Unit 4 Exam Review

ELECTROCHEMISTRY

Exam 4 Breakdown

Exam Study (progressive)

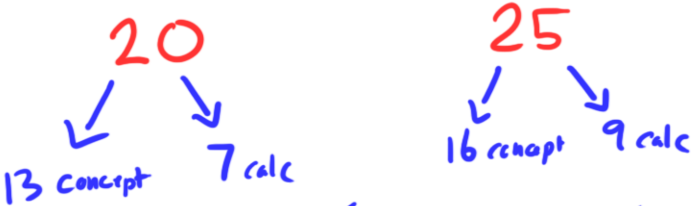
45 Followers • by Jimmy Wadman

Orion - Intro Mix

Sundriver • Orion

Round & Round - Sundriver Remix

19 Hz, Sundriver • Round and Round



STUDY: $pH = -\log[H^+]$, pH↓ $[H^+]$↑

$K_{sp} \rightarrow MX \rightarrow M^+ + X^-$

$Q = \frac{\text{Products}}{\text{Reactants}}$ } powers; solids & liquids not in expression

Please do my eCIS + comment

They are funny

http://mccord.cm.utexas.edu/courses/spring2019/ch302/exam4.php

Unit 4 Outline: Electrochemistry

1. Understand fundamental redox reactions
   - Assigning oxidation numbers
   - Balancing redox reactions
   - Identifying the roles of the different species in the reaction
2. Combine half-reactions into standard cells (voltaic and electrolytic)
3. Electrochemical Stoichiometry and Electrolytic applications
4. Apply the concepts of electrochemical cells to non-standard conditions
   - Concentration Cells
   - Nernst Potential
5. Complete the storylines of thermodynamics and equilibrium by converting electrical potential into K and ΔG.
6. Common applications of batteries
   - Primary and secondary cells
   - Fuel Cells
   - McCord: Alkaline Cell and Lead-Acid Chemistry

Unit 4 Mistakes (and how not to make them)

I. Check your charge balance when balancing redox reactions

II. 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, an electrolytic cell has a positive ΔG, increasing Q means a decrease in E, etc.)

III. 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, but you must use the full balanced reaction for ΔG, K, and Q calculations

IV. 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

V. Knowing your fundamental definitions will help

- Be able to put charge, voltage, constants, and current into your own words

Unit 4 Equations

1. Electrochemical Cell Potential

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

2. Faraday's Law, plating a metal

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

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

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

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

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

5. Non-standard Cell Potential

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

Redox Reactions

Electrochemistry Terms

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 balances both electron-transfer AND stoichiometric coefficients
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

Standard Potentials at 25°C	$E°$ (V)
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(\ell)$	+1.51
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(\ell)$	+1.33
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(\ell)$	+1.23
$Pd^{2+}(aq) + 2e^- \rightleftharpoons Pd(s)$	+0.915
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$Cu^+(aq) + e^- \rightleftharpoons Cu(s)$	+0.52
$O_2(g) + 2H_2O(\ell) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$Bi^{3+}(aq) + 3e^- \rightleftharpoons Bi(s)$	+0.20
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O(\ell)$	+0.17
$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	+0.150
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	**0.000**
$Fe^{3+}(aq) + 3e^- \rightleftharpoons Fe(s)$	–0.040
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	–0.44
$FeCO_3(s) + 2e^- \rightleftharpoons Fe(s) + CO_3^{2-}(aq)$	–0.756
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	–0.76
$2H_2O(\ell) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	–0.83
$Zr^{4+}(aq) + 4e^- \rightleftharpoons Zr(s)$	–1.45
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	–2.71
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	–3.05

Strongest oxidizing agent

Strongest reduction

Strongest reducing agent

Strongest oxidation

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: iron(III), aluminum(II)
3. When bonded, Group 1 is +1, Group 2 is +2…Group 7A is usually -1
   - Example: Na^+, K^+, F^-
4. When bonded, Hydrogen is +1, Oxygen is -2
   - ~~Exceptions: hydrides are -1, peroxides are -1~~
5. Rule 3 is not 100 %. To avoid making a mistake, assign peripheral charges first

$$\begin{tikzcd} SO^- \arrow[r] \arrow[d] & SO_3 \arrow[d] \\ 1 + (-2) = -1 \arrow[r, bend right, "5e^-\text{, oxidation}"'] & 6 + (-2)3 = 0 \end{tikzcd}$$

$$\begin{tikzcd} BrF_5 \arrow[r] \arrow[d] & NaBr \arrow[d] \\ 0 = 5 + (-1)5 \arrow[r, bend right, "6e^-\text{, reduction}"'] & -1 \end{tikzcd}$$

Balancing Reactions in Acid/Base

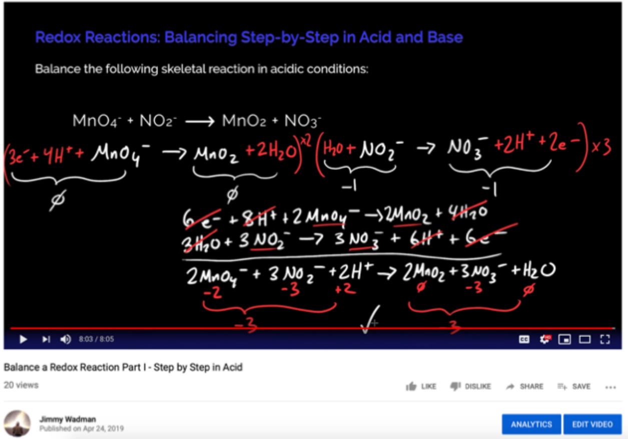
We will look in depth at balancing these three REDOX reactions. First, can you look at each reaction and determine:

a. What is being oxidized?
b. What is being reduced?
c. What is the oxidizing agent?
d. What is the reducing agent?

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

$$MnO_4^- + NO_2^- \rightarrow MnO_2 + NO_3^-$$

$$Pu + NpO_3^+ \rightarrow PuO_2 + NpO_2^{2+}$$



Redox Reactions: Balancing Step-by-Step in Acid and Base

Balance the following skeletal reaction in acidic conditions:

$$MnO_4^- + NO_2^- \longrightarrow MnO_2 + NO_3^-$$

$$\left(\underbrace{3e^- + 4H^+ + MnO_4^-}_{\emptyset} \rightarrow \underbrace{MnO_2}_{\emptyset} + 2H_2O\right)^{\times 2} \left(\underbrace{H_2O + NO_2^-}_{-1} \rightarrow \underbrace{NO_3^- + 2H^+ + 2e^-}_{-1}\right) \times 3$$

$$\cancel{6e^-} + \cancel{8}H^+ + 2MnO_4^- \rightarrow 2MnO_2 + \cancel{4H_2O}$$

$$\cancel{3H_2O} + 3NO_2^- \rightarrow 3NO_3^- + \cancel{6H^+} + \cancel{6e^-}$$

$$\underbrace{\underset{-2}{2MnO_4^-} + \underset{-3}{3NO_2^-} + \underset{+2}{2H^+}}_{-3} \rightarrow \underbrace{\underset{\emptyset}{2MnO_2} + \underset{-3}{3NO_3^-} + \underset{\emptyset}{H_2O}}_{3} \quad \checkmark$$

Balance a Redox Reaction Part I - Step by Step in Acid

20 views

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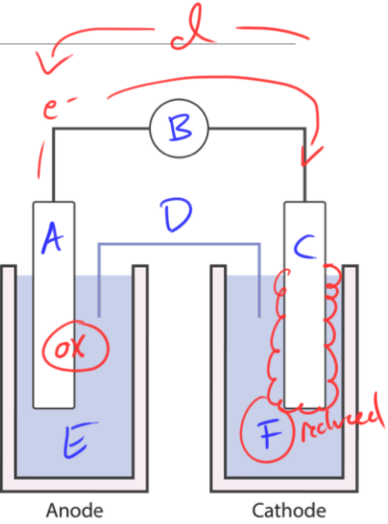
Published on Apr 24, 2019

Standard Cells

Electrochemical Cell Definitions

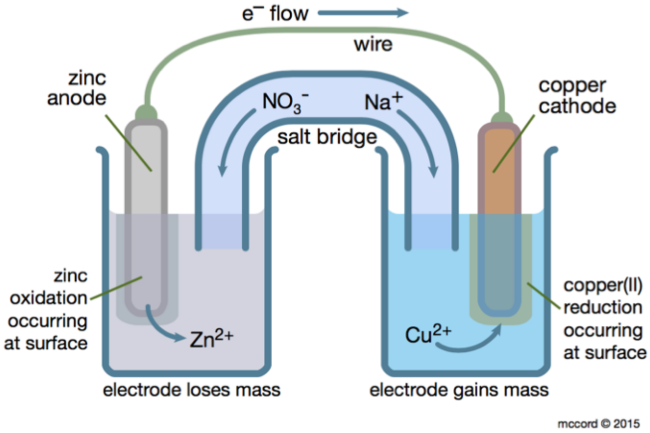
1. **Anode**: the site of oxidation (An Ox) ; gives electrons to the wire
2. **Cathode**: the site of reduction (Red Cat) ; takes in electrons from the wire
3. **Voltage**: the difference in potential per unit charge (J/C or V); a measurement of the "pulling power" on the electrons, where a positive potential means electrons are spontaneously flowing and a negative potential means the electrons must be pulled/pushed by an external power source
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)



The Electrochemical Cell Checklist

Make sure you can identify the following for a voltaic or electrolytic cell:

1. Cathode (including charge and half-reaction)
2. Anode (including charge and half-reaction)
3. Salt Bridge and flow of ions
4. Direction of electron flow and current flow
5. What is driving the push/pull of electrons
6. ε°, ΔG˚, and K
7. Voltmeter or power supply



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

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

Electrochemical Cells

	Voltaic Cell	Electrolytic Cell
Cathode (rxn and charge)	Cu^{2+}/Cu (+)	Al^{3+}/Al (−)
Anode (rxn and charge)	Al/Al^{3+} (−)	Cu/Cu^{2+} (+)
Direction of e^- flow	Anode → cathode	✓ A → C
Direction of current flow	C → A	✓ C → A
ε°	+2.00V	−2.00V
ΔG°	(−)	(+)
K	K > 1	K < 1
Flow of anions	Anode	✓ Anode
Flow of cations	Cathode	✓ Cathode

The Electrochemical Cell Summary

	Voltaic cells	**Electrolytic Cells**
free energy, ΔG	negative (–)	positive (+)
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.**

Conceptual Summary: Standard Cells

STD. Electrical Potential ε°	Free Energy ΔG°	Equilibrium Constant K	Spontaneous?	At equilibrium…
Positive	Negative	Greater than 1	Yes	$\Delta G = 0$ $\varepsilon = 0$
Negative	Positive	Less than 1	No	$\Delta G = 0$ $\varepsilon = 0$
Zero	Zero	Equal to 1	At Equilibrium	$\Delta G = 0 = \Delta G^\circ$ $\varepsilon = 0 = \varepsilon^\circ$

Concentration Cell

Electrochemical Applications and Nonstandard Cells

$e^- + AgCl \rightarrow Ag + Cl^-$

Tough Shorthand Notation

anode |anodic solution ||cathodic solution | cathode

$\overbrace{\mathrm{Al}|\ \mathrm{Al}^{3+}\ ||\underbrace{\mathrm{Cu}^{2+}\ |\ \mathrm{Cu}}_{n=2}}^{n=6}$

$\mathrm{Pt}\ |\ \mathrm{H}_2\ |\ \mathrm{H}^+\ ||\ \underbrace{\mathrm{Cu}^+\ |\ \mathrm{Cu}}_{n=1}$

$\mathrm{C\ (graphite)}|\ \mathrm{Cr}^{2+},\ \mathrm{Cr}^{3+}\ ||\ \underbrace{\mathrm{Al}^{3+}\ |\mathrm{Al}}_{n=3}$

$\mathrm{Ag}\ |\ \mathrm{Ag}^+\ ||\mathrm{Cl}^-\ \underbrace{\mathrm{(aq)}|\ \mathrm{AgCl\ (s)}\ |}_{n=1}\ \mathrm{Ag\ (s)}$

What is n if I am....

Plating Metal	Calculating ΔG˚
2	6
1	2
3	3
1	1

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

$$\frac{\text{charge applied}}{\text{charge per mol rxn}} = \frac{I \cdot t}{\underbrace{\boxed{n}}_{\frac{1}{2}\text{ rxn}} \cdot \underbrace{F}_{96485 \frac{C}{mol\ e^-}}} = \underline{\text{moles created}} = \text{moles rxn}$$

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**

$$\overbrace{2\underline{NaCl} \rightarrow 2Na(s) + Cl_2(g)}^{\text{Memorize!}}$$

red: $Na^+ + e^- \rightarrow Na$ $n=1$

ox: $2Cl^- \rightarrow Cl_2 + 2e^-$ $n=2$

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

$Ni^{2+}\cancel{Cl_2}$

Plating Ni from nickel(II) chloride

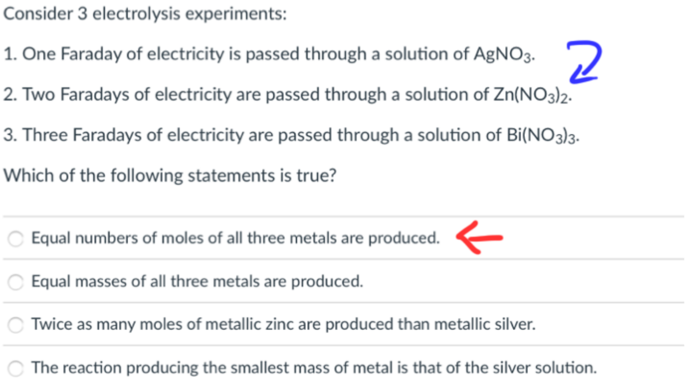
$Ni^{2+} \boxed{+2e^-} \rightarrow Ni$ $n=2$

Faraday's Law Exam Question

Suppose it takes 92 seconds to electroplate 42 mg of technetium (Tc, 98 g/mol) from a concentrated aqueous solution with an average current of 0.90 amps. What is the oxidation state of the technetium ions in solution?

Solution
@ end

Faraday’s Law Conceptual Question (Homework)



Consider 3 electrolysis experiments:

1. One Faraday of electricity is passed through a solution of $AgNO_3$. 2
2. Two Faradays of electricity are passed through a solution of $Zn(NO_3)_2$.
3. Three Faradays of electricity are passed through a solution of $Bi(NO_3)_3$.

Which of the following statements is true?

○ Equal numbers of moles of all three metals are produced. ←

○ Equal masses of all three metals are produced.

○ Twice as many moles of metallic zinc are produced than metallic silver.

○ The reaction producing the smallest mass of metal is that of the silver solution.

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

Optimize how much metal:

1) Charge applied (more current, more time)

2) Lower n-value

3) Molar mass MM ↑ mass plated ↑

Free Energy, Q, and K

Free Energy (non-expansion work)

$$\mathrm{KJ} \xleftarrow{\div 1000} \mathrm{J} \leftarrow \boxed{\Delta G^\circ} = -nF\boxed{\mathcal{E}^\circ} \rightarrow V = \frac{J}{C}$$

Non-standard cell potential

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

Equilibrium Constant; Dead Battery

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

n = balanced reaction!

* Make an electrolytic cell

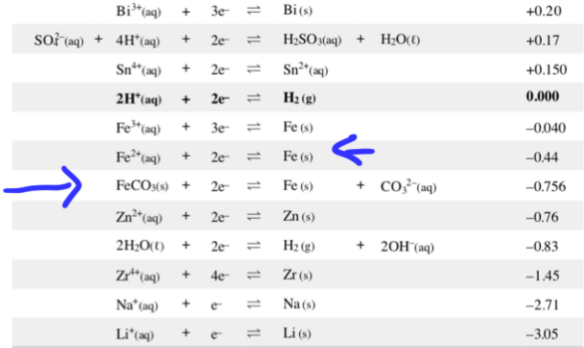
$K_{sp} <<< 1$, $\mathcal{E}^\circ(-)$

If rxn is the K_{sp} rxn

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 $FeCO_3$, for example.

$$\overset{-.316\,V}{\cancel{\mathcal{E}^\circ}} = \frac{0.05916}{\cancel{n} \to 2} \log K_{sp}$$



		$Bi^{3+}(aq)$	+	$3e^-$	⇌	$Bi(s)$			+0.20
$SO_4^{2-}(aq)$	+	$4H^+(aq)$	+	$2e^-$	⇌	$H_2SO_3(aq)$	+	$H_2O(\ell)$	+0.17
		$Sn^{4+}(aq)$	+	$2e^-$	⇌	$Sn^{2+}(aq)$			+0.150
		$2H^+(aq)$	**+**	**$2e^-$**	⇌	**$H_2(g)$**			**0.000**
		$Fe^{3+}(aq)$	+	$3e^-$	⇌	$Fe(s)$			−0.040
		$Fe^{2+}(aq)$	+	$2e^-$	⇌	$Fe(s)$ ←			−0.44
→		$FeCO_3(s)$	+	$2e^-$	⇌	$Fe(s)$	+	$CO_3^{2-}(aq)$	−0.756
		$Zn^{2+}(aq)$	+	$2e^-$	⇌	$Zn(s)$			−0.76
		$2H_2O(\ell)$	+	$2e^-$	⇌	$H_2(g)$	+	$2OH^-(aq)$	−0.83
		$Zr^{4+}(aq)$	+	$4e^-$	⇌	$Zr(s)$			−1.45
		$Na^+(aq)$	+	e^-	⇌	$Na(s)$			−2.71
		$Li^+(aq)$	+	e^-	⇌	$Li(s)$			−3.05

$$\overset{2+}{Fe}\overset{2-}{CO_3}(s) + \cancel{2e^-} \rightarrow \cancel{Fe(s)} + CO_3^{2-}(aq)$$

$$\cancel{Fe(s)} \rightarrow Fe^{2+} + \cancel{2e^-}$$

$$\rightarrow FeCO_3(s) \rightarrow Fe^{2+}(aq) + CO_3^{2-}$$

$$10^{-\frac{.316\times 2}{.05916}} = K_{sp} = 2.07\times10^{-11}$$

Non-Standard Cells Electrical Potential

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

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

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

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

$$Q = \frac{[Al^{3+}]^2}{[Cu^{2+}]^3}$$

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 or remove reactant (aq or g) , your voltage drops $Q\uparrow \mathcal{E}\downarrow$
- If you add reactant or remove product (aq or g), your voltage increases $Q\downarrow \mathcal{E}\uparrow$

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.

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

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

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

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

$\Delta G^{\circ} = 0$

$K = 1$

Question! What are two ways in which I can create a functional battery out of these two half-reactions?

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

Non-Standard Cell Potential Overview

Consider the following cell at standard conditions:

$Pt \mid H_2\,(g) \mid H^+\,(aq) \parallel Cl^- \mid AgCl(s) \mid Ag(s)$

$E^\circ = +\,0.27\ V$

$$H_2 \rightarrow 2H^+ + 2e^-$$

$$(e^- + AgCl \rightarrow Ag + Cl^-) \times 2$$

$$2AgCl(s) + H_2(g) \rightarrow 2H^+(aq) + 2Ag(s) + 2Cl^-$$

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

How does each of the following change the voltage:

I. Decrease the partial pressure of hydrogen $Q\uparrow\ \varepsilon\downarrow$

II. Add sodium chloride to the cathode compartment $Q\uparrow\ \varepsilon\downarrow$

III. Increase the pH $pH\uparrow\ [H^+]\downarrow\ Q\downarrow\ \varepsilon\uparrow$

Non-Standard Cell Potential pH

$\log(x)^2 = 2\log(x)$

$\log\left(\frac{1}{x^2}\right) = -2\log(x)$

Use the following electrochemical cell to answer the next two questions:

$2e^-$

Pt | H_2 (1 atm) | H^+ (? M) ||

Cl$^-$ (1 M) | Hg_2Cl_2 (s) | Hg (ℓ) | Pt

$2e^-$

If this cell has a voltage of 0.46 V at 298.15 K, what is the pH?

1. 0.721
2. 2.54
3. 1.69
4. 1.61
5. [✓ 3.21]
6. 1.18

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

E°= + 0.27 V

$$.46V = .27 - \frac{0.05916}{2}\log\frac{[H^+]^2\cancel{[Cl^-]}^2 \to 1}{\cancel{P_{H_2}} \to 1}$$

$$.46 = .27 - \frac{0.05916}{2}\log[H^+]^2$$

$$\frac{.46-.27}{.05916} = -\frac{\cancel{2}}{\cancel{2}}\log[H^+]^{\boxed{2}}$$

$$= -\log[H^+] = pH$$

Batteries – Primary Cells (one-way)

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

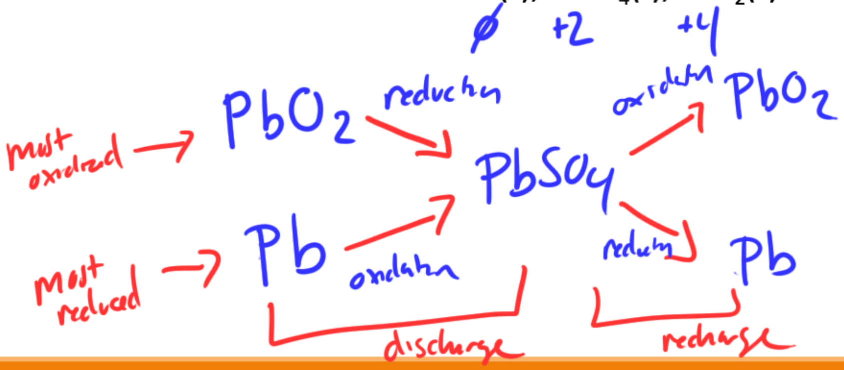
- The common primary cells in our lives are alkaline cells (D, C, AA, AAA, etc.)
- These all involve the same reaction, meaning they have the same standard potential.
- **They differ in size; therefore, they differ in current. A large surface area (D-batteries) will have a greater current (less internal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

Alkaline Cell: $Zn(s) + MnO_2(s) \rightleftharpoons Zn(OH)_2(s) + Mn_2O_3(s)$

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)



(McCord)

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.

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

→ Acid

$$(H_2 \rightarrow 2H^+ + 2e^-) \times 2$$

$$\underline{O_2 + 4H^+ + 4e^- \rightarrow 2H_2O}$$

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

→ Base

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

$$\underline{(H_2 + 2OH^- \rightarrow 2H_2O + 2e^-) \times 2}$$

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

Practice Questions

Tough Shorthand Notation

anode |anodic solution ||cathodic solution | cathode

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

$Pt | H_2 | H^+ || Cu^+ | Cu$

C (graphite)| $Cr^{2+}, Cr^{3+} || Al^{3+} | Al$

Ag | $Ag^+ || Cl^-$ (aq)| AgCl (s) | Ag (s)

What is n if I am….

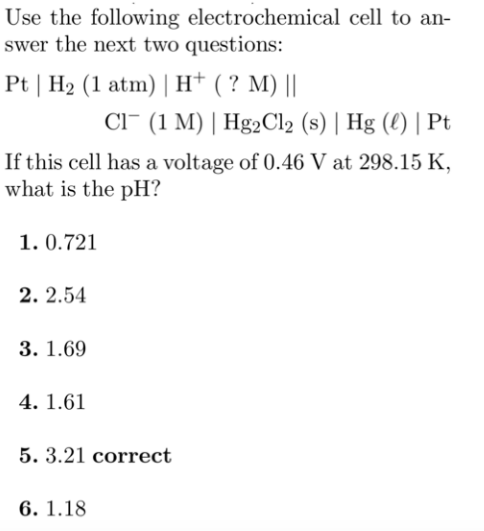
Plating Metal	Calculating Work

Faraday’s Law Exam Question

Suppose it takes 92 seconds to electroplate 42 mg of technetium (Tc, 98 g/mol) from a concentrated aqueous solution with an average current of 0.90 amps. What is the oxidation state of the technetium ions in solution?

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

Non-Standard Cell Potential pH



Use the following electrochemical cell to answer the next two questions:

$$\mathrm{Pt} \mid \mathrm{H_2}\ (1\ \mathrm{atm}) \mid \mathrm{H^+}\ (\ ?\ \mathrm{M}) \parallel \mathrm{Cl^-}\ (1\ \mathrm{M}) \mid \mathrm{Hg_2Cl_2}\ (s) \mid \mathrm{Hg}\ (\ell) \mid \mathrm{Pt}$$

If this cell has a voltage of 0.46 V at 298.15 K, what is the pH?

1. 0.721

2. 2.54

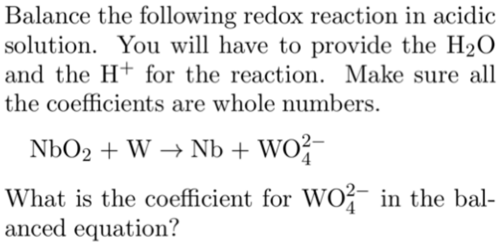
3. 1.69

4. 1.61

5. 3.21 **correct**

6. 1.18

Balanced Reaction in Acid

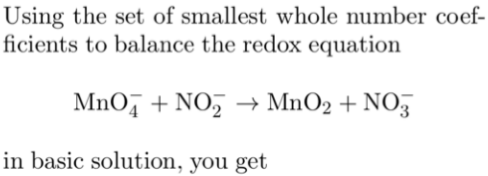


Balance the following redox reaction in acidic solution. You will have to provide the H_2O and the H^+ for the reaction. Make sure all the coefficients are whole numbers.

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

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

Balanced Reaction in Base

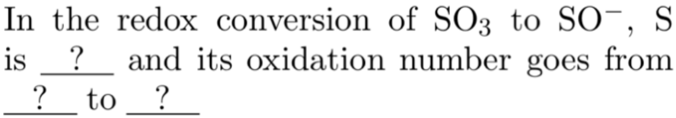


Using the set of smallest whole number coefficients to balance the redox equation

$$MnO_4^- + NO_2^- \rightarrow MnO_2 + NO_3^-$$

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+}?

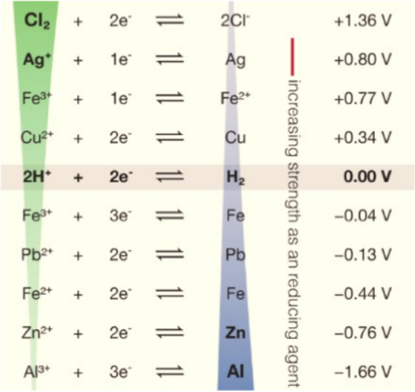
a. Fe^{2+}

b. H_2

c. Zn

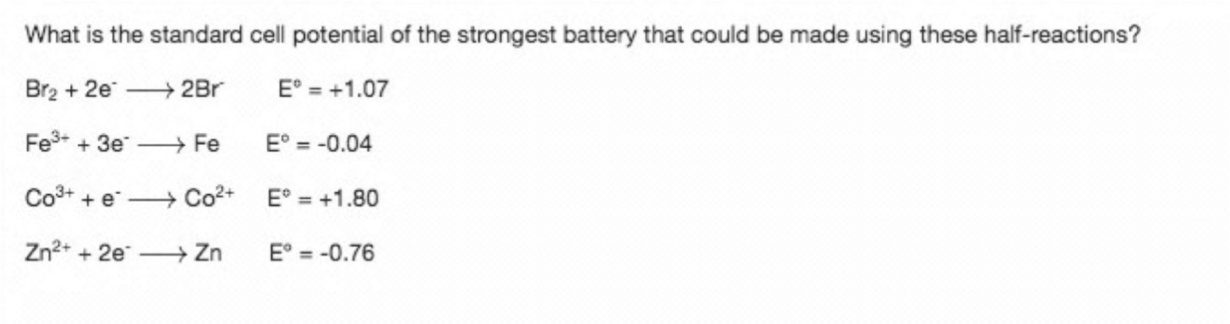
d. Fe^{3+}

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

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 ($E^\circ = 0.75$ 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?

Practice Calculations

1. Electroplating a metal using current (and stoichiometry)

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?

2. Predicting the non-expansion work of an electrochemical cell

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

$Pt|U^{3+},U^{4+}||Pd^{2+}|Pd$ $E^\circ = 1.525\ V$

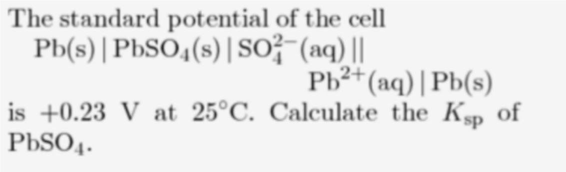
What is the value of non-expansion work for this cell at standard conditions?

3. Predicting the voltage of a non-standard cell

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

$Bi\ |\ Bi^{3+}(0.00200\ M)\ ||\ Cu^{+}(0.830\ M)\ |\ Cu$

Equilibrium Calculations



The standard potential of the cell

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

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:

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

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:

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

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?

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

Tough Shorthand Notation

anode |anodic solution ||cathodic solution | cathode

$3e^-$ $2e^-$
Al| Al^{3+} ||Cu^{2+} | Cu

$2e^-$ $1e^-$
Pt | H_2 | H^+ || Cu^+ | Cu

$1e^-$ $3e^-$
C (graphite)| Cr^{2+} , Cr^{3+} || Al^{3+} |Al

$1e^-$ $1e^-$
Ag | Ag^+ ||Cl^- (aq)| AgCl (s) | Ag (s)

What is n if I am….

Plating Metal	Calculating Work
2	6
1	2
3	3
1	1

Faraday’s Law Exam Question

Suppose it takes 92 seconds to electroplate 42 mg of technetium (Tc, 98 g/mol) from a concentrated aqueous solution with an average current of 0.90 amps. What is the oxidation state of the technetium ions in solution?

$Tc^{n+} + ne^- \rightarrow Tc$

$42\,mg \rightarrow .042\,g$

$\downarrow \div 98\ g/mol$

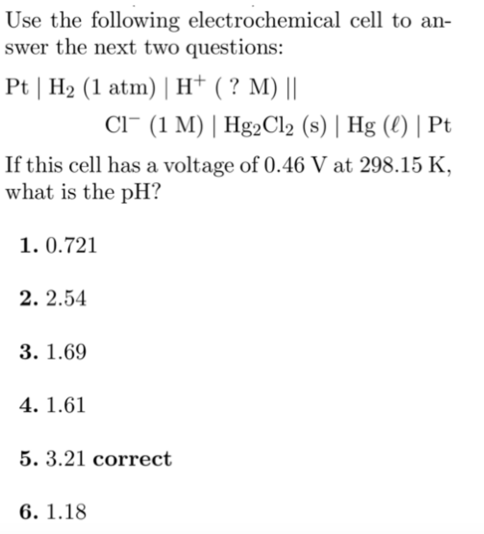
$$\frac{It}{nF} = \text{moles metal}$$

$$\frac{(.9)(92)}{n(96485)} = 4.28571 \times 10^{-4}\ mol$$

$n = 2$

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

Non-Standard Cell Potential pH



Use the following electrochemical cell to answer the next two questions:

$$\text{Pt} \mid \text{H}_2\ (1\ \text{atm}) \mid \text{H}^+\ (\ ?\ \text{M}) \parallel \text{Cl}^-\ (1\ \text{M}) \mid \text{Hg}_2\text{Cl}_2\ (\text{s}) \mid \text{Hg}\ (\ell) \mid \text{Pt}$$

If this cell has a voltage of 0.46 V at 298.15 K, what is the pH?

1. 0.721

2. 2.54

3. 1.69

4. 1.61

5. 3.21 **correct**

6. 1.18

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?

$$2H_2O + 3NbO_2 + 2W \rightarrow 3Nb + 2WO_4^{2-} + 4H^+$$

Balanced Reaction in Base

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

$$MnO_4^- + NO_2^- \rightarrow MnO_2 + NO_3^-$$

in basic solution, you get

$$\underbrace{H_2O + 2MnO_4^- + 3NO_2^-}_{-5} \rightarrow \underbrace{2MnO_2 + 3NO_2^- + 2OH^-}_{-5}$$

Exam Question: Change in Oxidation

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

reduced, 6 to 1

Question

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

reducing agent

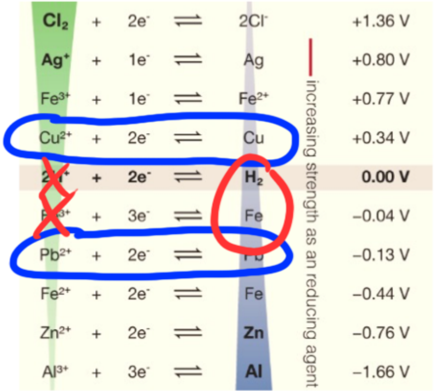
a. Fe^{2+}

[✓ b.] H_2

c. Zn

d. Fe^{3+}

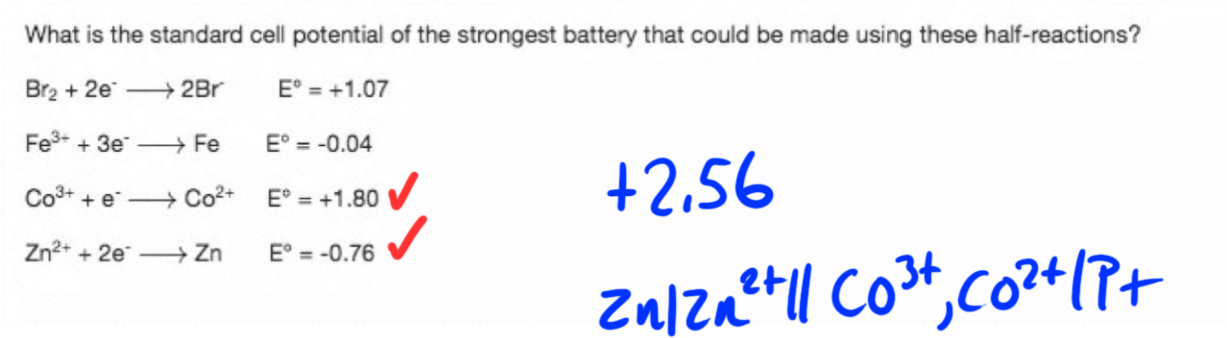
e. H^+



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

increasing strength as an reducing agent

Question



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

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

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

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

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

$+2.56$

$Zn|Zn^{2+}||Co^{3+},Co^{2+}|Pt$

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

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?

$$Cu|Cu^{2+}||\underbrace{Al^{3+}|\,Al}_{n=3}$$

$$\frac{It}{nF} = \frac{18\times(8\times60\times60)}{3\times96485}$$

$$\Big\downarrow \times 26.98\ g/mol$$

48g

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:

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

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad n=2$$

$$\frac{It}{nF} = \frac{7\times(6\times60\times60)}{2\times96485} = .7835\text{mol}$$

$$V=\frac{nRT}{P} = 17.56L$$

Electrochemical Work

Consider the following cell at standard conditions ($E^\circ = 0.75$ V) :

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

$$\underbrace{3e^- \qquad 2e^-}_{n=6}$$

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

$$-434182.5\text{ J} = -(6)(96485)(.75)$$

$$\hookrightarrow -434\text{ kJ}$$

Practice Calculations

1. Electroplating a metal using current (and stoichiometry)

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?

422g

2. Predicting the non-expansion work of an electrochemical cell

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

$Pt|U^{3+},U^{4+}||Pd^{2+}|Pd$ $E^{\circ} = 1.525$ V

What is the value of non-expansion work for this cell at standard conditions?

-294 kJ

3. Predicting the voltage of a non-standard cell

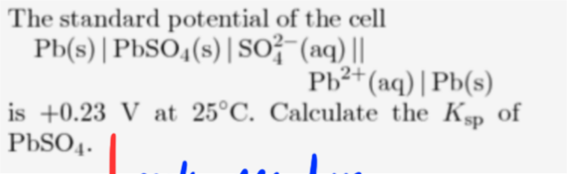
What is the non-standard cell potential for the following cell at 298.15 K and 1 atm?

.368V

$Bi \mid Bi^{3+} (0.00200\ M) \mid\mid Cu^{+} (0.830\ M) \mid Cu$

Use E° = 0.32 V. There is a discrepancy between the Bi half-reaction that we used last year and the new value on the table this year.

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 $PbSO_4$.

make negative

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

$$-.23 = \frac{.05916}{2}\log k_{sp}$$

$$K_{sp} = 1.7\times10^{-8}$$

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

II. Add sodium sulfate to the anode compartment $Q\downarrow\ \mathcal{E}\uparrow$

III. Decrease the pH

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

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

$$\underline{0.40}\ V = .36V - \frac{0.05916}{2}\log\frac{.08}{.6\times1.6^2}$$

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? .17 V, −32.8 kJ, 5.6×10^{5}

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?

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

$$0.12\ V = 0 - \frac{0.05916}{\cancel{2}} \log [H^+]^{\cancel{2}}$$

$$\frac{.12\ V}{.05916} = -\log [H^+] = pH = 2.03$$