5.111 Lecture Summary #25 **Friday, November 7, 2014**

Reading for Today: Sections 13.1-13.12 in 5th (4th ed: 12.1-12.12)
Reading For Lecture #26: 13.6-13.12 in 5th (4th ed: 12.6-12.12)

Topic: I. Introduction to Oxidation-Reduction (Redox) Reactions
II. Balancing Redox Reactions
III. Electrochemical Cells

I. INTRODUCTION TO OXIDATION-REDUCTION (REDOX) REACTIONS

Redox reactions are a major class of chemical reactions in which there is an exchange of electrons from one species to another.

For example, $2Mg (s) + O_2 (g) \rightarrow 2MgO$

Definitions

Oxidation:

Reduction:

Oxidizing agent:

Reducing agent:

Guidelines for Assigning Oxidation Numbers

1) In free elements, each atom has an oxidation number of zero. Example H_2

2) For ions composed of only one atom the oxidation number is equal to the charge on the ion. Thus Li^{+1} has an oxidation number of +1. Group 1 and group 2 metals have oxidation numbers of +1 and +2, respectively. Aluminum has an oxidation number of +3 in all its compounds.

3) The oxidation number of oxygen in most compounds is -2. However, in peroxides such as H_2O_2 and O_2^{-2}, oxygen has an oxidation state of -1.

4) The oxidation number of hydrogen is +1, except when it is bonded to metals in binary compounds, such as LiH, NaH, CaH_2. In these cases, its oxidation number is -1.

5) F has an oxidation number of -1 in all its compounds. Other halogens (Cl, Br, and I) have negative oxidation numbers when they occur as halide ions in compounds (Ex. NaCl). However, when combined with oxygen (oxoacids), they have positive oxidation numbers (Ex. ClO^-).

6) In a neutral molecule, the sum of the oxidation numbers of all the atoms must be zero. In a polyatomic ion, the sum of oxidation numbers of all the elements in the ion must be equal to the net charge of the ion.

Example NH_4^+

H is ________ N is ________ Sum is ___________

7) Oxidation numbers do not have to be integers. For example, the oxidation number of oxygen in superoxide O_2^{-1} is _________

Examples:

Li_2O PCl_5

HNO_3 N_2O

Disproportionation Reactions

A reactant element in one oxidation state is **both** oxidized and reduced.

$$NaClO \Rightarrow NaClO_3 + NaCl$$

Write the half reactions and determine the changes in oxidation state. Na^+ is a spectator ion so:

$$ClO^- \Rightarrow ClO_3^-$$

$$ClO^- \Rightarrow Cl^-$$

II. BALANCING REDOX REACTIONS

A. BALANCE IN **ACIDIC** SOLUTION

Fe^{2+} + $Cr_2O_7^{2-}$ ⇒ Cr^{3+} + Fe^{3+}

(1) Write two unbalanced half reactions for oxidized and reduced species.

$Cr_2O_7^{2-}$ ⇒ Cr^{3+}

Fe^{2+} ⇒ Fe^{3+}

(2) Insert coefficients to make the number of atoms of all elements except oxygen and hydrogen equal on the two sides of each equation.

$Cr_2O_7^{2-}$ ⇒ Cr^{3+}

Fe^{2+} ⇒ Fe^{3+}

(3) Add H_2O to balance oxygen

$Cr_2O_7^{2-}$ ⇒ $2Cr^{3+}$

Fe^{2+} ⇒ Fe^{3+}

(4) Balance hydrogen with H^+

$Cr_2O_7^{2-}$ ⇒ $2Cr^{3+}$ + $7H_2O$

Fe^{2+} ⇒ Fe^{3+}

(5) Balance the charge by inserting electrons

$14H^+$ + $Cr_2O_7^{2-}$ ⇒ $2Cr^{3+}$ + $7H_2O$

Fe^{2+} ⇒ Fe^{3+}

(6) Multiply the half reactions so that the number of electrons given off in the oxidation equals the number of electrons accepted in the reduction.

$$6e^- + 14H^+ + Cr_2O_7^{2-} \Rightarrow 2Cr^{3+} + 7H_2O$$

$$Fe^{2+} \Rightarrow Fe^{3+} + e^-$$

(7) Add half reaction, make appropriate cancellations.

$$\cancel{6e^-} + 14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \Rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+} + \cancel{6e^-}$$

B. BALANCE IN **BASIC** SOLUTION.

$$Fe^{2+} + Cr_2O_7^{2-} \Rightarrow Cr^{3+} + Fe^{3+}$$

Follow steps (1-7) to get your answer for acidic solution:

$$14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \Rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$$

(8) Then "adjust pH" by adding OH^- to both sides to neutralize H^+.

$$14OH^- + 14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \Rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+} + 14OH^-$$

OR

$$14H_2O + Cr_2O_7^{2-} + 6Fe^{2+} \Rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+} + 14OH^-$$

CANCEL

$$\overset{7}{\cancel{14H_2O}} + Cr_2O_7^{2-} + 6Fe^{2+} \Rightarrow 2Cr^{3+} + \cancel{7H_2O} + 6Fe^{3+} + 14OH^-$$

Thus: $7H_2O + Cr_2O_7^{2-} + 6Fe^{2+} \Rightarrow 2Cr^{3+} + 6Fe^{3+} + 14OH^-$

<u>Summary</u>

Acidic: $14H^{+} + Cr_2O_7^{2-} + 6Fe^{2+} \Rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

Basic: $7H_2O + Cr_2O_7^{2-} + 6Fe^{2+} \Rightarrow 2Cr^{3+} + 6Fe^{3+} + 14OH^{-}$

Oxidation-reduction (redox) reactions are essential for photosynthesis, fuel cells, and life!
Electrochemistry is the study of redox reactions at an electrode, including:

- Obtaining electricity directly from a spontaneous (ΔG____0) reaction.
- Using an electric current to drive a non-spontaneous (ΔG____0) reaction.

III. ELECTROCHEMICAL CELLS: are devices in which an electric current (a flow of electrons through a circuit) is either

- produced by a spontaneous chemical reaction (____________________cell); or
- used to bring about a non-spontaneous reaction (____________________cell).

Battery: a collection of galvanic cells joined in a series, so the voltage they produce is the sum of the voltages of each cell.

Electrodes: Conductors through which electrons can travel. Anodes and cathodes are two types of electrodes.

Anode: Electrons produced from ____________________ flow out of compartment through a wire.

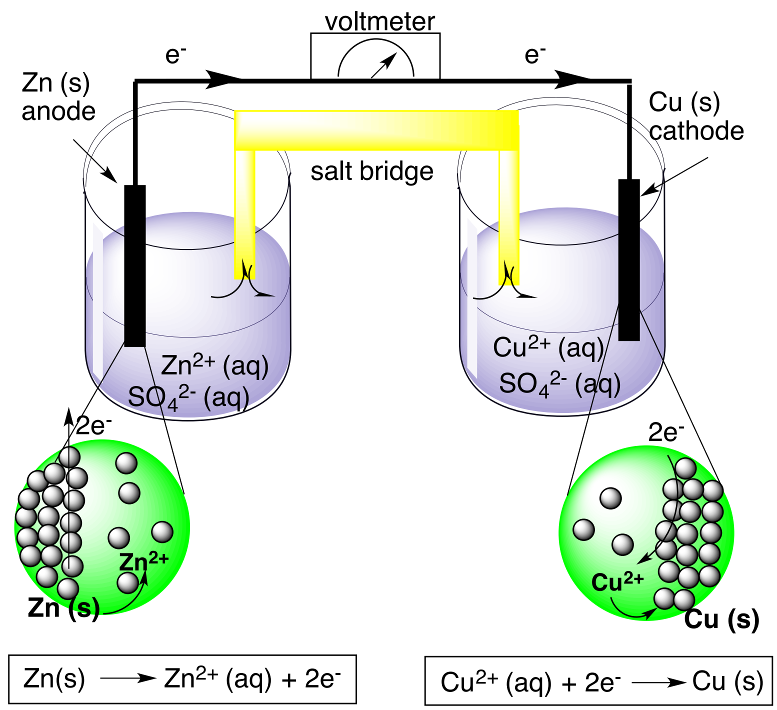
Zn (s) is ________________________ to Zn^{2+} (aq) at the anode

Cathode: Electrons entering the compartment are consumed in a ____________________ reaction.

Cu^{2+} (aq) is ________________________ to Cu(s) at the cathode.

The **voltmeter** measures the flow of electrons (the electric current).

Neutrality is maintained by the flow of ions through the **salt bridge**.



Overall, the electrochemical cell may be represented by:

Where phase boundaries are represented by "| ", and the salt bridge is represented by "| | "

Another cell has utilizes the following redox reactions:

$Zn (s) \rightarrow Zn^{2+} (aq) + 2e^-$ and $Sn^{4+} (aq) + 2e^- \rightarrow Sn^{2+} (aq)$

The reaction at the anode is:

The reaction at the cathode is:

The electrochemical cell may be represented by:

Faradays' Law

In the electrochemical cell on page 1, Zn is consumed and Cu is deposited. Faraday's Law states that Zn is consumed and Cu is deposited in a quantity ________________________ to the charge passed.

Example: How much Zn is consumed and how much Cu is deposited if a current of 1.0 A flows for 1.0 hours?

Step1. Determine the amount of charge that passed though the circuit.

Q	=	I	•	t
magnitude of charge in Coulombs (C)		current in amperes (A) (amperes = coulombs/ second)		time in seconds

Q = 1.0 A • 3600 sec = 3600 C

Step 2. Determine the number of moles of electrons to which this charge is equivalent.

Use Faraday's constant 96,485 C/ mol = 1 Faraday ($\mathfrak{I}$)

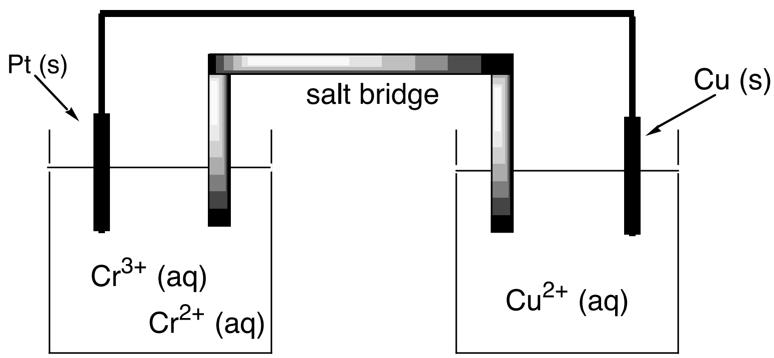
$$3600 \text{ C} \times \frac{1 \text{ mol}}{96{,}485 \text{ C}} = 0.0373 \text{ moles of electrons}$$

Step 3. Calculate the number of moles of Zn consumed and Cu deposited and convert to grams.

$$0.0373 \text{ moles of } e^- \text{ passed} \times \frac{1 \text{ mol Zn consumed}}{?? \text{ moles of } e^- \text{ passed}} \times \frac{65.39 \text{ g}}{\text{mol}} = 1.2 \text{ g}$$

$$0.0373 \text{ moles of } e^- \text{ passed} \times \frac{1 \text{ mol Cu deposited}}{?? \text{ moles of } e^- \text{ passed}} \times \frac{63.55 \text{ g}}{\text{mol}} = 1.2 \text{ g}$$

Electrodes (anodes, cathodes) are not always consumed or deposited upon during electrochemical experiments. <u>A Pt electrode</u>, which is ______________, can be used.



Anode (oxidation)
Cr^{2+} (aq) $\Rightarrow$ Cr^{3+} (aq) + e^-

Cathode (reduction)
Cu^{2+} (aq) + $2e^-$ $\Rightarrow$ Cu (s)

Notation for this type of cell is:

Pt (s) | Cr^{2+} (aq) , Cr^{3+} (aq) | | Cu^{2+} (aq) | Cu (s)

<u>A Hydrogen Electrode</u> constructed with Pt is commonly used. Many reduction potentials are measured against a **Standard Hydrogen Electrode** (S.H.E). The hydrogen electrode is denoted:

H^+ (aq) | H_2 (g) | Pt (s) when it acts as a cathode (H^+ is reduced) and

Pt (s) | H_2 (g) | H^+ (aq) when it acts as an anode (______________________).

Example of cell using hydrogen electrode.