Today

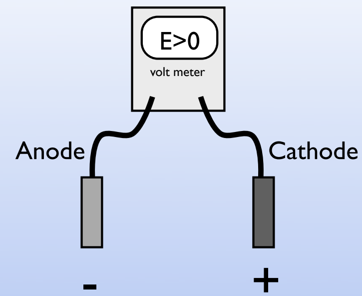
Quantitative Echem
How many electrons

Qualitative Echem
Which direction is spontaneous
What is the voltage
What is the best "oxidizer"

First some nomenclature

Galvanic Cell
Voltaic Cell
Battery

Spontaneous
$\Delta G<0$
$E > 0$



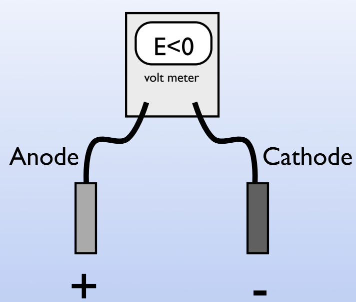
Cathode at a higher potential than the anode
So cathode get the PLUS sign

This is spontaneous. It can be used as a power supply

First some nomenclature

Electrolytic Cell

Non-Spontaneous
$\Delta G>0$
$E < 0$



Anode at a higher potential than the cathode
So anode get the PLUS sign

This reaction must be driven by
an external power supply

In the following standard Ecell,
what is the sign of the cathode?

$Zn(s) \mid Zn^{2+} \parallel H^+ \mid H_2\,(g)$

$Zn^{2+} + 2e^- \longrightarrow Zn(s) \qquad E° = -0.76\,V$
$2H^+ + 2e^- \longrightarrow H_2 \qquad E° = 0.0\,V$

A. +

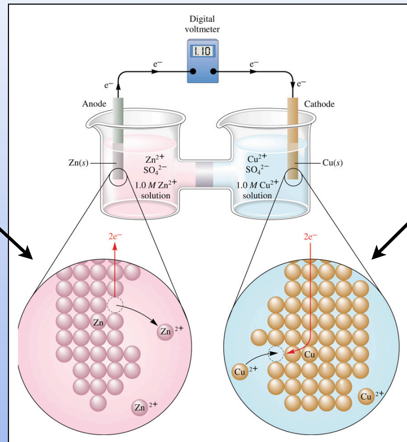
B. -

C. neither E°cell = 0

$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

$Zn(s) \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$

Oxidation
Anode



Reduction
Cathode

We've made a 1.1 V battery!

If I use this battery for a while
how much Zn reacts?

Charge = Current x Time

Coulomb (C) = Amp ($C\ s^{-1}$) x Second (s)

How many electrons are in a Coulomb?
What is the charge of 1 mole of electrons?

F is the charge of one mole of electrons
F = 96,485 C (Faraday's Constant)

If I run this cell for 100 s at a current of 30 mA
how many moles of electrons flow?

$Zn(s) \mid Zn^{2+} \parallel Cu^{2+} \mid Cu\ (s)$

A. $(30 \times 10^{-3}) \times 100 \times F$

B. $30 \times 100 \times F$

C. $30 / (100 \times F)$

D. $(30 \times 10^{-3}) / (100 \times F)$

E. $[(30 \times 10^{-3}) \times 100] / F$

$Q = A \times t = 10 \times 10^{-3}\ A \times 100\ s$

moles electrons
Q / F

$= 3 / F$

If I run this cell for 100 s at a current of 1 mA
how many moles of Zn react?

$Zn(s) \mid Zn^{2+} \parallel Cu^{2+} \mid Cu\ (s)$

A. (3/F)

B. (3/F) x 2

C. (3/F) / 2

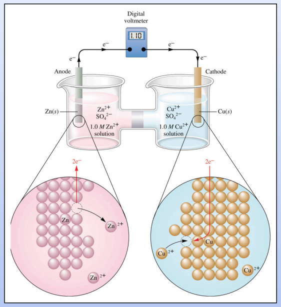
1 mole of Zn^{2+} requires 2 electron to be reduced to Zn

So 3/F moles of electrons will produce half that number of moles of Zn

$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) \quad + \quad Cu(s)$

$Zn(s) \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$

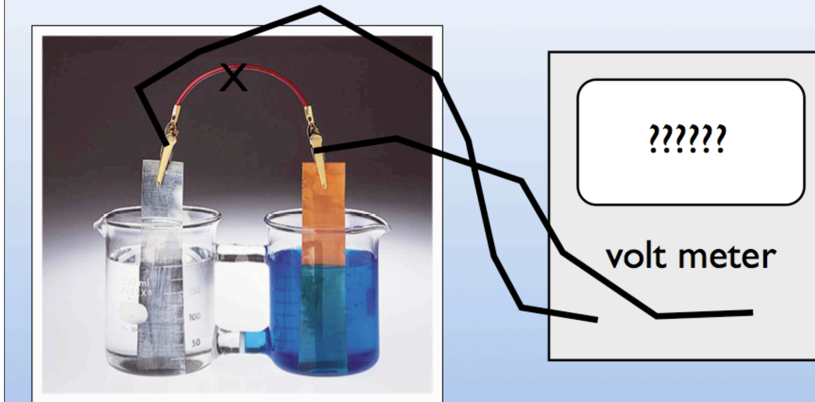
Oxidation
Anode



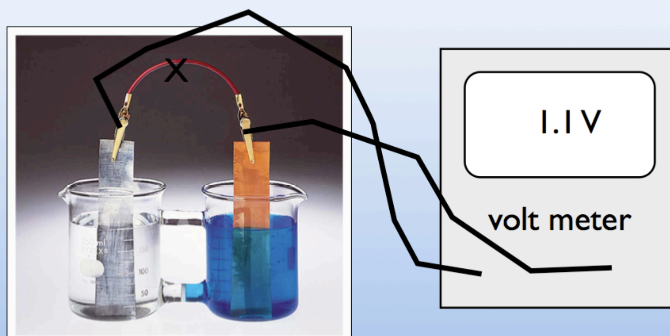
Reduction
Cathode

We've made a
1.1 V battery!

How do we know what the voltage is?



The voltage depends on the concentrations
(we've all had dead batteries)



Mix up "standard" concentrations
1 M Zn^{2+} and 1 M Cu^{2+}
(note this is very concentrated)

Now we can measure every possible combination
of electrochemical cells!

What if I would like to predict
the voltage from a cell using
the following reaction at standard conditions?

$Mn^{2+} \quad + \quad I_2 \longrightarrow MnO_4^- \quad + \quad I^-$

If want to know about the potential we
just have to identify the two reactions!

$Mn^{2+} + I_2 \longrightarrow MnO_4^- + I^-$

$I_2 \longrightarrow I^-$

$I_2 \longrightarrow 2I^-$

$I_2 + 2e^- \longrightarrow 2I^-$ This is the reduction (Cathode)

$Mn^{2+} + I_2 \longrightarrow MnO_4^- + I^-$

$Mn^{2+} \longrightarrow MnO_4^-$ everything but O & H

$4H_2O + Mn^{2+} \longrightarrow MnO_4^-$ balance O w/ H_2O

$4H_2O + Mn^{2+} \longrightarrow MnO_4^- + 8H^+$ balance H w/ H^+

$4H_2O + Mn^{2+} \longrightarrow MnO_4^- + 8H^+ + 5\,e^-$ charge w/e^-

This is the oxidation (Anode)

$Mn^{2+} + I_2 \longrightarrow MnO_4^- + I^-$

$4H_2O + Mn^{2+} \longrightarrow MnO_4^- + 8H^+ + 5\,e^-$

$I_2 + 2e^- \longrightarrow 2I^-$

To compare these two we don't
need to balance the number of electrons!

We only need to do this to relate
moles of electrons to moles of materials.

Potential difference depends only on the two reactions!

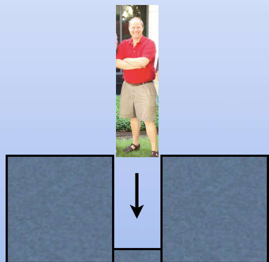
$4H_2O + Mn^{2+} \longrightarrow MnO_4^- + 8H^+ + 5\,e^-$

$I_2 + 2e^- \longrightarrow 2I^-$

How can we compare these two?

We'll compare every reaction to a standard

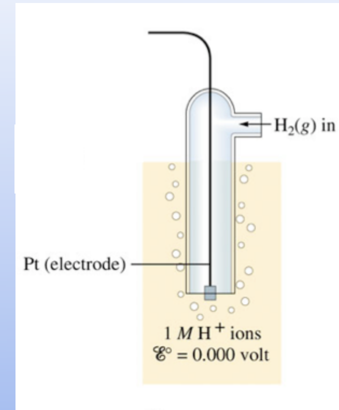
What is my gravitational potential energy?
zero if I am on the ground



But if a hole appears beneath me
then it is no longer zero and
I will move spontaneously from
high to low!

We need to pick a zero potential for electrochemistry

We chose this reaction



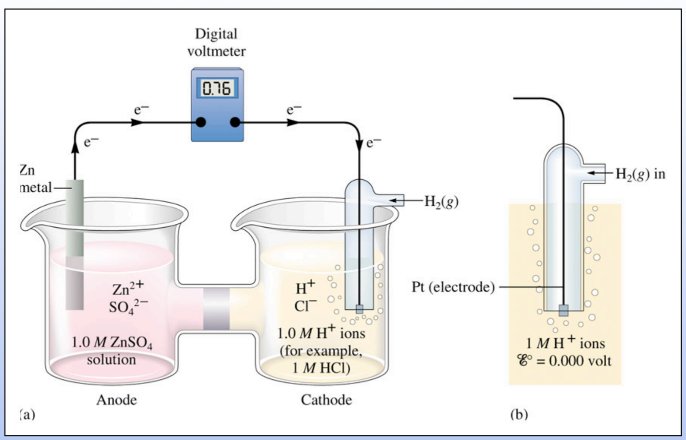
$2H^+ + 2e^- \rightarrow H_2(g)$

note standard conditions

we pick this as E°= 0V

potential energy

Now compare everything to this



So potential for $Zn \rightarrow Zn^{2+} + 2e^-$
is 0.76 V

Write everything as a reduction reaction

TABLE 11.1 Standard Reduction Potentials at 25°C (298 K) for Many Common Half-reactions

Half-reaction	ℰ° (V)	Half-reaction	ℰ° (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$IO_4^- + 2H^+ + 2e^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	−2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	−2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	−2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	−3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

TABLE 20.1 Standard Reduction Potentials in Water at 25°C

Standard Potential (V)	Reduction Half-Reaction
+2.87	$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$
+1.51	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$
+1.36	$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$
+1.33	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
+1.23	$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$
+1.06	$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$
+0.96	$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
+0.68	$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$
+0.59	$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$
+0.54	$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$
+0.40	$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
0	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$
−0.28	$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$
−0.44	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$
−0.76	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$
−0.83	$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$
−1.66	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$
−2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
−3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

Easy to reduce (Strongest oxidizing agents)

Easy to oxidize (strongest reducing agents)

How to find E°cell?

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

$$4H_2O + Mn^{2+} \longrightarrow MnO_4^- + 8H^+ + 5\,e^-$$

$$I_2 + 2e^- \longrightarrow 2I^-$$

$$I_2 + 2e^- \longrightarrow 2I^- \qquad E^\circ = 0.54\,V$$

$$MnO_4^- + 8H^+ + 5\,e^- \longrightarrow 4H_2O + Mn^{2+} \qquad E^\circ = 1.51\,V$$

E°cell = 0.54 - 1.51 = -0.97V

E < 0 not spontaneous. Electrolytic cell!