UNIT8-DAY3-LaB11am

Wednesday, April 17, 2013
4:04 PM

Thinking Like a Chemist
About Electrochemistry II

e^- on the move

UNIT8 DAY3

ke Spring 2012

IMPORTANT INFORMATION

LM36 & HW 11 Tues 9 AM

CH302 Vanden Bout/LaBrake Spring 2012

What are we going to learn today?

Oxidation – Reduction Chemistry
Voltaic and Electrolytic Cells

Quantifying the Voltage

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Principles of Chemistry II

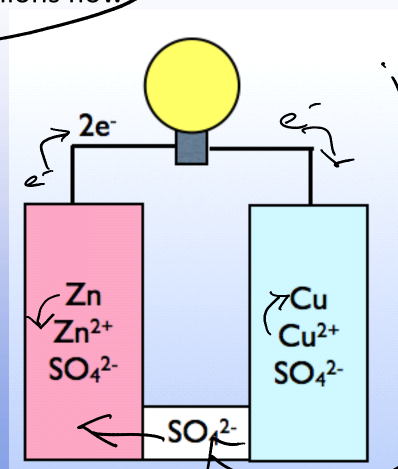
Quiz: Clicker Question 1 & 2

1. The following is a sketch of a voltaic cell.
In which direction will the sulfate anions flow?

a) Toward the anode
b) Toward the cathode
c) Depends, could go either way to balance charge

2. Is it possible for the "counter ions" to flow through the External wire to balance the charge?

a) Yes
b) No



ions do NOT flow through wires

ions pass through salt bridge

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Principles of Chemistry II

Half-reaction	$\mathscr{E}°$ (V)	Half-reaction	$\mathscr{E}°$ (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
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	[illegible]	[illegible]	−0.40

All Reduction

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		

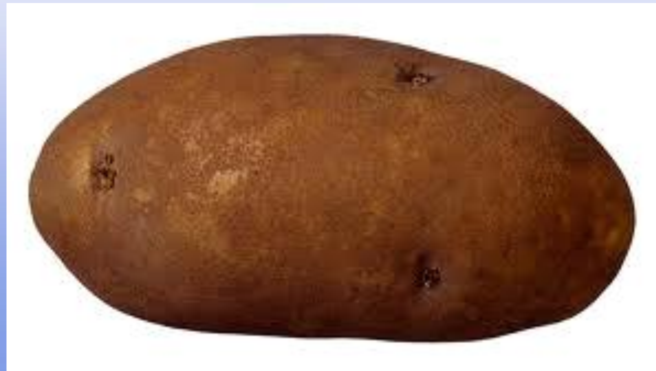
Reduction Reactions

Poll: Clicker Question 3

Battery/Potato Clock/Electrochemical Cell

What do these things have in common?
a) convert chemical energy to electrical energy
b) measurable voltage → diff. in energy
c) capable of going "dead" → equilibrium
d) all of the above

What happened with the potato?



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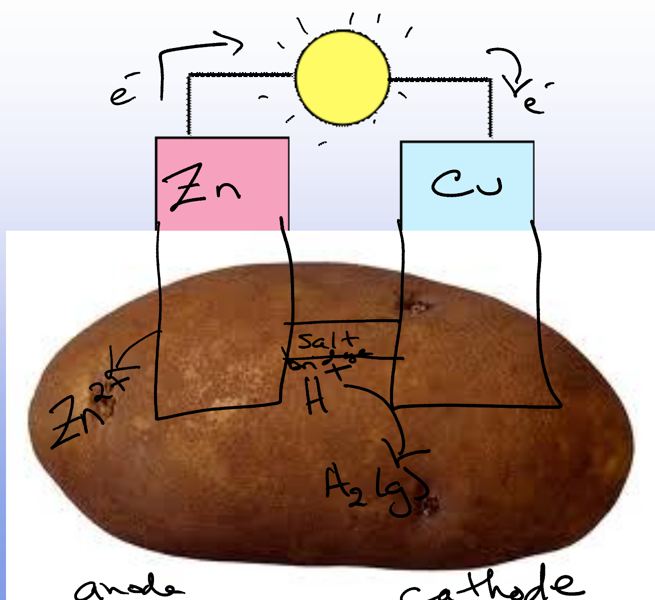
Principles of Chemistry II



Potato is salt bridge

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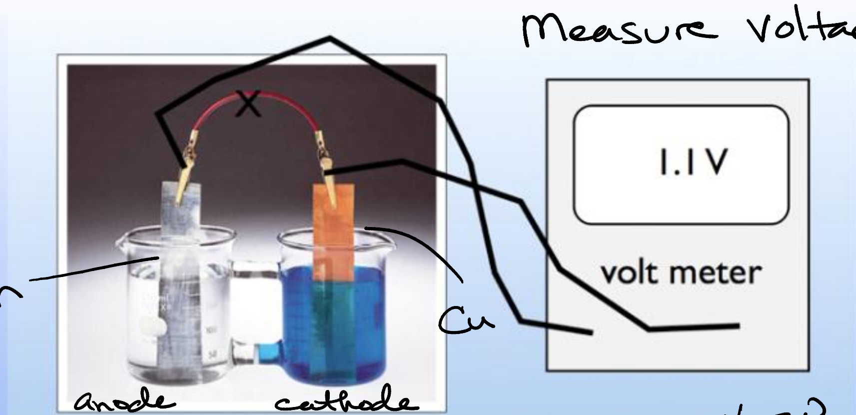
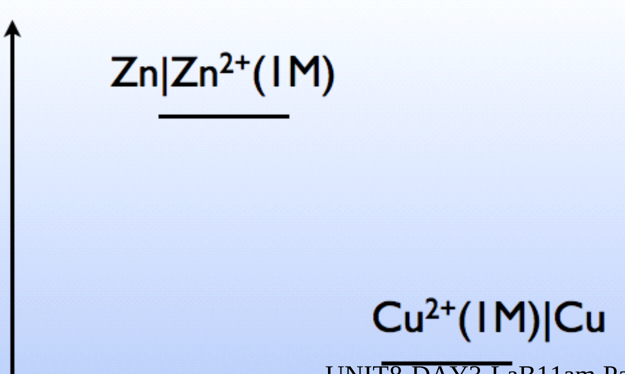
Measure voltage



voltage will depend on concentrations

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

Know standard conditions for electrochemistry



Voltage is a measure of the difference in potential

$Cu^{2+}(1M)|Cu$

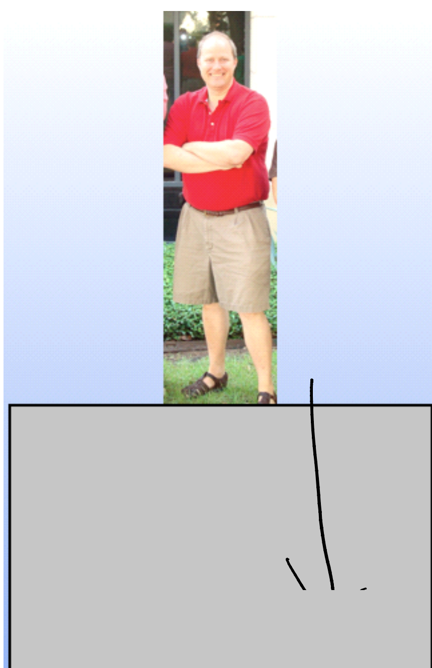
differ
in potential
energy

Potential Energy

Now we can measure every possible combination of electrochemical cells!

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

First we need to think about potential energy



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

Energy is relative!

We pick where zero is

then it is no longer zero

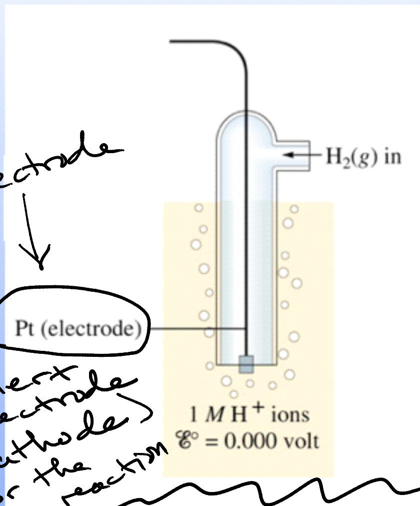
Energy is relative!

$\boxed{\text{We pick where zero is}}$

We need to pick a zero potential for electrochemistry

We chose this reaction

electrode



inert electrode (cathode) for the reaction

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

1M   1atm

note standard conditions

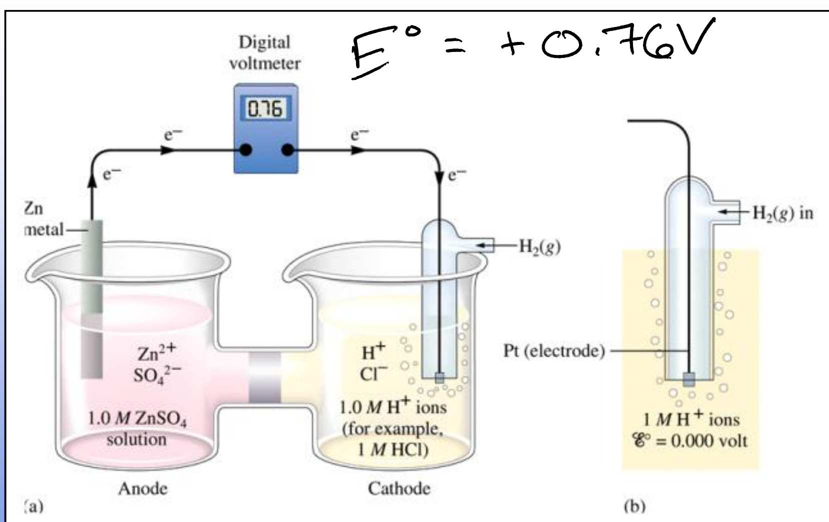
Standard Hydrogen Electrode

SHE

we pick this as E°= 0V

potential energy

Now compare everything to this



$E° = +0.76V$

Zn

H^+

E

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Poll: Clicker Question 4

IF:

$Zn \rightarrow Zn^{2+} + 2e^{-}$ E° = 0.76V

THEN:

$Zn^{2+} + 2e^{-} \rightarrow Zn$ E° = **?**

A .-0.76 V
B .0.76 V
C .0 V
D. it can't be measured

Reduction Table

easy to reduce

Half Reaction					potential
F_2	+	$2e^-$	$\rightleftharpoons$	$2F^-$	+2.87 V
Pb^{4+}	+	$2e^-$	$\rightleftharpoons$	Pb^{2+}	+1.67 V
Cl_2	+	$2e^-$	$\rightleftharpoons$	$2Cl^-$	+1.36 V
Ag^+	+	$1e^-$	$\rightleftharpoons$	Ag	+0.80 V
Fe^{3+}	+	$1e^-$	$\rightleftharpoons$	Fe^{2+}	+0.77 V
Cu^{2+}	+	$2e^-$	$\rightleftharpoons$	Cu	+0.34 V
$2H^+$	**+**	**$2e^-$**	$\rightleftharpoons$	**H_2**	**0.00 V**
Fe^{3+}	+	$3e^-$	$\rightleftharpoons$	Fe	−0.04 V
Pb^{2+}	+	$2e^-$	$\rightleftharpoons$	Pb	−0.13 V
Fe^{2+}	+	$2e^-$	$\rightleftharpoons$	Fe	−0.44 V
Zn^{2+}	+	$2e^-$	$\rightleftharpoons$	Zn	−0.76 V
Al^{3+}	+	$3e^-$	$\rightleftharpoons$	Al	−1.66 V
Mg^{2+}	+	$2e^-$	$\rightleftharpoons$	Mg	−2.36 V
Li^+	+	$1e^-$	$\rightleftharpoons$	Li	−3.05 V

increasing strength as an oxidizing agent

increasing strength as a reducing agent

easy to oxidize

Poll: Clicker Question 5

Reduction Potentials

Given that: $Fe^{2+} + 2e^{-} \rightarrow Fe$ E° = -0.44 V

$Zn^{2+} + 2e^{-} \rightarrow Zn$ E° = -0.76 V

which is easier to oxidize?

What can we oxidize?

Zn

A. Zn
B. Fe
C. Zn^{2+}

$Zn^{2+} + 2e^- \rightarrow Zn$ $E^\circ = -0.76$ V

which is easier to oxidize?

What can we oxidize:

A. Zn
B. Fe
C. Zn^{2+}
D. Fe^{2+}

Zn

Fe

already oxidized ... somewhat

Standard ½ reactions are listed as REDUCTION ½ reactions

HOW CAN YOU CALCULATE THE STANDARD POTENTIAL OF AN ELECTROCHEMICAL CELL?

difference in potentials depends on element not # e^-

Use the tabulated reduction potentials for each ½ reaction…

$\boxed{\textbf{THE \# OF ELECTRONS DOES NOT MATTER}}$

E° (cell) = E° (cathode) - E° (anode)

takes care of switching reduction to oxidation

reduction table

reduction table

Poll: Clicker Question 6

Write a cell reaction for a cell diagram

Write the chemical equation for the reaction corresponding to the cell:

same phase, use comma

$<Pt(s)|H_2(g)|H^+(aq)||Co^{3+}(aq),Co^{2+}(aq)|Pt(s)>$

NEED solid electrode

$H_2 \rightarrow 2H^+ + 2e^-$ $\quad 1e^- + Co^{3+} \rightarrow Co^{2+}$

$2e^- + 2Co^{3+} \rightarrow 2Co^{2+}$

a) $Pt + H_2 + H^+ \rightarrow Co^{3+} + Co^{2+} + Pt$

b) $H_2 + H^+ \rightarrow Co^{3+} + Co^{2+}$

c) $H_2 + Co^{3+} \rightarrow 2H^+ + Co^{2+}$ Balanced elements

d) $2H^+ + Co^{3+} \rightarrow H_2 + Co^{2+}$

e) $H_2 + 2Co^{3+} \rightarrow 2H^+ + 2Co^{2+}$ Balance CHARGE

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Poll: Clicker Question 7

Write a cell reaction for a cell diagram

Write the chemical equation for the reaction corresponding to the cell:

$<Pt(s)|H_2(g)|H^+(aq)||Co^{3+}(aq),Co^{2+}(aq)|Pt(s)>$

Given that $Co^{3+} + 1e^- \rightarrow Co^{2+}$ 1.82 V; calculate the standard cell potential, E°

$H_2 \rightarrow 2H^+ + 2e^-$ 0 V

$Co^{3+} + 1e^- \rightarrow Co^{2+}$ 1.8 V

a) Not enough information

b) - 1.82 V

c) + 1.82

$E^\circ_{cell} = E_{red} - E_{ox}$

$= 1.82 - 0$

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Two "kinds" of electrochemical cells

(Battery) Galvanic (Voltaic): Reaction is spontaneous we can use these to make a battery → use chemicals to generate electricity

Electrolytic: Reaction is not spontaneous we have to input work to get these reactions to proceed → use electricity to generate chemistry force e^- backwards

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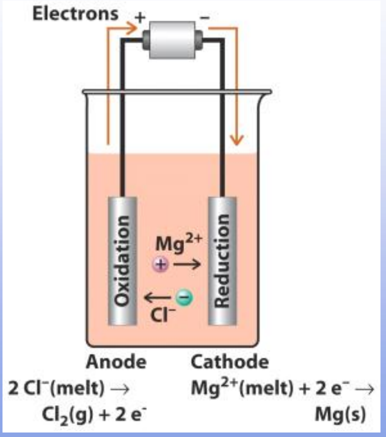
Electrolytic Cells

- Reaction is driven in a nonspontaneous direction by using an electric current.
- Anode is site of oxidation but labeled with “+”, and cathode is site of reduction but labeled with a “-”.
- Over potential is the extra emf over the emf of the cell that is needed to push the reaction in a nonspontaneous direction.



Example of Electrolytic Cell

Consider the electrolysis of aqueous copper(II)bromide. The observations are: one electrode becomes coated with copper metal, and the color of the solution around the electrode fades; around the other electrode the solution turns brown, as the bromine is formed and some O_2 bubbles are formed.

Design the cell, label electrodes, flow of e^-, and ½ reactions.

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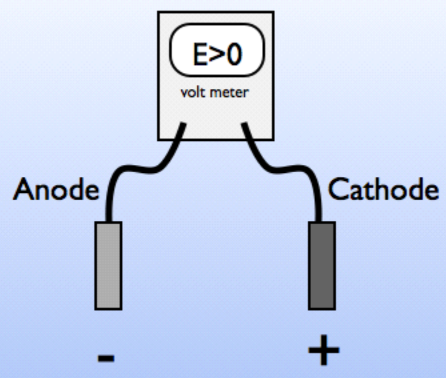
Nomenclature

Galvanic Cell
Voltaic Cell
Battery

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

electrons flow to cathode



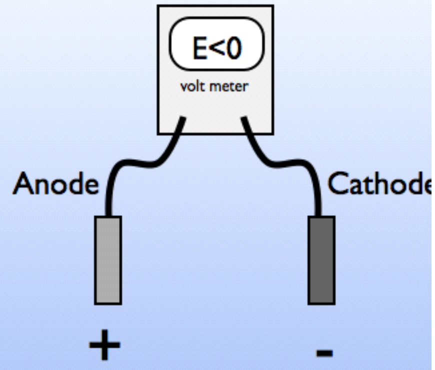
Cathode get the PLUS sign

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

Electrolytic Cell

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

electrons flow to cathode



Anode get the PLUS sign

This reaction must be driven by an external power supply

Poll: Clicker Question 8

ACTIVITY QUESTION 1:

A) YES
B) NO

Poll: Clicker Question 9

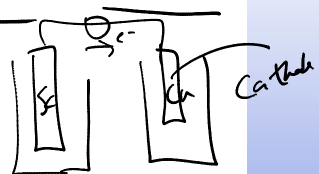
ACTIVITY QUESTION 2.

A) Cu & Sc
B) Cu & Pb
C) Cu & Cr
D) Pb & Sc

Poll: Clicker Question 10

ACTIVITY QUESTION 3: which will serve as anode and cathode, respectively:

A) Cu & Sc
B) Sc & Cu ✓
C) Cu^{2+} & Cr^{3+}
D) Pb & Sc^{3+}
E) Sc & Cu^{2+} ✓



$2e^- + Cu^{2+} \rightarrow Cu$.

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Poll: Clicker Question11

ACTIVITY QUESTION 4, $E^{\circ}_{(cell)}$:

A) + .34 V
B) - 2.1 V
C) + 1.7 V
D) - 2.44 V
E) + 2.44 V

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Poll: Clicker Question12

QUESTION 5, short hand cell notation:

A) $<Sc(s)|Sc^{3+}(aq)||Cu^{2+}(aq)|Cu(s)>$

B) $<Sc(s)|Sc^{3+}(aq)||Cu(s)|Cu^{2+}(aq)>$

A) $<Sc^{3+}(aq)|Sc(s)||Cu^{2+}(aq)|Cu(s)>$

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Poll: Clicker Question13

ACTIVITY QUESTION 6, overall balanced equation:

A) $Sc + Cu^{2+} \rightarrow Sc^{3+} + Cu$

B) $\cancel{2}Sc + 3Cu^{2+} \rightarrow \cancel{2}Sc^{3+} + 3Cu$

C) $3Sc + 2Cu^{2+} \rightarrow 3Sc^{3+} + 2Cu + 5e^-$

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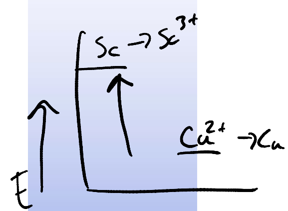
Poll: Clicker Question14

QUESTION 7, Applied potential must be at least:

A) ~~2.44 V~~ 0V

B) ~~2.44 V~~ exactly 2.44

C) ~~4.88 V~~ more than 2.44 V



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Poll: Clicker Question14

QUESTION 8: ½ Reactions at Anode & Cathode:

A) anode: $Cu^{2+} + 2e^- \rightarrow Cu$
cathode: $Sc^{3+} + 3e^- \rightarrow Sc$

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

B) anode: $Cu^{2+} + 2e^- \rightarrow Cu$

Poll: Clicker Question14

QUESTION 8: ½ Reactions at Anode & Cathode:

A) anode: $Cu^{2+} + 2e^- \rightarrow Cu$
cathode: $Sc^{3+} + 3e^- \rightarrow Sc$

B) anode: $Cu^{2+} + 2e^- \rightarrow Cu$
cathode: $Sc \rightarrow Sc^{3+} + 3e^-$

C) anode: $Cu \rightarrow Cu^{2+} + 2e^-$
cathode: $Sc^{3+} + 3e^- \rightarrow Sc$

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

96485 Coulomb = 1 mol e^-

1 Amp = $\frac{1 \text{ Coulomb}}{s}$

How much Charge do you need? (10)

A) 219,000 C
B) 643,800 C
C) 6430 C

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What did we learn today?

Construct an electrochemical cell diagram, including identifying the anode, cathode, direction of electron flow, sign of the electrodes, direction of ion flow in salt bridge, from a redox reaction or from short hand cell notation.

Describe the standard hydrogen electrode and state it's function.

Apply standard reduction potential data to calculate the standard cell potential for an electrochemical cell and from the sign of the potential predict if the cell is voltaic or electrolytic.

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