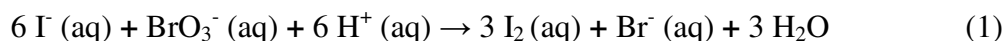


# Kinetics; A Clock Reaction

## Background

This experiment involves the study of the rate properties, or chemical kinetics, of the following reaction between iodide ion ( $\text{I}^-$ ) and bromate ion ( $\text{BrO}_3^-$ ) under acidic ( $\text{H}^+$ ) conditions:

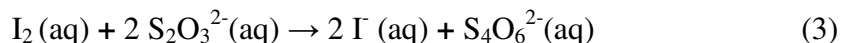


This reaction proceeds reasonably slowly at room temperature, its rate depending on the concentrations of the  $\text{I}^-$ ,  $\text{BrO}_3^-$  and  $\text{H}^+$  ions according to the rate law. For this reaction the rate law takes the form:

$$\text{rate} = k [\text{I}^-]^m [\text{BrO}_3^-]^n [\text{H}^+]^p \quad (2)$$

One of the main purposes of the experiment will be to evaluate the rate constant  $k$  and the reaction orders  $m$ ,  $n$ , and  $p$  for this reaction. We will also investigate the manner in which the reaction rate depends on temperature and will evaluate the activation energy  $E_a$  for the reaction.

Our method for measuring the rate of the reaction involves what is frequently called a clock reaction. In addition to Reaction 1, whose kinetics we will study, the following reaction will also be made to occur simultaneously in the reaction flask:



As compared with Equation 1 this reaction is essentially instantaneous. The  $\text{I}_2$  produced in (1) reacts completely with the thiosulfate,  $\text{S}_2\text{O}_3^{2-}$ , ion present in the solution, so that until the entire thiosulfate ion has reacted, the concentration of  $\text{I}_2$  is effectively zero. As soon as the  $\text{S}_2\text{O}_3^{2-}$  is gone from the system, the  $\text{I}_2$  produced by (1) remains in the solution and its concentration begins to increase. The presence of  $\text{I}_2$  is made strikingly apparent by a starch indicator that is added to the reaction mixture containing both  $\text{I}_2$  and  $\text{I}^-$  species. In the presence of  $\text{I}^-$ ,  $\text{I}_2$  reacts with starch solution to produce a blue color according to the following equation:



By carrying out Reaction 1 in the presence of  $\text{S}_2\text{O}_3^{2-}$  and a starch indicator, we introduce a “clock” into the system. Our clock tells us when a given amount of  $\text{BrO}_3^-$  ion has reacted (1/6 mole  $\text{BrO}_3^-$  per mole  $\text{S}_2\text{O}_3^{2-}$ ), which is just what we need to know, since the rate of reaction can be expressed in terms of the time it takes for a particular amount of  $\text{BrO}_3^-$  to be used up. In all our reactions, the amount of  $\text{BrO}_3^-$  that reacts in the time we measure will be constant and small as compared to the amounts of any of the other reactants. This means that the concentrations of all reactants will be essentially constant in Equation 2, and hence so will the rate during each reaction.

In our experiment we will carry out the reaction between  $\text{BrO}_3^-$ ,  $\text{I}^-$  and  $\text{H}^+$  ions under different concentration conditions. Measured amounts of each of these ions in water solution will be mixed in the presence of a constant small amount of  $\text{S}_2\text{O}_3^{2-}$ . The time it takes for each mixture to turn blue will be measured. The time obtained for each reaction will be inversely proportional to its rate. By changing the concentration of one reactant and keeping the other concentrations constant, we can investigate how the rate of the reaction varies with the concentration of a particular reactant. Once we know the order for each reactant we can determine the rate constant for the reaction.

In the last part of the experiment we will investigate how the rate of the reaction depends on temperature. You will recall that in general the rate increases sharply with temperature. By measuring how the rate varies with temperature we can determine activation energy,  $E_a$  for the reaction by making use of the Arrhenius equation:

$$\ln k = -E_a/RT + \text{constant} \quad (4)$$

In this equation,  $k$  is the rate constant at the Kelvin temperature  $T$ ,  $E_a$  is the activation energy, and  $R$  is the gas constant. By plotting  $\ln k$  against  $1/T$  we should obtain, by Equation 4, a straight line whose slope equals  $-E_a/R$ . From the slope of that line we can easily calculate the activation energy.

## Procedure

### A. Dependence of Reaction Rate on Concentration

In Table 1 we have summarized the reagent volumes to be used in carrying out the several reactions whose rates we need to know to find the general rate law for Reaction 1. For each of the reaction mixtures have 2 reaction flasks ready to deliver by pipettes the required volumes of reagents from the hoods.

**Table 1**

Reaction Mixture at room temperature (reagent volumes in ml)						
Mixture#	Reaction Flask 1 (250ml)			Reaction Flask #2 (125ml)		
	0.010 M KI	0.0010 M Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O	0.040 M KBrO <sub>3</sub>	0.10 M HCl	Starch Solution
1	10	10	10	10	10	3 drops
2	20	10	0	10	10	3 drops
3	10	10	0	20	10	3 drops
4	10	10	0	10	20	3 drops
5	8	10	12	5	15	3 drops

The actual procedure for each reaction mixture will be much the same, and we will describe it now for Reaction Mixture 1.

Since there are several reagents to mix, and since we don't want the reaction to start until we are ready, we will put some of the reagents into one flask and the rest into another, selecting them so that no reaction occurs until the contents of the two flasks are mixed. Using separate volumetric and/or **graduated pipets to measure volumes**, measure out 10 mL 0.010 M KI, 10 mL 0.0010 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, and 10 mL distilled water into a 250-mL Erlenmeyer flask (Reaction Flask #1).

Then measure out 10 mL 0.040 M KBrO<sub>3</sub> and 10 mL 0.10 M HCl into a 125-mL Erlenmeyer flask (Reaction Flask 2). To Flask 2 add three or four drops of starch indicator solution.

Pour the contents of Reaction Flask 2 into Reaction Flask 1 and swirl the solutions to mix them thoroughly. Note the time at which the solutions were mixed. Continue swirling the solution. It should turn blue in less than 2 minutes. Note the time at the instant that the blue color

appears. Record the temperature of the blue solution to  $0.2^{\circ}\text{C}$ .

Repeat the procedure with the other mixtures in Table 1. **Don't forget to add the starch indicator** before mixing the solutions in the two flasks. The reaction flasks should be rinsed with distilled water between runs. When measuring out reagents, **do not cross contaminate the pipets**. Try to keep the temperature just about the same in all the runs. Repeat any experiments that did not appear to proceed properly.

## B. Dependence of Reaction Rate on Temperature

In this part of the experiment, the reaction will be carried out at several different temperatures, using Reaction Mixture 1 in all cases. The temperatures we will use will be about  $20^{\circ}\text{C}$ ,  $40^{\circ}\text{C}$ , and  $3-4^{\circ}\text{C}$ .

We will take the time at about  $20^{\circ}\text{C}$  to be that for Reaction Mixture 1 as determined at room temperature. To determine the time at  $40^{\circ}\text{C}$  proceed as follows. Make up Reaction Mixture 1 as you did in Part A, including the indicator. However, instead of mixing the solutions in the two flasks at room temperature put the flasks into water at  $40^{\circ}\text{C}$ , drawn from the hot-water tap into one or more large beakers. Check to see that the water is indeed at about  $40^{\circ}\text{C}$ , and **leave the flasks in the water for several minutes to bring them to the proper temperature**. Then mix the two solutions, noting the time of mixing. Continue swirling the reaction flask in the warm water. When the color change occurs, note the time and the temperature of the solution in the flask.

Repeat the experiment at about  $3-4^{\circ}\text{C}$ , this time using an ice-water bath to **cool the reactants before starting the reaction**. Record the time required for the color to change and the final temperature of the reaction mixture.

## C. Dependence of the Reaction Rate on the Presence of Catalyst

Some ions have a pronounced catalytic effect on the rates of many reactions in water solution. Observe the effect on this reaction by once again making up Reaction Mixture 1. Before mixing, add one drop  $0.5\text{ M }(\text{NH}_4)_2\text{MoO}_4$ , ammonium molybdate, and a few drops of starch indicator to Reaction Flask 2. Swirl the flask to mix the catalyst thoroughly. Then mix the solutions, noting the time required for the color to change.

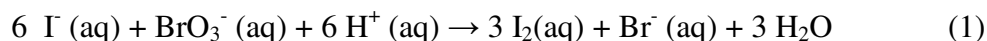
**DISPOSAL OF REACTION PRODUCTS.** The reaction products in this experiment are very dilute and may be poured into the sink as you complete each part of the experiment if so directed by your instructor.

Name \_\_\_\_\_

Section \_\_\_\_\_

Partner \_\_\_\_\_

Date \_\_\_\_\_

**Data and Calculations:** A clock Reaction**A. Dependence of Reaction Rate on Concentration**

$$\text{rate} = k(\text{I}^-)^m (\text{BrO}_3^-)^n (\text{H}^+)^p = \Delta(\text{BrO}_3^-)/t \quad (2)$$

In all the reaction mixtures used in the experiment, the color change occurred when a constant predetermined number of moles of  $\text{BrO}_3^-$  had been used up by the reaction. The color “clock” allows you to measure the **time required for this fixed number of moles of  $\text{BrO}_3^-$  to react**. The rate of each reaction is determined by the time required for the color to change; since in Equation 2 the change in concentration of  $\text{BrO}_3^-$  ion,  $\Delta(\text{BrO}_3^-)$ , is the same in each mixture, the relative rate of each reaction is inversely proportional to the time  $t$ . Since we are mainly concerned with relative rather than absolute rate, we will for convenience take all relative rates as being equal to  $1000/t$ . Fill in the following table, first calculating the relative reaction rate for each mixture.

Reaction Mixture	Time $t$ (sec) for Color to Change	Relative Rate of Reaction $1000/t$	Reactant Concentrations in Reacting Mixture (M)			Temp. in ( $^{\circ}\text{C}$ )
			$[\text{I}^-]$	$[\text{BrO}_3^-]$	$[\text{H}^+]$	
1	_____	_____	0.0020	_____	_____	_____
2	_____	_____	_____	_____	_____	_____
3	_____	_____	_____	_____	_____	_____
4	_____	_____	_____	_____	_____	_____
5	_____	_____	_____	_____	_____	_____

The reactant concentrations in the reaction mixture are *not* those of the stock solutions, since the reagents were diluted by the other solutions. The final volume of the reaction mixture is 50 mL in all cases. Since the number of moles of reactant does not change on dilution we can say, for example, for  $\text{I}^-$  ion, that

$$\text{no. moles I}^- = M_{\text{I}^- \text{ stock}} * V_{\text{stock}} = M_{\text{I}^- \text{ mixture}} * V_{\text{mixture}}$$

For Reaction Mixture 1,

$$(\text{I})_{\text{stock}} = 0.010 \text{ M} \quad V_{\text{stock}} = 10 \text{ ml} \quad V_{\text{mixture}} = 50 \text{ ml}$$

Therefore,

$$(\text{I})_{\text{mixture}} = (0.010\text{M} * 10\text{ml})/50\text{ml} = 0.0020\text{M}$$

Calculate the rest of the concentrations in the table by the same approach.

### Determination of the Orders of the Reaction

Given the data in the table, the problem is to find the order for each reactant and the rate constant for the reaction. Since we are dealing with relative rates, we can modify Equation 2 to read as follows:

$$\text{relative rate} = k' (\text{I})^m (\text{BrO}_3^-)^n (\text{H}^+)^p \quad (5)$$

We need to determine the relative rate constant  $k'$  and the orders  $m$ ,  $n$ , and  $p$  in such a way as to be consistent with the data in the table.

The solution to this problem is quite simple, once you make a few observations on the reaction mixtures. Each mixture (2 to 4) differs from Reaction Mixture 1 in the concentration of only one species (see table). This means that for any pair of mixtures that includes Reaction Mixture 1, there is only one concentration that changes. From the ratio of the relative rates for such a pair of mixtures we can find the order for the reactant whose concentration was changed. Proceed as follows.

Write Equation 5 below for Reaction Mixtures 1 and 2, substituting the relative rates and the concentrations of  $\text{I}$ ,  $\text{BrO}_3^-$ , and  $\text{H}^+$  ions from the table you have just completed.

$$\text{Relative Rate 1} \quad \underline{\hspace{2cm}} \quad = k' (\quad)^m (\quad)^n (\quad)^p$$

$$\text{Relative Rate 2} \quad \underline{\hspace{2cm}} \quad = k' (\quad)^m (\quad)^n (\quad)^p$$

*Divide* the second equation by the first, noting that nearly all the terms cancel out. The result is simply  $\frac{\text{Relative Rate 2}}{\text{Relative Rate 1}}$

If you have done this properly, you will have an equation involving only  $m$  as an unknown. Solve this equation for  $m$ , the order of the reaction with respect to  $\text{I}$  ion.

$$m_{\text{calculated}} =$$

$$m_{\text{estimated}} =$$

Applying the same approach to Reaction Mixtures 1 and 3, find the value of  $n$ , the order of the reaction with respect to  $\text{BrO}_3^-$  ion.

$$\text{Relative Rate 1} = \quad = k' ( \quad )^m ( \quad )^n ( \quad )^p$$

$$\text{Relative Rate 3} = \quad = k' ( \quad )^m ( \quad )^n ( \quad )^p$$

Dividing the third equation by the first:

$$n_{\text{calculated}} = \quad \quad \quad n_{\text{estimated}} =$$

Now that you have the idea, apply the method once again, this time to Reaction Mixtures 1 and 4, and find  $p$ , the order with respect to  $\text{H}^+$  ion.

$$\text{Relative Rate 4} = k' ( \quad )^m ( \quad )^n ( \quad )^p$$

Dividing the equation for Relative Rate 4 by that for Relative Rate 1, we get

$$p_{\text{calculated}} = \quad \quad \quad p_{\text{estimated}} =$$

Having found  $m$ ,  $n$ , and  $p$  (nearest integers), the relative rate constant,  $k'$ , can be calculated by substitution of  $m$ ,  $n$ ,  $p$ , and the known rates and reactant concentrations into Equation 5. Evaluate  $k'$  for Reaction Mixtures 1 to 4.

Reaction	1	2	3	4
$k'$	_____	_____	_____	_____
$k'_{\text{ave}}$	_____			

**Why should  $k'$  have nearly the same value for each of the above reactions?**

Using  $k'_{\text{ave}}$  in Equation 5, predict the relative rate and time  $t$  for Reaction Mixture 5. Use the concentrations in the table.

Relative rate <sub>pred</sub>	_____	$t_{\text{pred}}$	_____	$t_{\text{obs}}$
_____				

### B. Effect of Temperature on Reaction Rate: The Activation Energy

To find the activation energy for the reaction it will be helpful to complete the following table. The dependence of the rate constant,  $k'$ , for a reaction is given by Equation 4:

$$\ln k' = - ( E_a/RT ) + \text{constant} \quad (4)$$

Since the reactions at the different temperatures all involve the same reactant concentrations, the rate constants,  $k'$ , for two different mixtures will have the same ratio as the reaction rates themselves for the two mixtures. This means that in the calculation of  $E_a$  we can use the observed relative rates instead of rate constants. Proceeding as before, calculate the relative rates of reaction in each of the mixtures and enter these values in (c). Take the  $\log_{10}$  rate for each mixture and enter these values in (d). To set up the terms in  $1/T$  fill in (b), (e), and (f) in the table.

	Approximate Temperature in $^{\circ}\text{C}$		
	20	40	3-4
(a) Time $t$ in seconds for color to appear	_____	_____	_____
(b) Temperature of the reaction mixture in $^{\circ}\text{C}$	_____	_____	_____
(c) Relative rate = $1000/t$	_____	_____	_____
(d) $\ln$ of relative rate $t$	_____	_____	_____
(e) Temperature $T$ in $K$	_____	_____	_____
(f) $1/T$ in $K^{-1}$	_____	_____	_____

To evaluate  $E_a$  make a graph of  $\ln$  relative rate vs.  $1/T$  using Excel spreadsheet (see the **clock reaction spreadsheet**).

Find the slope of the line obtained by drawing the best straight line through the experimental points.

$$\text{Slope} = \underline{\hspace{2cm}}$$

The slope of the line equals  $-E_a/R$  where  $R = 8.31$  Joules/mole $K$  if  $E_a$  is to be in Joules per mole. Find the activation energy  $E_a$ , for the reaction.

$$E_a = \underline{\hspace{2cm}} \text{ Joules/mole}$$

### C. Effect of a Catalyst on Reaction Rate

	<b>Reaction 1</b>	<b>Catalyzed Reaction 1</b>
Time for color to appear (seconds)	_____	_____

Would you expect the activation energy,  $E_a$ , for the catalyzed reaction to be greater than, less than, or equal to the activation energy for the uncatalyzed reaction? Why?



Name \_\_\_\_\_

Section \_\_\_\_\_

### Advance Study Assignment: A clock Reaction

1. A student studied the clock reaction described in this experiment. She set up Reaction Mixture 2 by mixing 20 ml 0.010 M KI, 10 mL 0.001 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, 10 mL 0.040 M KBrO<sub>3</sub>, and 10 mL 0.10 M HCl using the procedure given. It took about 45 seconds for the color to turn blue.

- a. She found the concentrations of each reactant in the reacting mixture by realizing that the number of moles of each reactant did not change when that reactant was mixed with the others, but that its concentration did. For any reactant A,

$$\text{no. moles A} = M_{A \text{ stock}} * V_{A \text{ stock}} = M_{A \text{ mixture}} * V_{\text{mixture}}$$

The volume of the mixture,  $V_{\text{mixture}}$ , was 50 mL. Revising the above equation, she obtained

$$M_{A \text{ mixture}} = M_{A \text{ stock}} * V_{A \text{ stock}}(\text{ml})/50\text{ml}$$

Find the concentrations of each reactant by using the above equation.

$$[\text{I}^-] = \text{_____ M}; [\text{BrO}_3^-] = \text{_____ M}; [\text{H}^+] = \text{_____ M}$$

- b. What was the relative rate of the reaction (1000/t)?
- c. Knowing the relative rate of reaction for Mixture 2 and the concentrations of  $\text{I}^-$ ,  $\text{BrO}_3^-$  and  $\text{H}^+$  in that mixture, she was able to set up Equation 5 for the relative rate of the reaction. The only quantities that remained unknown were  $k'$ ,  $m$ ,  $n$ , and  $p$ . Set up Equation 5 as she did, presuming she did it properly.

2. For Reaction Mixture 1 the student found that 85 seconds were required. On dividing Equation 5 for Reaction Mixture 1 by Equation 5 for Reaction Mixture 2, and after canceling out the common terms ( $k'$ , terms in  $(\text{BrO}_3^-)$  and  $(\text{H}^+)$ ), she got the following equation:

$$11.8/22 = (0.0020/0.0040)^m = (1/2)^m$$

Recognizing that 11.8/22 is about equal to 1/2, she obtained an approximate value for  $m$ . What was that value?

$$m =$$

By taking logarithms of both sides of the equation, she got an exact value for  $m$ . What was that value?

$$m =$$

Since orders of reactions are often integers, she reported her approximate value as the order of the reaction with respect to  $\text{I}^-$ . What is the order of the reaction with respect to  $\text{I}^-$ ?