Determining a Rate Law
A "Sulfur Clock" Reaction

Introduction

The rate of a chemical reaction may depend on the concentration of one or more reactants or it may be independent of the concentration of a given reactant. Exactly how the rate depends on reactant concentrations is expressed in an equation called the rate law. How can the rate law for a reaction be determined?

Concepts

- Kinetics
- Order of reaction
- Rate law
- Concentration

Background

For a general reaction of the form

$$A + B \rightarrow C \qquad \textit{Equation 1}$$

the rate law can be written as

$$\text{Rate} = k\,[A]^n[B]^m \qquad \textit{Equation 2}$$

where k is the rate constant, [A] and [B] are the molar concentrations of the reactants, and n and m are exponents that define how the rate depends on the individual reactant concentrations. The values of n and m must be determined by experiment—they cannot be determined simply by looking at the balanced chemical equation. The rate constant for a reaction does not depend on the reactant concentrations, but does depend on temperature. The exponents n and m are also referred to as the *order of reaction* with respect to a particular reactant. In the above example, the reaction is said to be nth order in A and mth order in B. In general, n and m will be positive whole numbers—typical values of n and m are 0, 1, 2.

Rate laws for different reactions take on different forms. The reactions shown below and their experimentally determined rate laws demonstrate that the order of reaction cannot be predicted using the coefficients in the balanced chemical equation.

Chemical Equation	**Rate Law**
$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$	Rate $= k\,[NO_2]^2$
$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$	Rate $= k\,[NO]^2[O_2]$
$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$	Rate $= k\,[N_2O_5]$

The reaction order for each reactant in the rate law determines how the rate changes as the concentration of that reactant changes. If a reactant has an order of zero, the reactant does not appear in the rate law and the rate is independent of its concentration. Increasing or decreasing the concentration of a zero-order reactant does not affect the rate of the reaction.

When a reaction is first order in a reactant, the reactant appears in the rate law with an exponent of one—the rate is directly proportional to the reactant concentration. If the concentration of a first-order reactant is doubled, the rate will also double. For a reaction that is second order in a reactant, the reactant concentration appears in the rate law with an exponent of two. If the concentration of a second-order reactant is doubled, the rate of the reaction will increase by a factor of four.

The following general procedure may be used to determine the rate law for a reaction. First, the concentration of one reactant is held constant while the concentration of a second reactant is varied, and the reaction time is measured. Then, the first reactant's concentration is varied while the second reactant's concentration is held constant, and again the reaction time is measured. The average rate for each reaction is calculated by taking the inverse of the reaction time. The data is then analyzed to determine the reaction order for each reactant and the rate law.

Consider, for example, the reaction between nitric oxide and oxygen gas.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \qquad \textit{Equation 3}$$

$$\text{Rate} = k[NO]^n[O_2]^m \qquad \textit{Equation 4}$$

The following data was obtained by performing the reaction five times and varying the concentrations of the reactants as indicated. In each case, the reaction time was measured, then inverted to find the average rate.

Trial	[NO]	$[O_2]$	Reaction Time (sec)	Average Rate (sec^{-1})
1	0.020	0.010	35.7	0.028
2	0.020	0.020	17.5	0.057
3	0.020	0.040	8.8	0.11
4	0.040	0.020	4.4	0.23
5	0.010	0.020	71.4	0.014

In the first three trials, the concentration of NO was constant while the concentration of O_2 was varied. Therefore, any change in the rate in Trials 1–3 is due solely to the change in the concentration of O_2. Comparing the rates in Trials 1 and 2 gives the following results, where the subscripts 1 and 2 refer to Trials 1 and 2, respectively.

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{[O_2]_2^m}{[O_2]_1^m} = \left(\frac{[O_2]_2}{[O_2]_1}\right)^m$$

$$\frac{.057}{.028} = 2.0 = \left(\frac{.02}{.01}\right)^m = 2^m$$

$$m = 1$$

In trials 2, 4, and 5 the concentration of O_2 was held constant while the concentration of NO was varied. Therefore, any change in the rate in Trials 2, 4, and 5 is due solely to the change in the NO concentration. In the rate law, the $k[O_2]^m$ terms can be ignored because they do not vary. Comparing the rates in Trials 4 and 5 gives the following results.

$$\frac{\text{Rate}_4}{\text{Rate}_5} = \frac{[\text{NO}]_4{}^n}{[\text{NO}]_5{}^n} = \left(\frac{[\text{NO}]_4}{[\text{NO}]_5}\right)^n$$

$$\frac{.227}{.014} = 16 = \left(\frac{.04}{.01}\right)^n = 4^n$$

$$n = 2$$

The reaction of NO and O_2 to give NO_2 is first order in O_2, second order in NO. The overall rate equation for the reaction is rate $= k[NO_2]^2[O_2]$.

Experiment Overview

The purpose of this experiment is to determine the rate law for the reaction between hydrochloric acid, HCl, and sodium thiosulfate, $Na_2S_2O_3$.

$$2HCl(aq) + Na_2S_2O_3(aq) \rightarrow S(s) + SO_2(aq) + H_2O(l) + 2NaCl(aq) \qquad \textit{Equation 5}$$

In Part A, the HCl concentration will be held constant while the $Na_2S_2O_3$ concentration is varied. In Part B, the HCl concentration will be varied while the $Na_2S_2O_3$ concentration is held constant. Reaction times will be measured by monitoring the appearance of sulfur. As solid sulfur is produced in the reaction, the reaction mixture will become clouded with a yellow precipitate. The reaction time will be measured by noting the time at which it is no longer possible see through the solution.

Pre-Lab Questions

Read the *Background* section and the *Procedure,* then answer the following questions.

1. The following table summarizes the amounts and concentrations of the reactants that will be used in each trial in Parts A and B. Use the dilution equation $M_1V_1 = M_2V_2$ to calculate the concentration M_2 of each reactant in each well after mixing but *before* any reaction occurs. The first one has been worked for you as an example.

Sample		Volume of 1.0 M HCl	Volume of Water	Volume of 0.30 M $Na_2S_2O_3$
Part A	**Well 1**	2.0 mL	0	3.0 mL
	Well 2	2.0 mL	1.5 mL	1.5 mL
	Well 3	2.0 mL	2.0 mL	1.0 mL
Part B	**Well 4**	3.0 mL	0	2.0 mL
	Well 5	1.5 mL	1.5 mL	2.0 mL
	Well 6	1.0 mL	2.0 mL	2.0 mL

M_1 = concentation of reactant before mixing $\qquad$ M_2 = concentration of reactant after mixing

V_1 = volume of reactant before mixing $\qquad$ V_2 = volume of reactant after mixing

For well #1: $M_2(HCl) = (1.0\ M)(2.0\ mL)/(5.0\ mL) = 0.40\ M$

$M_2(Na_2S_2O_3) = (0.30\ M)(3.0\ mL)/(5.0\ mL) = 0.18\ M$

2. Enter the results of the calculations in the data table.

Materials

Hydrochloric acid solution, 1.0 M, HCl, 20 mL
Sodium thiosulfate solution, 0.30 M, $Na_2S_2O_3$, 20 mL
Distilled or deionized water and wash bottle
Beakers, 50-mL, 3
Labeling or marking pen
Cotton swabs or paper towels, 4
Piece of white paper
Reaction plate, six-well
Stopwatch or timer
Syringe, 3-mL

Safety Precautions

Hydrochloric acid solution is moderately toxic by ingestion and inhalation. It is corrosive to eyes and skin. Sodium thiosulfate is a body tissue irritant. The sulfur produced in this reaction has low toxicity, but may be a skin and mucous membrane irritant. The reaction generates aqueous sulfur dioxide, which is a skin and eye irritant. Wear chemical splash goggles and chemical-resistant gloves and apron. Wash hands thoroughly with soap and water before leaving the laboratory.

Procedure

Preparation

1. Label one small beaker "HCl". Add 20 mL of 1.0 M hydrochloric acid to this beaker.

2. Label another small beaker "$Na_2S_2O_3$". Pour 20 mL of 0. 30 M sodium thiosulfate solution into this beaker.

3. Label a third small beaker "water". Pour 30 mL of distilled or deionized water into this beaker.

4. On a piece of white paper draw a black "+" sign about the size of a well in the reaction plate. Verify that the "+" sign can be seen through the plate. Use the same "+" sign for every well reaction in Parts A and B.

Part A. Varying the Concentration of $Na_2S_2O_3$

Read the entire procedure before beginning the experiment.

5. Fill the 3-mL syringe up to the 2.0-mL mark with distilled water by submerging the syringe in the "water" beaker and drawing water into the syringe until the bottom of the plunger is at the 2.0-mL mark. Make sure there are no air bubbles in the syringe.

6. Now submerge the syringe in the "$Na_2S_2O_3$" beaker and draw 1.0 mL of the $Na_2S_2O_3$ solution into the syringe so that the plunger sits at the 3.0-mL mark.

7. Empty the syringe into well #3 of the six-well reaction plate. See Figure 1 below.

8. Repeat steps 5–7 to fill wells #1 and #2. Use the amounts of water and $Na_2S_2O_3$ solution shown below in Figure 1. Fill the wells in reverse order (well #2 next, then well #1). Filling the syringe with the most dilute mixture first and working up to the most concentrated means that the syringe does not need to be rinsed between fillings.

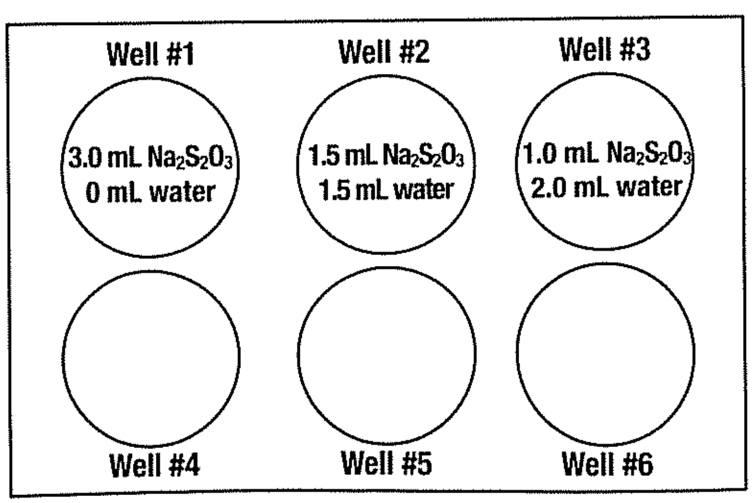

Figure 1.

9. Rinse the syringe thoroughly with water. Fill the 3-mL syringe to the 2.0-mL mark with the HCl solution. Prepare to start the timer. Empty the syringe into well #1. Time the reaction with a stopwatch by measuring the time from which the solution was added until the black "+" sign can no longer be seen through the solution. Record the exact time in seconds in the data table.

10. Repeat Step 9 for wells #2 and #3, adding 2 mL of the HCl solution to each well. Carefully time each reaction with a stopwatch by measuring the time from which the solution was added until the black "+" sign can no longer be seen through the solution. Record the exact time in seconds in the data table.

Part B. Varying the Concentration of HCl

11. Fill the 3-mL syringe to the 2.0-mL mark with distilled water by submerging the syringe in the "water" beaker and drawing water into the syringe until the plunger is at the 2.0-mL mark. Make sure that there are no air bubbles in the syringe.

12. Now submerge the syringe in the "HCl" beaker and draw 1.0 mL of HCl solution into the syringe so that the plunger sits at the 3-mL mark.

13. Empty the syringe into the well #6 of the six-well reaction plate. See Figure 2 below.

14. Repeat steps 11–13 to fill wells #5 and #6. Use the amounts of water and HCl solution shown below in Figure 2. Fill the wells in reverse order (well #5 next, then well #4).

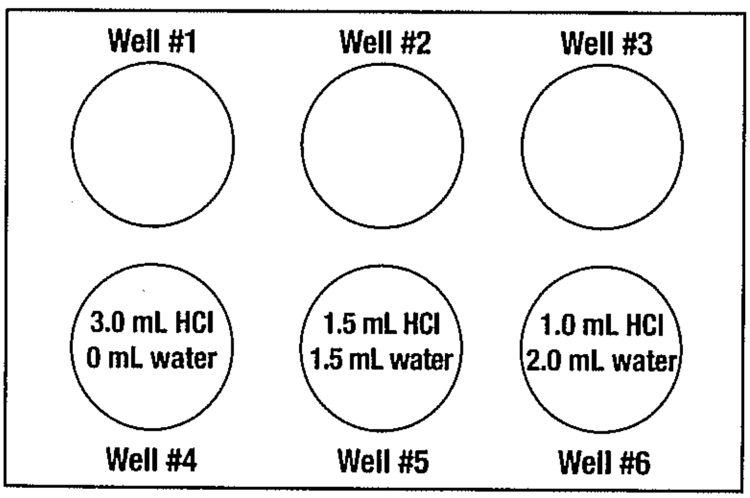

Figure 2.

15. Rinse the syringe thoroughly with water. Fill the 3-mL syringe to the 2.0-mL mark with the $Na_2S_2O_3$ solution. Prepare to start the timer. Empty the syringe into well #4. Time the reaction with a stopwatch or timer by measuring the time from which the solution was added until the black "+" sign can no longer be seen through the solution. Record the exact time in seconds in the data table.

16. Repeat Step 15 for wells #5 and #6, adding 2.0 mL of the $Na_2S_2O_3$ solution to each well. Carefully time each reaction with a stopwatch or timer by measuring the time from which the solution was added until the black "+" sign can no longer be seen through the solution. Record the exact time in seconds in the data table.

17. As soon as the reaction times have been measured, quickly empty the six-well reaction plate into the collection container provided by your teacher. Rinse and dry each of the wells with soap and water. Use a cotton swab or a paper towel to thoroughly clean and dry each well.

Name: ______________________________

Class/Lab Period: ______________________

Determining a Rate Law

Data Table

	Well	$[Na_2S_2O_3]$*	[HCl]*	Reaction Time
Part A	1			
	2			
	3			
Part B	4			
	5			
	6			

*These are the reactant concentrations in solution immediately after mixing and before any reaction has occurred. See the *Pre-Lab Questions* for calculations.

Post-Lab Questions *(Use a separate sheet of paper to answer the following questions.)*

1. The average rate of reaction is equal to the molar concentration of sulfur produced when the solution becomes cloudy divided by the reaction time.

$$\text{Rate} = \frac{[S]}{\text{Reaction Time}}$$

If the concentration of sulfur produced in each well is the same at the onset of "cloudiness," then the rate is proportional to 1/time.

$$\text{Rate} \propto \frac{1}{\text{Time}}$$

Calculate the "proportional" rate in 1/sec for each well.

2. Does the rate depend on the $Na_2S_2O_3$ concentration? Compare the concentration of $Na_2S_2O_3$ and the rate in wells #1–3. What is the reaction order for $Na_2S_2O_3$?

3. Does the rate depend on the HCl concentration? Compare the concentration of HCl and the rate in wells #4–6. What is the reaction order for HCl?

4. Write the rate law for this reaction.