

Spring 2022

Exam 2 Review



Goals for today:

- Review how to assign oxidation numbers
- Solving for electrical potential
- Two electrochemical cells
- Electrochemical cells in non-standard conditions
- Electrochemical application
- Battery types
- Study tips for the exam



Understanding Redox Reactions



maddie
@maddiefrancesse

you know you're not a kid anymore when you're watching hsm and understand wtf Gabriella's doing on the board



kevin
@_KevinSosa_

I guess I'm still a ~~kid~~ child then

Electrochemistry Terms

- OIL RIG**
- Redox Reaction:** a chemical reaction that involves the transfer of electrons from one species to another, resulting in a change in oxidation state. A redox reaction balances both electron-transfer AND stoichiometric coefficients
 - Reduction:** a species gains electrons in a half-reaction, resulting in a lower oxidation state
 - Oxidation:** a species loses electrons in a half-reaction, resulting in a higher oxidation state
 - Oxidizing Agent:** the species that drives the oxidation of another species in a redox reaction ; the oxidizing agent is always the species undergoing reduction as a reactant
 - Reducing Agent:** the species that drives the reduction of another species in a redox reaction ; the reducing agent is always the species undergoing oxidation as a reactant

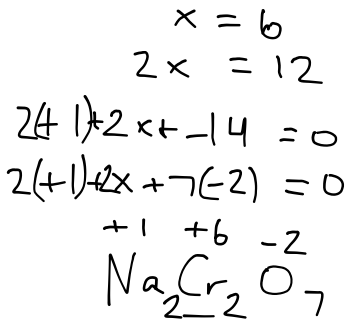
Standard Potentials at 25°C

Half-Reaction	E° (V)
$\text{F}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{F}^-(\text{aq})$	+2.87
$\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$	+1.51
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	+1.33
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	+1.23
$\text{Pd}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Pd}(\text{s})$	+0.915
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$	+0.80
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	+0.52
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightleftharpoons 4\text{OH}^-(\text{aq})$	+0.40
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	+0.34
$\text{Bi}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Bi}(\text{s})$	+0.20
$\text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2\text{SO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$	+0.17
$\text{Se}^{6+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Se}^{4+}(\text{aq})$	+0.150
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$	0.000
$\text{Fe}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Fe}(\text{s})$	-0.040
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Fe}(\text{s})$	-0.44
$\text{FeCO}_3(\text{s}) + 2\text{e}^- \rightleftharpoons \text{Fe}(\text{s}) + \text{CO}_3^{2-}(\text{aq})$	-0.756
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$	-0.76
$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83
$\text{Zr}^{4+}(\text{aq}) + 4\text{e}^- \rightleftharpoons \text{Zr}(\text{s})$	-1.45
$\text{Na}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Na}(\text{s})$	-2.71
$\text{Li}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Li}(\text{s})$	-3.05

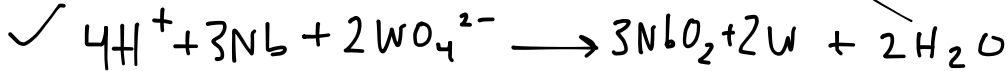
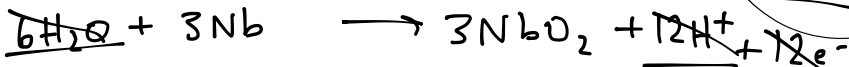
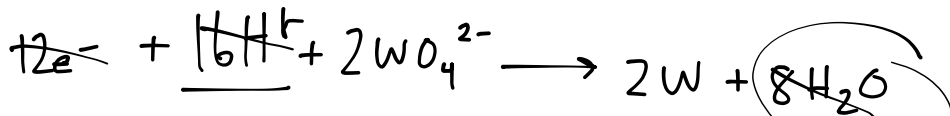
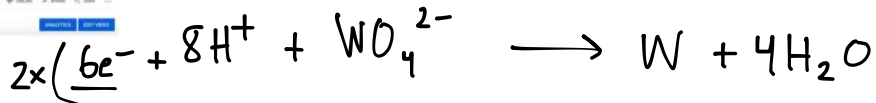
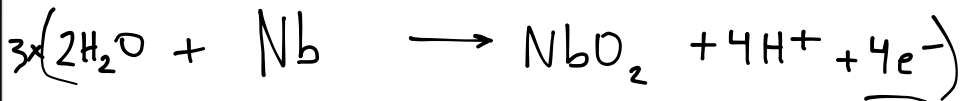
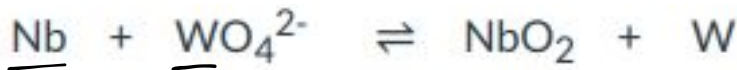
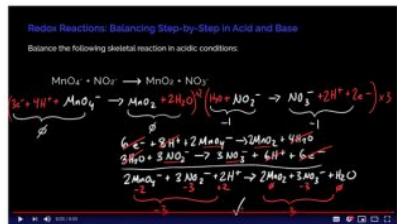
Handwritten notes on the table:
 - "Strongest oxidizing agent" with an arrow pointing to $\text{F}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{F}^-(\text{aq})$
 - "Strongest reduction" with an arrow pointing to $\text{F}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{F}^-(\text{aq})$
 - "Strongest oxidizing agent" with an arrow pointing to $\text{Li}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Li}(\text{s})$
 - "Strongest reducing agent" with an arrow pointing to $\text{Li}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Li}(\text{s})$

Assigning Oxidation Numbers

1. Atoms in their standard state are neutral
 - Example: O_2 , Na, Fe, Br_2
2. If the question directly assigns an oxidation number, that's its oxidation number
 - Example: iron³⁺(III), aluminum²⁺(II)
3. Group 1 is +1, Group 2 is +2...Group 7A is -1
 - Example: Na^+ , K^+ , F^-
4. ✓ Hydrogen is +1, Oxygen is -2 when bonded
 - ~~Exceptions: hydrides are -1, peroxides are -1~~
5. **Assign peripheral charges first** ✓



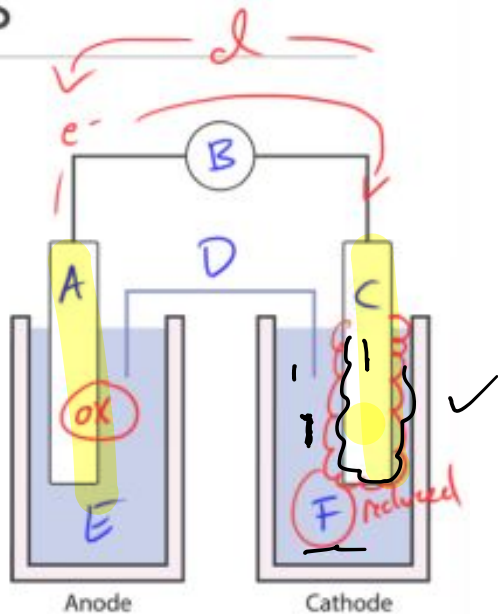
Balancing Reactions in Acid



Standard Cells

Electrochemical Cell Definitions

- Anode:** the site of oxidation (An Ox) ; gives electrons to the wire
- Cathode:** the site of reduction (Red Cat) ; takes in electrons from the wire
- Voltage:** the difference in potential per unit charge (J/C or V); a measurement of the "pulling power" on the electrons, where a positive potential means electrons are spontaneously flowing and a negative potential means the electrons must be pulled/pushed by an external power source
- Voltaic Cell (Galvanic Cell):** an electrochemical cell with a positive standard cell potential ; the redox reaction of the cell occurs without an external power source (spontaneous) ; $\epsilon^{\circ}_{\text{cathode}} > \epsilon^{\circ}_{\text{anode}}$ (reduction potentials)
- Electrolytic Cell:** an electrochemical cell with a negative standard cell potential ; the redox reaction of the cell relies on an external power source (non-spontaneous) $\epsilon^{\circ}_{\text{cathode}} < \epsilon^{\circ}_{\text{anode}}$ (reduction potentials)



Electrochemical Potential

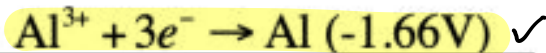
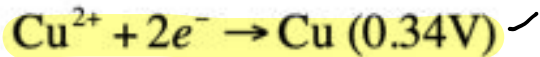
- **Electrical Cell Potential ($\epsilon^\circ_{\text{cell}}$):** the voltage associated with the redox reaction occurring in an electrochemical cell

Use \rightarrow $\epsilon^\circ_{\text{cell}} = \epsilon^\circ_{\text{cathode}} - \epsilon^\circ_{\text{anode}}$

Use data straight off reduction potential table

in this equation, both ϵ° values are reduction potentials read from a table

Using the following half-reactions, show the voltaic/ electrolytic cells that can be created:

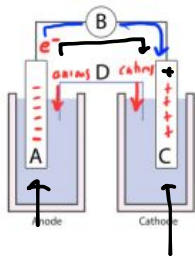


A voltaic cell **produces a positive voltage** through a spontaneous redox reaction

$$\mathcal{E}^{\circ}_{\text{cell}} = \mathcal{E}^{\circ}_{\text{cathode}} - \mathcal{E}^{\circ}_{\text{anode}}$$

Galvanic Voltage: $2.00\text{V} = (0.34\text{V}) - (-1.66\text{V})$; $\text{Al} \mid \text{Al}^{3+} \parallel \text{Cu}^{2+} \mid \text{Cu}$

✓



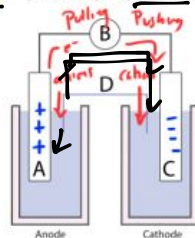
A → Al(s)
 B → Voltmeter
 C → Cu(s)
 D → Salt bridge

An electrolytic cell **requires a power source** to run a non-spontaneous redox reaction

$$\mathcal{E}^{\circ}_{\text{cell}} = \mathcal{E}^{\circ}_{\text{cathode}} - \mathcal{E}^{\circ}_{\text{anode}}$$

Electrolytic Voltage: $-2.00\text{V} = (-1.66\text{V}) - (0.34\text{V})$; $\text{Cu} \mid \text{Cu}^{2+} \parallel \text{Al}^{3+} \mid \text{Al}$

✓



A → Cu(s)
 B → Power Source
 C → Al(s)
 D → Salt bridge

The Electrochemical Cell Summary

	Voltaic cells Galvanic	Electrolytic Cells
spontaneous? free energy, ΔG	negative (-) yes	positive (+) No
potential, E	positive (+) ✓	negative (-) ✓
push/pull of electrons	Anode to cathode via spontaneous chemical reaction	Anode to cathode via an external power source
anode	negative (-) ✓	positive (+) ✓
cathode	positive (+) ✓	negative (-) ✓

Summary:

In **all** electrochemical cells, the electrons travel from the site of oxidation (anode) to the site of reduction (cathode).

The main difference is that voltaic cells are spontaneous cells, **where the redox reaction drives the current**. In an electrolytic cell, the redox reaction is non-spontaneous. **Therefore, the push/pull of current is driven by an external power source.**

Electrochemical Applications and Nonstandard Cells

1. Electroplating

You are using current to cause metal ions to reduce and become their solid form on a metal cathode.



A baseball bat is made by electroplating solid cobalt on a metal surface from a concentrated cobalt(II) chloride solution. If 6.40 amps of current is passed for a total of two and a half days, what is the mass of the solid cobalt surface? Molar Mass of Co = 58.93 g/mol

$$I = 6.4 \text{ A}$$

$$t = 2.5 \text{ days}$$

$$F = 96,485$$

$$n = 2 \text{ mole}^-$$

$$7.16 \text{ mol} \times \frac{58.93 \text{ g}}{1 \text{ mol}} = \boxed{422 \text{ g}}$$

moles of metal

$$\frac{I \cdot t}{n F}$$

↑
mole⁻
1/2 rxn

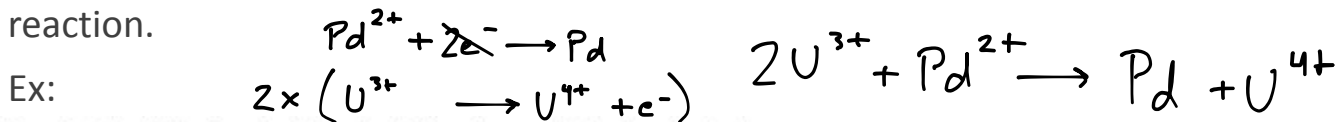
$$7.16 \text{ mol Co}$$

$$2.5 \text{ days} \times \frac{24 \text{ hrs}}{1 \text{ day}} \times \frac{60 \text{ min}}{1 \text{ hr}} \times \frac{60 \text{ s}}{1 \text{ min}} = 216,000 \text{ s}$$

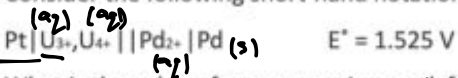
$$= \frac{(6.4)(216,000)}{(2)(96,485)}$$

2. Electrical Energy of a Cell

You are predicting the non-expansion work (also known as total energy) of an electrochemical cell based on the number of transferred electrons in the overall reaction.



Consider the following short-hand notation for an electrochemical cell:



What is the value of ~~non-expansion~~ ^{energy} work for this cell at standard conditions?

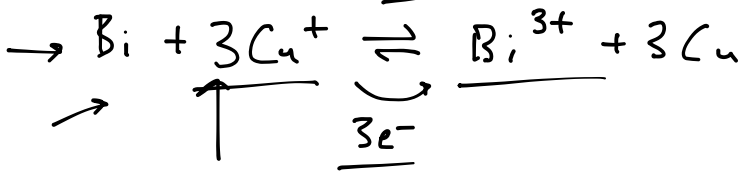
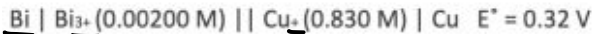
$$\begin{array}{l}
 \text{Energy} = n F E^\circ \\
 n = 2 \text{ mol e}^- \\
 F = 96485 \\
 E^\circ = 1.525 \text{ V} \\
 \frac{(2)(96485)(1.525)}{1000} \\
 \boxed{294.3 \text{ kJ/mol rxn}}
 \end{array}$$

3. Cells at Non-Standard Conditions

You are predicting the voltage of a non-standard cell using the Nernst Equation that allows us to see how concentrations affect cell potential.

Ex:

What is the non-standard cell potential for the following cell at 298.15 K and 1 atm?



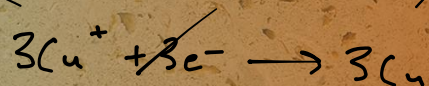
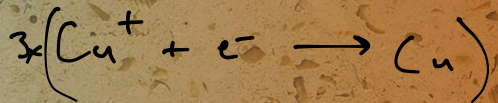
$$E = 0.32 - \frac{0.05916}{3} \log \frac{0.002}{(0.83)^3}$$

0.368 V

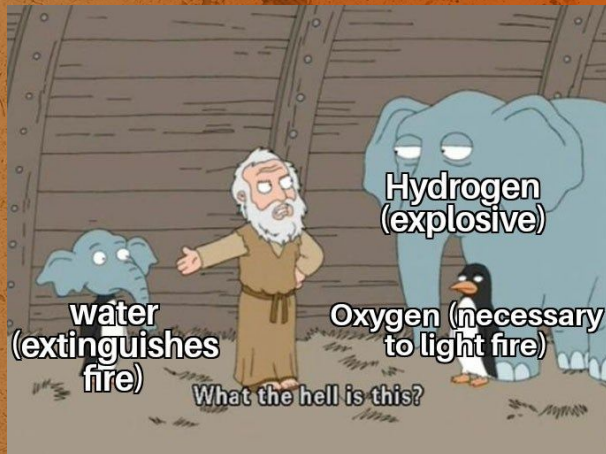
$$E = E^{\circ} - \frac{0.05916}{n} \log Q$$

\downarrow

$\frac{[\text{Prod}]^{\text{coefficient}}}{[\text{react}]^{\text{coefficient}}}$



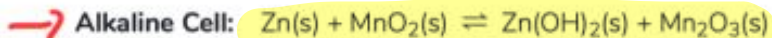
Batteries



Batteries – Primary Cells (one-way)

Primary Cell: a voltaic cell capable only of discharging. Primary cells are one-time use batteries.

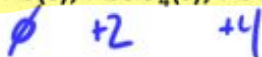
- The common primary cells in our lives are alkaline cells (D, C, AA, AAA, etc.)
- These all involve the same reaction, meaning they have the same standard potential.
- They differ in size; therefore, they differ in current. A large surface area (D-batteries) will have a greater current (less internal resistance)



Batteries – Secondary Cells (rechargeable)


Secondary Cell: a battery that can act like a voltaic cell when discharging, but can also act like an electrolytic cell when recharged (examples: cell phone battery, lead-acid car battery, Lithium-Ion). Secondary cells can be used numerous times (or continuously) until eventually the battery degrades.

- **Lead-Acid Car Battery:** a specific type of secondary cell that involves lead in three solid oxidation states: $\text{Pb}(s)$, $\text{PbSO}_4(s)$, $\text{PbO}_2(s)$



Batteries – Fuel Cells (refillable)

Fuel Cells: a battery that relies on a spontaneous combustion reaction. We are mostly concerned with the hydrogen fuel cell. The combustion of hydrogen to form water is very spontaneous, so we don't try to recharge these cells. Instead, we can refill them with our hydrogen fuel.



How to prepare for the exam in the next two nights:

* Learning Outcomes

* HWs

* gchem \rightarrow electrochemistry \rightarrow helpsheets

* Predict Exam Qs

Questions?

