

Lab #11: Chemical Kinetics**Objectives:**

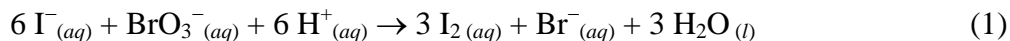
1. Determine the rate law of a chemical reaction.
2. Determine the activation energy of a chemical reaction.

Materials:

Beral (Micro) Pipets	0.010 M of potassium iodide (KI)
40 Micro Tubes (1.7 mL)	0.040 M of potassium bromate (KBrO ₃)
Micro Tubes Holder	Starch Solution (2%)
Electronic Balance	0.0010 M of sodium thiosulfate (Na ₂ S ₂ O ₃)
Watch Glass	0.10 M of hydrochloric acid (HCl)
Stopwatch	water (H ₂ O)
Thermometer	Bunsen Burner, Warm Water Bath, and Ice

Background Information:

In this experiment, we will study the kinetics of a chemical reaction. The reaction is called a “clock” reaction because of the means of observing the reaction rate. The reaction involves the oxidation (losing electrons) of iodide ion by bromate ion in the presence of an acid:



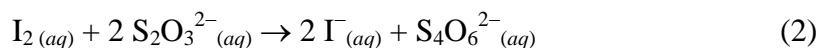
The reaction is somewhat slow at room temperature. Its rate depends on the concentration of the reactants and on the temperature. The rate law is a mathematical expression that relates the reaction rate to the concentrations of reactants. If we expressed the rate of reaction as the rate of decrease in concentration of bromate ion, the rate law has the form:

$$\text{Rate} = \frac{-\Delta[\text{BrO}_3^-]}{\Delta t} = k[\text{I}^-]^x[\text{BrO}_3^-]^y[\text{H}^+]^z$$

where the square brackets refer to the molar concentration of the indicated species. The rate is equal to the change in concentration of the bromate ion, $-\Delta[\text{BrO}_3^-]$, divided by the change in time for the reaction to occur, Δt . The term “ k ” is the rate constant for the equation, and changes as temperature changes. The exponents x , y , and z are called the “orders” of the reaction with respect to the indicated substance, and show how the concentration of each substance affects the rate of reaction.

One purpose of the experiment is to determine the total rate law for the process. To do this we must measure the rate, evaluate the rate constant, k , and determine the order of the reaction for each reactant, the values of x , y , and z . A second goal is to determine the activation energy for the reaction.

To find the rate of the reaction we need some way of measuring the rate at which one of the reactants is used up, or the rate at which one of the products is formed. The method that we will use is based on the rate at which iodine forms. If thiosulfate ions are added to the solution, they react with iodine as it forms in this way:



Reaction (1) is somewhat slow. Reaction (2) proceeds extremely rapidly, so that as quickly as iodine is produced in reaction (1), it is consumed in reaction (2). Reaction (2) continues until all of the thiosulfate is used up. This production of iodide ions keeps the starch indicator from turning dark blue, and the

colorless condition persists until all of the thiosulfate ions have reacted. Once all of the thiosulfate ions have reacted, more iodine is produced; and the starch indicator reacts and turns dark blue. Carrying out reaction (1) in the presence of thiosulfate ion and starch produces a chemical "clock". If an additional aliquot of thiosulfate ions is then added, the "clock" has been reset and the reaction can be timed again.

For each aliquot of thiosulfate ions added to the reaction, the number of moles of thiosulfate can be determined. From the stoichiometry of the reactions, the number of moles of bromate ions can be calculated. Knowing the $[\text{BrO}_3^-]$ and the time of the color change, we can calculate the rate of consumption of bromate ion.

In all of our reactions, we will use the same quantity of thiosulfate ion. The blue color appears when all the thiosulfate is used up. An examination of equations (1) and (2) shows that 6 moles of $\text{S}_2\text{O}_3^{2-}$ are needed to react with the I_2 formed from 1 mole of BrO_3^- . Knowing the amount of thiosulfate used allows the calculation of the amount of I_2 that is formed, and also the amount of BrO_3^- ion divided by the time it takes for the blue color to appear.

First, we have to determine the volume of a drop of solution. This must be done so that the number of moles of thiosulfate ion can be found, and so the amount of bromate ions that react can be calculated.

To find the order of the reaction for each reactants, and determine the rate constant. We will do this by carrying out an experiment at specific concentrations of each of the reactants by measuring the reaction rate. Then, we will change the concentration of one reactant and observe how the reaction rate changes. This will be repeated for all reactant. This data allows the calculation of the order of each reactant. Once the orders are known, the value of the rate constant can be calculated.

Next, we will study the relation between the rate of the reaction and temperature. Reaction rates always increase as temperature goes up. By measuring how the rate changes as the temperature is varied and we can determine the activation energy, E_a , for the reaction. The equation giving this relation is:

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

where $\ln k$ is the natural logarithm of the rate constant, E_a is the activation energy, R is the gas constant, $8.3145 \text{ J}/(\text{mol} \cdot \text{K})$ and T is the temperature on the Kelvin scale. A is a constant called the frequency factor which we will not need to determine.

This equation follows the straight-line relationship: $y = mx + b$. A plot of the natural logarithm of k versus $1/T$ will give a straight-line graph. The slope of the graph will be $-E_a/R$, and we will use the slope to determine the activation energy.

The experiment is designed so that the amounts of reactants that are consumed are small (microscale) in comparison with the total quantities present. Only 12 drops of reactants are delivered from the micro-pipets for each measurement. This means that the concentration of reactants is almost unchanged during the reaction, and therefore the reaction rate is almost a constant during this time.

Procedure:

Part 1: Calibrating the Volume of a Drop of Solution

1. Place a watch glass on a sensitive electronic balance and calibrate the balance to 0 g. Holding the Beral pipet vertically, deliver 10 drops of water on the watch glass, and record the mass.
2. Add an additional 5 drops of water, again record the mass for a total of 15 drops of water.

- Deliver 5 more drops and measure the mass again for a total of 20 drops of water.

Part 2: Determining the Rate Law and Rate Constant

- Using the following table, set up a series of micro tubes with the quantities indicated. Because we don't want the reaction to start until we are ready, **be sure that KBrO_3 solution is the last solution added**. It is important to use care in measuring out the solutions. Since the total solution volume is quite small, even one extra drop can cause a substantial change in concentrations.

(Last to add!)

Experiment Number	KI 0.010 M	H_2O	HCl 0.10 M	Starch 2%	$\text{Na}_2\text{S}_2\text{O}_3$ 0.0010 M	KBrO_3 0.040 M
1	2 drops	4 drops	2 drops	3 drop	1 drop	2 drops
2	4 drops	2 drops	2 drops	3 drop	1 drop	2 drops
3	6 drops	0 drop	2 drops	3 drop	1 drop	2 drops
4	2 drops	2 drops	2 drops	3 drop	1 drop	4 drops
5	2 drops	0 drop	2 drops	3 drop	1 drop	6 drops
6	2 drops	2 drops	4 drops	3 drop	1 drop	2 drops
7	2 drops	0 drop	6 drops	3 drop	1 drop	2 drops
8	3 drops	1 drop	3 drops	3 drop	1 drop	3 drops

- It is necessary to use consistently good technique to obtain reproducible data. Hold droppers vertically and be sure no air bubbles are introduced. Since such small quantities of reagents are used, it is very easy to repeat the measurements. Practice your technique by carrying out the first experiment at least three times (more, if necessary) until your values are reproducible, so be sure to get reproducible data from the beginning. All other experiments should be carried out at least twice.
- You may make a series of micro tubes ready with all reagents except the KBrO_3 . (If you are doing that, then be sure to set up a map indicating the experiment and trial numbers. Otherwise, label your micro tubes so they do not get mixed up.) Prepare a micro tube with the starch solution only. We will use this tube as a reference tube for the color change. (The color change may be subtle at first, so it is good to have a reference point to compare whether the solution has turned blue.)
- When you are ready to time the reaction, add the necessary amount of BrO_3 into the micro tube. Begin the timing with the stopwatch as soon as BrO_3 is added. Cap the micro tube and shake it a few times to ensure good mixing. Stop the stopwatch when the first sign of color change appears. Record the measurements.

Note: A study of the above table shows that all experiments contain the same total number of drops of solution. Only one drop of sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, and one drop of starch solution are added to each micro tube. In experiments 1, 2, and 3, the concentration of potassium iodide, KI, is gradually increased while all other volumes remain constant. Experiments 1, 4, and 5 have an increasing concentration of potassium bromate, KBrO_3 . Experiments 1, 6, and 7 show an increase in concentration of hydrochloric acid, HCl. **Experiment 8 will be a test to see if calculated orders of reactants agree with the experimental values from experiment 1 to 7.**

Part 3: Determining the Activation Energy

- Set up 15 micro tubes using the concentrations and volume outlined in Experiment 1 with the exception of KBrO_3 .
- Set up the Bunsen burner along with a ring stand, wire gauze, and a ring. Heat a small beaker of water to 40°C . Adjust the flame so the temperature of the water remains roughly at 40°C .

- Quickly add 2 drops of 0.040 M of KBrO_3 into a micro tube, capped and drop it into the warm water bath. Record the time it takes for the dark blue color to appear. Repeat this step for two more trials at 40°C .
- Remove the beaker from the Bunsen Burner and turn the gas off. Add a few ice cubes to the water bath. Wait until the temperature drops to about 30°C . Quickly add 2 drops of 0.040 M of KBrO_3 into a micro tube, capped and drop it into the beaker. Record the time it takes for the dark blue color to appear. Repeat this step for two more trials at 30°C .
- Add a few more ice cubes to the water bath. Wait until the temperature drops to about 20°C . Quickly add 2 drops of 0.040 M of KBrO_3 into a micro tube, capped and drop it into the beaker. Record the time it takes for the dark blue color to appear. Repeat this step for two more trials at 20°C .
- Repeat step 5 above with temperature around 10°C and near 0°C .

Observations:

Part 1: Calibrating the Volume of a Drop of Solution

Mass of 10 drops of water	
Mass of 15 drops of water	
Mass of 20 drops of water	

Part 2: Determining the Rate Law and Rate Constant

Experiment	Time (s)					Temperature ($^\circ\text{C}$)
	Trial 1	Trial 2	Trial 3	*Trial 4	*Trail 5	
1						
2						
3						
4						
5						
6						
7						
8						

* Trials 4 and 5 are optional to achieve consistent results

Part 3: Determining the Activation Energy

Measured Temperature ($^\circ\text{C}$)	Time of Reaction (s)		
	Trial 1	Trial 2	Trial 3
38.1	68	74	80
30.5	104	112	114
22.1	168	174	177
11.1	211	218	219
3.5	282	291	294

Analysis:**Part 1: Calibrating the Volume of a Drop of Solution**

1. Calculate the average mass of 1 drop of water for each measurement. Average the three averages into a final average of 1 drop of water for subsequent calculations.

	Average Mass of 1 drop of H ₂ O	Combined Average from 3 Measurements
Mass of 10 drops of H ₂ O		
Mass of 15 drops of H ₂ O		
Mass of 20 drops of H ₂ O		

Part 2: Determining *K* using Test Solutions

1. In each reaction, there is 1 drop of 0.0010 M Na₂S₂O₃ solution. Calculate the number of moles of Na₂S₂O₃ present in one drop. Show your work.
2. The dark blue color begins to appear when all thiosulfate ion is consumed. Examination of equations (1) and (2) allows us to calculate the moles of BrO₃⁻ which react as S₂O₃²⁻ ion is used up. Show your work.
3. Knowing the moles of BrO₃⁻, and that all experiments has a total volume of 14 drops, determine the -Δ[BrO₃⁻]. Show your work.
4. Calculate the rate of each experiment using -Δ[BrO₃⁻] found above and the average time for each experiment. Show all your work and summarize your results in Table 1.
5. Using the dilution formula, determine the initial concentrations of each reactant of each experiment, [I⁻], [BrO₃⁻] and [H⁺]. Show all your work. Record your result in Table 1.

Table 1: Reaction Rates and Initial Concentrations

Experiment	Average Time (s)	Temp (°C)	Reaction Rate (M/s)	Initial Concentrations, M		
				[I ⁻]	[BrO ₃ ⁻]	[H ⁺]
1						
2						
3						
4						
5						
6						
7						
8						

6. Next, we need to find the values for the exponents *x*, *y*, and *z*. The experiment is designed so that the concentration of one ion changes while the others remain constant. Comparing values in Experiments 1, 2 and 3, we see that Experiment 2 has twice the [I⁻] as Experiment 1, and Experiment 3 has 3 times the [I⁻] as Experiment 1. Use Experiments 1 and 2 to find *x*. Repeat the calculations using Experiments 1 and 3 to confirm your value of *x*. Show all your calculations.
7. Now, use the same procedure as above with Experiments 1, 4, and 5 to find the value of *y*. Lastly, use Experiments 1, 6, and 7 to find all value of *z*. Show how all your calculations are carried out.

- Substitute data from each experiment into the rate law equation to find the values of k with proper units. Average all 8 rate constants. Again, show all your work.
- Write the experimentally determined rate law.
- Experiment 8 is a check on your data. Substitute the concentrations of the reactants for this experiment into the rate law that you determined and calculate the value of the rate if reaction. Compare this calculated rate with the measured rate for Experiment 8 by finding their % difference.

Part 3: Determining the Activation Energy

- Fill in the Temperature (K) column in Table 2 and Table 3. Complete the Average Reaction Time (s) columns in Table 2 below.
- Using the $-\Delta[\text{BrO}_3^-]$ calculated in the previous section (Part 2: #3), and the average time for each temperature, determine their rates. Show all your work and summarize your results in Table 2.
- From the rate law determined in the last section, calculate the rate constant (with proper units) of the reaction at different temperature. Show all your work and summarize your results in Table 2 and Table 3.

$$\text{Rate} = \frac{-\Delta[\text{BrO}_3^-]}{\Delta t} = k[\text{I}^-]^x[\text{BrO}_3^-]^y[\text{H}^+]^z$$

Table 2: Reaction Rates and Rate Constant at Different Temperature

Measured Temperature (°C)	Temperature (K)	Average Reaction Time (s)	Rate of Reaction (M/s)	Rate Constant (k)
38.1				
30.5				
22.1				
11.1				
3.5				

- Calculate the $1/T$ and $\ln(k)$ and fill out Table 3.

Table 3: $1/T$ and $\ln(k)$ at Different Temperature

Temperature (K)	k	$1/T$ (K ⁻¹)	$\ln(k)$

- Graph $\ln(k)$ versus $(1/T)$. Find the linear regression equation and report the correlation coefficient (r). Include the graph in the lab report.
- Using the slope of the linear equation, determine the activation energy of this reaction.

Evaluation:

1. Why does reaction rate change as concentration changes?
2. Explain the procedure used to find the rate law.
3. Comment on the agreement between measured and calculated rates for Experiment 8.
4. Why does reaction rate change as temperature changes?
5. Explain the procedure used to determine the activation energy.
6. Differentiate between reaction rate and reaction rate constant.
7. How would you calculate the activation energy from any two points on the graph of $\ln(k)$ versus $(1/T)$?
8. Make a general statement about the consistency of your data as shown by calculating the orders of reactants, and by the graphical analysis that leads to activation energy. Were the calculated orders close to integers? Were the points on the graph of $\ln(k)$ versus $(1/T)$ close to a straight line?
9. Explain why iodine “clock” is important in this experiment.

Conclusion:

1. Summarize what you have learned from this lab.