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:

\[
\text{CV}^+ + \text{OH}^- \rightarrow \text{CVOH}
\]

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

\[
\text{CV}^+ + \text{OH}^- \rightarrow \text{CVOH}
\]

(crystal violet) (hydroxide)

The rate law for this reaction is in the form: \( \text{rate} = k[\text{CV}^+]^m[\text{OH}^-]^n \), where \( k \) is the rate constant for the reaction, \( m \) is the order with respect to crystal violet (\( \text{CV}^+ \)), 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, \([\text{OH}^-]\) 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 (\( k = -\text{slope} \)).
- **In Absorbance vs. time:** A linear plot indicates a first order reaction (\( k = -\text{slope} \)).
- **1/Absorbance vs. time:** A linear plot indicates a second order reaction (\( k = \text{slope} \)).

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.

**MATERIALS**

- Power Macintosh or Windows PC
- Vernier computer interface
- LoggerPro
- Vernier Colorimeter
- one plastic cuvette
- 0.02 M NaOH
- 2.0 x 10^{-5} M crystal violet
- distilled water
- stirring rod
- two 10-mL graduated cylinders
250-mL beaker

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 $2.0 \times 10^{-5}$ M crystal violet solution. CAUTION: Crystal violet is a biological stain. Avoid spilling it on your skin or clothing.

3. Prepare the computer for data collection by opening the file in the Experiment 30 folder of Chemistry with Computers. The vertical axis has absorbance scaled from 0 to 0.35. The horizontal axis has time scaled from 0 to 20 minutes.

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 right of the cuvette slot on the Colorimeter.

5. Calibrate the Colorimeter.
   a. Holding the cuvette by the upper edges, place it in the cuvette slot of the Colorimeter.
   b. If your Colorimeter has an AUTO CAL button, set the wavelength on the Colorimeter to 565 nm (Green), press the AUTO CAL button, and proceed directly to Step 6. If your Colorimeter does not have an AUTO CAL button, continue with this step to calibrate your Colorimeter.
   First Calibration Point
   c. Choose Calibrate from the Experiment menu and click Perform Now.
   d. Turn the wavelength knob on the Colorimeter to the “0% T” position.
   e. Type “0” in the edit box.
   f. When the displayed voltage reading for Input 1 stabilizes, click Keep.
   Second Calibration Point
   g. Turn the wavelength knob of the Colorimeter to the Green LED position (565 nm).
   h. Type “100” in the edit box.
   i. When the displayed voltage reading for Input 1 stabilizes, click Keep, then click OK.

5. 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.

6. 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.

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

8. 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.

9. Follow these directions to create a calculated column, ln Absorbance, and then plot a graph of ln Absorbance vs. time:
   a. Choose New Column ▶ Formula from the Data menu.
   b. Enter “ln Absorbance” as the Long Name, “ln Abs” as the Short Name, and leave the unit blank. Then click on the Definition tab.
   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 OK.
   d. A graph of ln absorbance vs. time should now be displayed. To see if the relationship is linear, click the Linear Regression button.

10. Use the method described in Step 9 to create a calculated column, 1/Absorbance, and then plot a graph of 1/Absorbance vs. time. To enter the correct formula for the column into the Equation edit box, type “1” and “/”, then select “Absorbance” from the Variables list.

11. Print a copy of the graph in Steps 8-10 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”, check only the box of the choice that gave a linear plot. Click OK.
   c. Print a copy of the Graph window. 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.

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

13. Optional: Print a copy of the two non-linear graphs.

**PROCESSING THE DATA**

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.)