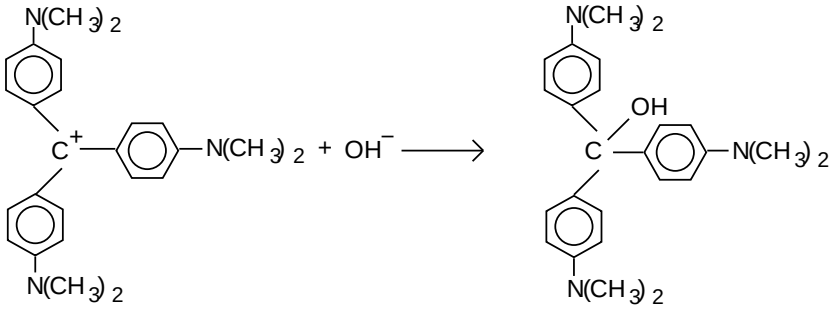
ASIM Rate Law Determination of the Crystal Violet Reaction

Introduction

In this experiment, you will observe the reaction between crystal violet and sodium hydroxide. One objective is to study the relationship between concentration of crystal violet and the time elapsed during the reaction. The equation for the reaction is shown here.



A simplified (and less intimidating!) version of the equation is:

$$CV^+ (aq) + OH^- (aq) \rightarrow CVOH (aq)$$

(crystal violet) (hydroxide)

The rate law for this reaction is in the form: rate = $k[CV^+]m[OH^-]n$, where k is the rate constant for the reaction, m is the order with respect to crystal violet (CV^+), and n is the order with respect to the hydroxide ion. Because the hydroxide ion concentration is more than 1000 times as large as the concentration of crystal violet, $[OH^-]$ will not change appreciably during this experiment. Thus, you will find the order with respect to crystal violet (m), but not the order with respect to hydroxide (n).

As the reaction proceeds, a violet-colored reactant will be slowly changing to a colorless product. You will measure the color change with a Vernier Colorimeter or a Vernier Spectrometer. The crystal violet solution used in this experiment has a violet color, of course, thus the Colorimeter users will be instructed to use the 565 nm (green) LED. Spectrometer users will determine an appropriate wavelength based on the absorbance spectrum of the solution. We will assume that absorbance is proportional to the concentration of crystal violet (Beer's law). Absorbance will be used in place of concentration in plotting the following three graphs:

- Absorbance vs. time: A linear plot indicates a zero order reaction (k = – slope).
- LN Absorbance vs. time: A linear plot indicates a first order reaction (k = –slope).
- 1/Absorbance vs. time: A linear plot indicates a second order reaction (k = slope).

Once the order with respect to crystal violet has been determined, you will also be finding the rate constant, k, and the half-life for this reaction.

Essential Question

How can graphical analysis be used to determine reaction order?

Safety

Goggles, gloves and aprons should be worn during this experiment. Sodium hydroxide solution is caustic. Avoid spilling it on your skin or clothing. Crystal violet is a biological stain. Avoid spilling it on your skin or clothing.

Materials

Vernier LabQuest	0.10 M sodium hydroxide, NaOH, solution
Vernier Colorimeter or Spectrometer	2.5×10^{-5} M crystal violet solution
Temperature Probe or thermometer	ice
5 plastic cuvettes	two 100 mL beakers
1 liter beaker	50 mL beaker
2 10 mL graduated cylinders	watch with a second hand

Procedure

Both Colorimeter and Spectrometer Users

1. Obtain and wear goggles.
2. Use a 10 mL graduated cylinder to obtain 10.0 mL of 0.10 M NaOH solution. **CAUTION:** *Sodium hydroxide solution is caustic. Avoid spilling it on your skin or clothing.* Use another 10 mL graduated cylinder to obtain 10.0 mL of 2.5×10^{-5} M crystal violet solution. **CAUTION:** *Crystal violet is a biological stain. Avoid spilling it on your skin or clothing.*
3. Prepare a *blank* by filling a cuvette 3/4 full with distilled water. To correctly use cuvettes, remember:
   - Wipe the outside of each cuvette with a lint-free tissue.
   - Handle cuvettes only by the top edge of the ribbed sides.
   - Dislodge any bubbles by gently tapping the cuvette on a hard surface.
   - Always position the cuvette so the light passes through the clear sides.

Colorimeter Users Only (Spectrometer users proceed to the Spectrometer section)

4. Connect the Colorimeter to LabQuest and choose New from the File menu.
5. Calibrate the Colorimeter.
   a. Place the blank in the cuvette slot of the Colorimeter and close the lid.
   b. Press the < or > buttons on the Colorimeter to set the wavelength to 565 nm (green). Then calibrate by pressing the CAL button on the Colorimeter. When the LED stops flashing, the calibration is complete.

6. Set up the data-collection mode.
   a. On the Meter screen, tap Rate. Change the data-collection rate to 1 sample/second.
   b. Change the data-collection length to 200 seconds. Select OK.
   c. Proceed to Step 7.

Spectrometer Users Only

4. Use a USB cable to connect the Spectrometer to your LabQuest. Turn on the LabQuest.
5. Calibrate the Spectrometer.
   a. Place the blank cuvette in the Spectrometer.
   b. Choose Calibrate from the Sensors menu. The following message is displayed: "Waiting 60 seconds for lamp to warm up." After 60 seconds, the message will change to "Warmup complete."
   c. Select Finish Calibration. When the message "Calibration completed" appears, select OK.

6. Determine the optimum wavelength for examining the crystal violet solution and set up the mode of data collection.
   a. Empty the blank cuvette and rinse it twice with small amounts of 2.5×10^{-5} M crystal violet solution. Fill the cuvette about 3/4 full with the crystal violet solution and place it in the Spectrometer.
   b. Start data collection. A full spectrum graph of the solution will be displayed. Stop data collection. The wavelength of maximum absorbance (λ max) is automatically identified.
   c. Tap the Meter tab. On the Meter screen, tap Mode. Change the mode to Time Based. The default data collection of 1 sample per second for 200 seconds will be suitable. Select OK.
   d. Remove the cuvette from the Spectrometer and dispose of the crystal violet solution as directed. Save the cuvette for Step 7.

Both Colorimeter and Spectrometer Users

7. *Do this quickly!* To initiate the reaction, simultaneously pour the 10 mL portions of crystal violet and sodium hydroxide into a 250 mL beaker and stir the reaction mixture with a stirring rod. Empty the water from the cuvette. Rinse the cuvette twice with ~1 mL amounts of the reaction mixture, fill it 3/4 full, and place it in the device (Colorimeter or Spectrometer). Close the lid on the Colorimeter. Start data collection.
8. Absorbance data will be collected for 200 seconds. You may stop data collection early if desired. Discard the beaker and cuvette contents as directed by your instructor.
9. Analyze the data graphically to decide if the reaction is zero, first, or second order with respect to crystal violet.
   - Zero Order: If the current graph of absorbance *vs.* time is linear, the reaction is *zero order*.
   - First Order: To see if the reaction is first order, it is necessary to plot a graph of the natural logarithm (LN) of absorbance *vs.* time. If this plot is linear, the reaction is *first order*.
   - Second Order: To see if the reaction is second order, plot a graph of the reciprocal of absorbance *vs.* time. If this plot is linear, the reaction is *second order*.
10. Follow these directions to create a calculated column, LN Absorbance, and then plot a graph of LN Absorbance *vs.* time:
    a. Tap the Table tab to display the data table.
    b. Choose New Calculated Column from the Table menu.
    c. Enter the Name (LN Abs) and leave the Units field blank. Select the equation, ALN(X). Use Absorbance as the Column for X, and **1** as the value for A. Select OK.
    d. A graph of LN absorbance *vs*. time will be displayed.

11. Follow these directions to create a calculated column, 1/Absorbance, and then plot a graph of 1/Absorbance *vs.* time:
    a. Tap the Table tab.
    b. Choose New Calculated Column from the Table menu.
    c. Enter "1/Absorbance" as the Name, and leave the Units field blank. Select the equation, A/X. Use Absorbance as the Column for X, and **1** as the value for A. Select OK.
    d. A graph of 1/Absorbance *vs.* time will be displayed.

12. To see any of the three plots again:
    a. Tap the vertical-axis label of the graph.
    b. Choose "Absorbance," "LN Absorbance," or "1/Absorbance."

13. Optional: Print a copy of the table.
14. Optional: Print a copy of the graph that was most linear.

Data Analysis Questions

1. Was the reaction zero, first, or second order, with respect to the concentration of crystal violet? Explain.

2. Calculate the rate constant, k, using the *slope* of the linear regression line for your linear curve (*k* = –slope for zero and first order and *k* = slope for second order). Be sure to include correct units for the rate constant. Note: This constant is sometimes referred to as the *pseudo rate constant*, because it does not take into account the effect of the other reactant, OH^-.

3. Write the correct rate law expression for the reaction, in terms of crystal violet (omit OH^-).

4. Using the printed data table, estimate the half-life of the reaction; select two points, one with an absorbance value that is about half of the other absorbance value. The *time* it takes the absorbance (or concentration) to be halved is known the *half-life* for the reaction. (As an alternative, you may choose to calculate the half-life from the rate constant, *k*, using the appropriate concentration-time formula.)