Lecture #6 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... 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
Experiments:

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

... 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...

RECALL:

Red line resists current flow
... for example, let’s say both electrodes are platinum...

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

... no one writes \( \Delta \), but a full-cell reaction is, of course, a difference

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

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

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

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

What is the half-reaction that defines it?
... now, if we apply +0.8 V to the WE (reconnect the wire)...
the potential of both electrodes likely changes, and not likely symmetrically...

\[ E_{\text{app}} = +0.8 \text{ V} \]

RECALL:
... even worse, we don’t now the potential of either electrode...

\[ E_{\text{app}} = +0.8 \text{ V} \]

RECALL:

\[ \Delta E = 0.8 \text{ V} \]

... we don’t know \textit{this} potential... ... and we don’t know \textit{this} potential!
... you get the picture!

\[ E_{\text{app}} = +1.2 \text{ V} \]

RECALL:

\[ \Delta E = 1.2 \text{ V} \]
In principle, this problem can be solved by using a second electrode that is an (ideal) reference electrode... (ideally) non-polarizable:

\[ J, \text{ A/cm}^2 \]

\[ E, \text{ V vs. RE} \]

RECALL:
\[ \Delta E \neq 0.0 \text{ V (likely)} \]

RECALL:

RE = saturated calomel electrode (SCE)

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

... which has a Pt wire in it...
$E_{oc} \neq 0.0 \text{ V} \ (\text{likely})$

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

What is the half-reaction that defines it?

RECALL:

$\text{RE} = \text{saturated calomel electrode (SCE)}$
... so get rid of the Pt reference electrode, and substitute in an SCE...

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

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

RECALL:

\[ E = E^0 - \frac{RT}{nF} \ln Q \]

\[ \text{Pt(s)}|\text{Hg(l)}|\text{Cl}^-(aq) \leftrightarrow \text{Pt(s)}|\text{Hg}_2\text{Cl}_2(s) \]

RE = saturated calomel electrode (SCE)

... but, where we know this potential because we can answer:

What is the half-reaction that defines it?
... so get rid of the Pt reference electrode, and substitute in an SCE...

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

RECALL:

$E_{SCE}^0 = +0.241 \text{ V vs. SHE}$

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

... the SCE has a defined potential of +0.241 V vs. SHE...
\[ E_{\text{app}} = 0.0 \text{ V} \]

(ammeter \(\neq 0\) A)

RECALL:

\[ E^0_{\text{SCE}} = +0.241 \text{ V vs. SHE} \]

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

... and its potential “does not” move (much, usually)...

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

... which has a Pt wire in it...
... how did we calculate that (meaning +0.641 V)?

\[ E_{\text{app}} = +0.4 \text{ V} \]

RECALL:

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

... and its potential “does not” move (much, usually)...

\[ \Delta E = 0.4 \text{ V} \]
... how did we calculate that (meaning +0.641 V)?

\[ E_{app} = +0.4 \text{ V} \]

**RECALL:**

\[ \Delta E = E_{WE} - E_{RE} \]

\[ E_{WE} = +0.4 \text{ V} + 0.241 \text{ V} = +0.641 \text{ V} \]
... you get the picture!

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

\[ E_{\text{app}} = -0.7 \text{ V} \]

**RECALL:**

\[
\Delta E = E_{\text{WE}} - E_{\text{RE}} \\
\Delta E = -0.7 \text{ V} \\
E_{\text{WE}} = -0.7 \text{ V} + 0.241 \text{ V} = -0.459 \text{ V}
\]

RE = saturated calomel electrode (SCE)
... here is what a commercial SCE looks like:

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

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

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.
... but no such thing exists.

The closest approximation: the *saturated calomel electrode* (SCE)
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- **Calomel** - a paste containing liquid mercury, $\text{Hg}_2\text{Cl}_2(s)$, and some saturated aqueous KCl
- **Calomel** - a paste containing liquid mercury, $\text{Hg}_2\text{Cl}_2(s)$, and some saturated aqueous KCl
- **Aqueous saturated KCl**
- **Vycor porous glass frit**
- **Heat shrink tubing**
- **Copper wire**
- **4–6 mm (o.d.) glass tubing shaped like an “h”**
- **Plastic caps**
... but no such thing exists. (see Figure E.1 on the inside back cover of B&F)

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

The *saturated calomel electrode (SCE)*

\[
\text{Hg}_2\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^- + 2\text{Hg}^0
\]

\[E^0 = +0.241 \text{ V vs. SHE}\]

the *saturated sodium calomel electrode (SSCE)*

\[
\text{Hg}_2\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^- + 2\text{Hg}^0
\]

\[E^0 = +0.236 \text{ V vs. SHE}\]

the *saturated mercurous sulfate electrode (MSE)*

\[
\text{Hg}_2\text{SO}_4 + 2e^- \rightarrow \text{SO}_4^{2-} + 2\text{Hg}^0
\]

\[E^0 = +0.64 \text{ V vs. SHE}\]
2H$^+ + 2e^- \rightarrow H_2$

$E_{\text{SHE}}^0 = 0.0000 \text{ V vs. SHE}$

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

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

\[ \text{AgCl} + e^- \rightarrow \text{Cl}^- + \text{Ag}^0 \]

\[ E^0 = +0.197 \text{ V vs. SHE} \]

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

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

Pt (s) | Hg (l) | Hg₂Cl₂ (s) | Cl⁻ (sat’d, aq) | AgCl (s) | Ag (s)

... and three final “specialty” reference electrodes include...

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

\[ E^0 = +0.098 \text{ V vs. SHE} \]

For **non-aqueous** (CH$_3$CN) electrolyte solutions
Ag/AgNO$_3$ (0.01 M) in CH$_3$CN

\[ E^0 = +0.3 \text{ V vs. SCE (aq), which is effectively } +0.54 \text{ V vs. SHE} \]

**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
* Calibrate with Fc (ferrocene)
How would one test the accuracy of a reference electrode?

- 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)
An example of two RE scales at once is helpful...

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.

... now, as mentioned earlier, unfortunately, real reference electrodes can do *none* of these things perfectly...
... so we resort to a 3-electrode potentiostat...

WE = working electrode
RE = reference electrode
CE = counter (or auxiliary) electrode

“Out of sight, out of mind” is a telling proverb/idiom!

http://www.porous-35.com/electrochemistry-semiconductors-10.html
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
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.
... invented in 1937 by Hickling...

this is a vacuum tube!

Fig. 1.—Potentiostat Circuit.
... invented in 1937 by Hickling...

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

https://www.tubeworld.com/european.htm

**Fig. 1.**—Potentiostat Circuit.

... this is how (many famous electrochemists) do this today...
... meaning with somewhat “old” instruments like described in B&F

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

https://www.ti.com/product/LMP7721#tech-docs
... this is how (many famous electrochemists) do this today...
... 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?


http://hyperphysics.phy-astr.gsu.edu/hbase/electronic/opampi.html#c2
... this is how (many famous electrochemists) do this today...
... three op-amps!

2. Three operational amplifier potentiostatic circuit

http://electronicdesign.com/Content/14978/59899_fig_02.jpg
... this is how (many famous electrochemists) do this today...

... three op-amps!

A current-to-voltage converter (current follower) with IN+ held at ground, and thus IN− at virtual ground; $I_{\text{in}}(\text{WE}) = V_{\text{out}}/R$, where $R$ is termed the feedback resistor.
... this is how (many famous electrochemists) do this today...  

... three op-amps!

\[ V_{IN+} = V_{IN-} \]
\[ I_{IN+} = I_{IN-} \approx 0 \]

\[ V_{IN+} = V_{in}(RE) + I_{IN+}R \]
\[ V_{IN-} = V_{out} + I_{IN-R} \]

Thus, \[ V_{in}(RE) = V_{out} \]

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

a voltage follower with unity gain due to the two \(10k\Omega\) 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
... this is how (many famous electrochemists) do this today... three op-amps!

\[ I_{in} = I_{out} \]
\[ I_{in} = \frac{V_{in}}{R} \quad I_{out} = -\frac{V_{out}}{R_f} \]
\[ \frac{V_{in}}{R} = -\frac{V_{out}}{R_f} \]
Thus, \[ V_{out} = -\frac{V_{in} \cdot R_f}{R} \]

a **voltage-to-current amplifier** \((I_{out} = \frac{V_{in}}{R_f})\) 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 = \(\frac{R_f}{R}\)

a **current-to-voltage converter** (current follower) with IN\(^+\) held at ground, and thus IN\(^-\) at virtual ground; \(I_{in}(WE) = \frac{V_{out}}{R}\), 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)

http://electronicdesign.com/Content/14978/59899_fig_02.jpg
If we want to be able to adjust the voltage on the WE, we introduce $E_{app}$ here...

**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; $I_{in}(WE) = V_{out}/R$, 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
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 (\( \sim 3 \text{ fA} \) for this particular op-amp; 0 fA is the ideal case).

4. Op-amp U1 produces, at the counter electrode (CE), an output current, \( I_{\text{out}} \), 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...
Beware of compliance voltage issues (maximum voltage to CE)...
... and compliance current too!

4.8 mM ferrocene, 0.1 M [NEt₄][BF₄], MeCN
flow rate = 1 ml/hr

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 assure 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
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](http://www.consultrsr.net/resources/pstats/design2.htm)
Active I/E Converter versus Passive I/E Converter

... meaning “newer”

http://www.consultrsr.net/resources/pstats/design2.htm
Potentiostat summary... for non-EE majors...

- 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
... and that is why we use a 3-electrode potentiostat...

"Out of sight, out of mind" is a telling proverb/idiom!

WE = working electrode
RE = reference electrode
CE = counter (or auxiliary) electrode

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

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

$$\eta = E_{\text{app}} - E_{\text{Eq}}$$

What if you dump in Cd$^{2+}$, whose $E^0(\text{Cd}^{2+}/\text{Cd}^0) \approx -0.4$ V vs. SHE?

... Current response will be kinetically determined and current will start to pass at about -0.4 V vs. SHE
Also, don’t forget about possible compliance voltage issues (maximum voltage to CE)... and compliance current too!

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

$I, \text{WE vs. RE}$

$-I, \text{CE vs. RE}$

(These data are flipped vertically on purpose)
Looking forward... Section 1.1 (and some of Chapter 15)

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