Absolute Measurement of the Faraday

Purpose

The total charge corresponding to one Avogardro's number of (i.e. 6.022×10^{23}) electrons is known as the *Faraday*. In this experiment you will measure the Faraday using an *absolute* technique, in which all of the quantities are measured in terms of the SI primary standards for mass (kilogram), length (meter), and time (second). Our goal is to give a simple example of how it is possible to measure derived quantities like the Coulomb, the Ampere, and the Faraday in terms of *primary standards*.

Introduction

In this lab, we will measure the Faraday by passing a known amount of charge through a solution of $CuSO_4$. Every time a copper ion (Cu^{++}) reaches the cathode, a charge +2e (e is the magnitude of the electron's charge) will have passed through the circuit. If we know the total charge Q that has passed through the circuit, and we weigh the cathode to find the total mass of copper deposited, we can then calculate the Faraday. The relationship between the total charge and the total mass of copper deposited is

 $Q = e N_A Z (\Delta m_{Cu}/M_{Cu}).$

In this expression Z is the charge state of the copper ion (+2), M_{Cu} is the mass of an Avogadro's number of copper atoms, Δm_{Cu} is the total mass of copper plated onto the cathode, and N_A is Avogadro's number. The Faraday F is defined as $F=e N_A$, so we have

$$F=(Q/Z) (M_{Cu}/\Delta m_{Cu}).$$

Using this expression, we can measure the Faraday. We will measure Δm_{Cu} in grams using a precision balance. Q will be found by measuring the current I in Amperes, and multiplying by the time t in seconds: Q = I t. To measure the current, we will construct a torsion-balance ammeter that allows us to measure the current in terms of time, mass, and length. We can also cross-check this ammeter with a multimeter.

In a true absolute measurement we would have to measure everything in terms of the primary SI standards. In the interest of keeping things simple, we will rely on the handbook value for the mass of an Avogadro's number of copper atoms, or equivalently, the copper/carbon atomic mass

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ratio. Recall that Avogadro's number is defined such that one Avogadro's number of pure carbon-12 atoms has a mass of 12 grams. The quantity we need for our experiment is the mass of one Avogadro's number of copper atoms, which is given by

$$M_{Cu}=12(A_{Cu}/A_C)$$
 grams,

Where A_{Cu} and A_C are the atomic masses of natural copper and carbon-12. If we measure A in atomic mass units then $A_C=12$ exactly, and $A_{Cu}=63.546$, to sufficient accuracy. We will assume that our rulers for measuring lengths, our balance for measuring mass, and our stopwatches for measuring time have all been calibrated in terms of the SI standards.

In the SI system, the Ampere is defined in terms of the force per unit length between two parallel wires that carry the same current. All other electrical quantities are defined in terms of the Ampere in the SI system. In particular, the Coulomb is equal to the charge transferred by a current of one Ampere in one second.

You can make a simple absolute ammeter by suspending a small bar magnet by a fiber at the center of a coil of wire. The unknown current I passes through the coil generating a magnetic field B, which exerts a torque on the bar magnet. When disturbed from equilibrium, the magnet performs small angular oscillations about the direction of the field. From the measured period T you can calculate the strength of the magnetic field B and hence the coil current I.

The presence of the earth's magnetic field and the torque of the suspension fiber must also be taken into account. When this has been done, the current I though the coil can be found from measurements of the period T_E in the earth's field and the period T in the combined fields of the earth and the coil using the equation:

$$I = C \left(\frac{1}{T^2} - \frac{1}{T_E^2} \right)$$

We will show below that the calibration constant C can be determined from absolute measurements.

References (on lab bookshelf)

- 1. D. J. Griffiths: "Introduction to Electrodynamics," 2nd edn., Prentice Hall (1989)
- 2. P. W. Atkins: "Physical Chemistry," 3rd edn., Oxford (1986)
- 3. G. W. C. Kaye and T. H. Laby: "Tables of Physical and Chemical Constants," 14th edn., Longman (1982).
- 4. J. H. Moore, and C. C. Davis and M. A. Coplan: "Building Scientific Apparatus," Addison-Wesley (1983).
- 5. M. Faraday: "Experimental Researches in Electricity," Vol.1 (1839) and Vol. 2 (1844), reprinted by Dover (1965)
- 6. J. C. Maxwell: "Treatise on Electricity and Magnetism," 1st edn., (1873), reprinted by Dover (1954). **Read Maxwell's preface.**

Outline of the Experiment

- A. First Week
 - 1. Design an absolute ammeter with 1% accuracy (problem set 1.1).
 - 2. Build the meter and make measurements needed to determine the calibration constant C.
 - 3. Analyze your data in the lab to find your value for *C* and its uncertainty.
 - 4. Decide how to improve your meter if the uncertainty is much more that 1%.
 - 5. If necessary, make improvements to obtain a better value for *C*.
- B. Second Week
 - 1. Report on the construction and calibration of your meter and plan the electroplating experiment (problem set 1.2).
 - 2. Do the electroplating to find the best conditions for the experiment. Record preliminary data for Faraday's constant.
 - 3. Calculate preliminary values for F in the lab. Examine the major sources of errors.
 - 4. Plan your final experiment to reduce the errors as much as possible. Record final data for determining *F*. Make at least two final runs under identical conditions.
- C. Final Report

Your report should describe the entire experiment in about five pages. Include a discussion of the reliability and significance of your result.

Apparatus



Fig 1(a) Apparatus for electrolysis. (b) Measurement of null distance

A power supply drives current through the electrolytic cell, which is in series with the coils of the absolute ammeter. A pair of "Helmholtz coils" replaces the singe coil described in the introduction in order to improve the accuracy. The Helmholtz pair produces a much more uniform B-field over the extended region occupied by the magnet.

Absolute Measurement of Current

1. The Helmholtz coils are connected in series such that the current flows in the same sense through both. The coils have equal radii (*a*), equal number of turns (*N* turns on each) and are separated by a distance exactly equal to the radius (s=a). The magnetic field (B_c) on the axis midway between the coils when current (*I*) flows through both coils is given by:

$$B_c = \left(\frac{4}{5}\right)^{3/2} \cdot \frac{\mu_0 NI}{a} \tag{4}$$

2. The field B_c is determined from the period of angular oscillations of the bar magnet suspended midway between the coils.

The coil field (\bar{B}_c) exerts a restoring torque $(\bar{m} \times \bar{B}_c)$ on a magnet of dipole moment (\bar{m}) . If there were no other forces, the period of small angular oscillations for a moment of inertia (I) about the vertical axis would be:

$$T = 2\pi \sqrt{I/mB_c}$$

The earth's magnetic field and twist in the fiber also affect the motion. Twist in fiber (torsion constant κ) contributes a relatively weak torque (- $\kappa\theta$) if the fiber is thin. If the coil axis is parallel to the horizontal component of the local earth's field (B_E), the resultant field at the center is just the algebraic sum of the two fields $(|\bar{B}_c + \bar{B}_E| = B_c + B_E)$. The magnetic torque is $-m(B_c + B_E)\sin\theta$. Adding the fiber torque (- $\kappa\theta$), the equation of motion becomes:

$$\Gamma = \left[-m(B_c + B_E) \cdot \sin\theta - \kappa\theta \right] = I\ddot{\theta}$$
(5)

The period for small amplitude oscillations $(\sin\theta \rightarrow \theta)$ is given by:

$$T = 2\pi \times \sqrt{\frac{\mathrm{I}}{m(B_C + B_E) + \kappa}} \tag{6}$$

The calibration equation is derived from (6). (Prob. 1).

$$I = C \left(\frac{1}{T^2} - \frac{1}{T_E^2} \right)$$
(7)

where T_E is the period in the earth's field alone (I=0, coil current OFF) and T is the period in the combined fields of the coil and the earth.

The "calibration constant" (*C*) must be found by experiment before you can measure current with the meter. *C* is a function of the moment of inertia (I), and the magnet's dipole moment (*m*), the local value of the earth's field (B_E) at the coil center and the torsion constant of the fiber (κ), as well as the radius (*a*) and the number of turns (*N*) on the Helmholtz coils.

$$C = C(I, m, B_E _, a, N)$$

a) <u>Moment of inertia</u> (I) can be found from the mass (m_m) and dimensions of the magnet (length l, radius r).

$$I = \frac{m_m l^2}{12} \left(1 + 3\frac{r^2}{l^2} \right)$$
(7a)

The quantities m_m , B_E , and κ may be found by combining the results of the following experiments. This procedure is not unique and you may choose to use different methods of your own.

b) <u>Measure $T_{\underline{E}}$, the period in the earth's field alone</u>. (Set current to zero in the coil so that $B_C = 0$ in equation (6).

$$T_E = 2\pi \sqrt{\frac{\mathrm{I}}{mB_E + \kappa}} \tag{7b}$$

c) <u>Measure T_{ϱ} </u>, period with zero magnetic torque, to find κ . Replace the magnet with a non-magnetic bar (copper or brass) having similar moment of inertia (I') as the magnet, but whose dipole moment is zero.

$$T_0 = 2\pi \sqrt{\frac{\mathbf{I}'}{\kappa}} \tag{7c}$$

d) <u>Determine the null distance</u> (Z_n) for the magnet. Here the magnetic dipole is considered as a *source* of *B*-field. The magnetic dipole field at distance *Z* along the dipole axis is: $B_m = \mu_0 m / (2\pi z^3)$.

If the dipole axis is set <u>anti-parallel</u> to the earth's field, there will be a point on the axis beyond each end of the magnet where the field of the earth and the magnet cancel exactly $(\bar{B}_E + \bar{B}_m) = 0$ -- the "null point." The null distance (Z_n) , from the magnet's center to the null point, is found by equating the dipole field at the null point to the magnitude of the earth's field.

$$|B_E| = B_m(Z)|_{Z_n} = \frac{\mu_0 m}{2\pi Z_n^3}$$
 (7d)

A second small magnet, the "test magnet", is needed to identify the position of the null point. The arrangement is shown in fig 1.1 (b) where the original dipole (m) is moved out along the coil axis, and the test magnet is suspended at the coil center. Since B_E varies around the lab, it is important to determine the null point at the same position used in measuring T_E , namely the center of the coils (see fig 1(b)).

Idealized Models and Systematic Errors

The equations (6) through (7d) are strictly correct only for an ideal situation where we have a <u>point</u> magnetic dipole suspended <u>exactly</u> at the center of <u>perfectly</u> constructed Helmholtz coils executing oscillations of <u>negligible</u> amplitude. The finite size of the real dipole, the finite amplitude of oscillation, and errors in the construction of the Helmholtz coils all represent systematic differences between the ideal model and the reality of the experiment. If these differences are ignored, they will cause hidden <u>systematic errors</u> in your result. Systematic errors are often evidenced by a "discrepancy" between two different experiments that is greater than the stated experimental uncertainties. You need to understand the physics of the apparatus thoroughly to avoid systematic errors. Two approaches for doing this are:

- a) Good design of the apparatus and appropriate procedure. For example, the Helmholtz coil pair generates a much more uniform magnetic field than would a single coil. And restricting the amplitude of the magnet oscillations can help to avoid errors due to the nonlinearity.
- b) Once you have the best design that time and money permit, you can correct residual systematic errors by using a more accurate theory. This often amounts to using terms of next higher order in a Taylor expansion, or a multipole expansion of the fields, to obtain a correction term.

Some particular higher order corrections

a) The period is independent of oscillation amplitude only when there is a linear restoring torque ($\Gamma = -\kappa \theta$). The sin θ term in the magnetic torque, $\Gamma_m = -mB \sin\theta$ causes the period to increase with increasing amplitude. Suppose *T* is the small-amplitude period (i.e. using the approximation $\sin\theta \approx \theta$). In the case of a somewhat larger amplitude, use of the approximation ($\sin\theta = \theta - \theta^3/3!$) leads to the period:

$$T_{\theta_0} = T(1 + \frac{\theta_0^2}{16} + \dots)$$
(8)

b) Residual non-uniformity of B field. When the permanent magnet has finite length l, you really need to know the field of the Helmholtz coil at the end so the magnet distance $\pm l/2$ away rather than at the center. If $B_Z(0)$ is the field precisely at the center, then the field at distance Z along the axis is:

$$B_{Z}(Z) = B_{Z}(0) \cdot \left[1 - \frac{144}{125} \left(\frac{Z}{a} \right)^{4} + \dots \right]$$
(9)

c) <u>Errors in construction of Helmholtz coils</u>. For perfectly constructed Helmholtz coils, the separation of the coils is precisely equal to the radius (s = a). If the actual separation had the different value ($s = a + \delta$), where ($\delta << a$), the field at the center changes to the value:

$$B'_{Z}(0) = B_{z}(0) \cdot \left[1 - \frac{3}{5} \frac{\delta}{a} + \dots\right]$$

where

$$B_Z(0) = \left(\frac{4}{5}\right)^{\frac{3}{2}} \cdot \frac{\mu_0 NI}{a}$$



is the field for the correct spacing.

d) <u>Field of a finite dipole</u>. The null distance for a dipole *m* of finite length is not the same as that of an infinitesimal dipole. A correction arises from the quadrupole team in the magnet's *B*-field. At distance *Z* along the axis:

$$B_m(finite) = B_m(ideal) \cdot \left[1 + \frac{1}{2}\left(\frac{l}{z}\right)^2 + \dots\right]$$

where

$$B_m(ideal) = \frac{\mu_0 m}{2\pi z^3}$$

e) <u>Coupling of different motions</u>. If the pendulum motion of the magnet has a period $T_p = 2\pi \sqrt{\frac{L}{g}}$ that is too close in value to the period of angular oscillations, the motions will interfere to generate beats, making it difficult to measure the period. If this is a problem, you can change the pendulum period (T_p) by increasing the length (L) of the fiber.

Electrolysis

a) <u>Basic process in the Cu/CuSO₄ electrolytic cell</u>

Faraday's law (eq. 1) relates to the mass (Δm_{Cu}) of copper transferred between the electrodes to the charge Q_{Cu++} specifically carried by copper ions. The subscript reminds

us of this. However, there are other ions present in the $CuSO_4$ solution (SO_4^- and H^+ and OH^- from water) which also contribute to the current flow (*I*) measured with the ammeter. These other ions can lead to a major systematic error in *F* if their presence is ignored:

$$Q_{Cu^{++}} = FZ\left(\frac{\Delta m_{Cu}}{M_{Cu}}\right) \quad ; \quad \left(Z = 2 \text{ for } Cu^{++}\right)$$

But the measured current (I) gives:



How can we distinguish the charge carried by copper ions from that carried by the others?

It turns out that we can suppress the movement of other ions by a suitable choice of conditions, such as concentration of solution and current density. If we are certain that the other ions are suppressed, then we can use the original relation with confidence.

$$(I \cdot t) = Q_{TOTAL} = (Q_{Cu^{++}} + 0) = F \cdot 2 \cdot \left(\frac{\Delta m_{Cu}}{M_{Cu}}\right)$$

The underlying physics is based on the different amounts of energy required to discharge different ions at the electrodes. The discharge energies are provided by the extremely high electric fields that occur in the polarization layers formed on the electrode surfaces. The strength of the "polarization layer" is in turn determined by the local current density and concentration of solution.

b) Polarization of the electrodes

Immediately after the current is switched on, the SO_4 ions start moving to the anode. They cannot be discharged at the anode because that would require too much energy (4 eV). The SO_4 ions collect on the anode surface, from which they electrically repel further sulfate ions that arrive later. In the steady state, diffusion to the left balances electrically driven motion to the right.



The layer of SO_4 ions on the anode surface is typically 20Å thick. It gives rise to a polarization voltage drop between the electrode and solution, whose magnitude increases with current density. The potential distribution across the cell is shown for various current densities in the figure below. There is a polarization potential drop at each electrode. The uniform gradient in the solution represents the effect of Ohm's Law for a solution of finite resistivity.



Note that the polarization potentials increase as the current is increased by turning up the power supply knob.

c) <u>Competing electrolytic processes</u>

The polarization potential difference between each electrode and the bulk solution can provide the energy needed to dissociate water $(H_2O_H^+ + OH^-)$ to a degree far greater than the equilibrium concentration $([H^+] [OH^-] = 10^{-14} (mole/dm^3)^2$. The H⁺ ions produced at the anode and OH⁻ at the cathode carry currents in addition to the copper ions. This means that the measured value of *I* is no longer the proper value to substitute into the Faraday equation. Evolution of gas at either electrode is the signal that water is being dissociated. Therefore, one needs to find by trial and error a condition in which no gas bubbles are observed.

As you increase the current (I) starting from zero, the polarization potentials increase. Gas is observed when the polarization potential crosses the energy threshold for the particular dissociation process involved.



This diagram shows chemical processes at anode and cathode when the polarization potential exceed the thresholds for ionization of water. Note: occurrence of gas bubbles is a sign that unwanted ions participate.

Problems: Design of the absolute ammeter with 1% accuracy

These are the kind of estimates that a competent experimenter would make before starting work in the lab.

Complete this set <u>before the first lab</u>. Write the solutions in your lab book. Turn in a Xerox copy for grading before the lab talk begins. Grades will be reduced by 50% for problems turned in after that talk.

Do your calculations in SI units (m, kg, sec, N, J, A, Tesla...). If an instrument measures in other units, or manufacturers data are so given, convert them to SI units before starting the calculations.

Permanent magnets have been chosen so that their angular periods in the earth's field (B_E) are easy to measure by eye. <u>Rough measurements</u> on a typical magnet (Edmund #A30724, \$2.25) gave values: length $l \approx 1$ ", diameter $d \approx 3/16$ ", quoted density of "alnico" $\rho = 7.3$ gm/cm³, period in earth's field $T_E \approx 1$ sec, $T_O > 20$ sec, null distance $Z_n \approx 15$ cm. Assume these values for planning purposes.

1. Measurement of Period

(a) Check that the given formula is correct. From the equation of motion of the magnet $(I\ddot{\theta} = \Gamma)$, show that the period (**T**) of small amplitude oscillations is given by the following equation. Check that the solution of the differential equation $(\ddot{\theta} + \omega^2 \theta) = 0$ is given by $\theta = \theta_0 \cos(\omega t)$. Identify any approximations that you use.

$$T = 2\pi \sqrt{\frac{\mathsf{I}}{m(B_c + B_E) + \kappa}}$$

- (b) Investigate possible systematic errors. For larger amplitudes (θ_0), the above equation predicts a period that is too short. Estimate the fractional difference in period between oscillations of negligible amplitude (say 1°), and oscillations with θ_0 =45°. How small must θ_0 be if the "error" in period is to be less than 1%? List other possible systematics.
- (c) Plan a procedure to control random errors of measurement. The uncertainty in period can be reduced by timing a sufficiently large number of oscillations. Suppose that a rough observation gives a period (T) of about 1 sec., and that your random uncertainty in timing with the stopwatch is $\delta t \approx \pm 1/10$ sec. For how long a total time

(*t*) must you run the stopwatch to get 1% accuracy in *t*? How many oscillations must you time to achieve 1% accuracy for period (T)?

- (d) Plan to control errors due to mistakes in measurement. Everyone makes mistakes: one needs a simple strategy to catch these quickly. A common mistake is to miscount by one the total number of cycles. What is the minimum number of measurements of T you should make: (i) if the first two values agree within the expected 1%; or (ii) if they disagree? How would you check unconscious perisistant mistakes in personal style of working?
- 2. Instrument equation and calibration constant of the ammeter
 - (a) Suppose that you have measured the values of I, I', T_E , T_0 , and Z_n . Show that the horizontal components of the earth's field B_E , and the dipole moment of the magnet, (*m*), can be found in terms of them by the equations:

$$B_{E} = \left(2\pi\mu_{0} \cdot \frac{\mathrm{I}}{Z_{n}^{3}}\right)^{\frac{1}{2}} \cdot \left(\frac{1}{T_{E}^{2}} - \frac{\mathrm{I}'}{\mathrm{I}} \cdot \frac{1}{T_{0}^{2}}\right)^{\frac{1}{2}}$$
$$m = \left(\frac{8\pi^{3}}{\mu_{0}} \cdot \mathrm{I}Z_{n}^{3}\right)^{\frac{1}{2}} \cdot \left(\frac{1}{T_{E}^{2}} - \frac{\mathrm{I}'}{\mathrm{I}} \cdot \frac{1}{T_{0}^{2}}\right)^{\frac{1}{2}}$$

(b) Show that the current, I, flowing through the Helmholtz coils when the small magnet is observed to oscillate with period T is given by the equation:

$$I = C \left(\frac{1}{T^2} - \frac{1}{T_E^2} \right), \quad where \quad C = \left(\frac{5^{\frac{3}{2}} \pi^2}{2\mu_0} \right) \cdot \frac{\mathrm{I}a}{mN}$$

(c) Required accuracies of measurements

What are the % uncertainties in *m* and B_E respectively for 1% errors in each of T_E , T_0 , I, Z_n , and *a*? First calculate the separate contributions ($\Delta Z_n/Z_n$, etc). Then combine them quadratically to give a total % uncertainty for *m* and B_E .

3. Design of Helmholtz Coils



Fig 1.2 A typical design of absolute ammeter built by a number of students in the past. Many variations of this design are possible.

- (a) Estimate the lab value of the earth's field (B_E) from data on the magnet given above problem 1. Check your result by comparing with the value of B_E in the data tables. It could differ by up to a factor of two due to magnetic materials in the lab.
- (b) What is the minimum radius a of the coils such that the field is uniform within 1% over the length of the dipole magnet (see equation 9).
- (c) The coil field (B_C) should be strong enough that the period (T) of the magnet in the field B_C is easily distinguishable from the period (T_E) in the earth's field alone.

(d) Assume that I = 1 amp. and the coil radius (a) has the value chosen in part (b). Calculate the number of turns, (N), of wire needed on each coil so that $B_C = 4 B_E$. Round off N to an integer.

Calculate the value of calibration constant *C* and its % uncertainty.