Name ___________________________**Chem 163 Section**: ______ **Team Number:** ______

ALE 24. Voltaic Cells and Standard Cell Potentials

(Reference: 21.2 and 21.3 Silberberg *5th edition*)

What does a voltmeter reading tell us?

The Model: Standard Reduction and Oxidation Potentials

In general, the reduction of a metal cation in aqueous solution to the elemental state of the metal can be written as eqn **1**.

$$M^{m+}(aq) + m\ e^- \rightarrow M(s) \qquad \textbf{(1)}$$

The reduction half-reaction has a **standard reduction potential**, E^o_{red}. (The superscript naught indicates that the concentration of metal cations in solution is 1 *M*.) The potential has units of **volts** (V). The greater the desire of a metal to become reduced, the more positive the metal's reduction potential is. As with most reactions, reduction reactions are reversible. The reverse of eqn **1** is written as eqn **2**.

$$M(s) \rightarrow M^{m+}(aq) + m\ e^- \qquad \textbf{(2)}$$

Being an oxidation half-reaction, eqn **2** has a **standard oxidation potential**, E^o_{ox}.

E^o_{ox} of eq 2 has the same magnitude but the opposite sign as E^o_{red} of eqn 1.

While it is convenient to think of a metal either undergoing reduction or oxidation, certainly other species can be reduced or oxidized. Hydrogen has been chosen to serve as a reference for all other species. *By definition*, the standard reduction potential of hydrogen is 0 V.

$$2\ H^+(aq) + 2\ e^- \rightarrow H_2(g) \qquad E^o_{red} = 0\ V$$

Key Questions

1. Use the table of standard reduction potentials in your textbook to rank the following 3*d* block transition metal cations in order from having the lowest potential to be reduced to having the highest potential to be reduced *to the elemental state*.

Cr^{3+} Mn^{2+} Fe^{2+} Co^{2+} Ni^{2+} Cu^{2+} Zn^{2+}

lowest potential to be reduced _____ < _____ < _____ < _____ < _____ < _____ < _____ highest potential to be reduced

2a. If a piece of zinc metal is placed in an aqueous solution of nickel(II), will the reaction shown as eqn **3** occur?

$$Ni^{2+}(aq) + Zn(s) \rightarrow Ni(s) + Zn^{2+}(aq) \qquad \textbf{(3)}$$

Explain your answer.

2b. If a piece of copper metal is placed in an aqueous solution of cobalt(II), will the reaction shown as eqn **4** occur? *Explain your answer.*

$$Co^{2+}(aq) + Cu(s) \rightarrow Co(s) + Cu^{2+}(aq) \qquad (\mathbf{4})$$

3. Metallic nickel dissolves in 1 *M* hydrochloric acid spontaneously according to eqn **5**.

$$Ni(s) + 2\,HCl(aq) \rightarrow NiCl_2(aq) + H_2(g) \qquad (\mathbf{5})$$

But metallic copper does not.

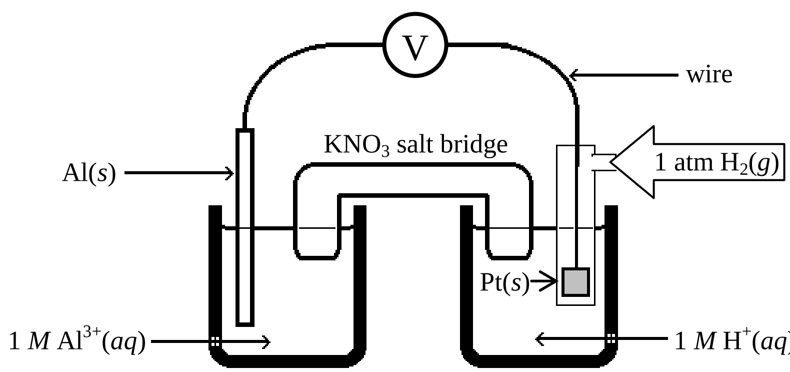
$$Cu(s) + 2\,HCl(aq) \not\rightarrow CuCl_2(aq) + H_2(g)$$

Use the table of standard reduction potentials in your textbook to explain these facts.

The Model: Voltaic Cells and Standard Cell Potentials

Because electrons can neither be created nor destroyed, a reduction cannot occur without an accompanying oxidation. If two substances which have different reduction potentials are connected to each other (via an electrically-conducting wire), then electrons can flow from the material which is undergoing oxidation to the second material. When this second material accepts the electrons, reduction will occur.

Consider the **voltaic cell** that is constructed by connecting the standard hydrogen electrode ("SHE") to a second **half-cell** consisting of an aluminum electrode submerged in a 1 *M* $Al^{3+}(aq)$ solution. A schematic of the Al-H^+ cell is shown to the right.



The two solutions are connected by a **salt bridge** (*e.g.*, an agar suspension of potassium nitrate, in which the ions are free to flow). The two electrodes are connected by a wire. Between the two electrodes may be placed a voltmeter. If the two electrodes are operating at their standard states, then the voltmeter would read "1.66 V".

Key Questions

4a. Which species, <u>aluminum</u> or <u>hydrogen</u>, has the greater potential to be reduced? (Circle your answer.)

4b. Which of the following reactions occur in the two half-cells of the Al-H^+ cell? (Circle your answer.)

	half-cell on left		half-cell on right
i.	$Al^{3+}(aq) + 3\,e^- \rightarrow Al(s)$	&	$2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)$
ii.	$Al^{3+}(aq) + 3\,e^- \rightarrow Al(s)$	&	$H_2(g) \rightarrow 2\,H^+(aq) + 2\,e^-$
iii.	$Al(s) \rightarrow Al^{3+}(aq) + 3\,e^-$	&	$2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)$
iv.	$Al(s) \rightarrow Al^{3+}(aq) + 3\,e^-$	&	$H_2(g) \rightarrow 2\,H^+(aq) + 2\,e^-$

5a. When the oxidation half-reaction and the reduction half-reaction occur simultaneously, by what number must you multiply the oxidation reaction? ________ By what number must you multiply the reduction reaction so that the number of electrons is conserved?___________

b. Write the overall balanced cell reaction that occurs in the Al-H^+ cell.

6a. What is the standard oxidation potential (in V) of the species that is oxidized in the Al-H^+ cell?

b. What is the standard reduction potential (in V) of the species that is reduced?

c. What is the sum of the standard oxidation potential of the oxidized species [the answer to part (a)] and the standard reduction potential of the reduced species [the answer to part (b)]? (Refer back to the Model to see what the voltmeter reads when connected to the Al-H^+ cell.)

d. True OR False: When determining the standard cell potential, before you add the standard oxidation and reduction potentials together, you need to multiply E^{o}_{ox} by the same number that you multiplied the oxidation half-reaction and you need to multiply E^{o}_{red} by the same number that you multiplied the reduction half-reaction. (Circle your answer.)

7. The solution that the aluminum electrode is submerged in is labeled "Al^{3+}(*aq*)", but there *must* be some anion (*e.g.*, nitrate) in solution so that it is electrically neutral. The same is true of the solution that is labeled "H^+(*aq*)". When oxidation occurs at the surface of the aluminum electrode, Al^{3+} goes into solution. When reduction occurs at the surface of the platinum electrode, H^+ leaves the solution (as hydrogen gas).

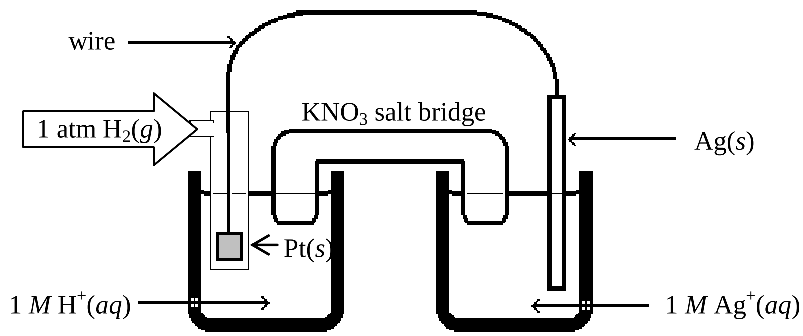
a. The potassium cations flow from the salt bridge into what half-cell? The nitrate anions flow from the salt bridge into what half-cell?

K^+ flows to: ______________________ NO_3^- flows to: _________________________

b. The electrode to which ***cat***ions flow is called the ***cat***hode. Something that can help you to remember that the ***r***eduction half-reaction occurs at the ***c***athode is that both words begin with a consonant. By analogy, why is the second electrode called the ***an***ode? What do the words "anode" and "oxidation" have in common that might help you remember which type of half-reaction occurs at the anode?

7c. Do electrons flow from the anode to the cathode or from the cathode to the anode through the wire? (Circle your answer.)

8. A schematic drawing of the H_2-Ag^+ cell is shown to the right.



a. Having to draw a schematic like the above every time you want to inform a reader of what cell you're considering is tedious. Instead, we can use a "shorthand" notation called a **cell diagram**. The cell diagram starts off with the anode written on the left. As you continue to write the cell diagram, you write additional species in the order in which they'd be encountered in the solutions in going from the anode to the cathode. The symbol "|" is used to indicate moving from one phase to another and the symbol "||" is used to indicate the salt bridge. The cell diagram *for the Al-H_2 cell* (See the Model.) in the standard state is:

$$Al(s) \mid Al^{3+}(aq, 1\ M) \parallel H^+(aq, 1\ M) \mid H_2(g) \mid Pt(s)$$

Write the cell diagram for the H_2-Ag^+ cell.

b. Write the half-reactions that occur at the anode and at the cathode, and write the balanced cell reaction (WITH NO "LEFT OVER ELECTRONS"!) that occurs in the H_2-Ag^+ cell.

Half-reaction at the anode: ______________________________

Half-reaction at the cathode: ______________________________

Balanced cell reaction: ______________________________

c. What are the values of E^o_{ox} of the species that is oxidized, E^o_{red} of the species that is reduced, and E^o_{cell} of the H_2-Ag^+ cell?

E^o_{ox} = E^o_{red} = E^o_{cell} =

9. The cell diagram of the Al-Ag^+ cell in its standard state is:

$$Al(s) \mid Al^{3+}(aq, 1\ M) \parallel Ag^+(aq, 1\ M) \mid Ag(s)$$

a. Write the balanced net cell reaction that occurs in the Al-Ag^+ cell.

b. What is the value of E^o_{cell} of the Al-Ag^+ cell?

E^o_{cell} =

10. Indicate below if the statement is true or false. *If false, correct the statement to make it true.*

a.) T or F In a voltaic cell, the anode is negative relative to the cathode.

b.) T or F Oxidation occurs at the anode in both voltaic cells and electrolytic cells.

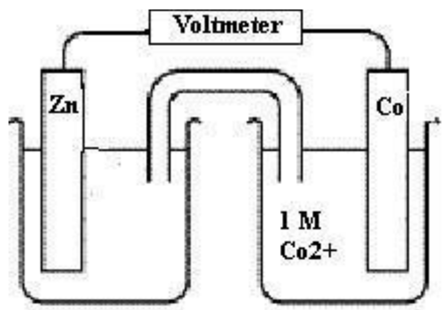
c.) T or F Electrons flow into the cathode of an electrolytic cell.

d.) T or F In a voltaic cell, the surroundings do the work on the system.

e.) T or F If a metal is plated out of an electrolytic cell, it appears on the cathode.

f.) T or F The cell electrolyte provides a solution of mobile electrons.

11. Consider the voltaic cell below.



a.) In which direction do electrons flow in the external circuit?

b.) In which half-cell does reduction occur?

c.) In which half-cell do the electrons leave the cell?

d.) At which electrode are the electrons generated?

e.) Which electrode is positively charged?

f.) Which electrode increases in mass?

g.) Suggest a solution for the anode electrolyte

h.) Suggest a pair of ions for the salt bridge.

i.) For which electrode could you use an inactive metal?

j.) In which direction do cations within the salt bridge move to maintain charge neutrality?

12. Write the balanced half-reactions and the overall spontaneous reaction for the voltaic cell in the previous question.

13. In acidic solution, ozone and the manganese (II) ion react spontaneously:

$$\mathbf{O_3(g) + Mn^{2+}(aq) + H_2O(l) \rightarrow O_2(g) + MnO_2(s) + 2H^+(aq) \qquad E^o_{cell} = 0.84\ V}$$

a.) Write the balanced reduction half-reaction. ***Hint***: use oxidation numbers to determine what is oxidized and what is reduced and then use Appendix D in your text to find the balanced oxidation and reduction half-reactions.

b.) Write the balanced oxidation half-reaction. (See the hint in part a!)

c.) Using Appendix D in your textbook to find E^o_{ozone}, and then calculate $E^o_{manganese}$.

14. When a clean iron nail is placed in an aqueous solution of copper (II) sulfate, the nail immediately begins to turn a brown-black color. In a few minutes, the nail is completely covered with a material of this color.

a.) What is the material coating the nail? ***Explain***.

b.) What is the oxidizing agent? ____________________

What is the reducing agent? ____________________

c.) Can this reaction be made into a voltaic cell? ***Explain***.

d.) Write the balanced equation for the reaction.

e.) Calculate E^o_{cell} for the process.