Lecture #8 of 17

Measurements in Electrochemistry

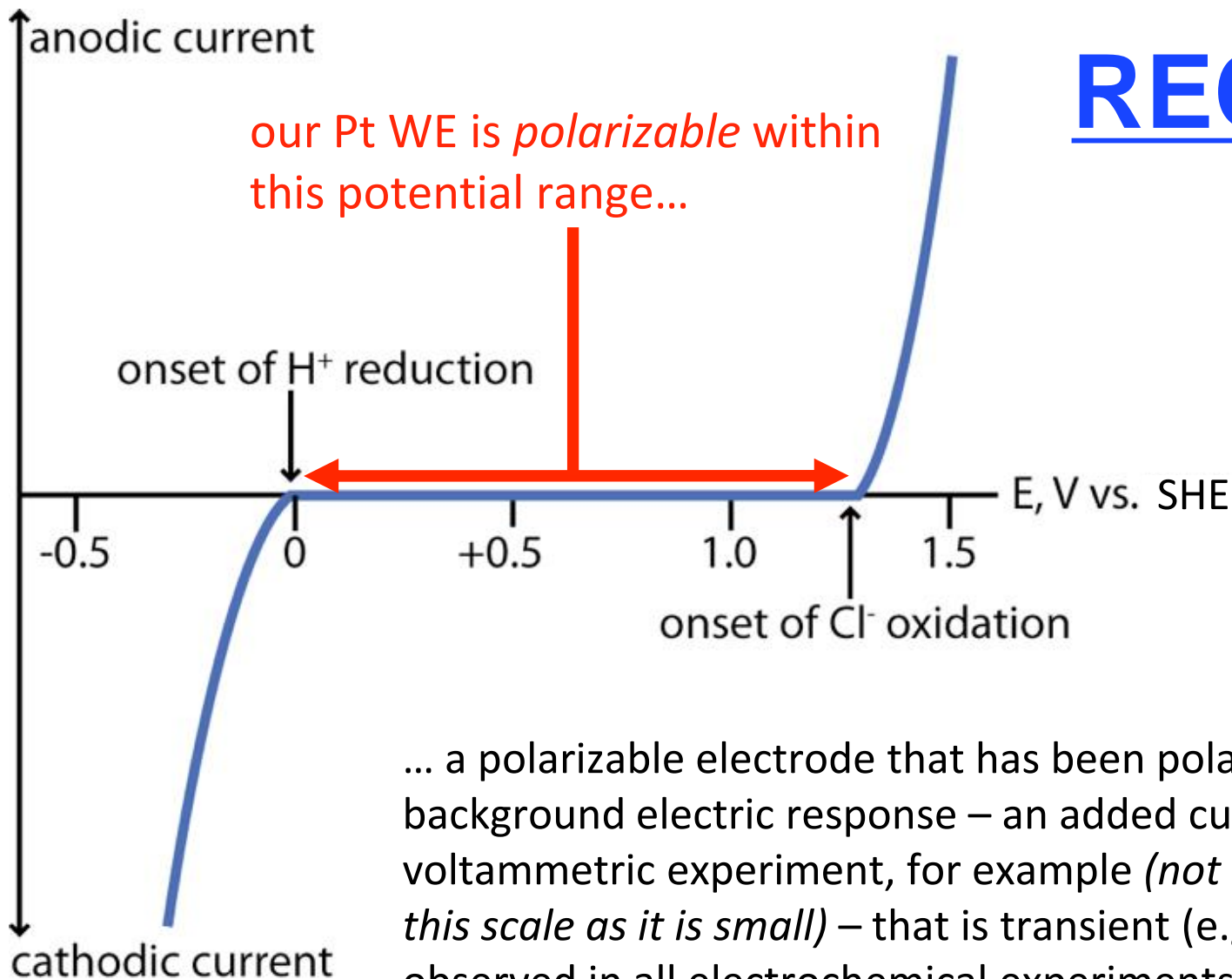## Chapters 1 and 15

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… Sections 1.2 and 1.3

- <u>RC circuits</u> *(~90% of slides) (halfway complete)*

- **Uncompensated resistance (R_u)**

- **Electrochemically active surface area (ECSA)**

- **Luggin–Haber capillary**

- **Placement of electrodes**

RECALL:

anodic current

our Pt WE is *polarizable* within this potential range…

onset of H⁺ reduction

E, V vs. SHE

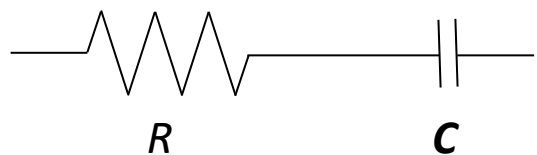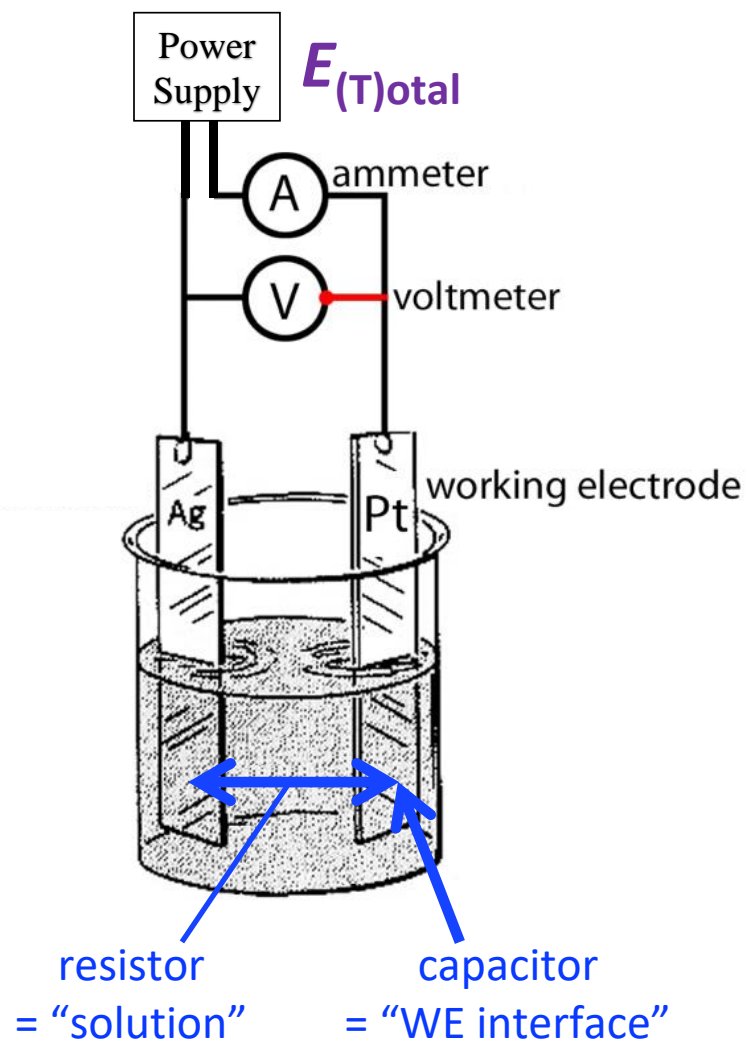-0.5   0   +0.5   1.0   1.5

onset of Cl⁻ oxidation

cathodic current

… a polarizable electrode that has been polarized imposes a background electric response – an added current in a voltammetric experiment, for example *(not observable on this scale as it is small)* – that is transient (e.g. a blip) and is observed in all electrochemical experiments…

*… **We need to understand this background current!***

The electrical response of a polarizable electrode is approximated by a series resistor and capacitor (a series *RC* circuit)…

RECALL:

Power Supply | $E_{(T)otal}$

A — ammeter

V — voltmeter

Ag | Pt — working electrode

resistor = "solution"

capacitor = "WE interface"

R   *C*

$$E_T = E_R + E_C + ...$$

The electrical response of a polarizable electrode is approximated by a series resistor and capacitor (a series *RC* circuit)…
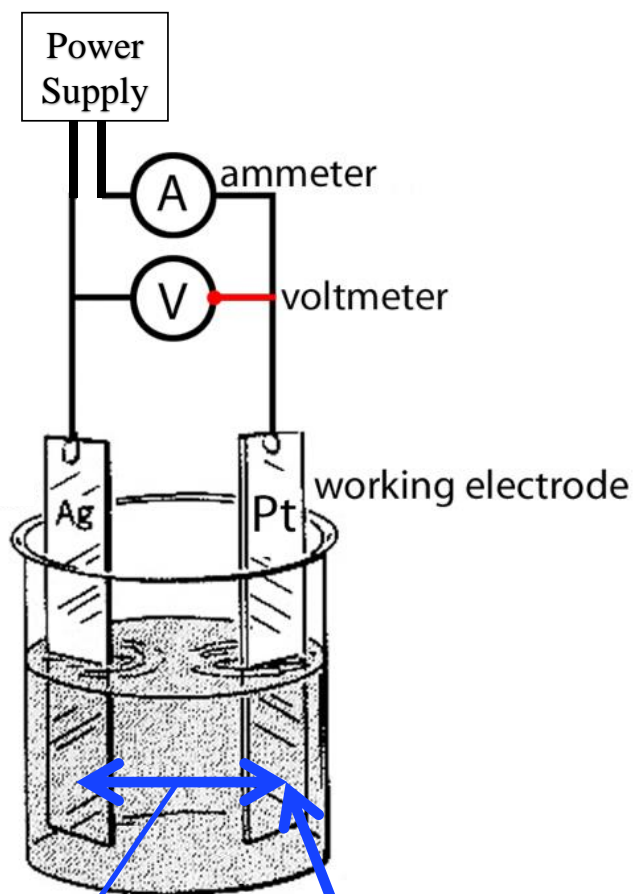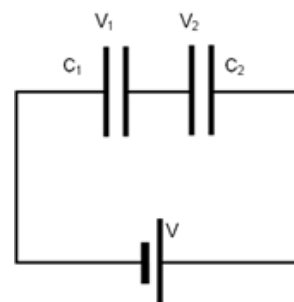
RECALL:

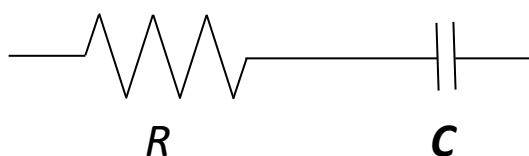R = the solution resistance (between the WE and RE)

Power Supply

ammeter A

voltmeter V

working electrode

Ag   Pt

resistor = "solution"

capacitor = "WE interface"

R C

C = the net capacitance (of the WE and the CE), $C_{(T)otal}$

V_1 V_2

C_1 C_2

V

$$\frac{1}{C_T} = \frac{1}{C_1} + \frac{1}{C_2}$$

… to measure $C_{2(WE)}$, make $C_{1(CE)}$ large… or use a three-electrode setup and a pstat

First, what are approximate values for $R_{(s)}$ and $C_{(d)}$? …

Power Supply

A ammeter

V voltmeter

Ag Pt working electrode

resistor = "solution"

capacitor = "WE interface"

R   C

RECALL:

R = the solution resistance (between the WE and RE)
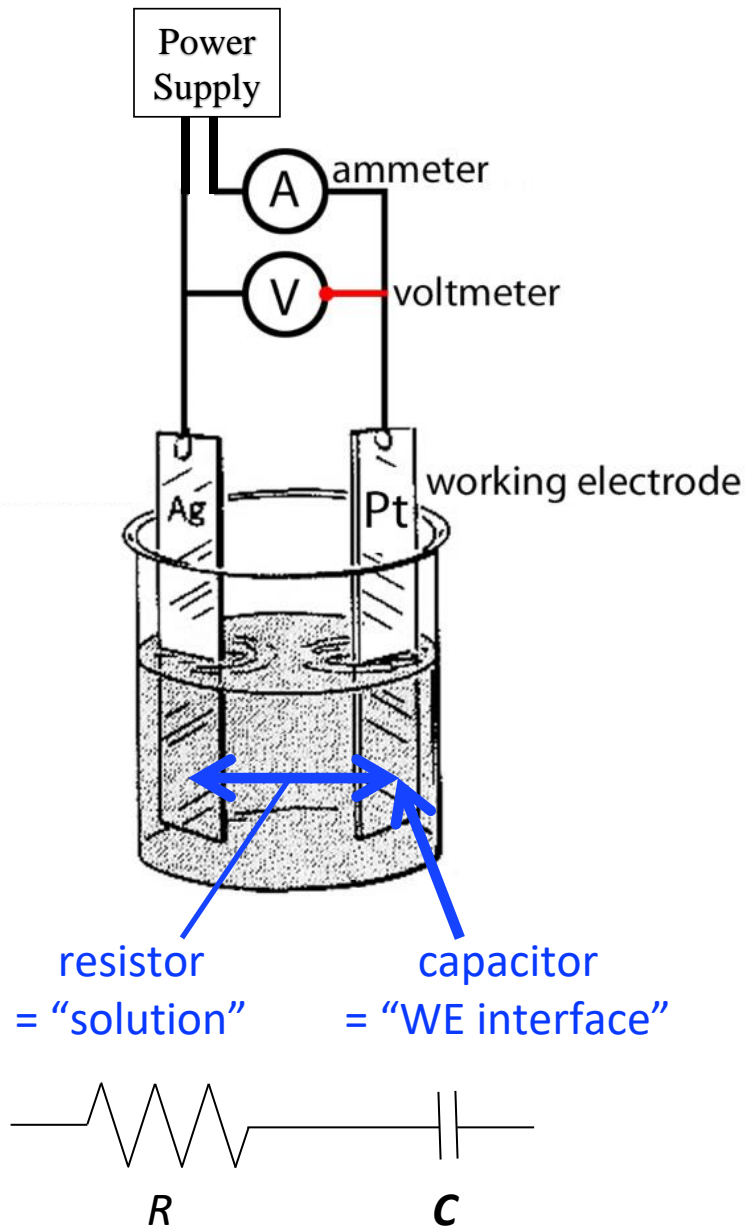
In aqueous solutions containing 0.1 M supporting electrolyte, R = *a few ohms*; for non-aq., R > 100 Ω

C = the net capacitance (of the WE and the RE), $C_{(T)otal}$

~20 µF/cm^2 of electrode area for gold or platinum; 2 – 5 µF/cm^2 for carbon, typically… but these change slightly with potential as we will see later
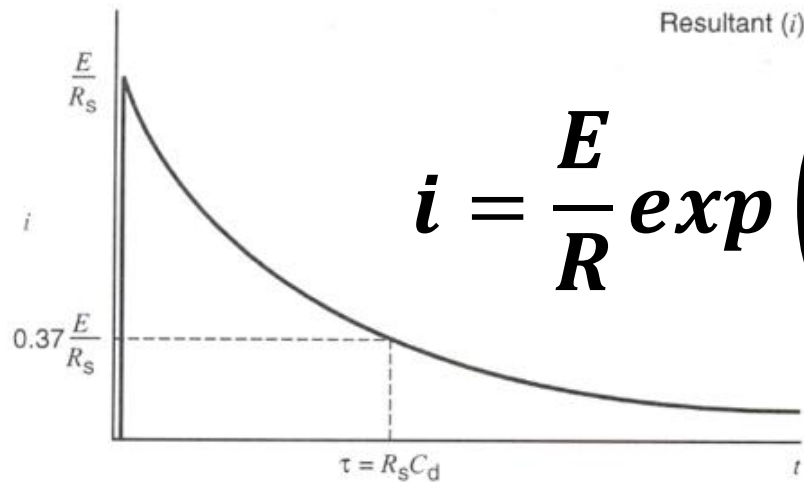
(Farad can be cast as C/V…

… and recall that Volt can be cast as J/C)

1. <u>Potential-step</u> potentiostatic chronoamperometry (chronocoulometry)

Voltage step (that is, increment the potential by an amount, *E*):

$$i = \frac{E}{R} exp\left(\frac{-t}{RC}\right)$$

RECALL:

Could there be a problem with an instantaneous 6 V potential step, for example?

… **Compliance current!**

(at t = 0, E = iR (Ohm's law))

What portion of E_{app} is actually present at the WE to drive interfacaial charge transfer at *t* = 0?
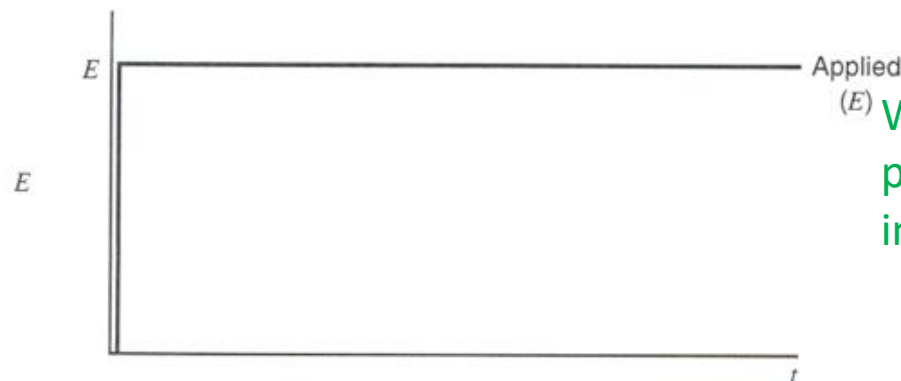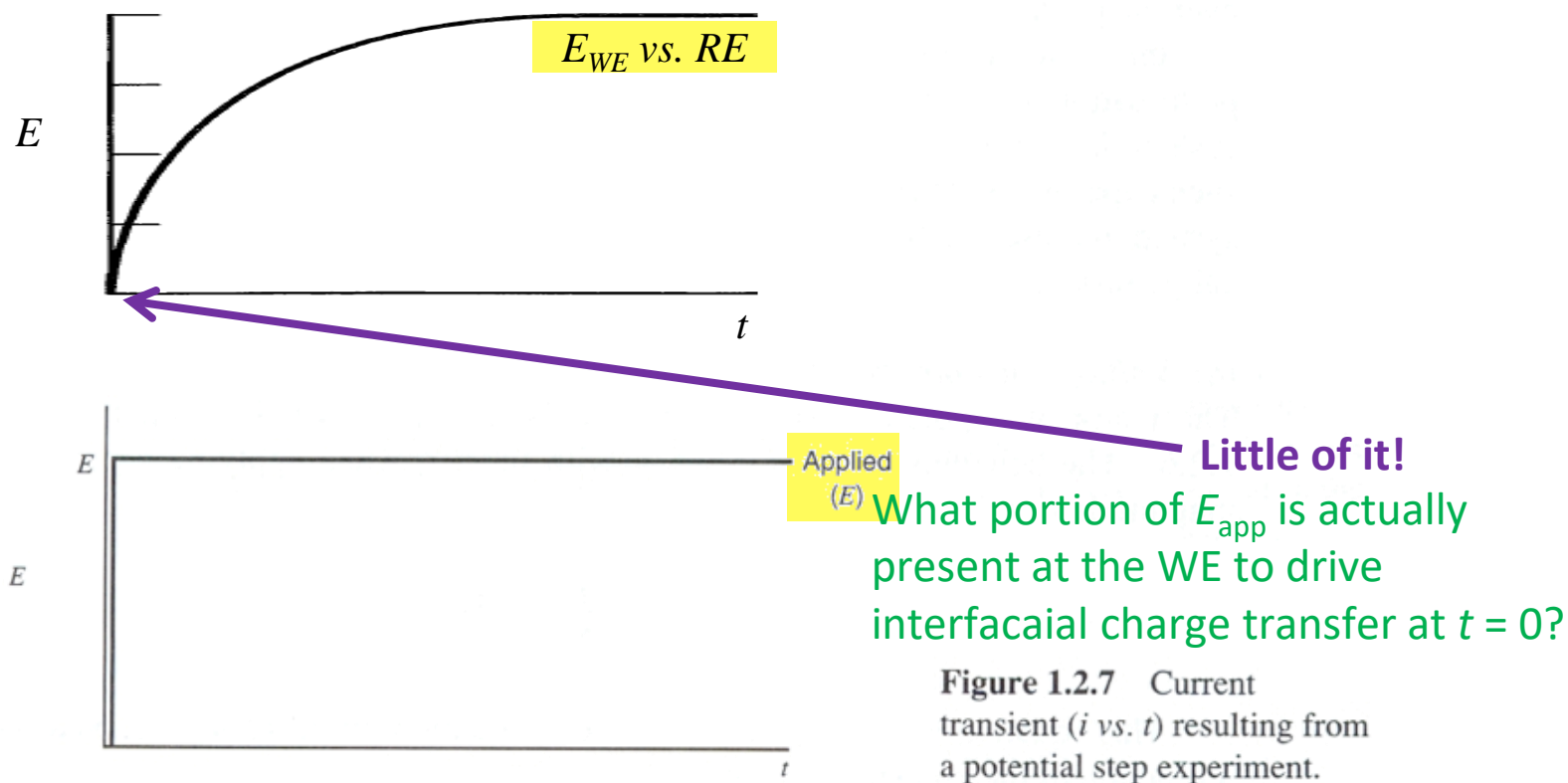
Figure 1.2.7 Current transient (*i vs. t*) resulting from a potential step experiment.

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 1.2.7

1. <u>Potential-step</u> potentiostatic chronoamperometry (chronocoulometry)

Voltage step (that is, increment the potential by an amount, *E*):

<u>NOTE</u>: Electronics can limit the observation of rapid chemical kinetics (i.e. the rate-determining step is charging and not electron transfer)

E_{WE} *vs. RE*

Applied
(E)

Little of it!

What portion of E_{app} is actually present at the WE to drive interfacaial charge transfer at $t = 0$?

Figure 1.2.7 Current transient (*i* vs. *t*) resulting from a potential step experiment.

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 1.2.7

1. <u>Potential-step</u> potentiostatic chronoamperometry (chronocoulometry)

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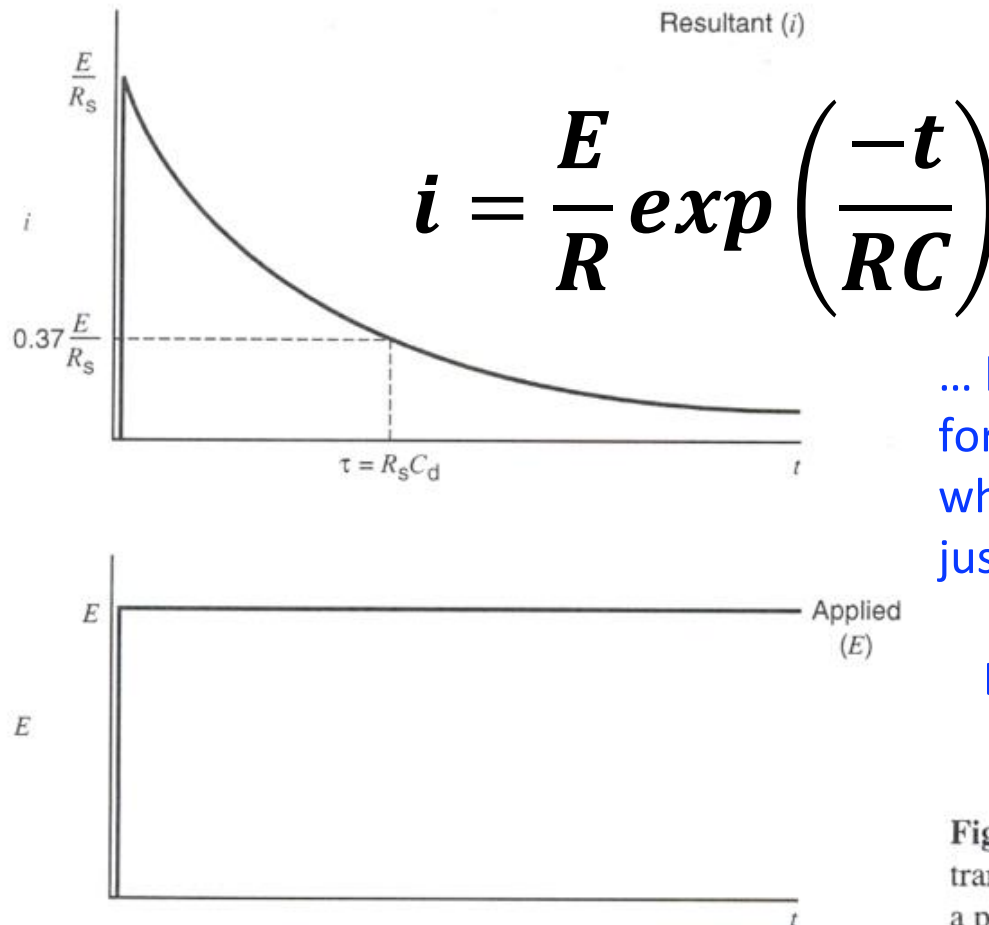
… but where did this equation for current come from? … who's comfortable with me just giving you this equation?

Let's manipulate units!

Figure 1.2.7 Current transient (*i* vs. *t*) resulting from a potential step experiment.

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 1.2.7

1. <u>Potential-step</u> potentiostatic chronoamperometry (chronocoulometry)

Voltage step (that is, increment the potential by an amount, *E*):

B&F eqn. (1.2.8)

$$E = E_R + E_C = \boldsymbol{i}R_s + \frac{q}{C_d}$$
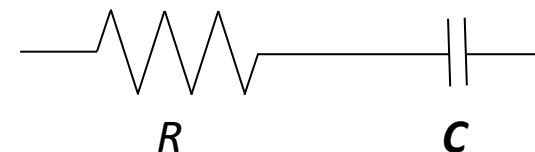
Units: C

Units: C/V

B&F eqn. (1.2.9)

$$\boldsymbol{i} = \frac{1}{R_s}\left(E - \frac{q}{C_d}\right) = \frac{dq}{dt}$$

Units: C/s

Need to integrate!

$E_T = E_R + E_c + ...$

$$\frac{1}{R_s}dt = \frac{1}{E - \frac{q}{C_d}}dq = \frac{-C_d}{-EC_d + q}dq$$

$$-\frac{1}{R_s C_d}t = \ln|-EC_d + q| - \ln|-EC_d| = \ln\left|\frac{-EC_d + q}{-EC_d}\right|$$

(assuming that at *t* = 0, *q* = 0)

Integrated!

Now, what response is obtained for various inputs to this circuit?

1. <u>Potential-step</u> potentiostatic chronoamperometry (chronocoulometry)

Voltage step (that is, increment the potential by an amount, E):

$$-\frac{1}{R_s C_d} t = \ln|-EC_d + q| - \ln|-EC_d| = \ln\left|\frac{-EC_d + q}{-EC_d}\right|$$

Integrated!

$$-EC_d e^{-\frac{t}{R_s C_d}} = -EC_d + q$$

$$\boldsymbol{q = EC_d \left(1 - e^{-\frac{t}{R_s C_d}}\right)}$$

B&F eqn. (1.2.10)

Now, what response is obtained for various inputs to this circuit?

1. <u>Potential-step</u> potentiostatic chronoamperometry (chronocoulometry)

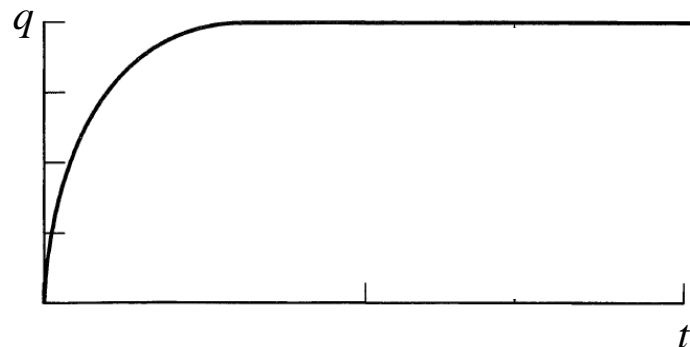Voltage step (that is, increment the potential by an amount, E):

$$-\frac{1}{R_s C_d} t = \ln|-EC_d + q| - \ln|-EC_d| = \ln\left|\frac{-EC_d + q}{-EC_d}\right|$$

Integrated!

$$-EC_d e^{-\frac{t}{R_s C_d}} = -EC_d + q$$

$$\boldsymbol{q = EC_d \left(1 - e^{-\frac{t}{R_s C_d}}\right)}$$
  B&F eqn. (1.2.10)

Need to differentiate!

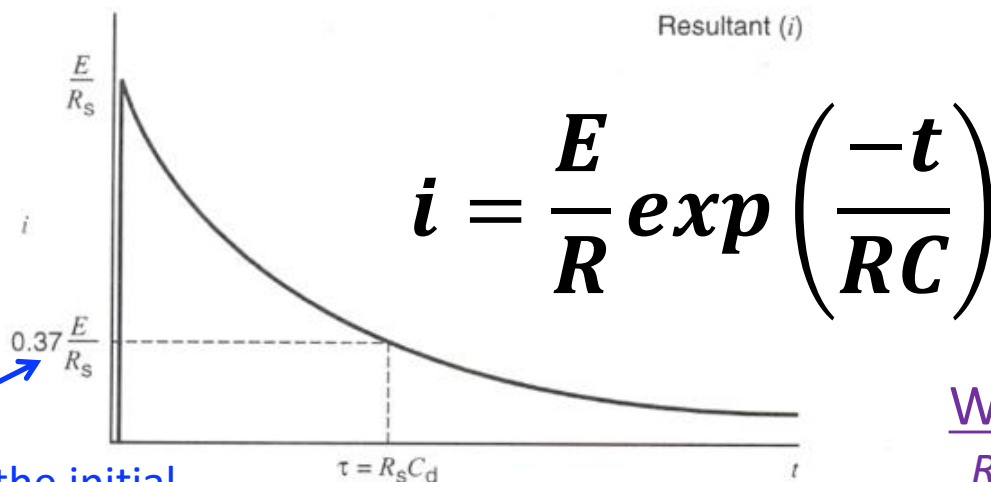$$\frac{dq}{dt} = EC_d\left(\frac{1}{R_s C_d} e^{-\frac{t}{R_s C_d}}\right) = \frac{E}{R_s} e^{-\frac{t}{R_s C_d}} = \boldsymbol{i}$$ **B&F eqn. (1.2.6)**

Done!

1. <u>Potential-step</u> potentiostatic chronoamperometry (chronocoulometry)

Voltage step (that is, increment the potential by an amount, *E*):

$$i = \frac{E}{R} exp\left(\frac{-t}{RC}\right)$$

Resultant (*i*)

Why is 37% of the initial signal noteworthy?

Plug in *t* = RC!
    … Ah ha!
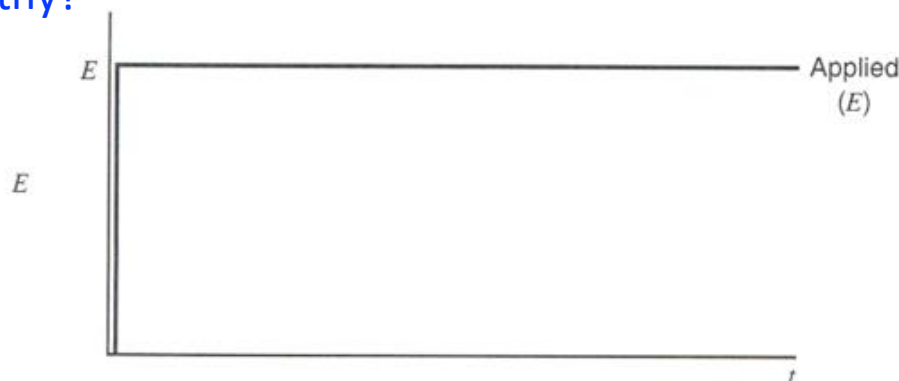
$\tau = R_s C_d$

Applied (*E*)

What are the units of *RC*?
  R (Ω) x *Cap* (F)
  R (V / C/s) x *Cap* (C/V)
  R·Cap (V-s/C x C/V)
  R·Cap (s)!

Figure 1.2.7 Current transient (*i* vs. *t*) resulting from a potential step experiment.
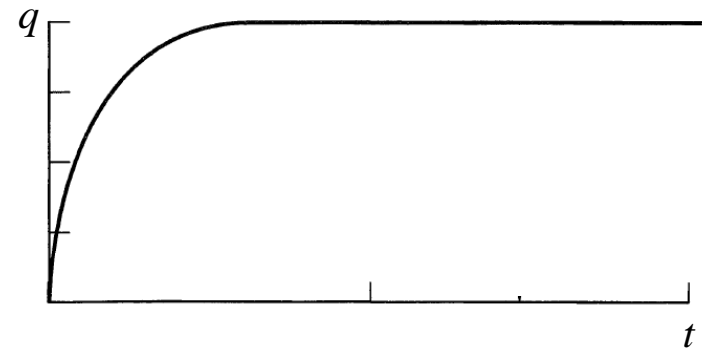
Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 1.2.7

1. <u>Potential-step</u> potentiostatic chronoamperometry (chronocoulometry)

Example: Consider the case where R = 1 Ω and C = 20 μF/cm^2.
How long will it take to charge C to 95% of its maximum capacity?

$$q = EC_d \left(1 - e^{-\frac{t}{R_sC_d}}\right)$$ **B&F eqn. (1.2.10)**

$$q_{t\to\infty} = EC_d$$

Example: Consider the case where R = 1 Ω and C = 20 µF/cm². How long will it take to charge C to 95% of its maximum capacity?

$$q = EC_d \left(1 - e^{-\frac{t}{R_s C_d}}\right)$$ **B&F eqn. (1.2.10)**

$$q_{t \to \infty} = EC_d$$

$$\frac{q}{q_{t \to \infty}} = 1 - e^{-\frac{t}{R_s C_d}}$$

$$0.95 = 1 - e^{-\frac{t_{0.95}}{R_s C_d}}$$

$$0.05 = e^{-\frac{t_{0.95}}{R_s C_d}}$$

$$\ln 0.05 = -\frac{t_{0.95}}{R_s C_d}$$

assuming 1 cm²

$$t_{0.95} = -(1\Omega)(20\mu F)\ln(0.05)$$
$$= \mathbf{60\mu s}$$

Example: Consider the case where $R = 1\ \Omega$ and $C = 20\ \mu F/cm^2$. How long will it take to charge C to 95% of its maximum capacity?

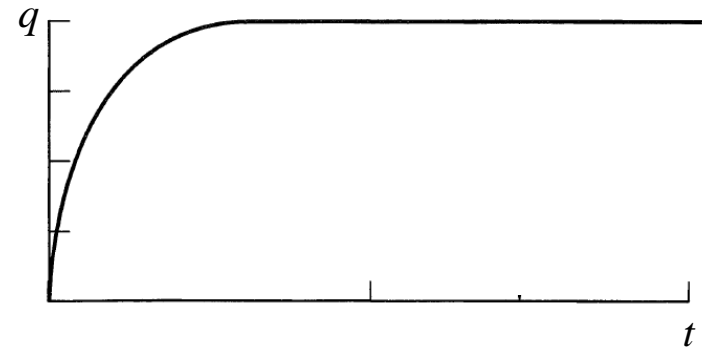$$q = EC_d\left(1 - e^{-\frac{t}{R_sC_d}}\right)$$

B&F eqn. (1.2.10)

$$q_{t\to\infty} = EC_d$$

As above, assuming a 6 V potential step, now what is the *average* current that flows up to $t_{0.95}$?

$$\frac{q}{q_{t\to\infty}} = 1 - e^{-\frac{t}{R_sC_d}}$$

$$0.95 = 1 - e^{-\frac{t_{0.95}}{R_sC_d}}$$

$I_{avg} = C/_s = {(C/V \times V)}/_s$

$\approx 20\ \mu F \times 6\ V\ /\ 60\ \mu s$

$\approx 120\ \mu C\ /\ 60\ \mu s$

$\approx$ **2 A! Compliance?**

$$0.05 = e^{-\frac{t_{0.95}}{R_sC_d}}$$

assuming 1 cm²

$$\ln 0.05 = -\frac{t_{0.95}}{R_sC_d}$$

$$t_{0.95} = -(1\Omega)(20\mu F)\ln(0.05)$$
$$= \boxed{60\mu s}$$

2. Current-step galvanostatic chronopotentiometry

Current step (that is, increment the current by an amount, i):
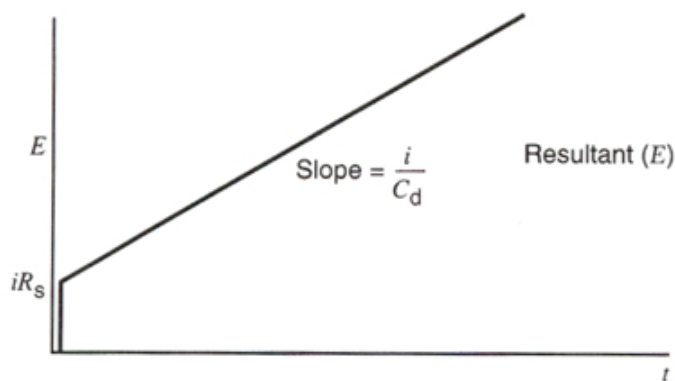
$$E = i\left(R + \frac{t}{C}\right)$$

B&F eqn. (1.2.12)

… So, a constant applied current results in a linear "sweep" of the potential…
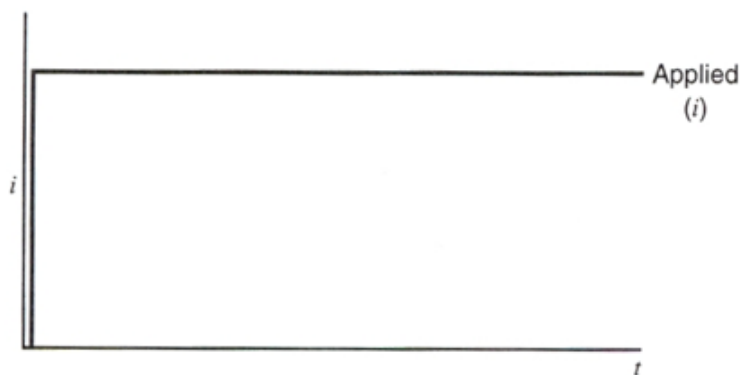   **… thus, what if we flipped this and instead applied a potential "sweep"?**

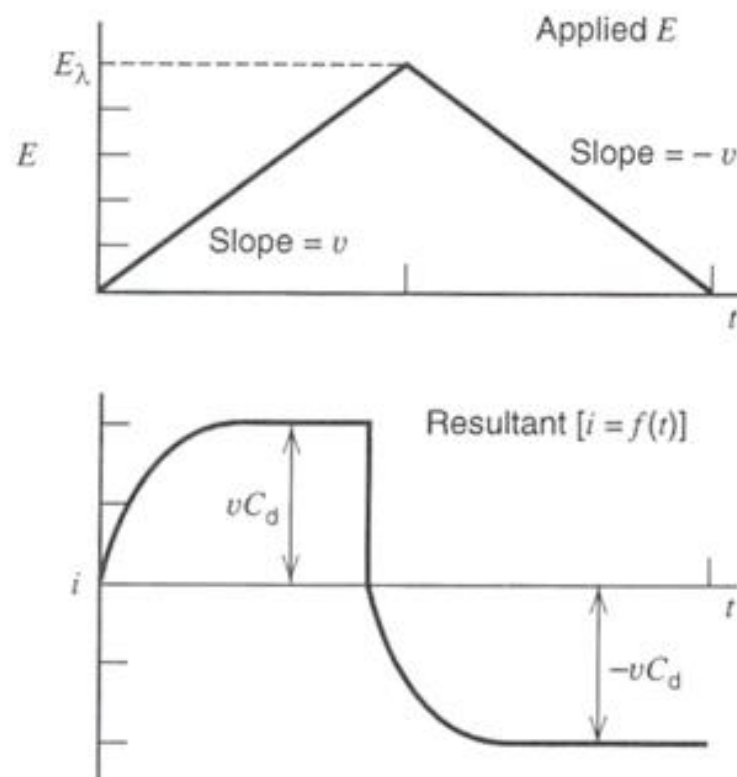**Figure 1.2.9**   *E-t* behavior resulting from a current step experiment.

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 1.2.9

3. <u>Linear-sweep</u> voltammetry…
   <u>cyclic</u> voltammetry

   Potential scan (that is, ramp the
   applied potential, $E(t) = vt$ for one
   direction): scan rate

$$i = vC_d \left[1 - exp\left(\frac{-t}{R_S C_d} \right) \right]$$

B&F eqn. (1.2.15)

Applied E

E_λ Slope $= -v$

E Slope $= v$ t

Resultant $[i = f(t)]$

vC_d

$-vC_d$ t

ASIDE: Recall, for a potential step, the same shape but for charge (q (C))

$$q = EC_d \left(1 - e^{-\frac{t}{R_S C_d}} \right)$$

B&F eqn. (1.2.10)

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 1.2.11

3. <u>Linear-sweep</u> voltammetry… <u>cyclic</u> voltammetry

Potential scan (that is, ramp the applied potential, E(t) = $v t$ for one direction): scan rate

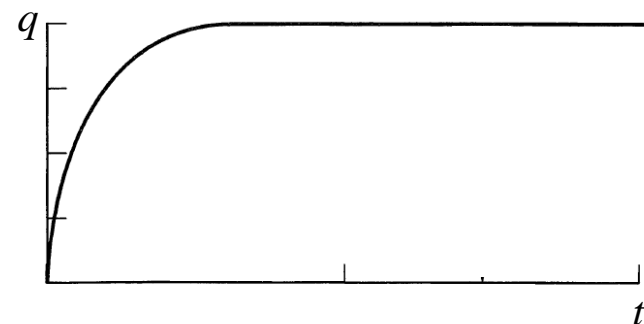$$i = v C_d \left[1 - exp\left(\frac{-t}{R_S C_d} \right) \right]$$

B&F eqn. (1.2.15)

So the total current "envelope" at any potential that is well-removed from the switching potential will be: i = $2 C_d v$, with v's units being V/s
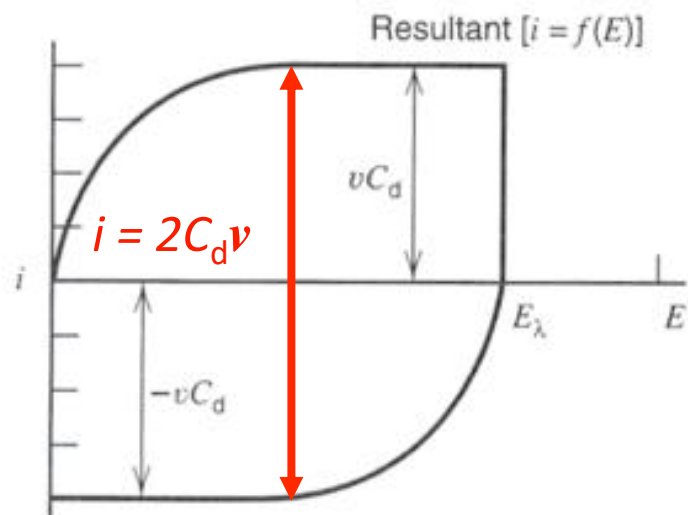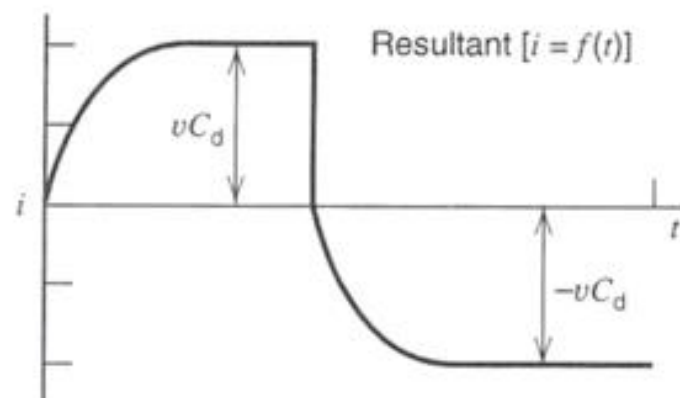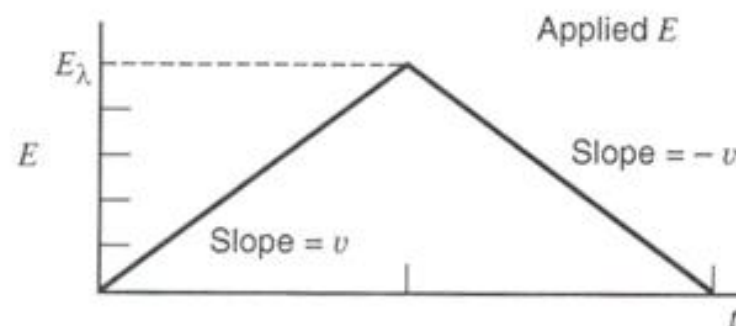
Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 1.2.11

Applied E
Slope = $- v$
Slope = v

Resultant [$i = f(t)$]
$v C_d$
$-v C_d$

Resultant [$i = f(E)$]
$i = 2C_d v$
$v C_d$
E_λ
$-v C_d$

Figure
plots r
triangu

3. <u>Linear-sweep</u> voltammetry...
   <u>cyclic</u> voltammetry
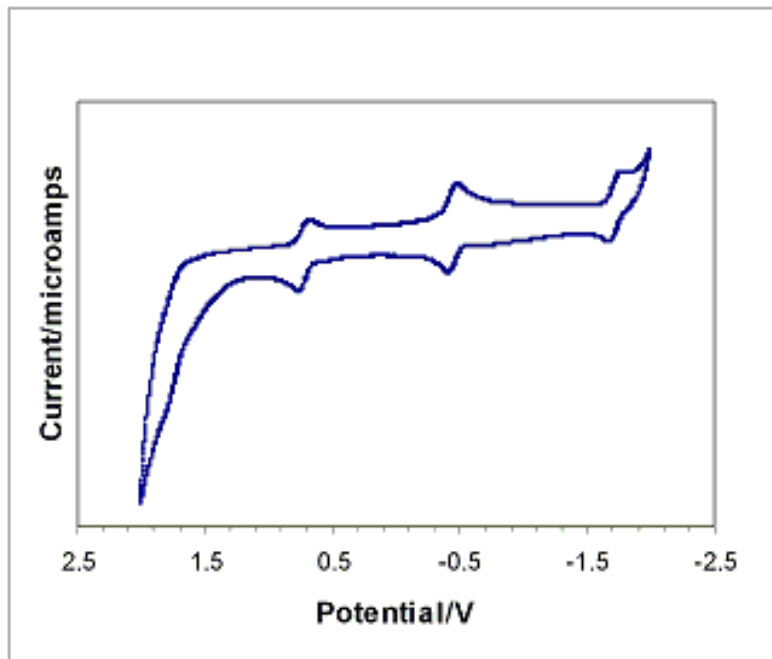
This is an example of a cyclic voltammogram with obvious RC charging

Applied E

Resultant $[i = f(t)]$

Resultant $[i = f(E)]$

$i = 2C_d v$

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 1.2.11

3. Linear-sweep voltammetry...
   cyclic voltammetry

Applied E

E_λ

Slope = $-v$

Slope = v

Resultant $[i = f(t)]$

vC_d

$-vC_d$

Resultant $[i = f(E)]$

vC_d

$i = 2C_dv$

$-vC_d$

E_λ E

Yuck! ... What can we do experimentally to decrease the magnitude of the resulting non-Faradaic capacitive *current* signal?

http://www.autoorb.com/cyclic-voltammetry-instrumentation-/thesuiteworld.com*wp-includes*theme-compat*dallas-texas-scenery-5417.jpg/

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 1.2.11
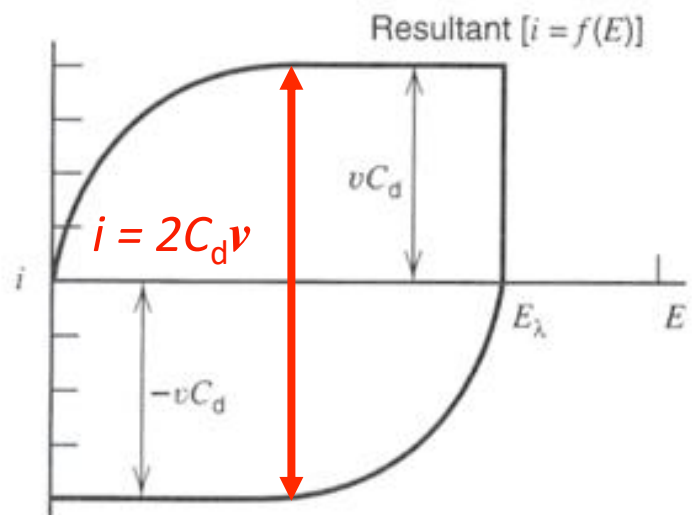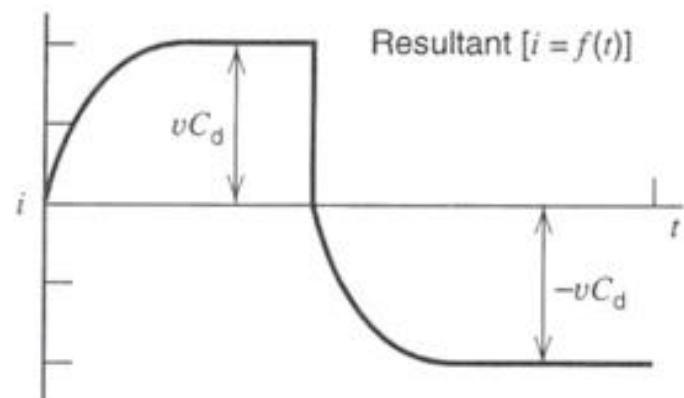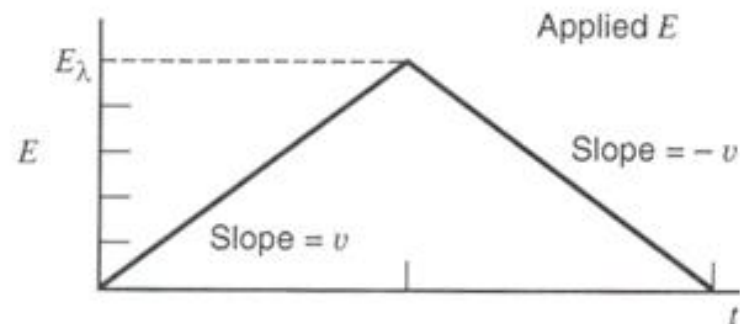
Figure
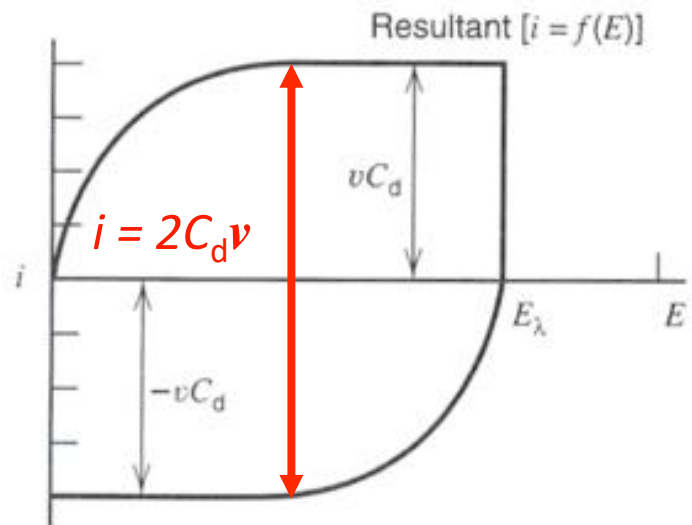
plots r

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Looking forward… Sections 1.2 and 1.3

- RC circuits *(~90% of slides)*

- **Uncompensated resistance (R_u)**

- **Electrochemically active surface area (ECSA)**

- **Luggin–Haber capillary**

- **Placement of electrodes**

Slow capacitive charging/discharging can convolute data/kinetics...
    ... think RC

Thus, minimize $R_{u(ncompensated)}$ (and thus possibly $R_{s(eries)}$ too) and $C_{d(ouble\ layer)}$ by doing the following...

(a)

(b)
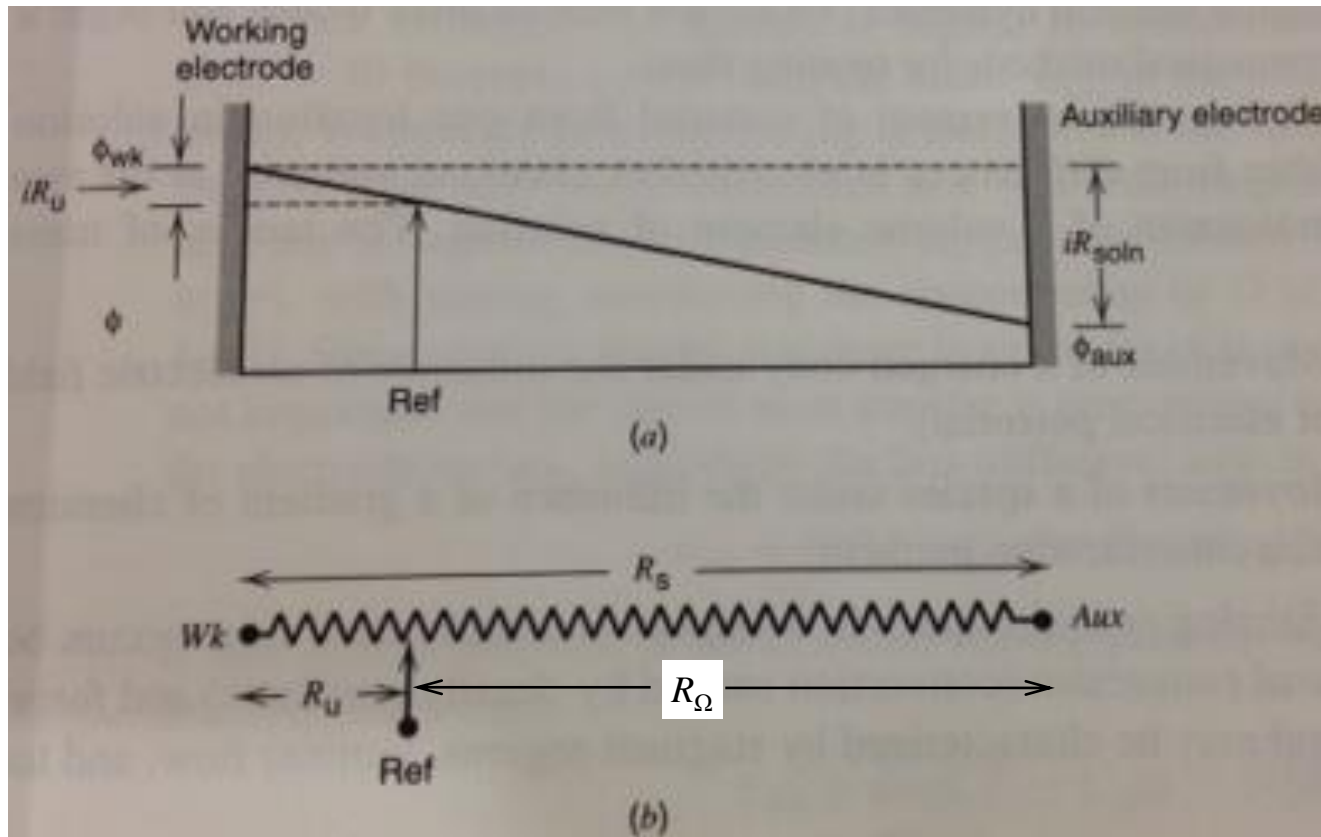
Slow capacitive charging/discharging can convolute data/kinetics…
     … think RC

Thus, minimize $R_{u(ncompensated)}$ (and thus possibly $R_{s(eries)}$ too) and $C_{d(ouble\ layer)}$ by doing the following…

1. Decrease the series resistance (between the WE and RE) by
        a) increasing the concentration of supporting electrolyte
        b) increasing the polarity of the solvent
        c) decreasing the viscosity of the solvent
        d) increasing the temperature

2. Move the RE tip "as close as possible" to the WE so that R_u (between the WE and RE) is a smaller fraction of R_s (between the WE and CE)

3. Decrease the electrochemically active surface area (ECSA) of the WE to decrease C_d proportionally

Electrochemically active surface area (ECSA) can be approximated… 273

… and used to determine the roughness (factor) as the ratio of it with the macroscopic geometric area of the electrode

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

PHYSICAL CHEMISTRY DIVISION
COMMISSION ON ELECTROCHEMISTRY*

REAL SURFACE AREA MEASUREMENTS IN ELECTROCHEMISTRY

Prepared for publication by
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Prof. Sergio Trasatti

(Università de Milano, Italy)

In Situ Methods
2.1 Drop weight (or volume)
2.2 Capacitance ratio
2.3 Parsons-Zobel plot
2.4 Hydrogen adsorption from solution
2.5 Oxygen adsorption from solution
2.6 Underpotential deposition of metals
2.7 Voltammetry
2.8 Negative adsorption
2.9 Ion-exchange capacity
2.10 Adsorption of probe molecules from solution
2.11 Mass transfer

Ex Situ Methods
3.1 Adsorption of Probe molecules from gas phase
3.2 X-ray diffraction
3.3 Porosimetry
3.4 Microscopy
3.5 Other methods

Prof. Oleg Petrii

(Moscow State University, Russia)

Trasatti and Petrii, *Pure & Appl. Chem.*, 1991, *63*, 711

… and used to determine the roughness (factor) as the ratio of it with the macroscopic geometric area of the electrode

lead to inaccuracy of 10-20%. The method is acceptable as an internal check (or for the estimation of the relative surface area) for different samples of the same metal or of the same ionic solid (eg oxide), provided the repeatibility of the experimental results is ascertained at a given constant frequency of the alternating signal.

In Situ Methods
  2.1 Drop weight (or volume)
  2.2 Capacitance ratio
  2.3 Parsons-Zobel plot
  2.4 Hydrogen adsorption from solution
  2.5 Oxygen adsorption from solution
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Ex Situ Methods
  3.1 Adsorption of Probe molecules from gas phase
  3.2 X-ray diffraction
  3.3 Porosimetry
  3.4 Microscopy
  3.5 Other methods

Trasatti and Petrii, *Pure & Appl. Chem.*, 1991, *63*, 711

WE

- Ideally polarizable (horizontal line on J–E plot), i.e. does not drive redox chemistry of/by itself (i.e. when no redox-active molecules are added)
- Well-defined size so that you can convert I (A) to J (A/cm$^2_{geom}$)

WE

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- Well-defined size so that you can convert I (A) to J (A/cm$^2_{geom}$)

CE

- Polarizable and non-polarizable both have advantages and disadvantages
- Large… <u>why</u>?
- Far from WE… <u>why</u>?
- Another compartment?

WE

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- Well-defined size so that you can convert I (A) to J (A/cm$^2_{geom}$)

CE
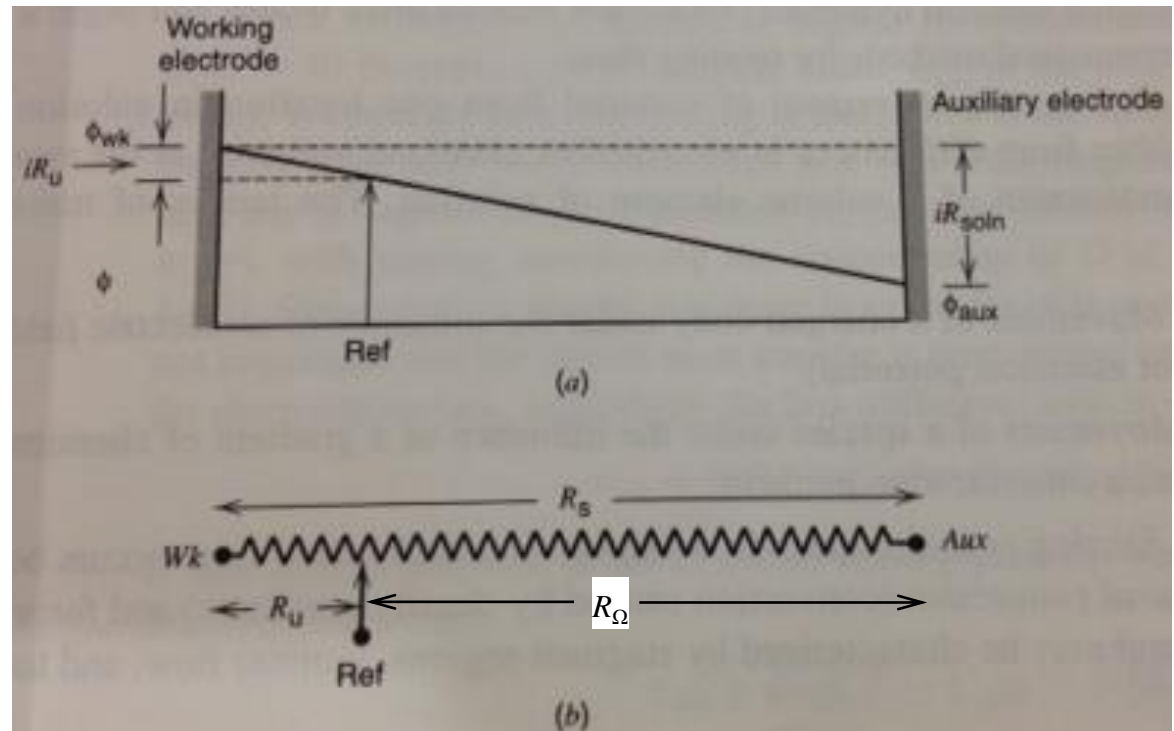
- Polarizable and non-polarizable both have advantages and disadvantages
- Large… <u>why</u>?
- Far from WE… <u>why</u>?
- Another compartment?

RE

- Ideally non-polarizable
- Close to WE, but not too close… <u>why</u>?
  - Minimize iR_u potential drop/loss between WE and RE
  - Luggin–Haber capillary about ~2 diameters away
  - Correct for iR_u drop electronically and/or manually

* Label numbers are for $^{Ru}/_{Ru(CE\ far)}$

Myland and Oldham, *Anal. Chem.*, 2000, *72*, 3972

… uncompensated resistance models
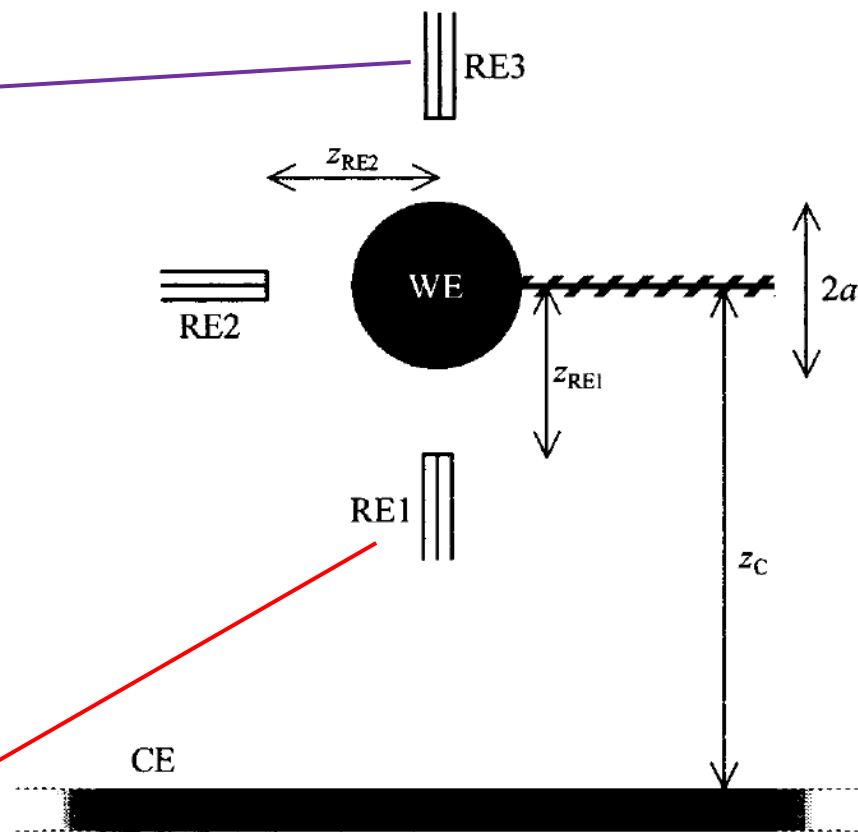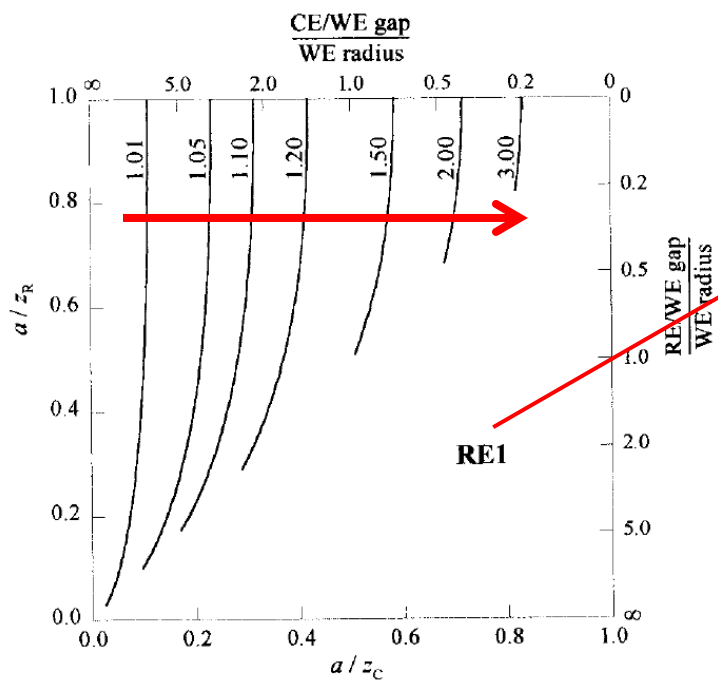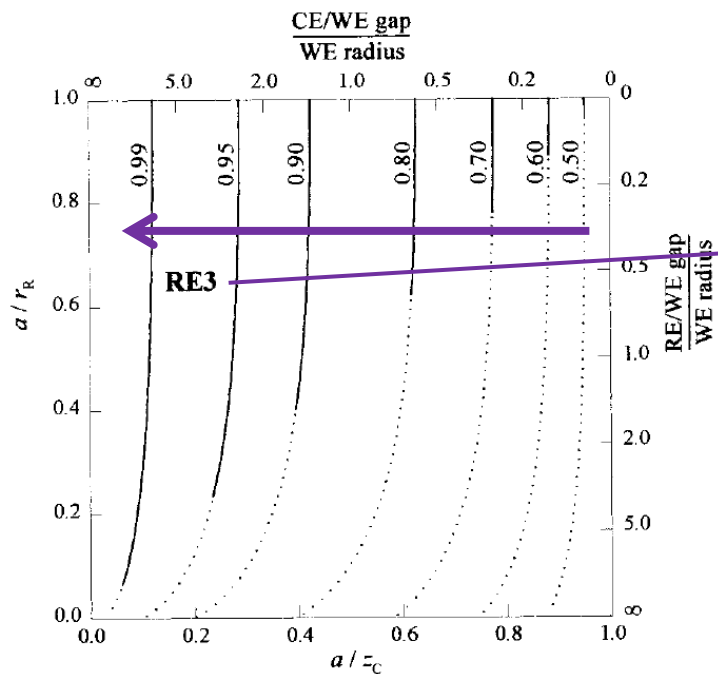
* Label numbers are for $^{R}u/_{Ru(CE\ far)}$

(1) For working electrodes benefitting from convergent transport, worthwhile compensation is impossible unless a midget RE is positioned extremely close to WE.

(2) Uncompensated resistance declines dramatically as RE approaches WE; however, the angle of approach may be important.

(3) A large CE is effectively remote when its distance from the working electrode is at least 5 times the radius of WE.

(4) When the CE is of a size comparable to that of WE, it is effectively remote when the interelectrode distance is at least 10 times the radius of WE.

(5) The resistance is effectively that of a cell in an infinitely large vessel, if the vessel's radius exceeds that of the electrodes 5-fold.

(6) An electrode must be covered by at least 10 times its own radius of solution, before it is immersed in an effectively infinite volume.

A review of Sections 1.2 and 1.3

- <u>RC circuits</u>

- <u>Uncompensated resistance (R_u)</u>

- <u>Electrochemically active surface area (ECSA)</u>

- <u>Luggin–Haber capillary</u>

- <u>Placement of electrodes</u>

… now on to a general qualitative analysis of electrochemical scenarios to help us better grasp relative reduction potentials…

... Bio-Logic potentiostats have a feature that allows us to measure the potential of the WE vs. RE **and the potential of the CE vs. RE**. Let's take a closer look at some of the data from my lab:
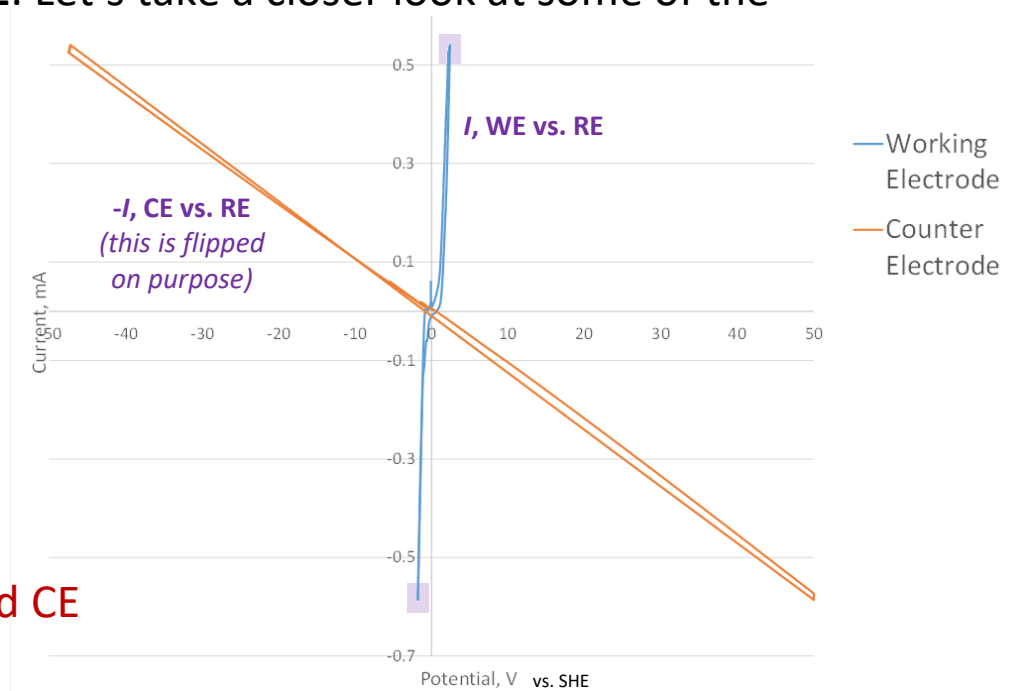
(1) Look at how large the potential of the CE vs. RE is! Wow! ... Why?

Potential drops in the cell between RE and CE

(2) Why did the data for the WE vs. RE "top out" when this potential became too large?

Compliance voltage of CE (vs. RE)

(3) If this experiment was measuring ferrocene (Fc) oxidation in CH_3CN at the WE, then what redox chemistry would be occurring at the CE?

Reduction of solvent, electrolyte, water impurities, or O_2, maybe; you may want a salt bridge; eventually enough Fc^+ will be built up from the WE that you could then begin to reduce Fc^+ at the CE... **Let's chat about this some more via a visual example...**

Example: Part 1 of 2

Figure E.1 Potentials of reference electrodes in aqueous solutions at 25°C. [See D. J. G. Ives and G. J. Janz, "Reference Electrodes," Academic, New York, 1961.]
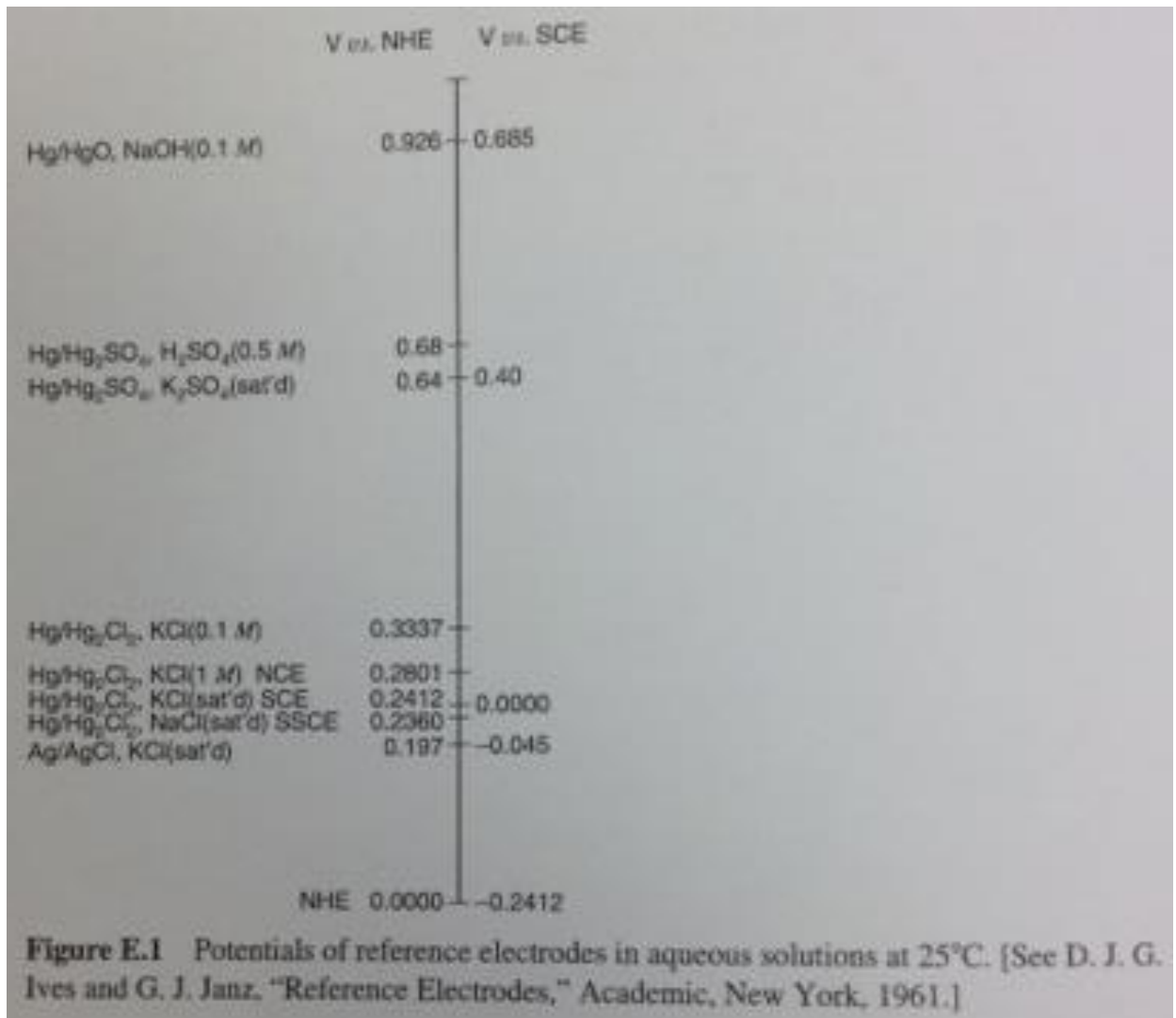
... Oh can we please flip this over?...   **B&F back inside**

Example: Part 2

Electrolyte   Electrode
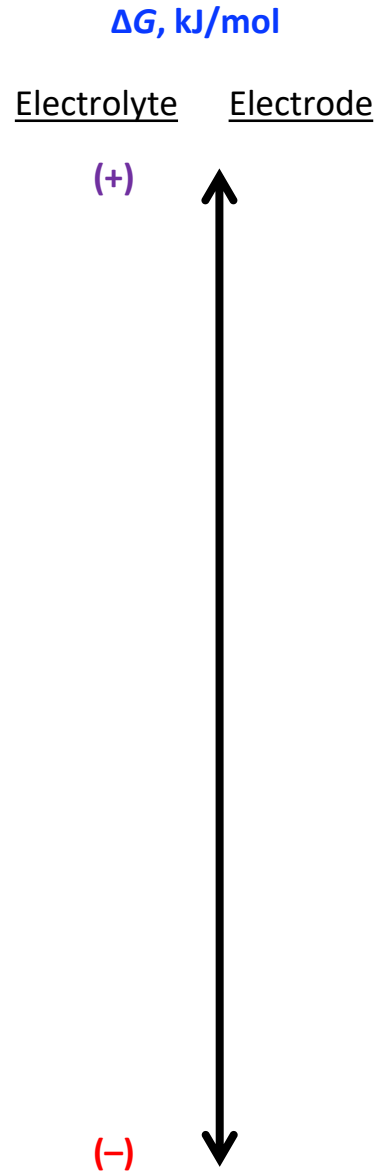
How would chemists label this plot?

Example: Part 2

ΔG, kJ/mol

Electrolyte   Electrode

(+)

How would chemists label this plot?

How would physicists label this plot?

(−)

Example: Part 2

vacuum, **0** ——

E, V

Electrolyte   Electrode

↑
|
|
|
|
|
|
|
↓

(+)

How would chemists label this plot?

How would physicists label this plot?

How would <u>electro</u>chemists label this plot?

Example: Part 2

vacuum —

E, V vs. SHE

<u>Electrolyte</u>   <u>Electrode</u>

(–)

SHE, 0 —

(+)

How would chemists label this plot?

How would physicists label this plot?

How would <u>electro</u>chemists label this plot?

Now let's put in some half-reaction reduction potentials from the CRC Table…

Example: Part 2

vacuum ▬

E, V vs. SHE

| Electrolyte | Electrode |

(−)

SHE, 0

$E^0(Fc^+/Fc) = +0.358$ V

$E^0(Fe^{3+/2+}) = +0.771$ V

$E^0(Br_2/Br^-) = +1.0873$ V

(+)

Nernst Equation:

$$E = E^0 - \frac{RT}{nF} \ln Q = E^0 - 0.0592 \, V \log \frac{a_{ox}}{a_{red}}$$

How would chemists label this plot?

How would physicists label this plot?

How would <u>electro</u>chemists label this plot?

Now let's put in some half-reaction reduction potentials from the CRC Table…

… what would the "solution potential" be if you had unity activity of the following?

(a) ferrocene (Fc) and ferrocenium (Fc⁺)

Example: Part 2

vacuum ▬

E, V vs. SHE

Electrolyte   Electrode

(−)

SHE, 0

E^0(Fc$^+$/Fc) = +0.358 V

E^0(Fe$^{3+/2+}$) = +0.771 V

E^0(Br$_2$/Br$^-$) = +1.0873 V

(+)

Nernst Equation:

$$E = E^0 - \frac{RT}{nF}\ln Q = E^0 - 0.0592\,V\log\frac{a_{\text{ox}}}{a_{\text{red}}}$$

How would chemists label this plot?

How would physicists label this plot?

How would <u>electro</u>chemists label this plot?

Now let's put in some half-reaction reduction potentials from the CRC Table…

… what would the "solution potential" be if you had unity activity of the following?

(a) Fc and Fc$^+$ **E = +0.358 V**
(b) Fe^{3+} and Fe^{2+}

Example: Part 2

vacuum —

E, V vs. SHE

Electrolyte   Electrode

(−)

SHE, 0

$E^0(Fc^+/Fc)$ = +0.358 V

$E^0(Fe^{3+/2+})$ = +0.771 V

$E^0(Br_2/Br^-)$ = +1.0873 V

(+)

Nernst Equation:

$$E = E^0 - \frac{RT}{nF}\ln Q = E^0 - 0.0592\,V\log\frac{a_{\text{ox}}}{a_{\text{red}}}$$

How would chemists label this plot?

How would physicists label this plot?
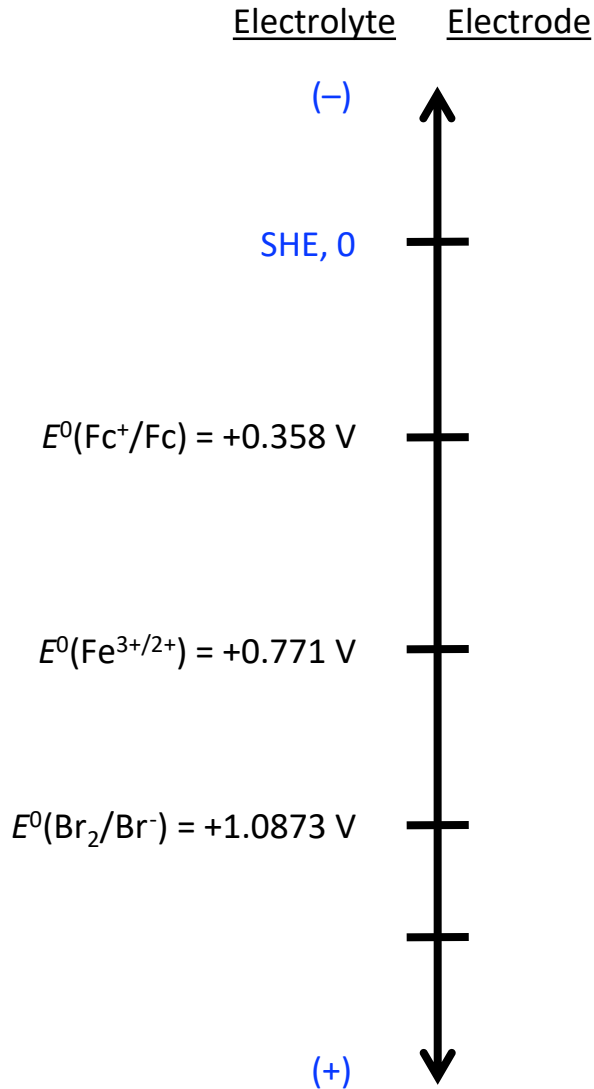
How would <u>electro</u>chemists label this plot?

Now let's put in some half-reaction reduction potentials from the CRC Table…

… what would the "solution potential" be if you had unity activity of the following?

(a) Fc and Fc⁺   *E* = **+0.358 V**
(b) Fe³⁺ and Fe²⁺   ***E* = +0.771 V**
(c) Both (a) and (b)

Example: Part 2

vacuum —

E, V vs. SHE

Electrolyte   Electrode

(−)

SHE, 0

E^0(Fc$^+$/Fc) = +0.358 V

E^0(Fe$^{3+/2+}$) = +0.771 V

E^0(Br$_2$/Br$^-$) = +1.0873 V

(+)

Electrons move down; think free energy…

… Once 90% of the Fc is oxidized and 90% of the Fe^{3+} is reduced, where are the *E* values for each half-reaction?

Nernst Equation:

$$E = E^0 - \frac{RT}{nF}\ln Q = E^0 - 0.0592\,V\log\frac{a_{\mathrm{ox}}}{a_{\mathrm{red}}}$$

How would chemists label this plot?

How would physicists label this plot?

How would <u>electro</u>chemists label this plot?

Now let's put in some half-reaction reduction potentials from the CRC Table…

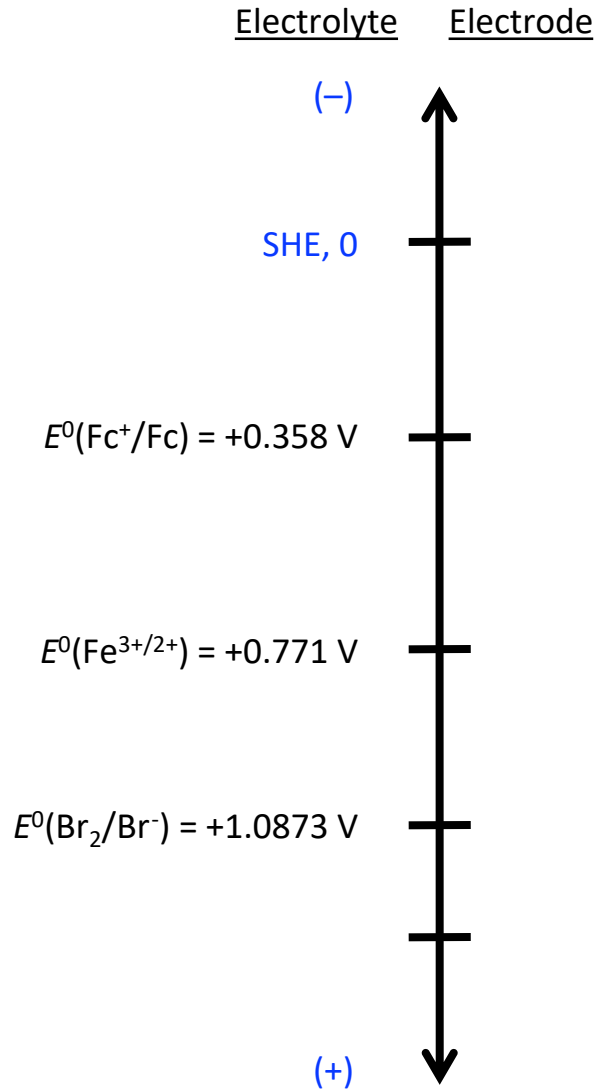… what would the "solution potential" be if you had unity activity of the following?
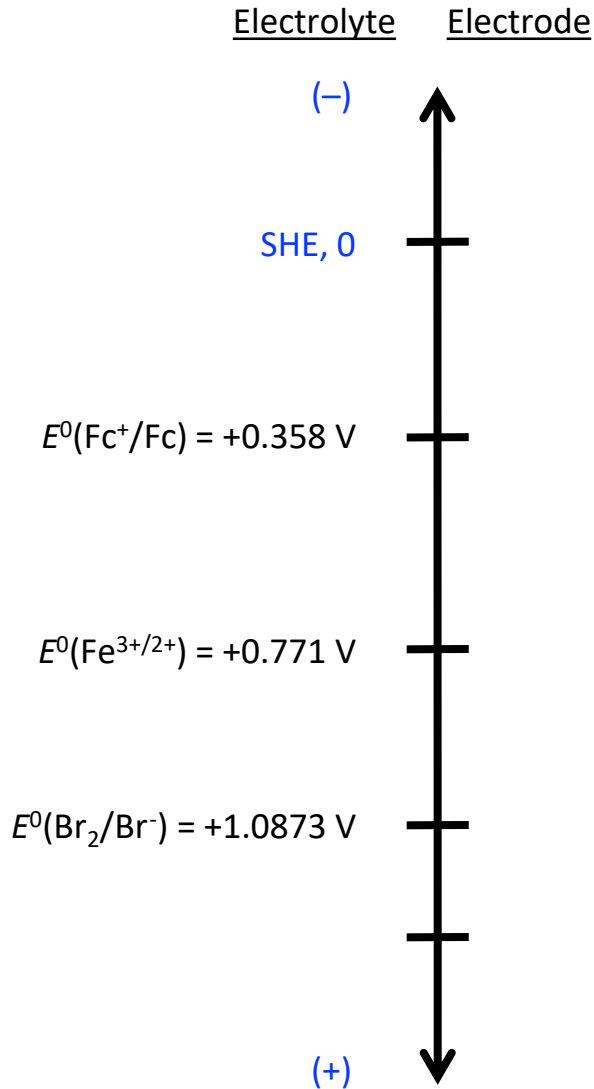
(a) Fc and Fc$^+$ *E* = **+0.358 V**
(b) Fe^{3+} and Fe^{2+} *E* = **+0.771 V**
(c) **Both (a) and (b)**   ***E* = +0.5645 V**, because Fc$^{+/0}$ and Fe$^{3+/2+}$ would equilibrate by electron transfer… **EXPLAIN THIS!**

Example: Part 2

vacuum ▬

E, V vs. SHE

Electrolyte	Electrode

(−)

SHE, 0

$E^0(Fc^+/Fc) = +0.358$ V

Electrons move down; think free energy…

$E^0(Fe^{3+/2+}) = +0.771$ V

… Roughly how far did each move?

$E^0(Br_2/Br^-) = +1.0873$ V

~60 mV

(+)

Nernst Equation:

$$E = E^0 - \frac{RT}{nF} \ln Q = E^0 - 0.0592 \, V \log \frac{a_{ox}}{a_{red}}$$

How would chemists label this plot?

How would physicists label this plot?

How would <u>electro</u>chemists label this plot?

Now let's put in some half-reaction reduction potentials from the CRC Table…

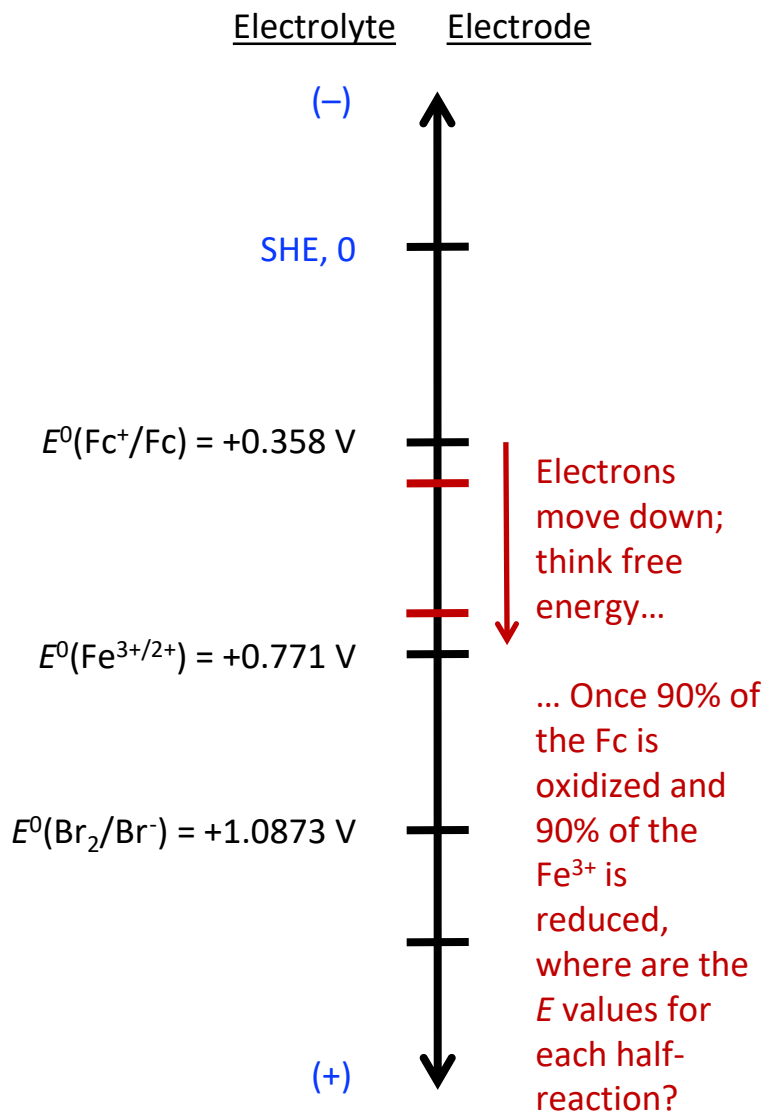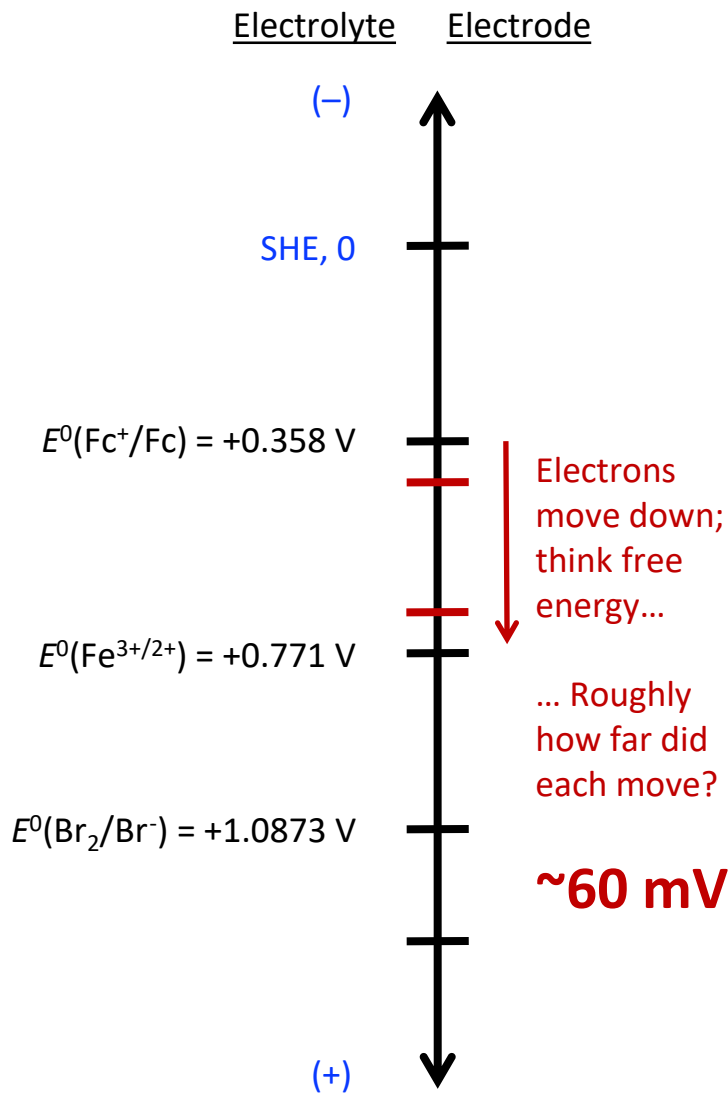… what would the "solution potential" be if you had unity activity of the following?

(a) Fc and Fc⁺   E = +0.358 V
(b) Fe³⁺ and Fe²⁺   E = +0.771 V
(c) **Both (a) and (b)**   **E = +0.5645 V**, because Fc⁺/⁰ and Fe³⁺/²⁺ would equilibrate by electron transfer… **EXPLAIN THIS!**

Example: Part 2

vacuum ▬

E, V vs. SHE

Electrolyte   Electrode

(−)

SHE, 0

$E^0(Fc^+/Fc) = +0.358$ V

$E(Fc^+/Fc/Fe^{3+}/Fe^{2+}) = +0.564$ V — **Equilibrated!**

$E^0(Fe^{3+/2+}) = +0.771$ V

$E^0(Br_2/Br^-) = +1.0873$ V

(+)

Nernst Equation:

$$E = E^0 - \frac{RT}{nF}\ln Q = E^0 - 0.0592\,V\log\frac{a_{\text{ox}}}{a_{\text{red}}}$$

How would chemists label this plot?

How would physicists label this plot?

How would <u>electro</u>chemists label this plot?

Now let's put in some half-reaction reduction potentials from the CRC Table…

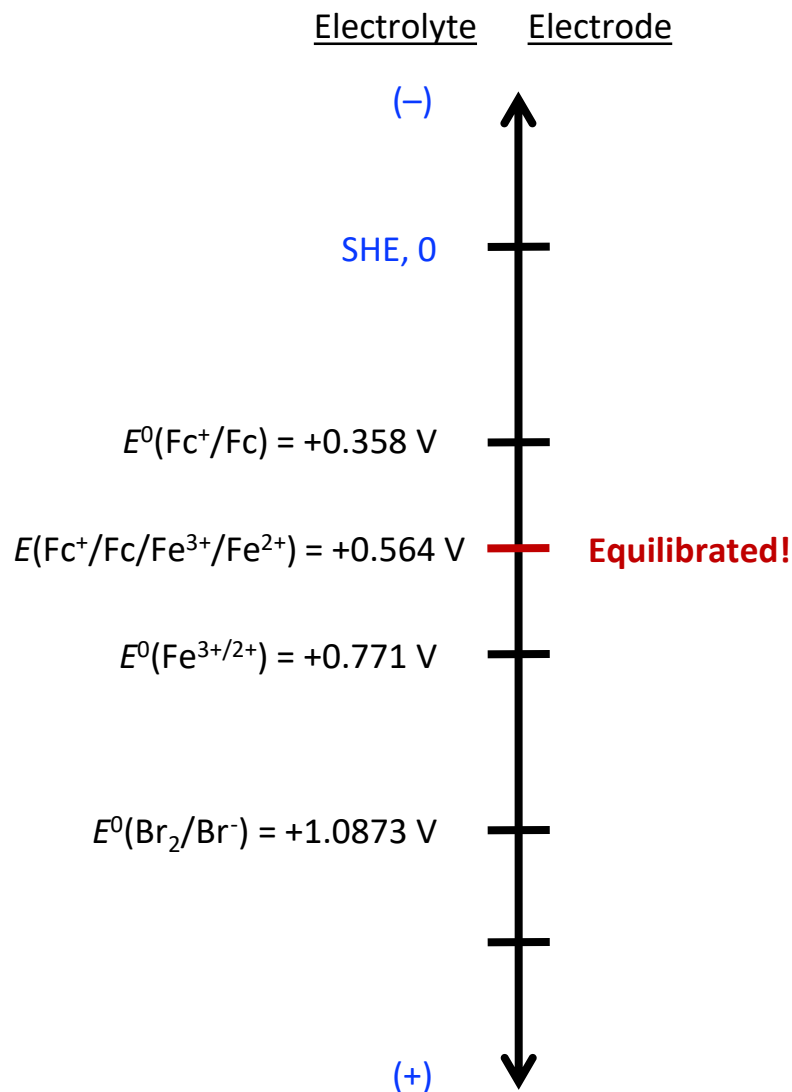… what would the "solution potential" be if you had unity activity of the following?

(a) Fc and Fc⁺   *E* = **+0.358 V**
(b) Fe^{3+} and Fe^{2+} *E* = **+0.771 V**
(c) **Both (a) and (b)**   *E* = **+0.5645 V**, because $Fc^{+/0}$ and $Fe^{3+/2+}$ would equilibrate by electron transfer… **EXPLAIN THIS!**

Example: Part 2

vacuum ▬

E, V vs. SHE

Electrolyte   Electrode

(−)

SHE, 0

$E^0(Fc^+/Fc)$ = +0.358 V

$E(Fc^+/Fc/Fe^{3+}/Fe^{2+})$ = +0.564 V

$E^0(Fe^{3+/2+})$ = +0.771 V

$E^0(Br_2/Br^-)$ = +1.0873 V

(+)

Nernst Equation:

$$E = E^0 - \frac{RT}{nF}\ln Q = E^0 - 0.0592\,V \log\frac{a_{\text{ox}}}{a_{\text{red}}}$$

Now, what is the open-circuit potential at Pt when each of the following has unity activity?

(a) Fc and Fc⁺ E = ???
(b) Fe³⁺ and Fe²⁺ E = ???
(c) Both (a) and (b) E = ???

Example: Part 2

vacuum ▬

E, V vs. SHE

Electrolyte   Electrode

(−)

SHE, 0

$E^0(Fc^+/Fc) = +0.358$ V

$E(Fc^+/Fc/Fe^{3+}/Fe^{2+}) = +0.564$ V

$E^0(Fe^{3+/2+}) = +0.771$ V

$E^0(Br_2/Br^-) = +1.0873$ V

(+)

Nernst Equation:

$$E = E^0 - \frac{RT}{nF}\ln Q = E^0 - 0.0592\ V \log\frac{a_{\text{ox}}}{a_{\text{red}}}$$

Now, what is the open-circuit potential at Pt when each of the following has unity activity?

(a) Fc and Fc^+ **$E = +0.358$ V**
(b) Fe^{3+} and Fe^{2+} **$E = +0.771$ V**
(c) <u>Equilibrated</u> (a) and (b)   **$E = +0.5645$ V**

Example: Part 2

vacuum —

E, V vs. SHE

Electrolyte   Electrode

(−)

SHE, 0

$E^0(\mathrm{Fc^+/Fc}) = +0.358\ \mathrm{V}$

$E(\mathrm{Fc^+/Fc/Fe^{3+}/Fe^{2+}}) = +0.564\ \mathrm{V}$

$E^0(\mathrm{Fe^{3+/2+}}) = +0.771\ \mathrm{V}$

$E^0(\mathrm{Br_2/Br^-}) = +1.0873\ \mathrm{V}$

(+)

Nernst Equation:

$$E = E^0 - \frac{RT}{nF}\ln Q = E^0 - 0.0592\ V \log\frac{a_{\mathrm{ox}}}{a_{\mathrm{red}}}$$

Now, what is the open-circuit potential at Pt when each of the following has unity activity?

(a) Fc and $\mathrm{Fc^+}$ **E = +0.358 V**
(b) $\mathrm{Fe^{3+}}$ and $\mathrm{Fe^{2+}}$ **E = +0.771 V**
(c) Equilibrated (a) and (b)   **E = +0.5645 V**

(d) Fc and $\mathrm{Fe^{3+}}$ E = ???
(e) $\mathrm{Fc^+}$ E = ???
(f) $\mathrm{Fc^+}$, $\mathrm{H^+}$, $\mathrm{Fe^{3+}}$, $\mathrm{Br^-}$ E = ???

Example: Part 2

Nernst Equation:

$$E = E^0 - \frac{RT}{nF}\ln Q = E^0 - 0.0592\,V \log\frac{a_{\text{ox}}}{a_{\text{red}}}$$

E, V vs. SHE

Electrolyte   Electrode

(−)

SHE, 0

$E^0(\text{Fc}^+/\text{Fc}) = +0.358\ \text{V}$

$E(\text{Fc}^+/\text{Fc}/\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.564\ \text{V}$

$E^0(\text{Fe}^{3+/2+}) = +0.771\ \text{V}$

$E^0(\text{Br}_2/\text{Br}^-) = +1.0873\ \text{V}$

(+)

Now, what is the open-circuit potential at Pt when each of the following has unity activity?

(a) Fc and Fc$^+$ **E = +0.358 V**
(b) Fe^{3+} and Fe^{2+} **E = +0.771 V**
(c) <u>Equilibrated</u> (a) and (b)   **E = +0.5645 V**

(d) Fc and Fe^{3+} **E = +0.5645 V**
(e) Fc$^+$ E = ???
(f) Fc$^+$, H$^+$, Fe^{3+}, Br$^-$ E = ???

Example: Part 2

vacuum

E, V vs. SHE

Electrolyte   Electrode

(−)

Nernst Equation:

$$E = E^0 - \frac{RT}{nF} \ln Q = E^0 - 0.0592\ V \log \frac{a_{ox}}{a_{red}}$$

SHE, 0

Now, what is the open-circuit potential at Pt when each of the following has unity activity?

(a) Fc and Fc⁺   **E = +0.358 V**

$E^0(Fc^+/Fc) = +0.358$ V

(b) Fe^{3+} and Fe^{2+} **E = +0.771 V**

(c) <u>Equilibrated</u> (a) and (b)   **E = +0.5645 V**

(d) Fc and Fe^{3+} **E = +0.5645 V**

$E^0(Fe^{3+/2+}) = +0.771$ V

?

(e) Fc⁺   *E* = ???

(f) Fc⁺, H⁺, Fe^{3+}, Br⁻   *E* = ???

$E^0(Br_2/Br^-) = +1.0873$ V

$E^0(O_2,H^+/H_2O) = +1.229$ V

(+)

Example: Part 2

vacuum ▬

Nernst Equation:

$$E = E^0 - \frac{RT}{nF}\ln Q = E^0 - 0.0592\ V \log\frac{a_{ox}}{a_{red}}$$

E, V vs. SHE

Electrolyte   Electrode

(−)

SHE, 0

Now, what is the open-circuit potential at Pt when each of the following has unity activity?

(a) Fc and Fc⁺   **E = +0.358 V**
(b) Fe³⁺ and Fe²⁺   **E = +0.771 V**
(c) Equilibrated (a) and (b)   **E = +0.5645 V**

(d) Fc and Fe³⁺   **E = +0.5645 V**
(e) Fc⁺   **E ≈ (+0.358, +1.229) V**
(f) Fc⁺, H⁺, Fe³⁺, Br⁻ E = ???

$E^0(Fc^+/Fc)$ = +0.358 V

$E^0(Fe^{3+/2+})$ = +0.771 V

$E^0(Br_2/Br^-)$ = +1.0873 V

$E^0(O_2, H^+/H_2O)$ = +1.229 V

(+)

vacuum —

Example: Part 2

E, V vs. SHE

Electrolyte   Electrode

(−)

SHE, 0

$E^0(Fc^+/Fc) = +0.358$ V

$E^0(Fe^{3+/2+}) = +0.771$ V

$E^0(Br_2/Br^-) = +1.0873$ V

$E^0(O_2,H^+/H_2O) = +1.229$ V

(+)

Nernst Equation:

$$E = E^0 - \frac{RT}{nF}\ln Q = E^0 - 0.0592\,V\log\frac{a_{ox}}{a_{red}}$$

Now, what is the open-circuit potential at Pt when each of the following has unity activity?

(a) Fc and Fc$^+$ *E* = +0.358 V
(b) Fe^{3+} and Fe^{2+} *E* = +0.771 V
(c) Equilibrated (a) and (b)   *E* = +0.5645 V

(d) Fc and Fe^{3+} *E* = +0.5645 V
(e) Fc$^+$ *E* ≈ (+0.358, +1.229) V
(f) Fc$^+$, H$^+$, Fe^{3+}, Br$^-$ *E* = ???

Example: Part 2

vacuum ▬

E, V vs. SHE

Electrolyte   Electrode

(−)

SHE, 0

$E^0(Fc^+/Fc) = +0.358\ V$

$E^0(Fe^{3+/2+}) = +0.771\ V$

$E^0(Br_2/Br^-) = +1.0873\ V$

$E^0(O_2,H^+/H_2O) = +1.229\ V$

(+)

Nernst Equation:

$$E = E^0 - \frac{RT}{nF}\ln Q = E^0 - 0.0592\ V \log\frac{a_{ox}}{a_{red}}$$

Now, what is the open-circuit potential at Pt when each of the following has unity activity?

(a) Fc and Fc⁺   **E = +0.358 V**
(b) Fe^{3+} and Fe^{2+} **E = +0.771 V**
(c) Equilibrated (a) and (b)   **E = +0.5645 V**

(d) Fc and Fe^{3+} **E = +0.5645 V**
(e) Fc⁺   **E ≈ (+0.358, +1.229) V**
(f) Fc⁺, H⁺, Fe^{3+}, Br⁻   **E ≈ (+0.771, +1.0873) V**

Example: Part 2

vacuum ▬

E, V vs. SHE

Electrolyte   Electrode

(−)

SHE, 0

$E^0(Fc^+/Fc) = +0.358$ V

$E^0(Fe^{3+/2+}) = +0.771$ V

$E^0(Br_2/Br^-) = +1.0873$ V

$E^0(O_2,H^+/H_2O) = +1.229$ V

(+)

anodic current

an *oxidation*:
$$2Cl^- (aq) \rightleftharpoons Cl_2 (g) + 2e^-$$

onset of H⁺ reduction

-0.5   0   +0.5   1.0   1.5   E, V vs. SHE

onset of Cl⁻ oxidation

a *reduction*:
$$2H^+ (aq) + 2e^- \rightleftharpoons H_2 (g)$$

cathodic current