Lecture #5 of 17
Looking forward... our review of Chapter “0”

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

**Disproportionation** – spontaneous and simultaneous reduction and oxidation of a molecule *(the opposite is comproportionation (AKA: symproportionation))*

(1) Does Mn$^{2+}$ disproportionate? **NO.** $E^o = E_{\text{red}} - E_{\text{ox}} = 1.18 - 1.51 = -0.33$ V

(2) What is the standard reduction potential of MnO$_4^-$ to MnO$_2$?

**Total Reaction:** $3\text{Mn}^{2+} \leftrightarrow \text{Mn}^0 + 2\text{Mn}^{3+}$ $E^o_{\text{total}} = ?$

**Reduction:** $\text{Mn}^{2+} \leftrightarrow \text{Mn}^0$ $E^o = +1.18$ V

**Oxidation:** $\text{Mn}^{2+} \leftrightarrow \text{Mn}^{3+}$ $E^o = +1.51$ V

**RECALL:**

from Wiki
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.

**Disproportionation** – spontaneous and simultaneous reduction and oxidation of a molecule (*the opposite is comproportionation* (AKA: *symproportionation*))

1. **Does Mn$^{2+}$ disproportionate?**  
   **NO.** \[ E^0 = E_{\text{red}} - E_{\text{ox}} = 1.18 - 1.51 = -0.33 \text{ V} \]

2. **What is the standard reduction potential of MnO$_4^-$ to MnO$_2$?**
   \[ \Delta G^0 = -nF E^0 = -3FE^0 \]
   \[ \Delta G^0 = -nFE^0_1 + -nFE^0_2 = -F((1 \times 0.56 \text{ V}) + (2 \times 2.26 \text{ V})) = -F(5.08 \text{ V}) \]
   Set them equal to each other, and thus, \[ 3E^0 = 5.08 \text{ and } E^0 = 1.69 \text{ V} \]

... for #1, you can work with $E^0$ only (do not need $\Delta G^0$), because the reaction is always equal in the number of electrons.
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.

Recall from before...

... anyway, why are these bottom $E^0$ values not on the Latimer diagram?

... because they are at basic/alkaline standard state with ~1 M OH$^-$. 

from Wiki
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.

Recall from before...

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

\[ E = E_{acid}^0 - \frac{0.05916 \text{ V}}{n} \log \left( \frac{[\text{MnO}_2]^1[H_2O]^2}{[\text{MnO}_4^{2-}]^1[H^+]^4} \right) = E_{acid}^0 - \frac{0.05916 \text{ V}}{2} \log \left( \frac{(1)^1}{(1)(10^{-14})^4} \right) = E_{acid}^0 - 0.02958 \text{ V} \]

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

$$E = E_{acid}^0 - \frac{0.05916 \text{ V}}{n} \log \left( \frac{[\text{MnO}_2]^1 [\text{H}_2\text{O}]^2}{[\text{MnO}_4^{2-}]^1 [\text{H}^+]^4} \right) = E_{acid}^0 - \frac{0.05916 \text{ V}}{2} \log \left( \frac{1}{(1)(10^{-14})^4} \right) = E_{acid}^0 - 0.02958 \text{ V}$$

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

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{MnO}_4^- + 2 \text{H}_2\text{O} + 3 e \rightleftharpoons \text{MnO}_2 + 4 \text{OH}^-$</td>
<td>0.595</td>
</tr>
<tr>
<td>$\text{MnO}_4^{2-} + 2 \text{H}_2\text{O} + 2 e \rightleftharpoons \text{MnO}_2 + 4 \text{OH}^-$</td>
<td>0.60</td>
</tr>
<tr>
<td>$\text{Mn(OH)}_2 + 2 e \rightleftharpoons \text{Mn} + 2 \text{OH}^-$</td>
<td>-1.56</td>
</tr>
<tr>
<td>$\text{Mn(OH)}_3 + e \rightleftharpoons \text{Mn(OH)}_2 + \text{OH}^-$</td>
<td>0.15</td>
</tr>
<tr>
<td>$\text{Mn}_2\text{O}_3 + 6 \text{H}^+ + e \rightleftharpoons 2 \text{Mn}^{2+} + 3 \text{H}_2\text{O}$</td>
<td>1.485</td>
</tr>
</tbody>
</table>

$E_{SHE} = 2.25648 \text{ V}$

... 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... mostly based on thermochemical data.

Pourbaix, Atlas of electrochemical equilibria in aqueous solutions, 1974
... Second one (not truly standard potentials)...

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... mostly based on thermochemical data.

Marcel Pourbaix (1904–1998)

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

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

Anyway, ... standard state is here, at ~1 M H⁺ (pH = 0) \(\rightarrow\) 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 ... *mostly based on thermochemical data*

![Marcel Pourbaix](http://corrosion-doctors.org/Biographies/PourbaixBio.htm)

Chemist

Marcel Pourbaix  
(1904–1998)

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 ... *mostly based on thermochemical data*

![Pourbaix Diagram](from Wiki)

(1) **What is the electrocatalyst for O₂ evolution through water oxidation?**  \( \text{MnO}_2 \)

(2) **At what pH values is a solid electrocatalyst for H₂ evolution stable?**  \( \text{pH} \sim 7.5 – \sim 13 \ldots \) *likely a smaller range; why?*

Pourbaix, Atlas of electrochemical equilibria in aqueous solutions, 1974
Looking forward... our review of Chapter “0”

- Cool applications
- Redox half-reactions
-Balancing electrochemical equations
- History of electrochemistry and Batteries
- IUPAC terminology and $E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$
- Thermodynamics and the Nernst equation
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- Latimer and Pourbaix diagrams
- Calculating $E_{\text{cell}}$ under non-standard-state conditions
- Conventions
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:

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

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

**Method 1: Total Reaction Method**

The total cell reaction is:

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

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

(1)

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

How else could we write this? … “(60 mV/2) log”! (at room temp.)
How to quantitatively attack non-standard-state cell problems…

Method 2: Half Cell Potential Method

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

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

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

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

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

Equivalence of the Two Methods

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

this eqn becomes:

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

(5)

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

(6)

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

(7)

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).
Common Reactive Electrodes: Copper, Zinc, Cadmium, Lead, Silver
Common Inert Electrodes: Platinum, Carbon, Gold

NOT The Daniell Cell

high impedance to measure potential

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

\[
E^0(\text{Cu}^{2+}/\text{Cu}) = +0.1 \text{ V vs. SCE}
\]
FYI, cells can be drawn any which way, even on top of each other, or radially… but in line notation the anode should be on the left-hand side.  

\[
\begin{align*}
\text{Pt(s)} & | \text{Hg(l)} | \text{Hg}_2\text{Cl}_2(s) | \text{Cl}^-(1 \text{ M, } aq) & | & | \text{Cu}^{2+} (0.1 \text{ M, } aq) & | \text{Cu(s)} \\
\end{align*}
\]
(a) What is $E_{\text{cell}}$ in this case (1 M KCl, 0.1 M CuSO$_4$)?

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

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

Pt(s) | Hg(l) | Hg$_2$Cl$_2$(s) | Cl$^-$ (1 M, aq) || Cu$^{2+}$ (0.1 M, aq) | Cu(s)
(a) What is \( E_{\text{cell}} \) in this case (1 M KCl, 0.1 M CuSO\(_4\))?  

\[
E_{\text{cell}} = E^o - \frac{RT}{nF} \ln \left( \frac{a_{Cu}a_{Hg_2Cl_2}}{a_{Cu}^2+a_{Hg}a_{Cl^-}^2} \right)
\]

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

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

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

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

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

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

Remember, there is no such thing as a half-cell reaction…  
… unless you are working with Trasatti

Pt(s) | Hg(l) | Hg\(_2\)Cl\(_2\)(s) | Cl\(^-\)(1 M, aq) | | Cu\(^{2+}\) (0.1 M, aq) | 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...

Then I prefer that you don’t say:
“The voltage of my cell is 0.1 V.” Let’s call it a potential...
In general, IUPAC will be our standard guide for this course... 

... and IUPAC prefers it too!
In general, IUPAC will be our standard guide for this course...

Quick quiz: Do the following make sense?
The grams (or grammage) of my material was 0.1 g.
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The m/s (or m/s-age) of that baseball was 10 m/s...

Then I prefer that you don’t say:
“The voltage of my cell is 0.1 V.” Let’s call it a potential...

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 I also prefer that you 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, where J is current density (A/cm²).
Electrochemistry:

conventions... oh, conventions!

Electrochemistry: conventions... oh, conventions!

WE WILL USE THIS ONE...

... which is like you’ve learned in every math class you’ve ever taken...

... and so yay!

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

... But sadly, B&F (2nd edition) use the convention on the left...

... at least you’ll be pros at mentally flipping over data

And finally... we are finished our review of Chapter “0”

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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
- 2-electrode versus 3-electrode measurements
- Potentiostats
- Compliance voltage/current
- J–E and I–E curves
- Kinetic overpotential
- Electrochemical window
- 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 \( (E_{\text{cell}}) \); an ideal voltmeter has infinite input impedance (i.e. it draws no current) \( \text{(impedance is “complex resistance”)} \)

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

Red line resists current flow

... Oftentimes, most of us wish to control the potential of this “working” electrode...
\[ \Delta E = 0.0 \ V = E_{WE} - E_{RE} \]

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

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

\[ E_{\text{app}} = +0.8 \text{ V} \]
... even worse, we don’t now the potential of either electrode...

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

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

... 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) reference electrode... (ideally) non-polarizable:
... so get rid of the Pt reference electrode, and substitute in an SCE...

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

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

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

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

... 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 in an SCE...

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

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

Pt(s) | Hg(l) | Cl$^-$ (aq)  $\rightleftharpoons$ Pt(s) | Hg$\text{Cl}_2$(s)

RE = saturated calomel electrode (SCE)

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

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

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

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

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

(ammeter $\neq 0 \text{ A}$)

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

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

\[ E_0^{\text{SCE}} = +0.241 \text{ V vs. SHE} \]

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

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

Current must flow!
$E_{\text{app}} = +0.4 \text{ V}$

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

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

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

$\Delta E = 0.4 \text{ V}$

RE = saturated calomel electrode (SCE)

WE

+0.241 V  +0.641 V
... how did we calculate that (meaning +0.641 V)?

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

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

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

\[ E_{\text{WE}} = +0.4 \text{ V} + +0.241 \text{ V} = +0.641 \text{ V} \]
\[ \Delta E = E_{\text{app}} = -0.7 \text{ V} \]

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

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

RE = saturated calomel electrode (SCE)