

Derivation and Application of the Nernst Equation to Fuel Cells

This write up derives the Nernst equation and discusses some of the different ways people apply the equation. Those of you familiar with the derivation for the equilibrium constant approach will see similarities here.

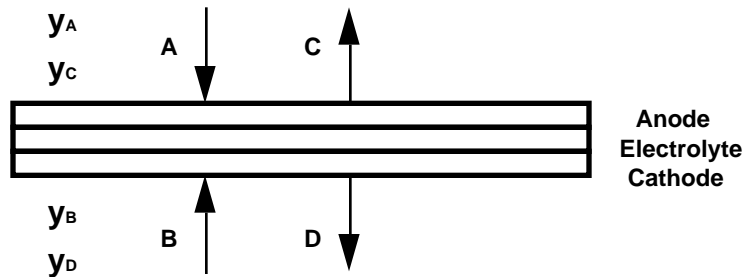
Consider a fuel cell reaction with two reactants and two products:



The reactant and product list can be expanded or contracted at will. For a hydrogen-fueled fuel cell, the corresponding real reaction would be:



Now consider a fuel cell that makes use of reaction (1):



In this system, A is consumed and C is produced at the anode, and B is consumed and D is produced at the cathode. y_A , y_B , y_C , and y_D are the mole fractions of each of the species present locally in the anode and cathode gas streams. These can be anything, and are *not* related to α , β , c or δ .

The local ideal cell voltage will be determined by the infinitesimal amount of reversible work produced for an infinitesimal amount of reagents consumed, *i.e.*, not enough to change the mole fractions. The differential reversible work is:

$$dW = dh - Tds \quad (3)$$

Expanding this:

$$dW = h_A dn_A + h_B dn_B + h_C dn_C + h_D dn_D - T[s_A dn_A + s_B dn_B + s_C dn_C + s_D dn_D] \quad (4)$$

(Note that the sign change for the products is taken care of by the sign on the differentials, *i.e.*, they would be negative.) Due to the stoichiometry presented by equation 1, the dn 's are related:

$$dn_A/\alpha = dn_B/\beta = -dn_C/c = -dn_D/\delta = dn \quad (5)$$

Here, dn represents a differential change in the reaction stoichiometry, as the reaction is written in equation 1. If we substitute dn for all the individual dn_i using equation 5, and then move the dn to the left side, we get:

$$dW/dn = \alpha h_A + \beta h_B - c h_C - \delta h_D - T[\alpha s_A + \beta s_B - c s_C - \delta s_D] \quad (6)$$

The enthalpy terms are calculated as usual:

$$h_A = h_{f,A}^0 + (h_T - h_{298})_A$$

The entropy terms expand as usual:

$$s_A = s_A^0 - R \ln\left(\frac{P_A}{P_0}\right)$$

Substituting this into equation 6, and collecting the partial pressure terms together gives:

$$dW/dn = \alpha h_A + \beta h_B - \gamma h_C - \delta h_D - T(\alpha s_A^0 + \beta s_B^0 - \gamma s_C^0 + \delta s_D^0) + RT \ln\left(\frac{P_A^\alpha P_B^\beta}{P_C^\gamma P_D^\delta P_0^{\alpha+\beta-\gamma-\delta}}\right)$$

Note that since the partial pressures are in atmospheres, and P_0 is always one atmosphere, the P_0 term will always be unity in the calculations and will generally not appear in printed equations. It must, however, be retained (or more correctly, remembered) to make the group in the log term dimensionless.

If we divide the equation by nF , where n is the number of electrons moved per unit stoichiometry (equation 1), and F is Faraday's constant, then the differential work terms become local voltages. Dropping the P_0 term, and collecting the enthalpy and one-atmosphere entropy terms together, we get:

$$E_0 = E_{T,1\text{atm}} + \frac{RT}{nF} \ln\left(\frac{P_A^\alpha P_B^\beta}{P_C^\gamma P_D^\delta}\right)$$

This is the Nernst equation.

The correct approach is to calculate the partial pressures separately for each stream. This would be via:

$$P_A = y_A P_{\text{anode}} \quad P_B = y_B P_{\text{cathode}} \quad \text{etc.}$$

Here, the mole fractions are based on the separate streams. It is common to calculate the mole fractions assuming the cathode and anode streams are mixed together, although this is not correct!