

114

# Lecture #5 of 17

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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](#)

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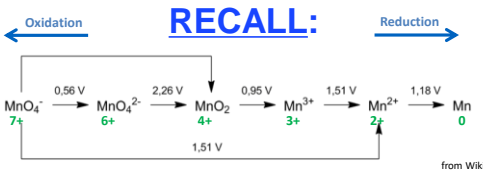
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115

Two diagrams of empirical standard potentials...

116

A **Latimer diagram** is a summary of the  $E^\circ$  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: *sympportionation*))

- (1) Does  $\text{Mn}^{2+}$  disproportionate? **NO.**  $E^\circ = E_{\text{red}} - E_{\text{ox}} = 1.18 - 1.51 = -0.33 \text{ V}$
- (2) What is the standard reduction potential of  $\text{MnO}_4^-$  to  $\text{MnO}_2$ ?




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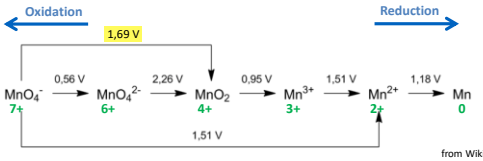
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116

Two diagrams of empirical standard potentials...

117

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.



from Wiki

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

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- (2) What is the standard reduction potential of  $MnO_4^-$  to  $MnO_2$ ?

$$\Delta G^0 = -nFE^0 = -3FE^0$$

$$\Delta G^0 = -nFE^0_1 + nFE^0_2 = -F((1 \times 0.56 V) + (2 \times 2.26 V)) = -F(5.08 V)$$

Set them equal to each other, and thus,  $3E^0 = 5.08$  and  $E^0 = 1.69 V$

... 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

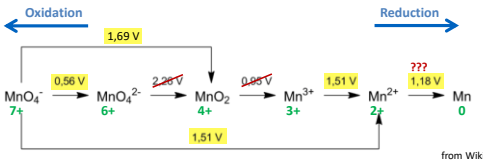
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Two diagrams of empirical standard potentials...

118

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.



from Wiki

Recall from before...

$Mn^{2+} + 2e \rightleftharpoons Mn$	???	-1.185
$Mn^{3+} + e \rightleftharpoons Mn^{2+}$		1.5113
$MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{2+} + 2H_2O$		1.224
$MnO_4^- + e \rightleftharpoons MnO_4^{2-}$		0.558
$MnO_4^- + 4H^+ + 3e \rightleftharpoons MnO_2 + 2H_2O$		1.679
$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$		1.507
$MnO_4^- + 2H_2O + 3e \rightleftharpoons MnO_2 + 4OH^-$		0.595
$MnO_2 + 2H_2O + 2e \rightleftharpoons Mn(OH)_2 + 4OH^-$		0.60
$Mn(OH)_2 + 2e \rightleftharpoons Mn + 2OH^-$		-1.56
$Mn(OH)_2 + e \rightleftharpoons Mn(OH) + OH^-$		0.15
$Mn_2O_3 + 6H^+ + e \rightleftharpoons 2Mn^{2+} + 3H_2O$		1.485

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

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

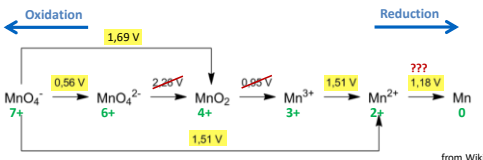
118



Two diagrams of empirical standard potentials...

119

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.



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		1.485

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

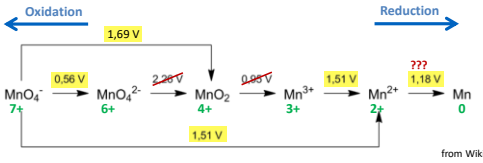
119



Two diagrams of empirical standard potentials...

120

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.



from Wiki

$$E = E_{acid}^0 - \frac{0.05916 \text{ V}}{n} \log \left( \frac{[\text{MnO}_2]^2 [\text{H}_2\text{O}]^2}{[\text{MnO}_4^{2-}]^2 [\text{H}^+]^4} \right) = E_{acid}^0 - \frac{0.05916 \text{ V}}{2} \log \left( \frac{(1)^2}{(1)^2 (10^{-14})^2} \right) = E_{acid}^0 - 0.02958 \text{ V} (56)$$

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

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

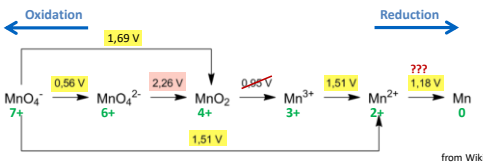
$\text{MnO}_4^- + 2 \text{H}_2\text{O} + 3 \text{e}^- \rightleftharpoons \text{MnO}_2 + 4 \text{OH}^-$	0.595
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$\text{Mn}_2\text{O}_3 + 6 \text{H}^+ + \text{e}^- \rightleftharpoons 2 \text{Mn}^{2+} + 3 \text{H}_2\text{O}$	1.485

120

Two diagrams of empirical standard potentials...

121

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from Wiki

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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?

$\text{MnO}_4^- + 2 \text{H}_2\text{O} + 3 \text{e}^- \rightleftharpoons \text{MnO}_2 + 4 \text{OH}^-$	0.595	$E_{HE}^0 = 2.25648 \text{ V}$
$\text{MnO}_4^- + 2 \text{H}_2\text{O} + 2 \text{e}^- \rightleftharpoons \text{MnO}_2 + 4 \text{OH}^-$	0.60	SWEET!
$\text{Mn}(\text{OH})_2 + 2 \text{e}^- \rightleftharpoons \text{Mn} + 2 \text{OH}^-$	-1.56	
$\text{Mn}(\text{OH})_2 + \text{e}^- \rightleftharpoons \text{Mn}(\text{OH}) + \text{OH}^-$	0.15	... but then why did the
$\text{Mn}_2\text{O}_3 + 6 \text{H}^+ + \text{e}^- \rightleftharpoons 2 \text{Mn}^{2+} + 3 \text{H}_2\text{O}$	1.485	CRC not list this? ...

121

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

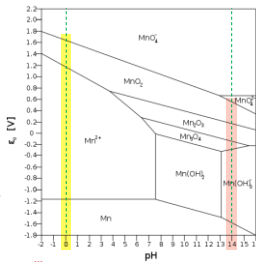
122

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

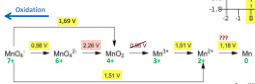


Marcel Pourbaix (1904–1998)

[http://commons.wikimedia.org/wiki/File:Marcel\\_Pourbaix.jpg](http://commons.wikimedia.org/wiki/File:Marcel_Pourbaix.jpg)



from Wiki



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

... but then why did the CRC not list this? ...

Pourbaix, Atlas of electrochemical equilibria in aqueous solutions, 1974

122

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

123

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

Chemist

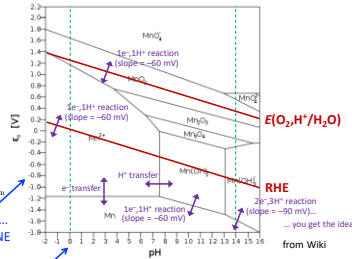


Marcel Pourbaix (1904–1998)

<http://comsolae-doctor.org/Biographie/PourbaixBto.htm>

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

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



from Wiki

Pourbaix, Atlas of electrochemical equilibria in aqueous solutions, 1974

123

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

124

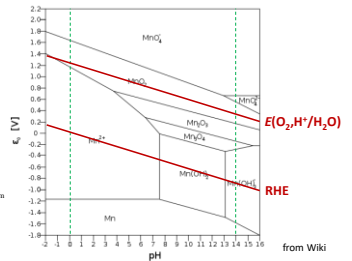
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Chemist



Marcel Pourbaix (1904–1998)

<http://comsolae-doctor.org/Biographie/PourbaixBto.htm>



from Wiki

- (1) What is the electrocatalyst for O<sub>2</sub> evolution through water oxidation? MnO<sub>2</sub>
- (2) At what pH values is a solid electrocatalyst for H<sub>2</sub> evolution stable? pH ~7.5 – ~13...

Pourbaix, Atlas of electrochemical equilibria in aqueous solutions, 1974 ... likely a smaller range; why?

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Looking forward... our review of Chapter "0"

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

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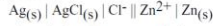
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How to quantitatively attack non-standard-state cell problems...

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

Electrochemical Cell Potential Calculation

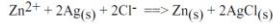
Consider the electrochemical cell:



The Cell Potential  $E_{\text{cell}}$  can be calculated by two methods:

Method 1: Total Reaction Method *These should all be  $E_{\text{cell}}$*

The total cell reaction is:



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

where  $E^{\circ}_{\text{cell}} = -\Delta G^{\circ}/2F$  *How else could we write this? ... "(60 mV/2) log<sup>-1</sup> (at room temp.)"*

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How to quantitatively attack non-standard-state cell problems...<sup>127</sup>

Method 2: Half Cell Potential Method

Nernst Equation:  $E = E^0 - \frac{RT}{nF} \ln Q$  (2)

Facile {

$$E_{\text{cell}} = E_{\text{Zn}} - E_{\text{AgCl}} \quad (2)$$



**Recall**  
 •  $E_{\text{cell}}$  does not require "n"  
 •  $\Delta G$  requires "n" ( $-nFE_{\text{cell}}$ )

$$E_{\text{Zn}} = E^{\circ}_{\text{Zn}} - (RT/2F) \ln (1/[\text{Zn}^{2+}]) \quad (3)$$



$$E_{\text{AgCl}} = E^{\circ}_{\text{AgCl}} - (RT/F) \ln ([\text{Cl}^-]) \quad (4)$$

Equivalence of the Two Methods

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

$$E_{\text{AgCl}} = E^{\circ}_{\text{AgCl}} + (RT/2F) \ln (1/[\text{Cl}^-]^2) \quad (5)$$

$$E_{\text{cell}} = (E^{\circ}_{\text{Zn}} - (RT/2F) \ln (1/[\text{Zn}^{2+}])) - (E^{\circ}_{\text{AgCl}} + (RT/2F) \ln (1/[\text{Cl}^-]^2)) \quad (6)$$

$$E_{\text{cell}} = (E^{\circ}_{\text{Zn}} - E^{\circ}_{\text{AgCl}}) - (RT/2F) \ln (1/([\text{Zn}^{2+}][\text{Cl}^-]^2)) \quad (7)$$

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).

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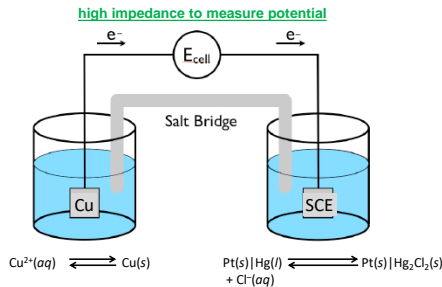
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**NOT** The Daniell Cell

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

Common Inert Electrodes: Platinum, Carbon, Gold

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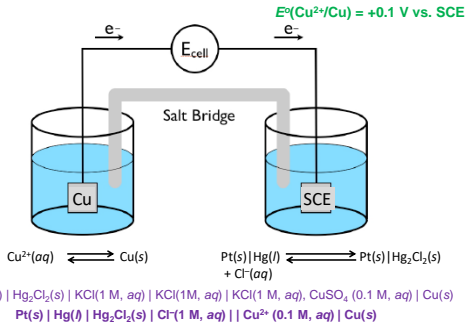
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128

Write and explain the line notation for the redox reaction between Cu/Cu<sup>2+</sup> and an SCE electrode, where Cu<sup>2+</sup> is CuSO<sub>4</sub> (0.1 M), and KCl (1 M) is present in all cells. 129




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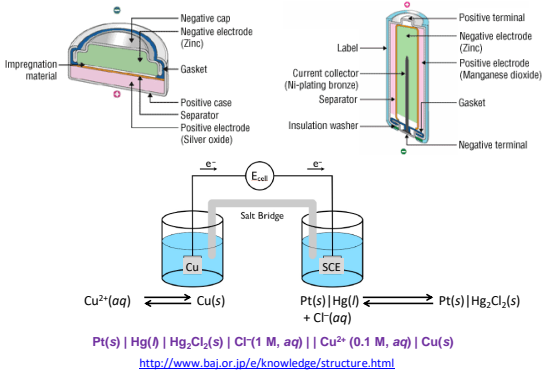
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129

FYI, cells can be drawn any which way, even on top of each other, or radially... 130  
 ... but in line notation the anode should be on the left-hand side. (SKIPPED)




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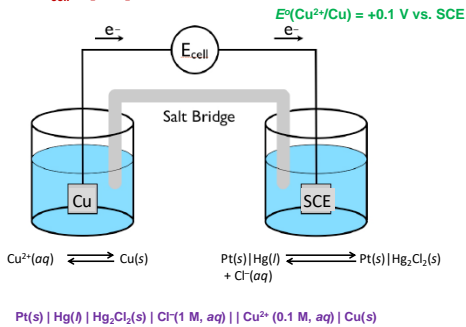
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130

(a) What is  $E_{\text{cell}}$  in this case (1 M KCl, 0.1 M CuSO<sub>4</sub>)? 131  
 (b) What is  $E_{\text{cell}}$  if [KCl] = 0.1 M? (SKIPPED)




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131

(a) What is  $E_{\text{cell}}$  in this case (1 M KCl, 0.1 M  $\text{CuSO}_4$ )? <sup>132</sup> *(SKIPPED)*

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

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

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

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

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

$$E_{\text{cell}} = +0.1 \text{ V} - 0.0296 \text{ V} = +0.0704 \text{ V} \quad E_{\text{cell}} = +0.1 \text{ V} - 0.0888 \text{ V} = +0.0112 \text{ V}$$

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



132

In general, IUPAC will be our standard guide for this course...

133

**Quick quiz:** Do the following make sense?

The grams (or grammage) of my material was 0.1 g.

The liters (or literage) 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...*

133

In general, IUPAC will be our standard guide for this course...

134

The screenshot shows the IUPAC Gold Book entry for 'voltage'. The definition states: "The use of the term is discouraged, and the term signed potential should be used instead, for non-specific signals; however, it is retained here for historical and other practical signals because no suitable substitute for it has been proposed." It also includes a diagram of a galvanic cell with a voltmeter and a table of units for potential and voltage.

... and IUPAC prefers it too!

<http://goldbook.iupac.org/V06635.html>

134

In general, IUPAC will be our standard guide for this course... 135

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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/cm<sup>2</sup>).*

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135

Electrochemistry: 136  
**conventions... oh, conventions!**



[http://upload.wikimedia.org/wikipedia/commons/thumb/c/c0/Map\\_of\\_USA\\_TX.svg/2000px-Map\\_of\\_USA\\_TX.svg.png](http://upload.wikimedia.org/wikipedia/commons/thumb/c/c0/Map_of_USA_TX.svg/2000px-Map_of_USA_TX.svg.png)

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136

Electrochemistry: 137  
**conventions... oh, conventions!**

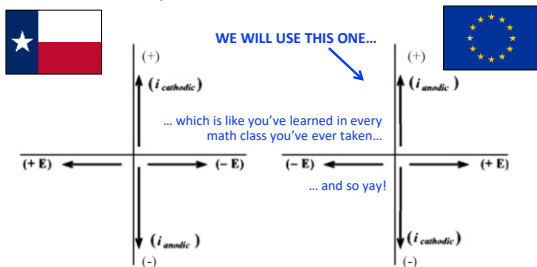


Figure 1.1 American (left) and IUPAC (right) voltammogram conventions.  
 ... But sadly, B&F (2<sup>nd</sup> edition) use the convention on the left...  
 ... at least you'll be pros at mentally flipping over data  
 Handbook of Electrochemistry, Zoski (ed.), Elsevier, 2007

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And finally... we are finished our review of Chapter "0"

- Cool applications
- Redox half-reactions
- Balancing electrochemical equations
- History of electrochemistry and Batteries
- IUPAC terminology and  $E_{cell} = E_{red} - E_{ox}$
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## Measurements in Electrochemistry

Chapters 1 and 15

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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

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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

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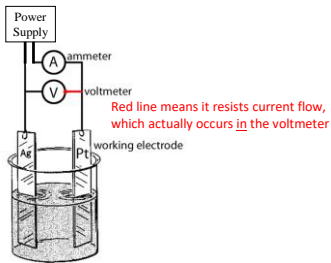
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141

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

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

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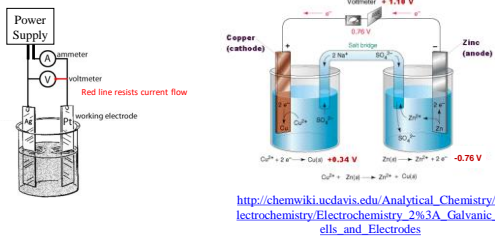
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142

These schematics introduce some terms that we must define:

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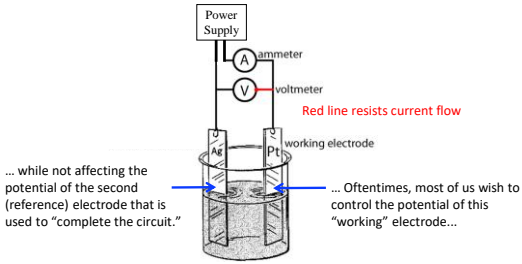
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- electrometer – a device for measuring a potential difference ( $E_{cell}$ ); an ideal voltmeter has infinite input impedance (i.e. it draws no current) (*impedance is "complex resistance"*)
- ammeter – a device for measuring a current; an ideal ammeter has zero input impedance (i.e. it imposes no potential drop)

143

Experiments: 144  
 95% of the measurements that you will perform have a problem




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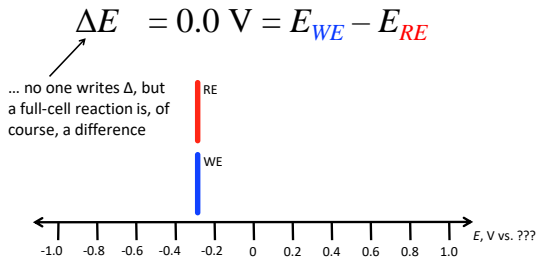
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144

... for example, let's say both electrodes are platinum... 145




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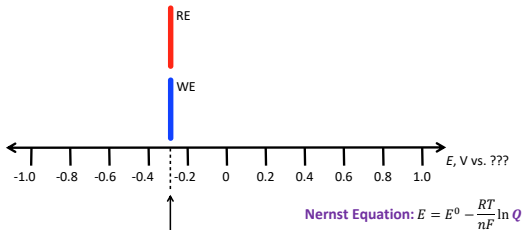
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145

... and at "open circuit," no potential bias is applied between them... (disconnect the wire!) 146

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



... 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?

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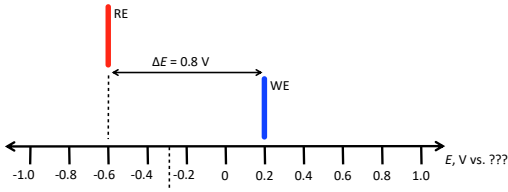
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146

... now, if we apply +0.8 V to the WE (reconnect the wire)...  
 the potential of both electrodes likely changes, and *not likely symmetrically*... 147

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




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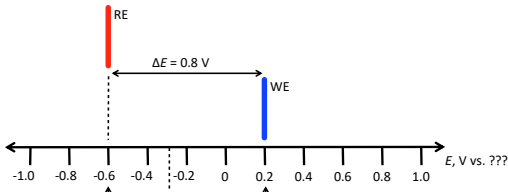
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147

... even worse, we don't now the potential of either electrode... 148

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



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

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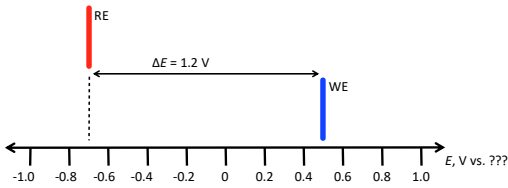
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148

... you get the picture! 149

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




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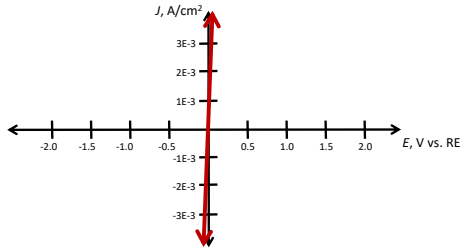
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149

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

150




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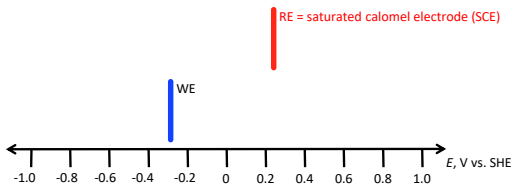
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150

... so get rid of the Pt reference electrode, and substitute in an SCE... 151  
... which has a Pt wire in it...

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




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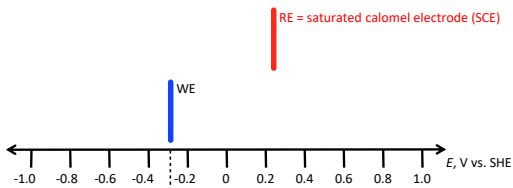
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151

... so get rid of the Pt reference electrode, and substitute in an SCE... 152  
... which has a Pt wire in it...

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



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

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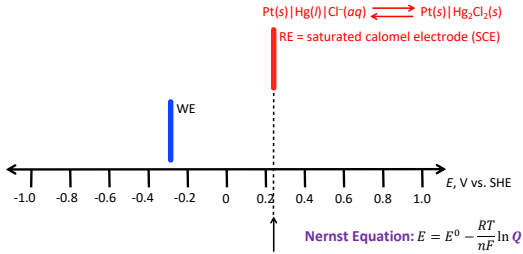
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152

... so get rid of the Pt reference electrode, and substitute in an SCE... 153  
 ... 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?

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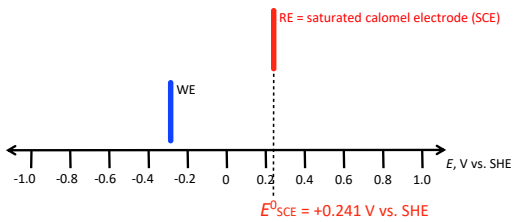
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153

... so get rid of the Pt reference electrode, and substitute in an SCE... 154  
 ... which has a Pt wire in it...

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



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

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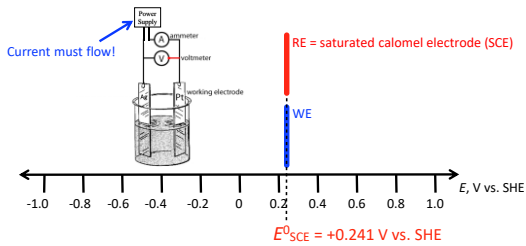
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154

... so get rid of the Pt reference electrode, and substitute in an SCE... 155  
 ... which has a Pt wire in it...

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



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

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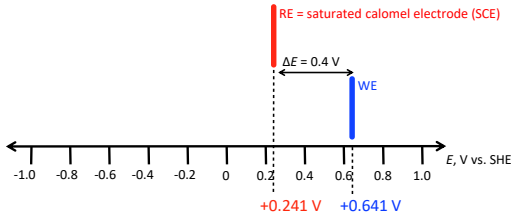
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155

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

156

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



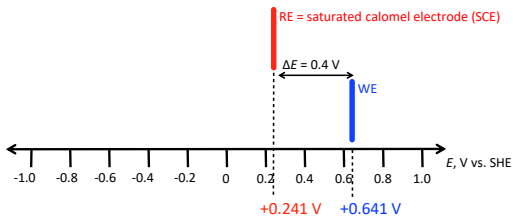
... the SCE has a defined potential of +0.241 V vs. SHE...  
 ... and its potential "does not" move (much, usually)...

156

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

157

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



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

$$E_{\text{WE}} = \underline{+0.4 \text{ V}} + +0.241 \text{ V} = +0.641 \text{ V}$$

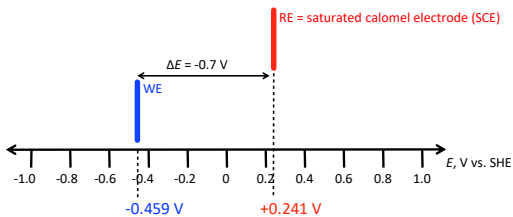
157

... you get the picture!...

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

158

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



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

$$E_{\text{WE}} = \underline{-0.7 \text{ V}} + +0.241 \text{ V} = -0.459 \text{ V}$$

158