Electrochemistry
Voltaic Cells

Many chemical reactions can be classified as oxidation-reduction or redox reactions. In these reactions one species loses electrons or is oxidized while another species gains electrons or is reduced. In some cases the same species can both gain and lose electrons in a disproportionation reaction. It is convenient to consider such reactions as two half-reactions, one oxidation and one reduction. In the following reaction zinc loses electrons while silver ions gains electrons. The overall redox reaction and the two half-reactions are shown. Note that electrons lost **must** equal electrons gained.

Eq 1 $Zn_{(s)} + 2Ag^{1+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$ **Redox**

Eq 2 $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^{-}$ **Oxidation**

Eq 3 $2Ag^{1+}_{(aq)} + 2e^{-} \rightarrow 2Ag_{(s)}$ **Reduction**

The tendency for a oxidation-reduction reaction to occur can be measured if the two half-reactions can be made to occur in two separate containers or cells and connected by a voltmeter, and a salt bridge or porous barrier. Electrons travel from the oxidation to the reduction reactions externally through electrodes and wires (or voltmeter) and ions migrate through a porous barrier or salt bridge. If a voltmeter is connected between the two half-cells the overall cell potential can be measured in volts. This type of system is called a voltaic cell since the redox reaction is spontaneous and produces a voltage as in a battery. An example of a voltaic cell is shown in Figure 1. Wires are connected to the electrodes using alligator clips.

Voltaic Cell

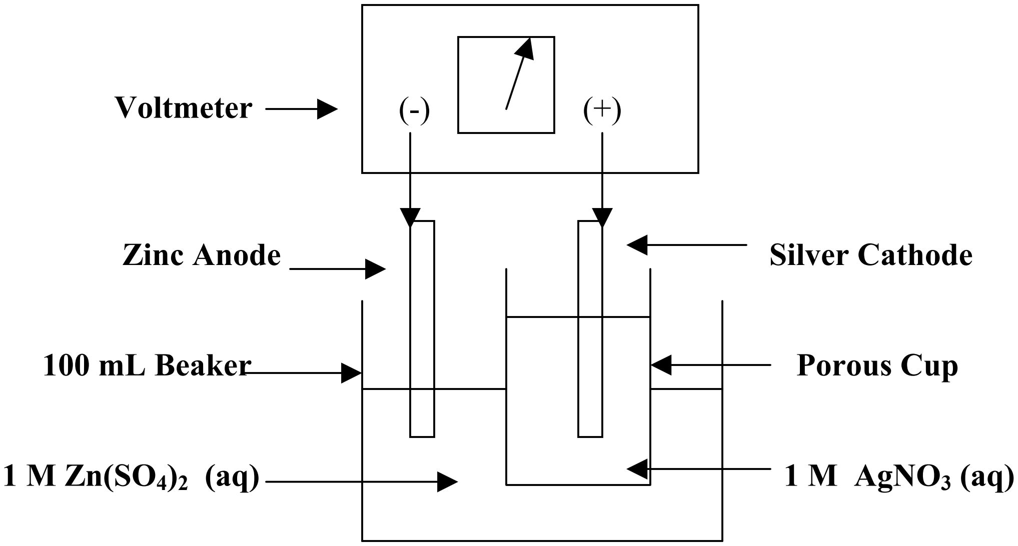


Figure 1

When a **positive** voltage is read (needle moves left to right) on the voltmeter, the electrode connected to the **negative** terminal is the anode and the oxidation reaction occurs here. The positive terminal of the voltmeter is thus connected to the cathode where reduction occurs. If a negative voltage (needle moves to left) the cell is hooked up backwards. Simply reverse the wires connecting the electrodes to the (+ and (-) terminals of the voltmeter. The cell depicted in Figure 1 is a standard cell as the concentrations of the solutions is 1.00 M.

The reading of the voltmeter, in the case of this system about 1.56 V, is a measure of the tendency to go as written in Eq. 1. It is the sum of the tendency for the oxidation plus the reduction reactions to occur. However it does not tell the tendency of either half-reaction to occur. In fact it is impossible to measure the tendency of a half-reaction to occur by itself. One has to arbitrarily assign one half-reaction a voltage of zero. The hydrogen ion , hydrogen gas half-reaction is assigned a standard potential of 0.000 V

$$\textbf{Eq 4} \quad 2H^{1+}_{(aq)} + 2e^{-} \rightarrow H_{2(g)} \quad E^{o} = 0.000\ V$$

The hydrogen ion concentration is 1.00 M and the pressure of the hydrogen gas is 1.00 atm. One can construct a cell using the reaction in equation 5 and determine its voltage to be +0.76 V.

$$\textbf{Eq 5} \quad Zn_{(s)} + 2H^{1+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)}$$

In a cell $E^{o}_{cell} = E^{o}_{oxidation} + E^{o}_{reduction}$ or in the above cell $+0.76\ V = E^{o}_{oxidation} + 0.00\ V$
Thus $Zn_{(s)} \rightarrow Zn^{2+} + 2e^{1-}$ is + 0.76 V or spontaneous. Voltages are by convention written as reduction half-reactions in tables. Reversing an equation changes the sign of E^{o} not its value. In standard reduction tables the zinc reaction would be written as:

$$\textbf{Eq 6} \quad Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^{-} \quad E^{o} = +0.76\ V$$

$$\textbf{Eq 7} \quad Zn^{2+}_{(aq)} + 2e^{-} \rightarrow Zn_{(s)} \quad E^{o} = -0.76\ V$$

For the cell in Figure 1: $1.56\ V = 0.76\ V + E^{o}_{reduction}$

Thus $E^{o}_{reduction}$ [$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$] is +0.80 V.

Electrolytic Cells

In a voltaic cell a spontaneous redox reaction generates an electric current as in a battery. However in an electrolytic cell an electric current is used to cause a nonspontaneous redox reaction. This type of reaction is also called electrolysis. The reaction will not occur if no electricity is supplied. The electrical current is applied so that electrons are supplied to the cathode (- electrode) where reduction occurs while oxidation occurs at the anode.

The amount of chemical change or reaction depends on the quantity of electricity supplied. The quantity of electricity is expressed in coulombs (C). Coulombs is equal to the rate of electrical current in amperes (coulombs/second) times the time in seconds.

Eq 8 Coulombs = (Amperes)(Seconds current is on)

Another important term in electrolysis is the Faraday (F), the charge in coulombs of one mole of electrons.

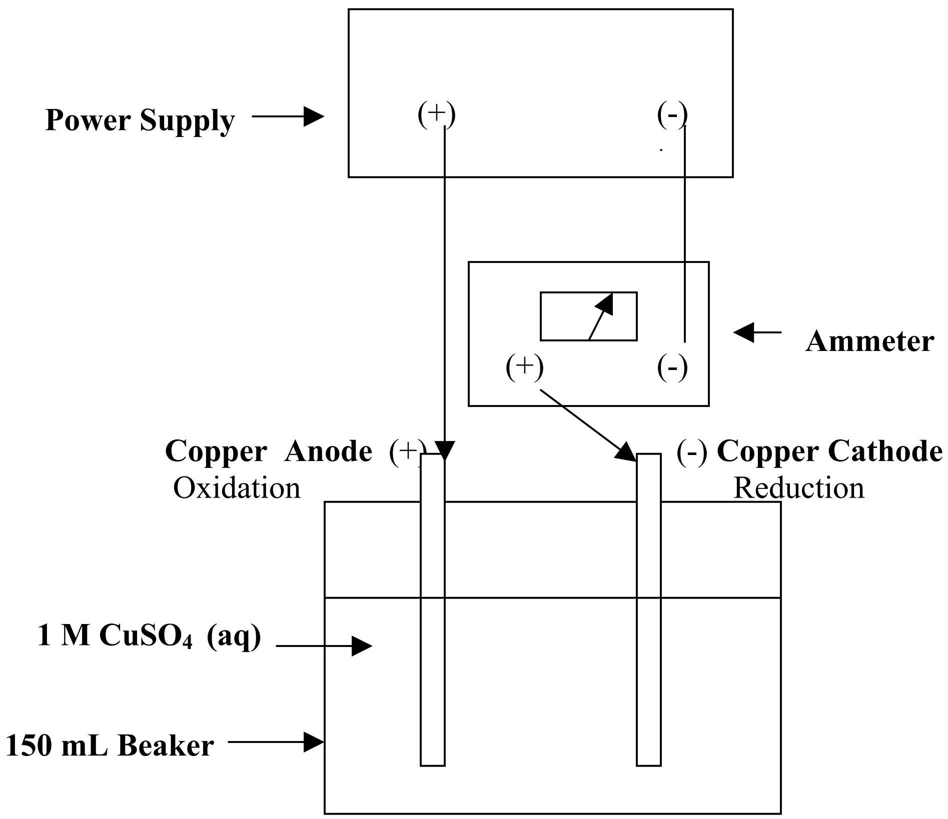
1F = (1.60 x 10^{-19} coulombs/1 electron)(6.02 x 10^{23} electrons/1 mole electrons
So 1 Faraday (F) = 96500 coulombs/mole electrons

One can determine the value of the Faraday experimentally by determining the moles of electrons involved when a certain amount of coulombs passes through an electrolytic cell. The moles of electrons can be determined by determining the mass of a substance reacting in the cell. As an example, in equation 9 it is seen that 2 moles of electrons are required to produce one mole or 65.39 grams of Zn solid from a zinc ion solution.

Eq 9 $Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$

For example if 0.183 grams of zinc metal is deposited on a zinc cathode from a 1 M $ZnSO_4$ solution using a 0.300 ampere current running for 30.0 minutes, what is the value of the Faraday ? Remember F = coulombs/moles of electrons. Coulombs is then (0.300Coul/sec) multiplied by (60.0 sec/min)(30.0 min) or 540 coulombs. The moles of electrons is (0.183 g Zn)(1 mole Zn/65.4 g Zn)(2.00 mole electrons/1 mole Zn) or 0.00560 moles of electrons. Thus F = (540Coul)/(0.00560 mol electrons) or 9.64 x 10^4 Coulombs per mole of electrons.

An electrolytic cell with copper electrodes for use in this experiment is shown in below. The electrons flow from the negative terminal of the power supply to the negative terminal of the ammeter and then from the positive terminal of the ammeter to the copper cathode. Wires are connected to the copper electrodes with alligator clips. Electrons return to the power supply from the copper anode.



Electrolytic Cell

Figure 2

Anode reaction: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

Cathode reaction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Procedure

Electrolytic Cell

Obtain a 150 mL beaker, two copper strips, a power supply, three copper wires (two with alligator clips), and an ammeter. Carefully polish, wash, and dry each copper strip and record their weights. Place about 40-50 mL of 1 M $CuSO_4$ solution into the beaker and drape two copper strips over opposite sides of the beaker. Connect the electrodes, ammeter, and power supply using copper wires as illustrated in Figure 2. Use the wires with alligator clips to connect the circuit to the electrodes.

Turn on the power supply and increase the voltage so that the ammeter reads 300 milliamps or 0.300 amperes. Check the ammeter periodically and adjust the voltage if necessary to maintain the current at 300 milliamps. Let the electrolysis run for 40.0 minutes. Shut off the power supply. **Very** carefully dry each electrode and record their weights. Try not to lose any loose copper plated on the cathode. While the electrolytic cell is running, assemble and measure the voltage of the three voltaic cells.

DISPOSE THE SOLUTION IN THE HEAVY METAL WASTE CONTAINER.

From the amperes and time calculate the coulombs passing through the cell. Calculate the moles of electrons passing through the cell from both the weight gain at the cathode and the weight loss at the anode. Calculate the Faraday value from each electrode and the average value in this experiment. Compare your value to the accepted Faraday value of 96500 coulombs/mole of electrons.

Voltaic Cells

Three standard voltaic cells will be assembled using Figure 1 as a guide and their voltages measured. Zinc-copper, zinc-iron, and iron-copper cells will be made. Obtain a 100 mL beaker and a porous cup for your cells. Place the porous cup in the beaker. Pour one of the solutions (say copper sulfate) in the beaker to a depth of 1-2 inches. Place a copper strip in the solution. Put some of the other solution (say zinc sulfate) inside the cup and place a zinc strip in it. Connect the two electrodes to a voltmeter using copper wires with alligator clips. If a positive voltage is not observed, reverse the wires to the electrode. The electrode connected to the negative voltmeter terminal is the anode and the other electrode is the cathode. Record the voltage and write the half-reactions and the redox reaction. Assemble the other two voltaic cells in a similar fashion. It does not matter which solution goes in the beaker and which goes in the porous cup.

DISPOSE ALL SOLUTIONS IN THE HEAVY METAL WASTE CONTAINER.

Compare the experimental cell voltage with the theoretical voltage calculated from standard reduction potential tables.

Name:____________________________ **Partner:**________________________

Data and Results

Voltaic Cells

1. $Zn(s) \mid ZnSO_4(aq) \parallel CuSO_4(aq) \mid Cu(s)$

   Measured Cell Voltage: ____

   Anode: ________ Half-Reaction:______________________________________

   Cathode: _________ Half-Reaction: ____________________________________

   Cell Redox Reaction: ____

   Standard Cell Voltage (E^o): ____

2. $Zn(s) \mid ZnSO_4(aq) \parallel FeSO_4(aq) \mid Fe(s)$

   Measured Cell Voltage: ____

   Anode: __________ Half-Reaction: ___________________________________

   Cathode: __________ Half-Reaction: _________________________________

   Cell Redox Reaction: ____

   Standard Cell Voltage (E^o): ____

3. $Fe(s) \mid FeSO_4(aq) \parallel CuSO_4(aq) \mid Cu(s)$

   Measured Cell Voltage: ____

   Anode: __________ Half-Reaction: ___________________________________

   Cathode: ___________ Half-Reaction: _________________________________

   Cell Redox Reaction: ____

   Standard Cell Voltage (E^o): ____

Name:____________________________ **Partner:**________________________

Data and Results

Electrolytic Cell

1. Average Current in milliamps: ________________________________

2. Average Current in Amperes: ________________________________

3. Time in minutes: ____

4. Time in Seconds: ____

5. Coulombs used in Cell: _______________________________________

Anode

1. Initial Mass of Anode in grams: ________________________________

2. Final Mass of Anode in grams: ________________________________

3. Mass of copper lost in grams: __________________________________

4. Moles of copper lost: ____

5. Moles of electrons: ____

6. Value of Faraday (Coulombs/mol of electrons): ______________________

Cathode

1. Initial Mass of cathode in grams: __________________________________

2. Final mass of cathode in grams: ____________________________________

3. Mass of copper gained in grams: ____________________________________

4. Moles of copper gained: ____

5. Moles of electrons: ____

6. Value of Faraday (Coulombs/mol of electrons): _______________________

Average Value of Faraday: _______________________________________

Percent Error in Experimental Value :

Standard Reduction Potentials at 25°C *

Half-Reactions	E^o, Volts
$F_2(g) + 2e^- \leftrightarrow 2F^- (aq)$	+2.87
$Co^{3+}(aq) + e^- \leftrightarrow Co^{2+}(aq)$	+1.84
$H_2O_2(aq) + 2H^+ 2e^- \leftrightarrow 2H_2O(l)$	+1.78
$MnO_4^-(aq) + 8H^+ + 5e^- \leftrightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.49
$Cl_2(g) + 2e^- \leftrightarrow 2Cl^-(aq)$	+ 1.36
$Cr_2O_7^{2-}(aq) + 14H^+ + 6e^- \leftrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$O_2(g) + 4H^+(aq) + 4e^- \leftrightarrow 2H_2O(l)$	+1.23
$Br_2(l) + 2e^- \leftrightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \leftrightarrow NO(g) + 2H_2O(l)$	+0.96
$Hg^{2+}(aq) + 2e^- \leftrightarrow Hg(l)$	+0.85
$Ag^+(aq) + e^- \leftrightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \leftrightarrow Fe^{+2}(aq$	+0.77
$O_2(g) + 4H^+(aq) + 2e^- \leftrightarrow H_2O_2(aq)$	+0.68
$I_2(s) + 2e^- \leftrightarrow 2I^- (aq)$	+0.54
$O_2(g) + 2H_2O(l) + 2e^- \leftrightarrow 4OH^- (aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \leftrightarrow Cu(s)$	+0.34
$2H^+(aq) + 2e^- \leftrightarrow H_2(g)$	0.00
$Pb^{2+} (aq) + 2e^- \leftrightarrow Pb(s)$	-0.13
$Sn^{+2}(aq) + 2e^- \leftrightarrow Sn(s)$	-0.14
$Ni^{2+}(aq) + 2e^- \leftrightarrow Ni(s)$	-0.23
$Co^{2+}(aq) 2e^- \leftrightarrow Co(s)$	-0.28
$Cd^{2+} + 2e^- \leftrightarrow Cd(s)$	-0.40
$Fe^{2+} + 2e^- \leftrightarrow Fe(s)$	-0.41
$Cr^{3+}(aq) + 3e^- \leftrightarrow Cr(s)$	-0.74
$Zn^{2+} + 2e^- \leftrightarrow Zn(s)$	-0.76
$2H_2O(l) + 2e^- \leftrightarrow H_2(g) + 2OH^- (aq)$	-0.83
$Mn^{2+} (aq) + 2e^- \leftrightarrow Mn(s)$	-1.03
$Al^{3+} (aq) + 3e^- \leftrightarrow Al(s)$	-1.66
$Mg^{2+} (aq) + 2e^- \leftrightarrow Mg(s)$	-2.38
$Na^+ (aq) + e^- \leftrightarrow Na(s)$	-2.71
$K^+ (aq) + e^- \leftrightarrow K(s)$	-2.92
$Li^+ (aq) + e^- \leftrightarrow Li(s)$	-3.04

- For all half-reactions the concentration of dissolved species is 1.00 M and the pressure of all gases is 1.00 atmospheres (atm).

Name:________________________

Electrochemistry

Prestudy

1. Write and name the half-reactions associated with the following redox reaction and write the balanced redox equation.

$$Cr(s) + Co^{2+}(aq) \leftrightarrow Cr^{3+}(aq) + Co(s)$$

2. Determine the standard cell potential for the reaction.

3. What would the cell potential be if 3.00 moles of Cr(s) instead of 1.00 mole were used ? Why ?

4. Is it a voltaic or electrolytic cell ?

5. Draw a cell diagram for the cell. Label the electrodes, give the sign of each electrode, and show the electron flow outside the cell and ion flow in the salt bridge. Use the other side of the paper to draw your diagram.

6. Calculate the value of the Faraday if 3.671 coulombs of electricity gave 4.828 mg of iodine, I_2, from an aqueous NaI solution.