

Reaction Kinetics: The Iodine Clock Reaction

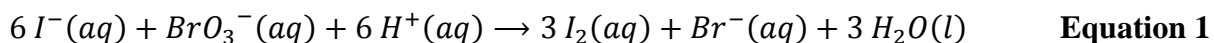
Introduction

The “clock reaction” is a reaction famous for its dramatic colorless-to-blue color change, and is often used in chemistry courses to explore the rate at which reactions take place. The color change occurs when I_2 reacts with starch to form a dark blue iodine/starch complex. The ability to record the time at which the blue complex appears allows the rate of reaction to be determined accurately with a stopwatch.

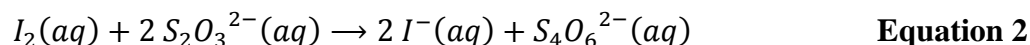
In this experiment, the rate law for a reaction is determined using the method of initial rates. The effect of concentration on the rate of this reaction is determined by measuring the initial reaction rate at several reactant concentrations. You will also examine the effect of a catalyst on the reaction rate. Lastly, you will investigate the effect of temperature on the rate of this reaction, which will allow you to determine the activation energy.

The Clock Reaction

The primary reaction to be studied is the oxidation of the iodide ion by the bromate ion in aqueous solution:



This reaction will be run in the presence of a known amount of $S_2O_3^{2-}$ (thiosulfate), which reacts very rapidly with I_2 . As long as $S_2O_3^{2-}$ is present, I_2 is consumed by $S_2O_3^{2-}$ as fast as it is formed. This competing reaction prevents the I_2 produced from our reaction of interest from reacting with starch, so no color change is observed until the thiosulfate is completely used up. The “clock” reaction is the reaction of a very small amount of $S_2O_3^{2-}$ (thiosulfate) with the I_2 produced in the primary reaction:



The “clock” reaction will signal when the primary reaction forms a specific amount of I_2 . The amount of I_2 formed before the color change can be calculated from the known amount of $S_2O_3^{2-}$ added using the molar ratio in Equation 2. To find the rate of Equation 1, the change in the concentration of I_2 is monitored over time. Below, $\Delta[I_2]$ is the change in the concentration of I_2 , and Δt represents the change in time:

$$\text{Rate} = \frac{1}{3} \cdot \frac{\Delta[I_2]}{\Delta t} \quad \text{Equation 3}$$

Recall that:

$$\text{Rate} = \frac{-1}{6} \cdot \frac{\Delta[I^-]}{\Delta t} = \frac{-1}{1} \cdot \frac{\Delta[BrO_3^-]}{\Delta t} = \frac{-1}{6} \cdot \frac{\Delta[H^+]}{\Delta t} = \frac{1}{3} \cdot \frac{\Delta[I_2]}{\Delta t} = \frac{1}{1} \cdot \frac{\Delta[Br^-]}{\Delta t} \quad \text{Equation 4}$$

As soon as all of the $S_2O_3^{2-}$ ions have reacted, the I_2 still being formed (Equation 1) starts to accumulate and reacts with starch. Starch serves as an indicator to help us “see” the I_2 , since the interaction between starch and I_2 forms a blue starch-iodine complex. Thus, “ Δt ” is simply the time elapsed between mixing the reagents and the appearance of the blue color. Because the $S_2O_3^{2-}$ ion concentration in the reaction mixture is known, you can calculate “ $\Delta[I_2]$ ” using the stoichiometry of the “clock” reaction. Since the same amount of $S_2O_3^{2-}$ should be added to each run, $\Delta[I_2]$ should also be the same for each run. The amount of time for the appearance of the blue color varies with initial reactant concentrations, with temperature, and in the presence of catalyst, so Δt is not constant.

Notes Regarding the Initial Concentrations, the Dilution Formula, and Ion Molarities:

The initial concentrations of reactants are calculated for the moment at which they are mixed. At that time, the solutions have mutually diluted each other (raised the volume of total solution, with or without adding moles of the solute), but have not yet started disappearing from solution (via reaction). For each ion in solution, a new molarity must be calculated that takes into consideration the new total volume of the solution, and the other ions that were added. The concentrations and volumes of the reactants which should be used are given in Table 1. Care should be taken to record the concentrations of the actual stock solutions provided. Also, care should be taken to use the volumes indicated in Table 1, and to note the exact volumes used in each trial to the proper precision.

To determine the concentration of an ion in solution, consider the stoichiometric relationship between the ionic compound and the number of ions formed in solution. For example, a 0.20 M solution of KI releases 0.20 M I^- and 0.20 M K^+ ions. The situation would be different if the source of I^- was CaI_2 , since 2 moles of I^- ions would be released for each mole of CaI_2 that dissociates.

Calculate the concentration of each reactant after combining the solutions, but before the chemical reaction begins. Note that if all volumes of solution used were precisely as indicated in Table 1, and if volumes were additive, the total volume of the reaction mixture for each trial would be 10 mL. To simplify both the calculations and the experimental procedure, the concentrations of the reactants in the reaction mixture should be calculated as if volumes were additive. Thus, in the dilution formula, $M_1V_1 = M_2V_2$, V_2 is approximately 10 mL, and V_1 is the volume of the individual solution added to the mixture.

Preliminary Calculations Involving the “Clock” Reaction

Using the dilution formula, the concentration of $S_2O_3^{2-}$ in the mixture is 2.0×10^{-4} M. According to the stoichiometry of the clock reaction in Equation 2, the number of moles of I_2 is one-half the the number of moles of $S_2O_3^{2-}$. The blue color will appear when 1.0×10^{-4} M of I_2 (with two significant figures) has been formed by the primary reaction. This number remains constant in all Runs, and so provides $\Delta[I_2]$ in all of rate calculations.

$$\text{All Runs: } \Delta[I_2] = 1.0 \times 10^{-4} \text{ M } I_2$$

Reaction Rate

The rate law for Equation 1 will be determined by measuring the initial rate of reaction with varying initial reactant concentrations. The concentration of $S_2O_3^{2-}$ in the reaction mixture is very small

compared to the other reactants present, such that the measured rate is the initial rate of the reaction. The rate law for Equation 1 is given below:

$$\text{Rate} = k \cdot [\text{I}^-]^x \cdot [\text{BrO}_3^-]^y \cdot [\text{H}^+]^z \quad \text{Equation 5}$$

In Equation 5, k is the rate constant, and x , y , and z represent the order of I^- , BrO_3^- , and H^+ , respectively. These values will be determined experimentally from your data.

Note: When the solution turns blue, only a very small percentage of the reactants have been used up. Thus, the initial concentrations of reactants can be used in the rate law with very little error. Typically, the error is less than 5%.

Effect of Concentration on the Reaction Rate: Finding the Rate Law

The rate law is determined using the method of initial rates. The following example will illustrate how to find a reaction order using the method of initial rates.

Example: The following data was obtained for the reaction: $\text{A} + \text{B} \rightarrow \text{C}$

Experiment	[A], M	[B], M	Rate (M/s)
1	0.020	0.10	1.20
2	0.030	0.10	1.80
3	0.030	0.25	11.25

The general rate law for this example is

$$\text{Rate} = k[\text{A}]^x[\text{B}]^y$$

Since [A] changes between Experiment 1 and 2, while [B] remains constant, the order for A is obtained by taking the ratio of the rates from these two experiments:

$$\frac{1.80 \text{ M/s}}{1.20 \text{ M/s}} = \frac{k[0.030]^x[0.10]^y}{k[0.020]^x[0.10]^y}$$

Since k is constant at a given temperature and $[\text{B}]^y$ is constant for Experiments 1 and 2, the equation simplifies to:

$$\frac{1.80 \text{ M/s}}{1.20 \text{ M/s}} = \frac{[0.030]^x}{[0.020]^x} \quad \text{or} \quad 1.50 = 1.5^x$$

Thus, $x = 1$ for this example.

Unfortunately, experimental results are not usually that "clean", and a more sophisticated method is needed to find x . Mathematically, solving for exponents requires the use of logarithms. Taking the log of both sides of the equation above yields:

$$\log(1.50) = x \times \log(1.5)$$

Rearranging this equation to solve for x yields

$$x = \frac{\log(1.50)}{\log(1.5)} = 1.0 \approx 1$$

Experiments 2 and 3 may then be used to find the order for B, as shown below

$$\frac{11.25 \text{ M/s}}{1.80 \text{ M/s}} = \frac{k[0.030]^x[0.25]^y}{k[0.030]^x[0.10]^y}$$

By cancelling out the common terms and dividing the rate and concentration values, we obtain

$$6.25 = 2.5^y$$

Taking the log of both sides and rearranging to solve for y gives

$$y = \frac{\log(6.25)}{\log(2.5)} = 2.0 \approx 2$$

Effect of Temperature on the Reaction Rate: Determination of E_a

The Arrhenius equation describes the relationship between the rate constant (k), the Kelvin temperature (T), the activation energy (E_a), and the frequency factor(A) :

$$\ln k = - \frac{E_a}{R} \frac{1}{T} + \ln A \quad \text{Equation 6}$$

$$y = m x + b$$

The reaction is run at four different temperatures, and for each, the rate constant is calculated. From these data, construct an Arrhenius plot of $\ln k$ vs $(1/T)$ by mapping the four data points onto the equation of a line, as shown under Equation 6. Use the slope of the Arrhenius plot to determine the value of the activation energy, E_a .

Effect of a Catalyst on the Reaction Rate

A comparison of the reaction rate with and without a catalyst will demonstrate catalytic action.

***Waste handling:** *Keep a large beaker at your station to collect the clock reaction waste. When you have completed all trials, pour the contents of the waste beaker into the waste container in the fume hood.*

Safety Precautions

CAUTION: I_2 is toxic and corrosive! It can damage eyes, skin, and clothes on contact. It is readily absorbed through skin and harmful if inhaled in high concentrations.

Disposal

Dispose of all chemicals and solutions in the appropriately marked waste container in the fume hood.

Procedure

It is recommended that you start the HOT water bath for part II immediately.

Make sure that the necessary glassware is clean and dry.

Label your glassware.

Record the concentrations of all stock solutions provided in your data table.

Record experimental values with the units and significant figures appropriate for the observation.

Use the precision of the measuring device to get the correct number of significant figures.

PREPARE SOLUTION A & SOLUTION B FOR ONLY ONE TRIAL AT A TIME.

Part I: Effect of Concentration on Reaction Rate

1. Prepare solutions A and B separately for Run 1 in TABLE 1 below, using the stock solutions provided.
2. Transfer solution A to a clean, dry, appropriately sized beaker. Add a magnetic stir bar to the beaker, place the beaker on the magnetic stirplate, and adjust the speed of the stirrer to obtain a slow but steady speed.
3. Simultaneously
 - * Add solution B to the reaction beaker as rapidly as possible.
 - * Begin timing as solutions A & B are combined.
4. Watch the solution continuously, when the solution initially turns blue-black:
 - * Note and record the elapsed time.
 - * Note and record the temperature of the solution.
5. Use forceps to remove the stir bar from the beaker. Between trials, rinse the beaker and the stir bar with tap water, and then DI water.
6. Repeat the steps above for Runs 2 – 5 in Table 1 below.

Part II: Effect of Temperature on Reaction Rate

1. Prepare a cold (0 °C) water bath, a cool (10 °C) water bath, and a hot (40 °C water bath). Select appropriately sized beakers for your temperature baths.

For each water bath:

1. Prepare solutions A and B separately for Run 1 in TABLE 1 below, using the stock solutions provided.
2. Allow the solutions to remain in the water bath (separately, not yet mixed!) until their temperatures have equilibrated (about 10 minutes), and measure the temperature of Tube A.
3. Transfer solution A to a clean, dry beaker. Add a magnetic stir bar to the beaker, place the beaker on the magnetic stirplate, and adjust the speed of the stirrer to obtain a slow but steady speed.
4. Simultaneously
 - * Add solution B to the reaction beaker as rapidly as possible.
 - * Begin timing as solutions A & B are combined.
5. Watch the solution continuously, when the solution initially turns blue-black:
 - * Note and record the elapsed time.
 - * Note and record the temperature of the solution.
6. Use forceps to remove the stir bar from the beaker. Between trials, rinse the beaker and the stir bar with tap water, and then DI water.

Part III: Effect of Catalysis on Reaction Rate

1. Prepare solutions A and B separately for Run 1 in TABLE 1 below, using the stock solutions provided.
2. Add one drop 0.5 M ammonium molybdate to solution B prior to mixing.
3. Transfer solution A to a clean, dry beaker. Add a magnetic stir bar to the beaker, place the beaker on the magnetic stirplate, and adjust the speed of the stirrer to obtain a slow but steady speed.
4. Simultaneously
 - * Add solution B to the reaction beaker as rapidly as possible.
 - * Begin timing as solutions A & B are combined.
5. Watch the solution continuously, when the solution initially turns blue-black:
 - * Note and record the elapsed time.
 - * Note and record the temperature of the solution.
6. Use forceps to remove the stir bar from the beaker. Between trials, rinse the beaker and the stir bar with tap water, and then DI water.

TABLE 1: Intended Composition of Reaction Mixtures

Solution A					Solution B	
Run No.	0.2% Starch, drops	0.001 M Na ₂ S ₂ O ₃ , mL	0.01 M KI, mL	H ₂ O, mL	0.04 M KBrO ₃ , mL	0.1 M HCl, mL
1	4 drops	2	2	2	2	2
2	4 drops	2	4	0	2	2
3	4 drops	2	2	0	4	2
4	4 drops	2	2	0	2	4
5	4 drops	2	1	0	3	4

Data

TABLE 2: Experimental Data

Reagents						
Solute:	Starch	Na ₂ S ₂ O ₃	KI	KBrO ₃	HCl	
Concentration:						

Part I								
	Solution A				Solution B		Time	Temperature
Reaction Mixture	Starch	Na ₂ S ₂ O ₃	KI	H ₂ O	KBrO ₃	HCl		
Run 1								
Run 2								
Run 3								
Run 4								
Run 5								

Part II								
	Solution A				Solution B		Time	Temperature
Reaction Mixture	Starch	Na ₂ S ₂ O ₃	KI	H ₂ O	KBrO ₃	HCl		
Run 1								
Run 1								
Run 1								

Part III								
	Solution A				Solution B		Time	Temperature
Reaction Mixture	Starch	Na ₂ S ₂ O ₃	KI	H ₂ O	KBrO ₃	HCl		
Run 1								

Calculations

Perform the following calculations in your lab notebook.

1. Use the dilution formula to calculate the concentration of $S_2O_3^{2-}$, I^- , BrO_3^- , and H^+ , for each Trial, and record these values in Table 1: Calculations. Show a sample calculation below for Trial 1. Respect significant figures based on the metric equipment used and during calculations. Show the units. These values will be determined experimentally from your data.
2. Convert the time for each trial to seconds. Calculate the rate of reaction ($\Delta[I_2]/\Delta t$) for each trial and record these values in Table 1. Recall, $\Delta[I_2]$ may be approximately $1.0 \times 10^{-4} M I_2$ for every trial. Show a sample calculation below for Run 1. Respect significant figures based on the metric equipment used and show the units.
3. Use Trials 1 and 2 to determine x, the order of I^- . Show calculated value with significant figures and then **state the order for I^- , rounding the value for x to the nearest whole number.**
4. Use Trials 1 and 3 to determine y, the order of BrO_3^- . Show calculated value with significant figures and then **state the order for BrO_3^- , rounding the value for y to the nearest whole number.**
5. Use Trials 1 and 4 to determine z, the order of H^+ . Show calculated value with significant figures and then **state the order for H^+ , rounding the value for z to the nearest whole number.**
6. Calculate k for each of Trials 1 to 4, and calculate the average of these values.
7. Write the complete Rate Law, including the experimentally numerical value of k, x, y, and z. Use this equation to calculate an expected rate for Trial 5, and compare it to the experimentally observed rate.
8. Calculate the Kelvin Temperature for each Trial. Using the data from part II with the data for Trial 1 from Part I, prepare an Arrhenius plot with **ln k on the y-axis and (1/T) on the x-axis** with Excel. (Note that "T" needs to be expressed in Kelvin rather than °C.) This plot should have four points, the original room temperature data for Trial 1, and the runs you carried out at the three additional temperatures. Print a full page graph with the straight line equation showing the slope and intercept. (Refer to the Excel Tutorial from earlier in the class if necessary.) The graph must have properly labeled axes and a descriptive title. Attach the graph to this report.
9. Use the Arrhenius plot to calculate the activation energy, E_a , for this reaction, and show the calculation below. Respect significant figures based on the linear regression analysis and show units. Note that the slope of this Arrhenius plot is equal to $-E_a/R$, where the gas constant, R, is $8.314 \frac{J}{mol \times K}$.

Report Sheets

Reaction Kinetics: The Iodine Clock Reaction

Calculations

In the tables below, neatly copy your calculated values.

TABLE 3: Calculations

Part I								
Reaction Mixture	$[S_2O_3^{2-}]_i$	$[I^-]_i$	$[BrO_3^-]_i$	$[H^+]_i$	Time	Rate		Temperature
Run 1								
Run 2								
Run 3								
Run 4								
Run 5								

Part II								
Reaction Mixture	$[S_2O_3^{2-}]_i$	$[I^-]_i$	$[BrO_3^-]_i$	$[H^+]_i$	Time	Rate		Temperature
Run 1								
Run 1								
Run 1								

Part III								
Reaction Mixture	$[S_2O_3^{2-}]_i$	$[I^-]_i$	$[BrO_3^-]_i$	$[H^+]_i$	Time	Rate		Temperature
Run 1								

Sample Calculations

In the space provided below, neatly write a copy of calculations 3, 4, 5, 6, and 9 (showing all work).

Results

The rate law for Equation (1) was experimentally determined to be _____

The activation energy (E_a) for Equation (1) was experimentally determined to be _____

Attach a copy of the graph of your Arrhenius plot to this report.

Discussion / Follow-up Questions

1. Compare the average reaction time for Trial 1 from Part I (without a catalyst) to the reaction time of Trial 1 from Part I II (with a catalyst), include the values. How did the addition of a catalyst affect the rate of reaction? Write in full sentences, using proper grammar.
2. Compare your average reaction time for Run 1 at room temperature to your reaction times at the colder and hotter temperatures. What effect does changing the temperature have on the rate of reaction? Write in full sentences, using proper grammar.
3. Theoretical Error: What assumptions or approximations may have contributed to error in your results?
4. Procedural Error: What parts of the experimental procedure may have contributed significantly to error in your results?
5. Human Error: What failures on your part to effectively follow the procedure as written do you think may have contributed to error in your results? (There should not be anything to write here, but if you did mess-up and for some reason did not redo the portion(s) of the experiment required to obtain uncorrupted data, the mistake(s) should be identified here.)

Pre-Laboratory Exercise

Reaction Kinetics: The Iodine Clock Reaction

1. Calculate the initial concentration of the ions below in the reaction mixture for each reaction (Runs 1 – 5) using the volumes and concentrations given in Table 1. Show a sample calculation for Run 1.

Run No.	Initial $[\text{S}_2\text{O}_3^{2-}]$ (M)	Initial $[\text{I}^-]$ (M)	Initial $[\text{BrO}_3^-]$ (M)	Initial $[\text{H}^+]$ (M)
1				
2				
3				
4				
5				

2. During the experiment, after each trial, where will the reaction mixture and runoff of rinsing your glassware be collected ?

3. If different than your answer to question 2, after the experiment where will the reaction mixture and runoff of rinsing your glassware be collected?