

Experiment 7

Rate Law Determination of the Crystal Violet Reaction

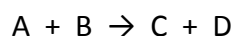
OUTCOMES

After completing this experiment, the student should be able to:

- use graphical analysis to determine the order of a reaction.
- determine the pseudo rate constant and half-life for a reaction.
- write an introduction for a lab report.

DISCUSSION

Chemical kinetics is the branch of chemistry that is concerned with the study of the **rate** of chemical reactions, or how quickly reactions occur. Experiments have shown that the rate of a homogeneous reaction in solution depends on the nature of the reactants, their concentrations, the temperature of the system, and the use of catalysts. For the hypothetical reaction



the rate of the reaction may be measured by observing the rate at which A or B disappears or the rate at which C or D appears. Generally, the rate of the reaction depends on the concentration of one or more of the reactants. Thus, the rate of the hypothetical reaction may be expressed using the rate law

$$\text{Rate} = k [A]^x [B]^y$$

where [A] and [B] are the molar concentrations of the reactants and k is the rate constant for the reaction. The powers x and y reflect the dependence of the reaction rate on the concentration of each particular reactant, or the order of the reaction for the reactant, and must be determined experimentally in one of two ways.

The first is known as the **method of initial rates** in which the reaction is run multiple times while varying the concentrations of A and B. The initial reaction rate is then calculated for each trial. The reaction order for A can be determined by looking at how the rate varies with changes in the concentration of A while the concentration of B is held constant. Similar analysis can be used to establish the reaction order for B. Once the reaction orders and rate are known for a given set of concentrations, the value of k can be calculated.

The other method of determining the order of a reaction for a reactant is through **graphical analysis**. This method works well for simple zero-, first-, and second-order reactions. It is based on the slope-intercept form of the integrated rate law equations. In this method, the reaction is run once and the concentration of the reactant at various points in time is collected. The data can be easily manipulated to give three different graphs: [A] vs. time, $\ln[A]$ vs. time, and $1/[A]$ vs. time. The graph which yields a straight line determines the order of the reaction and the numerical value of k .

- [A] vs. time: a straight line indicates a *zero-order* reaction where $k = -$ slope
- $\ln[A]$ vs. time: a straight line indicates a *first-order* reaction where $k = -$ slope
- $1/[A]$ vs. time: a straight line indicates a *second-order* reaction where $k = +$ slope

The one draw-back to using graphical analysis is that it only works for reactions with one reactant. In our hypothetical reaction with the rate dependent on both A and B, the orders cannot be determined simultaneously. In this case, we could use **pseudo reaction conditions** to make it appear as though the reaction only depends on one reactant. If we wanted to determine the reaction order for A using graphical analysis, we could run the reaction in the presence of a large excess of B. In this scenario, even though the concentration of B changes during the course of the reaction, the change is negligible compared to the change in the concentration of A. The concentration of B may therefore be considered constant, and the rate law can be rewritten as

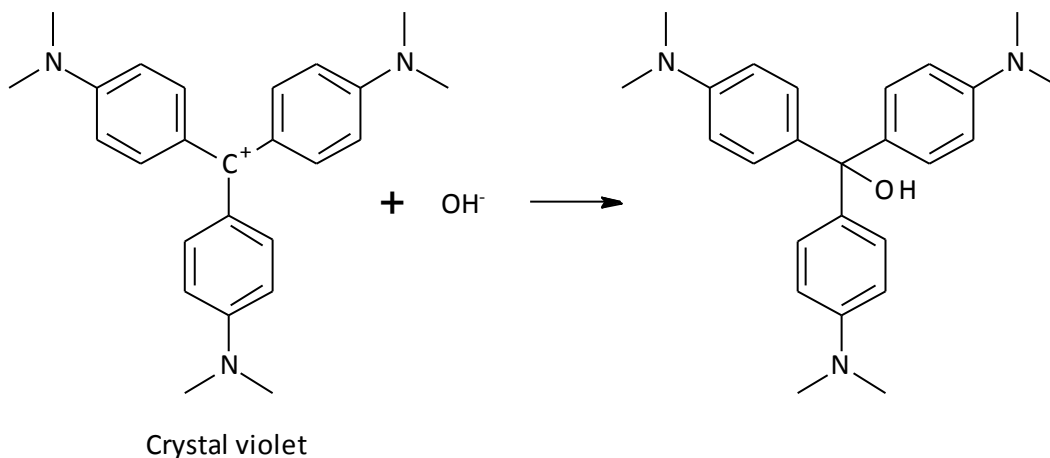
$$\text{Rate} = k' [A]^x$$

where k' is sometimes referred to as the *pseudo rate constant* and can be expressed as

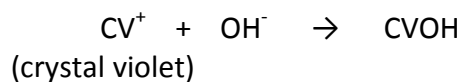
$$k' = k [B]^y$$

Because k' does have $[B]^y$ built into it, it *will* vary if the concentration of B is changed, unlike a true rate constant. However, this dependence of the pseudo rate constant on the concentration of B can be used to determine the reaction order of B in a manner similar to that used for the method of initial rates.

In this experiment, you will observe the reaction between the biological dye crystal violet and sodium hydroxide and determine the order of the reaction for both reactants.



A simplified version of the equation is



The rate law for this reaction would then be in the form

$$\text{Rate} = -\frac{\Delta[\text{CV}^+]}{\Delta t} = k [\text{CV}^+]^x [\text{OH}^-]^y$$

However, in order to use graphical analysis to determine reaction orders, pseudo reaction conditions are necessary. In this case, the reactant that will be in excess is the sodium hydroxide. Thus, the rate law can be rewritten as

$$\text{Rate} = -\frac{\Delta[\text{CV}^+]}{\Delta t} = k' [\text{CV}^+]^x \text{ where } k' = k [\text{OH}^-]^y$$

As the name implies, crystal violet (CV^+) is a purple compound. Thus, it reflects purple wavelengths of light and absorbs light in the green and yellow range of visible light. As the reaction proceeds, it is slowly changed to the product which is colorless. The disappearance of the purple color can be monitored by measuring the decrease in absorbance of green (565 nm) light over time using a computer-interfaced colorimeter. The decrease in absorbance can then be related to the decrease in concentration of CV^+ using Beer's Law ($A = \epsilon cl$) if the molar absorptivity (ϵ) of CV^+ is known.

MATERIALS

Logger Pro with LabPro® Interface	stirring rod
Vernier colorimeter	0.020 M NaOH
plastic cuvette	0.010 M NaOH
250-mL beaker	2.0×10^{-5} M crystal violet
two 10-mL graduated cylinders	deionized water

PROCEDURE

- ⚠ **Wear safety glasses or goggles at all times for this experiment.**
- ⚠ **Avoid skin contact with the chemicals in this experiment.**
- ⚠ **Crystal violet is a biological stain. Avoid spilling it on your skin or clothing.**

1. Before starting the experiment, develop a hypothesis for what you think will happen in the lab. You will be writing an introduction for this experiment and should have a hypothesis to include in it. It could be related to what the order of the reaction will be for CV^+ or OH^- , or any other question that you think will be answered during the course of the experiment.
2. Connect the colorimeter to the *LabPro* interface. Open "Exp 30b: Rate Crystal Violet" from the *Chemistry with Computers* experiment files of *LoggerPro*.
3. Prepare a *blank* cuvette by filling a cuvette 3/4 full with deionized water.

Handling Cuvettes: Examine your cuvette to ensure that the clear sides are free from scratches. Cuvettes should be wiped clean and dry on the outside with a KimWipe before each measurement. Do NOT use a paper towel! Handle the cuvettes near the top of the ribbed sides. Solutions should be free of bubbles. Align the cuvette in the colorimeter so that the light passes through the smooth sides. **To avoid inconsistencies from different cuvettes, only one cuvette should be used for the entire experiment.** If you are refilling a cuvette with a different solution, a small amount of the new solution should be used to rinse the cuvette before filling.

4. Place the blank cuvette in the colorimeter and calibrate the colorimeter at a wavelength of 565 nm. While most of the colorimeters used in the chemistry department are the rounded colorimeters which calibrate with the press of a button, you may occasionally encounter an older version which requires manual calibration. If this is the case, ask your instructor how to calibrate the colorimeter.

Calibration of Rounded Colorimeters: Use the arrow buttons to select the desired wavelength (565 nm). With the blank cuvette correctly positioned in the colorimeter and the lid closed, press the blue "Cal" button on top of the colorimeter. When the red light stops blinking, the colorimeter is calibrated and may be used.

5. In a small graduated cylinder, add 5.0 mL of deionized water to 5.0 mL of $2.0 \times 10^{-5} M$ crystal violet (CV^+) solution. Pour it into a small beaker and mix thoroughly.
6. Empty the contents of the cuvette and rinse it with a couple of 1-mL portions of the water- CV^+ mixture. Fill the cuvette with the water- CV^+ mixture and measure the absorbance (do not click on "Collect").
7. Set the Data Collection mode to "Time Based," and adjust the sampling rate to take two readings each minute for a total of 20 minutes.
8. Measure 10.0 mL each of $2.0 \times 10^{-5} M$ CV^+ and $0.020 M$ NaOH solutions in a small beaker and mix thoroughly.
9. Empty and discard the contents of the cuvette. As quickly as possible, rinse the cuvette with a couple of 1-mL portions of the CV^+ -NaOH mixture. Fill the cuvette with the CV^+ -NaOH mixture.
10. Place the cuvette into the colorimeter, close the lid, and click the green "Collect" button. Allow the reaction to proceed until the data collection ends on its own.
11. Repeat steps 8 to 10 using $0.010 M$ NaOH instead of $0.020 M$ NaOH.

- ⚠ Make sure to remove the cuvette from the colorimeter when done with the experiment.**
- ⚠ Dispose of all chemicals in the proper waste container.**

DATA ANALYSIS

1. Using the concentration of CV^+ after it was mixed with water and its absorbance (in step 6), calculate the molar absorptivity of CV^+ . What are the units of the molar absorptivity?
2. Copy and paste the time and absorbance data into an Excel spreadsheet. Place the data for each trial on a separate sheet. Add another column to each spreadsheet that calculates $[CV^+]$ using the molar absorptivity of the crystal violet.
3. Add columns to your spreadsheets that calculate $\ln[CV^+]$ and $1/[CV^+]$.
4. For each trial, graph $[CV^+]$ 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.
5. 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.

- Determine the pseudo rate constant, k' , for each trial from the *slope* of the trendline for your linear plot. Be sure to include correct units for the rate constant.
- What is the (initial) half-life of crystal violet in each trial?
- Write the correct rate law expression for the reaction in terms of crystal violet. Use the form: $\text{rate} = k' [\text{CV}^+]^m$. Omit $[\text{OH}^-]$.
- Add a column to your spreadsheet that calculates the rate. Label the column with the correct units. What happens to the reaction rate as the reaction proceeds? Why?
- 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.

POSTLAB ACTIVITY

You will be turning in a lab report. It may be an individual or group report, depending on instructor preference. The report should include the title, an introduction, results, discussion, and references. The information that you obtained from the data analysis should be included at some point in the report. It is up to you whether it is in the results or discussion or both. (The data tables may be included in an appendix at the end.) However, remember that the report is more than just answering some questions and that it should flow smoothly and logically as you discuss the data obtained, what it signifies, and potential errors or difficulties. Lab report guidelines for how to write the introduction, results, and discussion are found at <http://webs.anokaramsey.edu/chemistry/Chem1062>.

Follow your instructor's directions for submitting the report. If you are submitting electronically, please submit a single file with all of the required information. Use the following convention for naming your files: *Lastname1 Lastname2 Kinetics* for a group report or *Lastname Firstname Kinetics* for an individual report. If you are emailing the report, use a subject line of *Chem 1062: Kinetics Lab*.

You will need to show sample calculations in the report. For electronic submissions, you may embed data tables which contain the formulas in calculated cells. (Ask your instructor to demonstrate how to do this.) For paper submissions, you will need to show these calculations for one trial of each procedure. You will also need to show these calculations if you submit the report electronically but do NOT include formulas in embedded data tables.