

A Brief Explanation of the Nernst Equation

Its Importance in Explaining Anode and Cathode Polarization and Potential Changes

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The metal ion concentration in an electrolyte in the immediate vicinity of a metal surface has a strong effect on its energy or potential level and therefore, on its tendency to either gain (accept) or shed (give up) electrons. In general, the metal will be more active and therefore, have a more negative energy level as the metal ion concentration decreases. It will tend to corrode more rapidly because the metal has a greater tendency to dissolve into an "uncrowded" electrolyte.

The Nernst equation can be used to predict the energy level of a metal in a solution (electrolyte) containing a known quantity of the metal's ions. It can also be used to predict the shift in energy level that will occur as the concentration level increases or decreases.

Equation 1 = Nernst Equation

$$E = E_o + \frac{RT}{nF} \ln(Me^{++})$$

where:

E = Energy level or potential (in volts) of a metal in given concentration of it's metal ions (Volts)

E_o = Energy level or potential of a metal under standard conditions (Volts)

R = Universal Gas Constant (8.314 J/deg-mole)

T = Temperature (in degrees Kelvin)

N = Number of electrons released per atom oxidized or reduced

\ln = Napierian logarithm (Log to the base $e = 2.71828...$)

Me^{++} = Metal ion concentration in moles per liter of electrolyte

The above equation can be more easily interpreted once it is realized that the value of $RT \times 2.3/F$ (note the 2.3 multiplier converts \ln to \log_{10}) equals 0.059 volts at normal ambient temperatures (or approximately $298^\circ\text{K} = 25^\circ\text{C}$). The equation can therefore be simplified to:

Equation 2 = Nernst Equation modified for normal ambient conditions

$$E = E_o + \frac{.059}{n} \log_{10}(Me^{++})$$

In this simplified form, it can be seen that the potential or energy level of any metal is directly related to the ion concentration in the electrolyte surrounding the metal. This relationship is not linear but is rather logarithmic. Thus, for every decade (10 times) change in ion concentration, there will be $.059/n$ volts of change in the potential of the metal.

The unit of change is determined by "n" which is the valence (or number of electrons transferred per metal atom corroded or reduced during its reaction with the environment) of the metal involved. For example, the common values of "N" for some common metals are given in Table 1.

From Table 1, we can see that the potential shift of iron (Fe) can be predicted for any given change in the iron ion concentration around the metal.

Table 1 - Valence of Metals

Metal	Symbol	"n"
Iron	Fe	2 or 3
Magnesium	Mg	2
Aluminum	Al	3
Zinc	Zn	2
Hydrogen	H	1
Copper	Cu	2
Carbon	C	4
Silver	Ag	1
Lead	Pb	5

For example, if the Fe⁺⁺ concentration would increase from 1 mole per liter to 10 moles per liter (1 mole Fe⁺⁺ = 6.023 x 10²³ Fe⁺⁺ ions per liter) due to corrosion of the iron, the potential of the steel would shift by 0.0295 volts in the positive direction per the following calculations:

For one (1) mole iron ions (Fe⁺⁺) per liter of water (where E_o for Fe = -.340 volts):

$$E = E_o + \frac{0.059}{n} \log_{10}(Fe^{++})$$

$$E = E_o + \frac{0.059}{n} \log_{10}(Fe^{++})$$

$$E = -0.340 + \frac{0.059}{2} \log_{10}(1)$$

$$E = -0.340 + 0.0295(0)$$

$$E = -0.340$$

(Note:: The Log₁₀(1) = 0)

When the Fe⁺⁺ Ion Concentration increases from 1 to 10 moles per liter of water:

$$E = -0.340 + \frac{0.059}{2} \log_{10}(10)$$

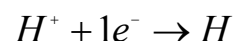
$$E = -0.340 + 0.295(1)$$

$$E = -0.3105$$

Note the potential shifts in the positive (passive) direction from -340 millivolts to -310.5 millivolts or a 29.5 millivolt shift in the positive direction at the corroding (anode) iron.

From the above, it can be appreciated that as iron and steel corrode, more Fe⁺⁺ ions are dissolved into the surrounding moisture or soil causing a positive (+) shift in the potential of the steel metal. This positive shift is always observed when an anodic (corrosion) reaction occurs. Conversely, a negative shift in potential always occurs at the cathode of the corrosion cell.

The most common reaction that causes a negative shift at the cathodic surfaces of a metal is generally:



There is a reduction in the hydrogen ion' (H⁺) concentration surrounding the cathode metal surface and simultaneously, an increase in the amount of hydrogen atoms (H) that accumulate on the metal surface. In this case, the cathode is no longer a metal surface, but is, instead, transitioning to a hydrogen atom surface. Thus, there is a simultaneous reduction in the H⁺ concentration and an increase in the

hydrogen atom surface. The Nernst equation is equally applicable for predicting the potential shift for this cathodic reaction.

For example, consider the following cathodic reaction:

For ten moles H⁺ ions per liter of water
(Note: E_o for H = 0.0 volts):

$$E = 0.0 + \frac{0.059}{1} \log_{10}(10)$$

$$E = 0 + .059(1)$$

$$E = 0.059 \text{volts}$$

If, under the influence of cathodic protection, there is a shift in concentration at the cathode metal surface from 10 moles

H⁺ ions per liter of water to 1 mole per liter, then the energy level of the material will revert to:

$$E = 0.0 + \frac{0.059}{1} \log_{10}(1)$$

$$E = 0 + 0.059(0)$$

$$E = 0.0 \text{Volts}$$

Note that a 59 millivolt shift will occur in the negative direction at the cathode (+59 mV → 0 mV is effectively a negative (-) 59 mV shift in potential)