

Rate Properties of an Iodide Oxidation Reaction (an “Iodine Clock” Reaction)

Goal and Overview

The rate law for the reduction reaction of peroxodisulfate (PODS) by iodide, $\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2 \text{I}^-(\text{aq}) \rightarrow \text{I}_2(\text{aq}) + 2 \text{SO}_4^{2-}(\text{aq})$, will be determined at room temperature. The reaction orders with respect to PODS and to I^- will be found by measuring rates for various concentrations of the reactants. Rates will also be measured at three additional temperatures, such that the Arrhenius equation can be used to calculate the activation energy and the pre-exponential factor for the reaction.

Objectives and Science Skills

Understand and explain common factors that influence the rates of chemical reactions. Apply linear fitting methods to find relationships between dependent and independent variables.

Quantitatively and qualitatively evaluate experimental data to determine the reaction orders, rate constant, Arrhenius factor, and activation energy of an iodine clock reaction. Identify and discuss factors or effects that may contribute to deviations between theoretical and experimental results and formulate optimization strategies.

Suggested Review and External Reading

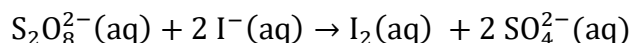
Reference materials and textbook sections covering kinetics and dilutions

Introduction

Thermodynamics includes the description of the equilibrium phases and concentrations of reactants and products under a given set of conditions, but it gives no information on how quickly equilibrium is attained.

Chemical kinetics is the study of reaction rates. Understanding how fast a reaction occurs, along with the factors that affect the rate, often helps in the determination of exactly how a reaction occurs (the reaction mechanism). The rate law quantifies the speed of the reaction.

For the reduction reaction in this experiment, which is quite slow, making it ideal for lab studies,



a rate equation can be written in terms of changes in concentrations per time interval.

$$\text{Rate} = -\frac{\Delta[\text{S}_2\text{O}_8^{2-}]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{I}^-]}{\Delta t} = \frac{\Delta[\text{I}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{SO}_4^{2-}]}{\Delta t}$$

It is also possible to write a rate equation in terms of reactant concentrations (assuming negligible back reaction).

$$\text{Rate} \propto [\text{S}_2\text{O}_8^{2-}]^m [\text{I}^-]^n = k[\text{S}_2\text{O}_8^{2-}]^m [\text{I}^-]^n$$

The reaction orders, m and n , give the rate's dependence on reactant concentrations and must be determined experimentally. The proportionality constant, k , is called the rate constant for the reaction. It is dependent on temperature and is given by the Arrhenius equation.

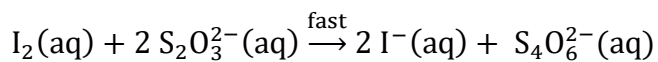
$$k = A e^{-\frac{E_a}{RT}}$$

A is the pre-exponential factor, E_a is the activation energy in kJ/mol, R is the universal gas constant in units of kJ/K·mol, and T is the absolute temperature in Kelvin.

I_2 is easy to detect because it forms an intensely colored deep blue complex with starch, providing an instant visual confirmation that the reaction has occurred. The rate at which I_2 is produced can be used to quantify changes in reactant concentration over time.

$$\text{Rate} = \frac{\Delta[\text{I}_2]}{\Delta t} = k[\text{S}_2\text{O}_8^{2-}]^m [\text{I}^-]^n = A e^{-\frac{E_a}{RT}} [\text{S}_2\text{O}_8^{2-}]^m [\text{I}^-]^n$$

However, the deep blue color appears as soon as I_2 is produced, making it difficult to determine how far the reaction has progressed. To control how quickly the blue appears, a second reaction, which is very fast, is used. A small amount of thiosulfate, $\text{S}_2\text{O}_3^{2-}$, is added to the initial reactant mixture. I_2 is consumed as fast as it is produced, so the blue color only appears once the $\text{S}_2\text{O}_3^{2-}$ is gone.



By using a known quantity of $\text{S}_2\text{O}_3^{2-}$, the rate can be calculated in terms of $[\text{S}_2\text{O}_3^{2-}]$.

$$\text{Rate} = -\frac{1}{2} \frac{\Delta[\text{S}_2\text{O}_3^{2-}]}{\Delta t} = \frac{1}{2} \frac{[\text{S}_2\text{O}_3^{2-}]_{\text{initial}}}{\Delta t} = \frac{\Delta[\text{I}_2]}{\Delta t} = k[\text{S}_2\text{O}_8^{2-}]^m [\text{I}^-]^n$$

The initial concentrations of PODS and I^- change very little because the amount of $\text{S}_2\text{O}_3^{2-}$ used is relatively small.

Note that PODS, $S_2O_8^{2-}$, is a reactant in the iodine clock reaction for which you are determining the rate law. PODS is not thiosulfate, $S_2O_3^{2-}$, which is the species used to delay the appearance of the blue I_2 -starch complex and to allow the quantification of the rate of I_2 production.

Equipment List

Stop watch or other timing device (use phones at your own risk)

Test tubes

150-mL beaker

Volumetric pipets and pipetters

Stoppers (corks)

Ice

Water baths

Miscellaneous other glassware and equipment, including labeling tape and waterproof markers

Procedure

Please bring stop watches or digital timers for measuring rates in seconds. If you choose to use your phone, understand that it is up to you to keep it safe, dry, and working.

Clean glassware is a must. Wash it well before and after each trial. Dedicate one pipet to each solution.

One person in your pair should mix and watch for the blue while the other person times. Make sure to swap roles.

You and your partner may be asked to do all parts of the experiment or you may be assigned by your TA to do one (or two) parts. You are responsible for getting a complete data set for all parts.

You will be asked to write your times in seconds up on the board so that the entire class will have good data.

Record room temperature to the ones place.

If you are to do part 2, set up the solutions in two test tubes per temperature (but do not do the final addition of KI) and get the test tubes in the baths (0°C , 35°C , and 45°C). The solutions need time to reach the temperature of their bath. After mixing, you must put the

test tube back in its bath so the temperature remains fairly constant. The 0°C (ice bath) trial can take some time, so mix and watch it while doing the 35°C and 45°C trials.

Label all glassware. It can be helpful to check off reagents as you add them so you don't miss any.

Caution

Incorrect use of the pipet and pipetter can result in **serious injury**.

Please **do NOT force or jam the pipet** into the pipetter.

If you push too hard, the pipet can break and **cut your hand**.

Use **just enough force** to create a seal. The pipet does not "click" into place.

Hold both the pipet and pipetter at all times.

If you pull any solution into the pipetter, please give it to your TA so that it can be cleaned.

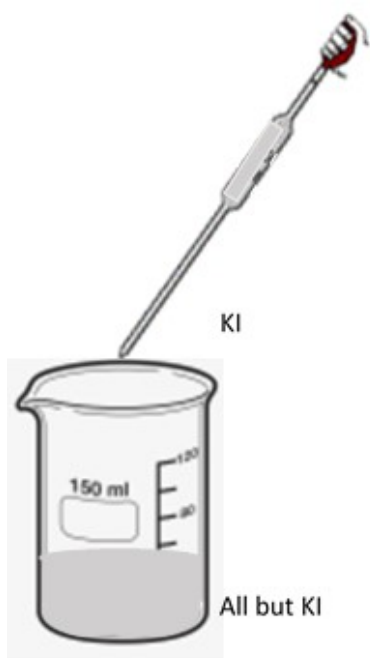
If you have trouble, **ask your TA for help**.

Part 1a. m, reaction order with respect to PODS, $S_2O_8^{2-}$

There are five trials in this series.

1. The following table lists the volumes of reagents that must be volumetrically pipetted into a clean, dry, 150-mL beaker. Do not add the KI until you are ready to time.

Run #	0.10 M $K_2S_2O_8$	0.10 M K_2SO_4	2% starch	0.010 M $Na_2S_2O_3$	0.20 M KI
1	1.00 mL	4.00 mL	1.00 mL	2.00 mL	5.00 mL
2	2.00 mL	3.00 mL	1.00 mL	2.00 mL	5.00 mL
3	3.00 mL	2.00 mL	1.00 mL	2.00 mL	5.00 mL
4	4.00 mL	1.00 mL	1.00 mL	2.00 mL	5.00 mL
5	5.00 mL	0 mL	1.00 mL	2.00 mL	5.00 mL



2. Once you have mixed the first four reagents, prepare your timing device.
3. Volumetrically pipet in 5.00 mL of the KI. Be consistent with when you start timing. It is usually easiest to set time = 0 when you begin the KI addition.
4. Gently swirl or stir the mixture to make sure there are no concentration gradients.
5. Record the time at which the blue first appears. Report it in a whole number of seconds. Notice that the concentration of PODS ($\text{S}_2\text{O}_8^{2-}$) increases as you progress through the trials. What do you expect the rate to do (increase, decrease, or remain the same)? Would a faster rate result in a longer or shorter time for the blue to appear?
6. Write your times in whole number of seconds (to the ones place) on the board.
7. Calculate $[\text{S}_2\text{O}_8^{2-}]$ to four significant figures using $M_1V_1 = M_2V_2$ (note $V_2 = 13.00$ mL). Keep four significant figures to use in your intermediate calculations but round the concentrations to two significant figures in your final reported values.
8. Calculate the rate of reaction in each trial to two significant figures (keep extra significant figures in your intermediate calculations). Note $[\text{S}_2\text{O}_3^{2-}]$ remains the same but $[\text{S}_2\text{O}_8^{2-}]$ and t_{blue} vary trial to trial.

$$\text{Rate} = \frac{1 [\text{S}_2\text{O}_3^{2-}]_{\text{initial}}}{2 t_{\text{blue}}} = \frac{1 [0.001538]}{2 t_{\text{blue}}}$$

9. Graphically determine m , the reaction order with respect to PODS, $\text{S}_2\text{O}_8^{2-}$. Take the \log_{10} of the rate equation. Calculate $\log_{10}(\text{Rate})$ and $\log_{10}[\text{S}_2\text{O}_8^{2-}]$ to two decimal places.

$$\begin{aligned} \text{Rate} &= k[\text{S}_2\text{O}_8^{2-}]^m[\text{I}^-]^n \\ \log_{10}(\text{Rate}) &= m \cdot \log_{10}[\text{S}_2\text{O}_8^{2-}] + \log_{10}(k[\text{I}^-]^n) \\ y &= m \cdot x + b \end{aligned}$$

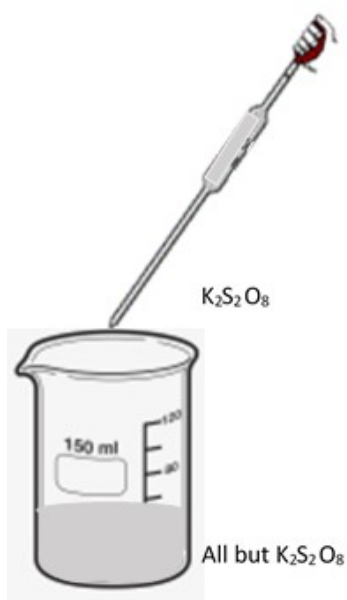
10. Plot $\log_{10}(\text{Rate})$ vs. $\log_{10}[\text{S}_2\text{O}_8^{2-}]$, draw or otherwise generate the best-fit line to the data, and determine the slope. The slope is m and should be rounded to the nearest integer (one significant figure).

Part 1b. n , reaction order with respect to iodide, I^-

There are five trials in this series.

11. The following table lists the volumes of reagents that must be volumetrically pipetted into a clean, dry, 150-mL beaker. Do not add the $\text{K}_2\text{S}_2\text{O}_8$ until you are ready to time.

Run #	0.20 M KI	0.2 M KCl	2% starch	0.010 M $\text{Na}_2\text{S}_2\text{O}_3$	0.10 M $\text{K}_2\text{S}_2\text{O}_8$
1	5.00 mL	0 mL	1.00 mL	2.00 mL	5.00 mL
2	4.00 mL	1.00 mL	1.00 mL	2.00 mL	5.00 mL
3	3.00 mL	2.00 mL	1.00 mL	2.00 mL	5.00 mL
4	2.00 mL	3.00 mL	1.00 mL	2.00 mL	5.00 mL
5	1.00 mL	4.00 mL	1.00 mL	2.00 mL	5.00 mL



12. Once you have mixed the first four reagents, prepare your timing device.
13. Volumetrically pipet in 5.00 mL of the $\text{K}_2\text{S}_2\text{O}_8$. Be consistent with when you start timing. It is usually easiest to set time = 0 when you begin the $\text{K}_2\text{S}_2\text{O}_8$ addition.
14. Gently swirl or stir the mixture to make sure there are no concentration gradients.
15. Record the time at which the blue first appears. Report it in a whole number of seconds. Notice that the concentration of iodide (I^-) decreases as you progress through the trials. What do you expect the rate to do (increase, decrease, or remain the same)? Would a faster rate result in a longer or shorter time for the blue to appear?
16. Write your times in whole number of seconds (to the ones place) on the board.
17. Calculate $[\text{I}^-]$ to two significant figures using $M_1V_1 = M_2V_2$ (note $V_2 = 13.00$ mL). Keep four significant figures to use in your intermediate calculations but round the concentrations to two significant figures in your final reported values.
18. Calculate the rate of reaction in each trial to two significant figures (keep extra significant figures in your intermediate calculations). Note $[\text{S}_2\text{O}_3^{2-}]$ remains the same but $[\text{I}^-]$ and t_{blue} vary trial to trial.

$$\text{Rate} = \frac{1}{2} \frac{[\text{S}_2\text{O}_3^{2-}]_{\text{initial}}}{t_{\text{blue}}} = \frac{1}{2} \frac{[0.001538]}{t_{\text{blue}}}$$

19. Graphically determine n , the reaction order with respect to iodide, I^- . Take the \log_{10} of the rate equation. Calculate $\log_{10}(\text{Rate})$ and $\log_{10}[\text{I}^-]$ to two decimal places.

$$\begin{aligned} \text{Rate} &= k[\text{S}_2\text{O}_8^{2-}]^m[\text{I}^-]^n \\ \log_{10}(\text{Rate}) &= n \cdot \log_{10}[\text{I}^-] + \log_{10}(k[\text{S}_2\text{O}_8^{2-}]^m) \\ y &= m \cdot x + b \end{aligned}$$

20. Plot $\log_{10}(\text{Rate})$ vs. $\log_{10}[\text{I}^-]$, draw or otherwise generate the best-fit line to the data, and determine the slope. The slope is n and should be rounded to the nearest integer (one significant figure).

Determination of the rate constant, k , at room temperature

21. Calculate the rate constant, k , to two significant figures for the ten trials in parts 1a and 1b. Use four significant figures for your concentrations and round k to two significant figures for your final reported values. Use your experimental values for m and n .

$$\text{Rate} = k[\text{S}_2\text{O}_8^{2-}]^m[\text{I}^-]^n \rightarrow k = \frac{\text{Rate}}{[\text{S}_2\text{O}_8^{2-}]^m[\text{I}^-]^n}$$

22. Calculate the average of k and its standard deviation. Do your values of k differ by very much (large or small σ_k)? Should they?

Part 2. Effect of temperature on reaction rate

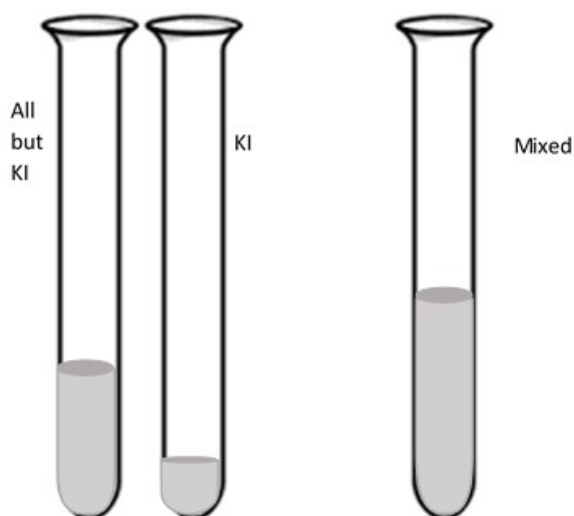
Immediately set up your solutions in large test tubes and get them in their respective baths so they have time to equilibrate to each temperature (0°C , 35° , and 45°C ; you already have room temperature data). Use the volumes of reagents listed in part 1a, trial #2.

Run #	0.10 M $\text{K}_2\text{S}_2\text{O}_8$	0.10 M K_2SO_4	2% starch	0.010 M $\text{Na}_2\text{S}_2\text{O}_3$	0.20 M KI
2	2.00 mL	3.00 mL	1.00 mL	2.00 mL	5.00 mL

The 0°C trial may take 15 minutes or more once the solutions are mixed. Watch it closely so that you don't miss the time when it turns blue, but do the warmer temperature trials while the reaction at 0°C proceeds.

23. Volumetrically pipet all reagents except KI into a labeled test tube, stopper with a cork, and mix well.

24. Volumetrically pipet the KI into a separate labeled test tube and stopper with a cork.
25. Place the pair of test tubes into an ice bath made in a 400-mL beaker (assume the bath is at 0°C).
26. Set up two more pairs of test tubes as above. Place one pair in the 35°C bath and one pair in the 45°C bath.
27. Leave each pair of test tubes in its bath for about 10-15 minutes.
28. Once the solutions have come to the correct temperature, prepare your timing device. Begin timing as you add the KI from one test tube into the test tube containing the other reagents. Make sure to stopper the solution with one of your corks. Hold the cork in, gently invert the test tube, and put it back in its bath. Used corks must go into the solid waste container, not the trash.



29. Record the time when the mixed solution turns blue and write your times in whole numbers of seconds on the board. As temperature increases, what do you expect the rate will do (increase, decrease, or stay the same)? Would a faster rate result in a longer or shorter time for the blue to appear?
30. Graphically determine E_a and A . You should have data for four trials at different temperatures (0°C, room temperature, 35°, and 45°C). Calculate k for each to two significant figures.

$$k = \frac{\text{Rate}}{[\text{S}_2\text{O}_8^{2-}]^m [\text{I}^-]^n} = \frac{\frac{1}{2} \frac{[\text{S}_2\text{O}_3^{2-}]}{t_{\text{blue}}}}{[\text{S}_2\text{O}_8^{2-}]^m [\text{I}^-]^n} = \frac{\frac{1}{2} [0.001538]}{[0.01538]^m [0.07692]^n}$$

31. Take the natural logarithm (ln) of the equation for the rate constant, k . Calculate $\ln k$ to two decimal places and $\frac{1}{T}$ in $\frac{1}{\text{Kelvin}}$ to three significant figures.

$$k = Ae^{-\frac{E_a}{RT}}$$
$$\ln k = -\frac{E_a}{R} \left(\frac{1}{T} \right) + \ln A$$
$$y = m \cdot x + b$$

32. Plot $\ln k$ vs. $\frac{1}{T}$, draw or otherwise generate the best-fit line to the data, and determine the slope to three significant figures and y-intercept to four.

The slope equals $-\frac{E_a}{R}$, so $E_a = -R \cdot \text{slope}$, where $R = 0.008314 \frac{\text{kJ}}{\text{mol}}$. Report E_a to three significant figures.

The y-intercept equals $\ln A$, so $A = e^{\text{y-intercept}}$. Report A to two significant figures.

33. Write the complete rate equation with your experimental values.

$$\text{Rate} = Ae^{-\frac{E_a}{RT}} [\text{S}_2\text{O}_8^{2-}]^m [\text{I}^-]^n$$

Please follow your TA's instructions for cleanup and waste disposal. Return any equipment and glassware borrowed clean.

Results / Sample Calculations

Complete the online inlab or write a lab report as directed by your TA.

part 1a: concentrations, times, rate, $\log(\text{Rate})$, $[\text{S}_2\text{O}_8^{2-}]$, $\log[\text{S}_2\text{O}_8^{2-}]$; slope

part 1b: concentrations, times, rate, $\log(\text{Rate})$, $[\text{I}^-]$, $\log[\text{I}^-]$; slope

part 1: individual room temperature rate constants with average and error ($k \pm \sigma_k$).

part 2: temperatures, k , $\ln k$, $\frac{1}{T}$, slope, E_a , A

Complete rate law, including reaction orders, pre-exponential factor, and activation energy

Graphs for parts 1a, 1b, and 2

Discussion Questions and Review Topics

What did you find out and how did you do it?

What could be done to improve the accuracy of the experiment?

What was the standard deviation in your room temperature rate constants? Should σ_k be large or small?

If you double both the PODS and I^- concentrations, what would you expect the reaction rate to do?

If you double the temperature while holding reactant concentrations constant, will the rate double?

Does changing the reactant concentrations and/or temperature affect the activation energy of the reaction?