Standard Cell Potentials, $E^\circ$ or $\mathcal{E}^\circ$

The cell potential is a measure of the driving force - or spontaneity - of a chemical reaction.

Our **STANDARD** conditions are the same as we saw in Thermodynamics, Solutes 1 $M$, gases 1 atm, pure liquid or solids.

We cannot measure potentials of individual half-cells, we can only measure the potential of two half cells coupled together.

We would like to know the potentials of standard half-cells - and we can get them by arbitrarily assigning a voltage of 0 to a **Standard Hydrogen Electrode**, then measure/report all voltages of all other standard half-cells relative to that. i.e. we assign a voltage of 0.000 to the reduction reaction

\[
2H^+\text{(aq)} + 2e^- \rightarrow H_2\text{(g)}, \quad E^\circ = 0.000 \text{ v}
\]
Now look back at the Standard Zn/Zn$^{2+}$(aq) and H$_2$(g)/H$^+$(aq) Cell

\[
\text{Zn(s)} \rightarrow \text{Zn}^{2+}$(aq) + 2e$^- \quad V = ?$
\]

\[
2e^- + 2\text{H}^+$(aq) $\rightarrow$ H$_2$(g) $\quad V = 0.00$
\]

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

so we can deduce that \(\text{Zn(s)} \rightarrow \text{Zn}^{2+}$(aq) + 2e$^- \quad V = +0.76 \text{ V}\)

**CONVENTION**: Always report half-cell potentials in the form: \(\text{Ox} + ne^- \rightarrow \text{Red}\)

i.e. we have **Standard Reduction Potentials**

If we *Reverse* a half-cell, we *change the SIGN of the voltage*.

\[
\text{Zn}^{2+}$(aq) + 2e$^- \rightarrow \text{Zn(s)}, \quad E^\circ = -0.76 \text{ V}
\]

*All 1M*
Now look back at the Standard Zn/Zn$^{2+}$(aq) and Cu(s)/Cu$^{2+}$(aq) Cell

Zn(s) → Zn$^{2+}$(aq) + 2e$^-$ $\quad E^\circ = + 0.76$ V

2e$^-$ + Cu$^{2+}$(aq) → Cu(s) $\quad E^\circ = ??$

\[\begin{align*}
\text{Zn(s) + Cu}^{2+}(&\text{aq}) \rightarrow \text{Zn}^{2+}(&\text{aq}) + \text{Cu(s)} \quad E^\circ = +1.10 \text{ V}
\end{align*}\]

by subtraction we obtain

Cu$^{2+}$(aq) + 2e$^-$ → Cu(s) $\quad E^\circ = +0.34$ V

By proceeding in this way we can build up a Table of

\textbf{Standard Reduction Potentials}

\textit{VERY USEFUL}!!!

Daniell Cell
### Sample of a **Standard Reduction Potential** Table

<table>
<thead>
<tr>
<th>Ox + ne⁻ → Red</th>
<th>E° (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₂(g) + 2e⁻ → 2F⁻(aq)</td>
<td>+2.87</td>
</tr>
<tr>
<td>Cl₂(g) + 2e⁻ → 2Cl⁻(aq)</td>
<td>+1.36</td>
</tr>
<tr>
<td>Au³⁺(aq) + 3e⁻ → Au(s)</td>
<td>+1.50</td>
</tr>
<tr>
<td>Ag⁺(aq) + e⁻ → Ag(s)</td>
<td>+0.80</td>
</tr>
<tr>
<td>Fe³⁺(aq) + e⁻ → Fe²⁺(aq)</td>
<td>+0.77</td>
</tr>
<tr>
<td>Cu²⁺(aq) + 2e⁻ → Cu(s)</td>
<td>+0.34</td>
</tr>
<tr>
<td>2H⁺(aq) + 2e⁻ → H₂(g)</td>
<td>0.000...</td>
</tr>
<tr>
<td>Sn⁴⁺(aq) + 2e⁻ → Sn²⁺(aq)</td>
<td>-0.15</td>
</tr>
<tr>
<td>Zn²⁺(aq) + 2e⁻ → Zn(s)</td>
<td>-0.76</td>
</tr>
<tr>
<td>Na⁺(aq) + e⁻ → Na(s)</td>
<td>-2.71</td>
</tr>
<tr>
<td>Li⁺(aq) + e⁻ → Li(s)</td>
<td>-3.05</td>
</tr>
</tbody>
</table>

**Best oxidizing agent**: F₂(g)

**Best reducing agent**: Li⁺(aq)
$F_2(g)$ is the BEST oxidizing agent (and the most easily reduced)

$Li^+(aq)$ is the WORST oxidizing agent (and the most difficult to reduce)

$Li(s)$ is the BEST reducing agent (and the most easily oxidized)

$F^-(aq)$ is the WORST reducing agent (and the most difficult to oxidize)
Example

1. $\text{Mg}^{2+} + 2e \rightarrow \text{Mg} \quad E^0 = -2.37$

2. $\text{Zn}^{2+} + 2e \rightarrow \text{Zn} \quad E^0 = -1.66$

3. $\text{Sn}^{4+} + 2e \rightarrow \text{Sn}^{2+} \quad E^0 = +0.15$

4. $\text{Ag}^+ + e \rightarrow \text{Ag} \quad E^0 = +0.8$

Strongest reducing agent

Strongest oxidizing agent

We will combine these together to see what reacts with what

- the half cell with the more -ve $E$ will be the anode

- the half cell with the more +ve $E$ will be the cathode

$E_{\text{cell}} = E_{\text{cat}} - E_{\text{an}}$
1 and 4

\[ 1 \text{Mg}^{2+} + 2e \rightarrow \text{Mg} \quad -2.37 \]

\[ 4 \text{Ag}^+ + e \rightarrow \text{Ag} \quad +0.8 \]

So reverse 1 (scale) and add up

\[ \text{Mg} \rightarrow \text{Mg}^{2+} + 2e \]
\[ 2\text{Ag}^+ + 2e \rightarrow 2\text{Ag} \]

\[ \text{Mg} + 2\text{Ag}^+ \rightarrow \text{Mg}^{2+} + 2\text{Ag} \quad E = 2.37 + 0.8 = +3.17 \]

Magnesium metal reduces silver
How do we obtain Standard Cell Potentials from Standard Reduction Potentials?

What would the Standard Cell Potential be for a Cu|Cu$^{2+}$ and Zn|Zn$^{2+}$ cell?

Step 1. Write out the two S.R.P. equations:

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

Step 2. The half-reaction with the more positive half-cell potential goes as written and the other half-cell is driven in the reverse direction.

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

Step 3. Are the electrons balanced?

Step 4. Now add

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

\[E^\circ = 1.10V\]
Comments:
Note that the $E^\circ$ value is POSITIVE, i.e. the reaction is spontaneous as we have written it (under Standard Conditions). Which is the Anode, which is the Cathode?

Now look at the Ni|Ni$^{2+}$(aq) and Ag|Ag$^+$ (aq) cell.
What is the spontaneous cell reaction, anode, cathode, $E^\circ$?

Step 1. Get SRPs from Tables

\[
\begin{align*}
\text{Ni}^{2+}(aq) + 2e^- &\rightarrow \text{Ni(s)} & -0.25 \\
\text{Ag}^+(aq) + e^- &\rightarrow \text{Ag(s)} & +0.80
\end{align*}
\]

Step 2: More +ve goes as written, other in reverse

\[
\begin{align*}
\text{Ag}^+(aq) + e^- &\rightarrow \text{Ag(s)} & +0.80 \\
\text{Ni(s)} &\rightarrow \text{Ni}^{2+}(aq) + 2e^- & +0.25
\end{align*}
\]

Step 3. Get electrons to balance:

\[
\begin{align*}
2\text{Ag}^+(aq) + 2e^- &\rightarrow 2\text{Ag(s)} & +0.80 \\
\text{Ni(s)} &\rightarrow \text{Ni}^{2+}(aq) + 2e^- & +0.25
\end{align*}
\]

Step 4. Now add

\[
2\text{Ag}^+(aq) + \text{Ni(s)} \rightarrow 2\text{Ag(s)} \text{ Ni}^{2+}(aq)
\]

$E^\circ = +1.05 \text{ V}$

Does anything strike you as odd about this??

YES !

Although we multiplied the coefficients in the Silver half-cell by 2, we did NOT double the half-cell voltage.

Why NOT ??
Compare

(1). \[ \text{Ag}^+ (aq) + e^- \rightarrow \text{Ag} (s) \]

(2). \[ 2\text{Ag}^+ (aq) + 2e^- \rightarrow 2\text{Ag} (s) \]

The energy released by (2) is certainly twice that of (1), but remember that

**Voltage = Joules/Coulombs**

(energy per coulomb of charge transferred)

Equation (2) involves twice the energy, but it also involves twice the coulombs - so the VOLTAGE does not change. An **Intensive** property.

**Bottom line: when scaling do not scale the voltage**

Batteries do not give out more volts if you make them bigger - they just last longer.
Example

Would the reaction
\[ \text{A}^{3+}(aq) + \text{Mg}(s) \rightarrow \text{A}(s) + \text{Mg}^{2+}(aq) \]
go as written under Standard Conditions, or would the reverse reaction occur?

Step 1. Get SRP equations:
\[ \begin{align*}
\text{Mg}^{2+}(aq) + 2\text{e}^- & \rightarrow \text{Mg}(s) \quad -2.37 \\
\text{A}^{3+}(aq) + 3\text{e}^- & \rightarrow \text{A} \quad -1.66
\end{align*} \]

Step 2.
More positive goes as written, reverse the other:
\[ \begin{align*}
\text{A}^{3+}(aq) + 3\text{e}^- & \rightarrow \text{A} \quad -1.66 \\
\text{Mg}(s) & \rightarrow \text{Mg}^{2+}(aq) + 2\text{e}^- +2.37
\end{align*} \]

Step 3. Balance electrons, leave \( E^\circ \) alone!
\[ \begin{align*}
2\text{A}^{3+}(aq) + 6\text{e}^- & \rightarrow 2\text{A} \quad -1.66 \\
3\text{Mg}(s) & \rightarrow 3\text{Mg}^{2+}(aq) + 6\text{e}^- +2.37
\end{align*} \]

Step 4. Now add:
\[ \begin{align*}
2\text{A}^{3+}(aq) + 3\text{Mg}(s) & \rightarrow 2\text{A}(s) + 3\text{Mg}^{2+}(aq) \\
E^\circ & = 0.71 \text{ V} \quad \text{and so is spontaneous as written}
\end{align*} \]
Homework

With access to an SRP table, deduce what reaction (if any) will occur when:-
(a) Metallic Sn is added to
   (i) 1 \text{ M} \text{ HCl} solution
   (ii) an aqueous solution of Cl₂

(b) A solution of 1.0 \text{ M} \text{ Sn}^{2+} is treated with
   (i) metallic Zn
   (ii) FeCl₃ solution

(c) A solution of 1.0 \text{ M} \text{ Sn}^{4+} is treated with
   (i) metallic Zn
   (ii) an aqueous solution of Cl₂

_Solution at front of next lecture: do not work from the answer_