Directionality vs. Speed

Prelab Assignment:

Read the entire experiment. Submit your completed prelab assignment to your TA before you begin the lab.

Experimental Overview

There are two reactions you will consider in this laboratory. The first is performed as a demonstration due to the waste it produces. This reaction is an example of an oscillating reaction. Consider what causes the reaction to continue and what will cause it to stop. The second set of reactions you will perform to determine the kinetic parameters of the reaction. Through these reactions, think about what causes the reactions and what makes them go faster.

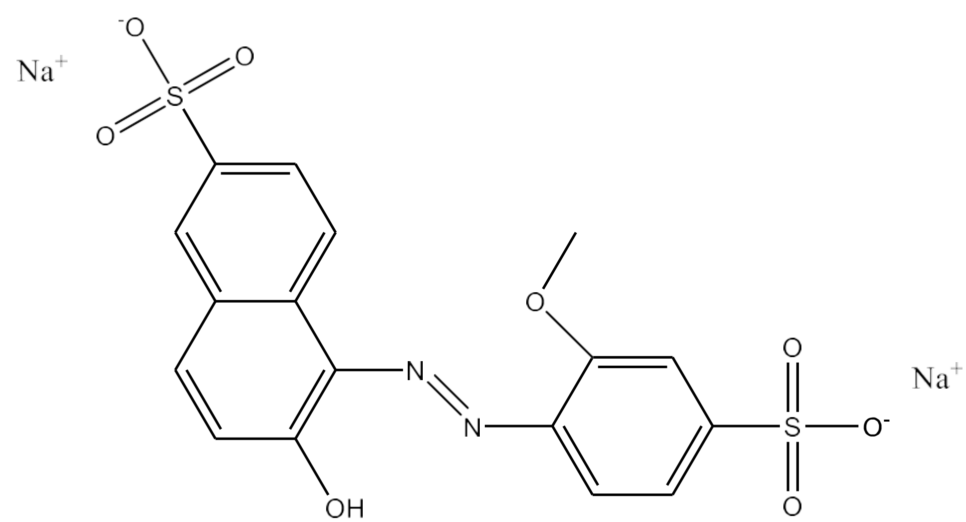
Bring your flashdrive to lab

Part I: Directionality

In most systems discussed in chemistry labs, the systems start at a position near equilibrium. Once allowed to start, the reaction or process spontaneously proceeds directly to its equilibrium position. When systems start far from their equilibrium position interesting things can happen.

Part II: Kinetics

Allura Red ($C_{18}H_{14}N_2O_8S_2$), also known as F.D.&C. Red Dye #40, is a commonly used commercial food dye. As is true of all seven of the certified food dyes in use in this country, it is an organic molecule with a system of alternating single and double bonds. The delocalization of electrons in this π-bonding system, known as a chromophore, is responsible for the color of these dyes.



Allura Red (F.D.&C. Red Dye #40)

Common household bleach is an aqueous solution of 3-6% sodium hypochlorite, NaOCl. The OCl^- ion oxidizes the chromophores in colored materials, breaking the double bonds and forming new molecules that do not absorb visible light, thus "bleaching" the colored material. In the process, the hypochlorite ion is reduced to chloride and hydroxide ions:

$$OCl^-(aq) + H_2O(l) + 2e^- \rightarrow Cl^-(aq) + 2OH^-(aq)$$

In this laboratory experiment you will study the kinetics of the reaction between Allura Red and bleach.

$$C_{18}H_{14}N_2O_8S_2(aq) + NaOCl(aq) \rightarrow \text{products}$$

(This reaction has not been investigated to determine the exact products formed.)

As the reaction proceeds, the intense color of Allura Red will fade. By using spectrophotometric methods to monitor this change, you will be able to determine how the concentration changes with time and use that information to find the rate law for the reaction.

The average rate of chemical reaction over a given period of time is expressed either in terms of the disappearance of reactants, rate = $-\frac{\Delta[A]}{\Delta t}$, ~~or~~ the appearance of products, rate = $\frac{\Delta[B]}{\Delta t}$. ~~The~~ choice of what to monitor experimentally is arbitrary, depending on which species lends itself to easy measurement. Because Allura Red is the only colored species in the reaction, we can monitor the rate of reaction by recording the decrease in the color of the solution with time.

The rate law for a chemical reaction is an expression that relates the rate of a reaction to the concentration of the reactants and the rate constant. For this reaction·

$$\text{rate} = -\frac{\Delta[Allura\ Red]}{\Delta t} = k[\text{Allura Red}]^x\,[\text{NaOCl}]^y$$

The exponents x and y represent the reaction order of the corresponding compounds and k is the rate constant for the reaction at a given temperature. These values must be determined experimentally, which is the objective of this experiment.

Imagine a situation in which the concentration of the bleach is in large excess over the concentration of Allura Red. For example, say we prepare the system such that initially,

time = 0, $[NaOCl]_0$ = 2.0 M, and $[\text{Allura Red}]_0$ = 0.001M.

Then, when the reaction has run to completion (at time = infinity),

$$[NaOCl]_i = [NaOCl]_0 - [\text{Allura Red}]_0 = 2.0\text{ M} - 0.001\text{ M} = 1.999\text{ M} \cong 2.0\text{ M}$$

In this case, the concentration of bleach did not change appreciably during the course of the reaction and can be considered to remain constant. In this case, the rate law simplifies to:

$$\text{rate} = -\frac{\Delta[Allura\ Red]}{\Delta t} = k'[\text{Allura Red}]^x$$

where $k' = k[NaOCl]^y$ and is referred to as the pseudo-first order rate constant.

This rate law expression can be mathematically converted into an integrated rate law, the form of which depends on the value of x.

zeroth order: $[\text{Allura Red}]_t = -k't + [\text{Allura Red}]_0$

and a plot of [Allura Red] vs time will give a straight-line plot with the slope = -k'.

first order: $\ln[\text{Allura Red}]_t = -k't + \ln[\text{Allura Red}]_0$

and a plot of ln[Allura Red] vs time will give a straight line plot with the slope = -k'.

second order: $\frac{1}{[Allura\ Red]_t} = k't + \frac{1}{[Allura\ Red]_0}$

and a plot of 1/ [Allura Red] vs time will give a straight-line plot with the slope = k'.

By measuring the concentration of Allura Red at various times during a reaction and graphing the results, the relationship between concentration and time that gives a linear fit allows you to determine the order of reaction with respect to Allura Red (i.e. a value for x).

A second set of rate data, collected for reactions where the concentration of Allura Red is held constant and the initial excess concentration of bleach is varied in a simple ratio between trials will allow you to determine the order of reaction with respect to bleach (i.e. a value for y).

For example, since rate = k'[Allura Red]^{X}, if [Allura Red] is doubled and the rate doesn't change, the Allura Red is not involved in the rate determining step of the reaction. On the other hand, if the observed rate doubles, x must be 1 and if the observed rate increases by a factor of 4, then x = 2.

The concentration of Allura Red will be determined spectrophotometrically using a Beer's Law calculation, as was done previously. You will use the values of lambda max and the molar absorptivity coefficient determined earlier this semester.

Application

The chemicals used in art undergo changes that affect the colors and textures of the products. Some of the products incorporate these changes in order to enhance the art, purposely anticipating the changes that will occur after the piece is completed by the artist, such as the use of verdigris.[1] Verdigris is the blue-green look of weathered copper. Though some artists want this weathered look, copper can cause problems in other applications. The presence of copper in paper can cause discoloration that is unwanted,[2] so efforts to remove verdigris from paper continue. Though copper weathers rapidly, other objects maintain their composition for a long time. The art processes of 75,000 years ago have recently been uncovered3 indicating the mixing of colored compounds. The mixing bowls (shells) were protected by dune sand in a cave. Whether the aging process is considered an advantage or a nuisance, the rate of aging can be influenced by temperature and the presence of other chemicals.

When an artist plans to use an aging material, it is important for them to consider the full lifetime of their art. The considerations include what the work will look like before it ages, as it ages and whether to try to stop the aging process at a particular point. In order to describe any chemical change, it is necessary to tell what the beginning looked like, what the endpoint looked like and how fast the beginning faded and the endpoint appeared. In chemistry we do this through describing the reactants, products and kinetics of the reaction. Given two related chemicals a trained scientist may be able to suggest which chemical is the reactant and which is the product, but thermodynamics (the energy change in the reaction) will determine whether the reaction proceeds from A → B or from B → A and kinetics (the rate of the reaction) tells how fast the process will occur.

References:

1. Mortensen, K. The Changing Nature of Copper, Copper in the Arts (2007) 8, online. https://www.copper.org/consumers/arts/2007/december/Verdigris.html accessed on 10/20/2016

2. Ahn et al. Investigation of the stabilization of verdigris-containing rag paper by wet chemical treatments, Heritage Science (2014) 2:12. Accessed online 10/20/2016 http://www.heritagesciencejournal.com/content/2/1/12

3. Pappas, S. Oldest Human Paint-Making Studio Discovered in Cave, LiveScience (2011) online. http://www.livescience.com/16538-oldest-human-paint-studio.html accessed 10/19/2016.

Safety Note

- Wear safety goggles at all times in the laboratory.
- Gloves are recommended when handling sulfuric acid. Sulfuric acid is a strong acid and should be handled carefully. Spills should be cleaned up immediately. If any strong acids or bases come in contact with your skin, rinse thoroughly with water.
- Chemicals are not to go down the sink. See your instructor for disposal instructions.

In-lab discussion:

Consider a glass of ice water.

- If ice (H_2O (s)) is one substance and liquid water (H_2O (l)) is the other substance, which direction will the reaction proceed?
- How long will it take for the reaction to go to completion?

These are questions that we will explore in part I. During part II, you will determine the quantitative method of describing a chemical reaction.

<u>TA Demonstration</u>

In this demonstration, you will see an example of the famous class of Belousov-Zhabotinsky reactions.

Carefully clean and dry a 400 mL beaker. Rinse with deionized water. Add 32 mL of deionized water to the beaker. Carefully measure 270 mL of 1.8 M sulfuric acid with a 50 mL or 100 mL graduated cylinder. Place the stir bar in the beaker of water. Adjust the magnetic stirrer until the water is gently being stirred. Slowly pour the acid in the beaker containing the water. The water will get warm. Allow the solution to stir until the beaker cools to near room temperature.

On separate pieces of weighing paper or into separate weighing boats, weigh out 3.25 g of malonic acid, $HOOCCH_2COOH$; 2.90 g potassium bromate, $KBrO_3$; and 0.65 g manganese (II) sulfate monohydrate, $MnSO_4 \cdot H_2O$. With stirring, add the malonic acid to the solution in the beaker. When the malonic acid has dissolved, add the $KBrO_3$ with stirring. Finally, add the $MnSO_4$ with stirring. (The order of addition of the solids is important.) Keep stirring slowly and continuously. Immediately after the addition of the $MnSO_4$, the solution should turn orange. After the solution turns orange, carefully observe the solution.

Observations: Look for any changes that indicate that a chemical reaction is occurring (e.g. color change, formation of a gas, or formation of a precipitate). Take care in describing the timing of events.

<u>**Part I Questions**</u> (record your observations and responses in your Labflow notebook)

1. Do all parts of the reaction appear to occur at the same rate?
2. Does the reaction proceed at the same rate throughout?
3. Explain both in diagram and in complete sentences how the reaction proceeds. Consider how the reactions are regulated.

Part II: Kinetics Procedure

You will be measuring concentration changes over time for four different sets of reactant concentrations. These data will be exported to Microsoft Excel for analysis.

1. The stockroom has prepared a 1×10^{-4} M stock solution of Allura Red and a 4.0×10^{-3} M solution of bleach. Using separate 100 mL beakers, obtain 45 mL of each solution.
2. Turn on LabQuest.
3. Calibrate the LabQuest Spectrometer: Insert "blank" cuvette into spectrometer (note: The "blank" cuvette should be filled with deionized water.) Remember that the cuvette should only be touched on the ridged sides and should be inserted into the spectrometer with the non-ridged sides facing top and bottom (toward the words "Vernier Spectrometer"). Be sure to wipe the outside of the cuvette with a Kimwipe to remove any smudges.

Tap the red box and choose “Calibrate”. The calibration dialog box will display the message: "Waiting ... seconds for lamp to warm up." Allow the spectrometer to warm up for one minute. Follow the instructions in the dialog box to complete the calibration.

4. Tap the red box again to select the wavelength. Set the wavelength to 502 nm. Click OK.
5. Click the data collection button. Change the Mode to Time Based. Make the Duration 660 seconds. In the section titled Interval, enter 30 seconds/ sample (NOT 30 samples/ second). Click OK.
6. Refer to Table 1 Trial 1. Using a graduated pipet, transfer the quantities of Allura Red from column A and water from column B into a 50 mL beaker and swirl to mix. Make sure to rinse your graduated pipet well between solutions to ensure solution concentrations are not altered.
7. Transfer the quantities of bleach from Table 1 column C and water from Table 1 column D into a second 50 mL beaker and swirl to mix.
8. *Simultaneously,* pour the bleach quickly into the beaker containing Allura Red and start the data collection by clicking the green Start button. (By pressing the green start button at the same time as mixing the solutions, data will automatically be recorded at T = 30 seconds and every 30 seconds thereafter until 660 seconds.)
9. Stir the solution rapidly using the tip of a transfer pipet. Use this pipet to fill the cuvette about 3/4 full. Wipe with a Kimwipe and place in the spectrometer in time for the data recording at thirty seconds.
10. If the absorbance drops below 0.03 before 660 seconds is over, you may press the red Stop button to end data collection.
11. Discard the solution in the cuvette and 50 mL beakers in the appropriate waste container. Rinse and dry beakers for use in subsequent mixing. Rinse cuvettes and allow them to dry on a paper towel.
12. Repeat steps 6-12 three more times using the quantities for trials 2 through 4 in Table 1.
13. After exporting your data to your USB, clear the memory on the LabQuest.
14. Open Microsoft Excel and open your text file within the spreadsheet program.

Table 1 Reagent Quantities

Trial	A: Stock Dye (mL)	B: H_2O for dye (mL)	C: Stock Bleach (mL)	D: H_2O for bleach (mL)
1	2.5	7.5	10.0	0
2	5.0	5.0	10.0	0
3	5.0	5.0	5.0	5.0
4	5.0	5.0	2.5	7.5

Calculations and Analysis

Before proceeding with the calculations, be sure that you have read and understand the introduction to this experiment (Part II). Without this background, this method of rate law determination may seem confusing. Use the stock solution concentrations and the values in table 1 to calculate the initial concentrations of Allura Red and NaOCl for trials 1-4.

1. Determination of the reaction order with respect to Allura Red:

   a. To find the reaction order with respect to Allura Red, you will need to prepare three graphs using data from trials 1 and 2. These graphs will represent:

      - Graph 1: [Allura Red] vs time (trials 1 and 2)
      - Graph 2: In [Allura Red] vs time (trials 1 and 2)
      - Graph 3: 1/[Allura Red] vs time (trials 1 and 2)

   b. Data for both trials 1 and 2 should be included on the same graph. In other words, you will have three graphs with two curves on each. To prepare these graphs, set up another column for each trial to calculate concentration from the absorbance readings using Beer's Law (A= εbc), 25,900 $M^{-1}cm^{-1}$ as the molar absorptivity coefficient, ε, for Allura Red and a path length of 1 cm for the cuvette. Remember that you manually calculated the concentration of Allura Red at zero seconds from the stock solution concentration, the aliquot taken, and the total reaction solution volume (Calculation 1).

   c. Create new columns for each trial to calculate ln[Allura Red] and 1/[Allura Red].

   d. Create the three graphs and determine the reaction order for Allura Red based on which graph yields a linear relationship.

2. Determination of the reaction order with respect to Sodium Hypochlorite:

- To determine the reaction order with respect to Allura Red, we could hold the concentration of sodium hypochlorite constant and note how the rate changed as a function of the concentration of Allura Red. Instead, we determined the reaction order by graphing the data vs. time.
- To determine the order with respect to sodium hypochlorite, we hold the concentration of Allura Red constant while varying the concentration of NaOCl. Because NaOCl is

colorless, it is not possible to monitor the experiment as was done previously. However, because k' is directly proportional to rate, we can determine how the rate changes by comparing k' for trials 3 and 4.

a. Prepare another graph of ln[Allura Red] vs time using data from trials 3 and 4. Find k' from the slopes of the two lines. Determine the reaction order with respect to sodium hypochlorite by noting how the values of k' change for trials 3 and 4.

3. Determination of the rate constant, k:

   a. Recall that k' = k[NaOCl]. Determine the value of k for trials 3 and 4 using the k' values derived from the linear relationships.

Questions to guide your Discussion/Conclusion:

1. Summarize your results and present your justification for using the graphs that you did to determine the order of the reaction.
2. Write the experimental rate law that you determined.
3. The rate constant, k, should remain constant unless the temperature is changed. Do your results support this statement within the limitations of expected experimental error? If not, propose the reasons why.
4. Does your data agree with the assumption made in Analysis 3a that the reaction is first order with respect to sodium hypochlorite, NaOCl?

Submission Details:

Submit your complete report to Canvas in the **"Lab Report 10 for Peer Review" assignment by 8:00 am, on the date of your Peer Review**.

Your Lab Instructor will assign you 2 other papers within your section to Peer Review during your lab meeting. You will have your normal Lab meeting time to complete the Peer Review Activity.

Final reports are due in the "Lab 1415-10 Final Report" assignment by the syllabus date.

Remember: References are required for full reports.

The OU Writing Center is also an excellent source of assistance. Feel free to get help from these experts.