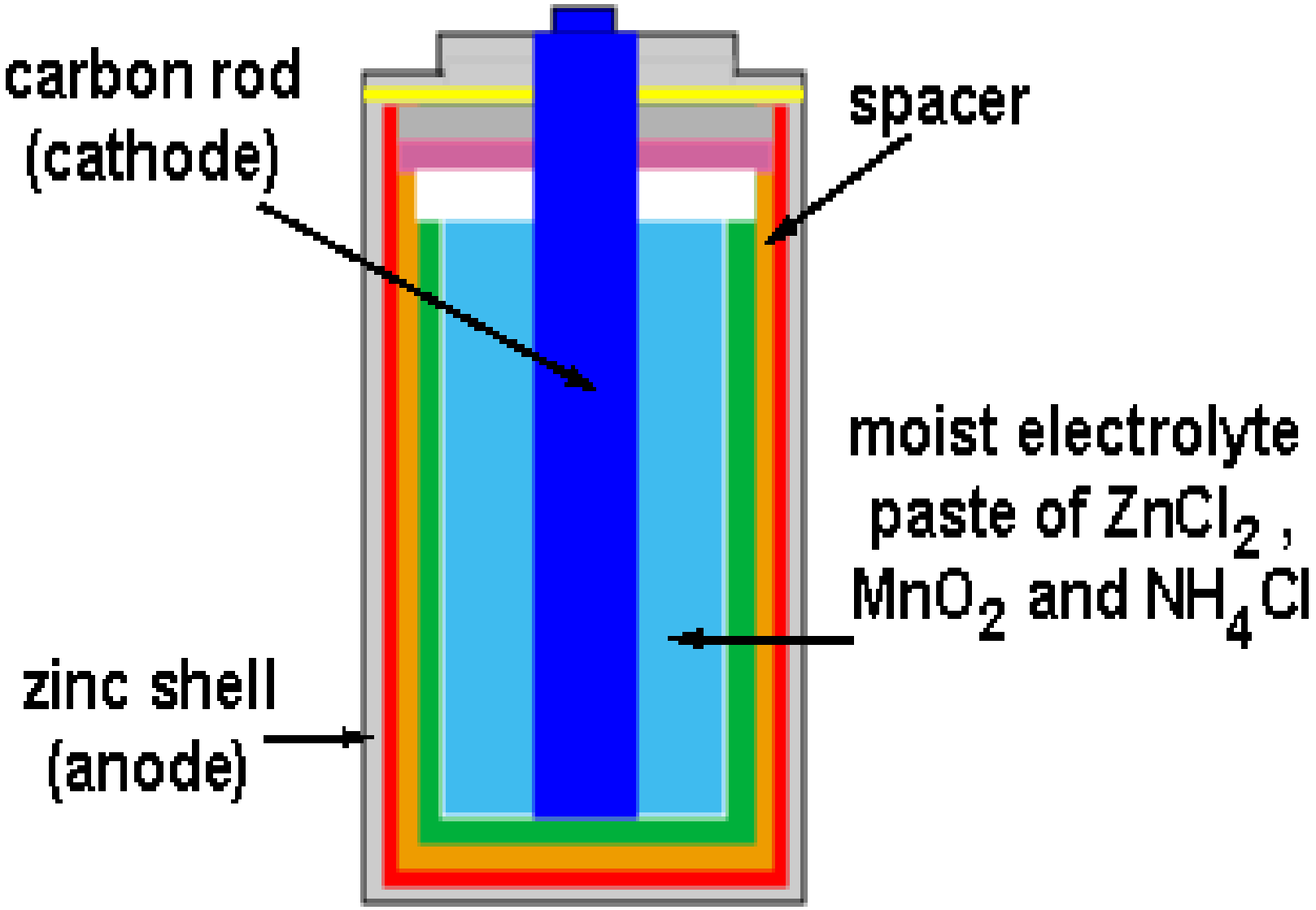
N43 - Electrochemistry

Cell Potential


carbon rod
(cathode)
spacer
moist electrolyte
paste of $ZnCl_2$,
MnO_2 and NH_4Cl
zinc shell
(anode)

Cell Potential

Cell Potential - The difference in potential energy between the anode and the cathode in a voltaic cell

Depends on how easy the oxidizing agent is reduced at the cathode and the reducing agent is oxidized at the anode.

Standard emf, $E°_{cell}$ - Cell potential @ standard conditions
(25 °C, 1 atm for gases, 1 M concentration of solution)

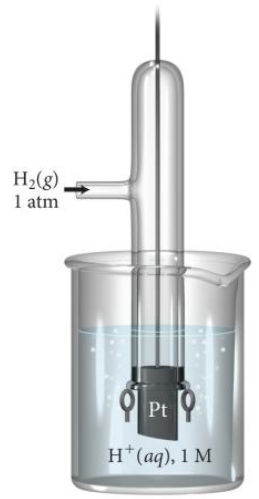
- You add the cell potentials for each half reaction

Standard Reduction Potential

- We cannot measure the absolute tendency of a half-reaction, we can only measure it relative to another half-reaction.

- We select as a standard half-reaction the reduction of H^+ to H_2 under standard conditions, which we assign a potential difference = 0 v. (An arbitrary choice!)

Standard hydrogen electrode, SHE



Half-Cell Potentials

- SHE reduction potential is defined to be exactly 0 V.
- Standard reduction potentials compare the tendency for a particular reduction half-reaction to occur relative to the reduction of H^+ to H_2.
  - Under standard conditions
- Half-reactions with a **stronger tendency toward reduction** than the SHE have a **positive value** for $E°_{red}$
- Half-reactions with a **stronger tendency toward oxidation** than the SHE have a **negative value** for $E°_{red}$
- For an oxidation half-reaction, $\mathbf{E°_{oxidation} = -E°_{reduction}}$.

Reduction Table

More + means more easily reduced

If you need to flip a rxn,
make sure to flip the sign on E.

If you multiply a rxn,
do NOT multiply E.
It is a “state function” and does not change based on quantity.

Stronger oxidizing agent	Reduction Half-Reaction		$E°$ (V)	Weaker reducing agent
	$F_2(g) + 2\ e^-$	$\longrightarrow 2\ F^-(aq)$	2.87	
	$H_2O_2(aq) + 2\ H^+(aq) + 2\ e^-$	$\longrightarrow 2\ H_2O(l)$	1.78	
	$PbO_2(s) + 4\ H^+(aq) + SO_4^{2-}(aq) + 2\ e^-$	$\longrightarrow PbSO_4(s) + 2\ H_2O(l)$	1.69	
	$MnO_4^-(aq) + 4\ H^+(aq) + 3\ e^-$	$\longrightarrow MnO_2(s) + 2\ H_2O(l)$	1.68	
	$MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^-$	$\longrightarrow Mn^{2+}(aq) + 4\ H_2O(l)$	1.51	
	$Au^{3+}(aq) + 3\ e^-$	$\longrightarrow Au(s)$	1.50	
	$PbO_2(s) + 4\ H^+(aq) + 2\ e^-$	$\longrightarrow Pb^{2+}(aq) + 2\ H_2O(l)$	1.46	
	$Cl_2(g) + 2\ e^-$	$\longrightarrow 2\ Cl^-(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ e^-$	$\longrightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)$	1.33	
	$O_2(g) + 4\ H^+(aq) + 4\ e^-$	$\longrightarrow 2\ H_2O(l)$	1.23	
	$MnO_2(s) + 4\ H^+(aq) + 2\ e^-$	$\longrightarrow Mn^{2+}(aq) + 2\ H_2O(l)$	1.21	
	$IO_3^-(aq) + 6\ H^+(aq) + 5\ e^-$	$\longrightarrow \frac{1}{2} I_2(aq) + 3\ H_2O(l)$	1.20	
	$Br_2(l) + 2\ e^-$	$\longrightarrow 2\ Br^-(aq)$	1.09	
	$VO_2^+(aq) + 2\ H^+(aq) + e^-$	$\longrightarrow VO^{2+}(aq) + H_2O(l)$	1.00	
	$NO_3^-(aq) + 4\ H^+(aq) + 3\ e^-$	$\longrightarrow NO(g) + 2\ H_2O(l)$	0.96	
	$ClO_2(g) + e^-$	$\longrightarrow ClO_2^-(aq)$	0.95	
	$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77	
	$O_2(g) + 2\ H^+(aq) + 2\ e^-$	$\longrightarrow H_2O_2(aq)$	0.70	
	$MnO_4^-(aq) + e^-$	$\longrightarrow MnO_4^{2-}(aq)$	0.56	
	$I_2(s) + 2\ e^-$	$\longrightarrow 2\ I^-(aq)$	0.54	
	$Cu^+(aq) + e^-$	$\longrightarrow Cu(s)$	0.52	
	$O_2(g) + 2\ H_2O(l) + 4\ e^-$	$\longrightarrow 4\ OH^-(aq)$	0.40	
	$Cu^{2+}(aq) + 2\ e^-$	$\longrightarrow Cu(s)$	0.34	
	$SO_4^{2-}(aq) + 4\ H^+(aq) + 2\ e^-$	$\longrightarrow H_2SO_3(aq) + H_2O(l)$	0.20	
	$Cu^{2+}(aq) + e^-$	$\longrightarrow Cu^+(aq)$	0.16	
	$Sn^{4+}(aq) + 2\ e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15	
	$2\ H^+(aq) + 2\ e^-$	$\longrightarrow H_2(g)$	0	
	$Fe^{3+}(aq) + 3\ e^-$	$\longrightarrow Fe(s)$	−0.036	
	$Pb^{2+}(aq) + 2\ e^-$	$\longrightarrow Pb(s)$	−0.13	
	$Sn^{2+}(aq) + 2\ e^-$	$\longrightarrow Sn(s)$	−0.14	
	$Ni^{2+}(aq) + 2\ e^-$	$\longrightarrow Ni(s)$	−0.23	
	$Cd^{2+}(aq) + 2\ e^-$	$\longrightarrow Cd(s)$	−0.40	
	$Fe^{2+}(aq) + 2\ e^-$	$\longrightarrow Fe(s)$	−0.45	
	$Cr^{3+}(aq) + e^-$	$\longrightarrow Cr^{2+}(aq)$	−0.50	
	$Cr^{3+}(aq) + 3\ e^-$	$\longrightarrow Cr(s)$	−0.73	
	$Zn^{2+}(aq) + 2\ e^-$	$\longrightarrow Zn(s)$	−0.76	
	$2\ H_2O(l) + 2\ e^-$	$\longrightarrow H_2(g) + 2\ OH^-(aq)$	−0.83	
	$Mn^{2+}(aq) + 2\ e^-$	$\longrightarrow Mn(s)$	−1.18	
	$Al^{3+}(aq) + 3\ e^-$	$\longrightarrow Al(s)$	−1.66	
	$Mg^{2+}(aq) + 2\ e^-$	$\longrightarrow Mg(s)$	−2.37	
	$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71	
	$Ca^{2+}(aq) + 2\ e^-$	$\longrightarrow Ca(s)$	−2.76	
	$Ba^{2+}(aq) + 2\ e^-$	$\longrightarrow Ba(s)$	−2.90	
Weaker oxidizing agent	$K^+(aq) + e^-$	$\longrightarrow K(s)$	−2.92	Stronger reducing agent
	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04	

Reduction Table

Example:

Which rxn is more likely to happen at the cathode and which at the anode??

$Ag^+ + e^-$	$\rightarrow$	$Ag(s)$	0.80
$Au^{3+} + 3\,e^-$	$\rightarrow$	$Au(s)$	1.50

Cathode = reduction = gain e- = more + E

Anode = oxidation = loss e- = more – E (less +)

Calculating Cell Potentials under Standard Conditions

$$E°_{cell} = E°_{oxidation} + E°_{reduction}$$

- When looking up values on reduction table, **flip the sign** for the one that is being oxidized because you have the opposite reaction taking place compared to what is written on the chart.
- When adding *E*° values for the half-cells, **do not multiply** the half-cell *E*° values, even if you need to multiply the half-reactions to balance the equation.

Calculating Cell Potential

Example:

What is the cell potential for a cell made with silver and gold?

$Ag^+ + e^-$	$\rightarrow$	$Ag(s)$	0.80
$Au^{3+} + 3\,e^-$	$\rightarrow$	$Au(s)$	1.50

Cathode = reduction = gain e- = more + E

Anode = oxidation = loss e- = more – E (less +)

$Au^{3+} + 3e^- \rightarrow Au$ **+1.50 V**

$Ag \rightarrow Ag^+ + e^-$ **- 0.80 V**

Flipped sign for Ag half rxn b/c oxidized but did NOT multiply it by 3.

(+1.50) + (-0.80)

= 0.70 V

Tendencies from the Table of Standard Reduction Potentials

A redox reaction will be spontaneous when there is a strong tendency for the oxidizing agent to be reduced and the reducing agent to be oxidized.

- Higher on the table of standard reduction potentials = stronger tendency for the reactant to be reduced
- Lower on the table of standard reduction potentials = stronger tendency for the product to be oxidized