EXPERIMENT 2

Chemical Kinetics, a clock reaction

PURPOSE:
The purpose of this experiment is to investigate the effect of concentration, temperature, and the presence of a catalyst on the rate of a reaction. By the method of initial rates you will determine the order with respect to each reactant, the overall order of the reaction, the rate constant and the activation energy of the reaction.

INTRODUCTION:
        The rate at which a chemical reaction takes place is expressed by a rate law. For example, for a general reaction:

$$aA \; + \; bB \; \rightarrow \; cC \; + \; dD \tag{1}$$

The rate law is:

$$rate = k[A]^x[B]^y \tag{2}$$

where [A] and [B] are the molarities of the reactants and x and y are the orders of the reaction with respect to [A] and [B]. The rate is defined as the change in concentration of either the reactants or products with respect to time. For the reaction, this will be:

$$rate = \; - (1/a) \, (\Delta[A]/\Delta t) \;\; = \; - (1/b) \, (\Delta[B]/\Delta t) \;\; = (1/c) \, (\Delta[C]/\Delta t) \;\; = (1/d) \, (\Delta[D]/\Delta t) \tag{3}$$

        In this experiment we will study the following reaction between iodide ion and bromate ion:

$$6I^-(aq) \; + \; BrO_3^-(aq) \; + \; 6H^+(aq) \; \rightarrow \; 3I_2(aq) \;\; + \; Br^-(aq) \; + \;\; 3H_2O(1) \tag{4}$$
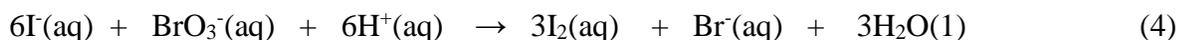
This reaction proceeds fairly slowly at room temperature and has a rate law of the form:

$$rate \quad = \quad k[I^-]^x[BrO_3^-]^y[H^+]^z \tag{5}$$

where x, y, and z are integers.

        One purpose of this experiment is to determine the orders x, y, and z and the value of the rate constant, k. This will be done by the method of initial rates. In this technique, the time required to form small, predetermined amount of product is monitored as a function of each of the concentrations of reactants. The amount of product formed (and reactant used) is small in relation to the overall amount of the reactant. For example, returning to a general reaction given in equation (1), if we begin with 0.100 M of A and B and monitor how long it takes for 0.002 M C to form, we will be measuring an initial rate, representing only 2% of the total reaction. In our reaction, we have three reactants. The concentrations of each will be varied to obtain the orders in each reactant. Once the orders for the rate law are determined, you can then calculate k, the rate constant, at room temperature. Use the methods of analysis that you learned in lecture.

The key to this experiment is to form the same small amount of product each time. A convenient way to control this by uses a property of the product, I_2. If I_2 is present in a solution, it can be detected by complexation with starch, which turns blue in the presence of I_2. However, we do not want a blue color to form until a small, predetermined amount of I_2 has formed. Starch will turn blue once any I_2 is present. This can be prevented by simultaneously running a second reaction:

$$I_2(aq) \quad + \quad 2S_2O_3^{2-}(aq) \quad \rightarrow \quad 2I^-(aq) + \quad S_4O_6^{2-}(aq) \tag{6}$$
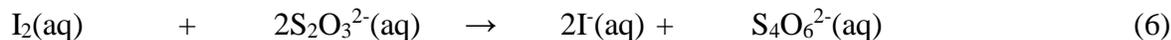
The thiosulfate ion, $S_2O_3^{2-}$, consumes I_2 as it is formed by main reaction in equation (4). This is a faster reaction than the main reaction, whose rate we are determining. By adding a small, predetermined amount of thiosulfate that will control the amount of I_2 that we wish to have formed in the main reaction, we have built a "clock" into the system. The blue color will not form until the thiosulfate has been consumed. Once the thiosulfate is consumed, we know that the desired amount of I_2 has been formed. This experiment then consists of measuring the time it takes for the blue color to appear as a function of varied concentrations of each of the three reactants.

From an inspection of equations (4) and (6)   we see that

$$\frac{3 \, mol \, I_2}{1 \, mol \, BrO_3^-} \times \frac{2 \, mol \, S_2O_3^{2-}}{1 \, mol \, I_2} \quad accounts \, for \quad \frac{\Delta[BrO_3^-]}{\Delta t} = \frac{1}{6}\frac{\Delta[S_2O_3^{2-}]}{\Delta t} \tag{7}$$

You will also investigate the rate of a reaction as a function of temperature in order to determine the activation energy, E_a, for the reaction. The activation energy is calculated from the Arrhenius equation:

$$\ln k = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln A \tag{8}$$

where A is a constant. The value of E_a can be determined graphing $\ln k$ vs $1/T$, where T is the temperature in Kelvin. The slope of this line then equals $-E_a/R$. (R=8.314J/mol K.)

Finally, the rate of the reaction will be observed in the presence of a catalyst. This should speed up the reaction.

PROCEDURE:
There are several parts to this experiment. The general plan is to:

1. Find the dependence of the reaction rate of concentration,
2. Determine the dependence of reaction rate on temperature,
3. Observe the dependence of reaction rate on a catalyst.

1. Dependence of Reaction Rate on Concentration: The table below indicates the volume of each of the reagents that must be mixed for each trial. Three of the reagents will be combined in one reaction flask (250 mL), the other two in a second flask (125 mL). By keeping the reagents separated, the reaction will not begin prematurely.

	Reaction Flask 1(250 mL)			Reaction Flask 2 (125mL)		
Mix	0.010 M KI	0.0010 M $Na_2S_2O_3$	H_2O	0.040 M $KBrO_3$	0.10 M HC1	Starch
1	10 mL	10 mL	10 mL	10 mL	10 mL	3 drops
2	20 mL	10 mL	0 mL	10 mL	10 mL	3 drops
3	10 mL	10 mL	0 mL	20 mL	10 mL	3 drops
4	10 mL	10 mL	0 mL	10 mL	20 mL	3 drops
5	8 mL	10 mL	12 mL	5 mL	15 mL	3 drops

First, obtain 100 mL of each of the reagents and save them in clean, labeled flasks or beakers. The procedure given below for Reaction Mixture 1 is the same that you will use for all other reaction mixtures. Only the volumes of reagents will change, as indicated in the table. Use a 10 mL graduated cylinder to measure out the volumes. For mixture 1, measure 10 mL of 0.010 M KI, 10.mL of 0.0010 M $Na_2S_2O_3$, and 10 mL of deionized water into a 250 mL Erlenmeyer flask (reaction flask 1).

At this time, be sure to rinse out the graduated cylinder with deionized water. Measure 10 mL of 0.040 M $KBrO_3$ (Reaction Flask 2) and 10 mL of 0.10 M HCl. Then add 3 drops of starch indicator solution to Flask 2.

Pour the contents of Reaction flask 2 into Reaction Flask 1 and swirl the solutions to mix them thoroughly. Immediately start your stopwatch. **Continue swirling the mixture until it turns blue.** Stop your stopwatch and record the time at the instant the mixture turns blue. Record the temperature of the blue solution, reading the thermometer to the nearest $0.2^{o}C$.

Repeat the procedure with Reaction Mixtures 2, 3, 4, and 5. **Remember to rinse out the graduated cylinder before adding reagents to each flask and to add the indicator to Reaction Flask 2.** Try to keep the temperature about the same for all reaction mixtures. Repeat any experiments that do not appear to proceed properly.

2. Dependence of Reaction Rate on Temperature: This part of the experiment is performed similarly to Part 1, but you use Reaction Mixture 1 in all cases. The reaction is performed at three additional temperatures, **approximately** $40^{o}C$, $10^{o}C$, and $0^{o}C$. Measure the exact temperature to the nearest $0.2^{o}C$. The fourth value, about $20^{o}C$, is the Reaction Mixture 1 you already studied in Part 1.

Prepare the reaction flasks for Mixture 1 as in Part 1, including the starch indicator. However, before mixing, place hot tap water (or water you have heated) into a large container. Verify that the bath water's temperature is around $40^{\circ}C$, and place the reaction flasks into this water for several minutes with swirling to bring them to the proper temperature. Then, mix the two solutions, **keeping the mixture in the hot water**. Swirl as before and record the time when the color changes. Record the temperature inside the reaction flask.

Repeat the experiment using cold tap water, cooled with ice if necessary, to lower it to about $10^{\circ}C$. Remove any ice before immersing the reaction flasks. Finally, use an ice/water bath to obtain a temperature near $0^{\circ}C$.

3. Dependence of the Reaction Rate on a Catalyst: Once again, use Reaction Mixture 1. Before mixing the two solutions, add to Reaction Flask 2 the starch indicator and one drop of 0.5 M $(NH_4)_2MoO_4$, ammonium molybdate, which will act as a catalyst. Swirl flask 2 to mix and then combine flask 1 and 2. Record the time of the color change.

REPORT: At your instructor's option write a formal lab report or complete the attached report form.

NAME_____ SECTION_____

PRE-LABORATORY ASSIGNMENT
EXPERIMENT 2

Chemical Kinetics, a Clock Reaction
Show all of your calculations on the back of this page.

A student mixed the following reactants, using the general procedure for the experiment: 10.0 mL 0.10 M KI, 10.0 mL 0.0010 M $Na_2S_2O_3$, 20.0 mL 0.040 M $KBrO_3$, and 10.0 mL 0.10 M HC1. It took about 75 seconds for the mixture to turn blue.

By using the dilution equation calculate the concentrations of each reactant in the mixture:
            $[I^-]$ = _____ $[BrO_3^-]$ = _____ $[H^+]$ = _____

Calculate the moles of $S_2O_3^{2-}$ consumed by reaction with I_2 within the 75 s it took for the mixture to turn blue:

                _____

Calculate the rate of the reaction $\Delta[BrO_3^-]/\Delta t$, by using the stoichiometry of the reaction and the total volume:

            Rate   = _____

The student then prepared Reaction Mixture 1, as described in the Part 1 of the Procedure, and it required about 155 seconds to change color.

By using the data from question 1, determine the order of the reaction with respect to the varied reagent, $[BrO_3^-]$, giving the closest integer as the answer:

y   = _____

You are solving an equation of the type:

$Rate_1/Rate_2$ $= \dfrac{\Delta t_2}{\Delta t_1}$ $=$ $\{[BrO_3^-]_1 / [BrO_3^-]_2\}^y$

        If logarithms are taken of both sides, an exact value for y can be determined.

        Calculate its value. Exact y = _____

NAME_____   SECTION_____

REPORT SHEET
EXPERIMENT 2

Chemical Kinetics

1. Dependence of Reaction Rate on Concentration: In all the reaction mixtures, the same number of moles of BrO_3^- has reacted once the color changes. From the stoichiometry of the two reactions, this is equal to one-sixth of the moles of $S_2O_3^{2-}$ used. Calculate the number of moles of thiosulfate reacted using the molarity and volume. Convert this to moles of BrO_3^- reacted, then to the change in molarity, $\Delta[BrO_3^-]$, during the reaction. Notice that the total volume in all reactions is 50 mL. Use the dilution equation, $M_1V_1 = M_2V_2$, to calculate all concentrations once the solutions are mixed.

Mix	Time (s)	Rate $-\Delta[BrO_3^-]/\Delta t$ $= 3.33 \times 10^{-5}$ (mol/L)/Δt	Reactant concentration (mol/L)			Temp ($\overset{\circ}{\text{C}}$)
			$[I^-]$	$[BrO_3^-]$	$[H^+]$	
1			0.0020			
2			0.0040			
3			0.0020			
4			0.0020			
5			0.0016			

In order to determine the orders of the reaction, x, y, and z, notice that in Reaction Mixtures 2, 3, and 4 only one of the concentrations has been changed relative to Mixture 1. By comparing the rate of reaction in each of the Mixtures 2, 3 and 4, relative to Mixture 1, the orders are determined as you learned in lecture. You must choose the closest whole-number integer for the orders. Do not give fractional orders. Write the values in the spaces below.

x = _____   y = _____   z = _____

Show your calculations here.

Now that you have determined the orders of the reactants, calculate the value of the rate constant, k, for each Reaction Mixture, 1, 2, 3, and 4. Simply use the concentrations of each reactant along with the rate. Put them into the rate law and solve for k. **Don't forget the units!**

Reaction   1   2   3   4

k   =   _____   _____   _____   _____

$k_{average}$=   _____

Show your calculations here.

Why should the values of k be nearly the same for each reaction? What accounts for any variation?

You have now calculated the value of the rate constant. Use Reaction Mixture 5 and the value of $k_{average}$ to predict how long it should take for the color to change. Do this by using the value of each of the concentrations, the orders, the value of $k_{average}$, and Δ [BrO_3^-] to solve for Δt. Next compare this value to the observed value.

Time predicted _____   Time observed _____

Show your calculations here.

2. Dependence of Reaction Rate on Temperature: The value of the activation energy, E_a, is determined by plotting 1n k vs. 1/T, where the temperature is in Kelvin. Complete the table below with your data taken at the four different temperatures. Remember, the first reaction is simply Reaction 1 from Part 1. This will be called Reaction Mixture 1A. Also, all concentrations are those of Reaction Mixture 1.

Mixture	Time (s)	Rate = $-\Delta[BrO_3^-]/\Delta t$ (mol/L-s)	Temp (°C)	Calculated k (units?)
1A				
1B				
1C				
1D				

Calculate the value of k for each reaction. Graph ln k vs. 1/T. Follow all rules for proper graphing, including labeling of axes, spreading out the data to fill the entire graph paper, a logical scale axes, etc. Draw the best straight line through the points and determine the slope. From the slope, calculate the value of E_a. Show all calculations on back of the graph and clearly indicate the slope and the value of E_a.

3. Dependence of the Reaction Rate on the Catalyst:

Time (s) for color to appear

Reaction Mixture 1 without catalyst: _____

Reaction Mixture 1 with catalyst: _____

Should you expect the activation energy of the catalyzed reaction to be greater, smaller, or equal to the uncatalyzed reaction? Explain.