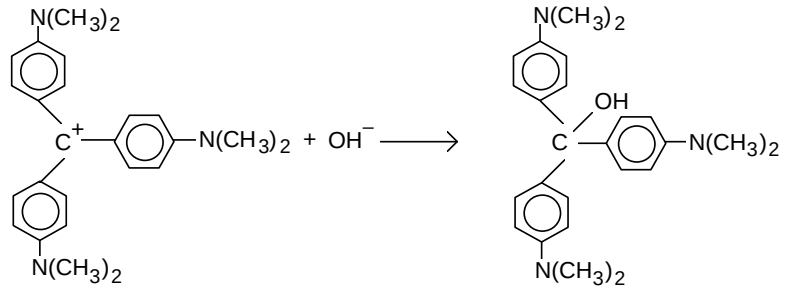
Rate Law Determination of the Crystal Violet Reaction

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 5000 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 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.

Materials

LabPro or CBL 2 interface
TI Graphing Calculator
DataMate program
Vernier Colorimeter
one plastic cuvette
100-mL beaker
0.10 M NaOH
2.5×10^{-5} M crystal violet solution
distilled water
stirring rod
test tube rack

Procedure

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. Plug the Colorimeter into Channel 1 of the LabPro or CBL 2 interface. Use the link cable to connect the TI Graphing Calculator to the interface. Firmly press in the cable ends.

4. Prepare a *blank* by filling an empty cuvette ¾ full with distilled 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. Turn on the calculator and start the DATAMATE program. Press CLEAR to reset the program.

6. Set up the calculator and interface for the Colorimeter.
   a. Place the blank in the cuvette slot of the Colorimeter and close the lid.
   b. Select SETUP from the main screen.
   c. If the calculator displays COLORIMETER in CH 1, set the wavelength on the Colorimeter to 565 nm. Then calibrate by pressing the AUTO CAL button on the Colorimeter and proceed directly to Step 7. If the calculator does not display COLORIMETER in CH1, continue with this step to set up your sensor manually.
   d. Press ENTER to select CH 1.
   e. Select COLORIMETER from the SELECT SENSOR menu.
   f. Select CALIBRATE from the SETUP menu.
   g. Select CALIBRATE NOW from the CALIBRATION menu.

   First Calibration Point

   h. Turn the wavelength knob of the Colorimeter to the 0% T position. When the voltage reading stabilizes, press ENTER. Enter "0" as the percent transmittance.

   Second Calibration Point

   i. Turn the wavelength knob of the Colorimeter to the Green LED position (565 nm). When the voltage reading stabilizes, press ENTER. Enter "100" as the percent transmittance.
   j. Select OK to return to the setup screen.

7. Set up the data-collection mode.
   a. To select MODE, press ▲ once and press ENTER.
   b. Select TIME GRAPH from the SELECT MODE menu.
   c. Select CHANGE TIME SETTINGS from the TIME GRAPH SETTINGS menu.
   d. Enter "4" as the time between samples in seconds.
   e. Enter "45" as the number of samples. The length of the data collection will be 3 minutes.
   f. Select OK to return to the setup screen.

g. Select OK again to return to the main screen.

8. You are now ready to begin monitoring data.
   a. To initiate the reaction, simultaneously pour the 10-mL portions of crystal violet and sodium hydroxide into a 100-mL beaker and stir the reaction mixture with a stirring rod.
   b. Empty the water from the cuvette. Rinse the cuvette with ~1 mL of the reaction mixture and then fill it 3/4 full.
   c. Place the cuvette in the cuvette slot of the Colorimeter and close the lid.
   d. Monitor the absorbance reading on the main screen of the calculator for about 10 seconds (the absorbance reading should be gradually decreasing), then select START to begin data collection.
   e. During the 3-minute data collection, observe the solution in the beaker as it continues to react.
   f. Data collection will end after 3 minutes
   g. Discard the contents of the beaker and cuvette as directed by your teacher.

Data and Calculations

1. 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*.
2. Now, use the RateLaw program on your calculator to determine the order of the reaction. Be sure to record all sets of results, along with r and r^2 values to support your conclusion.
3. Write the correct rate law expression for the reaction, in terms of crystal violet (omit OH^-).
4. 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^-.
5. Calculate the half-life from the rate constant, k, using the appropriate concentration-time formula.