

Name: _____ Section _____

Chemistry 118 Laboratory
University of Massachusetts Boston

IODINE CLOCK REACTION KINETICS

LEARNING GOALS

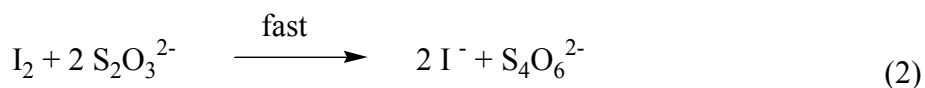
1. Investigate the effect of reactant concentration on the rate of a chemical reaction.
2. Investigate the effect of temperature on the rate of a chemical reaction.
3. Become familiar with manipulating rate equations.
4. Become familiar with applying and using the Arrhenius Equation.
5. Become familiar with linearizing exponential functions.
6. Become adept at graphing using Excel.

INTRODUCTION

In this experiment we will investigate the kinetics of the oxidation of iodide ion (I^-) to molecular iodine (I_2) by hydrogen peroxide (H_2O_2):



As this reaction proceeds, the colorless reactants gradually develop a brown color due to the product I_2 . Because of the difficulty of timing the appearance of the I_2 , we make use of another much faster reaction in the same solution to mark the progress of the slow reaction:



The reaction

Reaction 2 is so fast that I_2 produced by reaction 1 is consumed instantaneously by the thiosulfate ($S_2O_3^{2-}$), so that the I_2 color cannot develop. Because both $S_2O_3^{2-}$ and $S_4O_6^{2-}$ are colorless, the solution remains colorless. The goal is to measure the initial rate in which hydrogen peroxide reacts as a function of the initial hydrogen peroxide concentration and the reaction temperature. Therefore, we will only add enough thiosulfate to react less than 20 % of the I_2 produced from reaction 1. The reaction solution will stay colorless until the instant at which all the thiosulfate is consumed, and free I_2 begins to appear. We time the reaction from the initial mixing until the appearance of I_2 . In order to help see this appearance we add starch indicator which forms an intensely colored dark complex with I_2 and signals the appearance of I_2 by a dramatic color change. Since at this point, only a fraction of the hydrogen peroxide has reacted, we can use the time interval between the start of the reaction and appearance of the color to measure the initial reaction rate.

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The rate law

The general rate expression for this reaction is

$$\text{Rate (M/s)} = k[\text{H}_2\text{O}_2]^x[\text{H}^+]^y[\text{I}^-]^z$$

The initial rate of the reaction can be expressed in terms of the initial concentrations of the reactants.

$$\text{Rate}_i = k[\text{H}_2\text{O}_2]_i^x[\text{H}^+]_i^y[\text{I}^-]_i^z$$

In this experiment, we will find x by varying the concentration of $[\text{H}_2\text{O}_2]_i$ while holding $[\text{H}^+]_i$ and $[\text{I}^-]_i$ constant.

Because $[\text{H}^+]_i$ and $[\text{I}^-]_i$ are held constant in this experiment, $[\text{H}^+]_i^y$ and $[\text{I}^-]_i^z$ can be combined with k to conditional rate constant, k' , which is often referred to as a pseudo-first rate constant.

$$k' = k[\text{H}^+]_i^y[\text{I}^-]_i^z$$

Rate law written in terms of k'

$$\text{Rate}_i = k'[\text{H}_2\text{O}_2]_i^x$$

By measuring the initial rate at three different hydrogen peroxide concentrations ($[\text{H}_2\text{O}_2]_i$) we can determine the order in $[\text{H}_2\text{O}_2]$ (x) and calculate the pseudo-first order rate constant (k'). Perhaps the easiest way to determine x is to assume it is either 0, 1 or 2, calculate k' for each trial in each case ($x = 0, 1$ or 2) and examine which case gives the smallest standard deviation (ie. For which case is k' constant). Another strategy could be linearize the rate equation by taking the log of both sides.

$$\log\{\text{Rate (M/s)}\}_i = \log k' + x \log[\text{H}_2\text{O}_2]_i$$

If one plots $\log \text{Rate}_i$ (y variable) as a function of $\log[\text{H}_2\text{O}_2]_i$ (x variable), the slope of the line is equal to x .

The Arrhenius equation

The rate of any chemical reaction increases with increasing temperature. This relationship is generally expressed in the form of the Arrhenius Equation, k' is the rate constant, T is the temperature (K), R is the gas constant (8.314 J/Kmol), E_a is the activation energy (J/mol), and A is called frequency factor.

$$\ln k' = \ln A - E_a/R(1/T)$$

A plot of $\ln k'$ (y variable) as a function of $1/T$ (x variable) gives a slope that is equal to $-E_a/R$. Such a plot can be used to estimate the activation energy for a reaction.

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LABORATORY PROCEDURE

- Thoroughly clean and label glassware as follows:
Two 125 mL Erlenmeyer flasks, both labeled “A reaction Mixture”
Two small beakers, both labeled “B Peroxide”
Two small beakers, both labeled “C Thiosulfate”
One 25 or 50 mL graduated cylinder for water

Here is a summary of the setups for the five runs. Instructions for each are given below.

	Run 1	Run 2	Run 3	Run 4	Run 5
0.10 M HI into flask A, mL	50	50	50	50	50
0.20 M H ₂ O ₂ into beaker B, mL	20	30	40	30	30
Deionized water into beaker B, mL	20	10	0	10	10
0.15 M S ₂ O ₃ ²⁻ into beaker C, mL	10	10	10	10	10
Starch into beaker C, drops	2	2	2	2	2
Temperature	room	room	room	hot	cold

In order to avoid contaminating reagents use only the graduated cylinder placed near each reagent bottle to measure that reagent. Leave those cylinders in place.

PRELUDE TO RUN 5

- Set up an ice bath.
- Dispense reagents into one set of glassware A, B, and C as shown above for Run 5. Set these in the ice bath for later use.

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RUN 1

- Dispense reagents for Run 1 into another set of glassware.
- Have a clock or watch with a second hand ready. Then in quick succession:
 - Add the contents of both beakers B and C into flask A.
 - Swirl the mixture in A.
 - Start timing as soon as beaker B is emptied. This is time t_i .
- Place a thermometer in flask A but DO NOT STIR WITH IT.
- Swirl occasionally, and perhaps two minutes or more later the reaction mixture will suddenly turn dark. Note the time as the final time t_f . Record the temperature and the time interval $\Delta t = t_f - t_i$ in seconds.

RUN 2

- Thoroughly rinse flask A just used, and then dispense reagents.
- Follow the procedure for Run 1. This one is faster.

RUN 3

- Thoroughly rinse flask A, and then dispense reagents.
- Follow the procedure for Run 1. This is even faster than 2.

RUN 4

- Thoroughly rinse flask A, and dispense reagents.
- Place flask A and beaker C (but not B) on a hot plate and warm these up to between 45 °C and 50 °C. Use a thermometer to monitor the temperature in flask A only.
- When flask A is over 45 °C, remove both from the hot plate. Mix B and C into A and swirl.
- Leave the thermometer in the reaction mixture and record the temperature when the color turns. This one is very fast.

RUN 5

The temperature of solution A in the ice bath should be below 10 °C.

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- Leave flask A in the ice bath. Pour beakers B and C into A. Swirl to mix. Note the temperature.
- Swirl flask A from time to time while the reaction is proceeding. Record the time when the color turns. This one is very slow.
- If the final temperature is different than the initial temperature, record the average.

On the data sheet, fill in the following quantities in the table for each of the five runs:

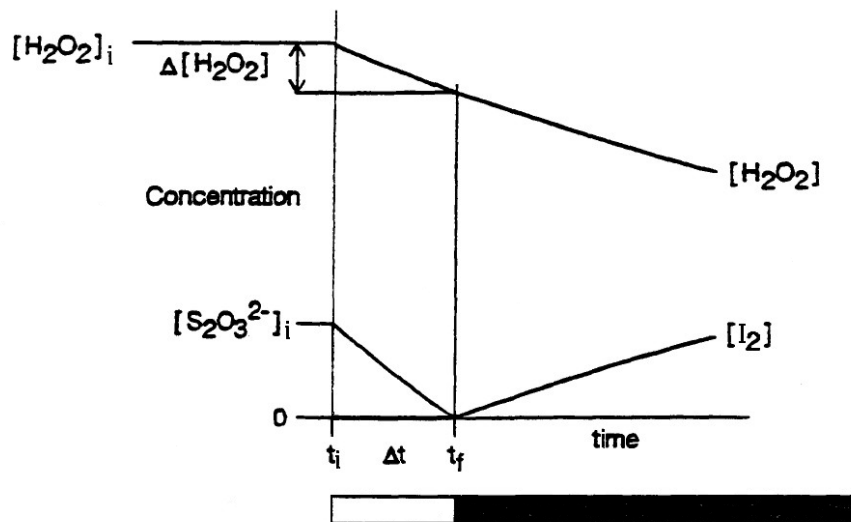
Row 1: Δt is your measured time interval in seconds.

Row 2: Temp, $^{\circ}\text{C}$ is the temperature of the reaction mixture.

Row 3: $[\text{H}_2\text{O}_2]_i$ is the H_2O_2 molarity in flask A at time t_i .
Calculate the total volume ignoring the 2 drops of starch.

Row 4: $[\text{S}_2\text{O}_3^{2-}]_i$ is the thiosulfate molarity in flask A at time t_i .

Row 5: $\Delta[\text{H}_2\text{O}_2]$ is the change in peroxide concentration during Δt .
This calculation is illustrated below.



Between t_i and t_f the following changes occur:

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- Thiosulfate molarity drops from $[S_2O_3^{2-}]_i$ to zero.
- The I_2 moles per liter consumed is $[S_2O_3^{2-}]_i/2$ (see the balancing coefficients in Reaction 2).
- The I_2 consumed in Reaction 2 is produced in Reaction 1.
- For each I_2 mole produced, a mole of H_2O_2 is consumed (see balancing coefficients in Reaction 1).
- Thus the H_2O_2 loss, $\Delta[H_2O_2]$, is $[S_2O_3^{2-}]_i/2$.

Row 6: $Rate_i$ is the initial rate of the reaction: $\Delta[H_2O_2]/\Delta t$

Row 7, 8 and 9:

Use the initial rate and $[H_2O_2]_i$ to calculate a k' value assuming the order, $x = 0, 1,$ or 2

$$k' = Rate_i / [H_2O_2]_i$$

Row 10:

Determine the order in H_2O_2 by examining the calculated k' 's calculated in row 7, 8 and 9 for the first three trials.

Row 11 Calculate $\ln k'$.

Row 12: Calculate $1/T$ from the temperature. T is the absolute temperature in Kelvin, where $T (K) = T (^{\circ}C) + 273.15$.

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	Run 1	Run 2	Run 3	Run 4	Run 5
1. t , seconds					
2. Temp, °C					
3. $[\text{H}_2\text{O}_2]_i$, M					
4. $[\text{S}_3\text{O}_3^{2-}]_l$, M					
5. $\Delta[\text{H}_2\text{O}_2]$, M					
6. Rate_i , M/s					
7. k , s^{-1} with $x = 0$					
8. k , s^{-1} with $x = 1$					
9. k , s^{-1} with $x = 2$					
10. order in H_2O_2					
11. $\ln k$					
12. $1/T$, K^{-1}					

- Use Excel to make a plot of $\log \text{Rate}_i$ vs. $\log[\text{H}_2\text{O}_2]_i$ from runs 1, 2 and 3.
- Use Excel to determine the slope of this plot _____
- Determine the rate order of H_2O_2 for this reaction using the slope
 $n =$ _____

Use Excel to make a plot of $\ln k'$ vs. $1/T$ from runs 1-5.

- Use Excel to determine the slope of this plot _____
- Calculate E_a from your slope.

The activation energy E_a is _____ Provide units to go along with this number

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Lab Report

No abstract is due for this report. You need to submit your data sheet (pg 7), two Excel plots and answer the following questions. Your data sheet is worth 30 points.

1. Determine the order of the reaction with respect to $[\text{H}_2\text{O}_2]$ by plotting the $\log \text{Rate}_i$ vs. $\log[\text{H}_2\text{O}_2]_i$ and obtaining the slope of the line using Excel with the data from Runs 1-3. (5 pts for plot, 5 pts for determining the order)
2. Determine the activation energy of the reaction by plotting the $\ln k'$ vs. $1/T$ and obtaining the slope of the line using Excel with the data from runs 1-5. (5 pts for plot, 5 pts for determining the order)
3. Discuss the whether you obtained results (for the reaction order and the relationship between the rate constant and the temperature) consistent with expectations. (10 points)