

# INVESTIGATION

## What Is the Rate Law of the Fading of Crystal Violet Using Beer's Law?

### Introduction

Crystal violet is a common, beautiful purple dye. In strongly basic solutions, the bright color of the dye slowly fades and the solution becomes colorless. The kinetics of this "fading" reaction can be analyzed by measuring the color intensity or absorbance of the solution versus time to determine the rate law.

### Central Challenge

The purpose of this laboratory activity is to determine the rate law for the reaction of crystal violet (CV) and sodium hydroxide (NaOH).

### Context for This Investigation

If you're making something, you might think making it to last would always be a good thing. But what if you're making a pesticide with known detrimental impacts on human health? Then you may only want it to stay intact for a few days after it has been applied to crops before it decomposes into what often are less harmful products. If its molecules stay intact for too long, the pesticide can persist in the environment and build up in drinking water. In 2000, over 20 million kilograms of the pesticide 1,3-dichloropropene (1,3-D) were applied to crops in the United States. Scientists investigated the rate of decomposition of 1,3-D in acidic, basic, and neutral solutions as well as in soil. For each case, they generated plots of the amount of intact 1,3-D persisting versus time and found that the reaction could be characterized as pseudo first-order. Knowing the order of the reaction allowed them to determine the half-life of intact 1,3-D. In acidic media, they found that the half-life for the decomposition of 1,3-D was about eight days, but in the presence of excess NaOH the half-life was reduced to about four days. Experimentally determined data like this is vital to the ability of society to use chemicals wisely in improving food production, while not endangering the end consumers or the people who work with the chemicals during the growing process.

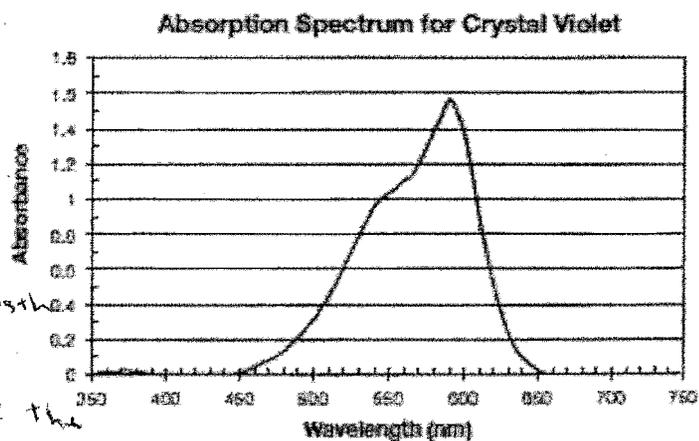
### Safety and Disposal

Crystal violet is a dye that stains skin and clothing. A sodium hydroxide solution is a corrosive skin irritant. You must wear an apron and splash-proof goggles during the lab and use disposable gloves in handling the aqueous solutions of crystal violet and sodium hydroxide. If any of the solutions spilled on your skin, wash with copious amounts of water.

### Part I: Guiding Questions

- Based on the absorption spectrum of 25  $\mu\text{M}$  crystal violet in Figure 1 and taking into account the considerations that follow, what wavelength should you use for the Beer's law calibration curve and subsequent reaction of CV with NaOH? Please explain your answer.

You should use a wavelength of 590 because on the graph, that would be the peak.



- A calibration curve requires the preparation of a set of known concentrations of CV, which are usually prepared by diluting a stock solution whose concentration is known. Describe how to prepare 10. mL of a 5-, 10-, 15-, and 20-  $\mu\text{M}$  CV solution using a 25  $\mu\text{M}$  CV stock solution.

Figure 1. The visible spectrum of a 12.5 micromolar CV solution

You would dilute it until you get the desired  $\mu\text{M}$  CV.  
 $(V_1)(25) = (10\text{mL})(5\text{m})$

3. During the reaction of CV with NaOH, do you expect the colorimeter's absorbance reading to change? How do you expect it to change if such a change is anticipated (i.e., increase, decrease, or no change) as the reaction proceeds? Explain your reasoning.

I expect the colorimeter's absorbance reading to decrease because the reaction should lower the concentration of the substance as we dilute it.

4. Answer the following questions for a reaction of CV with NaOH in these two scenarios: a solution with a 1:1 NaOH:CV mole ratio and a solution similar to what you will be using with a 1000:1 NaOH:CV mole ratio.

- a. Using your prior knowledge of reaction stoichiometry, what is the final percentage of each reactant remaining if each reaction went to completion? Show work and reasoning to justify your answer.

Based on the mole ratios, a 1:1 NaOH:CV mole ratio, both NaOH should have a final percentage of around 50% each. In the final mole ratio of 1000:1 NaOH:CV, the final percentage of NaOH should be around 99.9% and 0.1% for CV.

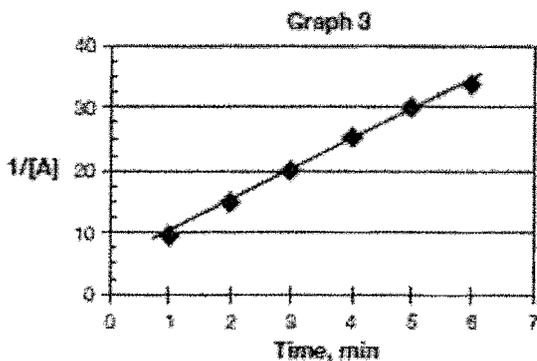
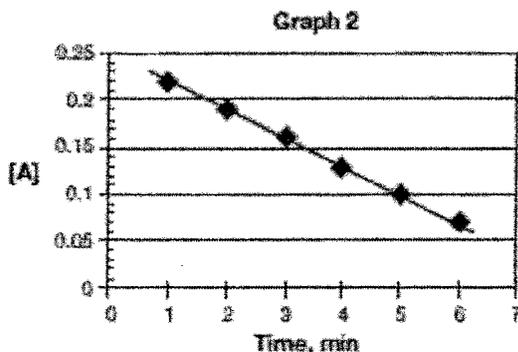
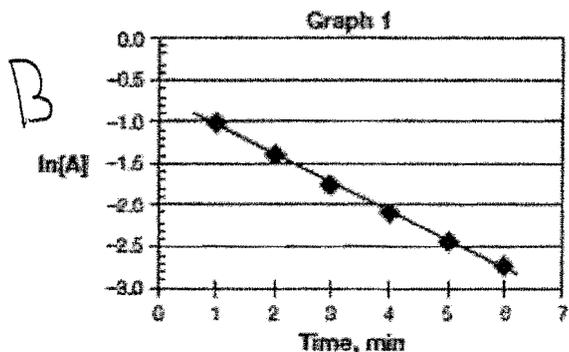
- b. Based on this result, describe how one gets Equations 3 and 4 from Equation 2 in the Explanation section.

One would take Equation 2 and make 2 other equations one for each reactant.

5. Using the kinetics chapter in your textbook and websites like "Chemical Kinetics – Integrated rate laws" <http://www.chm.davidson.edu/vce/kinetics/IntegratedRateLaws.html>, describe the graphical analysis that can be done to determine the order (considering only 0th, 1st, or 2nd order) and the value of the pseudo-rate constant,  $k^*$ , of a chemical reaction from concentration data collected through time.

You can determine the order of the graph by seeing the increase / decrease of the order intervals.

6. Match each linear graph shown below with that expected if the reaction is (a) zero order, (b) first order, and (c) second order with respect to [A].





A differential rate law describes the rate of a chemical reaction as a function of the concentration of the reactants, while an integrated rate law describes the concentration of a reactant as a function of time; both types of rate laws are related to each other by the use of calculus. Equation 3 is a differential rate law, in which a graphical analysis of the corresponding integrated rate law can be used to determine the value of the parameters in Equation 3 using least-squares linear regression analysis. The degree or extent of linear fit may be evaluated using the coefficient of determination (or square of the correlation coefficient), i.e., it may be used to identify the graph that has a linear relationship.

### Laboratory Technique

#### Calibrate the colorimeter:

Use a blank filled with 6 mL H<sub>2</sub>O and 4 mL 0.2 M NaOH to calibrate the colorimeter. Fill the cuvette with the prescribed solution. Set the wavelength on the colorimeter for the appropriate absorbance (see guiding question 1). Place the cuvette in the colorimeter and press the CAL button to calibrate, or zero, the colorimeter.

#### Trial One - Concentration vs Time:

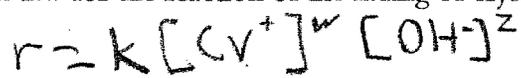
Carefully measure 6 mL of the stock solution of crystal violet, CV, and 4 mL of 0.2 M NaOH. DO NOT MIX until you are ready to place the reaction into the cuvette. Press "Play" on the Labquest, then mix the solutions, quickly fill the cuvette, and measure the absorbance until the color has faded so much that the absorbance is no longer measurable. Use the known concentration of stock CV to calculate the new initial concentration of CV upon mixing the two solutions.

#### Trial Two - Concentration vs Time:

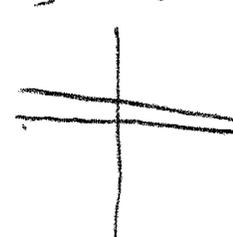
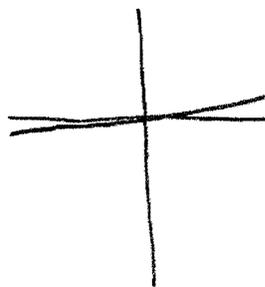
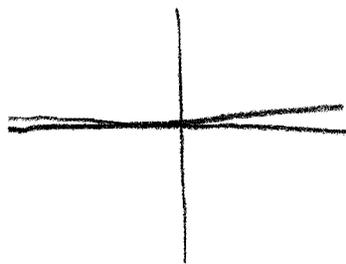
Carefully measure 6 mL of the stock solution of crystal violet, CV, and 2 mL of 0.2 M NaOH, and 2 mL H<sub>2</sub>O. DO NOT MIX until you are ready to place the reaction into the cuvette. Press "Play" on the Labquest, then mix the solutions, quickly fill the cuvette, and measure the absorbance until the color has faded so much that the absorbance is no longer measurable. Use the known concentration of stock CV to calculate the new initial concentration of CV upon mixing the two solutions.

#### Analysis

1. In your graphing calculator, enter time in L1 and absorbance in L2. Sketch a graph BY HAND of this same data.
2. In L3, calculate  $\ln[\text{Abs}]$ . Sketch a graph BY HAND of time (L1) vs  $\ln[\text{Abs}]$  (L3).
3. In L4, calculate  $[\text{Abs}]^{-1}$ . Sketch a graph BY HAND of time (L1) vs  $[\text{Abs}]^{-1}$  (L4).
4. Obtain the equation of each line and the corresponding  $R^2$  value using  $\text{STAT} \rightarrow \text{CALC} \rightarrow \text{LinReg}$ . Write the equation next to each graph.
5. Compare the three graphs and determine the order of the reaction with respect to CV. If necessary, view the Podcast 12.2B <http://www.screencast.com/t/lfc0fRysr>. ~~Second Order~~ **Second Order**
6. Compare the slopes of the lines for Trial One and Trial Two, being sure to use the appropriate linear graph (the one whose  $R^2$  value is closest to 1.00). Applying the differentiated rate law technique, determine the order of the reaction with respect to OH<sup>-</sup>. If necessary, view the Podcast 12.2A <http://www.screencast.com/t/KbA0P4HHZ>.
7. Write the overall rate law for the reaction of the fading of crystal violet.



$$1. y = 0.0417x + 0.114 \quad | \quad 2. y = 0.0208x + 0.5481$$



$$y = -0.008x + 1.393$$