N43 - Electrochemistry

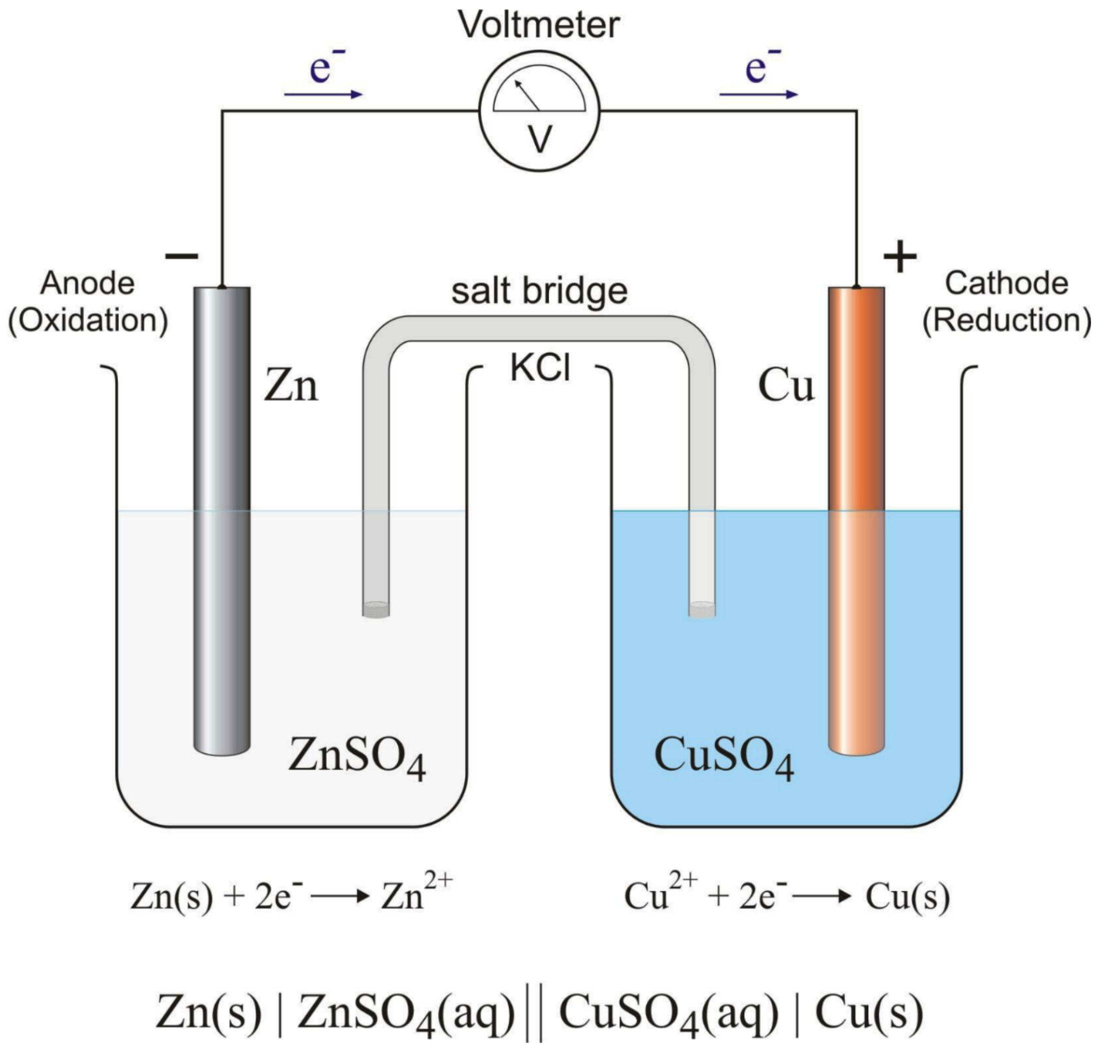
Cell Potential

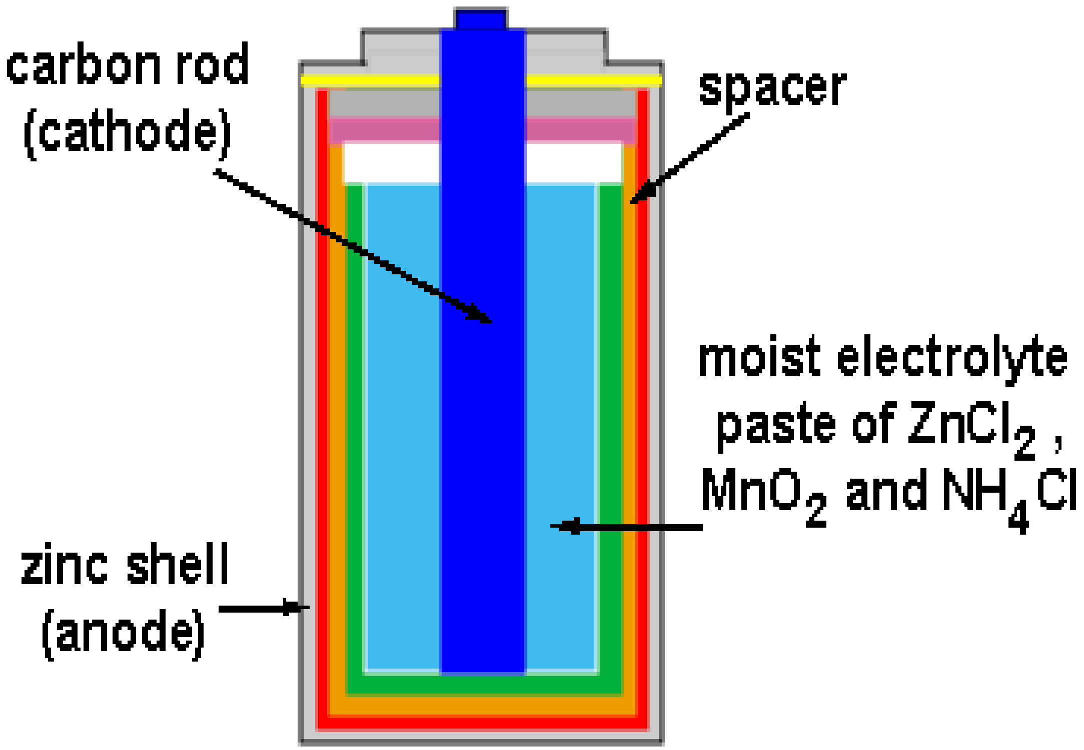
Link to YouTube Presentation: https://youtu.be/iqk4Li9toOQ

N43 - Electrochemistry

Cell Potential

Target: I can calculate the cell potential using standard reduction values.


Voltmeter
e⁻
e⁻
V
−
+
Anode
(Oxidation)
salt bridge
Cathode
(Reduction)
Zn
KCl
Cu
$ZnSO_4$
$CuSO_4$
$Zn(s) + 2e^- \longrightarrow Zn^{2+}$
$Cu^{2+} + 2e^- \longrightarrow Cu(s)$
$Zn(s) \mid ZnSO_4(aq) \parallel CuSO_4(aq) \mid Cu(s)$


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

Mnemonics

LEO goes GER

Loss of Electrons is Oxidation

Gain of Electrons is Reduction

OIL RIG

Oxidation is Loss of Electrons

Reduction is Gain of Electrons

A Few More Electrochemistry Terms

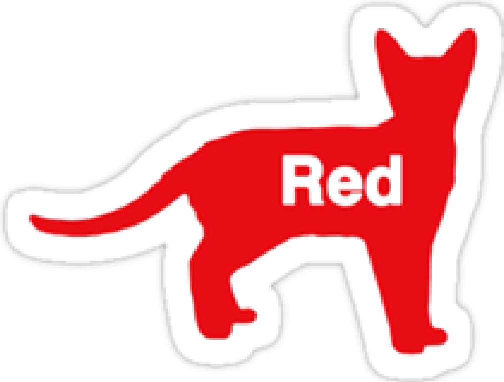
Anode

The electrode where oxidation occurs

Anode is Oxidation

Cathode

The electrode where reduction occurs



Reduction at the Cathode

Cell Potential

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

Depends on how easy one substance is reduced at the cathode and how easy the other 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

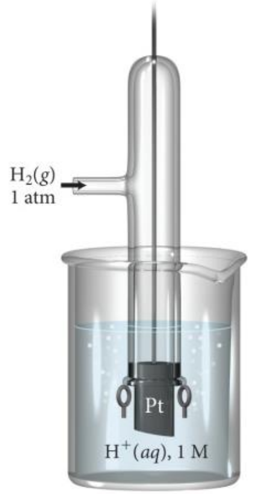
Standard Reduction Potential

- 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

$$2H^+ + 2e^- \rightarrow H_2(g)$$



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 oxidation** than the SHE have a **negative value for $E°_{red}$**
- Half-reactions with a **stronger tendency toward reduction** than the SHE have a **positive value for $E°_{red}$**
- For an oxidation half-reaction, $\mathbf{E°_{oxidation} = -\,E°_{reduction}}$

Reduction Values

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 / Weaker reducing agent

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

Weaker oxidizing agent / Stronger reducing agent

Reduction Table

More + means more easily reduced

More NIO

*More **N**egative **I**s **O**xidation*

More PER

*More **P**ositive **I**s **R**eduction*

Stronger oxidizing agent — Weaker reducing agent

Reduction Half-Reaction		$E°$(V)
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$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77
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$2\,H^+(aq) + 2\,e^-$	$\longrightarrow H_2(g)$	0
$Fe^{3+}(aq) + 3\,e^-$	$\longrightarrow Fe(s)$	−0.036
$Pb^{2+}(aq) + 2\,e^-$	$\longrightarrow Pb(s)$	−0.13
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Weaker oxidizing agent — Stronger reducing agent

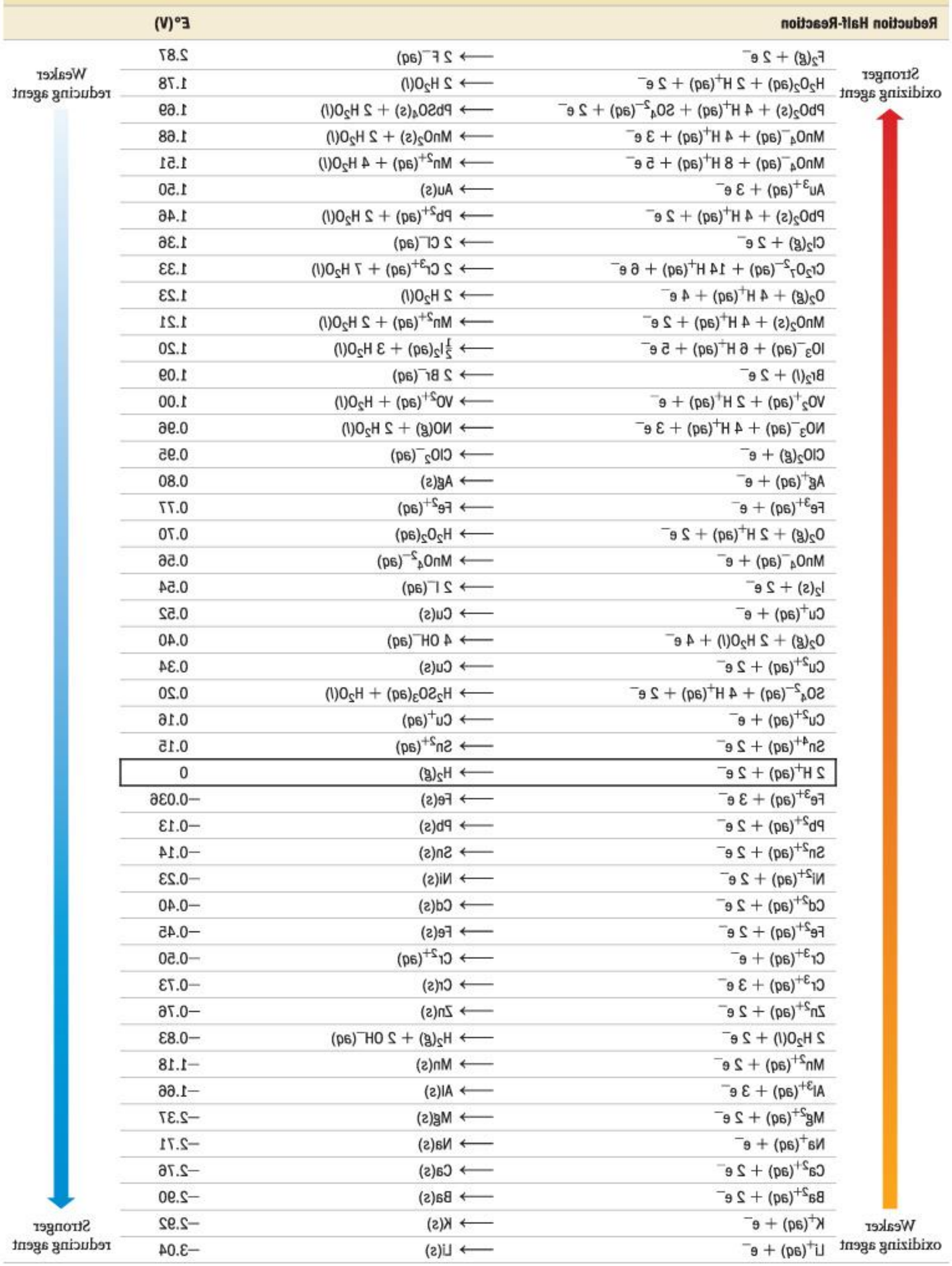
~~Reduction~~ Values Oxidation

Flip the equations?

NOW your values are Oxidation Values!

More positive NOW means more likely to be oxidized!

BE CAREFUL!



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

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

Cathode = reduction = gain e- = more (+) E

Calculating Cell Potentials under Standard Conditions

$$E^\circ_{\text{cell}} = E^\circ_{\text{oxidation}} + E^\circ_{\text{reduction}}$$

- 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

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

Cathode = reduction = gain e- = more + E

$Au^{3+} + 3e^{-} \rightarrow Au$ +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

Sneak Peak at Spontaneity...

If E°cell = (+) *we will see why in a later lecture ☺*

then ΔG° = (–)

So it is spontaneous!

If E°cell = (–)

then ΔG° = (+)

So it is NON-spontaneous!

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