Lecture 15: The Nernst Equation

• Reading: Zumdahl 11.4

• Outline:
  – Why would concentration matter in electrochemistry?
  – The Nernst equation.
  – Applications
Concentration and $E_{\text{cell}}$

- Consider the following redox reaction:

$$\text{Zn}(s) + 2\text{H}^+ (aq) \rightarrow \text{Zn}^{2+}(aq) + \text{H}_2(g) \quad E^\circ_{\text{cell}} = 0.76 \text{ V}$$

$$nFE_{\text{cell}} = -\Delta G_{\text{rxn}} > 0 \quad \text{(spontaneous)}$$

- What if $[\text{H}^+] = 2 \text{ M}$?

  Expect driving force for product formation to increase.
  Therefore $\Delta G_{\text{rxn}}$ decreases, and $E_{\text{cell}}$ increases
  How does $E_{\text{cell}}$ depend on concentration?
$E_{cell}$ depends on Concentration

The Nernst Equation

Recall, in general: \[ \Delta G_{rxn} = \Delta G_{rxn}^0 + RT \ln Q \]

Putting this with our recent result:

\[ nFE_{cell} = -\Delta G_{rxn} = -\Delta G_{rxn}^0 - RT \ln Q \]

\[ E_{cell} = E_{cell}^0 - \frac{RT}{nF} \ln Q \]

\[ E_{cell} = E_{cell}^0 - \frac{0.059}{n} \log_{10} Q \quad V \]

\[ \Delta G_{rxn} = \Delta G_{rxn}^0 + 5.7 \log_{10} Q \quad kJ \]
E_{cell}: The Nernst Equation

• With the Nernst Eq., we can determine the effect of concentration on cell potentials.

\[ E_{cell} = E_{cell}^0 - \frac{0.059}{n} \log_{10} Q \]

• Example. Calculate the cell potential for the following:

\[ Fe(s) + Cu^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cu(s) \]

Where \([Cu^{2+}] = 1 \text{ M and } [Fe^{2+}] = 1 \text{ M}\)

Where \([Cu^{2+}] = 0.3 \text{ M and } [Fe^{2+}] = 0.1 \text{ M}\)

Do you expect the potential to be greater than the Standard potential?
E\text{cell} example

\[ Fe(s) + Cu^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cu(s) \]

First, need to identify the 1/2 cells (table, 11.1).
Get the voltage under standard conditions

\[ Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad E_{cell}^0 = +0.34V \]
\[ Fe^{2+}(aq) + 2e^- \rightarrow Fe(s) \quad E_{cell}^0 = -0.44V \]
\[ Fe(s) \rightarrow Fe^{2+}(aq) + 2e^- \quad E_{cell}^0 = +0.44V \]

\[ \begin{array}{c}
Fe(s) + Cu^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cu(s) \\
E_{cell}^0 = +0.78V
\end{array} \]

Turn the iron half cell around and add.
E_{cell} example

\[ Fe(s) + Cu^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cu(s) \quad E_{cell}^0 = +0.78V \]

Now, calculate Q and then \( E_{cell} \).
Notice, the concentrations are in separate containers.

\[
Q = \left[ \frac{Fe^{2+}}{Cu^{2+}} \right] \cdot \frac{a_{Cu^0}}{a_{Fe^0}} = \left\{ \left[ \frac{Fe^{2+}}{a_{Fe^0}} \right] \right\}_{An} \cdot \left\{ \frac{a_{Cu^0}}{\left[ Cu^{2+} \right]} \right\}_{Cat} = \frac{(0.1)}{(0.3)} = 0.33
\]

\( n = 2 \)

\[
E_{Cell} = E_{Cell}^0 - \frac{0.059}{n} \log_{10} Q
\]

\[
E_{Cell} = 0.78 - \frac{0.059}{2} \log_{10} 0.33 = 0.78 + 0.014 = 0.794V
\]
If $[\text{Cu}^{2+}] = 0.3 \text{ M}$, what $[\text{Fe}^{2+}]$ is needed so that $E_{\text{cell}} = 0.76 \text{ V}$?

$$Fe(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Fe}^{2+}(aq) + \text{Cu}(s) \quad E_{\text{cell}}^0 = +0.78V$$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.059}{n} \log_{10} Q$$

$$0.76 = 0.78 - \frac{0.059}{2} \log_{10} Q$$

$$\log_{10} Q = \frac{2 \cdot 0.02}{0.059} = \frac{2}{3}$$

$$Q = 4.7 = \left[ \frac{[\text{Fe}^{2+}]}{[\text{Cu}^{2+}]} \right] = \left[ \frac{[\text{Fe}^{2+}]}{0.3} \right]$$

$$[\text{Fe}^{2+}] = 4.7 \cdot 0.3 = 1.4M$$
Concentration Cells

- Consider the cell presented on the left.

- The $1/2$ cell reactions are the same, it is just the concentrations that differ.

- Will there be electron flow?
Concentration Cells: Nernst Effect Only

\[ \text{Ag}^+ + e^- \rightarrow \text{Ag} \quad E^\circ_{1/2} = 0.80 \text{ V} \]

- \( E^\circ_{1/2} \) is measured when all species are in standard state, so this means both sides have 1 M concentrations of \( \text{Ag}^+ \). Therefore, \( E^\circ_{\text{cell}} = 0 \).
Silver Concentration Cell

Driving force for the reaction: Get the concentration up on the left, so produce more ions there. Will stop when concentrations in both beakers are equal (Q=1 but not Std State)

**Anode:**  \( \text{Ag} \rightarrow \text{Ag}^+ + e^- \)  \( E^\circ_{1/2} = -0.80 \text{ V} \)

**Cathode:**  \( \text{Ag}^+ + e^- \rightarrow \text{Ag} \)  \( E^\circ_{1/2} = +0.80 \text{ V} \)

\[
Q = \frac{[\text{Ag}^+]}{[\text{Ag}^+]_{\text{Cathode}}} = \frac{(0.1)}{(1.0)} = 0.1
\]

\( n = 1 \)

\[
E_{\text{cell}} = E^0_{\text{Cell}} - \frac{0.059}{n} \log_{10} Q
\]

\[
E_{\text{cell}} = 0.0 - \frac{0.059}{1} \log_{10} 0.1 = 0.0 - 0.059 = 0.06 \text{V}
\]
Concentration Cells (2\textsuperscript{nd} example)

Another Example:
The number of electrons per rxn is different

What is $E_{\text{cell}}$?
Iron Concentration Cells

\[ \text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe} \]

2 e\(^-\) transferred…\(n = 2\)

\[ Q = \frac{[\text{Fe}^{2+}]_{\text{Anode}}}{[\text{Fe}^{2+}]_{\text{Cathode}}} = \frac{(0.01)}{(0.1)} = 0.1 \]

\[ n = 2 \]

\[ E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.059}{n} \log_{10} Q \]

\[ E_{\text{cell}} = 0.0 - \frac{0.059}{2} \log_{10} 0.1 = 0.03 = 0.03V \]

\[ E_{\text{cell}} = 30\text{mV} \]
Measurement of pH

• pH meters use electrochemical reactions.

• Ion selective probes: respond to the presence of a specific ion. pH probes are sensitive to H⁺.

• Specific reactions:

\[
\begin{align*}
\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^- & \rightarrow 2\text{Hg}(\text{l}) + 2\text{Cl}^- (\text{aq}) \quad E^\circ_{1/2} = 0.27 \text{ V} \\
\text{H}_2(\text{g}) & \rightarrow 2\text{H}^+ (\text{aq}) + 2\text{e}^- \quad E^\circ_{1/2} = 0.0 \text{ V}
\end{align*}
\]

\[
\begin{align*}
\text{Hg}_2\text{Cl}_2(\text{s}) + \text{H}_2(\text{g}) & \rightarrow 2\text{Hg}(\text{l}) + 2\text{H}^+ (\text{aq}) + 2\text{Cl}^- (\text{aq}) \\
E^\circ_{\text{cell}} & = 0.27 \text{ V}
\end{align*}
\]
Measurement of pH

\[ \text{Hg}_2\text{Cl}_2(s) + \text{H}_2(g) \longrightarrow 2\text{Hg}(l) + 2\text{H}^+(aq) + 2\text{Cl}^-(aq) \]

- What if we let \([\text{H}^+]\) vary?

\[
Q = \frac{[\text{H}^+]^2[\text{Cl}^-]^2}{P_{\text{H}_2}} = [\text{H}^+][\text{Cl}^-]^2
\]

\[ n = 2 \]

\[
E_{\text{Cell}} = E_{\text{Cell}}^0 - \frac{0.059}{n} \log_{10} Q
\]

\[
E_{\text{Cell}} = E_{\text{Cell}}^0 - \frac{0.059}{2} \log_{10} \left\{ [\text{H}^+]^2[\text{Cl}^-]^2 \right\}
\]

\[
E_{\text{Cell}} = E_{\text{Cell}}^0 - 0.059 \log_{10} \left[ \text{H}^+ \right] - 0.059 \log_{10} \left[ \text{Cl}^- \right]
\]

Saturate the Chloride ion so that it is constant.
Application of pH Measurement

\[ E_{cell} = \left\{ E_{cell}^0 + E_{offset} \right\} - (0.0591) \log_{10}[H^+] \]

\[ E_{cell} = E_{ref} + 59.1 \cdot pH \quad mV \]

- \( E_{cell} \) is directly proportional to pH or \( \log [H^+] \)
None of these ideas is separate. They are all connected, and are all derived directly from thermodynamics.