

14.5: Evaluation of the Standard Cell Potential

As we have seen, the value of the standard cell potential $E_{\text{cell, eq}}^{\circ}$ of a cell reaction has useful thermodynamic applications. The value of $E_{\text{cell, eq}}^{\circ}$ for a given cell reaction depends only on temperature. To evaluate it, we can extrapolate an appropriate function to infinite dilution where ionic activity coefficients are unity.

To see how this procedure works, consider again the cell reaction $\text{H}_2(\text{g}) + 2 \text{AgCl}(\text{s}) \rightarrow 2 \text{H}^+(\text{aq}) + 2 \text{Cl}^-(\text{aq}) + 2 \text{Ag}(\text{s})$. The cell potential depends on the molality m_{B} of the HCl solute according to Eq. 14.4.5. We can rearrange the equation to

$$E_{\text{cell, eq}}^{\circ} = E_{\text{cell, eq}} + \frac{2RT}{F} \ln \gamma_{\pm} + \frac{2RT}{F} \ln \frac{m_{\text{B}}}{m^{\circ}} - \frac{RT}{2F} \ln \frac{f_{\text{H}_2}}{p^{\circ}} \quad (14.5.1)$$

For given conditions of the cell, we can measure all quantities on the right side of Eq. 14.5.1 except the mean ionic activity coefficient γ_{\pm} of the electrolyte. We cannot know the exact value of $\ln \gamma_{\pm}$ for any given molality until we have evaluated $E_{\text{cell, eq}}^{\circ}$. We do know that as m_{B} approaches zero, γ_{\pm} approaches unity and $\ln \gamma_{\pm}$ must approach zero. The Debye–Hückel formula of Eq. 10.4.7 is a theoretical expression for $\ln \gamma_{\pm}$ that more closely approximates the actual value the lower is the ionic strength. Accordingly, we define the quantity

$$E'_{\text{cell}} = E_{\text{cell, eq}} + \frac{2RT}{F} \left(-\frac{A\sqrt{m_{\text{B}}}}{1 + Ba\sqrt{m_{\text{B}}}} \right) + \frac{2RT}{F} \ln \frac{m_{\text{B}}}{m^{\circ}} - \frac{RT}{2F} \ln \frac{f_{\text{H}_2}}{p^{\circ}} \quad (14.5.2)$$

The expression in parentheses is the Debye–Hückel formula for $\ln \gamma_{\pm}$ with I_m replaced by m_{B} . The constants A and B have known values at any temperature (Sec. 10.4), and a is an ion-size parameter for which we can choose a reasonable value. At a given temperature, we can evaluate E'_{cell} experimentally as a function of m_{B} .

The expression on the right side of Eq. 14.5.1 differs from that of Eq. 14.5.2 by contributions to $(2RT/F) \ln \gamma_{\pm}$ not accounted for by the Debye–Hückel formula. Since these contributions approach zero in the limit of infinite dilution, the extrapolation of measured values of E'_{cell} to $m_{\text{B}}=0$ yields the value of $E_{\text{cell, eq}}^{\circ}$.

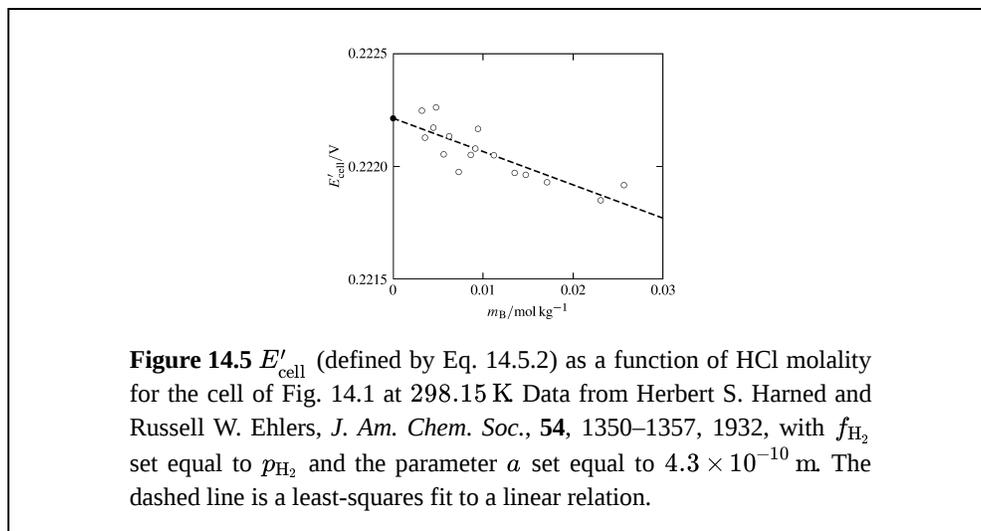


Figure 14.5 shows this extrapolation using data from the literature. The extrapolated value indicated by the filled circle is $E_{\text{cell, eq}}^{\circ} = 0.2222$ V, and the uncertainty is on the order of only 0.1 mV.

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