

17.15: The Nernst Equation

In [Chapter 14](#), we find that the Gibbs free energy change is a function of the activities of the reactants and products. For the general reaction $aA + bB \rightarrow cC + dD$

we have

$$\Delta_r G = \Delta_r G^\circ + RT \ln \frac{\tilde{a}_C^c \tilde{a}_D^d}{\tilde{a}_A^a \tilde{a}_B^b}$$

Using the relationship between cell potentials and the Gibbs free energy, we find

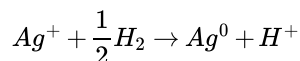
$$-n\mathcal{F}\mathcal{E} = -n\mathcal{F}\mathcal{E}^\circ + RT \ln \frac{\tilde{a}_C^c \tilde{a}_D^d}{\tilde{a}_A^a \tilde{a}_B^b}$$

or

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

This is the **Nernst equation**. We derive it from our previous results for the activity dependence of the Gibbs free energy, which makes no explicit reference to electrochemical measurements at all. When we make the appropriate experimental measurements, we find that the Nernst equation accurately represents the temperature and concentration dependence of electrochemical-cell potentials.

Reagent activities are often approximated adequately by molalities or molarities, for solute species, and by partial pressures—expressed in bars—for gases. The activities of pure solid and liquid phases can be taken as unity. For example, if we consider the reaction



it is often sufficiently accurate to approximate the Nernst equation as

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{n\mathcal{F}} \ln \frac{[H^+]}{[Ag^+] P_{H_2}^{1/2}}$$

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