CH 302 – Unit 5 Review 1

INTRODUCTION TO REDOX REACTIONS AND STANDARD CELLS

Unit 5 Outline: Electrochemistry

I. Understand fundamental redox reactions Tuesday
- 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) TH

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

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

V. Common applications of batteries
- Primary and secondary cells
- Fuel Cells

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**

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

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

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

LEO says GER

OIL RIG

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

$$4H^+ + MnO_4^- \rightarrow MnO_2 + 2H_2O$$

$+4OH^-$ $\qquad$ $+4OH^-$

$$\times 2\,(3e^- + 4H_2O + MnO_4^- \rightarrow MnO_2 + 2H_2O + 4OH^-)$$

$4-$ $\qquad$ $4-$

$$H_2O + NO_2^- \rightarrow NO_3^- + 2H^+$$

$+2OH^-$ $\qquad$ $+2OH^-$

$$3\times\,(2OH^- + H_2O + NO_2^- \rightarrow NO_3^- + 2H_2O + 2e^-)$$

$$H_2O + 2MnO_4^- + 3NO_2^- \rightarrow 2MnO_2 + 3NO_3^- + 2OH^-$$

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?

$$\left(4H^+ + NbO_2 + 4e^- \rightarrow Nb + 2H_2O\right) \times 3$$

$$\times 2\left(4H_2O + W \rightarrow WO_4^{2-} + 8H^+ + 6e^-\right)$$

$$\cancel{12H^+} + 3NbO_2 + \cancel{12e^-} \rightarrow 3Nb + \cancel{6H_2O}$$

$$8H_2O + 2W \rightarrow 2WO_4^{2-} + \cancel{16H^+} + \cancel{12e^-}$$

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

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

   ↳ NaH, AlH_4^-
5. Assign electronegative charges first

$$\emptyset = (+1)(2)(+6)(2)(-2)(7)$$

$K_2Cr_2O_7$

$$\emptyset = +3 + (-1)(3)$$

IF_3

Exam Question: Change in Oxidation

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

$$SO_3 \longrightarrow SO^-$$

$$0 = +6 + (-6)$$

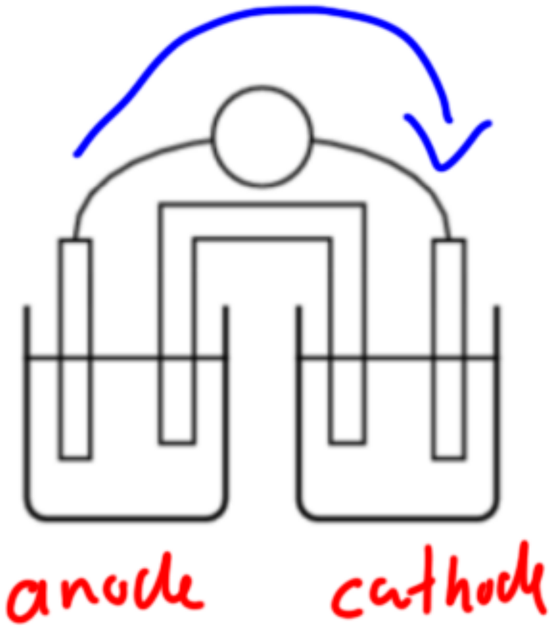
$$+1\ (-2) = -1$$

+6 to +1 via reduction

Inert electrode | R , P | spectator || spectator | R , P | Inert electrode

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)
6. Shorthand Notation:



anode|anodic solution ||cathodic solution | cathode

R | P || R | P

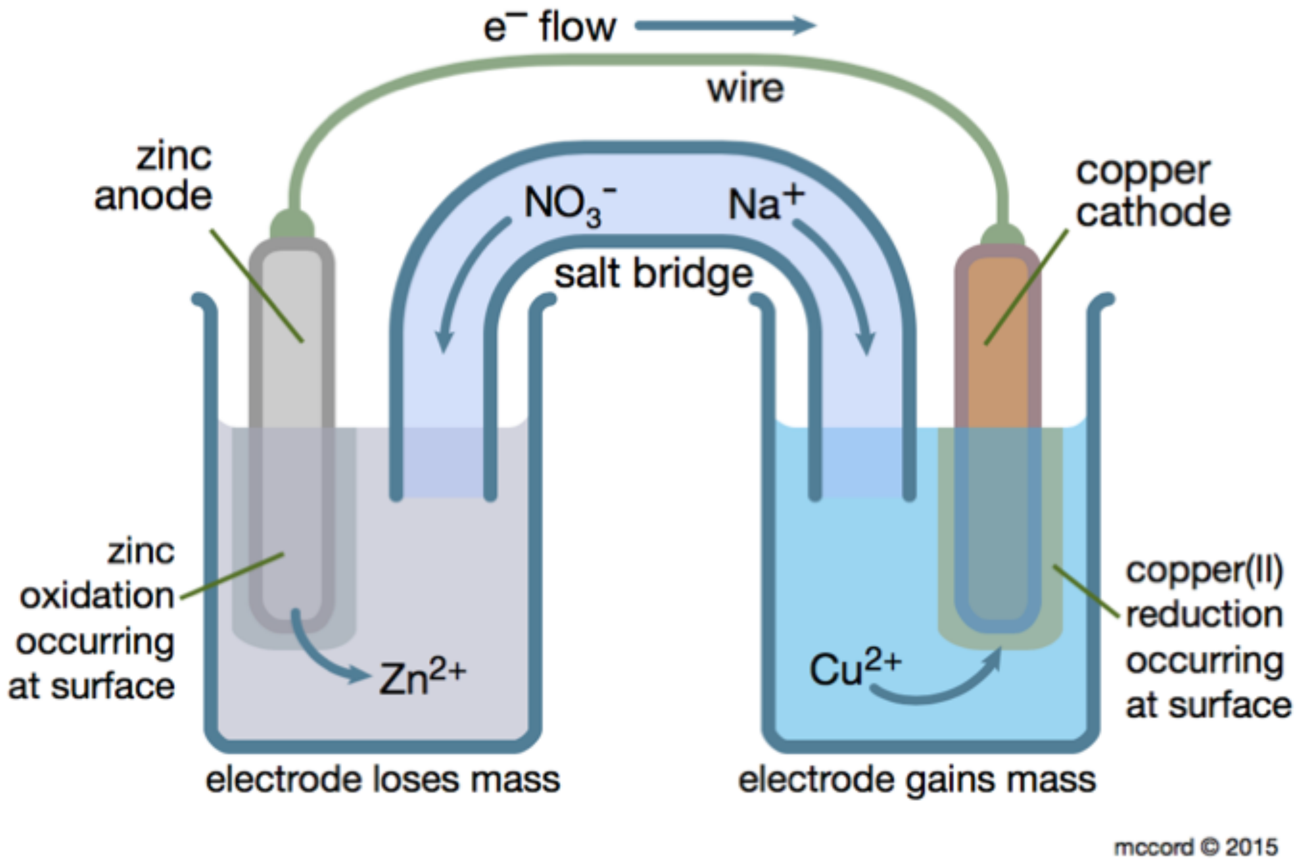
anode, oxidation

cathode, reduction

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
4. Conductive wire
5. Direction of electron flow
6. What is driving the push/pull of electrons
7. Flow of ions from a salt bridge
8. ε°, ΔG, and K, including spontaneity
9. Inert electrode (if applicable)
10. Voltmeter or power supply
11. What would be different between voltaic and electrolytic cells
12. Which electrode is gaining mass, which is losing mass (and why)



Electrochemical Potential

- **Electrical Cell Potential (ε°_{cell})**: the voltage associated with the redox reaction occurring in an electrochemical cell

$$\varepsilon^\circ_{cell} = \varepsilon^\circ_{cathode} - \varepsilon^\circ_{anode}$$

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

- This can also be written in the following way:

$$\varepsilon^\circ_{cell} = \varepsilon^\circ_{reduction} + \varepsilon^\circ_{oxidation}$$

**However, this equation uses the reduction potential plus the oxidation potential.

This means that you will not be able to directly use the data from a reduction potential chart.**

The Electrochemical Cell

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

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

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

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

voltaic

~~Galvanic~~ Voltage: **2.00V** = (0.34V) – (-1.66V) ; **Al | Al^{3+} || Cu^{2+} | Cu**

Electrolytic Voltage: **-2.00V** = (-1.66V) – (0.34V) ; **Cu | Cu^{2+} || Al^{3+} | Al**

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

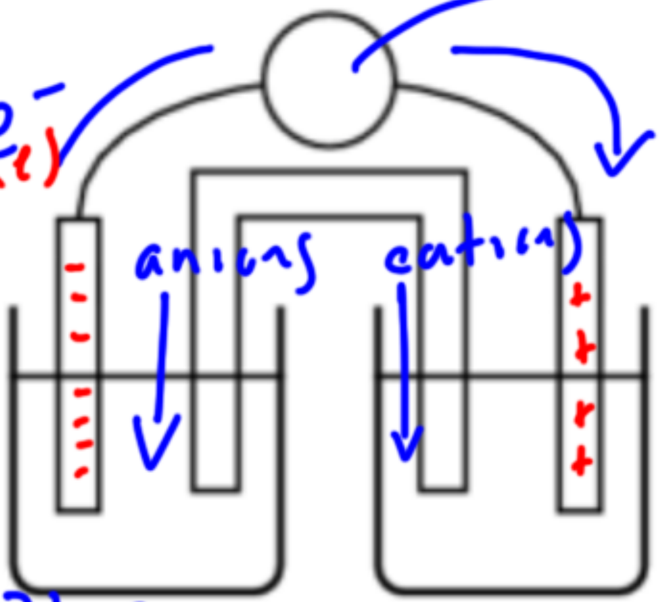
$$Al^{3+} + 3e^- \rightarrow Al\ (-1.66V)$$

The Voltaic Cell

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

$$\varepsilon^\circ_{cell} = \varepsilon^\circ_{cathode} - \varepsilon^\circ_{anode}$$

Galvanic Voltage: **2.00V** = (0.34V) – (-1.66V) ; **Al | Al³⁺ || Cu²⁺ | Cu**



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

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

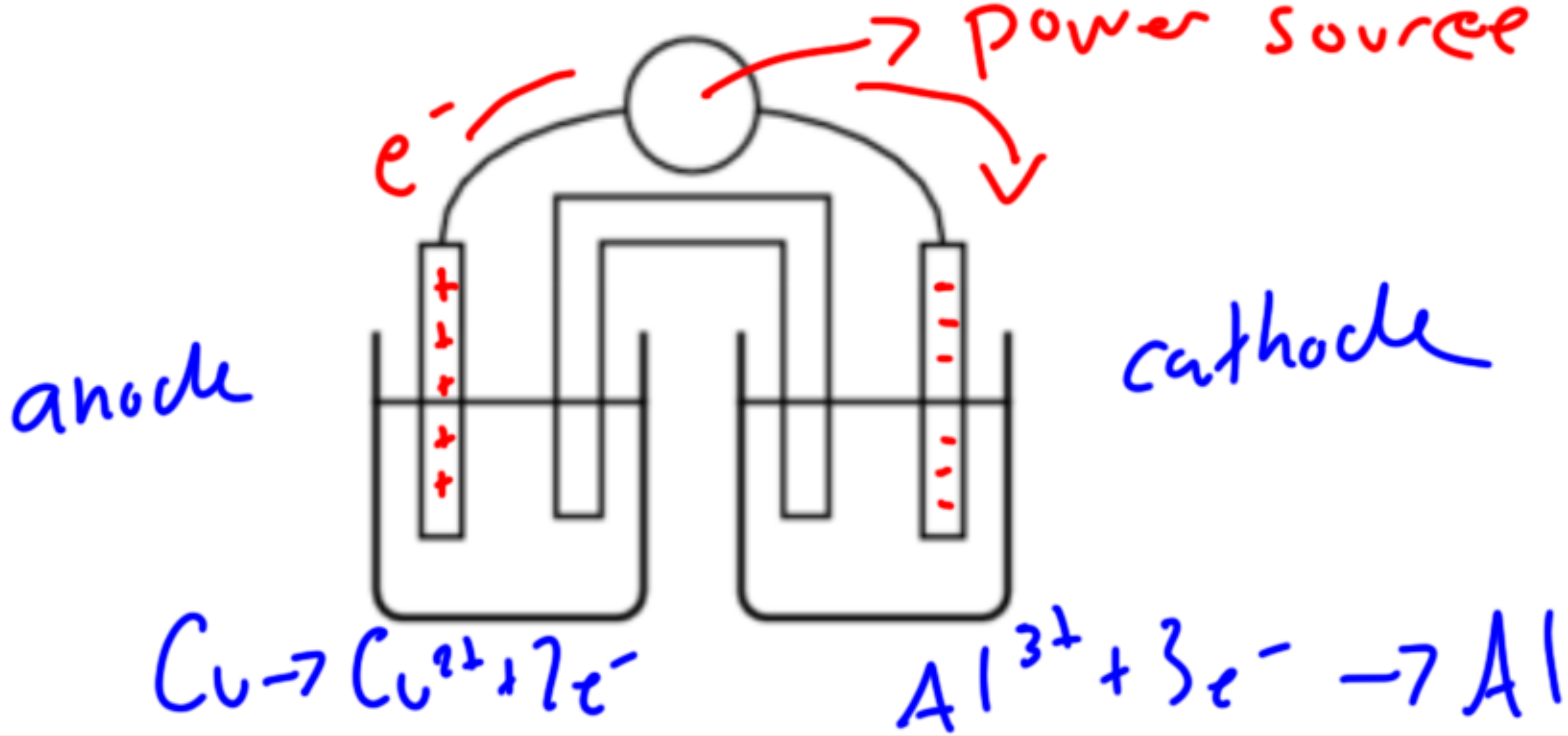
$$Al^{3+} + 3e^- \rightarrow Al\ (-1.66V)$$

The Electrolytic Cell

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

$$\varepsilon^\circ_{cell} = \varepsilon^\circ_{cathode} - \varepsilon^\circ_{anode}$$

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



reducing agent

(+)

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^+

reducing agent

Reductions

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

increasing strength as an reducing agent

ox agent)

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

increasing strength as an reducing agent

Question

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

red ox

$$2.56\,V = 1.80 + (-0.76)$$

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

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

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

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

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

red $Co^{3+} + e^- \rightarrow Co^{2+}$

ox $Zn \rightarrow Zn^{2+} + 2e^-$

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

Answer by showing the half-reactions and shorthand notation

Hint: look for the strongest reducing agent and the strongest oxidizing agent

Question

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

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

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

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

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

Answer:
$Zn \mid Zn^{2+} \| Co^{3+}, Co^{2+} \mid Pt$

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.**

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

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

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

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

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

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

5. Non-standard Cell Potential

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