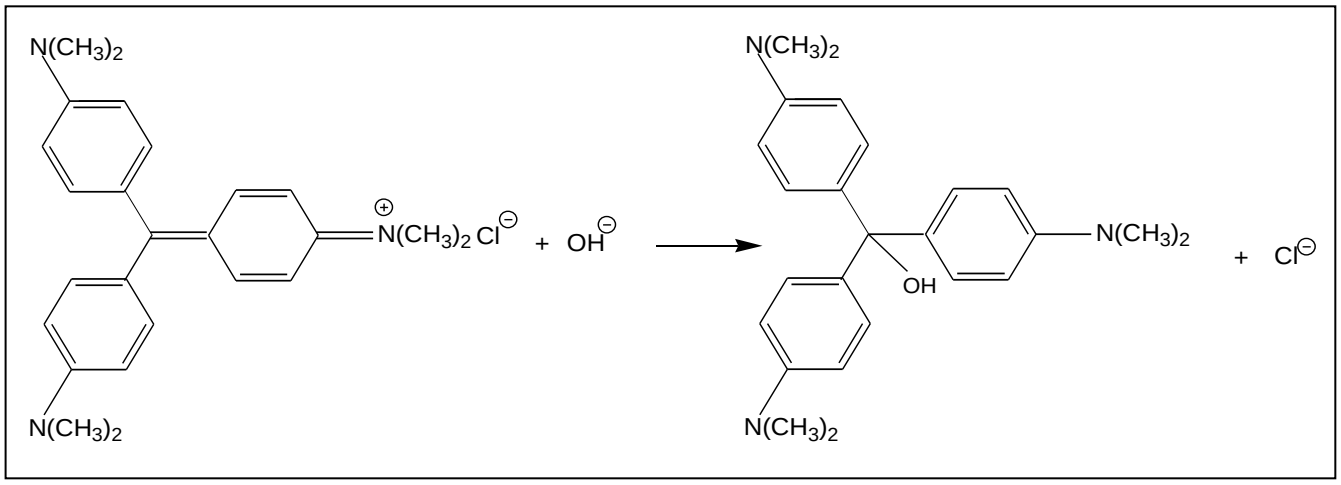
Experiment 8: Crystal Violet Kinetics

During this set of experiments we will be working with two members of the triphenylmethane dyes family, crystal violet and fuchsine. These are organic compounds that contain a colored cation: magenta in the case of fuchsine and violet in the case of crystal violet. The intense color of the cation is due to the extended conjugated system of alternate single and double bonds. Upon reaction with NaOH the conjugation gets disrupted and the color is lost.

The reaction between crystal violet and NaOH is the following:



A simplified version of the same reaction is:

$$CV^{+} + OH^{-}(aq) \longrightarrow CVOH \qquad (1)$$

(crystal violet) (hydroxide)

The rate law for reaction (1) is of 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^{+})

n is the order with respect to the hydroxide ion.

Since the absorbance of the cation follows Beer's Law (that is to say, the absorbance is directly proportional to the cation's concentration) the kinetics of the reaction can be determined by measuring the absorbance as a function of time.

In the first experiment we will determine the order of the reaction with respect to [CV^{+}]. You will then design an experiment to determine the order of the reaction with respect to [OH^{-}]. From these experiments you will be able to obtain the value of the rate constant k and the complete rate equation.

Finally in a third experiment you will determine the rate order with respect to fuchsine and will be able to compare the kinetics of both reactions.

Safety Hazards

Sodium hydroxide solution is caustic. Avoid spilling it on your skin or clothing. Crystal violet and fuchsine are biological stains. Avoid spilling them on your skin or clothing. They are also suspected carcinogens.

Experiment 1

To determine the order of the reaction with respect to CV we will work under such conditions that the hydroxide ion concentration is more than 1000 times the concentration of crystal violet. In this way the [OH^-] will not change appreciably during the five minutes that the experiment takes.

The constant [OH^-] term can be combined with the rate constant k as follows thus yielding a modified form of the rate law:

$$\textbf{rate} = k[CV^+]^m[OH^-]^n$$

$$\textbf{rate} = (k[OH^-]^n)[CV^+]^m$$

$$\textbf{rate} = k'[CV^+]^m$$

This constant k' is sometimes referred to as the *pseudo rate constant*, because it does not take into account the effect of the NaOH.

***pseudo rate constant*:** $k' = k[OH^-]^n$

As the reaction proceeds, a violet-colored reactant will slowly change to a colorless product. Using the green light source of a colorimeter (565 nm), you will monitor the absorbance of the crystal violet solution with respect to time. 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).

Procedure

1. Connect the colorimeter to the laptop, open Logger Pro and choose Open from the File menu. Click on Experiment #30 from Chemistry with Vernier.

2. You will be collecting data *only* for the first 5 minutes of the reaction. Go to Experiment>Data collection and choose "mode" = time based, "length" = 5 minutes, "units" = minutes, and "20 samples/minute".

3. 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 that:
   - 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 so that a non-ribbed side faces the arrow in the colorimeter.

4. 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. Then calibrate by pressing the CAL button on the colorimeter. When the LED stops flashing, the calibration is complete.

5. Use a 10 mL graduated pipet to obtain 10.0 mL of 0.10 M NaOH solution. Use another 10 mL graduated pipet to obtain 10.0 mL of 1.6 X 10^{-5} M crystal violet solution.

6. You are now ready to begin collecting the data.
   To initiate the reaction, simultaneously pour the 10 mL portions of crystal violet and sodium hydroxide into a 100 mL beaker. Press <collect> to start collecting the absorbance data and stir the reaction mixture with a stirring rod.
   a. Remove the blank from the colorimeter and empty the water from the cuvette. Rinse the cuvette with the reaction mixture and then fill it 3/4 full. Place the cuvette in the cuvette slot of the colorimeter and close the lid.
   b. During the 5 minute data collection, observe the solution in the beaker as it reacts.
   c. When data collection is complete, discard the contents of the beaker and cuvette into the proper waste container (aqueous waste).

7. You need to delete the data collected before the absorbance was maximum. In order to do that you should highlight all the cells that you want to delete, go to the "edit" menu and select "strike through data cells". You may also need to rescale the graph by choosing Analyze>Autoscale.

8. **Analyze the data graphically, using Excel or LoggerPro, to decide if the reaction is zero, first, or second order with respect to crystal violet. Print the plot that supports your decision.** The following instructions are for using LoggerPro.

   To see if the reaction is zero order: If the current graph of absorbance *vs.* time is linear, the reaction is *zero order*. Follow this procedure to plot a best-fit regression line on your graph of absorbance *vs.* time:
   a. Choose Curve Fit from the Analyze menu.
   b. Select Linear from 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^2 indicates how closely the data points fit the regression line. A value of 1.00 indicates a nearly perfect fit.
   c. Select OK.

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*.

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

   a. Choose New Calculated Column from the Data menu.
   b. Enter the Name (ln Abs) and leave the Units field blank. Select the equation, ln(x). Click "variables" and select Abs.
   c. Select OK.
   d. Go to the y variable of the plot and select "ln(Abs)" to display the new plot of ln(Abs) vs time.
   e. Repeat the curve fitting process described in part 8 to find the slope of the best-fitting line to the curve.

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 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, 1/x. Use Absorbance as the variable for x.

d. Select OK.

e. Go to the y variable of the plot and select "1/Abs"

f. Repeat the curve fitting process described in part 8 to find the slope of the best-fitting line to the curve.

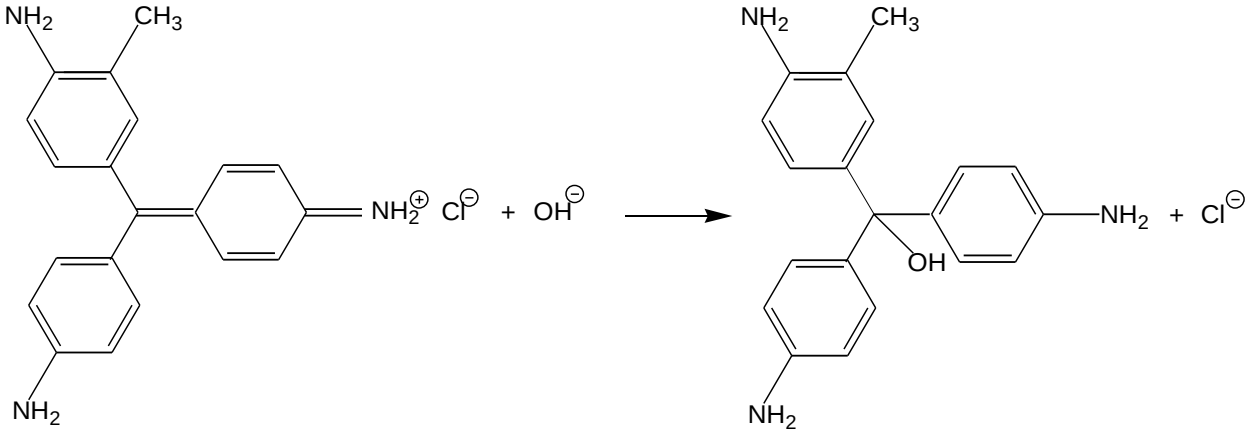
Experiment 2

From the first experiment you have determined the order of the reaction with respect to crystal violet. How could you determine the order with respect to NaOH (recall question 1b) from the Pre-lab assignment). Check with your instructor before doing your experiment. Describe the experiment, the materials that you used and the pertinent calculations.

Materials available: 1.6×10^{-5}M CV solution, 0.1M NaOH, 0.05M NaOH, 0.025M NaOH.

Experiment 3

We now introduce a different dye, fuchsine.



Procedure

1. You will be collecting data *only* for the first 3 minutes of the reaction. Go to Data collection and choose "mode" = time based, "length" = 3 minutes, "units" = minutes and "20 samples/minute".
2. Use a 10 mL graduated cylinder to obtain 10.0 mL of 0.05 M NaOH solution. Use another 10 mL graduated cylinder to obtain 10.0 mL of 2.0×10^{-5} M fuchsine solution.
3. To initiate the reaction, simultaneously pour the 10 mL portions of fuchsine and sodium hydroxide into a 100 mL beaker. Press <collect> to start collecting the absorbance data and stir the reaction mixture with a stirring rod.
4. Fill the cuvette about ¾ full with some of the reaction mixture. Place the cuvette in the cuvette slot of the colorimeter and close the lid.
5. During the 3 minute data collection, observe the solution in the beaker as it reacts.
When data collection is complete, discard the contents of the beaker and cuvette as directed by your instructor.
6. Analyze the data as you did for the crystal violet reaction (Experiment 1, steps 7-10).

REPORT SHEETS

Follow-up questions

1. Was the reaction zero, first, or second order, with respect to the concentration of crystal violet? Explain. **Include a copy of any relevant plots.**

2. Calculate the pseudo rate constant *k'* using the *slope* of the linear regression line for your linear curve. Be sure to include correct units for the pseudo rate constant.

3. What was the order of the crystal violet reaction with respect to $[OH^-]$? Briefly describe the experiment that you did and show any relevant calculations.

4. Calculate the value of the true rate constant and write the complete rate equation.

6. What was the order of the fuchsine reaction **with respect to fuchsine**? How can you tell?

7. Knowing that the fuchsine reaction is first order with respect to [OH^-], calculate the true rate constant, k. How does it compare to the rate constant for the crystal violet reaction?

8. Examine the molecular structure of both compounds. Make an educated guess about the approach of the hydroxide ion to the central carbon to explain the answer to question 8.

Prelab Exercise *To be completed BEFORE lab!*

Chlorine dioxide in aqueous solution oxidizes iodide ion on to iodine; chlorine dioxide is reduced to chlorite ion.

$$2ClO_2\,(aq) + 2I^-(aq) \rightarrow 2ClO_2^-(aq) + I_2(aq)$$

The order of this reaction with respect to ClO_2 is determined by starting with a large excess of I^- so that its concentration is essentially constant. Then the rate equation can be expressed as:

$$\text{rate} = k\,[ClO_2]^m[I^-]^n = k'[ClO_2]^m \qquad \text{where } k' = k[I^-]^n.$$

The following data was collected for the reaction.

1. Use Excel or LoggerPro to create the following plots and perform a linear fit (best-fit line, or "Add Trendline") for each. Provide the requested information about the linear fit for each.

Time (s)	$[ClO_2]$ (mol/L)
0	4.77×10^{-4}
1	4.31×10^{-4}
2	3.89×10^{-4}
5	2.87×10^{-4}
10	1.73×10^{-4}
15	1.02×10^{-4}
20	6.13×10^{-5}

Equation **R^2 value**

a. $[ClO_2]$ vs. time

b. $(1/[ClO_2])$ vs. time

c. $\ln[ClO_2]$ vs. time

2. What is the order of reaction with respect to $[ClO_2]$? Explain.

3. Calculate the pseudo rate constant, k', using the appropriate plot. Show your work.

4. You have at your disposition the following solutions: $[I^-] = 0.2M$, $[I^-] = 0.15M$, $[I^-] = 0.1M$, $[ClO_2] = 4.77\times10^{-4}M$. What kind of experiment can you do to determine the order of the reaction (n) with respect to I^-? Hint: *Eno rof tpecxe tnatsnoc selbairav lla gnipeek stnemirepxe owt mrofrep ot deen uoy*. Briefly describe the experiment.