

Standard reduction potentials

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Standard reduction potentials

Standard Hydrogen Electrode (SHE) has $E^\circ = 0 \text{ V}$
 $2 \text{ H}^+(1 \text{ M}) + 2 e^- \rightarrow \text{H}_2(1 \text{ atm}), E^\circ = 0 \text{ V}$

All other reductions defined *relative to SHE*

$\text{Zn}^{2+}(1 \text{ M}) + 2 e^- \rightarrow \text{Zn}(s), E^\circ = -0.763 \text{ V}$
 $\text{Cu}^{2+}(1 \text{ M}) + 2 e^- \rightarrow \text{Cu}(s), E^\circ = +0.340 \text{ V}$
etc.

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Combining reduction potentials

$\text{Zn}^{2+}(1 \text{ M}) + 2 e^- \rightarrow \text{Zn}(s), E^\circ = -0.763 \text{ V}$
 $\text{Cu}^{2+}(1 \text{ M}) + 2 e^- \rightarrow \text{Cu}(s), E^\circ = +0.340 \text{ V}$
 $\text{Cu}^{2+}(1 \text{ M}) + \text{Zn}(s) \rightarrow \text{Cu}(s) + \text{Zn}^{2+}(1 \text{ M}), E^\circ = ?$

$E^\circ = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$
 $= +0.340 \text{ V} - (-0.763 \text{ V}) = +1.103 \text{ V}$

So, Zn is **oxidized** by Cu^{2+}

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Combining reduction potentials

$E^\circ = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$
Why?

$\Delta G^\circ_{\text{cell}} = \Delta G^\circ_{\text{cathode}} + \Delta G^\circ_{\text{anode}}$
 $-n F E^\circ_{\text{cell}} = -n F E^\circ_{\text{cathode}} - (-n F E^\circ_{\text{anode}}) \dots$

“–” since anode runs as an oxidation

$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$

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Combining reduction potentials

$\text{Fe}^{3+}(1 \text{ M}) + e^- \rightarrow \text{Fe}^{2+}(1 \text{ M}), E^\circ_a = +0.771 \text{ V},$
 $\text{Fe}^{2+}(1 \text{ M}) + 2 e^- \rightarrow \text{Fe}(s), E^\circ_b = -0.409 \text{ V},$
 $\text{Fe}^{3+}(1 \text{ M}) + 3 e^- \rightarrow \text{Fe}(s), E^\circ = ?$
 $\Delta G^\circ = \Delta G^\circ_a + \Delta G^\circ_b$
 $-3 F E^\circ = -F E^\circ_a + (-2 F E^\circ_b) \dots$
since both are reductions
 $E^\circ = E^\circ_a/3 + 2 E^\circ_b/3$
 $= (+0.771 \text{ V})/3 + 2(-0.409 \text{ V})/3 = -0.016 \text{ V}$

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Combining reduction potentials

When result **does not** contain e^- ...
 $\text{Cu}^{2+}(1 \text{ M}) + \text{Zn}(s) \rightarrow \text{Cu}(s) + \text{Zn}^{2+}(1 \text{ M})$

$E^\circ = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$

When result **does** contain e^- ...
 $\text{Fe}^{3+}(1 \text{ M}) + 3 e^- \rightarrow \text{Fe}(s),$
use $\Delta G^\circ !!!$

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