

The Hydrogen Atom Spectrum: Experimental Analysis Using Iterative Model Building

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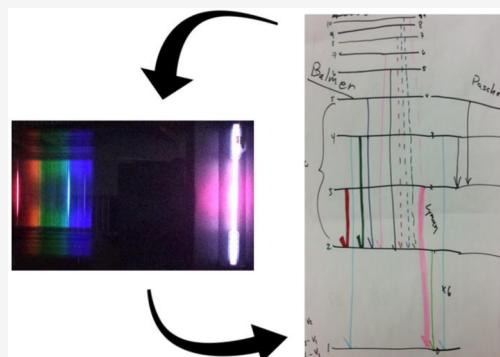
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ABSTRACT: The principles of process-oriented guided inquiry learning (POGIL) are applied to the analysis of the emission spectrum of atomic hydrogen. Over the course of three learning cycles, students construct the hydrogen atom's energy level diagram and assign quantum numbers using their measurements of the Balmer series plus additional information on the emission lines in the Lyman and Paschen series. This guided inquiry approach to the hydrogen emission spectrum, which was developed as part of the POGIL Physical Chemistry Laboratory Project, has been tested at several institutions with a variety of spectroscopic instruments. The analysis leading to the assignment of quantum numbers requires simple and inexpensive supplies: rulers, colored pens, and long strips of paper.



KEYWORDS: Undergraduate, Physical Chemistry, Laboratory, Atomic Structure, Guided Inquiry Learning, Hydrogen, Emission Spectrum, Constructivist, Iterative Model Building

In atomic and molecular spectroscopy, assigning quantum numbers is the crucial link between the data and the quantum model. Assigning quantum numbers to the Balmer emission lines of the hydrogen atom should be seen by students as an important conceptual puzzle, as it was for Balmer,¹ Rydberg,² and Bohr.³ The quantum numbers of the emission lines set the terms for the subsequent least-squares fit (or other data reduction procedure) that validates a model and produces the Rydberg constant. Going directly to data analysis without devoting time to assigning the numbers short-circuits this conceptual framework. Since model construction and refinement are at the heart of how we make sense of scientific data and observations, it is critical that students develop this skill.

However, a review of the literature indicates that very little attention has been devoted to this step in the analysis of the Balmer series in atomic hydrogen. With regard to the numbering of the energy levels—that is, assigning quantum numbers to the spectral lines—there is no common method or established procedure. In *Experiments in Physical Chemistry* by Shoemaker et al.,⁴ the quantum numbers are simply given to the students. Sime, in *Physical Chemistry: Methods, Techniques, and Experiments*, says that “If you choose n correctly, R is a constant.”⁵ He then provides the assignments. In *Physical Chemistry Laboratory* by Salzberg et al.,⁶ students are provided with a rather complicated difference formula to find the correct numbering of the upper state. In these three textbook examples, students are told that the energy levels are proportional to $1/n^2$; it is fair to say that the analysis is

designed to get the students to a value of R_H , the Rydberg constant, as quickly as possible. Boppegedera⁷ appears to give the students the quantum numbers but has them discover through least-squares fitting that the energies are proportional to $1/n^2$. In some chemistry laboratories and many physics laboratories, the goal of analyzing the Balmer series is to measure the isotope shift for deuterium to obtain its mass, so usually both the quantum numbers and $1/n^2$ dependence are given to the students.^{8,9}

Ramachandran and Halpern¹⁰ described what is probably the most extensive attempt to make the numbering, and hence model construction, a significant part of the analysis. They created a user-defined fit function in which the Rydberg equation contains n_l and $n + \Delta$, where Δ is the difference between n_u and a running index N . A least-squares fit of the spectral lines versus the running index yields values for n_l and Δ . Because $n_u = N + \Delta$, the fit establishes both n_l and n_u .

While this is an ingenious way to find the numbering by fitting, we believe that there may be more pedagogical value in separating the number assignment from the least-squares fit, which allows us to emphasize patterns within the experimental data along with model construction and refinement. In this

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Table 1. Content Goals for Each Stage of the Experiment

Stage	Goals
Pre-experiment	<ul style="list-style-type: none"> For a three-level model, $v_3 = v_1 + v_2$. For a model with 4 levels, the number of possible emission lines is 6.
Cycle 1	<ul style="list-style-type: none"> The first three lines of the Balmer series do not fit a three-level model. A four-level model for the Balmer series cannot have equal spacing between levels.
Cycle 2	<ul style="list-style-type: none"> The pattern of frequencies and intensities fits a model in which the energy-level spacing decreases at higher levels. The model can be used to predict transitions that could occur in the infrared.
Cycle 3	<ul style="list-style-type: none"> The Lyman series establishes the $n = 1$ ground state energy level. The Lyman, Balmer, and Paschen series show the same pattern of lines from the same upper states of emission.
Post-experiment	<ul style="list-style-type: none"> Answer the focus question. Use terms such as <i>energy level</i>, <i>transition</i>, and <i>spectroscopic line</i>, in other situations.

regard, the spirit of our approach is similar to the experiment described by Ball,¹¹ in which a PhET simulation¹² of the hydrogen atom interacting with light is used to map the energy levels of the atom. In their activity, it is the construction of the energy level diagram that is the goal, just as it is in ours.

To map the energy levels prior to fitting, we use a visual method of differences to match the patterns in the Balmer series to other emission series of the hydrogen atom. Careful analysis of the Balmer series suggests the general pattern of the energy levels, and the Lyman series establishes the ground state of the hydrogen atom. The Paschen series can be used to confirm the assignments made using the Balmer and Lyman data. Once the energy level diagram is constructed with a well-defined ground state, the quantum number assignments are obvious, and the data can be fitted.

The design of this experiment follows the process oriented guided inquiry learning (POGIL) framework developed in the POGIL Physical Chemistry Laboratory (PCL) Project.¹³ POGIL-PCL experiments emphasize modeling of chemical phenomena and involve learning cycles in which students make predictions, collect data, model the data, and discuss its meaning. Our experiment is designed around the focus question, “What does the emission spectrum of the hydrogen atom reveal about its energy levels?” It consists of several pre-experiment questions, three learning cycles, and several postexperiment questions. Each cycle comprises an experimental protocol and a series of Thinking About the Data (TATD) questions. Protocols are strategically vague to allow students freedom to propose and debate experimental design considerations. TATD questions, which are completed by students during the laboratory period, are written to call attention to key aspects of the data, expose blunders in the method, and refine the models being developed.

■ DEVELOPMENT AND IMPLEMENTATION

We developed the experiment at POGIL-PCL workshops^{14,15} for physical chemistry faculty, beginning in 2013 with ideas one of us (C.S.) had about the visual method of matching the Balmer series to the other series. An early draft of the experiment was tested by an undergraduate research student who had already taken physical chemistry. We tested later draft versions in our own physical chemistry courses, and the experiment was evaluated through the POGIL-PCL screening rubric at another workshop in 2015. Advanced drafts, including the instructor’s handbook, were beta-tested at several colleges around the United States. The experiment was then used in final form at two additional POGIL-PCL workshops. A recent survey of people associated with the POGIL-PCL effort indicated that at least 22 faculty members have used the experiment in their courses.

A comprehensive instructor’s handbook is available from the POGIL-PCL website;¹⁶ it provides learning objectives and pacing suggestions, lists equipment needs, identifies common problems, and includes expected responses for TATD questions. An implementation guide with learning objectives, suggested experimental parameters, and excerpts from the instructor’s handbook is available in the *Supporting Information*. Table 1 summarizes the specific goals for each stage of the experiment.

The main parts of the experiment may be completed within a 3 hour period if students answer the pre-experiment questions before the laboratory meeting and are familiar with the equipment. Scheduling 6 hours or more will allow students to address all of the experiment questions thoroughly or allow groups to rotate through the data collection process if equipment is to be shared. Instructors may implement the experiment over several periods using convenient break points, or they may omit portions of the experiment that they deem to be less important for their course objectives. The equipment used is similar to that for standard visible spectroscopy

measurements: inexpensive transmission gratings (or “rainbow glasses”), a hydrogen Geissler (discharge) tube and power supply, and an emission spectrometer or a monochromator with a detector. Emission spectra have been recorded by the authors using diode array spectrometers (Ocean Optics Red Tide or USB 2000, Vernier Emission Spectrometer, or SpectraVis Plus operating in emission mode) or the emission monochromator of a fluorimeter (JASCO FP-6500) equipped with a fiber optic cable.

■ HAZARDS AND SAFETY

Depending on the design, the discharge lamp power supply may have exposed high-voltage terminals, thus presenting an electrical hazard. An unfiltered hydrogen lamp will emit UV light; users should wear UV protective eyewear and avoid extended exposure to the lamp emission.

■ PRE-EXPERIMENT QUESTIONS

Students work alone before the lab period or in groups of three or four at the beginning of the period answering a series of questions that guide them through the creation of a qualitative energy level diagram using nascent knowledge of electronic transitions and energy states. The pre-experiment questions introduce terms and concepts of emission spectroscopy and atomic structure (e.g., ground/excited levels, wavenumber, spatial/temporal frequency), address common gaps in understanding and misconceptions, and guide students through calculations related to wavelength–energy relationships (unit conversions, Planck energy relationships, energy of a transition). By design, the term *energy level* is consistently used rather than *energy state* to avoid complicating the discussion with concepts such as degeneracy.

A key objective of the pre-experiment questions is to guide students through the creation of a simplistic model that reflects the number and separation of energy levels required to account for the number of lines observed in an emission spectrum. At this point, the accuracy of the model is not a primary concern, as deficiencies will be addressed later in the experiment.

■ CYCLE ONE

The experimental protocol has students observe the emission of an operating hydrogen discharge lamp both with and without a wavelength dispersion device (a hand-held spectroscope, piece of transmission grating film, or “rainbow glasses”). Students are to note the color, relative spacing, approximate wavelength (based on color if no wavelength scale is available), and relative intensities of the Balmer lines. TATD questions have students order the observed lines by frequency and intensity. Each group collaborates to produce a diagram that accounts for the type of transition (absorption or emission), the observed frequencies, intensity (thicker arrows represent brighter lines), and the number of levels required to account for the number of lines observed. Often the models have inconsistencies that may be attributed to inchoate understanding of electronic structure or spectroscopic transitions. Again, at this stage, flaws in the model are acceptable. [Figure 1](#) shows a typical model after Cycle One.

Instructors may wish to ask guiding questions about the models but are urged to refrain from correcting or explaining the errors. The experiment is designed so that students discover inconsistencies by answering carefully written TATD questions.

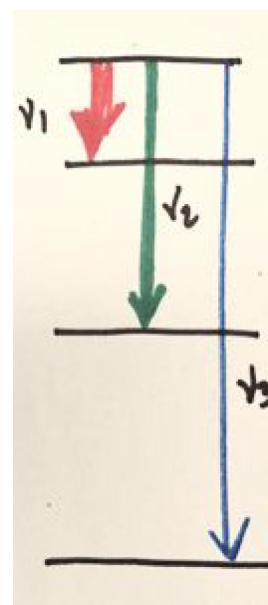


Figure 1. A possible four-level model for the first three emission lines of the Balmer series. Arrow width represents the intensity of the line. It should be noted that the model incorrectly shows the three lines originating from a common upper state.

■ CYCLE TWO

Students are informed that visible emission lines belong to the Balmer series, but the quantum numbers for levels involved in these transitions are not identified. The experimental protocol directs students to record the visible hydrogen emission spectrum with a spectrometer. Students use their experience from Cycle One to guide decisions on instrument settings to account for the differences in the intensities of the lines. Some groups may miss lines that were not obvious to the eye—for example, the indigo-colored line at 410 nm and lines in the near-UV region shown in [Figure 2](#).

Because of the large differences in intensity, students should optimize the instrument for each line. Inexpensive spectrometers typically resolve at least four Balmer lines, whereas more capable instruments can resolve five or more lines. Spurious lines may appear that result from molecular hydrogen emission, impurities in the discharge tube, or emission from

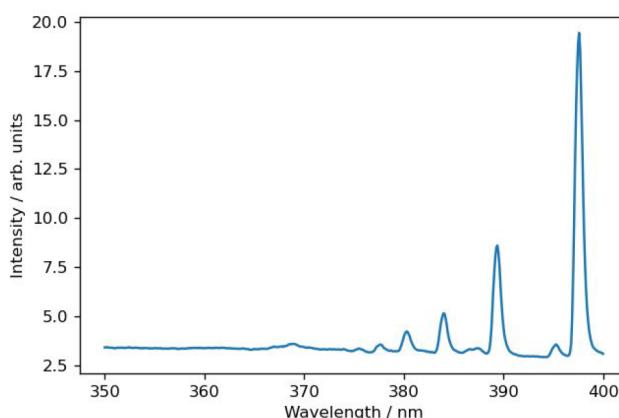


Figure 2. Hydrogen emission spectrum in the near-UV, showing the less-intense lines of the Balmer series (recorded using the emission monochromator of a JASCO FB-6500 fluorimeter).

fluorescent lighting or computer screens. Students usually deduce that these are not Balmer lines, but if not, there are TATD questions later in the cycle that lead students to disregard unrelated emission lines.

Groups then mark the frequency of each Balmer line on the long axis of a 30 cm strip of paper, as shown in Figure 3. Strip-chart recorder paper is ideal, but graph or plain paper can be used.



Figure 3. Seven lines of the Balmer series (frequencies in cm^{-1}) with the first (red) line on the left. Absolute frequencies are not indicated, but the differences among the lines are plotted with a scale of 1 inch = 1000 cm^{-1} .

Students are asked to identify a pattern in the spacing of the lines and to theorize about what this pattern implies about the separation of energy levels involved in the transitions. Students then revise the energy level diagram created in Cycle One to show vertical arrows connecting the levels involved in the Balmer transitions. The lengths and thicknesses of the arrows should depict the frequencies and intensities of the Balmer lines, respectively. Students discover that they need to add more levels and that the levels need to be spaced appropriately to represent the measured frequencies.

As noted above, this approach differs from other implementations in which the energy level diagram is provided to students as background information. Intentionally, we have students develop the diagram themselves by using their own data. Almost universally, students use terms such as “ground state” and “excited state” gleaned from other experiences, yet they do not realize that the ground level is missing from their model. Finally, the groups are asked to compare answers to generate a model that everyone agrees correctly represents the frequencies of lines in the hydrogen atom emission spectrum. At this point, errors such as that shown in Figure 1 are usually identified and corrected by the students, but instructors may confirm the veracity of the models prior to starting the next cycle.

CYCLE THREE

Lines from the Lyman and Paschen series are introduced. Transition wavelengths are provided in the handout because recording these data requires (less common) instruments capable of examining the ultraviolet and infrared regions of the electromagnetic spectrum. Again, students convert wavelengths to wavenumbers and plot each series on a separate strip of paper using the same scale as they used for the Balmer series in Cycle Two. Students may be inclined to start the plot at zero wavenumbers so the instructor may remind students to consider a more sensible starting point, especially for the Lyman series.

Students review the energy level diagram produced in Cycle Two in light of the new information related to the Lyman and Paschen series. Specifically, they are asked whether the energy level diagram includes the *ground* level of the hydrogen atom and to justify their answer. Most groups realize there must be another level below the lowest-energy Balmer level drawn. Next, students overlay the strips and slide them relative to each

other until the lines among all three are aligned as shown in Figure 4.

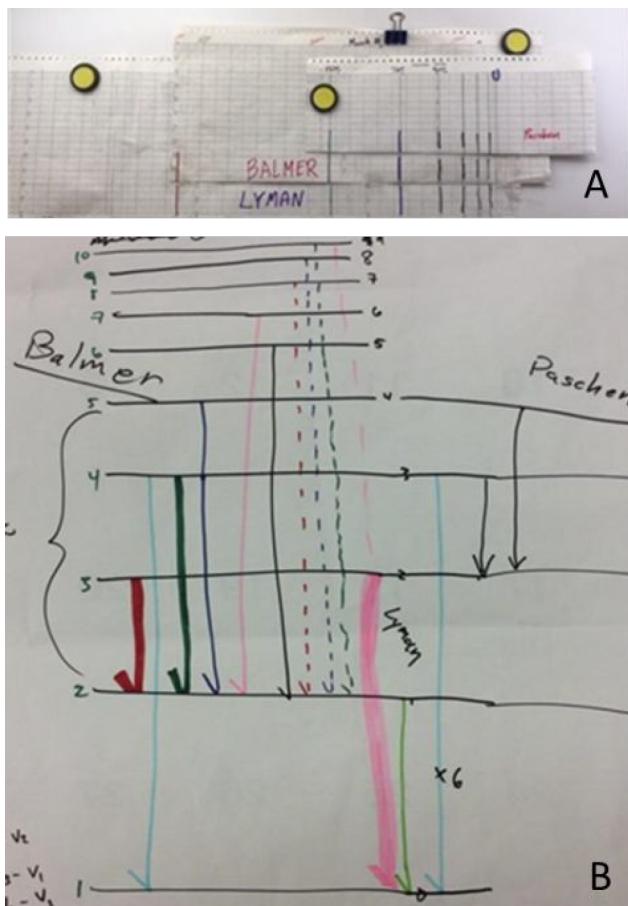


Figure 4. (A) Matching the lines for the Lyman and Paschen series with those of the Balmer series. Frequency differences are plotted on a scale of 1 inch = 1000 cm^{-1} . The first Lyman line is not shown in this image because it has no matching line in the other two series. (B) Energy level diagram after the addition of the corresponding lines in the Lyman and Paschen series. This diagram (which contains specious elements) shows the evolution of the students' model through the different cycles and provides a useful artifact for assessing understanding.

Aligning the Lyman lines with the Balmer lines shows that the two series have levels in common. This realization is used to update the model from Cycle Two so that the energy level diagram now includes the ground level of hydrogen and all Lyman emission lines terminate on that level (Figure 4).

By design, thus far the students have not assigned quantum numbers to the energy levels. Having established a viable model, only now are they prompted to number the levels using quantum numbers, starting with $n = 1$ at the ground level. With the quantum numbering scheme attached to the model, the Paschen series is explored through a sequence of questions that highlight connections between levels common to the Lyman and Balmer transitions. At this point students should be comfortable explaining relationships between the upper and lower levels for transitions in the various series as well as explaining how lines are assigned to a series according to the terminating level. A typical model is shown in Figure 5. Groups should now have a defensible energy level diagram with accurate labels for the quantum numbers.

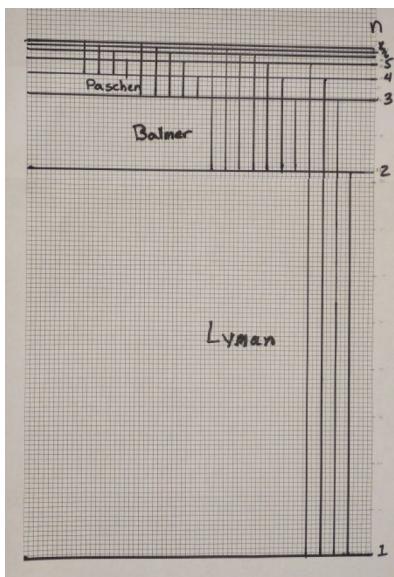


Figure 5. Final energy level diagram (1 inch = 1000 cm^{-1}). Although not requested in the activity, the (unlabeled) Pfund series is shown.

The next sequence of questions has students predict which relationship between frequency (in wavenumbers) and quantum number is linear: ν versus n , n^{-1} , n^2 , or n^{-2} . Despite having encountered the Rydberg equation in general chemistry or elsewhere, groups commonly make incorrect predictions at this point. This suggests a tenuous understanding of the Bohr and Rydberg models. To test their predictions, groups prepare plots of each of these relationships. They then interpret the meaning of the slopes and intercepts and how (or whether) these fit parameters are related to the model. If time allows, this is a good time to discuss accuracy and precision in experimental methods and fitting. Even with crude wavelength measurements from a hand-held spectrometer, the calculated value of the Rydberg constant is usually in excellent agreement with the accepted value.

■ POSTEXPERIMENT QUESTIONS

The final sequence of questions, which may be completed outside of the laboratory session, prompts students to use their model to make predictions about the Brackett series (which has a longest-wavelength transition at 4050 nm), to sketch a comprehensive spectrum for the hydrogen atom, and to contrast several concepts related to energy levels and atomic structure. Finally, using diagrams, fits, and models developed through the experiment, students are asked to respond to the focus question, “What does the emission spectrum of the hydrogen atom reveal about its energy levels?”

Additional questions that develop concepts in other contexts are also provided. These questions could be the basis for further exploration or “mini-projects”, including calculating the ionization energy of atomic hydrogen, recording the solar emission spectrum to identify the Fraunhofer lines associated with hydrogen (Figure 6), or extending the model to the hydrogen analogues He^+ and deuterium.

■ OUTCOMES AND CONCLUSIONS

The POGIL-PCL approach is constructivist: students make predictions about natural phenomena, create models based on those predictions, and perform experiments to validate the

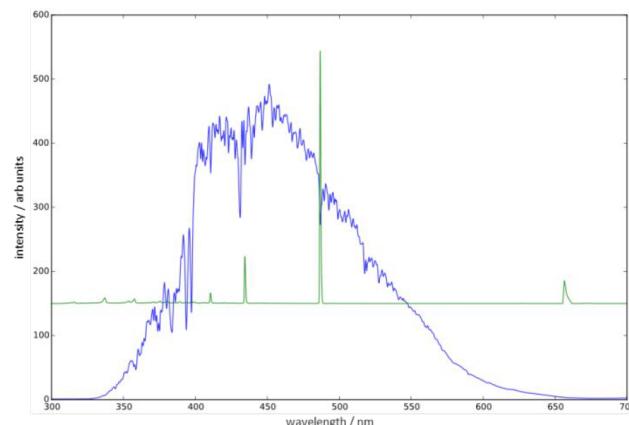


Figure 6. Solar emission spectrum (blue) and the hydrogen emission spectrum (green) obtained with a JASCO fluorometer. Dips in the solar emission spectrum correspond to lines of hydrogen.

models.^{17,18} In this laboratory activity, these tasks are performed several times to refine their models and improve their understanding of the structure of the hydrogen atom. We find that most students are able to

- discover patterns among spectral data
- unite those data in a model of the energy levels
- use that model to make predictions of additional spectral lines.

We also find that the most common difficulties include

- recognizing that the best model will show transitions terminating on a common level (Cycle 1)
- difficulty in optimizing the experimental procedure to obtain a suitable emission spectrum (Cycle 2)
- predicting and graphing the $1/n^2$ relationship between quantum numbers and frequency of emission lines (Cycle 3).

These stumbling blocks are addressed by reminding students to compare answers for specific TATD and postexperiment questions. By the end of the activity, it is rare for students to leave the laboratory with a flawed model or fit. Furthermore, we find that they readily meet expectations for answers to postexperiment questions and for explanations in laboratory reports.

In a recent survey, instructors who have used the experiment were asked for their insights about this approach and to compare it to non-PCL versions of the lab. Some representative responses were:

- “Even the most relatively simple concepts can be eye-opening the first time a student realizes the connection of data to a theoretical construct. That is, when students connect energy levels as determined by the Bohr model (or the quantum mechanical solution) to an actual spectrum and see how they match, it’s mind blowing...”
- “It helped me recognize how much trouble students have relating energy-level diagrams to spectra.”
- “Students [have] much less of an experience of discovery in the traditional lab.”
- “The strengths are getting students to connect data with energy level diagrams and transitions among them. The focus on intensities was interesting because that is usually not a focus in hydrogen atom spectral analysis. I liked the discovery-based determination of the depend-

ence of E on n (presumably as Rydberg did back in the day)."

- "I once or twice did an emission lab with hydrogen and a couple other elements, which was not PCL. It was confusing to the students and I'm not sure they learned much from it."
- "Students often think that the foundational knowledge in our field was determined a long time ago with really sophisticated equipment and complicated experimental design, stuff that they wouldn't be able to explain, understand, or run themselves unless they went to graduate school. It is an ah-ha moment for them when they realize that quite simple spectra can be really information rich if they know how to ask the right questions. I think it helps them build a little bit more of their science identity."

We too have observed that students experience several "a-ha" moments in each cycle. Students appreciate the dramatic energy differences among the different emission series of hydrogen, and many are amazed that they can construct a model that explains those differences. Students (and instructors) find it satisfying to see their model grow as more data are added to the analysis and to see the model evolve from primarily graphical to more mathematical as they progress through the cycles. Our approach with this experiment is focused on iterative model building from experimental data, and students completing this laboratory experience a taste of the discovery process at the heart of science.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available at <https://pubs.acs.org/doi/10.1021/acs.jchemed.2c00348>.

Implementation guide (PDF, DOCX)

Student handout (PDF, DOCX)

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Notes

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