Building Simple Electrochemical Cells

An electrochemical cell is made by combining an oxidation reaction with a separate reduction reaction to produce a flow of electrons(electricity). The two reactions are placed in separate cells to prevent direct contact. A salt bridge is used to allow for a movement of ions between the cells, that will complete the circuit. Half-cell potentials are additive to give the potential voltage difference expected for a given voltaic cell. In this experiment, simple metal-metal ion half cells $[M(s) / M^{2+}(aq)]$ will be used to establish voltaic cells, the potentials of which will be measured. For example, the reactions for a zinc/copper battery are below: $Zn \rightarrow Zn^{2+} + 2e$.

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

The sum of these two half-reactions is

$$Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu$$
 where $E^{o}_{cell} = E^{o}_{ox} + E^{o}_{rea}$

Materials:

20 drops 1M Zn(NO ₃) ₂	20 drops 1M Cu(NO ₃) ₂	20 drops Mg(NO ₃) ₂	20 drops 1M Fe(NO ₃) ₃
20 drops 1M KNO ₃	20 drops 1M Pb(NO ₃) ₂	20 drops 1M AgNO ₃	Multimeter or voltmeter
Small pieces of metals: Zn, Cu, Mg, Fe, Pb, Ag		Sandpaper, Filter paper, wire leads	

Procedure:

1. Use sandpaper or steel wool to clean small pieces of the various metals used in this lab.



Cut out the triangular wedges on a piece of filter paper to form five separate reaction areas. Label each spot with the symbol of one of the elements used in this lab. Place the filter paper on a glass plate. Wet each spot with 3 drops of the 1 M solutions of the respective metallic ions. Place a clean, shiny piece of metal on top of its own solution on the filter paper. The top of the metal pieces should remain dry. Add enough drops of 1M KNO3 to the center of the

paper to form a "salt bridge" between each met al half-cell. By placing the wire leads of a voltmeter in contact with any two met als, the voltage produced by the voltaic cell can be measured.

- 2. Touch one of the wires from a DC voltmeter to the copper metal and the other wire to the zinc metal. If the voltage is negative, switch the wire connections. Record the positive voltage, which is the <u>Ecell</u> at the experimental conditions, and note which metal is connected to the negative terminal(black wire) and which is connected to the positive terminal(red wire) of the voltmeter.
- Try ALL possible combinations of two half-cells and record the <u>Ecell</u> voltages in a data table.

Conclusions:

- When the negative terminal wire is connected to the anode (where oxidation occurs) and the positive terminal wire is connected to the cathode (where reduction occurs), a positive cell voltage is observed. Make a table of the net ionic reactions and their cell voltages, and note which half-cell is the oxidation reaction. Record their observed positive voltages.
- 2. Look up the reduction potentials for each half-reaction in your book, and calculate the theoretical voltages, E°_{cell} , for each electrochemical cell. Compare how your results fit the theoretical values. Explain what could cause differences between the theoretical and experimental voltage values.

Watch the video at <u>https://youtu.be/o1UGBtSVKZY</u> to see how each combination of half-cells were tested with a voltmeter in order to identify the oxidation and reduction half-reactions and E^o_{cell} voltage.

	Data Table					
Cells						
	Black = -	Measured				
Trial	Red = +	E ^g cell, V				
1	Zn/Cu	1.086				
2	Zn/Mg	0.487				
3	Zn/Pb	0.588				
4	Zn/Ag	1.501				
5	Zn/Fe	0.638				
6	Cu/Mg	1.577				
7	Cu/Pb	0.490				
8	Cu/Ag	0.412				
9	Cu/Fe	0.436				
10	Mg/Pb	1.063				
11	Mg/Ag	2.026				
12	Mg/Fe	1.138				
13	Pb/Ag	0.910				
14	Pb/Fe	-0.003				
15	Fe/Pb	0.018				
16	Fe/Ag	0.928				

A P P E N D I X

Standard Reduction Potentials at 25 °C

Half-Reaction	$E^{\circ}(\mathbf{V})$	Half-Reaction
$\operatorname{Ag}^+(aq) + e^- \longrightarrow \operatorname{Ag}(s)$	+0.799	$2 \operatorname{H}_2\operatorname{O}(l) + 2 \operatorname{e}^- \longrightarrow \operatorname{H}_2(g) + 2 \operatorname{OH}^-(aq)$
$\operatorname{AgBr}(s) + e^{-} \longrightarrow \operatorname{Ag}(s) + \operatorname{Br}^{-}(aq)$	+0.095	$HO_2^{-}(aq) + H_2O(l) + 2 e^{-} \longrightarrow 3 OH^{-}(aq)$
$\operatorname{AgCl}(s) + e^{-} \longrightarrow \operatorname{Ag}(s) + \operatorname{Cl}^{-}(aq)$	+0.222	$H_2O_2(aq) + 2 H^+(aq) + 2 e^- \longrightarrow 2 H_2O(l)$
$Ag(CN)_2^{-}(aq) + e^{-} \longrightarrow Ag(s) + 2 CN^{-}(aq)$	-0.31	$\mathrm{Hg_2}^{2+}(aq) + 2 e^- \longrightarrow 2 \mathrm{Hg}(l)$
$Ag_2CrO_4(s) + 2e^- \longrightarrow 2Ag(s) + CrO_4^{2-}(aq)$	+0.446	$2 \operatorname{Hg}^{2+}(aq) + 2 e^{-} \longrightarrow \operatorname{Hg}_{2}^{2+}(aq)$
$\operatorname{AgI}(s) + e^{-} \longrightarrow \operatorname{Ag}(s) + I^{-}(aq)$	-0.151	$Hg^{2+}(aq) + 2e^{-} \longrightarrow Hg(l)$
$\operatorname{Ag}(\operatorname{S}_2\operatorname{O}_3)_2^{3-}(aq) + e^- \longrightarrow \operatorname{Ag}(s) + 2\operatorname{S}_2\operatorname{O}_3^{2-}(aq)$	+0.01	$I_2(s) + 2 e^- \longrightarrow 2 I^-(aq)$
$Al^{3+}(aq) + 3 e^{-} \longrightarrow Al(s)$	-1.66	$2 \text{ IO}_3(aq) + 12 \text{ H}^+(aq) + 10 \text{ e}^- \longrightarrow$
$H_3AsO_4(aq) + 2 H^+(aq) + 2 e^- \longrightarrow$		$I_2(s) + 6 H_2O(l)$
$H_3AsO_3(aq) + H_2O(l)$	+0.559	$K^+(aq) + e^- \longrightarrow K(s)$
$3a^{2+}(aq) + 2e^{-} \longrightarrow Ba(s)$	-2.90	$\mathrm{Li}^+(aq) + \mathrm{e}^- \longrightarrow \mathrm{Li}(s)$
$\operatorname{BiO}^+(aq) + 2\operatorname{H}^+(aq) + 3\operatorname{e}^- \longrightarrow \operatorname{Bi}(s) + \operatorname{H}_2\operatorname{O}(l)$	+0.32	$Mg^{2+}(aq) + 2 e^{-} \longrightarrow Mg(s)$
$3r_2(l) + 2 e^- \longrightarrow 2 Br^-(aq)$	+1.065	$Mn^{2+}(aq) + 2 e^{-} \longrightarrow Mn(s)$
$2 \operatorname{BrO}_3^{-}(aq) + 12 \operatorname{H}^+(aq) + 10 \operatorname{e}^- \longrightarrow$		$MnO_2(s) + 4 H^+(aq) + 2 e^- \longrightarrow$
$Br_2(l) + 6 H_2O(l)$	+1.52	$Mn^{2+}(aq) + 2 H_2O(l)$
$2 \operatorname{CO}_2(g) + 2 \operatorname{H}^+(aq) + 2 \operatorname{e}^- \longrightarrow \operatorname{H}_2\operatorname{C}_2\operatorname{O}_4(aq)$	-0.49	$MnO_4^{-}(aq) + 8 H^{+}(aq) + 5 e^{-} \longrightarrow$
$\operatorname{Ca}^{2+}(aq) + 2 e^{-} \longrightarrow \operatorname{Ca}(s)$	-2.87	$Mn^{2+}(aq) + 4 H_2O(l)$
$\operatorname{Cd}^{2+}(aq) + 2 e^{-} \longrightarrow \operatorname{Cd}(s)$	-0.403	$MnO_4^{-}(aq) + 2 H_2O(l) + 3 e^- \longrightarrow$
$\operatorname{Ce}^{4+}(aq) + e^{-} \longrightarrow \operatorname{Ce}^{3+}(aq)$	+1.61	$MnO_2(s) + 4 OH (aq)$
$\operatorname{Cl}_2(g) + 2 e^- \longrightarrow 2 \operatorname{Cl}^-(aq)$	+1.359	$HNO_2(aq) + H^2(aq) + e \longrightarrow NO(g) + H_2O(l)$
$HClO(aq) + 2 H^+(aq) + 2 e^- \longrightarrow$		$N_2(g) + 4 H_2O(l) + 4 e \longrightarrow 4 OH(aq) + N_2H_4(aq)$
$Cl_2(g) + 2 H_2O(l)$	+1.63	$N_2(g) + 5 H'(aq) + 4 e \longrightarrow N_2H_5'(aq)$
$ClO^{-}(aq) + H_2O(l) + 2 e^{-} \longrightarrow Cl^{-}(aq) + 2 OH^{-}(aq)$	+0.89	$NO_3(aq) + 4 H^+(aq) + 3 e^- \longrightarrow NO(g) + 2 H_2O(l)$
$ClO_3^{-}(aq) + 12 H^+(aq) + 10 e^- \longrightarrow$		$Na^{+}(aq) + e^{-} \longrightarrow Na(s)$
$Cl_2(g) + 6 H_2O(l)$	+1.47	$Ni^{2+}(aq) + 2e^{-} \longrightarrow Ni(s)$
$\operatorname{Co}^{2^+}(aq) + 2 e^- \longrightarrow \operatorname{Co}(s)$	-0.277	$O_2(g) + 4 H^+(aq) + 4 e^- \longrightarrow 2 H_2O(l)$
$\operatorname{Co}^{3+}(aq) + e^{-} \longrightarrow \operatorname{Co}^{2+}(aq)$	+1.842	$O_2(g) + 2 H_2O(l) + 4 e^- \longrightarrow 4 OH^-(aq)$
$2r^{3+}(aq) + 3e^{-} \longrightarrow Cr(s)$	-0.74	$O_2(g) + 2 H^+(aq) + 2 e^- \longrightarrow H_2O_2(aq)$
$\operatorname{Cr}^{3+}(aq) + e^{-} \longrightarrow \operatorname{Cr}^{2+}(aq)$	-0.41	$O_3(g) + 2 H^+(aq) + 2 e^- \longrightarrow O_2(g) + H_2O(l)$
$\operatorname{CrO}_7^{2^-}(aq) + 14 \operatorname{H}^+(aq) + 6 \operatorname{e}^- \longrightarrow$		$Pb^{2+}(aq) + 2 e^{-} \longrightarrow Pb(s)$
$2 \operatorname{Cr}^{3}(aq) + 7 \operatorname{H}_2 O(l)$	+1.33	$PbO_2(s) + HSO_4^{-}(aq) + 3 H^+(aq) + 2 e^- \longrightarrow$
$\operatorname{Cr}O_4^2(aq) + 4 \operatorname{H}_2O(l) + 3 \operatorname{e}^- \longrightarrow$	0.12	$PbSO_4(s) + 2 H_2O(l)$
$Cr(OH)_{3}(s) + 5 OH (uq)$	-0.13	$PbSO_4(s) + H^+(aq) + 2 e^- \longrightarrow Pb(s) + HSO_4^-(aq)$
$\operatorname{Cu}^{-}(aq) + 2e \longrightarrow \operatorname{Cu}(s)$	+0.337	$PtCl_4^2(aq) + 2e^- \longrightarrow Pt(s) + 4Cl^-(aq)$
$\operatorname{Cu}^+(aq) + e^- \longrightarrow \operatorname{Cu}^-(aq)$	+0.155	$S(s) + 2 H^+(aq) + 2 e^- \longrightarrow H_2S(g)$
$\operatorname{Cu}(aq) + e \longrightarrow \operatorname{Cu}(s)$	+0.521	$H_2SO_3(aq) + 4 H^+(aq) + 4 e^- \longrightarrow S(s) + 3 H_2O(l)$
$E(a) + 2a^{-} \longrightarrow 2E^{-}(aa)$	-0.185	$HSO_4(aq) + 3 H^-(aq) + 2 e^- \longrightarrow$
$r_2(g) + 2e \longrightarrow 2F(aq)$	+2.8/	$\Pi_2 S \cup_3(aq) + \Pi_2 \cup (l)$
	-0.440	$\operatorname{Sn}^{-}(aq) + 2e \longrightarrow \operatorname{Sn}(s)$
$e^{-1}(aq) + e \longrightarrow Fe^{-1}(aq)$	+0.771	$\operatorname{Sn}^{-}(aq) + 2 \operatorname{e} \longrightarrow \operatorname{Sn}^{-}(aq)$
$fe(CIN)_6^{-1}(aq) + e \longrightarrow Fe(CIN)_6^{-1}(aq)$	+0.36	$vO_2^{-1}(aq) + 2H^{-1}(aq) + e \longrightarrow vO^{-1}(aq) + H_2O(l)$
$2 \operatorname{H}(aq) + 2 \operatorname{e} \longrightarrow \operatorname{H}_2(g)$	0.000	$Zn^{-}(aq) + 2 e \longrightarrow Zn(s)$

Reactions and voltage for an iron(III)-lead cell:

 $2Fe^{3+} + \underline{Pb}(s) \longrightarrow 2Fe^{2+} + \underline{Pb}^{2+}$

 $E_{\text{cell}}^{o} = 0.77 \text{ v} + 0.13 \text{ v} = 0.90 \text{ V}$

Reactions and voltage for an iron(III)-iron cell:

 $2Fe^{3+} + Fe (s) \longrightarrow 2Fe^{2+} + Fe^{2+}$ $\underline{E^o_{cell}} = 0.77 v + 0.44 v = 1.21 V$

E°(V) -0.83 +0.88 +1.776 +0.789 +0.920 +0.854 +0.536

+1.195 -2.925 -3.05 -2.37 -1.18

+1.23

+1.51

 $\begin{array}{r} +0.59\\ +1.00\\ -1.16\\ -0.23\\ +0.96\\ -2.71\\ -0.28\\ +1.23\\ +0.40\\ +0.68\\ +2.07\\ -0.126\end{array}$

+1.685-0.356+0.73+0.141+0.45

+0.17-0.136+0.154+1.00-0.763

The reaction between iron(III)-iron is more favorable and a short circuit occurs, showing very low voltage on the voltmeter.

Standard reduction potentials are determined at 25°C and using specific concentrations: 1)All soluble species are at 1 M. 2)Slightly soluble species must be at saturation. 3)Any gas is constantly introduced at 1 atm. 4)Any metal must be in electrical contact. 5)Other solids must also be present and in contact.

Operating galvanic cells at standard conditions <u>are not</u> systems in equilibrium. At equilibrium, the voltage of the galvanic cell would drop to zero (the battery would be dead.) Therefore, Le Chatelier's Principle cannot be used to correctly explain the effect of changes in the solution concentrations on the standard cell potential, E^{o}_{cell} .

Since all solutions and gases in a standard cell are 1 M or 1 atm, respectively, Q = 1 for the standard cell. In concentration cells, the direction of the spontaneous electron flow will be in the direction needed to reach equilibrium, where $E_{cell} = 0$ and Q = K. Deviations from standard conditions that take the cell further from equilibrium with Q > 1 will decrease the magnitude of the E_{cell} relative to E_{cell}° . Likewise, if the deviations result in Q < 1, then there will be an decrease the magnitude of the E_{cell} relative to E_{cell}° .

Another method of determining the change in voltage for galvanic cells at nonstandard condition is to apply the Nernst Equation, $E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{n^{\frac{2}{2}}} \ln Q = E_{\text{cell}}^\circ - \frac{0.0592}{n} \log Q @ 25^\circ \text{C}$

So.... When Q > 1, the voltage decreases since the log Q is a positive (+) value, and when Q < 1 the voltage increases since the log Q is a negative (-) value. Although the application of the Nernst Equation is not part of the new AP Chemistry Curriculum, it still comes in handy when trying to explain changes in the E^{o}_{cell} at nonstandard conditions by addressing the changes in the "log Q" variable found in this expression.