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Lecture #8 of 17

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Measurements in Electrochemistry

Chapters 1 and 15

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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

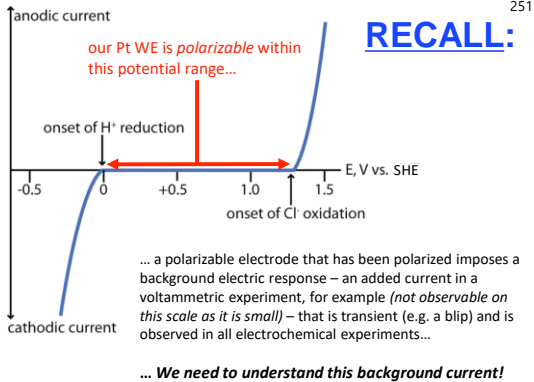
249

250

Looking forward... Sections 1.2 and 1.3

- RC circuits (~90% of slides) (halfway complete)
- Uncompensated resistance (R_u)
- Electrochemically active surface area (ECSA)
- Luggin-Haber capillary
- Placement of electrodes

250

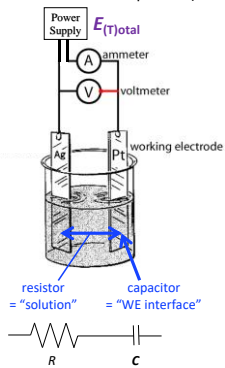


251

251

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

RECALL:

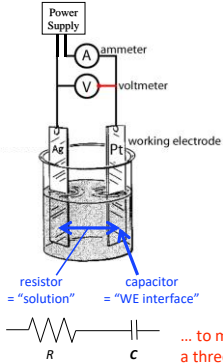


$$E_T = E_R + E_C + \dots$$

252

The electrical response of a polarizable electrode is approximated by a series resistor and capacitor (a series RC circuit)... 253

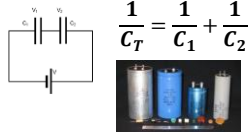
RECALL:



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



C = the net capacitance (of the WE and the CE), C_{Ttotal}

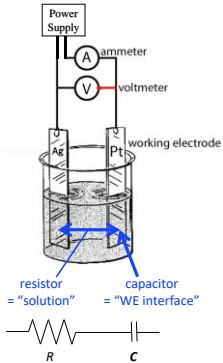


... to measure $C_{2(WE)}$, make $C_{1(CE)}$ large... or use a three-electrode setup and a pstat

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First, what are approximate values for $R_{(s)}$ and $C_{(a)}$? ... 254

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., $R > 100 \Omega$

C = the net capacitance (of the WE and the RE), C_{Ttotal}

$\sim 20 \mu F/cm^2$ of electrode area for gold or platinum; $2 - 5 \mu F/cm^2$ for carbon, typically... but these change slightly with potential as we will see later

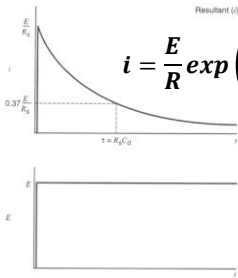
(Farad can be cast as C/V...
... and recall that Volt can be cast as J/C)

254

Now, what response is obtained for various inputs to this circuit? 255

1. **Potential-step potentiostatic chronoamperometry (chronocoulometry)**

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



RECALL:

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

Could there be a problem with an instantaneous 6 V potential step, for example?
... **Compliance current!**
(at $t = 0$, $E = iR$ (Ohm's law))
(3) What portion of E_{app} is actually present at the WE to drive interfacial 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

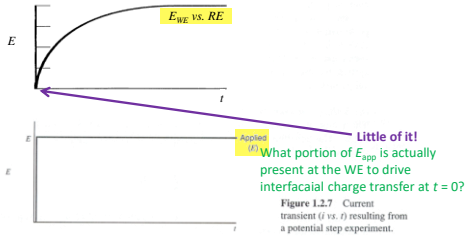
255

Now, what response is obtained for various inputs to this circuit? 256

1. **Potential-step** potentiostatic chronoamperometry (chronocoulometry)

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

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



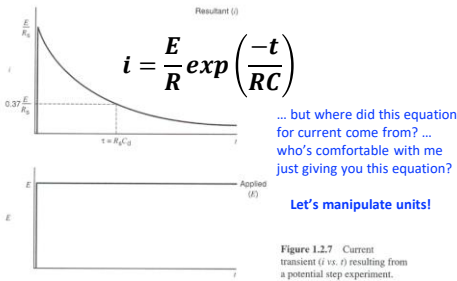
Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 1.2.7

256

Now, what response is obtained for various inputs to this circuit? 257

1. **Potential-step** potentiostatic chronoamperometry (chronocoulometry)

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

257

Now, what response is obtained for various inputs to this circuit? 258

1. **Potential-step** potentiostatic chronoamperometry (chronocoulometry)

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

B&F eqn. (1.2.8)
 $E = E_R + E_C = iR_s + \frac{q}{C_d}$ Units: C

B&F eqn. (1.2.9)
 $i = \frac{1}{R_s} \left(E - \frac{q}{C_d} \right) = \frac{dq}{dt}$ Units: C/V

Units: C/s

Need to integrate!

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

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

(assuming that at $t = 0, q = 0$) Integrated!

$E_T = E_R + E_C + \dots$

258

Now, what response is obtained for various inputs to this circuit? 259

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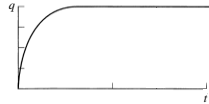
$$-\frac{1}{R_s C_d} t = \ln|-EC_d + q| - \ln|-EC_d| = \ln \left| \frac{-EC_d + q}{-EC_d} \right|$$

Integrated!

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

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

B&F eqn. (1.2.10)



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B&F eqn. (1.2.10)

Need to differentiate!

$$\frac{dq}{dt} = EC_d \left(\frac{1}{R_s C_d} e^{-\frac{t}{R_s C_d}} \right) = \frac{E}{R_s} e^{-\frac{t}{R_s C_d}} = i$$

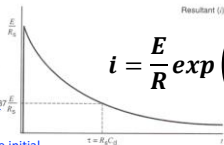
B&F eqn. (1.2.6)
Done!

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Now, what response is obtained for various inputs to this circuit? 261

1. **Potential-step potentiostatic chronoamperometry (chronocoulometry)**

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



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

What are the units of RC ?

- $R (\Omega) \times Cap (F)$
- $R (V / C/s) \times Cap (C/V)$
- $R \cdot Cap (V \cdot s / C \times C / V)$
- $R \cdot Cap (s)$

Why is 37% of the initial signal noteworthy?

Plug in $t = RC!$
... Ah ha!

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

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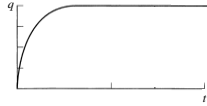
Now, what response is obtained for various inputs to this circuit? 262

1. **Potential-step potentiostatic chronoamperometry (chronocoulometry)**

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

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

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

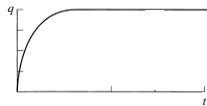


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Example: Consider the case where $R = 1 \Omega$ and $C = 20 \mu\text{F}/\text{cm}^2$. 263
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$$\frac{q}{q_{t \rightarrow \infty}} = 1 - e^{-\frac{t}{R_s C_d}}$$

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

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

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

assuming 1 cm^2

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

263

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

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

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

$$I_{\text{avg}} = \frac{q}{t} = \frac{(C \times V)}{t}$$

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

$$\approx 120 \mu\text{C} / 60 \mu\text{s}$$

$$\approx 2 \text{ A! Compliance?}$$

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

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

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

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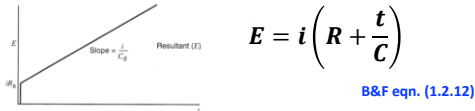
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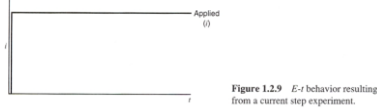
Now, what response is obtained for various inputs to this circuit? 265

2. Current-step galvanostatic chronopotentiometry

Current step (that is, increment the current by an amount, i):



... 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"?



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

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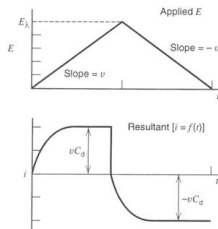
Now, what response is obtained for various inputs to this circuit? 266

3. Linear-sweep voltammetry... cyclic voltammetry

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

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

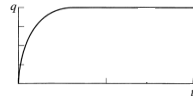
B&F eqn. (1.2.15)



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

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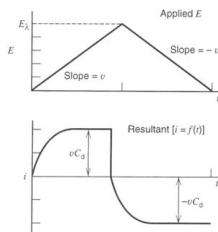
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$$i = vC_d \left[1 - \exp\left(\frac{-t}{R_S C_d}\right) \right]$$

B&F eqn. (1.2.15)



So the total current "envelope" at any potential that is well-removed from the switching potential will be: $i = 2C_d v$, with v 's units being V/s

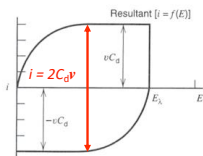


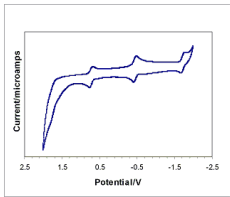
Figure plots D triane

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

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Now, what response is obtained for various inputs to this circuit? 268

3. Linear-sweep voltammetry...
cyclic voltammetry



This is an example of a cyclic voltammogram with obvious RC charging

<http://www.autotech.com/cyclic-voltammetry-instrumentation/>
[/thesite.world.com/wp-includes/theme-compat/dallas-texas-scenery-5417.jpg](https://thesite.world.com/wp-includes/theme-compat/dallas-texas-scenery-5417.jpg)
Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 1.2.11

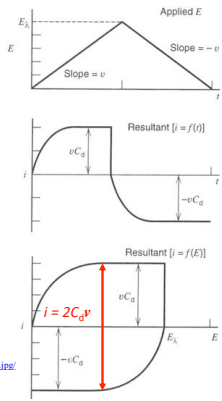
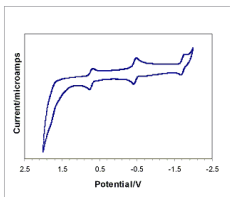


Figure plots n trianet

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Now, what response is obtained for various inputs to this circuit? 269

3. Linear-sweep voltammetry...
cyclic voltammetry



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

<http://www.autotech.com/cyclic-voltammetry-instrumentation/>
[/thesite.world.com/wp-includes/theme-compat/dallas-texas-scenery-5417.jpg](https://thesite.world.com/wp-includes/theme-compat/dallas-texas-scenery-5417.jpg)
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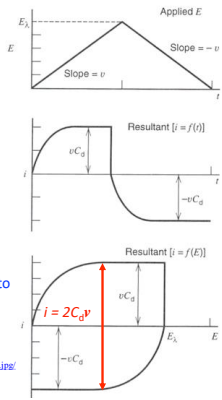


Figure plots n trianet

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Looking forward... Sections 1.2 and 1.3

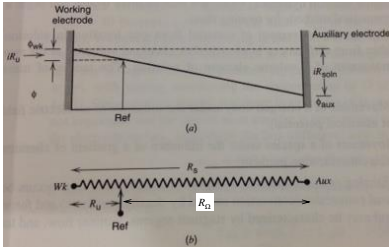
- RC circuits (~90% of slides)
- Uncompensated resistance (R_u)
- Electrochemically active surface area (ECSA)
- Luggin-Haber capillary
- Placement of electrodes

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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...



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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

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Electrochemically active surface area (ECSA) can be approximated...
... 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 S. TRASATTI¹ and O. A. PETRII²
¹Dipartimento di Chimica Fisica ed Electrochimica, Università di Milano, Italy
²Faculty of Chemistry, Lomonosov Moscow State University, USSR

- In Situ Methods**
- 2.1 Drop weight (or volume)
 - 2.2 Capacitance ratio
 - 2.3 Parsons-Zobell 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 Perimetry
 - 3.4 Microscopy
 - 3.5 Other methods



Prof. Sergio Trasatti (Università de Milano, Italy)



Prof. Oleg Petrii (Moscow State University, Russia)

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

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Electrochemically active surface area (ECSA) can be approximated... 274
 ... 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 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 repeatability of the experimental results is ascertained at a given constant frequency of the alternating signal.

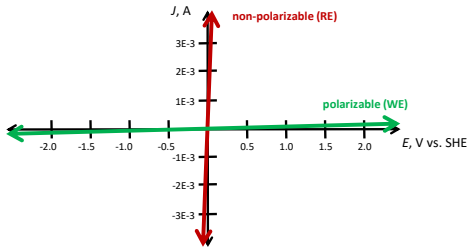
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Trasatti and Petrii, *Pure & Appl. Chem.*, 1991, 63, 711

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SUMMARY... Properties of electrodes 275

- 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})

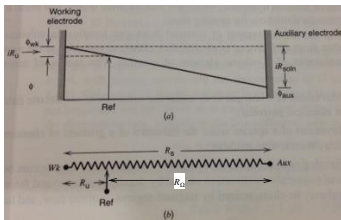


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SUMMARY... Properties of electrodes 276

- 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)
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- CE**
- Polarizable and non-polarizable both have advantages and disadvantages
 - Large... why?
 - Far from WE... why?
 - Another compartment?



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SUMMARY... Properties of electrodes

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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})

CE

- Polarizable and non-polarizable both have advantages and disadvantages
- Large... why?
- Far from WE... why?
- Another compartment?

RE

- Ideally non-polarizable
- Close to WE, but not too close... why?
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

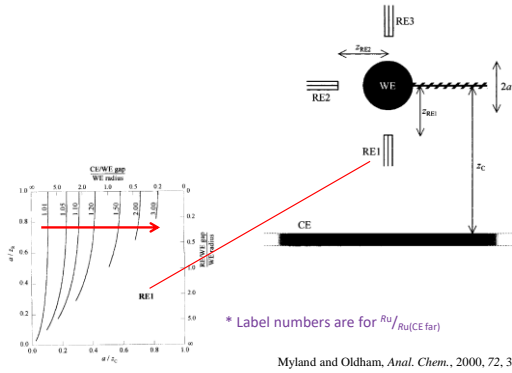


http://www.autolabj.com/construction_files/electrode_files/E-luggin%20agcl.htm

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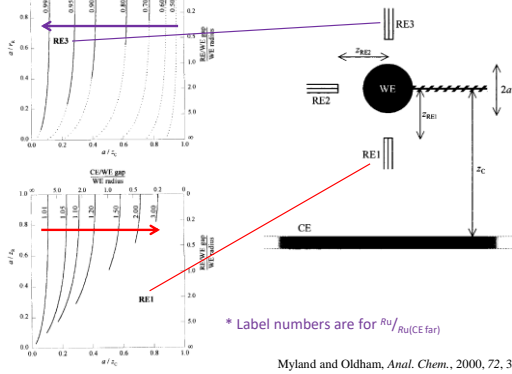
... Final thoughts...

Geometry and... 278
... uncompensated resistance models



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Geometry and... 279
... uncompensated resistance models



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Geometry and... 280
 ... uncompensated resistance models

- (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.

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

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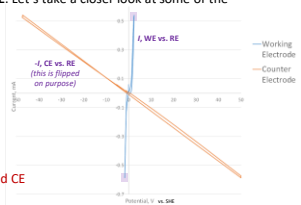
A review of Sections 1.2 and 1.3

- [RC circuits](#)
- [Uncompensated resistance \(\$R_u\$ \)](#)
- [Electrochemically active surface area \(ECSA\)](#)
- [Luggin-Haber capillary](#)
- [Placement of electrodes](#)

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

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... 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...

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vacuum, 0

Example: Part 2 286

E, V

Electrolyte Electrode

(-)

(+)

How would chemists label this plot?

How would physicists label this plot?

How would electrochemists label this plot?

286

vacuum

Example: Part 2 287

$E, V \text{ vs. SHE}$

Electrolyte Electrode

(-)

SHE, 0

(+)

How would chemists label this plot?

How would physicists label this plot?

How would electrochemists label this plot?

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

287

vacuum

Example: Part 2 288

$E, V \text{ vs. SHE}$

Electrolyte Electrode

(-)

SHE, 0

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

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

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

(+)

Nernst Equation:

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

How would chemists label this plot?

How would physicists label this plot?

How would electrochemists 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⁺)

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Example: Part 2

E, V vs. SHE

Electrolyte	Electrode
(-)	↑
SHE, 0	
$E^\circ(\text{Fc}^+/\text{Fc}) = +0.358 \text{ V}$	
$E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.771 \text{ V}$	
$E^\circ(\text{Br}_2/\text{Br}^-) = +1.0873 \text{ V}$	
(+)	↓

Nernst Equation:

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

How would chemists label this plot?
 How would physicists label this plot?
 How would electrochemists 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^+ $E = +0.358 \text{ V}$
 (b) Fe^{3+} and Fe^{2+}

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Example: Part 2

E, V vs. SHE

Electrolyte	Electrode
(-)	↑
SHE, 0	
$E^\circ(\text{Fc}^+/\text{Fc}) = +0.358 \text{ V}$	
$E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.771 \text{ V}$	
$E^\circ(\text{Br}_2/\text{Br}^-) = +1.0873 \text{ V}$	
(+)	↓

Nernst Equation:

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

How would chemists label this plot?
 How would physicists label this plot?
 How would electrochemists 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^+ $E = +0.358 \text{ V}$
 (b) Fe^{3+} and Fe^{2+} $E = +0.771 \text{ V}$
 (c) Both (a) and (b)

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Example: Part 2

E, V vs. SHE

Electrolyte	Electrode
(-)	↑
SHE, 0	
$E^\circ(\text{Fc}^+/\text{Fc}) = +0.358 \text{ V}$	
$E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.771 \text{ V}$	
$E^\circ(\text{Br}_2/\text{Br}^-) = +1.0873 \text{ V}$	
(+)	↓

Nernst Equation:

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

How would chemists label this plot?
 How would physicists label this plot?
 How would electrochemists 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^+ $E = +0.358 \text{ V}$
 (b) Fe^{3+} and Fe^{2+} $E = +0.771 \text{ V}$
 (c) Both (a) and (b) $E = +0.5645 \text{ V}$, because $\text{Fc}^{+/0}$ and $\text{Fe}^{3+/2+}$ would equilibrate by electron transfer... **EXPLAIN THIS!**

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?

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Example: Part 2

E, V vs. SHE

Electrolyte	Electrode	
(-)	↑	
SHE, 0		
$E^\circ(\text{Fc}^+/ \text{Fc}) = +0.358 \text{ V}$		
$E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.771 \text{ V}$		
$E^\circ(\text{Br}_2/\text{Br}^-) = +1.0873 \text{ V}$		
(+)	↓	

Nernst Equation:

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

How would chemists label this plot?
 How would physicists label this plot?
 How would electrochemists 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?

Electrons move down; think free energy...
 ... Roughly how far did each move?
 ~60 mV

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

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Example: Part 2

E, V vs. SHE

Electrolyte	Electrode	
(-)	↑	
SHE, 0		
$E^\circ(\text{Fc}^+/ \text{Fc}) = +0.358 \text{ V}$		
$E(\text{Fc}^+/ \text{Fc} / \text{Fe}^{3+} / \text{Fe}^{2+}) = +0.564 \text{ V}$		Equilibrated!
$E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.771 \text{ V}$		
$E^\circ(\text{Br}_2/\text{Br}^-) = +1.0873 \text{ V}$		
(+)	↓	

Nernst Equation:

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

How would chemists label this plot?
 How would physicists label this plot?
 How would electrochemists 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^+ $E = +0.358 \text{ V}$
 (b) Fe^{3+} and Fe^{2+} $E = +0.771 \text{ V}$
 (c) Both (a) and (b) $E = +0.5645 \text{ V}$, because Fc^{3+} and $\text{Fe}^{3+}/\text{Fe}^{2+}$ would equilibrate by electron transfer... **EXPLAIN THIS!**

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Example: Part 2

E, V vs. SHE

Electrolyte	Electrode	
(-)	↑	
SHE, 0		
$E^\circ(\text{Fc}^+/ \text{Fc}) = +0.358 \text{ V}$		
$E(\text{Fc}^+/ \text{Fc} / \text{Fe}^{3+} / \text{Fe}^{2+}) = +0.564 \text{ V}$		
$E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.771 \text{ V}$		
$E^\circ(\text{Br}_2/\text{Br}^-) = +1.0873 \text{ V}$		
(+)	↓	

Nernst Equation:

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

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

(a) Fc and Fc^+ $E = ???$
 (b) Fe^{3+} and Fe^{2+} $E = ???$
 (c) Both (a) and (b) $E = ???$

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Example: Part 2

E, V vs. SHE

Electrolyte Electrode

(-) ↑

SHE, 0

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

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

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

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

(+) ↓

Nernst Equation:

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

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

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

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Example: Part 2

E, V vs. SHE

Electrolyte Electrode

(-) ↑

SHE, 0

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

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

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

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

(+) ↓

Nernst Equation:

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

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

(a) Fc and Fc^+ $E = +0.358 \text{ V}$
 (b) Fe^{3+} and Fe^{2+} $E = +0.771 \text{ V}$
 (c) Equilibrated (a) and (b) $E = +0.5645 \text{ V}$
 (d) Fc and Fe^{3+} $E = ???$
 (e) Fc^+ $E = ???$
 (f) Fc^+ , H^+ , Fe^{3+} , Br^- $E = ???$

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Example: Part 2

E, V vs. SHE

Electrolyte Electrode

(-) ↑

SHE, 0

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

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

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

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

(+) ↓

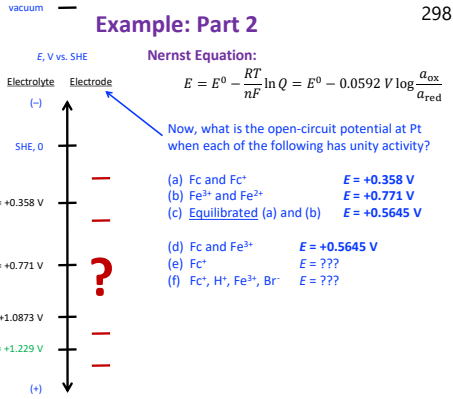
Nernst Equation:

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

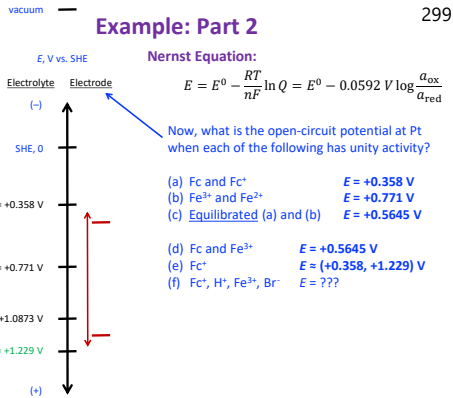
Now, what is the open-circuit potential at Pt when each of the following has unity activity?

(a) Fc and Fc^+ $E = +0.358 \text{ V}$
 (b) Fe^{3+} and Fe^{2+} $E = +0.771 \text{ V}$
 (c) Equilibrated (a) and (b) $E = +0.5645 \text{ V}$
 (d) Fc and Fe^{3+} $E = +0.5645 \text{ V}$
 (e) Fc^+ $E = ???$
 (f) Fc^+ , H^+ , Fe^{3+} , Br^- $E = ???$

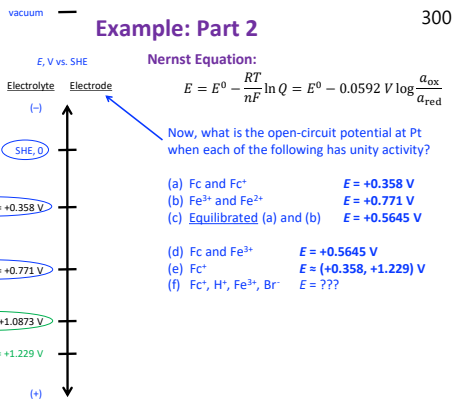
297



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300

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Example: Part 2

E, V vs. SHE

Electrolyte Electrode

(-)

SHE, 0

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

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

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

$E^\circ(\text{O}_2, \text{H}^+/\text{H}_2\text{O}) = +1.229 \text{ V}$

(+)

Nernst Equation:

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

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

(a) Fc and Fc⁺ $E = +0.358 \text{ V}$
 (b) Fe³⁺ and Fe²⁺ $E = +0.771 \text{ V}$
 (c) Equilibrated (a) and (b) $E = +0.5645 \text{ V}$
 (d) Fc and Fe³⁺ $E = +0.5645 \text{ V}$
 (e) Fc⁺ $E = (+0.358, +1.229) \text{ V}$
 (f) Fc⁺, H⁺, Fe³⁺, Br⁻ $E = (+0.771, +1.0873) \text{ V}$

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Example: Part 2

E, V vs. SHE

Electrolyte Electrode

(-)

SHE, 0

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

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

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

$E^\circ(\text{O}_2, \text{H}^+/\text{H}_2\text{O}) = +1.229 \text{ V}$

(+)

anodic current

an oxidation:
 $2\text{Cl}^- (\text{aq}) \rightleftharpoons \text{Cl}_2 (\text{g}) + 2\text{e}^-$

onset of H⁺ reduction

onset of Cl oxidation

cathodic current

a reduction:
 $2\text{H}^+ (\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2 (\text{g})$

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

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