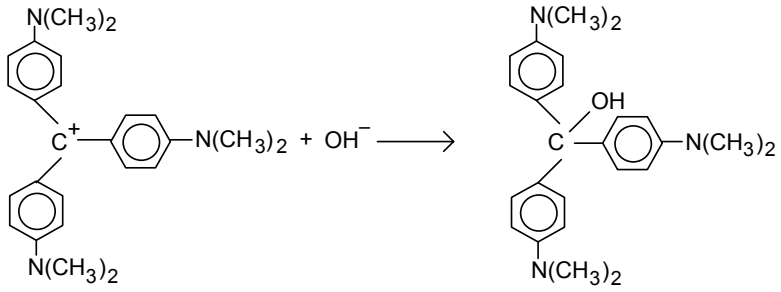
Rate Law Determination of the Crystal Violet Reaction

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:

$$CV^+ + OH^- \longrightarrow CVOH$$

(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. Since 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. Using the green (565 nm) light source of a computer-interfaced Colorimeter, you will monitor the absorbance of the crystal violet solution with time. 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.

OBJECTIVES

In this experiment, you will

- Observe the reaction between crystal violet and sodium hydroxide.
- Use a Colorimeter to monitor the absorbance of the crystal violet solution with time.
- Graph Absorbance *vs*. time, ln Absorbance *vs*. time, and 1/Absorbance *vs*. time.
- Determine the order of the reaction.
- Determine the rate constant, k, and the half-life for this reaction.

MATERIALS

computer
Vernier computer interface
Logger*Pro*
Vernier Colorimeter
one plastic cuvette
250 mL beaker
0.020 M NaOH
2.0×10^{-5} M crystal violet
distilled water
stirring rod
two 10 mL graduated cylinders

PROCEDURE

1. Obtain and wear goggles.
2. Use a 10 mL graduated cylinder to obtain 10.0 mL of 0.020 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 2.0×10^{-5} M crystal violet solution. **CAUTION:** *Crystal violet is a biological stain. Avoid spilling it on your skin or clothing.*
3. Connect the Colorimeter to the computer interface. Prepare the computer for data collection by opening the file "30 Rate Crystal Violet" from the *Chemistry with Computers* folder of Logger*Pro*.
4. Prepare a blank by filling an empty cuvette 3/4 full with water. Seal the cuvette with a lid. To correctly use a colorimeter cuvette, remember:
   - All cuvettes should be wiped clean and dry on the outside with a tissue.
   - Handle cuvettes only by the top edge of the ribbed sides.
   - All solutions should be free of bubbles.
   - Always position the cuvette with its reference mark facing toward the white reference mark at the top of the cuvette slot on the Colorimeter.
5. Calibrate the Colorimeter.
   a. Open the Colorimeter lid.
   b. Holding the cuvette by the upper edges, place it in the cuvette slot of the Colorimeter. Close the lid.
   c. If your Colorimeter has a CAL button, Press the < or > button on the Colorimeter to select a wavelength of 565 nm (Green) for this experiment. Press the CAL button until the red LED begins to flash. Then release the CAL button. When the LED stops flashing, the calibration is complete. Proceed directly to Step 6. If your Colorimeter does not have a CAL button, continue with this step to calibrate your Colorimeter.

First Calibration Point

   d. Choose Calibrate ▸ CH1: Colorimeter (%T) from the Experiment menu and then click Calibrate Now.
   e. Turn the wavelength knob on the Colorimeter to the "0% T" position.
   f. Type "0" in the edit box.
   g. When the displayed voltage reading for Reading 1 stabilizes, click Keep.

Second Calibration Point

   h. Turn the knob of the Colorimeter to the Green LED position (565 nm).
   i. Type "100" in the edit box.
   j. When the displayed voltage reading for Reading 2 stabilizes, click Keep, then click Done.

6. 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. Click

Collect. Note: Because the initial data are sometimes sporadic, you will not actually take a reading until 3 minutes have passed. Empty the water from the cuvette. Rinse the cuvette twice with ~1 mL amounts of the reaction mixture and then fill it 3/4 full. Do not put the cuvette in the Colorimeter yet. To keep the solution from warming inside the Colorimeter, the cuvette is left outside the Colorimeter between readings.

7. After about three minutes have passed since combining the 2 solutions, wipe the outside of the cuvette, place it in the cuvette slot of the Colorimeter, and close the lid. Wait for the absorbance reading to stabilize. When it is stable, click Keep—this saves both the absorbance and time data values. Remove the cuvette from the Colorimeter. After 45 seconds have elapsed, again place the cuvette in the Colorimeter, wait for the absorbance to stabilize, and click Keep. After saving this second data pair, remove the cuvette again. Continue in this manner, collecting data about once every minute, until 20 minutes have elapsed.

8. Data collection will end after 20 minutes. Discard the beaker and cuvette contents as directed by your teacher.

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. Choose New Calculated Column from the Data menu.
    b. Enter "ln Absorbance" as the Name, "ln Abs" as the Short Name, and leave the unit blank.
    c. Enter the correct formula for the column into the Equation edit box. Choose "ln" from the Function list. Then select "Absorbance" from the Variables list. In the Equation edit box, you should now see displayed: ln("Absorbance"). Click Done.
    d. Click on the y-axis label.Choose ln Absorbance. A graph of ln absorbance *vs.* time should now be displayed. To see if the relationship is linear, click the Linear Fit button,  .

11. Follow these directions to create a calculated column, 1/Absorbance, and then plot a graph of 1/Absorbance *vs.* time:
    a. Choose New Calculated Column from the Data menu.
    b. Enter "1/Absorbance" as the Name, "1/Abs" as the Short Name, and leave the unit blank.
    c. Enter the correct formula for the column into the Equation edit box. To do this, type in "1" and "/". Then select "Absorbance" from the Variables list. In the Equation edit box, you should now see displayed: 1/"Absorbance". Click Done.
    d. Click on the y-axis label. Choose 1/Absorbance and uncheck any other boxes. A graph of 1/Absorbance *vs.* time should now be displayed. To see if the relationship is linear, click the Linear Fit button,  .

12. Print a copy of the graph in Steps 9-11 that was linear (Absorbance, ln Absorbance, or 1/Absorbance *vs.* time).

a. Click the vertical-axis label of the graph.
b. Of "Absorbance", "ln Absorbance", or "1/Absorbance", choose only the choice that gave a linear plot. Click OK.
c. Print a copy of the graph. Enter your name(s) and the number of copies of the graph you want printed. Note: Be sure the linear regression curve is displayed on the graph, as well as the regression statistics box.

13. Print a copy of the table. Enter your name(s) and the number of copies of the table.

CALCULATIONS

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.)