Nernst Equation

The *Nernst Equation* enables the determination of cell potential under non-standard conditions. It relates the measured cell potential to the reaction quotient and allows the accurate determination of equilibrium constants (including solubility constants).

Introduction

The *Nernst Equation* is derived from the Gibbs free energy **under standard conditions**.

$$E^o = E^o_{reduction} - E^o_{oxidation} \tag{1}$$

ΔG is also related to E under general conditions (standard or not) via

$$\Delta G = -nFE \tag{2}$$

with

- n is the number of electrons transferred in the reaction (from balanced reaction),
- F is the Faraday constant (96,500 C/mol), and
- E is potential difference.

Under standard conditions, Equation 2 is then

$$\Delta G^o = -nFE^o. \tag{3}$$

Hence, when E^o is positive, the reaction is spontaneous and when E^o is negative, the reaction is non-spontaneous. From thermodynamics, the Gibbs energy change under non-standard conditions can be related to the Gibbs energy change under standard Equations via

$$\Delta G = \Delta G^o + RT \ln Q \tag{4}$$

Substituting $\Delta G = -nFE$ and $\Delta G^o = -nFE^o$ into Equation 4, we have:

$$-nFE = -nFE^o + RT \ln Q \tag{5}$$

Divide both sides of the Equation above by $-nF$, we have

$$E = E^o - \frac{RT}{nF} \ln Q \tag{6}$$

Equation 6 can be rewritten in the form of $\log_{10}$:

$$E = E^o - \frac{2.303RT}{nF} \log_{10} Q \tag{7}$$

At standard temperature T = 298 K, the $\frac{2.303RT}{F}$ term equals 0.0592 V and Equation 7 can be rewritten:

$$E = E^o - \frac{0.0592\,V}{n} \log_{10} Q \tag{8}$$

The Equation above indicates that the electrical potential of a cell depends upon the reaction quotient Q of the reaction. As the redox reaction proceeds, reactants are consumed, and thus concentration of reactants decreases. Conversely, the products concentration increases due to the increased in products formation. As this happens, cell potential gradually *decreases* until the reaction is at equilibrium, at which $\Delta G = 0$. At equilibrium, the reaction quotient $Q = K_{eq}$. Also, at equilibrium, $\Delta G = 0$ and $\Delta G = -nFE$, so $E = 0$.

Therefore, substituting $Q = K_{eq}$ and $E = 0$ into the Nernst Equation, we have:

$$0 = E^o - \frac{RT}{nF} \ln K_{eq} \tag{9}$$

At room temperature, Equation 9 simplifies into (notice natural log was converted to log base 10):

$$0 = E^o - \frac{0.0592\,V}{n}\log_{10} K_{eq} \tag{10}$$

This can be rearranged into:

$$\log K_{eq} = \frac{nE^o}{0.0592\,V} \tag{11}$$

The Equation above indicates that the equilibrium constant K_{eq} **is proportional to the standard potential** of the reaction. Specifically, when:

- $K > 1, E^o > 0$, reaction favors products formation.
- $K < 1, E^o < 0$, reaction favors reactants formation.

This result fits Le Châtlier's Principle, which states that when a system at equilibrium experiences a change, the system will minimize that change by shifting the equilibrium in the opposite direction.

Example 1

The $E^o_{cell} = +1.10\,V$ for the Zn-Cu redox reaction:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightleftharpoons Zn^{2+}_{(aq)} + Cu_{(s)}. \tag{12}$$

What is the equilibrium constant for this reversible reaction?

SOLUTION

Under standard conditions, $[Cu^{2+}] = [Zn^{2+}] = 1.0\,M$ and T = 298 K. As the reaction proceeds, $[Cu^{2+}]$ decreases as $[Zn^{2+}]$ increases. Lets say after one minute, $[Cu^{2+}] = 0.05\,M$ while $[Zn^{2+}] = 1.95\,M$. According to the Nernst Equation, the cell potential after 1 minute is:

$$E = E^o - \frac{0.0592V}{n}\log Q \tag{13}$$

$$E = 1.10V - \frac{0.0592V}{2}\log \frac{1.95\,M}{0.05\,M} \tag{14}$$

$$E = 1.05\,V \tag{15}$$

As you can see, the initial cell potential is $E = 1.10\,V$, after 1 minute, the potential drops to 1.05 V. This is after 95% of the reactants have been consumed. As the reaction continues to progress, more Cu^{2+} will be consumed and more Zn^{2+} will be generated (at a 1:1 ratio). As a result, the cell potential continues to decrease and when the cell potential drops down to 0, the concentration of reactants and products stops changing.

This is when the reaction is at equilibrium. From from Equation 9, the K_{eq} can be calculated from

$$\log K_{eq} = \frac{2 \times 1.10\,V}{0.0592\,V} \tag{16}$$

$$= 37.2 \tag{17}$$

$$K_{eq} = 10^{37.2} = 1.58 \times 10^{37} \tag{18}$$

This make sense from a Le Châtlier's Principle, since the reaction strongly favors the products over the reactants to result in a large E^o_{cell} of 1.103 V. Hence, the cell is greatly out of equilibrium under standard conditions. Reactions that are just weakly out of equilibrium will have smaller E^o_{cell} values (neglecting a change in n of course).

References

1. Atkins, Peter and de Paula, Julio. *Physical Chemistry for the Life Sciences*. New York: W.H. Freeman and Company. p. 214-222.
2. Sherwood, Lauralee. *Human Physiology 6th edition*. Thompson Corp. 2007. p. 77

Outside Links

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- Thompson, Martin L.; Kateley, Laura J. "The Nernst Equation: Determination of Equilibrium Constants for Complex Ions of Silver." *J. Chem. Educ.* **1999** *76* 95.