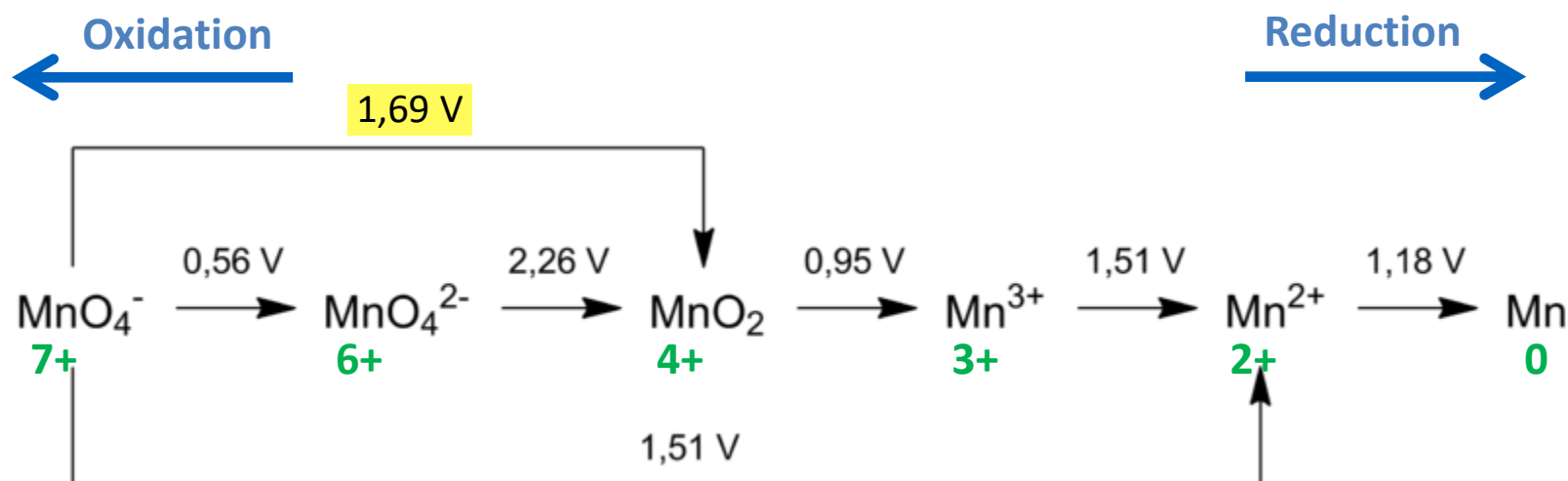


Lecture #5 of 17

Looking forward... our review of Chapter “0”

- Cool applications
- Redox half-reactions
- Balancing electrochemical equations
- History of electrochemistry and Batteries
- IUPAC terminology and $E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$
- Thermodynamics and the Nernst equation
- Common reference electrodes
- Standard and Absolute potentials
- Latimer and Pourbaix diagrams (*halfway complete*)
- **Calculating E_{cell} under non-standard-state conditions**
- **Conventions**

A **Latimer diagram** is a summary of the E^0 values for an element; it is useful for visualizing the complete redox series for an element and for determining when disproportionation will occur.



from Wiki

Disproportionation – spontaneous and simultaneous reduction and oxidation of a molecule (*the opposite is comproportionation (AKA: symproportionation)*)

(1) Does Mn^{2+} disproportionate? **NO.** $E^0 = E_{\text{red}} - E_{\text{ox}} = 1.18 - 1.51 = -0.33 \text{ V}$

(2) What is the standard reduction potential of MnO_4^- to MnO_2 ?

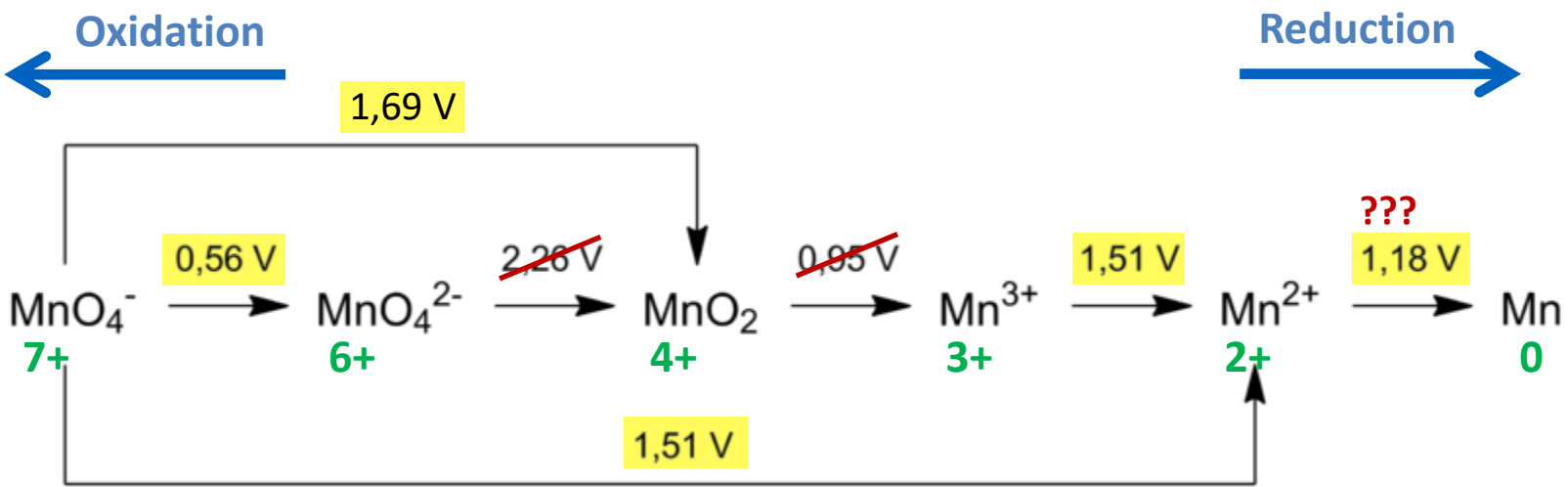
$$\Delta G^0 = -nFE^0 = -3FE^0$$

$$\Delta G^0 = -nFE^0_1 + -nFE^0_2 = -F((1 \times 0.56 \text{ V}) + (2 \times 2.26 \text{ V})) = -F(5.08 \text{ V})$$

Set them equal to each other, and thus, $3E^0 = 5.08$ and $E^0 = 1.69 \text{ V}$

... for #1, you can work with E^0 only (do not need ΔG^0), because the reaction is always equal in the number of electrons

A **Latimer diagram** is a summary of the E^0 values for an element; it is useful for visualizing the complete redox series for an element and for determining when disproportionation will occur.



from Wiki

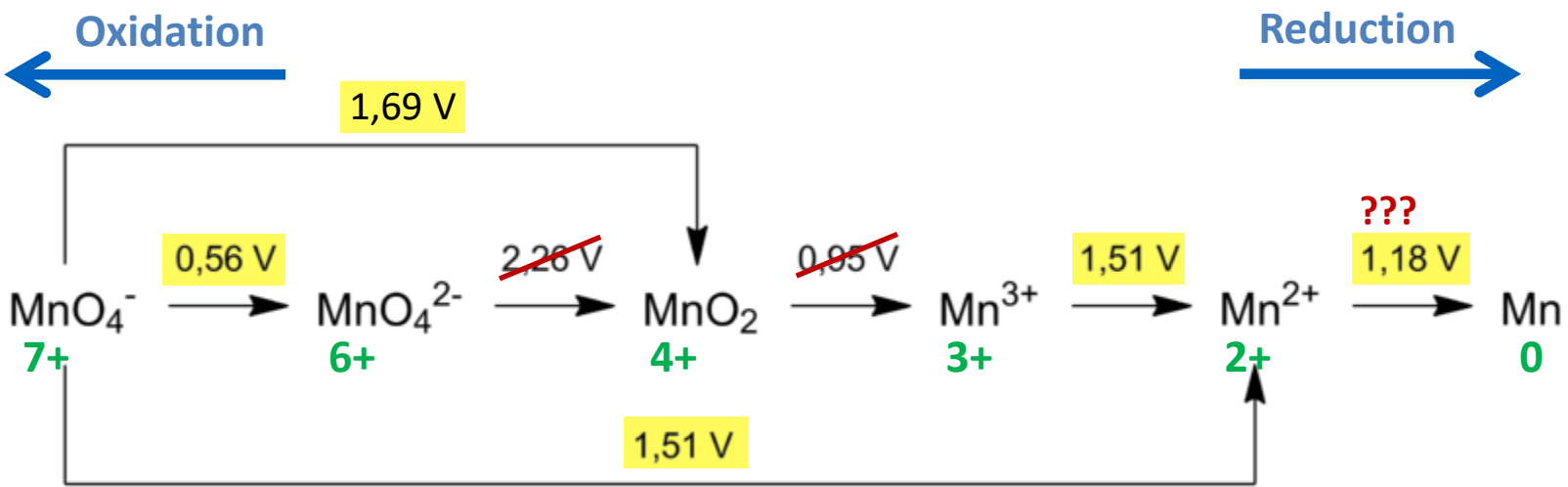
Recall from before...

$Mn^{2+} + 2 e \rightleftharpoons Mn$???	-1.185
$Mn^{3+} + e \rightleftharpoons Mn^{2+}$		1.5415
$MnO_2 + 4 H^+ + 2 e \rightleftharpoons Mn^{2+} + 2 H_2O$		1.224
$MnO_4^- + e \rightleftharpoons MnO_4^{2-}$		0.558
$MnO_4^- + 4 H^+ + 3 e \rightleftharpoons MnO_2 + 2 H_2O$		1.679
$MnO_4^- + 8 H^+ + 5 e \rightleftharpoons Mn^{2+} + 4 H_2O$		1.507
$MnO_4^- + 2 H_2O + 3 e \rightleftharpoons MnO_2 + 4 OH^-$		0.595
$MnO_4^{2-} + 2 H_2O + 2 e \rightleftharpoons MnO_2 + 4 OH^-$		0.60
$Mn(OH)_2 + 2 e \rightleftharpoons Mn + 2 OH^-$		-1.56
$Mn(OH)_3 + e \rightleftharpoons Mn(OH)_2 + OH^-$		0.15
$Mn_2O_3 + 6 H^+ + e \rightleftharpoons 2 Mn^{2+} + 3 H_2O$		1.485

... anyway, why are these bottom E^0 values not on the Latimer diagram?

... because they are at basic/alkaline standard state with ~1 M OH^- !

A **Latimer diagram** is a summary of the E^0 values for an element; it is useful for visualizing the complete redox series for an element and for determining when disproportionation will occur.



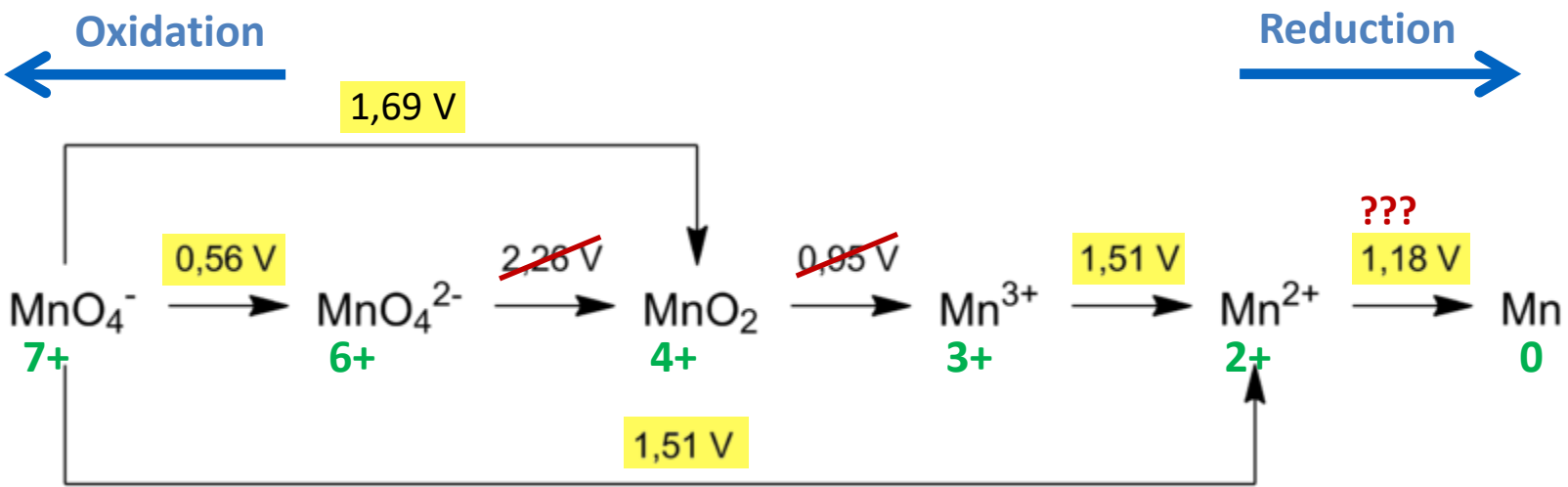
from Wiki

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$Mn_2O_3 + 6 H^+ + e \rightleftharpoons 2 Mn^{2+} + 3 H_2O$		1.485

What would this E^0 value be when at acidic standard state?

A **Latimer diagram** is a summary of the E^0 values for an element; it is useful for visualizing the complete redox series for an element and for determining when disproportionation will occur.



from Wiki

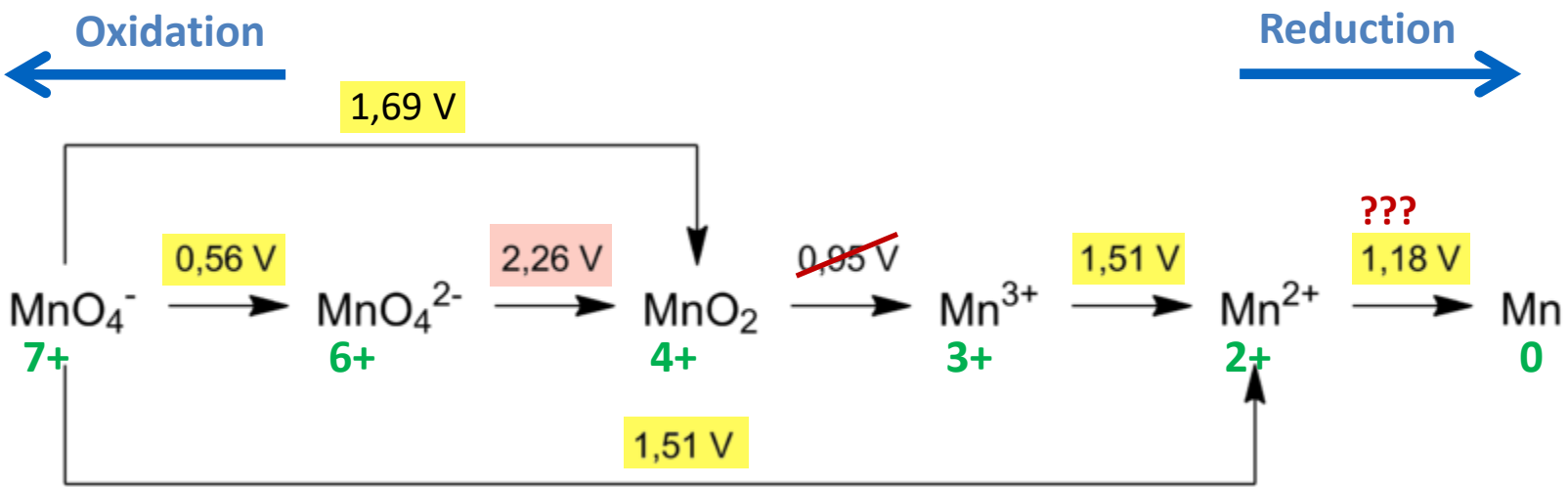
$$E = E_{acid}^0 - \frac{0.05916 \text{ V}}{n} \log \left(\frac{[MnO_2]^1 [H_2O]^2}{[MnO_4^{2-}]^1 [H^+]^4} \right) = E_{acid}^0 - \frac{0.05916 \text{ V}}{2} \log \left(\frac{(1)^1}{(1)^1 (10^{-14})^4} \right) = E_{acid}^0 - 0.02958 \text{ V} \quad (56)$$

$$E = E_{acid}^0 - 1.65648 \text{ V} = 0.60 \text{ V}$$

What would this E^0 value be when at acidic standard state?

$MnO_4^- + 2 H_2O + 3 e \rightleftharpoons MnO_2 + 4 OH^-$	0.595
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A **Latimer diagram** is a summary of the E^0 values for an element; it is useful for visualizing the complete redox series for an element and for determining when disproportionation will occur.



from Wiki

$$E = E_{acid}^0 - \frac{0.05916 \text{ V}}{n} \log \left(\frac{[MnO_2]^1 [H_2O]^2}{[MnO_4^{2-}]^1 [H^+]^4} \right) = E_{acid}^0 - \frac{0.05916 \text{ V}}{2} \log \left(\frac{(1)^1}{(1)^1 (10^{-14})^4} \right) = E_{acid}^0 - 0.02958 \text{ V} \quad (56)$$

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What would this E^0 value be when at acidic standard state?

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$Mn_2O_3 + 6 H^+ + e \rightleftharpoons 2 Mn^{2+} + 3 H_2O$	1.485

$$E_{SHE}^0 = 2,25648 \text{ V}$$

SWEET!

... but then why did the CRC not list this? ...

... Second one (not truly standard potentials)...

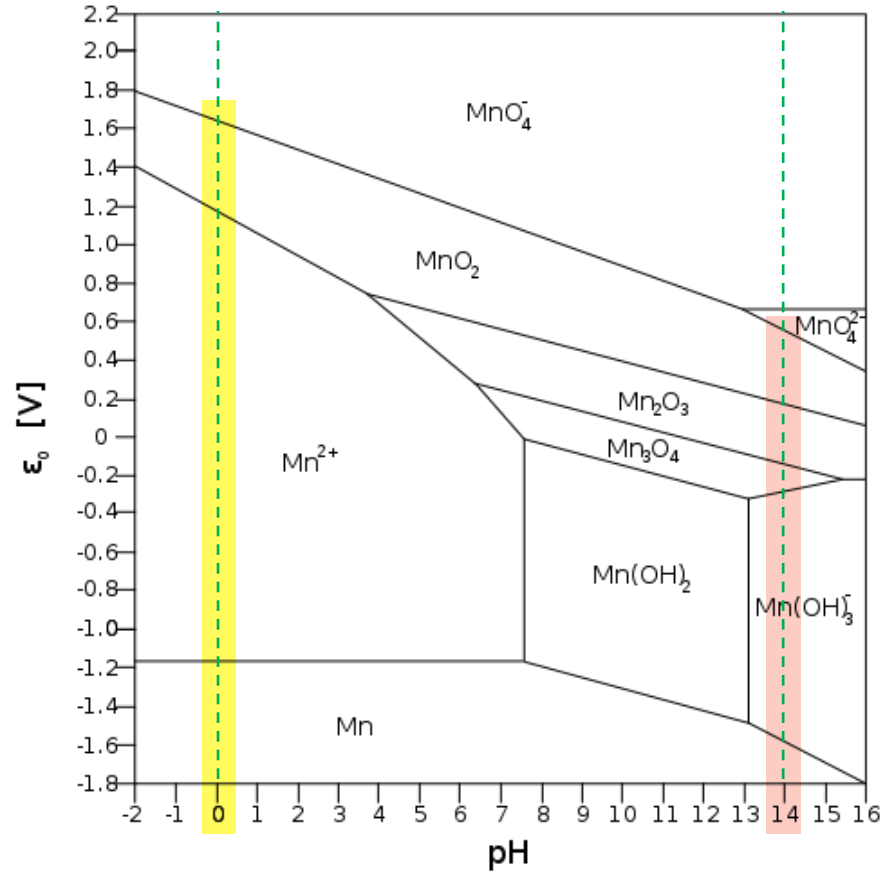
A **Pourbaix diagram** is a map of the predominant *equilibrium* species of an aqueous electrochemical system; it is useful for identifying which materials/species are present/stable ... mostly based on thermochemical data

Chemist

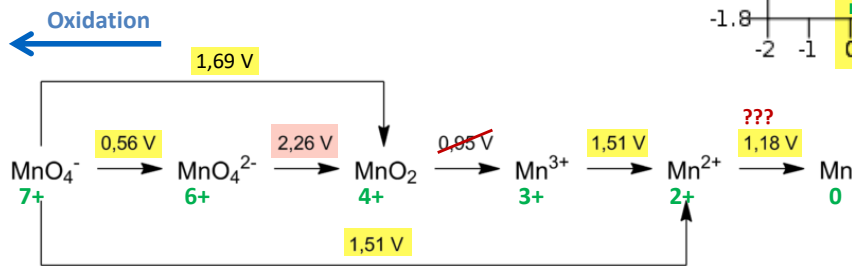


Marcel Pourbaix (1904–1998)

<http://corrosion-doctors.org/Biographies/PourbaixBio.htm>



from Wiki



from Wiki

... because in acid, the reaction does not occur!

... but then why did the CRC not list this? ...

... Second one (not truly standard potentials)...

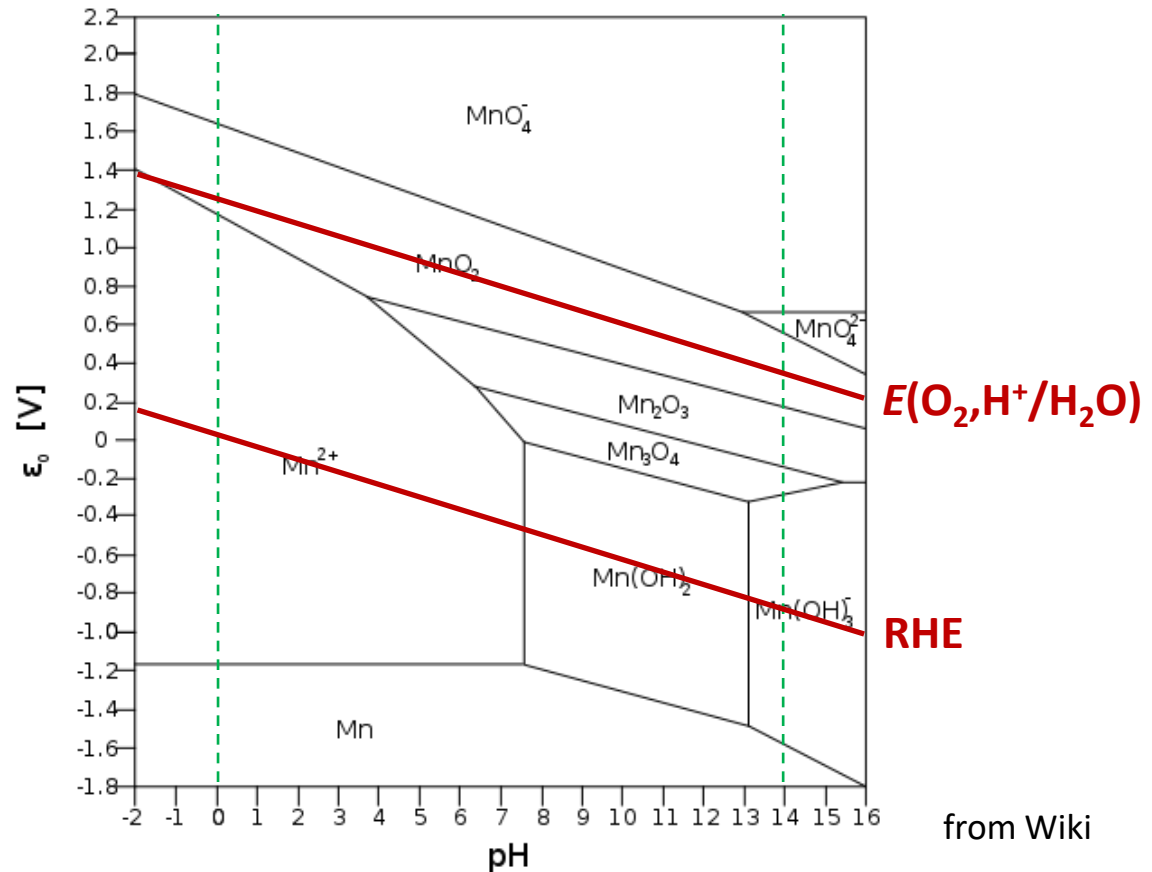
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Chemist



Marcel Pourbaix
(1904–1998)

<http://corrosion-doctors.org/Biographies/PourbaixBio.htm>



- (1) What is the electrocatalyst for O_2 evolution through water oxidation? MnO_2
- (2) At what pH values is a solid electrocatalyst for H_2 evolution stable? $pH \sim 7.5 - \sim 13...$

... likely a smaller range; why?

Looking forward... our review of Chapter “0”

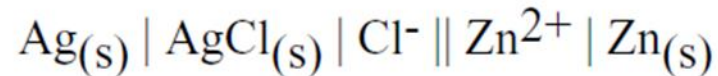
- Cool applications
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- **Conventions**

How to quantitatively attack non-standard-state cell problems...

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

Electrochemical Cell Potential Calculation

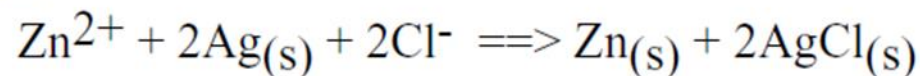
Consider the electrochemical cell:



The Cell Potential $\mathcal{E}_{\text{cell}}$ can be calculated by two methods:

Method 1: Total Reaction Method ← These should all be E_{cell}

The total cell reaction is:



$$\mathcal{E}_{\text{cell}} = \mathcal{E}^{\circ}_{\text{cell}} - (RT/2F) \ln (1/([\text{Zn}^{2+}][\text{Cl}^-]^2)) \quad (1)$$

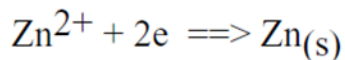
where $\mathcal{E}^{\circ}_{\text{cell}} = -\Delta G^{\circ}/2F$

How else could we write this? ...
“(60 mV/2) log”! (at room temp.)

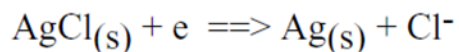
How to quantitatively attack non-standard-state cell problems... ¹²⁷

Method 2: Half Cell Potential Method

$$\mathcal{E}_{\text{cell}} = E_{\text{Zn}} - E_{\text{AgCl}}$$



$$E_{\text{Zn}} = E^{\circ}_{\text{Zn}} - (RT/2F) \ln (1/[\text{Zn}^{2+}])$$



$$E_{\text{AgCl}} = E^{\circ}_{\text{AgCl}} - (RT/F) \ln ([\text{Cl}^{-}]) \quad (4)$$

Equivalence of the Two Methods

Now since $(RT/F) \ln ([\text{Cl}^{-}]) = -(RT/F) \ln (1/[\text{Cl}^{-}]) = -(RT/2F) \ln (1/[\text{Cl}^{-}]^2)$
this eqn becomes:

$$E_{\text{AgCl}} = E^{\circ}_{\text{AgCl}} + (RT/2F) \ln (1/[\text{Cl}^{-}]^2) \quad (5)$$

$$\mathcal{E}_{\text{cell}} = (E^{\circ}_{\text{Zn}} - (RT/2F) \ln (1/[\text{Zn}^{2+}])) - (E^{\circ}_{\text{AgCl}} + (RT/2F) \ln (1/[\text{Cl}^{-}]^2)) \quad (6)$$

$$\mathcal{E}_{\text{cell}} = (E^{\circ}_{\text{Zn}} - E^{\circ}_{\text{AgCl}}) - (RT/2F) \ln (1/([\text{Zn}^{2+}][\text{Cl}^{-}]^2)) \quad (7)$$

If we define $(E^{\circ}_{\text{Zn}} - E^{\circ}_{\text{AgCl}}) = \mathcal{E}^{\circ}_{\text{cell}}$, Then we see that this is exactly the same equation that we found by Method 1 (Equation 1).

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

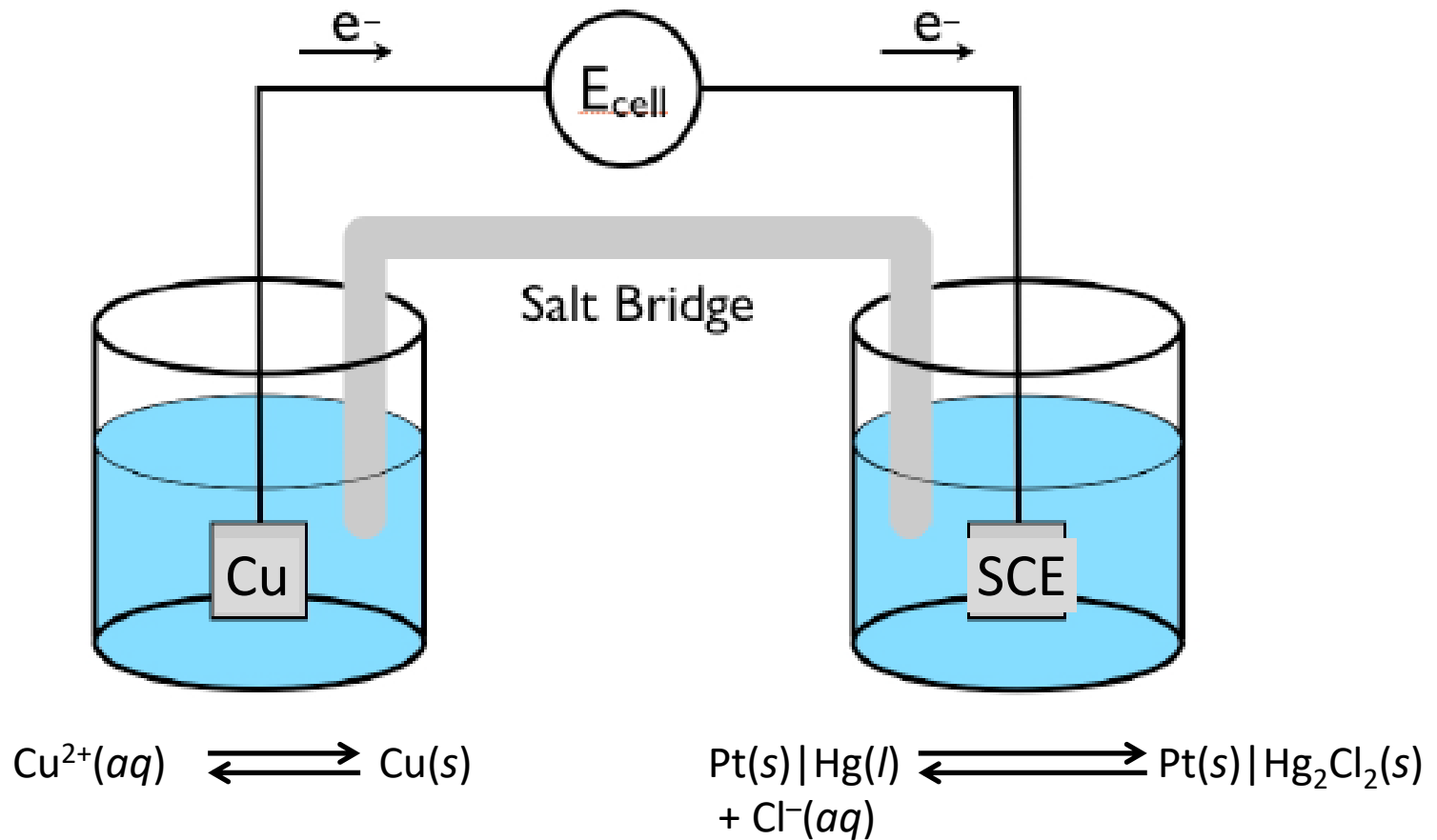
Recall (2)

- E_{cell} does not require “n”
- ΔG requires “n” ($-nFE_{\text{cell}}$)

Facile

NOT The Daniell Cell

high impedance to measure potential

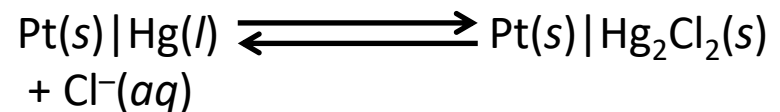
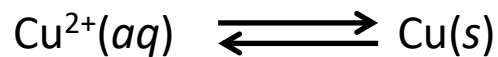
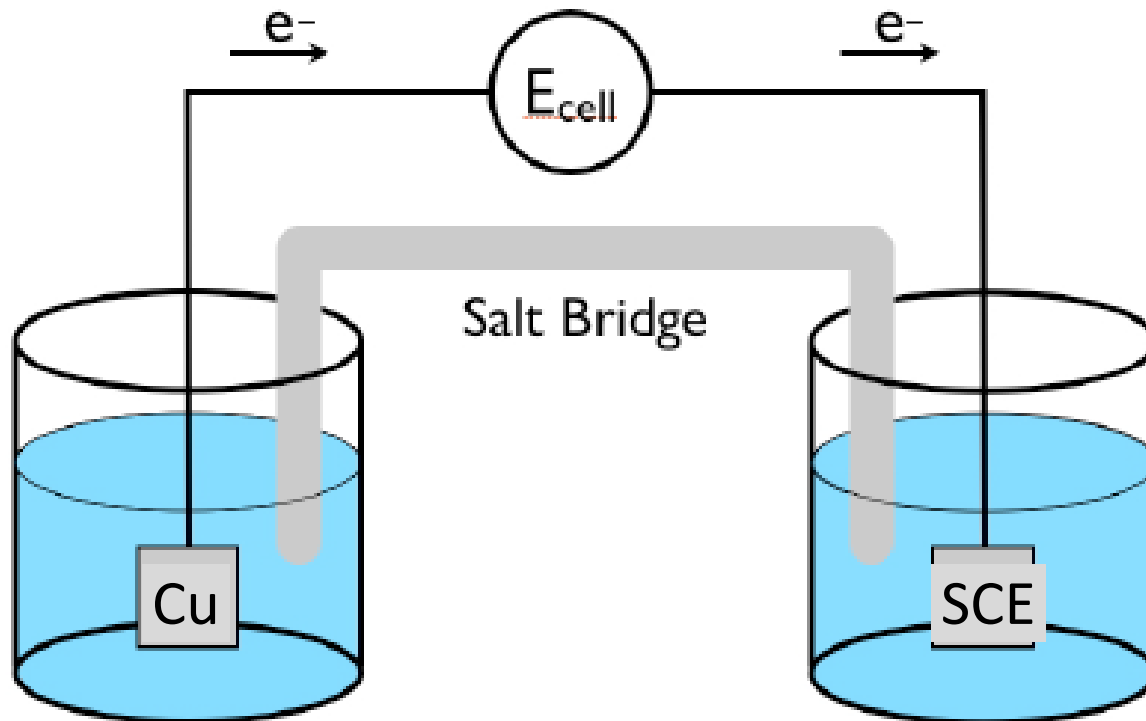


Common Reactive Electrodes: Copper, Zinc, Cadmium, Lead, Silver

Common Inert Electrodes: Platinum, Carbon, Gold

Write and explain the line notation for the redox reaction between Cu/Cu²⁺ and an SCE electrode, where Cu²⁺ is CuSO₄ (0.1 M), and KCl (1 M) is present in all cells.

$$E^\circ(\text{Cu}^{2+}/\text{Cu}) = +0.1 \text{ V vs. SCE}$$

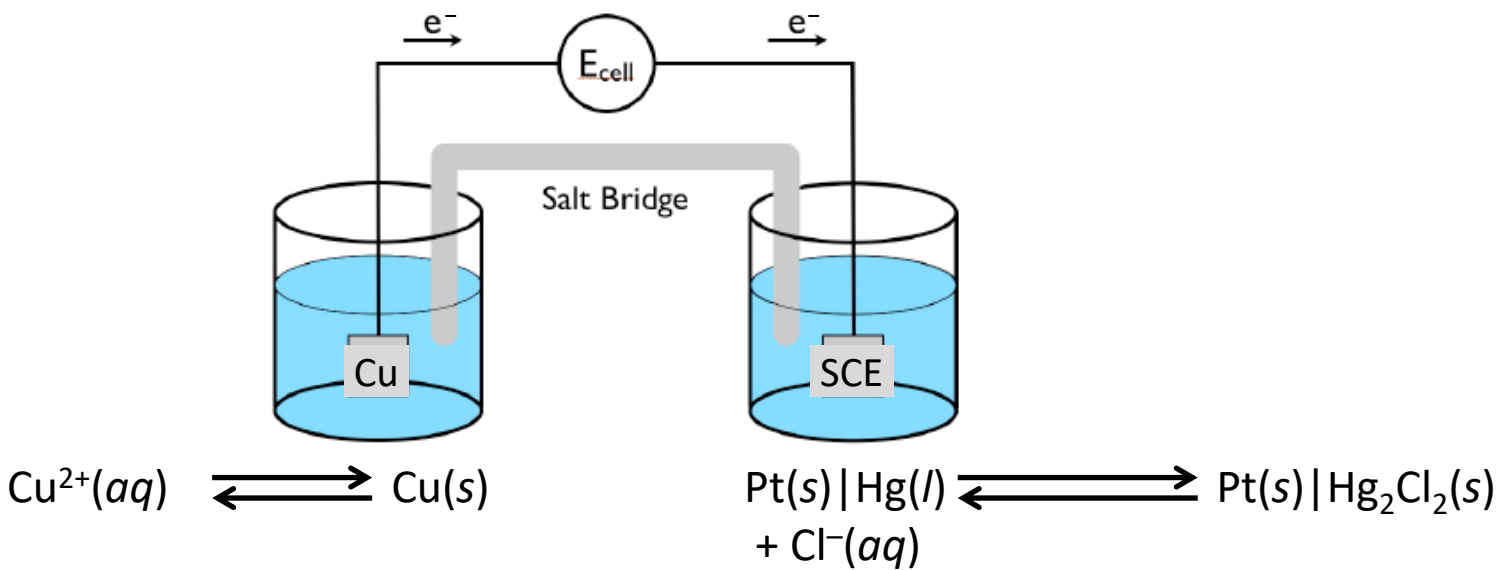
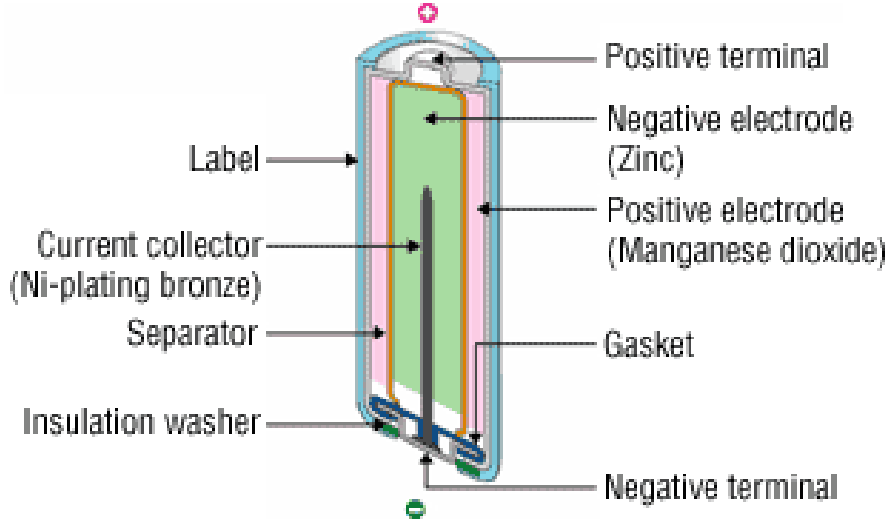
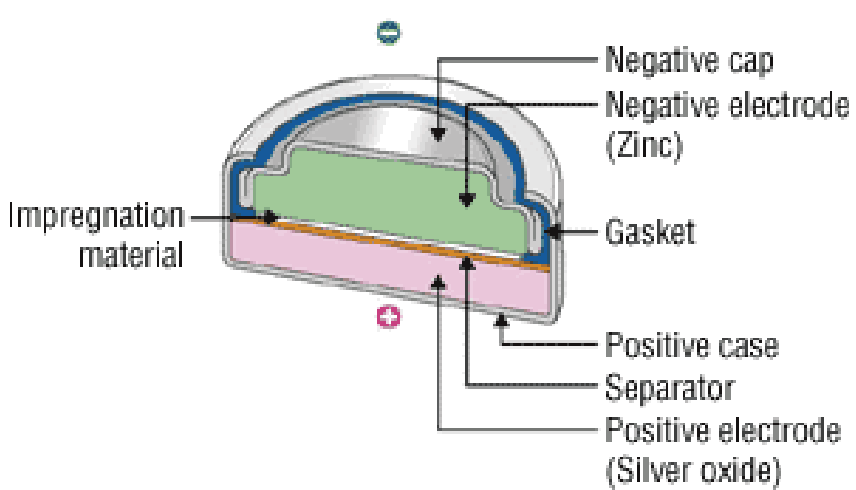


Pt(s) | Hg(l) | Hg₂Cl₂(s) | KCl(1 M, aq) | KCl(1M, aq) | KCl(1 M, aq), CuSO₄ (0.1 M, aq) | Cu(s)

Pt(s) | Hg(l) | Hg₂Cl₂(s) | Cl⁻(1 M, aq) || Cu²⁺ (0.1 M, aq) | Cu(s)

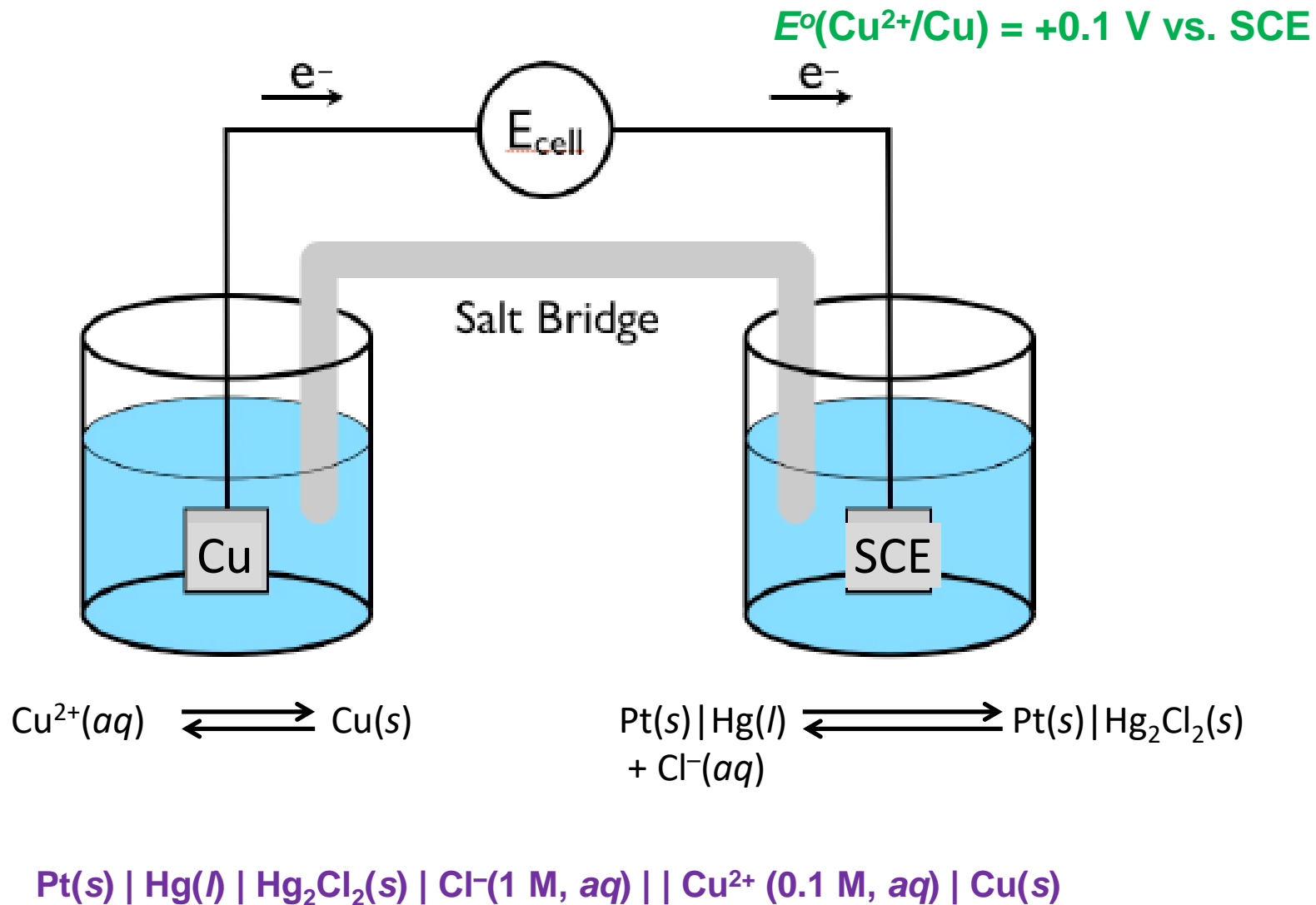
FYI, cells can be drawn any which way, even on top of each other, or radially... 130

... but in line notation the anode should be on the left-hand side. **(SKIPPED)**



(a) What is E_{cell} in this case (1 M KCl, 0.1 M CuSO_4)? (SKIPPED)

(b) What is E_{cell} if $[\text{KCl}] = 0.1 \text{ M}$?



(a) What is E_{cell} in this case (1 M KCl, 0.1 M CuSO_4)? *(SKIPPED)*

(b) What is E_{cell} if $[\text{KCl}] = 0.1 \text{ M}$?

$$E^\circ(\text{Cu}^{2+}/\text{Cu}) = +0.1 \text{ V vs. SCE}$$

(a)

$$E_{\text{cell}} = E^\circ - \frac{RT}{nF} \ln \left(\frac{a_{\text{Cu}} a_{\text{Hg}_2\text{Cl}_2}}{a_{\text{Cu}^{2+}} a_{\text{Hg}} a_{\text{Cl}^-}^2} \right)$$

$$E_{\text{cell}} \approx E^\circ - \frac{0.0592 \text{ V}}{n} \log \left(\frac{1}{[\text{Cu}^{2+}][\text{Cl}^-]^2} \right)$$

$$E_{\text{cell}} = +0.1 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \left(\frac{1}{(0.1)} \right)$$

$$E_{\text{cell}} = +0.1 \text{ V} - 0.0296 \text{ V} = +0.0704 \text{ V}$$

(b)

$$E_{\text{cell}} = +0.1 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \left(\frac{1}{(0.1)^3} \right)$$

$$E_{\text{cell}} = +0.1 \text{ V} - 0.0888 \text{ V} = +0.0112 \text{ V}$$

*Remember, there is no such thing as a half-cell reaction...
... unless you are working with Trasatti*



Quick quiz: Do the following make sense?

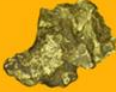
The grams (or grammage) of my material was 0.1 g.

The liters (or litterrage) of my beaker was 0.1 L.


The m/s (or m/s-age) of that baseball was 10 m/s...

Then I prefer that you don't say:

“The voltage of my cell is 0.1 V.” *Let's call it a potential...*



IUPAC
GOLD BOOK



search

IUPAC > Gold Book > alphabetical index > V > **voltage in electroanalysis**

PREVIOUS
volt


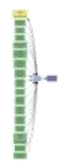
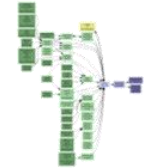
NEXT
voltammetric constant

voltage
in electroanalysis

The use of this term is discouraged, and the term **applied potential** should be used instead, for non-periodic signals. However, it is retained here for sinusoidal and other periodic signals because no suitable substitute for it has been proposed.

Source:
PAC, 1985, 57, 1491 (*Recommended terms, symbols, and definitions for electroanalytical chemistry (Recommendations 1985)*) on page 1505

Interactive Link Maps

First Level	Second Level	Third Level
		

Cite as:
IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). XML on-line corrected version: <http://goldbook.iupac.org> (2006-) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins. ISBN 0-9678550-9-8. doi:10.1351/goldbook.
Last update: 2014-02-24; version: 2.3.3.
DOI of this term: doi:10.1351/goldbook.V06635.

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... and IUPAC prefers it too!

Quick quiz: Do the following make sense?

The grams (or grammage) of my material was 0.1 g.

The liters (or litterrage) of my beaker was 0.1 L.

The m/s (or m/s-age) of that baseball was 10 m/s...

Then I prefer that you don't say:

“The voltage of my cell is 0.1 V.” Let's call it a potential...

Quick quiz: Do the following make sense?

The kinetic process was graphed as an M–s curve.

The kinetics were followed as the concentration versus s...

Then I also prefer that you don't say:

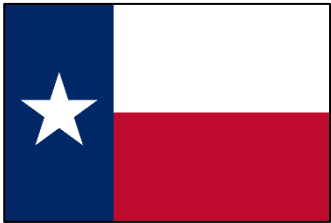
“The cell's behavior is shown as the I–V curve.” Let's call it an I–E curve, or best yet, a J–E curve, where J is current density (A/cm^2).

Electrochemistry:
conventions... oh, conventions!



[http://upload.wikimedia.org/wikipedia/commons/thu
mb/c/cc/Map_of_USA_TX.svg/2000px-
Map_of_USA_TX.svg.png](http://upload.wikimedia.org/wikipedia/commons/thumb/c/cc/Map_of_USA_TX.svg/2000px-Map_of_USA_TX.svg.png)

conventions... oh, conventions!



WE WILL USE THIS ONE...

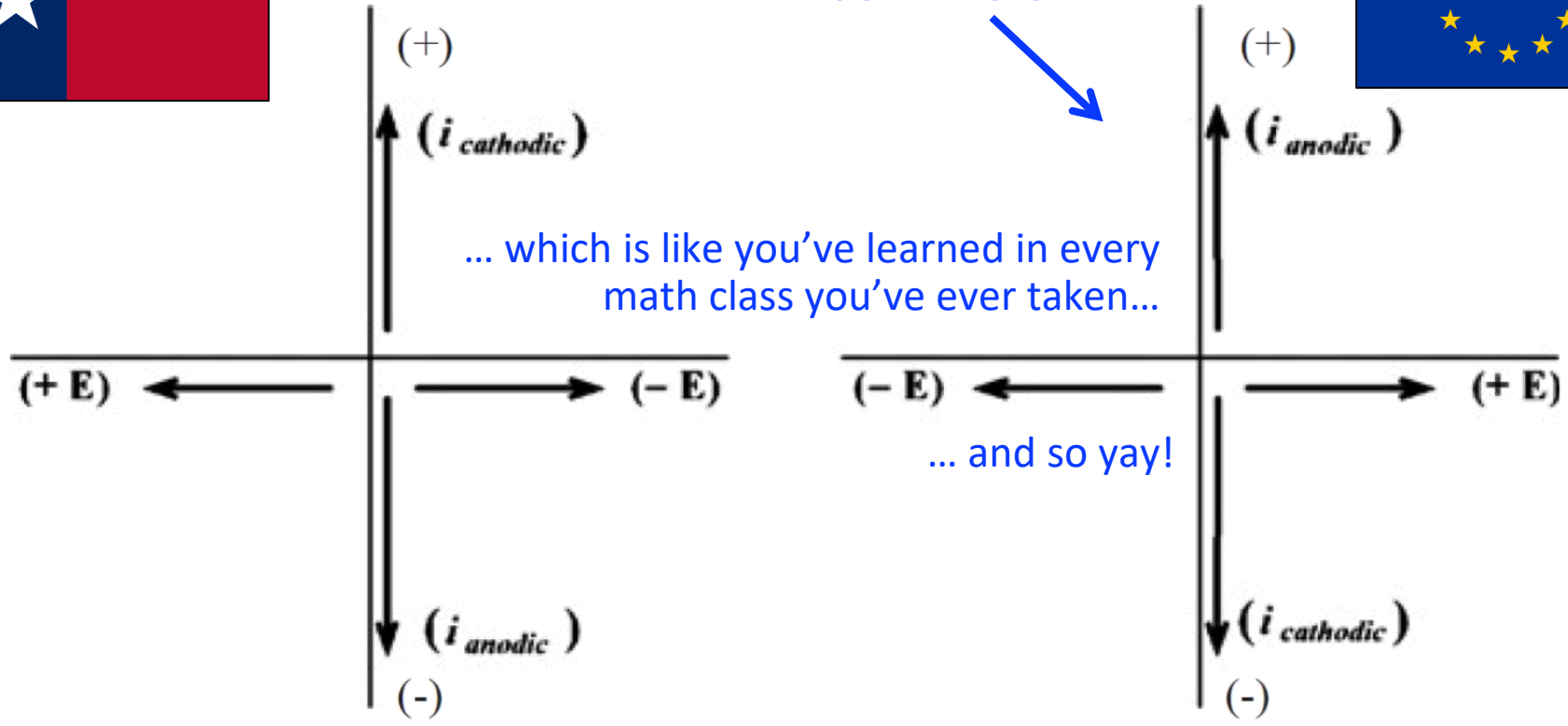


Figure 1.1 American (left) and IUPAC (right) voltammogram conventions.

... But sadly, B&F (2nd edition) use the convention on the left...

... at least you'll be pros at mentally flipping over data

Handbook of Electrochemistry, Zoski (ed.), Elsevier, 2007

And finally... we are finished our review of Chapter “0”

- Cool applications
- Redox half-reactions
- Balancing electrochemical equations
- History of electrochemistry and Batteries
- IUPAC terminology and $E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$
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Measurements in Electrochemistry

Chapters 1 and 15

Q: What's in this set of lectures?

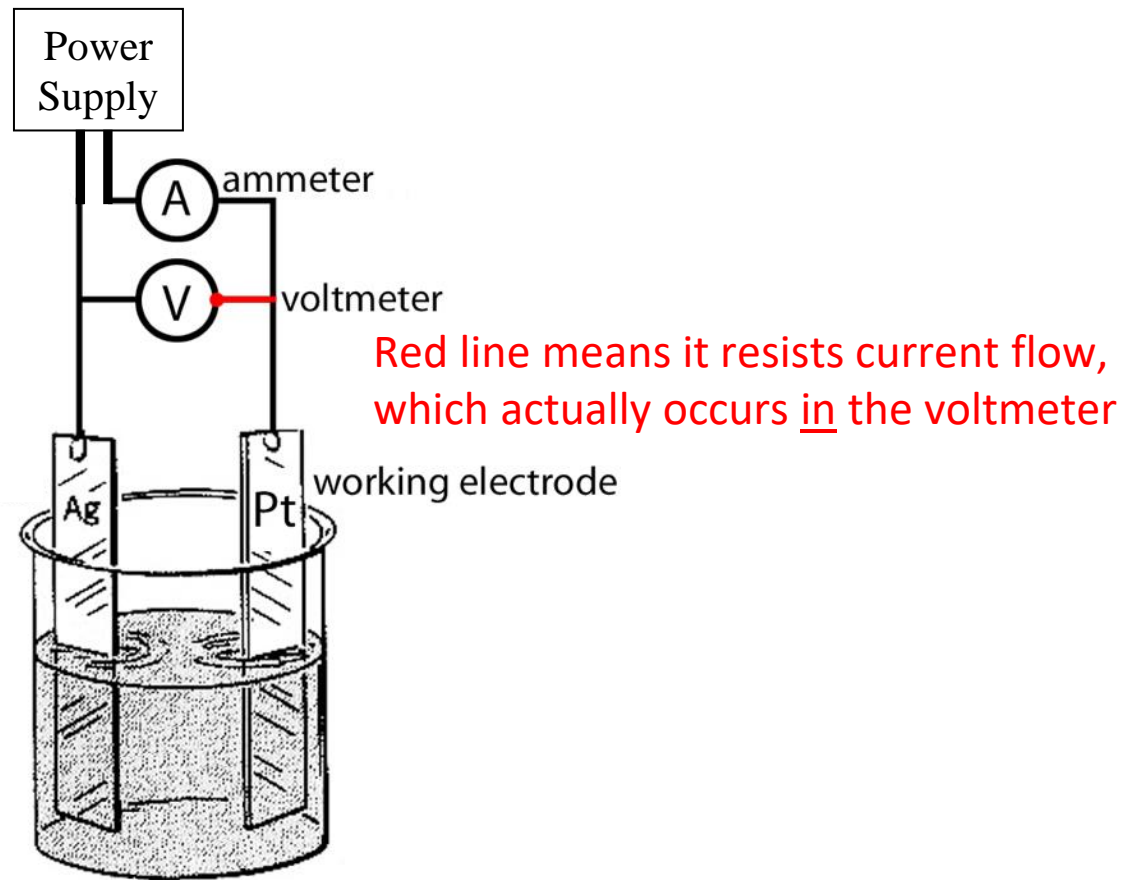
A: B&F Chapters 1 & 15 main concepts:

- 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)

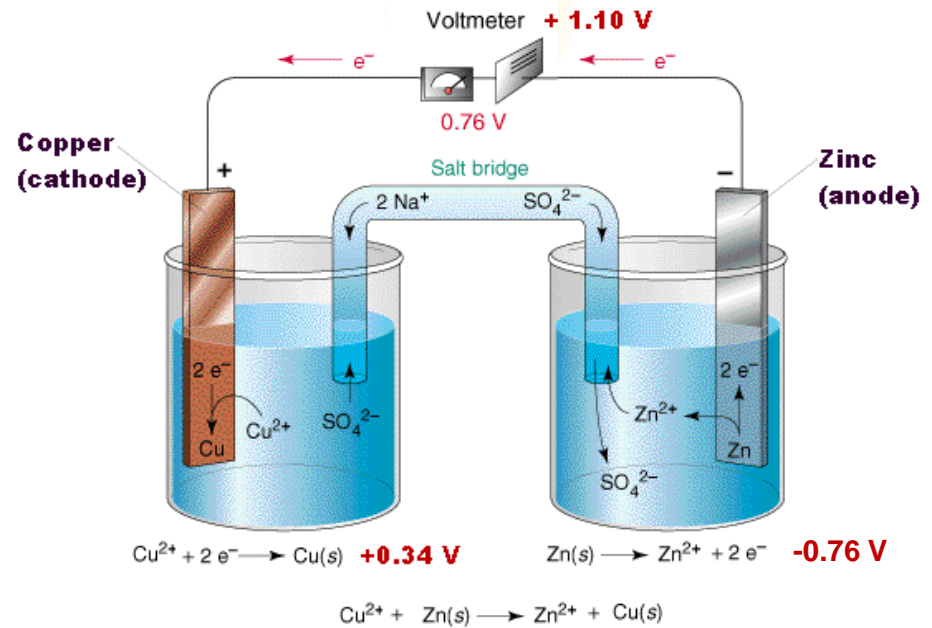
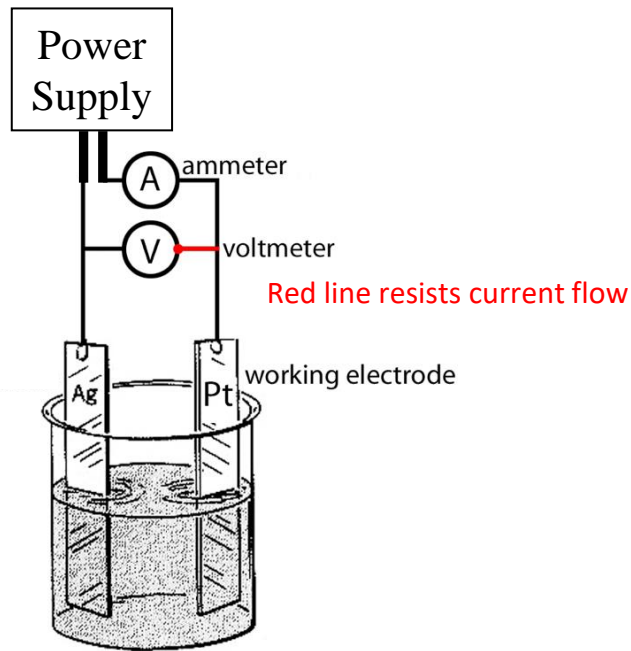
- **Reference electrodes**
- **2-electrode versus 3-electrode measurements**
- *Potentiostats*
- *Compliance voltage/current*
- *J–E and I–E curves*
- *Kinetic overpotential*
- *Electrochemical window*
- *Faradaic reactions*

Although we would like to measure electrochemical observables (e.g. the current, voltage, etc.) associated with a single “working” electrode (WE), we cannot.



We must always couple our working electrode to a second electrode in order to make a measurement. These two electrodes comprise an electrochemical “cell.”

These schematics introduce some terms that we must define:

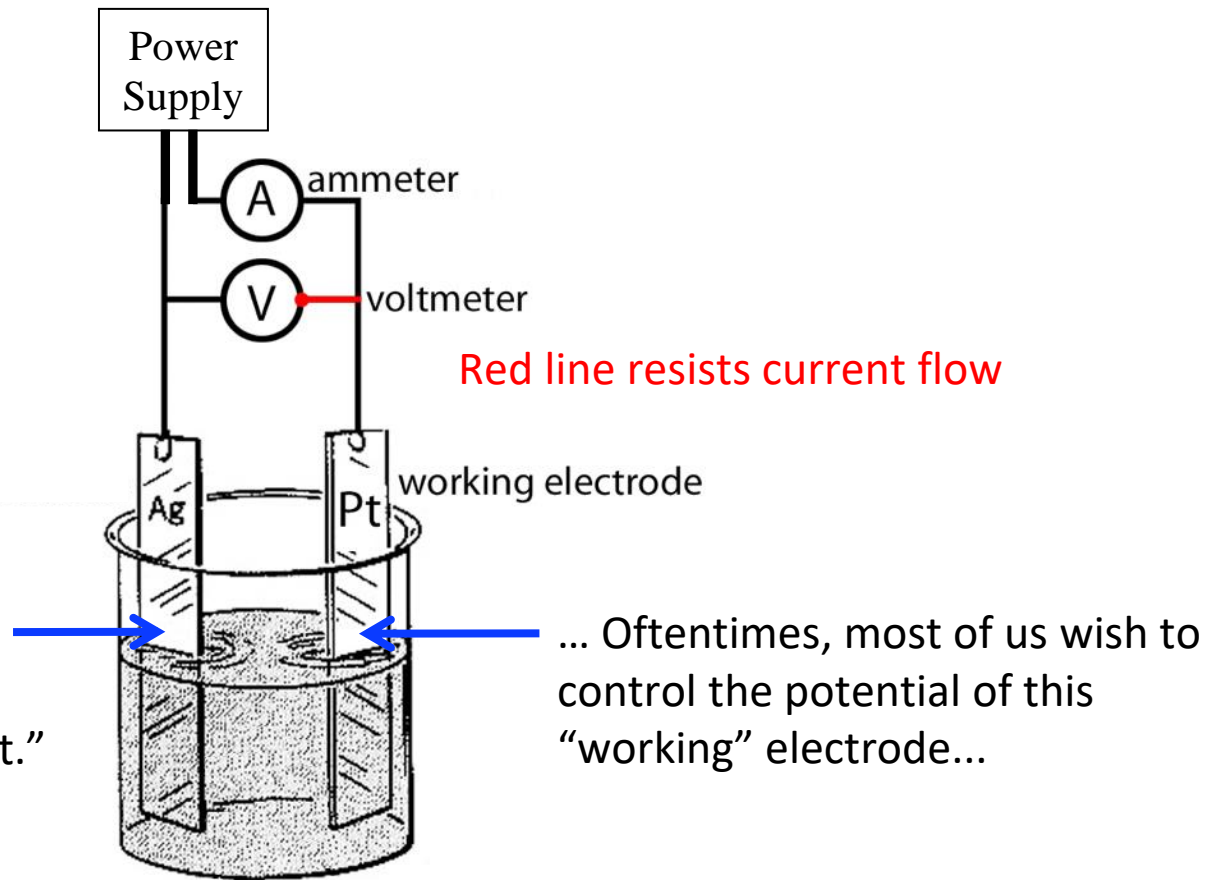


http://chemwiki.ucdavis.edu/Analytical_Chemistry/Electrochemistry/Electrochemistry_2%3A_Galvanic_cells_and_Electrodes

- electrometer – a device for measuring a potential difference (E_{cell}); an ideal voltmeter has infinite input impedance (i.e. it draws no current) (*impedance is “complex resistance”*)
- ammeter – a device for measuring a current; an ideal ammeter has zero input impedance (i.e. it imposes no potential drop)

Experiments:

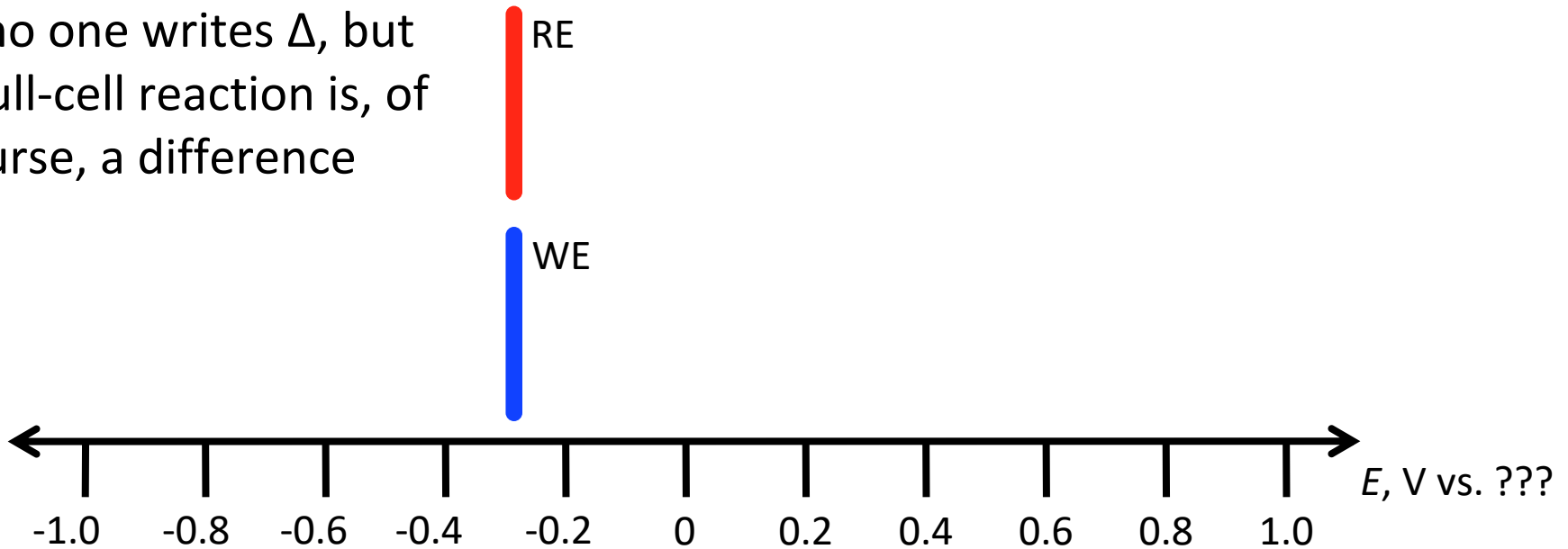
95% of the measurements that you will perform have a problem



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

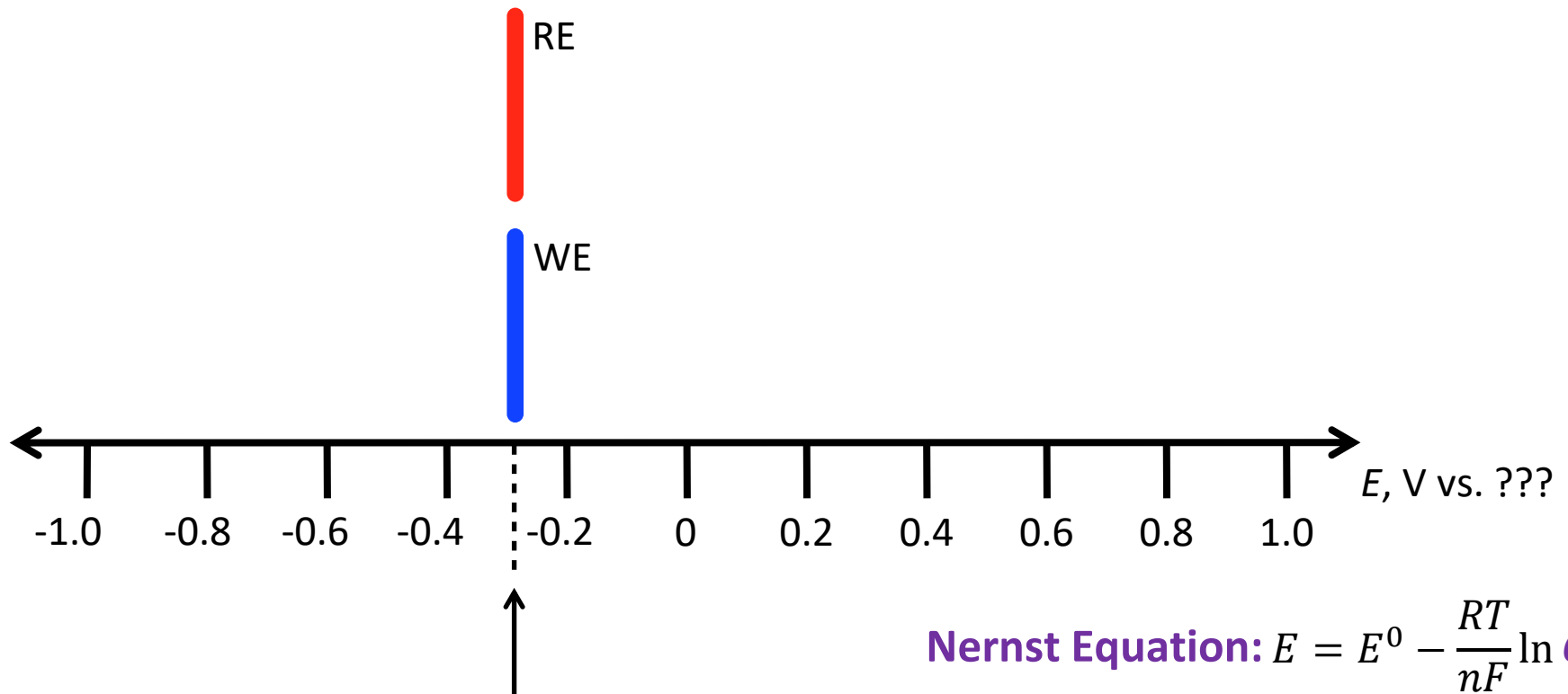
$$\Delta E = 0.0 \text{ V} = E_{WE} - E_{RE}$$

... no one writes Δ , but
a full-cell reaction is, of
course, a difference



... and at “open circuit,” no potential bias is applied between them...
(disconnect the wire!)

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



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

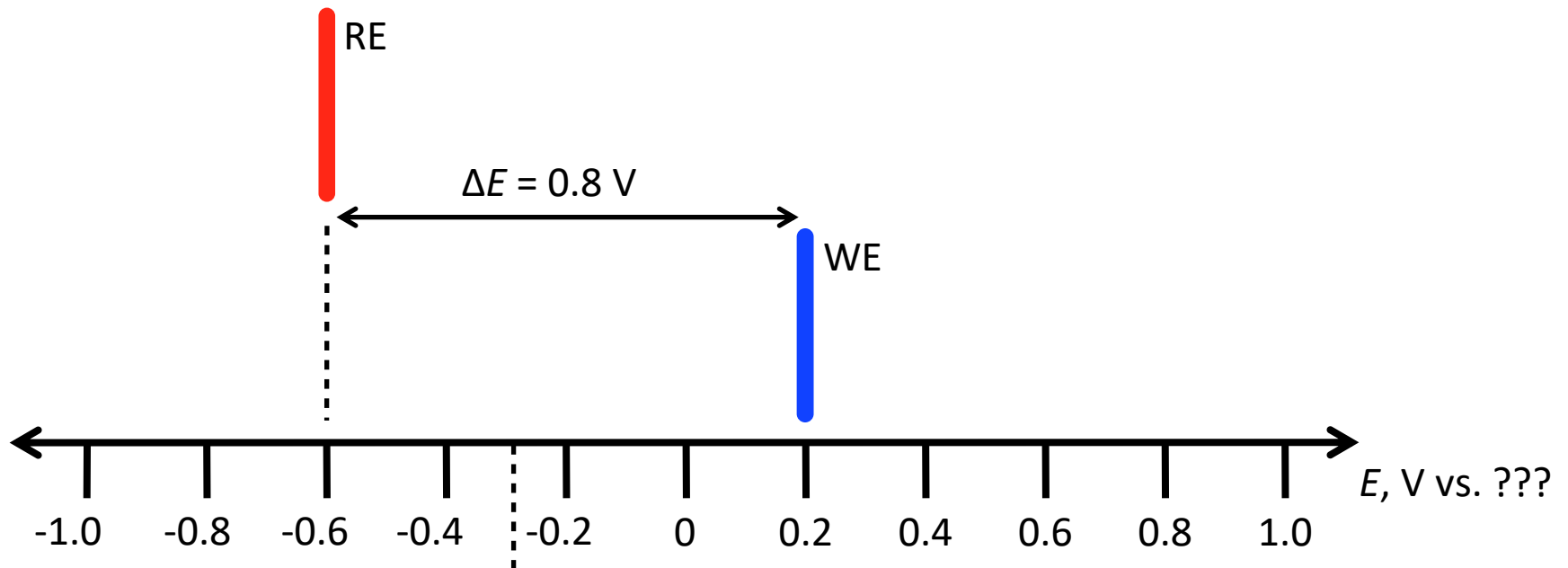
... and it is not well-defined because we cannot answer the question:

What is the half-reaction that defines it?

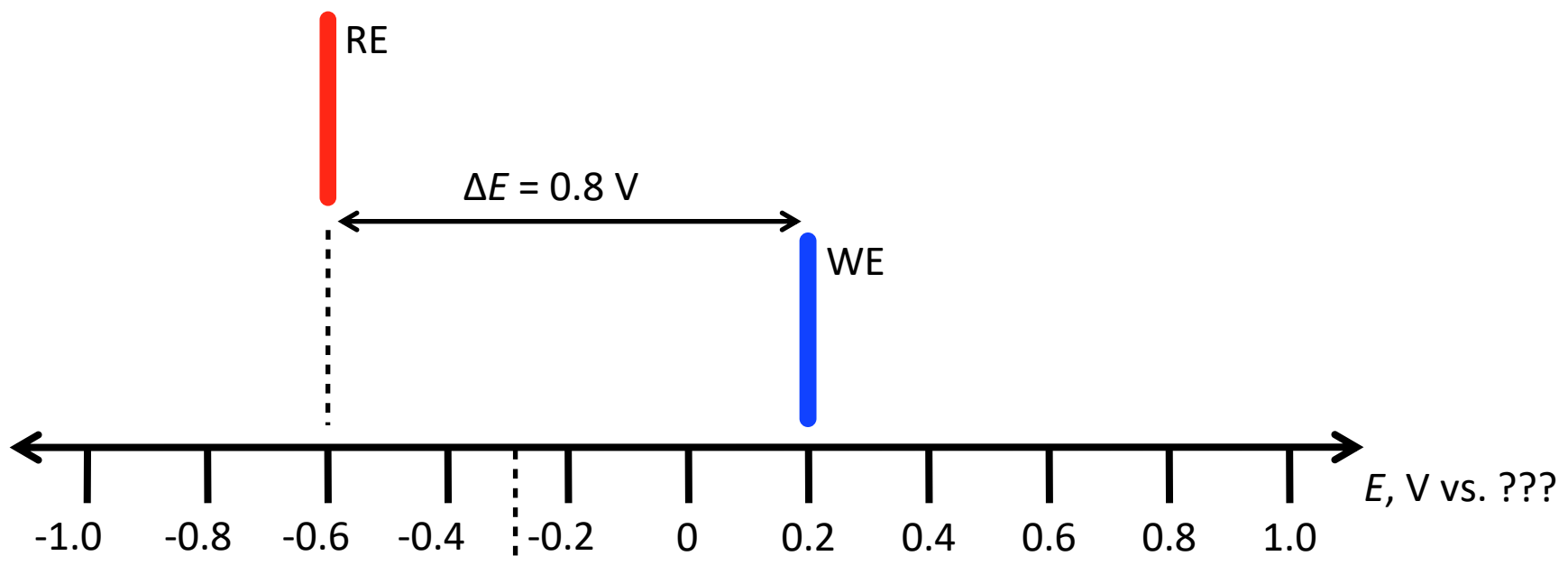
... now, if we apply +0.8 V to the WE (reconnect the wire)...

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

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



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

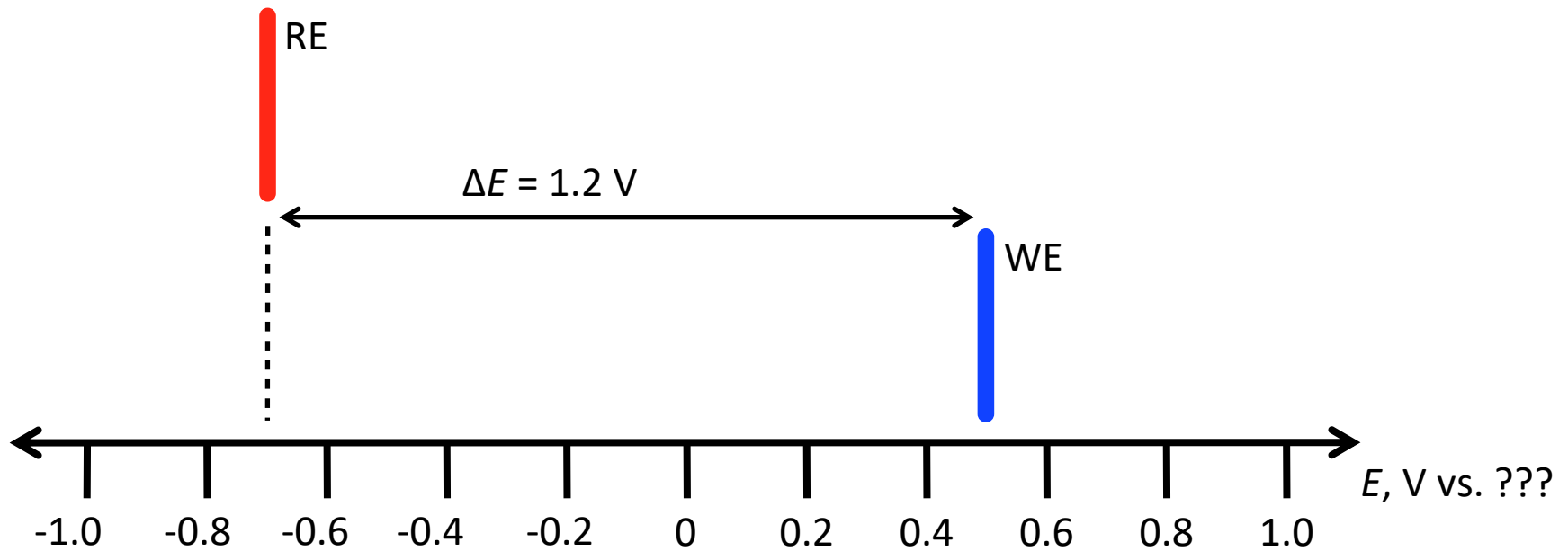


... we don't know *this* potential...

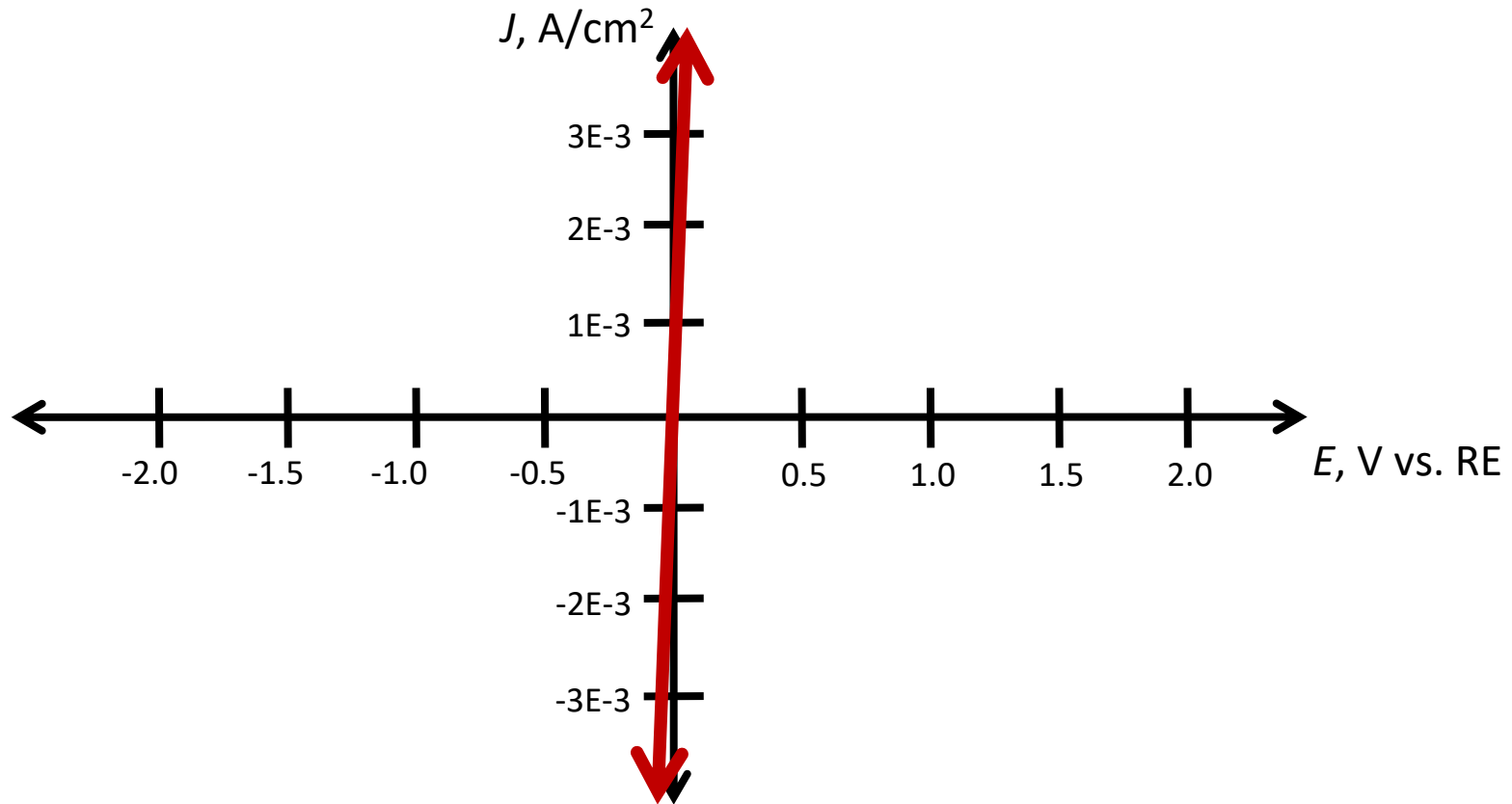
... and we don't know *this* potential!

... you get the picture!

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



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

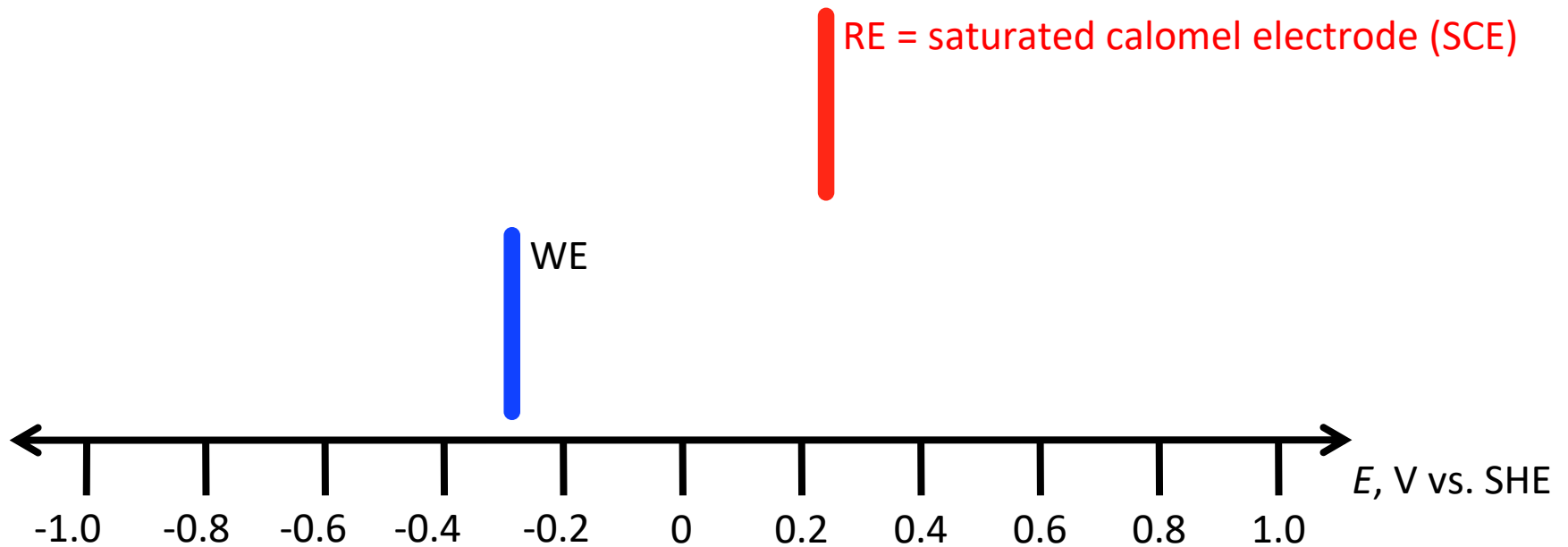


... so get rid of the Pt reference electrode, and substitute in an SCE...

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

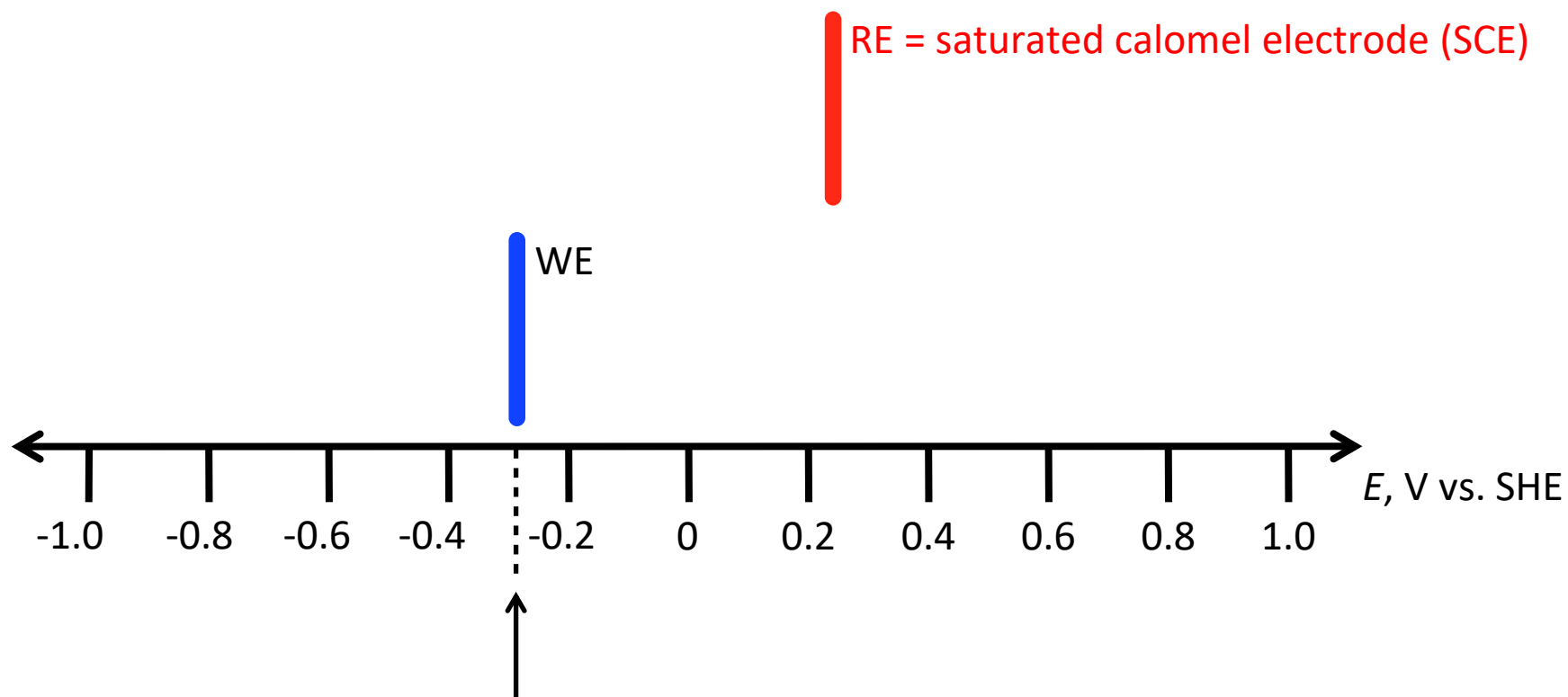
$$\Delta E \neq 0.0 \text{ V (likely)}$$



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

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

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



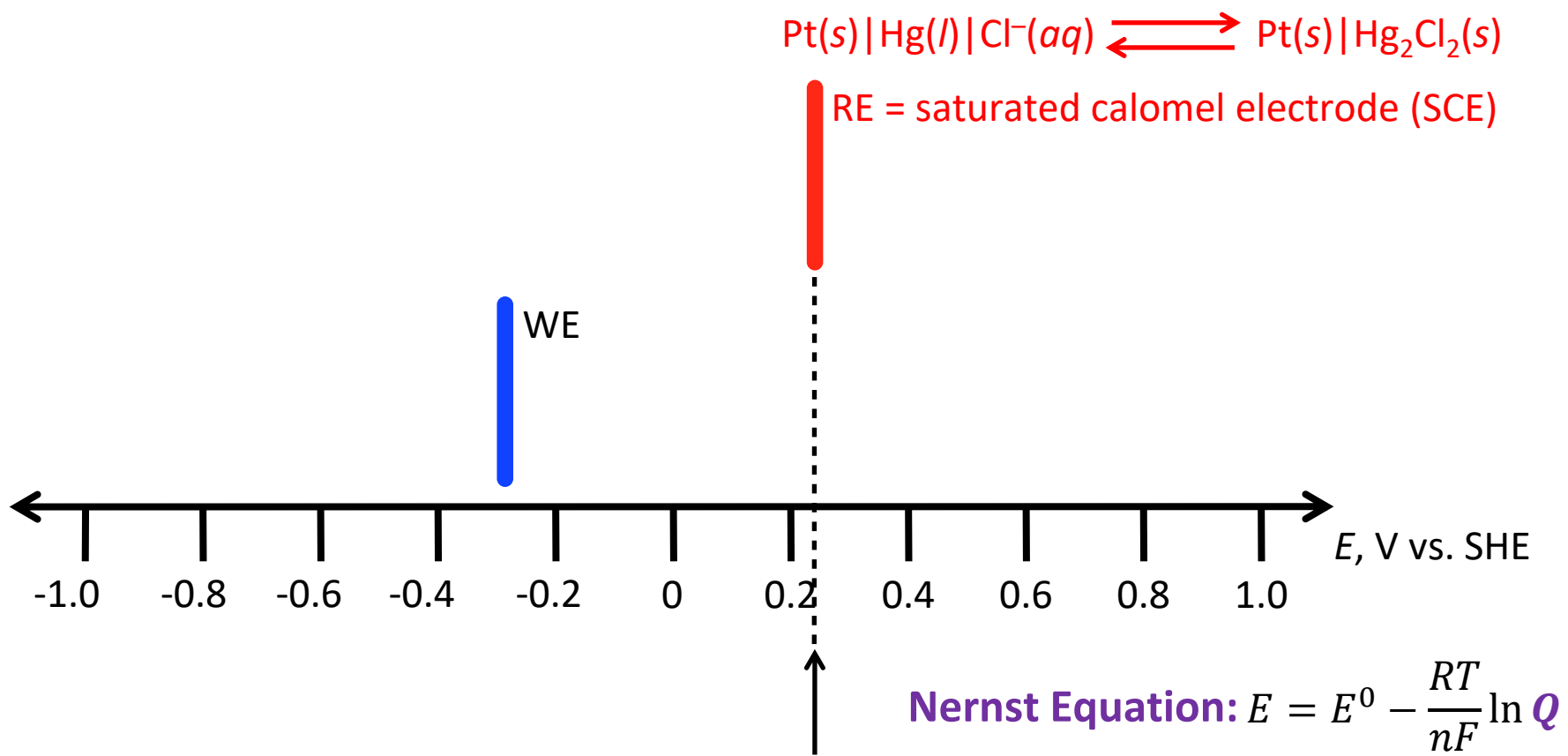
... where we still don't know this potential because we cannot answer:

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...

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

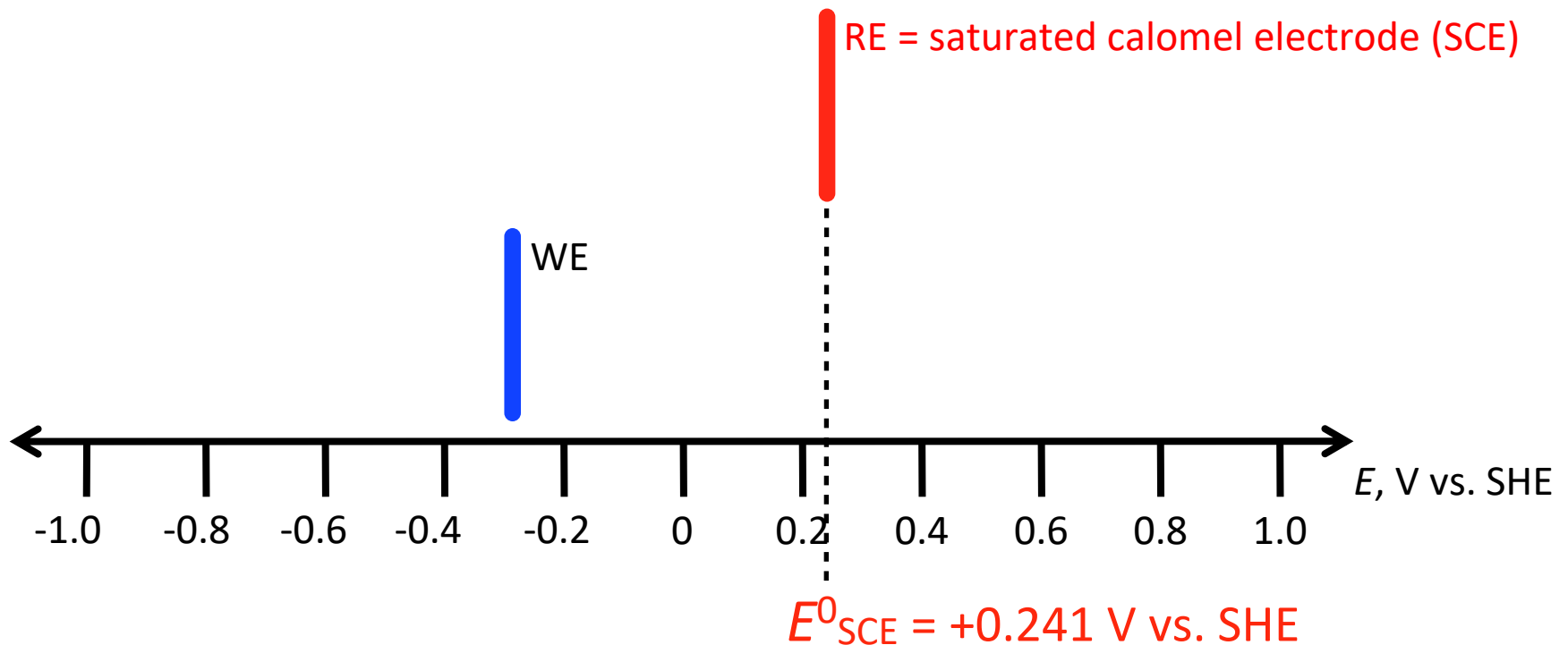


... but, where we know this potential because we can answer:
What is the half-reaction that defines it?

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

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

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

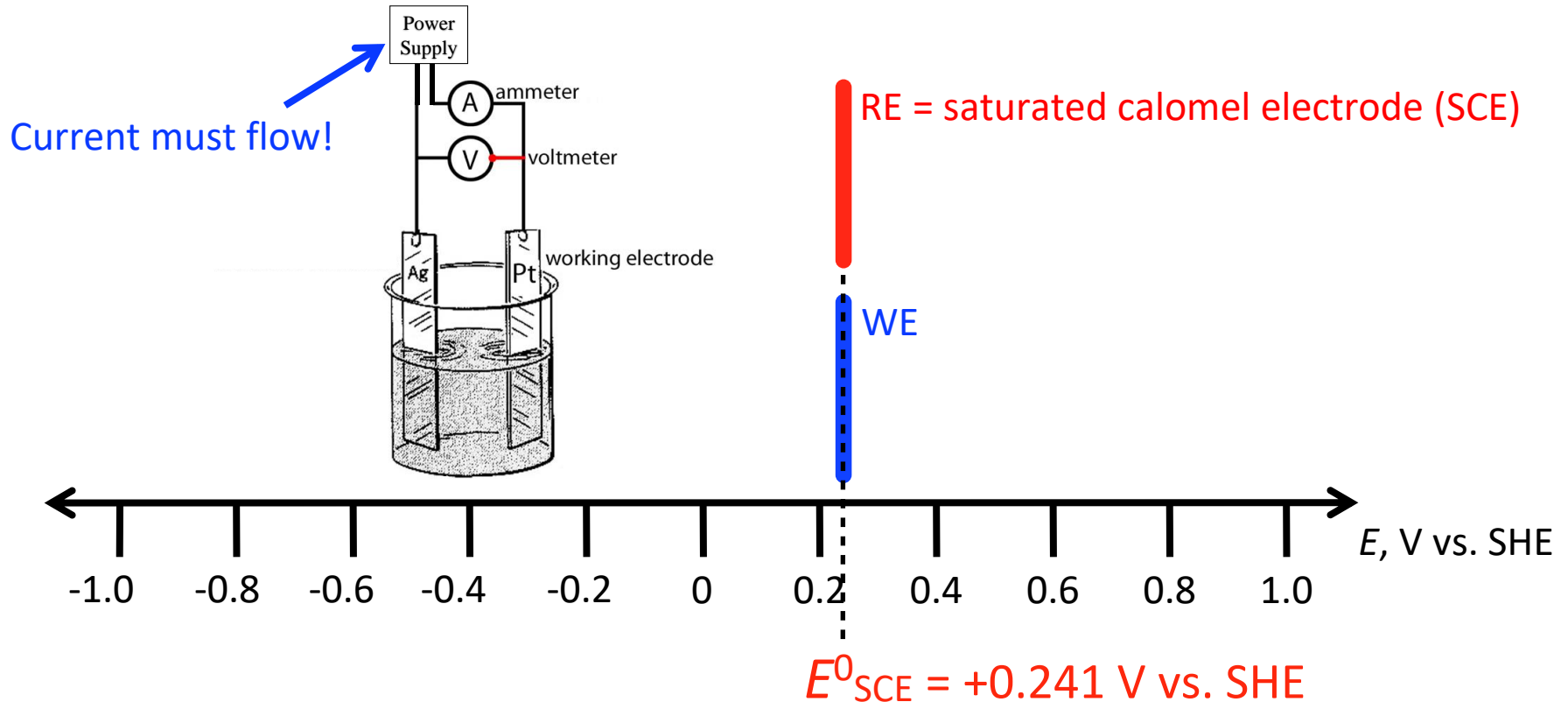


... the SCE has a defined potential of +0.241 V vs. SHE...

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

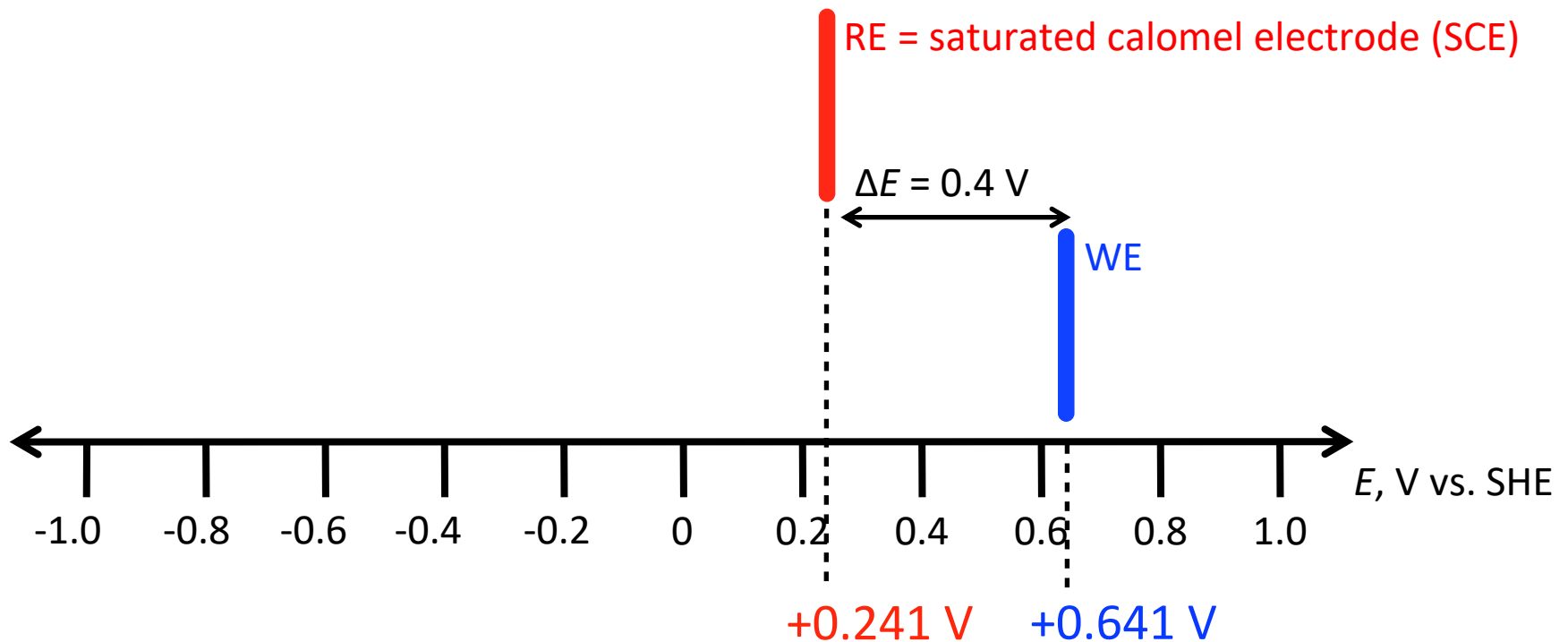
... which has a Pt wire in it...

$$E_{\text{app}} = 0.0 \text{ V} \quad (\text{ammeter} \neq 0 \text{ A})$$



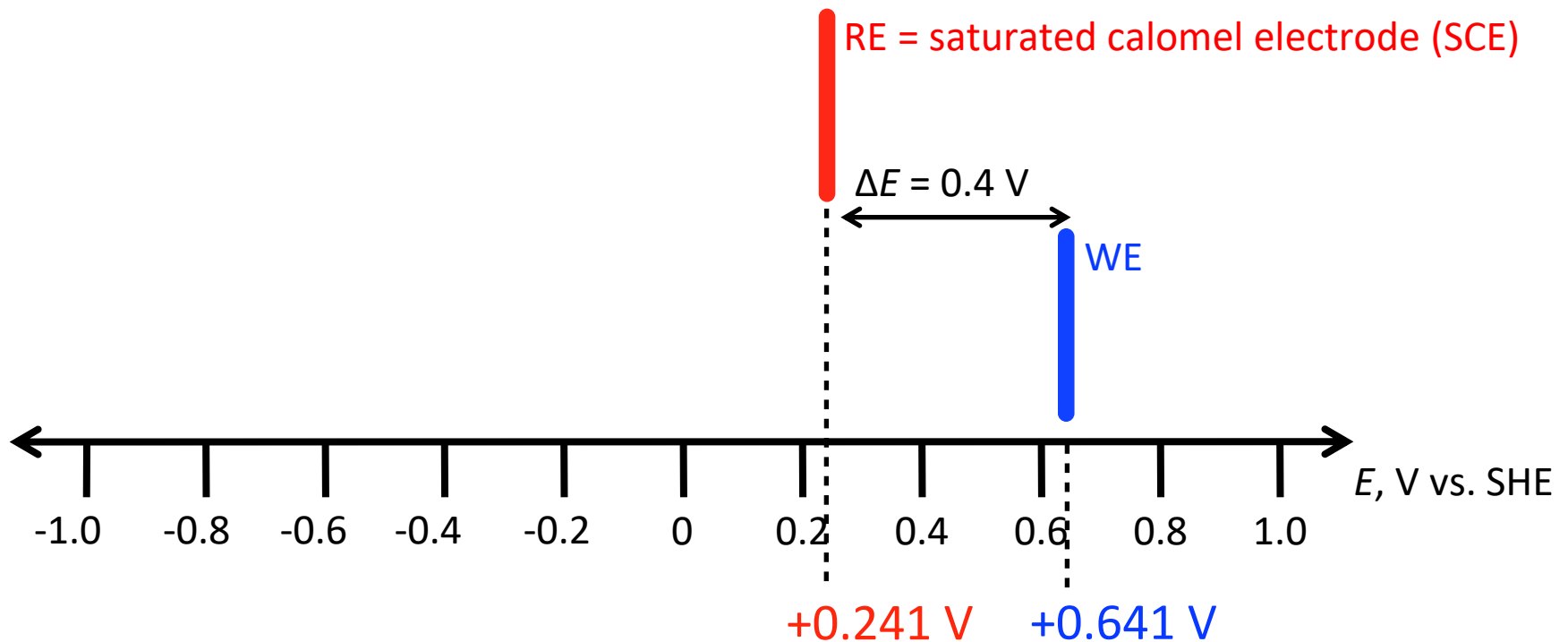
... the SCE has a defined potential of +0.241 V vs. SHE...
 ... and its potential "does not" move (much, usually)...

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



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

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



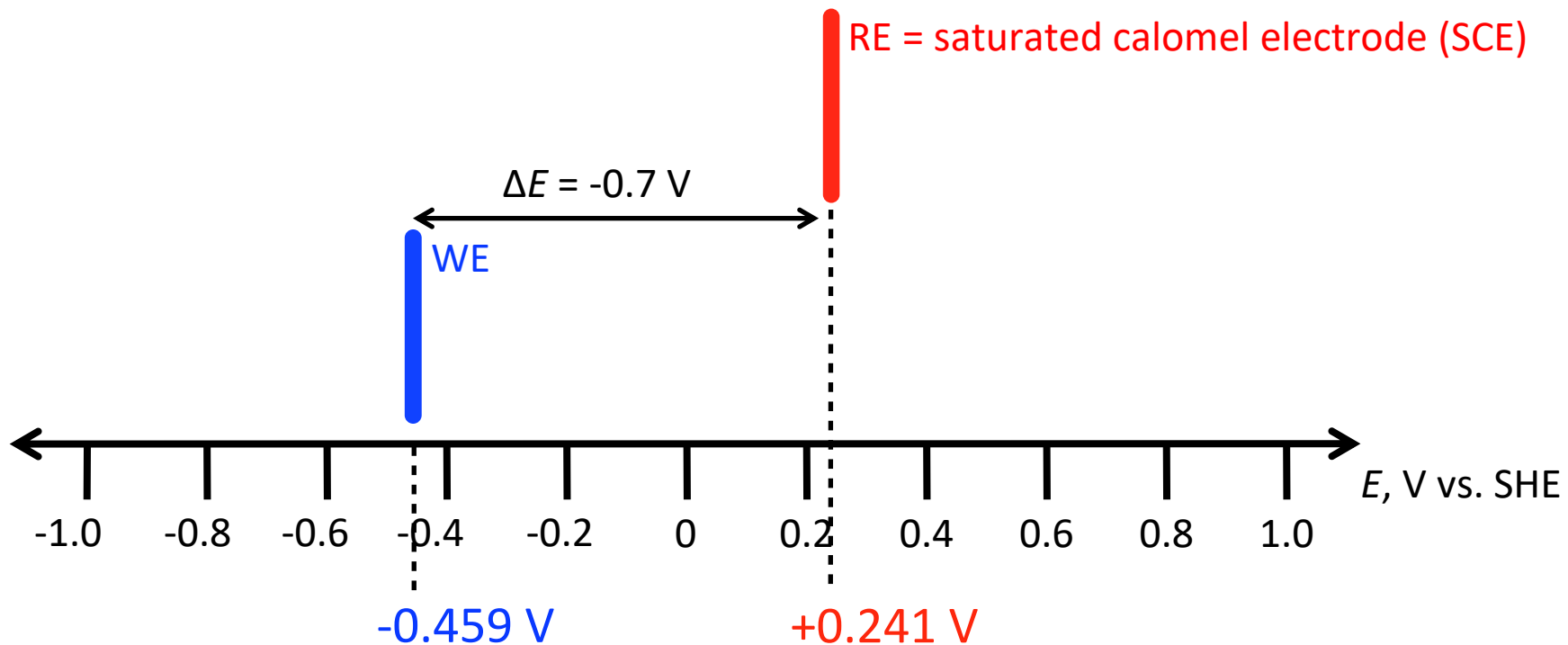
$$\underline{\Delta E} = E_{\text{WE}} - E_{\text{RE}}$$

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

... you get the picture!...

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

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



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

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