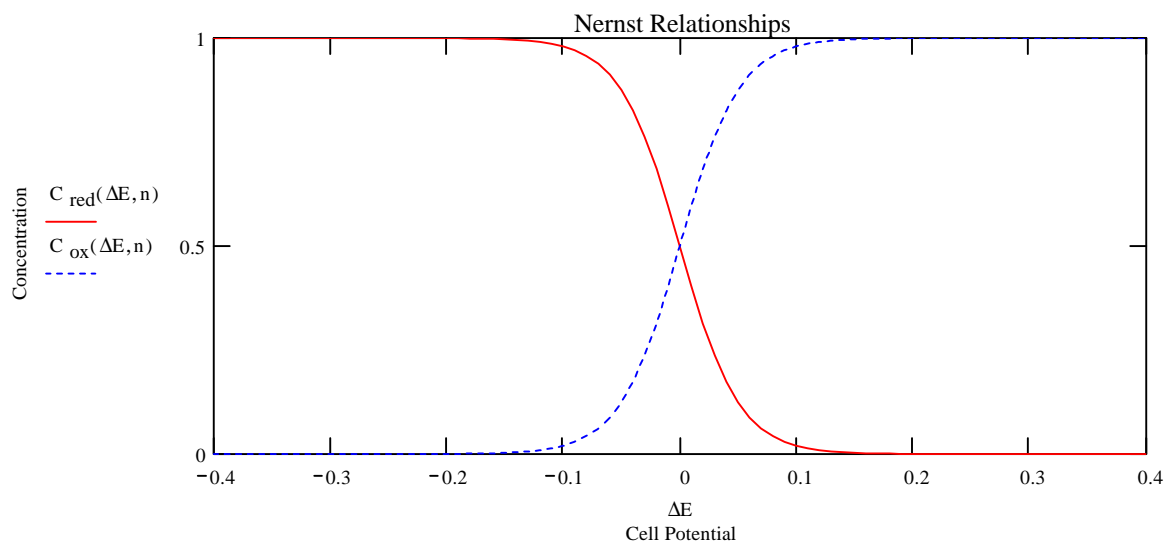
$$\Delta E := -0.4 \cdot \text{volt}, -0.39 \cdot \text{volt}.. 0.4 \cdot \text{volt} \quad n := 1$$

Some Constants for electrochemistry:

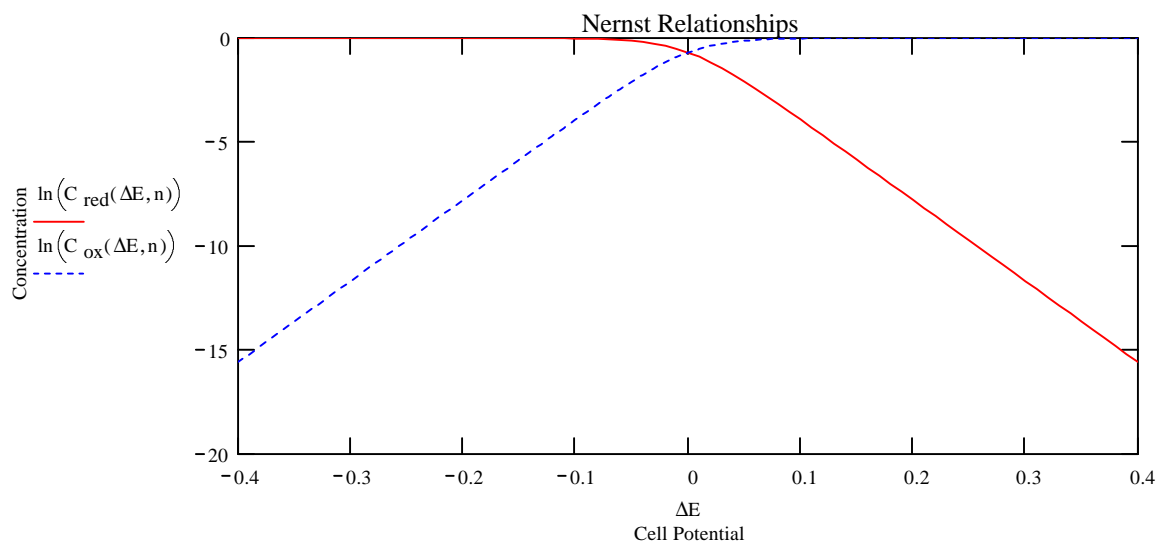
$$R := 8.31441 \cdot \text{joule} \cdot \text{K}^{-1} \cdot \text{mole}^{-1} \quad T := 298 \cdot \text{K} \quad F := 96484.6 \cdot \text{coul} \cdot \text{mole}^{-1}$$

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

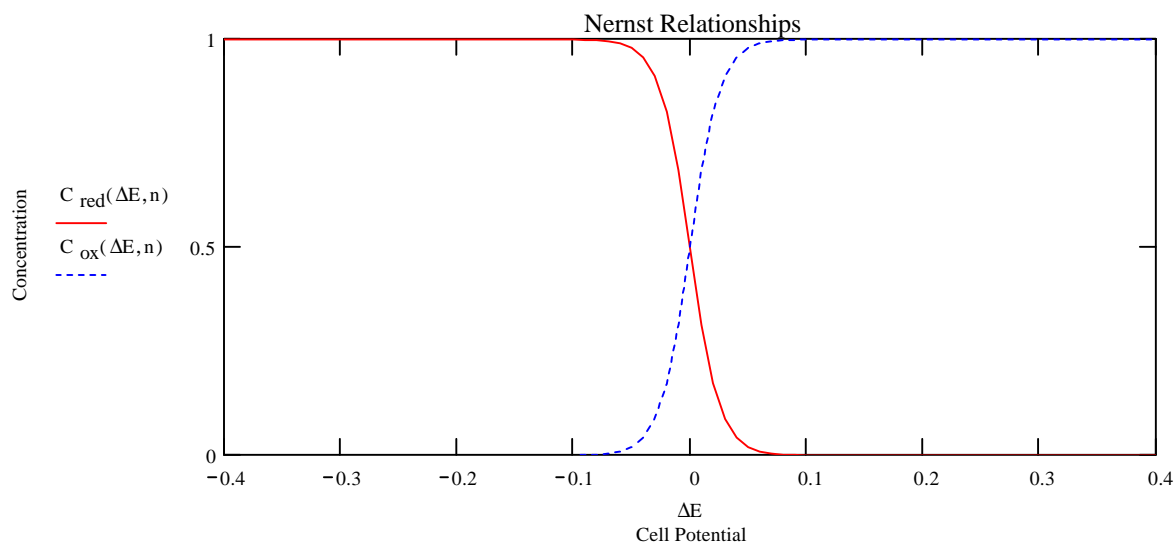
$$\alpha(\Delta E, n) := e^{\frac{\Delta E \cdot (n \cdot F)}{R \cdot T}} \quad C_{\text{red}}(\Delta E, n) := \frac{1}{1 + \alpha(\Delta E, n)} \quad C_{\text{ox}}(\Delta E, n) := 1 - C_{\text{red}}(\Delta E, n)$$



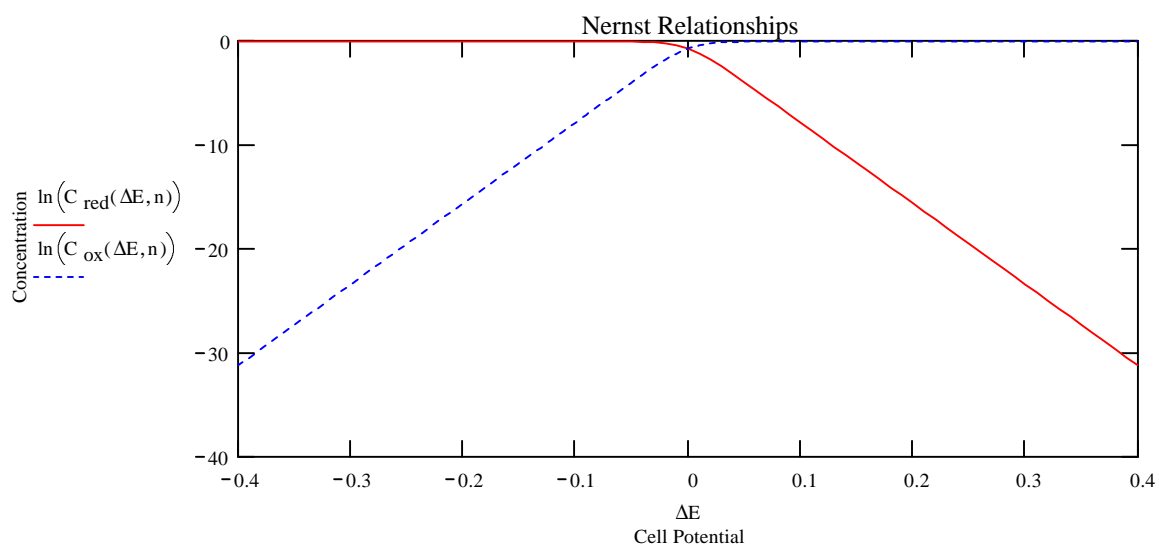
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Now, let's see what happens if the number of electrons changes:  $n := 2$

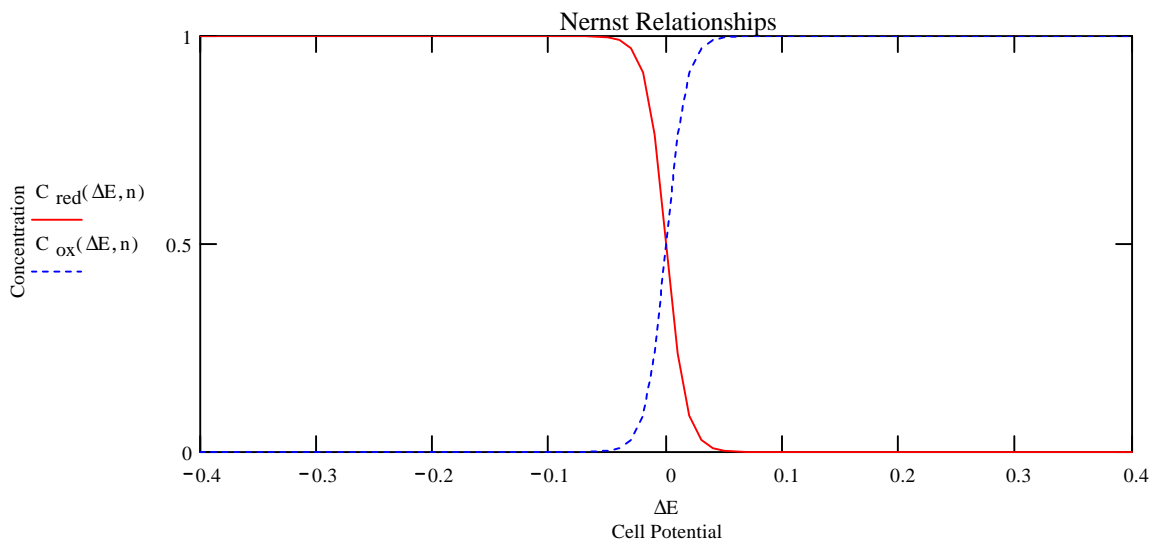


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$n := 3$

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



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