Experiment 2

The Kinetics of the Iodine Clock Reaction

Pre-lab Assignment
Before coming to lab:

- Read the lab thoroughly.
- Answer the pre-lab questions that appear at the end of this lab exercise. The questions should be answered on a separate (new) page of your lab notebook. Be sure to show all work, round answers, and include units on all answers. Background information can be found in Chapter 14, especially sections 14.1-14.4 in your textbook (Brown and LeMay).
- Follow the guidelines in the "Lab Notebook Policy and Format for Lab Reports" section of the lab manual to complete in your lab notebook the following sections of the report for this lab exercise: Title, Lab Purpose, Procedure and Data Tables.

Background
In this experiment you will determine the effect of concentration upon the rate of the reaction of bromate ions (BrO\textsuperscript{3-}) with iodide ions (I\textsuperscript{-}) and hydrogen ions (H\textsuperscript{+}). In addition you will determine the effect of temperature changes on the rate of the reaction, the amount of energy required for molecules to react (called the activation energy), and the effect of a catalyst on the rate of the reaction.

Factors Affecting Rates of Reactions
On the basis of previous experiments you've performed, you probably have already noticed that reactions occur at varying speeds. There is an entire spectrum of reaction speeds, ranging from very slow to extremely fast. For example, the rusting of iron is reasonably slow, whereas the decomposition of TNT is extremely fast. The branch of chemistry that is concerned with the rates of reactions is called chemical kinetics. Understanding reaction rates helps us control them and adjust conditions to make them useful. For example, refrigeration of foods allows us to slow down the reactions involved in food spoilage while catalytic converters in cars increase the rate at which pollutants are converted to harmless gases. Experiments show that rates of reactions in solution depend upon:

1. The nature of the reactants
2. The concentration of the reactants
3. The temperature
4. The presence of a catalyst.

All of these factors rely on one basic underlying principle: before a reaction can occur, the reactants must come into direct contact with each other by way of collisions. In addition, the reacting particles must collide with sufficient energy to result in a reaction (break bonds within a molecule); if the reactant particles do not collide frequently or do not collide with very much energy, the reaction will be proceed slowly or not at all. Looking at these factors individually:

Concentration: Changing the concentration of a solute in solution alters the number of particles per unit volume. The more particles present in a given volume, the greater the probability of them colliding. Hence, increasing the concentration of a solute in solution increases the number of collisions per unit time and therefore, increases the rate of reaction.
**Temperature**: Since temperature is a measure of the average kinetic energy of a substance, an increase in temperature increases the kinetic energy of the reactant particles. The results in an increase in the velocity of the particles and therefore, increases the number of collisions between them in a given period of time. Thus, the rate of reaction increases. Also, an increase in kinetic energy results in a greater proportion of the collisions having the required energy for reaction. A good rule of thumb is that for each 10°C increase in temperature, the rate of reaction doubles.

**Catalyst**: A catalyst is a substance that speeds up a reaction but undergoes no permanent chemical change itself. Catalysts increase the rate of a reaction by providing an alternative route to the reaction-one that requires less energetic collisions between reactant particles. If less energy is required for a successful collision, a larger percentage of the collisions will have the required energy, and the reaction will occur faster.

**The Rate Law**

In order to relate the rate of a reaction to the factors discussed above, chemists write rate laws for reactions. The rate law of a chemical reaction is a mathematical equation that describes how the reaction rate depends upon the concentration of each reactant.

Consider the hypothetical reaction:

\[ A + B \rightarrow C + D \]

In general, the rate of the reaction will depend upon the concentration of the reactants. Thus, the rate of our hypothetical reaction above may be expressed as:

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

where \([A]\) and \([B]\) are the concentrations of A and B in units of molarity, and \(x\) and \(y\) are called the order of the reaction (the powers to which the respective concentrations must be raised to describe the rate). The orders of the reaction (\(x\) and \(y\)) can only be determined experimentally and are typically 0, 1, 2, or a fraction such as \(\frac{1}{2}\). They are not the coefficients of the reaction! The rate constant is given the symbol \(k\) and its value changes depending upon the reaction being studied and the temperature of the reaction as we shall see in this experiment.

In this experiment, we shall use the method of initial rates to determine the numerical values of \(x\) and \(y\) and the value of \(k\).
Example

Finding the Rate Law Using the Method of Initial Rates

Consider the reaction:

\[2\text{NO} + 2\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}\]

The rate law would be: \[\text{Rate} = k[\text{NO}]^x[\text{H}_2]^y\]

To give be more complete rate law, you will need to find the values of \(x\), \(y\), and \(k\) using experiment data. Consider the following data where the rate of the reaction was measured as the initial concentration of \(\text{NO}\) and \(\text{H}_2\) were varied.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[NO]</th>
<th>[H(_2)]</th>
<th>Initial rate in M/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.15 M</td>
<td>0.35 M</td>
<td>0.56</td>
</tr>
<tr>
<td>2</td>
<td>0.24 M</td>
<td>0.35 M</td>
<td>1.43</td>
</tr>
<tr>
<td>3</td>
<td>0.24 M</td>
<td>0.48 M</td>
<td>1.96</td>
</tr>
</tbody>
</table>

To see the effect of changing the concentration of \(\text{NO}\), find two experiments where only the concentration of \(\text{NO}\) is changing – experiment 1 and experiment 2 in this example. The rate laws for these experiments would be

\[\text{Rate}_1 = 0.56 = k[0.15]^x[0.35]^y\]
\[\text{Rate}_2 = 1.43 = k[0.24]^x[0.35]^y\]

You can determine the effect of changing the concentration of \(\text{NO}\) by taking a ratio and solving for \(x\):

\[\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{1.43}{0.56} = \frac{k[0.24]^x[0.35]^y}{k[0.15]^x[0.35]^y} = \frac{[0.24]^x}{[0.15]^x} = 1.6^x = 2.55\]

Taking the logarithm of each side of the equation allows us to solve for \(y\). Kinetics requires familiarity with powers and logarithms. Review both if necessary.

\[\log 2.55 = x \log 1.6\]

\[x = \frac{\log(2.55)}{\log(1.6)} = 2.0\]

Similarly, to see the effect of changing the concentration of \(\text{H}_2\), you can examine experiments 2 and 3 where only the concentration of \(\text{H}_2\) is changing.

The rate laws for these experiments would be

\[\text{Rate}_3 = 1.96 = k[0.24]^y[0.48]^y\]
\[\text{Rate}_2 = 1.43 = k[0.24]^x[0.35]^y\]

You can determine the effect of changing the concentration of \(\text{H}_2\) by taking a ratio and solving for \(y\):

\[\frac{\text{Rate}_3}{\text{Rate}_2} = \frac{1.96}{1.43} = \frac{k[0.24]^y[0.48]^y}{k[0.24]^x[0.35]^y} = \frac{[0.48]^y}{[0.35]^y} = 1.37^y\]

\[1.37 = 1.37^y\]

You can see that \(y = 1\). (You could take the log of both sides as done above to show this.)
The Kinetics of the Iodine Clock Reaction

Part A: Finding the Rate Law Using the Method of Initial Rates

The iodine clock reaction is a well-known and memorable chemical reaction where two colorless solutions are mixed and, after a period of time ranging from seconds to minutes, the solution suddenly turns from colorless to colored (yellow or bluish–black). It is represented by the following balanced chemical equation:

\[ 6I^- (aq) + BrO_3^- (aq) + 6H^+ (aq) \rightarrow 3I_2 (aq) + Br^- (aq) + 3H_2O (l) \] (slow) Equation 1

A starch indicator, which turns yellow or blue-black in the presence of the product iodine \((I_2)\), is also added to the reaction mixture. However, the color does not show right away because a second reaction takes place in which thiosulfate ions \((S_2O_3^{2-})\) consume the product iodine molecules \((I_2)\) as soon as they are produced as shown by Equation 2:

\[ I_2 (aq) + 2 S_2O_3^{2-} (aq) \rightarrow 2 I^- (aq) + S_4O_6^{2-} (aq) \] (fast) Equation 2

\[ I_2 (aq) + \text{Starch} \rightarrow \text{Starch-I}_2 (aq) \text{ (bluish-black)} \] (fast) Equation 3

Since the first reaction is slow, and the second is fast, the iodine molecules \((I_2)\) are not present long enough to react with the starch and produce the color. **It is only after all of the \(S_2O_3^{2-}\) in Equation 2 has been used up that iodine accumulates, then combines with the starch, and the solution turns yellow or bluish–black.**

Although three reactions are involved, the reaction between bromate and iodide ions (eqn 1) is the one we will be studying in this experiment. The second reaction (eqn 2) is only used to delay the reaction between iodine and starch (eqn 3).
For the reaction we will be studying

$$6I^- (aq) + BrO_3^- (aq) + 6H^+ (aq) \rightarrow 3I_2 (aq) + Br^- (aq) + 3H_2O (l) \quad \text{(slow)}$$

Equation 1

The rate law for this reaction will be of the form:

$$\text{Rate} = k[I^-]^x[BrO_3^-]^y[H^+]^z$$

Your goal is to find the values of $x, y, z$ and $k$ in order to complete the rate law. We will also get the value of a 'hidden parameter,' the activation energy ($E_a$), which tells us how the rate changes when we change the temperature. Finally, we can investigate the effect of adding a catalyst, which increases the rate by providing a different set of 'steps' requiring less energy for converting the reactants into products.

The **method of initial rates** allows the values of these orders to be found by running the reaction multiple times under controlled conditions and measuring the rate of the reaction in each case. All variables are held constant from one run to the next, except for the concentration of one reactant. The order of that reactant in the rate law can be determined by observing how the reaction rate varies as the concentration of that one reactant is varied. This method is repeated for each reactant until all the orders are determined. At that point, the rate law can be used to find the value of the rate constant ($k$) for each trial. If the temperatures are the same for each trial, then the values of $k$ should be the same too. The values of the reaction orders, $x, y, z$ are usually, though not always, small integers.

For today's lab, we will base our calculations on the change in concentration of $BrO_3^-$. This is a somewhat arbitrary decision since we could do our calculations based upon the rate of appearance or disappearance of any species involved in the reaction. It will be easier to think in terms of a species that has a coefficient of one in the reaction- hence the choice of $BrO_3^-$. 

$$\text{Rate of Reaction} = \frac{\Delta [BrO_3^-]}{\Delta t} \quad \text{Note: brackets are used to represent the unit Molarity (M)}$$

However, as discussed above, our observation of the endpoint of the reaction is based on when all the $S_2O_3^{2-} (aq)$ to be used up by the clock reaction. We will need to use the stoichiometry of Equations (1) and (2) to relate the rate of change of the $S_2O_3^{2-} (aq)$ concentration (Molarity) in the clock reaction to that of the $BrO_3^- (aq)$.

Using the coefficients of equations (1) and (2) we see that

$$\Delta [S_2O_3] \times \frac{\Delta 1 [I_2]}{\Delta 2 [S_2O_3]} \times \frac{\Delta 1 [BrO_3]}{\Delta 3 [I_2]} = \Delta [BrO_3]$$

using coeff. from rx 2 using coeff. from rx 1

The relationship above is based on using the coefficients of the reactions. Looking at the coefficients in equation 2, we can see that $S_2O_3^{2-}$ is used up twice as fast as $I_2$. Similarly, looking at the coefficients in equation 1 we can see that $I_2$ is produced at three times the rate $BrO_3^-$ is used up.
Part B: Determination of the Activation Energy (Ea) and Frequency factor (A) of the Reaction

In the first section, the reaction was performed at different reactant concentrations but at a constant temperature. In this section, the concentrations will be kept constant and the temperature will be varied. This will allow us to determine the activation energy of a reaction using the Arrhenius equation:

\[ k = A e^{\frac{-E_a}{RT}} \]  

Equation 5

where \( E_a \) is the activation energy of the reaction (the minimum energy that must be present in a collision for a reaction to occur), \( A \) is the frequency factor and is related to the number of collisions between reactant molecules with the correct orientation that occur per second, and \( R \) is the universal gas constant with a value of 8.314 J/mol K.

We will need to rearrange this equation to be able to use it for today’s lab. Taking the natural logarithm of both sides of Equation (5) gives:

\[ \ln(k) = \frac{-E_a}{R} \left( \frac{1}{T} \right) + \ln A \]

\[ y = mx + b \]

Note that this equation is that of a straight line of the form \( y = mx + b \). Thus, if the rate constant, \( k \), is measured at several temperature and \( \ln k \) (\( y \)) is plotted versus \( 1/T \), (x) the slope of the resulting line will be \(-E_a/R\).

Part C: The Effect of a Catalyst upon Reaction Rate

The effect of a catalyst on reaction rate will be studied in Part C of the lab. A catalyst is a substance that can increase the rate of reaction by changing the mechanism (pathway) of the reaction. Usually, a catalyzed mechanism will have a lower activation energy than an uncatalyzed mechanism. Hence, at any given temperature, there will be more molecules having enough energy to react via the catalyzed mechanism than via the uncatalyzed route. The rate of the catalyzed reaction will therefore, be faster. In this experiment, the catalyst will be a small amount of ammonium molybdate (NH₄)₂MoO₄.

Procedure

Materials and Equipment

You will need the following items for this experiment:

- stopwatch (or digital timer)
- thermometer
- one 250 mL Erlenmeyer flask
- one 125 mL Erlenmeyer flask
- hot-water baths set at different temperatures (available in lab room)
- ice-water bath (obtain a bucket of ice from the stockroom)
Safety
GENERAL SAFETY: Students must wear safety goggles at all times.

WASTE DISPOSAL: All solutions used in this lab may be disposed of in the sink except in Part C of the experiment which involves ammonium molybdate (NH₄)₂MoO₄ which is toxic. There is a waste container for this part of the lab.

General note about the lab: The procedure is to put various amounts of water, Na₂S₂O₃, and KI in one flask and various amounts of KBrO₃, HCl, and starch indicator in a second flask. With the stopwatch ready, the contents of the two flasks are mixed and the time required for the solution to turn faint blue is measured.

Due to time constraints for Part A, you and your partner will only need to do a portion of the runs outlined in the table below. You will obtain the other data from another pair of students. Your instructor will help coordinate this “divide and conquer” approach.

Preparation of Glassware
Because soap residue and other chemicals can interfere with the reaction we are observing it is critical that all glassware used in this experiment be rinsed several times using deionized water (and not soap!) prior to performing the experiment. Also, because the production of deionized water is very energy intensive glassware should be rinsed using a squirt bottle in order to minimize waste; never rinse glassware directly under the deionized water tap. The glassware needs to be relatively dry.

Part A
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). This keeps your reactants separated so no reaction occurs until you pour the mixtures together.

<table>
<thead>
<tr>
<th>Mix</th>
<th>Reaction Flask 1 (250 mL)</th>
<th>Reaction Flask 2 (125 mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.010 M KI</td>
<td>0.0010 M Na₂S₂O₃</td>
</tr>
<tr>
<td>1</td>
<td>10 mL</td>
<td>10 mL</td>
</tr>
<tr>
<td>2</td>
<td>20 mL</td>
<td>10 mL</td>
</tr>
<tr>
<td>3</td>
<td>10 mL</td>
<td>10 mL</td>
</tr>
<tr>
<td>4</td>
<td>10 mL</td>
<td>10 mL</td>
</tr>
</tbody>
</table>
1. Using the labeled burets that are around the lab room, measure out the above amount of reagents for mixture 1 (or one of the mixtures you have been assigned). Accuracy is critical so if your amounts are off, you will need to start over. Be sure to check the volume of solution in the buret and if it is low, refill the buret from the stock bottles using a funnel before measuring out your sample.

2. Pour the contents of Reaction Flask 2 into Reaction Flask 1 and swirl the solutions to mix them thoroughly. Immediately start your stopwatch. Set the flask containing the solution down on a sheet of white paper and watch carefully for the blue color of the starch-iodine complex to appear. It should take about one to three minutes. Stop the timer the instant that the blue color appears. Record the elapsed time on your data sheet.

3. Record the temperature of the blue solution, reading the thermometer to the nearest 0.1 °C. Dispose of the contents down the sink.

4. Clean both flasks and thermometer with deionized water.

5. Unless otherwise instructed, repeat the experiment one a second time.

6. Repeat the procedure with Reaction Mixtures 2, 3, 4, and 5.

7. Perform the calculations for Part A to determine the rate law before proceeding to the next part.

Testing Your Rate Law (Optional)

1. Your instructor will tell you what volumes of reagents to use for this part of the experiment. Write those volumes in your data table in your notebook.

<table>
<thead>
<tr>
<th>Reaction Mixture</th>
<th>Reaction Flask 1 (250 mL)</th>
<th>Reaction Flask 2 (125mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.010 M KI</td>
<td>0.0010 M Na₂S₂O₃</td>
</tr>
<tr>
<td>5</td>
<td>mL</td>
<td>mL</td>
</tr>
</tbody>
</table>

2. Use your rate law to predict the time that will be required for this reaction mixture to blue. For help with this, see the calculations section on your data sheet for Part B of this experiment.

3. Repeat the steps above but use the volumes for Reaction Mixture 5.
Part B: Determination of the Activation Energy \((E_a)\) and Frequency Factor \((A)\) of the Reaction

This part of the experiment is performed similarly to Part 1, but you will use the amounts from Reaction Mixture 1 in all cases. The reaction is performed at three additional temperatures, approximately 5°C, 30°C and 40°C.

1. Prepare Flasks 1 and 2 as in Mixture 1 of part A.

2. Make an ice water bath by mixing ice and water in a shallow tub. The bath should contain mostly ice with enough water to fill in all the spaces between the ice cubes.

3. Place both flasks in the ice water bath and wait several minutes until the temperature of the contents of Flask 1 have reached a steady temperature. Monitor the temperature of the mixture by placing your thermometer in Flask 1. Do not remove the thermometer from Flask 1 since this will remove some of your reagents, too.

4. Get your stopwatch ready and pour the contents of Flask 2 into Flask 1 to begin the reaction. Swirl the flask gently to mix the solutions and start the stopwatch as soon as the solution in Flask 2 has entered Flask 1. Keep your thermometer in Flask 1 and maintain a constant temperature for the duration of the reaction by keeping the flask in the ice bath.

5. When the color changes, stop your stopwatch and record the time it took for the color change to appear on your data sheet.

6. Record the approximate temperature at which you ran the reaction to the nearest 0.1°C.

7. Dispose of the contents of your flask down the sink and rinse your glassware thoroughly with distilled water.

8. Repeat this procedure in a hot water bath at approximately 30°C(±5°C), then once more at about 40°C (±5°C). Be sure to record the actual temperature of each reaction mixture (not the water bath) on your report form.

Part C. The Effect of a Catalyst Upon Reaction Rate

<table>
<thead>
<tr>
<th>Safety</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ammonium Molybdate</strong> can affect you when inhaled and may be absorbed through the skin.</td>
</tr>
<tr>
<td><strong>Ammonium Molybdate</strong> can irritate the nose and throat causing coughing and wheezing.</td>
</tr>
<tr>
<td>High or repeated exposure to <strong>Ammonium Molybdate</strong> may cause headache, weakness, fatigue, and joint and muscle pains.</td>
</tr>
</tbody>
</table>

Dispose of waste in the proper container.

1. Prepare Flasks 1 and 2 as in step 2 of part A using the amounts for reaction mixture 1, but this time add one drop of 0.5 M ammonium molybdate \((\text{NH}_4)_2\text{MoO}_4\) to Flask 2. Don't forget to add the 3-4 drops of starch indicator to Flask 2 as well.
2. As before, get your stopwatch ready. (Watch out! This will be a fast reaction!) Pour the contents of Flask 2 into Flask 1 to begin the reaction. Swirl the flask to mix the solutions and start the stopwatch as soon as the solution in Flask 2 has entered Flask 1. Place the flask on a piece of white paper and watch carefully for the blue color of the iodine-starch complex to appear.

3. When the color changes, stop your stopwatch and record the time it took for the color change to appear on your data sheet.

4. Pour the contents of your flask into the appropriate waste container.
Data Tables and Calculations

These tables and space for sample calculations should be placed in your notebook.

A. Finding the Rate Law Using the Method of Initial Rates

1. Times for Color Change and Reaction Temperatures

<table>
<thead>
<tr>
<th>Reaction Mixture</th>
<th>Time for Color Change $\Delta t$ (in seconds, recorded to nearest 0.1 sec)</th>
<th>Temperature ($^\circ$ C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>How many digits should be in your readings?</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trial 1</td>
<td>_______</td>
<td>Trial 1</td>
</tr>
<tr>
<td>Trial 2</td>
<td>_______</td>
<td>Trial 2</td>
</tr>
<tr>
<td>AVERAGE</td>
<td>_______</td>
<td>AVERAGE</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trial 1</td>
<td>_______</td>
<td>Trial 1</td>
</tr>
<tr>
<td>Trial 2</td>
<td>_______</td>
<td>Trial 2</td>
</tr>
<tr>
<td>AVERAGE</td>
<td>_______</td>
<td>AVERAGE</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trial 1</td>
<td>_______</td>
<td>Trial 1</td>
</tr>
<tr>
<td>Trial 2</td>
<td>_______</td>
<td>Trial 2</td>
</tr>
<tr>
<td>AVERAGE</td>
<td>_______</td>
<td>AVERAGE</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trial 1</td>
<td>_______</td>
<td>Trial 1</td>
</tr>
<tr>
<td>Trial 2</td>
<td>_______</td>
<td>Trial 2</td>
</tr>
<tr>
<td>AVERAGE</td>
<td>_______</td>
<td>AVERAGE</td>
</tr>
</tbody>
</table>

2. Determine the rate of the reaction. Complete questions a, b, and c below to determine the rate of the reaction. Remember, Rate of Reaction $= \frac{\Delta [\text{BrO}_3^-]}{\Delta t}$

Please show your work in your notebook, labeled, with units, and rounded.

a. Write the balanced chemical equations for Reactions 1 and 2 below.

   Equation 1:

   Equation 2:

b. Determine the change in concentration of $\text{S}_2\text{O}_3^{2-}$ that occurred during the time period measured. This should be the same for all the reaction mixtures. You will need to use $M_1V_1 = M_2V_2$ to determine the initial
concentration of the $S_2O_3^{2-}$ after mixing the contents of the two flasks. This is because as the solutions are combined, they are diluting each other. Recall that all the $S_2O_3^{2-}$ is consumed when the color change occurs.

$$[S_2O_3^{2-}]_{initial} = \ldots$$

Recall that all the $S_2O_3^{2-}$ is consumed when the color change occurs. Therefore,

$$\Delta[S_2O_3^{2-}] = \ldots$$

c. Use the stoichiometry of Reactions 1 and 2 to determine the change in concentration of $BrO_3^-$ during the same time period. (see eqn. 1-2)

$$\Delta[BrO_3^-] = \ldots$$

3. Complete the following table to find the initial reaction rate for each of your mixtures.

<table>
<thead>
<tr>
<th>Reaction Mixture</th>
<th>$\Delta[BrO_3^-]$</th>
<th>$\Delta t$ (seconds)</th>
<th>Rate $= \frac{\Delta[BrO_3^-]}{\Delta t}$ (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>See previous table and use average if more than one trial</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4. Now that we know the rate of the reaction, we also need to know the concentration of each reactant in each mixture. This is not the same as the concentration on the stock bottles because as the reactants were combined, they were diluting each other. Recall that you use $M_1V_1=M_2V_2$ to find the concentration when diluting a solution. Also, enter the initial rates computed above in the following table. Remember that when you are doing the same calculation over and over, it is only necessary to show one set of sample calculations- for example the work for reaction mixture 1.

<table>
<thead>
<tr>
<th>Reaction Mixture</th>
<th>$[I^-]$</th>
<th>$[BrO_3^-]$</th>
<th>$[H^+]$</th>
<th>Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>after mixing</td>
<td>after mixing</td>
<td>after mixing</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>3</td>
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<td></td>
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<td>4</td>
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</tbody>
</table>
The Kinetics of the Iodine Clock Reaction

Notice that you now have a table identical to the example on pg 3. Congratulations! You are now ready to use the method of initial rates to compute the order for each reactant. Clearly show your calculations, including which trials you have used. You will need to take the log of the ratio of the rates and the log of the ratio of concentrations to calculate x, y, and z. (see Example in pg 3).

The reaction order with respect to I^-

\[ x = \text{__________} \text{ (two decimal places)} \quad x = \text{__________} \text{ (rounded to closest integer)} \]

The reaction order with respect to BrO_3^-

\[ y = \text{__________} \text{ (two decimal places)} \quad y = \text{__________} \text{ (rounded to closest integer)} \]

The reaction order with respect to H^+

\[ z = \text{__________} \text{ (two decimal places)} \quad z = \text{__________} \text{ (rounded to closest integer)} \]

The Rate Law: _______________________________

5. Using the rate law you just discovered and the final (diluted) concentrations of each reaction mixture, calculate the value and units of the rate constant (k) for each reaction mixture. Then, find the average value of k.

<table>
<thead>
<tr>
<th>Reaction Mixture</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value of k</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average value of k (including units)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6. Should the value of k be the same for each of the trials? Explain.

Testing Your Rate Law (Optional)

7. Use your rate law to predict the time required for the color change to occur in Mixture 5. Use your average value of the rate constant, k.

<table>
<thead>
<tr>
<th>Reaction Mixture</th>
<th>[I^-]</th>
<th>[BrO_3^-]</th>
<th>[H^+]</th>
</tr>
</thead>
<tbody>
<tr>
<td>after mixing</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>after mixing</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>after mixing</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5
Rate predicted for color change for Mixture 5  ___________ M/s

Predicted Δt for color change for mixture 5.  ___________ sec

Recall that Rate of Reaction = \frac{\Delta [\text{BrO}_3^-]}{M}
And that the change in bromate ion concentration is the same for all five reaction mixtures.

Observed time for color change for Mixture 5  ___________ sec

8. Comment on the level of agreement between your predicted time and the actual time for color change in Mixture 5. Considering the precision of your data, do you think this level of agreement is reasonable? If not, why do you think the results disagree?

Part B: Determination of the Activation Energy ($E_a$) and Frequency Factor ($A$) of the Reaction

Complete the table on the following page with your data taken at the four different temperatures. Remember, the first reaction is simply Reaction 1 from Part A and that all concentrations are those of Reaction Mixture 1. The value of the activation energy, $E_a$, is determined by plotting $\ln k$ vs. $1/T$ (in Kelvin), where the temperature is in Kelvin.

At Room Temp

(already done in Part A)

<table>
<thead>
<tr>
<th>Actual Temperature °C</th>
<th>Actual Temperature K</th>
<th>Time for Color Change</th>
<th>$\Delta [\text{BrO}_3^-]$</th>
<th>Reaction Rate (M/s)</th>
<th>Rate Constant (k) units?</th>
<th>$\ln k$ (no units)</th>
<th>$1/T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>In ice water</td>
<td>At about 30 °C</td>
<td>At about 40 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Recall that \( k \) and \( T \) are related via the Arrhenius Equation:

\[
\ln(k) = -\frac{E_a}{R} \left( \frac{1}{T} \right) + \ln A
\]

Which is of the form

\[
y = mx + b
\]

Using Excel, create a graph of "ln \( k \) versus \( 1/T \)." Be sure to label the axis and title your graph. Add a trendline to your plotted data, and obtain both the equation of the trendline and the \( R^2 \) value. Do not set the \( y \)-intercept to zero! A printout of this graph should be stapled to your report form. Use the appropriate information obtained from the graph and linear equation to determine the activation energy, \( E_a \), and the frequency factor, \( A \), for this reaction (include units!). Show your calculations.

\( R^2 \) (Correlation Coefficient) __________________________

Equation of the line: __________________________

\( E_a \): (J/mol) __________________________

\( E_a \) (KJ/mol) (a more common unit) __________________________

A (frequency factor) __________________________

If you unfamiliar with Excel ask your instructor for help.

Part C: The Effect of a Catalyst Upon Reaction Rate

<table>
<thead>
<tr>
<th>Reaction Mixture</th>
<th>Without Catalyst (use data from Part A Mixture 1)</th>
<th>With Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time for color change</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rate constant (( k ))</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

By what factor did the rate of the reaction increase? i.e. what is the ratio of \( k_{cat} / k_{uncat} \)?
Post-Lab Questions

1. Explain how and why a decrease in reactant concentration will affect the rate of a chemical reaction?

2. Looking at your results from Part B, explain the relationship between the temperature and rate of a reaction. Give a physical explanation for this. What is occurring at the molecular level?

3. In Part A, even though the concentrations of the reactants are changing in each trial, the experimental values of the rate constant (k) for each trial should be similar. Do you results from Part A support this?

4. Based on your results from Part C, how does the presence of a catalyst affect the values of the activation energy of this reaction?

5. What additional experiments could you perform to determine the value of the activation energy for the catalyzed reaction?

6. What is one difficulty you would face in performing the experiment you described in your answer to the previous question (Hint: THINK FAST!)? How might you attempt to overcome this difficulty?

7. From the $E_a$ and A you determined in this experiment, calculate the rate constant at 85°C?

8. Would your observed reaction rates for the experiment have changed if you had doubled the volume of each solution used in the experiment? Explain.

9. Consider the following graphs of $\ln k$ versus $1/T$ for reactions A, B, C, and D.

![Graphs of ln k versus 1/T for reactions A, B, C, and D](image)

Which reaction of the four (A, B, C, or D) would have the largest activation energy? Explain how you know your answer.

The Kinetics of the Iodine Clock Reaction
10. Consider the following reaction coordinate diagram:

![Reaction Coordinate Diagram]

a. Is A, B, C, or D the activation energy? Also, is this reaction exothermic or endothermic?

b. Sketch the above diagram in your notebook. Next to you sketch, draw and label what the diagram for a reaction that is faster and endothermic would look like.

11. The following rate data were collected for the reaction at 100 °C.

\[ 2\text{NO}_2 + \text{F}_2 \rightarrow 2\text{NOF}_2 \]

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[NO]</th>
<th>[F₂]</th>
<th>Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0480</td>
<td>0.0317</td>
<td>0.00190</td>
</tr>
<tr>
<td>2</td>
<td>0.0120</td>
<td>0.0317</td>
<td>0.000469</td>
</tr>
<tr>
<td>3</td>
<td>0.0480</td>
<td>0.127</td>
<td>0.00757</td>
</tr>
</tbody>
</table>

a. Determine the reaction order for NO and F₂.

b. Determine the overall order of the reaction.

c. Write the rate law for the reaction.

d. Using the data from experiment 3, calculate the value of the rate constant (k). Include units in your answer.

12. Suppose the rate law for a particular reaction between nitrogen dioxide and chlorine is

\[ \text{Rate} = k [\text{NO}_2]^2[\text{Cl}_2]. \]

How would each of the following affect the rate of the reaction?

a. If the concentration of NO₂ is doubled then the reaction rate would ____________________ by a factor of ______________.

b. The concentration of NO₂ and Cl₂ are both tripled, then the reaction rate would ____________________ by a factor of ______________.

c. The concentration of Cl₂ is halved, then the reaction rate would ____________________ by a factor of ______________.
Pre-Lab Questions

These questions should be answered in your notebook on a separate (new) sheet of paper. Be sure to show all work, round answers and include units.

1. A student mixed the following reactants, using the general procedure for the experiment: 10.0 mL of 0.10 M KI, 10.0 mL of 0.0010 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, 20.0 mL of 0.040 M KBrO<sub>3</sub>, and 10.0 mL of 0.10 M HCl. It took about 75 seconds for the mixture to turn blue.

   a. By using the dilution equation \((M_1V_1 = M_2V_2)\) calculate the concentrations of each reactant in the mixture after all of the solutions have been combined:

   \[
   [I^-] = \text{________} \quad [\text{BrO}_3^-] = \text{________} \quad [\text{H}^+] = \text{________}
   \]

   b. Recall the reactions for this lab:

   The one you are studying:

   \[
   6I^- (\text{aq}) + \text{BrO}_3^- (\text{aq}) + 6\text{H}^+ (\text{aq}) \rightarrow 3\text{I}_2 (\text{aq}) + \text{Br}^- (\text{aq}) + 3\text{H}_2\text{O} (\text{l}) \quad \text{(slow)} \quad \text{Equation 1}
   \]

   The one that delays the solution turning blue:

   \[
   \text{I}_2 (\text{aq}) + 2\text{S}_2\text{O}_3^{2-} (\text{aq}) \rightarrow 2\text{I}^- (\text{aq}) + \text{S}_4\text{O}_6^{2-} (\text{aq}) \quad \text{(fast)} \quad \text{Equation 2}
   \]

   Calculate the initial concentration of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> after all the solutions have been mixture together

   \[ [\text{S}_2\text{O}_3^{2-}]_{\text{initial}} = \]

   c. Recall that all the S<sub>2</sub>O<sub>3</sub><sup>2-</sup> is consumed when the color change occurs. Therefore,

   \[ \Delta [\text{S}_2\text{O}_3^{2-}] = \]

   d. Use the stoichiometry of Reactions 1 and 2 to determine the change in concentration of BrO<sub>3</sub><sup>-</sup> during the same time period. (see pg 5)

   \[ \Delta [\text{BrO}_3^-] = \]

   e. Assuming the reaction took 75 seconds, calculate the rate of the reaction \(\Delta [\text{BrO}_3^-]/\Delta t\).

   Rate of Reaction = \[\frac{\Delta [\text{BrO}_3^-]}{\Delta t} = \]

2. A student repeated the experiment mixed the following reactants 10.0 mL of 0.10 M KI, 10.0 mL of 0.0010 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, 10.0 mL of 0.040 M KBrO<sub>3</sub>, 10.0 mL of 0.10 M HCl and 10 mL of H<sub>2</sub>O. It took about 155 seconds for the mixture to turn blue.

   a. By using the dilution equation \((M_1V_1 = M_2V_2)\) calculate the concentrations of each reactant in the mixture after all of the solutions have been combined:

   \[
   [I^-] = \text{________} \quad [\text{BrO}_3^-] = \text{________} \quad [\text{H}^+] = \text{________}
   \]
b. Calculate the initial concentration of $S_2O_3^{2-}$ after all the solutions have been mixture together.

$$[S_2O_3^{2-}]_{\text{initial}} = \ldots$$

c. Recall that all the $S_2O_3^{2-}$ is consumed when the color change occurs. Therefore,

$$\Delta[S_2O_3^{2-}] = \ldots$$

d. Use the stoichiometry of Reactions 1 and 2 to determine the change in concentration of $BrO_3^-$ during the same time period. (see pg 6)

$$\Delta[BrO_3^-] = \ldots$$

e. Assuming the reaction took 155 seconds, calculate the rate of the reaction $\Delta [BrO_3^-]/\Delta t$.

$$\text{Rate of Reaction} = \frac{\Delta[BrO_3^-]}{\Delta t} = \ldots$$

f. Using the answers above for the rate of the reaction and the diluted concentration of $BrO_3^-$, determine the order of the reaction with respect to $BrO_3^-$. (called $y$ in the lab)

The reaction order with respect to $BrO_3^-$

$$y = \ldots$$ (two decimal places)  

$$y = \ldots$$ (rounded to closest integer)

3. Consider the following reaction $A + B \rightarrow \text{products}$. The rate law was found to be

$$\text{rate} = k[A][B]^2.$$ 

a. What is the order with respect to $A$?

b. What is the order with respect to $B$?

c. What is the overall order of the reaction?

d. If the concentration of $A$ is doubled while the concentration of $B$ is kept constant, how will this affect the rate of the reaction?

e. If the concentration of $B$ is doubled while the concentration of $A$ is kept constant, how will this affect the rate of the reaction?

f. If the concentration of $B$ is doubled while the concentration of $A$ is halved, how will this affect the rate of the reaction?

4. Why is it better to transfer one group of solutions into one flask and a second group of solutions into a second flask and then mixing them inset of pipetting the solutions sequentially into the same flask?

5. What safety precautions should you take during the experiment? Of the chemicals used in this experiment, which one may not be disposed of down the sink?