

Constant-Current Coulometric Titration of Hydrochloric Acid

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The titration of a strong acid with a strong base and the electrolysis of water are two classic laboratory exercises that are either performed or demonstrated in secondary school classrooms in order to introduce two important areas of chemistry: acid–base chemistry and electrochemistry. In this experiment we have combined these two classical experiments into one complete laboratory experience. Here we report how the electrolysis of an aqueous solution can be used to determine the concentration of hydrochloric acid in a coulometric titration.

This experiment is an adaptation of one developed at the University of Arkansas–Fayetteville and is currently used in the sophomore analytical chemistry laboratory (Paul, D.; Wisman, J., unpublished). The experiment has been refined so that it can be performed quickly and inexpensively, with materials available in secondary school classes, serving as good examples of both electrochemistry and acid–base titration. The student procedure for the coulometric titration of hydrochloric acid is easy to perform and gives results as good as those first reported by Badoz–Lambling (1).

Chemists frequently wish to know the concentration of an acid in solution. One reliable method used is volumetric titration in which the number of acid equivalents reacts with the same number of base equivalents, as shown in eq 1:

$$\text{no. of equiv of acid} = \text{no. of equiv of base} \quad (1)$$

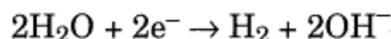
For an acid–base reaction, an equivalent (equiv) is the number of moles of reagent that can donate or accept one mole of protons.

In a titration, the volume of standardized base needed to completely react with the acid is accurately measured using a buret. If the volume of the titrated acid solution is known, then the concentration of the acid can be determined by rewriting eq 1:

$$n_A \times M_A \times V_A = n_B \times M_B \times V_B \quad (2)$$

In eq 2, the molarity M of acid (subscript A) or base (subscript B) times n is the normality (equiv/L), where n_A or n_B are the number of hydrogen ions donated or accepted by the acid and base, respectively.

In the electrolysis of water, two molecules of water take two electrons from the cathode and form hydrogen gas and hydroxide ion (2), or:



At the anode, hydrogen ions and oxygen gas are produced, and the reaction at the anode is:



In a traditional electrolysis demonstration the oxygen and hydrogen are collected in a Hoffman apparatus, showing the students that twice as much hydrogen as oxygen is produced during the electrolysis.

For oxidation–reduction reactions, an equivalent (equiv) is the number of moles of reagent that can donate

or accept one mole of electrons. Normality is then n times the molarity of a red–ox reagent, where n is the number of electrons donated or accepted by that species in a particular reaction.

As with any chemical reaction, the quantity of products produced will depend upon the limiting reagent. The most convenient limiting reagent in the electrochemical production of hydroxide ions is the number of electrons added to water. Electrons are very hard to count but the charge they carry with them is very easy to monitor (3). The rate at which charge passes is called the current (in amperes) and has the units of *coulombs/second* ($A = C/s$). The charge that passes, Q , can be calculated by:

$$Q = i \times t \quad (3)$$

where i is the value of the current and t is the elapsed time since the start of the electrolysis (4). If a constant current is forced through the electrode, then the charge that passes during the electrolysis is directly proportional to the elapsed time.

Michael Faraday related the charge that passes through an electrode to the amount of chemistry done at the surface of the electrode by the relationship:

$$F = Q/\text{equiv} \quad (4)$$

Here F is the value of the faraday or Faraday's constant, which is equal to 96,483 coulombs/equiv. One faraday is then the charge on one mole of electrons. At the cathode, the charge that passes through the electrodes is directly proportional to the number of moles of hydroxide generated. This resulting charge can be calculated from eq 4 as shown below:

$$Q = (96,483 \text{ C/equiv}) \times (2 \text{ equiv/2mol OH}^-) \times \text{mol OH}^- \text{ produced}$$

Noting that there is a 1:1 ratio between the number moles of OH^- produced and the number of electrical equivalents, eq 2 can then be rewritten as:

$$n_A M_A V_A = \text{equiv} \quad (5)$$

Substituting eq 3 and 4 into eq 5 we can calculate the molar concentration of the acid as:

$$M_A = it/FV_A n_A \quad (6)$$

which relates the time needed to reach the end point of the titration to the concentration of the acid. Therefore if a constant current is passed through the cell causing the production of hydroxide ions, the time needed to neutralize all the acid is directly proportional to the concentration of the acid. The students must measure the time needed to reach the end point of the titration in order to determine the concentration of the acid. In the example give here, the electrochemical production of hydroxide ions continues until the indicator change signals the end point of the titration.

In contrast to volumetric acid–base titrations in which an additional titration is needed to standardize the titrant, determination by coulometric titration can be done in a single experiment. Using a current to generate a reactant can save time and the cost of the chemicals and achieves the same result as adding the reagent by volume (5).

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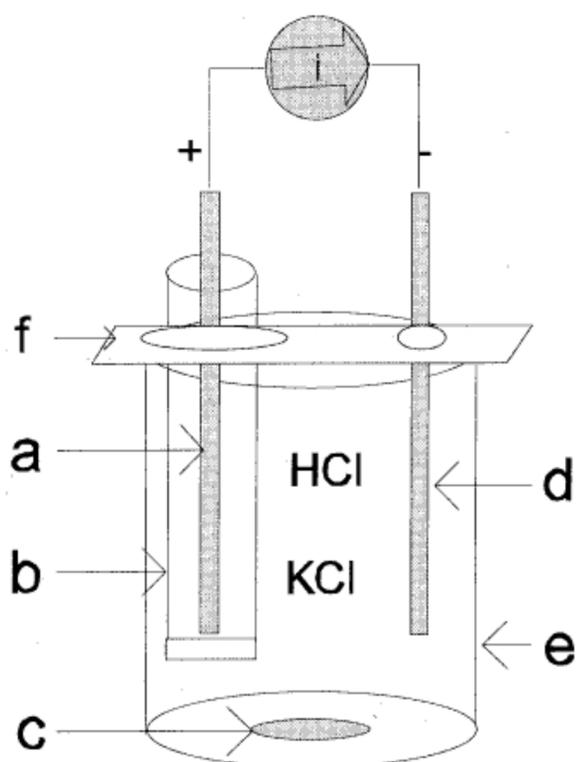


Figure 1. Electrochemical Cell. (a) Counter electrode (anode). (b) Anode compartment. (c) Stir bar. (d) Generator electrode (cathode). (e) Reaction vessel. (f) Cork stopper or piece of dense foam insulation. (i) Current source.

Electrochemical Cell

The electrochemical cell shown in Figure 1 uses a 200-mL Berzelius beaker and two carbon electrodes (6–12). The cell is placed in series with a current source (see below) that generates a constant current through the cell. Electrochemical oxidation occurs at the anode and electrochemical reduction occurs at the cathode. The passage of charge through the solution is facilitated by using an electrolyte solution of saturated KCl. The salt can par-

ticipate in the electrochemical reaction and this will be discussed further.

Constant Current Source

A schematic diagram for the current source is shown in Figure 2a along with the wiring requirements in Figure 2b. The active components of the current source are housed in a plastic box $19 \times 11 \times 6.0$ cm, as shown in Figure 3. After construction the current source was calibrated for an output current to four significant figures using a Keithley 179 Digital Multimeter. The current source constructed with the components in Table 1 furnished a constant current of 124 mA. The current was found to be constant to ± 0.01 mA throughout a 70-s titration of the acid.

The leads from the current source should be color-coded so that the students will know how to attach the current source to the cell. In this work, a red wire was used for the anode lead, marked with a “+” in Figure 2, and a black wire was used for the cathode lead, marked with a “-” in Figure 2. Further details are available from the authors upon request.

Instructor's Notes

Good results were obtained using 10-mL aliquots for the student's unknown HCl with aliquot concentrations up to 0.05 M HCl. The higher concentrations required 10 min to reach the end point. Since the experiment should be performed several times, higher concentrations of the student's unknown HCl should be avoided, as the total amount of time needed is not available in a typical high school laboratory. The results presented here were obtained by adding a 10-mL aliquot of 0.006 M HCl to the reaction vessel, needing only about 1 min for neutralization. Lower concentrations allow the students ample of time to run several trials in a 50 min class period.

The student's unknown HCl solution was standardized by using a sodium hydroxide solution that had been previously standardized by a volumetric titration with solid potassium hydrogen phthalate as a primary standard.

Equipment

The following is a list of equipment needed per lab group to perform the experiment. Two students per “lab

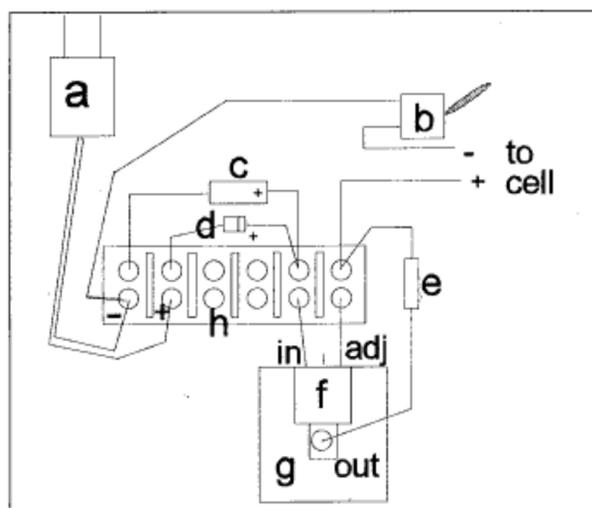
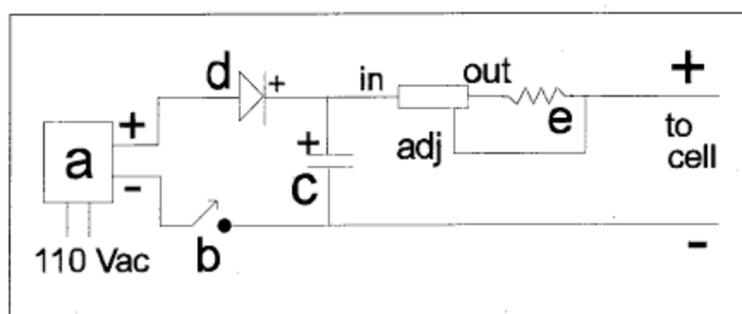


Figure 2. Current source (above) and wiring requirements for current source (below). (a) 9-V AC adapter. (b) Switch. (c) $4.7 \mu\text{F}/35 \text{ V}$ capacitor. (d) Diode. (e) 10Ω resistor. (f) LM317T regulator. (g) Heat sink. (h) Terminal strip.

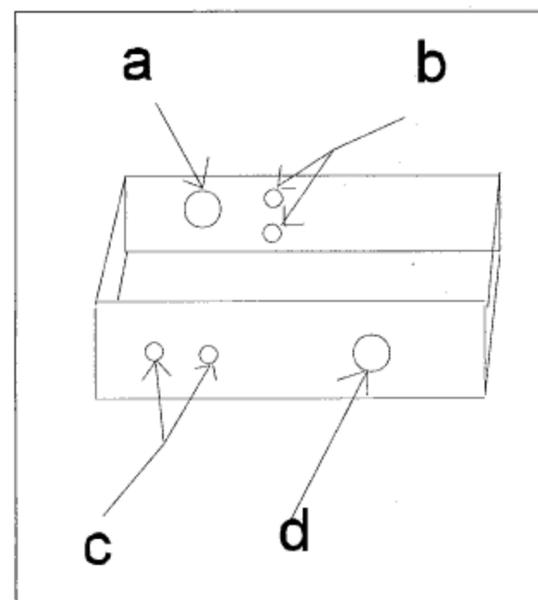


Figure 3. (a) Hole for 9-V AC adapter line. (b) Holes for cable ties, holding AC adapter line. (c) Holes for leads to cell. (d) Hole for spst switch.

group" is ideal, as one student can operate the current source and the other the stop watch.

- 1 current generator
- 1 200-mL beaker (Berzelius)
- 1 electrode apparatus
- 1 10-mL pipet or graduated cylinder
- 1 stop watch or second hand
- 1 magnetic stirrer or stirring rod
- 2 250-mL beakers (for solutions)

Chemical Reagents Required

Very few chemicals are required to perform the experiment. The following is a list of chemicals required for each lab group.

- 50 mL student's hydrochloric acid (HCl) unknown (enough for five trials)
- phenolphthalein indicator
- 150 mL potassium chloride (KCl) saturated solution (enough to fill the cell three times)

The Student Laboratory

The following is the general outline of the text given to the students in the laboratory.

Introduction

In this experiment the molarity of an HCl solution will be determined by coulometric titration (1). Hydrogen ions from the acid are consumed by electrochemical reduction reactions that occur at the cathode. The electrolysis of the acidic solution is made possible by a constant current source that drives a current through the cell. The anode is isolated in a separate compartment by a porous glass sheath (13).

Procedure

1. Set up the equipment as shown in Figure 1.
2. Attach the electrodes to the leads from the current source, making sure that the red lead is connected to the anode (the electrode protected by the porous glass sheath) and the black lead to the cathode.
3. Check that the switch is in the off position.

4. Add 50 mL of saturated potassium chloride solution to the cell. The electrodes must be covered.
5. Add 2–3 drops of phenolphthalein indicator.
6. Pipet 10 mL of unknown HCl solution into the reaction vessel.
7. Turn on the magnetic stirrer.
8. In one motion, turn the switch to the "on" position and start a stop watch.
9. As soon as the indicator changes color, turn off the current, and the stop watch. The solution must remain pink after the current has stopped.
10. Record the time needed to reach the end point in seconds.
11. Repeat the procedure until three values are within 5 s of one another.
12. Record the level of current produced by your current source.

Fresh electrolyte solution need not be used with each sample. If the end point is not overshoot and there is room in the coulometer cell, another aliquot may be added to the cell, the timer reset to zero, and another titration performed. This may be done two additional times before the electrolyte solution is changed. When the electrolyte solution is changed, be certain to clean the anode compartment with distilled water before continuing the titration.

Safety Precautions

1. Dilute HCl will stain, cause mild burns, and irritate lungs and eyes. Avoid contact and inhalation. Rinse spills with plenty of water.
2. Wear chemical splash goggles and laboratory aprons during this experiment.
3. Small amounts of hydrogen, oxygen, and/or chlorine gas are produced at the electrodes; be sure to work in a well ventilated area and make sure no open flames are present.

Disposal

Any leftover hydrochloric acid and/or potassium chloride solution can be washed down the drain with plenty of water.

Table 1. Component List for Current Source and Electrodes

Item	Supplier	Catalog	Cost (\$)
2 carbon electrodes	Sargent-Welch	2208	16.15 pkg 12
1 fritted glass tube 12-mm o.d. Por. D	Ace Glass	7209-08	15.18
1 plastic box	Radio Shack	270-224	3.49
1 heat sink	Radio Shack	276-1363	0.99
1 LM317T regulator	Radio Shack	276-1778	1.99
1 10- Ω resistor	Radio Shack	271-001	0.49 pkg 5
1 capacitor 4.7 μ F/35 V	Radio Shack	272-1012	0.49
12 machine nuts 6-32 sz	Radio Shack	64-3019	1.39 pkg 30
12 machine screws 6-32 sz	Radio Shack	64-3012	1.39 pkg 42
2 alligator clips	Radio Shack	270-347	2.29 pkg 10
1 switch	Radio Shack	275-1533	1.89
1 9-V AC 300 mA adapter	Radio Shack	273-1455	7.99
1 diode IN4001	Radio Shack	276-1101	0.49 pkg 2
1 terminal plate 6 place	Radio Shack	274-659	1.59
24 in. red wire	Radio Shack	278-563	2.99 spool
24 in. black wire	Radio Shack	278-564	2.99 spool
2 plastic ties	Radio Shack	278-1652	2.99 pkg 30
4 spade terminal ends	Radio Shack	64-3031	1.39 pkg 24

Sample Calculations

For example, if the current source generated a current of 0.1030 A, and 64.5 s was needed to reach the end point, the acid concentration may be determined by eq 6:

$$\begin{aligned} \text{acid molarity} &= \frac{0.1030 \text{ C/s} \times 64.5 \text{ s}}{98,483 \text{ C/equiv} \times 0.0100 \text{ L} \times 1 \text{ equiv/mole acid}} \\ &= 6.89 \times 10^{-3} \text{ M} \end{aligned}$$

If the actual molarity (known to your instructor) of the unknown acid was $6.72 \times 10^{-3} \text{ M}$, then the percentage error (% err) in this experiment may be calculated as follows:

$$\% \text{ err} = \frac{\text{experimental value} - \text{actual value}}{\text{actual value}} \times 100 \quad (7)$$

A sample calculation would be:

$$\% \text{ err} = \frac{6.89 \times 10^{-3} \text{ M} - 6.72 \times 10^{-3} \text{ M}}{6.72 \times 10^{-3} \text{ M}} \times 100 = 2.53\%$$

Questions for Students

In the student write-up for this experiment, the following are some good questions that may be asked of the students.

What is the electrochemical reaction at the anode? Why is it important to keep the anode encased in a separate compartment? What sources of systematic error are found in this experiment? Write an overall cell reaction. What other electrode reactions may occur at the generator electrode? Would these effect the calculated molarity for the HCl unknown? Calculate the molarity of your unknown HCl solution. Obtain the actual molarity of your acid solution, and calculate your percentage error for this experiment.

Results and Discussion

A limiting factor in performing a coulometric experiment at the secondary school level is the cost of the coulometer. Research-grade coulometers cost several thousand dollars. However, an inexpensive current source can be constructed using the materials shown in Table 1 for approximately \$20 per unit. The constant current source has only four components: an integrated circuit called a regulator, a capacitor, a diode, and a resistor. A terminal strip used in the construction avoids the need for a soldering iron or a printed circuit board. This current source will deliver a constant current without the need for additional adjustments, simplifying the procedure for high school students. Batteries were initially used as the power

Table 2. Coulometric Titration of HCl Using 6-mm Carbon Electrodes

Trial Run	Time (s) ^a	[HCl] (M)	Current (A)
1	60.11	6.33×10^{-3}	0.1030
2	58.80	6.33×10^{-3}	0.1030
3	58.03	6.33×10^{-3}	0.1030
4	58.83	6.33×10^{-3}	0.1030

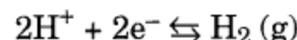
^aAll four times were used in the calculations.

source, but over a period of time they required repeated replacement (14–16). A 9-V AC adapter not only eliminates the need for batteries but also lowers the voltage and current to a safe level for student use.

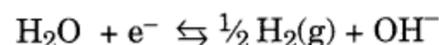
Initially the apparatus used platinum electrodes, so two inexpensive materials were tried as substitutes (14, 17). Copper wire electrodes proved to be unsuitable because, being more easily oxidized than water, they distorted the results 37% above the predicted value for the analysis. Electrodes constructed of easily available mechanical pencil leads was also tried in an effort to keep costs down. Despite good precision, times obtained were about 27% above the accepted value. The poor performance was thought to be due to a plastic coating that might be on the pencil lead. Therefore, we sanded the plastic coating off the end of the pencil leads and repeated the experiment. The results were still about 16% above the accepted value.

Two carbon electrodes, 6 mm in diameter and 127 mm long, gave the best results. Table 2 shows four trials that were done without changing the KCl electrolyte solution. The average calculated concentration obtained from this data for the acid was $6.29 \times 10^{-3} \text{ M}$. This represents a 0.6% error from the volumetrically determined molarity of the HCl. In step number 11 of the student's procedure, students were asked to repeat the experiment until three time trials are within 5 s of each other. For a 60-s titration, a 5-s spread gives a precision of 9%. With patience and care, a 1% level of precision is easy to achieve, but because the students have diverse levels of interest in the laboratory, the precision of the experiment was relaxed a bit, in hope of reducing student frustration.

There are two possible reactions that may take place at the cathode. In acidic solutions the primary reaction at the cathode is the reduction of the hydrogen ion to hydrogen:

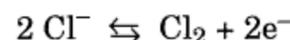
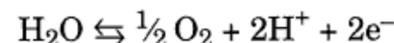


When the supply of hydrogen ions at the electrode surface is inadequate to maintain the constant current, then the reduction of water will occur.

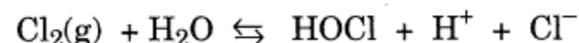


In the weak acid solution used here, the second reaction dominates and bubbles are observed streaming from the cathode. Both electrochemical reactions result in the quantitative consumption of the acid, either by direct reduction or by indirect reaction with electrochemically produced hydroxide.

At the anode the two possible oxidation reactions are:



If only water is available, water is oxidized, but in chloride solutions chlorine is produced (18). Chlorine is a powerful oxidizing agent and reacts with water to produce acids.



Either reaction results in the production of acid in the anode compartment.

We discovered that hydrogen ions leaking from the anode compartment seriously compromised accuracy when electrolysis took longer than 15 min. At a fixed current, the neutralization of larger concentrations of acid took so long that the acid in the anode compartment had time to diffuse into the main reaction chamber and con-

taminate the sample. For higher concentrations of acid, electrolysis could be shortened by increasing the level of the current, but an adjustable current source would cost more and be more difficult for students to operate. The area of the electrode also affects the duration of electrolysis. Because they are so thin, pencil leads require longer electrolysis times than the larger commercial carbon electrodes.

Another possible complication is the presence of dissolved carbon dioxide in the solutions in the form of carbonic acid. This problem was not addressed, since we are dealing with a high school laboratory that does not require the degree of accuracy expected in the college setting.

In summary, the low-cost constant-current source described here can be successfully used to determine the concentration of hydrochloric acid in a coulometric titration. The use of carbon electrodes and readily available chemicals makes the experiment a good choice for illustrating, with one experiment, electrochemistry and acid-base titrations, as well as analytical techniques not normally covered in a high school curriculum.

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Testing the Electrical Resistivity of Wax and Copper Composites

An Experiment for Simulating the Electrical Behavior of Metal-Filled Plastics

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Conducting polymers are playing an important role in the evolution of understanding of materials. One class of these materials is metal-filled plastics. These mixtures have gained a large area of application—for example, for electromagnetic/radio-frequency interferences (EMI/RFI) shielding in electronic instruments, antistatic purposes in electronic devices, preparation of hybrid microelectronic circuits, and die attach adhesives (1-7).

The predominance of solution chemistry in both lecture examples and laboratory experiments, together with the high cost and complexity inherent in the apparatus, provides an obstacle to the integration of new technologies (such as processing techniques for the fabrication of filled particulate plastics) that normally include compression molding or extrusion (8, 9). The purpose of this article is to provide teachers at many levels with both theoretical and practical information for classroom use, through an experiment simulating the electrical behavior of metal-filled plastics. The experiment is inexpensive to construct and easy to perform. General references have been included as an introduction to the vast literature on the electrical conductivity of insulator-conductor composites.

The basic problem of a conductive polymer mixture (compounding of polymer with conductive filler such as metal powder or carbon black) is the dependence of the electrical conductivity (or inverse resistivity) of the mixtures on the conductivity filler content. This dependence

is surprising. It is generally known that electrical resistivity does not decrease continuously with increasing filler content. Rather, there is a critical composition of the conductive filler (the "percolation concentration") at which resistivity drops by several orders of magnitude from the insulating range (most polymers are insulators) to a value in the semiconductor or metallic range. An insulator has resistivities in the range of 10^{18} – 10^7 Ω cm, a semiconductor in the range of 10^7 – 10^3 Ω cm, and the range for a conductor is usually given as 10^3 – 10^{-6} Ω cm (10). Decreases of 13–16 orders of magnitude in the resistivity of polymers are not uncommon when conducting fillers are added.

A classical theoretical explanation of this characteristic of electrically conductive polymer composites is that electrical resistivity is not much affected by addition of the conductive filler until the lower percolation concentration is reached, at which point chains and nets of contacting conductive filler particles first appear in the polymeric host. This marks the beginning of the sharp decline in electrical resistivity. As the filler concentration is increased beyond this lower concentration, the number of conducting particles in the particle chains and nets increases until a second critical point, the upper percolation concentration, is reached. At this point the best quality conductive particle network should be established. Figure 1 illustrates the essence of the percolation theory. The circles represent conductive particle fillers. At low fractions of fillers, the conductive particles are disconnected