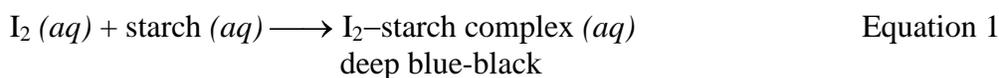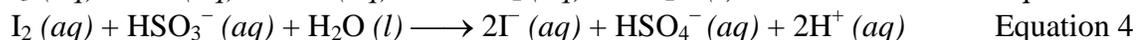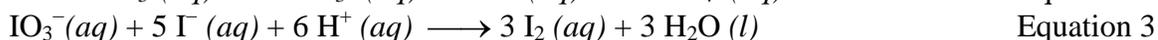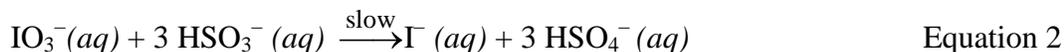# Experiment 6: THE RATE LAWS OF AN IODINE CLOCK REACTION

Purpose: The rate law for the reaction of an "iodine clock" reaction is to be established. It involves the determination of the order of reaction with respect to each of two reactants, as well as the determination of the rate constant for a particular temperature.

Introduction: The reaction used in this experiment is a classic example of a *chemical clock*. The term, *chemical clock*, refers to a reaction where the concentration of one of the chemical components undergoes an abrupt change in concentration after a time period and leads to a sudden change in color. The reaction in this experiment is termed an *iodine clock reaction*, because it is the molecular iodine (I_2) that undergoes the sudden concentration change. When the iodine concentration increases, it reacts with the starch in the solution to form a complex, turning it a deep blue-black color. This reaction is shown in Equation 1.

$$I_2 \ (aq) + \text{starch} \ (aq) \longrightarrow I_2\text{–starch complex} \ (aq) \qquad \qquad \text{Equation 1}$$
$$\text{deep blue-black}$$

There are several variations of iodine clock reactions. This experiment will focus on the reaction of iodate ion (IO_3^-) with an acidified solution of sodium bisulfite ($NaHSO_3$) containing the starch indicator. The reaction occurs in two steps. The first step generates iodide ion (I^-) in Equation 2, which occurs slowly and is the *rate determining step*. A *rate determining reaction* is the slowest step in a reaction mechanism and is assumed to be equal to the overall reaction rate because the reaction cannot go faster than the slowest step.

$$IO_3^-(aq) + 3 \ HSO_3^- \ (aq) \xrightarrow{\text{slow}} I^- \ (aq) + 3 \ HSO_4^- \ (aq) \qquad \text{Equation 2}$$
$$IO_3^-(aq) + 5 \ I^- \ (aq) + 6 \ H^+ \ (aq) \longrightarrow 3 \ I_2 \ (aq) + 3 \ H_2O \ (l) \qquad \text{Equation 3}$$
$$I_2 \ (aq) + HSO_3^- \ (aq) + H_2O \ (l) \longrightarrow 2 I^- \ (aq) + HSO_4^- \ (aq) + 2H^+ \ (aq) \qquad \text{Equation 4}$$

As the iodide ion is produced, it is quickly oxidized to iodine (I_2) by the iodate ion (Equation 3). However, the iodine is reduced immediately back to iodide by bisulfite (HSO_3^-) as seen in Equation 4. Since this step occurs extremely fast, the molecular iodine does not exist long enough to react with the starch and no color change is observed until all of the bisulfite has reacted. At that point, the iodine in Equation 4 is no longer being converted to iodide (as there is no more bisulfite available). The iodine reacts with the starch in Equation 1 and the blue-black iodine-starch complex appears. <u>This means that the appearance of the blue-black color is a signal that all of the bisulfite ions have reacted</u>. If we measure the time it takes for the blue-black color to appear, it would give us the rate of the reaction based on the change in concentration of HSO_3^-, which can be expressed as follows:

$$\text{Rate} = \frac{\Delta[HSO_3^-]}{\Delta t} \quad \text{where } \Delta[HSO_3^-] = \text{change in concentration of } HSO_3^-$$

and Δt = time period for the change in concentration of HSO_3^-

Since Δt is the time it takes for the blue-black color to appear and that corresponds to the time when <u>all</u> of the bisulfite has reacted, $\Delta[HSO_3^-]$ must equal to the initial concentration of the bisulfite. The rate is therefore the initial concentration of HSO_3^- divided by time, Δt.

A rate law expresses the reaction rate as a function of the concentration of each reactant. The rate at any instant is proportional to the product of the molar concentrations of the reactants, each concentration raised to some exponent that has to be determined experimentally. These exponents do **not** necessarily correspond to the coefficients of the overall equation because many reactions have reaction mechanisms that occur in multiple steps. The rate determining step that determines the rate law is only one step of a series of steps, not necessarily represented by the overall equation.

The exponents are determined by holding the concentration of all but one reactant constant (so that the concentration of only one reactant is changed). In this way, any change in the rate will be a direct result of a change in a single reactant. Since it is necessary to determine the rate order of each reactant, several sets of data must be collected, one set for each reactant.

The rate law for this reaction will be in the form:
$$\text{Rate} = k\,[IO_3^-]^x\,[HSO_3^-]^y \qquad\qquad \text{Equation 5}$$
where k is the rate constant for this reaction at a particular temperature, and x and y are the reaction orders for the iodate and bisulfite ions respectively. The x- and y-values are what you will be determining in this experiment.

Once the data has been collected there are two ways to determine the rate order, x and y. Both methods will be utilized in this experiment to expose you to how they work. The first is **mathematically**. To do this, you use data from two different trials (with Rate 1 and Rate 2) performed at the same temperature and the concentration of one reactant is kept constant:
$$\text{Rate 1} = k_1[IO_3^-]_1^x\,[HSO_3^-]_1^y \quad \text{and} \quad \text{Rate 2} = k_2[IO_3^-]_2^x\,[HSO_3^-]_2^y$$

> where $[IO_3^-]_1$ and $[IO_3^-]_2$ are the molar concentrations of iodate in Trials 1 and 2 respectively, and $[HSO_3^-]_1$ and $[HSO_3^-]_2$ are the molar concentrations of bisulfite in Trials 1 and 2 respectively.

Dividing Rate 1 by Rate 2 gives us Equation 6.

$$\frac{\text{Rate 1}}{\text{Rate 2}} = \frac{k_1[IO_3^-]_1^x[HSO_3^-]_1^y}{k_2[IO_3^-]_2^x[HSO_3^-]_2^y} \qquad\qquad \text{Equation 6}$$

Note that the rate constants k_1 and k_2 are the same if we perform the experiments at the same temperature (room temperature). Equation 6 becomes much simpler by canceling k_1 and k_2. In addition when one reactant concentration is held constant it cancels out as well, thus allowing us to solve for one of the exponents (either x or y).

For example, if $[IO_3^-]$ is kept constant, Equation 6 simplifies to Equation 7:

$$\frac{\text{Rate 1}}{\text{Rate 2}} = \frac{\cancel{k_1}\cancel{[IO_3^-]_1^x}[HSO_3^-]_1^y}{\cancel{k_2}\cancel{[IO_3^-]_2^x}[HSO_3^-]_2^y} = \left(\frac{[HSO_3^-]_1}{[HSO_3^-]_2}\right)^y$$

$$\frac{\text{Rate 1}}{\text{Rate 2}} = \left(\frac{[HSO_3^-]_1}{[HSO_3^-]_2}\right)^y \qquad\qquad \text{Equation 7}$$

where y is the only unknown in the equation. Solve for y by finding the antilog of both sides of the equation.

A similar operation can be done by keeping the bisulfite concentration constant in order to solve for x.

The second way to determine the rate order is **graphically**, by using the integrated rate laws. The integrated rate law can be rearranged to place the rate data into a linear equation. Each rate order law has a different linear equation. If [A] is the concentration of reactant A at a given point in time, k is the rate constant, and $[A]_0$ is the initial concentration, we have the following equations:

Zero order:	$[A] = -kt + [A]_0$	Equation 8
First order:	$\ln [A] = -kt + \ln [A]_0$	Equation 9
Second order:	$1/[A] = kt + 1/[A]_0$	Equation 10

If you prepare the three graphs; [A] *vs.* time, ln [A] *vs.* time, and 1/[A] *vs.* time, only one should produce a straight line. The graph that is linear tells you the order of reaction of that reactant. For example, if the "[A] *vs.* time" graph is linear, then the reaction is zero order with respect to reactant A. The slope equals to −k and the y-intercept equals $[A]_0$.

Safety Precautions:
Wear goggles at all times. Potassium iodate and sodium bisulfite may be harmful if swallowed, may cause irritation to skin, eyes and respiratory tract, may affect blood, kidneys, central nervous system, toxic effects may be delayed. In addition, the bisulfite solution contains sulfuric acid, which is also caustic.

Procedure: *Work with one partner.*

1. Obtain approximately 60 mL each of 0.020 M potassium iodate solution and 0.010 M starch-sodium bisulfite in clean dry beakers. Fill a 50.0 mL buret with deionized water (remember to first rinse the buret twice with 10 mL of deionized water). Since rates are temperature dependent, it is important that all reagents used are at room temperature.

2. Record the room temperature before you begin the trials and record the room temperature again after you finish all the trials.

3. There are seven trials that are to be set up, and each reaction will be done in duplicate.
   Trials 1 through 4:   bisulfite concentration is constant
                          iodate concentration is varied
   Trials 1, 5 through 7:   iodate concentration is constant
                          bisulfite concentration is varied
   The success of this experiment depends greatly on how accurately you measure out volumes. Water is dispensed by a buret. It is assumed that you have mastered the technique of dispensing accurately with a buret. Ask your instructor if you are not sure.

   The following procedure shows you how to use the 10-mL syringe correctly in dispensing the other reagents: the iodate and bisulfite solutions.

4. Examine the 10-mL syringes carefully to determine how this can be done accurately and precisely. The key is to keep your eye on Part A of the plunger in your measurements:
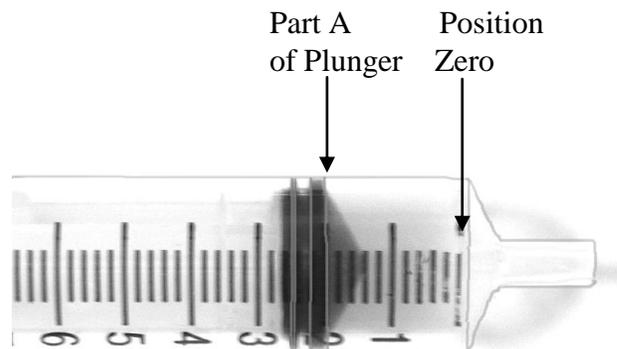
To accurately dispense 2.00 mL of a reagent:
a) First push the plunger all the way in (Part A would line up with Position Zero).
b) Immerse the tip of the syringe in the reagent and pump it a few times to get rid of any air bubbles in the tip.
c) Pull the plunger back until Part A is PRECISELY at 2.00 mL-mark. (During this process, keep the tip below the surface of the reagent so that no air gets back into the plunger.)
d) To deliver this volume, push the plunger all the way in (again Part A would line up with Position Zero). There will be a small amount of liquid remaining at the tip, but that is SUPPOSED TO REMAIN IN THE TIP. DO NOT PUMP THE PLUNGER because in so doing you would be delivering more than you are supposed to.

The seven trials are to be set up as indicated in Table 6.1. For each trial, you will first mix the water and bisulfite solutions in a clean 50 mL Erlenmeyer flask and then swirl to mix. Set the flask on a sheet of white paper (so that it is easier to see the color change). One partner will operate a stopwatch, while the other partner adds the iodate solution. It is important that the stopwatch is started exactly at the time the iodate is added because some of the reactions will occur in as quickly as 20 seconds.

When adding the iodate, it is important to add it as quickly as possible but without splashing the sides of the container as this may cause incomplete mixing. Swirl several times to mix. It is not necessary to swirl continuously during the trial. Stop the stopwatch at the first sign of a permanent color change, and record the time to the nearest second.

For the duplicate trials, the times should agree to within ± 5 seconds. If they do not agree, additional trials must be run until you obtain two trials that are within 5 seconds. Between trials, the 50-mL Erlenmeyer needs to be thoroughly rinsed with deionized water and excess water needs to be shaken out.

Table 6.1: Volume to be Added for Each Trial

Trial	Water (mL)	IO_3^- (mL) (0.020M)	HSO_3^- (mL) (0.010M)
1a	16.0	2.0	2.0
1b	16.0	2.0	2.0
2a	14.0	4.0	2.0
2b	14.0	4.0	2.0
3a	12.0	6.0	2.0
3b	12.0	6.0	2.0
4a	10.0	8.0	2.0
4b	10.0	8.0	2.0
5a	14.0	2.0	4.0
5b	14.0	2.0	4.0
6a	12.0	2.0	6.0
6b	12.0	2.0	6.0
7a	10.0	2.0	8.0
7b	10.0	2.0	8.0

Volume is assumed to be additive in this experiment. Thus, the total volume of all the solutions is assumed to be 20.0 mL. This introduces a small error that can be considered insignificant. The concentrations of IO_3^- and HSO_3^- (after mixing but before the reaction begins) can be calculated using the relationship: $M_{dilute}V_{dilute} = M_{conc}V_{conc}$. A sample calculation is shown below for the concentration of IO_3^- in Trial 1:

M_{dilute} = to be calculated V_{dilue} = 20.0 mL M_{conc} = 0.020M V_{conc} = 2.0 mL

$$\text{diluted } [IO_3^-] = \frac{0.020 \text{ M x } 2.0 \text{ mL}}{20.0 \text{ mL}} = 0.0020 \text{ M } IO_3^-$$

Similarly, the concentration of HSO_3^- in Trial 1 is calculated thus:

$$\text{diluted } [HSO_3^-] = \frac{0.010 \text{ M x } 2.0 \text{ mL}}{20.0 \text{ mL}} = 0.0010 \text{ M } HSO_3^-$$

Copy this **Data Table** neatly into your lab notebook prior to the prelab.

Trial	$[IO_3^-]$	$[HSO_3^-]$	Time (s)	Rate $[HSO_3^-]$/Time	Average Rate
1a	0.0020 M	0.0010 M			
1b	0.0020 M	0.0010 M			
2a	0.0040 M	0.0010 M			
2b	0.0040 M	0.0010 M			
3a	0.0060 M	0.0010 M			
3b	0.0060 M	0.0010 M			
4a	0.0080 M	0.0010 M			
4b	0.0080 M	0.0010 M			
5a	0.0020 M	0.0020 M			
5b	0.0020 M	0.0020 M			
6a	0.0020 M	0.0030 M			
6b	0.0020 M	0.0030 M			
7a	0.0020 M	0.0040 M			
7b	0.0020 M	0.0040 M			

DATA ANALYSIS: *Steps 1 & 2 of the calculations are to be completed in class. Steps 3 – 5 can be completed at home if you run out of time.*

1. The rate of each reaction is $\Delta[HSO_3^-]/\Delta t$. Remember that the experimental design is set up so that the bisulfite is always completely used up, therefore you can divide the initial concentration of bisulfite by the time to get the reaction rate. Calculate the average rate for the duplicate trials by using the average time.
2. Use the results from trials 1, 5, 6, and 7 to **graphically** determine the reaction order with respect to the **bisulfite** as explained in the introduction. Since there are four sets of data, each of the three graphs that you prepare will have 4 data points. You will prepare these graphs using Excel. Each graph should also include a linear trendline with the linear equation and R^2 value displayed. The graph with R^2 closest to the value one tells you the order of reaction with respect to the bisulfite ion.
3. Use the average rates from trials 1-4 to **mathematically** determine the reaction order with respect to the **iodate**.
4. Combine the results from your mathematical and graphical analyses and give the rate law. In other words, give Equation 5, substituting in place of x and y with the values you have determined in this experiment (rounded to the closest integer).
5. Next, for each of the seven trials, calculate the rate constant (k) based on the rate law you have just stated, and then find the average rate constant. Be sure to include the units for your rate constant.

Preparation for Pre-Lab Quiz:

1. You should be able to calculate the initial concentrations of IO_3^- and HSO_3^- shown in the **Data Table** for yourself. (See sample calculation shown on the previous page.)
2. What color change are you expecting to signify that the reaction is finished and you are to stop the stopwatch?
3. What exactly is the blue-black color due to? Why is it not present while HSO_3^- is still present?
4. You will be doing two trials for each set of concentrations. What is the criterion to decide whether you need to do more than two trials?
5. Be familiar with the names and formulas of the ions you are working with. Give the formulas of the following: iodine, iodate, iodide, bisulfite
6. How many significant figures are in 0.020 M?
7. You are using 0.020 M KIO_3. What is the molarity of IO_3^-?
8. How do you solve for y in Equation 7? Use the following data and solve for y.

$$\frac{\text{Rate 1}}{\text{Rate 2}} = \left(\frac{[HSO_3^-]_1}{[HSO_3^-]_2}\right)^y \quad \text{where Rate 1} = 1.7\text{x}10^{-4} \text{ M/s, Rate 2} = 4.9\text{x}10^{-5} \text{ M/s}$$
$$\text{and } [HSO_3^-]_1 = 0.0050 \text{ M}, [HSO_3^-]_2 = 0.0032 \text{ M}$$

First calculate y to the correct sig. fig. before rounding it to the closest integer. Show your work.

9. For the reaction   4 A + 3 B ⟶ 2 C   the following data were obtained at 35.0°C temperature. Use this data to determine the rate law for the reaction and to calculate, k, the rate constant – include units for the rate constant. Show your work.

Trial	Initial [A] (mol/L)	Initial [B] (mol/L)	Initial Rate of Formation of C (mol/L · min)
1	0.100	0.100	5.00
2	0.300	0.100	45.0
3	0.100	0.200	10.0
4	0.300	0.200	90.0

10. For Trial 2a, initial $[IO_3^-]$ is 0.0040 M and initial $[HSO_3^-]$ is 0.0010 M. If it takes 25 seconds for the blue-black color to appear, what is the rate for Trial 2a? Show your setup and include units.

Post-Lab Questions: *Please type on a separate sheet of paper.*

1. Suppose the rate law for a particular reaction between nitrogen dioxide and chlorine is Rate = k $[NO_2]^2[Cl_2]$. How would each of the following affect the rate of the reaction?
    a) If the concentration of NO_2 is tripled, then the reaction rate would (increase/decrease?)_____ by a factor of _____.

    b. If the concentration of NO_2 and Cl_2 are both doubled, then the reaction rate would (increase/decrease?)_____ by a factor of _____.

    c. If the concentration of Cl_2 is halved, then the reaction rate would (increase/decrease?)_____ by a factor of _____.

2. Use the rate law to explain quantitatively how increasing the iodate ion concentration affects the rate of the iodine clock reaction? (State whether it doubles or triples, etc.)

3. Use the rate law to explain quantitatively how decreasing the bisulfite ion concentration affects the rate of the iodine clock reaction? (Again, state whether it doubles or triples, etc.)

4. How would doubling the total volume of the solution by doubling the volume of water, iodate and bisulfite solutions affect the rate of the iodine clock reaction? Explain in full sentences.

5. Why is it important to record the temperature when you did not have to use it in any of your calculations? Explain in full sentences.

6. Explain, at the particulate level, why increasing the concentrations of the reactants would cause an increase in the rate of the reaction. (Think carefully what is meant by "at the particulate level.")

Calculations & Results:

Name: _____

CHEM 124 Sec: _____   **Lab Partner's Name:** _____

What is the average room temperature? _____

1. Show calculation setup for Trial 1 to show how the initial molarities and average rate are calculated and then fill in the rest of the table.
   Setup:

Trial	Initial $[IO_3^-]$	Initial $[HSO_3^-]$	Average Time	Average rate (including units)
1				
2				
3				
4				
5				
6				
7				

2. Graphically determine the order with respect to the bisulfite ion using Trials 1 and 5-7. You will turn in all three graphs that you prepare to do this (remember that this is an individual assignment and that your graph should be unique). You should add a trendline to each graph and display the equation and the R^2 value. The R^2 value is to be used to help you determine the order of reaction.

Order	Integrated Rate Law	Trendline	R^2
Zero	$[A] = -kt + [A]_0$		
1st	$\ln [A] = -kt + \ln [A]_0$		
2nd	$1/[A] = kt + 1/[A]_0$		

Name: _____

3. Use Trials 1-4 to mathematically calculate the order with respect to the iodate ion. Use multiple sets of data (at least three sets) and then calculate the average. Be wise in choosing which trials to use. If the time or rate of one particular trial seems out of place, do not use it. *Specify which combinations of trials you are using for this calculation and show your work on a separate sheet of paper.*

Combination of Trials *e.g. Trial 1 + Trial 2*	Order of Reaction with Respect to IO_3^- (to correct sig. fig.)	Order of Reaction with Respect to IO_3^- (rounded to closest integer)

Average Order of Reaction (rounded to the closest integer) =

4. Use the orders you have determined in Steps 2 & 3 above to write the rate law.

5. Use the rate law you derived on the previous page to calculate the rate constant. Fill in the table below, and show at least one sample set of calculations in the space below. Include units at all times.

	rate constant
k_1	
k_2	
k_3	
k_4	
k_5	
k_6	
k_7	
$k_{average}$	