Calculating cell potential \( (E_{\text{cell}}) \)

1. Consider an electrochemical cell (a.k.a. galvanic cell, voltaic cell, battery) with Zn(s) and 0.25 M \( \text{Zn(NO}_3\text{)}_2(\text{aq}) \) in one compartment and Cu(s) and 0.25 M \( \text{Cu(NO}_3\text{)}_2(\text{aq}) \) in the other compartment.

   a. Calculate the cell potential (EMF, voltage) at 298 K.

   Reduction (cathode): \( \text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)} \) \( E^o_{\text{cathode}} = +0.337 \text{ V} \)

   Oxidation (anode): \( \text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \) \( E^o_{\text{anode}} = -0.763 \text{ V} \)

   Net (overall cell reaction): \( \text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)} \)

   \[ E_{\text{cell}} = E^o_{\text{cell}} - (0.0592/n)\log Q = 1.100 \text{ V} - \frac{0.0592 \text{ V}}{2} \log(1) = \left[ 1.100 \text{ V} \right] \]

   \( Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = \frac{0.25}{0.25} = 1 \) (even though this is not a standard cell, it behaves exactly like a standard cell because \( Q = 1 \! )

   b. What would be the cell potential if the concentration of \( \text{Zn(NO}_3\text{)}_2 \) was increased to 2.5 M?

   \[ Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = \frac{2.5}{0.25} = 10 \]

   \[ E_{\text{cell}} = 1.100 \text{ V} - \frac{0.0592 \text{ V}}{2} \log(10) = 1.070 \text{ V} \]

   A 10-fold increase in \( Q \) results in a very small voltage change.

   c. Calculate the equilibrium constant (at 298 K) for the overall cell reaction.

   \[ \Delta G^o = -nF E^o_{\text{cell}} = -2(96,500 \frac{\text{C}}{\text{mol}})(1.100 \frac{\text{J}}{\text{C}}) = -212,300 \frac{\text{J}}{\text{mol}} \]

   \[ = -212.3 \frac{\text{kJ}}{\text{mol}} \]

   \[ K_e = e^{-\frac{\Delta G^o}{RT}} = e^{-\frac{(-212.3 \frac{\text{kJ}}{\text{mol}})}{(0.008314 \frac{\text{J}}{\text{mol} \cdot \text{K} \cdot \text{K}})(298 \text{ K})}} = 1.64 \times 10^{37} \]

   This reaction goes to completion.

   Recall that \( E_{\text{cell}} = 0 \) when the reaction is at equilibrium \( (Q = K) \)

   Plug this value of \( K_e \) into the Nernst equation and you should get \( E_{\text{cell}} = 0 \). Now you can see why it takes a huge change in \( Q \) to change \( E_{\text{cell}} \) significantly.
2. Consider a voltaic cell with Cr(s) and Cr\(^{3+}\)(aq) in one compartment and Zn(s) and Zn\(^{2+}\)(aq) in the other compartment.

a. Draw and label a diagram of this cell.

Zn is more active than Cr, so Zn is the anode.

\[
\begin{align*}
\text{Zn} & \rightarrow \text{Zn}^{2+} + 2e^- \\
\text{Cr}^{3+}(aq) + 3e^- & \rightarrow \text{Cr}(s)
\end{align*}
\]

(The voltage assumes that \( Q = 1 \))

b. Calculate the standard cell potential and the equilibrium constant for the overall reaction.

\[
\begin{align*}
\text{red: } & \quad 2 \times (\text{Cr}^{3+}(aq) + 3e^- \rightarrow \text{Cr}(s)) & E_{\text{cell}}^\circ = -0.74 \text{ V} \\
\text{ox: } & \quad 3 \times (\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^-) & E_{\text{anod}}^\circ = -0.763 \text{ V} \\
\text{net: } & \quad 3\text{Zn}(s) + 2\text{Cr}^{3+}(aq) \rightarrow 3\text{Zn}^{2+}(aq) + 2\text{Cr}(s) & E_{\text{cell}}^\circ = +0.023 \text{ V}
\end{align*}
\]

\[
\Delta G^\circ = -nF E_{\text{cell}}^\circ = -(6)(96,500 \text{ J/mol})(0.023 \text{ V}) = -13,317 \text{ J/mol}
\]

\[
K_{eq} = e^{-\frac{\Delta G^\circ}{RT}} = e^{-\frac{13,317 \text{ J/mol}}{2.48 \text{ kJ/mol}}} = 2.15
\]

(Note: at 298 K, \( RT = 2.48 \text{ kJ/mol} \))

Even though there is only a small difference in the reduction potentials, the reaction still has a pretty big \( K_{eq} \).
c. Calculate the cell potential if $[\text{Zn}^{2+}] = 5.00 \ M$ and $[\text{Cr}^{3+}] = 0.50 \ M$? What does this result tell you? How would your diagram change? How does $Q$ compare to $K$?

$$Q = \frac{[\text{Zn}^{2+}]^3}{[\text{Cr}^{3+}]^2} = \frac{(5.00)^3}{(0.50)^2} = 500 \quad n = 6$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592 \ V}{n} \log Q = 0.023 \ V - \frac{0.0592 \ V}{6} \log (500)$$

$$= -0.00363 \ V$$

Not spontaneous so reaction proceeds in the reverse direction.

All arrows in diagram reverse.

Now $Q > K_{eq} \ (500 > 215)$

d. If zinc is the anode and $[\text{Cr}^{3+}] = 0.010 \ M$, what must the $[\text{Zn}^{2+}]$ be in order to achieve 0.050V?

$$0.050 \ V = 0.023 \ V - \frac{0.0592 \ V}{6} \log Q$$

$$Q = 1.834 \times 10^{-3} = \frac{[\text{Zn}^{2+}]^3}{(0.010)^2}$$

$$[\text{Zn}^{2+}]^3 = \sqrt[3]{5.68 \times 10^{-3} \ M}$$

Notice $E_{\text{cell}} = 0.023 \ V$ when $Q = 1$

$E_{\text{cell}} = 0.050 \ V$ when $Q = 1.8 \times 10^{-3}$

$Q$ had to drop a lot to double the voltage.

If all but one concentration is known, then $E_{\text{cell}}$ tells you the unknown concentration.

(see the last problem.)

e. What must the value of $Q$ be in order for the voltage to be zero?

$$Q = K_{eq} = 215$$
3. A standard zinc half-cell was coupled to a standard hydrogen electrode. When the red wire was attached to the hydrogen electrode, the cell potential was 0.763 V. What is the standard reduction potential for the zinc half-cell?

\[ \text{Zn/Zn}^{2+} \parallel \text{H}_2/\text{H}^+ \quad [\text{Zn}^{2+}] = 1.0 \text{ M}, [\text{H}^+] = 1.0 \text{ M}, P_{\text{H}_2} = 1 \text{ atm} \quad (\text{standard hydrogen electrode}) \]

Reduction (cathode): \( 2 \text{H}^+ + 2e^- \rightarrow \text{H}_2 \quad \quad E^\circ_{\text{cathode}} = 0.00 \text{ V} \)

Oxidation (anode): \( \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \quad \quad E^\circ_{\text{anode}} = X \)

Net (overall cell reaction): \( \text{Zn} + 2 \text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2 \quad \quad E^\circ_{\text{cell}} = 0.763 \text{ V} \)

\[ 0.00 - X = 0.763 \]

\[ X = -0.763 \text{ V} \]

This is how all standard reduction potentials are measured!

4. A Zn/Zn\(^{2+}\) half-cell was coupled to a hydrogen electrode in which \( P_{\text{H}_2} = 1 \text{ atm} \). The \([\text{Zn}^{2+}]\) in the anode compartment was 0.10 M and the cell emf was 0.542 V. Calculate the pH in the cathode compartment.

\[ [\text{Zn}^{2+}] = 0.10 \text{ M} \]

\[ P_{\text{H}_2} = 1.00 \text{ atm} \]

\[ [\text{H}^+] = ? \]

\[ E_{\text{cell}} = 0.542 \text{ V} \]

\[ Q = \frac{[\text{Zn}^{2+}]P_{\text{H}_2}}{[\text{H}^+]^2} \quad \text{(This is not } Q_c \text{ or } Q_p \text{. It is a "mixed" } Q) \]

\[ E_{\text{cell}} = E^\circ_{\text{cell}} - 0.0592 \text{ V } \log Q \]

\[ 0.542 \text{ V} = 0.763 \text{ V} - \frac{0.0592 \text{ V } \log Q}{2} \]

\[ Q = 2.93 \times 10^{-7} = \frac{(0.10)(1.00)}{[\text{H}^+]^2} \]

\[ [\text{H}^+] = 5.90 \times 10^{-5} \text{ M} \]

\[ \text{pH} = 4.233 \quad \text{This is how a pH meter works!} \]