Lecture 15: The Nernst Equation

• Reading: Zumdahl 11.4

• Outline:
  – Why would concentration matter in electrochemistry?
  – The Nernst equation (contains Concentration effects on Battery Voltage)
  – Applications
  – An entropically-driven battery

• Problems (Ch 11 Zumdahl 5th Ed.)
  – 49, 50, 52 (Show you can do this), 53 (how much does entropy contribute), 55, 57d.
Concentration and $E_{\text{cell}}$

- Consider the following redox reaction:

$$\text{Zn(s)} + 2\text{H}^+ (\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{H}_2(\text{g})$$

(spontaneous)

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

Expect driving force for product formation to increase.

LeChatelier Principle

Therefore $\Delta G_{\text{rxn}}$ decreases, and $E_{\text{cell}}$ increases

How does $E_{\text{cell}}$ depend on concentration?
$E_{\text{cell}}$ depends on Concentration

The Nernst Equation

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

Putting this with our recent result:

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

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

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

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

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

\[ E_{cell} = E_{cell}^0 - \frac{60}{n} \log_{10} Q \ mV \]

• Example. Calculate the cell potential for the following:

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

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

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

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

Fe(s) + Cu\textsuperscript{2+} (aq) \rightarrow Fe\textsuperscript{2+} (aq) + Cu(s)

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

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

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

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

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

Turn the iron half cell around and add. Note n=2
**E\text{cell} example**

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

Now, calculate Q and then E\text{cell}.

Notice, the concentrations are in separate containers.

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

\[n = 2\]

\[E_{\text{cell}} = E_{\text{cell}}^{0} - \frac{0.06}{n} \log_{10} Q V\]

\[E_{\text{cell}} = 0.78 - \frac{0.06}{2} \log_{10} 0.33 = 0.78 + 0.014 = 0.80 \text{V}\]
If $[\text{Cu}^{2+}] = 0.3 \text{ M}$, what $[\text{Fe}^{2+}]$ is needed so that $E_{\text{cell}} = 0.76 \text{ V}$?

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

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

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

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

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

\[
[\text{Fe}^{2+}] = 4.7 \cdot 0.3 = 1.4 \text{M}
\]
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? Why?
Concentration Cells: Concentration Effects Only

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

\[
\begin{array}{c}
\text{Anode} \\
0.1 \text{ M Ag}^+ \\
0.1 \text{ M NO}_3^- \\
\end{array}
\quad
\begin{array}{c}
\text{Cathode} \\
1 \text{ M Ag}^+ \\
1 \text{ M NO}_3^- \\
\end{array}
\]

- \(E^{\circ}_{1/2}\) is measured when all species are in standard state, so this means both sides have 1 M concentrations of 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: $\text{Ag} \rightarrow \text{Ag}^+ + e^- \quad E_{1/2}^0 = -0.80 \text{ V}$

Cathode: $\text{Ag}^+ + e^- \rightarrow \text{Ag} \quad E_{1/2}^0 = +0.80 \text{ V}$

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

$n = 1$

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

$$E_{\text{cell}} = 0.0 - \frac{0.059}{1} \log_{10} 0.1 = 0. + 0.059 = 0.06 \text{ V}$$
Concentration Cells (2\textsuperscript{nd} example)

Another Example:
The number of electrons per rxn is different

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

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

2 \( e^- \) transferred…\( n = 2 \)

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

\[ E_{\text{cell}} = 30 \text{mV} \]  
Same Result for Cu/Cu^{2+} battery
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:

\[
\begin{align*}
Hg_2Cl_2(s) + 2e^- & \rightarrow 2Hg(l) + 2Cl^-(aq) \quad \text{E}^{\circ} = 0.27 \text{ V} \\
H_2(g) & \rightarrow 2H^+(aq) + 2e^- \quad \text{E}^{\circ} = 0.0 \text{ V}
\end{align*}
\]

\[
\begin{align*}
Hg_2Cl_2(s) + H_2(g) & \rightarrow 2Hg(l) + 2H^+(aq) + 2Cl^-(aq) \quad \text{E}^{\circ}_{\text{cell}} = 0.27 \text{ V}
\end{align*}
\]
Measurement of pH

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

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

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

\[ n = 2 \]

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

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

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

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 \( \log [H^+] \)
Summary

\[ w^\text{electric}_{\text{rev}} = \Delta G = \Delta G_{\text{rxn}} \Delta X \]

\[ \Delta G_{\text{rxn}} = \Delta G^0_{\text{rxn}} + RT \ln Q \]

\[ \Delta G_{\text{rxn}} = \Delta G^0_{\text{rxn}} + 2.48 \ln Q \quad kJ \]

\[ \Delta G_{\text{rxn}} = -nF \cdot \mathcal{E}_{\text{cell}} \quad \mathcal{E}_{\text{cell}} = \mathcal{E}_{\text{cell}}^0 - \frac{0.0591}{n} \cdot \log Q \quad V \]

None of these ideas is separate. They are all connected, and are all derived directly from thermodynamics.
Nernst Equation and half reactions (Z11.52)

Show that the Nernst Equation can be applied to half reactions as well:

\[
E_{\text{Cell}} = E^0_{\text{Cell}} - \frac{0.06}{n} \cdot \log Q \quad V
\]

\[
E_{\text{Cell}} = E^1 - E^2 \quad Q = Q_1 Q_2^{-1}
\]

\[
E^1 = E^0_1 - \frac{0.06}{n} \cdot \log Q_1 \quad E^2 = E^0_2 - \frac{0.06}{n} \cdot \log Q_2
\]

However each half reaction has to be multiplied by some factor so that the number of electrons is the same for both half reactions.

\[
n = n_1 m_1 = n_2 m_2
\]

\[
E^1 = E^0_1 - \frac{0.06}{n_1 m_1} m_1 \cdot \log Q_1 = E^0_1 - \frac{0.06}{n_1 m_1} \cdot \log \left( Q_1^{m_1} \right) = E^0_1 - \frac{0.06}{n} \cdot \log \left( Q_1^{m_1} \right)
\]

So this shows that yes one can do each half reaction separately and get the same result as doing both half reactions together as a single reaction.
Nernst Equation half reactions (Z11.52a)

Apply the Nernst Equation to the Half reaction Cu/Cu2+

So you need to write and balance the half reaction in the same direction as the half cell EMF is specified, which is written as a reduction potential in table 11.1

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

\[ n = 2 \quad \left[ Cu^{2+} (aq) \right] = 0.1M \quad Q = \frac{1}{\left[ Cu^{2+} (aq) \right]} = 10 \]

\[ E^1 = E^0 - \frac{0.06}{n_1} \cdot \log Q_1 = 0.34 - \frac{0.06}{2} \cdot \log 10 = 0.34 - 0.07 = 0.27V \]
Sample Problems (Z11.49, 52)

• Analyze the galvanic cell for the reaction:

\[ Au^{3+} + 3e^- \rightarrow Au \quad E^\circ = 1.5V \]
\[ Tl^+ + e^- \rightarrow Tl \quad E^\circ = -0.34V \]

As you can see it really doesn’t matter what the metals are: The overall cell is just the sum of the half cell potentials

For later we need to know that \( n=3 \) and have the balance reaction for the cell:

\[ Au^{3+} + 3Tl \rightarrow Au + 3Tl^+ \quad E^\circ_{cell} = 1.84V \]

Get Gibbs energy and K:

\[ \Delta G^\circ_{rxn} = -nF \cdot E_{cell}^\circ = -RT \ln K \]
\[ \Delta G^\circ_{rxn} = -550kJ \]

So a 2V battery is VERY Spontaneous.

\[ \ln K = n \frac{E_{cell}^\circ}{0.025} = 3 \frac{1.84}{0.025} = 220 \]
Sample (Z11.49, 52)

- How much change in EMF if product and reactant concentrations are low? There is a trade off.

\[ Au^{3+} + 3Tl \rightarrow Au + 3Tl^+ \]

\[ \mathcal{E}_\text{cell}^o = 1.84V \]

\[
\begin{bmatrix}
\text{[Au}^{3+}\text{]} = 1 \cdot 10^{-2} \\
\text{[Tl}^+\text{]} = 1 \cdot 10^{-4} \ M
\end{bmatrix}
\]

\[
\mathcal{E}_\text{cell} - \mathcal{E}_\text{cell}^0 = -\frac{0.0591}{n} \cdot \log Q \\
Q = \frac{\text{[Tl}^+\text{]}^3}{\text{[Au}^{3+}\text{]}} = \frac{10^{-12}}{10^{-2}} = 10^{10}
\]

\[
\mathcal{E}_\text{cell} - \mathcal{E}_\text{cell}^0 = \frac{0.6}{3} \cdot \log 10 = 0.46 \\
\mathcal{E}_\text{cell} = 1.8 + 0.46 = 2.3V
\]

The voltage will stay up until the Gold ion concentration goes way down. That’s the way batteries are: When they start to go out, they go quickly.
Lead Acid Car Battery (Z11.53)

- For the car battery, calculate the standard EMF at -20C.

\[ \text{Pb}(s) + \text{PbO}_2(s) + 4\text{H}^+ \rightarrow 2\text{Pb}^{2+}(aq) + 2\text{H}_2\text{O} \]

\[ \text{Pb}^{2+}(aq) + \text{SO}_4^{2-}(aq) \rightarrow \text{PbSO}_4(aq) \quad K_{sp} = 1.3 \cdot 10^{-8} \]

\[ \text{Pb}(s)|\text{Pb}^{2+}\parallel\text{PbO}_2(s) \quad \text{Shorthand/no salt bridge} \]

\[ \varepsilon_{\text{cell}}^o = 2.04V \]

The EMF is the total for both reactions; does the second reaction increase the EMF or decrease it?

\[ \Delta G_{\text{Rxn}}^o = -nF \cdot \varepsilon_{\text{cell}}^o = \Delta H_{\text{Rxn}}^o - T \Delta S_{\text{Rxn}}^o \]

The reaction is exothermic and the entropy is positive. So both parts contribute to the battery functioning. Because the entropy is positive the EMF of the cell will be smaller at lower temperatures. It is not surprising that a battery works worse at low temperatures.

An extra question: What percentage of the battery is driven entropically under standard conditions?

\[ \frac{T \Delta S_{\text{Rxn}}^o}{-\Delta G_{\text{Rxn}}^o} = \frac{0.298 \cdot 263}{316 + 0.298 \cdot 263} = \frac{78}{395} = 0.2 = 20\% \]
The Concentration Battery (Z11.55)

\[ \text{Ni}_A (s) \bigg| \text{Ni}^{2+}_A (aq) \bigg| \text{Ni}^{2+}_B (aq) \bigg| \text{Ni}_B (s) \]

- Two cells, each contains Ni metal and Ni \(^{2+}\) ions.
- Why would there be any potential at all?
- The concentration in the different Beakers is different.
- Eg (c) 1 M Ni \(^{2+}\) in beaker A and 0.1M Ni \(^{2+}\) in beaker B.
  - What is the standard EMF?
  - What is the EMF?
  - Which way do the electrons go?
  - What is the concentration of Ni \(^{2+}\) in A/B at equilibrium?
  - What is EMF at equilibrium?

Not spontaneous in direction written.

\[ \varepsilon_{cell} = \varepsilon_{cell}^0 - \frac{0.0591}{n} \cdot \log Q = -0.03 \log_{10} 10 = -0.03V = -30mV \]

\[ \varepsilon_{cell}^0 = 0 \quad Q = \left[ \frac{\text{Ni}^{2+}}{\text{Ni}^{2+}} \right]_A = 10 \quad n = 2 \]

It is a totally Entropic battery!!!!!