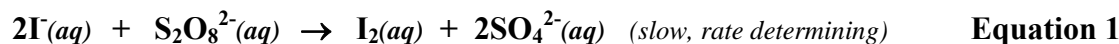# Reaction Kinetics: The Iodine Clock Reaction

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 metal ion 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 I^- by $S_2O_8^{2-}$ (persulfate) in aqueous solution:

$$2I^-(aq) \ + \ S_2O_8^{2-}(aq) \ \rightarrow \ I_2(aq) \ + \ 2SO_4^{2-}(aq) \quad \textit{(slow, rate determining)} \qquad \textbf{Equation 1}$$

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:

$$I_2(aq) \ + \ 2S_2O_3^{2-}(aq) \ \rightarrow \ 2I^-(aq) \ + \ S_4O_6^{2-}(aq) \quad \textit{(fast)} \qquad \textbf{Equation 2}$$
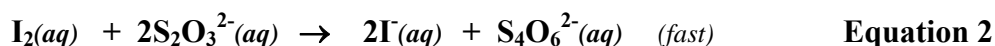
The "clock" reaction will signal when the primary reaction forms a specific amount of I_2. The amount of I_2 formed before the color change can be calculated from the known amount of $S_2O_3^{2-}$ added using the molar ratio in Equation 2. To find the rate of Equation 1, the change in the concentration 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:

$$\textbf{Rate} = \frac{\Delta[I_2]}{\Delta t} \qquad\qquad \textbf{Equation 3}$$

$$\text{Recall:} \ \ \text{Rate} \ = \ 1/2\left(\frac{\Delta[SO_4^{2-}]}{\Delta t}\right) = \ -\frac{\Delta[S_2O_8^{2-}]}{\Delta t} \ = \ -1/2\left(\frac{\Delta[I^-]}{\Delta t}\right)$$

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 $S_2O_3^{2-}$ is added to each run, $\Delta[I_2]$ is also the same for each run. However, 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 are given in Table 1.

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 the total volume of each solution is 20 mL. Thus, in the dilution formula, $M_1V_1 = M_2V_2$, V_2 is always 20 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 1.2×10^{-3} 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 6.0×10^{-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.

$$\textbf{All Runs}: \ \Delta[\textbf{I}_2] = \textbf{6.0} \times \textbf{10}^{-4} \textbf{ M I}_2$$

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:

$$\textbf{Rate} = \ \textbf{k}[\textbf{I}^-]^{\textbf{x}} \, [\textbf{S}_2\textbf{O}_8^{2-}]^{\textbf{y}} \hspace{3cm} \textbf{Equation 4}$$

In Equation 4, k is the rate constant, and x and y represent the order of I^- and $S_2O_8^{2-}$, 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

For Runs 1-3, the initial I^- concentration is varied while the initial $S_2O_8^{2-}$ concentration remains constant.

The order with respect to I^- 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: $A + B \rightarrow C$

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

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

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 $[B]^y$ is constant for Experiments 1 and 2, the equation simplifies to:

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

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 yeilds:

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

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

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

For Runs 2, 4, and 5, the initial $S_2O_8^{2-}$ concentration will vary while the initial I^- concentration remains constant. Use the initial rates method shown above to find the order for $S_2O_8^{2-}$.

Once the values for x and y are known, these can be substituted back into Equation 4, and the rate constant (k) calculated for each set of initial concentrations. The average value of k is reported for the five runs conducted at room temperature, along with the average rate. Use average values for Run 3 in Parts II and III.

Effect of a Catalyst on the Reaction Rate

A comparison of the reaction rate with and without a catalyst will demonstrate catalytic action. The Cu^{2+} ion, added in the form of a dilute $Cu(NO_3)_2$ solution, makes a suitable catalyst.

Effect of Temperature on the Reaction Rate: Determination of E_a

The Arrhenius equation describes the relationship between k, T, E_a and A, the frequency factor:

$$\ln k = - \frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A \qquad\qquad \textbf{Equation 5}$$

$$y \ = \ m \ \ x \ + \ b$$

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 5. Use the slope of the Arrhenius plot to determine the value of the activation energy, E_a.

*Waste handling: Keep a 600 mL 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: Ammonium persulfate is moderately toxic by ingestion, and corrosive to body tissues. Avoid body tissue contact. Potassium iodide is irritating to body tissues, avoid all body tissue contact.

Disposal

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

Procedure

Part I: The Effect of Concentration

Work in groups of 2. Make sure that the necessary glassware is clean and dry. **Each group will carry out Run 2, plus another Run** as determined by the instructor, and will obtain data for the remaining Runs from other groups. **Three trials of each Run** will be used to give a good average time. To keep the ionic strength of all runs relatively constant, the non-reactive compounds KNO_3 and $(NH_4)_2SO_4$ are added to replace the reactants KI and $(NH_4)_2S_2O_8$ when less than 10 mL of the former and 8 mL of latter are used.

Table I gives the composition in *milliliters* of the reaction mixtures that will be used to determine the order of reaction with respect to iodide and persulfate.

Table I. Compostion of the Reaction Mixtures

	Test Tube A				Test Tube B	
Run No.	0.2% Starch, drops	0.012 M $Na_2S_2O_3$, mL	0.20 M KI, mL	0.20 M KNO_3, mL	0.20 M $(NH_4)_2S_2O_8$, mL	0.20 M $(NH_4)_2SO_4$, mL
1	5 drops	2	8	2	4	4
2	5 drops	2	4	6	4	4
3	5 drops	2	2	8	4	4
4	5 drops	2	4	6	8	0
5	5 drops	2	4	6	2	6

1. Heat a 400 mL beaker of water on a hot plate to prepare for Part III. Place the hot plate out of the way, and watch that cords do not get in the way. There may be room to set up your hotplate on the counter along the wall.

2. Label three clean, dry test tubes A and three clean dry test tubes B (for Run 2). Use a test tube rack to hold these grouped appropriately, and avoid contamination between Set A and Set B.

3. Use the self-zeroing burets containing $Na_2S_2O_3$ and KI to deliver the appropriate amounts of these reactants (see Table 1) to **Test Tube A,** according to Table 1. Use a graduated cylinder or graduated pipet to measure the appropriate volume of KNO_3 for Run 2 into **Test Tube A**. Repeat this process with two more test tubes to prepare the other two trials for Run 2. Add 5 drops of starch to each test tube.

   Note: Make sure you use solutions from the same set of burets. Label your test tubes. Use the precision of the measuring device to get the correct number of significant figures for the total volume. Write down all concentrations shown on the burets in your data tables.

4. Obtain a thermometer to record the temperature of the mixture in one of these test tubes. Note that this will be room temperature and this temperature will remain relatively constant for Runs 1-5, so only one measurement is needed.

5. Use the self-zeroing burets containing $(NH_4)_2S_2O_8$ and $(NH_4)_2SO_4$ to combine the appropriate volumes for Run 2 in **Test Tube B**. Prepare two more test tubes to use for the other two trials for Run 2.

6. Obtain a stir plate from one of the benches. Transfer the contents of Test Tube A to a clean, dry 50 mL beaker. Add a magnetic stir bar to the 50 mL beaker, place the beaker on the magnetic stirplate, and adjust the speed of the stirrer to obtain a slow but steady speed.

7. Have one partner hold the stopwatch, and practice using it to make sure it can be set to zero and then started quickly when the reaction begins.

8. When ready, one student starts the timer as the other student completely empties the contents of Test Tube B into the 50 mL beaker as rapidly as possible. Watch the solution continuously, and stop the timer when the solution <u>initially</u> turns blue-black. Record the time in your data table.

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

9. Use forceps to remove the stir bar from the beaker. Rinse the stir bar and test tubes with tap water, then DI water, and then acetone between trials. Place the test tubes upside down to dry.

10.   Repeat this process for the other two trials of Run 2, *so you will have **three reaction times** for Run 2*.

11.   Repeat the procedure for Run 1, 3, 4, or 5 as assigned by your instructor.

12.   Write your raw data on the board, or post on the class forum if your class uses one. Copy posted data into your data table for use in the calculations.

Note: The same test tube B can be used for all trials of Runs 1-3 because the same amounts of $(NH_4)_2S_2O_8$ and $(NH_4)_2SO_4$ are used in all three Runs. However, use a different test tube B for each subsequent Run, Runs 4 and 5, because the composition of the $(NH_4)_2S_2O_8$ and $(NH_4)_2SO_4$ mixture is different for these runs.

Part II: Effect of a Catalyst

Repeat Run 2 (at room temperature) **one more time**, adding one drop of 0.020 M $Cu(NO_3)_2$ to the mixture in the **Test Tube B**.   Since there are no calculations using this result, one trial should be sufficient. Record your time, and calculate the rate with the catalyst.

Part III: Effect of Temperature and the Activation Energy

Run 2 provides the reaction time at room temperature, and the temperature study requires reaction times for Run 2 **at another temperature** . Perform a single run at one of the following temperatures, **as assigned by your instructor:** one at least 15°C colder than room temperature, one about 15°C warmer than room temperature, and another about 25°C warmer than room temperature.

Make sure to do the cold temperature run first and only perform one trial at each temperature.

1. **If preparing a cold water bath**: Use a small beaker that is large enough to prop up two test tubes. Use tap water to mostly-fill the beaker, and add small pieces of ice. The test tubes should sit in an ice-water slurry, but don't add too much ice.   Rather, maintain a cool temperature by adding pieces of ice periodically as they melt.

2. **If preparing a warm water bath**: Use a small beaker by mixing the warm water on the hot plate with an appropriate amount of tap water. Verify that the temperature of the water baths are within the appropriate ranges.

3. Prepare three each of **Test Tubes A** and **Test Tubes B**, as described in **Part I** for **Run 2**. Place both Test Tubes A & B in a water bath containing either an ice-water slurry or warm water, depending on the desired temperature. 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. Make sure to record into your data table the temperatures of the solutions just before you combine them. Then combine the mixtures, and time the reaction as before. For the reactions *at temperatures above room temperature, the reaction will occur very quickly*.

4. Repeat this for each temperature of water bath.

Report Sheets

Reaction Kinetics: The Iodine Clock Reaction

Write the concise scientific purpose of this experiment. Be sure to include each part of the experiment, and indicate what quantities (results) will be reported.

Purpose

Data Fill in the concentrations of reagents used (include units):

$Na_2S_2O_3$	KI	$(NH_4)_2S_2O_8$	$(NH_4)_2SO_4$

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Report Sheets

Reaction Kinetics: The Iodine Clock Reaction

Parts I & II: The Effect of Concentration and a Catalyst on Reaction Rate

Record the time of each Trial of each reaction in the table below. Fill in calculated values after the raw data (time and temperatures) have been recorded. Record the units.

Temperature of reactions (room temperature): _____ (   )

Table 1: Measured Reactions Times and Calculated Rates for Concentration Study and Effect of a Catalyst*

Run No.	Initial [I-] ( )	Initial [S2O8^{2-}] ( )	time ( )	rate ( )	Average Rate ( )	Average Rate Constant (k) ( )
Run 1a						
Run 1b						
Run 1c						
Run 2a						
Run 2b						
Run 2c						
Run 3a						
Run 3b						
Run 3c						
Run 4a						
Run 4b						
Run 4c						
Run 5a						
Run 5b						
Run 5c						
Run 2*						

Report Sheets

Reaction Kinetics: The Iodine Clock Reaction

Parts III: The Effect of Temperature on Reaction Rate; Finding the Activation Energy

Transfer the reaction time for Run 2 above (at room temperature) to the data table below.

Table 2: Temperature Study: Measured Reactions Times and Calculated Rates for Run 2

Temperature ( )	Time ( )	rate ( )	rate constant (k) ( )

Calculations

Perform the following calculations in your lab notebook, if your class is using them, and show a neat sample calculation for each below.

Parts I: The Effect of Concentration

1. Convert the time for each trial to seconds. Calculate the rate of reaction ($\Delta[I_2]/\Delta t$) for each trial in Runs 1-5, and record these values in Table 1. Recall, $\Delta[I_2] = 6.0 \times 10^{-4}\,M\,I_2$ for every run. Show a sample calculation below for Run 1. Respect significant figures based on the metric equipment used and show the units.

2. Use the dilution formula to calculate the concentration of I^- and $S_2O_8^{2-}$ for each of the five Runs, and record these values in Table 1. Show a sample calculation below for Run 1. Respect significant figures based on the metric equipment used and during calculations. Show the units.

Report Sheets

Reaction Kinetics: The Iodine Clock Reaction

3. Use Runs 1, 2 and 3 to determine x, the order of I^-. Pick two of these Runs and use the initial rates method (shown in the example on page 3) to find the value for x. Pick a different combination among Runs 1, 2 and 3 to verify the value obtained for x. 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 Runs 2, 4 and 5 to determine y, the order of $S_2O_8^{2-}$. Pick two of these Runs and use the initial rates method (shown in the example on page 3) to find the value for y. Pick a different combination among Runs 2, 4 and 5 to verify the value obtained for y. Show calculated value with significant figures and then **state the order for $S_2O_8^{2-}$, rounding the value for y to the nearest whole number.**

5. Substitute x, y, the rate of reaction, and your calculated ion concentrations back into the rate law (Equation 4) to calculate the rate constant, k, for each Run. Respect significant figures based on the metric equipment used and show units.

6. Write out the rate law substituting in the values for the 3 constants: x, y, and k. Respect significant figures and make sure to include units for your average room temperature rate constant.

Report Sheets

Reaction Kinetics: The Iodine Clock Reaction

Parts III: The Effect of Temperature on Reaction Rate; Finding the Activation Energy

7. Calculate the rate for the cold and hot temperature trials. Using the rate law from Question 6, calculate the rate constant, k, at each temperature, using [I⁻] and [$S_2O_8^{2-}$] from Run 2. Record these values in Table 2. Respect significant figures based on the metric equipment used and show units.

8. Use Excel to prepare an Arrhenius plot with **ln k on the y-axis and (1/T) on the x-axis**. (Note that "T" needs to be expressed in Kelvin rather than °C.) This plot should have four points, the original room temperature data for Run 2, 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 $\dfrac{J}{mol \cdot K}$.

Results and Discussion

1. The rate law for Equation (1) was found to be   _____ .

2. Which of the following mechanisms is compatible with the rate law obtained in this experiment? Give an explanation for your choice.

   a) $2I^-$*(aq)* + $S_2O_8^{2-}$*(aq)* → I_2*(aq)* + $2SO_4^{2-}$*(aq)*   *one-step reaction*

   b) I^-*(aq)* + $S_2O_8^{2-}$*(aq)* → I^+*(aq)* + $2SO_4^{2-}$*(aq)*   *slow step*

   I^-*(aq)* + I^+*(aq)* → I_2 *(aq)*   *fast step*

Report Sheets

Reaction Kinetics: The Iodine Clock Reaction

3. Compare the average reaction time for Run 2 without a catalyst to the reaction time with a catalyst (include the values). How did the addition of $Cu(NO_3)_2$ affect the rate of reaction? Based on your choice in question 1, explain how the rate is affected in terms of collision theory and the properties of the copper(II) ion. Write in full sentences, using proper grammar.

4. Compare your average reaction time for Run 2 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? Explain this effect in terms of collision theory.

5. Based on your choice in question 1, how do you expect the rate to change for Run 1 if 4 mL of deionized water is used in place of the 4 mL of aqueous $(NH_4)_2SO_4$? Explain.

Name _____

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Pre-Laboratory Exercise

Reaction Kinetics: The Iodine Clock Reaction

1. Write a concise scientific purpose for this experiment in the space available in the Report Sheet. Be sure to include each part of the experiment, and indicate what results will be reported.

2.   Calculate the initial concentration of $[I^-]$ and $[S_2O_8^{2-}]$ 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 $[I^-]$ (M)	Initial $[S_2O_8^{2-}]$ (M)
1		
2		
3		
4		
5		

3.   In the reaction   **A + B → C**, it is found experimentally that doubling the concentration of A, while holding other variables constant, doubles the rate. Doubling the concentration of B while holding other variables conctant increases the rate by a factor of four. Write the rate law for this reaction.