Lecture #3 of 17
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
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.

Latimer, The oxidation states of the elements and their potentials in aqueous solution, 1938
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**Chemist**

Wendell Mitchell Latimer  
(1893–1955)

http://academictree.org/chemistry/peopleinfo.php?pid=24644

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Disproportionation – spontaneous and simultaneous reduction and oxidation of a molecule

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(1) Does Mn$^{2+}$ disproportionate?
(2) What is the standard reduction potential of MnO$_4^-$ to MnO$_2$?
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Reduction: Mn$^{2+}$ $\rightleftharpoons$ Mn$^0$ $E^0 = +1.18$ V

Oxidation: Mn$^{2+}$ $\rightleftharpoons$ Mn$^{3+}$ $E^0 = +1.51$ V
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Disproportionation – spontaneous and simultaneous reduction and oxidation of a molecule

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

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

   **Reduction:** Mn$^{2+} \leftarrow \rightarrow$ Mn$^0$  
   \[ E^o = +1.18 \text{ V} \]

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$$\Delta G^0 = -nFE^0 = -3FE^0$$
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\[ \Delta G^0 = -nFE^0 = -3FE^0 \]
\[ \Delta G^0 = -nFE^0_1 + -nFE^0_2 = -F((1 \times 0.56 \text{ V}) + (2 \times 2.26 \text{ V})) = -F(5.08 \text{ V}) \]
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\[
\Delta G^0 = -nF E^0 = -3FE^0 \\
\Delta G^0 = -nF E_{\text{1}}^0 + -nF E_{\text{2}}^0 = -F((1 \times 0.56 \text{ V}) + (2 \times 2.26 \text{ V})) = -F(5.08 \text{ V})
\]
Set them equal to each other, and thus, $3E^0 = 5.08$ and $E^0 = 1.69 \text{ V}$

... you do not need to do this process for #1 above, because the reaction is always balanced/equal in the number of electrons.
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.

Recall from before...

\[
\begin{align*}
\text{Mn}^{2+} + 2 \text{e} & \rightleftharpoons \text{Mn} & -1.185 \\
\text{Mn}^{3+} + \text{e} & \rightleftharpoons \text{Mn}^{2+} & 1.5415 \\
\text{MnO}_2 + 4 \text{H}^+ + 2 \text{e} & \rightleftharpoons \text{Mn}^{2+} + 2 \text{H}_2\text{O} & 1.224 \\
\text{MnO}_4^- + \text{e} & \rightleftharpoons \text{MnO}_4^{2-} & 0.558 \\
\text{MnO}_4^- + 4 \text{H}^+ + 3 \text{e} & \rightleftharpoons \text{MnO}_2 + 2 \text{H}_2\text{O} & 1.679 \\
\text{MnO}_4^- + 8 \text{H}^+ + 5 \text{e} & \rightleftharpoons \text{Mn}^{2+} + 4 \text{H}_2\text{O} & 1.507 \\
\text{MnO}_4^- + 2 \text{H}_2\text{O} + 3 \text{e} & \rightleftharpoons \text{MnO}_2 + 4 \text{OH}^- & 0.595 \\
\text{MnO}_4^{2-} + 2 \text{H}_2\text{O} + 2 \text{e} & \rightleftharpoons \text{MnO}_2 + 4 \text{OH}^- & 0.60 \\
\text{Mn(OH)}_2 + 2 \text{e} & \rightleftharpoons \text{Mn} + 2 \text{OH}^- & -1.56 \\
\text{Mn(OH)}_3 + \text{e} & \rightleftharpoons \text{Mn(OH)}_2 + \text{OH}^- & 0.15 \\
\text{Mn}_2\text{O}_3 + 6 \text{H}^+ + \text{e} & \rightleftharpoons 2 \text{Mn}^{2+} + 3 \text{H}_2\text{O} & 1.485
\end{align*}
\]
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.

Recall from before…

- $\text{Mn}^{2+} + 2 \text{e} \rightleftharpoons \text{Mn}$
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- $\text{MnO}_4^- + \text{e} \rightleftharpoons \text{MnO}_4^{2-}$
- $\text{MnO}_4^- + 4 \text{H}^+ + 3 \text{e} \rightleftharpoons \text{MnO}_2 + 2 \text{H}_2\text{O}$
- $\text{MnO}_4^- + 8 \text{H}^+ + 5 \text{e} \rightleftharpoons \text{Mn}^{2+} + 4 \text{H}_2\text{O}$
- $\text{MnO}_4^- + 2 \text{H}_2\text{O} + 3 \text{e} \rightleftharpoons \text{MnO}_2 + 4 \text{OH}^-$
- $\text{MnO}_4^{2-} + 2 \text{H}_2\text{O} + 2 \text{e} \rightleftharpoons \text{MnO}_2 + 4 \text{OH}^-$
- $\text{Mn(OH)}_2 + 2 \text{e} \rightleftharpoons \text{Mn} + 2 \text{OH}^-$
- $\text{Mn(OH)}_3 + \text{e} \rightleftharpoons \text{Mn(OH)}_2 + \text{OH}^-$
- $\text{Mn}_2\text{O}_3 + 6 \text{H}^+ + \text{e} \rightleftharpoons 2\text{Mn}^{2+} + 3 \text{H}_2\text{O}$
- $-1.185$
- $1.5415$
- $1.224$
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- $1.507$
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- $1.485$
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?
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.

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⁻!
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?
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.

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

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>$\text{MnO}_4^- + 2 \text{H}_2\text{O} + 3 \text{e} \rightleftharpoons \text{MnO}_2 + 4 \text{OH}^-$</td>
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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.

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

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

- $\text{MnO}_4^{-} + 2 \text{H}_2\text{O} + 3 \text{e} \rightleftharpoons \text{MnO}_2 + 4 \text{OH}^{-}$
- $E = 0.595$ V
- $\text{MnO}_4^{2-} + 2 \text{H}_2\text{O} + 2 \text{e} \rightleftharpoons \text{MnO}_2 + 4 \text{OH}^{-}$
- $E = 0.60$ V
- $\text{Mn(OH)}_2 + 2 \text{e} \rightleftharpoons \text{Mn} + 2 \text{OH}^{-}$
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- $\text{Mn(OH)}_3 + \text{e} \rightleftharpoons \text{Mn(OH)}_2 + \text{OH}^{-}$
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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.

The Latimer diagram shows the redox series of Mn:

- Oxidation:
  - MnO$_4^-$ (7+) → MnO$_4^{2-}$ (6+) → MnO$_2$ (4+) → Mn$^{3+}$ (3+) → Mn$^{2+}$ (2+) → Mn (0)
  - $E^0 = 1.69$ V

- Reduction:
  - Mn$^{2+}$ → Mn$^0$ (0)
  - $E^0 = 1.18$ V

The equation for calculating $E^0$ values is:

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

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

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

$$E_{SHE}^0 = 2.25648 \text{ V}$$

SWEET!
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.

Two diagrams of empirical standard potentials...

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... 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*.

Marcel Pourbaix (1904–1998)

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

Pourbaix, Atlas of electrochemical equilibria in aqueous solutions, 1974
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**Chemist**

Marcel Pourbaix (1904–1998)

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Pourbaix, Atlas of electrochemical equilibria in aqueous solutions, 1974

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... because in acid, the reaction does not occur!

... 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*

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**Marcel Pourbaix**
(1904–1998)

[Image: Marcel Pourbaix]

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

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**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... mostly based on thermochemical data.

(1) What is the electrocatalyst for O₂ evolution through water oxidation?
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... *mostly based on thermochemical data*

(1) What is the electrocatalyst for O_2 evolution through water oxidation? MnO_2

(2) At what pH values is a solid electrocatalyst for 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:

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

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

**Method 1: Total Reaction Method**

The total cell reaction is:

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

\[ \mathcal{E}_{\text{cell}} = \mathcal{E}_{\text{cell}}^0 - \frac{RT}{nF} \ln \left( \frac{1}{[\text{Zn}^{2+}][\text{Cl}^-]^2} \right) \]

(1)

where \( \mathcal{E}_{\text{cell}}^0 = -\Delta G^%/2F \)

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

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

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

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

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

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

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

Equivalence of the Two Methods

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

this eqn becomes:

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

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

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

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).
Facile

Method 2: Half Cell Potential Method

\[ \mathcal{E}_{\text{cell}} = E_{Zn} - E_{AgCl} \]

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

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

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

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

Nernst Equation:

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

Recall

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

Equivalence of the Two Methods

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

this eqn becomes:

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

(5)

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

(6)

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

(7)

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

The Daniell Cell

**Common Reactive Electrodes**: Copper, Zinc, Cadmium, Lead, Silver

**Common Inert Electrodes**: Platinum, Carbon, Gold

High impedance to measure potential
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.

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

$$
\begin{align*}
\text{Cu}^{2+}(aq) & \rightleftharpoons \text{Cu}(s) \\
\text{Pt}(s) | \text{Hg}(l) & \rightleftharpoons \text{Pt}(s) | \text{Hg}_2\text{Cl}_2(s) + \text{Cl}^-(aq)
\end{align*}
$$
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)

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)
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)

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

\[
Pt(s) | Hg(l) | Hg_2Cl_2(s) | Cl^-(1M, aq) \rightleftharpoons Cu^{2+} (0.1M, aq) | Cu(s)
\]

http://www.baj.or.jp/e/knowledge/structure.html
(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?

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

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

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 (1 M KCl, 0.1 M CuSO$_4$)?

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

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

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

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

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

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 (1 M KCl, 0.1 M CuSO$_4$)?

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

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

$$(a) \quad E_{\text{cell}} = E^o - \frac{RT}{nF} \ln \left( \frac{a_{\text{Cu}} a_{\text{Hg}_{2}Cl_2}}{a_{\text{Cu}^2+} a_{\text{Hg}} a_{\text{Cl}^-}^2} \right)$$

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

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

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

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 (1 M KCl, 0.1 M CuSO$_4$)?

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

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

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

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

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

\[
E_{\text{cell}} = +0.1 \text{ V} - 0.296 \text{ V} = +0.0704 \text{ V}
\]

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

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

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

\[
\text{Pt(s)} | \text{Hg(l)} | \text{Hg}_2\text{Cl}_2(s) | \text{Cl}^- (1\text{ M, aq}) | | \text{Cu}^{2+} (0.1\text{ M, aq}) | \text{Cu(s)}
\]
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…
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!

http://goldbook.iupac.org/V06635.html
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.
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*…

**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…
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.
- 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**...

**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**.
Electrochemistry: conventions… oh, conventions!

Electrochemistry: conventions... oh, conventions!

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

WE WILL USE THIS ONE...

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

... and so yay!
And FINALLY… A 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
Overview of Electrochemistry and Mass Transfer Processes

Chapters 1, 15, and 4
Q: What’s in this set of lectures?
A: B&F Chapters 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… 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 \((E_{\text{cell}})\). 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).

http://chemwiki.ucdavis.edu/Analytical_Chemistry/Electrochemistry/Electrochemistry_2%3A_Galvanic_cells_and_Electrodes
Experiments:
95% of the measurements that you will perform have a problem

Power Supply

Ammeter

Voltmeter

working electrode

Red line resists current flow

... Oftentimes, most of us wish to control the potential of this “working” electrode...
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...
... for example, let's say both electrodes are platinum...

\[ \Delta E = 0.0 \text{ V} = E_{WE} - E_{RE} \]
... 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 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 \emph{this} potential… … and we don’t know \emph{this} potential!
\[ E_{\text{app}} = +1.2 \text{ V} \]
In principle, this problem can be solved by using a second electrode that is an (ideal) reference electrode... (ideally) non-polarizable:
\[ \Delta E \neq 0.0 \text{ V} \quad (\text{likely}) \]

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

\[ E, \text{ V vs. SHE} \]
\[ E_{oc} \neq 0.0 \text{ V (likely)} \]

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

What is the half-reaction that defines it?
\[ E_{oc} \neq 0.0 \text{ V} \ (\text{likely}) \]

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

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

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

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

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

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

... the SCE has a defined potential of +0.241 V vs. SHE...
... so get rid of the Pt reference electrode, and substitute in an SCE... which has a Pt wire in it...

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

Current must flow!

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

... 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 (meaning +0.641 V)?

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

... and it “does not” “move” (much, usually)...
$E_{\text{app}} = +0.4 \text{ V}$

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

$E_{\text{WE}} = +0.4 \text{ V} + +0.241 \text{ V} = +0.641 \text{ V}$
... you get the picture!...
... but let’s learn some more about reference electrodes...

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

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

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

4 – 6 mm (o.d.) glass tubing shaped like an “h”

plastic caps

platinum wire

white Epotec epoxy or TorrSeal, heat gunned...

copper wire

heat shrink tubing

Vycor frit
… but no such thing exists.

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

4 – 6 mm (o.d.) glass tubing shaped like an “h”

**plastic caps**

**filling solution:** aqueous saturated KCl

**4 – 6 mm (o.d.) glass tubing shaped like an “h”**

**copper wire**

**heat shrink tubing**

**Vycor frit**

**calomel** - a paste containing liquid mercury, Hg\(_2\)Cl\(_2\) and some sat’d *aq.* KCl
... 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)

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

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

the *saturated sodium calomel electrode* (SSCE)

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

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

the *saturated mercurous sulfate electrode* (MSE)

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

\[ E^0 = +0.64 \text{ V vs. SHE} \]
... 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)!

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

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

But for those of you doing photoelectrochemistry, beware!

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

Moody, Oke, & Thomas, Analyst, 1969, 94, 803
... 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\textsubscript{3}CN) electrolyte solutions
Ag/AgNO\textsubscript{3} (0.01 M) in CH\textsubscript{3}CN

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

**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
* 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))
How would one test the accuracy of a reference electrode?

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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 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.
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, 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.