

# Determination of Avogadro's Number

## Introduction

In this experiment you will use information derived from the electrolytic decomposition of water to determine the numerical value of Avogadro's Number,  $N_A$ . As you may remember, this quantity is defined as the number of atoms in exactly twelve grams of isotopically-pure  $^{12}\text{C}$ . Its numerical value, which must be obtained by experiment (rather than in some "theoretical" way), depends upon two things: an international agreement that the mass of one atom of  $^{12}\text{C}$  shall be exactly 12 atomic mass units, and another international agreement as to the amount of mass that equals exactly one gram.

A statement that the atomic mass of  $^1\text{H}$  is 1.00780 atomic mass units means that one  $^1\text{H}$  atom has a mass 1.00780/12 times that of the mass of one  $^{12}\text{C}$  atom. The tabulated atomic masses of elements, which are often also loosely called their atomic weights, are dimensionless, abundance-weighted, averages of the atomic masses of the various isotopes that make up a naturally occurring macroscopic sample of the element in question.

A mole of any substance (abbreviated mol) is by definition the amount of that substance which contains Avogadro's number of its constituent units. On the basis of the information in the two preceding paragraphs, it also follows that the mass of one mole of any substance in grams is numerically equal to the sum of the atomic weights of all of its elemental components. The molar mass of a substance (often termed its molecular weight) has the same numerical value both in atomic mass units and in grams/mol. Thus, the number of moles of a molecular substance can be obtained by dividing the mass of the sample by the molar mass of the molecule.

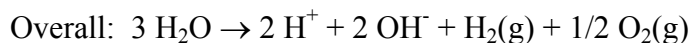
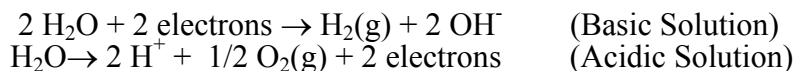
If the substance in question is a gas, then P-V-T measurements can also be used to determine the number of moles of gas in a sample if its Equation of State is known. In this experiment we will assume that the Ideal Gas Law applies.

When two chemically inert electrodes are immersed in water and a sufficiently high DC voltage is applied across them, an electric current is observed to flow and gases are evolved at both electrodes. As you undoubtedly know already, chemical tests show that one of the gases is molecular hydrogen and the other is molecular oxygen. The overall process is termed "electrolysis." (The noun "lysis" derives from the Greek word for disintegration.) A fairly straightforward way to think about the electrolysis experiment is as follows:

The "negative" pole of a battery looks negative because there are surplus electrons being made available there as a result of chemical reactions within the battery itself. If an electrode attached to the negative pole of a battery is placed in a solution containing an electron deficient species that species can take on some of the excess electrons and become "reduced". This process occurs to an immeasurably small extent if only one electrode from the battery is placed in the solution.

The positive pole of a battery, on the other hand, is electron deficient. A chemical substance that is capable of surrendering electrons could thus get "oxidized" at an electrode attached to such a pole. Again, this process would only occur to a minute extent with an isolated electrode.

On the other hand, when both battery terminals are connected to electrodes immersed in the solution, the internal reactions within the battery will continuously replenish the electron surplus at the negative side and generate an electron deficiency at the positive side, leading to ongoing chemical processes at the two electrodes. If water is the chemical substance being electrolyzed, the following two electrode processes are:



(Note that as with all chemical reactions, the two electrode reactions are both atom-balanced and charge-balanced.)

If the solution is stirred, the  $\text{H}^+$  and  $\text{OH}^-$  products that accumulate near the two electrodes will react with each other to make water again. The net effect of the electrolysis then will be to turn 3 moles of water into one mole of hydrogen gas and half a mole of oxygen gas for every two moles of electrons transferred around the circuit in the form of an electric current.

Since the number of moles of gas produced is directly related to the number of electrons transferred around the circuit, it looks as if all one has to do to determine Avogadro's Number is count the number of electrons that get transferred from one electrode to the other, and measure the number of moles of either hydrogen gas or oxygen gas that accompanies their transfer. The chemical product is easily quantified by collecting and measuring the volume of gas formed together with its pressure and temperature.

The number of electrons concomitantly transferred is equally easy to measure. The customary unit of electric current is called the Ampere. One Ampere of current flow corresponds to the passage of one Coulomb of electrical charge through the circuit in a one-second time interval; in other words,

$$\text{Amperes} = \text{Coulombs} / \text{Seconds}.$$

Since the Coulombic charge on an electron is known from independent physical measurements, one can determine how many electrons have been transferred in an experiment such as this one by measuring the current in Amperes, multiplying it by the time in seconds during which the current flows, and dividing the resulting product by the charge on one electron. (If you want to be picky, what you really should do is calculate the integral of [current.d(time)] over the course of the experiment.)

### DATA ANALYSIS FOR PART B

At the end of the experiment you will have information in your hands concerning the volume of evolved hydrogen and the current vs. time profile for its evolution. In order to calculate Avogadro's number you need to compute the number of moles of evolved hydrogen and the number of electrons that were transferred while it was being evolved.

The first thing you will want to calculate is the number of electrons transferred, since it is relatively easy to obtain. Begin this calculation by determining the average value of the current along with its standard deviation. (Many hand calculators have a built-in program that will do this calculation for you.) Please note that even if the observed current did not change at all over the course of the experiment, it would nevertheless have a standard

deviation of at least  $\pm 0.001$  Ampere since you cannot measure it with any greater accuracy than that.

Next, multiply the average current by the total electrolysis time (in seconds) to obtain the number of Coulombs passed through the solution during the electrolysis. The resulting product must have the same relative standard deviation as the corresponding quantity for the current itself. In other words, if the current is uncertain by 5% the Coulombs passed must also be uncertain by 5%. (This statement assumes that there is no significant error in the time measurement.)

If you then divide the number of Coulombs transferred by the charge on an electron,  $1.6022 \times 10^{-19}$  Coulombs, you will get the number of electrons transferred. Again, the relative error in the number of electrons involved in the electrolysis must be the same as that in the current from which it was calculated.

An accurate determination of the hydrogen production involves a Dalton's Law calculation. You have already done a similar calculation in determining the composition of an aluminum/ zinc alloy. This calculation is simpler in that only one reaction produces the hydrogen gas you have collected. Before you try to follow the discussion on the calculations for this lab, read the procedure so that you have an idea of what you are doing and what information you will have in hand. Also review your alloy lab report and re-familiarize yourself with the calculations.

At the end of the experiment, the buret contains hydrogen and water vapor. Just as in the alloy experiment, you can determine the amounts of each vapor that is initially present. The calculation is the same. As in the previous experiment, the pressure outside the system must be equal to the pressure inside the system. Therefore, the sum of the partial pressures of water vapor and hydrogen gas plus the pressure exerted by the column of water in the buret must be equal to the outside atmospheric pressure.

The partial pressure of hydrogen in the buret at the end of the experiment is given by the total barometric pressure minus the sum of the pressure exerted by the column of water in the buret and the vapor pressure of water. Remember that the vapor pressure of water is dependent on temperature and can be looked up in a table.

The number of moles of hydrogen produced in the electrolysis can now be calculated from the Ideal Gas Law, with "P" equal to its partial pressure and "V" equal to the total gas volume at the end of the electrolysis.

With the number of moles of hydrogen produced and the number of electrons accompanying its production both in hand, Avogadro's Number is readily calculated. The relative standard deviation of your calculated value of  $N_A$  may be taken to be the same as that of the current measurements.

**Safety:** The hydrogen gas produced is flammable; NO FLAMES in the lab. As always, exercise care when handling acids and bases. Clean up spills promptly. Wear your goggles.

### Procedure

Work in pairs on this experiment. The actual data analyses and the written reports must be done entirely independently of your lab partner or other students. Make sure that you avoid unauthorized collaboration and plagiarism. All suspected violations of the Code of Academic Conduct will be referred to Student Judicial Affairs.

#### PART A: Qualitative observations

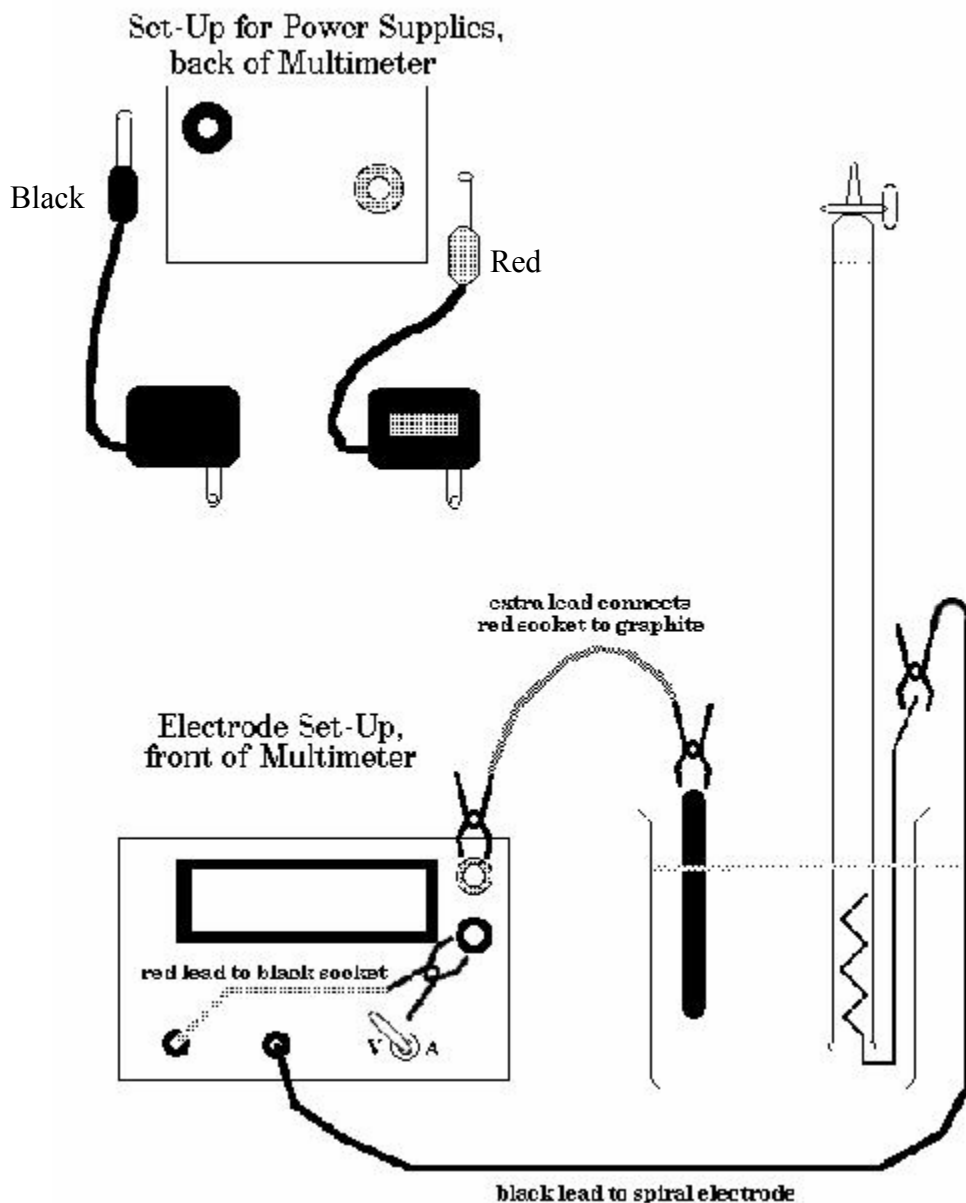
1. Set up the power supply and the multimeter (volt/ammeter). Pick up a multimeter and two different power supplies from the shelf. The two power supplies need to be plugged into the back of the multimeter. One of the power supplies is labeled CUI and other is labeled OEM. One is to power the multimeter and the other is to supply the electron potential needed for the electrolysis of water. Each power supply has a connector that is to be plugged into the back of the multimeter. The two connectors for the power supplies, fortunately, are not interchangeable. They are slightly different in size. This means that one of the connectors will only fit into one of the mountings on the back of the multimeter. See Diagram 1 on next page.
  - A) Plug each power supply into its appropriate mounting in the back of the multimeter.
  - B) Take the red lead that comes out of the front of the multimeter and clip it onto the black terminal in front of the meter.
  - C) Take the black lead that comes out of the front of the multimeter and clip it either to the graphite electrode for Part A or the spiral electrode for Part B.
  - D) Take another lead that has been supplied to you with alligator clips on both ends, clip one end to the red terminal in front of the meter and the other end to the graphite electrode.
  - E) It is important that you make the proper connections here. If the leads are improperly connected then the multimeter will be damaged and will not show the correct readings.

The TAs will demonstrate this set up for your for comparison.

2. Obtain an apparatus that consists of two funnels connected by a short length of plastic tubing, as shown in Figure 1. Attach clamps to the rubber stoppers on the stems of

the two funnels and then to a support rod, producing a U-shaped configuration of the apparatus. The tops of the two funnels should be at the same height, a foot or so off the tabletop. Also, obtain two graphite (carbon) electrodes and two "clip leads." These are just fairly short lengths of insulated wire that have alligator clips attached to each end.

### Determination of Avogadro's, Wiring Diagram



KR17Dec01

Diagram 1. Schematic of the multimeter and lead connectivity.

3. Obtain about 50 mL of 0.5 M potassium sulfate solution in a 100 mL beaker and add several drops of "universal indicator" in order to give the solution a fairly intense color. (Record the color you see.) We must use ionic solutions in this experiment because the conductivity of pure water is so small that it would take an impossibly long time to obtain any observable results. The ions play no part in the electrode processes. They are present to carry electric current through the solution.

The indicator used in this experiment has the behavior that its color changes in the same order as the colors in a rainbow (red, orange, yellow, green, blue, indigo, violet) as the solution changes its acid/base content by powers of ten from  $10^{-4}$  M acid (red) through  $10^{-7}$  M acid and/or base (a "neutral" solution) to  $10^{-4}$  M base (violet). If you are familiar with the terminology, the indicator color changes like the rainbow as the solution pH goes from 4 to 10 in unit steps.

4. Fill the apparatus with the colored  $K_2SO_4$  solution until the two funnels are almost full. Insert a graphite electrode into one end of each of the two clip leads, then connect the other ends of the two clip leads to the two leads coming off of the multimeter. The red lead coming off of the multimeter is the positive pole and the black lead coming off of the black terminal is the negative pole. Now dip the graphite electrode connected to the (+) terminal of the multimeter into the left-hand funnel and the one connected to the (-) pole of the multimeter into the right-hand funnel, keeping the metal alligator clips out of the solution. **It is important to swirl the electrode in each funnel to mix the solution.**

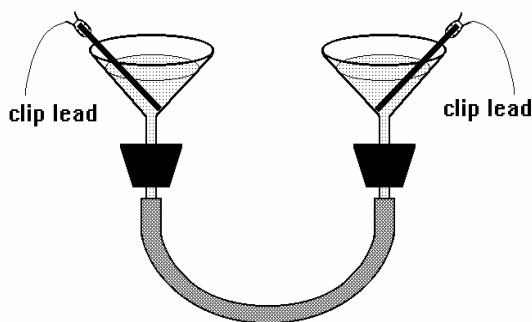


Figure 1. Funnel Apparatus with Electrodes

Question A: How do you interpret the color changes in each funnel? Draw the diagram in Figure 1 and indicate what color changes occur and write balanced chemical reactions for the processes that cause the changes.

5. Allow the electrolysis to proceed for a few minutes until no further color changes seem to be occurring, then remove the two electrodes from solution and disconnect them from the power supply. Quickly rinse the electrodes off with water from your wash bottle and store them in a clean beaker.

Very carefully unclamp one of the funnels from the supporting rod and by lowering and tipping it (using the clamp as a handle), drain all the contents of the apparatus back into the beaker from which they came.

Question B: Explain the color of the solution in the beaker. Write a balanced chemical reaction for the process that caused the color change.

The apparatus may now be dismantled. Wash it thoroughly, rinse it with deionized water, and return it to its source.

#### Part B: Quantitative measurements

For this part of the experiment you will need a 25 or 50 mL buret, a 50 mL Erlenmeyer flask, a thermometer, a stainless steel spiral electrode, a graphite (carbon) electrode, two clip leads, your power supply and multimeter apparatus, and about 60 mL of 0.25 M sulfuric acid solution stored in a 150 mL beaker. You will prepare this solution yourself by diluting the 3 M stock solution supplied on the lab benches.

As in the alloy experiment, you will be collecting gas into an inverted buret. You will be using a 25 mL or a 50 mL buret and will need to determine the volume of the uncalibrated portion of the buret (the head space) between the 25 mL (or 50 mL) mark and stopcock. Last time you did this calibration, you measured the volume of water using a graduated cylinder. This time calibrate the buret by measuring the mass of water contained in the uncalibrated region. Use the table of conversion factors found in the Introductory Laboratory Techniques experiment.

As you plan your procedure, remember that the water coming out of the tap is not necessarily at room temperature.

Question C: Comment on the relative accuracy of your buret calibration this time compared to last time.

You will now electrolyze water and collect one of the evolved gases in your buret. Figure 2 shows selected parts of the assembled apparatus as it should appear at the instant the electrolysis is begun.

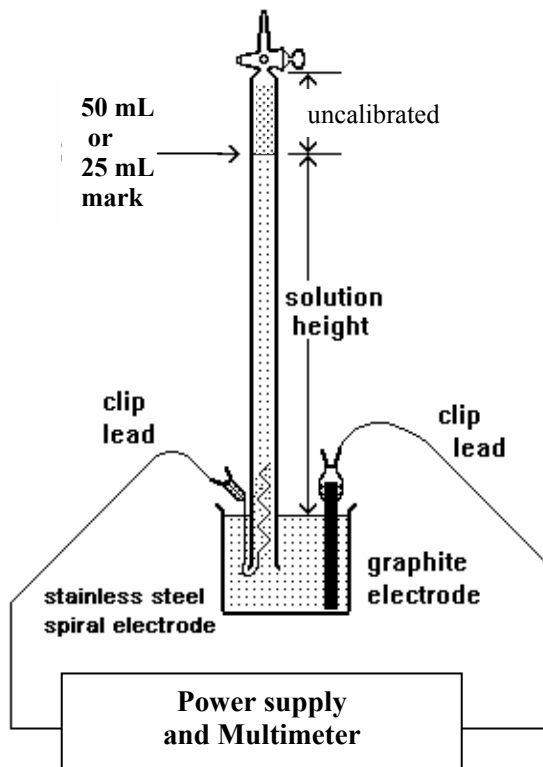


Figure 2. Electrolysis Apparatus

**SAFETY:** The buret will be used to catch and determine the volume of hydrogen gas that will be produced in a timed electrolysis during which the current will be monitored. The oxygen gas will be generated at a graphite electrode and will be allowed to escape into the atmosphere. **We do not want to let any hydrogen loose in the lab at the same time, so think very carefully about Part A of this experiment to determine how to connect your multimeter.**

1. Invert the buret, clamp it to a support rod, and insert the stainless steel coil electrode into the buret mouth. Now lower the buret partway into the beaker of dilute sulfuric acid and clamp it firmly in place. Be very careful when handling the buret from here on; the outside will have acid on it. Do not get this acid on yourself or drip it onto the floor, lab bench, neighbors and so on! Open the buret stopcock, and with a rubber bulb carefully draw the sulfuric acid solution up into the buret to top then close the stopcock, leaving no air bubbles.
2. Record the barometric pressure, the room temperature and the temperature of the sulfuric acid solution. You will find a barometer mounted on one of the walls in the laboratory room. **Please do not touch any of the buttons on the barometer.**
3. Connect the proper lead from the multimeter to the spiral electrode. Connect the other lead from the multimeter to the graphite electrode. Be sure you are collecting the hydrogen gas at the spiral electrode! Do not put the graphite electrode into the solution in the beaker just yet.

Question D: (Answer this question before you continue with the experiment.) To which pole of the power supply should the electrode be connected in order to collect the hydrogen gas in the buret?

4. Throw the switch on the multimeter to "A", and simultaneously lower the graphite electrode into the beaker as far as you can without wetting the metal clip, and either start a stopwatch or note the time (including the position of the second hand) on your wristwatch or the wall clock. Record the initial multimeter reading in amps.
5. Record the meter reading every minute for a total of seven minutes, then remove the graphite electrode from the solution, thereby ending the electrolysis. Store the graphite electrode in another empty beaker for future use. Wait a few minutes for all the hydrogen bubbles to rise to the top of the liquid column. Also inspect the turns of the stainless steel spiral to see if any gas bubbles are trapped there. If there are some bubbles, you can tap the buret gently and try to dislodge them. If you cannot do so, try to estimate their number and sizes and increase the gas production volume accordingly. (Recall that one buret drop is about 0.05 mL, and it is unlikely that any of the trapped gas bubbles will be that big.) When no more hydrogen bubbles are visible in the liquid column, read and record the final buret reading. Also, measure the height in millimeters of the liquid level in the buret above that in the beaker.
6. Open the buret stopcock, allow the solution to flow back into the beaker, and close the stopcock. Swirl the beaker to homogenize the solution. You will now again use a rubber bulb to refill the buret to near the 25 mL mark. However, you must do this carefully so that none of the hydrogen gas in the buret escapes into the room. You want to trap all of the gas that you remove from the buret in the rubber bulb, and then vent the bulb's contents in the fume hood. While carrying the rubber bulb to the hood, use your finger to seal the bulb's opening. Squeeze and release the bulb several times in the hood to expel any hydrogen gas. It may require more than one application of the bulb to fill the buret. If this occurs, vent the bulb each time in the hood. Then, repeat Steps 3, 4 and 5 of this part of the experiment. In this repetition you should use a different (measured!!) collection time. It's up to you to decide whether to use a longer or shorter time depending on the amount of gas evolved in seven minutes. You don't want to have an evolved volume that is too small because the accuracy of your final answer depends on how big that volume is. You should not run for too long either, since as the electrolysis proceeds the solution compositions change near the electrodes (remember what happened in the two funnels in Part A of this experiment), and the current could vary somewhat erratically.
7. At the end of the second run, again use the rubber bulb to collect the hydrogen gas and expel it in the hood. Then drain the buret into the beaker, raise the buret up, and rinse off its outside with your wash bottle. While wearing gloves, remove the spiral electrode and place it in an empty beaker along with the graphite electrode. Rinse out the buret, wash off the electrodes with deionized water, and return everything to its proper place. **Do not throw out the graphite electrodes.**

Write-up. Include in your lab report a very clear calculations section and your average value for Avogadro's number. Estimate the standard deviation of your result based on the estimated standard deviation you get for the number of electrons transferred. As always, also include the answers to the questions posed in the procedure.