Today

Galvanic Cells

Spontaneous Electrochemistry

Electrolytic Cells

“Backwards” Electrochemistry

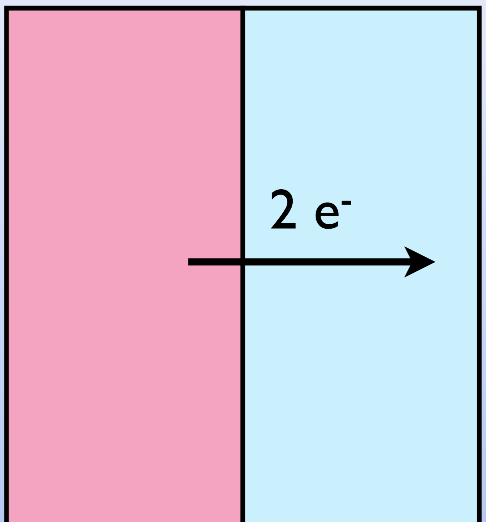
Balancing Redox Reactions

There is a method (actually several)

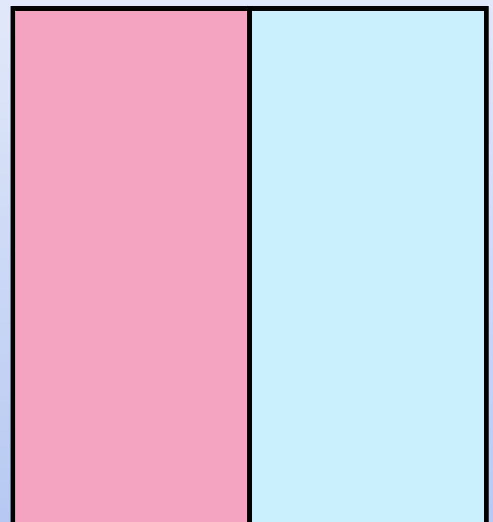
Learn one (4.10-4.12)

Practice (worksheet)

Electrons have a lower free energy in Zn^{2+} (and Cu) than Cu^{2+} (and Zn)



Zn Cu^{2+}



Zn^{2+} Cu

Depends on the concentrations!

Which has the lower Standard Gibb's free energy?

A. $Zn^{2+}(1M) + Cu$

B. $Zn + Cu^{2+}(1\,M)$

C. They are exactly equal

A moment to think again about
Free Energy
and Standard Free Energy

ΔG

Difference in Free Energy between reactants and product under the current conditions (depends on the **concentrations** of the reactants and products)

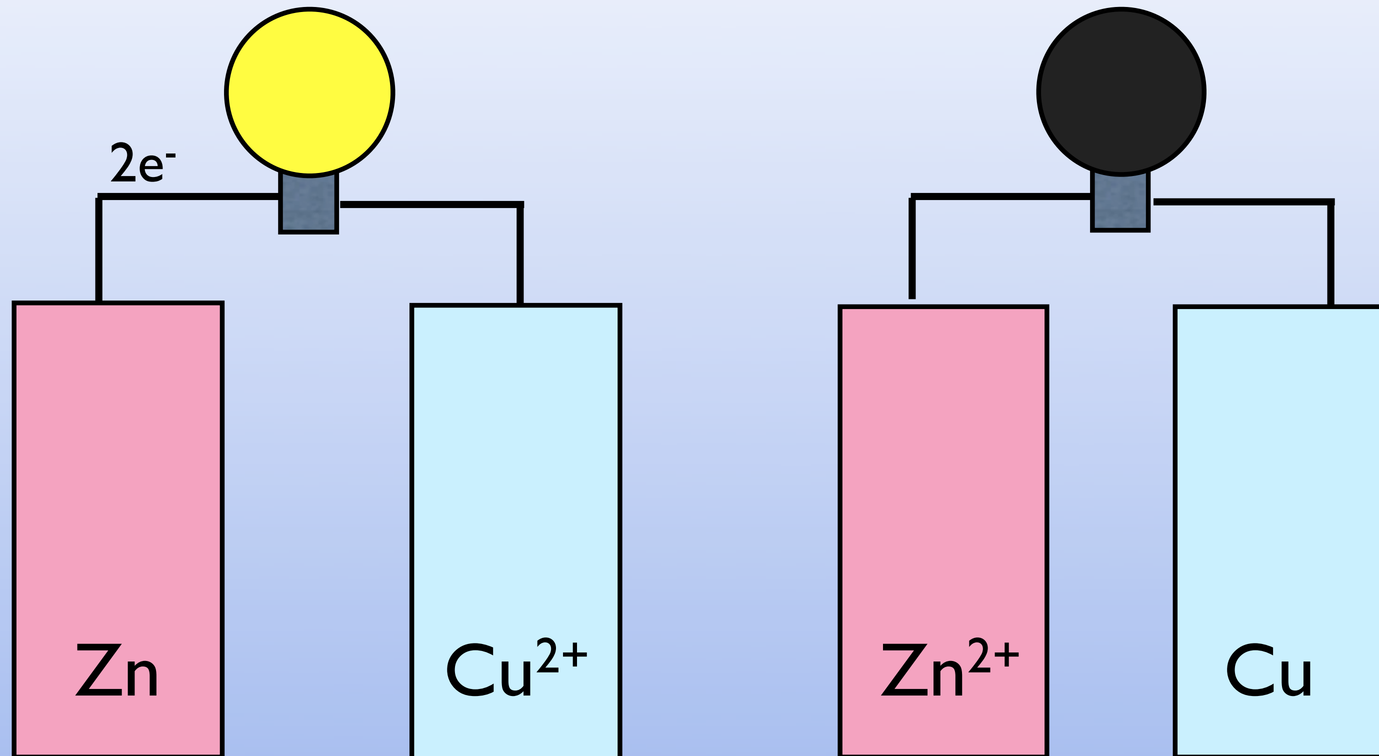
The concentration will change until $\Delta G = 0$

$\Delta G°$

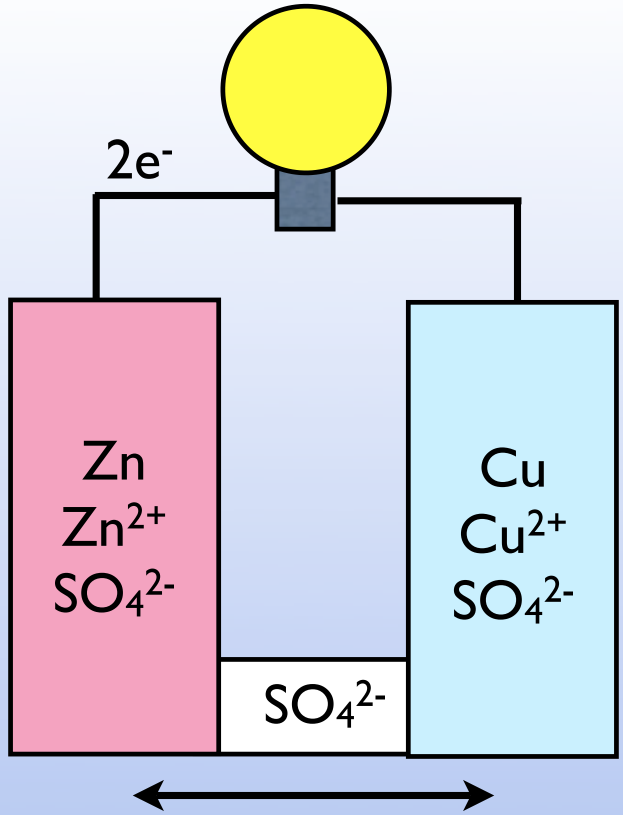
Difference in Free Energy between reactants and product under standard conditions

standard conditions are **1 M for all aqueous species** or 1 atm pressure for all gases

Last time, we look at this idea
Use a wire to connect the two sides
and have e- flow in an external circuit

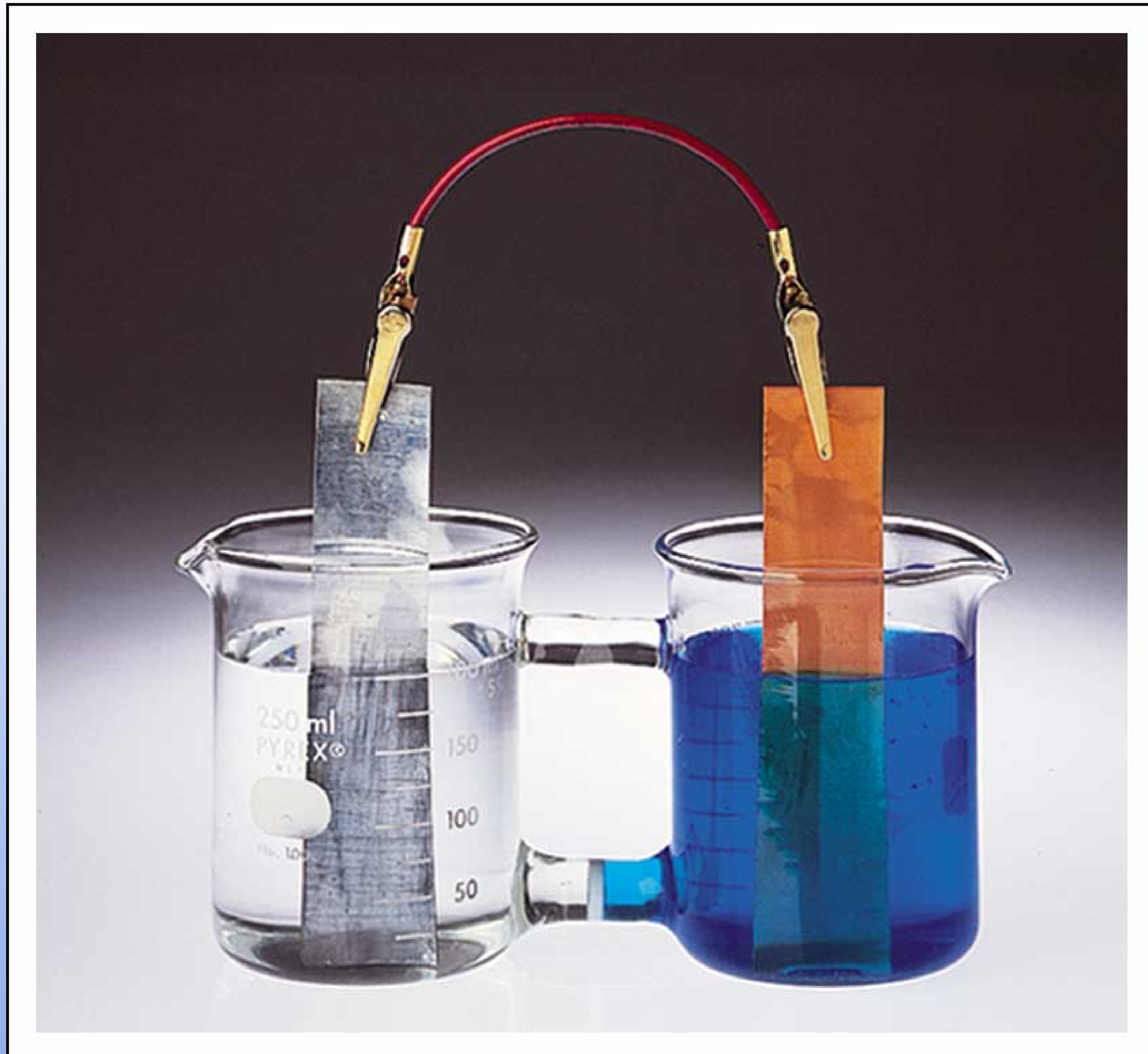


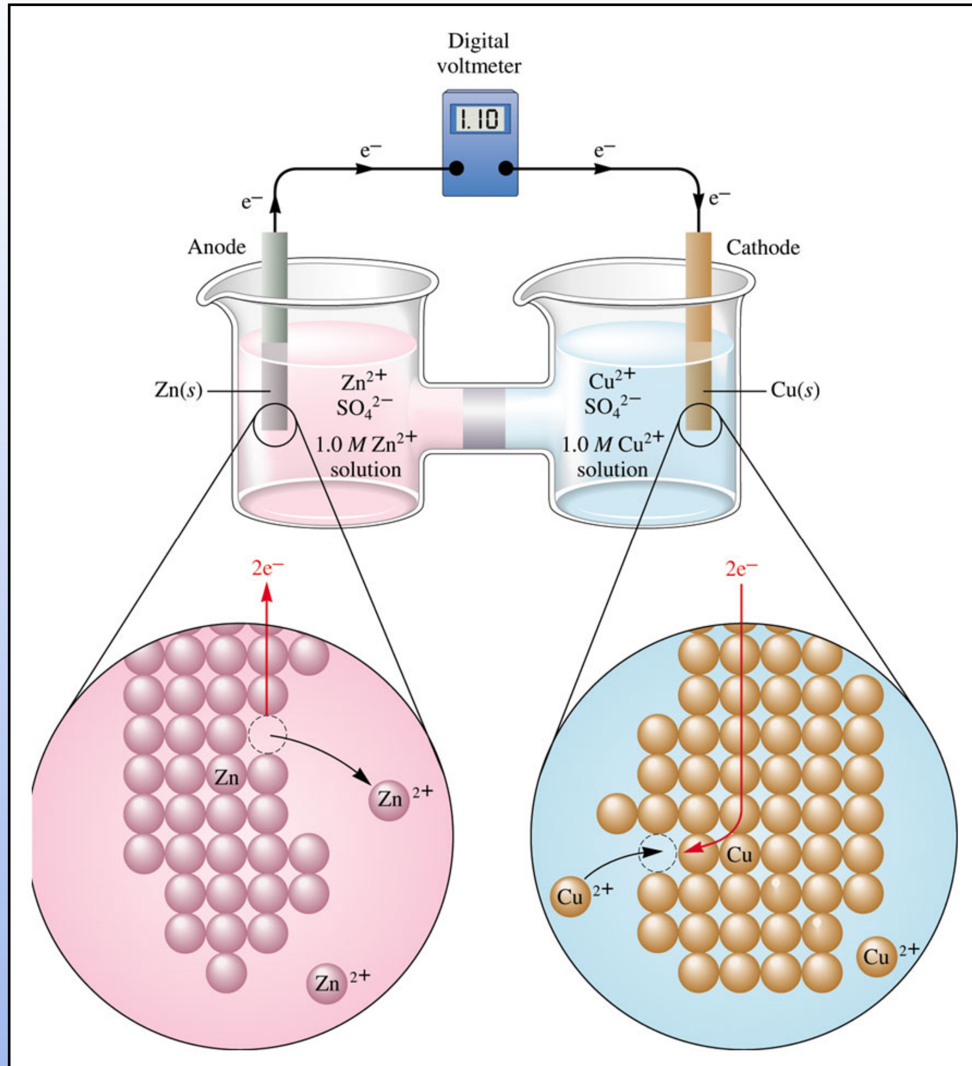
Problem, one side is getting more positive
one side is getting more negative.
We need to keep each side neutral



Add a connection that let's a "counter" ion move between the two sides

As the reaction proceeds Zn is oxidized into Zn^{2+}
Cu^{2+} is reduced into Cu
note I have two solid pieces of metal (electrodes) connected to the wire


250 ml
PYREX®
150
100
50



Oxidation

Zn -> Zn^{2+} + 2 e^-

Reduction

Cu^{2+} + 2e^- -> Cu

Initially we start with 0.5M $CuSO_4$
and ~ 0 M $ZnSO_4$

As the reaction proceeds ...

A. $[Zn^{2+}]$ is increasing

B. $[Cu^{2+}]$ is increasing

C. neither is changing

Initially we start with 0.5M $CuSO_4$
and ~ 0 M $ZnSO_4$

As the reaction proceeds ...

A. the voltage is increasing

B. the voltage is decreasing

C. neither is changing

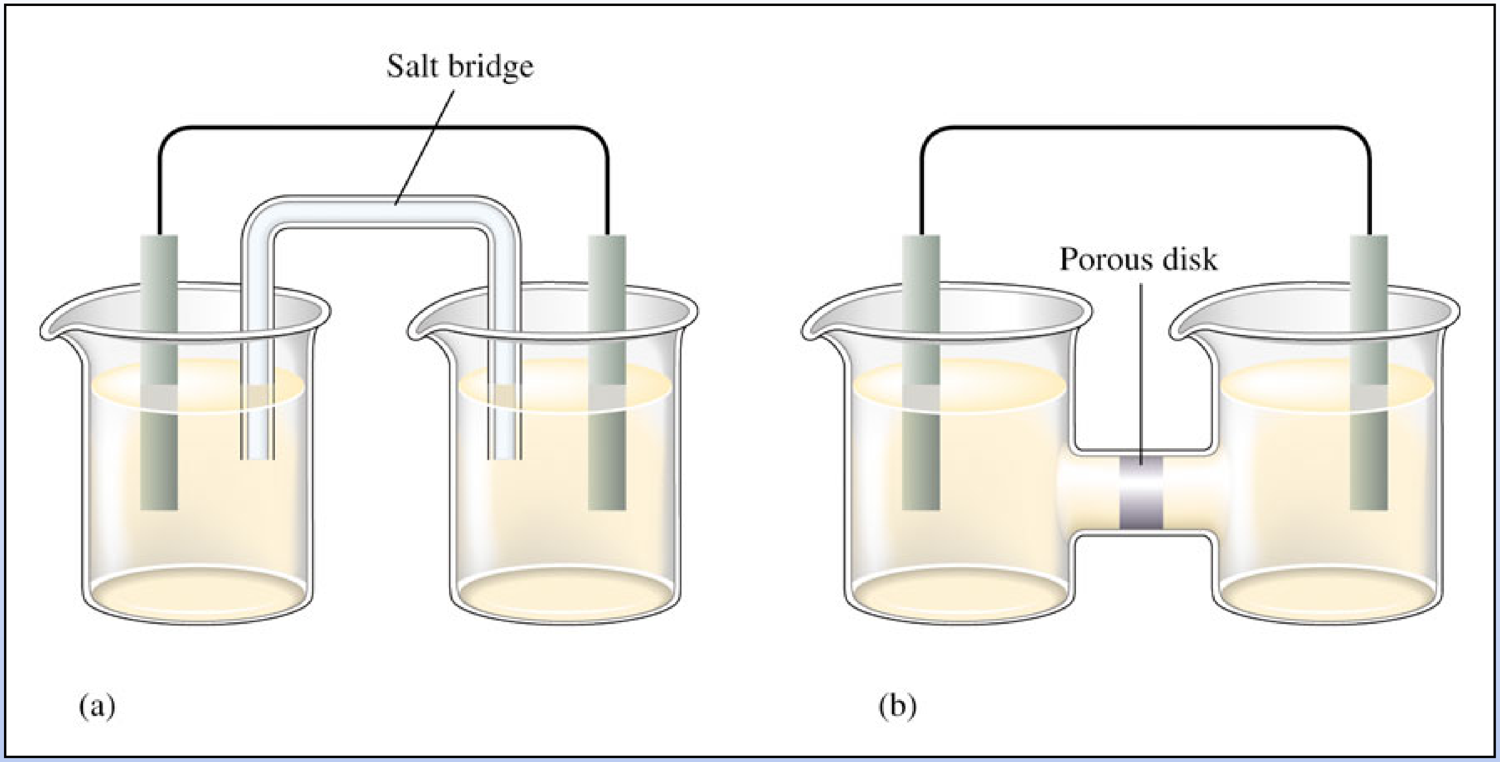
Initially we start with 0.5M $CuSO_4$
and ~ 0 M $ZnSO_4$

When the reaction stops

A. the voltage is zero

B. the free energy difference is zero

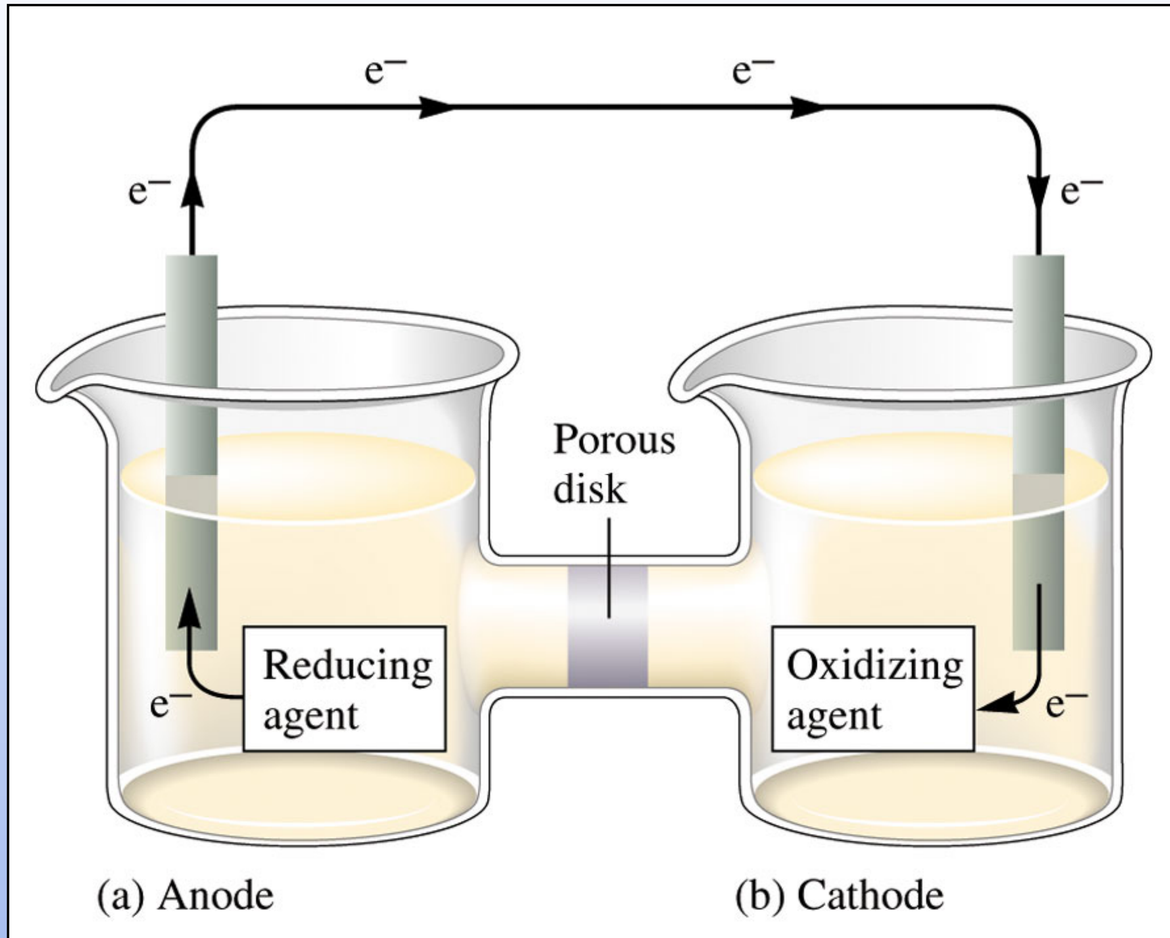
C. both are zero



Salt Bridge or Porous Disk allow ions to flow back and forth between the two beakers.

As e^- move from one side to the other, counter anions move the opposite direction

Define by the chemistry we want to happen



Anode.
Oxidation
reaction

Cathode.
Reduction
Reaction

How will I ever remember?

AN OX and RED CAT

ANode OXidation

REDuction CAThode

Cathode Ray Tube
Shoots out electrons

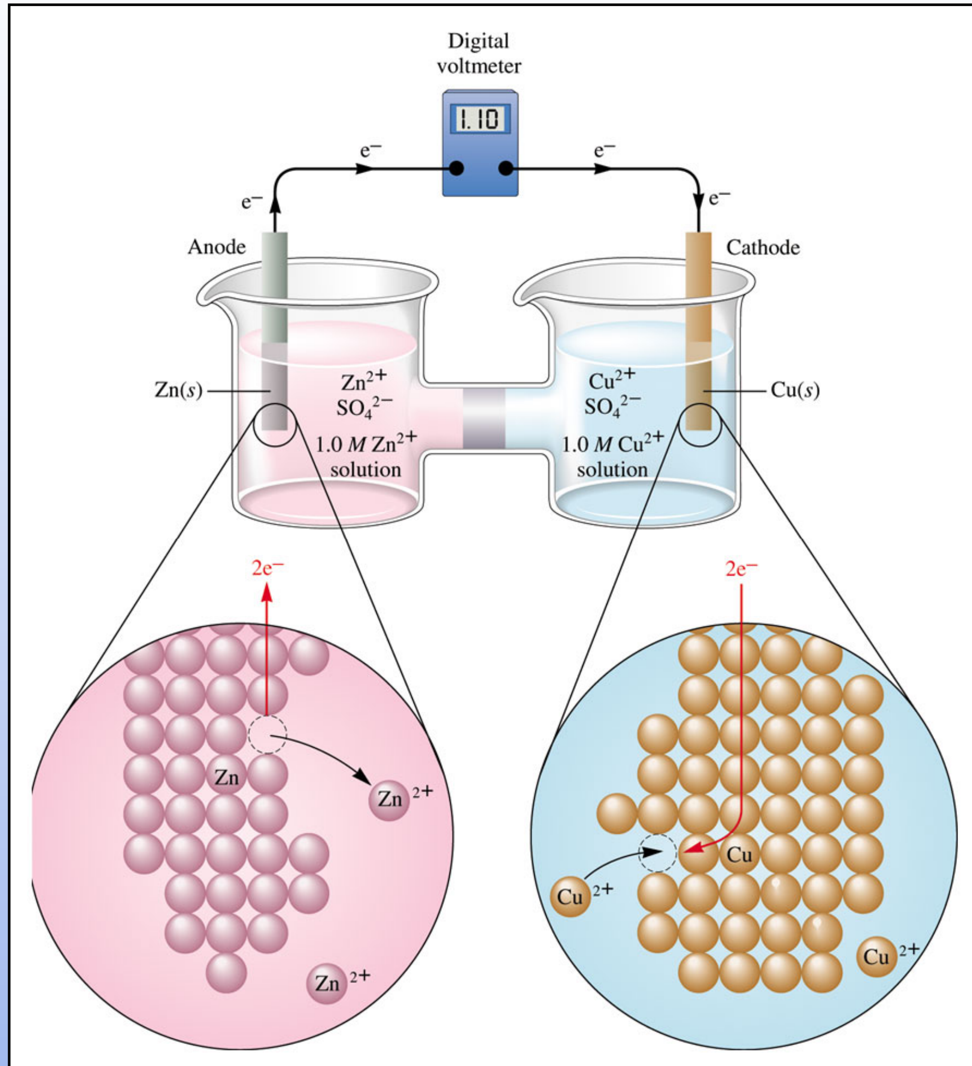
Alternatively just remember it!

In our reaction of Zn goes to Zn^{2+}
and Cu^{2+} goes to Cu
What is the cathode?

A. The Cu strip

B. The Zn strip

C. neither



Oxidation

$Zn \rightarrow Zn^{2+} + 2\,e^-$

Reduction

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

To write this out we develop a short hand

symbol for the short hand

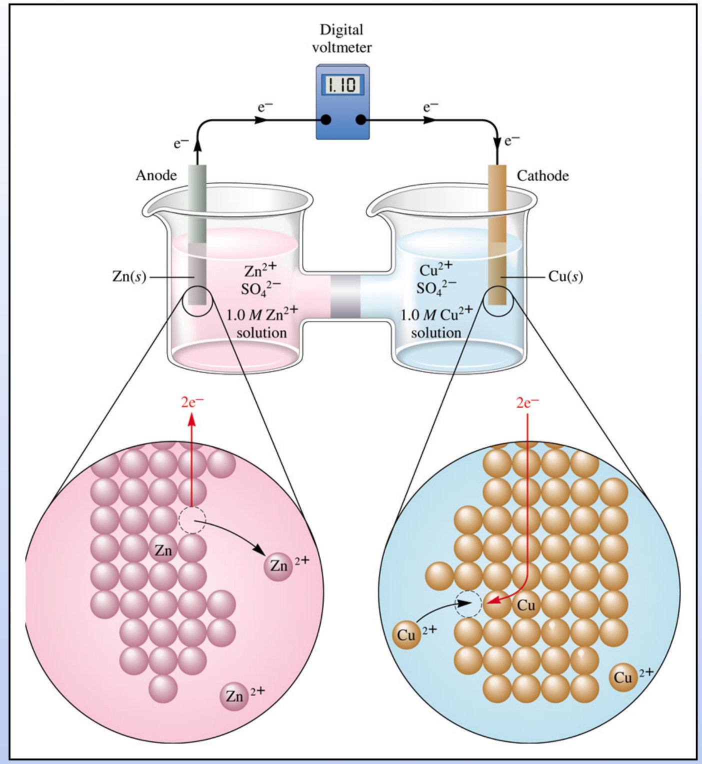
|| = "salt bridge" this divides the cell into to halves
| = show the different compounds of each 1/2 reaction

By convention the anode is always on the "left"

So for the cell we just had

We can write this as

$<Zn|Zn^{2+}||Cu^{2+}|Cu>$



if we knew the
concentrations of the ions

$<Zn|Zn^{2+}(1\ M)\ ||Cu^{2+}(10^{-3}\ M)\ |Cu>$

Other reactions

One half is
Oxidation (Anode) Ag goes to Ag+

Reduction (Cathode) Fe^{3+} goes to Fe^{2+}

$$< Ag \mid Ag^{+} \mid\mid Fe^{3+} \mid Fe^{2+} >$$

but we would like this to represent the actual cell
I cannot hook a wire up to Fe^{2+}. I need an electrode in the solution. Let's say I use a Pt electrode

$$< Ag \mid Ag^{+} \mid\mid Fe^{3+} \mid Fe^{2+} \mid Pt >$$

Two “kinds” of electrochemical cells

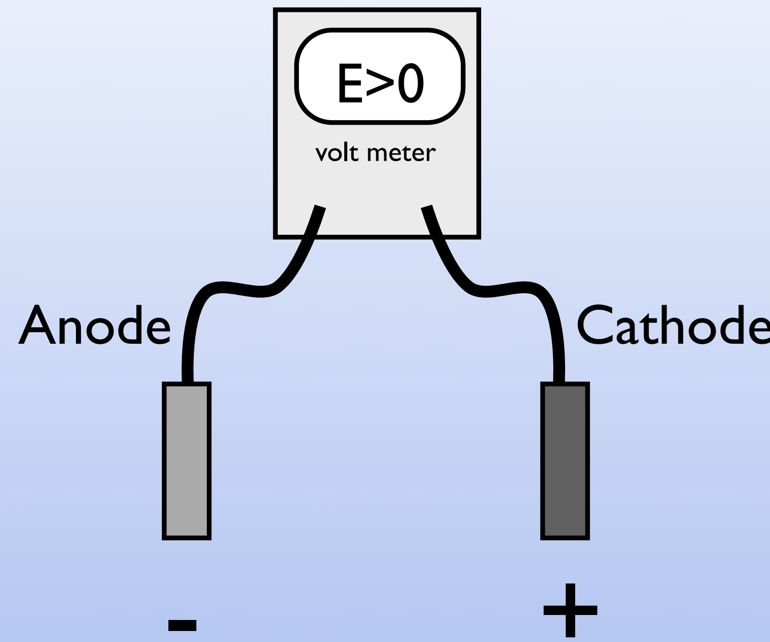
Galvanic (Voltaic)
Reaction is spontaneous
we can use these to make a battery

Electrolytic
Reaction is not spontaneous
we have to input work to get these reactions to proceed

Nomenclature

Galvanic Cell
Voltaic Cell
Battery

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



electrons flow to cathode

Cathode get the PLUS sign

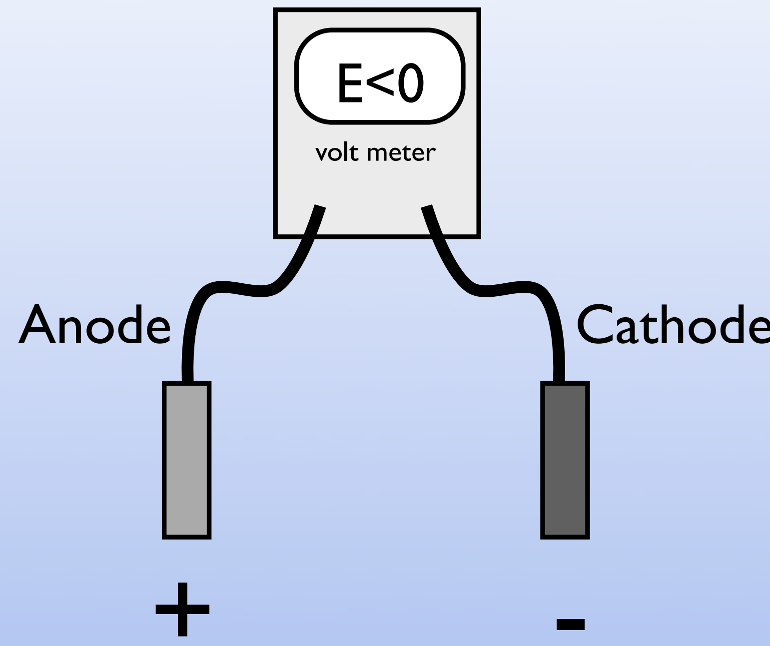
This is spontaneous. It can be used as a power supply

First some nomenclature

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

In the following cell, how many electrons flow for each Zinc atom that reacts?

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

A. 0.5

B. 1

C. 2

D. 4

E. Zinc doesn't react, Zn^{2+} do

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

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

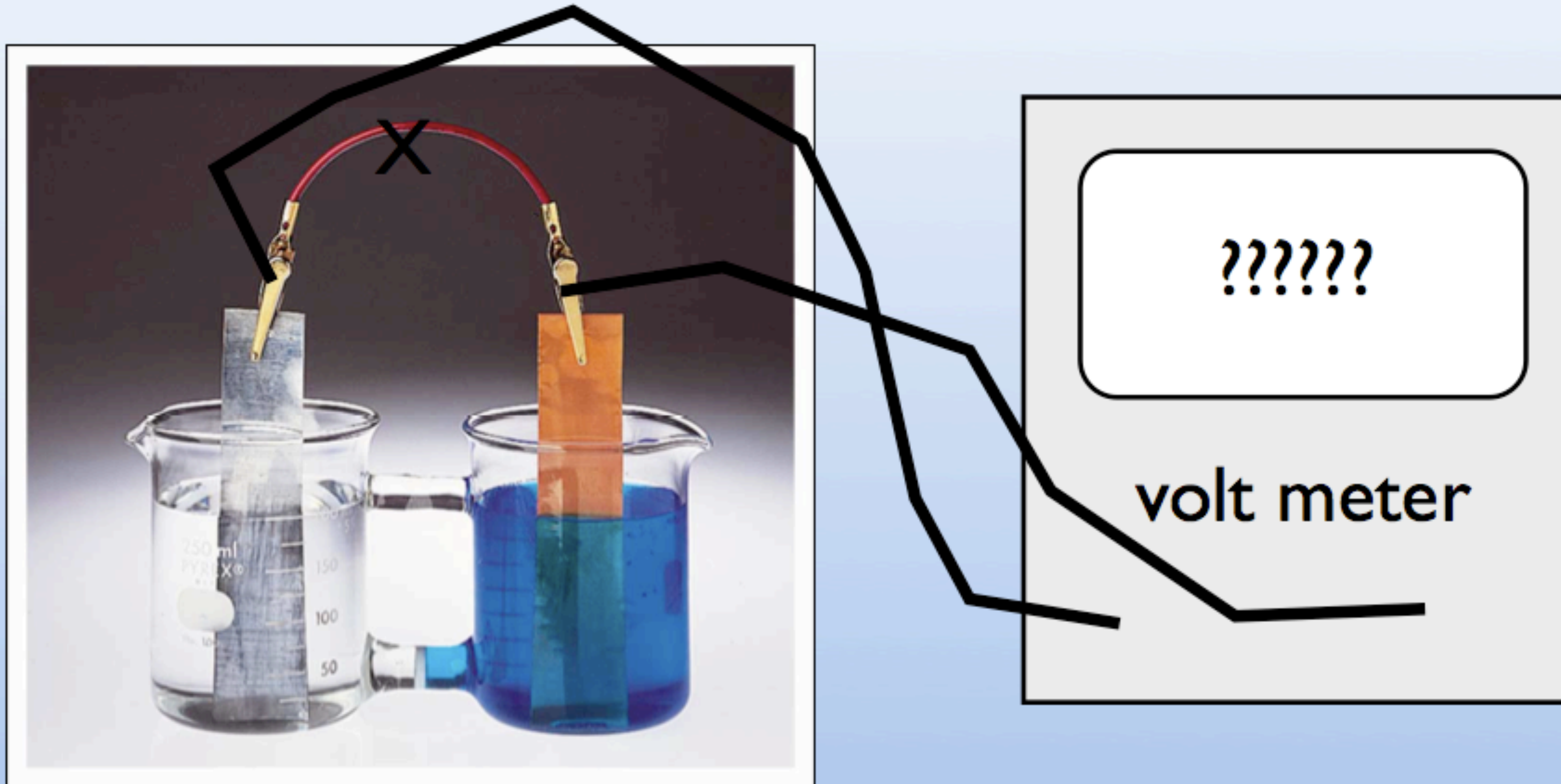
$Zn(s) \mid Zn^{2+} \parallel Cu^{2+} \mid Cu\,(s)$

A. (3/F)

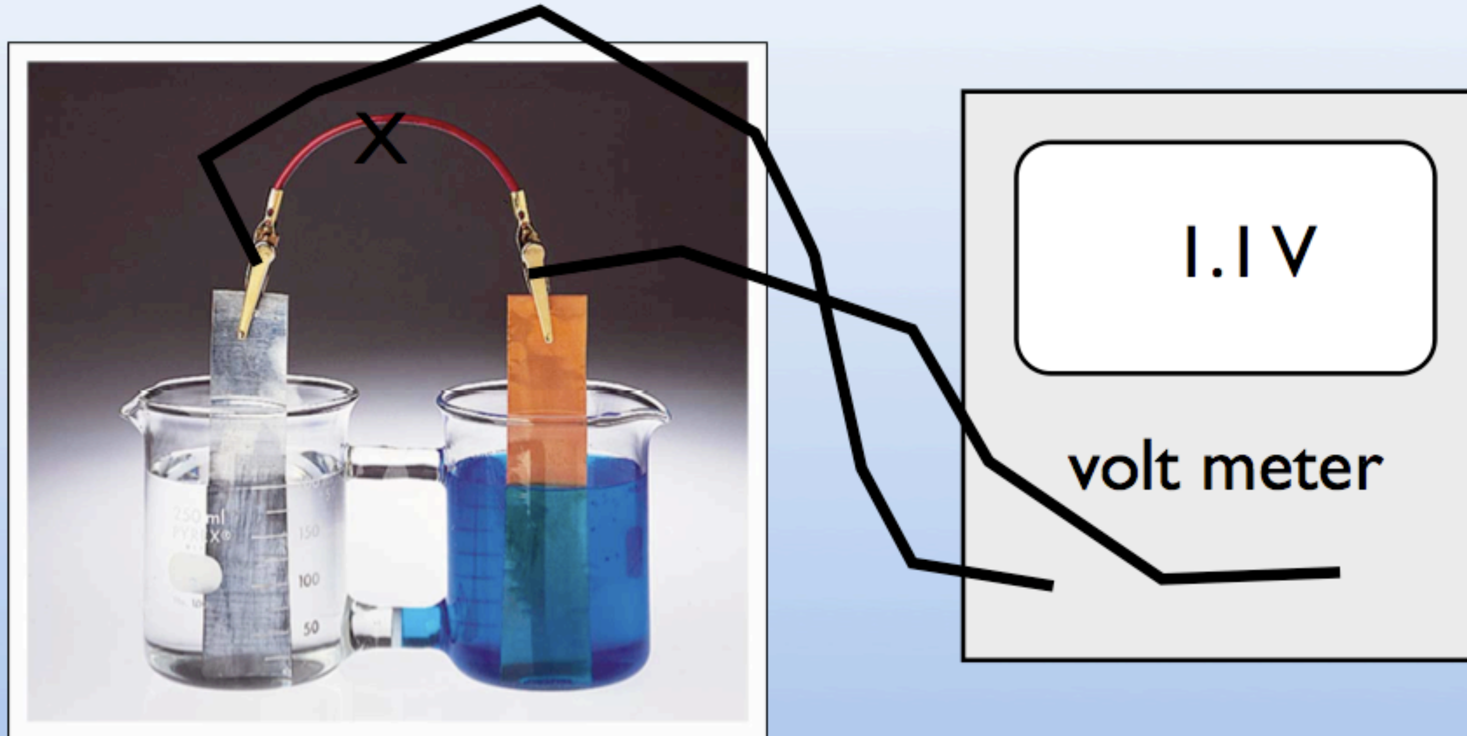
B. (3/F) x 2

C. (3/F) / 2

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)