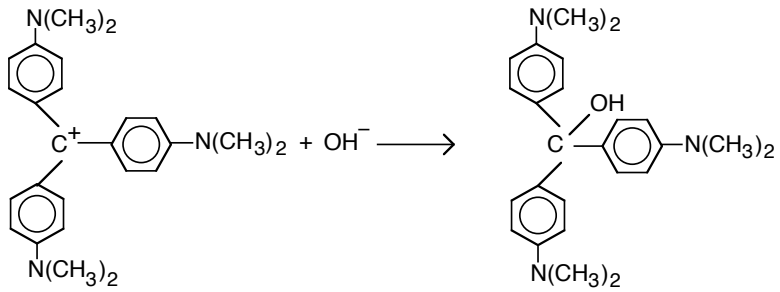
Rate Law of the Crystal Violet Reaction

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:

$$\underset{\text{(crystal violet)}}{CV^+} + \underset{\text{(hydroxide)}}{OH^-} \longrightarrow CVOH$$

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 graphs:

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.

Prelab Questions

1) What do you plot to get a straight line for a first order reaction?

2) What do you plot to get a straight line for a second order reaction?

3) What do you plot to get a straight line for a zeroth order reaction?

4) What is Beer's Law?

5) What type of relationship exists between absorbance and concentration?

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 2.0 x 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 the adapter cable in Channel 1 of the CBL System. Use the link cable to connect the CBL System to the calculator. Firmly press in the cable ends.

4. Turn on the CBL unit and the calculator. Start the CHEMBIO program and proceed to the MAIN MENU.

5. Set up the calculator and CBL for the colorimeter.

   - Select SET UP PROBES from the MAIN MENU.
   - Enter "1" as the number of probes.
   - Select COLORIMETER from the SELECT PROBE menu.
   - Enter "1" as the channel number.

6. You are now ready to calibrate the colorimeter. First prepare a *blank* by filling a cuvette 3/4 full with distilled water. To calibrate the cuvette at 0% and 100% transmittance:

   - Place the blank cuvette in the cuvette slot of the colorimeter and close the lid. Turn the wavelength knob of the colorimeter to the 0% T position. In this position, the light source is turned off, so no light is received by the photocell. When the voltage reading displayed on the CBL screen stabilizes, press [TRIGGER] on the CBL and enter "0" in the TI calculator.
   - Turn the wavelength knob of the colorimeter to the Green LED position (565 nm). In this position, the colorimeter is calibrated to show 100% of the green light being transmitted through the blank cuvette. When the displayed voltage reading stabilizes, press [TRIGGER] and enter "100" in the calculator. Leave the wavelength knob of the colorimeter set to the Green LED position for the remainder of the experiment.
   - Press [ENTER] to return to the MAIN MENU.

7. Set up the calculator and CBL for data collection.

   - Select COLLECT DATA from the MAIN MENU.
   - Select TIME GRAPH from the DATA COLLECTION menu.
   - Enter "4" as the time between samples, in seconds.
   - Enter "45" as the number of samples (the CBL will collect data for a total of 3 minutes).
   - Press [ENTER]. Select USE TIME SETUP to continue. If you want to change the sample time or sample number, select MODIFY SETUP.
   - Enter "0" as the minimum absorbance (Ymin).
   - Enter "0.5" as the maximum absorbance (Ymax).
   - Enter "0.1" as the absorbance increment (Yscl).

8. You are now ready to begin monitoring data. 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. Empty the water from the cuvette. Rinse the cuvette with ~1-mL of the reaction mixture and then fill it 3/4 full. Place the cuvette in the cuvette slot of the colorimeter and close the lid. Monitor the percent transmittance reading on the CBL for about 10 seconds (the percent transmittance reading should be gradually increasing). Then press [ENTER] to begin collecting data. During the 3-minute data collection, observe the solution in the beaker as it continues to react. When data collection stops after 3 minutes ("DONE" appears on the CBL screen), press [ENTER] to display a graph of absorbance vs. time. Discard the contents of the beaker and cuvette 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*.

Follow these directions to create the lists ln absorbance in L3 and 1/absorbance in L4.

- Select NO when asked if you want to repeat, then select QUIT from the MAIN MENU.

TI-82 or TI-83 Calculators:

- To view the lists, press [STAT] to display the EDIT menu and then select Edit.
- To create a list of natural log (ln) of absorbance values (in L3), move the cursor until the L3 column heading is highlighted, then press [LN] [2nd] [L2] [ENTER].
- To create a list of reciprocal of absorbance values (in L4), move the cursor until the L4 column heading is highlighted, then press [2nd] [L2] [x^{-1}] [ENTER]. Proceed to Step 10.

COPY THIS NUMERICAL DATA INTO YOUR LAB BOOK IMMEDIATELY.

10. Follow this procedure to calculate regression statistics and to plot a best-fit regression line on your graph of absorbance, ln absorbance, or reciprocal of absorbance vs. time:

    - Start the CHEMBIO program again and proceed to the MAIN MENU.
      Important: Do *not* select SET UP PROBES—doing so will clear the data lists.
    - Select FIT CURVE from the MAIN MENU.
    - Select LINEAR L1, Ln, where Ln is list 2, 3, or 4. The linear-regression statistics for these two lists are displayed for the equation in the form:

      $$y = ax + b$$

      where *x* is time, *y* is absorbance, ln absorbance or reciprocal absorbance, *a* is the slope, and *b* is the y-intercept. Note: For the plot that is linear, record the value of the slope, *a*, to use in the calculation of the rate constant, *k*, in Processing the Data.
    - To display a best-fit regression line on the graph, press [ENTER], then select SCALE FROM DATA from the SCALE DATA menu. Examine your graph to see if the relationship is linear.
    - To view a graph of two other lists, press [ENTER], return to the MAIN MENU and repeat Step 10.

POST LAB QUESTIONS

1) Create three graphs for this lab. One if it was 0^{th} order, one if it was 1^{st} order, and one if it was 2^{nd} order.

2) Determine if the reaction is first, second, or zeroth order and write the rate law.

3) Determine the numerical value of k and it's units.

4) Write the integrated rate law (y = mx + b) for the reaction.

5) How would the value of k change if we increased the temperature for the reaction.