

Foundations of calculus in chemistry: Where and how is calculus used in the chemistry undergraduate curriculum

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The discipline of chemistry – 5 sub-disciplines

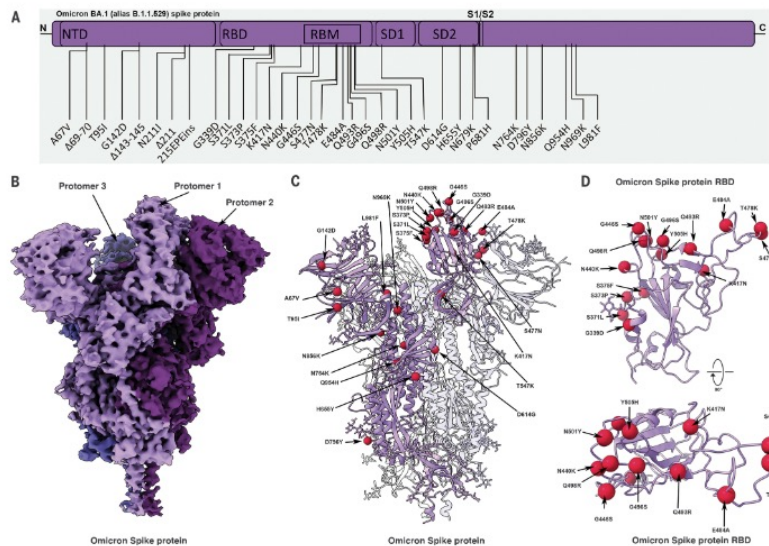


Fig. 1. Cryo-EM structure of the Omicron spike protein.

Biochemistry

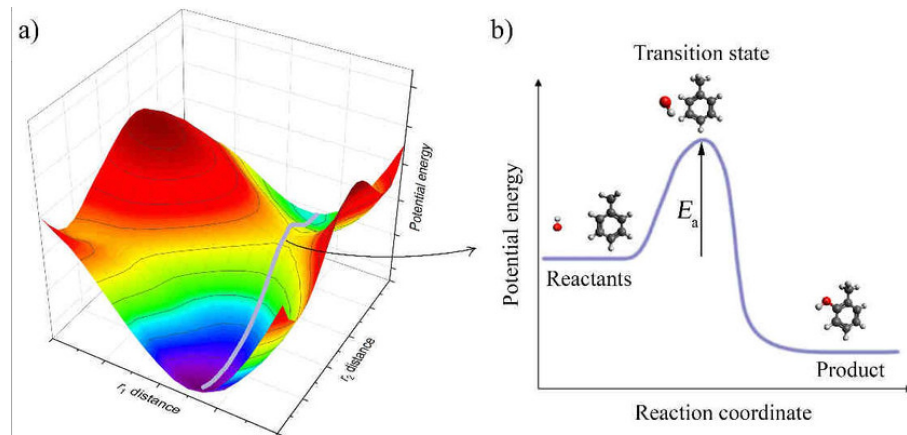
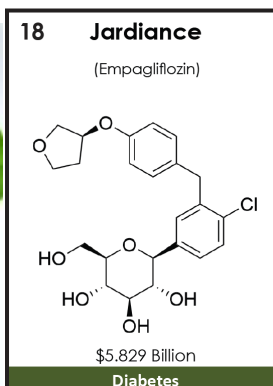
Analytical chemistry



Inorganic chemistry



Organic chemistry



Physical chemistry

Undergraduate curriculum – standard 4-year

3 semesters of calculus,
Differential equations,
&
Linear algebra

Physics (calculus based)

A lot of hours of
Laboratory

*Important that math is
a scaffold, not a filter.*

Year	Fall	Spring
1	General Chemistry + lab	General Chemistry + lab
	Calculus I	Calculus II
		Physics I + lab
2	Organic Chemistry + lab	Organic Chemistry + lab
	Calculus III	Inorganic I
	Physics II + lab	Differential equations
3	Analytical I + lab	Physical Chem. II + lab
	Physical Chem. I + lab	Linear algebra
4	Biochemistry	Inorganic II
	Analytical II + lab	Inorganic lab

Where and how is calculus used?

- Analyzed the “Anchoring Concepts Content Maps” (ACCM)
 - General chemistry, organic chemistry, inorganic chemistry, analytical chemistry, physical chemistry
 - Biochemistry publication has been delayed by COVID – was not available
- Where is it used most often across the curriculum? To understand rates of reactions, kinetics.

Zero-Order

$$\frac{d[A]}{dt} = -k$$

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

$$\text{rate} = -\frac{d[A]}{dt} = k[A]^1$$

$$k = Ae^{-E_a/RT}$$

$$[A] = -kt + [A]_0$$

First-Order

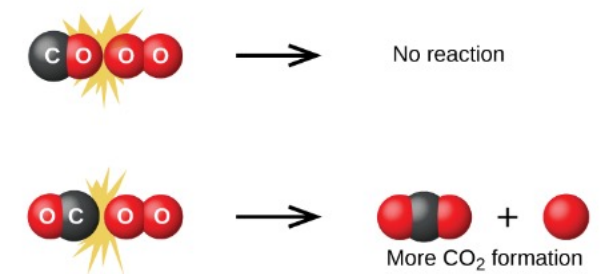
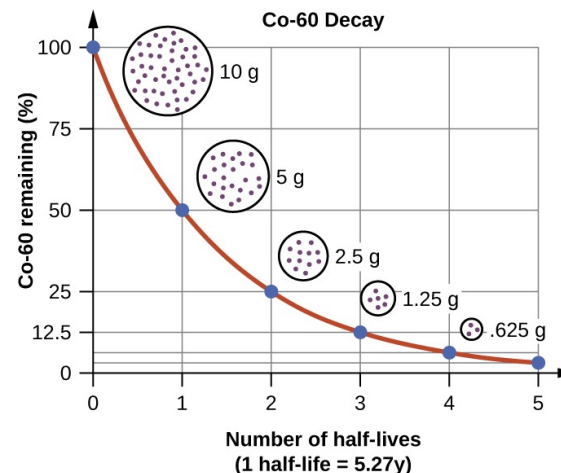
$$\frac{d[A]}{dt} = -k[A]$$

$$\ln[A] = -kt + \ln[A]_0$$

Second-Order

$$\frac{d[A]}{dt} = -k[A]^2$$

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

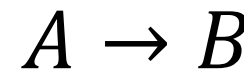


Quick Chemistry Primer: What is Kinetics?

(Gentle note: Here's where the disciplines discuss the same thing differently.)

Kinetics:
*The study of rates
of chemical processes*

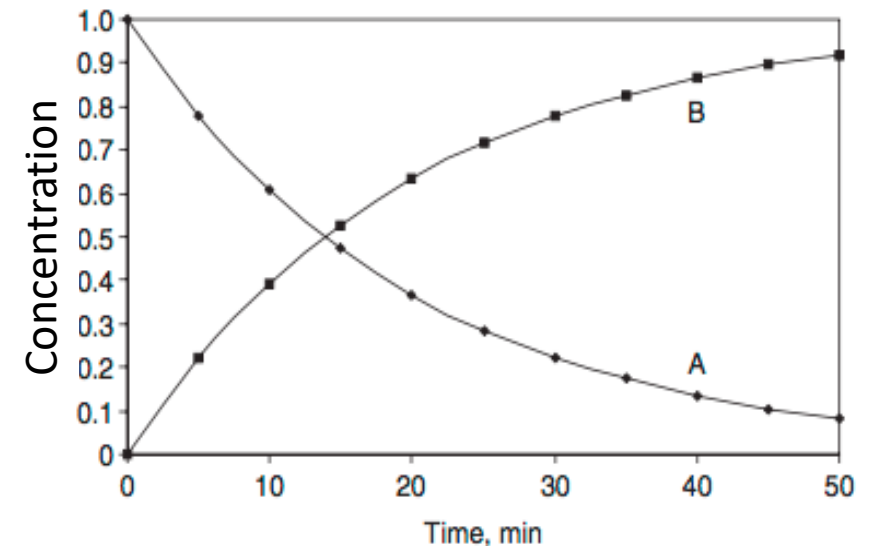
$$\frac{-d[A]}{dt}$$



$$\frac{+d[B]}{dt}$$

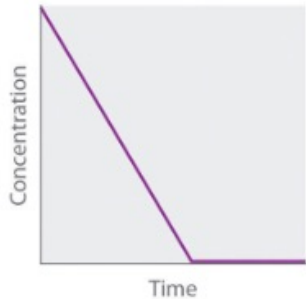
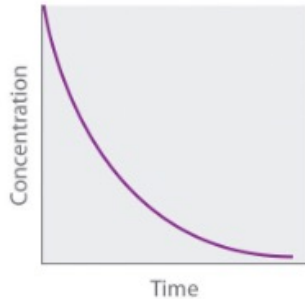
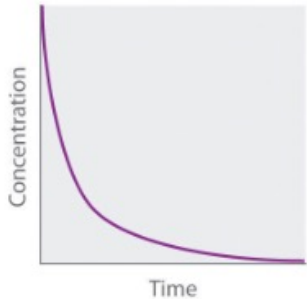
$$\frac{-d[A]}{dt} = k[A]^x$$

$\frac{-d[A]}{dt} = \text{Rate}$
 $k = \text{rate constant}$
 $[A] = \text{concentration of reactant A}$
 $x = \text{order of the reaction}$



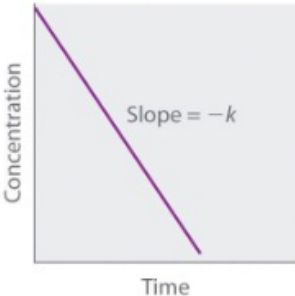
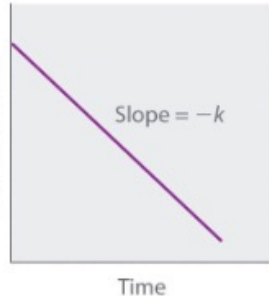
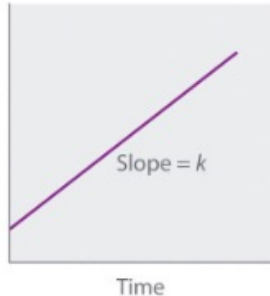
How do students learn about rates in chemistry?

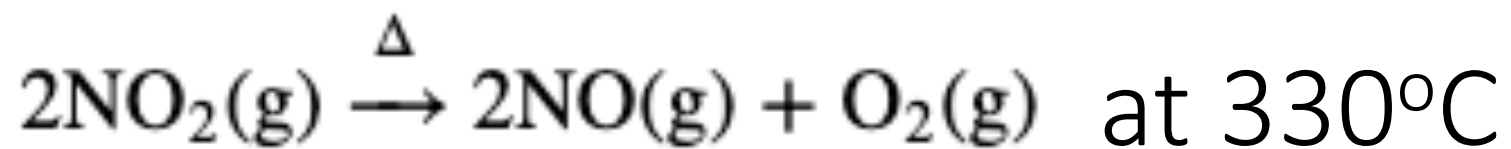
1. Often learn through order.
2. Concentration vs. time is seldom explored.
3. Integrated rate laws, in a linear form, are used to determine the order of a reaction.

	Zeroth Order	First Order	Second Order
Differential rate law	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$
Concentration vs. time			

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Differential rate law	Rate = $-\frac{\Delta[A]}{\Delta t} = k$	Rate = $-\frac{\Delta[A]}{\Delta t} = k[A]$	Rate = $-\frac{\Delta[A]}{\Delta t} = k[A]^2$
Concentration vs. time	<i>Not emphasized</i>		
Integrated rate law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$ or $\ln[A] = \ln[A]_0 - kt$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
Straight-line plot to determine rate constant			

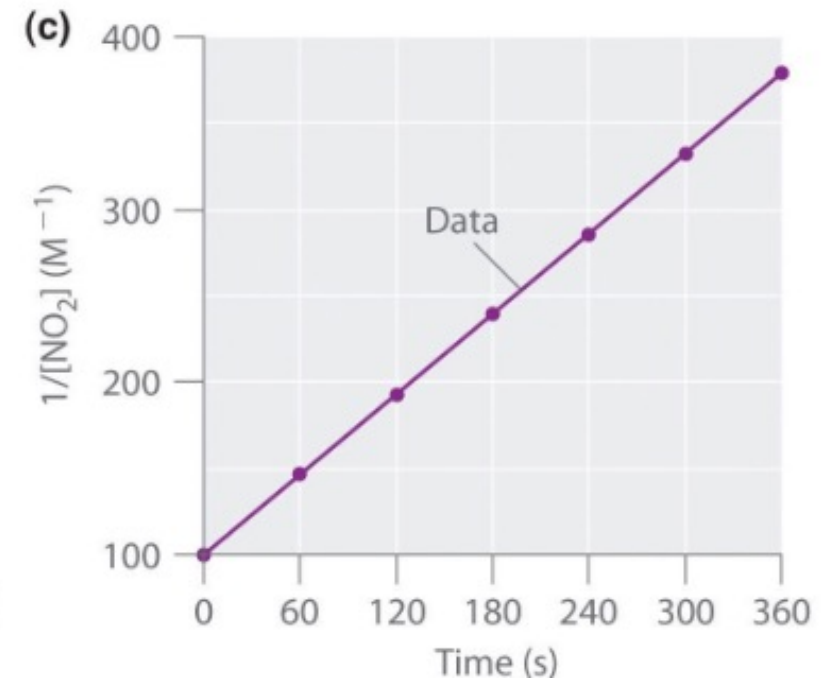
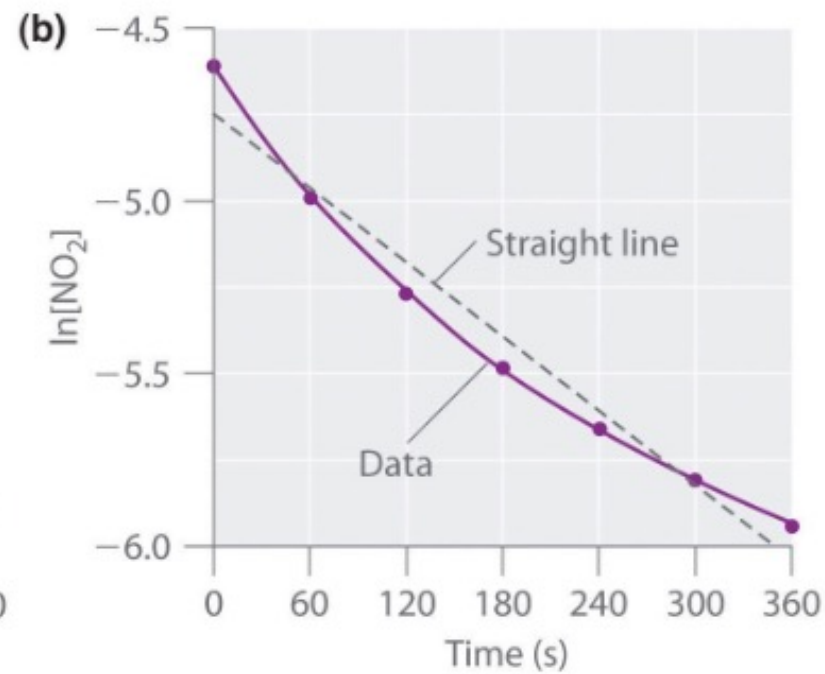
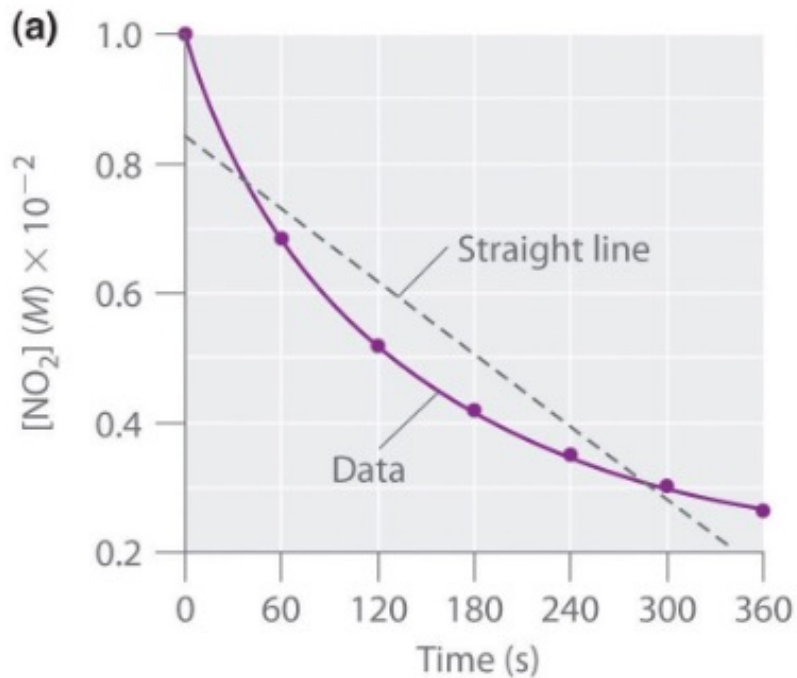


Time (s)	[NO ₂] (M)
0	1.00 x 10 ⁻²
60	6.83 x 10 ⁻³
120	5.18 x 10 ⁻³
180	4.18 x 10 ⁻³
240	3.50 x 10 ⁻³
300	3.01 x 10 ⁻³
360	2.64 x 10 ⁻³

1. Measure concentration of [NO₂] as it changes with time. This is the experiment.
2. Find ln [NO₂] and 1/[NO₂] as it changes with time.
3. Create graphs (plots) of [NO₂] vs. time, ln [NO₂] vs time, and 1/[NO₂] vs. time

Plot the data

- Which model produces the best fit?
 - What order is the reaction? What is the rate constant at 330°C?
 - Rate = $k[\text{NO}_2]^2$, it is second order.
 - Rate constant, k = slope of $1/[\text{NO}_2]$ vs. time

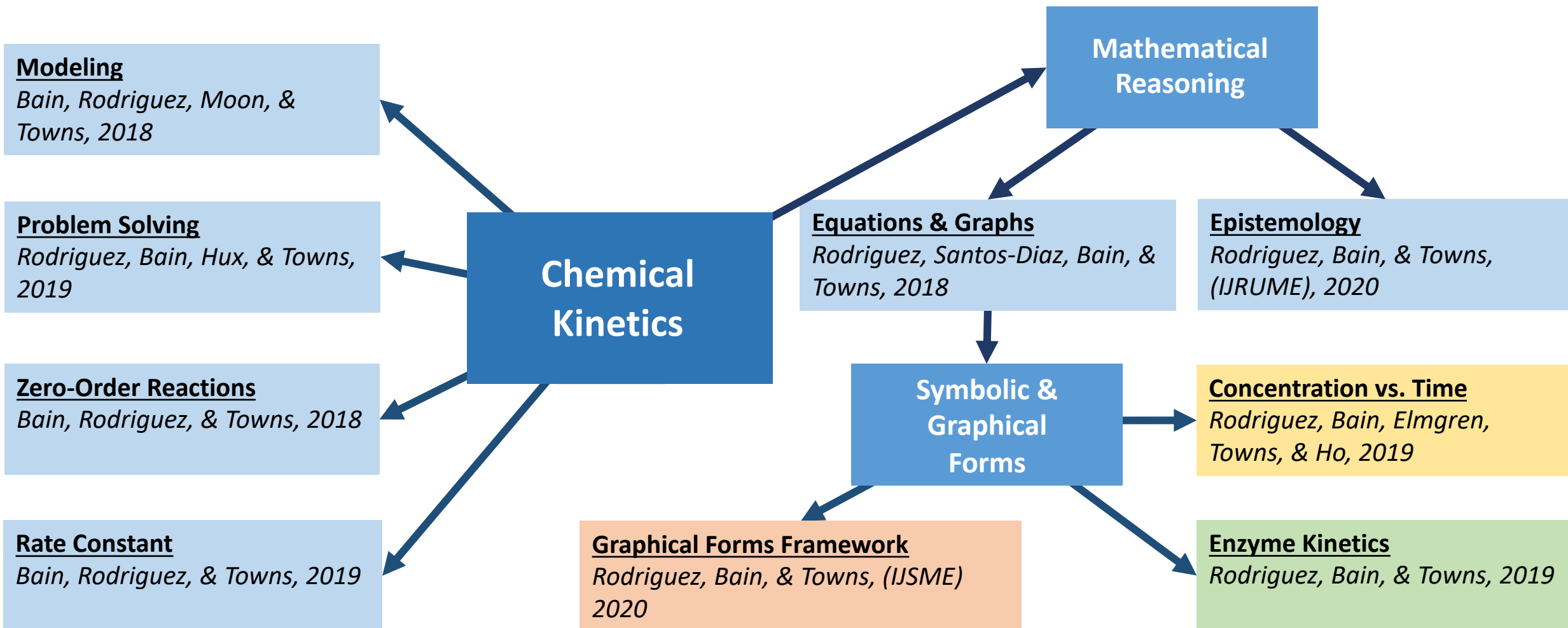


How do undergraduate chemistry students understand and use mathematics in chemical kinetics?

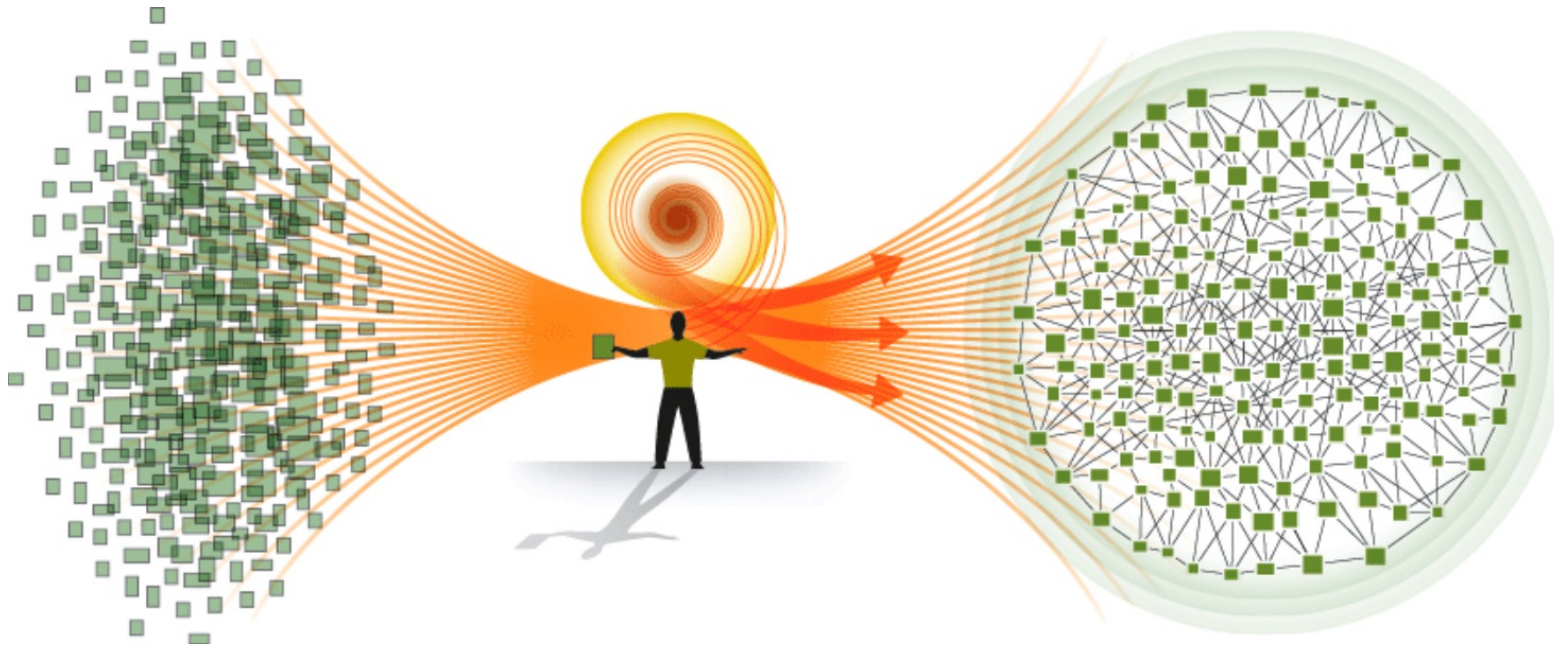
Background

- Investigating student understanding and use of mathematics in chemical kinetics
- N=48 (general chemistry, upper-level)
- Semi-structured interviews using think-aloud protocol and Livescribe™ smartpen

Background



Resources Framework



- **Knowledge** is a dynamic network of interacting cognitive elements, which vary in complexity and are activated in specific contexts
- **Expert knowledge** is highly interconnected, organized by fundamental ideas in the discipline, and both contextualized and transferrable

We conducted semi-structured interviews with STEM majors in a general chemistry II course

n=40
STEM Majors
General Chemistry II

Math Prompt

Here's an equation you may have seen in class.

How would you explain this equation to a friend from class?

How would you explain this on an exam?

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

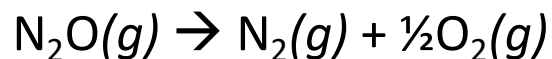
$$[A] = kt + [A]_0$$

We conducted semi-structured interviews with STEM majors in a general chemistry II course

n=40
STEM Majors
General Chemistry II

Chemistry Prompt

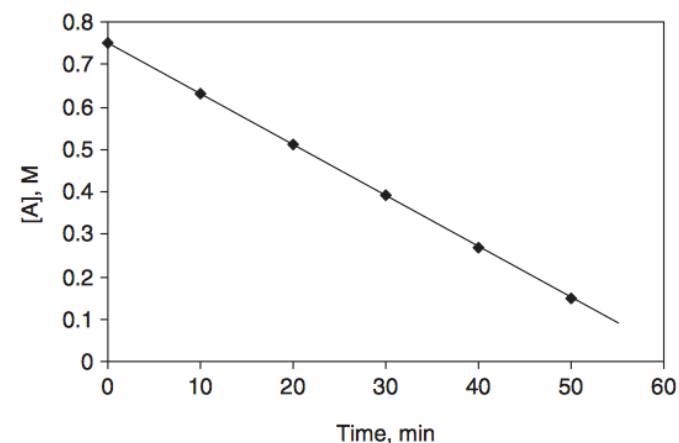
Below is a **zero-order rate plot** for the reaction



where $[\text{N}_2\text{O}]_0 = 0.75 \text{ M}$ and $k = 0.012 \text{ M/min}$. $[\text{A}]$, M on the graph below represents $[\text{N}_2\text{O}]$ (M).

The reaction is conducted at $575 \text{ }^\circ\text{C}$ 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?

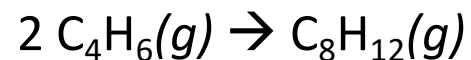


We conducted semi-structured interviews with STEM majors in a general chemistry II course

n=40
STEM Majors
General Chemistry II

Chemistry Prompt

A second-order reaction



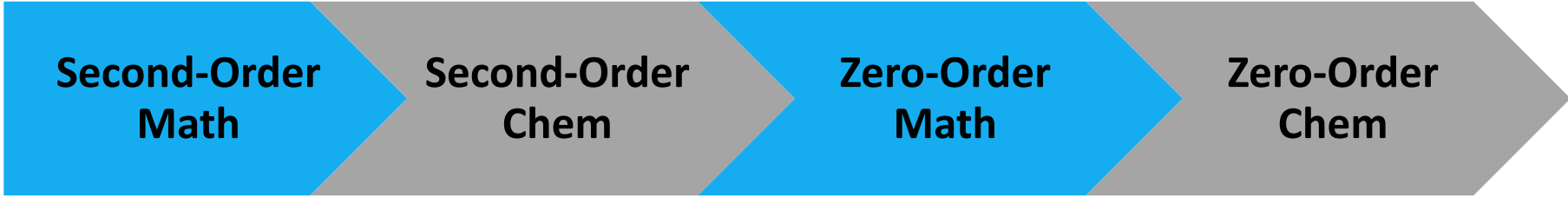
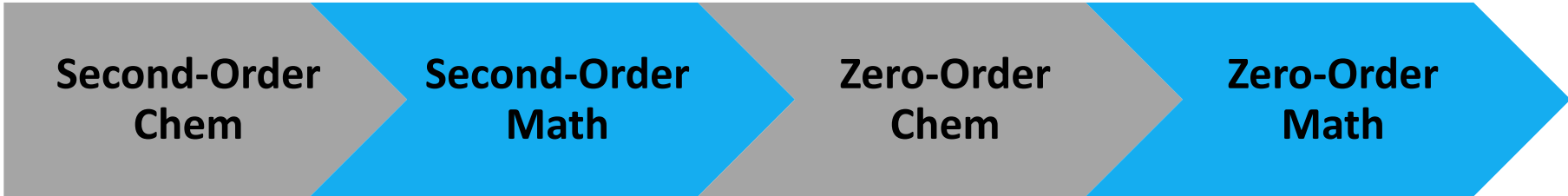
was run first at an initial concentration of 1.24 M and then again at an initial concentration of 2.48 M. They were run under the same reaction conditions (e.g., same temperature). Data collected from these reactions are provided in the table.

Is the rate constant for reaction 1 (1.24 M) greater than, less than, or equal to the rate constant for reaction 2 (2.48 M)?

Time (hrs)	[C ₄ H ₆] (M)	
	Rxn 1	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

We alternated the prompts to avoid priming effects

n=40
STEM Majors
General Chemistry II



Symbolic Forms

- Intuitive ideas about equations

Symbol Template + Conceptual Schema

$\square \pm \Delta$ modified base value

$$[A] = [A]_0 + kt x$$

Symbolic Forms

Symbolic Form	Symbol Template	Conceptual Schema
Balancing	$\square = \square$	Competing influences are seen as equal and opposite
Parts-of-a-whole	$\square + \square + \square \dots$	A whole is created by combining two or more parts
Prop-	$\left[\frac{\dots}{\dots x \dots} \right]$	Indirectly proportional to a quantity, x , appears as an individual symbol in the denominator
Dependence	$[\dots x \dots]$	A whole depends on a quantity associated with an individual symbol
Template Key		
[...]	Expression in brackets corresponds to an entity in the schema	
x	Individual symbols in an expression	
\square	A term or group of terms	
\dots	Omitted Portions of an expression that are inconsequential	

Becker, & Towns, 2012; Dorko & Speer, 2015; Dreyfus, Elby, Gupta, & Sohr, 2017; Hu & Rubello, 2013; Izak, 2004; Jones, 2013, 2015a, 2015b; Schermerhorn & Thompson, 2016; Von Korff & Rubello, 2014

Students had productive mathematics ideas for reasoning about the problem

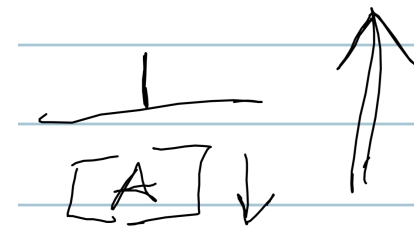
Why is the sign of k different for the second-order ($\frac{1}{[A]} = kt + \frac{1}{[A]_0}$) and zero-order ($[A] = -kt + [A]_0$) integrated rate laws?

Howie: “Concentration of A almost always goes down as long as it's a reactant, unless you're dealing with the reverse of an equilibrium something. Molarity of A almost always goes down, but **if it's one over the molarity of A, this is why that's positive [k in the second-order integrated rate law], if it's one over the molarity of A, then as A gets smaller, one over the molarity, this whole thing is going to get bigger.** As the concentration of A goes down, the y of the integrated second-order rate law goes up.”

Symbolic Form
Prop-

$$\left[\frac{\dots}{\dots x \dots} \right]$$

Indirectly proportional to a quantity, x, appears as an individual symbol in the denominator



Students had productive mathematics ideas for reasoning about the problem

Steven: “Well, the concentrations other than the initial and final, they don't affect the rate at all. It's just basically the rate changes the amount with time, or the k constant, not the rate. The rate constant just changes with time, and it's not being multiplied by concentration. It reminds me of a physics equation, v_f equals v_i plus at. Basically saying, this is where you start off, this is the amount of change you have, and so, here's what your final is.”

$$[A] = kt + [A]_0$$

Symbolic Form
no dependence

[...]

A whole does not depend on a quantity associated with an individual symbol

Symbolic Form
dependence

[... X ...]

A whole depends on a quantity associated with an individual symbol

Symbolic Form
base ± change

$\square \pm \Delta$

A change increases or decreases an initial value

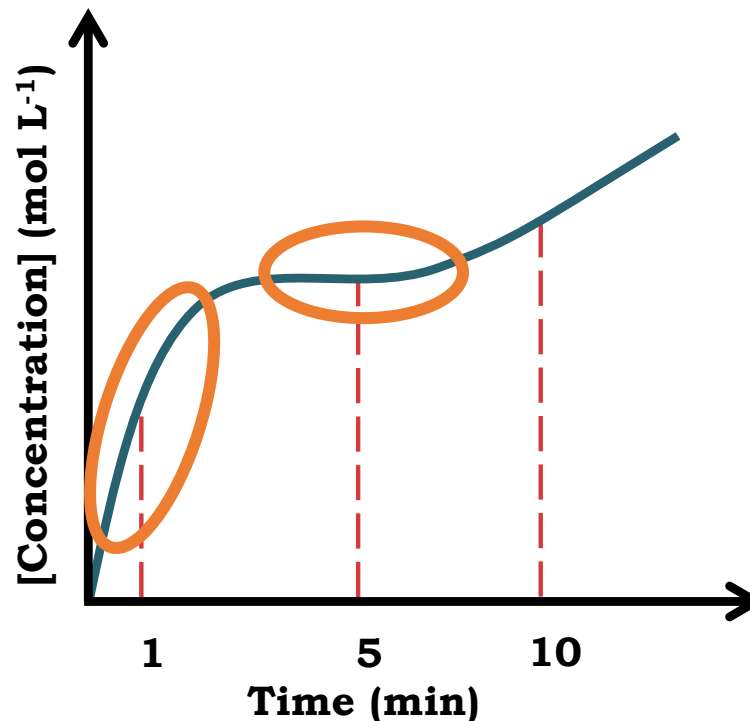
Students had productive mathematics ideas for reasoning about the problem

At which of the time points $t = 1$ min, 5 min, 10 min was the rate of reaction the highest? At which time point was it the lowest? Explain carefully how you arrived at your answer.

Nancy: *“The reaction rate was greatest at $t = 1$ min because **the slope of the curve is the steepest there**. The reaction rate is the lowest at $t = 5$ min because **the slope is the smallest there**.”*

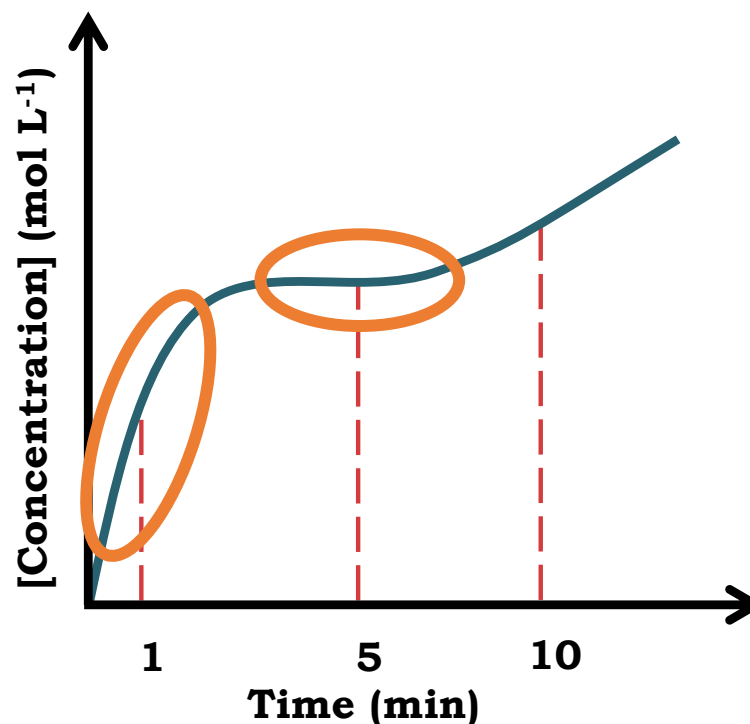
Graphical Form
steepness as rate

Varying levels of steepness in a graph correspond to different rates



Students had productive mathematics ideas for reasoning about the problem

“The reaction rate was high at first because there was a lot of reactants. A lot of reactants means that many molecules can collide and create products. The fewer reactant molecules, the more the reaction rate evens out. When the curve stays at the same reaction rate the reaction has probably reached equilibrium and products are created as fast as reactants are reformed. The increase in reaction rate can be due to some change for example compression, temperature change or addition of more reactant, etc.”

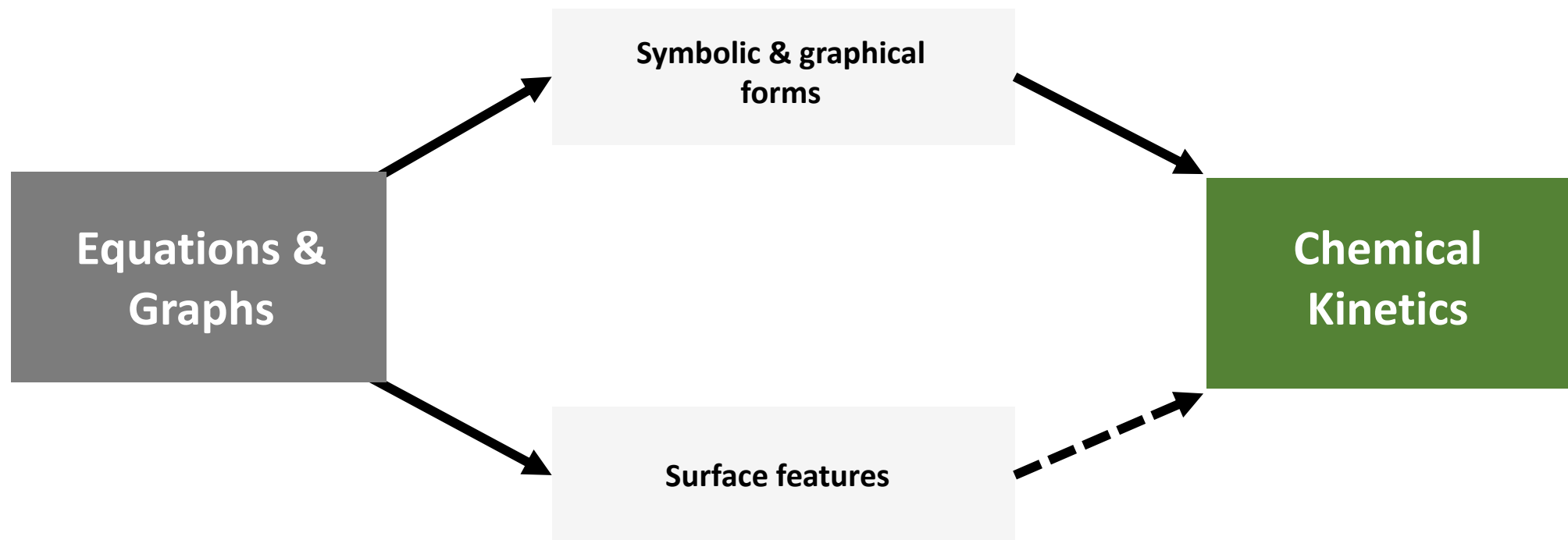


Summary of our work in kinetics

Mathematics

Students' Reasoning

Chemistry



We coded the data by focusing on the problem-solving approaches students used

Problem-Solving Routes

Conceptual Reasoning

Data to Check

Equation & Data

Equation Recall

Graphical Approach

Method of Initial Rates

Patterns & Trends

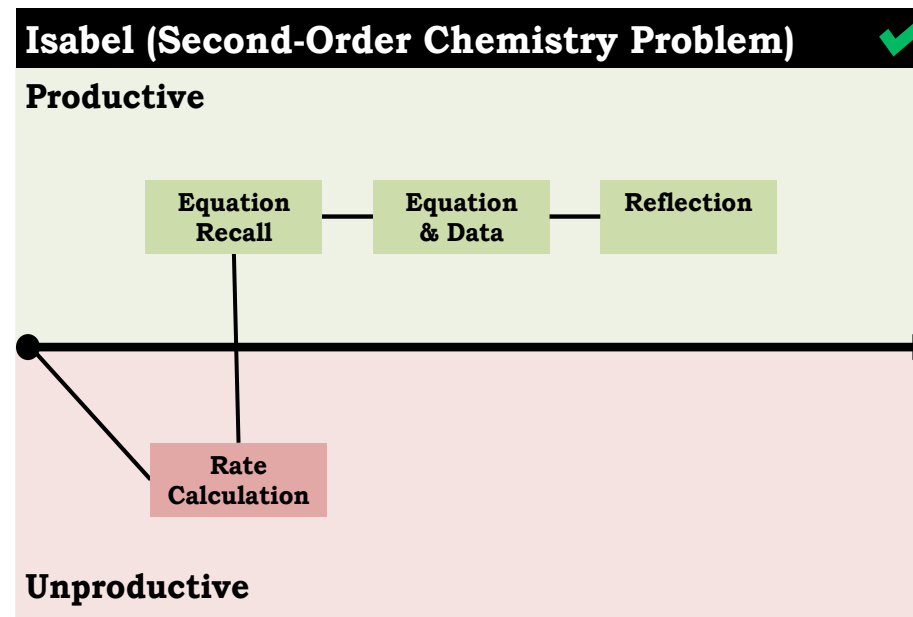
Rate Calculation

Ratio Calculation

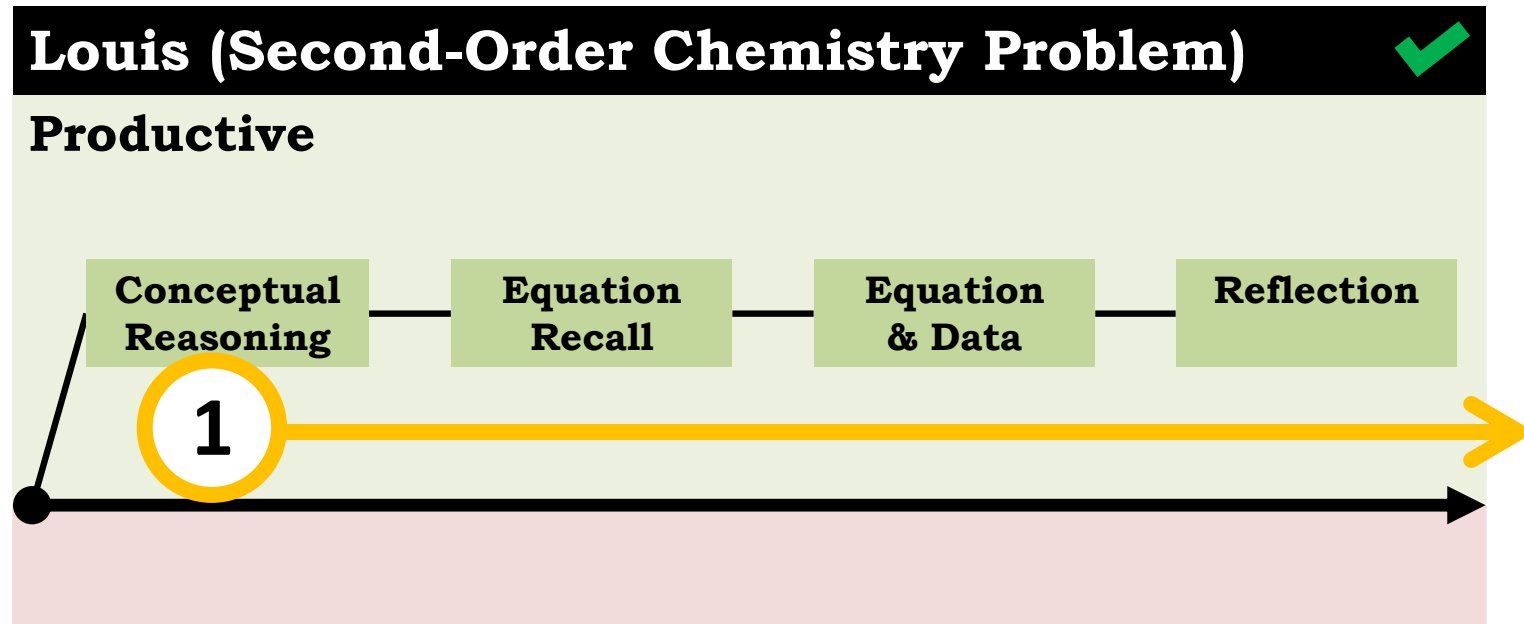
Reflection

Slope Calculation

Problem-Solving Map

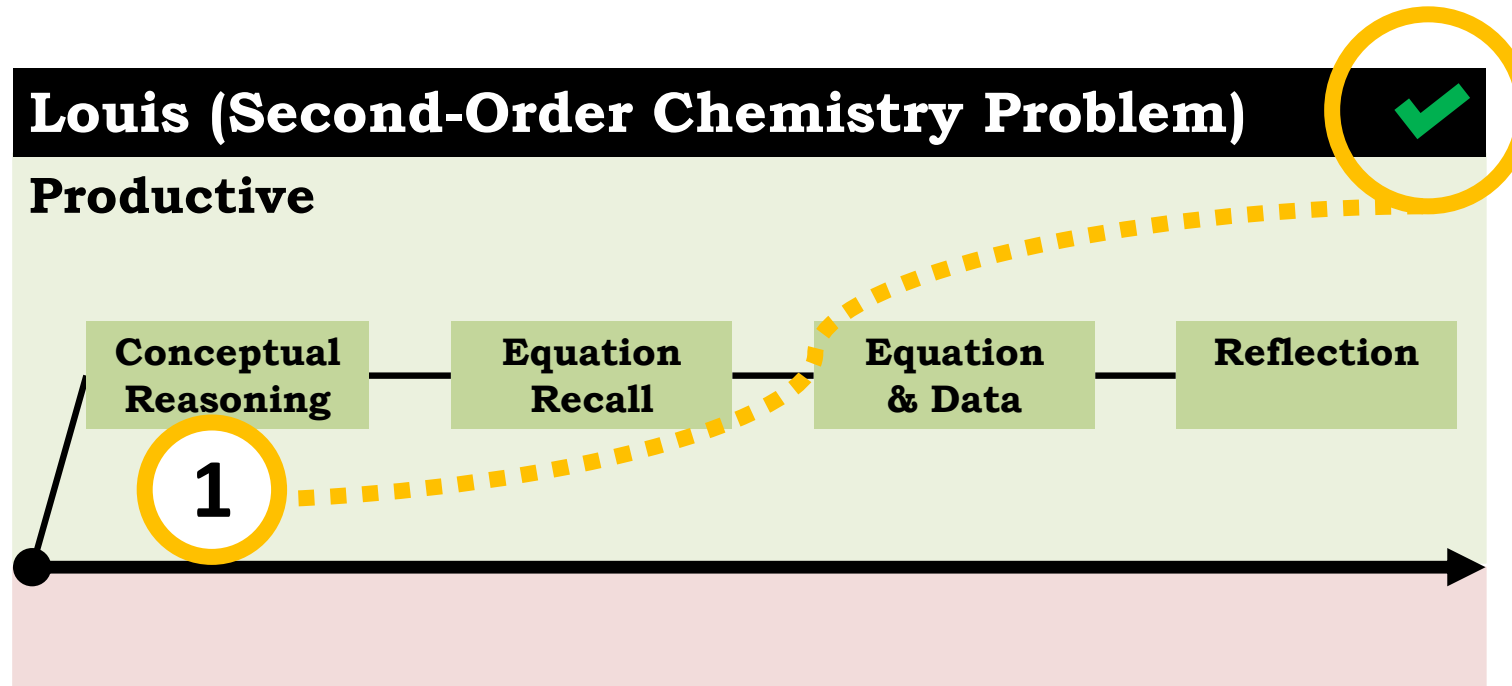


Productive problem-solving typically involved the use of conceptual reasoning



n = 9 students exclusively used productive problem-solving routes, most began with conceptual reasoning and followed a straightforward, linear progression

Productive problem-solving typically involved the use of conceptual reasoning

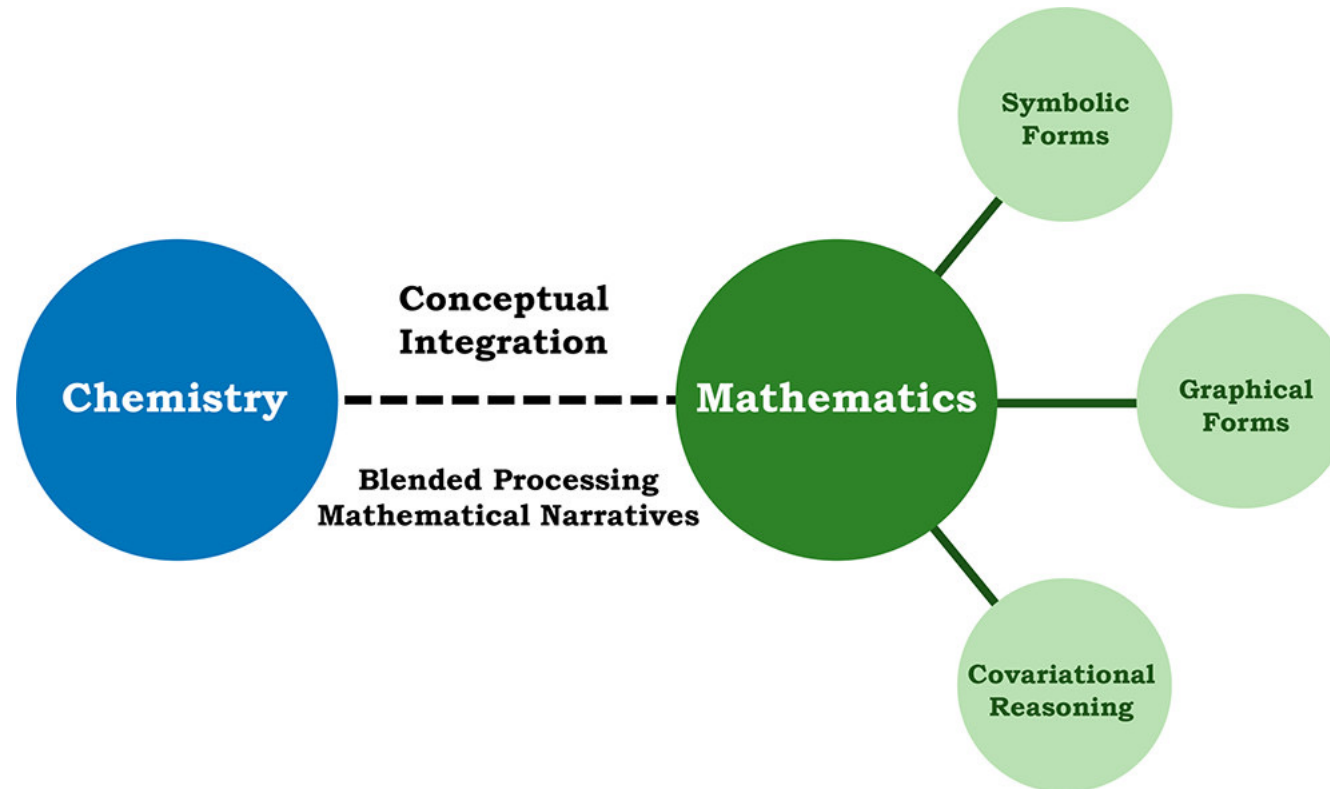


n = 16 had conceptual reasoning as first-problem-solving step, typically resulting in correct answer

Conceptual Reasoning

Description	Example
Addresses prompt or attempts to answer the prompt by predicting and/or providing justification involving a conceptual understanding.	Russel: <i>“They were run under the same reaction conditions, same temperature, so the rate constant will be the same. So just initially I would think it'd be equal ... because if you're holding temperature the same, and the initial concentration I didn't think had an effect on the rate constant.”</i>
	Andrew: <i>“Yeah, I would say k changes based on concentrations.”</i>

Blending mathematics and chemistry



Bain, K.; Rodriguez, J-M. G.; Towns, M. H. *J. Chem. Educ.* **2019**, *96*(10), 2086-2096. (see references herein)

Experiments in Chemistry (include all sciences and engineering too)



Learning outcomes

- Learn hands-on techniques
- Improve critical thinking
- Create an evidence-based argument



M. E. Fay, N. P. Grove, M. H. Towns, S. L. Bretz. *Chem. Educ. Res. Pract.*, **2007**, 8(2), 212-219.
L. Bruck, S. L. Bretz, M. H. Town*, *J Coll. Sci. Teach.* **2008**, 38(1), 52-58.
L. B. Bruck, M. Towns, S. L. Bretz, *J.Chem. Educ.*, **2010**, 87(12), 1416-1424.
S. L. Bretz, M. Fay, L. Bruck, M. Towns, *J. Chem. Educ.* **2013**, 90, 281-288.
A. Bruck, M. H. Towns, *J. Chem. Educ.*, **2013**, 90(6), 685-693

Chemistry and Mathematics: Research and Frameworks to Explore Student Reasoning

- Covariational reasoning: Coordinating relationships between values
 - “Holding in mind a sustained image of two quantities (magnitudes) simultaneously “ (Saldanha and Thompson, 1998)
 - Covariational reasoning involves attending to the relationship between values, with an emphasis on how both values change (Bain, Rodriguez, Towns, 2019)
 - Foundational to mathematics and the sciences – reasoning about graphs, functions, conceptualizing problems

Bain, K.; Rodriguez, J-M. G.; Towns, M. H. *J. Chem. Educ.* **2019**, *96*(10), 2086-2096. (see references herein)

Saldanha, L. A.; Thompson, P. W. *Proceedings of the Annual Meeting of the Psychology of Mathematics Education*; North Carolina University,: Raleigh, NC, 1998; pp 298–304.

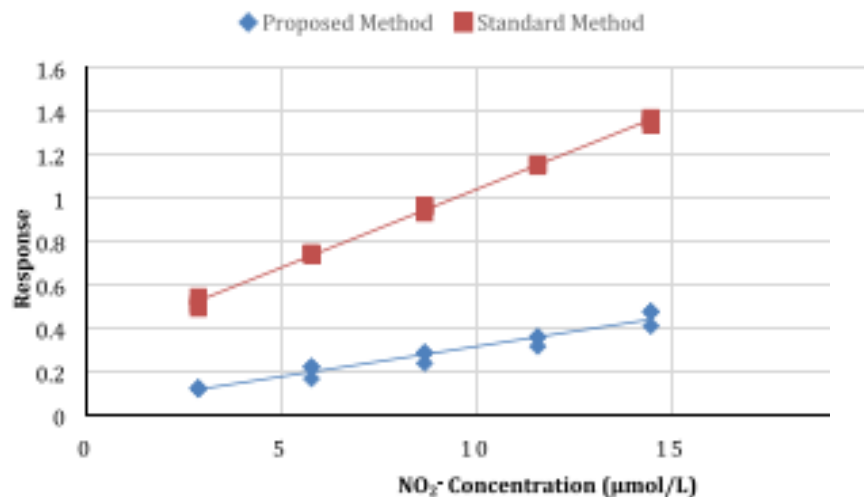
Carlson, M.; Jacobs, S.; Coe, E.; Larsen, S.; Hsu, E. *J. Res. Math. Educ.* **2002**, *33* (5), 352–378.

Confrey, J.; Smith, E. *J. Res. Math. Educ.* **1995**, *26* (1), 66.

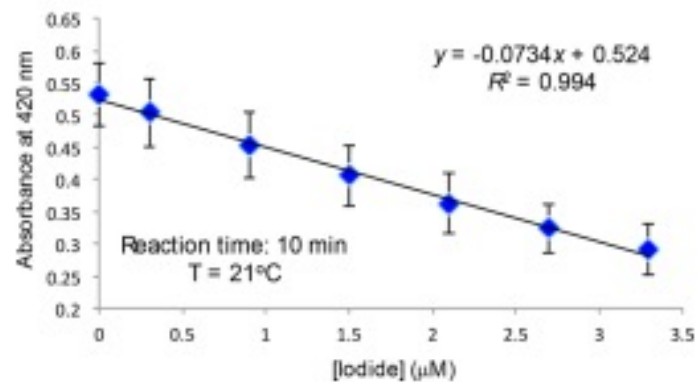
Habre, S. *Int. J. Math. Educ. Sci. Tech.* **2017**, *48* (1), 48–66.

Thompson, P. W. *Educ. Stud. Math.* **1994**, *26* (2–3), 229–274.

Covariational reasoning in chemistry – chunky versus smooth



External Calibration Curve for Iodide: Pooled Student Data



Average Absorbance vs. Glyphosate Concentration

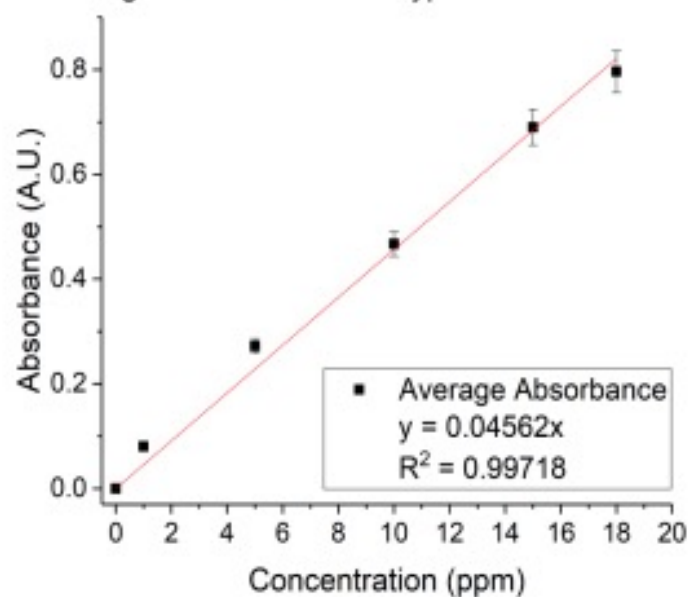
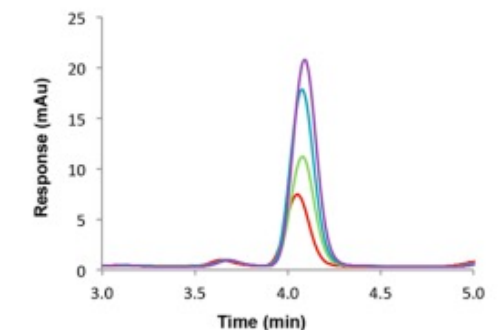


Figure 1. Normalized average absorbance at 264 nm vs concentration for three trials of glyphosate standards. Error bars indicate standard deviation.

A Thymol Standard Addition HPLC Chromatograms



B Standard Addition Plot of Thyme Extracts with Added Thymol

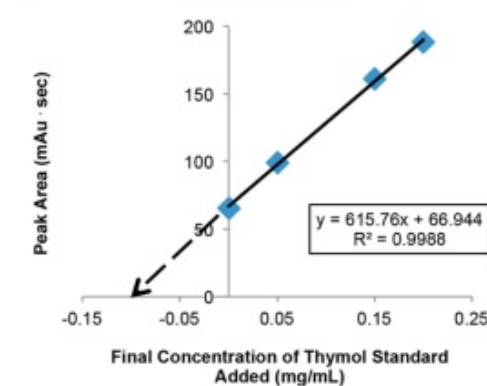


Figure 1. (A) Sample student HPLC chromatograms of thyme extracts with varying amounts of thymol standard added using the method of standard addition. (B) Student data of standard addition calibration curve of HPLC peak area for thymol. Data are used to determine the amount of thymol in the extracts, then in thyme leaves by weight.

Nori de Macedo; Mathiapparanam; Ly; Britz-McKibbin, *J. Chem. Educ.*, **2018**, *95*, 1029-1034.
 Fernandes Filgueiras, Cesar de Jesus, Marcel Borges, *J. Chem. Educ.*, **2021**, *98*, 3303-3311.
 Purcell et al., *J. Chem. Educ.*, **2016**, *93*, 1422-1427.
 Felton et al., *J. Chem. Educ.*, **2018**, *95*, 136-140.

Chunky or Smooth Covariation?

- Mathematics favors smooth covariation over chunky.
 - Smooth conceptualizations of covariation produce more powerful mathematics
 - Prioritization of having students “see” functions as emerging smoothly, continuously.
- This is problematic for scientists where we acquire data that is by necessity chunky. We carry out experiments and our data is inherently discrete.
 - All experiments have a context – real attributes of real objects.
 - Numbers in many/most cases have units (true for bio, chem, econ, eng, phys).

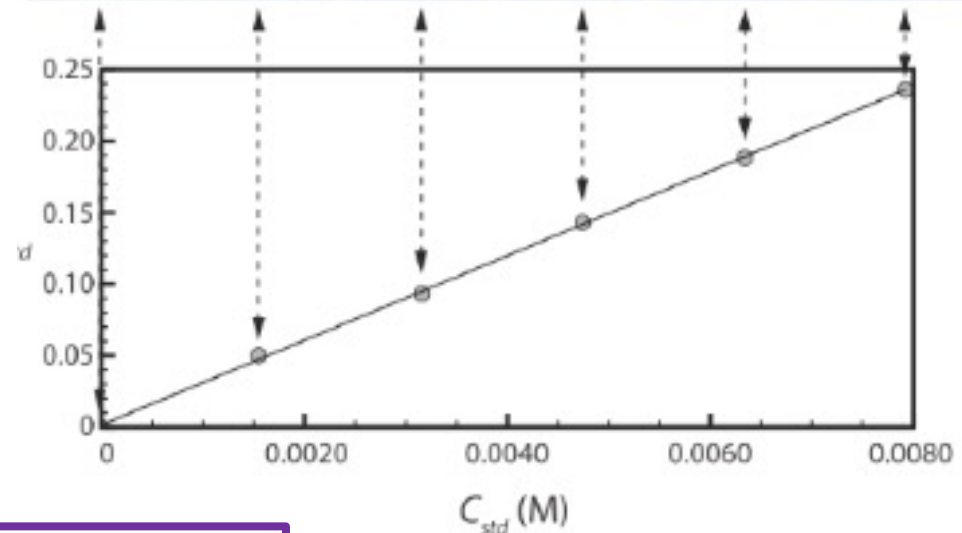
Castillo-Garsow, C.; Johnson, H.; Moore, K. C. Chunky and Smooth images of change. *For the Learning of Mathematics*, **2013** 33, 31-37.

Dray, T.; Gire, E.; Kustus, M. B.; Manogue, C. A.; Roundy, D.; Interpreting Derivatives, *PRIMUS*, **2019**, 29(8), 830-850.

Jones, S. R. What education research related to calculus integrals implies for chemistry instruction. In *It's Just Math: Research on Student Understanding of Chemistry and Mathematics*; Towns, M. H.; Bain, K.; Rodriguez, J-G. Eds.; ACS Symposium Series Vol. 1316; American Chemical Society: Washington, DC, 2019; pp. 187-212.

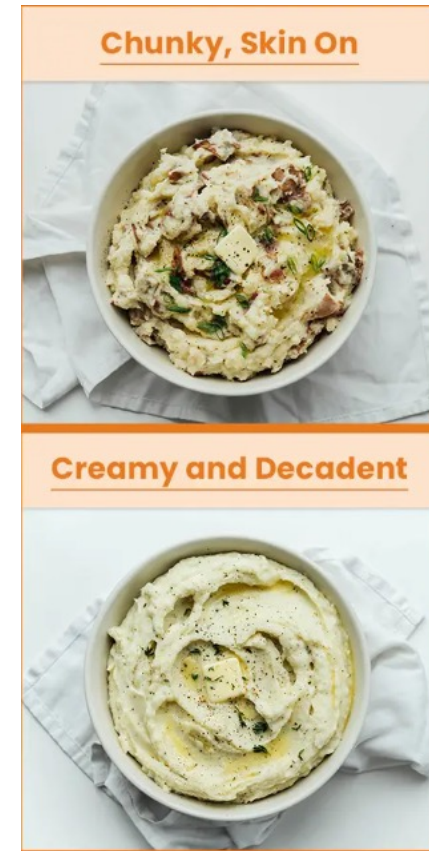
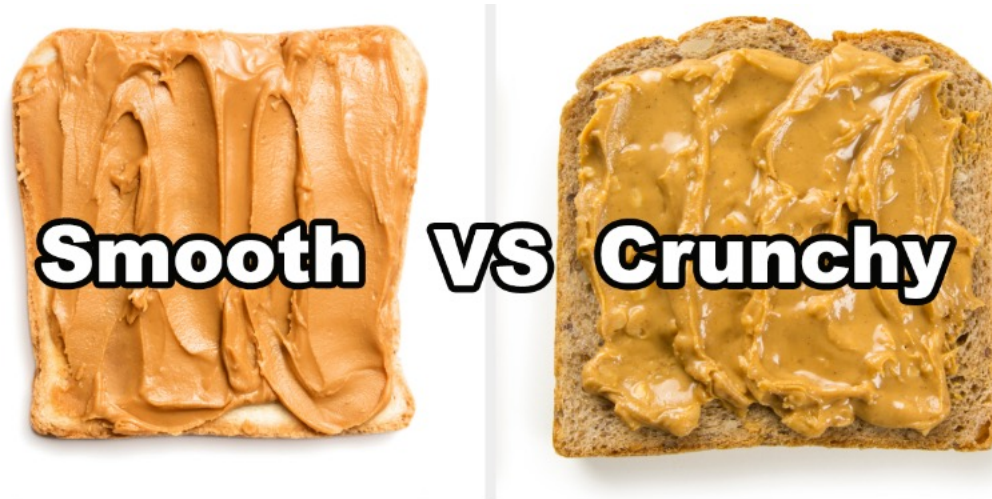
Why don't chemists use a smooth conceptualization of covariation? (You may be asking this.)

- Experimental design and time constraints
- Designed to collect data, then analyze by using a model
 - Model is used to reveal characteristics of the system under study.
 - Beer's law: Absorbance is directly related to the concentration.
- 1-3 hour lab period
 - Collect data; analyze and interpret.



Story about Pat's comment

Looking forward to more conversation about this!



Acknowledgments



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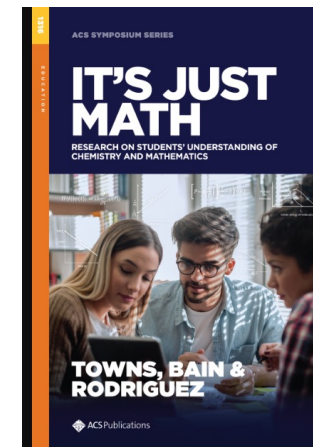
Dr. Thomas A. Holme
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Evaluator



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ACS Symposium
Book!



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The Learning and Teaching of Calculus Across the Disciplines

Programme Committee

Tommy Dreyfus

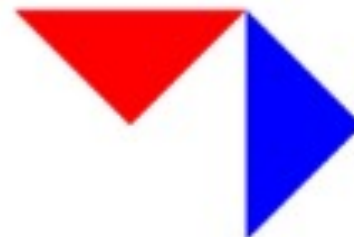
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MatRIC Centre for Research,
Innovation and Coordination
of Mathematics Teaching

Extra slides, not in presentation, but happy to share.

What is considered a “rate” in chemistry, and what is not.

- Chemists usually reserve the term *rate* for derivatives *with respect to time*.
- Not a rate example:
 - Chemical potential - partial molar Gibbs function defined for a multi-component mixture for compound i as

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{P, T, n_j \neq i}$$

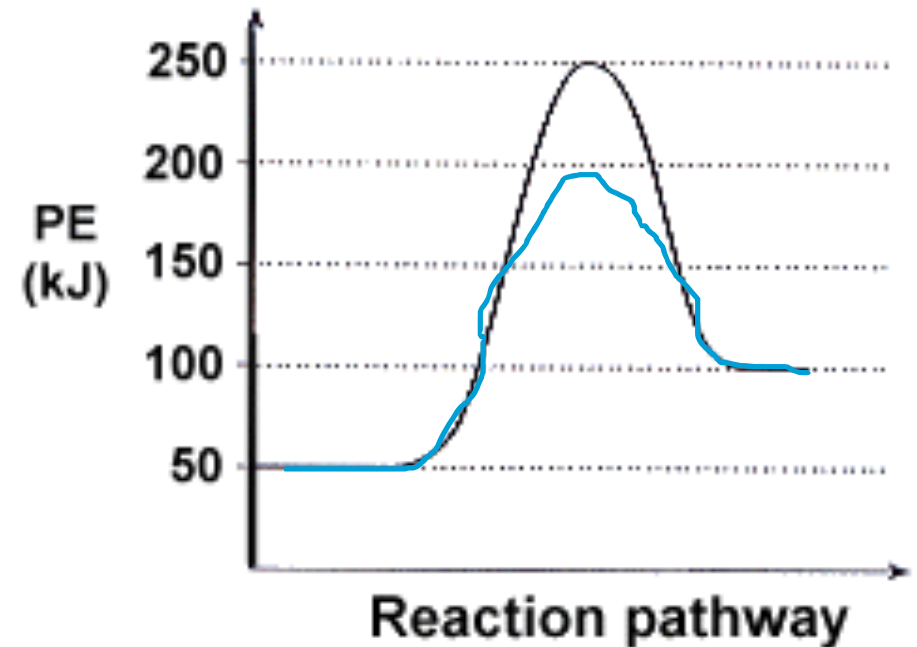
This is partial derivative describes how the Gibbs energy changes as the composition of a mixture changes (the amount of component i where n_i is the amount of substance) at constant P, T, and all other components other than i.

Students invoke time, frequently. But why do rates increase? (Hint: Blend chem/math)

The reaction diagram shown at right is for the reaction $A \rightarrow B$.

- A. How would the diagram change if a catalyst was present? Explain in words and **show what the new reaction diagram would look like on the graph by directly drawing on it.**
- B. What does a catalyst do to change the the rate of the reaction? (Assume the temperature does not change.)

Essentials: The maximum is at a lower potential energy (PE) value. Lowering the maximum lowers the activation energy for the reaction thus speeding up the reaction. Enzyme molecules provide an alternate pathway for the reaction to occur.

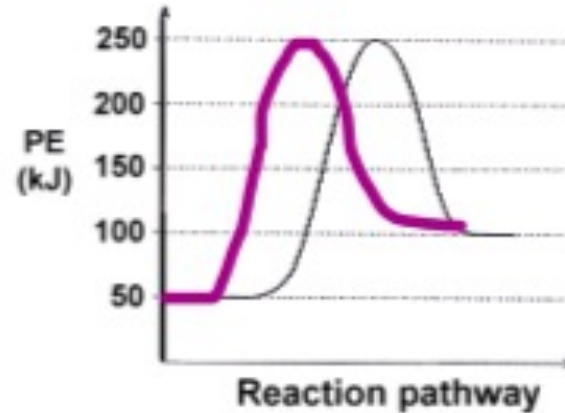


Compression to the origin, towards the left

4. A reaction diagram is shown at right for the reaction $A \rightarrow B$.

- a. (2 pt) How would the diagram change if a catalyst was present? Explain in words and **show what the new reaction diagram would look like on the graph by directly drawing on it.**

A catalyst would cause the diagram to have a steeper slope sooner.



- b. (1 pt) Exactly what does a catalyst do to change the rate of the reaction? (Assume the temperature does not change.)

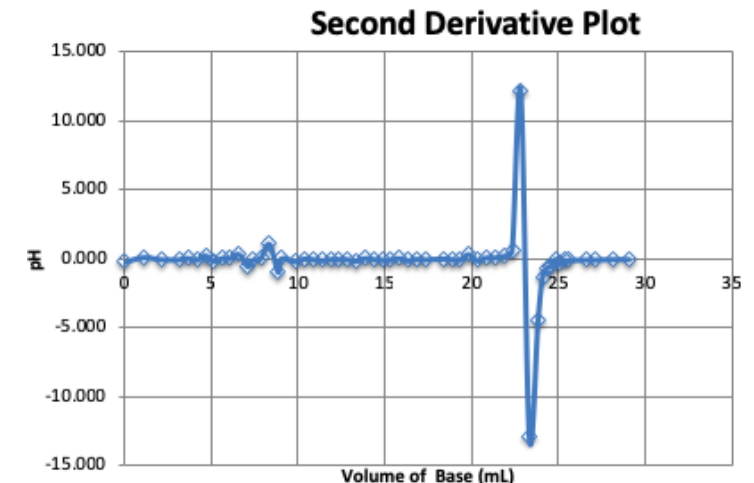
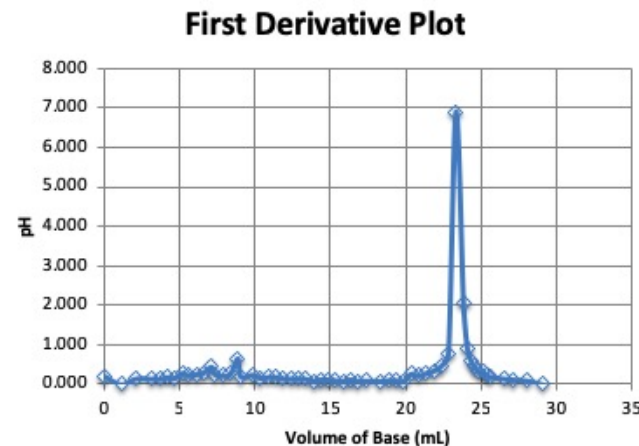
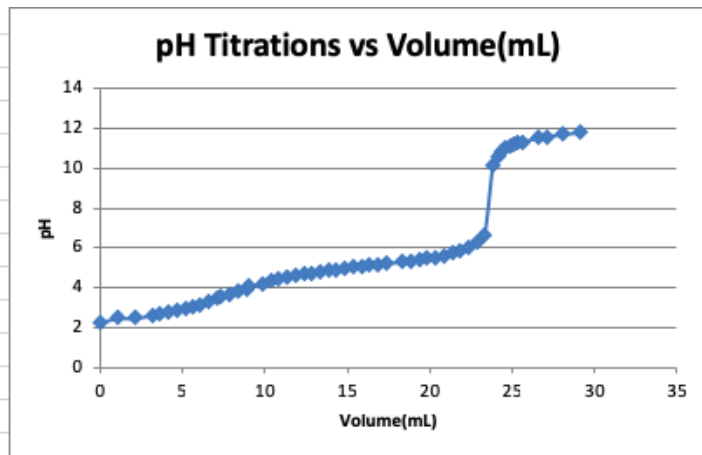
A catalyst causes the rate of reaction to go quicker.

Indicative of thinking that the x-axis is time, not reaction pathway.

See Jones, S. J. *Math. Behavior*, **2017**, 45, 95-110.

Use of second derivative – more accurate determination of concentration of acid.

- pH is recorded against the volume of base added to an acid.
- Data is manipulated in Excel to find the first derivative ($\Delta\text{pH}/d\Delta\text{V}$) and the second derivative $\Delta(\Delta\text{pH}/\Delta\text{V})/\Delta\text{V}$
- Find concentration of acid more accurately using this method.



<https://www.chegg.com/homework-help/questions-and-answers/>

1-transfer-data-excel-template-provided-template-set-plot-titration-curve-first-derivative-q46457589