# Prelab Assignment: Reaction Rates (A Clock Reaction)

Watch this YouTube Video: <https://www.youtube.com/watch?v=qT5xwZgMIEw>

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 Na2S2O3, 10. mL 0.040 M KBrO3, and 10. mL of 0.10 M HCl as outlined in the experimental procedure. It took 43 seconds for the solution to turn blue.
   1. 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.

**M1V1 = M2V2**

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

[I–] = \_\_\_\_\_\_\_\_\_M; [BrO3–] = \_\_\_\_\_\_\_\_\_ M; [H+] = \_\_\_\_\_\_\_\_\_\_ M

* 1. What was the relative rate of the reaction (1000/t)? \_\_\_\_\_\_\_\_\_\_\_
  2. Knowing the relative rate for the reaction mixture 2 and the molarities

of I–, BrO3–, 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.

* 1. 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’*, [BrO3–], and [H+]), the

following equation was obtained.



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

**Introduction**

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

6I–(aq) + BrO3–(aq) + 6 H+(aq) 🡪 3 I2(aq) + Br–(aq) + 3 H2O(*l*) (1)

Its rate law can be written as:

Rate = *k*[I–]*m*[BrO3–]*n*[H+]*p*

(2)

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

(3)

I2(aq) + 2 S2O32–(aq) 🡪 2 I–(aq) + S4O62–(aq)

Reaction (3) occurs simultaneously with reaction (1), but is much faster, almost instantaneous, compared to reaction (1). Therefore the I2 produced in (1) is immediately removed by reaction with the thiosulfate, S2O32–, reaction (3), and the time required for a constant amount of S2O32– 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 S2O32– has reacted, the I2 concentration increases in solution and the starch indicator produces a blue color. In all trials, the amount of S2O32– 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:

(4)

ln k = –**Ea**/RT + constant

where T = temperature in Kelvin, R = the ideal gas constant, and Ea 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 (relative rate) = – **Ea**/RT + constant

The value of the activation energy, Ea, will be calculated from the slope of the graph of ln (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.*

**Regents:**

Obtain about 100 mL of each of the reagents mentioned below in a clean, dry, labeled beaker or flask. The regent volumes to be used for each trial are shown in the table below. Use the G-pipets to measure KBrO3 and HCl solutions, the V-pipet to measure the S2O32– solution, graduated cylinders to measure the KI solution and water.

The regent 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  Na2S2O3 | H2O | 0.040 M  KBrO3 | 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 regent volumes as follows: place the required amounts of KI and Na2S2O3 solutions, and water into a 250-mL Erlenmeyer flask (Reaction Flask I). Place the corresponding amounts of KBrO3 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 0.5oC.

**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 5oC. Check, using your thermometer, that both solutions are at about 5oC, record the exact temperature, then mix the two solutions as before, swirl and keep the flask with the reactants in the 5oC 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 35oC and then the 45oC water baths. Use the time measured in Part A of the experiment for calculations at about 25oC. 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, S2O32–, had reacted with the I2 produced by the slow reaction (1). After that, the I2 concentration increased and changed the color of the starch indicator to blue. The amount of I2 produced by reaction (1) is proportional to the amount of BrO3– consumed, thus, t, the time measured, is the time required for a fixed number of moles of BrO3– to react.

The rate of reaction (1) = *k*[I–]*m*[BrO3–]*n*[H+]*p* = –[BrO3–] / 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

(5)

Relative rate = *k’*[I–]*m*[BrO3–]*n*[H+]*p*

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 oC |
| [I–] | [BrO3–] | [H+] |
| 1 | 91 |  | 0.0020 |  |  | 24.0 |
| 2 | 42 |  |  |  |  | 24.0 |
| 3 | 48 |  |  |  |  | 24.0 |
| 4 | 22 |  |  |  |  | 24.0 |
| 5 | 87 |  |  |  |  | 24.0 |

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–]stock x Vstock = [I–]mixture x Vmixture

where Vmixture = 50.0 mL for all mixtures, for Reaction Mixture 1, [I–]stock = 0.010 mol/L, Vstock = 10.0 mL.

Therefore,

(sample calculation of [I-]) Mmixture = 0.010 mol/L x 10.0 mL/50.0 mL = 0.0020 mol/L

**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).

Relative rate 1 = \_\_\_\_\_\_\_\_\_\_ = *k’*( )*m*( )*n*( )*p*

Relative rate 2 = \_\_\_\_\_\_\_\_\_\_ = *k’*( )*m*( )*n*( )*p*

Divide the first equation by the second to obtain

Relative rate 1 =

Relative rate 2

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

*m* = \_\_\_\_\_\_\_\_\_\_\_\_\_, nearest integer = \_\_\_

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

*n* = \_\_\_\_\_\_\_\_\_\_\_\_\_, nearest integer = \_\_\_

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

*p* = \_\_\_\_\_\_\_\_\_\_\_\_\_, nearest integer = \_\_\_

**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’average*  \_\_\_\_\_\_\_\_\_\_

**Why should the *k’* values calculated above be nearly constant?**

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 ratepredicted \_\_\_\_\_\_\_\_\_\_\_\_ tpredicted \_\_\_\_\_\_\_\_\_\_\_ tobserved \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

**Write the Rate law as you have determined it to be for reaction (1) below:**

**Part B:**

**Activation Energy – the Effect of Temperature on the Reaction Rate**

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

(6)

ln *k’* = – **Ea**/RT + constant

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

(7)

ln (relative rate) = – **Ea**/RT + constant

Equation (7) shows that a plot of ln(relative rate) *vs* 1/T is expected to be a straight line with

slope = – **Ea**/R

(8)

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

Complete the following table.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Temp. of  Reaction  Mixture, (oC) | Temp. T of  Reaction  mixture, (K) | 1/T (K–1) | Time t  (sec) | Relative rate  RR = 1000/t | ln (RR) |
| 35.0 |  |  | 42 |  |  |
| 45.0 |  |  | 25 |  |  |
| 5.0 |  |  | 272 |  |  |
| 24.0 |  |  | 91 |  |  |

Plot a graph of ln(RR) *vs* 1/T using excel. Insert the graph into this document.

Use excel to calculate the trendline (linear) and the slope.

slope = \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

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

Activation energy, **Ea**, = \_\_\_\_\_\_\_\_\_\_\_

Reaction Rates and Activation Energy Summary

|  |  |  |  |
| --- | --- | --- | --- |
| **Reaction Flask #1** (250-mL Erlenmeyer) | | **Reaction Flask #2** (125-mL Erlenmeyer) | |
|  | ***add using a*** |  | ***add using a*** |
| 0.010M KI | graduated cylinder | 0.040M BrO3– | graduated pipet |
| 0.0010M S2O32- | volumetric pipet | 0.10M HCl | graduated pipet |
| H2O | graduated cylinder | 10 drops starch | bottle dropper |

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

**Add Flask #2 🡪 Flask #1**

**Count the seconds until the solution turns blue**

# For part 1 you will calculate:

a. the **orders** with respect to I–, BrO3–, and H+.

b. the **rate constant, k**, from run 1, 2, 3, 4, and the average rate constant

c. the **rate law**

d. then, using the average k, predict the **relative rate** and **time** for run #5

e. compare the calculated and actual time – determine the % difference

# Part #2 Temperature runs

1. For all runs use **Reaction Mixture #1**

2. You can use your results from **run 1** in Part #1 for the room temperature data.

3. 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.

4. The temperature of the run is the temperature of the water bath.

5. 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**.