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Lecture #5 of 20

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

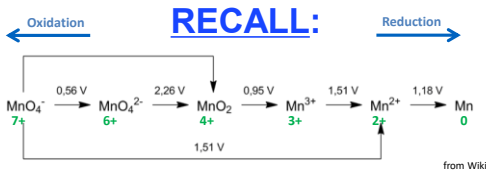
- Cool applications
- Redox half-reactions
- Balancing electrochemical equations
- History of electrochemistry and Batteries
- IUPAC terminology and $E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$
- Thermodynamics and the Nernst equation
- Common reference electrodes
- Standard and Absolute potentials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

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Two diagrams of empirical standard reduction potentials...

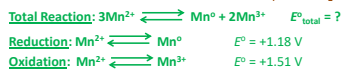
118

A Latimer diagram is a summary of the E° 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 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 MnO_4^- to MnO_2 ?

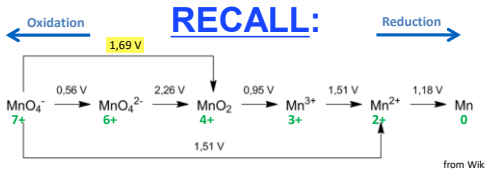


118

Two diagrams of empirical standard reduction potentials...

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

$$\Delta G^\circ = -nFE^\circ_1 + -nFE^\circ_2 = -F((1 \times 0.56 \text{ V}) + (2 \times 2.26 \text{ V})) = -F(5.08 \text{ V})$$

$$\text{Set them equal to each other, and thus, } 3E^\circ = 5.08 \text{ and } E^\circ = 1.69 \text{ V}$$

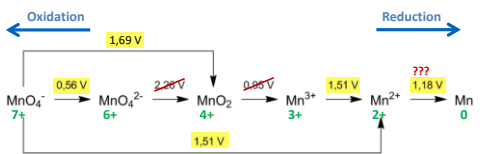
... for #1, you can work with E° only (do not need ΔG°), because the reaction is always equal in the number of electrons

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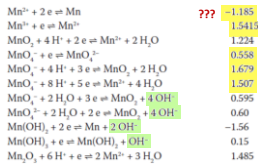
Two diagrams of empirical standard reduction potentials...

120

A **Latimer diagram** is a summary of the E° 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° values not on the Latimer diagram?

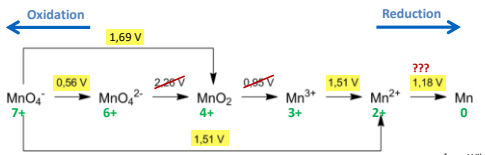
... because they are at basic/alkaline standard state with $\sim 1 \text{ M OH}^-$

120

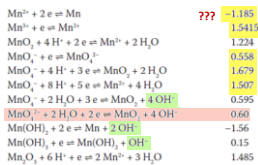
Two diagrams of empirical standard reduction potentials...

121

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Recall from before...

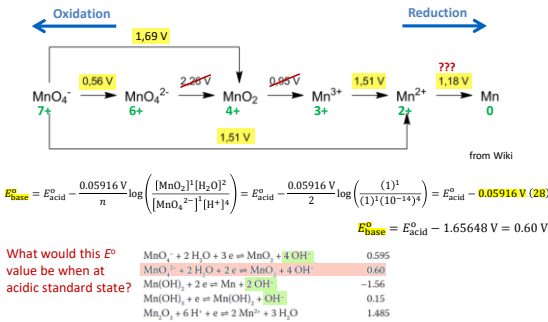


What would this E° value be when at acidic standard state?

121

Two diagrams of empirical standard reduction potentials... (UPDATED) 122

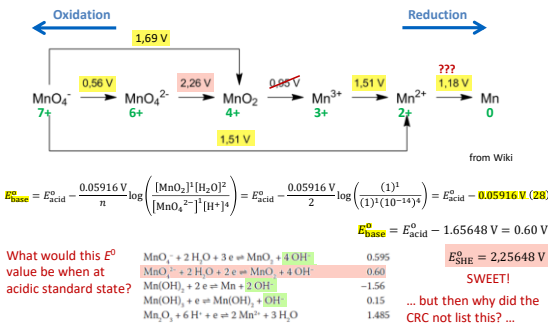
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Two diagrams of empirical standard reduction potentials... (UPDATED) 123

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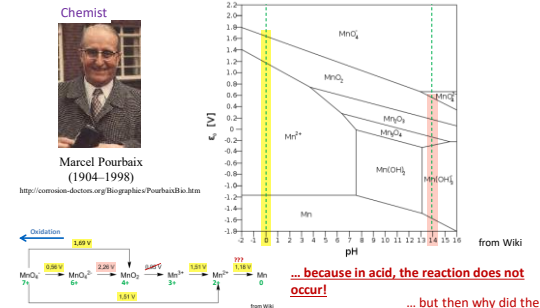


123

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

124

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

124

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

125

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*

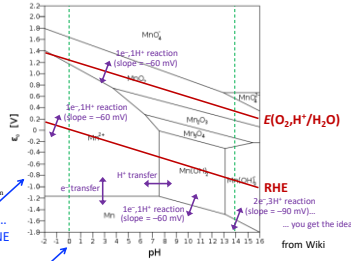
Chemist



Marcel Pourbaix
(1904–1998)

<http://commons-dection.org/Biographies/PourbaixBio.htm>

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



Anyway, ... standard state is here, at $\sim 1 \text{ M H}^+$ (pH = 0) $\rightarrow$ SHE
... but if written under alkaline conditions, $\sim 1 \text{ M OH}^-$ is standard state (pH 14)

Pourbaix, Atlas of electrochemical equilibria in aqueous solutions, 1974

125

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

126

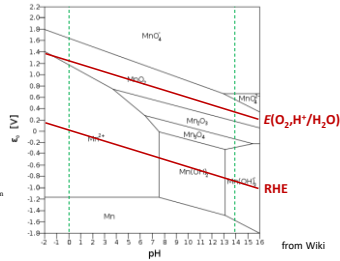
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Chemist



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- (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 $\sim 7.5 - \sim 13$...

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"

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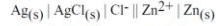
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How to quantitatively attack non-standard-state cell problems...

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

Electrochemical Cell Potential Calculation

Consider the electrochemical cell:

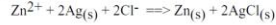


The Cell Potential $\mathcal{E}_{\text{cell}}$ can be calculated by two methods:

Method 1: Total Reaction Method

These should all be E_{cell}

The total cell reaction is:



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

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

How else could we write this? ...
"[60 mV/2] log⁻¹ (at room temp.)

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How to quantitatively attack non-standard-state cell problems...¹²⁹

Method 2: Half Cell Potential Method

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

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

Recall
• E_{cell} does not require "n"
• ΔG 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 $(RT/F) \ln ([\text{Cl}^-]) = -(RT/2F) \ln (1/[\text{Cl}^-]^2)$
this eqn becomes:

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

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

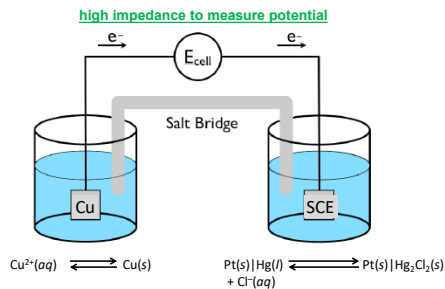
$$\mathcal{E}_{\text{cell}} = (E^\circ_{\text{Zn}} - E^\circ_{\text{AgCl}}) - (RT/2F) \ln (1/([\text{Zn}^{2+}][\text{Cl}^-]^2)) \quad (7)$$

If we define $(E^\circ_{\text{Zn}} - E^\circ_{\text{AgCl}}) = \mathcal{E}^\circ_{\text{cell}}$. Then we see that this is exactly the same equation that we found by Method 1 (Equation 1).

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NOT The Daniell Cell

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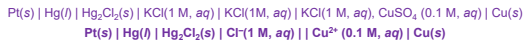
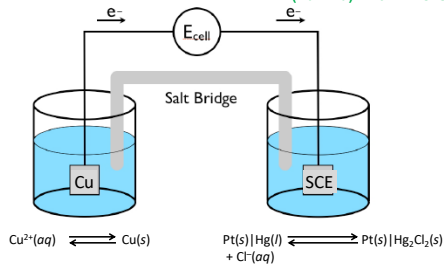
Common Reactive Electrodes: Copper, Zinc, Cadmium, Lead, Silver

Common Inert Electrodes: Platinum, Carbon, Gold

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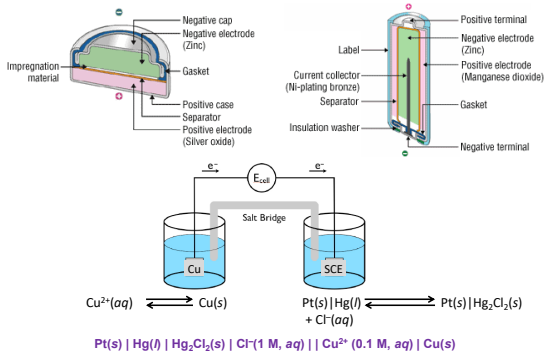
Write and explain the line notation for the redox reaction between Cu/Cu^{2+} and an SCE electrode, where Cu^{2+} is CuSO_4 (0.1 M), and KCl (1 M) is present in all cells. ¹³¹

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



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FYI, cells can be drawn any which way, even on top of each other, or radially... ¹³²
 ... but in line notation the anode should be on the left-hand side.

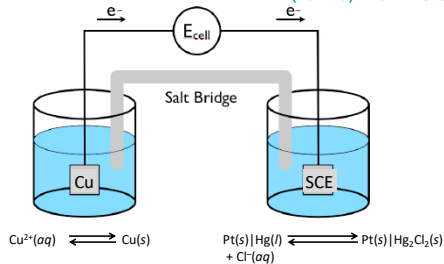


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(a) What is E_{cell} in this case (1 M KCl , 0.1 M CuSO_4)? ¹³³ *(SKIPPED)*

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

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



133

(a) What is E_{cell} in this case (1 M KCl, 0.1 M CuSO_4)? **(SKIPPED)** 134

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

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

(a)

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

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

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

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

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



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In general, IUPAC will be our standard guide for this course... **(UPDATED)** 135

Quick quiz: Do the following make sense?

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

The liters (or litterrage) of my beaker was 0.1 L.

The m/s (or m/s-age) of that baseball was 10 m/s...

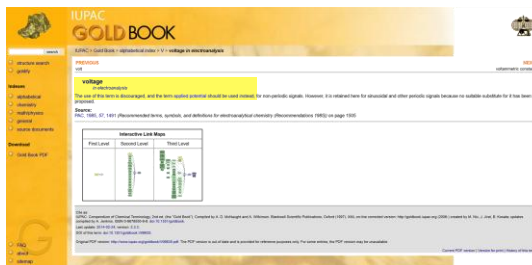
Then I prefer that you don't say:

"The voltage of my cell is 0.1 V." Let's call it a potential...

<https://doi.org/10.1021/acscenergylett.0c02443> ("Potentially Confusing: Potentials in Electrochemistry" by Boettcher; Oener; Lonergan; Surendranath; Ardo; Brozek; Kempler)

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In general, IUPAC will be our standard guide for this course... 136



... and IUPAC prefers it too!

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

136

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137

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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 I-E curve, where I is current density (A/cm^2).*

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Electrochemistry:

conventions... oh, conventions!

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from Wiki

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Electrochemistry:

conventions... oh, conventions!

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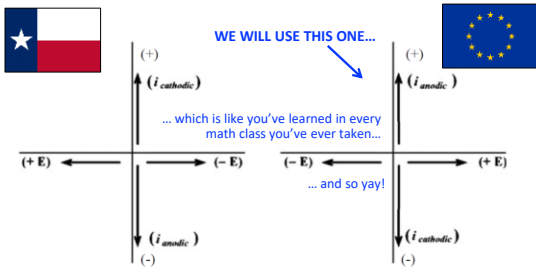


Figure 1.1 American (left) and IUPAC (right) voltammogram conventions.

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

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

Handbook of Electrochemistry, Zoski (ed.), Elsevier, 2007

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

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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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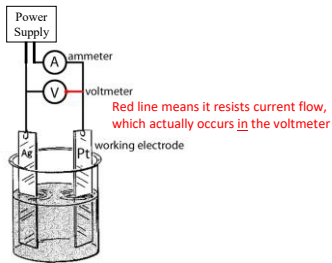
Looking forward... Section 1.1 (and some of Chapter 15)

- 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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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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