Determination of the Fundamental Electronic Charge via the Electrolysis of Water

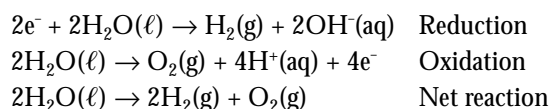**Brittney Hoffman,[†] Elizabeth Mitchell,[†] Petra Roulhac,[†] Marc Thomes,[†] and Vincent M. Stumpo*[‡]**

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The allure of universal physical constants is unmistakable. Membership in this set is reserved for only the most fundamental data in science. To the novice student, these entities often appear more metaphysical than physical; experimentally inaccessible abstractions, frequently confined by orders of magnitude to either the realm of the quantum (e.g., the electronic charge and Planck's constant) or the cosmological (e.g., the speed of light and the universal gravitational constant).

It was the intention, therefore, of the AP Chemistry class at our school to demystify one small component of the scientific data bank by designing and executing an experiment sensitive enough to determine, within acceptable accuracy, the value of one of nature's theoretical building blocks, and simple enough to be conducted in a typical secondary school laboratory. The electronic charge was selected because of its ubiquitous application in chemistry and the elegance of the experimental system.

Theory

A Hoffman electrolysis apparatus, filled with deionized water and a small amount of acid, is placed in series with a low-voltage power supply (Science Kit & Boreal Laboratories, Model 64250-10) and a digital multimeter (Goldstar, Model DM-311). A current of 25 mA passing through the system simultaneously reduces the hydrogen and oxidizes the oxygen in the water. The molecular hydrogen and oxygen gases thus produced are trapped in separate inverted burets, so that their volumes can easily be measured. The half-reactions and overall process appear below.

$2e^- + 2H_2O(\ell) \rightarrow H_2(g) + 2OH^-(aq)$	Reduction
$2H_2O(\ell) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$	Oxidation
$2H_2O(\ell) \rightarrow 2H_2(g) + O_2(g)$	Net reaction

In comparing the electrode half-reactions, stoichiometry indicates that twice as much gas is generated by hydrogen reduction at the cathode. The volume of hydrogen is directly proportional to the time that the current flows, and thus to the number of electrons consumed in the formation of this gas. Consequently, the fundamental electronic charge can be deduced by gas law, stoichiometric and dimensional considerations.

The number of moles of hydrogen gas is given by the ideal gas law as

$$n_{H_2} = PV/RT \qquad (1)$$

where P, V, and T are the pressure, volume, and temperature of the collected hydrogen.

The moles of electrons passing through the circuit in a given time can be expressed as

$$n_{e^-} = it/Ne^- \qquad (2)$$

where i, t, N, and e^- represent the current, time, Avogadro's number, and the electronic charge, respectively.

The balanced coefficients of the reduction require that

$$n_{e^-} = 2n_{H_2} \qquad (3)$$

Inserting eqs 1 and 2 into eq 3 yields the desired expression for the electronic charge.

$$e^- = (itRT)/(2NPV) \qquad (4)$$

Experimental Procedure

A current of 25 mA is applied to the circuit for 20 to 30 minutes, an interval sufficient to produce a significant volume of hydrogen gas. The current must be consistently monitored and the variable power source adjusted to compensate for fluctuations and drift. At the conclusion of each trial it is evident that the total pressure (hydrogen gas and water vapor) within the cathodic buret is slightly greater than atmospheric, as the water level in the central section of the Hoffman apparatus is higher than that in the hydrogen-containing buret. This height differential must be measured so that the pressure of the hydrogen can be calculated by

$$P_H + P_{water} = \rho gh + P_{atm} \qquad (5)$$

where P_{water} is the vapor pressure of water (2.5 and 2.6 kPa at 21 and 22 °C, respectively), ρ is the density of water, g is the gravitational acceleration of the planet, h is the height difference in the water levels, and P_{atm} is the barometric pressure.

Data and Results

The following data were obtained in our classroom.

	Trial 1	Trial 2	Trial 3	Trial 4
Current/mA	25	25	25	25
Time/s	1200	1200	1800	1800
Volume/mL	3.9	3.8	5.7	5.6
Temperature/°C	21.5	22.0	20.5	22.0
Hydrogen pressure/kPa (calculated from eq 5)	100.5	101.4	100.8	100.5
Electronic charge/10^{-19} C (calculated from eq 4)	1.6	1.6	1.6	1.6

Sample Calculation: e⁻ = (itRT)/2 NPV, Trial 2

Error Analysis

Equation 4 represents the electronic charge as a function of five variables: current, time, and the volume, temperature, and pressure of the hydrogen produced. The estimated uncertainties in these measured values are indicated below.

$$\mathrm{d}i = \pm 0.5 \text{ mA}$$
$$\mathrm{d}V = \pm 0.1 \text{ mL}$$
$$\mathrm{d}P = \pm 100 \text{ Pa}$$
$$\mathrm{d}t = \pm 1 \text{ s}$$
$$\mathrm{d}T = \pm 0.5 \text{ °C}$$

From the outset of this project, it was anticipated that the greatest errors would be due to the instability of the current and the uncertainty in the volume measurement. This was confirmed by treating the electronic charge as a function of these five variables (eq 4) and computing the total differential of this function. This analysis demonstrated that the uncertainties in the current and the volume cause a maximum error in the electronic charge value on the order of 2% each. The predicted errors in time, temperature and pressure contribute a significantly smaller error of approximately 0.1% each. This results in a maximum error of less than 5%, a very respectable level of accuracy for secondary school investigations.

To two significant digits, our experimentally determined value for the electronic charge of 1.6×10^{-19} C is in excellent agreement with the accepted value.

Conclusion

This experiment offers instructors several enticements. It is easy to set up, each trial can be accomplished within a class period, and the students are engaged in a marvelously comprehensive exercise in stoichiometry, gas laws, electrochemistry, and error analysis. Perhaps as important, it establishes the notion that unlocking nature's secrets need not always require sophisticated equipment and elaborate procedures. It is common practice for chemistry teachers to demonstrate electrolysis with a Hoffman apparatus. However, with little additional effort, students can experience the wonder that accompanies accurately measuring a universal physical constant.