

Introducing Undergraduate Students to Electrochemistry: A Two-Week Discovery Chemistry Experiment

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The Holy Cross Chemistry Department has designed and implemented a series of experiments for our four-course introductory chemistry sequence that we call Discovery Chemistry¹ (1–9). Discovery Chemistry is a teaching approach based on guided-inquiry, which reverses the traditional order of introducing chemical concepts in lecture followed by laboratory exercises as reinforcement. Instead, a question is posed at the beginning of a laboratory session. Students suggest possible solutions or methods for examining the question. They work in small groups and their data are pooled. The data are used as the basis for discussion in the lecture, giving students ownership of the learning process and training them to use the scientific method in their studies.

Electrochemistry often is considered a difficult topic to learn and teach, and it has been shown that learning through textbook reading and lecture can lead to student misconceptions (10–12). Therefore, we have designed a two-week laboratory exercise to address these difficulties by the Discovery model (2). This experiment has been improved extensively over fifteen years by examining a variety of systems and modifying experimental conditions, and now gives reproducible results.

Experimental Design and Results

In the first week of the lab experiment, students create a plot of E_{cell} as a function of Q for one of five reduction half-reactions measured against a common oxidation half-reaction. By the use of data pooling from five different systems, students discover the general form of the Nernst equation. In part two of the first week, student groups team to predict and measure the E_{cell} value for a reaction that couples two of the reduction half-cells from part one, and discover which half-reaction serves as the oxidation. In the second week, students use their discoveries from week one and the intervening lectures to calculate formation constants of two complex ions of silver using electrochemical data, and discover concentration cells using a quinone/hydroquinone system to measure the potential difference due to a pH difference between two half-cells.

For the first week of lab, student data are used to discover the Nernst equation, to calculate E° values for half-reactions, and to calculate the overall E_{cell}° . We begin with a 45-minute pre-lab. The previous week's qualitative analysis lab makes use of redox reactions, so we have reviewed reduction and oxidation half-reactions and how to balance them. For this week's pre-lab, we

start by describing a diagram of a typical galvanic cell. We show a model plot of Gibbs energy versus reaction coordinate, and ask the students to make the connection between the large potential difference between the anode and cathode and the cell's ability to do work. This is an opportunity to reinforce issues that confuse many introductory students, including the difference between a reaction with a large equilibrium constant that is at equilibrium (using the analogy of a dead battery) and a reaction with a smaller equilibrium constant at conditions far from equilibrium. We also discuss that reactions can be either spontaneous or have large equilibrium constants, yet proceed very slowly.

The discovery question that is posed for the lab is "What is the relationship between the cell potential and the value of the reaction quotient, Q ?" To test this, we use a standard silver/silver chloride reference electrode as the oxidation half-cell, saturated with 4.2 M KCl, and couple this to five separate reduction half-cells: $\text{Ag}^+|\text{Ag}$, $\text{Fe}^{3+}|\text{Fe}^{2+}$, quinone/hydroquinone, $\text{I}_3^-|\text{I}^-$, and $\text{Cu}^{2+}|\text{Cu}$. The first two reductions are one-electron processes, and the last three are two-electron processes, which aids in the discovery of the Nernst equation. Students are instructed to generate a plot of E_{cell} as a function of the reaction quotient, Q , as well as E_{cell} as a function of $\ln Q$ (or $\log Q$, depending on instructor preference). Students are given stock solutions for one of the five reduction half-reactions and detailed instructions for how to prepare working solutions.²

Students make the E_{cell} measurements and return to the prelab classroom to calculate their values of Q . They generate the plots using Microsoft Office Excel and are instructed to make a linear best-fit trendline to both plots, using the R^2 value to decide which plot is more linear.³ They add their slope and y -intercept data to a table on the board, and the instructor prepares overhead transparencies of the plots. (Examples of these plots are given in Figure 1.) Pooled student data from 2007 are reported in Table 1.

Students are asked to make observations about the values for the slope. They are able to group the slopes into two categories, one for the one-electron reactions and another for the two-electron reactions, and conclude that the slope must contain a term of $1/n$. Next they compare the y intercepts, and see that there is no trend and that the value depends upon the reaction. Various approaches have been used to discover that the Nernst equation can account for each group's data. We discuss the other factors that influence the slope, and show how the y -intercept is E_{cell}° by setting $Q = 1$.

In part two of the first lab, the discovery question is, “Can the reduction potentials we determined against a common oxidation half-cell be used to estimate E_{cell} if two reduction half-cells are used to construct a cell?” Students are instructed to prepare another reduction half-cell and measure it against the Ag|AgCl reference. Each group is assigned a partner group that has a different reduction half-reaction. From pre-lab discussion, the students know that a spontaneous reaction should give a

positive E_{cell} . Together, the partner groups are asked to predict E_{cell} for a reaction composed of the two assigned reduction reactions. First, they attach the red lead to the electrode of the predicted reduction reaction (i.e., the one with the higher E_{cell} versus the reference). Then they attach the black lead to the predicted oxidation reaction and connect the half-cells using a string soaked in 1 M KNO_3 as a salt bridge. They measure E_{cell} and compare it to their prediction. They are asked to predict

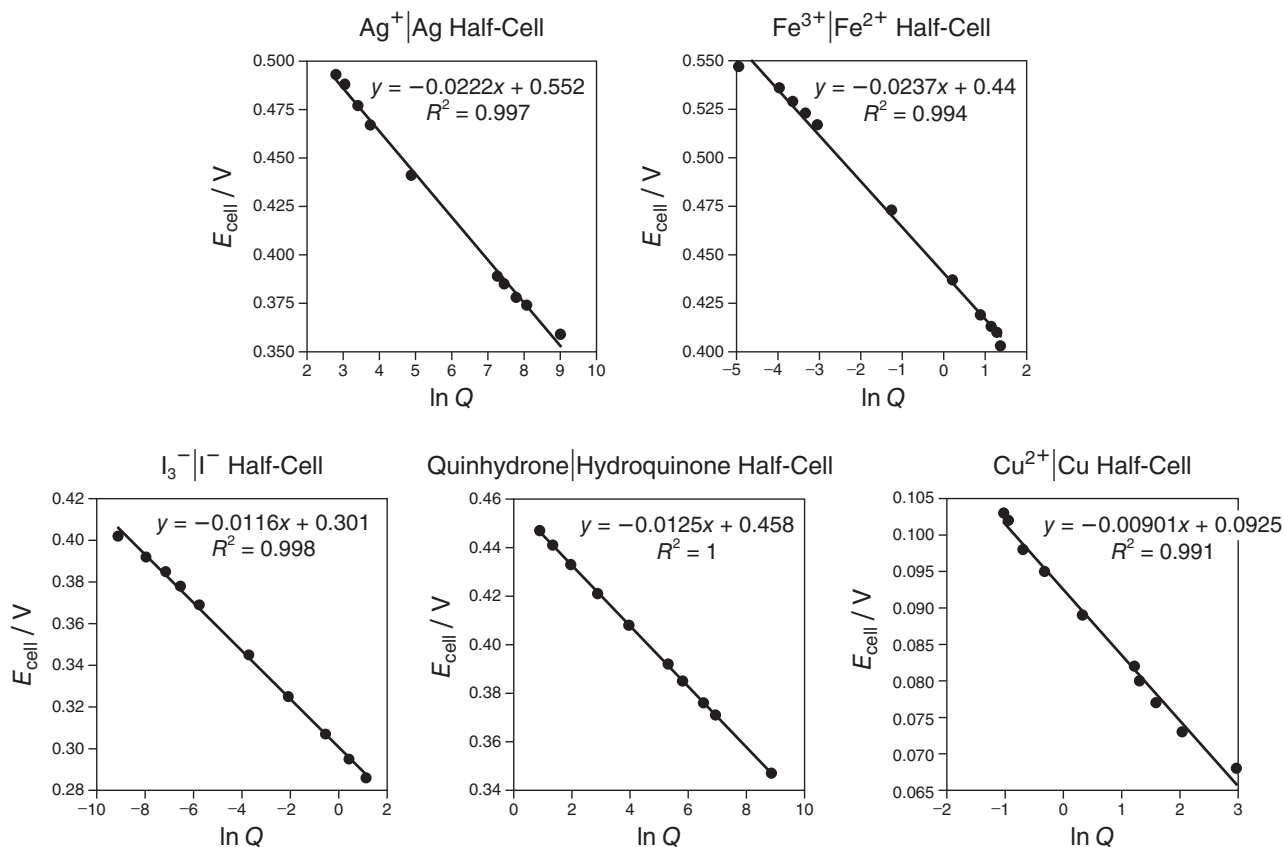


Figure 1. Representative student data for plots from part one of lab one in which students discover the Nernst equation. Data were fit by a linear least-squares analysis using KaleidaGraph (Synergy Software).

Table 1. Distribution of Pooled Student Data Collected in Spring 2007

Type of Reduction Half-Cell (Numbers of Student Groups)	Average Slope Values (SD)/V ¹	Average y-Intercept Values (SD)/V	Literature Values ² for $E_{\text{cell}}^{\circ} / \text{V}$
Ag ⁺ Ag (12)	-0.024 (0.003)	0.556 (0.017)	0.60
Fe ³⁺ Fe ²⁺ (11)	-0.023 (0.002)	0.442 (0.011)	0.48 ⁴
I ₃ ⁻ I ⁻ (10)	-0.011 (0.002)	0.291 (0.014)	0.34
Cu ²⁺ Cu (12)	-0.013 (0.003)	0.092 (0.012)	0.14
Qu H ₂ Qu ³ (9)	-0.012 (0.001)	0.450 (0.010)	0.50

¹Average slope of plot of E_{cell} versus $\ln Q$. Expected values -0.026 V or -0.013 V.

²Based on E_{cell}° (16) vs Ag|AgCl standard oxidation, with 4.2 M KCl, assuming E_{ox}° of -0.199 V vs standard hydrogen electrode, the literature value for a reference electrode with saturated KCl at 25 °C (17).

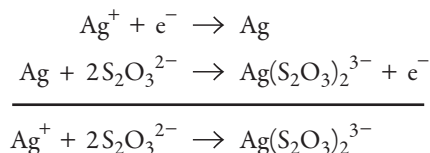
³Quinhydrone|hydroquinone.

⁴The standard potential would be 0.57 V in neutral water, but in 1 M sulfuric acid the formal potential is 0.48 V (17). Our protocol uses a varying amount of sulfuric acid. Following the protocol distributed to students, we obtained a potential of 0.456 V. Maintaining a constant 1 M sulfuric acid concentration, we obtained a potential of 0.460 V.

what would happen to the value if they switched the leads, and then check their prediction. The assigned groupings and concentrations avoid any E_{cell} values close to zero volts.

During the three lectures between the labs, we review the student data and conclusions about the Nernst equation. As a post-lab assignment, students are asked to calculate E_{cell}° for their assigned redox reaction in part two using the y -intercept values from both their plot and that of their partner group from part one. They are also asked to calculate the predicted E_{cell}° given their measured E_{cell} and the calculated Q value from part two. We review these calculations in the lecture, which leads into a discussion of the standard hydrogen electrode and using tables of standard reduction potentials to predict the size of the equilibrium constant, K , and the spontaneity at standard states for reactions of interest, including those related to corrosion and galvanic protection. We use the data from the $\text{Ag}^+|\text{Ag}$ group to show how their predicted E_{cell}° value can be used to calculate the solubility product constant, K_{sp} , of AgCl , which leads into the lab for week 2.⁴ Using the data in Table 1, one calculates a K_{sp} of 3.9×10^{-10} , compared to a literature value of 1.8×10^{-10} (13).

During week two, the first discovery question posed to the students is, "Can we use the electrochemical data of a system far from equilibrium to predict the equilibrium constant of a reaction that is not a redox reaction?" The equilibrium constant they calculate is the formation constant of either $\text{Ag}(\text{NH}_3)_2^+$ or $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$. In the pre-lab session, we remind them of our calculation of the K_{sp} of silver chloride and the definition of the formation constant, K_{f} , of $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$, which we used in our qualitative analysis lab. We ask them to suggest two half-reactions to calculate the E_{cell} of the formation reaction. After prompting they suggest:



Drawing on the discovery from the previous week, the students predict E_{cell} for the overall reaction using E_{cell} values for each of the reduction reactions measured against the common oxidation $\text{Ag}|\text{AgCl}$. Students make two half-cells that are each 0.0010 M in AgNO_3 . To create the silver complex, they pipet either 5.0 mL of 6.0 M ammonia or 5.0 mL of 0.1 M sodium thiosulfate into one of the two beakers. They measure the potential of each half-reaction versus the reference electrode, and then predict E_{cell} for the overall reaction. Students verify both their data and their prediction by measuring E_{cell} of the two cells coupled directly. The students calculate the Q value for the overall reaction, with the silver ion concentration from the cathode and the complex ion and free ammonia or thiosulfate concentrations from the anode. They are told to assume that K_{f} is very large, so that the complex ion forms to completion when calculating the concentrations in the anode. With E_{cell} and Q in hand, they can predict E_{cell}° and calculate the K_{f} . They are asked to compare this to a literature value. The class works in small groups, half studying the thiosulfate system and the other half studying the ammonia system.⁵

For our spring 2007 sections, the average E_{cell}° value for the $\text{Ag}(\text{NH}_3)_2^+$ system was 0.425 V ($N = 26$, standard deviation = 0.018 V), and for $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ was 0.819 V ($N = 28$, standard

deviation = 0.158 V). This results in average K_{f} values of 1.5×10^7 for $\text{Ag}(\text{NH}_3)_2^+$ and 7.1×10^{13} for $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$, compared to literature values of 1.6×10^7 and 1.7×10^{13} , respectively (13), assuming a temperature of 298 K.

In part 2, the discovery question is, "Will two identical half-reactions that differ in concentration generate a potential difference?" In the pre-lab session, we use the example of a $\text{Ag}^+|\text{Ag}$ half-cell with 1.0 M silver ion as the cathode, and a $\text{Ag}|\text{Ag}^+$ with 0.1 M silver ion as the anode. We ask students to balance the redox reaction, and whether they would expect a value for E_{cell} . This is a good opportunity to remind students of the difference between E_{cell} and E_{cell}° , and reinforces the concept that E_{cell} is zero at equilibrium. We connect to our earlier lab about thermodynamics and entropy. Students proceed into the lab to make two quinhydrone/hydroquinone half-cells, one half-cell using 0.10 M HNO_3 and one with 0.0010 M HNO_3 . They measure each against the standard oxidation of the $\text{Ag}|\text{AgCl}$ electrode, and are asked to predict which half-cell would serve as the cathode in a combined cell based on the relative reduction potentials against the common oxidation. They check their prediction, and compare this to the E_{cell} that they would predict based on their calculated value for the reaction quotient using the Nernst equation. Students generally calculate and observe a value very close to the predicted 118 mV.

Hazards

Solutions of quinone, hydroquinone, iron(II) ammonium sulfate, potassium iodide, potassium nitrate and sodium thiosulfate are irritants. Solutions of ammonia, copper(II) nitrate, iodine, iron(III) chloride, silver nitrate, and sulfuric acid are corrosive. Solutions of iodine, sulfuric acid, and nitric acid are toxic. Solutions of ammonia and iodine are lachrymators. Solutions of copper(II) nitrate, nitric acid, potassium nitrate, silver nitrate, and sulfuric acid are oxidizers. Goggles, gloves and appropriate lab attire should be worn at all times, and all solutions used in this lab should be disposed of as hazardous waste according to official procedures.

Discussion

This two-week electrochemistry sequence has been well-received by our students. We have made the decision to focus the lab sequence on the connections between electrochemistry and the other parts of this course, particularly equilibrium and thermodynamics. Therefore, we have chosen to leave for the upper-level analytical course the discussion of more advanced topics in electrochemistry, such as junction potentials, that could obscure these valuable connections for our introductory students. In some years, faculty members have successfully used these two experiments to introduce the concepts of entropy and Gibbs energy.

We find that the discovery process of teaching the Nernst equation allows students to understand it as more than just an equation to be memorized, as their data are used to derive it. We have chosen ranges of concentrations for which the data are linear in the Nernst plot. Depending on the solution, the cell potential will either increase or decrease as students add their solutions. Once the Nernst equation has been discovered, it is instructive to ask the students to explain this trend based on the form of the reaction quotient for their system.

In part two of the first lab, we assign particular concentrations in the student half-cells, as well as particular combinations of half-cells. The particular concentrations assure that we get the same sign and magnitude for each combination of half-cells.⁶ Assigning particular combinations of half-cells prevents combinations with an E_{cell}° close to zero.

In the second week, half of the students start with the concentration cells and the others start with the silver complex ion formation reactions.⁷ Many of our students are concomitantly taking Cell Biology, so discussions of concentration cells with biological applications are of particular interest to them. In our discussion after lab two, we ask the students to consider how the quinhydrone concentration cell could be used as a pH electrode.

The first lab requires a 45-minute pre-lab introduction, which could take longer if it is the first introduction of redox reactions. The data collection takes about an hour for both parts combined, and the remaining two hours are spent on calculations, generating plots, and a brief post-lab discussion. We find that reviewing the form of the reaction quotient equations in pre-lab helps with the calculations. We provide a suggested headings list for a lab notebook table, and ask students to prepare a sample pre-lab calculation. For the second week, we have similar timing. Students tend to struggle with the stoichiometry calculations for the complex ion formation, so it serves as a nice review of equilibrium and stoichiometry.

Acknowledgments

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Notes

1. This article is dedicated to the memory of Lisa P. Nestor, co-founder of and vital participant in the Holy Cross Discovery Chemistry Program.

2. We used to give students freedom design their own concentrations, but decided that performing the calculations is a sufficient challenge and that we get more consistent data in the concentration ranges that we prescribe. Groups studying the $\text{Ag}^+|\text{Ag}$ are directed to use double junction probes, and the KNO_3 solution in the outer chamber is replaced after every lab.

3. Sometimes a discontinuity in the linearity of the best-fit line is observed when students change from using the more concentrated working solution to a diluted solution. This lab serves as a good reinforcement of the essential skills of making dilutions and calculating the concentration of diluted solutions—not student strengths in our experience.

4. For a more precise determination of K_{sp} using electrochemistry data that accounts for junction potentials and temperature dependence, an experiment determining the solubility product of lead (II) chloride has been published in this *Journal* (14).

5. Alternatively, this system can be viewed as a concentration cell, using the E_{cell} value to calculate the free silver ion concentration in the presence of a known concentration of thiosulfate or ammonia,

and using these data to approximate K_{f} . This is the approach taken by the authors of an experiment measuring the formation constant of $\text{Ag}(\text{NH}_3)_2^+$, published in this *Journal* (15). We have found that students do not find this approach intuitive until they have completed part 2 of this lab.

6. In the past, we gave students latitude in these choices, and different groups would have different cathodic or anodic solutions based on the concentrations they chose. This was instructive for students as they compared data, but confusing for teaching assistants and instructors.

7. If a lab had a full complement of double-junction probes, it might be better for all groups to discover the concentration cell first so they could appreciate the complexation reaction set-up as a concentration cell.

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