162

Lecture #6 of 17

162

163

Measurements in Electrochemistry

Chapters 1 and 15

163

164

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

164

(UPDATED) 165

Looking forward… Section 1.1 (and some of Chapter 15)

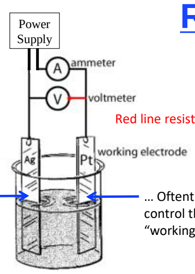
- Reference electrodes *(halfway complete)*
- 2-electrode versus 3-electrode measurements *(halfway complete)*
- **Potentiostats**
- **Compliance voltage/current**
- *J–E and I–E curves*
- *Kinetic overpotential*
- *Electrochemical window*
- *Faradaic reactions*

165

Experiments: 166

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

RECALL:



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

… Oftentimes, most of us wish to control the potential of this "working" electrode…

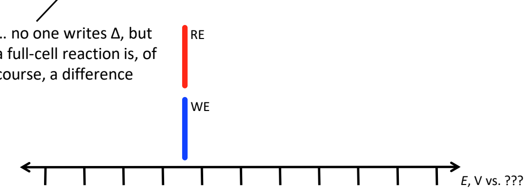
166

… for example, let's say both electrodes are platinum… 167

RECALL:

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

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

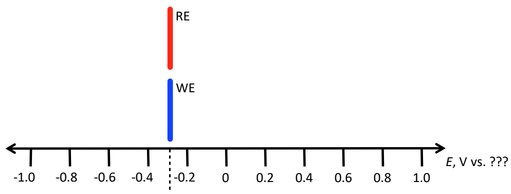


167

… and at “open circuit,” no potential bias is applied between them… 168
(disconnect the wire!)

RECALL:

$$E_{\mathrm{OC}} = 0.0\ \mathrm{V} = E_{WE} - E_{RE}$$



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

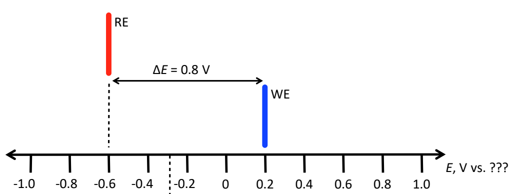
… and by the way, *we don’t know this potential…*
… and it is not well-defined because we cannot answer the question:
What is the half-reaction that defines it?

168

… now, if we apply +0.8 V to the WE (reconnect the wire)… 169
the potential of *both* electrodes likely changes, and *not likely symmetrically…*

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

RECALL:

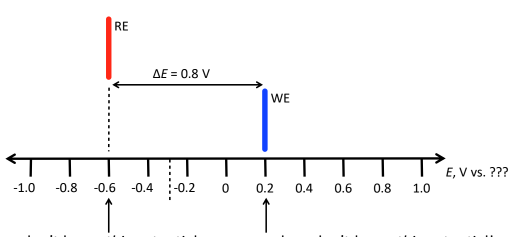


169

… even worse, we don’t now the potential of either electrode… 170

RECALL:

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



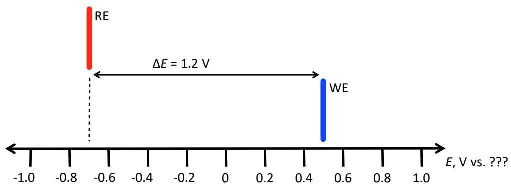
… we don’t know *this* potential… … and we don’t know *this* potential!

170

… you get the picture! 171

RECALL:

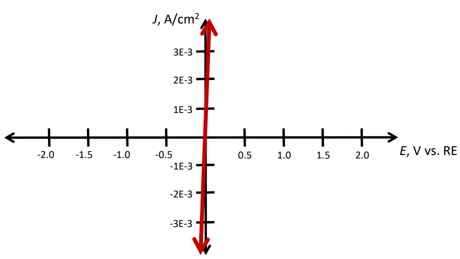
$$E_{app} = +1.2\ V$$



171

In principle, this problem can be solved by using a second electrode that is an (ideal) *reference electrode*… (ideally) non-polarizable: 172

RECALL:

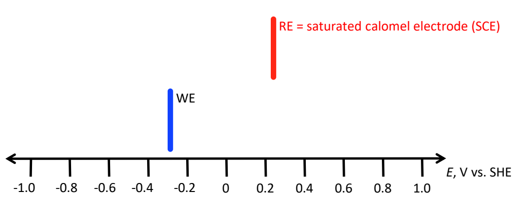


172

… so get rid of the Pt reference electrode, and substitute in an SCE… 173
… which has a Pt wire in it…

$$\Delta E \neq 0.0\ V$$ *(likely)*

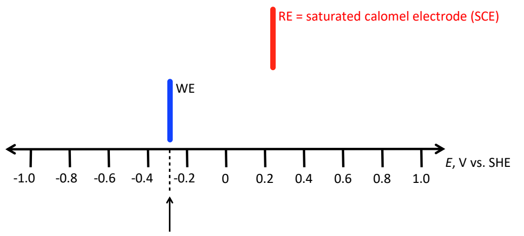
RECALL:



173

... so get rid of the Pt reference electrode, and substitute in an SCE... 174
... which has a Pt wire in it...

$E_{\mathrm{oc}} \neq 0.0\ \mathrm{V}$ *(likely)* **RECALL:**

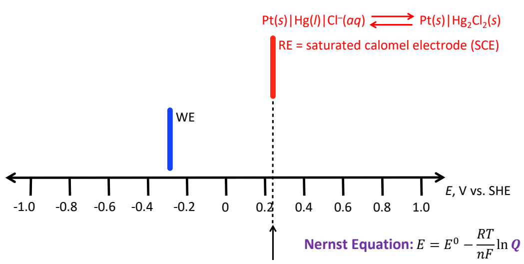


... where we still don't know this potential because we cannot answer:
What is the half-reaction that defines it?

174

... so get rid of the Pt reference electrode, and substitute in an SCE... 175
... which has a Pt wire in it...

$E_{\mathrm{oc}} \neq 0.0\ \mathrm{V}$ *(likely)* **RECALL:**



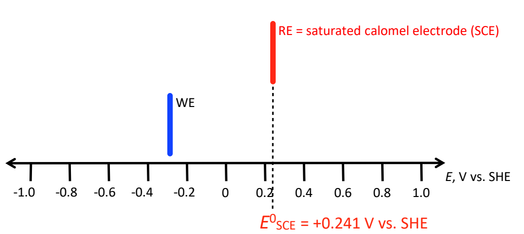
Nernst Equation: $E = E^0 - \frac{RT}{nF}\ln Q$

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

175

... so get rid of the Pt reference electrode, and substitute in an SCE... 176
... which has a Pt wire in it...

$E_{\mathrm{oc}} \neq 0.0\ \mathrm{V}$ *(likely)* **RECALL:**



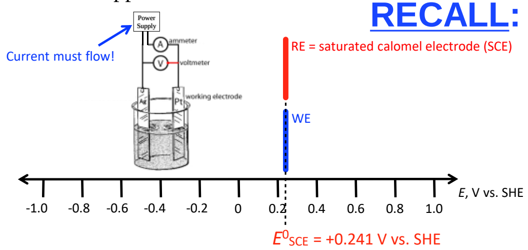
... the SCE has a defined potential of +0.241 V vs. SHE...

176

… so get rid of the Pt reference electrode, and substitute in an SCE… 177
… which has a Pt wire in it…

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

RECALL:



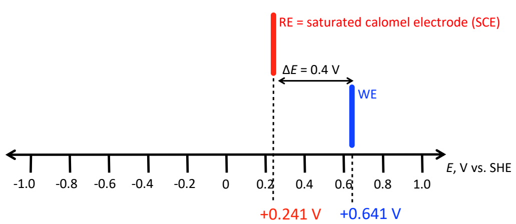
… the SCE has a defined potential of +0.241 V vs. SHE…
… and its potential "does not" move (much, usually)…

177

… how did we calculate that (meaning +0.641 V)? 178

RECALL:

E_{app} = +0.4 V



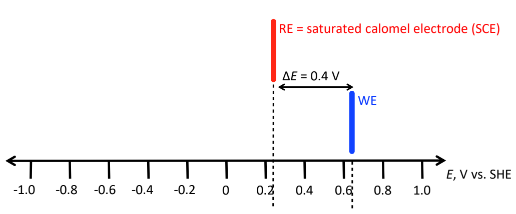
… the SCE has a defined potential of +0.241 V vs. SHE…
… and its potential "does not" move (much, usually)…

178

… how did we calculate that (meaning +0.641 V)? 179

RECALL:

E_{app} = +0.4 V



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

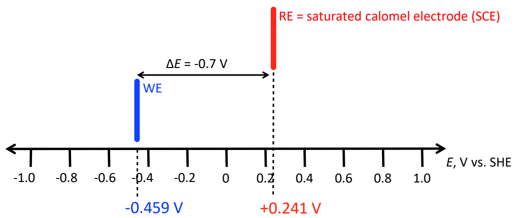
$E_{WE} = \underline{+0.4\ \text{V}} + 0.241\ \text{V} = +0.641\ \text{V}$

179

... you get the picture!... 180

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

E_{app} = -0.7 V **RECALL:**

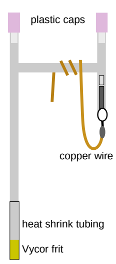


$$\underline{\Delta E} = E_{WE} - E_{RE}$$

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

180

... here is what a commercial SCE looks like: 181



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

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

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

181

Specifically, we would really like to have a reference electrode that has the following attributes. 182

1. It has a well-defined and invariant potential. That is, no matter how much current we draw from this electrode, its potential must not vary.

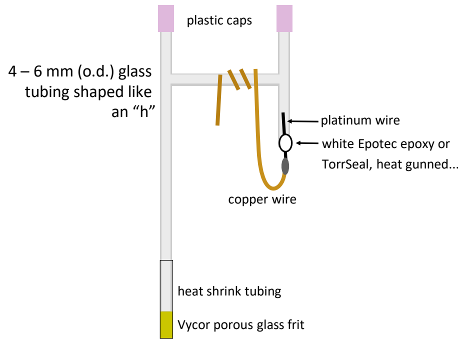
2. It has zero impedance. That is, it imposes no resistive load on our cell.

3. It does not "contaminate" our solution. That is, it is not a source of undesired ions in our electrochemical cell.

182

... but no such thing exists. 183

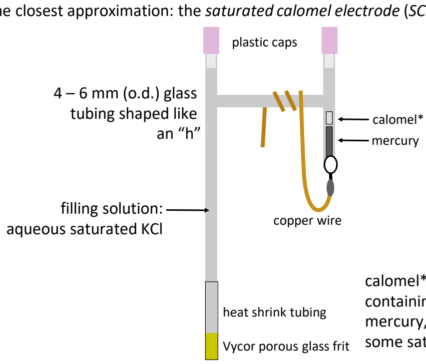
The closest approximation: the *saturated calomel electrode* (*SCE*)



183

... but no such thing exists. 184

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



calomel* - a paste containing liquid mercury, Hg_2Cl_2(s), and some sat’d *aq.* KCl

184

... but no such thing exists. (see Figure E.1 on the inside back cover of B&F) 185

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

the *saturated calomel electrode* (*SCE*)

$$\mathbf{Hg_2Cl_2 + 2e^- \rightarrow 2Cl^- + 2Hg^0}$$

E^0 = +0.241 V vs. SHE

the *saturated sodium calomel electrode* (*SSCE*)

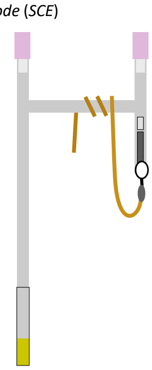
$$\mathbf{Hg_2Cl_2 + 2e^- \rightarrow 2Cl^- + 2Hg^0}$$

E^0 = +0.236 V vs. SHE

the *saturated mercurous sulfate electrode* (*MSE*)

$$\mathbf{Hg_2SO_4 + 2e^- \rightarrow SO_4^{2-} + 2Hg^0}$$

E^0 = +0.64 V vs. SHE



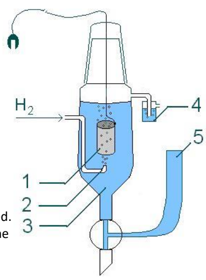
185

… great. But what is an SHE (standard hydrogen electrode)? 186

$$2H^+ + 2e^- \rightarrow H_2$$

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

The scheme of the standard (or normal) hydrogen electrode:
1) platinized platinum electrode (large area)
2) hydrogen blow (bubbling)
3) solution of aqueous acid with proton activity equal to one (dimensionless)
4) means to prevent O_2 interference (sealant)
5) reservoir through which the second half-element of the electrochemical cell is attached. This creates an ionically conductive path to the working electrode of interest (salt bridge).



* one rendition of an SHE

http://en.wikipedia.org/wiki/Standard_hydrogen_electrode

186

… another common RE is the aq. Ag/AgCl electrode (KCl sat'd)! 187

$$AgCl + e^- \rightarrow Cl^- + Ag^0$$

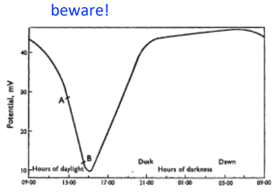
E^0 = +0.197 V vs. SHE

AgCl (white)

Ag (gray), from photodecomposition of AgCl

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

But for those of you doing **photo**electrochemistry, beware!



Pt (s) | Hg (*l*) | Hg_2Cl_2 (s) | Cl^- (sat'd, *aq*) | AgCl (s) | Ag (s)

Moody, Oke, & Thomas, *Analyst*, 1969, *94*, 803

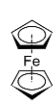
187

… and three final "specialty" reference electrodes include… 188

For aqueous **alkaline** electrolyte conditions
Mercury/Mercury Oxide (Hg/HgO, 20 wt% KOH)
E^0 = +0.098 V vs. SHE

For **non-aqueous** (CH_3CN) electrolyte solutions
Ag/$AgNO_3$ (0.01 M) in CH_3CN
E^0 = +0.3 V vs. SCE (*aq*), which is effectively +0.54 V vs. SHE

B&F 2.1.7
When a reference electrode cannot be used or is not wanted
"**Quasi-reference**" electrode as a Pt wire and any redox couple



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

188

How would one test the accuracy of a reference electrode? 189

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

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

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

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

189

190

An example of two RE scales at once is helpful…

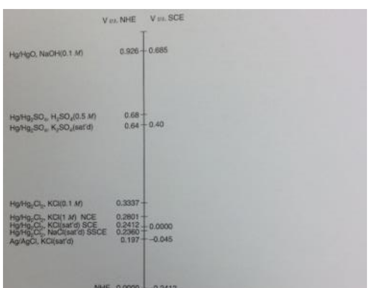


Figure E.1 Potentials of reference electrodes in aqueous solutions at 25°C. [See D. J. G. Ives and G. J. Janz, "Reference Electrodes," Academic, New York, 1961.]

B&F back inside

190

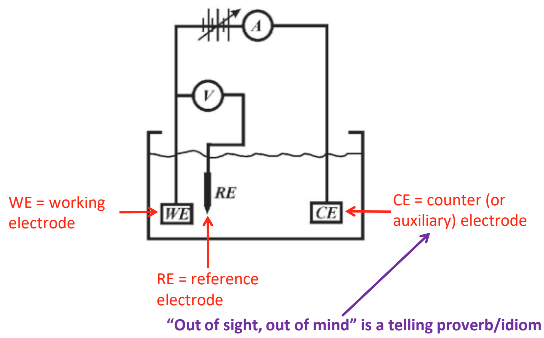
… now, as mentioned earlier, unfortunately, real reference electrodes can do *none* of these things perfectly… 191

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

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

191

… so we resort to a *3-electrode potentiostat…* 192



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

192

(UPDATED) 193

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*

193

… invented in 1937 by Hickling… 194

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

By A. Hickling.

Received 16th September, 1941.

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

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

Hickling, *Trans. Faraday Soc.*, 1942, *38*, 27

194

… invented in 1937 by Hickling… 195

this is a vacuum tube!

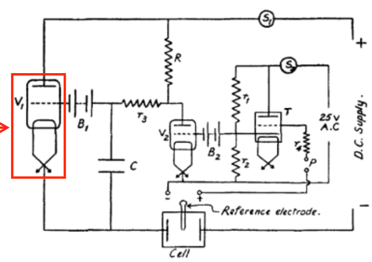


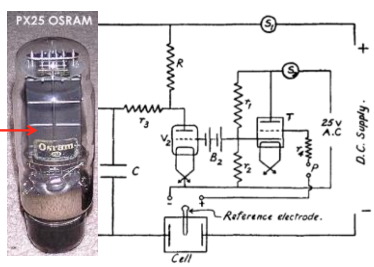
Fig. 1.—Potentiostat Circuit.

Hickling, *Trans. Faraday Soc.*, 1942, *38*, 27

195

… invented in 1937 by Hickling… 196

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



https://www.tubeworld.com/european.htm Fig. 1.—Potentiostat Circuit.

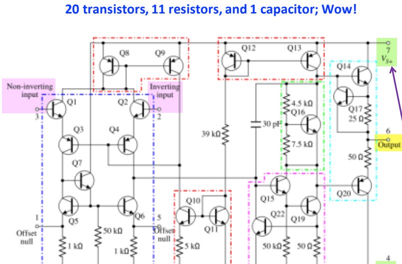
Hickling, *Trans. Faraday Soc.*, 1942, *38*, 27

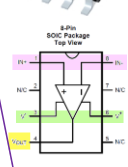
196

… this is how (many famous electrochemists) do this today… 197
… meaning with somewhat "old" instruments like described in B&F

an op-amp

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





fixed values (vs. ground)

http://en.wikipedia.org/wiki/Operational_amplifier
https://www.ti.com/product/LMP7721#tech-docs

197

… this is how (many famous electrochemists) do this today… 198

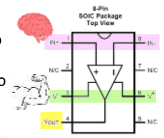
… meaning with somewhat "old" instruments like described in B&F

an op-amp

Op-amp Golden Rules

Ideal rules that are close to correct in practice.

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



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

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

… How does the output then pass current?

http://www.clipartsfree.net/small/1174-brain-in-profile-clipart.html
http://shujaabbas.hubpages.com/hub/Cartoon-Boxing-Champion

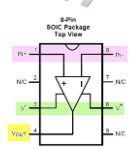
Horowitz and Hill, The Art of Electronics, Cambridge University Press, 1980
http://hyperphysics.phy-astr.gsu.edu/hbase/electronic/opampi.html#c2

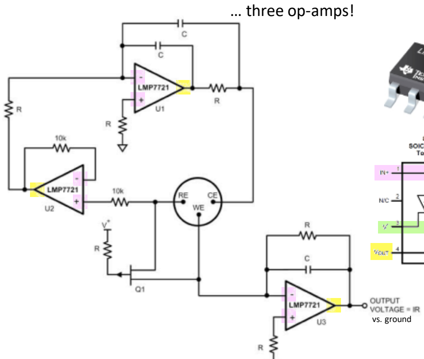
198

… this is how (many famous electrochemists) do this today… 199

… three op-amps!

an op-amp





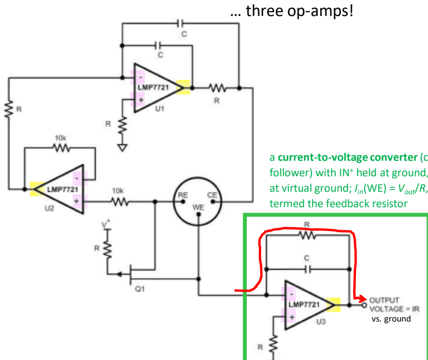
2. Three operational amplifier potentiostatic circuit

http://electronicdesign.com/Content/14978/59899_fig_02.jpg

199

… this is how (many famous electrochemists) do this today… 200

… three op-amps!



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

2. Three operational amplifier potentiostatic circuit

http://electronicdesign.com/Content/14978/59899_fig_02.jpg

200

... this is how (many famous electrochemists) do this today... 201

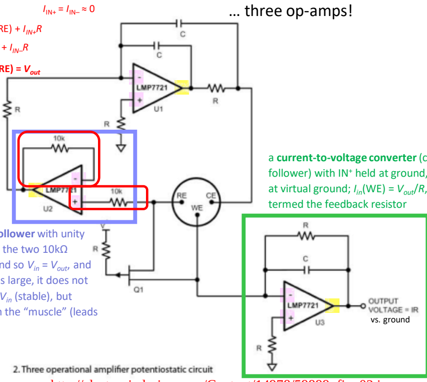
... three op-amps!

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

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

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

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



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

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

2. Three operational amplifier potentiostatic circuit

http://electronicdesign.com/Content/14978/59899_fig_02.jpg

201

... this is how (many famous electrochemists) do this today... 202

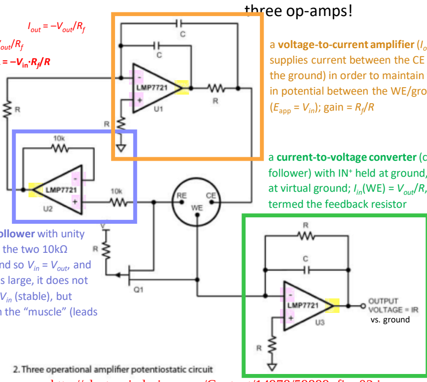
... three op-amps!

$I_{in} = I_{out}$

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

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

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



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

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

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

2. Three operational amplifier potentiostatic circuit

http://electronicdesign.com/Content/14978/59899_fig_02.jpg

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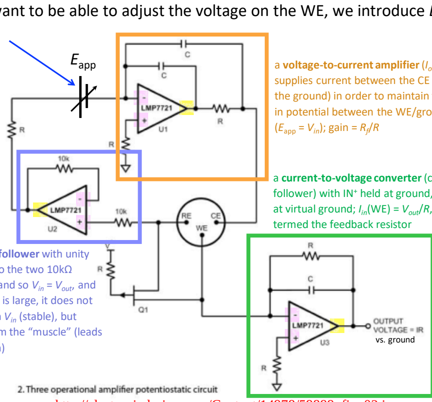
If we want to be able to adjust the voltage on the WE, we introduce E_{app} here... 203



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

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

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

2. Three operational amplifier potentiostatic circuit

http://electronicdesign.com/Content/14978/59899_fig_02.jpg

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Note especially the following **for "older" (simpler) potentiostats**:

1. The working electrode (WE) is at (virtual) ground and has a very low impedance, $Z = R + iX$. You "cannot" get an electrical shock at this electrode or at this input to the potentiostat.

2. Amplifier U3 takes the current at the WE and converts it into a potential so it can be recorded. $V = IR$ at the output of U3.

3. The reference electrode (RE), connected to the non-inverting input (+) of the op-amp U2, is asked to source a *minute* amount of current (~3 fA for this particular op-amp; 0 fA is the ideal case).

4. Op-amp U1 produces, at the counter electrode (CE), an output current, I_{out}, that is proportional to the potential difference between RE and WE (i.e. ground). *Caution: You CAN get a lethal shock at this electrode. However, this power is not infinite (your wall sockets have a limited power they can supply). The potentiostat limits are termed the* *compliance voltage and compliance current…*

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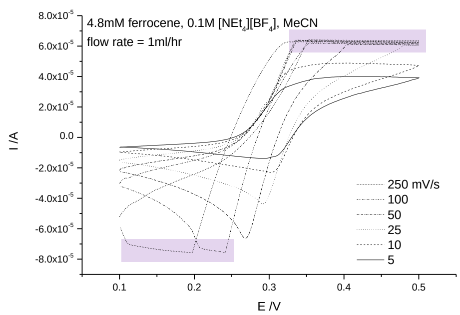
Beware of compliance voltage issues (maximum voltage to CE)…
… and compliance current too!



https://www.metrohm.com/en_us/products/electrochemistry.html

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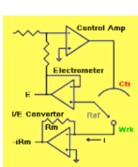
Active I/E Converter versus Passive I/E Converter

… meaning "older"



- **Advantages**

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

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

- **Disadvantages**

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

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

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

On the Instability of Current Followers in Potentiostat Circuits

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

E. Clifford Toren, Jr.[1]
Departments of Medicine and Pathology, University of Wisconsin, Madison, Wis. 53706

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

Davis and Toren, *Anal. Chem.*, 1974, *46*, 647

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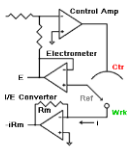
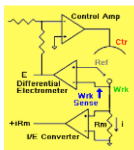
Active I/E Converter versus Passive I/E Converter

... meaning "newer"



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

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



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

http://www.consultrsr.net/resources/pstats/design2.htm

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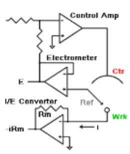
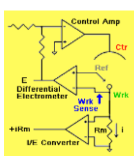
Active I/E Converter versus Passive I/E Converter

... meaning "newer"





- **Advantages**

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

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

- **Disadvantages**

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

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

http://www.consultrsr.net/resources/pstats/design2.htm

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Potentiostat summary… for non-EE majors…

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

Rowe, ..., Plaxco, *PLoS One*, 2011, *6*, e23783
Mott, ..., Sykes, *J. Chem. Educ.*, 2014, *91*, 1028

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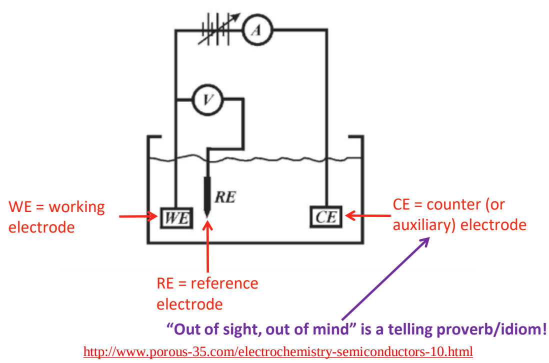
… and that is why we use a *3-electrode potentiostat*… 210



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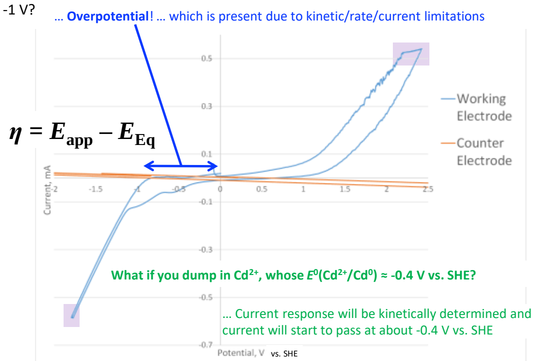
Now, pretend this experimental *I–E* curve (from my labs; in fact) was measured when the Pt WE was switched with a Hg WE… why does little current flow until ~ -1 V? 211

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



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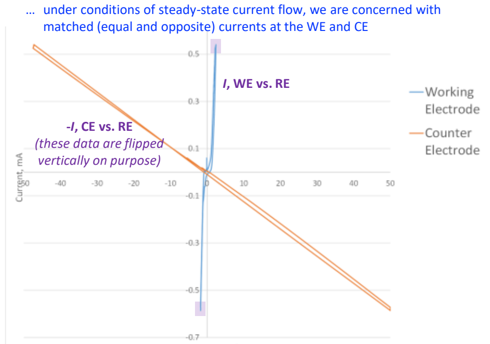
Also, don't forget about possible compliance voltage issues (maximum voltage to CE)… and compliance current too! 212

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



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(UPDATED) 213

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*

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