

149

Lecture #6 of 20

149

150

Measurements in Electrochemistry

Chapters 1 and 15

150

151

- 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

151

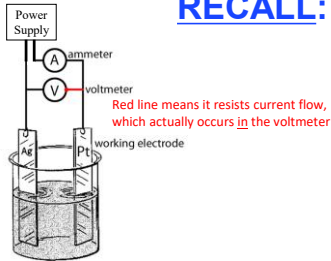
152

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

152

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



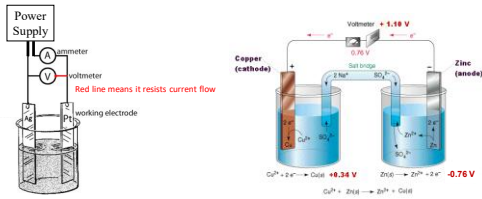
RECALL:

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

153

These schematics introduce some terms that we must define:

154



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

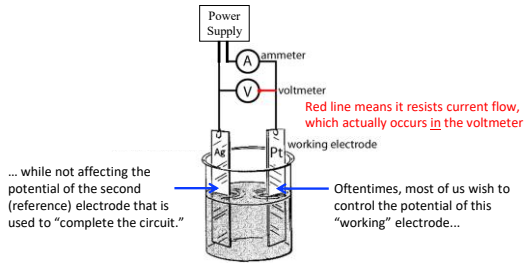
ammeter – a device for measuring a current; an ideal ammeter has zero input impedance (i.e. it imposes no potential drop)

154

Experiments:

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

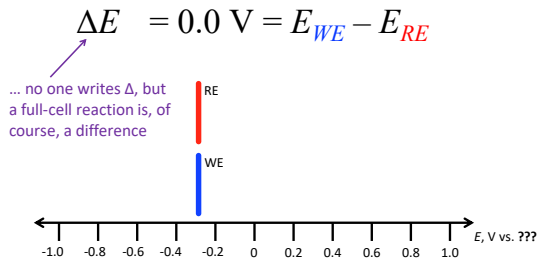
155



155

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

156

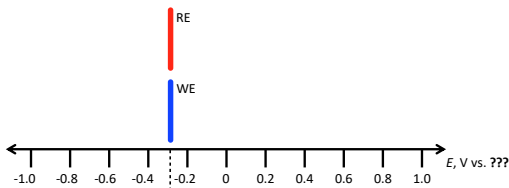


156

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

157

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



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

... and by the way, we can't predict this potential...

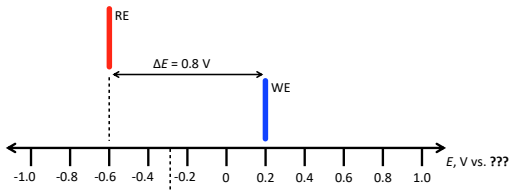
... it is not well-defined because we cannot answer the question:

What is the half-reaction that defines it?

157

... now, if we apply +0.8 V to the WE (reconnect the wire)... 158
the potential of *both* electrodes likely changes, and *not likely symmetrically*...

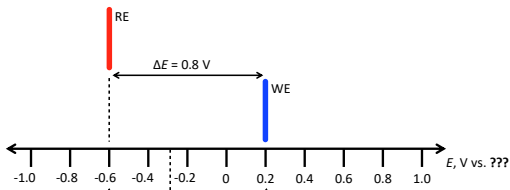
$$E_{\text{app}} = +0.8 \text{ V}$$



158

... even worse, we don't now the potential of either electrode... 159

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



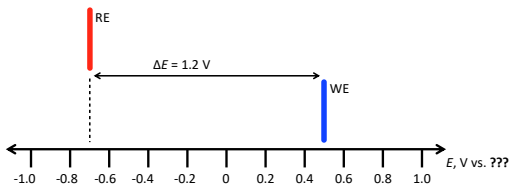
... we don't know *this* potential...

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

159

... you get the picture! 160

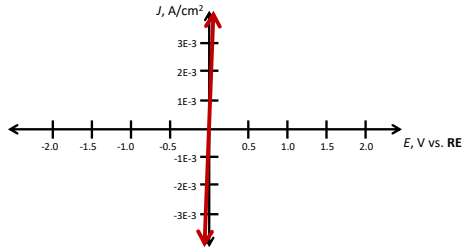
$$E_{\text{app}} = +1.2 \text{ V}$$



160

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

161



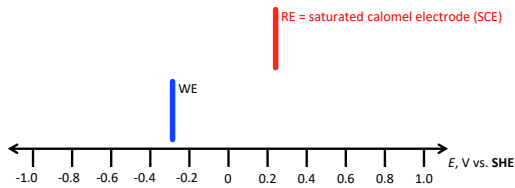
161

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

162

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

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



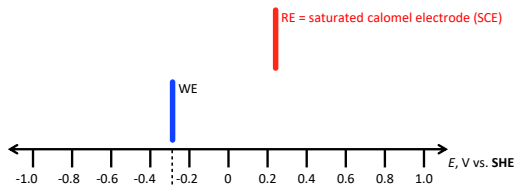
162

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

163

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

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

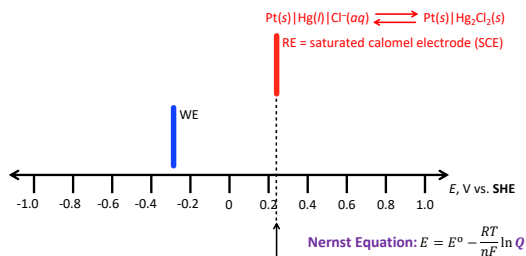


... where we still can't predict this potential because we cannot answer:
What is the half-reaction that defines it?

163

... so get rid of the Pt reference electrode, and substitute in an SCE... 164
... which has a Pt wire in it...

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

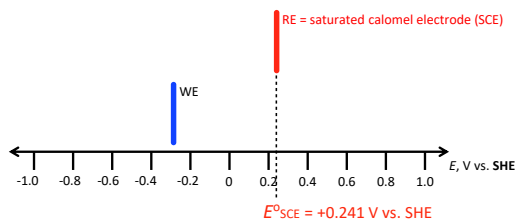


... but, where we know this potential because we can answer:
What is the half-reaction that defines it?

164

... so get rid of the Pt reference electrode, and substitute in an SCE... 165
... which has a Pt wire in it...

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

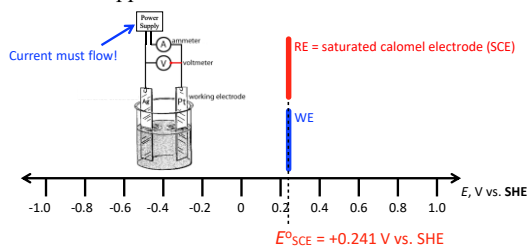


... the SCE has a defined reduction potential of +0.241 V vs. SHE...

165

... so get rid of the Pt reference electrode, and substitute in an SCE... 166
... which has a Pt wire in it...

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



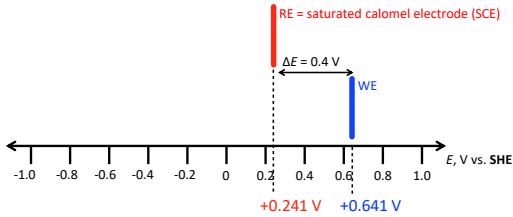
... the SCE has a defined reduction potential of +0.241 V vs. SHE...
... and its potential "does not" move (much, usually)...

166

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

167

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



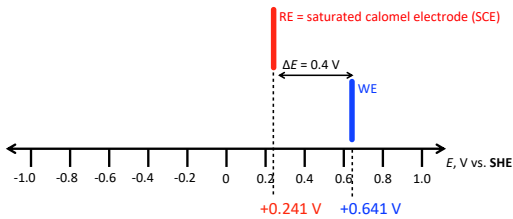
... the SCE has a defined reduction potential of +0.241 V vs. SHE...
... and its potential "does not" move (much, usually)...

167

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

168

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



$$\begin{aligned} \Delta E &= E_{\text{WE}} - E_{\text{RE}} \\ E_{\text{WE}} &= \underline{+0.4 \text{ V}} + \underline{+0.241 \text{ V}} = +0.641 \text{ V} \end{aligned}$$

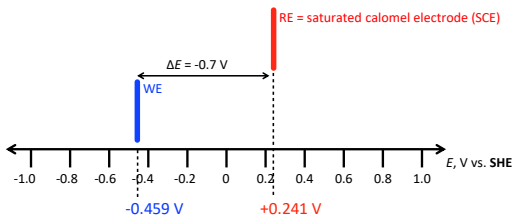
168

... you get the picture!...

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

169

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

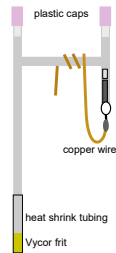


$$\begin{aligned} \Delta E &= E_{\text{WE}} - E_{\text{RE}} \\ E_{\text{WE}} &= \underline{-0.7 \text{ V}} + \underline{+0.241 \text{ V}} = -0.459 \text{ V} \end{aligned}$$

169

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

170



Some major companies that have excellent additional information on their websites:
AMETEK (PAR, Solartron), BASI, Bio-Logic, CH Instruments, Gamry, Metrohm, Pine, etc.

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

170

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

171

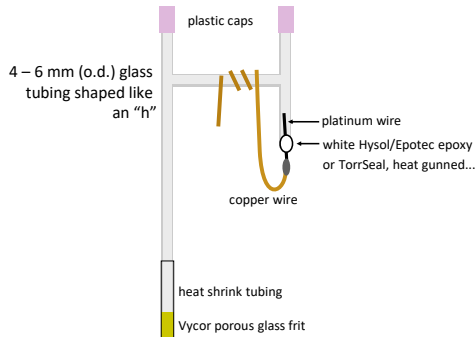
1. It has a well-defined and invariant potential. That is, no matter how much current we draw from this electrode, its potential must not vary.
2. It has zero impedance. That is, it imposes no resistive load on our cell.
3. It does not "contaminate" our solution. That is, it is not a source of undesired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

171

... but no such thing exists.

172

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

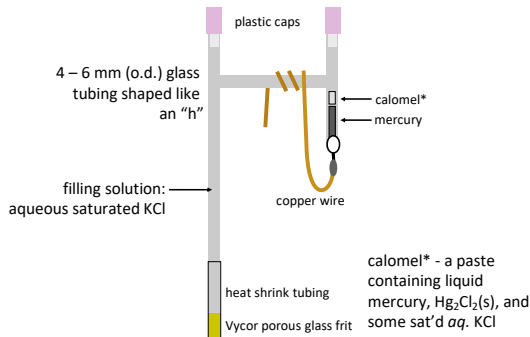


172

... but no such thing exists.

173

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



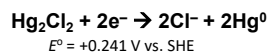
173

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

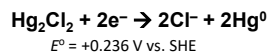
174

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

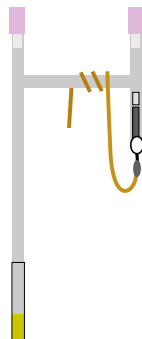
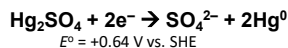
the *saturated calomel electrode (SCE)*



the *saturated sodium calomel electrode (SSCE)*



the *saturated mercurous sulfate electrode (MSE)*



174

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

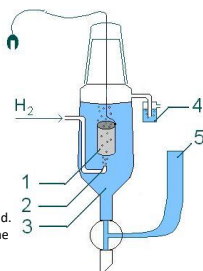
175



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

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

- 1) platinized platinum electrode (large area)
- 2) hydrogen blow (bubbling)
- 3) solution of aqueous acid with proton activity equal to one (dimensionless)
- 4) means to prevent 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).



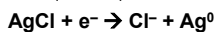
* one rendition of an SHE

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

175

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

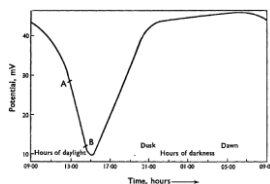
176



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

AgCl (white)

But for those of you doing
photoelectrochemistry,
beware!



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



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

176

... and three final "specialty" reference electrodes include...

177

For aqueous **alkaline** electrolyte conditions
Mercury/Mercury Oxide (Hg/HgO, 20 wt% KOH)

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

For **non-aqueous** (CH_3CN) electrolyte solutions
Ag/AgNO₃ (0.01 M) in CH_3CN

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

B&F 2.1.7

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

- * Used when you already have a cell with two halves of a redox couple that will not change during your experiment and thus you know the half-reaction that defines your RE (or else it's a "pseudo-reference" electrode)
- * Calibrate with Fc (ferrocene)



177

How would one test the accuracy of a reference electrode?

178

- 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 in your lab, with a voltmeter
(e.g. Ag (s) | AgCl (s) | Cl⁻ (sat'd) | AgCl (s) | Ag (s))

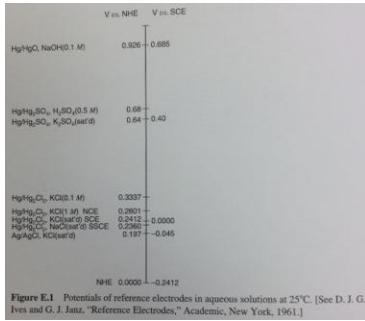
What if no matter what you do, the potential is unstable or the equipment overloads (i.e. gives you an error; often a **red light** turns on)?

- 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)

178

An example of two RE scales at once is helpful... 179



B&F back inside

179

... now, as mentioned earlier, unfortunately, real reference electrodes can do *none* of these things perfectly... 180

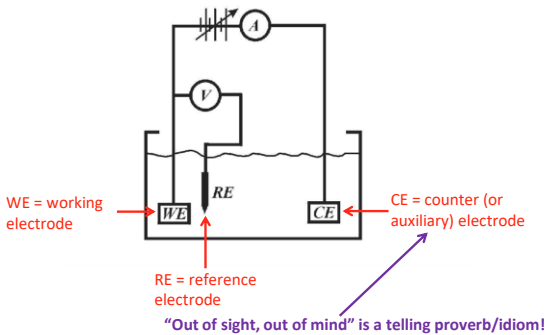
Specifically, we would really like to have a reference electrode that has the following attributes:

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.

180

... so we resort to a 3-electrode potentiostat...

181



181

182

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

182

... invented in 1937 by Hickling...

183

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.

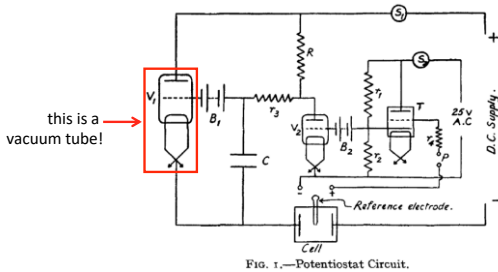
... Would a person drive a car without knowing how an ICE works?... Okay, bad example...

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

183

... invented in 1937 by Hickling...

184



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

184

... invented in 1937 by Hickling...

185

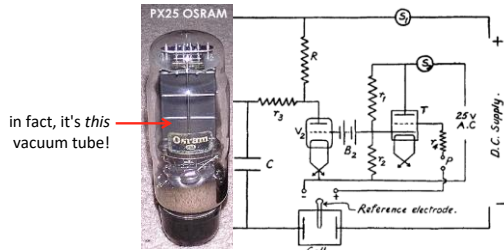


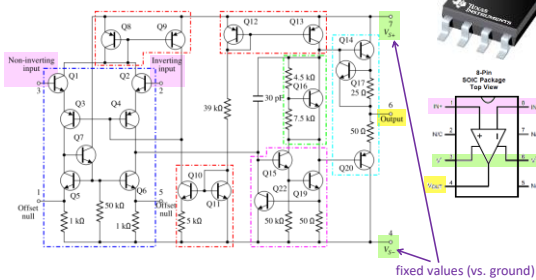
FIG. 1.—Potentiostat Circuit.

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

185

... this is how (many famous electrochemists) do this today... **(BRIEFLY)** 186
... meaning with somewhat "old" instruments like described in B&F

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



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

186

... this is how (many famous electrochemists) do this today... **(BRIEFLY)** 187
... meaning with somewhat "old" instruments like described in B&F

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?

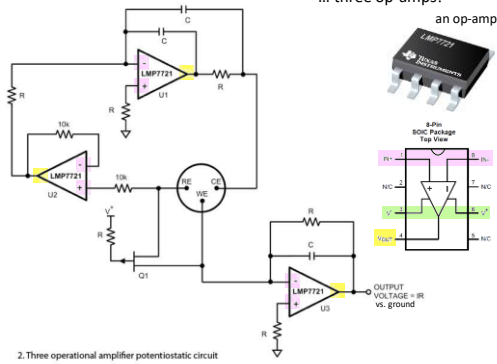
Horowitz and Hill, *The Art of Electronics*, Cambridge University Press, 1980
<http://hyperphysics.phy-astr.gsu.edu/hbase/electronic/opamp.html#c2>

187

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

... three op-amps!

188

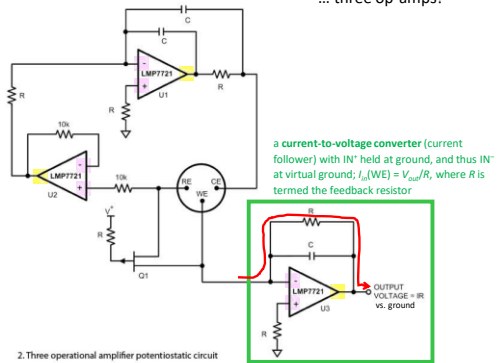


188

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

(BRIEFLY) 189

... three op-amps!

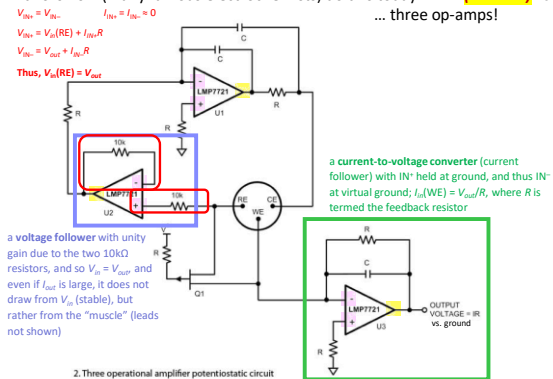


189

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

(BRIEFLY) 190

... three op-amps!

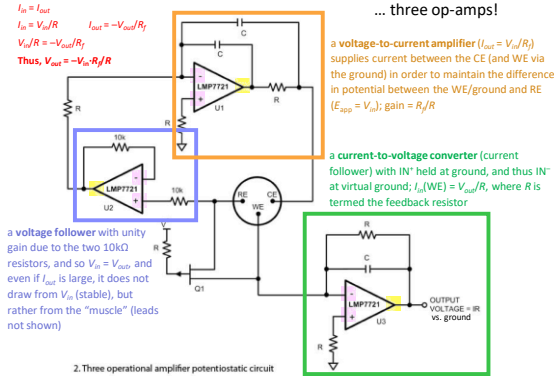


190

... this is how (many famous electrochemists) do this today... **[BRIEFLY]** 191

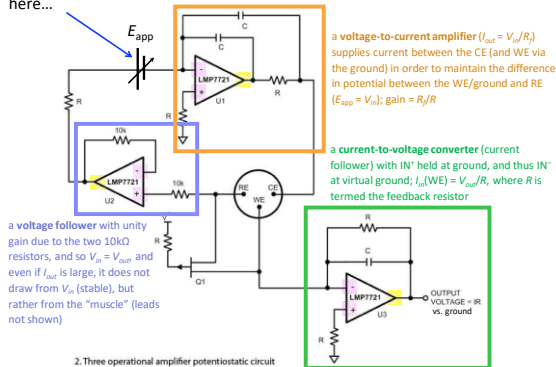
$$I_{in} = I_{out} \\ I_{in} = V_{in}/R \quad I_{out} = -V_{out}/R_f \\ V_{out}/R = -V_{in}/R_f \\ \text{Thus, } V_{out} = -V_{in} R_f/R$$

... three op-amps!



191

If we want to be able to adjust the voltage on the WE, we introduce E_{app} 192 here...



192

Note especially the following for "older" (simpler) potentiostats: 193

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...*

193

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

194

- The potentiostat does not control the potential of the working electrode! (*a little, in newer models*)
- The potentiostat controls the potential of the counter electrode **only** (relative to the working electrode) (*not entirely, in newer models*)
- 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" (*newer*) potentiostats do not hold the WE at earth ground, but can also measure potentials across electrolyte interfaces using 4-electrodes

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

194