CH 302 – Unit 5 Exam Review

ELECTROCHEMISTRY

ECIS is open (course instructor surveys)

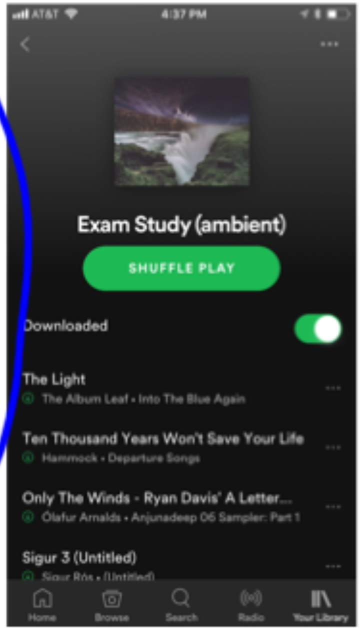
Sorry for the technical issues :(

Here are all the best playlists from the year

Please do mine + comment

They are funny

And make me happy



Exam Study (ambient)

Downloaded

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The Album Leaf • Into The Blue Again

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Hammock • Departure Songs

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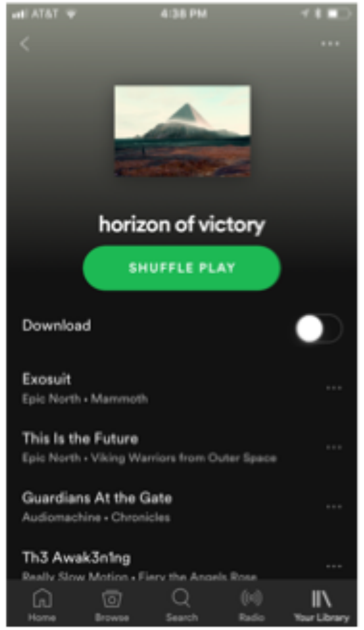
Ólafur Arnalds • Anjunadeep 06 Sampler: Part 1

Sigur 3 (Untitled)
Sigur Rós • (Untitled)



horizon of victory

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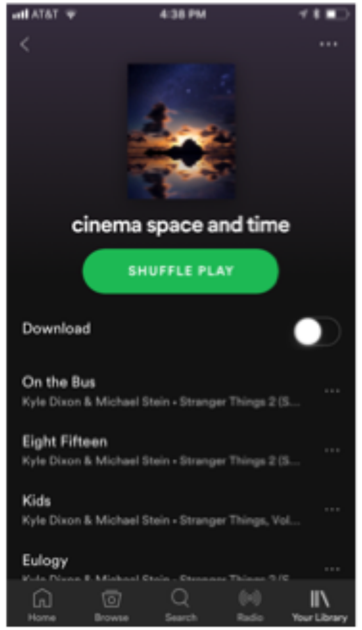

cinema space and time

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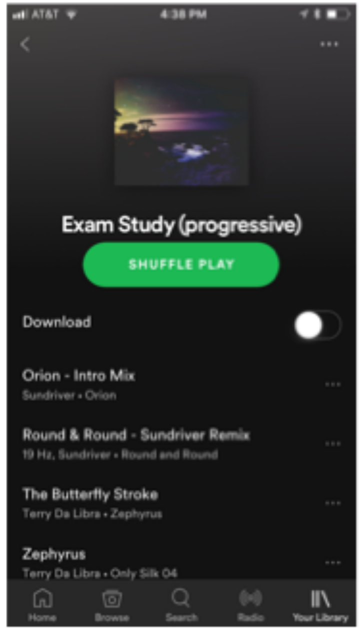

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Round & Round - Sundriver Remix
19 Hz, Sundriver • Round and Round

The Butterfly Stroke
Terry Da Libra • Zephyrus

Zephyrus
Terry Da Libra • Only Silk 04

Exam 5 Breakdown

22-26 Q's

~15 concept

~9 calc

46% fundamental, 20% very hard

46% medium

Remember.....

↳ $PV = nRT$, $pH = -\log[H^+]$, Ksp represents $MX_{(s)} \rightarrow M^+_{(aq)} + X^-_{(aq)}$

Unit 5 Outline: Electrochemistry

I. Understand fundamental redox reactions
   - Balancing redox reactions
   - Assigning oxidation numbers
   - Identifying the roles of the different species in the reaction

II. Combine half-reactions into standard cells (voltaic and electrolytic)
   - Important: Electrolytic applications (electrolysis and electroplating)

III. Apply the concepts of electrochemical cells to non-standard conditions
   - Concentration Cells
   - Nernst Potential

IV. Complete the storylines of thermodynamics and equilibrium by converting electrical potential into K and ΔG.

Main challenges

V. Common applications of batteries
   - Primary and secondary cells
   - Fuel Cells
   - Lead-Acid (car) Batteries

Unit 5 Mistakes (and how not to make them)

I. Make sure your answer makes sense with your sign convention
   - Reflect on your answer and make sure it aligns with your fundamentals (voltaic is positive, work done on the system is positive ΔG, increasing Q means a decrease in E, etc.)

II. Make sure to use the correct number for “n” moles of electrons
   - Knowing how to balance a reaction properly is essential for electrical work (ΔG), equilibrium constant calculations, and non-standard cell potentials
   - You can get away with using the “n” for your half-reaction when using Faraday’s Law for electrolysis and electroplating

III. Remember how to solve for Q using concentrations and pressures
   - Both Q and K are based on the mass action expression, meaning you take the concentrations (or pressures) of the products raised to the powers of their coefficients divided by the concentrations (or pressures) of the reactants raised to the powers of their coefficients
   - Balance your reaction before solving for Q
   - Ignore liquids and solids, which have activities equal to 1

IV. Knowing your fundamental definitions will help
   - Be able to put charge, voltage, and current into your own words

Unit 5 Equations

1. Electrochemical Cell Potential

$$\mathcal{E}^\circ_{cell} = \mathcal{E}^\circ_{cathode} - \mathcal{E}^\circ_{anode}$$

2. Faraday's Law, plating a metal, electrolysis

$$\frac{I \cdot t}{n \cdot F} = \text{moles created}$$

$$n = \frac{\text{moles } e^-}{\text{mol product}}$$

3. Convert between electrical potential (ε) and free energy/ maximum electrical work (ΔG)

$$\Delta G = -nF\mathcal{E} \qquad \Delta G^\circ = -nF\mathcal{E}^\circ$$

$$n = \frac{\text{moles } e^-}{\text{balanced rxn}}$$

4. Convert between electrical potential (ε) and the equilibrium constant (K)

$$\cancel{\mathcal{E}^\circ = \frac{RT}{nF}\ln K} \qquad \boxed{\mathcal{E}^\circ = \frac{0.05916}{n}\log K}$$

5. Non-standard Cell Potential

$$\cancel{\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{nF}\ln Q} \qquad \boxed{\mathcal{E} = \mathcal{E}^\circ - \frac{0.05916}{n}\log Q}$$

Electrochemistry Definitions

1. **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 involves one species undergoing reduction and another undergoing oxidation.
2. **Reduction**: a species gains electrons in a half-reaction, resulting in a lower oxidation state
3. **Oxidation**: a species loses electrons in a half-reaction, resulting in a higher oxidation state
4. **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**
5. **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**

$$3\mathrm{Cu}^{2+} + 2\mathrm{Al} \rightarrow 3\mathrm{Cu} + 2\mathrm{Al}^{3+}$$

$$\mathrm{Cu}^{2+} + 2e^{-} \rightarrow \mathrm{Cu}$$

$$\mathrm{Al} \rightarrow \mathrm{Al}^{3+} + 3e^{-}$$

LEO says GER
OIL RIG

spontaneous

Question

Which of the following species will reduce Cu^{2+} but not Pb^{2+}?

a. Fe^{2+}

[✓ b. H_2]

c. Zn

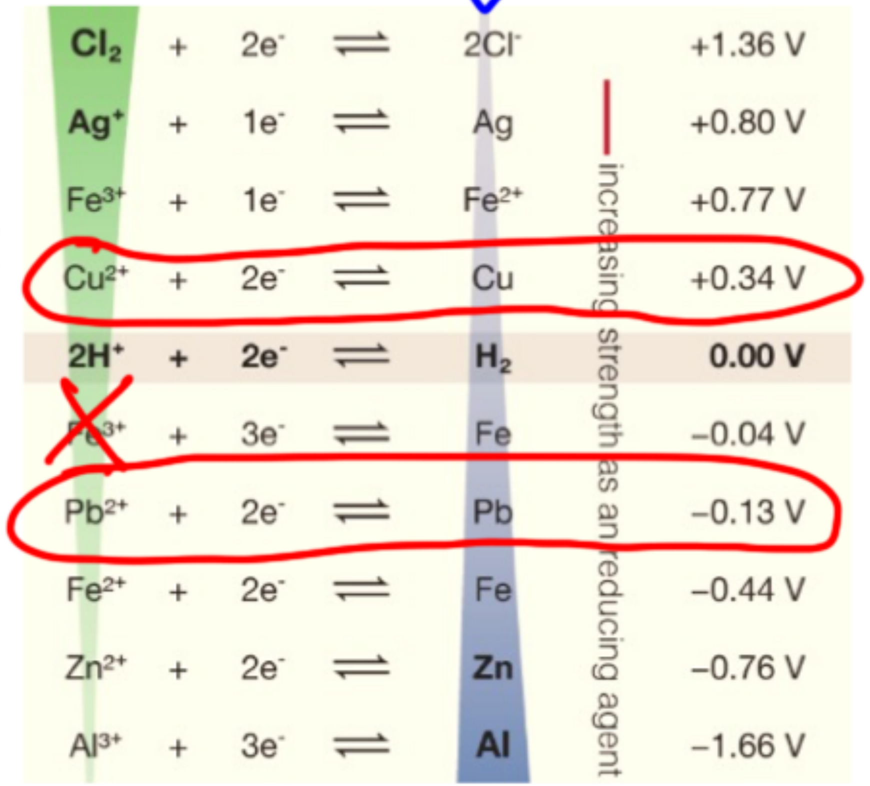
d. Fe^{3+}

e. H^+

reduction in an electrolytic cell w/ answer

reduction in a voltaic cell w/ answer

Looking for a reducing agent



Cl_2	+	$2e^-$	⇌	$2Cl^-$	+1.36 V
Ag^+	+	$1e^-$	⇌	Ag	+0.80 V
Fe^{3+}	+	$1e^-$	⇌	Fe^{2+}	+0.77 V
Cu^{2+}	+	$2e^-$	⇌	Cu	+0.34 V
$2H^+$	+	$2e^-$	⇌	H_2	0.00 V
Fe^{3+}	+	$3e^-$	⇌	Fe	−0.04 V
Pb^{2+}	+	$2e^-$	⇌	Pb	−0.13 V
Fe^{2+}	+	$2e^-$	⇌	Fe	−0.44 V
Zn^{2+}	+	$2e^-$	⇌	Zn	−0.76 V
Al^{3+}	+	$3e^-$	⇌	Al	−1.66 V

Electrochemical Cell Definitions

1. **Anode**: the site of oxidation (An Ox) ; gives electrons to the wire
2. **Cathode**: the site of reduction (Red Cat) ; takes in electrons from the wire
3. Voltage: the difference in potential per unit charge (J/C or V); a measurement of the "pulling power" on the electrons
4. **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) ; $\varepsilon^\circ_{cathode} > \varepsilon^\circ_{anode}$ (reduction potentials)
5. **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) $\varepsilon^\circ_{cathode} < \varepsilon^\circ_{anode}$ (reduction potentials)

→ work done by system

$\Delta G = -$

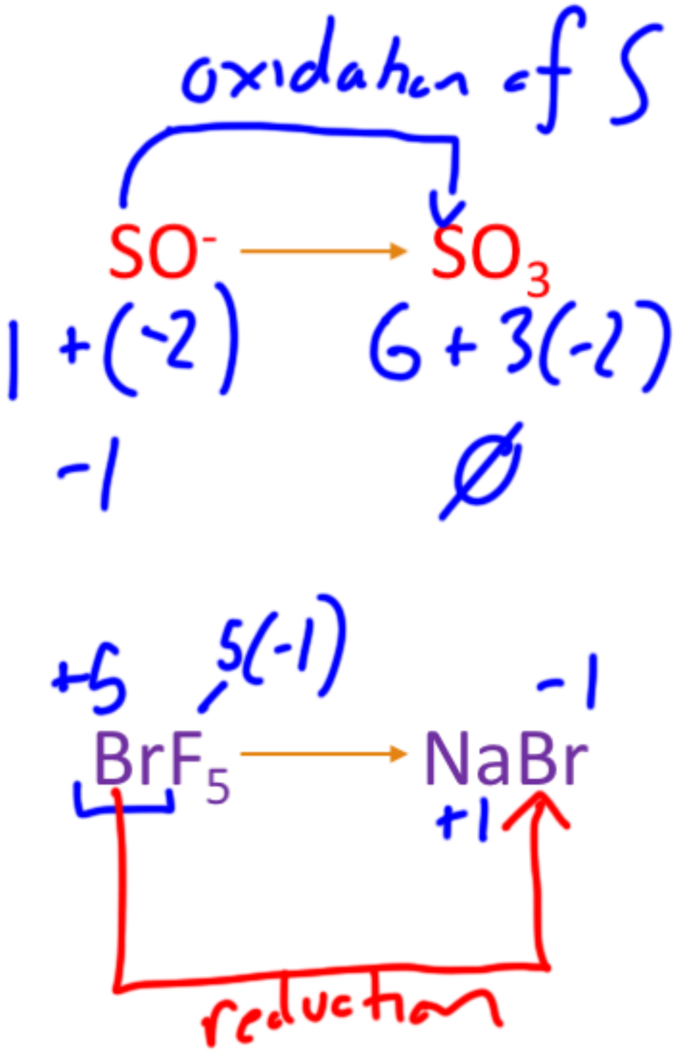
→ work done on system

$\Delta G = +$

Be able to balance any redox reactions:
Neutral, Basic, and Acidic (see review 1)

Oxidation Numbers

1. Atoms in standard state are neutral
   - Example: O_2, Fe, Br_2
2. If you have already assigned a charge to a monatomic species, that's its oxidation number
   - Example: Fe^{3+}, Al^{2+}
3. Group 1 is +1, Group 2 is +2...Group 7A is -1
   - Example: Na^+, K^+, F^-
4. Hydrogen is +1, Oxygen is -2
   - Exceptions: hydrides are -1, peroxides are -1
5. Assign electronegative charges first



oxidation of S

$SO^- \rightarrow SO_3$

$1 + (-2)$ $6 + 3(-2)$

-1 0

$+5$ $5(-1)$ -1

$BrF_5 \rightarrow NaBr$

$+1$

reduction

The Electrochemical Cell

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

$$\mathrm{Cu}^{2+} + 2e^{-} \rightarrow \mathrm{Cu}\ (0.34\mathrm{V})$$

$$\mathrm{Al}^{3+} + 3e^{-} \rightarrow \mathrm{Al}\ (-1.66\mathrm{V})$$

$$\varepsilon^{\circ}_{cell} = \varepsilon^{\circ}_{cathode} - \varepsilon^{\circ}_{anode}$$

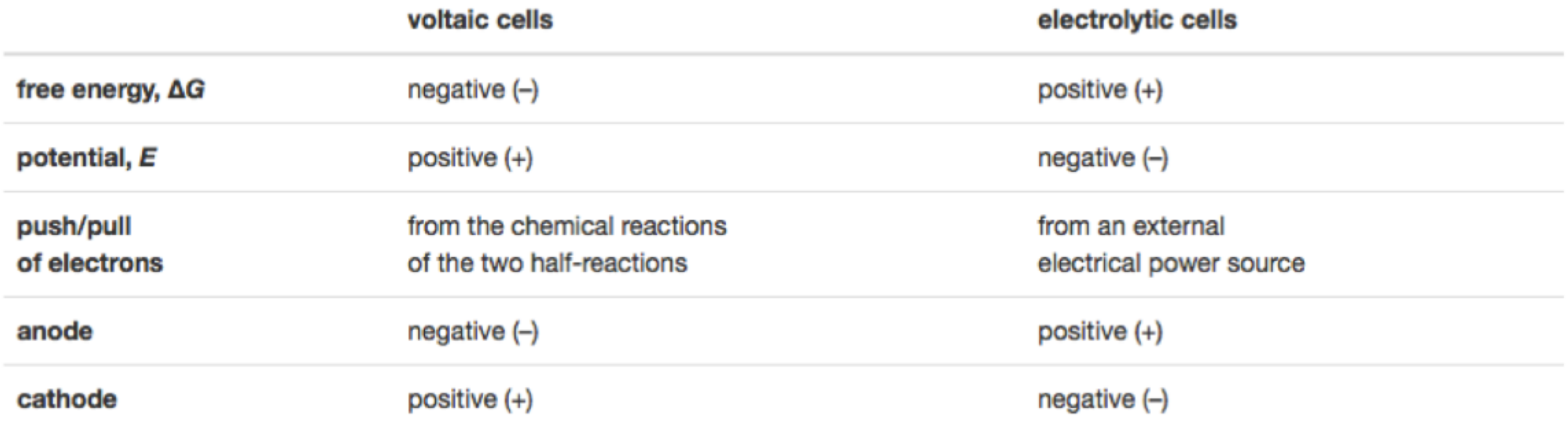
Voltaic Potential: **2.00V** = (0.34V) – (-1.66V) ; **$\mathrm{Al} \mid \mathrm{Al}^{3+} \parallel \mathrm{Cu}^{2+} \mid \mathrm{Cu}$**

Electrolytic Potential: **-2.00V** = (-1.66V) – (0.34V) ; **$\mathrm{Cu} \mid \mathrm{Cu}^{2+} \parallel \mathrm{Al}^{3+} \mid \mathrm{Al}$**

Electrochemical Cells

	Voltaic Cells	Electrolytic Cells
Cathode (rxn and charge)	reduction (+)	reduction (−)
Anode (rxn and charge)	oxidation (−)	oxidation (+)
Direction of e^- flow	Anode → Cathode	A → C
Direction of current flow	C → A	C → A
$\varepsilon°$	+	−
ΔG	−	+
K	$K > 1$	$K < 1$
Work	− by sys	+ on sys
Flow of anions	to anode	to anode
Flow of cations	to cathode	to cathode

The Electrochemical Cell Summary



	voltaic cells	**electrolytic cells**
free energy, ΔG	negative (–)	positive (+)
potential, *E*	positive (+)	negative (–)
push/pull of electrons	from the chemical reactions of the two half-reactions	from an external electrical power source
anode	negative (–)	positive (+)
cathode	positive (+)	negative (–)

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.**

Conceptual Summary: Standard Cells

STD. Electrical Potential ε°	Free Energy ΔG°	Equilibrium Constant K	Spontaneous?
Positive	Negative	Greater than 1	Yes
Negative	Positive	Less than 1	No
Zero	Zero	Equal to 1	At Equilibrium

Concentration Cell

Tough Shorthand Notation

anode |anodic solution ||cathodic solution | cathode

½ rxn of interest

balanced rxn

What is n if I am….

	Plating Metal	Calculating Work
$\overbrace{Al \vert Al^{3+} \Vert \underbrace{Cu^{2+} \vert Cu}_{+2}}^{6}$	2	6
$Pt \vert H_2 \vert H^+ \Vert Cu^+ \vert Cu$	1	2
$C\ (graphite) \vert Cr^{2+}, Cr^{3+} \Vert Al^{3+} \vert Al$	3	3
$Ag \vert Ag^+ \Vert Cl^-\ (aq) \vert AgCl\ (s) \vert Ag\ (s)$	1	1

We want you to know these conversions backward and forward. This means you can solve for I, t, n, ~~n~~ moles, mass, or volume

Faraday's Law

Two common applications of electrolytic cells are **electroplating** and **electrolysis**

- Faraday's Law states that the charge provided (I t) times the charge per mole product (n F) is equal to the moles of that product created.

$$\frac{\cancel{C}}{\cancel{s}}\cdot\cancel{s}$$

$$\frac{I\cdot t}{n\cdot F} = \text{moles created} = \frac{\text{charge applied}}{\text{charge it takes per mole product}}$$

$$\frac{\cancel{\text{mol } e^-}}{\text{mol product}}\cdot\frac{\cancel{C}}{\cancel{\text{mol}}\ e^-}$$

We want you to know these conversions backward and forward. This means you can solve for I, t, n, ~~F,~~ moles, mass, or volume

current

time

oxidation state

Faraday's Law

Two common applications of electrolytic cells are **electroplating** and **electrolysis**

- Here (and only in this equation), our "n" value represents the moles of electron in the **half-reaction that produces the desired product**

$1e^-$

$$2NaCl \xrightarrow{2e^-} 2Na(s) + Cl_2$$

$2e^-$

→ to volume

PV=nRT

$$\frac{I \cdot t}{n \cdot F} = \text{moles created}$$

→ to mass (g, mg, kg, etc.)

$2e^-$

Plating Ni from nickel(II) chloride

Free Energy and Electrical Work

1. **There is a simple relationship between free energy and electrical potential:**

$$\underbrace{\boxed{\Delta G^\circ}}_{\text{Joules/mol rxn}} = -\overset{\text{balanced rxn}}{\boxed{n}}F\mathcal{E}^\circ$$

÷1000 → kJ

2. **This equation can be applied to tell us about the capacity for an electrochemical system to do work:**

$$w = -q \cdot \mathcal{E}$$

3. These values are ideal, meaning we are calculating the maximum electrical work, **or the maximum reversible non-expansion work.**

Electrical Potential and Equilibrium

Now that we know the relationship between electrical potential and free energy:

$$\Delta G^{\circ} = -nF\mathcal{E}^{\circ}$$

We can very clearly connect the dots between free energy and the equilibrium constant, K:

$$\mathcal{E}^{\circ} = \frac{0.05916}{n}\log K$$

K_{sp} from electrical potential

If your overall reaction corresponds to a special type of reaction, you can solve for that special K value. Take the K_{sp} for $PbSO_4$, for example:

$PbSO_4 + 2e^- \rightarrow \cancel{Pb} + SO_4^{2-}$, E° = -0.36 V

Flip ~~$Pb^{2+} + 2e^- \rightarrow Pb$~~, E° = - 0.13 V

$\cancel{Pb} \rightarrow Pb^{2+} + 2e^-$

$PbSO_4 \rightarrow Pb^{2+} + SO_4^{2-}$

$\mathcal{E}^\circ = -0.23V$

$n = 2$

$$\mathcal{E}^\circ = \frac{0.05916}{n}\log K_{\underline{\underline{sp}}}$$

$$-0.23V = \frac{0.05916}{2}\log K_{sp}$$

Non-Standard Cells Electrical Potential

You can use Q to determine the non-standard potential with the Nernst Equation:

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

Remember how Q works (and remember that Q depends only on aqueous and gaseous species!):

- Q is the given concentrations (or pressures) of the products raised to the power of their coefficients divided by the reactants raised to the power of their coefficients.
- If you add product, your voltage drops
- If you add reactant, your voltage increases

$Q\downarrow \ \mathcal{E}\uparrow$

$Q\uparrow \ \mathcal{E}\downarrow$

If you change the temperature, the "adjustment term" changes with it

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{nF}\ln Q$$

Non-Standard Cell Potential Overview

Consider the following cell at standard conditions:

$Pt \mid H_2(g) \mid H^+(aq) \parallel Cl^- \mid AgCl(s) \mid Ag(s)$ E° = + 0.222 V

How does each of the following change the voltage:

I. Decrease the partial pressure of hydrogen $P_{H_2}\downarrow \quad Q\uparrow \quad \mathcal{E}\downarrow$

II. Add sodium chloride to the cathode compartment $[Cl^-]\uparrow \quad Q\uparrow \quad \mathcal{E}\downarrow$

III. Increase the pH $pH\uparrow \quad [H^+]\downarrow \quad Q\downarrow \quad \mathcal{E}\uparrow$

Write an expression that represents the non-standard cell potential at any given concentrations/pressures.

$$H_2 + 2\cancel{Ag}Cl \xrightarrow{2e^-} 2\cancel{Ag} + 2Cl^- + 2H^+$$

↑ solids ↑

$$Q = \frac{[Cl^-]^2[H^+]^2}{P_{H_2}}$$

The Concentration Cell

A concentration cell is simply a cell that has identical half-reactions and achieves a positive cell potential by having a favorable Q-value in the Nernst Equation.

$$reduction: \mathrm{Cu}^{2+} + 2e^{-} \rightarrow \mathrm{Cu}\ (0.34\mathrm{V})$$

$$oxidation: \mathrm{Cu} \rightarrow Cu^{2+} + 2e^{-} (\text{-}0.34\mathrm{V})$$

$\varepsilon^{\circ}_{cell}$ is 0V

ΔG° is 0

K is 1

$$\mathcal{E} = \underbrace{\cancel{\mathcal{E}^{\circ}}}_{=0V} - \frac{0.05916}{n} \log Q$$

$$\frac{[Cu^{2+}]_{an}}{[Cu^{2+}]_{cat}}$$

but if....

$[Cu^{2+}]_{cathode} > [Cu^{2+}]_{anode}$

$\mathcal{E} > 0$

$[Cu^{2+}]_{cathode} < [Cu^{2+}]_{anode}$

$\mathcal{E} < 0$

The Biological Concentration Cell

Animal cells behave like concentration cells with a reaction based on the flow of ions into and out of the cell. These look like:

ε°_{cell} is 0V, ΔG° is 0, K is 1

but if...

$$K^+_{inside} \rightarrow K^+_{outside}$$

$$\mathcal{E} = \underbrace{\cancel{\mathcal{E}^\circ}}_{=0V} - \frac{0.05916}{n}\log Q$$

$$Q = \frac{[K^+]_{out}}{[K^+]_{in}}$$

$[K^+]_{in} > [K^+]_{out}$

$\varepsilon > 0$

$[K^+]_{out} > [K^+]_{in}$

$\varepsilon < 0$

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: Pb(s), $PbSO_4$(s), PbO_2(s)

$$\text{High Energy}\left\{\begin{array}{l}\overset{0}{\mathrm{Pb(s)}} \xrightarrow{\text{oxidation}} \\ \overset{+4}{\mathrm{PbO_2}} \xrightarrow[\text{reduction}]{} \end{array}\right. \overset{+2}{\mathrm{PbSO_4}} \;\text{Low Energy}$$

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.

$$2H_2 + O_2 \rightarrow 2H_2O$$

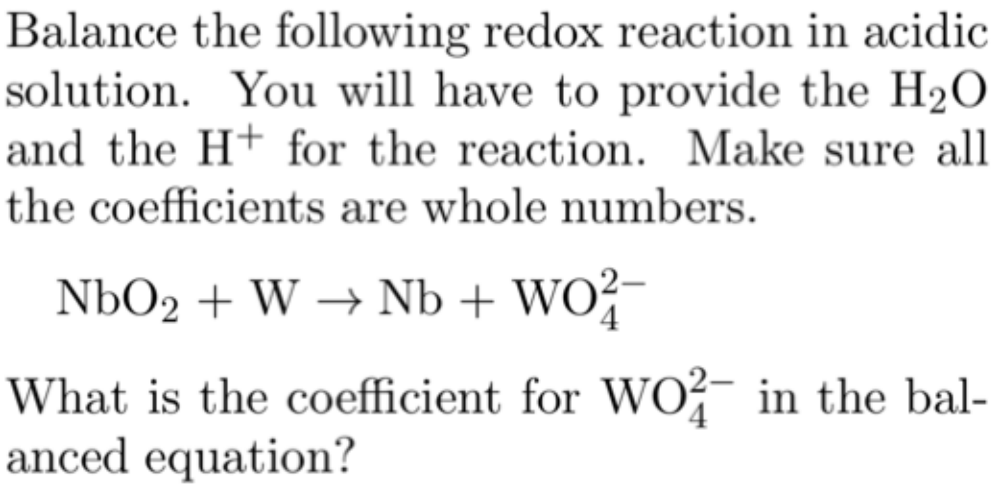
WORK THESE!

Practice Questions

SEE SOLUTIONS IN PREVIOUS REVIEWS

First five questions are from Review 1

Balanced Reaction in Acid



Balance the following redox reaction in acidic solution. You will have to provide the H_2O and the H^+ for the reaction. Make sure all the coefficients are whole numbers.

$$NbO_2 + W \rightarrow Nb + WO_4^{2-}$$

What is the coefficient for WO_4^{2-} in the balanced equation?

Balanced Reaction in Base

Using the set of smallest whole number coefficients to balance the redox equation

$$\mathrm{MnO_4^- + NO_2^- \rightarrow MnO_2 + NO_3^-}$$

in basic solution, you get

Exam Question: Change in Oxidation

In the redox conversion of SO_3 to SO^-, S is ___?___ and its oxidation number goes from ___?___ to ___?___

Question

Which of the following species will reduce Cu^{2+} but not Pb^{2+}?

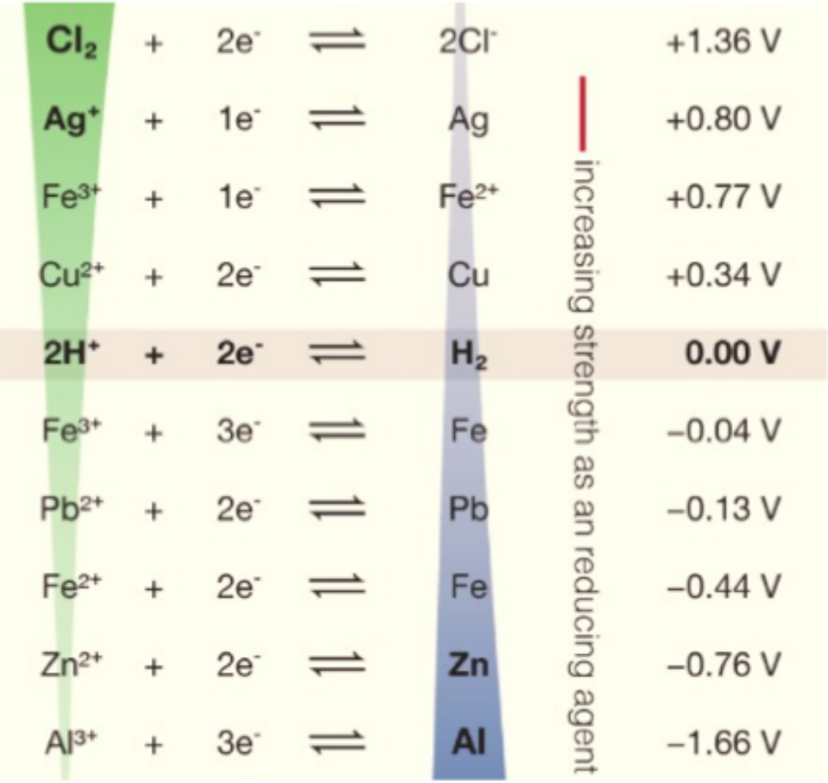
a. Fe^{2+}

b. H_2

c. Zn

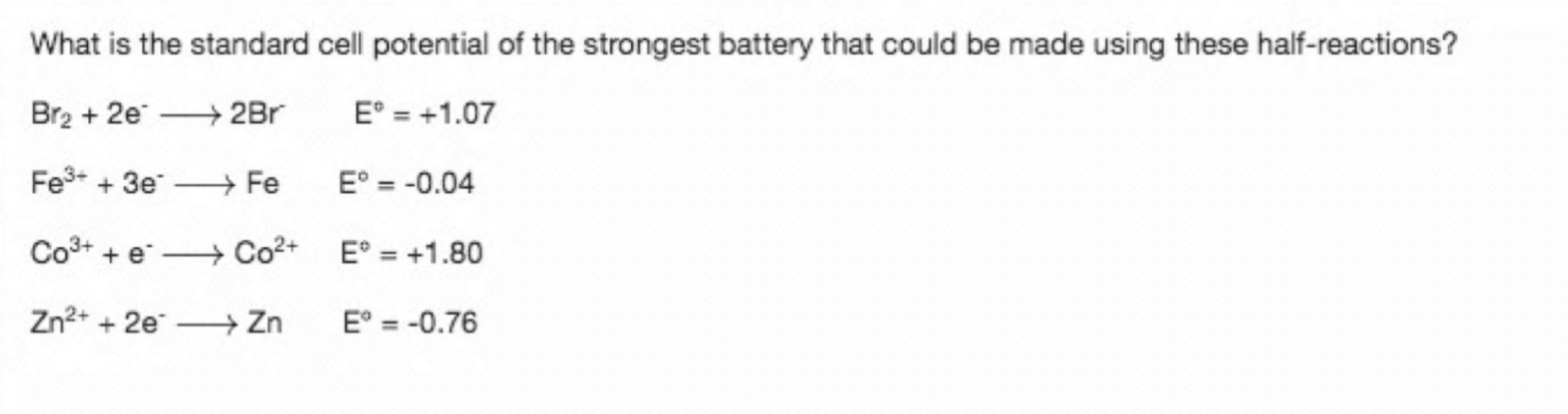
d. Fe^{3+}

e. H^+



Cl_2	+	$2e^-$	$\rightleftharpoons$	$2Cl^-$	+1.36 V
Ag^+	+	$1e^-$	$\rightleftharpoons$	Ag	+0.80 V
Fe^{3+}	+	$1e^-$	$\rightleftharpoons$	Fe^{2+}	+0.77 V
Cu^{2+}	+	$2e^-$	$\rightleftharpoons$	Cu	+0.34 V
$2H^+$	**+**	**$2e^-$**	$\rightleftharpoons$	**H_2**	**0.00 V**
Fe^{3+}	+	$3e^-$	$\rightleftharpoons$	Fe	−0.04 V
Pb^{2+}	+	$2e^-$	$\rightleftharpoons$	Pb	−0.13 V
Fe^{2+}	+	$2e^-$	$\rightleftharpoons$	Fe	−0.44 V
Zn^{2+}	+	$2e^-$	$\rightleftharpoons$	**Zn**	−0.76 V
Al^{3+}	+	$3e^-$	$\rightleftharpoons$	**Al**	−1.66 V

Question



What is the standard cell potential of the strongest battery that could be made using these half-reactions?

$Br_2 + 2e^- \longrightarrow 2Br^-$ E° = +1.07

$Fe^{3+} + 3e^- \longrightarrow Fe$ E° = -0.04

$Co^{3+} + e^- \longrightarrow Co^{2+}$ E° = +1.80

$Zn^{2+} + 2e^- \longrightarrow Zn$ E° = -0.76

Answer by showing the half-reactions and shorthand notation
Hint: look for the strongest reducing agent and the strongest oxidizing agent

All after this are from Review 2

Exam Question

What is the mass of aluminum (Al, 26.98 g/mol) formed when 18 A is run through the following cell for 8.0 hours?

$$Cu|Cu^{2+}||Al^{3+}|\ Al$$

Electrolysis Question

What is the volume of $Cl_2(g)$ produced at STP by the electrolysis of concentrated sodium chloride if 7.00 A are passed through the solution for 6 hours? The reaction is shown below:

$$2NaCl(aq) + 2H_2O(l) \rightleftharpoons 2NaOH(aq) + H_2(g) + Cl_2(g)$$

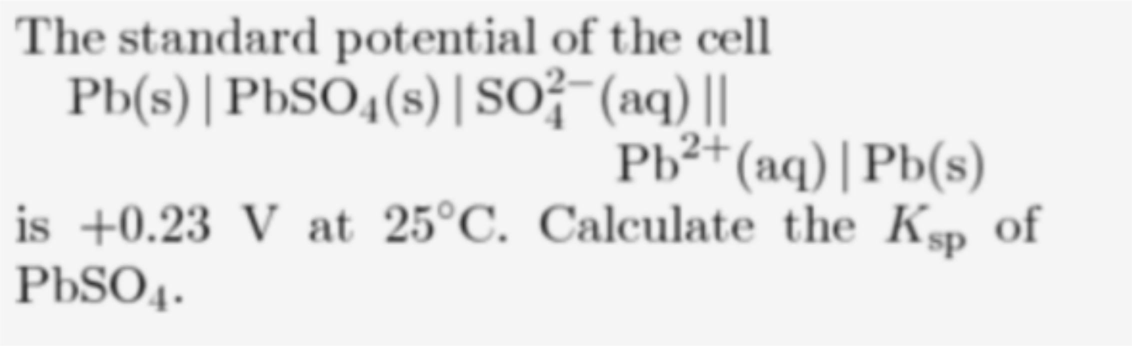
Electrochemical Work

Consider the following cell at standard conditions (E˚ = 0.75 V) :

$Al | Al^{3+} || Cr^{2+} | Cr$

What is the value of ΔG˚? Is work done on the system or being applied to the system?

Equilibrium Calculations



The standard potential of the cell

$$\mathrm{Pb(s)\,|\,PbSO_4(s)\,|\,SO_4^{2-}(aq)\,||\,Pb^{2+}(aq)\,|\,Pb(s)}$$

is +0.23 V at 25°C. Calculate the K_{sp} of $PbSO_4$.

Non-Standard Cell Potential

Consider the following cell at standard conditions:

$Pb(s)\ |\ PbSO_4(s)\ |\ SO_4^{2-}\ ||\ H^+(aq)\ |\ H_2(g)\ |\ Pt$

How does each of the following change the voltage:

I. Increase partial pressure of hydrogen
II. Add sodium sulfate to the anode compartment
III. Decrease the pH

Non-Standard Calculations

If E° for the following cell is 0.36 V at 25°C, what is the value of E for the conditions given:

$Pb(s) \mid PbSO_4(s) \mid SO_4^{2-}(aq, 0.60\ M) \mid\mid H^+(aq, 1.6\ M) \mid H_2(g, 0.08\ atm) \mid Pt$

Overview Question

Suppose you create a battery out of nickel and cadmium with the following half-reactions:

$Cd^{2+} + 2e^{-} \rightarrow Cd$ -0.40V

$Ni^{2+} + 2e^{-} \rightarrow Ni$ -0.23V

What are the values of E°, ΔG°, and K?

What is the ratio of Cd^{2+} : Ni^{2+} when your battery reaches equilibrium?

Concentration Cell Question

An electrochemical cell is created out of two SHE compartments (shown below). What is the pH of the anode compartment if the measured potential is 0.12 V?

$$\text{Pt} \mid H_2\ (1\ \text{atm}) \mid H^+\ (???) \parallel H^+\ (1M) \mid H_2\ (1\ \text{atm}) \mid \text{Pt}$$