Lecture #3 of 18
Q: What’s in this set of lectures?
A: Introduction, Review, and B&F Chapter 1, 15 & 4 main concepts:

- Section 1.1: Redox reactions
- Chapter 15: Electrochemical instrumentation
- Section 1.2: Charging interfaces
- Section 1.3: Overview of electrochemical experiments
- Section 1.4: Mass transfer and Semi-empirical treatment of electrochemical observations
- Chapter 4: Mass transfer
Looking forward… our review of Chapter “0”

- Cool applications
- Redox half-reactions
- Balancing electrochemical equations
- History of electrochemistry
- IUPAC terminology and $E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$
- Nernst equation and Common reference electrodes
- Standard and Absolute potentials
- Latimer and Pourbaix diagrams
- Calculating $E_{\text{cell}}$ under non-standard state conditions
- Conventions
Two diagrams of empirical standard potentials...

A Latimer diagram is a summary of the $E^0$ values for an element; it is useful for visualizing the complete redox series for an element and for determining when disproportionation will occur.

\[ E = E_{acid}^0 - \frac{0.05916}{n} \log \left( \frac{[MnO_2]^1 [H_2O]^2}{[MnO_4^{2-}]^1 [H^+]^4} \right) = E_{acid}^0 - \frac{0.05916}{2} \log \left( \frac{(1)^1 (10^{-14})^4}{(1)^1 (10^{-14})^4} \right) = E_{acid}^0 - 0.02958 \text{V}\] (56)

\[ E = E_{acid}^0 - 1.65648 \text{V} = 0.60 \text{V} \]

What would this $E^0$ value be when at acidic standard state?

\[ E_{\text{SHE}}^0 = 2.25648 \text{V} \]

... but then why did the CRC not list this? ...
A **Pourbaix diagram** is a map of the predominant *equilibrium* species of an aqueous electrochemical system; it is useful for identifying which materials/species are present/stable.

Marcel Pourbaix (1904–1998)

http://corrosion-doctors.org/Biographies/PourbaixBio.htm

Pourbaix, Atlas of electrochemical equilibria in aqueous solutions, 1974

... Second one (not truly standard potentials)...

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Pourbaix, Atlas of electrochemical equilibria in aqueous solutions, 1974
A Pourbaix diagram is a map of the predominant equilibrium species of an aqueous electrochemical system; it is useful for identifying which materials/species are present/stable.

Why don’t I like this? …
Even though EVERYONE plots it this way

Anyway, … standard state is here, at ~1 M H⁺ (pH = 0) → SHE
... but if written under alkaline conditions, ~1 M OH⁻ is standard state (pH 14)

Pourbaix, Atlas of electrochemical equilibria in aqueous solutions, 1974
A Pourbaix diagram is a map of the predominant equilibrium species of an aqueous electrochemical system; it is useful for identifying which materials/species are present/stable.

(1) What is the electrocatalyst for O₂ evolution through water oxidation?
(2) At what pH values is a solid electrocatalyst for H₂ evolution stable?

Pourbaix, Atlas of electrochemical equilibria in aqueous solutions, 1974
(1) What is the electrocatalyst for \( \text{O}_2 \) evolution through water oxidation? \( \text{MnO}_2 \)

(2) At what pH values is a solid electrocatalyst for \( \text{H}_2 \) evolution stable?

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A *Pourbaix diagram* is a map of the predominant *equilibrium* species of an aqueous electrochemical system; it is useful for identifying which materials/species are present/stable.

(1) What is the electrocatalyst for $\text{O}_2$ evolution through water oxidation? $\text{MnO}_2$

(2) At what pH values is a solid electrocatalyst for $\text{H}_2$ evolution stable? pH 7.5 – 13

Pourbaix, Atlas of electrochemical equilibria in aqueous solutions, 1974
How to quantitatively attack non-standard-state cell problems...

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

Electrochemical Cell Potential Calculation

Consider the electrochemical cell:

\[
\text{Ag}(s) \mid \text{AgCl}(s) \mid \text{Cl}^- \ || \ \text{Zn}^{2+} \mid \text{Zn}(s)
\]

The Cell Potential \( \mathcal{E}_{\text{cell}} \) can be calculated by two methods:

**Method 1: Total Reaction Method**

The total cell reaction is:

\[
\text{Zn}^{2+} + 2\text{Ag}(s) + 2\text{Cl}^- \rightarrow \text{Zn}(s) + 2\text{AgCl}(s)
\]

\[
\mathcal{E}_{\text{cell}} = \mathcal{E}^\circ_{\text{cell}} - \frac{(RT/2F)}{\ln (1/([\text{Zn}^{2+}][\text{Cl}^-]^2))}
\]

(1)

where \( \mathcal{E}^\circ_{\text{cell}} = -\Delta G^\circ/2F \)

How else could we write this?

... 60 mV/2 log! (at room temp.)
Method 2: Half Cell Potential Method

\[ \varepsilon_{\text{cell}} = E_{\text{Zn}} - E_{\text{AgCl}} \] (2)

\[ \text{Zn}^{2+} + 2e^{-} \rightarrow \text{Zn(s)} \]

\[ E_{\text{Zn}} = E^\circ_{\text{Zn}} - \left(\frac{RT}{2F}\right) \ln \left(\frac{1}{[\text{Zn}^{2+}]}\right) \] (3)

\[ \text{AgCl(s)} + e^{-} \rightarrow \text{Ag(s)} + \text{Cl}^- \]

\[ E_{\text{AgCl}} = E^\circ_{\text{AgCl}} - \left(\frac{RT}{F}\right) \ln ([\text{Cl}^-]) \] (4)

**Equivalence of the Two Methods**

Now since \( \left(\frac{RT}{F}\right) \ln ([\text{Cl}^-]) = -(\frac{RT}{F}) \ln (1/[\text{Cl}^-]) = -(\frac{RT}{2F}) \ln (1/[\text{Cl}^-]^2) \)

this eqn becomes:

\[ E_{\text{AgCl}} = E^\circ_{\text{AgCl}} + (\frac{RT}{2F}) \ln (1/[\text{Cl}^-]^2) \] (5)

\[ \varepsilon_{\text{cell}} = (E^\circ_{\text{Zn}} - (\frac{RT}{2F}) \ln (1/[\text{Zn}^{2+}])) - (E^\circ_{\text{AgCl}} + (\frac{RT}{2F}) \ln (1/[\text{Cl}^-]^2)) \] (6)

\[ \varepsilon_{\text{cell}} = (E^\circ_{\text{Zn}} - E^\circ_{\text{AgCl}}) - (\frac{RT}{2F}) \ln (1/([\text{Zn}^{2+}][\text{Cl}^-]^2)) \] (7)

If we define \( E^\circ_{\text{Zn}} - E^\circ_{\text{AgCl}} = \varepsilon^\circ_{\text{cell}} \), Then we see that this is exactly the same equation that we found by Method 1 (Equation 1).
How to quantitatively attack non-standard-state cell problems…

Method 2: Half Cell Potential Method

\[ \varepsilon_{\text{cell}} = E_{\text{Zn}} - E_{\text{AgCl}} \]

\[ \text{Zn}^{2+} + 2e^{-} \rightarrow \text{Zn(s)} \]

\[ E_{\text{Zn}} = E^{\circ}_{\text{Zn}} - (RT/2F) \ln \left(1/[\text{Zn}^{2+}]\right) \]

\[ \text{AgCl(s)} + e^{-} \rightarrow \text{Ag(s)} + \text{Cl}^{-} \]

\[ E_{\text{AgCl}} = E^{\circ}_{\text{AgCl}} - (RT/F) \ln \left([\text{Cl}^{-}]\right) \]

Nernst Equation: \[ E = E^{\circ} - \frac{RT}{nF} \ln Q \] (2)

Recall

- \( E_{\text{cell}} \) does not require “n”
- \( \Delta G \) does require “n” \((-nFE_{\text{cell}})\) (3)

Equivalence of the Two Methods

Now since \((RT/F) \ln ([\text{Cl}^{-}]) = -(RT/F) \ln (1/[\text{Cl}^{-}]) = -(RT/2F) \ln (1/[\text{Cl}^{-}]^2)\)

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If we define \((E^{\circ}_{\text{Zn}} - E^{\circ}_{\text{AgCl}}) = E^{\circ}_{\text{cell}}\), Then we see that this is exactly the same equation that we found by Method 1 (Equation 1).
**NOT The Daniell Cell**

**High impedance to measure potential**

![Electrochemical Cell Diagram](image)

- **Common Inert Electrodes:** Platinum, Carbon, Gold
- **Common Reactive Electrodes:** Copper, Zinc, Cadmium, Lead, Silver

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

\[
\text{Cu}^{2+}(aq) \rightleftharpoons \text{Cu}(s)
\]
Write and explain the line notation for the redox reaction between Cu/Cu$^{2+}$ and an SCE electrode, where Cu$^{2+}$ is CuSO$_4$ (0.1 M), and KCl (1 M) is present in all cells.

\[ E^\circ(Cu^{2+}/Cu) = +0.1 \text{ V vs. SCE} \]

\[
\begin{align*}
\text{Cu}^2+(aq) & \rightleftharpoons \text{Cu}(s) \\
\text{Pt(s)-Hg(l)} & \rightleftharpoons \text{Hg}_2\text{Cl}_2(s) + \text{Cl}^-(aq)
\end{align*}
\]
Write and explain the line notation for the redox reaction between Cu/Cu$^{2+}$ and an SCE electrode, where Cu$^{2+}$ is CuSO$_4$ (0.1 M), and KCl (1 M) is present in all cells.

\[ E^{\circ}(\text{Cu}^{2+}/\text{Cu}) = +0.1 \text{ V vs. SCE} \]

Pt(s) | Hg(l) | Hg$_2$Cl$_2$(s) | KCl(1M, aq) | KCl(1M, aq) | KCl(1M, aq), CuSO$_4$ (0.1M, aq) | Cu(s)

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---|---|---|---|---|---|---
Pt(s) | Hg(l) | Hg$_2$Cl$_2$(s) | Cl$^-$(1M, aq) | | Cu$^{2+}$ (0.1M, aq) | Cu(s)
(a) What is $E_{\text{cell}}$ in this case?

(b) What is $E_{\text{cell}}$ if [KCl] = 0.1 M?

$E^\circ(\text{Cu}^{2+}/\text{Cu}) = +0.1 \text{ V vs. SCE}$
(a) What is $E_{\text{cell}}$ in this case?

(b) What is $E_{\text{cell}}$ if $[\text{KCl}] = 0.1 \text{ M}$?

$$E_{\text{cell}} = E^o - \frac{RT}{nF} \ln \left( \frac{a_{\text{Cu}} a_{\text{Hg}_2\text{Cl}_2}}{a_{\text{Cu}^2+} a_{\text{Hg}} a_{\text{Cl}^-}^2} \right)$$

$E^o(\text{Cu}^{2+}/\text{Cu}) = +0.1 \text{ V vs. SCE}$

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E_{\text{cell}} = E^\circ - \frac{RT}{nF} \ln \left( \frac{a_{\text{Cu}}a_{\text{Hg}_2\text{Cl}_2}}{a_{\text{Cu}^2+}a_{\text{Hg}}a_{\text{Cl}^-}^2} \right) 
\]

\[
E_{\text{cell}} \approx E^\circ - \frac{0.0592 \text{ V}}{n} \log \left( \frac{1}{[\text{Cu}^{2+}][\text{Cl}^-]^2} \right) 
\]

Pt(s) | Hg(l) | Hg$_2$Cl$_2$(s) | Cl$^-$(1M, aq) | | Cu$^{2+}$ (0.1M, aq) | Cu(s)
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$E^\circ(\text{Cu}^{2+}/\text{Cu}) = +0.1 \text{ V vs. SCE}$

(a) 

$$E_{\text{cell}} = E^\circ - \frac{RT}{nF} \ln \left( \frac{a_{\text{Cu}}a_{\text{Hg}_2\text{Cl}_2}}{a_{\text{Cu}^2+}a_{\text{Hg}}a_{\text{Cl}^-}^2} \right)$$

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$$E_{\text{cell}} = +0.1 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \left( \frac{1}{0.1} \right)$$

$$E_{\text{cell}} = +0.1 \text{ V} - 0.0296 \text{ V} = +0.0704 \text{ V}$$

Pt(s) | Hg(l) | Hg$_2$Cl$_2$(s) | Cl$^-$(1M, aq) | Cu$^{2+}$ (0.1M, aq) | Cu(s)
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\[
E_{\text{cell}} = E^\circ - \frac{RT}{nF} \ln \left( \frac{a_{\text{Cu}}a_{\text{Hg}_2\text{Cl}_2}}{a_{\text{Cu}^{2+}}a_{\text{Hg}}a_{\text{Cl}^-}^2} \right)
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\[
E_{\text{cell}} = +0.1 \text{ V} - 0.0296 \text{ V} = +0.0704 \text{ V}
\]

\[
E_{\text{cell}} = +0.1 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \left( \frac{1}{(0.1)^3} \right)
\]

\[
E_{\text{cell}} = +0.1 \text{ V} - 0.0888 \text{ V} = +0.0112 \text{ V}
\]

* Remember, there is no such thing as a half-cell reaction, unless you’re working with Trasatti

\[
\text{Pt(s) | Hg(l) | Hg}_2\text{Cl}_2(s) | \text{Cl}^-(1\text{M, aq}) | | \text{Cu}^{2+} (0.1\text{M, aq}) | \text{Cu(s)}
\]
Quick quiz: Do the following make sense?

The grams (or grammage) of my material was 0.1 g.
The liters (or literrage) of my beaker was 0.1 L.
The m/s (or m/s-age) of that baseball was 10 m/s…
In general, IUPAC will be our standard guide for this course…

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Then please don’t say:
“The **voltage** of my cell is 0.1 V.” Let’s call it a **potential**…
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http://goldbook.iupac.org/V06635.html
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Quick quiz: Do the following make sense?
  The kinetic process was graphed as an M–s curve.
  The kinetics were followed as the concentration versus s…

Then please don’t say:
  “The cell’s behavior is shown as the I–V curve.” Let’s call it an I–E curve, or best yet, a J–E curve.
Electrochemistry:

conventions… oh, conventions!

Electrochemistry: conventions... oh, conventions!

Figure 1.1 American (left) and IUPAC (right) voltammogram conventions.

And FINALLY… A review of Chapter “0”

- Cool applications
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- Balancing electrochemical equations
- History of electrochemistry
- IUPAC terminology and \( E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}} \)
- Nernst equation and Common reference electrodes
- Standard and Absolute potentials
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- Section 1.4: Mass transfer and Semi-empirical treatment of electrochemical observations
- Chapter 4: Mass transfer
Looking forward… Section 1.1 (and some of Chapter 15)

- 2-electrode versus 3-electrode measurements
- Reference electrodes
- Potentiostats
- Compliance voltage/current
- \( J-E \) and \( I-E \) curves
- Kinetic overpotential
- Faradaic reactions
Although we would like to measure electrochemical observables (e.g. the current, voltage, etc.) associated with a single “working” electrode (WE), we cannot.

We must always couple our working electrode to a second electrode in order to make a measurement. These two electrodes comprise an electrochemical “cell.”
These schematics introduce some terms that we must define:

**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).

[Diagram of a galvanic cell with an ammeter and voltmeter, showing the flow of electrons and the potential differences.]
Experiments:
95% of the measurements you will perform have a problem

Red line resists current flow

Oftentimes, most of us wish to control the potential of this “working” electrode...
Experiments:
95% of the measurements 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...

Red line resists current flow
\[ \Delta E = 0.0 \text{ V} = E_{\text{WE}} - E_{\text{RE}} \]

... for example, let's say both electrodes are platinum...
... 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 at “open circuit,” no potential bias is applied between them… (disconnect the wire!)

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

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?

Nernst Equation: \[ E = E^0 - \frac{RT}{nF} \ln Q \]
... now, if we apply +0.8 V to the WE (reconnect the wire)... the potential of both electrodes likely changes, and not likely symmetrically...

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

we don’t know this potential… … and we don’t know this potential!
... you get the picture!

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

\[ \Delta E = 1.2 \text{ V} \]
In principle, this problem can be solved by using a second electrode that is an (ideal) \textit{reference electrode}... (ideally) non-polarizable:
... so get rid of the Pt reference electrode, and substitute an SCE... which has a Pt wire in it...

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

RE = saturated calomel electrode (SCE)
... so get rid of the Pt reference electrode, and substitute an SCE... which has a Pt wire in it...

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

\[ \text{RE} = \text{saturated calomel electrode (SCE)} \]

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

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

... 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?

\[ RE = \text{saturated calomel electrode (SCE)} \]

\[ \text{Pt(s)-Hg(l)} \rightarrow \text{Hg}_2\text{Cl}_2(s) \]

\[ + \text{Cl}^- (aq) \]

Nernst Equation:

\[ E = E^0 - \frac{RT}{nF} \ln Q \]
... so get rid of the Pt reference electrode, and substitute an SCE...

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

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

\[ E^{0}_{SCE} = +0.241 \ \text{V vs. SHE} \]
… so get rid of the Pt reference electrode, and substitute an SCE…

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

Current must flow!

RE = saturated calomel electrode (SCE)

$$E_{0\text{SCE}} = +0.241 \text{ V vs. SHE}$$
The SCE has a defined potential of +0.241 V vs. SHE...
... and it "does not" "move" (much, usually)...

\[ E_{\text{app}} = +0.4 \text{ V} \]
... how did we calculate that?

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

\[ \Delta E = 0.4 \text{ V} \]

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

\[ E_{\text{WE}} = +0.4 \text{ V} + +0.241 \text{ V} = +0.641 \text{ V} \]

RE = saturated calomel electrode (SCE)
... you get the picture!

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

\[
\Delta E = -0.7 \text{ V}
\]

\[
RE = \text{saturated calomel electrode (SCE)}
\]

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

\[
E_{\text{WE}} = -0.7 \text{ V} + +0.241 \text{ V} = -0.459 \text{ V}
\]
… 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

http://www.gamry.com/Products/RefElec_SCE.htm
Specifically, we need 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)*
The closest approximation: the *saturated calomel electrode* (*SCE*)

... but no such thing exists.

**Diagram:**
- Plastic caps
- 4–6 mm (o.d.) glass tubing shaped like an “h”
- Filling solution: aqueous saturated KCl
- Copper wire
- Calomel* - a paste containing liquid mercury, Hg₂Cl₂ and some sat’d aq. KCl
- Heat shrink tubing
- Vycor frit
... 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)*

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

\[E^0 = +0.64 \text{ V vs. SHE}\]
... great. But what is an SHE (standard hydrogen electrode)?

\[
2H^+ + 2e^- \rightarrow H_2
\]

\[E^0_{\text{SHE}} = 0.0000 \text{ V vs. SHE}\]

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

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

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

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

AgCl (white)

But for those of you doing photoelectrochemistry, beware!

Ag (gray), from photodecomposition of AgCl

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

Pt (s) | Hg (l) | Hg\textsubscript{2}Cl\textsubscript{2} (s) | Cl\textsuperscript{−} (sat’d, aq) | AgCl (s) | Ag (s)

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\textsubscript{3}CN) electrolyte solutions
Ag/AgNO\textsubscript{3} (0.01 M) in CH\textsubscript{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
“Quasireference” electrode as 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 exp.
* 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., \( \text{Ag (s)} | \text{AgCl (s)} | \text{Cl}^- (\text{sat’d}) | \text{AgCl (s)} | \text{Ag (s)} \))
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)?
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)
Specifically, we need 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.
... 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 bad motto!

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

Fig. 1. — Potentiostat Circuit.
... 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…

an op-amp

http://www.ti.com/product/LMP7721/technicaldocuments
20 transistors, 11 resistors, and 1 capacitor; Wow!

---

http://www.ti.com/product/LMP7721/technicaldocuments
... this is how (many famous electrochemists) do this today...

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

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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! ...

http://hyperphysics.phy-astr.gsu.edu/hbase/electronic/opampi.html#c2
Op-amp Golden Rules

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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 $\text{IN}^+$ held at ground, and thus $\text{IN}^-$ 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!

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.

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

... three op-amps!

---

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).

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

... three op-amps!

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

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

\[ V_{IN-} = V_{out} + I_{IN-R} \]

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

A current-to-voltage converter (current follower) with \( IN^+ \) held at ground, and thus \( IN^- \) at virtual ground; \( I_{in}(WE) = V_{out}/R \), 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
... this is how (many famous electrochemists) do this today... ... three op-amps!

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

supplies current between the CE (and WE via the ground) in order to maintain the difference in potential between the WE/ground and RE \( (E_{\text{app}} = V_{\text{in}}) \); gain = \( R_f/R_a \)

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

**a voltage follower** with unity gain due to the two 10k\( \Omega \) resistors, and so \( V_{\text{in}} = V_{\text{out}} \)

and even if \( I_{\text{out}} \) is large, it does not draw from \( V_{\text{in}} \) (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!

\[
\begin{align*}
I_{\text{in}} &= I_{\text{out}} \\
I_{\text{in}} &= \frac{V_{\text{in}}}{R} \\
I_{\text{out}} &= -\frac{V_{\text{out}}}{R_f} \\
V_{\text{in}} / R &= -\frac{V_{\text{out}}}{R_f}
\end{align*}
\]

Thus, \( V_{\text{out}} = -V_{\text{in}} \cdot R_f / R \)

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

supplies current between the CE (and WE via the ground) in order to maintain the difference in potential between the WE/ground and RE \((E_{\text{app}} = V_{\text{in}})\); gain = \(R_f / R\)

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

a **voltage follower** with unity gain due to the two 10kΩ resistors, and so \( V_{\text{in}} = V_{\text{out}} \)

and even if \(I_{\text{out}}\) is large, it does not draw from \(V_{\text{in}}\) (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)

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

4.8mM ferrocene, 0.1M [NEt$_4$][BF$_4$], MeCN
flow rate = 1ml/hr

http://www.autolab-instruments.com
Active I/E Converter versus Passive I/E Converter

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

http://www.consltrsr.net/resources/pstats/design.htm
Active I/E Converter versus Passive I/E Converter

“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
Active I/E Converter versus Passive I/E Converter

![Active I/E Converter Diagram]

- **Advantages**

  The I/E Converter amplifier must only report the iR drop across the current sense resistor. It is not involved in the control of the working electrode and it does not need 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
Potentiostat summary

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, followed by the reference electrode

Compliance voltage 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...

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

"Out of sight, out of mind" is a bad motto!

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