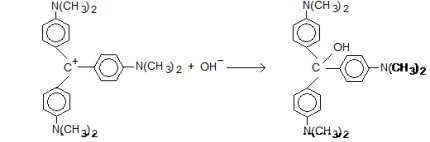
  Spectral Analysis 30

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)  (crystal violet) | + | OH– (aq)  (hydroxide) | → | CVOH (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 Spectrometer. 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

Vernier Spectral Analysis app

Go Direct SpectroVis Plus

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. Launch Spectral Analysis. Connect the Go Direct SpectroVis Plus to your Chromebook, computer, or mobile device. Click or tap Absorbance vs. Time.
5. To calibrate the Spectrometer, place the blank cuvette in the Spectrometer and select Finish Calibration. Note: If necessary, wait for the Spectrometer to warm up before selecting Finish Calibration.
6. Determine the optimum wavelength for examining the crystal violet solution.
   1. Empty the blank cuvette and rinse it twice with small amounts of 2.5 × 10–5 M crystal violet solution. Fill the cuvette about 3/4 full with the crystal violet solution and place it in the Spectrometer.
   2. The live graph will update with the spectrum of the sample. Click or tap the desired wavelength or enter the Wavelength. Click or tap Done.
   3. Remove the cuvette from the Spectrometer and dispose of the crystal violet solution as directed.
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. Click or tap Collect to start data collection.
8. Stop data collection when the reaction is complete (about 200 seconds). Discard the beaker and cuvette contents as directed by your instructor.
9. Analyze the data 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:
    1. In the Absorbance column header in the table, click or tap More Options, , and choose Add Calculated Column.
    2. Enter ln Absorbance as the Name and leave the Units field blank.
    3. Click or tap Insert Expression and choose Aln(X) as the expression.
    4. Confirm that Parameter A is set to 1 and that Absorbance is set to Column X.
    5. Click or tap Apply. A graph of ln absorbance vs. time is displayed.
    6. To see if the relationship is linear, click or tap Graph Tools, , and choose Apply Curve Fit.
    7. Select Linear as the curve fit.
    8. 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:
    1. In the data table, click or tap More Options, , in the Absorbance column header, and then choose Add Calculated Column.
    2. Enter 1/Absorbance as the Name and leave the Units field blank.
    3. Click or tap Insert Expression and choose A/X as the expression.
    4. Confirm that Parameter A is set to 1 and that Absorbance is set to Column X.
    5. Click or tap Apply.
    6. To display a graph of 1/Absorbance vs. time, click or tap the y-axis label and select only 1/Absorbance.
    7. To see if the relationship is linear, click or tap Graph Tools, , and choose Apply Curve Fit.
    8. Select Linear as the curve fit and click or tap Apply.
    9. 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.)

Sample data for analysis is available at <https://youtu.be/jObaX9HdgxY> and Vernier’s Graphical Analysis App can be used to analyze the curve fits and determine the rate order of this reaction. A concluding video that explains how to perform the mathematical analysis of the first derivative and the inverse of the absorbances vs. time can be viewed at <https://youtu.be/_InznF1A6VQ>