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## Experiment #14 – Determination of Equivalent Mass by Electrolysis

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The equivalent mass of an element can be related to the chemical effects observed in electrolysis. Because they can contain ions, some liquids will conduct an electric current. If the two terminals on a storage battery or any other source of DC voltage are connected through metal electrodes to a conducting liquid, an electric current will pass through the liquid and chemical reactions will occur at the two metal electrodes. In this process, electrolysis is said to occur, and the liquid is said to be electrolyzed.

At the electrode connected to the negative pole or cathode of the battery, a reduction reaction will invariably be observed. In this reaction, electrons will be accepted by one of the species present in the aqueous solution. The species reduced will ordinarily be a metallic cation, the  $H^+$  ion, or possibly water itself. The reaction that is observed is the one that occurs with the least expenditure of electrical energy and will depend on the composition of the solution and overpotentials that may be involved. For this experiment, hydrogen gas is produced by the reduction of the hydrogen ion:



At the positive pole of an electrolysis cell (i.e. the metal electrode that is connected to the positive terminal of the battery), an oxidation reaction will occur at the anode, in which some species give up electrons. Again, this may involve an ionic or neutral species in the solution or the metallic electrode itself. For this experiment, the pertinent oxidation reaction for an unknown metal occurs as follows:



During the course of the electrolysis, the atoms in the metal electrode will be converted to metallic cations and will go into the solution. The mass of the metal electrode will decrease, depending on the amount of electricity passing through the cell and the nature of the metal. To oxidize one mole or one molar mass of the metal, it would take  $n$  faradays, where  $n$  is the charge on the cation that is formed. By definition, one faraday of electricity would cause one gram equivalent mass, GEM, of metal to go into solution. The molar mass, MM, and the equivalent mass of the metal are related by the equation:

$$MM = GEM \times n \quad (3)$$

In an electrolysis experiment, since  $n$  is not determined independently, it is not possible to find the molar mass of a metal. It is possible, however, to find gram equivalent masses of many metals.

In this experiment, a sample of an unknown metal is oxidized at the positive pole (anode) of an electrolysis cell, weighing the metal before and after the electrolysis, thereby

determining its loss in mass. Using the same amount of electricity and number of electrons, the hydrogen ion is reduced at the negative pole of the electrolysis cell. From the volume of  $\text{H}_2$  gas that is produced under known conditions, we can calculate the number of moles of  $\text{H}_2$  formed and hence the number of faradays that passed through the cell. The equivalent mass of the metal is then calculated as the amount of metal that would be oxidized if one faraday were used. In the last part of the experiment, your instructor will tell you which metal you used. Using equation 3, it will be possible to determine the charge on the metallic cations that was produced during electrolysis.

### Procedure

Obtain a buret and sample of unknown metal. Lightly sand the metal to clean it. Rinse the metal with water and then in acetone. Let the acetone evaporate. When the sample is dry, weigh the unknown metal on the analytical balance to 0.001 g.

Set up the electrolysis apparatus as indicated in Figure One (next page). Add about 100 mL of a pre-mixed solution of 0.5 M  $\text{HC}_2\text{H}_3\text{O}_2$  in 0.5 M  $\text{Na}_2\text{SO}_4$  in the beaker with the gas buret. This will serve as the conducting solution. Insert the bare coiled end of the heavy copper wire up into the end of the buret; all but the coiled end of the wire should be covered with watertight insulation. Immerse the end of the buret in the solution and attach a length of rubber tubing to its upper end. SLOWLY AND CAREFULLY open the stopcock on the buret and, with vacuum suction, carefully draw the acid up to the top of the graduations. Close the stopcock. Check the solution level after a few minutes to make sure the stopcock does not leak. Record the level.

The unknown metal will serve as the anode in the electrolysis cell. Connect the metal to the positive pole of the power source with an alligator clip and immerse the metal but not the clip in the conducting solution. Note: The alligator clip must connect to the metal and not the non-conducting tape that indicates the unknown number of the metal. The bare coiled wire inside the buret will be the cathode in the cell. Connect the cathode to the negative pole of the power source. Hydrogen gas should immediately begin to bubble from the cathode. Collect the gas until about 30 mL have been produced. At that point, stop the electrolysis by disconnecting the copper electrode from the power source. Record the level of the liquid in the buret. Measure and record the temperature and the barometric pressure in the laboratory. Note that in some cases, cloudiness may develop in the solution during the electrolysis; this is caused by the formation of a metal hydroxide and will have no adverse effect on the experiment.

Raise the buret and discard the conducting solution from the beaker into the labeled waste container. Rinse the beaker with water, and pour in 100 mL of fresh conducting solution. Take the alligator clip off the metal anode and wash the anode with 0.1 M  $\text{HC}_2\text{H}_3\text{O}_2$ . Rub off any loose adhering coating with your fingers, and then rinse off your hands. Rinse the electrode in water and then in acetone. Let the acetone evaporate. Weigh the dry metal electrode to the nearest 0.001 g.

Reassemble the apparatus and repeat the electrolysis, once again generating about 30 mL of  $\text{H}_2$  and recording the initial and final liquid levels in the buret. Perform the necessary calculations to determine the charge of your unknown cation.

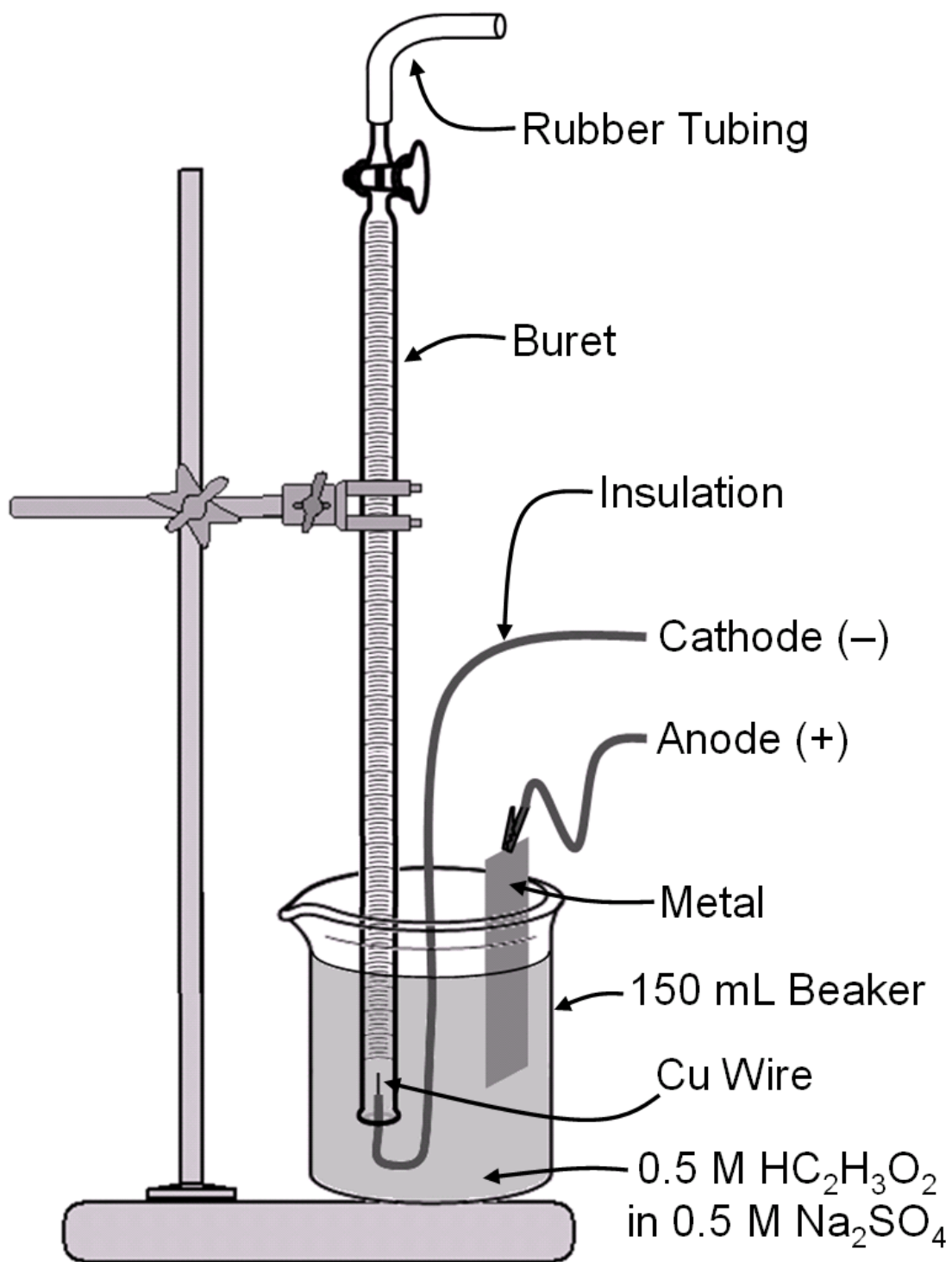


Figure 1

Name: \_\_\_\_\_

Section: \_\_\_\_\_

**Pre-Lab Questions:** Determination of an Equivalent Mass by Electrolysis

1. In an electrolysis cell similar to the one employed in this experiment, a student observed that his unknown metal anode lost 0.233 g while a total volume of 94.50 mL of H<sub>2</sub> was being produced. The temperature in the laboratory was 25 °C, and the barometric pressure was 740 mm Hg. At 25 °C, the vapor pressure of water is 23.8 mm Hg. To find the equivalent mass of his metal, the student filled in the blanks below:

$$P_{\text{hydrogen gas}} = P_{\text{bar}} - VP_{\text{water}} = \text{_____ mm Hg} = \text{_____ atm}$$

$$V_{\text{hydrogen gas}} = \text{_____ mL} = \text{_____ L}$$

$$T = \text{_____ K}$$

$$n_{\text{hydrogen gas}} = \text{_____ moles}$$

$$1 \text{ mol H}_2 \text{ requires passage of _____ faradays}$$

$$\text{Faradays passed (moles of electrons)} = \text{_____}$$

$$\text{Loss of mass of metal anode} = \text{_____ g}$$

$$\text{Grams of metal lost per faraday passed} = \text{grams lost/faradays passed} =$$

$$\text{_____ g} = \text{GEM}$$

The student was told that the identity of the metal anode is copper.

$$\text{MM Cu} = \text{_____ g. The charge } n \text{ on the Cu ion is _____}. \text{ (Eq. 3)}$$

Name: \_\_\_\_\_

Section: \_\_\_\_\_

**Data and Calculations:** Determination of an Equivalent Mass by Electrolysis

Mass of metal anode \_\_\_\_\_ g

Mass of anode after first electrolysis \_\_\_\_\_ g

Mass of anode after second electrolysis \_\_\_\_\_ g

Initial buret reading \_\_\_\_\_ mL

Buret reading after first electrolysis \_\_\_\_\_ mL

Initial buret reading for the second electrolysis \_\_\_\_\_ mL

Buret reading after second electrolysis \_\_\_\_\_ mL

Barometric pressure \_\_\_\_\_ mmHg

Temperature  $T$  \_\_\_\_\_ °C

Vapor pressure of H<sub>2</sub>O at  $T$  \_\_\_\_\_ mmHg

Total volume of H<sub>2</sub> produced,  $V$  \_\_\_\_\_ mL

Temperature  $T$  \_\_\_\_\_ K

Pressure exerted by dry H<sub>2</sub>:  $P = P_{\text{bar}} - VP_{\text{water}}$   
(ignore any pressure effect due to liquid levels in the buret) \_\_\_\_\_ mmHg

Moles of H<sub>2</sub> produced,  $n$  \_\_\_\_\_ moles

Faradays passed (moles of electrons) \_\_\_\_\_

Loss in mass by anode \_\_\_\_\_ g

Equivalent mass of metal (GEM = g lost / faradays passed) \_\_\_\_\_ g

Unknown metal number \_\_\_\_\_

Metal \_\_\_\_\_

MM \_\_\_\_\_ g

Charge  $n$  on cation (equation 3) \_\_\_\_\_

Name: \_\_\_\_\_

Section: \_\_\_\_\_

**Pre-Lab Questions:** Determination of an Equivalent Mass by Electrolysis

1. In ordinary units, the faraday is equal to 96,485 coulombs. A coulomb is the amount of electricity passed when a current of one ampere flows for one second. Given the charge on an electron,  $1.6022 \times 10^{-19}$  coulombs, calculate a value for Avogadro's number.

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2. Consider the electrolysis of  $\text{Na}_2\text{SO}_4(\text{aq})$ . Write the overall net ionic equation that occurs for this electrolysis. Note: Consider all the possible reactions; the oxidation of water or sulfate ions, the reduction of water or sodium ions. Determine which is more likely to occur.

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