

Prelab Assignment: Reaction Rates (A Clock Reaction)

1. A student in lab was studying the clock reaction. She prepared reaction mixture #2 by mixing 20. mL of 0.010 M KI, 10. mL of 0.0010 M $\text{Na}_2\text{S}_2\text{O}_3$, 10. mL 0.040 M KBrO_3 , and 10. mL of 0.10 M HCl as outlined in the experimental procedure. It took 43 seconds for the solution to turn blue.
 - a. She then calculated the concentration of each reactant in the reaction mixture. The number of moles for a reactant was the same before and after mixing but the concentration changed since the reactants were diluted by the mixing of the solutions.

$$M_1V_1 = M_2V_2$$

The above equation was used to find the concentration of each reactant.

$$[\text{I}^-] = \text{_____ M}; [\text{BrO}_3^-] = \text{_____ M}; [\text{H}^+] = \text{_____ M}$$

- b. What was the relative rate of the reaction ($1000/t$)? _____
- c. Knowing the relative rate for the reaction mixture 2 and the molarities of I^- , BrO_3^- , and H^+ in the mixture the student used equation #5 to show the relative rate of the reaction. Only k' , m , n , and p remained unknown. Using equation #5 show the relative rate for the reaction.
- d. The student found that Reaction Mixture #1 took 90 seconds to turn blue. On dividing Equation 5 for Reaction Mixture 1 by equation 5 for Reaction Mixture 2, and canceling out all common terms (k' , $[\text{BrO}_3^-]$, and $[\text{H}^+]$), the following equation was obtained.

$$\frac{11}{24} = \left(\frac{0.0020}{0.0040} \right)^m = \left(\frac{1}{2} \right)^m$$

Recognizing that $11/24$ is approximately equal to $1/2$, she obtained an approximate value for m . What is the **approximate value** for m ? _____

By taking the logarithms of both sides of the equation, she got an **exact value** for m . What is the exact value for m ? _____

Since orders of reactants are frequently integers, the approximate value of I^- was used in reporting the order with respect to I^- . _____

Reaction Rates and Activation Energy

Note: All data tables should be copied into your laboratory notebook.

Introduction

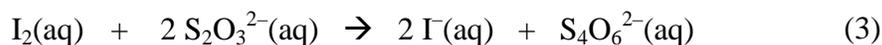
The purpose of this experiment is to study the rate properties of the following reaction:



Its rate law can be written as:

$$\text{Rate} = k[\text{I}^{-}]^m[\text{BrO}_3^{-}]^n[\text{H}^{+}]^p \quad (2)$$

The values of the rate constant, k , and reaction orders, m , n , p , will be calculated from measurements using the “clock” reaction:



Reaction (3) occurs simultaneously with reaction (1), but is much faster, almost instantaneous, compared to reaction (1). Therefore the I_2 produced in (1) is immediately removed by reaction with the thiosulfate, $\text{S}_2\text{O}_3^{2-}$, reaction (3), and the time required for a constant amount of $\text{S}_2\text{O}_3^{2-}$ to react with the iodine, can be used as a measure of the rate of the reaction which produces the iodine, reaction (1). As soon as all of the $\text{S}_2\text{O}_3^{2-}$ has reacted, the I_2 concentration increases in solution and the starch indicator produces a blue color. In all trials, the amount of $\text{S}_2\text{O}_3^{2-}$ is kept constant and small compared to the amounts of other reactants. Therefore only relatively very small amounts of the reactants of (1) are used up before the solution becomes blue, and the initial concentrations are used for calculations of the rate constant and the rate orders using equation (2).

In the first part of the experiment, the trials are carried out at constant temperature (room temperature), varying the concentrations of the reagents of reaction (1). From these values the rate orders and the rate constant is calculated. In the second part, the concentrations of reagents are kept constant, but measurements are made at various temperatures. Arrhenius equation gives:

$$\ln k = -\mathcal{E}_a/RT + \text{constant} \quad (4)$$

where T = temperature in Kelvin, R = the ideal gas constant, and \mathcal{E}_a is the activation energy. Because the concentrations of all reactants are essentially constant, the rate of the reaction is proportional to the rate constant and the measured relative rate can be used in a modified Arrhenius equation:

$$\ln (\text{relative rate}) = -\mathcal{E}_a/RT + \text{constant}$$

The value of the activation energy, \mathcal{E}_a , will be calculated from the slope of the graph of $\ln (\text{relative rate})$ vs $1/T$.

Experimental Procedure:

Part A:

Determination of the Rate Law – Dependence of Reaction Rate on Concentration

Equipment needed:

one 10-mL volumetric pipet (V-pipet)
two 10-mL graduated pipets (G-pipets)*
two thermometers
two graduated cylinders

**Note: When using graduated pipets fill to the 0mL mark, allow to drain to the final volume mark - do NOT drain completely.*

Reagents:

Obtain about 100 mL of each of the reagents mentioned below in a clean, dry, labeled beaker or flask. The reagent volumes to be used for each trial are shown in the table below. Use the G-pipets to measure KBrO_3 and HCl solutions, the V-pipet to measure the $\text{S}_2\text{O}_3^{2-}$ solution, graduated cylinders to measure the KI solution and water.

The reagent volumes are given in the mL.

Reaction Mixture	Reaction Flask I (250-mL Erlenmeyer)			Reaction Flask II (125-mL Erlenmeyer)	
	0.010 M KI	0.0010 M $\text{Na}_2\text{S}_2\text{O}_3$	H_2O	0.040 M KBrO_3	0.10 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	15

For each trial, mix the indicated reagent volumes as follows: place the required amounts of KI and $\text{Na}_2\text{S}_2\text{O}_3$ solutions, and water into a 250-mL Erlenmeyer flask (Reaction Flask I). Place the corresponding amounts of KBrO_3 and HCl solutions into a 125-mL Erlenmeyer flask (Reaction Flask II). Add about ten drops of starch indicator to Flask II.

When you are prepared to start timing the reaction, pour the contents of Flask II into Flask I. Swirl to mix the solutions thoroughly. Record the time required for the blue color to appear in seconds. For Reaction Mixture I at room temperature, this time should be in the range from 90 seconds to 150 seconds. Record also the temperature of the final blue solution.

Discard the blue solution and rinse Flasks I and II. Repeat the procedure for the next trials. If time permits after completing these five trials and Part B of the experiment, you may repeat any of the measurements, but check that the temperature is the same for the whole set of Part A to within 0.5°C.

Part B:

Determination of the Activation Energy – Dependence of the Reaction Rate on Temperature

In this part of the experiment, Reaction Mixture I will be used for all trials and the reaction rate will be measured at three temperatures other than the room temperature.

Prepare solutions in Flask I and II for Reaction Mixture I as for Part A of the experiment, but before mixing the contents of Flasks I and II, they need to be warmed or cooled to the required temperature. Use the water baths available in the lab to cool Flask I and II to about 5°C. Check, using your thermometer, that both solutions are at about 5°C, record the exact temperature, then mix the two solutions as before, swirl and keep the flask with the reactants in the 5°C water bath. Measure the time needed for the blue color to appear. This will take considerably longer than at room temperature. Record the temperature of the blue solution.

Discard the blue solution, rinse the flasks, and repeat the trial using the 35°C and then the 45°C water baths. Use the time measured in Part A of the experiment for calculations at about 25°C. In the calculations, use the actual temperature measured.

Results and Calculations

A. Rate Constant and Order of the Reaction – the Rate Law

In all the reaction mixtures used in this experiment, the color change occurs when a constant amount of thiosulfate, $S_2O_3^{2-}$, had reacted with the I_2 produced by the slow reaction (1). After that, the I_2 concentration increased and changed the color of the starch indicator to blue. The amount of I_2 produced by reaction (1) is proportional to the amount of BrO_3^- consumed, thus, t , the time measured, is the time required for a fixed number of moles of BrO_3^- to react.

$$\text{The rate of reaction (1)} = k[I^-]^m[BrO_3^-]^n[H^+]^p = -\Delta[BrO_3^-] / t$$

Where t is the time required for the blue color to appear. In the following calculations only the relative rate values are required, therefore $1000/t$ will be used as a convenient relative rate value. Equation (2) then becomes

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

Where k' is the relative rate constant.

Complete the following table.

Reaction Mixture	Time t (sec)	Relative rate of Reaction $1000/t$	Reactant Concentrations (mol/L)			Temp. in $^{\circ}C$
			$[I^-]$	$[BrO_3^-]$	$[H^+]$	
1			0.0020			
2						
3						
4						
5						

Note that the reactant concentrations in the Reaction Mixtures are not the same as the initial concentrations of the stock solutions because all have been diluted by the presence of other solutions. All final volumes of the Reaction Mixtures are 50.0 mL. The actual reactant concentrations must be calculated as follows, for example, for the I^- ion.

$$[I^-]_{\text{stock}} \times V_{\text{stock}} = [I^-]_{\text{mixture}} \times V_{\text{mixture}}$$

where $V_{\text{mixture}} = 50.0$ mL for all mixtures, for Reaction Mixture 1, $[I^-]_{\text{stock}} = 0.010$ mol/L, $V_{\text{stock}} = 10.0$ mL.

Therefore,

$$M_{\text{mixture}} = 0.010 \text{ mol/L} \times 10.0 \text{ mL}/50.0 \text{ mL} = 0.0020 \text{ mol/L}$$

As shown for Reaction Mixture 1 in the table.

Calculate the rest of the reactant concentrations to complete the table.

To obtain the values of m , n , and p , the orders of the reactants, use the ratios of the measured relative rates in such a way that the concentrations of some reactants cancel out and the required values are obtained from equations which only have one unknown value.

Substitute the relative rate and concentration values of Reaction Mixtures 1 and 2 from the table into equation (5).

$$\text{Relative rate 1} = \text{_____} = k'(\text{_____})^m(\text{_____})^n(\text{_____})^p$$

$$\text{Relative rate 2} = \text{_____} = k'(\text{_____})^m(\text{_____})^n(\text{_____})^p$$

Divide the first equation by the second to obtain

$$\frac{\text{Relative rate 1}}{\text{Relative rate 2}} =$$

Calculate the value of m to three figures, then round it to the nearest integer value:

$$m = \text{_____}, \text{ nearest integer} = \text{___}$$

Similarly calculate the value of n from the results of Reaction Mixtures 1 and 3,

$$n = \text{_____}, \text{ nearest integer} = \text{___}$$

and value of p from the results of Reaction Mixtures 1 and 4.

$$p = \text{_____}, \text{ nearest integer} = \text{___}$$

Using the integer values of m , n , and p and equation (5), calculate the relative rate constant, k' , for Reaction Mixtures 1 to 4.

Reaction Mixture	1	2	3	4
k'	_____	_____	_____	_____

$$k'_{\text{average}} \text{ _____}$$

Why should the k' values calculated above be nearly constant? (*answer this question in your lab notebook*)

Using the k'_{average} value in equation (5), predict the relative rate and the time t for Reaction Mixture 5. Use the concentration values in the table. Compare the predicted and actually observed times.

Relative rate_{predicted} _____ $t_{\text{predicted}}$ _____ t_{observed} _____

Write the Rate law as you have determined it to be for reaction (1) in your laboratory notebook.

Part B:

Activation Energy – the Effect of Temperature on the Reaction Rate

For the relative rate constant, k' , Arrhenius equation (4) becomes

$$\ln k' = -\mathcal{E}_a/RT + \text{constant} \quad (6)$$

Because all trials for this part of the experiment used the same reactant concentrations (Reaction Mixture 1), according to equation (5), k' is proportional to the relative rate and equation (6) becomes

$$\ln(\text{relative rate}) = -\mathcal{E}_a/RT + \text{constant} \quad (7)$$

Equation (7) shows that a plot of $\ln(\text{relative rate})$ vs $1/T$ is expected to be a straight line with

$$\text{slope} = -\mathcal{E}_a/R \quad (8)$$

The ideal gas constant, R , is 8.314 joules/mol-K.

Complete the following table.

Temp. of Reaction Mixture, ($^{\circ}\text{C}$)	Temp. T of Reaction mixture, (K)	$1/T$ (K^{-1})	Time t (sec)	Relative rate $\text{RR} = 1000/t$	$\ln(\text{RR})$

Plot a graph of $\ln(\text{RR})$ vs $1/T$.

Draw the best average straight line through the experimental points.

Calculate the slope of the straight line,

slope = _____

Calculate the Activation Energy for the reaction from equation (8),

Activation energy, \mathcal{E}_a , = _____

Reaction Rates and Activation Energy Notes

Reaction Flask #1 (250-mL Erlenmeyer)		Reaction Flask #2 (125-mL Erlenmeyer)	
	<i>add using a</i>		<i>add using a</i>
0.010M KI	graduated cylinder	0.040M BrO ₃ ⁻	graduated pipet
0.0010M S ₂ O ₃ ²⁻	volumetric pipet	0.10M HCl	graduated pipet
H ₂ O	graduated cylinder	10 drops starch	bottle dropper

Record the temperature of the solutions. For Part 1 the temperature should remain within a 0.5°C range.

Add Flask #2 → Flask #1
Count the seconds until the solution turns blue

For part 1 you will calculate:

- the **orders** with respect to I⁻, BrO₃⁻, and H⁺.
- the **rate constant, k**, from run 1, 2, 3, 4, and the average rate constant
- the **rate law**
- then, using the average k, predict the **relative rate** and **time** for run #5

Part #2 Temperature runs

- For all runs use **Reaction Mixture #1**
- You can use your results from **run 1** in Part #1 for the room temperature data.
- The solutions in flask #1 and flask #2 must reach the temperature of the water bath before mixing. Keep the mixture in the water bath until the solution turns blue.
- The temperature of the run is the temperature of the water bath.
- For the cold temperature bath record the time when the solution *first* turns blue (This will be a light color blue initially).

In part #2 you will plot ln(RR) versus 1/T(K). From the slope you will calculate the **activation energy**.

Reaction Rates and Equilibrium Constant

Laboratory Preparation Instructions

Equipment needed by each pair of students: (Typically 16 sets)

- 1) One 10-mL volumetric pipets
- 2) Two 10-mL graduated pipets
- 3) One pipette pump, or pipette bulb
- 4) Two thermometers
- 5) One stop watch
- 6) Two 10-mL graduated cylinders

Class reagents or general supply: (*divide all solutions equally into four sets - one per table*)

- 1) 3-L 0.010M KI
- 2) 3.0-L 0.0010 M $\text{Na}_2\text{S}_2\text{O}_3$
- 3) 3.0-L 0.040 M KBrO_3
- 4) 4.0-L 0.10 M HCl
- 5) carboy of DW
- 6) starch indicator
(4 dropper bottles with 100 mL in each)

Special requirements:

- 1) On the previous day of the experiment mixture #1 must be tested and the concentration of HCl adjusted so that the time for mixture #1 is between 90 and 110 seconds.