EXPERIMENT

Determination of Avogadro's Number via Electrolysis

26

OBJECTIVE

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To determine the value of Avogadro's Number from electrolysis.

APPARATUS AND CHEMICALS

A P P A R A T U S

Ring stand / 3-fingered clamp	Thermometer
Buret / clamp	100 mL graduated cylinder
AC/DC power converter	Suction bulb

C H E M I C A L S

Copper electrodes (1 insulated, 1 bare)

1 M H_2SO_4

Electrolysis uses the energy associated with moving electrons (electromotive force) to drive two chemical reactions – one at the anode, the other at the cathode. Electrons generated from an external source move onto the cathode causing it to become negative. Two nearby hydrogen ions (H^+) accept two electrons from the cathode and become H_2 – hydrogen gas that bubbles out of the solution. At this point, a charge imbalance begins to form. The two H^+ ions had formerly served as counterions for two HSO_4^- ions (these were placed in the aqueous solution as H_2SO_4). Now an excess of negative ions (HSO_4^-) causes the energy of the system to increase. **The reaction will cease if the energy increase of the system is not quickly addressed.** To alleviate this buildup of energy, electrons must be given to the anode by a reactant – this will complete the electrical circuit and form a new species (a product). Two options exist for this new species: either it was negatively charged and became neutral, or it was neutral and became positively charged. In theory, two water molecules (H_2O) could be converted into O_2 and 4 H^+ ions effectively completing the electrolysis of water – H_2 generated at the cathode and O_2 at the anode. However, as in all chemical reactions, the pathway of lowest energy will be followed by the chemical participants. In the system devised for this laboratory, the lowest energy pathway involves the loss of electrons from the metal that serves as the anode. Specifically, copper atoms from the anode will give up two electrons each to form copper ions (Cu^{2+}). These ions will serve as counterions to the HSO_4^- ions mentioned previously. This process will continue as long as electrons move onto the cathode from an external source. The two half-cell reactions are shown below:

$$2H^{+}(aq) + 2e^{-} \longrightarrow H_2(g) \qquad E° = 0.00\text{ V} \qquad \textbf{Equation 26.1}$$

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^{-} \qquad E° = -0.34\text{ V} \qquad \textbf{Equation 26.2}$$

To determine Avogadro's Number, we will need to determine how many electrons have traveled from the cathode to the anode **AND** how many moles of electrons have traveled from the cathode to the anode. Then,

$$\text{Avogadro's Number} = \frac{\text{Number of electrons}}{\text{moles of electrons}} \qquad \textbf{Equation 26.3}$$

The numerator in the above equation is determined from the amperage and time. An amp is a unit used to measure the flow or current or rate of the electrons as they pass a given point. Let's look at a few definitions before we proceed.

Volt – a unit used to measure the potential difference between two points - the greater the potential difference (or voltage) between two points, the greater the **tendency** for the electrons to move between those two points.

Resistance – a force that retards the flow of electrons. Small wires (like small water pipes) have large resistances because it becomes increasingly more difficult to move larger and larger numbers of electrons through the wire in a given time. Large diameter wires have lower resistance and many more electrons can move along these wires in a given time. Resistance is measured in **ohms**.

Ampere – a measure of the number of electrons that pass a given point in a given time. An Ampere is equivalent to the voltage divided by the resistance – it is the tendency of electrons to move divided by the retarding force.

$$\text{Ampere} = \frac{\text{Volt}}{\text{Ohm}} \qquad \textbf{Equation 26.4}$$

Coulomb – a measure of the electric charge that can be delivered. A large electric charge (or shock) can be delivered from high voltage, low resistance (large diameter) wires. The magnitude of the charge (or shock) increases in proportion to the length of time that the current flows. Therefore, a coulomb is equal to the amperage multiplied by the time.

$$\text{Coulomb} = \text{Ampere} \times \text{time (sec)} \qquad \textbf{Equation 26.5}$$

Faraday – named after Michael Faraday who discovered the basic laws of electrolysis – is the magnitude of charge on one mole of electrons. It has been determined that the charge on one mole of electrons is equal to 96,500 Coulombs.

A conversion factor useful to this laboratory can be derived from Faraday's work: ***the charge on only one electron is 1.60 x 10^{-19} Coulombs***.

The following series of conversions will allow us to determine the numerator (number of electrons that were lost at the cathode to the 2 H^+ ions which is also the number of electrons delivered to the anode by the Cu atom) in **Equation 26.3**.

$$\_\_\ \cancel{\text{amps}} \times \_\_\ \cancel{\text{seconds}} \times \frac{1\ \cancel{\text{Coulomb}}}{1\ \cancel{\text{amp-sec}}} \times \frac{1\ \text{electron}}{1.60\times10^{-19}\ \cancel{\text{Coulombs}}} = \#\ \text{electrons}$$ **Equation 26.6**

The denominator in **Equation 26.3** will be determined two different ways allowing us to calculate Avogadro's Number from two different measurements.

First, the volume of Hydrogen gas formed at the cathode can be measured and converted into moles of Hydrogen using the ideal gas equation PV = nRT. Then, using **Equation 26.1**, the moles of electrons involved in the production of the Hydrogen gas can be calculated since 2 moles of electrons are needed in the production of 1 mole of Hydrogen gas.

Second, the loss in mass of the copper electrode can be measured and this mass converted into moles. Then, using **Equation 26.2**, the moles of electrons involved in the conversion of Copper metal into copper ions can be calculated since 2 moles of electrons are required to convert 1 mole of Copper metal into Cu^{2+} ions. Sample Problem 26.1 illustrates the calculations involved in this laboratory.

Sample Problem 26.1: A current of 0.35 A is passed through a 1 M sulfuric acid solution for 20 minutes. If the temperature of the acid solution is 22 ºC, the atmospheric pressure is 101,992 Pa, and the volume of hydrogen collected is 53.9 ml, what is the value of Avogadro's number?

Using **Equation 26.6**, the number of electrons are calculated as follows:

$$0.35\ \cancel{\text{amps}} \times 1200\ \cancel{\text{seconds}} \times \frac{1\ \cancel{\text{Coulomb}}}{1\ \cancel{\text{amp-sec}}} \times \frac{1\ \text{electron}}{1.60\times10^{-19}\ \cancel{\text{Coulombs}}} = 2.625\times10^{21}\ \text{electrons}$$

The moles of electrons are calculated from the hydrogen gas data that was collected. Use the ideal gas equation to calculate the moles of hydrogen gas and then **Equation 26.1** allows us to calculate the moles of electrons produced. Note that the pressure of the gas is found by subtracting the vapor pressure of water at 22 ºC (found in Appendix B of your text book) from the atmospheric pressure.

$$n_{H_2} = \frac{P\ V}{R\ T}$$ **Equation 26.7**

$$n_{H_2} = \frac{\left[\left(101{,}992\ \text{Pa} \times \frac{1\ \text{atm}}{101{,}325\ \text{Pa}}\right) - \left(19.83\ \text{mm Hg} \times \frac{1\ \text{atm}}{760\ \text{mm Hg}}\right)\right]\left[53.9\ \text{mL} \times \frac{1\times 10^{-3}\ \text{L}}{1\ \text{mL}}\right]}{\left(0.0821\ \frac{\text{L atm}}{\text{mole K}}\right)\left(22^{o}\ \text{C} + 273.15\right)}$$

$$n_{H_2} = 2.181\times 10^{-3}\ \text{moles}$$

$$n_{electrons} = 2.181\times 10^{-3}\ \text{moles H}_2 \times \frac{2\ \text{moles electrons}}{1\ \text{mole H}_2}$$

$$n_{electrons} = 4.362\times 10^{-3}\ \text{moles electrons}$$

$$\text{Avogadro's Number} = \frac{\text{Number of electrons}}{\text{moles of electrons}} = \frac{2.625\times 10^{21}\ \text{electrons}}{4.362\times 10^{-3}\ \text{moles electrons}}$$

$$\text{Avogadro's Number} = 6.018\times 10^{23}\ \text{electrons / mole}$$

The following "Maps" illustrate pictorially the ways in which the various data collected in this lab are arranged to answer the question posed: **What is Avogadro's Number?????**

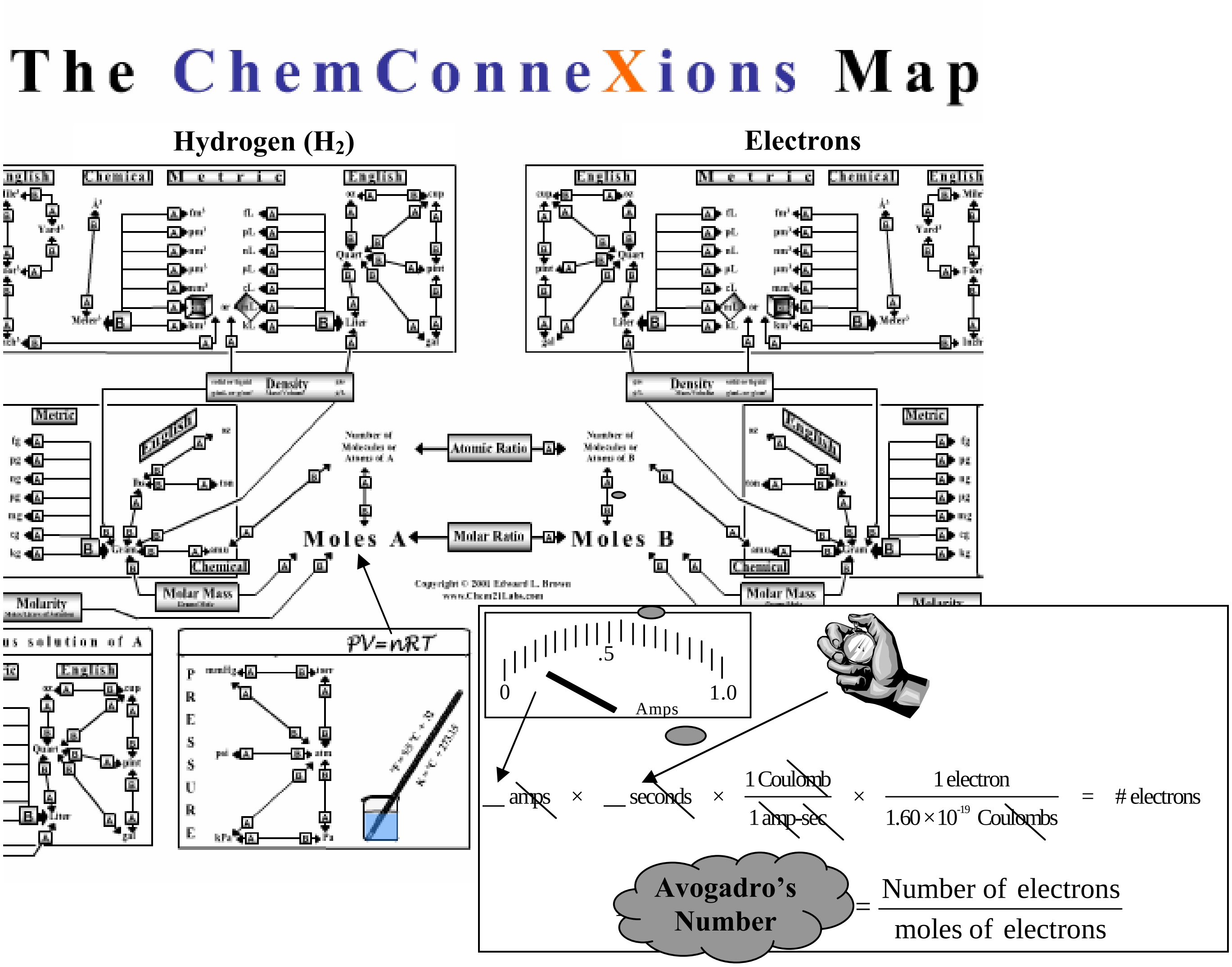

Figure 26.1

In **Figure 26.1**, the amps and seconds are converted into the number of electrons involved in the process. On the left side of the Map, the mL, temperature, and pressure of the collected Hydrogen are used to determine the moles of Hydrogen collected using **PV = nRT**. Conversion of moles H_2 to moles of electrons provides all the information necessary to calculate Avogadro’s Number.

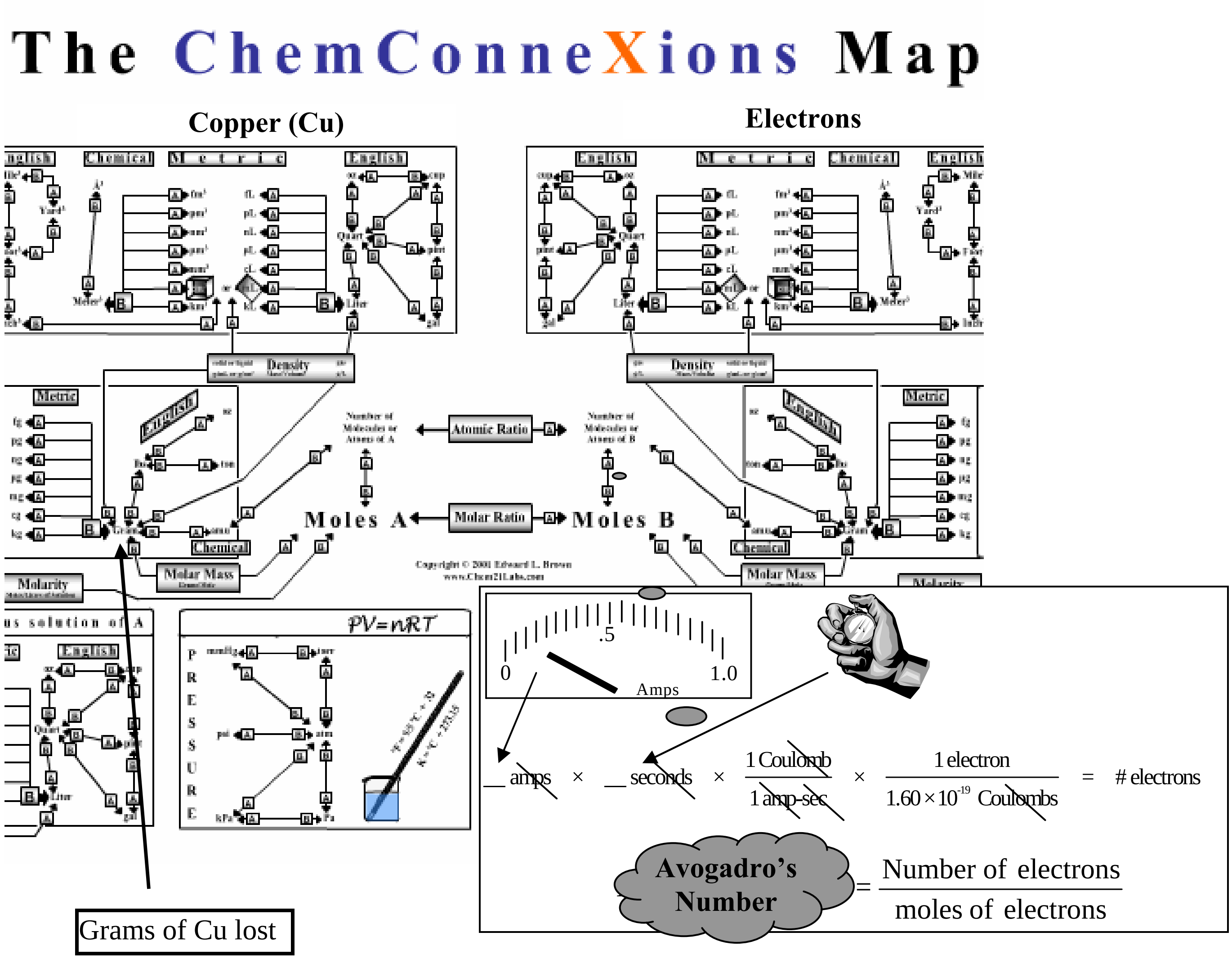

Figure 26.2

In **Figure 26.2**, the moles of electrons involved in the process will be determined by measuring the amount of copper loss from the anode. Conversion of moles Cu to moles of electrons provides all the information necessary to calculate Avogadro’s Number.

PROCEDURE

1. Obtain a DC source, ammeter, stopwatch, one bare copper electrode, one insulated copper electrode, three wires with alligator clips, a 50 mL buret and a 100 mL graduated cylinder. **Use the steel wool to polish all exposed copper on the two electrodes.**

Calibration Of The Non-Graduated Portion Of A Buret:

2. Weigh a clean dry 100 mL beaker [**Data Sheet Q1**].
3. Fill the buret to the 45 mL mark with water. **At the sink**, open the stopcock and allow water to go into the sink until the water in the buret is at the 50 mL mark. Place the tip of the buret over the weighed beaker and open the stopcock to allow the water to exit into the beaker. Close the stopcock **immediately** when the exiting water just reaches the top of the stopcock – this is the part of the buret that will be filled with H_2 later in the experiment.
4. Weigh the beaker again [**Data Sheet Q2**] and calculate the mass of water (1 mL = 1 g for water) collected [**Online Report Sheet Q3**].

Setting Up The Lab:

5. Place **80 mL 1M H_2SO_4** in the 100 mL graduated cylinder and clamp it as shown in **Figure 26.3**.
6. Insert the **curved** bare end of the **insulated** copper electrode into the mouth of the inverted buret, **open the stopcock on the buret** and lower the buret to the 20 mL mark on the graduated cylinder. Clamp it in place [**Figure 26.3**].
7. Attach a rubber suction bulb to the tip of the buret and pull the 1 M H_2SO_4 solution into the buret. You may have to close the buret's stopcock once or twice to evacuate the rubber bulb and continue drawing the acid solution toward the stopcock.
8. When the solution reaches the stopcock, close the stopcock and remove the rubber bulb – **Don't Allow the Solution to Enter the Rubber Bulb!!**
9. Lower the buret so that the bare metal of the inserted electrode is completely contained inside the buret (all of the H_2 gas bubbling from this electrode must travel to the top of the buret).
10. **Weigh the completely bare electrode to the nearest 0.001 g** [**Data Sheet Q4**] and place it into the graduated cylinder so that it contacts the sulfuric acid solution.
11. Use an alligator clip to connect the negative terminal of the DC source (this is the all black wire from the DC source) to the COM port of the ammeter.
12. Another alligator clip will connect the "**.5**" port on the ammeter to the cathode (this is the **insulated** copper wire).
13. Attach the positive terminal of the DC source (this is the black wire with a white stripe from the DC source) to the anode with the third alligator clip.
14. Place a thermometer into the H_2SO_4 solution.

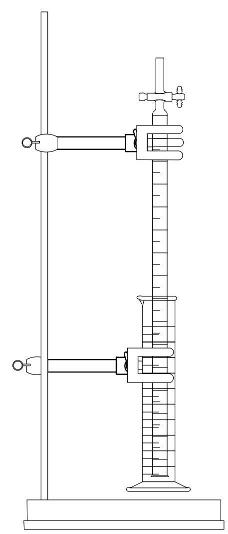

Figure 26.3

Performing The Lab:

15. Plug the DC source into a 110 V outlet and **start the stopwatch**. Immediately adjust the voltage on the DC source so that the amps are between 0.30 and 0.45 and quickly make certain all connections are secure by squeezing the alligator clamps and watching the ammeter.
16. **DO NOT MOVE OR ADJUST ANYTHING UNTIL THE EXPERIMENT IS FINISHED!!**
17. Allow the reaction to proceed until the hydrogen collected has forced the solution level in the buret to the **1-mL mark on the buret**.
18. Unplug the DC source and **record the time in seconds** [**Data Sheet Q5**], **temperature of the 1M H_2SO_4 to the nearest ºC** [**Data Sheet Q6**], **average current (amps)** [**Data Sheet Q7**], **and the barometric pressure (in Pa)** [**Data Sheet Q8**]. The barometric pressure can be found at http://www.wunderground.com.
19. Adjust the buret vertically until the level of liquid inside the buret is the same as the level of liquid in the graduated cylinder. **Record the volume of H_2 in the buret (<u>this number will be ~ 49 mL</u>)**[**Data Sheet Q9**].
20. Remove the bare electrode (anode) and dry it with a paper towel. Wrap the paper towel around the top of the electrode and pull the electrode through the towel to remove any loose particles adhering to the surface. **Weigh this electrode to the nearest 0.001 g** [**Data Sheet Q10**].

Temperature (°C)	Vapor Pressure (mm Hg)
18	15.5
19	16.5
20	17.5
21	18.6
22	19.8
23	21.1
24	22.4
25	23.8
26	25.2
27	26.7
28	28.4
29	30.0

Table 26.1

Lab Calculations:

21. Use **Table 26.1** to report the vapor pressure of water inside the buret [**Online Report Sheet Q11**].
22. Convert the temperature of the Hydrogen to Kelvin [**Online Report Sheet Q12**].
23. Convert the barometric pressure to atmospheres [**Online Report Sheet Q13**].
24. Determine the mass of copper loss at the anode [**Online Report Sheet Q14**].
25. Determine the total volume of Hydrogen collected in the buret (**in L**) [**Online Report Sheet 15**].
26. Determine the pressure of the Hydrogen collected (in atm) – **don't forget to account for the vapor pressure of water** [**Online Report Sheet Q16**].
27. Calculate Avogadro's Number from the Hydrogen gas data and the amperage and time [**Online Report Sheet Q17**].
28. Calculate Avogadro's Number from the loss of copper from the anode and the amperage and time [**Online Report Sheet Q18**].
29. Repeat the experiment a second time – **use the H_2SO_4 solution already present in the graduated cylinder**. Record this data as **Trial 2**.
30. Calculate the average Avogadro's Number from the Hydrogen gas data for **Trials 1 & 2** [**Online Report Sheet Q19**].
31. Calculate the average Avogadro's Number from the loss of Cu data for **Trials 1 & 2** [**Online Report Sheet Q20**].

Laboratory 26
Student Data Sheet

		Trial 1	Trial 2
1.	Mass of empty beaker	________ g	
2.	Mass of beaker and water from buret	________ g	
4.	Initial Mass of the Bare Electrode	________ g	________ g
5.	Time of the reaction (**<u>seconds</u>**)	________ sec	________ sec
6.	Temperature of Hydrogen Collected	________ °C	________ °C
7.	Average Current	________ A	________ A
8.	Barometric Pressure	________ Pa	
9.	Volume H_2 in Buret (~ **49 mL**)	________ mL	________ mL
10.	Final Mass of the Bare Electrode	________ g	________ g

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Laboratory 26

Name: ________________

Instructor Data Sheet

		Trial 1	Trial 2
1.	Mass of empty beaker	________ g	
2.	Mass of beaker and water from buret	________ g	
4.	Initial Mass of the Bare Electrode	________ g	________ g
5.	Time of the reaction (**<u>seconds</u>**)	________ sec	________ sec
6.	Temperature of Hydrogen Collected	________ °C	________ °C
7.	Average Current	________ A	________ A
8.	Barometric Pressure	________ Pa	
9.	Volume H_2 in Buret (~ **49 mL**)	________ mL	________ mL
10.	Final Mass of the Bare Electrode	________ g	________ g