

Determining Equivalent Weight by Copper Electrolysis

Purpose

The purpose of this experiment is to determine the equivalent mass of copper based on change in the mass of a copper electrode and the volume of hydrogen gas generated during an electrolysis reaction. The volume of hydrogen gas will be used to calculate the number of moles of electrons passing through the cell.

Introduction

An electrochemical cell is a device that converts the energy of a chemical reaction into electrical energy. In such a cell, the chemical reaction proceeds by the transfer of electrons which produces an electric current. A reaction that involves the transfer of electrons is an oxidation-reduction (redox) reaction. If the oxidizing and reducing species are separated from each other, the electron transfer can occur through a wire that is in contact with the oxidizing and reducing species. The flow of electrons through the wire (current) can be used to produce electrical work. The common dry cell battery is an electrochemical cell. When the terminals of a battery are connected to a motor, electrons will move from the cell through the motor producing work.

If an electric current passes through a solution containing ions, positive ions move in one direction while negative ions move in the other direction. This movement of ions allows the current to pass through the solution. In order to maintain the current, chemical reactions must occur at the solution/electrode interface. These chemical reactions accompanying the passage of current are said to be the result a process called electrolysis, and the reactions that occur are oxidation-reduction reactions.

Faraday's Laws describe the extent to which a chemical reaction occurs and the amount of electric current passed through the solution. These laws state that when Avogadro's number of electrons is supplied to a chemical system, one gram-equivalent of a chemical reaction will occur. The transfer of Avogadro's number of electrons corresponds to one Faraday of electricity. In this experiment, the number of Faradays will be determined from the number of moles of hydrogen gas produced as a result of the electrolysis reaction.

In the electrolysis cell under study, the reduction reaction occurs in a slightly acidic medium. Hydrogen gas will be produced by the reduction of hydrogen ion:



Reduction always occurs at the *cathode* of an electrochemical cell. This is the negative pole in an electrolytic cell (as in this experiment), but is the positive pole in a voltaic (galvanic) cell. For every hydrogen ion (H^+) reduced one electron will be required, but for every molecule of hydrogen gas (H_2) produced *two* electrons will be required. By measuring the volume of hydrogen gas and knowing the temperature and pressure of the gas, the moles of hydrogen gas produced can be calculated using the idea gas law ($PV = nRT$).

While hydrogen ion is being reduced at the cathode, a metal will be oxidized at the *anode* according to the reaction:



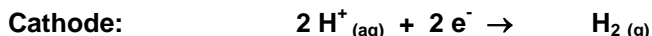
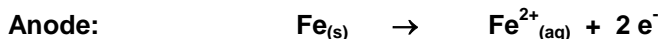
The relationship between the atomic weight (AW) and the equivalent mass (EM) of a metal is shown by the equation (3).

$$\text{AW} = \text{EM} \times n \quad (3)$$

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Where n is the number of electrons the metal loses during the oxidation reaction. If the value of n is determined or known from a specific metal oxidation number, equation (3) can be used to determine the atomic weight of a metal with this experiment.

For illustration, let us consider an electrolysis cell with an iron anode and an inert cathode. The chemical reactions that will occur are:



If during the experiment 1.34×10^{-3} moles of hydrogen gas is produced, the number of Faradays of electrons passing through the cell will be 2.68×10^{-3} since each mole of hydrogen gas produced requires 2 moles of electrons. By weighing the iron electrode carefully before and after the experiment, it is observed that the mass of the electrode decreases by 0.0748 grams. The equivalent weight of iron can be calculated as shown in (4).

$$EM_{(\text{iron})} = \frac{\text{Grams iron oxidized}}{\# \text{ Faradays passed}} = \frac{0.0748}{0.00268} = 27.9 \text{ grams} \quad (4)$$

Since the ferrous ion has a charge of +2, equation (3) can be used to show the consistence of the data with the accepted atomic weight of iron, 55.85 grams/mole.

To obtain the pressure of the dry hydrogen gas to insert into the ideal gas law equation, a careful analysis is required. The total pressure of the gas collected is the sum of the hydrogen gas collected, water vapor, and any air left in the buret. According to Dalton's law of partial pressures, these pressures are independent. In this experiment we assume that the pressure of the air left in the buret is negligible so Dalton's law reduces to :

$$P_{(\text{total})} = P_{(\text{Hydrogen})} + P_{(\text{Water Vapor})} \quad (5)$$

The question remains as to how to get the total pressure of the gas inside the buret. If the water levels are the same inside and outside then the total pressure equals the pressure of the atmosphere, which we can measure with a barometer. In this experiment this is often difficult to achieve so we must relate the total pressure of the gas inside to the barometric pressure by measuring the difference between the solution level inside and outside. If the solution level is higher inside the buret, we know that the atmosphere is pushing down harder than the gas, and you will need to subtract a correction from the atmospheric pressure. If the solution level inside the buret is lower than the solution level outside, then the gas inside the buret is pushing down harder, and you must add a correction to the atmospheric pressure to obtain the total pressure of the gas inside the buret.

The magnitude of this correction is determined by the difference in the solution level inside and outside the buret as well as the fact that it is a difference in a **water solution** level. The atmospheric pressure should be read in units of mm of Hg (also called Torr) from the barometer. Since the density of mercury about 13.6 times greater than the water solution, 1 mm Hg is equivalent to 13.6 mm of water solution. Using this conversion factor, you will convert the solution level difference from mm of solution to mm of Hg. This is the correction that is applied to the atmospheric pressure to obtain the total pressure of the gas inside the buret.

$$P_{(\text{total})} = P_{(\text{Barometer})} \pm \text{correction} \quad (6)$$

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Now you can apply equation (5) to find the pressure of the dry hydrogen gas. This is the pressure that goes into the ideal gas law equation.

$$P_{(\text{Hydrogen})} = P_{(\text{total})} - P_{(\text{Water Vapor})} \quad (7)$$

Finally when the ideal gas law ($PV=nRT$) calculations are performed to solve for "n"; the units for volume, pressure and temperature must be in the same units of the ideal gas constant. There are many sets of units for "R" but the most convenient set in this experiment is to use the value of **$R = 62.36 \times 10^3 \text{ (mL Torr) / (mol K)}$** . (Note - Some of you may be stuck on $R = 0.08206 \text{ atm L / mol K}$ but try this new value of R. It's easier in this experiment.) Since $1 \text{ Torr} = 1 \text{ mm Hg}$ the only real unit conversion is the conversion of your temperature from Celsius to Kelvin. All the other units you have measured match. All units should cancel when using this calculation except for the desired quantity - moles.

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Procedure

1. Obtain a copper electrode to use as the anode, and sand it lightly to remove any oxide. Do NOT sand directly on the benchtop. Rinse the electrode with distilled water and acetone. Allow the electrode to dry completely and then weigh it to the nearest milligram. Record value on data sheet
2. Obtain a cathode wire, buret and 250-mL beaker and assemble the apparatus as shown in the experimental apparatus below. Be certain all the bare wire of the cathode is contained within the buret for least 0.25 inches, but not more than 1.0 inch.
3. Lower the buret cathode wire assembly to the bottom of the beaker. Connect the free end of the cathode wire to the negative (black) DC power terminal (NOTE: MAKE SURE POWER SUPPLY IS OFF WHILE MAKING THESE CONNECTIONS). Add ~ 150 mL of the H₂SO₄ electrolysis solution to the beaker. Carefully place a compressed rubber pipetting bulb on the tip of the buret. Slowly open the buret and allow the electrolysis solution to rise until its level is between the 49-mL and 50-mL graduations. Close the stopcock and note the initial volume reading.
4. Attach one end of a connector wire to the positive (red) DC power terminal. Attach the free end of the connector wire to the previously weighed copper electrode. Check the electrolysis solution level in the buret. It should be exactly the same as the previous value recorded. If a difference exists, your system has a gas leak. Consult with the instructor before proceeding further. If the readings are identical, record this value on the data sheet.

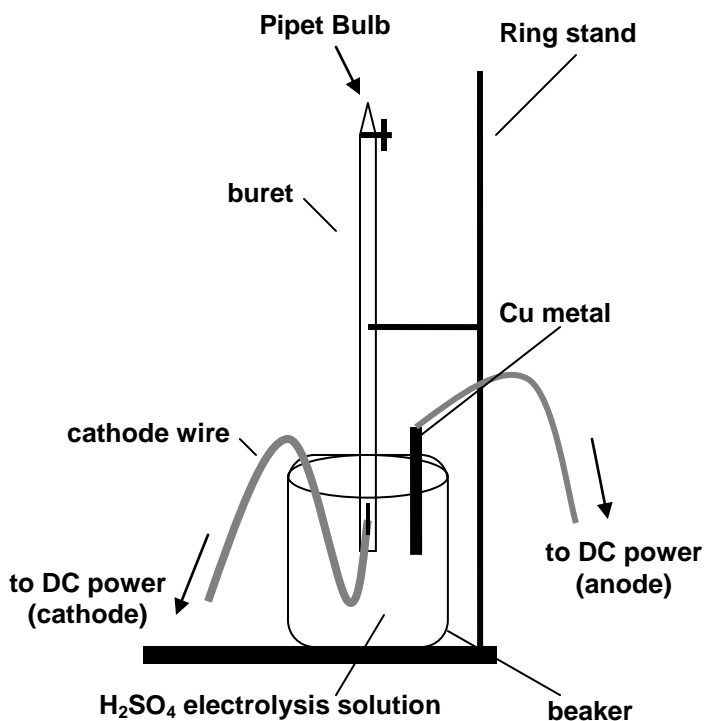
NOTE: The buret and the numbers are upside down. It is very important the readings of electrolyte solution level are accurately read and recorded. If you need assistance, ask your instructor.

5. Place the copper electrode in the electrolysis solution and turn on the DC power supply. If bubbles start forming on the copper strip, immediately remove the strip and examine the set up for an electrical connection error. The actual rate of electrolysis will vary during the experiment for a variety of reasons. When the water level approaches the 2 mL mark on the buret, be prepared to turn off the power supply and remove the copper electrode to stop the generation of hydrogen gas *while the solution level is still within the buret markings*. It is necessary to generate a total volume of hydrogen gas of at least **92 mL**. If the first run begins at 49.05 and ends at 1.52 mL, 47.53 mL will have been generated and the second electrolysis run will require slightly less.
6. Record the final electrolysis solution level for the first run on your data sheet. At this point, you should notice a coloration of the electrolysis solution from the copper ions created by oxidation of the copper electrode (Remember: Cu (II) ion is blue in aqueous solution).
7. Record the approximate distance (accurate to +/- 3 mm) between the solution level in the beaker and the gas in the buret.
8. Compress the pipette bulb and again draw the solution to a level between the 49 mL and 50 mL marks. Record the solution level on your data sheet. Wait a couple of minutes to check for gas leaks. Be certain the cathode wire is properly located within the end of the buret.
9. Place the copper electrode in the solution and repeat the electrolysis as before. Stop whenever the total volume of hydrogen generated exceeds 92 mL, but **do not allow the level to drop below the buret markings**. Record the final gas level reading on the data sheet.
10. Use a small ruler to measure the approximate distance (accurate to +/- 3 mm) between the solution level in the beaker and the level in the buret. Record value on data sheet

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- Record the barometric pressure of the laboratory in units of mm Hg and measure the temperature of the electrolysis solution using a thermometer. Record this temperature and use it for estimating the vapor pressure of water in the buret.
- Carefully remove the connector wire from the copper electrode. Rinse the electrode with distilled water and acetone. Allow the electrode to dry completely and measure its mass on the same balance used for the initial determination. Record the final mass of the Cu electrode on the data sheet.

Experimental Apparatus:



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Data Sheet

Name: _____

Lab Partner: _____

Initial mass of copper electrode _____ g

Final mass of copper electrode _____ g

Mass of copper oxidized during electrolysis _____ g

Atmospheric pressure ($P_{\text{barometer}}$) _____ mm Hg

Temperature of solution after final electrolysis _____ °C

Vapor pressure of water ($P_{\text{water vapor}}$) _____ mm Hg

(Reference: _____)

First Run

Initial solution level _____ mL

Final solution level _____ mL

Volume of hydrogen gas (1st time) _____ mL

Difference between solution level in beaker and buret _____ mm H₂O

Solution level was higher in buret or beaker? _____

Second Run

Initial solution level _____ mL

Final solution level _____ mL

Volume of hydrogen gas (2nd time) _____ mL

Difference between solution level in beaker and buret _____ mm H₂O

Solution level was higher in buret or beaker? _____

Total volume of hydrogen gas generated _____ mL

Correction to apply to atmospheric pressure from barometer
(avg solution height difference divided by 13.6) _____ mm Hg

Total pressure of gas inside buret (P_{total})
(Barometric pressure \pm correction) see Eq. 6 _____ mm Hg

Determining Equivalent Weight by Copper Electrolysis**Calculations***(Show all work)*

Name: _____

Pressure of dry hydrogen gas ($P_{\text{total}} - P_{\text{water vapor}}$) _____ mm Hg

Volume of hydrogen gas generated _____ mL

Temperature _____ Kelvin

Moles of hydrogen generated (use $PV=nRT$) _____ moles

Faradays of current passed through cell _____ faradays

(2 times # moles of hydrogen gas generated)

EM of copper (see equation #4) _____ g / mole of charges

Calculate the experimentally determined atomic weight of copper. (use equation #3)**Calculate the percent error in the experimentally determined atomic weight of copper.**

