

The Rate and Order of a Chemical Reaction

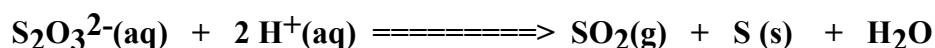
A basic kinetic study of a chemical reaction often involves conducting the reaction at varying concentrations of reactants. In this way, you can determine the order of the reaction in each species, and determine a rate law expression. Once you select a reaction to examine, you must decide how to follow the reaction by measuring some parameter that changes regularly as time passes, such as temperature, pH, pressure, conductance, or absorbance of light.

All chemical reactions occur at specific rates. The rate of a chemical reaction depends on several physical and chemical factors. These factors include:

- The concentration of the reactants
- The pressure on the reaction
- The temperature of the reaction
- The presence of a catalyst

In this activity you will determine the effect of changes in concentration of the reactants on the rate of the chemical reaction. The reaction for this activity is the acidic reduction of the thiosulfate ion to sulfur and sulfur dioxide.

The equation for the reaction is:



One way to determine the effect of concentration on the rate of the reaction is to use a Colorimeter to measure the formation of the solid sulfur generated. The solid sulfur will block the light in the Colorimeter and the amount of blockage is directly proportional to the amount of sulfur in suspension.

The rate of this chemical reaction is given by the equation:

$$\text{Rate} = k [\text{thiosulfate}]^a [\text{acid}]^b$$

The letters a and b seen as exponents are numerals which can only be determined experimentally. Each reactant must be varied separately while the other is kept constant. The effect on the rate of the reaction is noted and the value of the exponent is determined in this way:

- If a change in concentration of one of the reactants has no effect, the exponent is 0.
- If doubling the concentration doubles the rate, the exponent is 1.
- If doubling the concentration quadruples the rate, the exponent is 2.

The overall order of the reaction is determined by adding a + b.

Use the Colorimeter to measure the change in absorbance of light by a solution of sodium thiosulfate and hydrochloric acid as the two components react. Begin with a mixture with specific concentrations of the two components, and then test mixtures with different concentrations of one component or the other. Use the data to determine the overall order of the rate of reaction.

Kinetics Analysis

As this reaction proceeds, it undergoes a change that can be precisely measured by a Vernier Colorimeter (see Figure 1). By carefully varying the concentrations of the reactants, you will determine the effect each reactant has on the rate of the reaction, and consequently the order of the reaction. From this information, you will write a rate law expression for the reaction.

OBJECTIVES

In this experiment, you will

- Conduct the reaction using various concentrations of reactants.
- Determine the order of the reaction .
- Determine the rate law expression for the reaction.

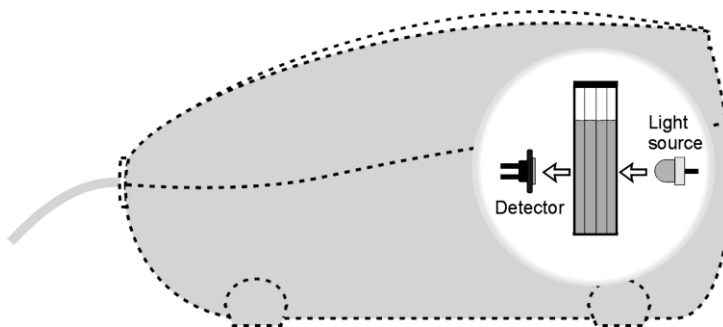


Figure 1

MATERIALS

Vernier computer interface
Computer or Lab Quest
Vernier Colorimeter or Spectrovisor or
stopwatch
1 cuvettes
3 – Syringe pipettes

Hydrochloric acid, 6 molar
Sodium thiosulfate, 0.24 molar
Distilled Water

Cotton Swab

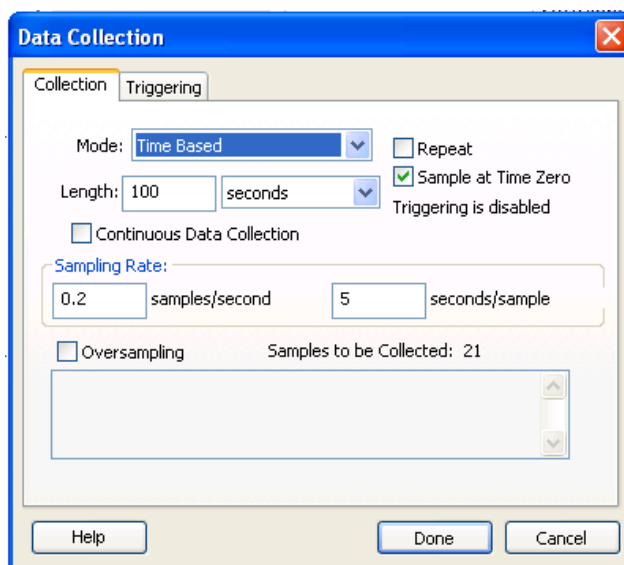
PROCEDURE

1. Obtain and wear goggles.
2. Connect a Colorimeter to Channel 1 of the Vernier computer interface. Connect the interface to the computer with the proper cable.

The Colorimeter analyzes colors of light that pass through a solution. The solution is put into a rectangular container called a cuvette, which is then placed inside the Colorimeter. The measure of the amount of light that passes through a solution is called “transmittance”. Transmittance is a ratio of the intensity of the transmitted light to the intensity of the original light, and is usually expressed as a percentage.

3. Start the *Logger Pro* program on your computer. Open the file “25 Rate and Order” from the *Advanced Chemistry with Vernier* folder. Click the experiment tab and select data collection. Adjust the data collection to .2 samples/second and click done.

4. Set up and calibrate the Colorimeter.
 - a. Prepare a *blank* by filling an empty cuvette $\frac{3}{4}$ full with distilled water. Place the blank in the cuvette slot of the Colorimeter and close the lid.
 - b. If your Colorimeter has a CAL button, set the wavelength on the Colorimeter to Red nm, press the CAL button.



5. Conduct the reactions according to the chart below. Use micro pipets to measure out the volumes of reactants and distilled water into small labeled breakers. Add the distilled water to the acid solution, to standardize your process. Place the two reactants in separate labeled beakers.

Note: If a spectrovis is used instead of the colorimeter with a LabQuest.

Connect the spectrovis to the LabQuest. Change the mode to time based.

Tap the orange bar and select wavelength and set to 635 nm.

Tap the orange bar again to Calibrate the spectrometer.

- a. Fill a blank cuvette $\frac{3}{4}$ full with the distilled water blank.
- b. Place the cuvette in the spectrometer. Be certain to align the cuvette so that the clear sides are facing the light bulb icon and arrow on the spectrometer. To correctly use a cuvette, remember:
 - All cuvettes should be wiped clean and dry on the outside with a lint-free tissue.
 - Always position the cuvette with the clear sides or reference point facing the white reference mark on the top of the spectrophotometer.
 - Handle cuvettes only by the top edge of the ribbed sides.
 - All solutions should be free of bubbles.

Kinetics Analysis

- c. Tap the Orange box and select Calibrate. The following message appears in the Calibrate dialog box: "Waiting ... seconds for lamp to warm up." After the allotted time, the message changes to: "Finish Calibration."

6. Prepare for Trial 1 and collect absorbance data.

An alternate method is to place a line on a white background the width of the bottom of the micro syringe. Determine the time with a timer the length of time it takes to longer you are able to view the black line do to the colloidal sulfur.

The general procedure is as follows:


- a) Measure the water needed for each trial and the acid place into one cuvette.
- b) Place the cuvette into the spectrovis or colorimeter or on white paper.
- c) Add the required thiosulfate to the same cuvette .
- d) Quickly close the top and record the absorption readings.

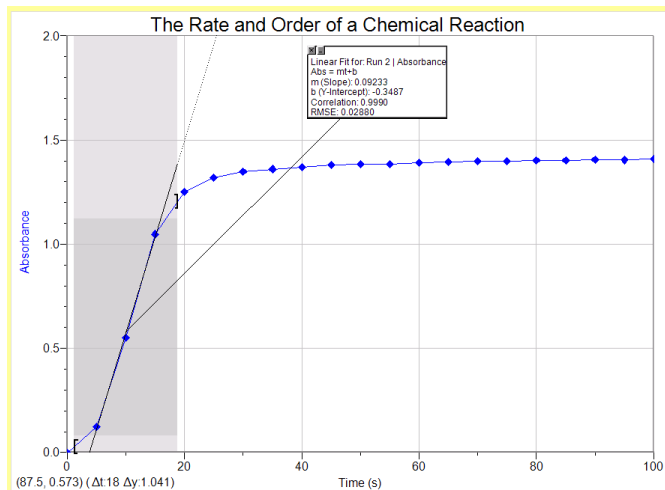
TABLE #1. A Kinetics Study of the Thiosulfate-HCl Reaction

Trial	B	A		Total Number mls
	mls 0.24 M $\text{Na}_2\text{S}_2\text{O}_3$	mls 6.0 M HCl	mls of water	
1	.80	.40	.40	1.60
2	.80	.80	0	1.60
3	.70	.80	.10	1.60
4	.60	.80	.20	1.60
5	.50	.80	.30	1.60
6	.40	.80	.40	1.60

7. Click to begin collecting absorbance data. Data will be gathered for 200 sec. If you are using stop watch determine the time it takes for you not to be able to see the black line you have written on the white background. This time is your time interval.
8. When the data collection is complete, carefully remove the cuvette from the Colorimeter. Clean the cuvette with the cotton swab provided. Remove all colloidal sulfur. Rinse and clean the cuvette for the next trial.

The Rate and Order of a Chemical Reaction

9. Examine the graph of the first trial. Select a linear region of the graph that covers about 20-40 seconds of the reaction. Click the Linear Regression button, . Record the slope, as the initial rate of the Trial 1 reaction, in your data table. Determine the time the linear region began and when it ended. This time interval is time of reaction. Use the last point highlighted as your time interval.



10. Repeat Steps 6-9 to conduct Trials 2-6.

QUESTIONS AND CALCULATIONS:

- Q1. Complete Table #2 by determining rate of the reaction for each trial. Where
 For each trial, calculate the concentration of the diluted Thiosulfate solution.
 For each trial, calculate the concentration of the diluted Hydrochloric acid.
- Q2. (a) Plot the molar concentration of the thiosulfate, $[S_2O_3^{2-}]$, for trial 2 through 6 as a function of the time of the reaction.
 (b) Plot the natural log of the molar concentration of the thiosulfate ion, $\ln [S_2O_3^{2-}]$, as a function of the time of the reaction.
 (c) Plot the reciprocal of the molar concentration of the thiosulfate ion, $1/[S_2O_3^{2-}]$, as a function of the time of the reaction.
 (d) Determine the slope of the graph plotted in questions Q2a, Q2b, or Q2c, which produced a linear relationship. The slope of your graph is equal to the rate constant, k , for the reaction.
 (e) From the type of graph which produced a linear relationship in questions Q2a, Q2b, or Q2c, predict the "order" of the reaction with respect to the molar concentration of thiosulfate, $[S_2O_3^{2-}]$

Information Plotted	Reaction Order
concentration vs time	zero order
ln concentration vs time	first order
1/concentration vs time	second order

- Q3. (a) Calculate the ratio of the concentrations of thiosulfate ion in wells 2 & 6. Likewise, calculate the ratio of the concentrations of HCl in wells 2 & 1
- (b) Calculate the ratio of the rates of the reaction between the solutions in wells 2 & 6. Likewise, calculate the ratio of the rates of the reaction between solutions in wells 2 & 1.

Kinetics Analysis

- (c) Determine the exponents in the rate equation for the reaction between sodium thiosulfate and hydrochloric acid where, the exponents x and y are determined by comparing the ratios of the molar concentration of the reactants to the ratio of the rates of reaction in the same trials.

Use the Average Rate and then the Graphical Rate.

By comparing the ratios of the concentrations calculated in Q3a with the ratio of their rates calculated in Q3b, you can determine the "order" of the reaction. For example, if the ratio of the concentrations is 2 and the ratio of the rates is also 2, then the reaction is first order ($2^1 = 2$). However, if the ratio of the concentrations is 2 and the ratio of the rates is 4 (2^2), then the reaction is a second order reaction. Likewise, if the ratio of the concentrations is 2 and the ratio of the rates is roughly 1, then the reaction is a "0" order reaction (a change in concentration has little or no effect on the rate of the reaction).

- (d) Determine the rate constant, k , in the rate equation for each trial in Table #2 and calculate the average rate constant of all trials.
- (e) Give your rate equation or rate law complete with your value of the rate constant, k .
- (f) What is the overall order of the reaction? (The overall order of the reaction is the sum of the exponents, x and y .)
- Q4. Determine the "half life", $t_{1/2}$, of the thiosulfate ion in an acid medium from the order of the reaction and the table below:
- Q5. According to your data, what general statement can you make regarding the effect of the concentration of thiosulfate ion, $[S_2O_3^{2-}]$, on the rate or speed at which the colloidal sulfur is formed?
- Q6. According to your data, what general statement can you make regarding the effect of the concentration of hydrochloric acid, $[HCl]$, on the rate or speed at which the colloidal sulfur is formed?
- Q7. Compare the "order" and rate constant of the reaction determined graphically with the "order" and rate constant you determined algebraically. Which method, the graphic method or the algebraic method, do you feel is more reliable? Justify your answer.

The Rate and Order of a Chemical Reaction

TABLE #1. A Kinetics Study of the Thiosulfate-HCl Reaction

Cuvette	Cuvette first		Then Add	Total Number mls
	mls 6.0 M HCl	mls of water	mls 0.24 M Na ₂ S ₂ O ₃	
1	.40	.40	.80	1.60
2	.80	0	.80	1.60
3	.80	.10	.70	1.60
4	.80	.20	.60	1.60
5	.80	.30	.50	1.60
6	.80	.40	.40	1.60

TABLE #2. The Thiosulfate-HCl Kinetics Summary

Well	Time Interval	Average Rate 1/(Time Interval)	Graphical Rate	[S ₂ O ₃ ²⁻]	[H ⁺]	Rate Constant	Well Ratio	Conc. Ratio	Rate Ratio
1		/s	/s	M	M		2:1 [H ⁺]		
2		/s	/s	M	M				
3		/s	/s	M	M				
4		/s	/s	M	M		2:6 [S ₂ O ₃ ²⁻]		
5		/s	/s	M	M				
6		/s	/s	M	M				

Average Rate Constant k=