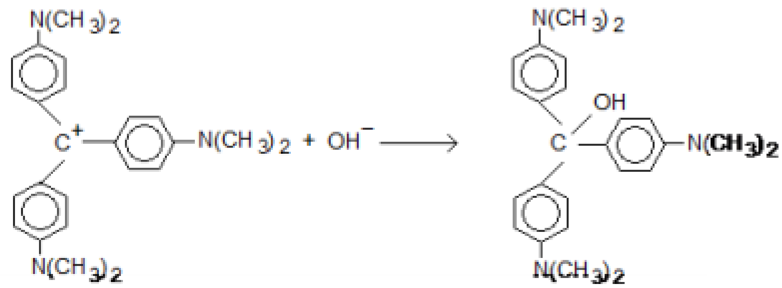
Rate Law Determination of the Crystal Violet Reaction

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^+ (aq)	+	OH^- (aq)	→	CVOH
(crystal violet)		(hydroxide)		(aq)

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. Because the hydroxide ion concentration is more than 1000 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. You will measure the color change with a Colorimeter. The crystal violet solution used in this experiment has a violet color, of course, thus the Colorimeter users will be instructed to use the 565 nm (green) LED. Spectrometer users will determine an appropriate wavelength based on the absorbance spectrum of the solution. 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

- Observe the reaction between crystal violet and sodium hydroxide.
- 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

Chromebook, computer, **or** mobile device
Graphical Analysis app
Vernier data-collection interface
Colorimeter
Temperature Probe or thermometer
5 plastic cuvettes
1 L beaker
two 10 mL graduated cylinders
0.10 M sodium hydroxide, NaOH, solution
2.5×10^{-5} M crystal violet solution
ice
two 100 mL beakers
50 mL beaker
watch with a second hand

PROCEDURE

1. Obtain and wear goggles.

2. Use a 10 mL graduated cylinder to obtain 10.0 mL of 0.10 M NaOH solution. **WARNING**: *Sodium hydroxide solution,* NaOH: *Causes skin and eye irritation.* Use another 10 mL graduated cylinder to obtain 10.0 mL of 2.5×10^{-5} M crystal violet solution. **WARNING**: *Aqueous crystal violet: May be harmful if swallowed. May cause skin irritation and eye damage*.

3. Prepare a blank by filling a cuvette 3/4 full with distilled water. To correctly use cuvettes, remember:

   - Wipe the outside of each cuvette with a lint-free tissue.
   - Handle cuvettes only by the top edge of the ribbed sides.
   - Dislodge any bubbles by gently tapping the cuvette on a hard surface.
   - Always position the cuvette so the light passes through the clear sides.

4. Connect the Colorimeter to the data-collection interface, and then connect the interface to your Chromebook, computer, or mobile device. Launch Graphical Analysis.

5. Calibrate the Colorimeter.

   a. Place the blank in the cuvette slot of the Colorimeter and close the lid.

   b. Press the < or > buttons 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. Click or tap Mode to open Data Collection Settings. Change Rate to 1 samples/s and End Collection to 200 s. Click or tap Done.

7. *Do this quickly!* 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. Empty the water from the cuvette. Rinse the cuvette twice with ~1 mL amounts of the reaction mixture, fill it 3/4 full, and place it in the device. Close the Colorimeter lid. Click or tap Collect to start data collection.

8. Absorbance data will be collected for 200 seconds. You may stop data collection early if desired. Discard the beaker and cuvette contents as directed by your instructor.

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*.

10. Create a calculated column, ln Absorbance, and add a linear curve fit to the graph ln Absorbance *vs*. time:

   a. Click or tap View, ⊞, and turn on Data Table. Then, dismiss the View menu.

   b. In the Absorbance column header in the table, click or tap Column Options, ⋯, and choose Add Calculated Column.

   c. Enter **ln Absorbance** as the Name and leave the Units field blank.

   d. Click or tap Insert Expression and choose Aln(X) as the expression.

   e. Enter **1** as Parameter A and select Absorbance as Column X.

   f. Click or tap Apply. A graph of ln absorbance *vs*. time is displayed. Double-click the graph to autoscale the graph.

   g. To see if the relationship is linear, click or tap Graph Tools, ⟋, and choose Apply Curve Fit.

   h. Select Linear as the curve fit and Dismiss the Curve Fit box.

   i. Record the slope as the rate constant, *k*, and dismiss the Linear curve fit box.

11. Create a calculated column, 1/Absorbance, and then plot a graph of 1/Absorbance *vs*. time:

    a. In the data table, click or tap More Options, , in the Absorbance column header, and then choose Add Calculated Column.

    b. Enter **1/Absorbance** the Name and leave the Units field blank.

    c. Click or tap Insert Expression and choose A/X as the expression.

    d. Enter 1 as Parameter A and select Absorbance as Column X.

    e. Click or tap Apply.

    f. Click or tap the y-axis label and select only 1/Absorbance to display a graph of 1/Absorbance *vs*. time.

    g. To see if the relationship is linear, click or tap Graph Tools, , and choose Apply Curve Fit.

    h. Select Linear as the curve fit and Dismiss the Curve Fit box.

    i. Record the slope as the rate constant, *k*, and dismiss the Linear curve fit box.

12. (Optional) To see any of the three graphs again, click or tap the y-axis label and choose the column you want to display. Export, download, or print the most linear graph.

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.)