EXPERIMENT 1

The Kinetics of a Thiosulfate Solution

INTRODUCTION:

Various approaches are used to study the kinetics of reactions. A usual procedure is to monitor some property, such as intensity of color due to a reactant or product, which changes during the course of a reaction. In the present experiment, the property studied is the precipitation of a product, sulfur, which forms when solutions of hydrochloric acid and thiosulfate are mixed. The acidification of thiosulfate solutions leads to the formation of colloidal sulfur. The rate of this reaction is studied by measuring the time required for the reaction mixture to become so turbid that it ceases to transmit light. The reaction is acid catalyzed and the acid is kept at constant concentration throughout the experiment.

When a solution of thiosulfate is acidified, the following reaction takes place: $S_2O_3^2$ - (aq) + 2H⁺ (aq) \rightarrow H₂O + SO₂ (g) + S (s) (1)

On mixing a solution of acid, such as HCI, and a thiosulfate solution, there is an initial time-delay, then a precipitate of sulfur appears fairly sharply. The time interval between initial mixing and sulfur precipitation is a measure of the initial rate of reaction (i.e. the amount of time for a given amount of product, sulfur, to form). The color appears after a fixed amount of colloidal sulfur has been produced. Because the amounts of reactant used up in causing this amount of precipitate is small, the reactant concentrations remains essentially constant throughout the time of reaction. Recall that a rate for a chemical reaction is expressed as an amount of product formed (or reactant used up) divided by the time interval of the change:

$$\Delta \text{ Concentration } / \Delta t = \Delta[M] / \Delta t = \Delta[S_2O_3^{2-}] / \Delta t$$
 (2)

In this experiment you will determine the dependence of the initial rate of reaction on the initial concentration of thiosulfate ion. The concentration of the other reactant, H^+ , will be kept constant. Recall that, in this case:

Average Rate =
$$(\Delta [M] / \Delta t)$$
 (3)

Rate law
$$= k [M]^{m}$$
 (4)

For Example, suppose the following data was collected for this experiment and we assume (1) the concentration of thiosulfate, at the point of data acquisition, has not significantly changed from its initial concentration and (2) since we are collecting the data at constant product production, the change at that point will be consistent for each trial therefore:

trial	$\mathbf{M}_{\text{initial}} = [\mathbf{S}_2 \mathbf{O}_3^{2-}]$	Time	~ Rate
1	0.1 M	160 s	6.25x10 ⁻⁴ M/s
2	0.2 M	40 s	5.00x10 ⁻³ M/s
3	0.4 M	10 s	4.00x10 ⁻² M/s

Using equation (3), we can get an approximate rate of $0.1/16 = 6.25 \times 10^{-4}$ M/s. Now using the initial rate method equation 4: (Rate₂ = k [M²] ^m / Rate₁ = k [M₁] ^m) we can calculate the order of m.

 $(5.00 \times 10^{-3} \text{ M/s}/6.25 \times 10^{-4} \text{ M/s}) = (.2/.1)^{\text{m}}$ 8 = 2^m ln(8) / ln(2) = m In a generic graph plotting rate vs concentration, we can see some kinetic rate trends as a function of time. If we plot the above date we would see the graph corresponds to 3^{rd} order curve. Great correlation!



Fig 1 - Kinetic Rate Trends (Order of Rxn) as a Function of Concentration



In this experiment you will use the initial rate method to determine the order of thiosulfate and then plot the data as either concentration vs time, natural log of concentration vs time or inverse concentration vs time to verify the order obtained by the initial rate method. Then in part 2, you will vary temperature to determine the activation energy of this reaction.

PROCEDURE:

Part I: Effect of Thiosulfate Concentration on Reaction Rate

- (1) Prepare a piece of white paper with a large "X" marked on it (pen or pencil, makeit dark).
- (2) A solution of 1 M sodium thiosulfate, is available (center bench or hood). Add 70 mL of this solution to 210 mL of water to make a solution approximately 0.25 M in thiosulfate. We will refer to this as your "stock thiosulfate solution".
- (3) Trial 1: Measure 50 mL of this stock thiosulfate solution into a 250 mL Erlenmeyer flask.
- (4) Carefully noting the time with a stopwatch or clock with a second hand, add about 5 mL of 2 M HCl, (provided for you by the stock room personnel or instructor), make sure it is the same amount each trial.
- (5) Swirl the contents of the flask vigorously to mix, then place it on the white paper prepared in step(1).
- (6) Look down vertically through the flask. When the "X" disappears (due to the sulfur precipitate obstructing your vision), note the time.
- (7) The experiment is now repeated four more times, using progressively more dilute thiosulfate solutions. Note, however, that for each experiment, the disappearance of the "X" corresponds to formation of the same amount of precipitated sulfur in the reaction mixture. The diluted solutions are prepared as follows:

Trial #2: take 40 mL stock thiosulfate solution and dilute to 50 mL by adding water Trial #3: take 30 mL stock thiosulfate solution and dilute to 50 mL by adding water Trial #4: take 20 mL stock thiosulfate solution and dilute to 50 mL by adding water Trial #5: take 10 mL stock thiosulfate solution and dilute to 50 mL by adding water

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In each experiment, addition of 5 mL of 2 M HCI solution assures that the concentration of H^+ does not vary. Only the initial concentration of thiosulfate varies. Use the data collected above to estimate the order of reaction with respect to thiosulfate solution.

Part II: Temperature Dependence of Reaction

- (1) Measure 10 mL of your stock thiosulfate solution (0.25 M) into a 100-mLErlenmeyer flask.
- (2) Add 40 mL of water.
- (3) Measure the temperature of the solution.
- (4) Noting the time carefully, add 5 mL of 2M HCI, swirl, and place on the marked white paper as in Part 1.
- (5) Note the time of disappearance of the "X" on the white paper.
- (6) Repeat the experiment four more times, heating the thiosulfate solution before the addition of HCI to a little over 30°, 40°, 50°, and 60 °C so that the reaction can be started as near to these temperatures as possible.
- (7) Use these data to investigate temperature dependence of the reaction (see Report Sheet).

List of Chemicals & Equipment per student 70 mL of 1M Na₂S₂O₃ 50 mL of 2M HCl White paper & sharpie Stopwatch 3 - 250mL Erlenmeyer Flask Thermometer Hot plate

NAME

REPORT SHEET EXPERIMENT 1

The Kinetics of a Thiosulfate Solution

General/Pre-Lab Questions:

- 1. Based on Equation (1), write the oxidation and reduction half-reactions for the $S_2O_3^{2-}/H^+$ reaction.
- 2. When the results are analyzed for part 1, you will plot the time taken for the "X" to disappear against either the concentration, the reciprocal of concentration, and then against the natural log of concentration. Why the reciprocal? Why the natural log of concentration? In what way is a change in the rate of reaction reflected by the time of reaction? For example, if the rate doubles, what happens to the time for a fixed amount of product to form?

3. Suppose that the order of reaction with respect to thiosulfate, stock solution of 0.25 M, is two. Further suppose that the time taken for the "X" to disappear when we use 50 mL thiosulfate solution is 25 sec. How long would it take for the "X" to disappear if we instead use 30 mL thiosulfate diluted to 50 mL with water? How would this change if the order with respect to thiosulfate is 1.5?

EXPERIMENT DATA:

Volume thiosulfate	Time for "X" to disappear,	Concentration of	Rate of disappearance
used	in seconds	thiosulfate	of "X"
50 mL			
40 mL			
30 mL			
20 mL			
10 mL			

Part I - Changes due to concentration differences (include units)

1. Estimate the order of reaction with respect to thiosulfate based on the initial rate method. Show a sample calculation here, the rest of the calculations should be in your lab notebook.



2. Next display your results graphically, in excel or similar program, by plotting (1) concentration vs time, (2) the reciprocal of the concentration against the time, and then (3) plot the natural log of concentration against time and compare your graphs. Attach those graphs to this report sheet. Describe any conclusions/comparisons can you draw from these graphs. How do the answers acquired from the graphs compare to the initial rate method?

3. How would the shape of these graphs change if the order of the reaction were:

- a. higher?
- b. lower?

Part II - Changes due to temperature difference [M] = _____

Temperature (°C)	Temperature (K)	Time (t) for "X" to disappear	Rate	k

Calculate the rate and rate constant per temperature.

1. Plot the natural log of k vs. the reciprocal of temperature in Kelvin. Attach that graph to this report sheet. Briefly describe the appearance of the graph. What equation correlates to this graph, (show two variations)?

2. Use this graph to estimate the activation energy (include units). Describe and demonstrate how you analyzed this graph and acquired your E_a value.

$E_a =$		