

# Lecture #6 of 17

# Measurements in Electrochemistry

Chapters 1 and 15

Q: What's in this set of lectures?

A: B&F Chapters 1 & 15 main concepts:

- Section 1.1: Redox reactions
- Chapter 15: Electrochemical instrumentation
- Section 1.2: Charging interfaces
- Section 1.3: Overview of electrochemical experiments

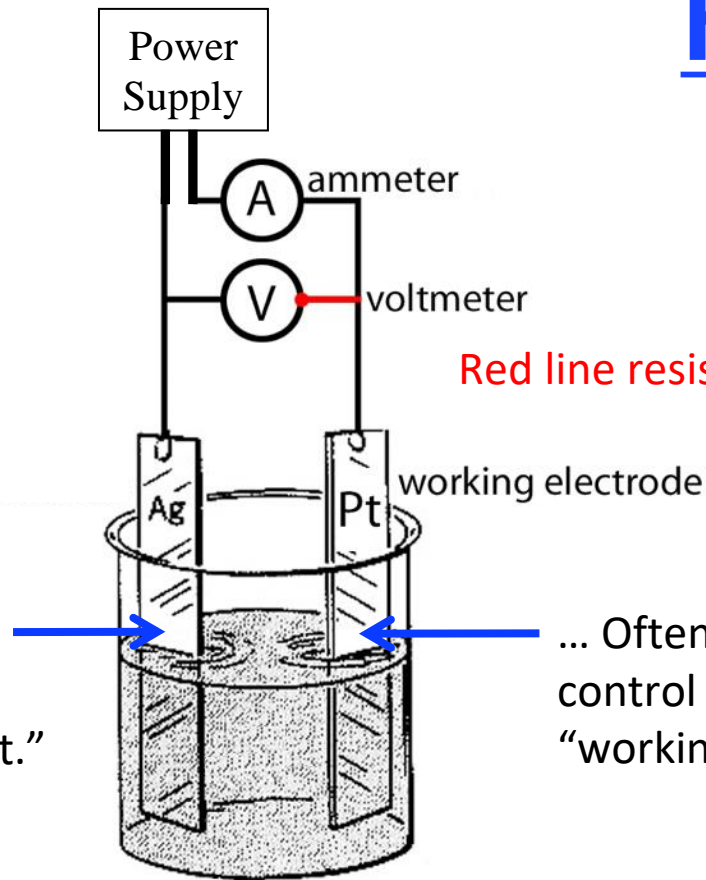
## Looking forward... Section 1.1 (and some of Chapter 15)

- Reference electrodes (*halfway complete*)
- 2-electrode versus 3-electrode measurements (*halfway complete*)
- **Potentiostats**
- **Compliance voltage/current**
- *J–E and I–E curves*
- *Kinetic overpotential*
- *Electrochemical window*
- *Faradaic reactions*

## Experiments:

95% of the measurements that you will perform have a problem

**RECALL:**



... while not affecting the potential of the second (reference) electrode that is used to “complete the circuit.”

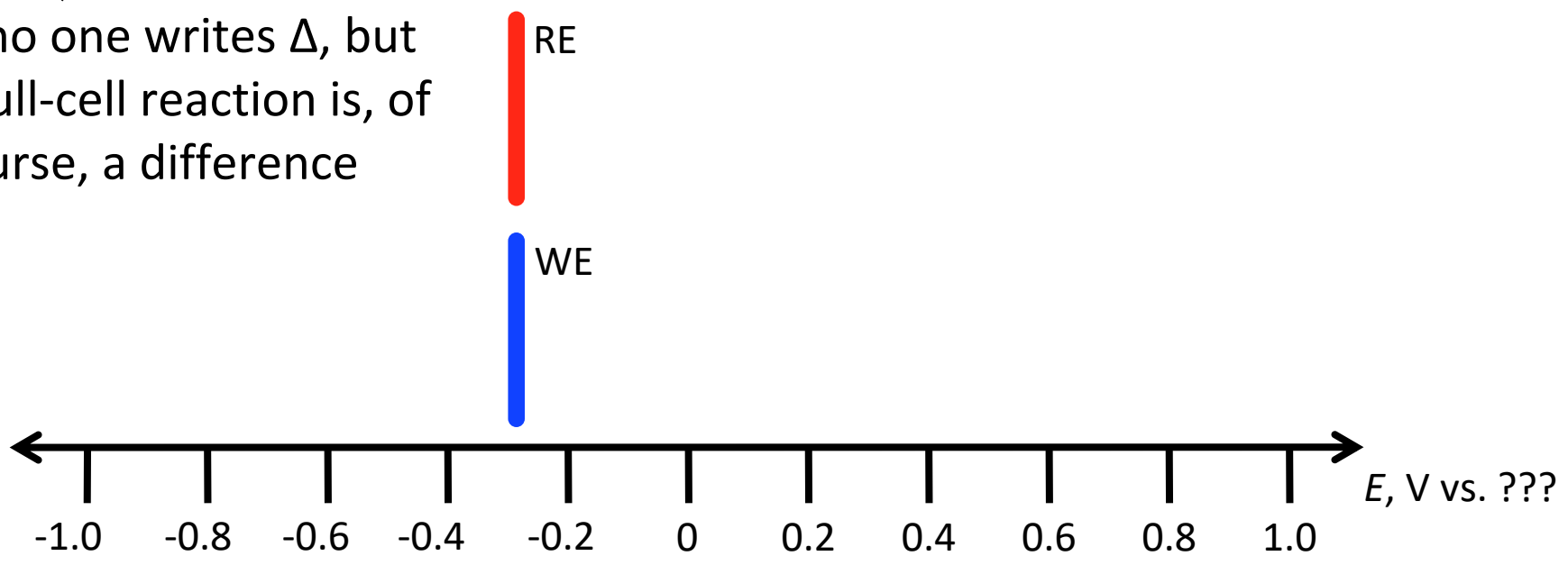
... Oftentimes, most of us wish to control the potential of this “working” electrode...

... for example, let's say both electrodes are platinum...

# RECALL:

$$\Delta E = 0.0 \text{ V} = E_{WE} - E_{RE}$$

... no one writes  $\Delta$ , but a full-cell reaction is, of course, a difference

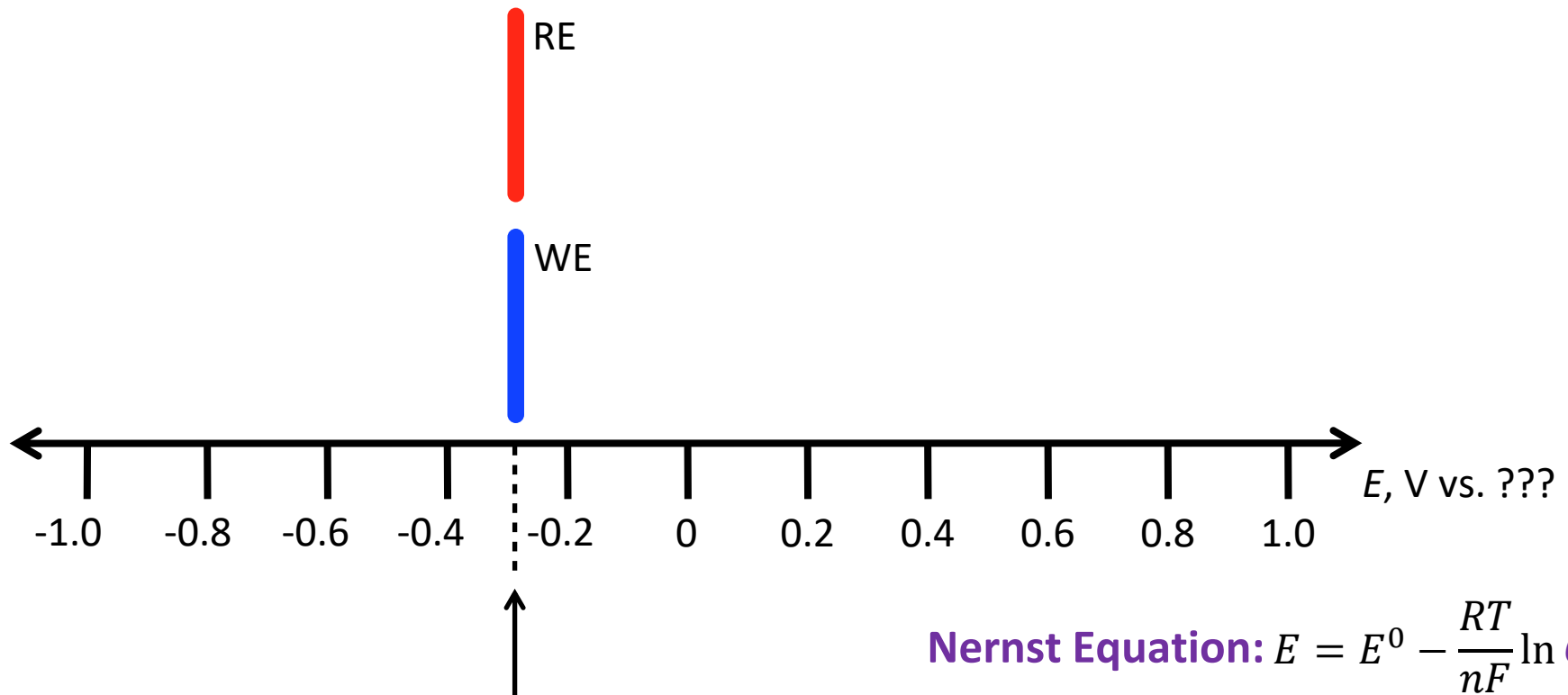


... and at “open circuit,” no potential bias is applied between them...

(disconnect the wire!)

**RECALL:**

$$E_{\text{oc}} = 0.0 \text{ V} = E_{\text{WE}} - E_{\text{RE}}$$



**Nernst Equation:**  $E = E^0 - \frac{RT}{nF} \ln Q$

... and by the way, *we don't know this potential...*

... and it is not well-defined because we cannot answer the question:

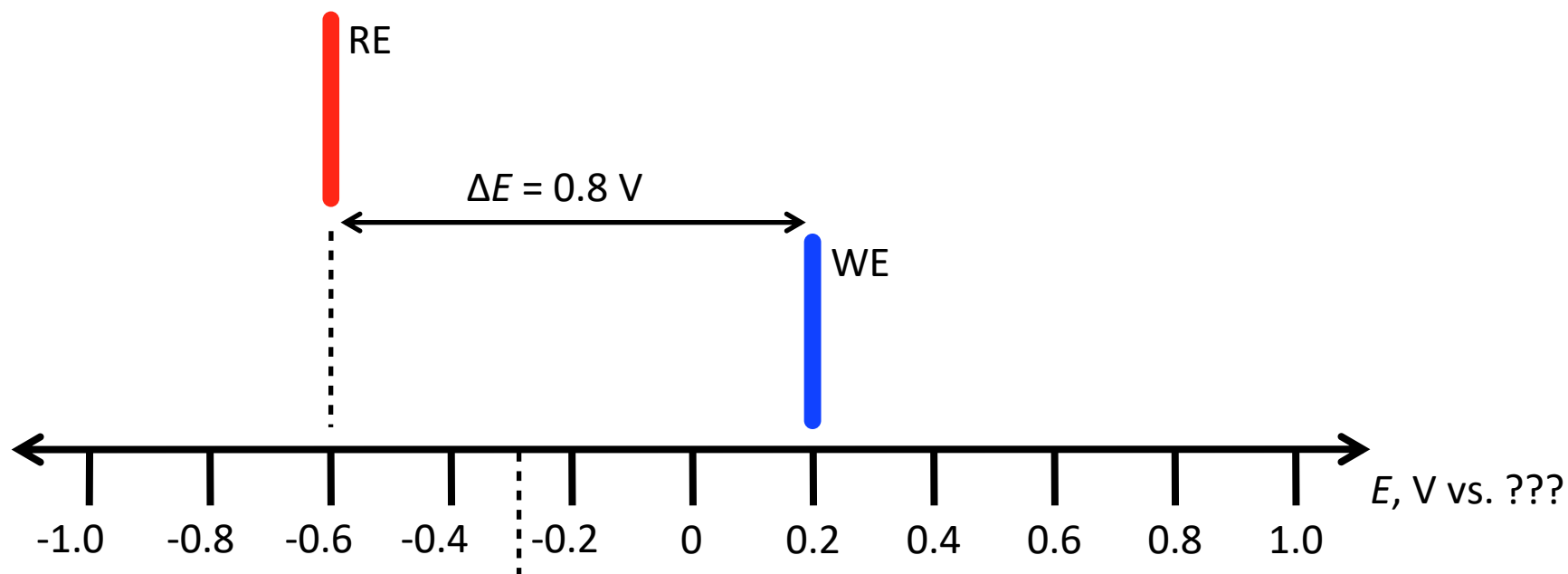
**What is the half-reaction that defines it?**

... now, if we apply +0.8 V to the WE (reconnect the wire)...

the potential of *both* electrodes likely changes, and *not likely symmetrically*...

$$E_{\text{app}} = +0.8 \text{ V}$$

**RECALL:**

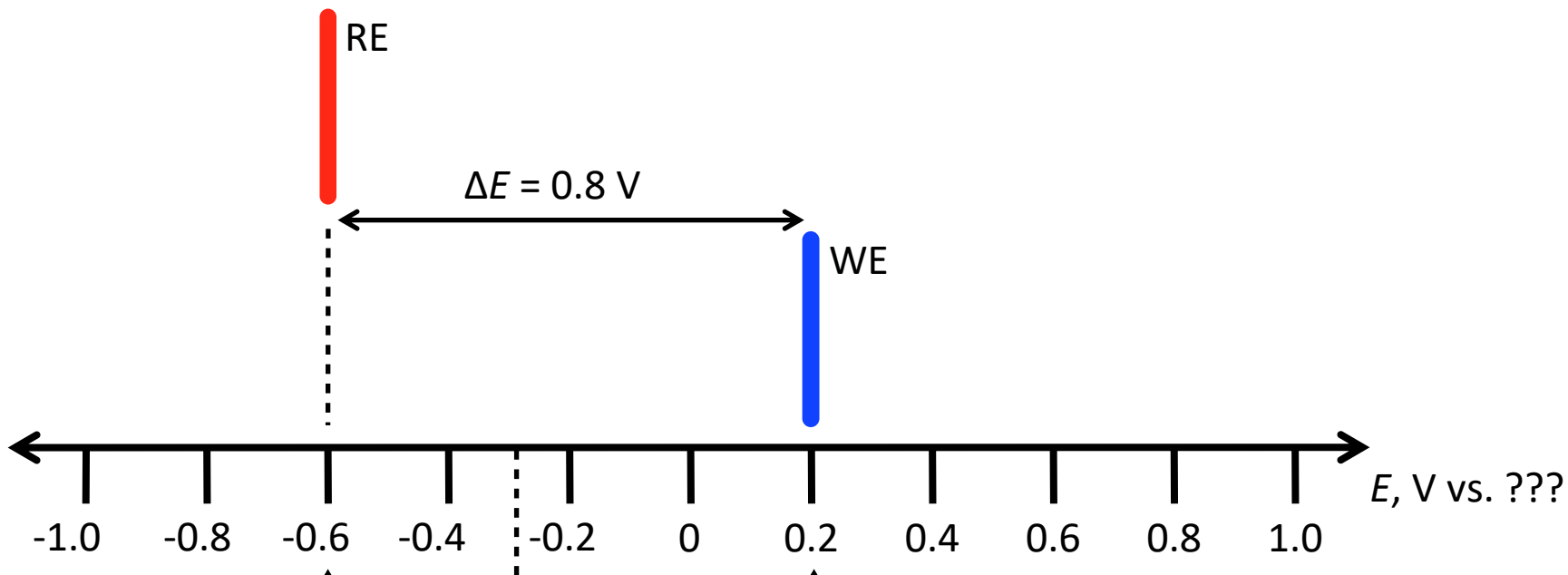




... even worse, we don't know the potential of either electrode...

RECALL:

$$E_{\text{app}} = +0.8 \text{ V}$$

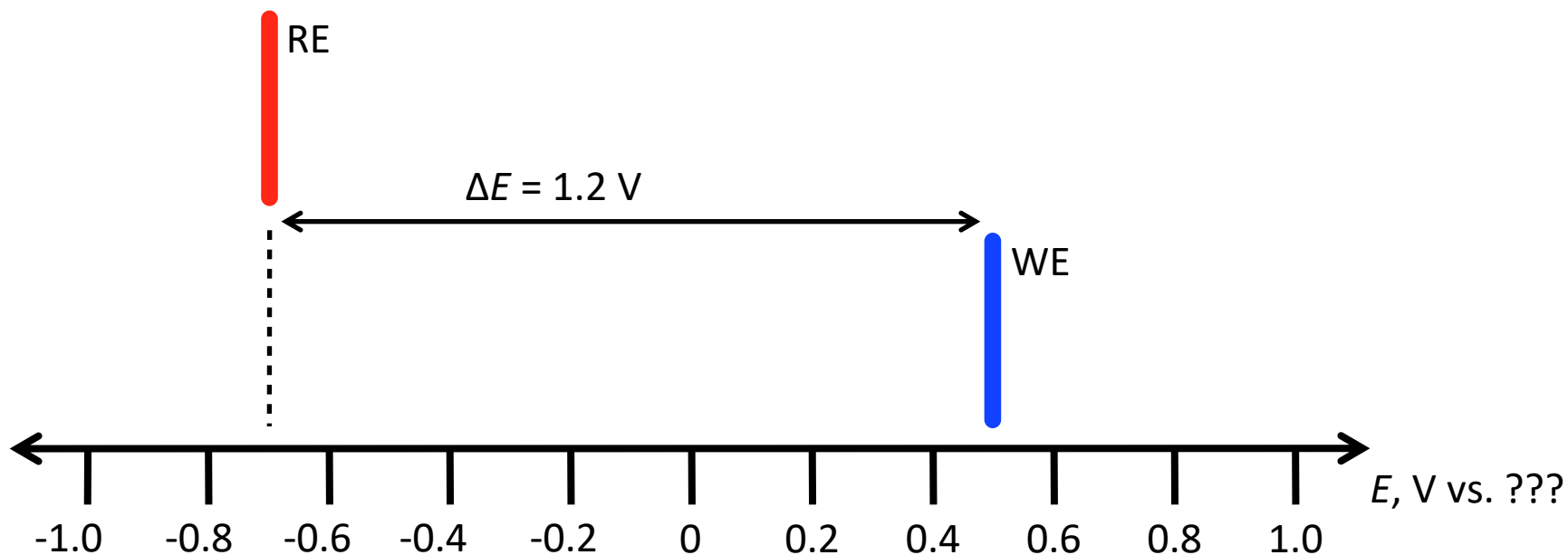


... we don't know *this* potential...

... and we don't know *this* potential!

RECALL:

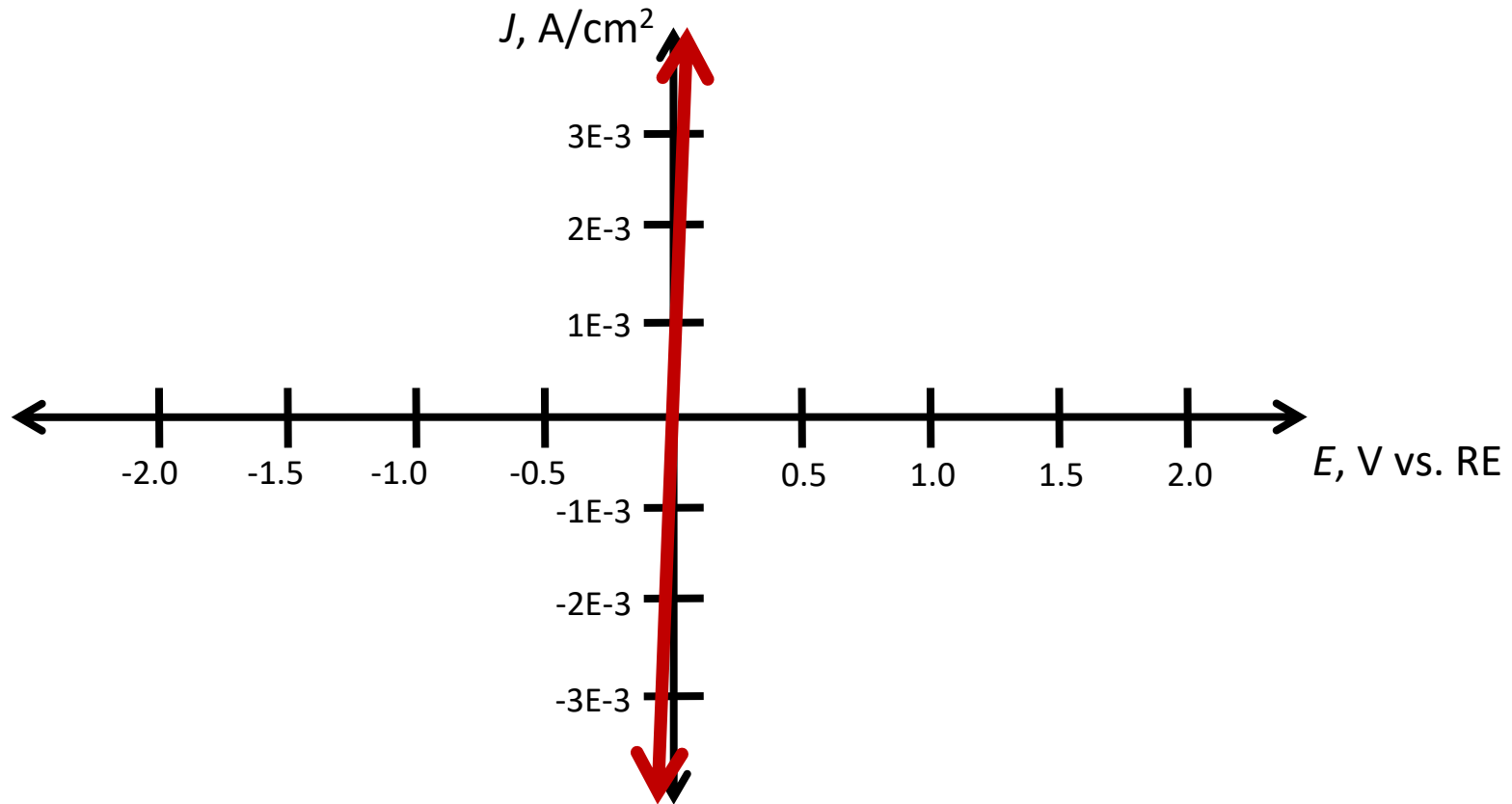
$$E_{\text{app}} = +1.2 \text{ V}$$



... you get the picture!

In principle, this problem can be solved by using a second electrode that is an (ideal) *reference electrode*... (ideally) non-polarizable:

**RECALL:**



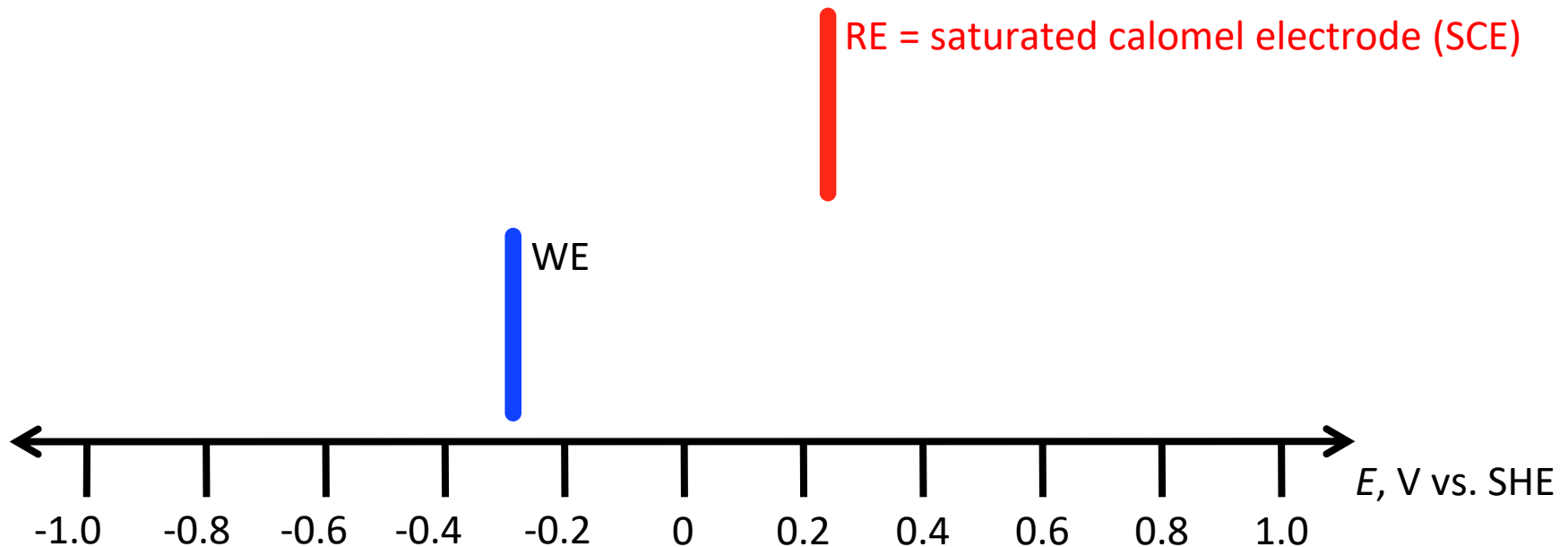
... so get rid of the Pt reference electrode, and substitute in an SCE...

173

... which has a Pt wire in it...

$$\Delta E \neq 0.0 \text{ V (likely)}$$

**RECALL:**

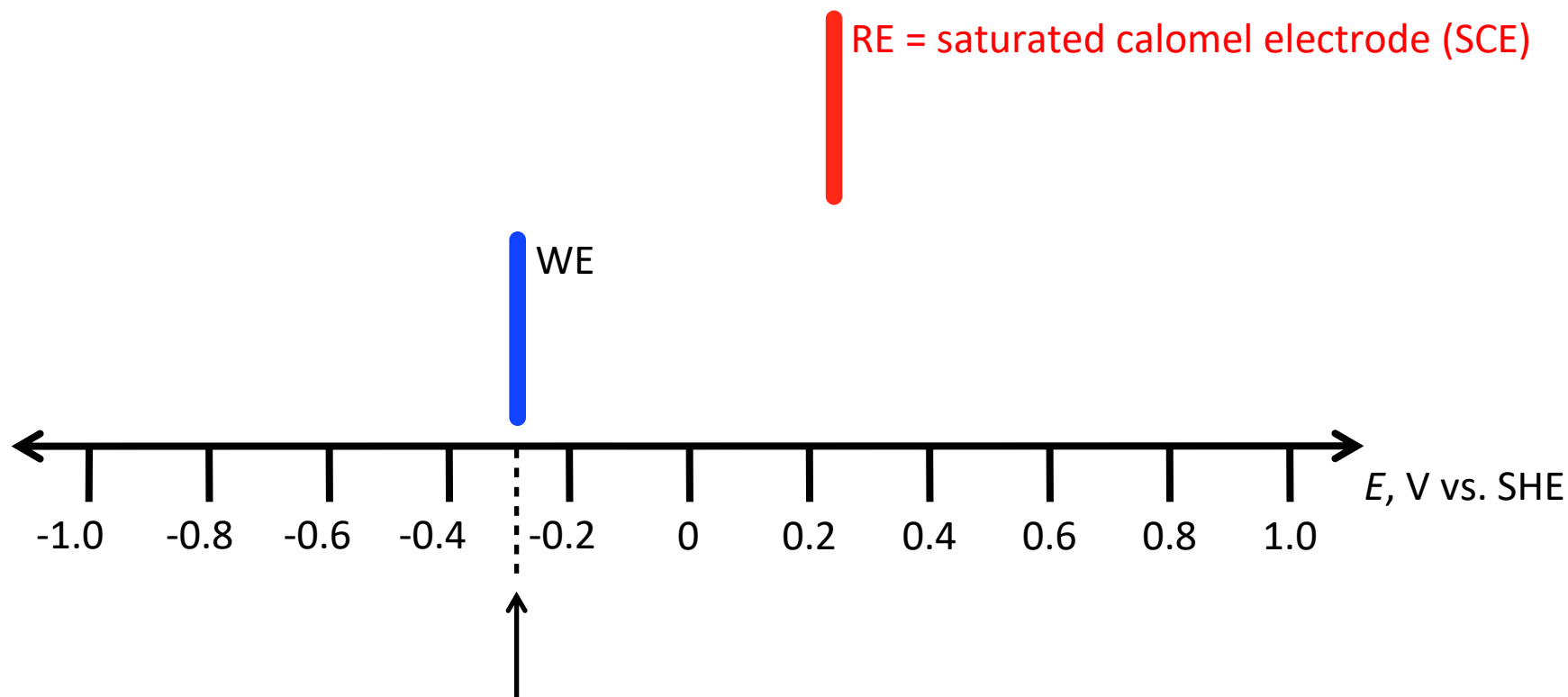


... so get rid of the Pt reference electrode, and substitute in an SCE...

... which has a Pt wire in it...

$$E_{oc} \neq 0.0 \text{ V (likely)}$$

**RECALL:**



... where we still don't know this potential because we cannot answer:

What is the half-reaction that defines it?

... so get rid of the Pt reference electrode, and substitute in an SCE...

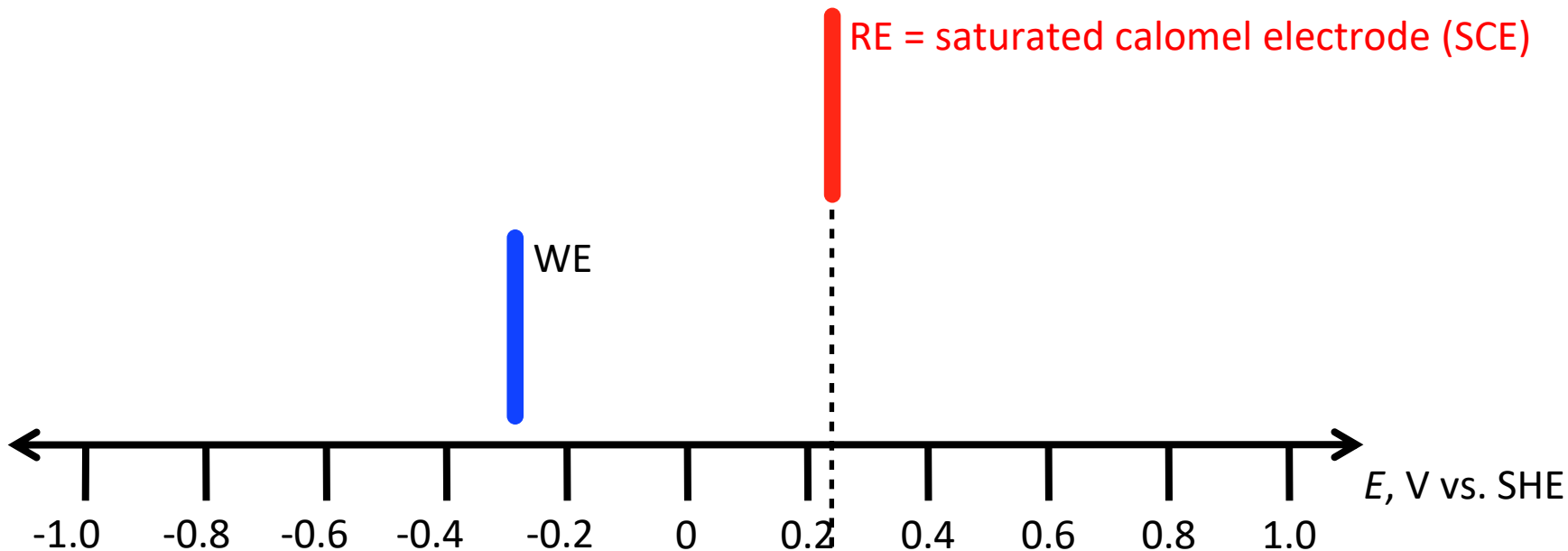
... which has a Pt wire in it...

$$E_{oc} \neq 0.0 \text{ V (likely)}$$

**RECALL:**



RE = saturated calomel electrode (SCE)



Nernst Equation:  $E = E^0 - \frac{RT}{nF} \ln Q$

... but, where we know this potential because we can answer:

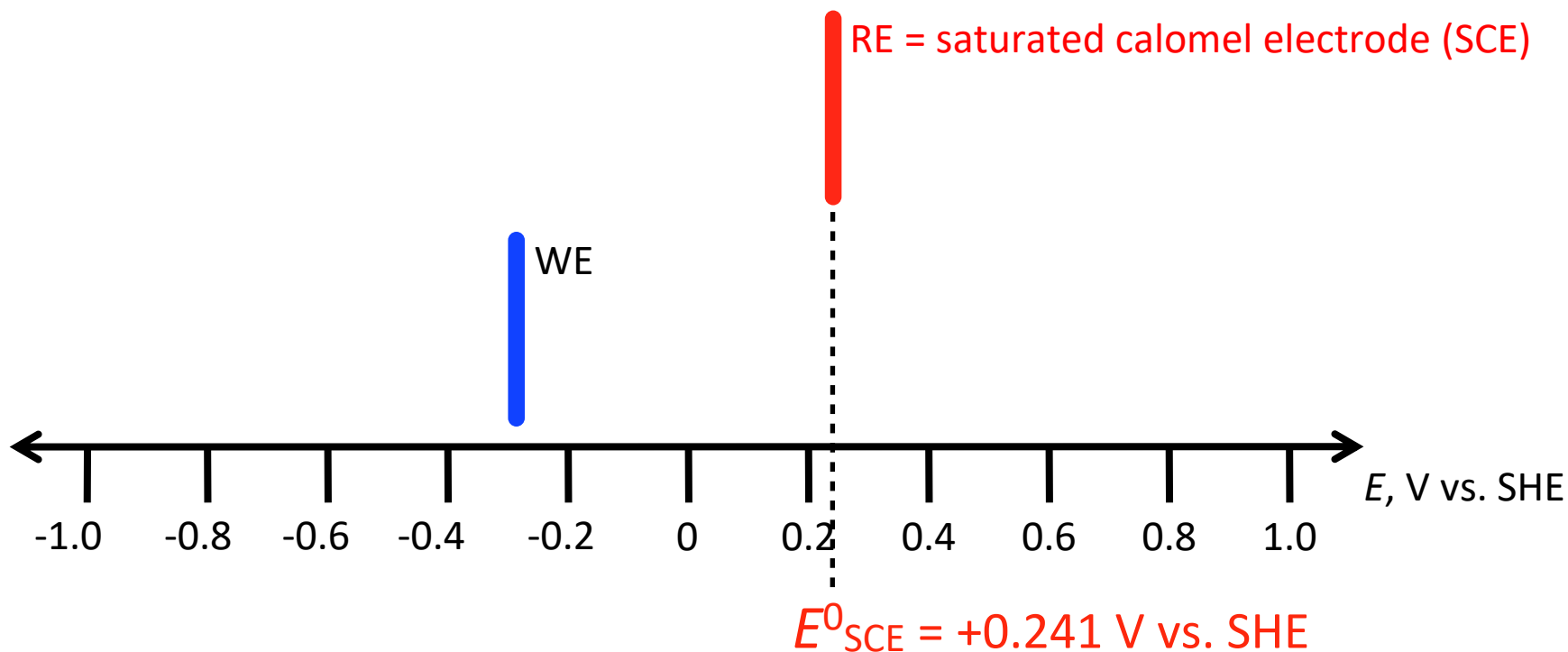
What is the half-reaction that defines it?

... so get rid of the Pt reference electrode, and substitute in an SCE...

... which has a Pt wire in it...

$$E_{oc} \neq 0.0 \text{ V (likely)}$$

**RECALL:**



... the SCE has a defined potential of +0.241 V vs. SHE...

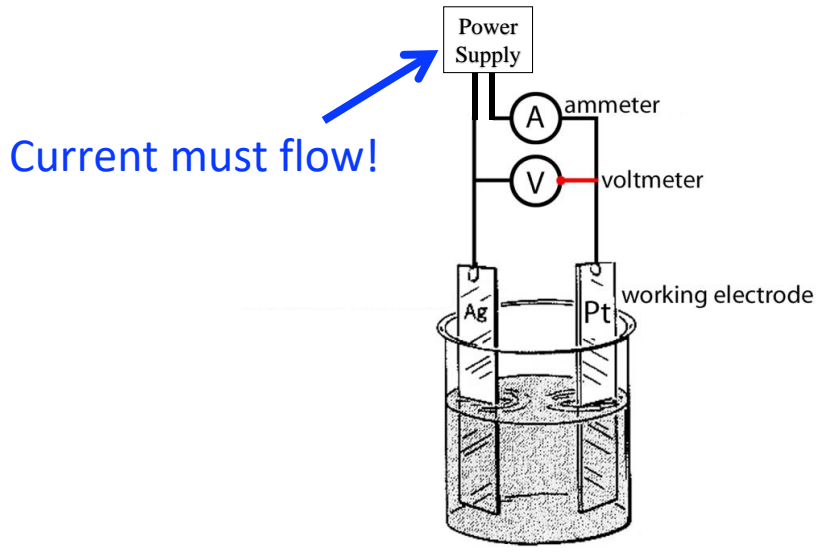
... so get rid of the Pt reference electrode, and substitute in an SCE...

... which has a Pt wire in it...

$$E_{app} = 0.0 \text{ V}$$

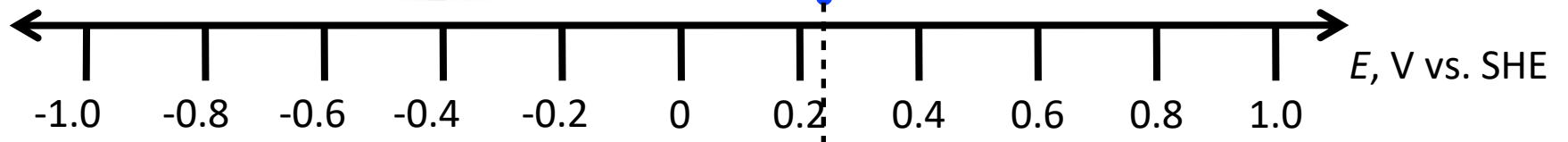
(ammeter  $\neq 0 \text{ A}$ )

**RECALL:**



RE = saturated calomel electrode (SCE)

WE



$$E^0_{SCE} = +0.241 \text{ V vs. SHE}$$

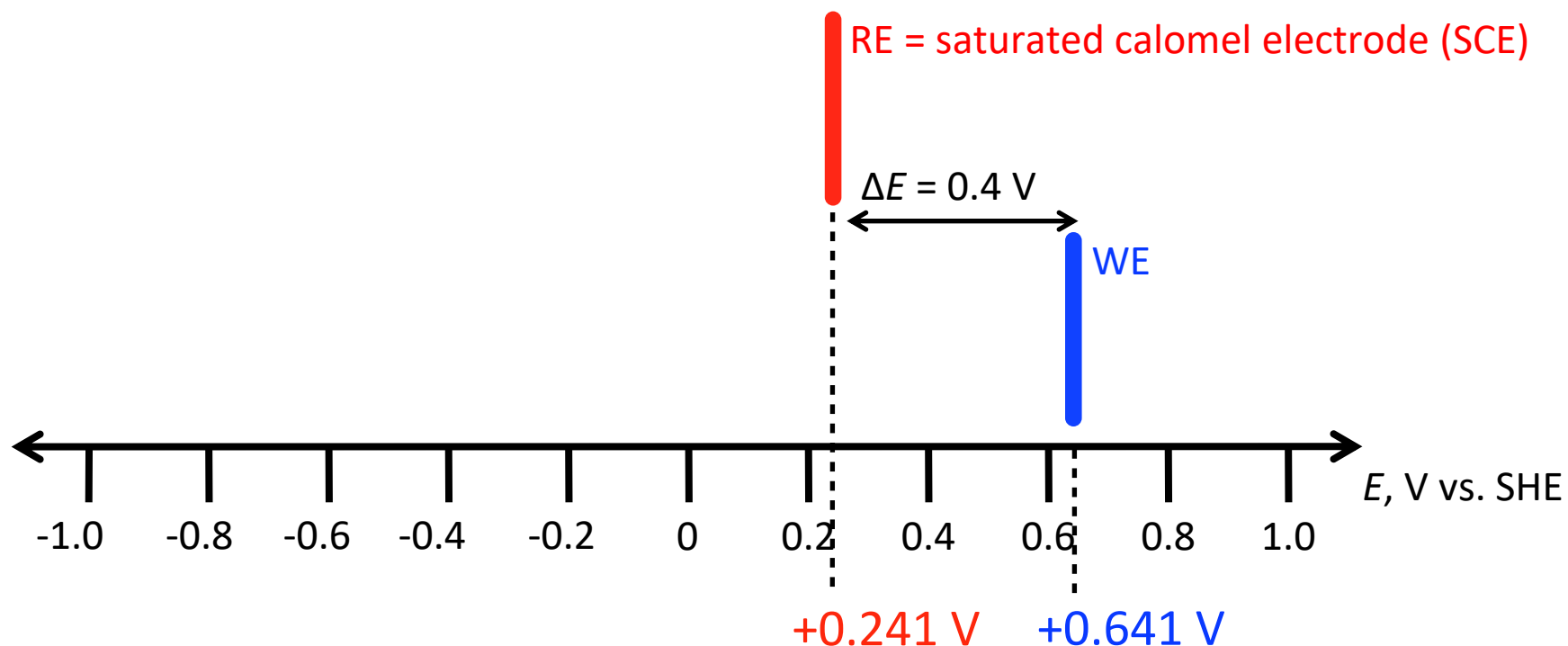
... the SCE has a defined potential of +0.241 V vs. SHE...  
... and its potential "does not" move (much, usually)...



... how did we calculate that (meaning +0.641 V)?

**RECALL:**

$$E_{\text{app}} = +0.4 \text{ V}$$

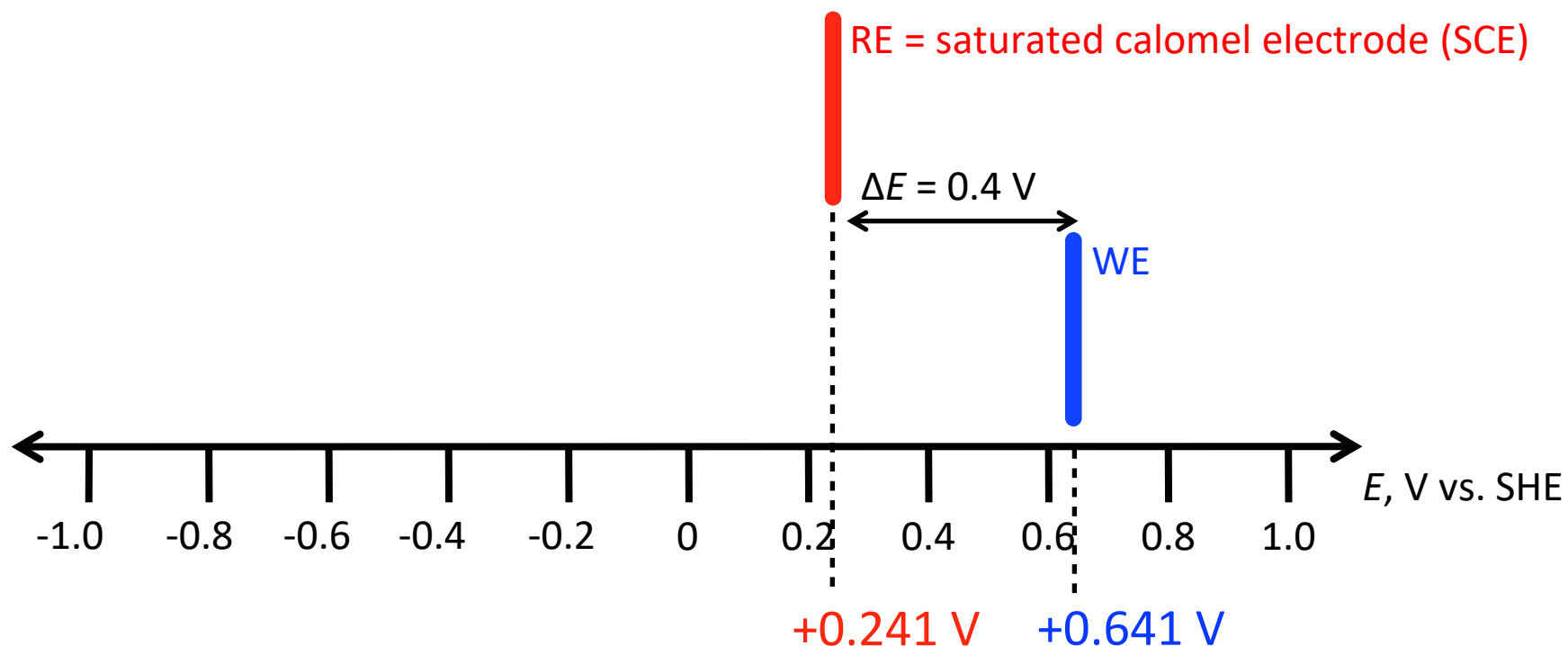


... the SCE has a defined potential of +0.241 V vs. SHE...  
 ... and its potential “does not” move (much, usually)...

... how did we calculate that (meaning +0.641 V)?

**RECALL:**

$$E_{\text{app}} = +0.4 \text{ V}$$



$$\underline{\Delta E} = E_{\text{WE}} - E_{\text{RE}}$$

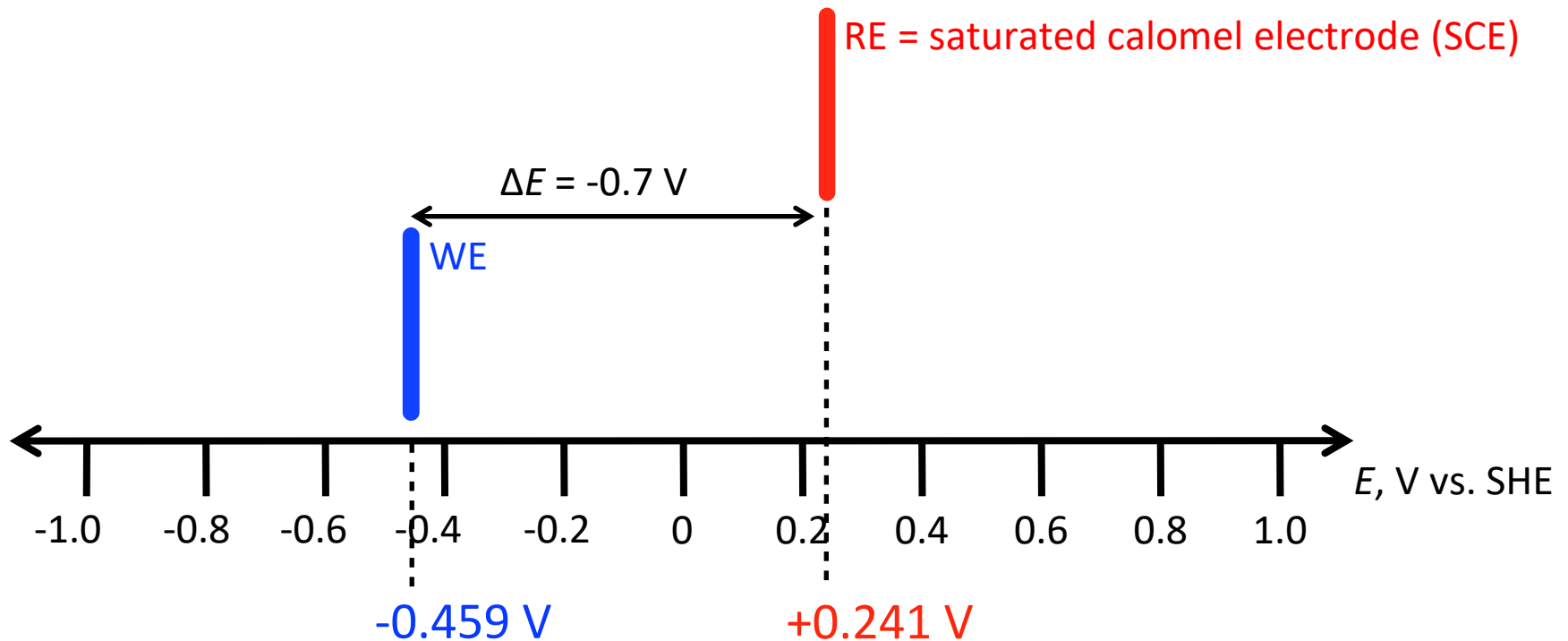
$$E_{\text{WE}} = \underline{+0.4 \text{ V}} + +0.241 \text{ V} = +0.641 \text{ V}$$

... you get the picture!...

... but let's learn some more about reference electrodes...

$$E_{\text{app}} = -0.7 \text{ V}$$

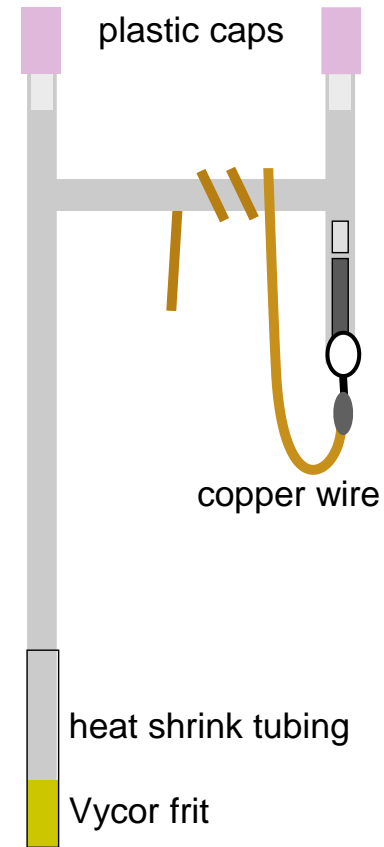
**RECALL:**



$$\underline{\Delta E} = E_{\text{WE}} - E_{\text{RE}}$$

$$E_{\text{WE}} = \underline{-0.7 \text{ V}} + +0.241 \text{ V} = -0.459 \text{ V}$$

... here is what a commercial SCE looks like:



Some major companies that have excellent additional information on their websites:

**AMETEK (PAR, Solartron), BASi, Bio-Logic, CH Instruments, Gamry, Metrohm, Pine**

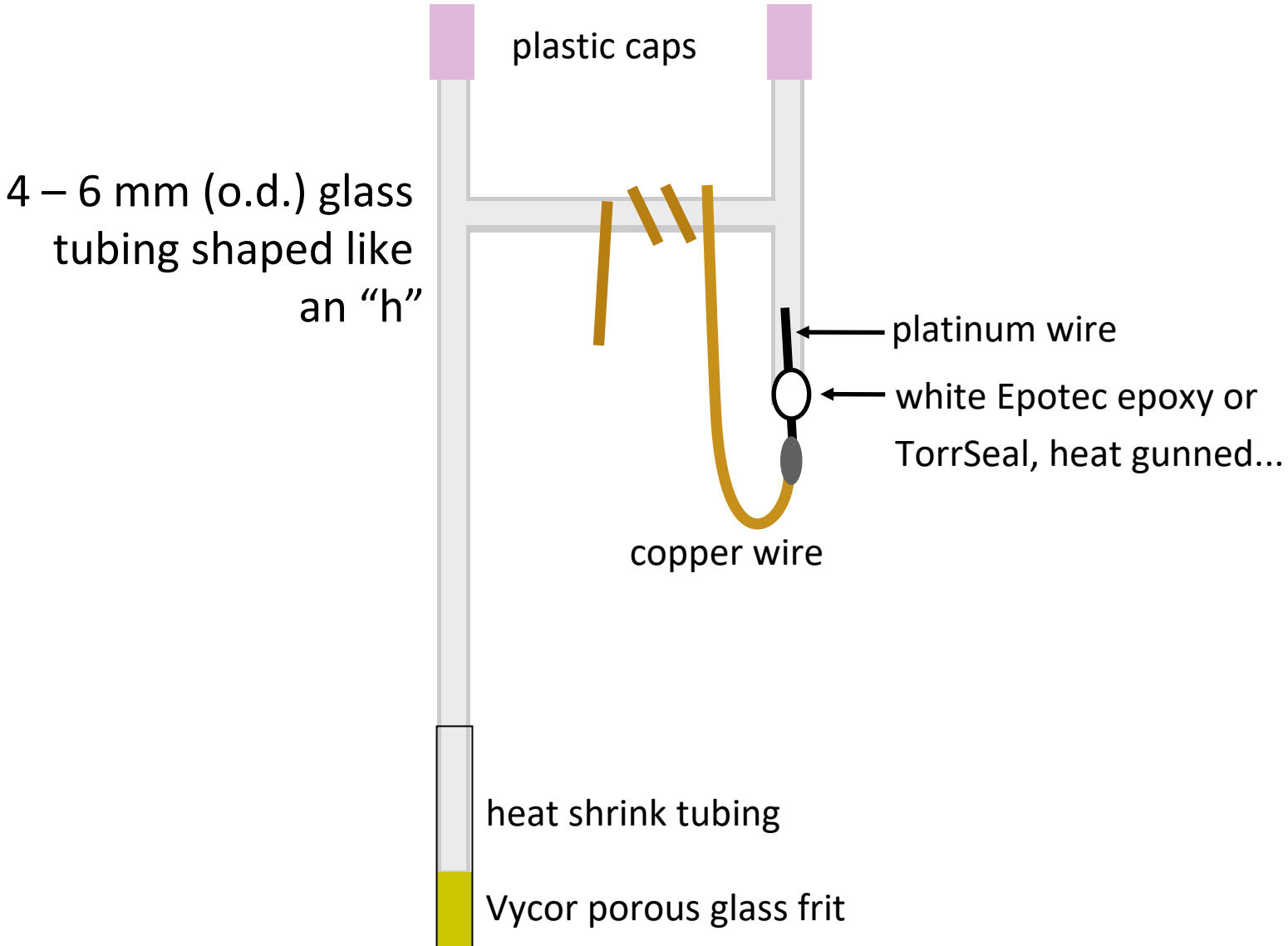
<https://www.gamry.com/cells-and-accessories/electrodes/reference-electrodes/>

Specifically, we would really like to have a reference electrode that has the following attributes.

1. It has a well-defined and invariant potential. That is, no matter how much current we draw from this electrode, its potential must not vary.
2. It has zero impedance. That is, it imposes no resistive load on our cell.
3. It does not “contaminate” our solution. That is, it is not a source of undesired ions in our electrochemical cell.

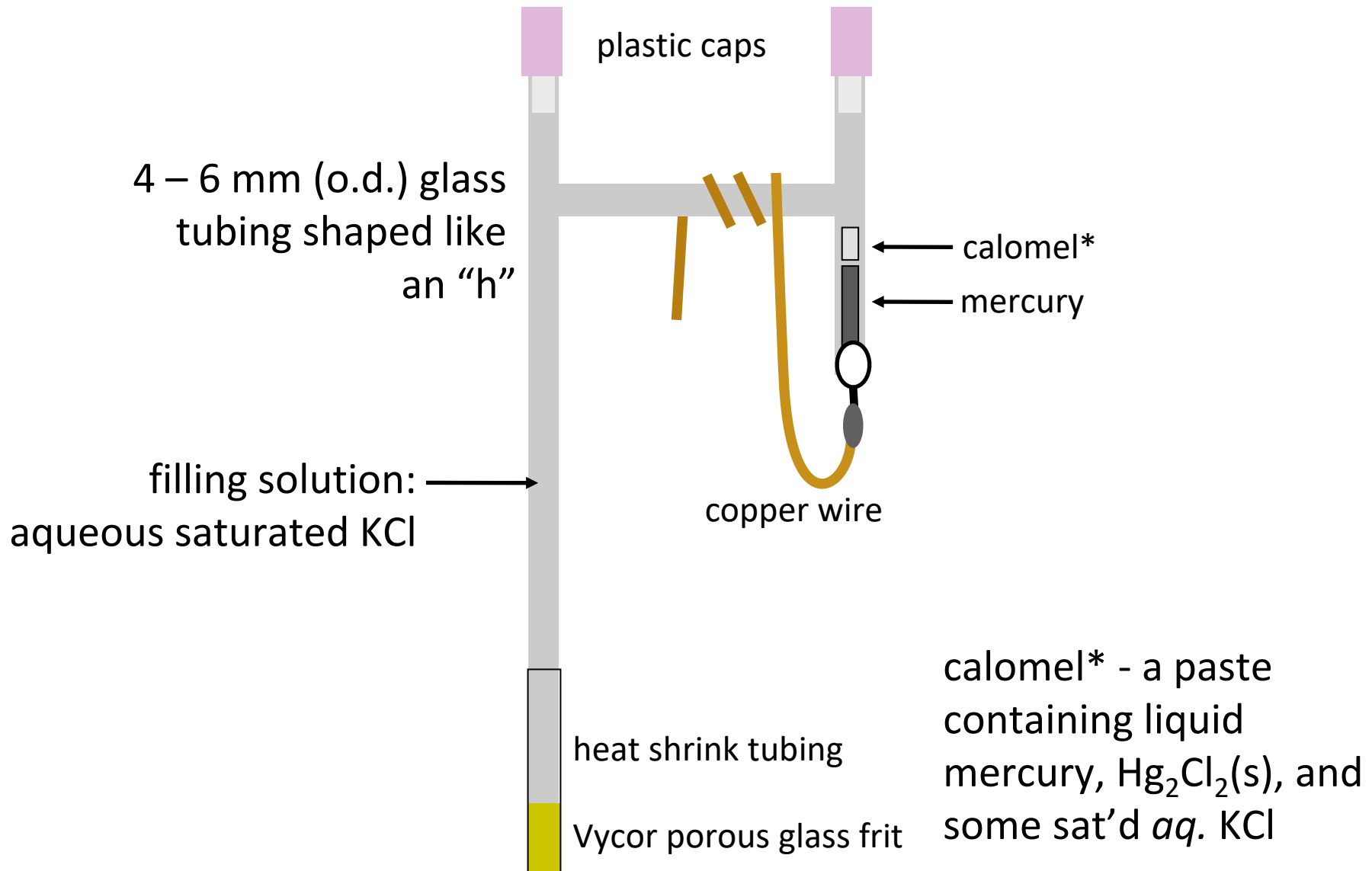
... but no such thing exists.

The closest approximation: the *saturated calomel electrode (SCE)*



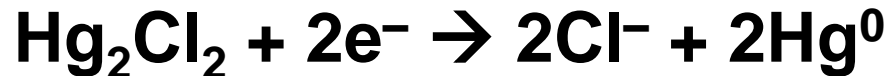
... but no such thing exists.

The closest approximation: the *saturated calomel electrode (SCE)*



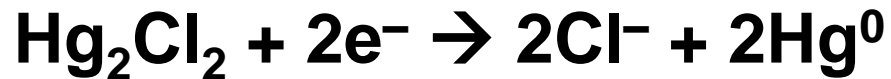
The closest approximation: the *saturated calomel electrode (SCE)*

the *saturated calomel electrode (SCE)*



$$E^0 = +0.241 \text{ V vs. SHE}$$

the *saturated sodium calomel electrode (SSCE)*

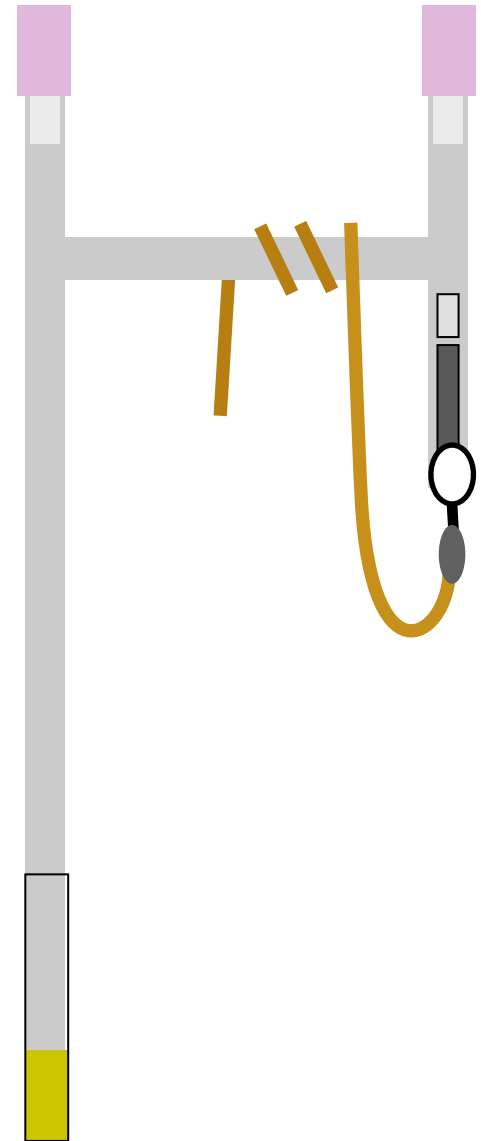


$$E^0 = +0.236 \text{ V vs. SHE}$$

the *saturated mercurous sulfate electrode (MSE)*



$$E^0 = +0.64 \text{ V vs. SHE}$$





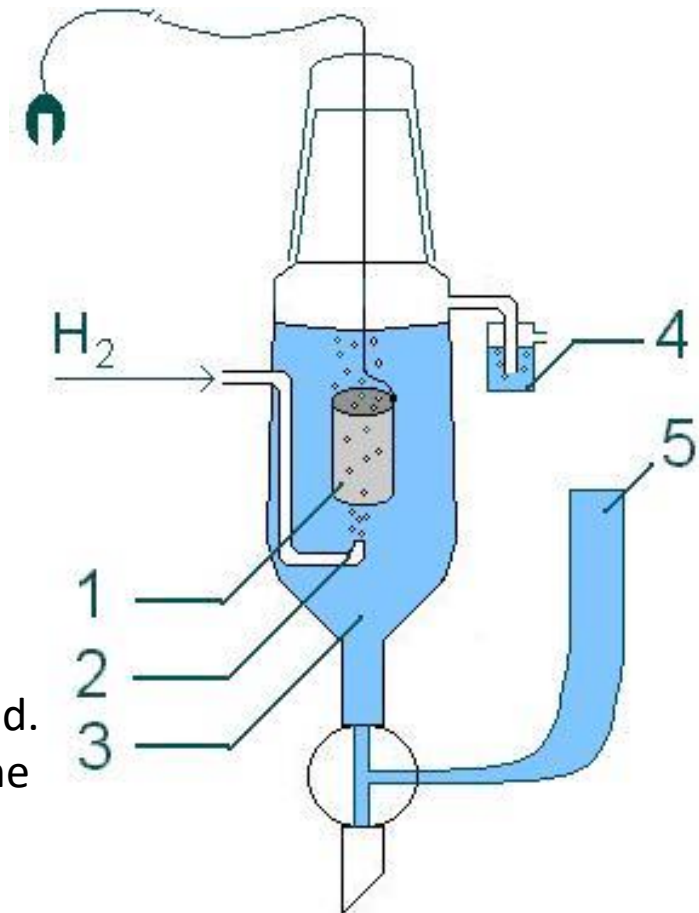
... great. But what is an SHE (standard hydrogen electrode)?



$$E^0_{\text{SHE}} = 0.0000 \text{ V vs. SHE}$$

The scheme of the standard (or normal) hydrogen electrode:

- 1) platinized platinum electrode (large area)
- 2) hydrogen blow (bubbling)
- 3) solution of aqueous acid with proton activity equal to one (dimensionless)
- 4) means to prevent  $\text{O}_2$  interference (sealant)
- 5) reservoir through which the second half-element of the electrochemical cell is attached. This creates an ionically conductive path to the working electrode of interest (salt bridge).



\* one rendition of an SHE

... another common RE is the aq. Ag/AgCl electrode (KCl sat'd)!



$$E^0 = +0.197 \text{ V vs. SHE}$$

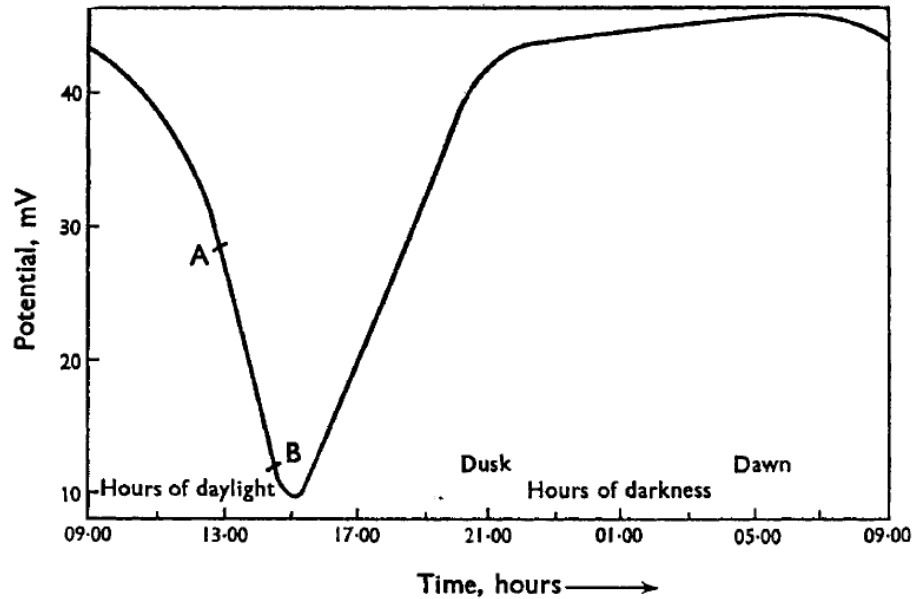


AgCl (white)

Ag (gray), from photodecomposition of AgCl

But for those of you doing **photoelectrochemistry**, beware!

<https://www.youtube.com/watch?v=8e0-AbwBDYM>



... and three final “specialty” reference electrodes include...

For aqueous **alkaline** electrolyte conditions

Mercury/Mercury Oxide (Hg/HgO, 20 wt% KOH)

$$E^0 = +0.098 \text{ V vs. SHE}$$

For **non-aqueous** (CH<sub>3</sub>CN) electrolyte solutions

Ag/AgNO<sub>3</sub> (0.01 M) in CH<sub>3</sub>CN

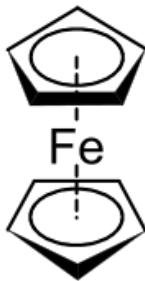
$$E^0 = +0.3 \text{ V vs. SCE (aq), which is} \\ \text{effectively } +0.54 \text{ V vs. SHE}$$

### B&F 2.1.7

When a reference electrode cannot be used or is not wanted

“**Quasi-reference**” electrode as a Pt wire and any redox couple

- \* Used when you already have a cell with two halves of a redox couple that will not change during your experiment and thus you know the half-reaction that defines your RE
- \* Calibrate with Fc (ferrocene) \_\_\_\_\_



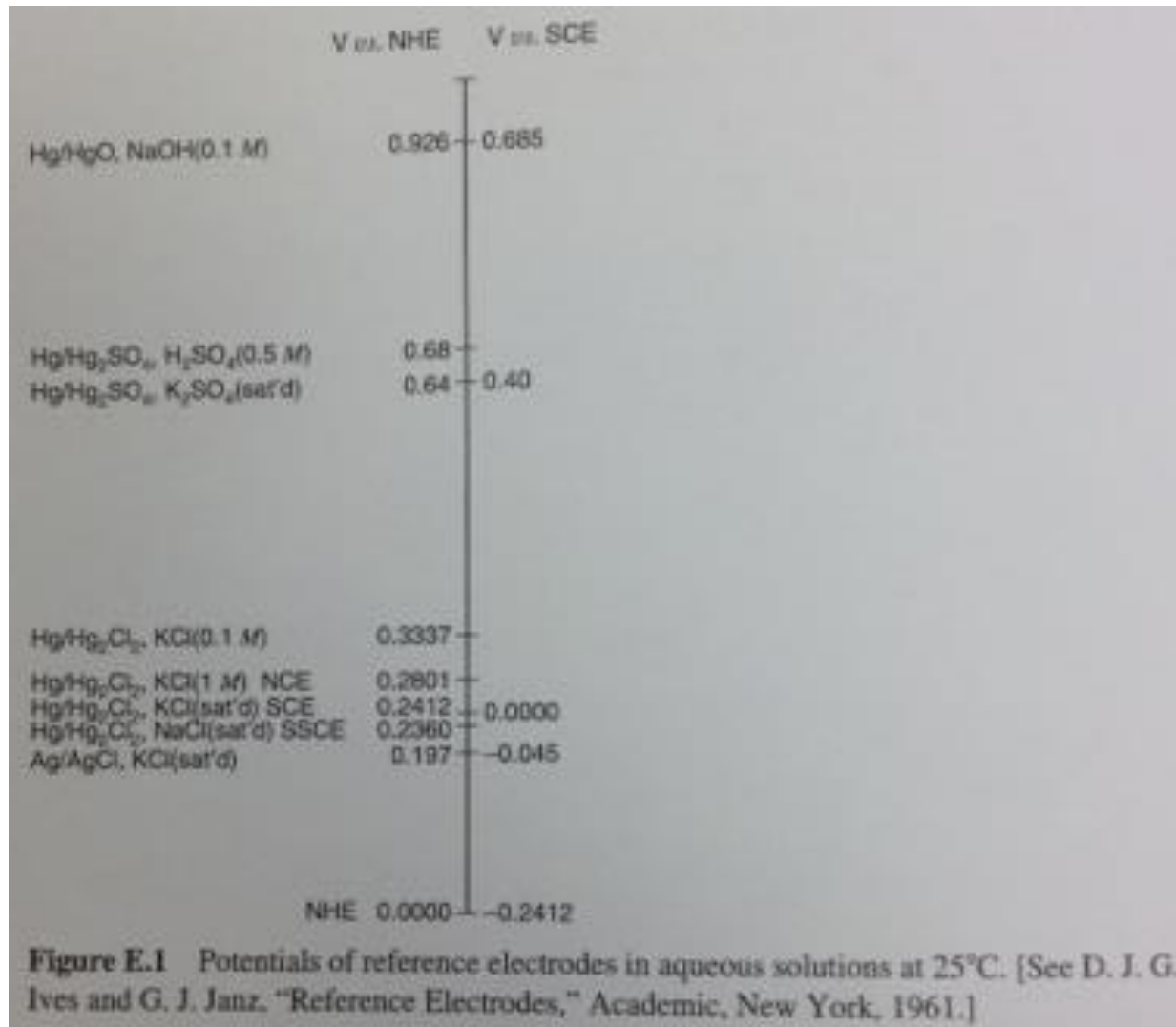
- Measure the potential of an internal standard versus this reference electrode  
(e.g. ferrocene in non-aqueous electrolyte)
- Measure the potential of this reference electrode versus several other reference electrodes with a voltmeter  
(e.g.  $\text{Ag (s)} \mid \text{AgCl (s)} \mid \text{Cl}^- (\text{sat'd}) \mid \text{AgCl (s)} \mid \text{Ag (s)}$ )

What if no matter what you do, the potential is unstable or the equipment overloads (i.e. gives you an error; often a **red light** turns on)?

- Throw the electrode away? **NO WAY!**
- Fix it!
- Check for (insulating) bubbles... change the frit... remake the redox couple... something else?

**... check out tidbits on troubleshooting EChem systems (B&F 15.9)**

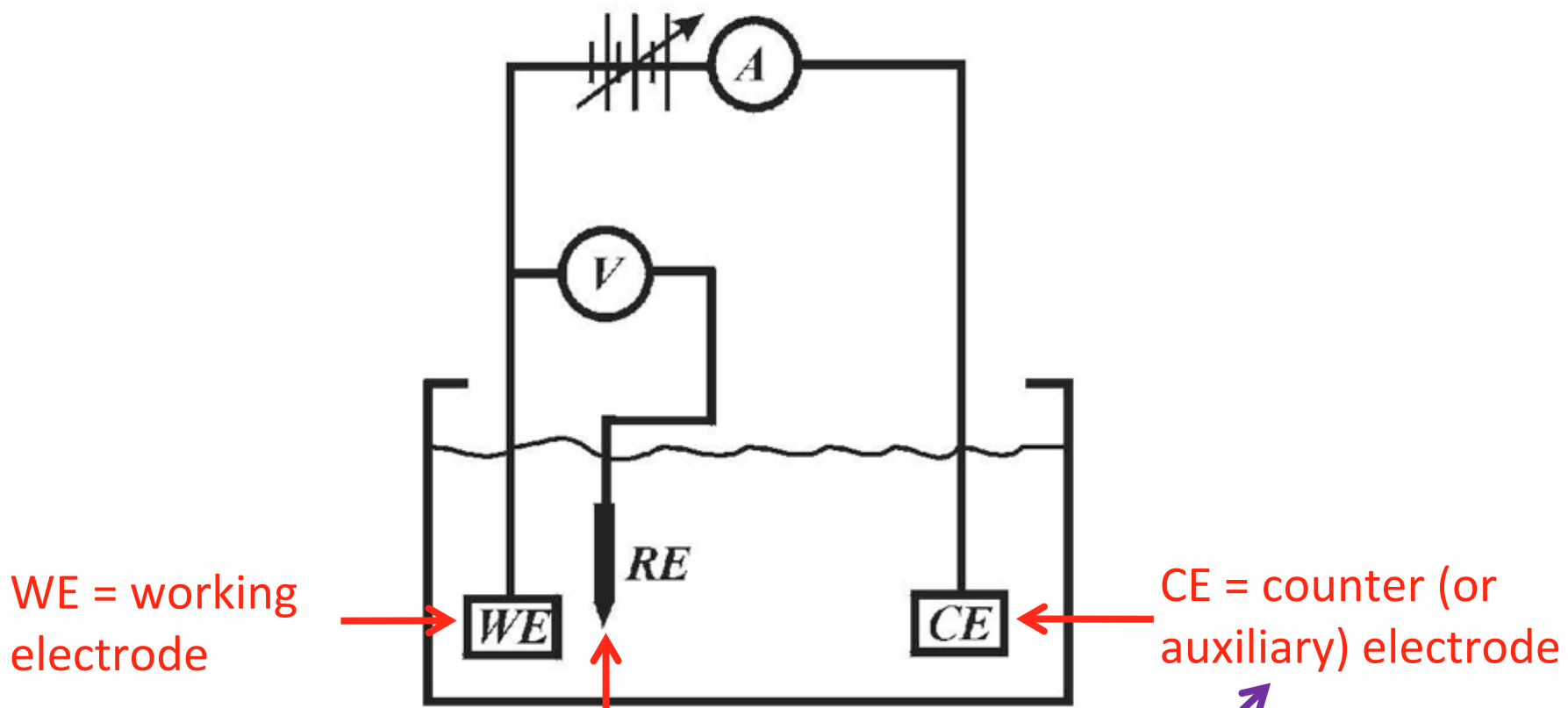
An example of two RE scales at once is helpful...



... now, as mentioned earlier, unfortunately, real reference electrodes can do *none* of these things perfectly...

Specifically, we would really like to have a reference electrode that has the following attributes:

1. It has a well-defined and invariant potential. That is, no matter how much current we draw from this electrode, its potential must not vary.
2. It has zero impedance. That is, it imposes no resistive load on our cell.
3. It does not “contaminate” our solution. That is, it is not a source of undesired ions in our electrochemical cell.



WE = working electrode

RE = reference electrode

CE = counter (or auxiliary) electrode

“Out of sight, out of mind” is a telling proverb/idiom!

<http://www.porous-35.com/electrochemistry-semiconductors-10.html>

## Looking forward... Section 1.1 (and some of Chapter 15)

- Reference electrodes
- 2-electrode versus 3-electrode measurements
- **Potentiostats**
- **Compliance voltage/current**
- *J–E and I–E curves*
- *Kinetic overpotential*
- *Electrochemical window*
- *Faradaic reactions*



**STUDIES IN ELECTRODE POLARISATION.  
PART IV.—THE AUTOMATIC CONTROL OF THE  
POTENTIAL OF A WORKING ELECTRODE.**

BY A. HICKLING.

*Received 16th September, 1941.*

Although the electrode potential is considered to be the dominating factor governing many electrolytic processes, it is one of the variables least amenable to direct experimental control. In general it can only be indirectly changed or maintained during electrolysis by alteration of such factors as current density, temperature, electrode material and electrolyte composition. A device whereby the potential of a working electrode can be fixed at any desired arbitrary value would seem, therefore, to have many valuable applications in the exploration of electrolytic processes, and the present paper describes an electrical circuit by means of which this aim can be achieved.

... Would a person drive a car without knowing how an ICE works?... Okay, bad example...

this is a vacuum tube! →

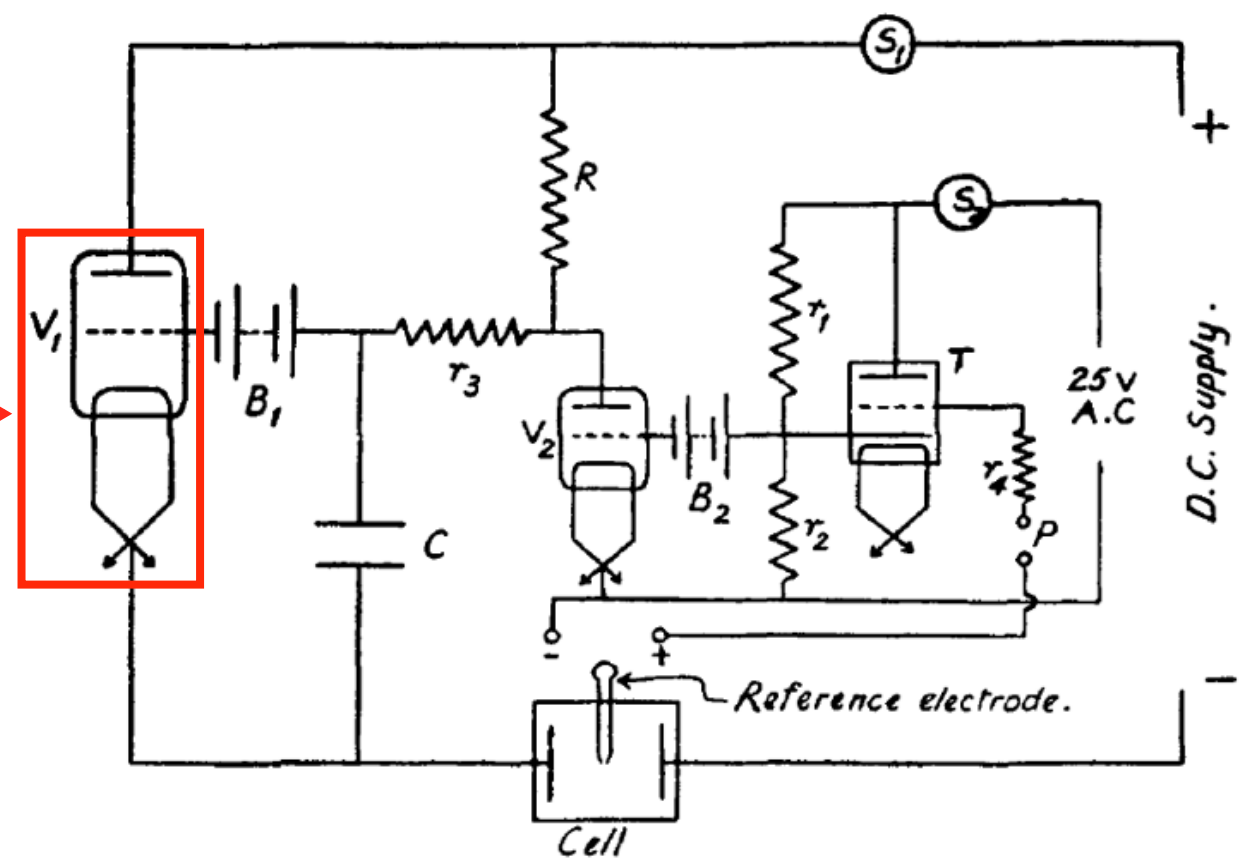


FIG. 1.—Potentiostat Circuit.

... invented in 1937 by Hickling...

in fact, it's *this* vacuum tube!

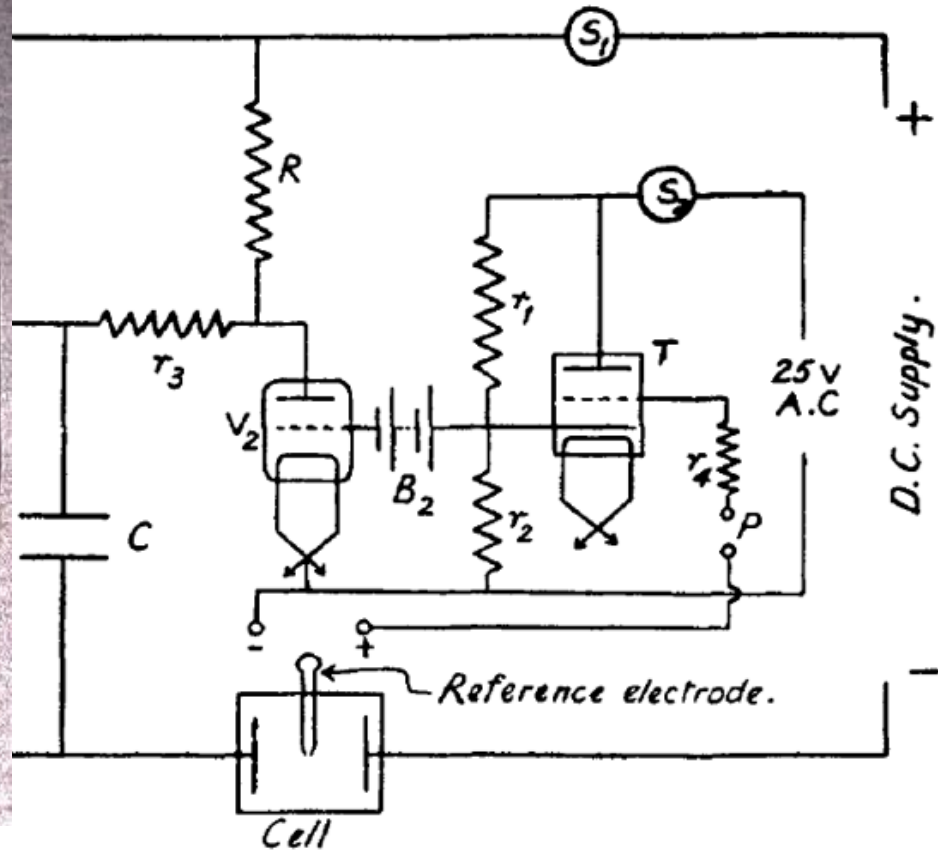


FIG. 1.—Potentiostat Circuit.

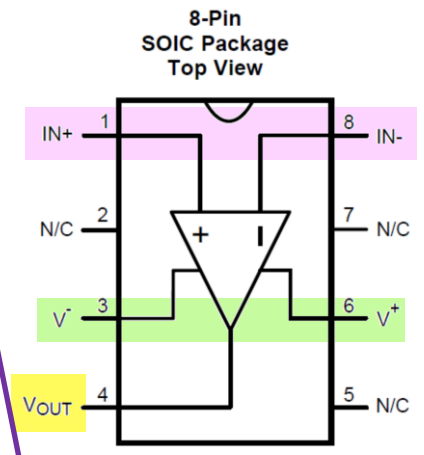
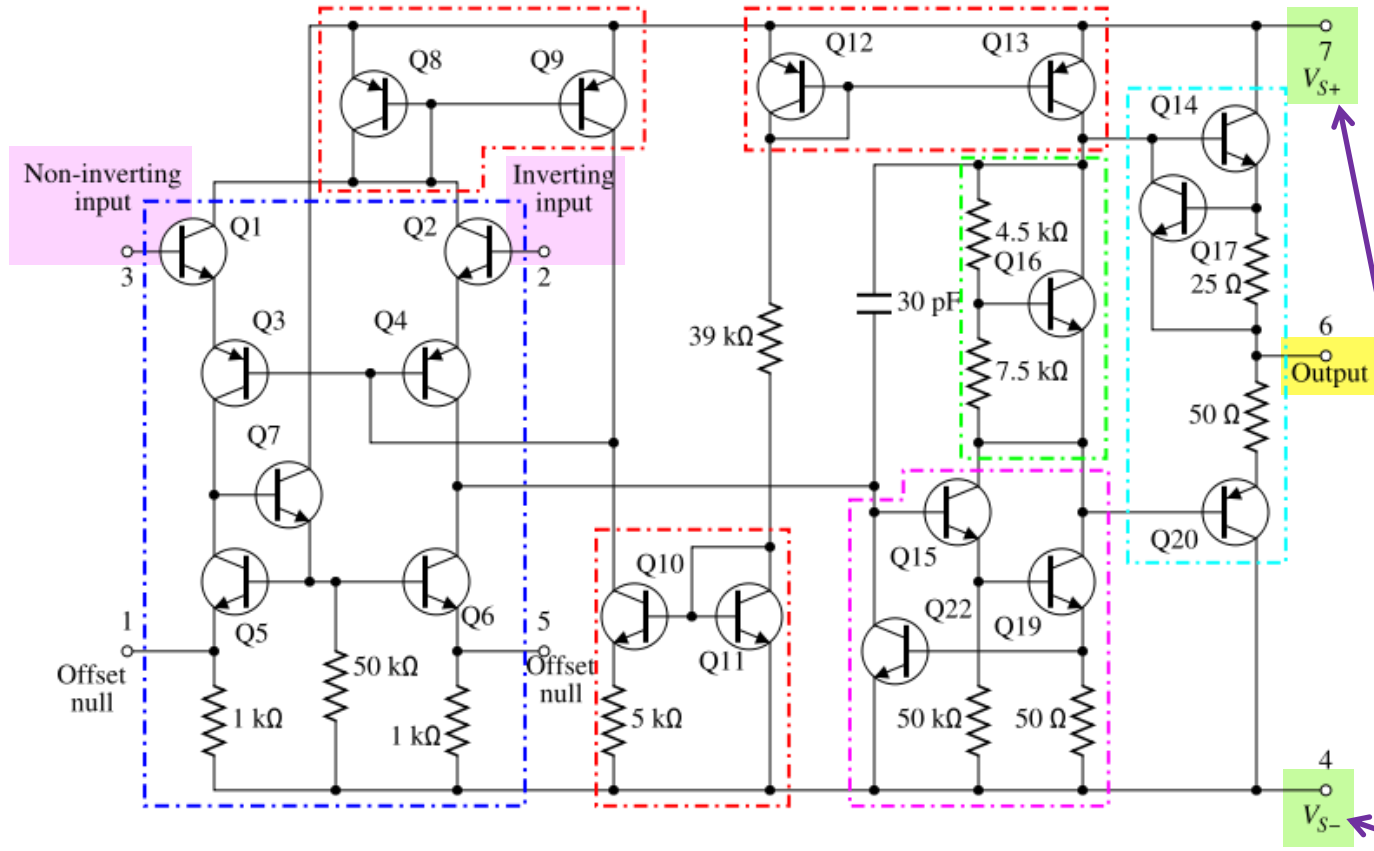
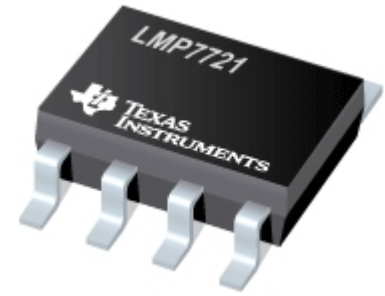
<https://www.tubeworld.com/european.htm>

... this is how (many famous electrochemists) do this today...

... meaning with somewhat "old" instruments like described in B&F

an op-amp

20 transistors, 11 resistors, and 1 capacitor; Wow!



fixed values (vs. ground)

[http://en.wikipedia.org/wiki/Operational\\_amplifier](http://en.wikipedia.org/wiki/Operational_amplifier)  
<https://www.ti.com/product/LMP7721#tech-docs>

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an op-amp

## Op-amp Golden Rules

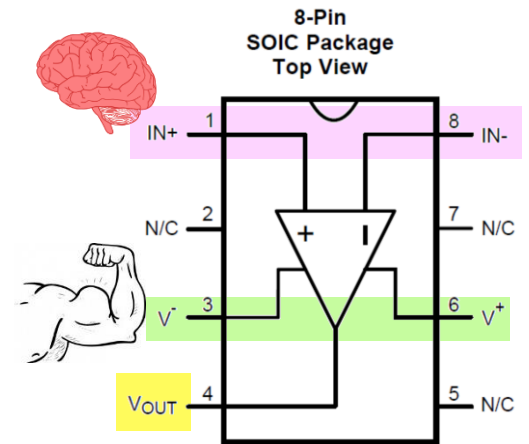
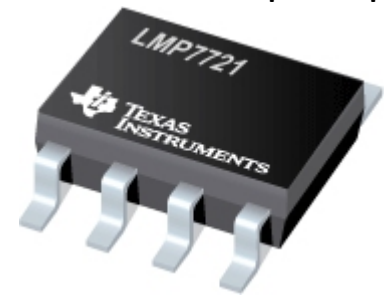
Ideal rules that are close to correct in practice.

For an op-amp with feedback (which we have),

(1) The Voltage Rule: The output ( $V_{OUT}$ ) attempts to do whatever is necessary to make the potential difference between the inputs ( $IN+$  and  $IN-$ ) zero (because  $V^-$  and  $V^+$  are fixed).

(2) The Current Rule: The inputs to  $IN+$  and  $IN-$  draw no *net* current. Thus, by Ohm’s law, the impedance is essentially infinite! ...

... How does the output then pass current?



<http://www.clipartfree.net/small/1174-brain-in-profile-clipart.html>

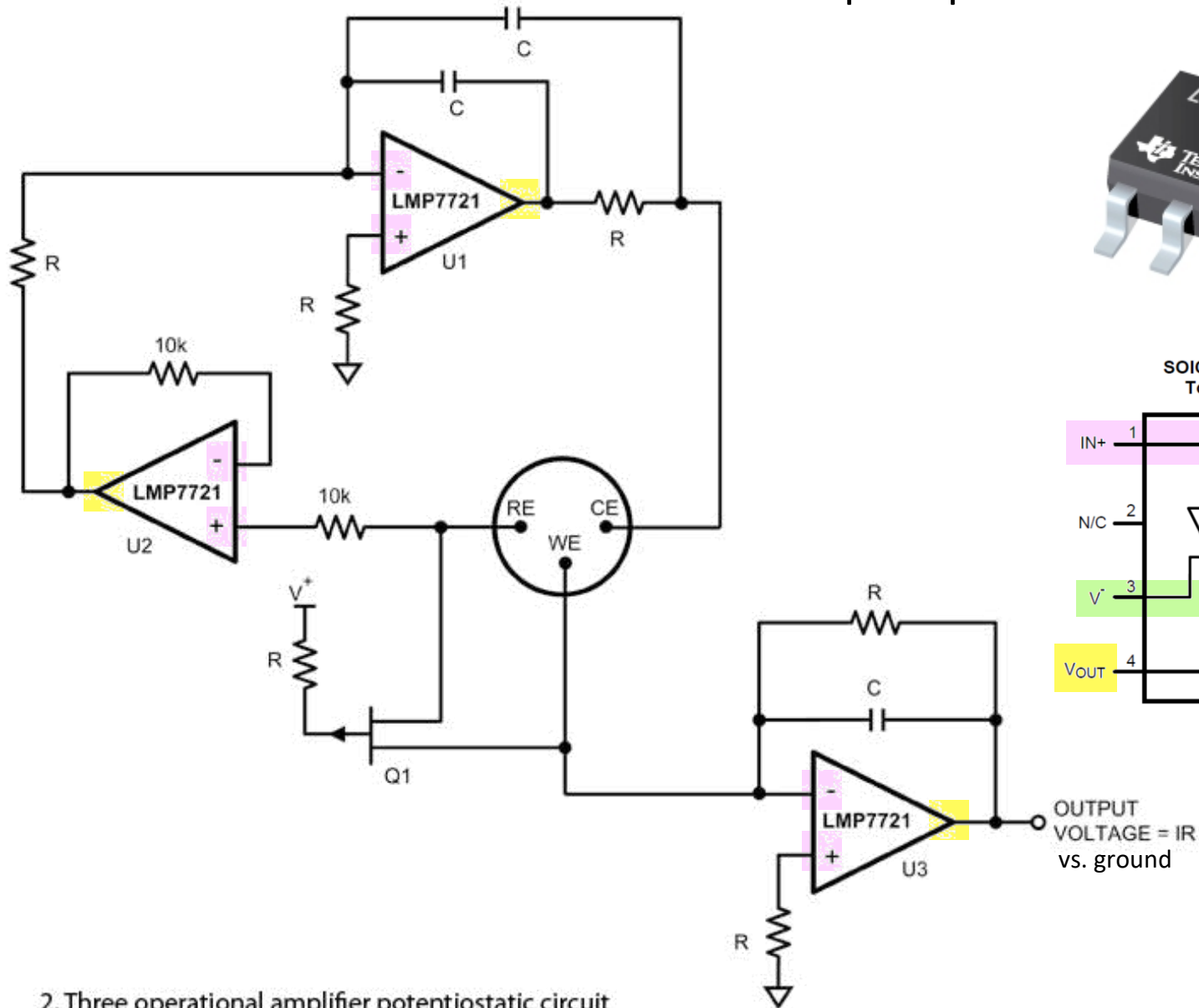
<http://shujaabbas.hubpages.com/hub/Cartoon-Boxing-Champion>

Horowitz and Hill, The Art of Electronics, Cambridge University Press, 1980

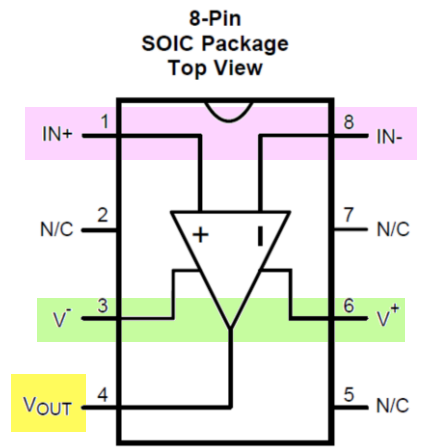
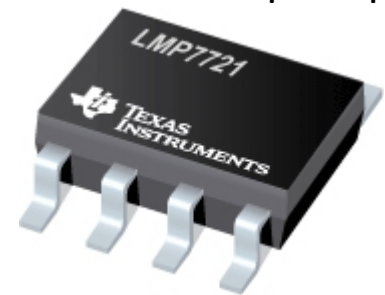
<http://hyperphysics.phy-astr.gsu.edu/hbase/electronic/opamp.html#c2>

... this is how (many famous electrochemists) do this today...

... three op-amps!



an op-amp

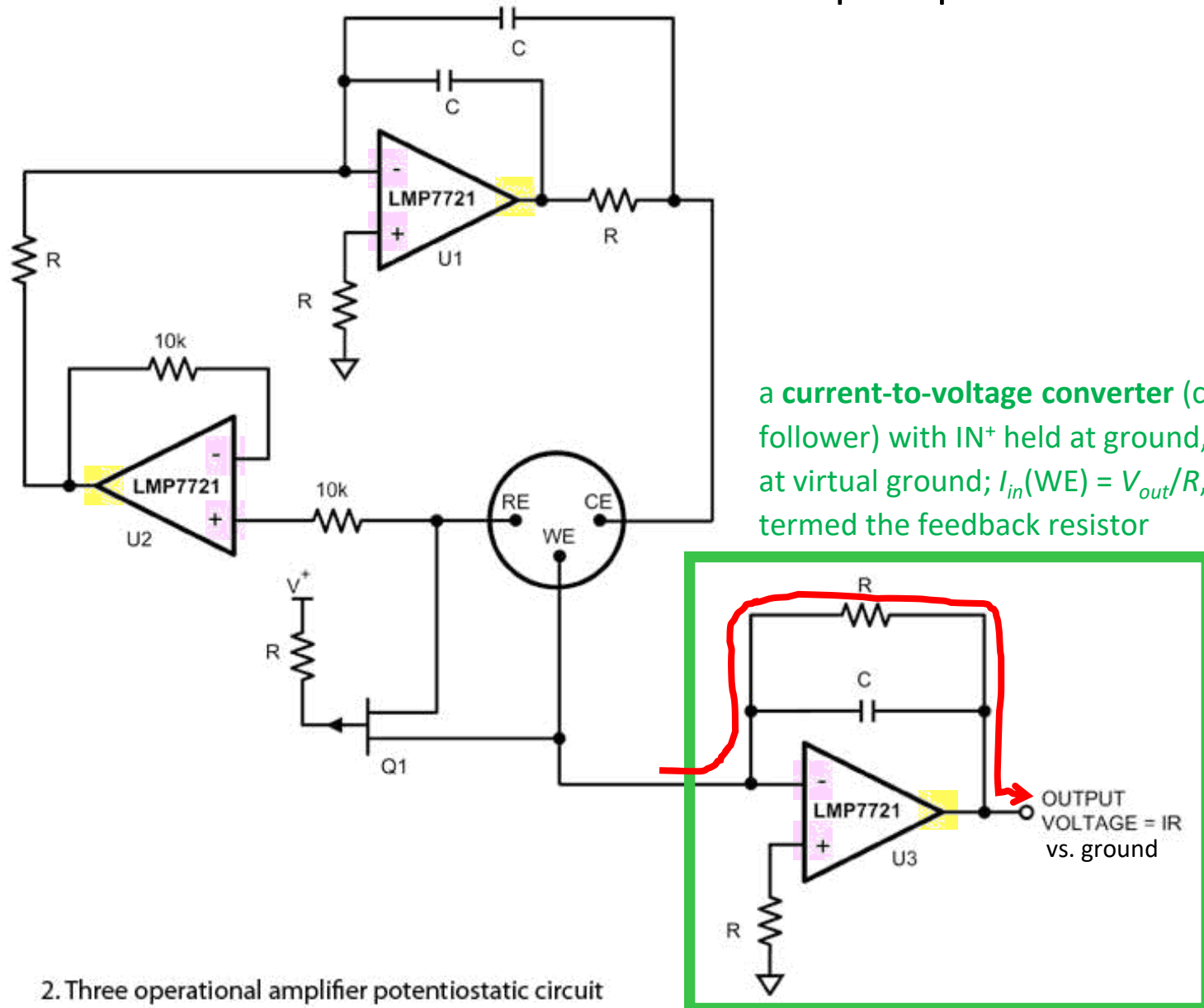


2. Three operational amplifier potentiostatic circuit

[http://electronicdesign.com/Content/14978/59899\\_fig\\_02.jpg](http://electronicdesign.com/Content/14978/59899_fig_02.jpg)

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2. Three operational amplifier potentiostatic circuit

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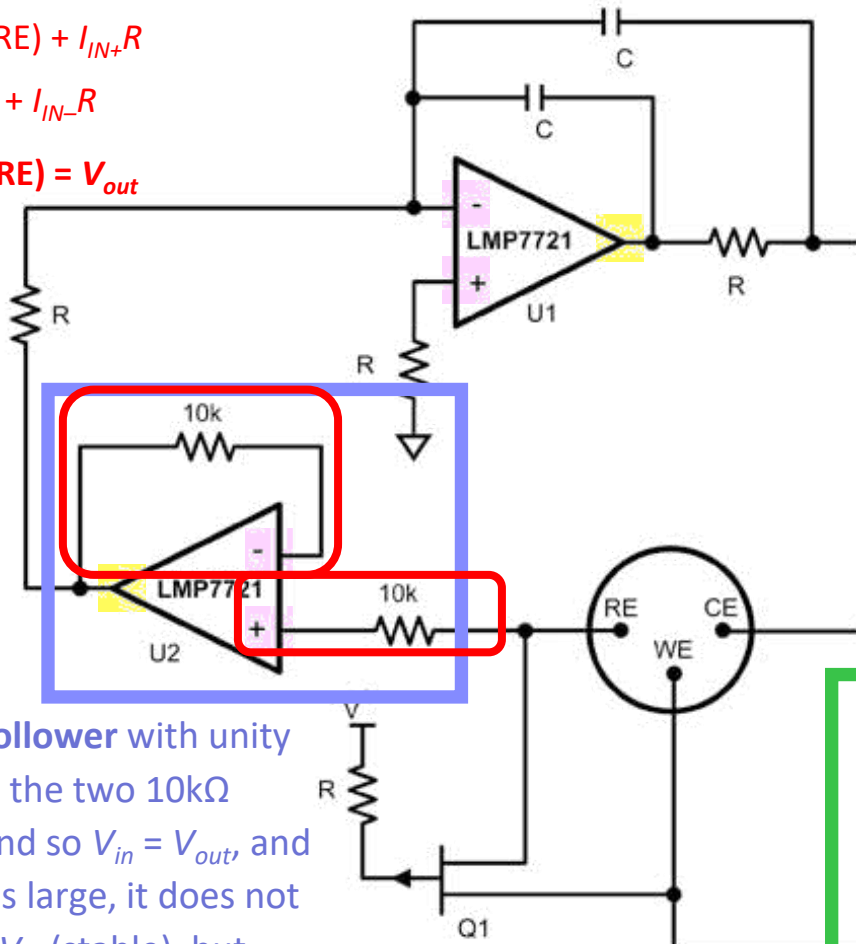
... three op-amps!

$$V_{IN+} = V_{IN-} \quad I_{IN+} = I_{IN-} \approx 0$$

$$V_{IN+} = V_{in}(RE) + I_{IN+}R$$

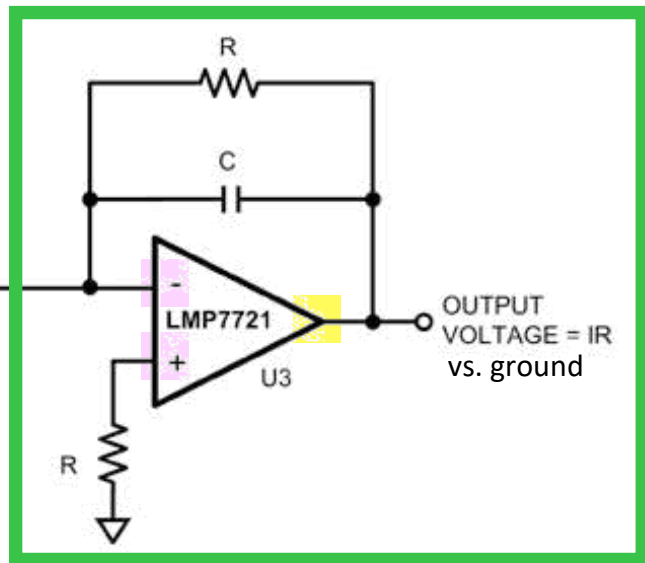
$$V_{IN-} = V_{out} + I_{IN-}R$$

Thus,  $V_{in}(RE) = V_{out}$



a **current-to-voltage converter** (current follower) with  $IN^+$  held at ground, and thus  $IN^-$  at virtual ground;  $I_{in}(WE) = V_{out}/R$ , where  $R$  is termed the feedback resistor

a **voltage follower** with unity gain due to the two  $10k\Omega$  resistors, and so  $V_{in} = V_{out}$ , and even if  $I_{out}$  is large, it does not draw from  $V_{in}$  (stable), but rather from the "muscle" (leads not shown)



2. Three operational amplifier potentiostatic circuit



... this is how (many famous electrochemists) do this today...

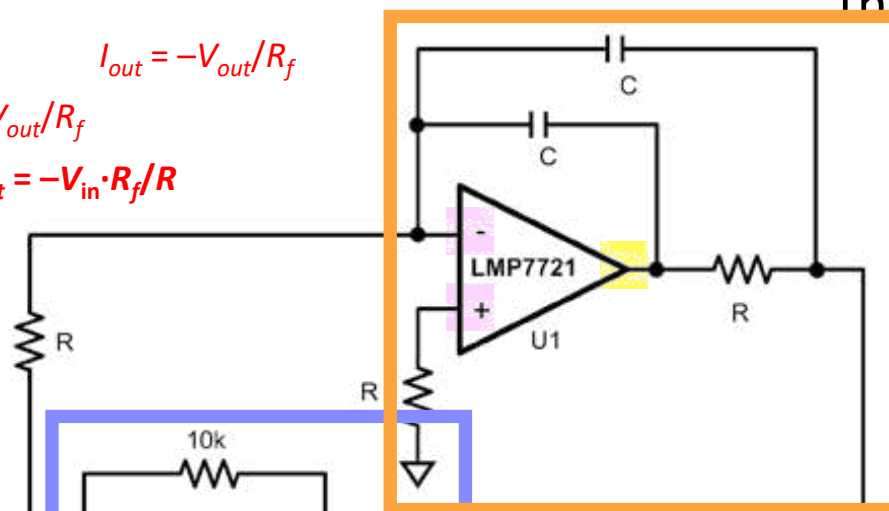
three op-amps!

$$I_{in} = I_{out}$$

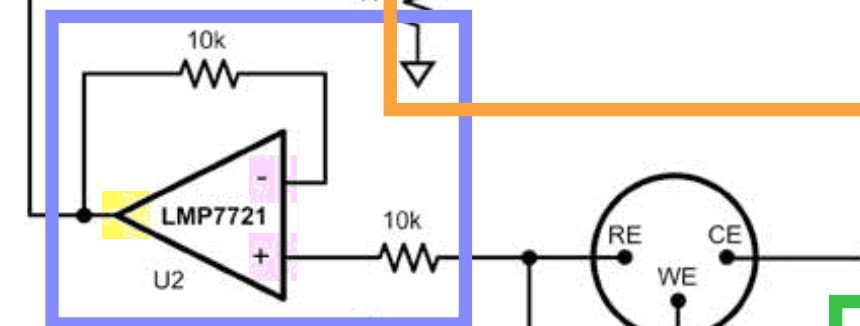
$$I_{in} = V_{in}/R \quad I_{out} = -V_{out}/R_f$$

$$V_{in}/R = -V_{out}/R_f$$

$$\text{Thus, } V_{out} = -V_{in} \cdot R_f/R$$

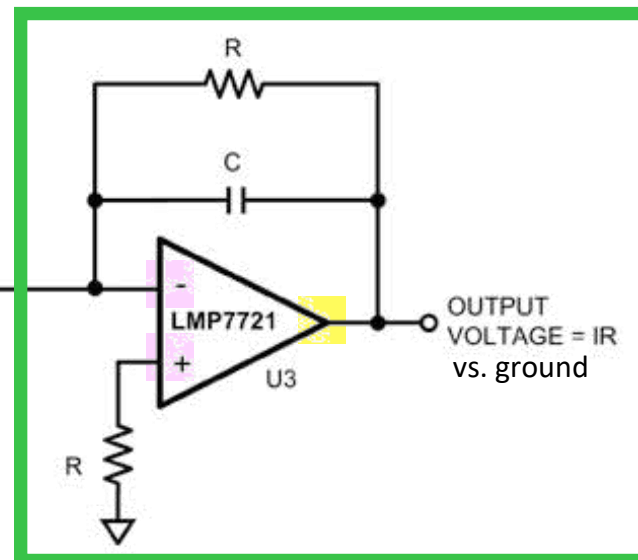


a **voltage-to-current amplifier** ( $I_{out} = V_{in}/R_f$ ) supplies current between the CE (and WE via the ground) in order to maintain the difference in potential between the WE/ground and RE ( $E_{app} = V_{in}$ ); gain =  $R_f/R$



a **current-to-voltage converter** (current follower) with  $IN^+$  held at ground, and thus  $IN^-$  at virtual ground;  $I_{in}(WE) = V_{out}/R$ , where  $R$  is termed the feedback resistor

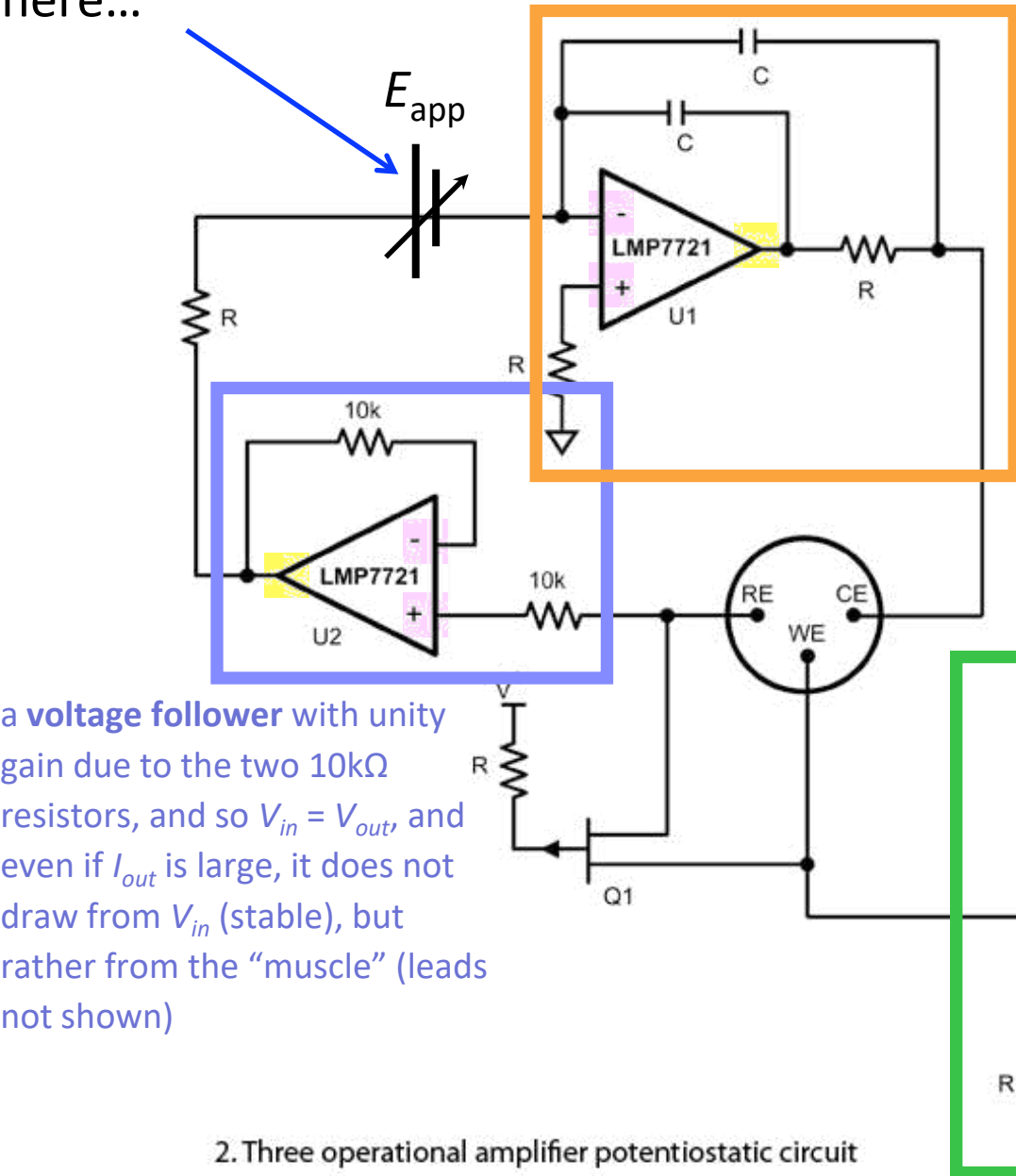
a **voltage follower** with unity gain due to the two  $10k\Omega$  resistors, and so  $V_{in} = V_{out}$ , and even if  $I_{out}$  is large, it does not draw from  $V_{in}$  (stable), but rather from the "muscle" (leads not shown)



2. Three operational amplifier potentiostatic circuit

[http://electronicdesign.com/Content/14978/59899\\_fig\\_02.jpg](http://electronicdesign.com/Content/14978/59899_fig_02.jpg)

If we want to be able to adjust the voltage on the WE, we introduce  $E_{app}$  here...



a **voltage-to-current amplifier** ( $I_{out} = V_{in}/R_f$ ) supplies current between the CE (and WE via the ground) in order to maintain the difference in potential between the WE/ground and RE ( $E_{app} = V_{in}$ ); gain =  $R_f/R$

a **current-to-voltage converter** (current follower) with  $IN^+$  held at ground, and thus  $IN^-$  at virtual ground;  $I_{in}(WE) = V_{out}/R$ , where R is termed the feedback resistor

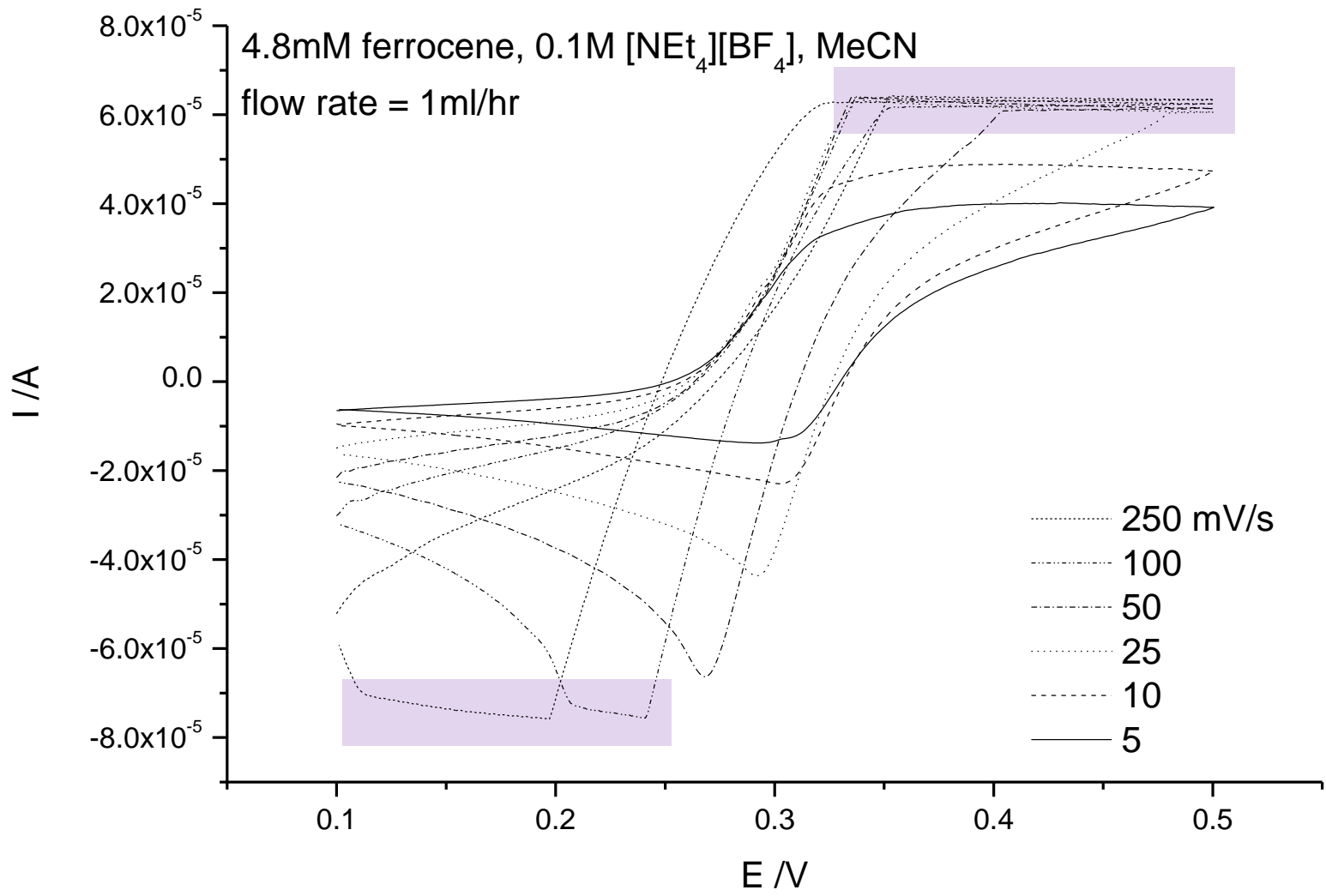
a **voltage follower** with unity gain due to the two  $10k\Omega$  resistors, and so  $V_{in} = V_{out}$ , and even if  $I_{out}$  is large, it does not draw from  $V_{in}$  (stable), but rather from the "muscle" (leads not shown)

2. Three operational amplifier potentiostatic circuit

Note especially the following for “older” (simpler) potentiostats:

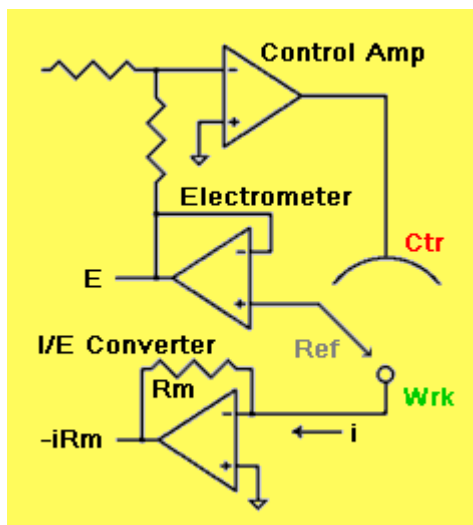
1. The working electrode (WE) is at (virtual) ground and has a very low impedance,  $Z = R + iX$ . You “cannot” get an electrical shock at this electrode or at this input to the potentiostat.
2. Amplifier U3 takes the current at the WE and converts it into a potential so it can be recorded.  $V = IR$  at the output of U3.
3. The reference electrode (RE), connected to the non-inverting input (+) of the op-amp U2, is asked to source a *minute* amount of current ( $\sim 3$  fA for this particular op-amp; 0 fA is the ideal case).
4. Op-amp U1 produces, at the counter electrode (CE), an output current,  $I_{\text{out}}$ , **that is proportional to the potential difference between RE and WE** (i.e. ground). ***Caution: You CAN get a lethal shock at this electrode.*** *However, this power is not infinite (your wall sockets have a limited power they can supply). The potentiostat limits are termed the compliance voltage and compliance current...*

Beware of compliance voltage issues (maximum voltage to CE)...  
... and compliance current too!



# Active I/E Converter versus Passive I/E Converter

... meaning "older"



## • Advantages

Both the measured current signal and the measured voltage signal are referenced to the potentiostat's ground. This makes for easy interconnection to an oscilloscope or data acquisition system without the need for differential amplifiers.

The Working Electrode is easily protected from noise by using coax cable and grounding the shield.

## • Disadvantages

Whenever the current measurement circuit is overloaded the working electrode is no longer maintained at virtual ground. The net result is loss of potential control.

Even if the I/E circuit is not overloaded, it can have severe influence on potentiostat stability. This was noted in the mid 60's [ [Ref 1](#) ]. The I/E converter must be de-tuned in order to insure potentiostat stability.

This design is not well suited for high current potentiostats since two high current amplifiers must be designed and built; one for the Control Amplifier and one for the I/E Converter.

## On the Instability of Current Followers in Potentiostat Circuits

J. E. Davis,

Departments of Pathology and Medicine, Washington University; Division of Laboratory Medicine, Barnes Hospital, St. Louis, Mo. 63110

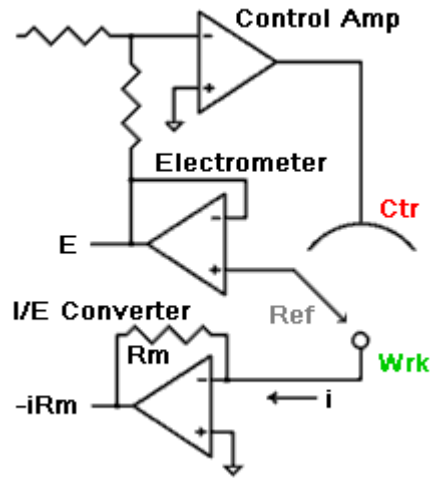
E. Clifford Toren, Jr.<sup>1</sup>

Departments of Medicine and Pathology, University of Wisconsin, Madison, Wis. 53706

<http://www.consultrsr.net/resources/pstats/design.htm>

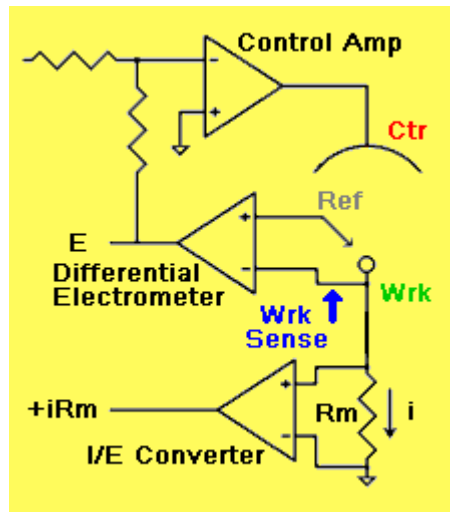
# Active I/E Converter versus Passive I/E Converter

... meaning “newer”



“Many modern potentiostats use the architecture shown here, yet it is rarely discussed at length in textbooks!”

“This scheme has been used by Gamry, PAR, Solartron, and perhaps others [and likely Bio-Logic].”

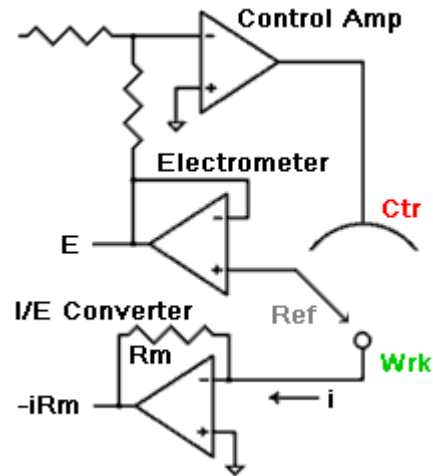


Unlike the active I/E converter design,

- this I/E converter is passive... current only flows through passive circuit elements (e.g. R, C, not op-amp)
- the working electrode is NOT at (virtual) (earth) ground
- the electrometer is differential between the RE and the WE sense (RE #2)

# Active I/E Converter versus Passive I/E Converter

... meaning "newer"



## • Advantages

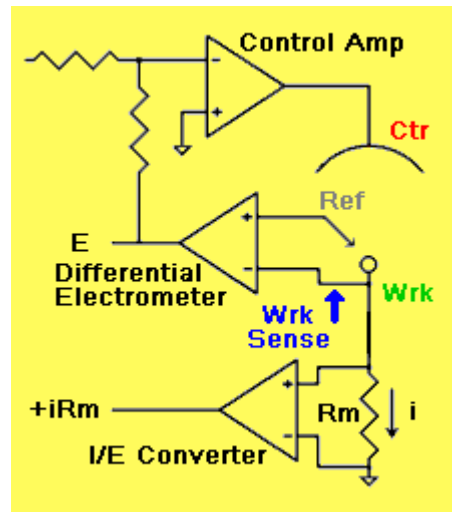
The I/E Converter amplifier must only **report** the  $iR$  drop across the current sense resistor. It is not involved in the control of the working electrode and it does not have to be a high current amplifier. The frequency response of this style of I/E converter can be faster than the "active" design because of this. Its frequency response does not have to be sacrificed for potentiostat stability since the I/E converter is not involved in the "control loop."

Because the electrometer is differential, a potentiostat of this design can be used to control the voltage across a membrane or across the interface between two immiscible liquids. In this application two reference electrodes are used. One is connected to the Reference input, and the other (on the other side of the membrane or interface) is connected to the Working Sense input.

## • Disadvantages

The Common Mode Rejection Ratio (CMRR) of the differential electrometer can have a profound influence on the stability of this potentiostat. There are two feedback paths through the differential electrometer. The path through the reference electrode is a net **negative feedback** path if you follow it from the reference electrode to the counter electrode via the electrometer and control amplifier. This path gives stability. The path through the **Wrk Sense** input, however, is a **positive feedback** path and is destabilizing.

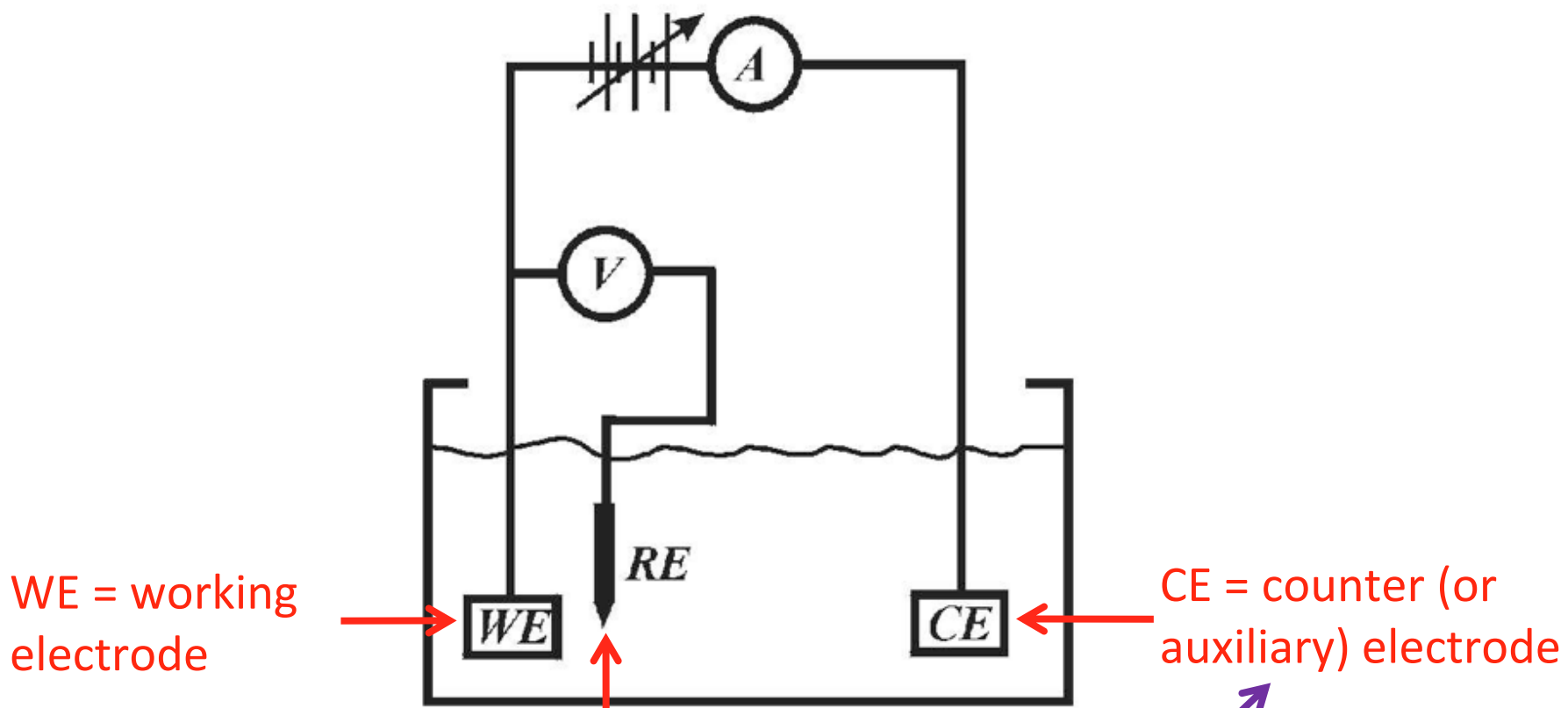
The overall 'gain' of the control amplifier is higher with this scheme. This is another way of saying that the control amplifier must work harder to keep the working-reference voltage correct. Not only must it overcome the counter-reference resistance, but the voltage drop across the current measuring resistor as well. In many commercial designs, the voltage drop across this resistor is 100 mV or less, even at 'full scale' current. The differential amplifier often amplifies the voltage level (to a nominal 1V at full scale current) as well as buffering it.



# Potentiostat summary... for non-EE majors...

- The potentiostat does not control the potential of the working electrode!
- The potentiostat controls the potential of the counter electrode **only** (relative to the working electrode)
- The counter electrode is the most important electrode for the potentiostat EE, followed by the reference electrode
- Compliance voltage and compliance current limits are very important in the choice of the potentiostat / application
- With a few components you can build your own potentiostat for < \$100!
- “Passive” potentiostats do not hold the WE at earth ground, but can measure potentials across electrolyte interfaces





WE = working electrode

RE = reference electrode

CE = counter (or auxiliary) electrode

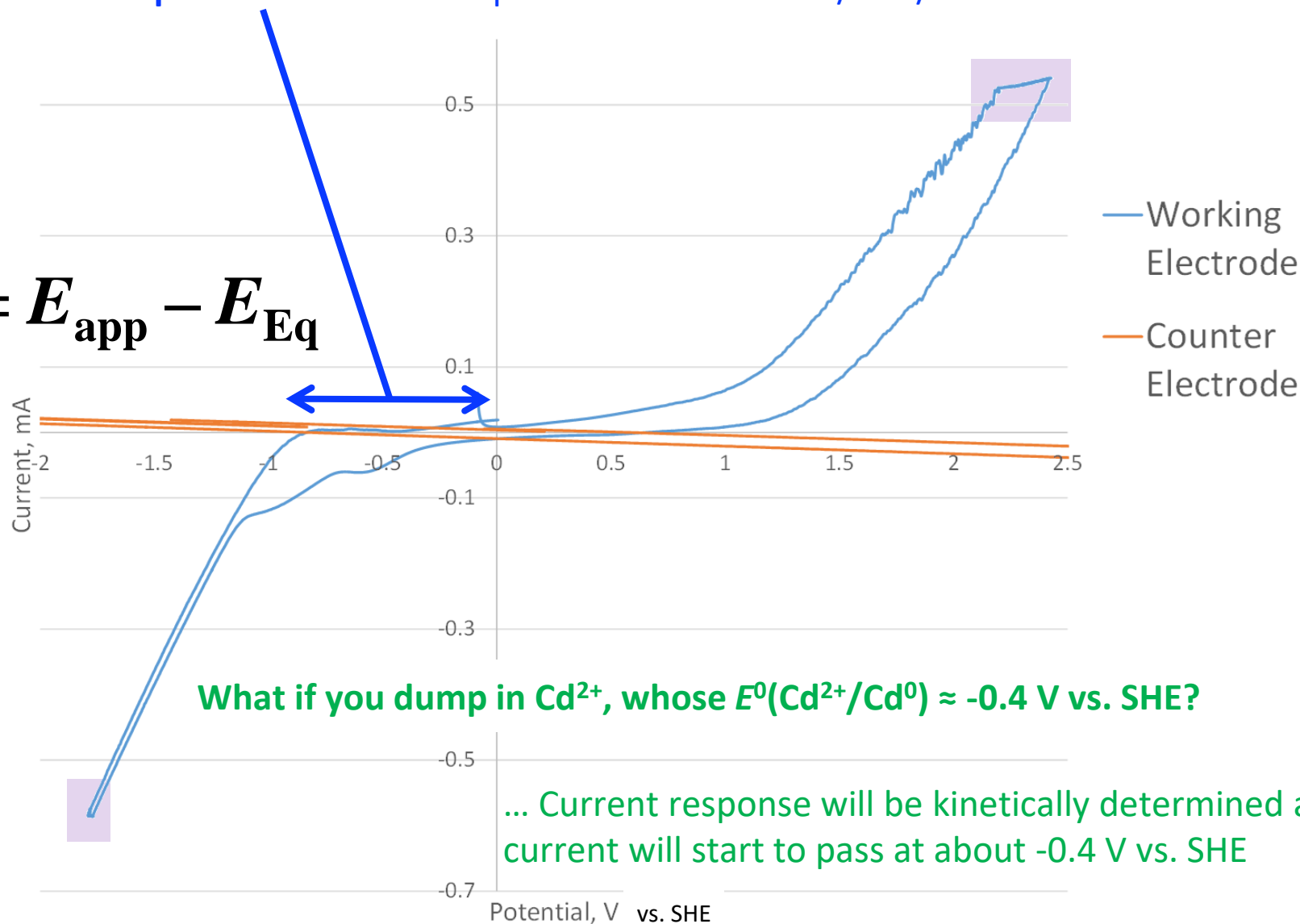
“Out of sight, out of mind” is a telling proverb/idiom!

<http://www.porous-35.com/electrochemistry-semiconductors-10.html>

Now, pretend this experimental  $I-E$  curve (from my labs; in fact) was measured when the Pt WE was switched with a Hg WE... why does little current flow until  $\sim -1$  V?

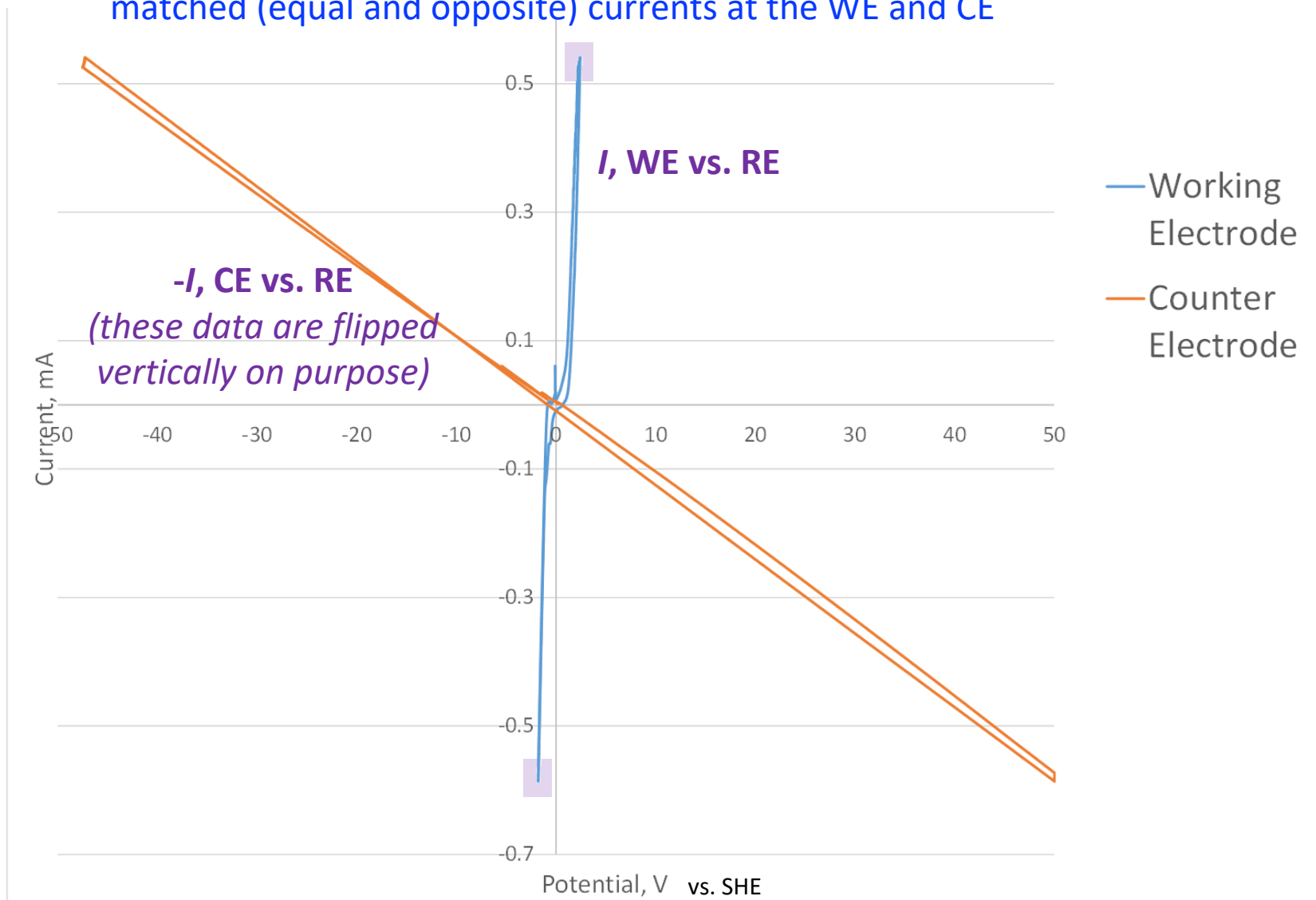
... **Overpotential!** ... which is present due to kinetic/rate/current limitations

$$\eta = E_{\text{app}} - E_{\text{Eq}}$$



Also, don't forget about possible compliance voltage issues (maximum voltage to CE)... and compliance current too!

... under conditions of steady-state current flow, we are concerned with matched (equal and opposite) currents at the WE and CE



## Looking forward... Section 1.1 (and some of Chapter 15)

- Reference electrodes
- 2-electrode versus 3-electrode measurements
- Potentiostats
- Compliance voltage/current
- *J–E and I–E curves*
- *Kinetic overpotential*
- *Electrochemical window*
- *Faradaic reactions*