Rate Properties of an Iodide Oxidation Reaction

GOAL AND OVERVIEW

The rate law for the reduction reaction of peroxodisulfate (PODS) by iodide: $S_2O_8^{2-}(aq) + 2\,I^-(aq) \rightarrow I_2(aq) + 2\,SO_4^{2-}(aq)$ will be determined. The orders of reaction with respect to PODS and to iodide 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 of the Data Analysis

- understand the theory and use of kinetics

- perform dilution calculations

- work with equations expressing rates in terms of equation order

- graph data and interpret graphs

- use the Arrhenius equation for the temperature dependence of the rate constant

SUGGESTED REVIEW AND EXTERNAL READING

- relevant reference and textbook information on kinetics and dilutions

BACKGROUND

Thermodynamics describes the equilibrium phases and concentrations of reactants and products under a given set of conditions. It gives *no information on how quickly* the equilibrium concentrations are reached.

Chemical kinetics is the study of chemical reaction rates. Understanding how fast a reaction occurs, along with the factors that affect the rate, often helps to determine exactly how a reaction is occurring (the mechanism of the reaction). The speed with which a reaction occurs is described by the *reaction rate.*

For a simple reaction like a + b → c + d, the reaction rate can be expressed as concentration change with respect to change in time. Since the stoichiometry of the reaction above involves coefficients of 1 only, there is a simple relationship between the *rates of formation* of each product and the *rates of consumption* of each reactant. The negative signs on the reactant terms ensure that the calculated rate is positive for the forward reaction (the reactant concentration change is *negative* when the reaction proceeds from left to right).

$$\text{Rate} = \frac{\text{change in concentration}}{\text{time interval}} = \frac{\Delta[\text{c}]}{\Delta t} = \frac{\Delta[\text{d}]}{\Delta t} = -\frac{\Delta[\text{a}]}{\Delta t} = -\frac{\Delta[\text{b}]}{\Delta t} \qquad (1)$$

Reaction rates often depend on reactant concentrations. In a number of simple cases, the rate is proportional to a reactant's concentration, raised to some power. The overall dependence is the product of these terms.

$$\text{Rate } \propto [\text{a}]^{\text{m}}[\text{b}]^{\text{n}} \quad \text{or} \quad \text{Rate } = k[\text{a}]^{\text{m}}[\text{b}]^{\text{n}} \tag{2}$$

Here, the reaction is m^{th} order in a and n^{th} order in b; its overall order is m + n.

The proportionality constant, k, which is called the *reaction rate constant*, depends on temperature and is given by the Arrhenius equation.

$$k = Ae^{-E_{\text{a}}/RT} \quad \text{so} \quad \text{Rate } = Ae^{-E_{\text{a}}/RT}[\text{a}]^{\text{m}}[\text{b}]^{\text{n}} \tag{3}$$

Where A is a constant called the *pre-exponential factor*; E_{a} the *activation energy* for the reaction; R is the universal gas constant in units of $J/K \cdot mol$; and, T is the absolute temperature in Kelvin.

You will determine the rate law for the PODS/I$^-$ reaction (m, n, A, and E_{a}). This enables *the rate* for *any concentrations* of PODS and I$^-$ *at any temperature* to be calculated.

The Peroxodisulfate Iodide Clock Reaction (PODS/I$^-$ reaction)

In this reaction, two iodide ions provide one electron each to reduce the peroxodisulfate ion, $S_2O_8{}^{2-}$, to form two stable sulfate ions and molecular iodine. The overall redox reaction is shown below.

$$S_2O_8{}^{2-}(aq) + 2\text{ I}^-(aq) \rightarrow I_2(aq) + 2\text{ SO}_4{}^{2-}(aq) \tag{4}$$
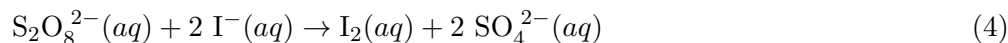
The rate law can be written as follows.

$$\begin{aligned}
\text{Rate } &= -\frac{\Delta[S_2O_8{}^{2-}]}{\Delta t} = -\frac{\Delta[\text{I}^-]}{2\Delta t} = \frac{\Delta[I_2]}{\Delta t} = \frac{\Delta[SO_4{}^{2-}]}{2\Delta t} \\
&= k[S_2O_8{}^{2-}]^{\text{m}}[\text{I}^-]^{\text{n}} = Ae^{-E_{\text{a}}/RT}[S_2O_8{}^{2-}]^{\text{m}}[\text{I}^-]^{\text{n}}
\end{aligned} \tag{5}$$

The stoichiometric coefficients for iodide and for sulfate appear in the denominators for their rate expressions. I$^-$ is consumed twice as fast as PODS; $SO_4{}^{2-}$ is formed twice as fast as I_2. The reaction is m^{th} order in $S_2O_8{}^{2-}$, n^{th} order in I$^-$, and $(\text{m + n})^{\text{th}}$ order overall. The specific rate constant, k, for this reaction, as it is balanced, contains the rate's dependence on temperature.

This reaction is quite slow, making its rate ideal to measure in a lab setting. It is also convenient to study because molecular iodine, I_2, is easy to detect. I_2 reacts with starch to form a deeply blue-colored complex. By adding starch to the reaction mixtures, a deep blue color is observed as soon as iodine is produced by the reaction. However, the blue color appears almost immediately and it gets extremely intense very quickly. In order to control how quickly the blue color appears, a

second reaction is used.

A small amount of thiosulfate ions, $S_2O_3^{2-}$ is added to the initial mixture. The $S_2O_3^{2-}$ ions react immediately with any I_2 present to regenerate two I^- ions. This prevents the solution from turning blue until all of the $S_2O_3^{2-}$ is consumed.

$$I_2(aq) + 2\ S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2\ I^-(aq) \tag{6}$$
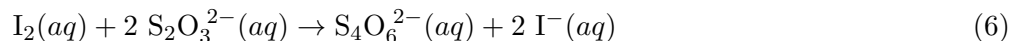
Once $[S_2O_3^{2-}]$ goes to zero, the I_2 produced will no longer be removed and the solution turns blue. By using a known quantity of $S_2O_3^{2-}$, the rate can be calculated in terms of $[S_2O_3^{2-}]$.

$$\text{Rate} = \frac{\Delta[I_2]}{\Delta t} = -\frac{\Delta[S_2O_3^{2-}]}{2\Delta t} = \frac{[S_2O_3^{2-}]_{\text{initial}}}{2t} = k[S_2O_8^{2-}]^{\text{m}}[I^-]^{\text{n}} \tag{7}$$

Because the coefficient of $S_2O_3^{2-}$ in the I_2 scavenging reaction is 2 (while the coefficient for I_2 is 1), there is a 2 in the denominator of this term. The *change in $S_2O_3^{2-}$ concentration* is the negative of the $[S_2O_3^{2-}]_{\text{initial}}$ because $[S_2O_3^{2-}]_{\text{final}} = 0$. The *change in time* is simply the *measured time, t*, from the beginning of the experiment because $t_{\text{initial}} = 0$. The initial $S_2O_8^{2-}$ and I^- concentrations change very little during the reaction because the amount of $S_2O_3^{2-}$ added is relatively small, so their concentrations can be calculated using the dilution equation.

Use Eq. 7 for your experiments. Each run uses the same initial concentration of $S_2O_3^{2-}$.

- To determine m, use different concentrations of PODS.

- To determine n, use different concentrations of I^-.

- Once you have found m and n, determine the average value of the rate constant k at room temperature.

To determine A and E_{a}, data at different temperatures are required. By doing trials with *constant $[S_2O_8^{2-}]$ and $[I^-]$* at several temperatures, you can determine k values under these conditions. The activation energy E_{a} and pre-exponential factor A will be determined graphically.

Once m, n, E_{a}, and A are known, the reaction rate for any concentrations of PODS and I^- at any temperature can be calculated.

Notes:

- Bring **stop watches** or **digital watches** for recording reaction times in **seconds.**

- You will do this experiment with a partner – one person will mix while the other times.

- Half of the pairs will do Part 1a and half will do Part 1b (unless otherwise instructed).

- Every pair will do Part 2 (unless otherwise instructed).

- Every pair will put their times on the board so that the entire class will have good data.

- ***Before starting Part 1, set up the solutions for Part 2 (but do not mix them).*** The solutions need time to reach the temperature of their water bath.

PROCEDURE

Note: Wash your glassware before you use it, and return it clean. Dedicate one pipet to each solution (don't mix and match).

Part 1a: Reaction Order with Respect to Peroxodisulfate Ion (PODS), m

There are five runs in this series. The following table gives the volumes of reagents that must be accurately pipetted into a clean, dry 150-mL beaker for each trial.

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 mL	4 mL	1 mL	2 mL	5 mL
2	2 mL	3 mL	1 mL	2 mL	5 mL
3	3 mL	2 mL	1 mL	2 mL	5 mL
4	4 mL	1 mL	1 mL	2 mL	5 mL
5	5 mL	0 mL	1 mL	2 mL	5 mL

Once you have mixed the first four reagents, initiate the experiment.

1 Prepare the timepiece.

2 Obtain 5 mL of 0.20 M KI solution in a volumetric pipet.

3 Start to record the time halfway through the addition of the KI.

4 You may want to record the draining time to get an approximate error in reaction times.

5 Gently swirl the beaker to keep the solution mixed.

6 Record the time of the first appearance of the dark blue color *in seconds.*

Part 1b: Reaction Order with Respect to Iodide Ion, n

There are five runs in this series. The following table gives the volumes of reagents that must be accurately pipetted into a clean, dry 150-mL beaker for each trial.

Run #	0.20 M KI	0.2 M KCl	2% starch	0.010 M Na$_2$S$_2$O$_3$	0.10 M K$_2$S$_2$O$_8$
1	5 mL	0 mL	1 mL	2 mL	5 mL
2	4 mL	1 mL	1 mL	2 mL	5 mL
3	3 mL	2 mL	1 mL	2 mL	5 mL
4	2 mL	3 mL	1 mL	2 mL	5 mL
5	1 mL	4 mL	1 mL	2 mL	5 mL

Once you have mixed the first four reagents, initiate the experiment.

1 Prepare the timepiece.

2 Obtain 5 mL of 0.10 M K$_2$S$_2$O$_8$ solution in a volumetric pipet.

3 Start to record the time half way into the addition of the 5 ml of K$_2$S$_2$O$_8$.

4 You may want to record the draining time to get an approximate error in recorded reaction times.

5 Gently swirl the beaker to keep the solution mixed.

6 Record the time of the first appearance of the dark blue color *in seconds.*

Note: Put your results on the board and compare your results with those of others.

Part 1 Data Analysis: To Determine m and n From Your Measured Times (Parts 1a and 1b)

7 Calculate $[S_2O_8^{2-}]$ and $[I^-]$ to two significant figures using $M_1V_1 = M_2V_2$ to find M_2 for each trial. Note that V_2 is the final volume (13 mL). In Part 1a (trials 1a$_1$ - 1a$_5$), $[S_2O_8^{2-}]$ varied; in Part 1b (trials 1b$_1$ - 1b$_5$), $[I^-]$ varied.

8 For each run, determine the rate to two significant figures using $\text{Rate} = \dfrac{[S_2O_3^{2-}]_{\text{initial}}}{2t}$. $[\,S_2O_3^{2-}\,]$ stays the same (use two significant figures); calculate it using $M_1V_1 = M_2V_2$. Time, t, is the only value that changes trial to trial.

9 To find m, use part 1a data. Take the logarithm of the rate equation.

$$\log(\text{Rate}) \quad = \quad \text{m} \ \log \ [\text{S}_2\text{O}_8{}^{2-}] \quad + \quad \log(k[\text{I}^-]^\text{n})$$

$$y \quad = \quad mx \quad + \quad b \tag{8a}$$

10 Plot log(rate) vs. log $[\text{S}_2\text{O}_8{}^{2-}]$. Your log valuse should have two decimal places. Graph your data, draw the best-fit straight line, and determine the slope (which equals m). Round m to the nearest integer.

11 To find n, use part 1b data. Take the logarithm of the rate equation.

$$\log(\text{Rate}) \quad = \quad \text{n} \ \log \ [\text{I}^-] \quad + \quad \log(k[\text{S}_2\text{O}_8{}^{2-}]^\text{m})$$

$$y \quad = \quad mx \quad + \quad b \tag{8b}$$

12 Plot log(rate) vs. log $[\text{I}^-]$. Your log values should have two decimal places. Graph your data, draw the best-fit straight line, and determine the slope (which equals n). Round n to the nearest integer.

13 To find the rate constant at room temperature for each trial, use a rearrangement of the rate equation.

$$k = \frac{\text{Rate}}{[\text{S}_2\text{O}_8{}^{2-}]^\text{m}[\text{I}^-]^\text{n}} = \frac{[\text{S}_2\text{O}_3{}^{2-}]/2t}{[\text{S}_2\text{O}_8{}^{2-}]^\text{m}[\text{I}^-]^\text{n}} \tag{9}$$

Substitute in your values of m and n, along with the correct time and concentrations for each trial.

Calculate values of k for each of the ten room-temperature runs to two significant figures; then find the average value of k and its standard deviation. Do the values of k differ very much? Should they?

Part 2: Effect of Temperature on the Reaction Rate

Initial Part: Begin this immediately so that the solutions reach the temperature of the water baths.

You already have the data for run #2 of Part 1a (room temperature).

Use the concentrations listed in Part 1a, trial #2 to find the rate at 0°C, 35°C, and 45°C.

Run #	0.10 M K$_2$S$_2$O$_8$	0.10 M K$_2$SO$_4$	2% starch	0.010 M Na$_2$S$_2$O$_3$	0.20 M KI
2	2 mL	3 mL	1 mL	2 mL	5 mL

1 Into one test tube (labeled with contents and your name) pipet the reagents given in the table for run #2 of Part 1a.

2 Into another test tube (similarly labeled) pipet 5 mL of 0.20 M KI solution.

3 Stopper them both.

4 Place the pair in an ice water bath made in a 250 or 400 mL beaker.

5 Repeat the process with two test tubes and place them in the 35°C temperature bath.

6 Repeat the process once more and place the tubes in the 45°C temperature bath.

Final Part: Be sure to record the temperature of each bath.

7 Remove a pair of tubes from each bath.

8 Begin to record the time as you add the 5 mL of KI from one test tube into the other.

9 Stopper the tube and gently invert it to mix. Put it back into the water bath.

10 Record the time when you see the onset of the blue color.

   The low-temperature run may take 20 minutes or more – keep your eye on it, but do other things while you wait.

11 Repeat for both the other baths.

12 Record room temperature.

Note: Put your results on the board and compare your results with those of others.

Part 2 Data Analysis: E_a and A Determination (temperature dependence of the rate)

1 In addition to the value of k obtained above at room temperature, calculate the value of k to two significant figures for the runs at 0°C, 35°C, and 45°C. (See Equation 9.)

2 You now have four data points consisting of k and the corresponding T (in Kelvin). To perform the graphical analysis, take the ln of both sides of the Arrhenius equation and rearrange the following.

$$
\begin{aligned}
k &= Ae^{-E_a/RT} \\
\ln k &= \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A \\
y &= mx + b
\end{aligned}
\tag{10}
$$

3 Plot $\ln k$ vs $1/T$; $\ln k$ should contain two decimal places, $1/T$ should contain three. You should have four points. The slope of the best-fit line should be straight and equal to $-E_a/R$; report your slope to three significant figures. The y-intercept should be $\ln A$.

4 Determine the activation energy, E_a, to three significant figures in kJ/mol; $R = 8.314$ J/K · mol. Calculate the pre-exponential factor, A to two significant figures.

5 Write the complete rate law, substituting your experimental values for m, n, E_a, and A.

Waste disposal: follow your TA's instructions. Nothing goes down the sink.

RESULTS

Complete your lab summary or write a report (as instructed).

Abstract

Results

    Tables including concentrations, times, temperatures and rates

    Graphs for part 1 and 2

    Report the Arrhenius Equation for the reaction (including reaction orders, pre-exponential factor, and activation energy)

Sample Calculations

    part 1a: rate, log(rate), $[S_2O_8^{2-}], \log[S_2O_8^{2-}]$; slope determination

    part 1b: rate, log(rate), $[I^-], \log[I^-]$; slope determination

    part 1: individual room temperature rate constants with average and error

    part 2: k, $\ln k$, $1/T$, slope of graph, A determination

Discussion/Conclusions

    What did you find out and how?

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

Review