Terror in the Toilet Bowl: Instructor Guide

Title:

Terror in the Toilet Bowl

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Discipline:

Chemistry and Biochemistry

Target Audience

Introductory, majors or nonmajors

Keywords

Integrated rate laws, kinetic plots, kinetics, method of initial rates, rate laws, reaction mechanisms

Length of Time/Staging

Two 50 minute class periods for work and discussion for each part of the problem.

Abstract

Part 1 of the problem provides students with an opportunity (1) to learn how to derive the rate law of a mechanism from initial rate and concentration data, and (2) to learn what sort of information might be obtained from plotting concentration vs. time data from a kinetic experiment. In Part 2, students are asked to use the rate law they derived in evaluating several possible mechanisms for the reaction in question, leading to the discovery of rate laws for elementary reactions and the role of intermediates in mechanisms.

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Format of Delivery

Students work on the problem in groups of four, then submit a written report of their solutions.

Student Learning Objectives

Part 1

1. To understand the effect of concentration on the rate of a reaction, and its quantitative expression in terms of rate laws.
2. To learn how to derive a rate law for a mechanism from initial concentration and rate data.
3. To interpret concentration effects through integrated rate laws.
4. To recognize the utility of graphing rate data in various ways to determine the order of a reaction with respect to a given component.
5. To learn how to do graphing and best line fits on Excel, and how to evaluate lines through R factors.

Part 2

1. To understand what a reaction mechanism represents and how it is used.
2. To learn how to determine the rate law for an elementary step.
3. To learn how to predict the rate law for a mechanism, and how to evaluate mechanisms proposed for a given reaction.
4. To learn how to deal with intermediates that appear in predicted rate law.

Student Resources

A standard general chemistry textbook

Instructor Resources

Cain and Powell, "The Raschig Synthesis of Hydrazine", *J. Amer. Chem. Soc. 76*, 2565-2567 (1954).

Yagil and Anbar, "The Kinetics of Hydrazine Formation from Chloramine and Ammonia", *J. Amer. Chem. Soc. 84*, 1797-1803 (1962).

Author's Teaching Notes

This problem follows a brief (one 50 minute class) introduction to kinetics that includes a discussion of "rate" in a chemical context, an example of calculating the average rate over different intervals vs. plotting concentration vs. time to get the instantaneous rate, and several demonstrations of the effects of factors such as concentration, temperature, surface area, and the presence of a catalyst on rates.

Students must look up what a rate law is in order to analyze the data, discovering rate constants in the process. Plotting the concentrations vs. time leads to graphs that do not immediately suggest anything to the students, but discussions of integrated rate laws and the corresponding plots are eventually discovered in the text, allowing for an analysis of the data this way as well.

Part 2:

Here, students must evaluate several proposed mechanisms for the formation of hydrazine in light of the rate law that was determined in part 1. This section follows a lecture on collision theory and the effect of temperature on reaction rates. The energy profiles used in this discussion are then extended: students are presented with a two-hump energy profile, which leads into a discussion of multistep reactions and the concept of a reaction mechanism. Students are told that, to be feasible, a mechanism must give a predicted rate law that conforms to the experimental rate law, and are reminded that the latter are always expressed in terms of measurable reactant (and possibly product/catalyst) concentrations.

To evaluate the mechanisms, they must learn about elementary reactions, how to write the rate law for an elementary step, and how to deal with intermediates that appear in a predicted rate law by utilizing equilibrium steps.

Assessment Strategies

Groups submit written reports of their work, in addition to reporting out orally during class. Exam questions include requests to design kinetic experiments to obtain specific information, including discussions of what data to collect and how to analyze it. Students are also asked to interpret data provided, to derive rate laws both through graphs and calculations, and to evaluate mechanisms for given situations.

Assessment in Kinetics: Sample Exam Questions

Question 1:

Consider the reaction

$$A + B + 2C \rightarrow 2D + 3E$$

In a study of this reaction, three experiments were run at the same temperature:

Expt.#	$[A]_0$	$[B]_0$	$[C]_0$
	M	**M**	**M**
1	2.0	0.0010	1.0
2	0.010	3.0	1.0
3	10.0	5.0	0.50

In each experiment, the concentration of one species was monitored over time; from various plots of the resulting data, the rate law was determined to be Rate = $k[A][B]^2$

a. Indicate which species was monitored in each experiment, and how you know that.
b. For each experiment, sketch the expected results for plots of [ ], ln [ ], and 1/[ ] vs. time; explain your reasoning.
c. Describe how you could determine the value of the rate for the first reaction, using the data discussed in the problem.

Question 2:

The reaction

$H_2SeO_{3(aq)} + 6\ I^-_{(aq)} + 4\ H^+_{(aq)} \rightarrow Se_{(s)} + 2\ I^-_{3\ (aq)} + 3\ H_2O_{(l)}$

was studied at 0 °C, and the following data were obtained:

Trial #	$[H_2SeO_3]_0$	$[H^+]_0$	$[I^-]_0$	initial rate
	M	**M**	**M**	**M/s**
1	1.0×10^{-4}	2.0×10^{-2}	2.0×10^{-2}	1.66×10^{-7}
2	2.0×10^{-4}	2.0×10^{-2}	2.0×10^{-2}	3.33×10^{-7}
3	3.0×10^{-4}	2.0×10^{-2}	2.0×10^{-2}	4.99×10^{-7}
4	1.0×10^{-4}	4.0×10^{-2}	2.0×10^{-2}	6.66×10^{-7}
5	1.0×10^{-4}	1.0×10^{-2}	2.0×10^{-2}	0.42×10^{-7}

6	1.0×10^{-4}	2.0×10^{-2}	4.0×10^{-2}	13.2×10^{-7}
7	1.0×10^{-4}	1.0×10^{-2}	4.0×10^{-2}	3.36×10^{-7}

a. Determine the rate law for this reaction, indicating briefly how you arrived at the answer.
b. What is the value of the rate constant for the first experiment?
c. These data were obtained by monitoring the decrease in $[H_2SeO_3]$ as the reaction proceeded. Would the value for the rate shown for the first set of data change if the disappearance of $H^+_{(aq)}$ had been monitored instead? Explain.

Question 3:

Suppose you have initiated a kinetic analysis of the formation of formaldehyde, CH_2O (a major eye irritant in smog), produced in a reaction between ethylene, C_2H_4, and ozone:

$$C_2H_{4(g)} + O_{3(g)} \rightarrow 2\ CH_2O_{(g)} + 1/2\ O_{2(g)}$$

a. You have collected data showing the concentration of C_2H_4 at a series of different time points. To what use(s) can you put these data? Explain, indicating in detail the steps you would take in doing this, and what results you might expect to see.
b. Indicate another bit of kinetic information that you might wish to obtain concerning this system, that is not available from the data in part a; what additional data would you need to get that information, and how you would use it?
c. Relate the rate of O_3 loss to the rate of formation of O_2.