

14.4: The Nernst Equation

The standard cell potential $E_{\text{cell, eq}}^\circ$ of a cell reaction is the equilibrium cell potential of the hypothetical galvanic cell in which each reactant and product of the cell reaction is in its standard state and there is no liquid junction potential. The value of $E_{\text{cell, eq}}^\circ$ for a given cell reaction with given choices of standard states is a function only of temperature. The measured equilibrium cell potential $E_{\text{cell, eq}}$ of an actual cell, however, depends on the activities of the reactants and products as well as on temperature and the liquid junction potential, if present.

To derive a relation between $E_{\text{cell, eq}}$ and activities for a cell without liquid junction, or with a liquid junction of negligible liquid junction potential, we substitute expressions for $\Delta_r G$ and for $\Delta_r G^\circ$ from Eqs. 14.3.13 and Eq. 14.3.15 into $\Delta_r G = \Delta_r G^\circ + RT \ln Q_{\text{rxn}}$ (Eq. 11.8.8) and solve for $E_{\text{cell, eq}}$:

$$E_{\text{cell, eq}} = E_{\text{cell, eq}}^\circ - \frac{RT}{zF} \ln Q_{\text{rxn}} \quad (14.4.1)$$

(no liquid junction, or $E_j=0$)

Equation 14.4.1 is the **Nernst equation** for the cell reaction. Here Q_{rxn} is the reaction quotient for the cell reaction defined by Eq. 11.8.6: $Q_{\text{rxn}} = \prod_i a_i^{\nu_i}$.

The rest of this section will assume that the cell reaction takes place in a cell without liquid junction, or in one in which E_j is negligible.

If each reactant and product of the cell reaction is in its standard state, then each activity is unity and $\ln Q_{\text{rxn}}$ is zero. We can see from the Nernst equation that the equilibrium cell potential $E_{\text{cell, eq}}$ in this case has its standard value $E_{\text{cell, eq}}^\circ$, as expected. A decrease in product activities or an increase in reactant activities decreases the value of $\ln Q_{\text{rxn}}$ and increases $E_{\text{cell, eq}}$, as we would expect since $E_{\text{cell, eq}}$ should be greater when the forward cell reaction has a greater tendency for spontaneity.

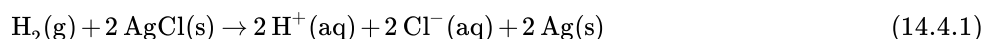
If the cell reaction comes to reaction equilibrium, as it will if we short-circuit the cell terminals with an external wire, the value of Q_{rxn} becomes equal to the thermodynamic equilibrium constant K , and the Nernst equation becomes $E_{\text{cell, eq}} = E_{\text{cell, eq}}^\circ - (RT/zF) \ln K$. The term $(RT/zF) \ln K$ is equal to $E_{\text{cell, eq}}^\circ$ (Eq. 14.3.16), so $E_{\text{cell, eq}}$ becomes zero—the cell is “dead” and is incapable of performing electrical work on the surroundings.

At $T=298.15 \text{ K}$ (25.00°C), the value of RT/F is 0.02569 V , and we can write the Nernst equation in the compact form

$$E_{\text{cell, eq}} = E_{\text{cell, eq}}^\circ - \frac{0.02569 \text{ V}}{z} \ln Q_{\text{rxn}} \quad (14.4.2)$$

($T=298.15 \text{ K}$)

As an illustration of an application of the Nernst equation, consider the reaction equation



This reaction takes place in a cell without liquid junction (Fig. 14.1), and the electrolyte solution can be aqueous HCl. The expression for the reaction quotient is

$$Q_{\text{rxn}} = \frac{a_+^2 a_-^2 a_{\text{Ag}}^2}{a_{\text{H}_2} a_{\text{AgCl}}^2} \quad (14.4.3)$$

We may usually with negligible error approximate the pressure factors of the solids and solutes by unity. The activities of the solids are then 1, the solute activities are $a_+ = \gamma_+ m_+ / m^\circ$ and $a_- = \gamma_- m_- / m^\circ$, and the hydrogen activity is $a_{\text{H}_2} = f_{\text{H}_2} / p^\circ$. The ion molalities m_+ and m_- are equal to the HCl molality m_{B} . The expression for Q_{rxn} becomes

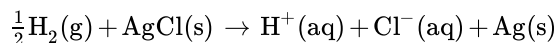
$$Q_{\text{rxn}} = \frac{\gamma_+^2 \gamma_-^2 (m_{\text{B}} / m^\circ)^4}{f_{\text{H}_2} / p^\circ} = \frac{\gamma_{\pm}^4 (m_{\text{B}} / m^\circ)^4}{f_{\text{H}_2} / p^\circ} \quad (14.4.4)$$

and the Nernst equation for this cell is

$$\begin{aligned} E_{\text{cell, eq}} &= E_{\text{cell, eq}}^\circ - \frac{RT}{2F} \ln \frac{\gamma_{\pm}^4 (m_{\text{B}} / m^\circ)^4}{f_{\text{H}_2} / p^\circ} \\ &= E_{\text{cell, eq}}^\circ - \frac{2RT}{F} \ln \gamma_{\pm} - \frac{2RT}{F} \ln \frac{m_{\text{B}}}{m^\circ} + \frac{RT}{2F} \ln \frac{f_{\text{H}_2}}{p^\circ} \end{aligned} \quad (14.4.5)$$

By measuring $E_{\text{cell, eq}}$ for a cell with known values of m_{B} and f_{H_2} , and with a derived value of $E_{\text{cell, eq}}^\circ$, we can use this equation to find the mean ionic activity coefficient γ_{\pm} of the HCl solute. This is how the experimental curve for aqueous HCl in Fig. 10.3 was obtained.

We can always multiply each of the stoichiometric coefficients of a reaction equation by the same positive constant without changing the meaning of the reaction. How does this affect the Nernst equation for the reaction equation above? Suppose we decide to multiply the stoichiometric coefficients by one-half:



With this changed reaction equation, the value of z is changed from 2 to 1 and the Nernst equation becomes

$$E_{\text{cell, eq}} = E_{\text{cell, eq}}^\circ - \frac{RT}{F} \ln \frac{\gamma_{\pm}^2 (m_{\text{B}}/m^\circ)^2}{(f_{\text{H}_2}/p^\circ)^{1/2}} \quad (14.4.6)$$

which yields the same value of $E_{\text{cell, eq}}$ for given cell conditions as Eq. 14.4.5. This value must of course be unchanged, because physically the cell is the same no matter how we write its cell reaction, and measurable physical quantities such as $E_{\text{cell, eq}}$ are unaffected. However, molar reaction quantities such as $\Delta_{\text{r}}G$ and $\Delta_{\text{r}}G^\circ$ do depend on how we write the cell reaction, because they are changes per extent of reaction.

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