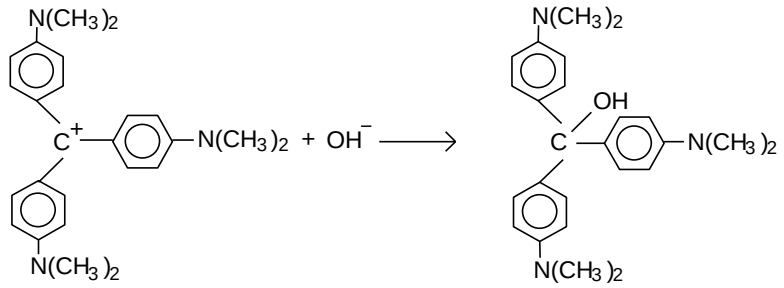
Rate Law Determination of the Crystal Violet Reaction

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:

$$CV^+ \quad + \quad OH^- \longrightarrow \quad CVOH$$

(crystal violet) (hydroxide ion)

The rate law for this reaction is in the form:

$$\text{rate} = -\frac{\Delta[CV^+]}{\Delta t} = k[CV^+]^m[OH^-]^n,$$

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 at the beginning is1000 times larger than the concentration of crystal violet, $[OH^-]$ will not change appreciably during this experiment — $[OH^-]$ is essentially constant. This enables us to rewrite the rate law as:

$$\text{rate} = -\frac{\Delta[CV^+]}{\Delta t} = k'[CV^+]^m, \text{ where } k' = k[OH^-]^n$$

*Note: k' is sometimes referred to as the **pseudo rate constant**, because $[OH^-]$ is also built into it. Since the psuedo rate constant includes $[OH^-]$, k' does not actually remain constant, like a **true** rate constant would, as k' will vary if $[OH^-]$ is varied.*

Thus, you will be able to determine the order with respect to crystal violet (m), but not the order with respect to hydroxide (n), by collecting concentration vs. time data for crystal violet, CV^+. 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 computer-interfaced colorimeter, you will monitor the absorbance of the crystal violet solution with time. We will assume that absorbance is directly proportional to the concentration of crystal violet at the concentrations used in the experiment (Beer's law). Thus, the two terms are related using the equation $A = \varepsilon cl$ where A is the absorption, ε is the molar absorptivity, c is the concentration, and l is the path length of the cuvette. You will prepare three graphs:

- $[CV^+]$ vs. time: A linear plot indicates a *zero order* reaction (k' = -slope).
- $\ln[CV^+]$ vs. time: A linear plot indicates a *first order* reaction (k' = -slope).
- $1/[CV^+]$ 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 pseudo rate constant, k', and the half-life for this reaction.

MATERIALS

IBM-compatible computer	0.020 *M* NaOH
LabPro interface	2.0×10^{-5} *M* crystal violet
Logger Pro Software	Deionized water
Vernier colorimeter	Stirring rod
One plastic cuvette	Two 10-mL graduated cylinders
250-mL beaker	Safety goggles

PROCEDURE

1. Obtain and wear goggles.

2. Connect the colorimeter to the *LabPro* interface. Open "Exp 30b: Rate Crystal Violet" from the *Chemistry with Computers* experiment files of Logger *Pro*.

3. Prepare a *blank cuvette* by filling a cuvette 3/4 full with deionized water. Then calibrate the colorimeter at a wavelength of 565 nm.

HANDLING CUVETTES: Cuvettes should be wiped clean and dry on the outside with a Kimwipe®. Do not use a paper towel! Handle the cuvettes near the top of the ribbed sides. Solutions should be free of bubbles. If a cuvette is not dry on the inside, a small amount of the solution to be used should be used to rinse the cuvette before filling. Always align the reference mark on the cuvette with the reference mark on the slot of the colorimeter.
CALIBRATION: • **For square colorimeters:** Click the icon on the toolbar used to calibrate the probes. (Alternatively, select "Calibrate" from the "Experiments" menu.) 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. Type "0" in the % edit box. When the voltage stabilizes, click Keep. Turn the knob of the colorimeter to the desired wavelength. In this position, the sample transmits 100% of the light. Type "100" in the % edit box. When the voltage stabilizes, click Keep, then click OK. • **For rounded colorimeters:** Use the arrow buttons to select the desired wavelength. With the blank cuvette correctly positioned in the colorimeter, press the blue "Cal" button on top of the colorimeter.

4. Set the Data Collection mode to "Time Based", and adjust the sampling rate to take two readings a minute for a total of 20 minutes.

CAUTION: *Sodium hydroxide solution is caustic. Avoid spilling it on your skin or clothing. Crystal violet is a biological stain. Avoid spilling it on your skin or clothing.*
NOTE: *Use the same cuvette for all your measurements. Before filling a cuvette with a solution, pour a little bit of the solution into the cuvette, swirl it around, and empty it out.*

5. Empty the contents of the cuvette. In a small graduated cylinder, add 5.0 mL of water to 5.0 mL of 2.0×10^{-5} *M* crystal violet (CV) solution. Pour it into a small beaker and mix thoroughly. Rinse the cuvette with a couple ~1-mL portions of the mixture, fill the cuvette, and measure the absorbance (**do *not* click** Collect). Use this measurement to determine the molar absorptivity of crystal violet.

6. Empty and discard the contents of the cuvette as directed by your instructor. Measure 10.0-mL each of 2.0×10^{-5} *M* CV and 0.020 *M* NaOH solutions into a small beaker and mix thoroughly. As soon as possible, rinse the cuvette with a couple ~1-mL portions of the mixture, and fill the cuvette ¾ full with the mixture.

7. Place the cuvette into the colorimeter, close the lid and click Collect. Allow the reaction to proceed until the the data collection ends on its own. Discard the beaker and cuvette contents as directed by your instructor.

8. Repeat steps 6 and 7 using 0.010 *M* NaOH instead of 0.020 *M* NaOH.

DATA ANALYSIS AND QUESTIONS

1. Copy and paste the time and absorbance data into an *Excel* speadsheet. Add another column to the spreadsheet that calculates $[CV^+]$, using the molar absorptivity of the crystal violet. Place the data for each trial on a separate sheet.

2. Add a column to your spreadsheet(s) that calculates $\ln[CV^+]$ and another column that calculates $1/[CV^+]$.

3. Try graphing $[CV^+]$ vs. time, $\ln[CV^+]$ vs. time, and $1/[CV^+]$ vs. time to determine whether the reaction is zero-, first-, or second-order. Keep the graph that is linear.

4. Was the reaction zero, first, or second order, with respect to the concentration of crystal violet? Did the concentration of NaOH have any effect on the reaction order of CV^+? Explain.

5. Determine the pseudo rate constant, *k*', for each trial, from the *slope* of the trendline for your linear plot (*k*' = –slope for zero and first order and *k*' = slope for second order). Be sure to include correct units for the rate constant.

6. Write the correct rate law expression for the reaction, in terms of crystal violet. (Use the form: rate = $k'[CV^+]^m$; omit $[OH^-]$).

7. What is the (initial) half-life of crystal violet in each trial?

8. Finally, add a column to your spreadsheet that calculates the rate. Label the column with the correct units. What happens to the reaction rate as each reaction proceeds? Why?

9. Determine the reaction order of $[OH^-]$. You will not likely obtain an integer value for the reaction order of $[OH^-]$. Report the reaction order to two decimal places. There are resources on the web that may guide you.

LAB REPORT

You may choose to submit an individual or group report for this lab. Follow the guidelines for Laboratory Reports located at http://webs.anokaramsey.edu/chemistry/Chem1062. For this lab report, you will need to include a **title**, ***introduction***, **procedure**, **results** (include the graphs—raw data tables can be included as an appendix), **discussion**, and **references**. You may use the above questions to *guide* your discussion, but the discussion should be more than just answering the questions and should flow logically as you discuss the lab and the results.

Follow your instructor's directions for submitting this lab report. Remember to name the file as specified (*Lastname_Kinetics* or *Lastname1_LastName2_Kinetics*). If you are emailing your report, use the subject line "Chem 1062: Kinetics Lab". If you worked in pairs and are submitting this assignment on an individual basis, please underline your own name and include your lab partner's name on the assignment.

Major portions of this lab courtesy of Vernier Software, "Chemistry With Computers". Edited by Lance S. Lund, Anoka-Ramsey Community College. Updated April 11.