

# Reaction Kinetics: the Iodine Clock Reaction

**Objective:** To investigate the factors that affect the rate of reactions, including concentrations of reactants and temperature; to use kinetics data to derive a rate law for the iodine clock reaction; to estimate the activation energy of the reaction.

**Materials:** Solutions of 0.22 M KI (potassium iodide), 0.18 M  $K_2S_2O_8$  (potassium peroxydisulfate) 0.18 M  $K_2SO_4$  (potassium sulfate), 0.22 M  $KNO_3$  (potassium nitrate), 0.010 M  $Na_2S_2O_3$  (sodium thiosulfate), and 5% starch indicator.

**Equipment:** Stopwatch or time piece with a second hand; two 100-mL beakers; pipettes (5-mL, 10-mL, 20-mL volumetric pipettes, and/or graduated pipettes); two 100-mL beakers; two 600-mL beakers for hot water bath and ice bath.

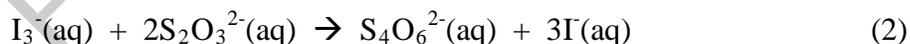
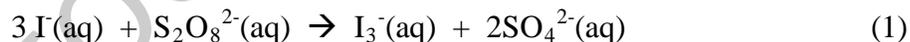
**Safety:** Iodine solutions can stain skin and clothing; wash thoroughly if contact is made with skin. Safety goggles should be worn at all times in the lab.

**Waste Disposal:** Excess reagents/reaction solutions may be flushed down the sink with water.

## INTRODUCTION

Chemical kinetics is the study of **reaction rate**, or how fast a reaction proceeds. Knowing the factors that control the rate of reactions has tremendous implications in both industry and the environment. Manipulating these factors to increase the rate of a reaction can increase the yield of desirable products of industrial processes, or decrease the rate of undesirable reactions to minimize negative environmental impacts.

A reaction that readily lends itself to kinetic investigations is the iodine clock reaction, so called because of its kinetics are so well known and reliable. In reality, two reactions are involved, although we will only be studying the kinetics of one of them.



We are interested in the kinetics of Reaction (1) between the iodide ion ( $I^-$ ) and the peroxydisulfate, or persulfate ion ( $S_2O_8^{2-}$ ). We can write a generic **rate law** which relates the rate of the reaction (in units of M/sec) to the concentration of reactants:

$$Rate = k [I^-]^m [S_2O_8^{2-}]^n \quad (3)$$

In this rate law, the  $m$  and  $n$  are integers and represent the **order** of the reaction with respect to the respective reactants. Unfortunately, the values of these integers cannot be determined simply by examination of the balanced equation, but must be determined experimentally. To simplify the experiment, the concentration of one reactant is typically held constant while the other reactant concentration is varied. Any changes in the rate of the reaction must be related to the change in the concentration of the variable reactant.

The problem is, how can we measure the rate of this reaction? This is where Reaction (2) is useful. Reaction (2) is nearly instantaneous. As soon as any triiodide ion is produced by Reaction (1) it reacts with the thiosulfate ion ( $S_2O_3^{2-}$ ) via Reaction (2). We can monitor the rate of Reaction (1) by observing how long it takes to produce enough triiodide to completely react with a given amount of thiosulfate. But how do we know when all the thiosulfate is consumed?

A starch indicator added to the reaction mixture will turn deep blue in the presence of triiodide ion ( $I_3^-$ ), one of the products of Reaction (1).



As long as there is any thiosulfate in solution, there is no triiodide to react with the starch indicator. Once all the thiosulfate has been consumed, Reaction (2) ceases. Subsequent production of triiodide by Reaction (1) will result in the formation of the blue starch complex, signaling the end of the experiment.

By systematically varying the concentrations of reactants in Reaction (1), and observing the effect of the change in concentration on the rate of the reaction, we can mathematically determine the values of  $m$  and  $n$  in the rate law. Once the rate law is known, we can use the rate law and experimental data (rates, concentrations) to calculate the value of the rate constant,  $k$ , at a given temperature. By performing additional experiments at different temperatures, we can determine the value of  $k$  as a function of temperature. The activation energy for the reaction,  $E_a$ , can then be determined using the Arrhenius equation

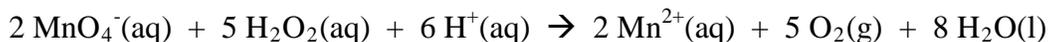
$$\ln(k) = \ln A - \frac{E_a}{RT} \quad (5)$$

where  $A$  is the Arrhenius constant,  $R = 8.31 \text{ J/mol}\cdot\text{K}$ , and  $T$  is absolute temperature in Kelvin.

## Pre-Lab Questions

1. Why is the starch indicator added to the reaction solution?

2. Consider the following balanced chemical reaction:



a) A student wrote the following rate law for this reaction:

$$\text{Rate} = k [\text{MnO}_4^-]^2 [\text{H}_2\text{O}_2]^5 [\text{H}^+]^6$$

Is this correct? Explain.

b) Briefly describe what must be done to obtain the correct rate law.

3. Define the following terms:

a) *Rate* :

b) *Rate law* :

c) *Rate constant, k* :

4. What would you expect to happen to the rate of the reaction between iodide ion and persulfate ion (Reaction 1), as temperature increases? Explain your answer in terms of kinetic theory.

## PROCEDURE

1. Working in pairs, obtain two clean, dry 100-mL beakers. Label one "A" and one "B." For each of the experiments, beaker A will contain the KI,  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{KNO}_3$ , and the starch indicator. Beaker B will contain the  $\text{K}_2\text{S}_2\text{O}_8$  and the  $\text{K}_2\text{SO}_4$ . The  $\text{KNO}_3$  and  $\text{K}_2\text{SO}_4$  are only added to maintain constant ionic strength of the solutions and do not participate in any of the reactions. The volumes of each reagent solution needed for each experiment are summarized in Table 1.
2. For Experiment 1, pipet the indicated amount of each reagent into the beakers labeled A and B. When ready, one partner should start timing while the other partner mixes the two solutions. Mix the solutions by pouring one beaker into another, and then back and forth several times. When the solutions have been thoroughly mixed, set the beaker down on a piece of white paper and wait for the appearance of the blue color that signals the end of the experiment. Record to the nearest second the time it takes for the blue color to appear.
3. Flush the reaction solution down the drain with plenty of water. Rinse and dry the two beakers and repeat Experiment 1.
4. Repeat steps 2 and 3 for Experiments 2–7, using the volumes of reagent solutions indicated in Table 1.

### Activation Energy

5. Runs 8, 9, and 10 will be used to determine the activation energy ( $E_a$ ) for the reaction. Obtain solution volumes from Experiment 3 in beakers A and B. Measure the temperature of one of these solutions. This temperature will be the room temperature, and the reaction times in Table 1 for Experiment 3 will be used for Experiment 8 in Table 2.
6. Prepare a hot water bath as instructed by your TA. Run #9 will be the hot solution. Using the solutions from Step 5, place the beakers in the hot water bath and allow them to warm up for 3–5 minutes. Be careful not to allow the beakers to tip over while in the hot water bath. Measure the temperature of the solutions in the two beakers. If they are different, record the average temperature in Table 2.
7. Mix the solutions and start the timer as before, and return the reaction solution to the hot bath. Wait for the color change; watch carefully, since the hot reaction will occur more rapidly and you must be ready to record the reaction time. Repeat this run and record the second reaction time in Table 2.
8. Prepare a cold water bath as instructed. Obtain a fresh set of reagent solutions in beakers A and B, using the solution volumes for Experiment 3 in Table 1. Place the beakers in the cold water bath and allow 6–8 minutes for them to cool. They will cool faster if the solutions in the beakers are swirled occasionally. Measure the temperature of one of the solutions. When the temperature of the solutions are about  $5\text{--}10^\circ\text{C}$ , record the actual temperature in

Table 2. Mix the solutions as before and start the timer. Return the solutions to the cold water bath, swirling occasionally to keep the solutions homogeneous. Record the time at which the first blue color appears. Repeat this experiment, and record the reaction times in Table 2.

9. Dispose of all solutions as instructed. Rinse and dry all glassware and thermometers, and return them to the lab drawers from which they were obtained.

## CALCULATIONS

### Part A. Rate Law

In order to determine the rate law we will need to determine the rate (in units of M/sec), the order of the reaction with respect to the reactants (m and n), and the value of the rate constant, k.

To determine the rate, we will need to know the original concentration of the reactants and how long it took them to react.

1. **Reaction time.** Calculate the average of the reaction times (trials 1 and 2) for each of the experiments 1–7. Record this average in Table 1 of the Data Sheet.
2. **Concentrations.** When calculating the concentrations of the two major reactants in Reaction (1),  $\text{I}^-$  and  $\text{S}_2\text{O}_8^{2-}$ , we must consider the dilution of the original solutions. This calculation is summarized in Equation (6)

$$M_d = M_o (V_o / V_f) \quad (6)$$

Where  $M_d$  is the final molar concentration of the reactant,  $M_o$  is the concentration of the original solution, and  $V_o$  and  $V_f$  are the volume of the original stock solution and the final volume of the reaction solution, respectively.

For example, we can calculate the final molar concentration of  $\text{I}^-$  in Exp. 1 as follows. We used 20 mL of 0.22 M KI. The final volume of the reaction solution, after mixing all reactants, is the sum of the volumes in beakers A and B, or 52 mL. Substituting these data into Eq. (6) we obtain:

$$[\text{I}^-]_f = (0.22 \text{ M}) (20 \text{ mL} / 52 \text{ mL}) = 0.085 \text{ M}$$

The  $[\text{I}^-]$  and  $[\text{S}_2\text{O}_8^{2-}]$  for Exp. 1–7 can now be calculated in a similar fashion. Record the results of these calculations in the data table under **Calculations: Part A**. Be sure to also calculate the natural logs (ln) for these concentrations and include the results in the data table.

3. **Rate.** The rate of the reaction can be defined as the time required for a given amount of one of the reactants to react, or for a given amount of product to be formed. If we select the triiodide ion, the product of Reaction (1), then we can define the rate as:

$$\text{Rate} = \Delta[\text{I}_3^-] / \Delta\text{time}$$

Examining Reaction (2), we see that the  $\text{I}_3^-$  reacts immediately with thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ) in a 1:2 stoichiometry, so that  $\Delta[\text{I}_3^-] = \Delta[\text{S}_2\text{O}_3^{2-}] / 2$ . The initial concentration of thiosulfate can be calculated by substituting the volume and molarity of  $\text{S}_2\text{O}_3^{2-}$  into Eq. (6):

$$[\text{S}_2\text{O}_3^{2-}]_f = (0.010 \text{ M}) (10 \text{ mL} / 52 \text{ mL}) = 0.0019 \text{ M}$$

When all the thiosulfate has reacted, the starch indicator turns blue. At that point  $\Delta[\text{S}_2\text{O}_3^{2-}] = 0.0019 \text{ M}$ , and  $\Delta[\text{I}_3^-] = (0.0019 \text{ M}) / 2 = 0.00095 \text{ M}$ . Since the same volume of thiosulfate was used in each of experiments 1–7 we can now calculate the rates for each experiment as

$$\text{Rate} = (0.00095 \text{ M}) / (\text{time})$$

Calculate the reaction rate using the average reaction time (in seconds) for each of the experiments 1–7. Record these rates, and the corresponding  $\ln \text{rate}$  values, in the appropriate table in **Calculations: Part A**.

4. **Reaction order.** To determine the values of  $m$  and  $n$  we take advantage of the fact that only one reactant concentration was changed at a time. Note that the  $[\text{I}^-]$  was the same for Exp. 1–4, while the  $[\text{S}_2\text{O}_8^{2-}]$  varied. The generic rate law can be written as:

$$\text{Rate} = k [\text{I}^-]^m [\text{S}_2\text{O}_8^{2-}]^n$$

Taking the natural log of both sides of the equation yields:

$$\ln \text{rate} = \ln k + m \ln [\text{I}^-] + n \ln [\text{S}_2\text{O}_8^{2-}] \quad (7)$$

Since  $m$  and  $[\text{I}^-]$  are both constants for experiments 1–4, we can combine them with  $\ln k$  to make a new constant  $\ln k'$ , which yields:

$$\ln \text{rate} = \ln k' + n \ln [\text{S}_2\text{O}_8^{2-}] \quad (8)$$

This new equation resembles the equation for a straight line,  $y = mx + b$ . Plotting  $\ln \text{rate}$  vs  $\ln [\text{S}_2\text{O}_8^{2-}]$  for experiments 1–4 yields a straight line with a slope =  $n$ . For experiments 1, 5, 6, and 7 we held the  $[\text{S}_2\text{O}_8^{2-}]$  constant and varied  $[\text{I}^-]$ . Using a similar approach, we can rewrite the rate law for these experiments as:

$$\ln \text{rate} = \ln k' + m \ln [\text{I}^-] \quad (9)$$

Plotting  $\ln \text{rate}$  vs  $\ln [\text{I}^-]$  yields a straight line with a slope =  $m$ . Record your values for  $m$  and  $n$  on bottom of the **Calculations: Part A** section. Be sure to round your values to the nearest integer.

## Part B. Rate Constants and Activation Energy

5. **Rate Constants at Room Temperature.** We now know the exact form of the rate law from Part A. We can rearrange the rate law expression to solve for the rate constant,  $k$ .

$$k = \frac{\text{rate}}{[I^-]^m [S_2O_8^{2-}]^n} \quad (10)$$

Using Eq. (10), calculate the value of  $k$  for each of the experiments 1-7. Record these values of  $k$  in the table in **Calculations: Part B**. Calculate the average value of  $k$ , and record this as the value of  $k$  for the room temperature you measured for experiment 8.

6. **Rate Constants at “Hot” and “Cold” Temperatures.** Using the average reaction times from Table 2 of the Data Sheet, calculate the reaction rates for experiments 9 and 10. Remember that you are using the  $\Delta[I_3^-]$  from Exp. 3 to calculate rates. Record these rates in the appropriate table in **Calculations: Part B**. Once the reaction rates at these temperatures are known, you can calculate values of  $k$  at these temperatures using Eq. (10). Record these values in the appropriate table in **Calculations: Part B**. Also calculate  $\ln k$  and  $1/T$  values and include them in this table. Be sure to convert temperatures to Kelvin for this table.
7. **Activation Energy,  $E_a$ .** Recall Eq. (5) from the **Introduction**:

$$\ln(k) = \ln A - \frac{E_a}{RT}$$

This equation also takes the form of a straight line. Plotting  $\ln(k)$  vs  $1/T$  (in Kelvin) should yield a straight line having slope =  $E_a/R$ . By rearrangement, we can find  $E_a = (\text{slope})(R)$ . Using the value of  $R = 8.31 \text{ J/mol} \cdot \text{K}$  will allow us to obtain the value of  $E_a$  in J/mol, which we can convert to kJ/mol. Record your value of  $E_a$  under the **Calculations: Part B**. Turn in all plots, along with Data Sheets and Calculations.

## Data Sheet: Iodine Clock Reaction

Table 1. Reaction Conditions for Rate Law Determination

Exp. #	Beaker A	Beaker B	Time (trial 1)	Time (trial 2)	Average
1	20 mL KI 10 mL Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> 2 mL starch	20 mL K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>			
2	20 mL KI 10 mL Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> 2 mL starch	15 mL K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> 5 mL K <sub>2</sub> SO <sub>4</sub>			
3	20 mL KI 10 mL Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> 2 mL starch	10 mL K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> 10 mL K <sub>2</sub> SO <sub>4</sub>			
4	20 mL KI 10 mL Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> 2 mL starch	5 mL K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> 15 mL K <sub>2</sub> SO <sub>4</sub>			
5	15 mL KI 10 mL Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> 5 mL KNO <sub>3</sub> 2 mL starch	20 mL K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>			
6	10 mL KI 10 mL Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> 10 mL KNO <sub>3</sub> 2 mL starch	20 mL K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>			
7	5 mL KI 10 mL Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> 15 mL KNO <sub>3</sub> 2 mL starch	20 mL K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>			

Table 2. Energy of Activation Determination

Exp.#	Temp (°C)	Time (trial 1)	Time (trial 2)	Average
8 (same as 3)				
9				
10				

# Calculations

## Part A.

Exp. #	[I <sup>-</sup> ]	[S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> ]	ln [I <sup>-</sup> ]	ln[S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> ]
1				
2				
3				
4				
5				
6				
7				

Exp. #	1	2	3	4	5	6	7
<i>Rate</i>							
<i>ln rate</i>							

**RESULTS:**       $m =$  \_\_\_\_\_       $n =$  \_\_\_\_\_

## Calculations (con't.)

### Part B.

Exp. #	$k$
1	
2	
3	
4	
5	
6	
7	

At T = \_\_\_\_\_ °C, average  $k$  = \_\_\_\_\_ (include appropriate units!)

### Activation Energy

Exp. #	Temp (K)	Rate	$k$	$\ln k$	1/T
8					
9					
10					

$E_a$  = \_\_\_\_\_ J/mol = \_\_\_\_\_ kJ/mol

## Post-Lab Questions

1. Based on your results, what is the order of the reaction with respect to iodide? What is the order of the reaction with respect to persulfate ion? What is the overall order of the reaction?
2. Draw an activation energy diagram for the iodide-persulfate reaction, assuming that  $\Delta H$  for the reaction is negative.
3. Some of the reagents used in this lab are easily confused: such as persulfate ( $S_2O_8^{2-}$ ) and thiosulfate ( $S_2O_3^{2-}$ ). A student inadvertently switched these reagents, adding the persulfate to beaker A and thiosulfate to beaker B. How would this affect the results? What would the student observe with respect to the mixture in beaker A?
4. The thermometer used by Student A was indicating temperatures that were  $5^\circ\text{C}$  higher than the thermometer used by Student B when measuring the same solutions. Would this affect the  $E_a$  values obtained by the two students? Explain.
5. Using procedures similar to this lab exercise, a student determined an  $E_a = 9.25 \times 10^4 \text{ J/mol}$ . When the reaction was performed at  $27^\circ\text{C}$ , the student calculated a rate constant of  $k = 1.22 \times 10^{-2} \text{ L/mol}\cdot\text{sec}$ . Calculate the value of  $k$  at  $200^\circ\text{C}$ .