

Today

*Voltaic*

Galvanic Cells

Spontaneous Electrochemistry

Electrolytic Cells

“Backwards” Electrochemistry

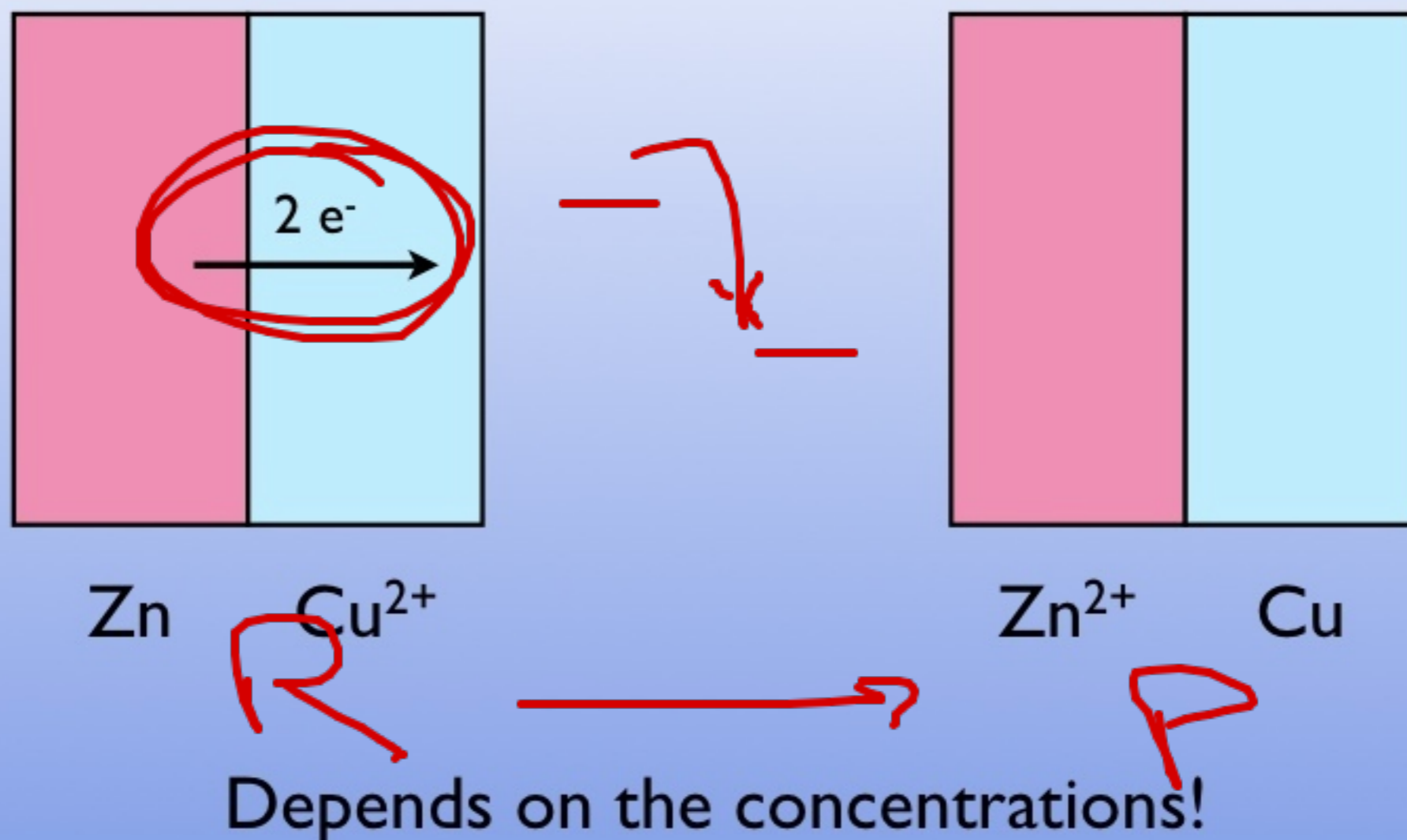
# Balancing Redox Reactions

There is a method (actually several)

Learn one (4.10-4.12)

Practice (worksheet)

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



Which has the lower  
Standard Gibb's free energy?

- A.  $\text{Zn}^{2+}(\text{1M}) + \text{Cu}$
- B.  $\text{Zn} + \text{Cu}^{2+}(\text{1M})$
- C. They are exactly equal

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

$$\Delta G$$

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

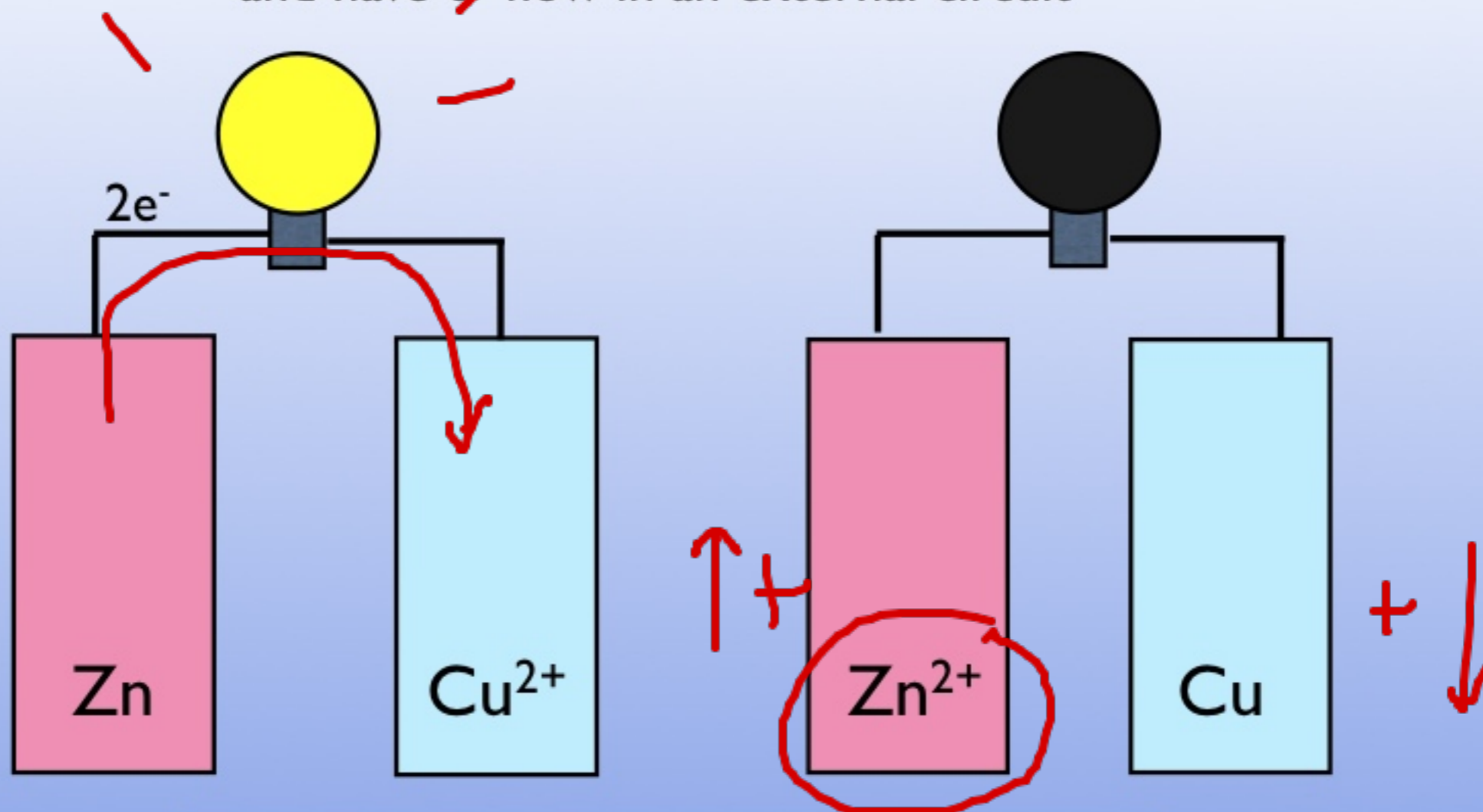
The concentration will change until  $\Delta G = 0$

$$\Delta G^\circ$$

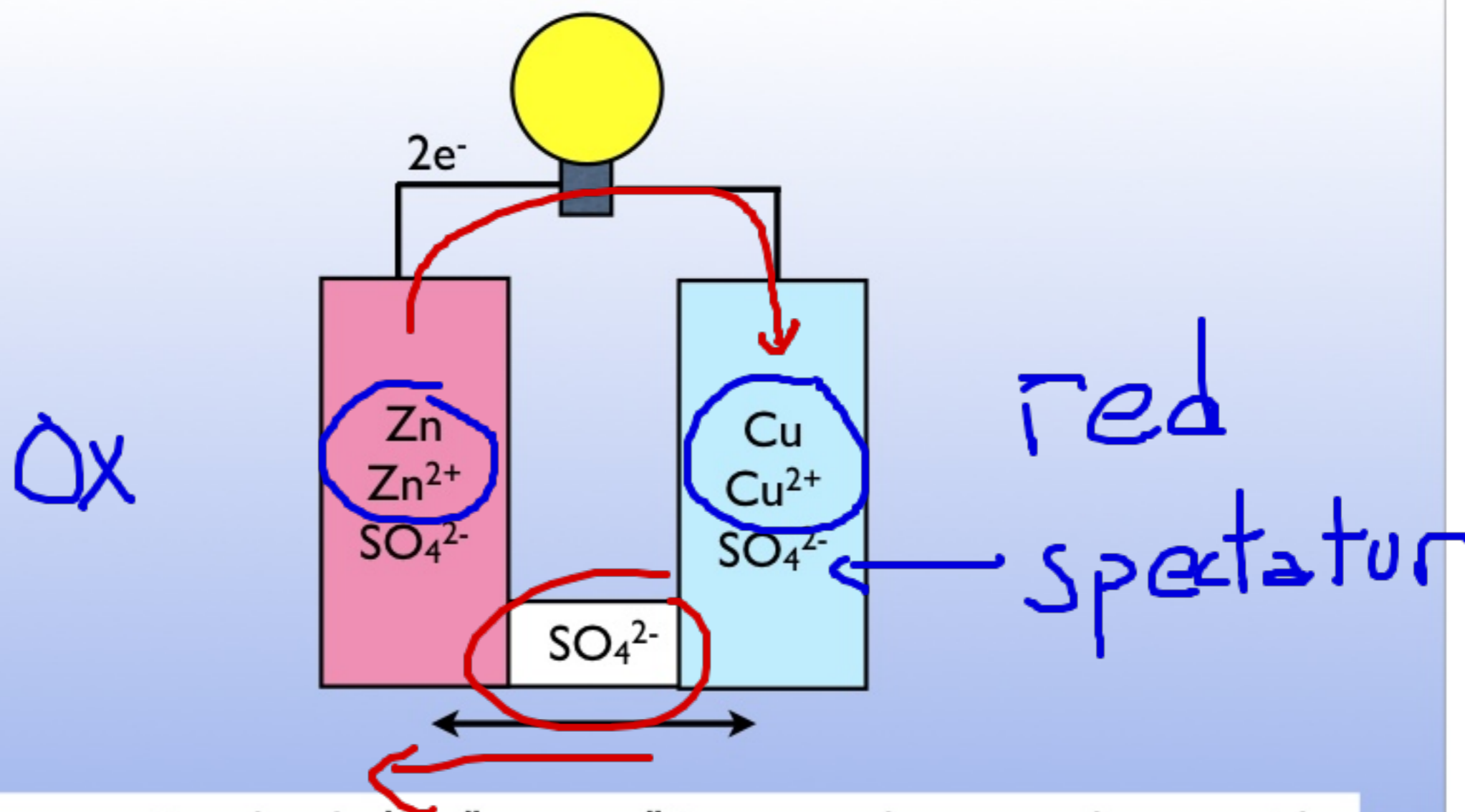
Difference in Free Energy between reactants and product under standard conditions

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

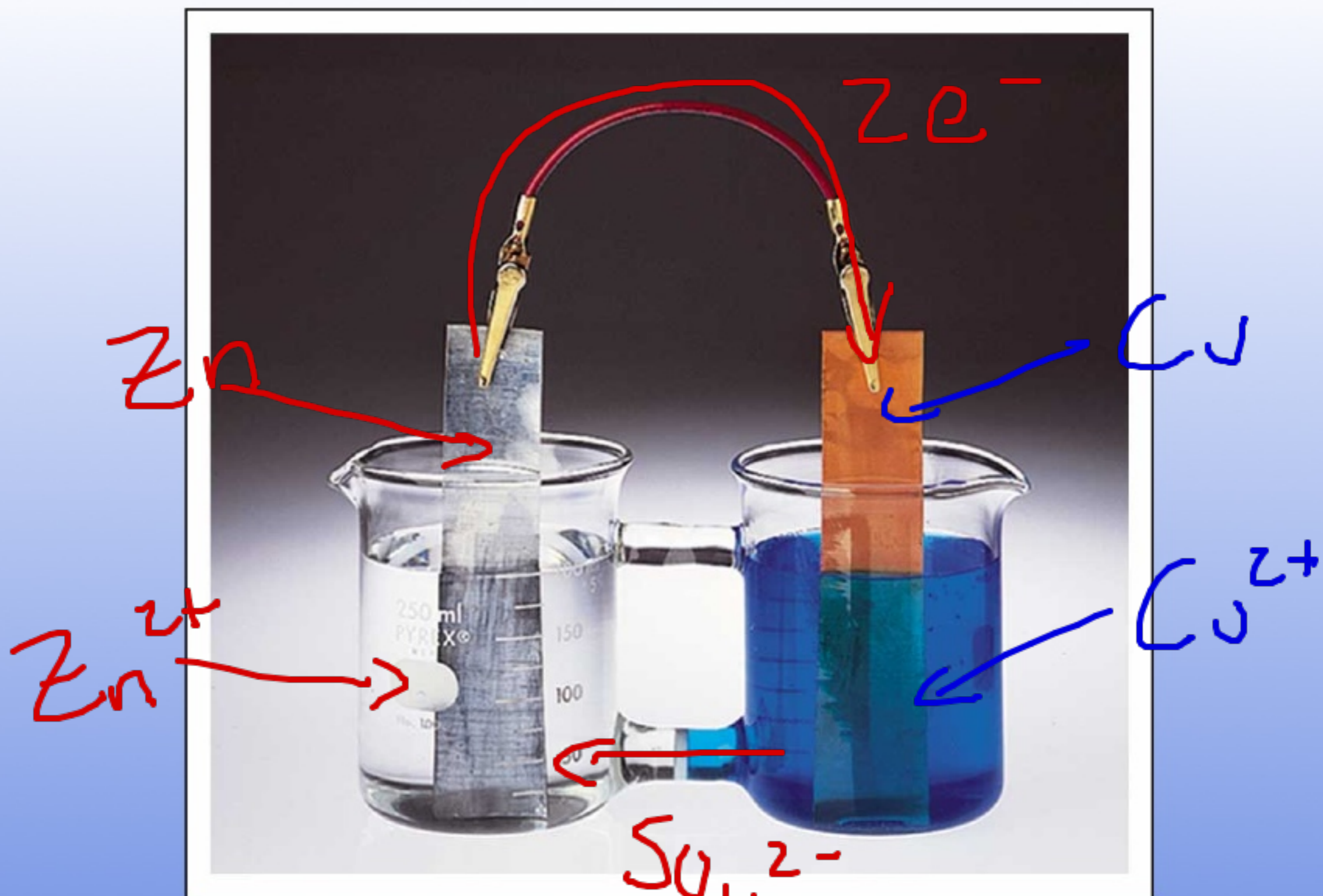


Problem, one side is getting more positive  
one side is getting more negative.  
We need to keep each side neutral

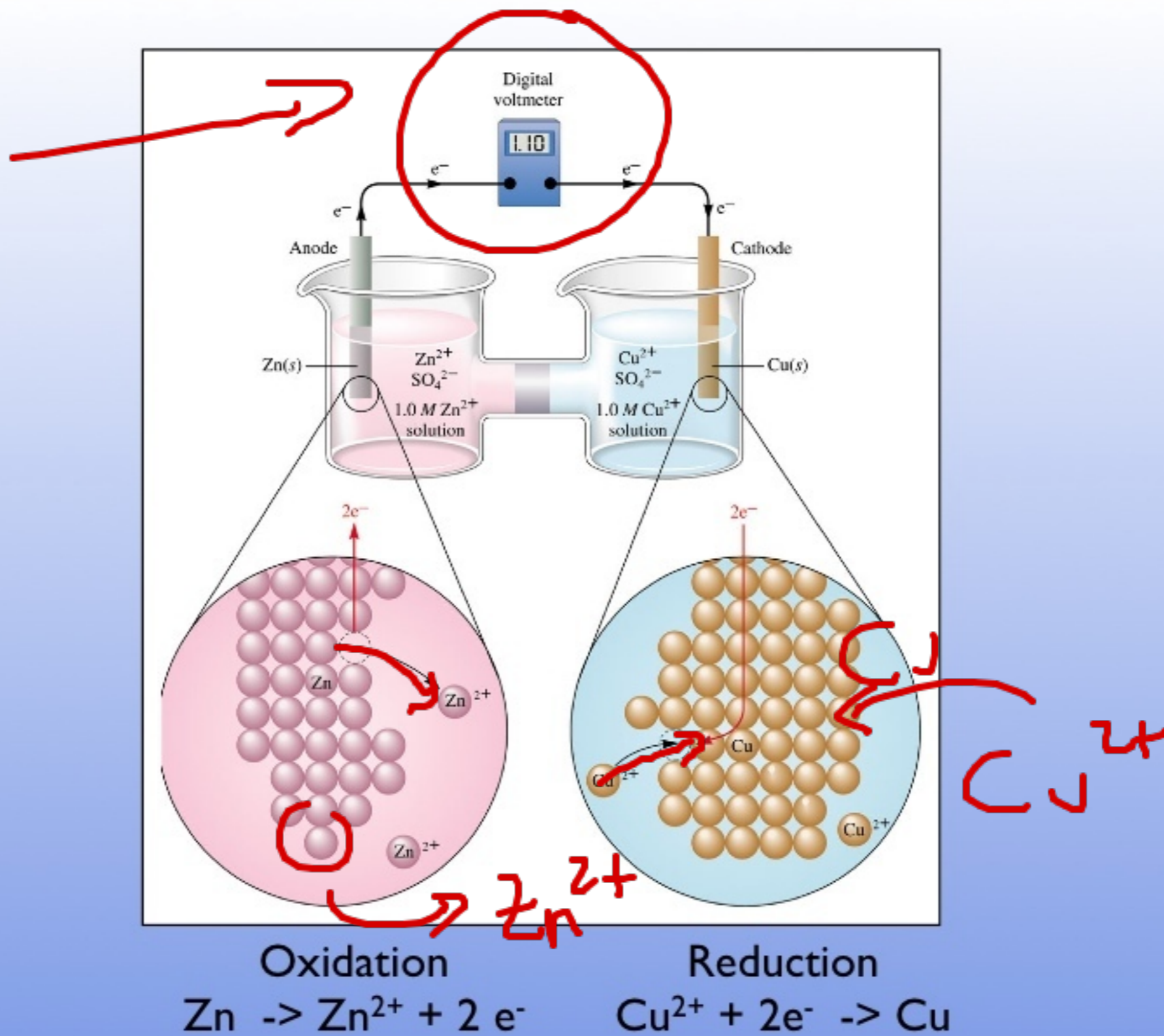


Add a connection that let's a "counter" ion move between the two sides

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







Initially we start with 0.5M  $\text{CuSO}_4$   
and  $\sim 0$  M  $\text{ZnSO}_4$

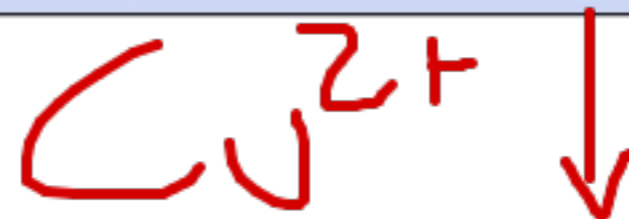
As the reaction proceeds ...

$$K = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

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

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

C. neither is changing



Initially we start with 0.5M  $\text{CuSO}_4$   
and  $\sim 0$  M  $\text{ZnSO}_4$

As the reaction proceeds ...

A. the voltage is increasing

B. the voltage is decreasing

C. neither is changing

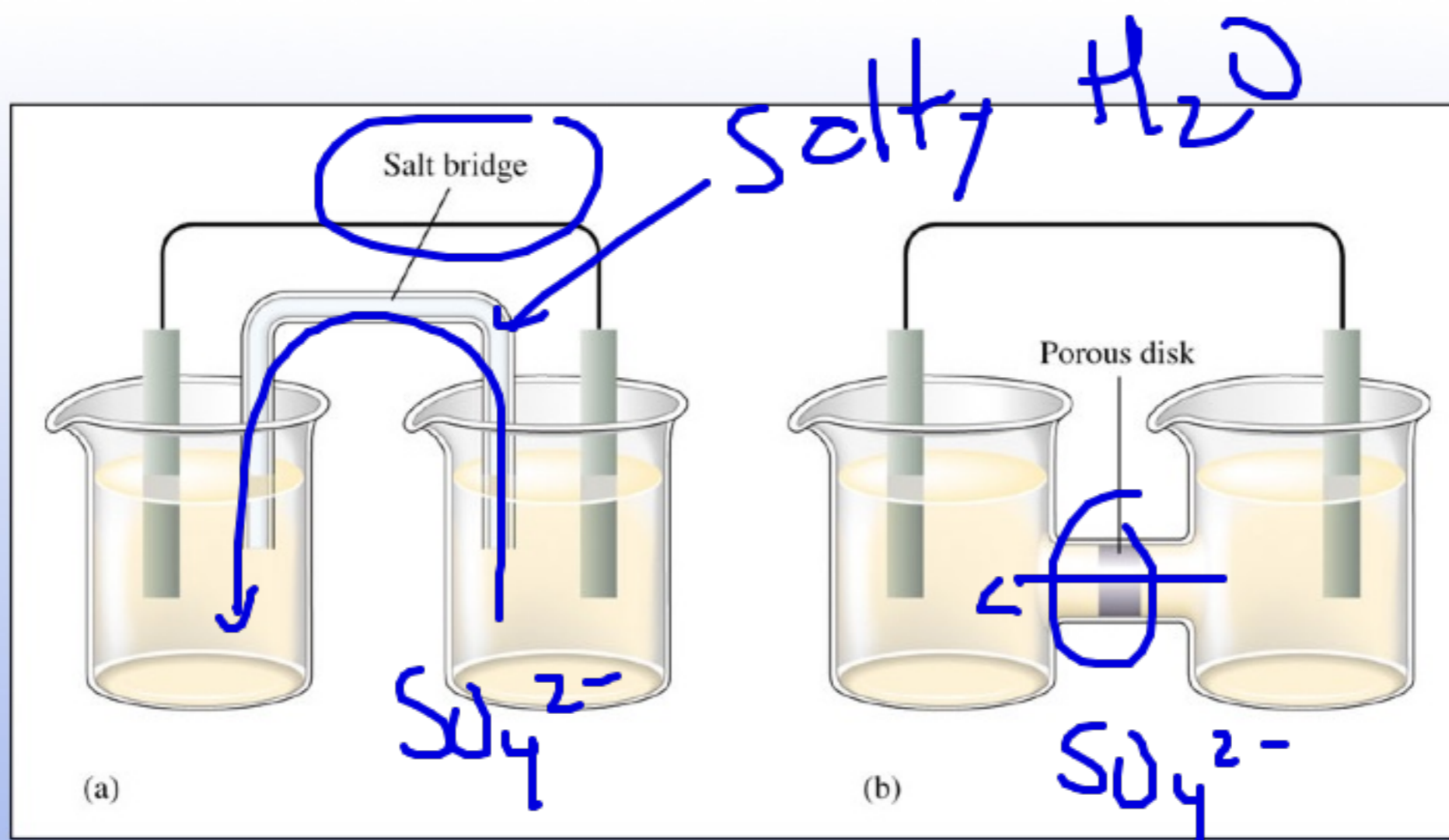
At equil

$$V = 0$$

Initially we start with 0.5M  $\text{CuSO}_4$   
and  $\sim 0$  M  $\text{ZnSO}_4$

When the reaction stops

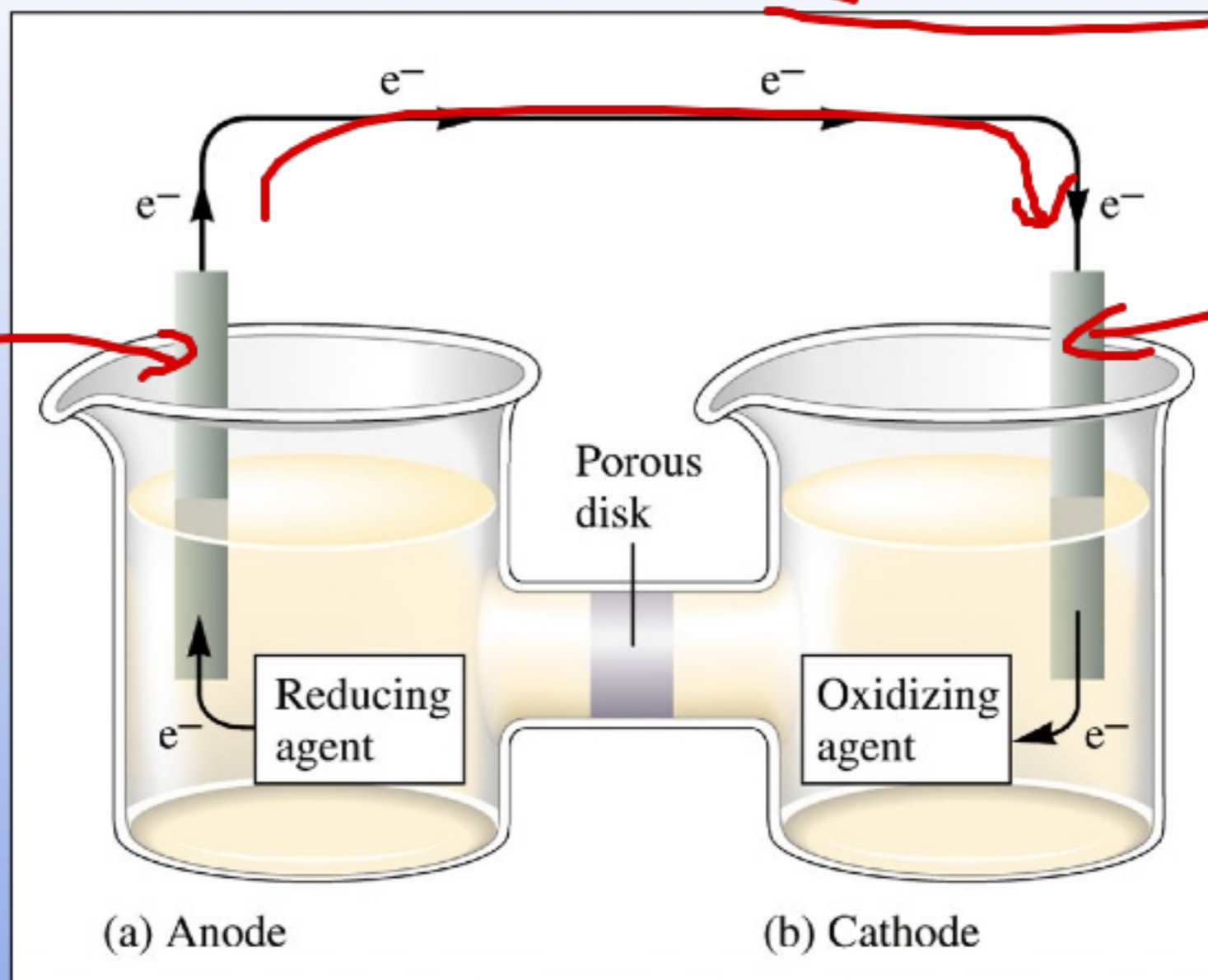
- A. the voltage is zero
- B. the free energy difference is zero
- C. both are zero



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

Cathode

$e^-$  flow  
cathode

(a) Anode

(b) Cathode

Anode.  
Oxidation  
reaction

Cathode.  
Reduction  
Reaction

How will I ever remember?

AN OX and RED CAT



ANode      REDuction  
OXidation      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

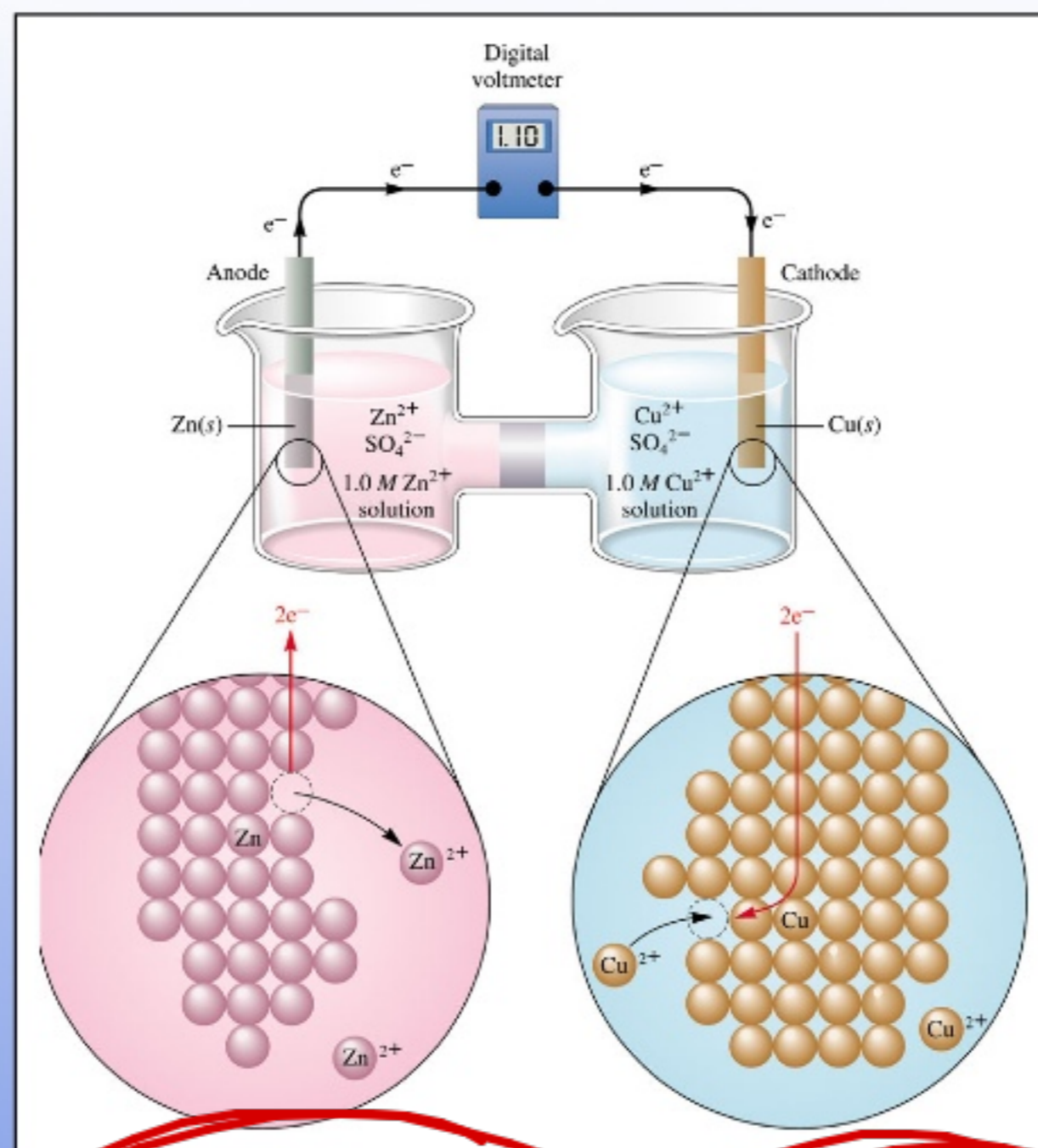
B. The Zn strip

C. neither

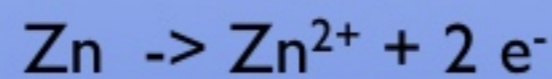
Reduction



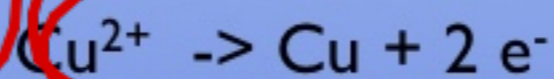




Oxidation



Reduction



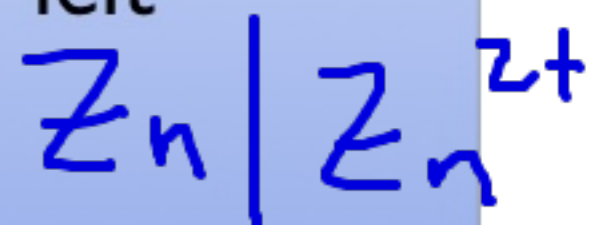
To write this out we develop a short hand

symbol for the short hand

$\text{||}$  = "salt bridge" this divides the cell into two halves  
 $\text{⊥}$  = show the different compounds of each 1/2 reaction

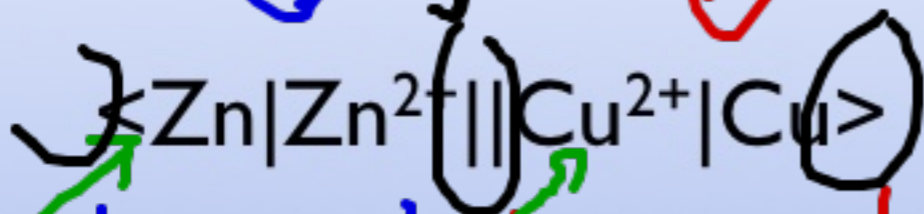
By convention the anode is always on the "left"

So for the cell we just had



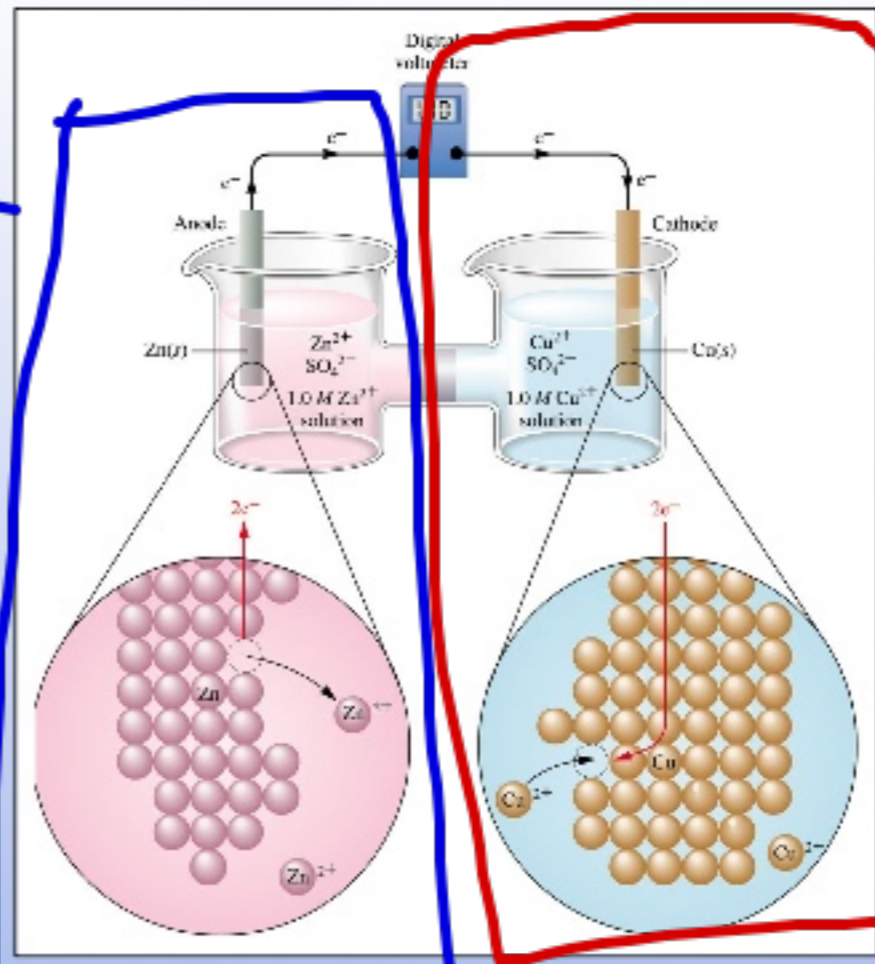
salt bridge

We can write this as



ANODE

CATHODE



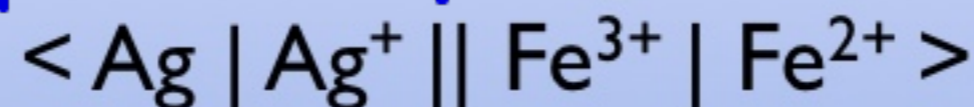
if we knew the concentrations of the ions



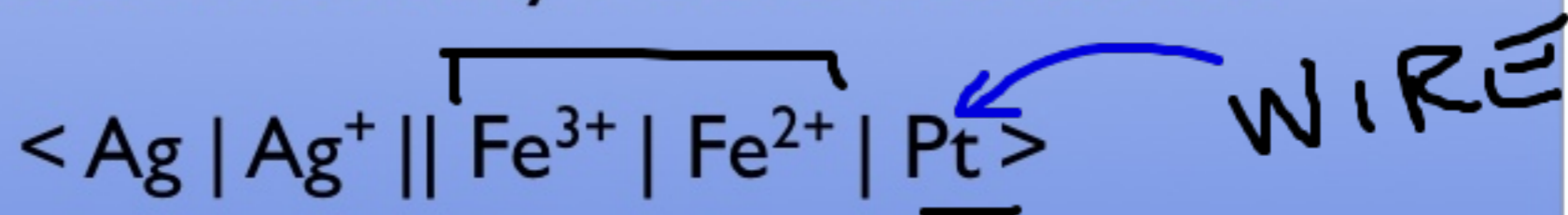
## Other reactions

One half is  
Oxidation (Anode) Ag goes to Ag<sup>+</sup>

Reduction (Cathode) Fe<sup>3+</sup> goes to Fe<sup>2+</sup>



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



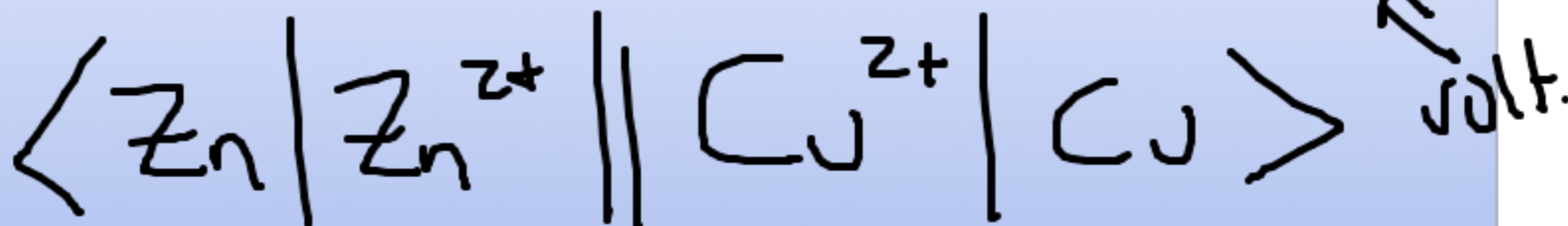
## Two “kinds” of electrochemical cells

Galvanic (Voltaic)

Reaction is spontaneous  
we can use these to make a battery

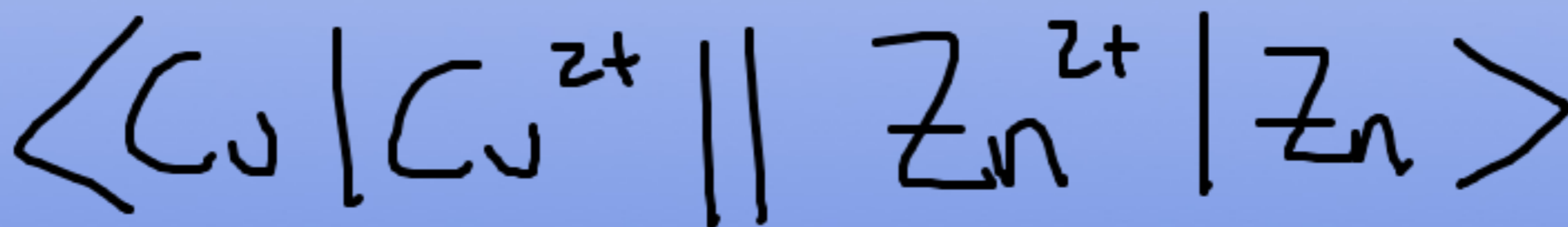
$$\Delta_r G^\circ < 0$$

$$\sum^\circ > 0$$



Electrolytic

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



## Nomenclature

Galvanic Cell  
Voltaic Cell  
Battery

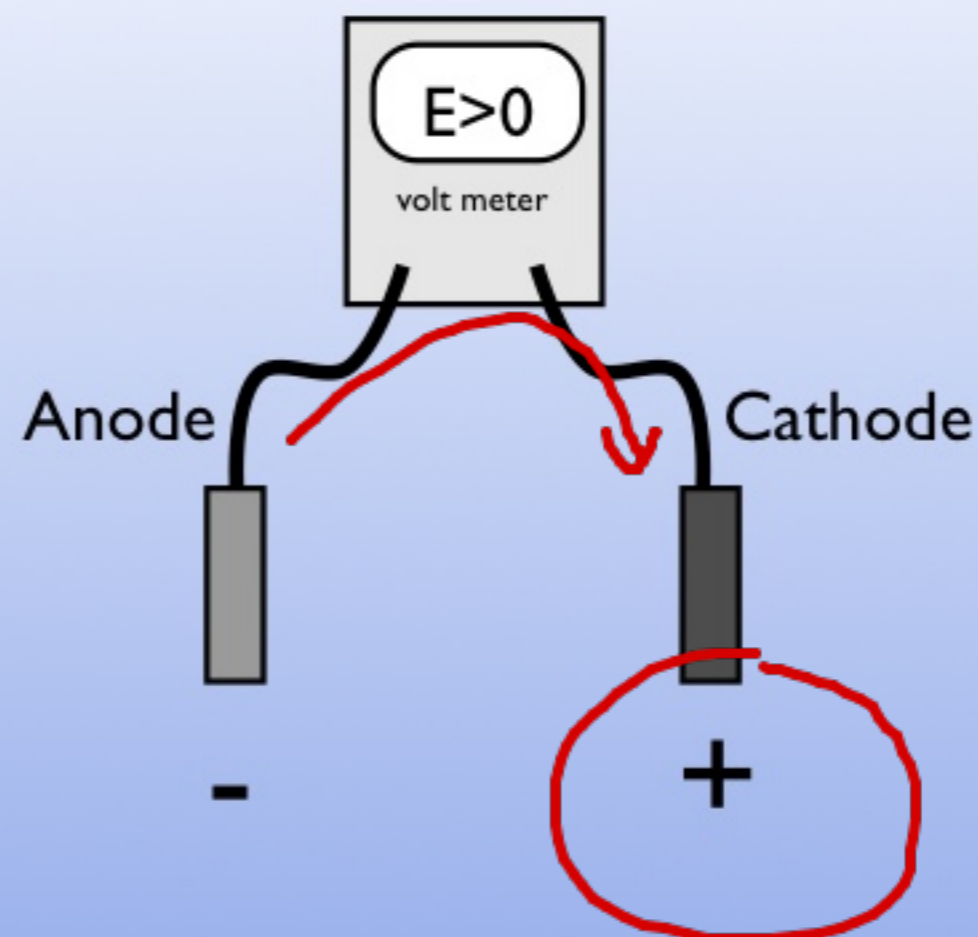
Spontaneous

$$\Delta G < 0$$

$$E > 0$$

VOLTAGE

electrons flow to  
cathode



Cathode get the PLUS sign

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

## First some nomenclature

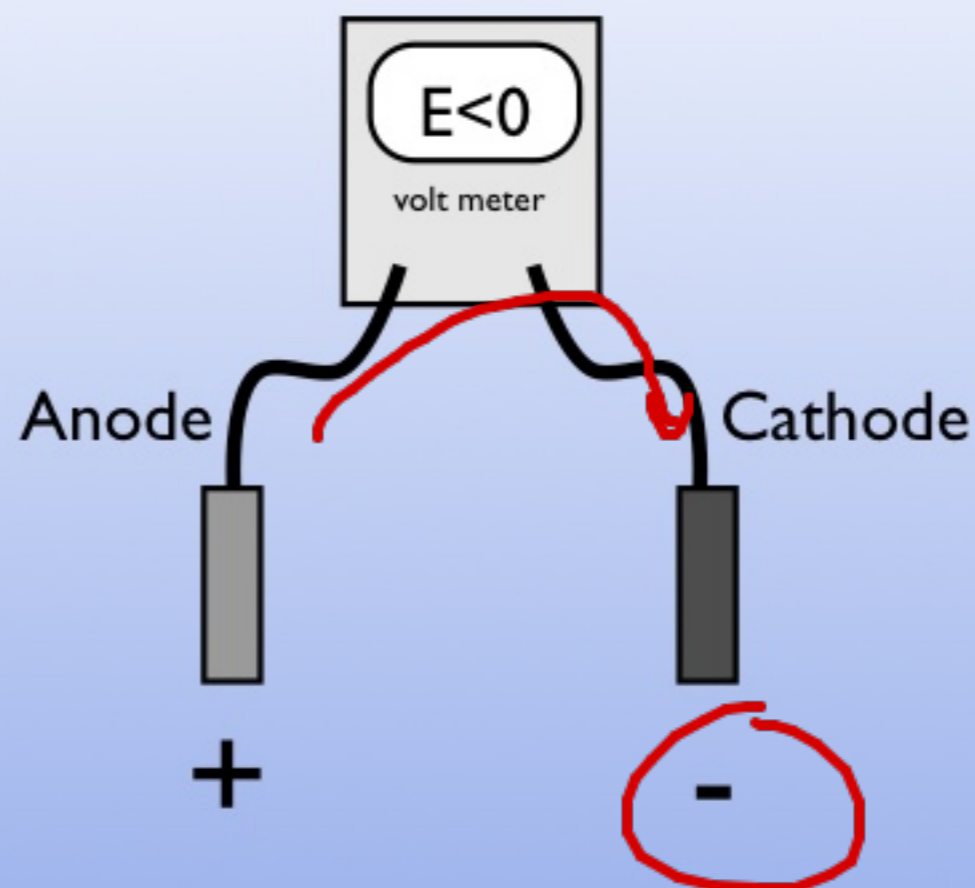
Electrolytic Cell

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?



A. 0.5

B. 1

C. 2

D. 4

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





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

$$\text{Charge} = \text{Current} \times \text{Time}$$

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

# of  
 $e^-$

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

$$F = 96,485 \text{ C} \quad (\text{Faraday's Constant})$$

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



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

F C mol<sup>-1</sup>

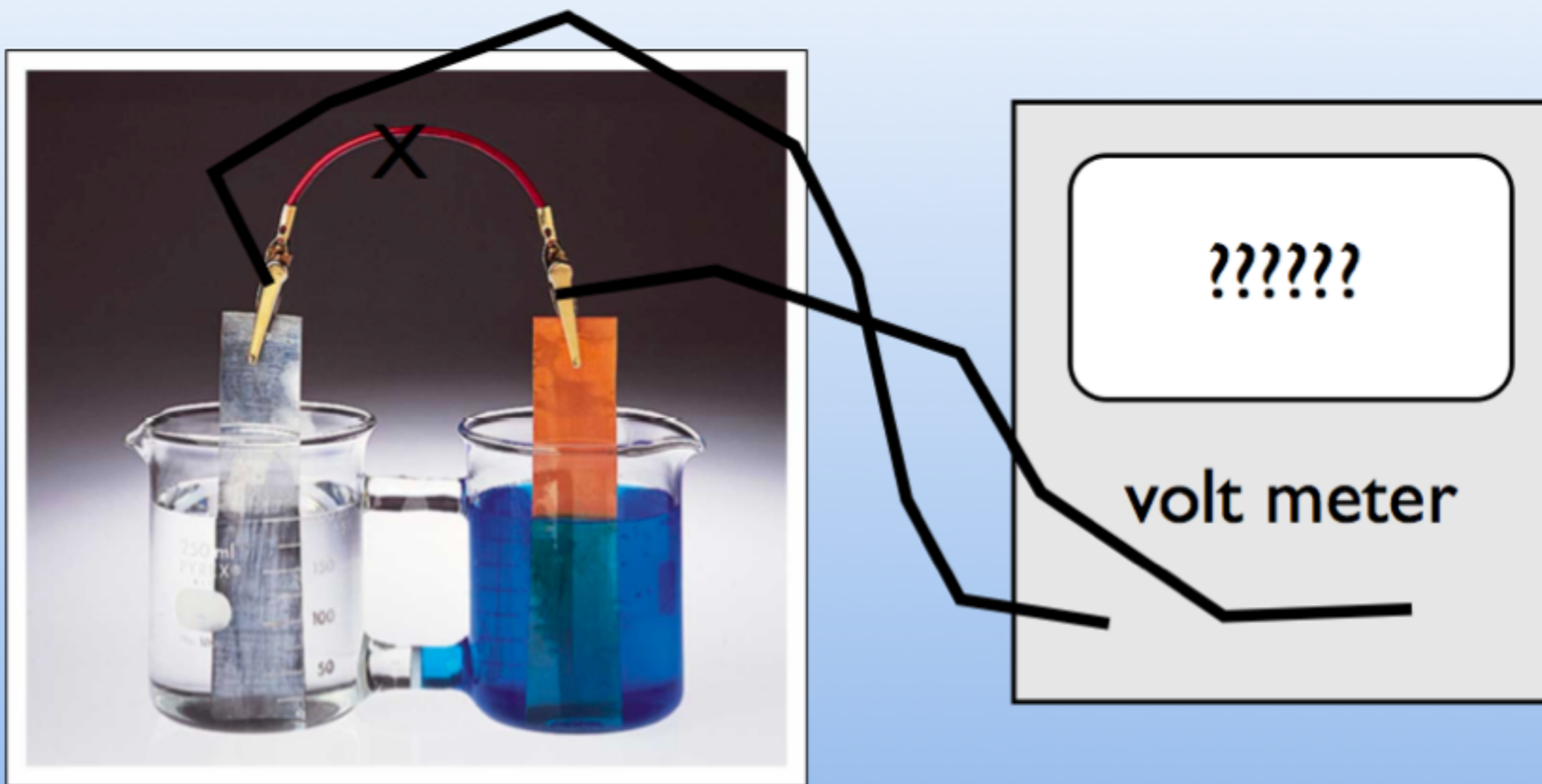
TOTAL CHARGE

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

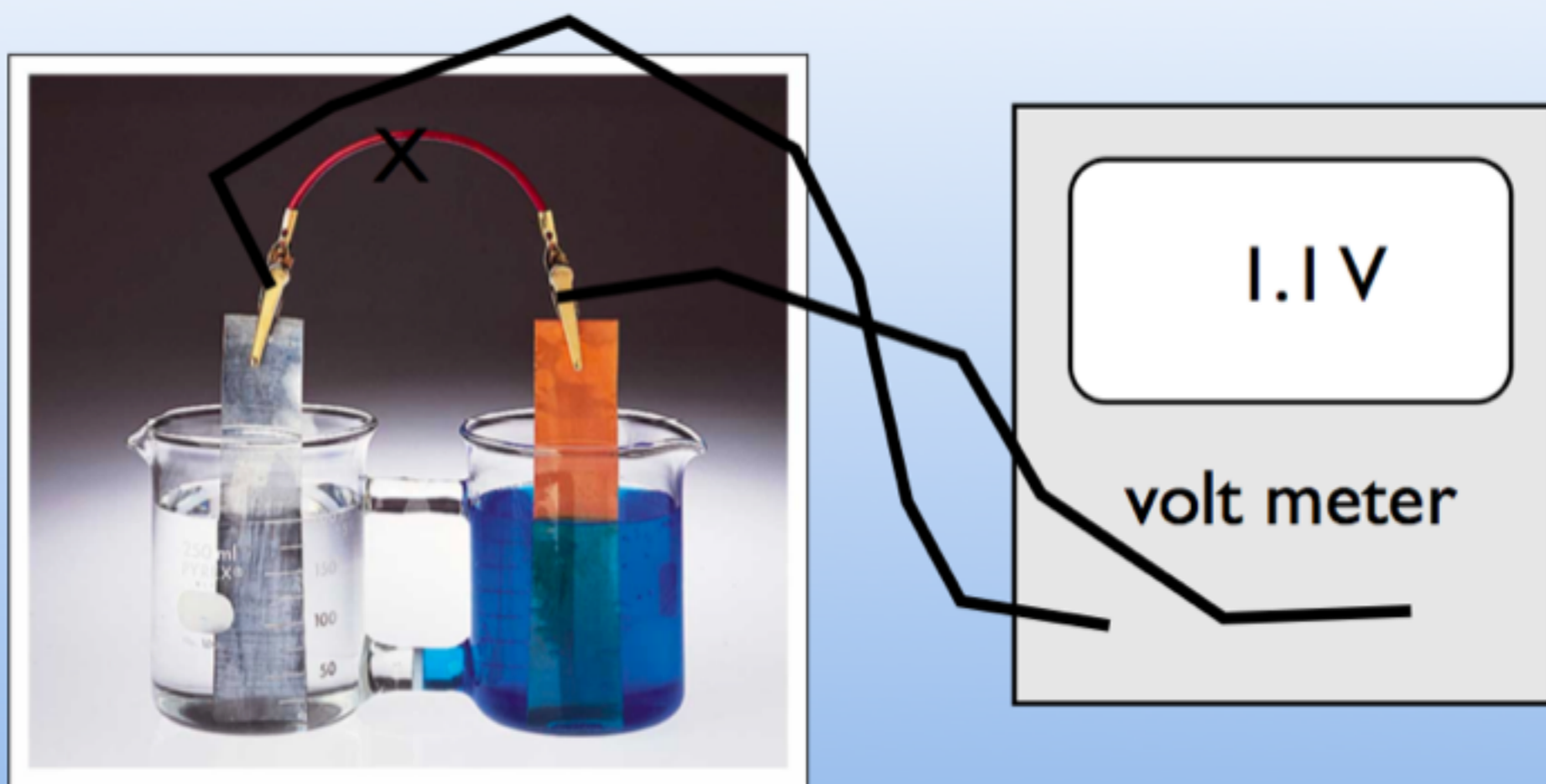


- A.  $(3/F)$
- B.  $(3/F) \times 2$
- C.  $(3/F) / 2$

How do we know what the voltage is?



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



Mix up “standard” concentrations  
 $1\text{ M Zn}^{2+}$  and  $1\text{ M Cu}^{2+}$   
(note this is very concentrated)