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Charting an Alternate Pathway to Reaction Orders and Rate Laws in Introductory Chemistry Courses

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Ⓢ *Supporting Information*

ABSTRACT: Reaction kinetics is an axiomatic topic in chemistry that is often addressed as early as the high school course and serves as the foundation for more sophisticated conversations in college-level organic, physical, and biological chemistry courses. Despite the fundamental nature of reaction kinetics, students can struggle with transforming their corpuscular reaction concepts into mathematical rate models. Here, we describe an approach to teaching rate laws at the introductory college level that draws upon model-based reasoning as the pedagogical underpinning. Collision theory, graphical analysis of kinetics plots, and transformations between concentration/time and rate/concentration representations are used to facilitate the growth in understanding about rate laws and reaction mechanisms. The learning outcome expected by the conclusion of the instructional sequence is the ability to collect and analyze kinetic data to determine reaction orders and rate laws using mathematical concepts familiar to students just beginning a course sequence in calculus. While the ideas that are discussed in this paper focus on kinetics principles as they might be presented in undergraduate general chemistry courses, we believe they would also prove useful at the advanced high school level.

KEYWORDS: *High School/Introductory Chemistry, First-Year Undergraduate/General, Inquiry-Based/Discovery Learning, Kinetics, Mechanisms of Reactions, Nucleophilic Substitution*
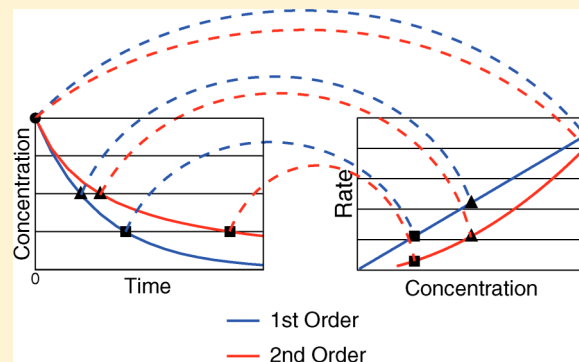
■ INTRODUCTION

Recent reform documents by the National Academies and the College Board advocate that students learning chemistry at the introductory levels be taught relatively few core disciplinary concepts and develop aptitudes in scientific practices such as carrying out investigations, analyzing data, and constructing explanations from evidence.[1−3] Reaction kinetics, the study of the rate at which chemical processes occur, is a fundamental topic in chemistry and is often addressed as early as the high school course when qualitative discussions involving particle size, agitation, temperature, and the presence of catalysts are introduced as factors that can affect how quickly solutions form or metallic objects corrode, for example. The introductory college course is often expected to serve as the foundation for more sophisticated conversations about kinetics later in the curriculum, such as those studies supporting one particular mechanism over another when learning about unimolecular and bimolecular nucleophilic substitution reactions (S_N1 vs S_N2) in organic chemistry,[4] analyzing systems obeying Michaelis—Menten kinetics in biochemistry,[5] or when discussing photolytic chain reaction mechanisms in physical chemistry.[6] Given its fundamental importance to a number of courses in the advanced high school and undergraduate chemistry curriculum,

consideration must be given to whether this topic is being taught in a manner that creates the strongest possible foundation for instructors and students to draw upon when it is revisited in future courses.

Obstacles to learning reaction kinetics may involve the transformation of student corpuscular (molecular, atomic, etc.) conceptions into more scientific and mathematical models.[7−9] In an analysis of erroneous student conceptions about kinetics, BouJaoude[10] drew several conclusions regarding the underlying causes for those errors, including: (i) students did not understand the relationship between experimental results and the rate of reaction; and (ii) students' misconception that an arithmetic relationship existed between concentrations of reactants and products led to a mathematical rather than a chemical solution to one problem.[10] Previous strategies to overcome kinetic misconceptions appealed to secondary students from an affective point of view by first engaging them with a macroscopic phenomenon and then facilitating a search for corpuscular explanations.[7] Such model-based reasoning prompts students to use mental representations as a means to visualize, think, and understand "through the lens of

a conceptual structure".[11] The use of model-based reasoning, coupled with guided inquiry, is advocated in the science education literature to encourage the development and revision of mental models as further empirical data is presented during the instructional sequence.[9,12]

Herein, we present an approach to teaching reaction orders and rate laws that is grounded in model-reasoning and guided inquiry. Our approach has been successful with both undergraduate students in general chemistry courses and high school teachers in professional development workshops. The structure for presenting the key ideas is such that visualizations and representations are always at the forefront of the conversation. Additionally, any transformations from or into mathematical formulations are based on these visualizations and the mathematics that should be familiar to students. Using visual, mathematical transformations that are familiar is an approach that has been advocated previously in this *Journal*,[13,14] and we expand significantly on this previous effort by outlining an entire instructional sequence on the topic of kinetics.

■ THE APPROACH

Prior to this instructional sequence on kinetics, students in our course have been familiarized with concepts that will be drawn upon to support their understanding of the new ideas introduced here. For example, students have been exposed to kinetics-related principles when they learn about solution formation and dissolution, precipitation and crystallization, vapor pressure, and colligative properties, albeit in a less explicit way. When studying solutions, for example, the condition of saturation can be understood as the balancing of the relative rates of the dissolving and precipitation processes. When being introduced to the idea of vapor pressure, graphical representations, similar to that shown in Figure 1, are often
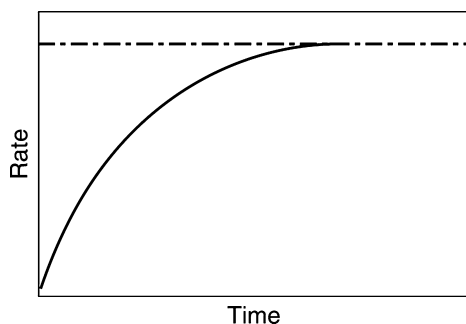

Figure 1. Kinetics principles in the context of phase change equilibria. The relative rate of evaporation (dashed line) for a volatile liquid in a closed vessel is constant compared to condensation (solid curve), which slows upon approach to equilibrium.

invoked to illustrate the relative rates of evaporation and condensation as equilibrium is reached. Assuming a constant temperature, the rate of evaporation remains constant but the rate of condensation starts low (owing to the low concentration of gaseous particles) and increases over time until it equals the evaporation rate when the vapor pressure is reached.

■ PHASE I—INTRODUCTION TO KINETICS PLOTS

The first phase in our approach (maximum of 15 min) involves orienting the participants (students, or those attending a workshop) to the types of kinetic relationships that they will be asked to master by the end of their experience with rate laws

and rate orders. The first is how reactant (or product) concentrations change as a function of time. We start by presenting reaction 1, shown in eq 1, which has the same form as a single displacement reaction that is familiar to students by this point in the introductory course, despite involving organic compounds:

$$I^- + CH_3Br \rightarrow CH_3I + Br^- \qquad (1)$$
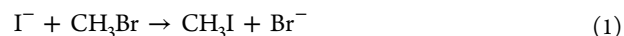
We also furnish them with drawing supplies and a blank plot with the appropriately labeled axes (Figure 2, top).
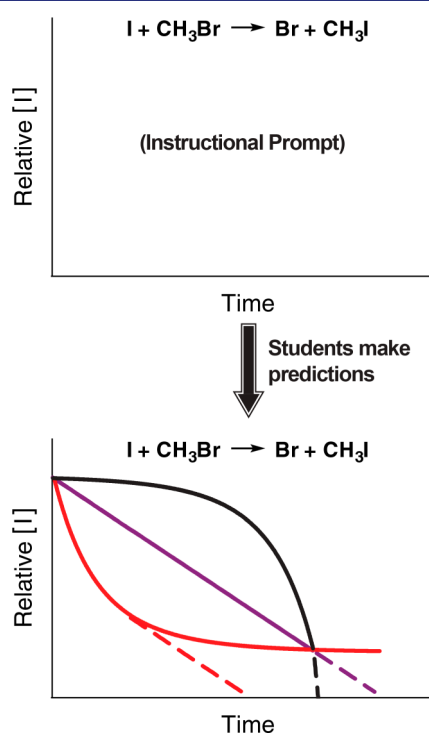

Figure 2. Assessment of student ideas regarding kinetics prior to instruction. (Top) The instructional prompt given to students depicts a balanced single displacement reaction and appropriately labeled axes. (Bottom) Typical student responses: reaction starts slow, then speeds up (black line), stays constant throughout the reaction (purple line), or starts fast and then slows down (red line). Student responses regarding the end point of the reaction (dashed lines) may include complete reaction (x-axis intercept) or an approach to equilibrium (horizontal asymptote).

Then, presented with the prompt, "What are the possible graphs you might expect for the reactant concentrations as the reaction progresses over time?", we seek to understand the level of sophistication with which students can model chemical reactions graphically. Specifically, do students consider or ignore ideas about these considerations?

   Whether the concentrations should increase or decrease over time
   Whether the concentrations' rate of change (i.e., slope) should change or remain the same over time
   The relationship between the changes for each reactant with respect to each other
   The concentrations at the "end" of the reaction, that is, whether to stop drawing their graphs above, at, or below the x-axis (these represent positive, zero, and negative concentrations, respectively)
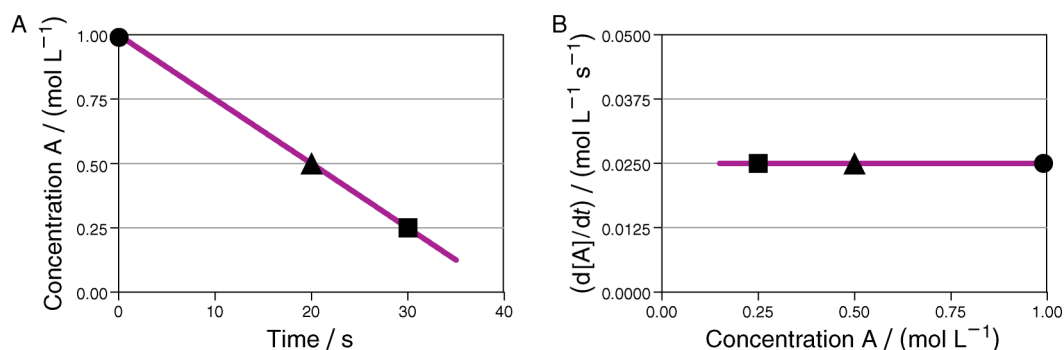
Figure 3. Zeroth-order plots based on the instructional prompt in Phase I and simulated data. (A) Simulated changes in the concentration of reactant A show a constant decrease throughout the reaction. The initial (●) and first (▲) and second half-life concentrations (■) are depicted. (B) Conceptual reconstruction of the first derivative of the function in (A), using the reaction rate and concentration at each half-life, and defining reaction rates to be positive. The initial and half-life concentrations are depicted as above for clarity. In a classroom setting, it may be informative to graphically link the corresponding data points from plots (A) and (B) and reiterate that the constant negative and zero slopes, respectively, both indicate the rate is independent of the reaction concentration.

The concavity of the graphs, that is, whether they could anticipate a negative or positive concavity, and what that would imply about the reaction system

After compiling the student responses, graphs such as that depicted in Figure 2 (bottom) are typical, and have stimulated conversations about the rationale for particular choices that were made during the process. The populations of students with which we have worked through these "prediction plots" have often been able to invoke arguments that draw upon preliminary models about reaction mechanisms and collision theory even though formal instruction about these concepts has not occurred prior to this time. It seems that many students at this point in their introductory chemistry education can, for example, recognize that reactant concentrations should decrease over the course of a reaction (and likewise, product concentrations increase), because the reactive species are rearranging, recombining, or otherwise changing to reduce their amounts over time. The details about how this process occurs are often poorly articulated, but we attempt to affirm students' rudimentary ideas about mechanistic processes by building upon examples they can provide. We remind the students that some of their intuitive notions of relative reaction rates are often well informed from their everyday life experiences, such as making sweet tea (or powdered soft drink mix) with hot and cold water. Most of them recognize that sugar dissolves faster in hot water than when it is colder, because the hotter water has more kinetic energy to solvate the solid sucrose crystals through more energetic collisions. We try to make clear that for simple dissolving phenomena and the other types of systems studied *in this course*, the "constant slope" (i.e., Figure 2, purple line, corresponding to the zeroth-order condition) and one of the "curved or variable slope" plots (i.e., graphs with the same shape as the red line in Figure 2) will be considered. Further, although rate laws can be written in terms of reactants or products, we will constrain ourselves to only those involving reactants.

■ **PHASE II—CONCEPTUAL UNDERSTANDING OF RATE LAWS PART I: INTERPRETING HYPOTHETICAL KINETICS DATA**

In the second phase of this approach (15–30 min), students build from the foundations laid in phase I (concentration/time) to develop a conceptual grounding of zeroth-, first-, and second-order processes (rate/concentration). From straightforward interpretations of rate versus concentration plots, we also expect them to write the form of the associated (differential) rate laws. This involves conceptually focused (as opposed to mathematically focused) manipulations of a minimal data set. Using only the graphs corresponding to zeroth-, first-, and second-order processes generated during Phase I, we ask the students to consider the slope of each graph at three points:

1. The initial concentration
2. One-half of the initial concentration (i.e., at the first half-life)
3. One-quarter of the initial concentration (i.e., at the second half-life)

We have found it can be useful to mark the axes with some values to aid in the estimation of the slopes, such as 1, 0.5, and 0.25 M for the *y*-axis, and time intervals (e.g., every 10 s) for the *x*-axis.

Step 1: Zeroth Order

We begin with the zeroth-order plots, in contrast to the first-order process presented first by the textbooks we surveyed, mostly because it is the simplest graphical relationship to work with when attempting to determine rate laws conceptually. For the zeroth-order (concentration/time) plot, the students can quickly see that the slope (reaction rate) is constant over the course of the reaction, and they do not usually have difficulty with our assertion that for processes that obey these kinetics, *the rate is independent of reactant concentration* (Figure 3A). To assess this understanding, we ask the students to construct the plot of rate (*y*-axis) versus concentration (*x*-axis) that would represent this relationship between reactant concentration and time, reminding them that rates are defined to be positive values. Implicitly, we are prompting them to plot the first derivative of this function, but we find that our students, if they can recognize how the rate is changing over time (i.e., that it is constant), can draw this graph with relative ease. Once plotted, we ask them to write an equation for this graph in terms of the *y*-variable (rate) and *x*-variable (concentration). Some students immediately recognize the form as simply Rate = k, where k is the rate constant for the zeroth-order process, while others require the explicit connection between the more familiar "y = constant" language from their previous mathematics classes to feel comfortable with it. Next, we show the students that this equation is equivalent to Rate = $k[R]^0$, where [R] represents
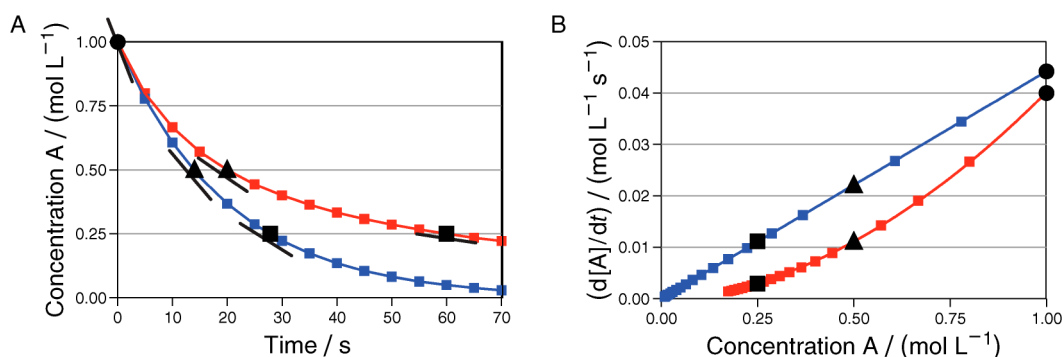
Figure 4. First- and second-order plots based on simulated data. (A) First-order (blue) and second-order (red) kinetic processes are overlaid to show the difficulty in determining the relationship between slope (i.e., rate) and concentration, and the challenge of distinguishing the first- from the second-order curves. Data approximating initial (●) and first (▲) and second half-life concentrations (■) are depicted. Changes in slope are illustrated by tangential lines at each depicted concentration. Only the slope for the initial concentration of the first-order process is shown for simplicity. A tool for generating first- and second-order data is provided in the Supporting Information. (B) Conceptual reconstruction of the first derivative of each process in (A) using the same labeling scheme for comparison. In a classroom setting, it may be informative to graphically link the corresponding data points from plots (A) and (B) and reiterate that the familiar first- (linear) and second-order polynomials clearly differentiate the first- and second-order processes, respectively.

the reactant concentration and the exponent (0) represents the order of the reaction with respect to the reactant R. Therefore, we explain, a zeroth-order process is just one in which the rate of the reaction *does not* depend on the concentration of that *particular* reactant.

The latter point usually stimulates a conversation about what kinds of reactions might obey zeroth-order rate laws. We return to reaction 1 and ask whether the nucleophilic substitution of methyl bromide by the iodide ion (S_N2) might be a candidate for a zeroth-order process, either with respect to the methyl bromide concentration, the iodide concentration, or both. Having taught kinetics with this approach to both students and teachers alike, we cannot recall anyone positing a scenario in which the rate would not depend on the reactant concentrations when ideas consistent with collision theory are proposed. If reactants must collide to react, the more concentrated the reactants are, the higher the rate must be, it is reasoned. In our setting, state curriculum standards at the high school level explicitly relate concentration and rate with a positive correlation,[15] so with that background, this line of reasoning is expected and even appropriate. What we communicate about the zeroth-order process, however, is that it represents the case in which reactant concentration does not influence the overall rate of the process. While counterintuitive for many of our students, zeroth order processes can lead nicely into a conversation about multiple-step reactions and rate-determining steps.

Step 2: First- and Second-Order Plots

Because the first- and second-order processes are both curved when plotted on the graph of concentration/time, it is difficult to distinguish between the two when displayed in this format (Figure 4). Specifically, it is not obvious what the relationship is between the slope of the graph and the concentration of the reactant, in contrast to the zeroth-order plot. Our strategy has been to tell the students that for the introductory course, only two relationships outside of the zeroth-order case will be considered: one in which the rate changes proportionally to concentration (i.e., first order), and one in which it changes as the square of the concentration (second order). Both of these types of functions (i.e., first- and second-order polynomials) are familiar, having been introduced multiple times in our students'

mathematics courses prior to their precalculus or calculus experiences in which they are enrolled during the introductory chemistry sequence.[16,17]

For the first-order plot, we use simulated data to show that at each successive half-life, the instantaneous rate (i.e., the slope in the concentration/time graph) decreases also by a factor of 2, and that this relationship is consistent across the entire concentration/time curve (Figure 4A). Using the three points corresponding to 0.25, 0.5, and 1.0 M as a guide, we then prompt the students to construct the appropriate rate/ concentration graph for it, and find that as a whole, the requisite graph is easily conceptualized and appropriately drawn. On the basis of the slopes (rates) from the three highlighted points on the concentration versus time plot, students are usually comfortable with the concept of a direct relationship between rate and concentration when they are plotted against each other (Figure 4B). For example, moving from 0.25 to 0.5 M, a doubling of concentration, the corresponding rate also doubles (from ~0.01 to ~0.02 M s^{-1}). The same relationship is shown to hold when the concentration doubles from 0.5 to 1.0 M as well (see the Supporting Information).

In the case of second-order processes, sketching an accurate second-order plot on the same graph as the first-order plot helps the students to recognize how the curvature differs (Figure 4A). For instance, the second-order rate has decreased to one-quarter of its initial value at the first half-life, and a mere one-sixteenth at the second half-life. Translating this function to a correctly drawn rate/concentration graph gives our students more trouble than in the zeroth- or first-order situations, but because the $y = x^2$ curve is familiar to them, they soon recognize it as such. As with the zeroth-order graph, we then prompt the students to write the form of the mathematical equation between rate and concentration that would be consistent with what they have drawn. When the rate versus concentration plot for the second-order process is overlaid with that of the first-order one (Figure 4B), we explicitly direct the students to consider how the rate changes when the concentration changes from 0.5 to 1.0 M and compare that to the linear plot. In the second-order case, the rate quadruples (from ~0.01 to 0.04 M s^{-1}), while in the first-order case, it only doubles (see the Supporting Information).
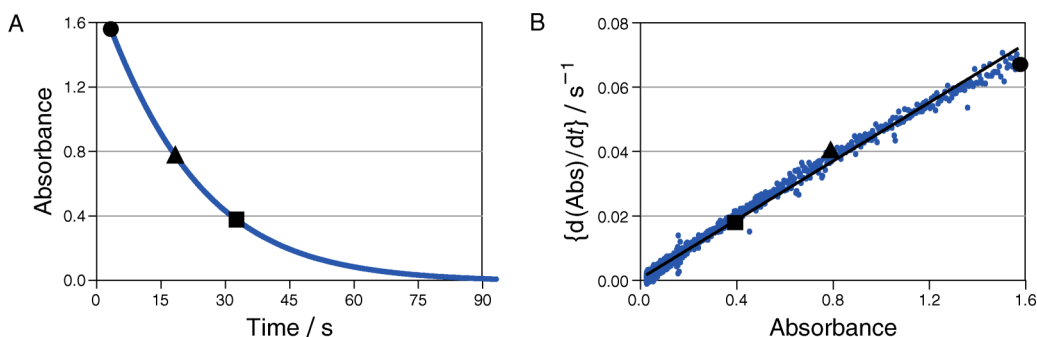
Figure 5. First-order example plots based on student data from the dye bleaching experiments. (A) Pseudo-first order kinetic process showing a decrease in blue food color intensity in the presence of bleach. Data approximating initial (●) and first (▲) and second half-life concentrations (■) are depicted. Dye absorbance at 610 nm serves as a proxy for concentration and was detected using a PASCO GLX datalogger with colorimeter. (B) Conceptual reconstruction of the first derivative of (A) using the same labeling scheme for comparison. Best-fit linear regression corresponds to R^2 = 0.9925.
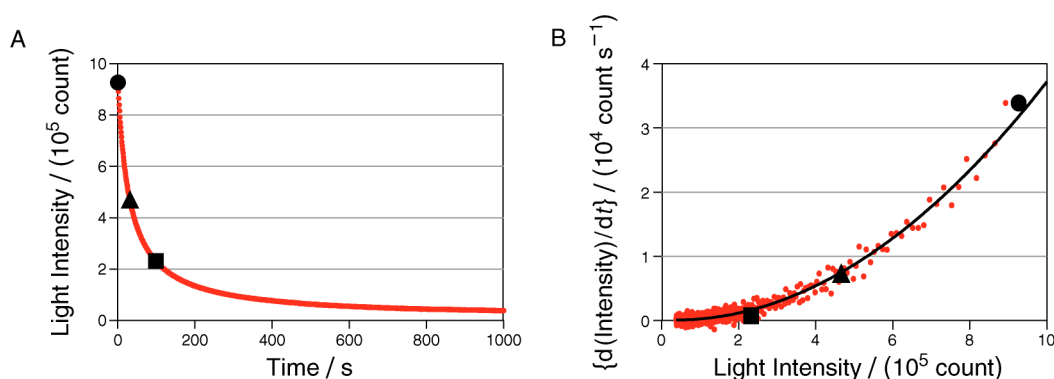

Figure 6. Second-order example plots based on student data from phosphorescence experiments. (A) Second-order kinetic process showing a decrease in phosphorescent paint intensity. Data approximating initial (●) and first (▲) and second half-life concentrations (■) are depicted. Paint fluorescence at 485 nm serves as a proxy for concentration and was detected using an Olis DM 45 spectrofluorimeter. (B) Conceptual reconstruction of the first derivative of (A) using the same labeling scheme for comparison. Best-fit nonlinear regression using a second-order polynomial corresponds to R^2 = 0.9657.

Because these functions are familiar to students from previous mathematics courses, most of them are comfortable with the typical representations given in general chemistry textbooks for these rate laws, namely (eqs 2 and 3):

$$\text{Rate} = -d[A]/dt = k[A]^1 = k[A] \tag{2}$$

$$\text{Rate} = -d[A]/dt = k[A]^2 \tag{3}$$

where [A] is the concentration of reactant A at a given time in the reaction.

■ PHASE III—CONCEPTUAL UNDERSTANDING OF RATE LAWS PART II: INTERPRETING EXPERIMENTAL KINETICS DATA

Once oriented to the limited scope of rate laws that will be considered in the introductory course (30 min or longer depending on approach), the students generate and evaluate kinetics data from three model systems previously reported in this *Journal*: dye bleaching,[18] phosphorescent paint[19] and the glyoxal clock reaction.[20] From these data, the expectation is for the students to write the appropriate rate laws for each system, and to recognize that most balanced chemical equations are not written as elementary steps and therefore cannot be used directly in rate law development. The other expected outcome for this segment of the instructional sequence is to connect the three related concepts of reaction mechanisms, collision theory,

and rate laws to construct a coherent mental model that accounts for the empirical results. That model should be based on a conceptual understanding of the underlying molecular-level processes that occur over the course of a reaction. Students should be supported here in the intellectual work of moving beyond the simplistic preliminary models they were likely to have drawn on earlier in this instructional sequence and onto more sophisticated models with features that align with the kinds of visualizations that would be generated from collision theory.

Although we have a strong preference for the students to generate and analyze their own kinetics data prior to formal instruction in the lecture portion of the course, we recognize that this can be logistically problematic to enact. In these situations, the students can be given the raw data to analyze during classroom-based, guided-inquiry experiences.[21] We recommend not presenting the reaction system investigations in the predictable sequence of zeroth-, first-, and then second-order reactions, as that may interfere with student task engagement. Students should not anticipate a particular sequence of experiments that would give away the answers prior to working through them. In our experience, beginning with the technically straightforward bleach/blue food coloring experiment[18] (pseudo-first order) has worked well with populations of teachers and students alike (Figure 5).

Because the absorbance measurement in the dye bleaching investigation[18] is directly related to concentration via the Beer–Lambert law, we use absorbance as a "proxy" for blue dye concentration.[22] We exploit the ability of modern dataloggers (in this case, the PASCO GLX with a colorimeter[23]) to take readings multiple times each second so that the necessary data to construct rate/concentration graphs and the corresponding rate laws can be collected (Figure 5). What the hand-held technology has enabled students to do is to accurately approximate the instantaneous rate of change (i.e., the slope in the concentration/time plot) during the reaction with a series of average rates taken over very short time intervals (see the sample data in the Supporting Information).

As a result, the rate/concentration plots are generated with ease, facilitating the elucidation of the rate law with a minor and comfortable manipulation of the raw data the students collect during the investigation. In a more mathematical approach, by comparison, students might be required to generate the concentration/time plot, and rather than being prompted to consider the relationship between the rate and the reactant concentration, they are instead asked to only look at the transformation of that plot that leads to the "most linear" relationship. Students then, in the ideal outcome, infer a rate law from an understanding of which transformation achieves linearity (namely [A] vs time, ln [A] vs time, and 1/[A] vs time where [A] is the concentration of reactant "A"). The authors' experience, however, is that most of our students, lacking the mathematical understanding of the connection between the differential and integrated forms of the rate law, default to the mechanical process of generating the transformed plots and engaging in the heuristic task of matching the transformed plot to the appropriate entry in a summary table of kinetic formulas.

For the second-order phosphorescent paint experiment,[19] we found the portable sensor to be insensitive for detecting the relatively low intensity of the blue glow paint. Instead, we used a commercial spectrofluorimeter that generated data for an analysis similar to the bleach experiment described above (Figure 6).

As the zeroth-order process is easy to recognize in the concentration/time graph (being the only linear function, Figure 3), the glyoxal–bisulfite clock reaction may have utility in facilitating the conceptual understanding that is anticipated with the other two investigations. In our search of the literature, it was one of the very few zeroth-order processes reported for study in the introductory course,[20,24,25] and the only one we were comfortable advocating to our colleagues with varied access to specialized equipment. Instead of reproducing the experimental data again here, we direct the reader to the original manuscript but have included sample student outcomes and analytical procedures for determining kinetic relationships in the Supporting Information.

By the end of this part of the experience, the students may be expected to construct and interpret time/concentration and rate/concentration graphs appropriately, make and justify claims about the order of the reaction and the form of the rate law, and rationalize the observation that the half-life for a first-order reaction is concentration independent, while those for the zeroth- and second-order processes are concentration dependent.[26]

■ PHASE IV—CONNECTING RATE ORDERS, LAWS, COLLISION THEORY, AND REACTION MECHANISMS

In the final stage of the instructional sequence (15–30 min), students are asked to consider why the study of reaction mechanisms is often a central focus of kinetics studies. To facilitate this understanding, we return to the process introduced in reaction 1, the nucleophilic substitution of methyl bromide by the iodide ion. Students are first asked to reconsider their initial graphs of the reactant concentrations over time based on their new understanding of kinetics. When prompted to draw on the board and explain their answers, most answers reflect a first-order process based on an inspection of the balanced chemical equation and an intuitive notion of how chemical processes occur, namely through the collision of two species to make novel structures. We affirm both conceptions and expand this result by showing a reaction coordinate graph overlaid with a ball-and-stick model of each species taken from a publicly available Web site (Figure 7).[27]
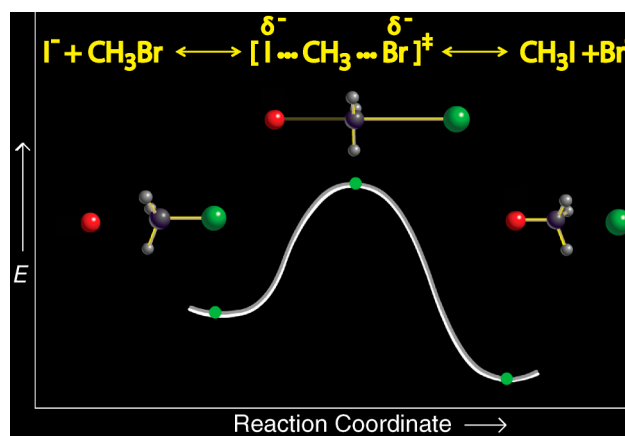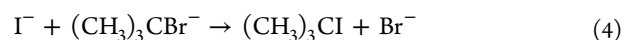

Figure 7. Reaction coordinate for a single step nucleophilic substitution reaction. Reaction 1 is depicted in ball-and-stick representation to show the concerted substitution of bromide (green) with iodide (red) in a single rate-limiting step. Atomic radii are not to scale. Adapted from reference 24

While stepping students through the bond-breaking and bond-forming processes, we highlight that the process occurs in a single (concerted) step in which bond breaking and bond forming occur more or less simultaneously; therefore, the rate of the reaction is dependent on both the concentrations of the nucleophile and electrophile (i.e., it is a bimolecular process). Once convinced that most student concerns over the concepts or terminology introduced here are resolved, we present them a seemingly similar system (reaction 2, in eq 4) and prompt them for a proposed mechanism and reaction coordinate, along with the two kinetics plots of concentration/time and rate/concentration:

$$I^- + (CH_3)_3CBr^- \rightarrow (CH_3)_3CI + Br^- \qquad (4)$$

Predictably, students propose another bimolecular, single-step process that yields the same rate law forms and graphs as in the S_N2 case, and are justifiably surprised when shown that the experimentally determined rate law is zeroth order with respect to iodide, but first order with respect to *tert*-butyl bromide (Figure 8). After some speculation and discussion, the reaction coordinate showing that the process proceeds through
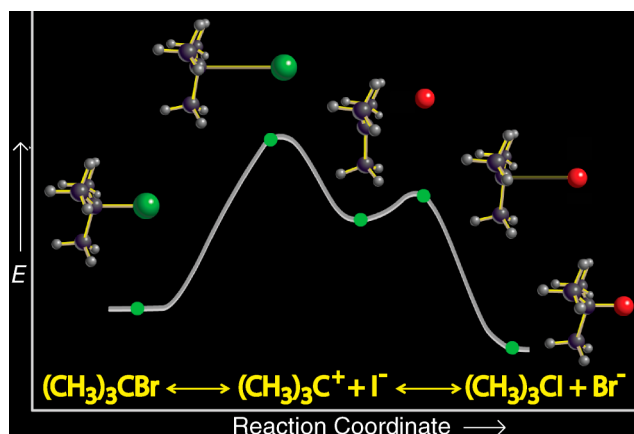
Figure 8. Reaction coordinate for a multistep nucleophilic substitution reaction. Reaction 2 is depicted in ball-and-stick representation to show the (first) rate-determining step involves a single reactant molecule, *tert*-butyl bromide, and is therefore zeroth order with respect to the other reactant, iodide. Labeling scheme as Figure 7 for direct comparison. Adapted from reference 25

two steps with different relative rates helps the students to understand how zeroth-order processes could occur and to recognize that, in many cases, the overall balanced equation is not sufficient to explain the kinetics of the reaction (i.e., balanced equations do not capture the elementary steps in the reaction).[28] It is here that we try to be explicit about why the study of reaction mechanisms can be so important to chemists: namely, that by understanding the steps through which the reaction proceeds, the rate by which products are produced can be altered. We suggest, for example, that if the product of this process (*t*-butyl iodide) was important industrially and company profit was in part dependent on the rate of production, it would be important to recognize that changing the concentration of iodide in the reaction mixture would not affect the rate.

■ CONCLUSIONS

In this article we have presented a conceptually based (rather than mathematically based) approach to developing foundational concepts of chemical kinetics. This approach has proven fruitful with students in university-level general chemistry classes as well as teachers in professional development workshops. It is an approach that we believe would also be productive in advanced high school courses, and we have planned studies to investigate the efficacy of the approach in that context. In concluding this article, we wish to expand on the pedagogical thinking that supports the approach and how that thinking can be used to ensure the strongest conceptual understanding of chemical kinetics possible for students. In particular, we build upon key insights from BouJaoude's[10] analysis of student errors in kinetic concepts: (i) students must be provided a great deal of support in learning how to transform traditional experimental data associated with chemical kinetics (concentration vs time) into the data that allows determination of the appropriate kinetics relationships (rate vs concentration); and (ii) students must be facilitated in developing strong links between their mathematical representations of kinetic phenomena and their conceptual models.[10]

The insights identified above were incorporated into the instructional approach at each stage of the lesson sequence. In Phase I, student corpuscular conceptions were prompted with a

familiar chemical reaction structure that involved new organic molecules. Through inquiry, students were guided to connect molecular phenomenon to mathematical models using principles from collision theory. The many possible concentration vs time plots generated by students were narrowed to first- and second-order processes during a class discussion of reactants, rates, and reaction end points. In Phase II, students were challenged to consider reaction rates at each half-life when distinguishing between zeroth, first-, and second-order processes. By beginning with the concentration versus time plot corresponding to the zeroth-order process, students visualize how to transform the data into rate versus concentration relationships. While this process is conceptually straightforward for zeroth-order processes, the transformation is necessary to distinguish between the seemingly similar curves of first- and second-order processes. In our experience, moving from the conceptual rate plot to the first derivative can be facilitated by the use of limited data points, such as the initial concentration, first half-life and second half-life. Phase III reinforced newly developed mathematical formulations and corresponding molecular visualizations through application to three experimental systems. As a result, students strengthened their understanding of the multiple ways of representing kinetics phenomena by working with extensive empirical data sets. In the final Phase IV, students revisited their initial conceptions of reaction 1 and refined them based on the work in the previous phases with collision theory and reaction mechanisms. This instructional approach was designed after Gilbert's[29] strategy to help students assemble simple principles into conceptual models, which could then be refined into more sophisticated mental models through comparison to additional facts.[29]

We propose that this approach is aligned not only with the principles of model-based reasoning as discussed earlier, but also with the ideas emerging from studies on how scientists engage in the work of understanding natural phenomenon. Specifically, scientists often work at refining a visual image as the answer to a problem well before translating the solution into a mathematical equation.[30] In such instances, the use of mathematics becomes a means to more efficiently describe the "answer-image". Root-Bernstein and Root-Bernstein[30] go on to describe this ability of first feeling or seeing what the equations mean as a strategy that distinguishes successful scientists and engineers from their peers. We believe that structuring our curriculum and building our pedagogical practices to support the sequential work of visualization, representation, and mathematical formulation will likely lead to deeper conceptual understanding of those phenomena,[31,32] in this case producing successful science experiences with chemical kinetics.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Instructor notes describing the instructional approach; alternative experiments and data analysis; properly formatted tables for simulating first- and second-order data; student data and sample graphs from the dye/bleach, phosphorescent paint, and glyoxal clock experiments. This material is available via the Internet at http://pubs.acs.org.

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Notes

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