Investigating Student Understanding of Rate Constants in Chemical Kinetics: When is a Constant "Constant"?

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The concept of rate constants is important for developing a deep understanding of chemical kinetics, an area of chemistry that models the rates of reactions. Reaction rates are modeled mathematically, typically using an equation called a "rate law". One of the terms in this equation, the rate constant, embodies important variables that affect rate, such as temperature-dependence, Our primary research focus in this work is investigating the question: How do students reason about rate constants in chemical kinetics? Preliminary analysis reveals that students often conflate ideas from chemical kinetics and equilibrium, such as rate constants and equilibrium constants. Furthermore, students demonstrated varying levels of sophistication regarding the distinction and relationship between rate and rate constants. Finally, students conveyed different ideas about the mathematical nature of the rate constant quantity.

Keywords: Constants, Parameters, Variables, Rate, Chemistry

Introduction and Rationale

One of the core ideas in the discipline of chemistry is change and stability of chemical systems (Cooper, Posey, Underwood, 2017; Holme, Luxford, & Murphy, 2015; Holme & Murphy, 2012; Laverty et al., 2016). This foundational idea that "energy and entropy changes, *the rates of competing processes* [emphasis added], and the balance between opposing forces govern the fate of chemical systems" takes many shapes and forms (Laverty et al., 2016). One area of study called chemical kinetics models rates of reaction, often utilizing rate law equations. For example, a generic chemical reaction, $x\text{ X} + y\text{ Y} \rightarrow P$, the rate law would be $\text{rate} = k[X]^m[Y]^n$ (concentration of a reactant is represented by surrounding the reactant with square brackets). Rate laws are empirically derived and demonstrate the dependence of reaction rates on the concentration (or pressure) of reactants and other parameters, typically a coefficient (k) and reaction orders (m and n) (Holme et al., 2015). In the case of elementary reactions or reaction steps, the order is also empirically derived and relates to the molecularity, or the number of molecules that react. The coefficient that appears in the rate law is typically termed the rate constant (k). The temperature dependence of reaction rate is contained in the rate constant and is typically modeled by the Arrhenius equation, $k = Ae^{-E_a/RT}$, where E_a is the activation energy of the reaction, A is a preexponential or frequency factor, R is the gas constant, and T is temperature (Holme et al., 2015). As temperature is controlled in an experimental setting, rate constants are generally held constant during a reaction.

Understanding the information encoded in rate constants is an important part of understanding the chemistry being modeled by kinetics equations (Holme et al., 2015). However, studies of chemistry students at both secondary and tertiary levels demonstrate that students have difficulty with this. Students often have an incorrect understanding of the relationship between reaction rate and temperature, a relationship that is contained in the rate constant (Bain & Towns, 2016). Students also often falsely relate temperature and activation energy or mischaracterize the mathematical nature of rate's time-dependence (Bain & Towns, 2016). While these studies give some insight into the nature of student thinking in this area, more work is needed at the undergraduate level (Bain & Towns, 2016; Singer, Nielson, & Schweingruber, 2012).

A robust understanding of rate constants would, among other things, include mathematical resources related to constants, parameters, variables, and functions. Mathematical symbols, like those present in a rate law, encode meaning. These quantities, represented by different symbols, could represent a constant (does not vary ever), a parameter (does not vary within a given setting), or a variable (varies with a given setting) (Thompson & Carlson, 2017). A rate constant would typically be considered a parameter, or a "generalized constant" (Philipp, 1992; Thompson & Carlson, 2017). As discussed by colleagues from the physics education research community (Redish, 2005; Redish & Gupta, 2009), the labeling and use of constants, parameters, and variables is very different in scientific communities, such as physics or chemistry, compared to mathematics communities. Further, scientists also load meaning onto these symbols, which can lead to different interpretation of equations and changes how equations are viewed; such differences arise because the goals and purposes for the use of mathematics are so divergent (Redish, 2005; Redish & Gupta, 2009). These distinctions and differences are often not apparent to students, who are concurrently enrolled in math and science courses (Redish, 2005; Tuminaro & Redish, 2007). Considering student reasoning from both a chemistry and mathematics perspective, this work was guided by the following research question: *How do students reason about rate constants in chemical kinetics?*

Theoretical Perspectives

We have framed our data analysis and discussion of results in terms of the resources framework, which is a model of cognition that defines knowledge as a network of fine-grained *resources*, or cognitive units, that are activated and constructed in response to a task or prompting (Hammer & Elby, 2003; Hammer, Elby, Scherr, and Reddish, 2005). The resources perspective builds on diSessa's (1993) *knowledge-in-pieces* conceptualization, which accounts for the observed inconsistency of student responses, since different resources or groups of resources may be activated when reasoning about different contexts (Hammer et al., 2005).

The resources perspective is in contrast to an alternate model of cognition that presupposes student understanding as composed of unitary, stable conceptions that are applied generally across contexts (Hammer & Elby, 2003; Hammer et al., 2005). This has implications for understanding the role of instruction in relation to how student ideas change over time; instead of targeting and replacing large entities or conceptions, conceptual change involves adding fine-grained resources and modifying connections between resources, ultimately restructuring students' local cluster of ideas to create a more coherent network of meaningfully connected resources (Wittmann, 2006). We are interested in identifying the resources students used to reason about rate constants, and we are particularly interested in understanding the connections between these resources. One useful representation of resources discussed in the literature is a *resource graph*, which visually indicates the links between different resources activated in a specific context (Wittmann, 2006; Sayre & Wittmann, 2008). Ongoing analysis involves determining the utility of such a representation for our work. A better understanding of how students cognitively organize resources would provide insight regarding which resources need to be targeted and which connections between resources need to be emphasized.

Methods

The study that we discuss in this preliminary report is part of larger project interested in investigating how students integrate chemistry and mathematics when solving chemical kinetics problems. For this project we have previously reported on student engagement in modeling (Bain, Rodriguez, Moon, & Towns, 2018), student conceptions regarding zero-order systems (Bain, Rodriguez, & Towns, 2018), productive features of problem solving (Rodriguez, Bain, Hux, & Towns, 2018), and student use of symbolic and graphical forms (Rodriguez, Santos-Diaz, Bain, & Towns, Submitted); here we focus on student reasoning related to rate constants. Our primary data source for this study is semi-structured interviews involving students working through a series of prompts (Table 1), with data collection involving the use of a Livescribe™ smartpen to digitally synchronize audio and written data (Linenberger and Bretz, 2012; Harle and Towns, 2013; Cruz-Ramirez de Arellano and Towns, 2014). Participants were undergraduate chemistry students from a second-semester general chemistry course (n=40), an upper-level physical chemistry course (n=5), and an upper-level reactions engineering course (n=3).

Table 1. Second-order and zero-order math and chemistry prompts.

Second-Order Math Prompt	**Zero-Order Math Prompt**
Here is another equation you've probably seen in class: $\frac{1}{[A]} = kt + \frac{1}{[A]_0}$ How would you explain this equation to a friend from class? How would you explain this on an exam?	Here is another equation you've probably seen in class: $[A] = -kt + [A]_0$ How would you explain this equation to a friend from class? How would you explain this on an exam?
Second-Order Chemistry Prompt	**Zero-Order Chemistry Prompt**

Second-Order Chemistry Prompt

A second-order reaction

$2\ C_4H_6(g) \rightarrow C_8H_{12}(g)$

was run first at an initial concentration of 1.24 M and then again at an initial concentration of 2.48 M. They were run under the same reaction conditions (e.g. same temperature). Data collected from these reactions are provided in the table. Is the rate constant for reaction 2 (1.24 M) greater than, less than, or equal to the rate constant for reaction 1 (2.48 M)?

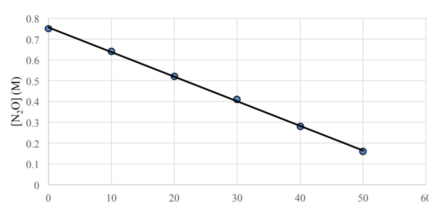
Time (hrs)	$[C_4H_6]$ (M) Rxn 1	$[C_4H_6]$ (M) Rxn 2
0	1.24	2.48
1	0.960	1.55
2	0.775	1.13
3	0.655	0.89
4	0.560	0.73
5	0.502	0.62
6	0.442	0.54
7	0.402	0.48
8	0.365	0.43
9	0.335	0.39
10	0.310	0.35

Zero-Order Chemistry Prompt

Below is a zero-order rate plot for the reaction

$N_2O(g) \rightarrow N_2(g) + ½O_2(g)$

where $[N_2O]_0$ = 0.75 M and k = 0.012 M/min. The reaction is conducted at 575 ˚C with a solid platinum wire, which acts as a catalyst. If you were to double the concentration of N_2O and run the reaction again, how would the half-life change? At the half-lives for each reaction run, how do the chemical systems compare?



Student interviews were transcribed and open coded using constant comparison (Bain et al., 2018; Strauss and Corbin, 1990). Data analysis involved two researchers coding in tandem, discussing coding discrepancies and requiring 100% consensus for code assignments (Campbell, Quincy, Osserman, & Pederson, 2013). The coding scheme for the larger project had three primary themes, where one was comprised of codes that characterized the type of chemistry and mathematics content resources expressed. The codes primarily related to rate and rate constants were further analyzed for themes surrounding student understanding of rate constants.

Preliminary Results

Our preliminary analysis reveals three primary themes: (1) conflation of rate constants with equilibrium constants, (2) potential levels of sophistication in differentiating the concepts of rate and rate constants, and (3) various types of understanding regarding the mathematical nature of rate constants.

Conflation of Rate Constant (k) with Equilibrium Constant (K)

One commonly used idea is in the study of chemical equilibrium is the equilibrium constant, *K*. It is used to determine the extent of a reaction and the amount of reactants and products present at equilibrium from a given initial state; it is also a function of temperature and change in free energy (Holme et al., 2015). As reported in prior research, students often confuse kinetics and equilibrium concepts (Bain & Towns, 2016; Becker, Rupp, & Brandriet, 2017). In light of this, it was unsurprising to see that almost a quarter of our participants demonstrated rate constant (*k*) and equilibrium constant (*K*) conflation, a finding similar to Becker et al. (2017). The reason for this appears to be two-fold. First, the symbols for each constant are represented by the letter "k", which are only distinguishable by capitalization (or lack thereof). Second, from the perspective of Sherin's (2001) symbolic forms, the pattern of terms in the equations (symbol templates) is somewhat similar (Figure 1).

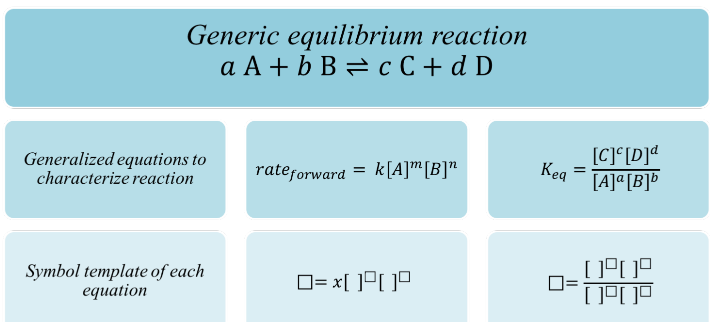


Figure 1. Side-by-side comparison of two mathematical equations and their corresponding symbol templates that model various aspects of this generic equilibrium reaction.

The sentiment that symbols and topics in general chemistry are similar and difficult to differentiate is summarized in a statement made by a general chemistry student, Nelly:

Nelly: *"That's like equilibrium* [constant]. *Not rate constant. I don't know. That's also another thing that's hard about chemistry. It just seems that everything is the same almost, and it's hard to distinguish each equation and each principle."*

This discussion stemmed from her reasoning about if and how rate constants change for different reactions. She began reasoning about rate constants as equilibrium constants, but realized that she was thinking about the inappropriate constant, correcting herself. The similar nature of the symbols and equation structure caused temporary conflation of the ideas during her interview.

Another general chemistry student, Georgina, demonstrated conflation of equilibrium and rate constants as well, utilizing an an equilibrium-like expression to solve for reaction order.

Georgina: *"I remember from zero order, you didn't have to do anything to do the concentration of a for it to be a straight line."*

Interviewer: *"Why do you think that is?"*

Georgina: *"I know it has something to do ... I kinda remember vaguely that ... Say that your equation would be A plus B equals C plus D.* [writing chemical equation, top of Figure 2] *Concentrations of your products go over your concentration of the reactants.* [writing variation of equilibrium expression, bottom of Figure 2] *I know it has something to do with whatever exponents you ended up with here."*

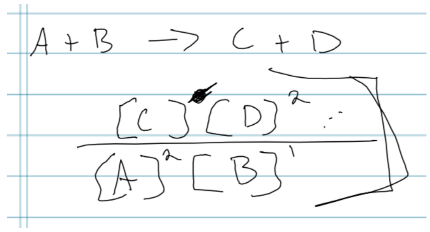


Figure 2. Chemical and mathematical equations written by Georgina (general chemistry student). The mathematical equation is structured like that of an equilibrium expression.

In this passage, Georgina was using the inappropriate equation to solve for order; she should have been using rate law equation, which contains a rate constant term, rather than the equilibrium constant. As shown in Figure 1, the symbol templates of the two equations are similar in structure. In general, each equation contained a variable related to the product of bracketed quantities, each raised to a power (Becker & Towns, 2012; Dorko & Speer, 2015; Rodriguez, Bain, & Towns, 2018; Rodriguez et al., 2018; Sherin, 2001). It is this similarity that often caused participants to activate the inappropriate resource for this context.

Possible Levels of Sophistication in Student Understanding of Rate Constants

There were a wide variety of resources characterized regarding student understanding of rate constants. Analysis revealed varying participant understanding of the relationship between rate and rate constant. Some students expressed conflation of these ideas, while others conveyed distinctive understanding of these two concepts with differing degrees of sophistication. The exact nature of these ideas is presently being explored.

Levels of Sophistication in Understanding the Mathematical Nature of Rate Constants

When analyzing participant understanding of rate constants among students who did conceive of rate and rate constants as distinct, there were three levels of understanding conveyed with respect to what type of quantity rate constants were. First, participants sometimes conveyed the idea that rate constants were like *universal constants*, that is quantity was the same at all times. This is distinct from other participants who stated that rate constants were only constant for a given reaction, demonstrating a more *parameter-like* understanding. Finally, some participants went further to describe on what rate constants depend. These participants cited specific variables, such as temperature, or provided the Arrhenius equation, demonstrating an even more sophisticated *parameter-like* understanding.

Conclusions and Questions

While the analysis for this work is ongoing, the preliminary findings for this project indicate that an important instruction target for undergraduate chemistry (and likely other science and mathematics courses) is a nuanced understanding of the distinction between constants, parameters, and variables. While terms like "rate constant" and "equilibrium constant" may be misleading for students, explicit discussion of the mathematical nature of equation terms is important in developing deep understanding of the chemistry being mathematically modeled.

Further analysis involves addressing the following questions:

(1) What insight into students' knowledge structures can be gained using resource maps?
(2) What is the relationship between participant understanding of rate and rate constants?
(3) Are there other lenses in the RUME community that would be helpful for investigating students' mathematical understanding in chemistry contexts?

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