Lecture – 7 Electrochemistry

Difference between E_{cell} and E^0_{cell}

E^0 cell is the standard state cell potential, which means that the value was determined under standard states. The standard states include a concentration of 1 Molar (mole per liter) and an atmospheric pressure of 1. Similar to the standard state cell potential, E^0_{cell}, the E_{cell} is the non-standard state cell potential, which means that it is not determined under a concentration of 1 M and pressure of 1 atm. The two are closely related in the sense that the standard cell potential is used to calculate for the cell potential in many cases.

$$E_{cell} = E^o_{cell} - \frac{RT}{nF} \ln Q \qquad (3)$$

Other simplified forms of the equation that we typically see:

$$E_{cell} = E^o_{cell} - \frac{0.0257}{n} \ln Q \qquad (4)$$

or in terms of log10log10 (base 10) instead of the natural logarithm (base e)

$$E_{cell} = E^o_{cell} - \frac{0.0592}{n} \log_{10} Q \qquad (5)$$

Both equations applies when the temperature is 25ºC. Deviations from 25ºC requires the use of the original equation. Essentially, E^0 is E at standard conditions

Example 1

What is the value of E_{cell} for the voltaic cell below:

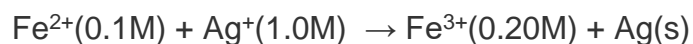$$Pt(s) \mid Fe^{2+}(0.1M), Fe^{3+}(0.2M) \mid\mid Ag^+(0.1M) \mid Ag(s)$$

SOLUTION

To use the **Nernst equation**, we need to establish E^o_{cell} and the reaction to which the cell diagram corresponds so that the form of the reaction quotient (Q) can be revealed. Once we have determined the form of the **Nernst equation**, we can insert the concentration of the species.

Solve: $E^o_{cell} = E^o_{cathode} - E^o_{anode}$

$$= E^o_{Ag+ / Ag} - E^o_{Fe3+ / Fe2+}$$

$$= 0.800V - 0.771V = 0.029V$$

Now to determine Ecell for the reaction

$$Fe^{2+}(0.1M) + Ag^{+}(1.0M) \rightarrow Fe^{3+}(0.20M) + Ag(s)$$

Use the Nernst equation

$$E_{cell} = 0.029V - (0.0592V / 1) \log [Fe^{3+}] / [Fe^{2+}][Ag+]$$

$$= 0.029V - 0.0592V * \log [0.2] / [0.1]*[1.0]$$

$$= 0.011V$$

K: The Equilibrium Constant

K is the equilibrium constant of a general reaction

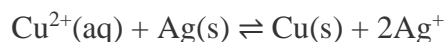$$aA + bB \leftrightharpoons cC + dD \tag{6}$$

and is expressed by the reaction quotient:

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{7}$$

Example 2

Given $K = 2.81 \times 10^{-16}$ for a following reaction

$$Cu^{2+}(aq) + Ag(s) \rightleftharpoons Cu(s) + 2Ag^{+}$$
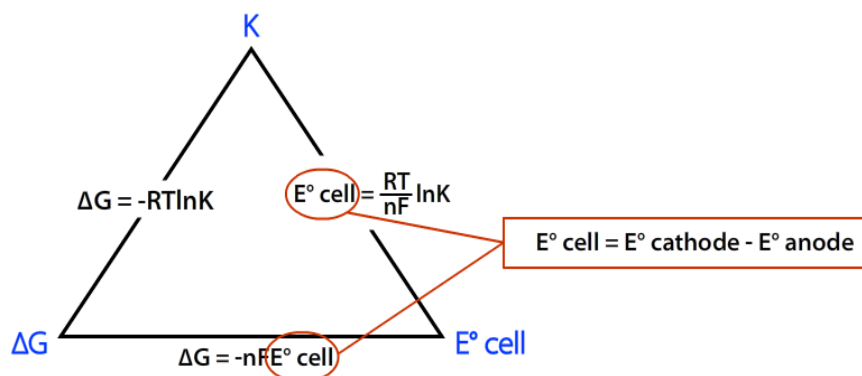
Find ΔG.

Solution:

Use the following formula: Δ**G = - RT lnK**

$$= 8.314 \times 298 \times \ln(2.81 \times 10^{-16}) = - 8.87 \times 10^{5}$$

$$= \mathbf{8.871\ kJ}$$

The Relationship Between the Three

The relationship between ΔG, K, and E° cell can be represented by the following diagram.

where

- $R = 8.314$ J mol C^{-1}
- $T = $ Temp in K
- $n = $ moles of e$^-$ from balanced redox reaction
- $F = $ Faraday's constant $= 96{,}485$ C/mol

  $E°_{cell}$ can be calculated using the following formula:

$$E^o_{cell} = E^o_{cathode} - E^o_{anode} = E^o_{Reduction} - E^o_{Oxidation} \qquad (8)$$

Summary Table				
E° cell	**ΔG**	**Q & K Relationship**	**Reaction Direction**	**Spontaneity (as written)**
> 0	-	$Q < K$	Forward	Spontaneous
< 0	+	$Q > K$	Backward	Non-spontaneous
$= 0$	$= 0$	$Q = K$	No Reaction	N/A

Example 3: Using ΔG = - RT lnK

Question Find the E° cell for the following coupled half-reactions

SOLUTION

1. Determine the cathode and anode in the reaction

   $Zn_{(s)} \leftrightarrow Zn^{2+}_{(aq)} + 2e^-$ Anode, Oxidation (since $Zn_{(s)}$ increase oxidation state from 0 to +2)

   $Cu^{2+}_{(aq)} + 2e^- \leftrightarrow Cu_{(s)}$ Cathode, Reduction (since $Cu^{2+}_{(aq)}$ decreases oxidation state from +2 to 0)
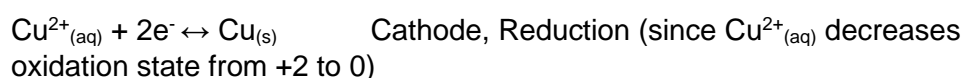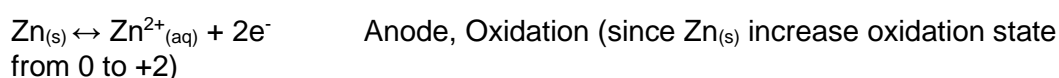
2. Determine the E° cell values using the standard reduction potential table (Table P1)

$$Zn_{(s)} \leftrightarrow Zn^{2+}{}_{(aq)} + 2e^- \qquad -0.763$$

$$Cu^{2+}{}_{(aq)} + 2e^- \leftrightarrow Cu_{(s)} \qquad +0.340$$
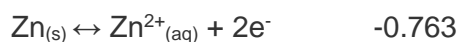
3. Use **E° cell = E°cathode - E°anode**

$$= 0.340 - (-0.763)$$

$$= 1.103 \text{ V}$$

Example 5: Using E° cell = (RT/nF) lnK

Given the E° cell for the reaction

$$Cu(s) + 2H+(aq) \rightleftharpoons Cu2+(aq) + H2(g)$$
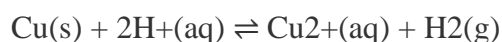
is -0.34V, find the equilibrium constant (K) for the reaction.

SOLUTION

Step 1: Split into two half reaction

$$Cu_{(s)} \leftrightarrow Cu^{2+(aq)}$$

$$2H^+{}_{(aq)} \leftrightarrow H_{2(g)}$$
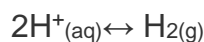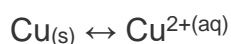
Step 2: Balance the half reactions with charges to determine n

$$Cu_{(s)} \leftrightarrow Cu^{2+}{}_{(aq)} + 2e^-$$

$$2H^+{}_{(aq)} + 2e^- \leftrightarrow H_{2(g)}$$
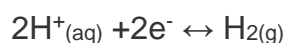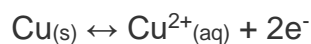
    Therefore n=2

Step 3: From the example above, E° cell = - 0.34V

- 0.34 = (0.025693/2) lnK

$K = e^{(-0.34 \times 2 / 0.025693)}$

K = 3.19 x 10⁻¹²

Effect of Concentration on Electrode Potentials:
The Nernst Equation

Consider the reversible half-reaction

$$aA + bB + … + ne^- \Leftrightarrow cC + dD +…$$

where the capital letters represent formulas for the participating species,

e^- represents the electrons, and the lower case italic letters indicate the number of moles of each species appearing in the half-reaction as it has been written.

The electrode potential for this process is given by the equation

$$E = E^0 - \frac{RT}{nF} \ln \frac{[C]^c[D]^d…}{[A]^a[B]^b…}$$

$$E = E^0 - \frac{0.0592}{n} \log \frac{[C]^c[D]^d…}{[A]^a[B]^b…}$$

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**.

$$E^o = E^o{}_{reduction} - E^o{}_{oxidation} \qquad (1)$$

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

$$\Delta G = - nFE \qquad (2)$$

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

$$\Delta G^o = - nFE^o. \qquad (3).$$

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

$$\Delta G = \Delta G^o + RT\ \ln Q \qquad\qquad (4)$$

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

$$-\ \ nFE = -nFE^o + RT\ \ln Q \qquad\qquad (5)$$

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

$$E = E^0 - \frac{RT}{nF}\ln Q$$

Equation 6 can be _rewritten_ in the form of $\log 10\log 10$:

$$E = E^0 - \frac{2.303RT}{nF}\log Q \qquad\qquad \text{(Generalized Nernst Equation)}$$

At standard temperature T = 298 K, the $\frac{2.303RT}{F}$ term equals 0.0592 V and this equation turns into:

$$E = E^0 - \frac{0.0592\,V}{n}\log Q \qquad\qquad \text{(Nernst Equation @ 298 K)}$$

 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:

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

$$\qquad\qquad\qquad\qquad\qquad\qquad (7)$$

At room temperature, the equation above simplifies into (notice natural log was converted to log base 10):

$$0 = E^0 - \frac{0.0592\,V}{n}\log K_{eq} \qquad\qquad (8)$$

This equation can be rearranged into:

$$\log K_{eq} = \frac{nE^{o}}{0.0592\,V} \tag{9}$$

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 <u>Le Châtlier's Principle</u>, 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 $E^{o}cell = +1.10V$ for the Zn-Cu redox reaction:

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s).$$
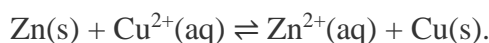
What is the equilibrium constant for this reversible reaction?

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, $[Cu^{2+}] = 0.05M$ while $[Zn^{2+}] = 1.95M$. According to the Nernst equation, the cell potential after 1 minute is:

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

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

$$E = 1.05\ V$$

$$E = 1.05V$$

As you can see, the initial cell potential is $E = 1.10V$, 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

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

Log Keq = 37.2

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

This make sense from a <u>Le Châtlier's Principle</u>, since the reaction strongly favors the products over the reactants to result in a large $E°$ 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^0 cell values (neglecting a change in n of course).

EXAMPLE 18-2

Typical half-cell reactions and their corresponding Nernst expressions follow.

(1) $Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$ $E = E^0 - \dfrac{0.0592}{2} \log \dfrac{1}{[Zn^{2+}]}$

No term for elemental zinc is included in the logarithmic term because it is a pure second phase (solid). Thus, the electrode potential varies linearly with the logarithm of the reciprocal of the zinc ion concentration.

(2) $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}(s)$ $E = E^0 - \dfrac{0.0592}{1} \log \dfrac{[Fe^{2+}]}{[Fe^{3+}]}$

The potential for this couple can be measured with an inert metallic electrode immersed in a solution containing both iron species. The potential depends on the logarithm of the ratio between the molar concentrations of these ions.

(3) $2H^+ + 2e^- \rightleftharpoons H_2(g)$ $E = E^0 - \dfrac{0.0592}{2} \log \dfrac{p_{H_2}}{[H^+]^2}$

In this example, p_{H_2} is the partial pressure of hydrogen (in atmospheres) at the surface of the electrode. Usually, its value will be the same as atmospheric pressure.

(4) $MnO_4^- + 5e^- + 8H^+ \rightleftharpoons Mn^{2+} + 4H_2O$

$$E = E^0 - \dfrac{0.0592}{5} \log \dfrac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$
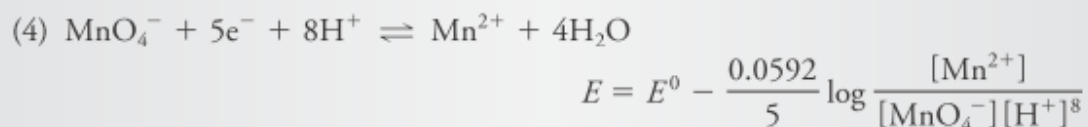
In this situation, the potential depends not only on the concentrations of the manganese species but also on the pH of the solution.

(5) $AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$ $E = E^0 - \dfrac{0.0592}{1} \log [Cl^-]$

This half-reaction describes the behavior of a silver electrode immersed in a chloride solution that is *saturated* with AgCl. To ensure this condition, an excess of the solid AgCl must always be present. Note that this electrode reaction is the sum of the following two reactions:

$$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$$
$$Ag^+ + e^- \rightleftharpoons Ag(s)$$
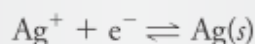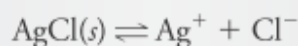
Note also that the electrode potential is independent of the amount of AgCl present as long as there is at least some present to keep the solution saturated.

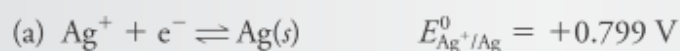## *Systems Involving Precipitates or Complex Ions*

Figure 18-9 The measurement of the standard electrode potential for the Ag/AgCl electrode.
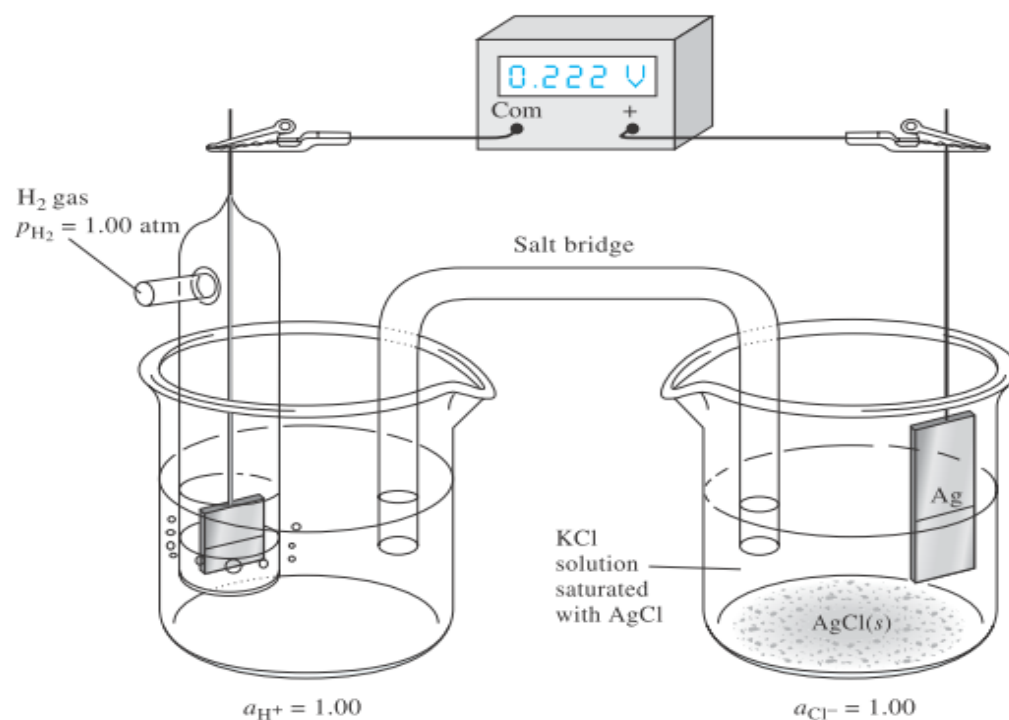
EXAMPLE 18-3

Calculate the electrode potential of a silver electrode immersed in a 0.0500 M solution of NaCl using (a) $E^0_{Ag^+/Ag} = 0.799$ V and (b) $E^0_{AgCl/Ag} = 0.222$ V.

Solution

(a) $Ag^+ + e^- \rightleftharpoons Ag(s)$ $E^0_{Ag^+/Ag} = +0.799$ V

The Ag^+ concentration of this solution is given by

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.82 \times 10^{-10}}{0.0500} = 3.64 \times 10^{-9}\,M$$

Substituting into the Nernst expression gives

$$E = 0.799 - 0.0592 \log \frac{1}{3.64 \times 10^{-9}} = 0.299\,V$$

(b) We may write this last equation as

$$E = 0.222 - 0.0592 \log [Cl^-] = 0.222 - 0.0592 \log 0.0500$$
$$= 0.299$$

References

- Fundamental of Analytical Chemistry,8th Edition,Skoog.
- Petrucci, et al. General Chemistry: Principles & Modern Applications. 9th ed. Upper Saddle River, New Jersey: Pearson/Prentice Hall, 2007.

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