

## 17.18: The Nernst Equation and the Criterion for Equilibrium

In [Section 17.15](#) we find for the general reaction  $aA + bB \rightarrow cD + dD$  that the Nernst equation is

$$\mathcal{E} = \mathcal{E}^o - \frac{RT}{n\mathcal{F}} \ln \frac{\tilde{a}_C^c \tilde{a}_D^d}{\tilde{a}_A^a \tilde{a}_B^b}$$

We now want to consider the relationship between the potential of an electrochemical cell and the equilibrium position of the cell reaction. If the potential of the cell is not zero, short-circuiting the terminals of the cell will cause electrons to flow in the external circuit and reaction to proceed spontaneously in the cell. Since a spontaneous reaction occurs, the cell is not at equilibrium with respect to the cell reaction.

As we draw current from any electrochemical cell, cell reactants are consumed and cell products are produced. Experimentally, we see that the cell voltage decreases continuously, and inspection of the Nernst equation shows that it predicts a potential decrease. Eventually, the voltage of a short-circuited cell decreases to zero. No further current is passed. The cell reaction stops; it has reached chemical equilibrium. If the cell potential is zero, the cell reaction must be at equilibrium, and *vice versa*.

We also know that, at equilibrium, the activity ratio that appears as the argument of the logarithmic term is a constant—the equilibrium constant. So when  $\mathcal{E} = 0$ , we have also that

$$K_a = \frac{\tilde{a}_C^c \tilde{a}_D^d}{\tilde{a}_A^a \tilde{a}_B^b}$$

Substituting these conditions into the Nernst equation, we obtain

$$0 = \mathcal{E}^o - \frac{RT}{n\mathcal{F}} \ln K_a$$

or

$$K_a = \exp \frac{(n\mathcal{F}\mathcal{E}^o)}{RT}$$

We can obtain this same result if we recall that  $\Delta G^o = -RT \ln K_a$  and that  $\Delta G^o = -n\mathcal{F}\mathcal{E}^o$ . We can determine equilibrium constants by measuring the potentials of standard cells. Alternatively, we can measure an equilibrium constant and determine the potential of the corresponding cell without actually constructing it. Standard potentials and equilibrium constants are both measures of the Gibbs free energy change when the reaction occurs under standard conditions.

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