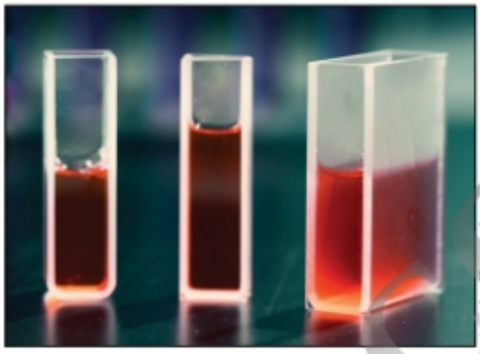

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Laboratory 3

(BAR)

Determining the Kinetics for the Bleaching of Allura Red Dye

Expected Learning Outcomes

- Compare and contrast zero-, first-, and second-order rate laws
- Calculate, using Beer's law, the concentration of a colored reactant over time
- Determine the rate constant of a reaction using measured rates for various concentrations of reactants
- Through graphing techniques, analyze a complex set of data to make claims and identify patterns

Introduction

Chemical kinetics is the study of the speed, or rate, of reactions. We know that some reactions happen faster than others. The addition of baking soda to vinegar produces a rapid reaction that we observe almost instantly. In contrast, rust forming on cars is a very slow reaction, one that takes years instead of minutes. Knowing the speed of a chemical reaction can be critical. Pharmaceutical researchers, for example, must know how fast a drug will work when it enters the body. Likewise, mechanics need to know the rate at which automotive parts will rust and need to be replaced. In this lab, you will study chemical kinetics. We will use absorbance measurements to track the progress of a reaction as a function of time and determine the rate law and rate constant for a chemical reaction.

Discussion

What is the rate law for a reaction?

The goal of this experiment is to determine the rate law and rate constant for a real reaction. To do this, we need to select a reaction that allows us to detect—quantitatively—how much reactant has been consumed or product has been formed. In solution, we must be able to measure concentration of a reactant or product during the course of the reaction, while it is changing. Color is an intrinsic physical property of a substance; therefore, we can quantitatively determine the concentration of a colored species using spectrophotometry. Furthermore, a change in color can indicate a chemical reaction, and we can monitor the rate of a color change to study the rate of a reaction.

In this lab, we will be studying the aqueous reaction between the commercial food dye Allura Red ($C_{18}H_{14}N_2Na_2O_8S_2$) and bleach, also known as sodium hypochlorite (NaClO). The reaction (shown with the reactants balanced) can be represented as follows:

$$C_{18}H_{14}N_2Na_2O_8S_2(aq) + NaClO(aq) \rightarrow \text{products}$$

Spot Check 3.1: Why do we not need to know the identity or concentration of the products formed by this reaction to determine the rate constant?

Allura Red dye is a large, organic molecule with the structure shown in Figure 3.1.

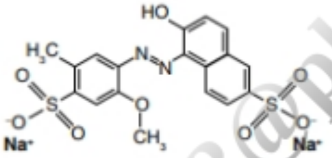

Figure 3.1 The chemical structure of the Allura Red dye molecule.

As the bleach interacts with the Allura Red, the dye reacts with NaClO to form a number of colorless products. While the products are not well-defined for this reaction, the effects of the reaction can be seen visually; the solution of dye transitions from a vibrant red to a colorless solution. A spectrophotometer can be used to measure the absorbance, A, of the red dye, which is directly proportional to concentration, c:

$$A \propto c$$

The proportionality constant is represented by εb, where ε is the molar absorptivity and b is the path length of light through the solution. This relationship is known as **Beer's law**. When graphed, εb is the slope, m:

$$A = \varepsilon bc = mc = m[\text{Allura Red dye}]$$

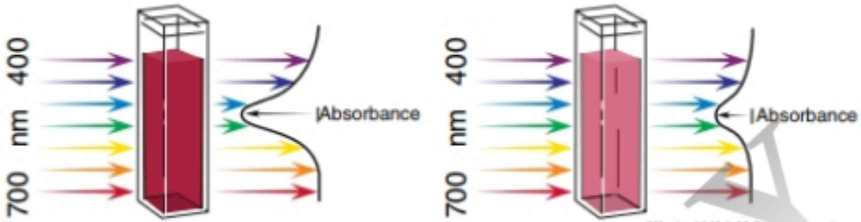

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Figure 3.2 Dependence of absorbance on concentration. The solute has a max absorbance at 505 nm.

Differently colored species absorb light of different wavelengths. As shown in Figure 3.2, solutions of Allura Red strongly absorb light at a wavelength of 505 nm, giving them their characteristic red color. As the reaction between bleach and Allura Red proceeds, the solution will absorb detectably less 505 nm light, decreasing the absorbance reading throughout the experiment.

In this lab, we will be studying how changing the concentration of Allura Red dye affects the rate of the reaction. As you can see in the chemical equation on page 20, two reactants are needed to produce the colorless products. However, we want to determine the effect of *just* Allura Red dye concentration. How do we do this? The easiest way to accomplish this task is to use an excess of bleach for all trials. In fact, an excess of 50 times the stoichiometric amount of bleach needed will be used in this experiment; this means the concentration of bleach is essentially constant. In addition, the excess bleach will keep the pH nearly constant, as bleach has psuedo-zero-order kinetics and will not affect the rate of the reaction.

Rate Laws

The rate of a reaction is the change in concentration over change in time and generally depends on the concentration of reactants. The **rate law** is a mathematical expression of how the rate changes with changing concentration. For the general reaction represented below:

$$a\,A + b\,B \rightarrow \text{products}$$

the rate law has the form:

$$\text{rate} = k[A]^{x}[B]^{y}$$

where square brackets indicate concentrations (in this experiment, molar concentrations) of reactants A and B:

x is the order with respect to A

y is the order with respect to B

k is the rate constant, a proportionality constant between rate and concentration terms

Spot Check 3.2: Are the "x" and "y" values the same as the "a" and "b" coefficients listed in the general reaction?

Values of x, y, and k can only be determined experimentally. Defining the values of x and y establishes the rate law and determines the overall reaction order.

Using an excess of bleach in our experiment allows us to study the effect of concentration of just one reactant on the rate. Therefore, only x will define the order, as in the following expression:

$$\text{rate} = k[A]^x$$

The rate is the change in concentration over time and can be expressed as:

$$\text{rate} = -\frac{[A]_t - [A]_0}{t_t - t_0} = -\frac{\Delta[A]}{\Delta t} = k[A]^x$$

The negative sign arises because the concentration of A is decreasing (a negative change in concentration). What we are really interested in is the instantaneous change in concentration, which is the limit as the time interval Δt approaches zero. This is the derivative of [A] with respect to time:

$$-\frac{d[A]}{dt} = k[A]^x$$

Reaction Order

One goal of this lab is to quantitatively determine the rate constant of the bleaching of Allura Red. However, to calculate the correct rate constant, we must know the reaction order. The three rate laws we commonly consider are zero-order, first-order, and second-order. After collecting data over time, enough information is known to construct graphs of each order.

Because the value of x must be determined experimentally, these graphs must be analyzed to determine the rate law. The graph with four straight lines (with a good linear fit) that are closely parallel establishes the order of the reaction and the rate law.

Spot Check 3.3: "Straight" lines indicate the data fits well to a linear trendline. Mathematically, how do we assess "straightness"?

Zero-Order Reactions

In some cases, rate does not depend on concentration and the rate will be independent of the initial concentration of A. Here, x = 0 and the reaction follows a zero-order rate law:

$$\text{rate} = k[A]^0$$

the derivative of which yields the following form:

$$-\frac{d[A]}{dt} = k[A]^0 = k$$

Integration of the above equation from time = 0 to time = t, followed by rearrangement gives:

$$[A]_t = -kt + [A]_0$$

where $[A]_t$ is the concentration of reactant A at time = t and $[A]_0$ is the initial concentration of A when time = 0. This equation has the form of a straight line.

$$\begin{tikzcd}
{[A]_t} & = & -k & t & + & {[A]_0} \\
y \arrow[u] & = & m \arrow[u] & x \arrow[u] & + & b \arrow[u]
\end{tikzcd}$$

For a zero-order reaction, a graph of concentration at time t, $[A]_t$, versus time, t, is a straight line.

Spot Check 3.4: What is the slope and y-intercept of the line for a zero-order plot?

First-Order Reactions

If x = 1, the reaction follows a first-order rate law. This means that the rate depends on the concentration of A to the first power. The first-order expression becomes:

$$\text{rate} = k[A]^1$$

the derivative of which produces the following form:

$$-\frac{d[A]}{[A]} = -k\,dt$$

and integration from t = 0 to t gives:

$$ln\frac{[A]_t}{[A]_0} = -kt$$

This expression can be rearranged to produce a linear equation:

$$ln\,[A]_t - ln\,[A]_0 = -kt$$

$$\begin{tikzcd}
{ln\,[A]_t} & = & -k & t & + & {ln\,[A]_0} \\
y \arrow[u] & = & m \arrow[u] & x \arrow[u] & + & b \arrow[u]
\end{tikzcd}$$

For a first-order reaction, a graph of the natural log of concentration of A at time t, *ln* $[A]_t$, versus time, t, is a straight line.

Spot Check 3.5: For a first-order process, a graph of *ln* $[A]_t$ versus t will give a straight line. What are the slope and y-intercept of this line?

Second-Order Reactions

Similarly, with respect to just the concentration of A, $x = 2$ for a second-order reaction. The rate law takes the form of:

$$\text{rate} = k[A]^2$$

And can be written, arranged, and integrated as follows:

$$-\frac{d[A]}{dt} = k[A]^2$$

$$-\frac{d[A]}{[A]^2} = k\,dt$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

Again, a rearrangement produces the form of an equation of a straight line:

$$\underset{\boxed{y}}{\underset{\uparrow}{\frac{1}{[A]_t}}} \;=\; \underset{\boxed{m}}{\underset{\uparrow}{k}}\;\underset{\boxed{x}}{\underset{\uparrow}{t}} \;+\; \underset{\boxed{b}}{\underset{\uparrow}{\frac{1}{[A]_0}}}$$

For a second-order reaction, a graph of the inverse of concentration at time t ($1/[A]_t$) versus time, t, is a straight line.

Spot Check 3.6: What are the slope and y-intercept for a second-order plot?

Rate Constant, k

As you can see, the rate constant, k, can be determined by analyzing the graphs of the integrated rate laws. Only after the reaction order is established can the rate constant for the reaction be determined. Looking back at the linear integrated equation for each order, you will notice that the slope equals the negative of the rate constant, –k, for both a zero-order and first-order graph. For a second-order graph, slope = k. Graphical determination of the slope establishes the rate constant.

Overview

In lab, you will be working in groups to collect data. You may split up the tasks, but all members must leave with all pertinent data in their individual notebooks. The Day 1 procedure has three parts:

A. Four solutions are prepared with different concentrations of Allura Red dye. These will provide data for four determinations of the rate constant. Be sure to start the timer at the time of mixing for each solution—to make sure the data can be accurately analyzed, the time of mixing is $t = 0$.

B. The absorbance is read for each solution over a 10-minute interval. The temperature of the spectrophotometer cavity is measured before inserting a sample.

C. A series of dilute solutions will be made and their absorbance values measured. The proportionality constant (εb) can then be determined from the slope (m) of a Beer's law plot.

Data Analysis

Zero-order reactions are most common when a gas undergoes decomposition (for a further discussion of this, please see Section 14.4 of your textbook). Since this is not the case in this experiment, we can assume that the reaction is not zero-order. Therefore, the reaction **does** depend on the concentration of Allura Red, and we are interested in quantifying that dependence.

However, both first- and second-order reactions can commonly occur in solutions. How can we know the rate order? Through graphing the integrated rate laws, we can determine if the bleaching of Allura Red is a **first-order or second-order reaction**. This means $x = 1$ or $x = 2$ in the rate equation:

$$\text{Rate} = k[\text{Dye}]^{x}$$

Your goal is to identify whether this reaction is first- or second-order by using the integrated rate laws described previously to construct graphs. Many calculations (>150) are required to get your data into the "y = mx + b" format before the graphs can even be made. Therefore, Microsoft Excel, a spreadsheet program, should be used for both your calculations and graphs. Make sure to follow the graph guidelines outlined in the front of this lab manual and in Appendix D.

Construct a table like the one below for each solution, 1 through 4. Data of "Time" and "Abs" will be collected in lab, and the other columns of "$[\text{Dye}]_t$," "*ln* $[\text{Dye}]_t$," and "$1/[\text{Dye}]_t$" will be calculated in Excel. Remember to include units (units of concentration, [Dye], should be recorded in molarity; absorbance is unitless) and have the correct significant figures. The dashed line indicates that the table should be extended appropriately. Note: do not pre-fill your time values. Your data will be easier to process if you record the exact time the absorbance readings were taken.

Time	Abs	$[\text{Dye}]_t$	*ln* $[\text{Dye}]_t$	$1/[\text{Dye}]_t$

To determine the rate constant, three graphs will be constructed:

Beer's Law (Graph 1)

In the four solutions analyzed in Part C, the Allura Red concentration has been decreased through the addition of water. Calculate the final molar concentration of the Allura Red dye by using the molarity, initial volume, and final volume for each volumetric flask; this is a dilution calculation. Construct a Beer's law plot by graphing absorbance (y-axis) versus concentration (x-axis) for these solutions (Graph 1). Your plot should include the bleach "blank" solution and its absorbance. Force the trendline through the origin and display both the line equation and R^2 value on the graph. Determine the slope of the line, m, which is equal to the proportionality constant, εb.

Use your Beer's law plot and absorbance values to determine $[\text{Dye}]_t$ for each of the data points you collected in Part B.

First-Order (Graph 2)

Construct a first-order graph by plotting $\ln\,[\text{Dye}]_t$ versus t for each solution. Include all data points from the four solutions on the same graph (each a different series). Add a linear trendline for each solution. Set the options to display the equation and R^2 value for each trendline on the graph.

Second-Order (Graph 3)

Construct a second-order graph by plotting $1/[\text{Dye}]_t$ versus t for each solution. Include all data points from the four solutions on the same graph (each a different series). Add a linear trendline for each solution. Set the options to display the equation and R^2 value for each trendline on the graph.

Selecting the Reaction Order

After constructing your graphs, compare them. Which one looks as you expect? When doing this comparison, do not ONLY use the R^2 values to determine the reaction order. Instead, look at the lines and choose the graph (order) for which the lines are most parallel. *You will not be graded on determining the actual order correctly, but instead on how you present your analysis and the reasoning behind your choice.*

The Rate Constant

The rate constant will be related to the slope of the trendline and should be the same for all four solutions. Calculate the average rate constant and average deviation.

The experimental portion of Day 1 is performed in groups; data must be recorded in your individual lab notebook. On Day 2, you will work individually to work up your data in Excel. Discussions with your peers and lab instructor are encouraged on both days. ALL calculations, graphs, and other parts of the report must be completed individually.

Materials Required

Equipment

- 5-mL pipet
- 10-mL pipet
- pipet bulb
- 3 50-mL volumetric flasks
- 8 large (75-mL) test tubes
- 1 25-mL test tube
- 2 100-mL beakers
- digital flip thermometer

Chemicals

- 1.0×10^{-4} M Allura Red dye (65 mL/group)
- 5.0×10^{-3} M bleach (75 mL/group)
- deionized water

Common Equipment

- 1.00 cm cuvette
- Jenway 6320D spectrophotometer
- Kimwipes
- digital timer

Cautions

The solutions used in this experiment can cause stains, skin and eye irritation, and chemical burns. Gloves are highly recommended, and goggles must be worn at all times.

Procedure

DAY 1

Part A. Preparing the solutions and the spectrophotometer.

1. Turn on the spectrophotometer and set the wavelength to 505 nm. Let the spectrophotometer warm up while you prepare your solutions. Consult Appendix C for more instruction on the use of the spectrophotometer.

2. Label and fill four large (75-mL) test tubes according to the table below. Record both the actual concentration listed on the bottle and the actual volumes used in your notebook with appropriate significant figures:

Tube Label	1.0×10^{-4} M Allura Red (mL)	Deionized Water (mL)
1A	5	15
2A	10	10
3A	15	5
4A	20	0

3. Label and fill four large (75-mL) test tubes according to the table below. Record the actual concentration listed on the bottle and the actual volumes used in your notebook with appropriate significant figures:

Tube Label	5.0×10^{-3} M Bleach (mL)
1B	20
2B	20
3B	20
4B	20

Part B. Measurement of absorbance as a function of time.

4. Using the spectrophotometer, calibrate to "zero" absorbance using a "blank"—a cuvette containing only bleach solution. Rinse the cuvette three times with deionized water, then rinse with bleach solution. Fill the cuvette about ¾ full with bleach solution. The cuvettes have two frosted and two clear sides. Make sure a frosted side of the cuvette faces toward you when the cuvette is placed in the spectrophotometer, ensuring that the beam of light passes from left to right through the clear faces of the cuvette. If your cuvette does not have any frosted sides, make sure the triangle faces the LCD screen. Close the door and press the "CAL" button to zero the absorbance. After calibration, pour the bleach solution into the sink and rinse the cuvette **a minimum of three times** with deionized water and blot it dry with a Kimwipe.

5. One group member must check out a digital flip thermometer from the storeroom window (BuckID required) and pick up a digital timer from your lab instructor. Use the thermometer to record the ambient temperature of the spectrophotometer cavity. Hold it in the cavity until the temperature stabilizes. Record this temperature in your notebook.

6. Carefully pour the Allura Red solution from test tube 1A into test tube 1B. As soon as the solution has been poured, **start your timer**. Swirl the solution, and then pour the resulting solution back into the Allura Red test tube—thus thoroughly mixing the solutions. Use the solution to rinse and fill the cuvette about ¾ full. Wipe the outside with a Kimwipe, insert it into the spectrophotometer, and take an absorbance reading at 505 nm. Record the time displayed by your timer and the absorbance displayed by the instrument; this should be your first data point. Remember, "0.50 min" is not the same as "0:50 min"; be sure your notation reflects the notation on the timer.

   If the initial absorbance reading exceeds 1.200, consult your lab instructor. No more than a minute should elapse between mixing (t = 0) and the first measurement.

7. Continue taking time and absorbance readings every 30 seconds for at least 7 minutes, and no more than 10 minutes (your absorbance readings must be below 0.100 in order to stop before 10 minutes have elapsed). Pour the exhausted reaction mixture from your cuvette down the drain with copious amounts of running water. Rinse the cuvette **a minimum of three times** with deionized water and blot it dry with a Kimwipe.

8. Repeat Steps 4–7 for tubes 2–4. Note: you will complete data collection for Solution 1 before moving on to Solution 2, etc. Be sure to calibrate with a "blank" between solutions. *Do not mix any solution before the prior one is complete and the spectrophotometer has been calibrated.*

Part C. Creating a dilution series and Beer's law plot.

While one group member monitors the reactions in Part B, the other may begin sample preparation for Part C. It is strongly recommended that both group members complete a dilution.