Today: Pick up CH19 @ Reduction Potential

→ Eqn 19.1 vs. Reverse & Add.
→ Spontaneous / ΔG
→ Nernst

Monday: Batteries
Corrosion
Electrolysis

As I said before - Electrocen has always been a bane
→ I get anode/cathode backwards
→ I get sign of E° wrong (repeatedly)
→ My solution is to write it out carefully with baby steps

To calculate E\text{cell}, we can go 2 ways:

1. Use Eqn 19.1:

\[ E_{\text{cell}} = E^º_{\text{cathode}} - E^º_{\text{anode}} \]

E° values come straight out of table.

e.g. Zn & Pb

\begin{align*}
\text{Table:} & \\
\text{Pb}^{2+} & + 2e^- \rightarrow \text{Pb} & -0.13 V \\
\text{Zn}^{2+} & + 2e^- \rightarrow \text{Zn} & -0.76 V
\end{align*}

Pb is higher so gets reduced = cathode

\[ \text{Pb}^{2+} + \text{Zn} \rightarrow \text{Pb} + \text{Zn}^{2+} \]

\[ E_{\text{cell}} = (-0.13) - (-0.76 V) \]

\[ = 0.63 V \]

2. \[ \text{Write out Equations & reverse} \]

\[ \text{Pb}^{2+} + 2e^- \rightarrow \text{Pb} \quad E^º = -0.13 \]

\[ \text{Zn} + 2e^- \rightarrow \text{Zn}^{2+} \quad E^º = +0.76 \]

\[ \text{Pb}^{2+} + \text{Zn} \rightarrow \text{Pb} + \text{Zn}^{2+} \quad E_{\text{cell}} = 0.63 \]

Anode 1st: \[ \text{Zn} \parallel \text{Zn}^{2+} \parallel \text{Pb}^{2+} \parallel \text{Pb} \]
A note about electricity:

\[ \text{can envision as water: (Voltage = height of water-fall)} \]

\[ \text{\( \text{Pb}^{2+} + 2e^- \rightarrow \text{Pb(s)} \)} \quad \text{E}^0 = -0.13 \text{V} \]

\[ 2 \times (\text{Na}(s) \rightarrow \text{Na}^+ + e^-) \quad \text{E}^0 = +2.71 \text{V} \]

\[ \text{Pb}^{2+} + 2\text{Na}(s) \rightarrow \text{Pb(s)} + 2\text{Na}^+ \quad \text{E} = -0.13 \text{V} + 2.71 \text{V} = 2.58 \text{V} \]

\[ \text{not \( 2x \)!} \]

- Voltage is a "potential" not energy.

Spontaneity: to predict reactions, we use \( \Delta G \).

Converting \( V \to \text{energy gets us to } \Delta G \)

\[ \text{Electrical Energy} = \text{Volts} \times \text{(Current)} = \]

\[ 1 \text{V} \times 1 \text{Coulomb} = 1 \text{J} \]

1 mole of electrons = 96,485.3 Coulombs (electrical charge)

1 Faraday (F) = 9.65 x 10^4 C/mol or 1 mol C

\[ \text{Work done by cell} = W = -nFE_{cell} \]

\[ \text{at of mole} \]
\[ \Delta G = \text{work} \]
\[ \Delta G = -nFE_{\text{cell}}, \quad \Delta G^o = -nFE^o_{\text{cell}} \]

we can fool w/ \( \Delta G (\Delta G = -RT \ln(K)) \)

\[ -RT \ln(K) = -nFE^o_{\text{cell}} \]

\[ E^o_{\text{cell}} = \frac{RT}{nF} \ln(k) \quad @ \ 298K, \quad R = 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}, \]
\[ F = 96500 \frac{\text{C}}{\text{mol}}, \quad \text{convert log to ln} \]

\[ = \frac{(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}})(298 K)}{nF} \log(K) \cdot \ln(10) \]

\[ E^o_{\text{cell}} = \frac{0.0592 V \log(K)}{n} \]

For Pb \( \text{II} \) \( \text{Na}^+ \):

\[ E^o_{\text{cell}} = +0.63 \]
\[ n = 2 \]

\[ +0.63 V = \frac{0.0592 V \log(K)}{2} \]

\[ \log(K) = -2.138 \quad K = 10^{-2.138} = 1.9 \times 10^{-2} \]

That's all for 1 M solutions. To work w/ other solutions, we start with:

\[ \Delta G = \Delta G^o + RT \ln(Q) \]
\[ -nFE = -nFE^o + RT \ln(Q) \]
\[ E = E^o - \frac{RT}{nF} \ln(Q) \]

\[ E = E^o - \frac{0.0592 V \log(Q)}{n} \]
The Nernst Equation:

\[ E = E^0 - \frac{RT}{nF} \ln(Q) \]

allows us to measure/predict voltage of solutions that aren’t 1.0 M

E.G.:

If we do electrode \( \text{v} / \text{Zn}^{2+} \text{Cu}^+ \):

\[
\begin{align*}
\text{Zn}^{2+} + 2e^- & \rightarrow \text{Zn}(s) & -0.76 \text{ e}^{-} \text{reduced} \\
\text{Cu}^{2+}(aq) + 2e^- & \rightarrow \text{Cu}(s) & +0.34 \text{ e}^{-} \text{reduced}
\end{align*}
\]

\[ n = 2e^- \]

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

\[ E^0 = 0.34 + 0.76 = \boxed{1.10 \text{ V}} \]

Nernst:

\[
E_{cell} = E^0 - \frac{0.0592}{2} \log \left( \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right)
\]

\[ = 1.10 - \frac{0.0592}{2} \log \left( \frac{0.5}{1.5} \right) \]

\[ = 1.10 - (-0.014 \text{ V}) \]

\[ = 1.11 \text{ V} \]

Watch this:

\[ [\text{Cu}^{2+}] = 5.0 \text{ M}, \]
\[ [\text{Zn}^{2+}] = 0.001 \text{ M} \]

\[
E_{cell} = 1.10 - \frac{0.0592}{2} \log \left( \frac{0.001}{5} \right) = 1.10 - (-0.11) = 1.21 \text{ V}
\]

or

\[ [\text{Cu}^{2+}] = 5.0 \text{ M} \]
\[ [\text{Zn}^{2+}] = 10^{-9} \text{ M} \]

\[ E_{cell} = 1.39 \text{ V} \rightarrow \text{extra 0.29 V} \]

but as soon as it starts,

\[ [\text{Zn}^{2+}] \uparrow \uparrow \text{ V} \downarrow \]