Determination of the rate law for a chemical reaction.
Useful reading from text: Sections 14.1-14.3
Introduction

      In this lab we will examine the factors that influence the rate properties, or kinetics of reaction 1 between iodide ion and the bromate ion under acidic conditions (All ions as aqueous ions):

   1.) $6\ I^- + BrO_3^- + 6\ H^+ \rightarrow 3\ I_2 + Br^- + 3\ H_2O$

      This reaction occurs reasonably slowly at room temperature, and its rate depends on the concentrations of iodide, bromate, and hydrogen ions according to a rate law of the form:

      2.)   rate $= k[I^-]^m[BrO_3^-]^n[H^+]^p$

The main goal for today's lab is to determine the rate constant k and the exponents m, n, and p for this reaction. (These are referred to as the **reaction orders** for this reaction). We will also examine how the rate depends on temperature, and the temperature dependence will allow us to estimate the **activation energy** for this reaction.

      This reaction is an example of what is often referred to as a clock reaction. In addition to reaction 1, an additional reaction will also be made to occur in the same reaction mixture, given by equation 3 below:

      3) $I_2 + 2\ S_2O_3^{-2} \rightarrow 2\ I^- + S_4O_6^{-2}$
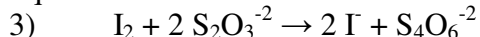
      In comparison to reaction1, reaction is extremely fast. The I_2 produced in reaction 1 will react completely with the thiosulfate ($S_2O_3^{-2}$) by reaction 3 until all of the thiosulfate is used up. As long as reaction 3 is occurring, the concentration of iodine is essentially zero. As soon as all of the thiosulfate is used up, reaction 3 can no longer occur and the concentration of iodine begins to increase. This iodine reacts with the added starch indicator to produce a bright blue color even with very low concentrations of iodine, giving us a very sensitive way to time the reaction.

      If you compare the stoichiometry of the two reactions, you can notice that 1/6 of a mole of bromate ion has to react to remove 1 mole of thiosulfate. Since our clock reaction tells us how long it takes to remove thiosulfate from solution, it also tells us how long it takes the corresponding number of moles of bromate to react. This gives us the rate of equation 1, which is the goal of the experiment.

      In part B of the lab, we will investigate how the reaction rate depends on temperature. By measuring the reaction rate at different temperatures we can use the Arrhenius equation (4) to determine the activation energy E_{act}.

      4) $\log_{10} k = (-E_{act}/2.30\ RT) + $ constant.

In this equation k is your experimentally determined rate constant at a given Kelvin temperature T, and R is the gas law constant. By graphing log k against 1/T, you should obtain a straight line in which the slope is equal to $-E_{act}/2.303\ R$.

Experimental Procedure

A. Dependence of rate on concentration

In the table below is a summary of the volumes needed for each of the experiments used to find the rate law for reaction 1. First, obtain about 100 mL of each of the needed reagents in clean labeled flasks or beakers.

Table 1: Reaction Mixtures (All volumes in mL)

Reaction Mixture	Reaction Flask 1 (250 mL)			Reaction Flask II (125 mL) Note: this flask will also contain the starch indicator.	
	0.010 M KI	0.001 M $Na_2S_2O_3$	H_2O	0.040 M $KBrO_3$	0.010 M HCl
1	10	10	10	10	10
2	20	10	0	10	10
3	10	10	0	20	10
4	10	10	0	10	20
5	8	10	12	5	5

The procedure will be the same for each trial, and will be described in detail for mixture 1. Since there are many items to mix and we want to start the reaction at a defined time, some components will be placed in one flask and some in the other flask, with the reaction starting when the components of both flasks are mixed. Using a 10 mL graduated cylinder to measure the volumes, place the components of flask 1 in one container. Bs sure to rinse the graduated cylinder between flasks or use a second cylinder for the components of flask II. Do the same for the second container. BE SURE TO ADD 3-4 DROPS OF THE STARCH INDICATOR TO FLASK II!

Pour the contents of reaction flask II into flask I, swirl to mix thoroughly and start the timing process. Continue swirling and note the time the solution turns blue. Also record the temperature of your reaction mixture.

Repeat this process for each of the suggested mixtures. The reaction flasks can be reused but be sure to rinse thoroughly with DI water between each run. Try to keep the temperatures the same for each run, and repeat any experiments that did not appear to run properly.

B. Dependence of reaction rate on temperature

In this part the same reaction mixture will have its rate measure at different temperatures. Use the solution mixture for reaction 1 from Table 1. The temperatures used will be about 20, 40, 10, and 0 ^{o} C. Use the time for reaction 1 at room temperature in part A as your 20 C run. For the other temperatures, prepare flasks I and II as in part A, including the indicator. BEFORE mixing, place the flasks in a water bath at the desired temperature range and leave them for several minutes to equilibrate at the new temperature. Then mix and begin the timing process. Continue swirling in the water bath at the desired temperature. When the reaction turns blue record the time and actual temperature. Repeat this process at the suggested temperature ranges.

C. Influence of a catalyst on reaction rate.

Some ions have a catalytic effect on the rate of reactions in aqueous solution. To observe this effect here again make the components of reaction mix 1 in the two flasks. Before mixing, add one drop of 0.5 M $(NH_4)_2MoO_4$ (ammonium molybdate) along with the starch solution to flask II. Swirl to mix and measure the rate at room temperature.

Data and calculation

In all of the reaction, the color change occurred when a set number of moles of bromate ion reacted. The rate of each reaction was measure by the time t for that trial. This defines the rate of our reaction $k = -\Delta(BrO_3^-)/t$. To simplify our life, and since here we are only interested in relative rate, we will set our amount of bromate as 1000 units, and thus our reaction rate $k = 1000/t$ (units are sec^{-1})

Fill in the table below for the starting and measure values for your trials in part A. Note that the concentrations of the reactants are the concentrations in the final mixed reaction mixture, not those of the stock solutions. The iodide value for trial 1 has been given for reference.

Table 2: Kinetic Data

Reaction Mixture	Time for color change (sec)	Relative rate of reaction 1000/t	Reactant concentrations in starting mixture (M)			Temperature
			I^-	BrO_3^-	H^+	
1			0.0020			
2						
3						
4						
5						

Determination of the order of the reaction.

Here we will use equation 2 with a slight modification, just changing rate to relative rate and the rate constant to k', the relative rate constant.

$$5) \quad \text{Relative rate} = k'[I^-]^m[BrO_3^-]^n[H^+]^p$$

Here we will take advantage of the mixtures that were chosen to find the values of the exponents m, n, and p. For example, write out equation 5 above filling in the values for trial 1. Do a similar step for trial 2.

Relative rate 1=_____=k' ( )^m ( )^n ( )^p
Relative rate 2=_____=k' ( )^m ( )^n ( )^p

Now divide the first equation by the second equation, and note that virtually all of the terms cancel out. If you have done this properly, you will now have an equation in which relative rate 1/relative rate 2 is only a function of m. Solve this for m, which gives you the order of this reaction in iodide ion-how does this the rate of this reaction depend on the concentration of iodide?

Carry out a similar process with trials 1 and 3, and with 1 and 4.
NOTE: normally the orders rate laws are integers or very simple fractions. In this lab, round each exponent to the nearest integer.

Now that you have found the values for the exponents m, n, and p, you can solve for the relative rate constant k'. Based on you data table, find k' for trials 1 through 4. It should have a constant value, or at least be fairly close.

As a test of this value, use equation 5 and your determined values for m, n, p, and k' to predict the relative rate and reaction time for trial 5 using your known starting concentrations. How good was the prediction?

Effect of temperature on reaction rate and determination of activation energy.
For each of your temperature samples find the relative rate. In all cases here, the concentrations of all reactants were identical and the only variable was temperature. Plot log k' vs. 1/T and determine the activation energy using equation 4.

What was the effect of the catalyst? Would you expect the activation energy for the reaction with the catalyst to be greater or small than the activation energy without the catalyst?