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:

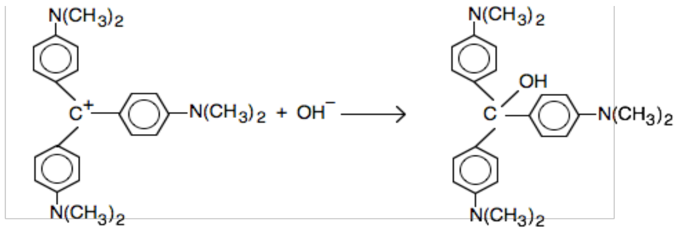

Figure 1

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

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

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 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

LabQuest	0.10 M NaOH	one plastic cuvette
LabQuest App	2.5×10^{-5} M crystal violet solution	100 mL beaker
Vernier Colorimeter	distilled water	stirring rod

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. Connect the Colorimeter to LabQuest and choose New from the File menu.

4. Prepare a *blank* by filling an empty cuvette 3/4 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 top of the cuvette slot on the Colorimeter.

5. Calibrate the Colorimeter.
   a. Place the blank in the cuvette slot of the Colorimeter and close the lid.
   b. Press the < or > button 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. On the Meter screen, tap Length. Change the data-collection length to 180 seconds. Select OK. Data collection will last 3 minutes.

7. 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 for about 10 seconds (the absorbance reading should be gradually decreasing), then start data collection.
   e. During the 3 minute data collection, observe the solution in the beaker as it reacts
   f. When data collection is complete, discard the contents of the beaker and cuvette 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*.

   Follow these directions to create a column of the natural log (ln) of absorbance.

   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.
   d. Select OK.

9. Follow this procedure to plot a best-fit regression line on your graph of ln absorbance *vs.* time:
   a. Choose Curve Fit from the Analyze menu.
   b. Select Linear as the Fit Equation menu. The linear-regression statistics for these two data columns are displayed for the equation in the form

$$y = mx + b$$

   where x is time, y is absorbance, m is the slope, and b is the y-intercept. The correlation coefficient, r, indicates how closely the data points match up with (or *fit*) the regression line. A value of 1.00 indicates a nearly perfect fit.
   c. Select OK.

10. Follow these directions to create a calculated column, 1/Absorbance.
   a. Tap Table to display the data table.
   b. Choose New Calculated Column from the Table menu.
   c. Enter the Column Name (l/Abs) and leave the Units field blank. Select the equation, A/X. Use Absorbance as the column for X, and enter **1** as the value for A.
   d. Select OK.

11. Repeat Step 9 to plot a best-fit regression line on the graph of 1/Absorbance *vs.* time.

PROCESSING THE DATA

(on a separate piece of paper COPY DOWN ALL of the graphs, including axes)

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.)