

17.16: The Nernst Equation for Half-cells

If the S.H.E. is one of the half-cells, the corresponding Nernst equation can be viewed as a description of the other half-cell. Using the cell in which the silver–silver ion electrode opposes the S.H.E., as in the preceding example, the cell potential is the algebraic sum of the potential of the silver terminal and the potential of the platinum terminal. We can represent the potential of the silver–silver ion electrode as $\mathcal{E}_{Ag|Ag^+}$. Since the S.H.E. is always at standard conditions, its potential, which we can represent as $\mathcal{E}_{Pt|H_2|H^+}^o$, is zero by definition. The cell potential is

$$\mathcal{E} = \mathcal{E}_{Ag|Ag^+} + \mathcal{E}_{Pt|H_2|H^+}^o$$

The potential of the cell with both half-cells at standard conditions is

$$\mathcal{E}^o = \mathcal{E}_{Ag|Ag^+}^o + \mathcal{E}_{Pt|H_2|H^+}^o$$

and, again since the S.H.E. is at standard conditions, $\tilde{a}_{H^+} = 1$ and $P_{H_2} = 1$. Substituting into the Nernst equation for the full cell, we have

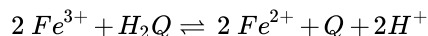
$$\mathcal{E}_{Ag|Ag^+} + \mathcal{E}_{Pt|H_2|H^+}^o = \mathcal{E}_{Ag|Ag^+}^o + \mathcal{E}_{Pt|H_2|H^+}^o - \frac{RT}{\mathcal{F}} \ln \frac{1}{\tilde{a}_{Ag^+}}$$

or

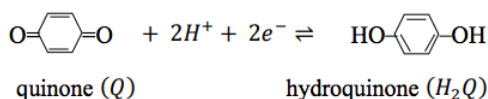
$$\mathcal{E}_{Ag|Ag^+} = \mathcal{E}_{Ag|Ag^+}^o - \frac{RT}{\mathcal{F}} \ln \frac{1}{\tilde{a}_{Ag^+}}$$

where the algebraic signs of $\mathcal{E}_{Ag|Ag^+}$ and $\mathcal{E}_{Ag|Ag^+}^o$ correspond to writing the half-reaction in the direction $Ag^+ + e^- \rightarrow Ag^0$. Note that this is precisely the equation that we would obtain by writing out the Nernst equation corresponding to the chemical equation $Ag^+ + e^- \rightarrow Ag^0$.

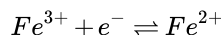
To see how these various conventions work together, let us consider the oxidation of hydroquinone (H_2Q) to quinone (Q) by ferric ion in acidic aqueous solutions:



The quinone–hydroquinone couple is

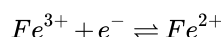


and the ferric ion–ferrous ion couple is

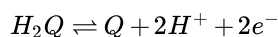


The standard electrode potentials are $\mathcal{E}_{Pt|Q,H_2Q,H^+} = +0.699$ v and $\mathcal{E}_{Pt|Fe^{3+},Fe^{2+}} = +0.783$ v. In each case, the numerical value is the potential of a full cell in which the other electrode is the S.H.E. The algebraic sign of the half-cell potential is equal to the sign of the half-cell's electrical potential when it operates *versus* the S.H.E.

To carry out this reaction in an electrochemical cell, we can use a salt bridge to join a $Pt | Fe^{3+}, Fe^{2+}$ cell to a $Pt | Q, H_2Q, H^+$ cell. To construct a standard $Pt | Fe^{3+}, Fe^{2+}$ cell, we need only insert a platinum wire into a solution containing ferric and ferrous ions, both at unit activity. To construct a standard $Pt | Q, H_2Q, H^+$ cell, we insert a platinum wire into a solution containing quinone, hydroquinone, and hydronium ion, all at unit activity. For standard half-cells, the cathode and anode reactions are



and



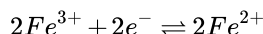
We can immediately write the Nernst equation for each of these half-reactions as

$$\mathcal{E}_{Pt|Fe^{3+},Fe^{2+}} = \mathcal{E}_{Pt|Fe^{3+},Fe^{2+}}^o - \frac{RT}{\mathcal{F}} \ln \frac{\tilde{a}_{Fe^{2+}}}{\tilde{a}_{Fe^{3+}}}$$

and

$$(-\mathcal{E}_{Pt|Q,H_2Q,H^+}) = (-\mathcal{E}_{Pt|Q,H_2Q,H^+}^o) - \frac{RT}{2\mathcal{F}} \ln \frac{\tilde{a}_Q \tilde{a}_{H^+}^2}{\tilde{a}_{H_2Q}}$$

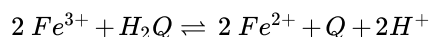
If we add the equations for these half-reactions, the result does not correspond to the original full-cell reaction, because the number of electrons does not cancel. This can be overcome by multiplying the ferric ion–ferrous ion half-reaction by two. What do we then do about the corresponding half-cell Nernst equation? Clearly, the values of $\mathcal{E}_{Pt|Fe^{3+},Fe^{2+}}$ and $\mathcal{E}_{Pt|Fe^{3+},Fe^{2+}}^o$ do not depend on the stoichiometric coefficients in the half-reaction equation. However, the activity terms in the logarithm's argument do, as does the number of electrons taking part in the half-reaction. We have



with

$$\begin{aligned} \mathcal{E}_{Pt|Fe^{3+},Fe^{2+}} &= \mathcal{E}_{Pt|Fe^{3+},Fe^{2+}}^o - \frac{RT}{2\mathcal{F}} \ln \frac{\tilde{a}_{Fe^{2+}}^2}{\tilde{a}_{Fe^{3+}}^2} \\ &= \mathcal{E}_{Pt|Fe^{3+},Fe^{2+}}^o - \frac{RT}{\mathcal{F}} \ln \frac{\tilde{a}_{Fe^{2+}}}{\tilde{a}_{Fe^{3+}}} \end{aligned}$$

We see that we can apply any factor we please to the half-reaction. The Nernst equation gives the same dependence of the half-cell potential on reagent concentrations no matter what factor we choose. This is true also of the Nernst equation for any full-cell reaction. In the present example, adding the appropriate half-cell equations and their corresponding Nernst equations gives



and

$$\begin{aligned} \mathcal{E} &= \mathcal{E}_{Pt|Fe^{3+},Fe^{2+}} - \mathcal{E}_{Pt|Q,H_2Q,H^+} \\ &= \mathcal{E}_{Pt|Fe^{3+},Fe^{2+}}^o - \mathcal{E}_{Pt|Q,H_2Q,H^+}^o - \frac{RT}{2\mathcal{F}} \ln \frac{\tilde{a}_{Fe^{2+}}^2}{\tilde{a}_{Fe^{3+}}^2} - \frac{RT}{2\mathcal{F}} \ln \frac{\tilde{a}_Q \tilde{a}_{H^+}^2}{\tilde{a}_{H_2Q}} \\ &= \mathcal{E}^o - \frac{RT}{2\mathcal{F}} \ln \frac{\tilde{a}_Q \tilde{a}_{H^+}^2 \tilde{a}_{Fe^{2+}}^2}{\tilde{a}_{H_2Q} \tilde{a}_{Fe^{3+}}^2} \end{aligned}$$

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