# EXPERIMENT 13:  THE IODINE CLOCK REACTION

## Background

In this experiment you will study the rate of the reaction between iodide ion, $I^-$, and persulfate (peroxydisulfate), $S_2O_8^{2-}$.  The products of the reaction are $I_2$ and sulfate ion. Write the balanced chemical equation for this reaction in the space provided.  Below the chemical equation draw the Lewis structure for persulfate and sulfate ions.

Chemical equation(1):

Starch will combine with iodine forming a starch-$I_2$ complex which has a blue color.  This chemical information will be used in this experiment to determine the rate of the reaction between iodide ion and persulfate ion.

Using the above equation between iodide and persulfate, and the behavior of iodine in the presence of starch, what do you think would happen if we prepared a solution of iodide ion of a given concentration and a solution of persulfate ion of a given concentration, added a starch solution to one of these two ions solution, then mixed them together?

Explanation:

Since the starch-$I_2$ complex is so intense we need to control the formation of the complex so the reaction between $I^-$ and $S_2O_8^{2-}$ can occur to some extent before the concentration of iodine is large enough to react with the starch.  The chemical way to do this is to introduce another reagent which does <u>not</u> react with either iodide ion, $I^-$, or persulfate ion, but reacts with any iodine, $I_2$, as it is formed.  So the idea is that persulfate reacts with iodide ion to form iodine, but as soon as any iodine forms it reacts with this other chemical species ($Na_2S_2O_3$) to reform $I^-$ ion and the $S_4O_6^{2-}$ ion.  This reaction continues until all of the $S_2O_3^{2-}$ reacts at which point the iodine, which continues to be formed (from reaction (1)), reacts with the starch in the solution to form the starch-$I_2$ complex and the bright blue color "turns-on" like a clock.  Knowing the stoichiometry of the reaction of the $I_2$ and the $S_2O_3^{2-}$ and the reaction between $I^-$ and $S_2O_8^{2-}$, allows the determination of how much $S_2O_8^{2-}$ reacts.  Measuring the length of time from mixing (t = 0) to when the starch–$I_2$ complex forms allows the determination of the time it takes for the $S_2O_8^{2-}$ to react.  The quotient of change in concentration of $S_2O_8^{2-}$ and the change in time is the rate of the reaction.

Use the space on is page to write the second reaction which occurs between $I_2$ and $S_2O_3^{2-}$.

Chemical equation(2):

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Next we need to think about the two reactions and how $I_2$, $S_2O_3^{2-}$ and $S_2O_8^{2-}$ are related stoichiometrically.

From reaction (2) how many moles of $I_2$ must react when 1 mol of $S_2O_3^{2-}$ reacts?

From reaction (1) how many moles of $S_2O_8^{2-}$ must react when 1 mol of $I_2$ forms?

By combining these two stoichiometric relationships $I_2$ acts as a 'bridge' between the moles of $S_2O_3^{2-}$ reacting and the moles of $S_2O_8^{2-}$ reacting.

Calculate how many moles of $S_2O_8^{2-}$ reacted when $1.25 \times 10^{-4}$ moles of $S_2O_3^{2-}$ react? (One must assume an excess of $I^-$ is available and that some starch was added to the solution.)

Since we are interested in rate of reaction, calculate the quotient of $\Delta[S_2O_8^{2-}]$ and the change in time if it took 56 seconds for all of the $S_2O_3^{2-}$ to react.

# Procedure
## PART I:  Concentration Effects and the Rate Law.

It is suggested you use three labeled beakers, one for the iodide ion, one for the persulfate ion and one for the mixture.

Here is the procedure for the basic experiment.  It is modified as described later when doing further experiments.  Use a buret, or pipet, to measure 20.0 mLs of the KI solution.  Use a second burette, or pipet, to measure 20.0 mLs of the $K_2S_2O_8$ solution.  Pipet 10.00 mLs of the $Na_2S_2O_3$ solution into the mixing beaker, add a few drops of the starch indicator.  Obtain a thermometer from your locker.  Simultaneously pour the KI and $Na_2S_2O_8$ solutions into the mixing beaker, start measuring the time the moment the solutions are poured into the mixing beaker.  Carefully swirl the solution in the mixing beaker to thoroghly mix the reagentsRecord the time when the starch-$I_2$ complex forms.  Record the temperature of the solution.  Rinse all the beakers in preparation for the next experiment

In the 2nd experiment everything is the same with the exception of the amount of thiosulfate, $K_2S_2O_3$.  In this experiment measure 5.0 mLs of the $K_2S_2O_3$ solution and put in the mixing beaker. Add 5.0 mLs of water to keep the toal volume of the reagents constant.  Mix the solutions and measure the time required for the thiosulfate to react.

The 3rd experiment varies the concentration of amount of thiosulfate, $K_2S_2O_3$ once again.  You decide on the amount for this run. Remember to add a volume of water to keep the total volume constant.  Check with your TA if you have any questions.

The fourth experiment uses the same amounts of solutions as described in the first experiment, except for the KI solution.  In this experiment measure out 10.0 mLs of the KI solution and 10 mLs of water and place in the labeled beaker.  Mix the solutions and measure the time.

The fifth experiment again seeks to determine the rate of the reaction at a different concentration of KI.   You decide on the amount of KI for this run.  Remember the relationship between the volume of KI solution and volume of water.  Check with your TA if you have any questions.

Data: Be sure to record the concentrations of the stock solutions!

$$[KI] = \text{\underline{\hspace{3cm}}}$$
$$[Na_2S_2O_8] = \text{\underline{\hspace{3cm}}}$$
$$[K_2S_2O_3] = \text{\underline{\hspace{3cm}}}$$

| Experiment | volume of [KI] | volume of [Na$_2$S$_2$O$_8$] | volume of [K$_2$S$_2$O$_3$] | volume of water | Temper-ature | TIME (seconds)-1 | TIME (seconds)-2 |
|---|---|---|---|---|---|---|---|
| 1 | 20.0 mL | 20.0 mL | 10.0 mL | 0 mL | 23 ˚C | | |
| 2 | 20.0 mL | 20.0 mL | 5.00 mL | 5.00 mL | 23 ˚C | | |
| 3 | 20.0 mL | 20.0 mL | | | 23 ˚C | | |
| 4 | 10.0 mL | 20.0 mL | 10.0 mL | 10.0 mL | 23 ˚C | | |
| 5 | | 20.0 mL | 10.0 mL | 10.0 mL | 23 ˚C | | |
| 6 | 20.0 mL | 20.0 mL | 10.0 mL | 0 mL | ˚C | | |
| 7 | 20.0 mL | 20.0 mL | 10.0 mL | 0 mL | ˚C | | |
| 8 | 20.0 mL | 20.0 mL | 10.0 mL | 0 mL | ˚C | | |
| 9 | 20.0 mL | 20.0 mL | 10.0 mL | 0 mL | ˚C | | |

### PART II:   Temperature Effects.

Four measurements will be made over a range of temperatures between 0 ˚C and 50 ˚C.  Replace the beakers for the Na$_2$S$_2$O$_8$ solution and KI solution with labeled test tubes. These test tubes will be immersed in a water bath (600 mL of distilled water) to obtain the different temperatures.  Use the solutions as described in the first experiment.

To obtain the highest temperature heat the water bath to approximately 60 ˚C and then place the test tubes containing the Na$_2$S$_2$O$_8$ solution and KI solution into the water bath for a few minutes.  Mix the solutions with the cold indicator solution.  Use the thermometer to measure the temperature of the solution.  Measure the time to the formation of the starch-I$_2$ complex.  This is sixth experiment.

In the seventh experiment repeat the experiment with the new solutions only use a water bath temperature of between 25 ˚C and 40 ˚C.

In the eighth use a temperature slightly cooler than room temperature.  Immerse the test tubes into a water bath which is near 15 ˚C.

In the ninth experiment immerse the test tubes into an ice bath.

**PART III:   Calculations.**

| Exp. # | moles of I⁻ added | moles of $S_2O_3^{2-}$ added | moles of $S_2O_8^{2-}$ consumed | $[S_2O_8^{2-}]$ consumed | Temperature | time | rate $= \frac{\Delta[S_2O_8^{2-}]}{\Delta t}$ |
|---|---|---|---|---|---|---|---|
| 1 | | | | | | | |
| 2 | | | | | | | |
| 3 | | | | | | | |
| 4 | | | | | | | |
| 5 | | | | | | | |
| 6 | | | | | | | |
| 7 | | | | | | | |
| 8 | | | | | | | |
| 9 | | | | | | | |

Complete the above table.  Remember the rate of the reaction with respect to $S_2O_8^{2-}$ is;

$$\text{rate of the reaction with respect to } S_2O_8^{2-} = \frac{\Delta[S_2O_8^{2-}]}{\Delta t}$$

Sample calculations: (Show a sample calculation for one of the experiments in the above table.)

Graphine the data:

Several plots will have to be made to interpret the data and determine the order of the reaction with respect to $I^-$ and $S_2O_8{}^{2-}$. To better understand what information needs to be plotted to determine order, consider the general reaction;

$$A + B \rightarrow products \tag{1}$$

The rate law for this reaction is;

$$rate = k[A]^m[B]^n \tag{2}$$

Equation (2) can be manipulated by taking the natural log of both sides. When this is done the following equation is obtained;

$$\ln (rate) = \ln k + m{\cdot}\ln[A] + n{\cdot}\ln[B] \tag{3}$$

When one of the species concentrations is held constant, say A in this example, the equation becomes;

$$\ln (rate) = (\ln k + m{\cdot}\ln[A]) + n{\cdot}\ln[B] \tag{4}$$

Which has the form of a straight line

$$\ln (rate) = (n\,k + m{\cdot}\ln[A]) + n{\cdot}\ln[B] \tag{3}$$
$$y \quad = \quad b \quad + \quad mx$$

Plotting ln(rate) versus ln[B] the slope is the order.
This can be done to determine the order of the reaction between $I^-$ and $S_2O_8{}^{2-}$.
From your plots (attach your graphs) determine the order of the reactions with respect to $I^-$ and $S_2O_8{}^{2-}$.
Once the orders are determined use the rate law to determine the rate constant for each of experiments.

| Exp. # | [I⁻] added | [S$_2$O$_8{}^{2-}$] | rate | rate constant |
|---|---|---|---|---|
| 1 | | | | |
| 2 | | | | |
| 3 | | | | |
| 4 | | | | |
| 5 | | | | |
| 6 | | | | |
| 7 | | | | |
| 8 | | | | |
| 9 | | | | |

Activation Energy:

To determine $E_a$ plot $\ln k$ versus $\frac{1}{T}$ for the sixth through ninth experiment. The heat of vaporization of a liquid can be obtained from such a plot. The relationship is given as,

$$\text{slope} = -\frac{E_a}{8.314 \ \frac{J}{\text{mol·K}}}$$