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

Analytical chemistry

Inorganic chemistry

Biochemistry

Organic chemistry

Physical chemistry
## Undergraduate curriculum – standard 4-year

<table>
<thead>
<tr>
<th>Year</th>
<th>Fall</th>
<th>Spring</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>General Chemistry + lab</td>
<td>General Chemistry + lab</td>
</tr>
<tr>
<td></td>
<td>Calculus I</td>
<td>Calculus II</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Physics I + lab</td>
</tr>
<tr>
<td>2</td>
<td>Organic Chemistry + lab</td>
<td>Organic Chemistry + lab</td>
</tr>
<tr>
<td></td>
<td>Calculus III</td>
<td>Inorganic I</td>
</tr>
<tr>
<td></td>
<td>Physics II + lab</td>
<td>Differential equations</td>
</tr>
<tr>
<td>3</td>
<td>Analytical I + lab</td>
<td>Physical Chem. II + lab</td>
</tr>
<tr>
<td></td>
<td>Physical Chem. I + lab</td>
<td>Linear algebra</td>
</tr>
<tr>
<td>4</td>
<td>Biochemistry</td>
<td>Inorganic II</td>
</tr>
<tr>
<td></td>
<td>Analytical II + lab</td>
<td>Inorganic lab</td>
</tr>
</tbody>
</table>

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.*
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.

\[
\begin{align*}
\text{Zero-Order} & \quad B \quad \frac{1}{[A]} = kt + \frac{1}{[A]_0} \quad \text{rate} = -\frac{d[A]}{dt} = k[A]_0 \\
\text{First-Order} & \quad [A] = -kt + [A]_0 \quad \frac{d[A]}{dt} = k[A] \\
\text{Second-Order} & \quad \text{rate} = -\frac{d[A]}{dt} = k[A]^2 \\
\end{align*}
\]

2A → B \quad \ln[A] = -kt + \ln[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

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

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

<table>
<thead>
<tr>
<th>Differential rate law</th>
<th>Zeroth Order</th>
<th>First Order</th>
<th>Second Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate $\frac{\Delta[A]}{\Delta t} = k$</td>
<td>Rate $\frac{\Delta[A]}{\Delta t} = k[A]$</td>
<td>Rate $\frac{\Delta[A]}{\Delta t} = k[A]^2$</td>
<td></td>
</tr>
</tbody>
</table>

Concentration vs. time:

![Graphs showing concentration vs. time for zeroth, first, and second order reactions.](image-url)
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.
\[ 2\text{NO}_2(g) \xrightarrow{\Delta} 2\text{NO}(g) + \text{O}_2(g) \] at 330°C

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>[NO₂] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.00 x 10⁻²</td>
</tr>
<tr>
<td>60</td>
<td>6.83 x 10⁻³</td>
</tr>
<tr>
<td>120</td>
<td>5.18 x 10⁻³</td>
</tr>
<tr>
<td>180</td>
<td>4.18 x 10⁻³</td>
</tr>
<tr>
<td>240</td>
<td>3.50 x 10⁻³</td>
</tr>
<tr>
<td>300</td>
<td>3.01 x 10⁻³</td>
</tr>
<tr>
<td>360</td>
<td>2.64 x 10⁻³</td>
</tr>
</tbody>
</table>

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?
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

**Chemical Kinetics**

- **Modeling**
  - Bain, Rodriguez, Moon, & Towns, 2018

- **Problem Solving**
  - Rodriguez, Bain, Hux, & Towns, 2019

- **Zero-Order Reactions**
  - Bain, Rodriguez, & Towns, 2018

- **Rate Constant**
  - Bain, Rodriguez, & Towns, 2019

- **Equations & Graphs**
  - Rodriguez, Santos-Diaz, Bain, & Towns, 2018

- **Symbolic & Graphical Forms**

- **Mathematical Reasoning**

- **Epistemology**
  - Rodriguez, Bain, & Towns, (IJRUME), 2020

- **Concentration vs. Time**
  - Rodriguez, Bain, Elmgren, Towns, & Ho, 2019

- **Enzyme Kinetics**
  - Rodriguez, Bain, & Towns, 2019

- **Graphical Forms Framework**
  - Rodriguez, Bain, & Towns, (IJSME) 2020
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.

Chemistry Prompt

Below is a zero-order rate plot for the reaction

\[ \text{N}_2\text{O}(g) \rightarrow \text{N}_2(g) + \frac{1}{2}\text{O}_2(g) \]

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

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 \(\text{N}_2\text{O}\) 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.

Chemistry Prompt

A second-order reaction

\[ 2 \text{C}_4\text{H}_6(g) \rightarrow \text{C}_8\text{H}_{12}(g) \]

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

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>[C_4H_6] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rxn 1</td>
</tr>
<tr>
<td>0</td>
<td>1.24</td>
</tr>
<tr>
<td>1</td>
<td>0.960</td>
</tr>
<tr>
<td>2</td>
<td>0.775</td>
</tr>
<tr>
<td>3</td>
<td>0.655</td>
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<tr>
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<td>0.560</td>
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<tr>
<td>5</td>
<td>0.502</td>
</tr>
<tr>
<td>6</td>
<td>0.442</td>
</tr>
<tr>
<td>7</td>
<td>0.402</td>
</tr>
<tr>
<td>8</td>
<td>0.365</td>
</tr>
<tr>
<td>9</td>
<td>0.335</td>
</tr>
<tr>
<td>10</td>
<td>0.310</td>
</tr>
</tbody>
</table>

n=40
STEM Majors
General Chemistry II
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

\[ \pm \quad \Delta \]

modified base value

\[ [Ay] = [A]_0 + mt \]

Sherin, 2001
## Symbolic Forms

<table>
<thead>
<tr>
<th>Symbolic Form</th>
<th>Symbol Template</th>
<th>Conceptual Schema</th>
</tr>
</thead>
<tbody>
<tr>
<td>Balancing</td>
<td>$\square = \square$</td>
<td>Competing influences are seen as equal and opposite</td>
</tr>
<tr>
<td>Parts-of-a-whole</td>
<td>$\square + \square + \ldots$</td>
<td>A whole is created by combining two or more parts</td>
</tr>
<tr>
<td>Prop-</td>
<td>$\left[ \ldots \right] \ldots x \ldots$</td>
<td>Indirectly proportional to a quantity, $x$, appears as an individual symbol in the denominator</td>
</tr>
<tr>
<td>Dependence</td>
<td>$[\ldots x \ldots]$</td>
<td>A whole depends on a quantity associated with an individual symbol</td>
</tr>
</tbody>
</table>

### 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
- $\ldots$ Omitted Portions of an expression that are inconsequential

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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.”

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*Rodriguez, Santos-Diaz, Bain, & Towns, 2018*
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**

\[
[... \times ...]
\]

A whole depends on a quantity associated with an individual symbol

---

Rodriguez, Santos-Diaz, Bain, & Towns, 2018
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

Rodriguez, Bain, Elmgren, Towns, & Ho 2019
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.”

Rodriguez, Bain, Elmgren, Towns, & Ho 2019
Summary of our work in kinetics

Mathematics

Equations & Graphs

Symbolic & graphical forms

Surface features

Students’ Reasoning

Chemistry

Chemical Kinetics
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**

Isabel (Second-Order Chemistry Problem)

Productive

- Equation Recall
- Equation & Data
- Reflection

Unproductive

Rate Calculation

Rodriguez, Bain, Hux, Towns, 2019
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.

Rodriguez, Bain, Hux, Towns, 2019
### Conceptual Reasoning

<table>
<thead>
<tr>
<th>Description</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Addresses prompt or attempts to answer the prompt by predicting and/or providing justification involving a conceptual understanding.</td>
<td><strong>Russel:</strong> “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.”</td>
</tr>
<tr>
<td></td>
<td><strong>Andrew:</strong> “Yeah, I would say k changes based on concentrations.”</td>
</tr>
</tbody>
</table>
Blending mathematics and chemistry

Experiments in Chemistry (include all sciences and engineering too)

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

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

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).

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!

Smooth VS Crunchy

Chunky, Skin On

Creamy and Decadent
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- Alejandro S. Gonzalez-Martin
- John Monaghan
- Elena Nardi
- Pat Thompson

*Admin Asst: Elisabeth and Ninni Marie*
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

\[
\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{P,T, n_{i \neq i}}
\]

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 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.
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 ($\Delta \text{pH}/d\Delta V$) and the second derivative $\Delta(\Delta \text{pH}/\Delta V)/\Delta V$
- Find concentration of acid more accurately using this method.