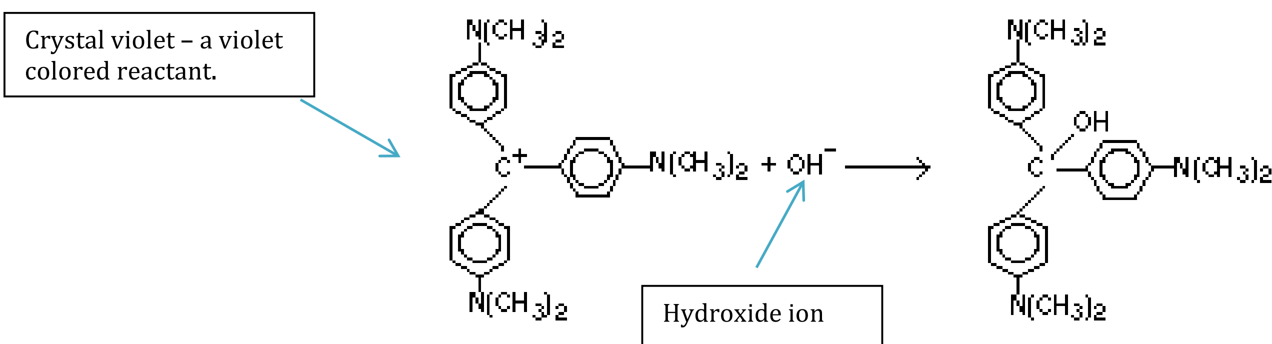
Rate law Determination of the Crystal Violet Reaction Using the Isolation Method

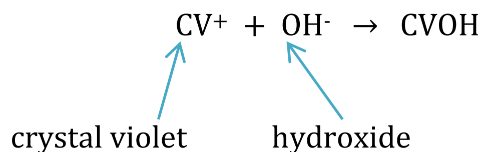
Introduction

A common challenge in chemical kinetics is to determine the rate law for a reaction with multiple reactants. With the concentrations of several species changing simultaneously, real rate laws often do not follow the simple zero-, first, and second-order rate laws discussed in lecture. For reactions where many reactants are involved, the order of the reaction is often determined using a technique called ***"the method of isolation"*** developed by the Nobel Prize winning chemist Wilhelm Ostwald. In this method the concentration of one reactant is made much smaller than the concentrations of the other reactants.[1] Under this condition, all reactant concentrations except one are essentially constant, and the simple zero-, first-, and second-order kinetic plots can usually be used to interpret the concentration-time data.

In this experiment, you will observe the reaction between crystal violet and sodium hydroxide. The reaction is shown below:



An alternative version of this reaction is:



[1] How large a concentration excess is required to effectively "isolate" the effects of a single reactant? As a general rule, a minimum of a 20-fold stoichiometric excess is necessary. A 50-fold or 100-fold stoichiometric excess is preferable.

The ***general*** rate law for this reaction may be written as:

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

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, OH^-.

In this experiment you will use the Isolation Method to determine the exponent's ***m,*** and ***n***. In this experiment the concentration of the hydroxide ion will be more than 1000 times as large as the concentration of the crystal violet. Thus the $[OH^-]$ will not change appreciable during the experiment which is a requirement if we are to use the Isolation Method. Our rate law will then be modified as follows:

$$(1)\ \text{Rate} = k[CV^+]^m[OH^-]^n$$

Since $[OH^-]$ is a constant we may modify equation (1) as follows:

$$(2)\ \text{Rate} = k'[CV^+]^m \quad \text{where } k' = k[OH^-]^n$$

k' is called the "pseudo" rate constant which equals $k[OH^-]$ for each trial.

In part A of this experiment, you will determine the value for exponent **m** by monitoring the violet-colored reactant, CV^+. As the reaction proceeds, CV^+ will be slowly changing to a colorless product. You will use a Spectronic 20 to monitor the absorbance of the CV^+ solution with time. Since absorbance of CV^+ is proportional to its concentration (Beer's Law) you will generate a Beer's Law plot which will allow you to calculate the concentration of CV^+. $[CV^+]$ will then be plotted three ways to determine the order of the reaction (the m exponent) for CV^+.

$[CV^+]$ 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)

In part B of this experiment, you will use the method of ***"serial dilutions"*** to generate a Beer's Law plot for CV^+. [2]

[2] Refer to Appendix I

Purpose

In this lab, you will determine the rate law for the reaction between crystal violet and hydroxide ion using the Isolation Method. You will also learn how to use the serial dilution technique to accurately prepare diluted samples of known concentration. Finally you will use a Spectronic 20 spectrophotometer to generate a Beer's Law plot.

Apparatus

Balance
2 clean, 10-mL graduated cylinders
1 clean, 5-mL volumetric pipet
Stirring rod
Clean 25 mL beaker
Spectronic 20 spectrophotometer

Chemicals

0.0200 M NaOH stock solution
2.00×10^{-5} M crystal violet stock solution

Part A : Procedure for Determining Reaction Order with Respect to CV^+ (m exponent)

1. Turn on the Spectronic 20 spectrophotometer and allow it to warm-up for 15 minutes.
2. Calibrate the Spectronic 20 using the procedure outlined in Appendix A. Always remember the following when using a spectrophotometer cuvette:
   - All cuvettes should be wiped clean and dry on the outside with a tissue
   - Use a tissue when handling cuvettes or hold it at the very top
   - All solutions should be free of bubbles
   - Always position the cuvette with its reference mark aligned with the reference mark in the chamber
   - For crystal violet solution adjust wavelength setting to 580 nm.
3. Use a 10-mL graduated cylinder to obtain 10.0 mL of 0.0200 M NaOH solution. CAUTION: Sodium hydroxide solution is caustic. Avoid spilling it on your skin and clothing. Wear goggles.
4. Use another 10-mL graduated cylinder to obtain 10.0 mL of 2.00×10^{-5} M crystal violet solution. CAUTION: Crystal violet is a biological stain. Avoid spilling it on your skin and clothing.
5. Initiate the reaction by simultaneously pouring the 10-mL portions of crystal violet and sodium hydroxide into a clean 150 mL beaker. Start your timer. Stir the mixture with a glass stirring rod. Remove the cuvette containing water from the Spectronic 20 and empty the water from the cuvette. Rinse the cuvette twice with ~ 1 mL amounts of the reaction mixture and then fill it ¾ full. Do not put the cuvette in the Spec 20 yet. To keep the solution from warming inside the Spec 20, the cuvette is left outside of the Spec 20 between readings.
6. After one minute has passed, wipe the outside of the cuvette, place it in the Spec 20 , close the lid and take an absorbance reading (A) and ***record the time the reading is taken***. Immediately remove the cuvette from the Spec 20.[3]
7. After 60 more seconds have elapsed, again place the cuvette in the Spec 20, close the lid and take another absorbance. Be sure to record the time the reading is taken. Continue in this manner,

[3] Alternatively a transmittance reading may be taken and converted to absorbance using the relationship at the bottom of page 10.

collecting data every minute, ***until the absorbance reading dropped to 0.15 or less.*** Discard the beaker and cuvette contents as directed by your instructor.

Part B: Procedure for Generating the Beer's Law Plot

You are to prepare five crystal violet solutions of known concentration (standard solutions). Each is transferred to a small, cuvette that is placed into the colorimeter. The amount of light that penetrates the solution and strikes the photocell is used to compute the absorbance of each solution. When a graph of absorbance vs. concentration is plotted for the standard solutions, a direct relationship should result, as shown in Figure 1. The direct relationship between absorbance and concentration for a solution is known as Beer's law.

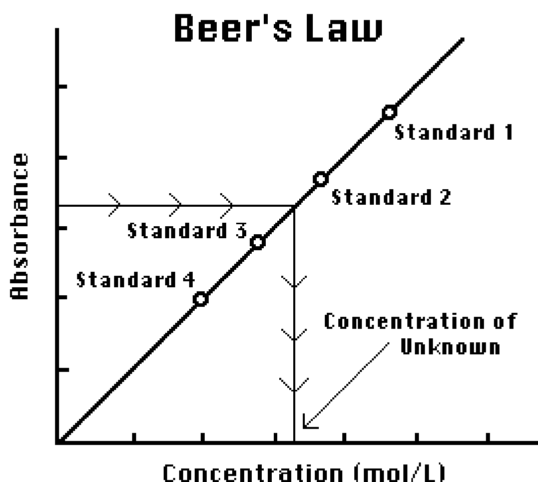


Figure 1

The concentration of an *unknown* crystal violet solution is then determined by measuring its absorbance with the colorimeter. By locating the absorbance of the unknown on the vertical axis of the graph, the corresponding concentration can be found on the horizontal axis (follow the arrows in Figure=2). The concentration of the unknown can also be found using the slope of the Beer's law curve.

Procedure:

1) Add about 30 mL of ~ 2.00 x 10^{-5} M crystal violet stock solution to a 100-mL beaker. Add about 30 mL of distilled water to another 100-mL beaker.

2) Label four clean, dry, test tubes 1-4 (the fifth solution is the beaker of 2.0 x 10^{-5} M crystal violet stock solution). Pipet 2, 4, 6, and 8 mL of 2.0 x 10^{-5} M crystal violet stock solution into Test Tubes 1-4, respectively. With a second pipet, deliver 8, 6, 4, and 2 mL of distilled water into Test Tubes 1-4, respectively. *Thoroughly* mix each solution with a stirring rod. Clean and dry the stirring rod between stirrings. Keep the remaining 2.0 x 10^{-5} M crystal violet stock solution in the 100-mL beaker to use in the fifth trial. Volumes and concentrations for the trials are summarized below:

Trial #	mL 2.0 x 10^{-5} M stock CV solution	mL H_2O	Concentration
1	2	8	?
2	4	6	?
3	6	4	?
4	8	2	?
5	10	0	?

3) Calculate the concentration of CV for trials 1 – 4.
4) Calibrate the Spec 20 (Refer to Appendix II).
5) You are now ready to collect absorbance-concentration data for the five standard solutions. Empty the water from the cuvette. Condition the cuvette with ~1-mL of solution from test tube #1 and then fill it ¾ full. Wipe the outside with a tissue and place it in the colorimeter. After closing the lid, wait for the reading displayed on the Spectronic 20 to stabilize. Record either the absorbance or the percent transmittance value.
6) Discard the cuvette contents as directed by your teacher and rinse the cuvette with deionized water. Again, condition the cuvette with ~ 1 mL of solution from test tube #2 and then fill it ¾ full. Wipe the outside, place it in the colorimeter, and close the lid. Record either the absorbance or the percent transmittance value.
7) Repeat the Step 6 procedure for the remaining standard solutions, e.g., test tubes 3, 4, & 5.
8) Before leaving lab, determine if your data is consistent with Beer>s law, use Excel and plot a graph of absorbance vs. concentration with a linear regression curve displayed. If your data is consistent with Beer>s law (a direct relationship between absorbance and concentration), the regression line should closely fit the five data points *and* should pass through (or near) the origin of the graph. Your R^2 value should be > 0.98.[4] Refer to Data Analysis & Calculations, Part 1 below.

Data Analysis & Calculations

1. **Beer's Law Plot (Part B Data)** - Using the absorbance data from part B, construct a Beer's Law plot.[5,6] Type the absorbance and [CV^+] values into an Excel spreadsheet. Create a graph plotting the absorbance values on the y – axis and the concentrations (Molarity) on the x – axis. Plot a trend line (best fit straight line through the data) setting the y intercept to 0 and determine the equation for the line. Display the equation and R^2 value on your plot. Change y and x in the equation to represent the variables actually being graphed. Remember to save your file.

[4] When constructing a Beer's Law plot, set the intercept to go through zero.
[5] Refer to Appendix I for an example of a Beer's Law plot.
[6] Refer to Appendix II for the relationship between absorbance and % transmittance

2. **<u>Determining the Order of the Reaction with Respect to [CV^+], Part A</u>**– Open up a new Excel spreadsheet and create columns in your spreadsheet that display the following: time, absorbance (Abs.), [CV^+], ln[CV^+], and 1/[CV^+]. Using the Beer's Law equation (from step 1 above) and the data from Part A, compute the [CV^+] for each time point and enter results in the table. Next compute values for ln[CV^+] and 1/[CV^+] for each time point and enter into spreadsheet. Using Excel create the following graphs: [CV^+] versus time, ln[CV^+] versus time and 1/[CV^+] versus time. Remember, in order to make each graph, you must insert a time column preceding the data you want to display on your y-axis. Plot a best fit line on each graph and display the line equation and R^2 value. Also, at this point, change y and x in the equation to represent the variables actually being graphed, concentration and absorbance. Based on the graphs generated (which graph yields a straight line) determine the order of the reaction, the exponent "m", with respect to [CV^+]. Round m to the nearest integer.

3. **<u>Pseudo Rate Constant k_1'</u>** – Determine the pseudo rate constant, k', from the line equation. Use proper units.

4. **<u>Rate Law</u>** - Write the ***complete*** rate law using the pseudo rate constant k'. Be sure to include the order of the reaction in the rate law.

5. **<u>Rate of RX from Rate Law</u>** – Plot [CV^+] versus time and draw a best-fit line using Excel. Use a polynomial fit, order = 2. Display the best-fit line and the R^2 value. Using the line equation, determine the [CV^+] at 5 minutes. Determine the rate of reaction at 5 minutes using the rate law from step 4.

6. **<u>Rate of RX from Tangent Line</u>** – Using the plot from step 5, determine the rate of reaction at 5 minutes using a graphical method employing a tangent line.

7. **<u>Analysis</u>** - Compare and comment on the rates determined using the pseudo rate law (Step 5) and graphical method employing the tangent line (Step 6).

8. **<u>Integrated Rate Law</u>** – Write the integrated rate law using the plot in step 2.

9. **<u>Half-Life</u>** – Determine the half-life for the reaction using the integrated rate law.

10. **<u>Half-Life</u>** – Determine the half-life for the reaction graphically using the plot of [CV^+] versus t.

11. **<u>Half –Life</u>** – Compare and comment on the values for half-life as determined in steps 9 and 10.

Preparation of Finished Lab Report

Follow the steps below to prepare your finished lab report. Your report should contain the sections listed in the ***exact*** order they are listed below: Each section should start on a ***new*** page.

Title (front) page (typed)

a) Experiment title
b) Your name & name of your lab partner(s)
c) Date experiment conducted
d) Chemistry 220, Canada College, Summer Session, 2012

Section I)

a) Excel spreadsheet containing concentration and absorbance data from Part B.
b) Plot your Beer's Law data; absorbance versus concentration.
c) Include the best fit trend line (but remember to set y intercept = 0 when using Excel) on your graph. Include the line equation and R^2 value on your graph along with properly label axis and a title.

Section II) Excel spreadsheet containing data for Part A.

a) Include columns for absorbance, time, absorbance, $[CV^+]$, $\ln[CV^+]$, and $1/[CV^+]$ for data from
b) Properly label your data table.

Section III) Data Plots – Use Excel

a) For Part A, show plots for $[CV^+]$ vs. t, $\ln[CV^+]$ vs. t, and $1/[CV^+]$ vs. t.
b) Include the best fit trend line on each graph with the line equation and R^2 value.
b) Properly label your graphs and provide titles.

Section IV) Summary of Results Table (typed) – complete the table on page 8

Section V) Calculations (typed or handwritten)

a) Show your calculations for steps 5, 6, 9 & 10 on page 6.

Section VI) Post-Lab Questions (typed or handwritten)

1. Why does the reaction rate change as concentrations of the reactants change?

2. Suppose the rate law for a particular reaction between nitrogen dioxide and chlorine is Rate = $k[NO_2]^2[Cl_2]$. How would each of the following affect the rate of the reaction?

a. If the concentration of NO_2 is doubled then the reaction rate would ______________________ by a factor of ___________.

b. The concentration of NO_2 and Cl_2 are both tripled, then the reaction rate would ______________________ by a factor of ___________.

c. The concentration of Cl_2 is halved, then the reaction rate would ___________________ by a factor of ___________.

Summary of Results Table

1	Equation for trend line (best fit straight line) in Beer's Law plot (Part B)	
2	Order of the RX with respect to [CV^+], round to closest integer (Part A)	
3	Equation for trend line (best fit straight line) – Part A	
4	Pseudo rate constant – Part A	
5	Pseudo rate law – Part A	
6	Polynomial equation for best fit line in step 5	
7	[CV^+] @ 5 minutes	
8	Rate of RX for Run #1 after 5 minutes, using pseudo rate law	
9	Rate of RX for Run #1 after 5 minutes, using tangent method	
10	Compare and comment on the rates determined using the pseudo rate law and graphical method employing the tangent line.	
11	Half-life for Run #1 from integrated rate law	
12	Half-life for Run #1 from graph of [CV] vs time	

SUGGESTED FORMAT FOR DATA COLLECTION – KINETIC DATA

Run # ________

Data Point	Time	% T	Absorbance
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
11			
12			
13			
14			
15			
16			
17			

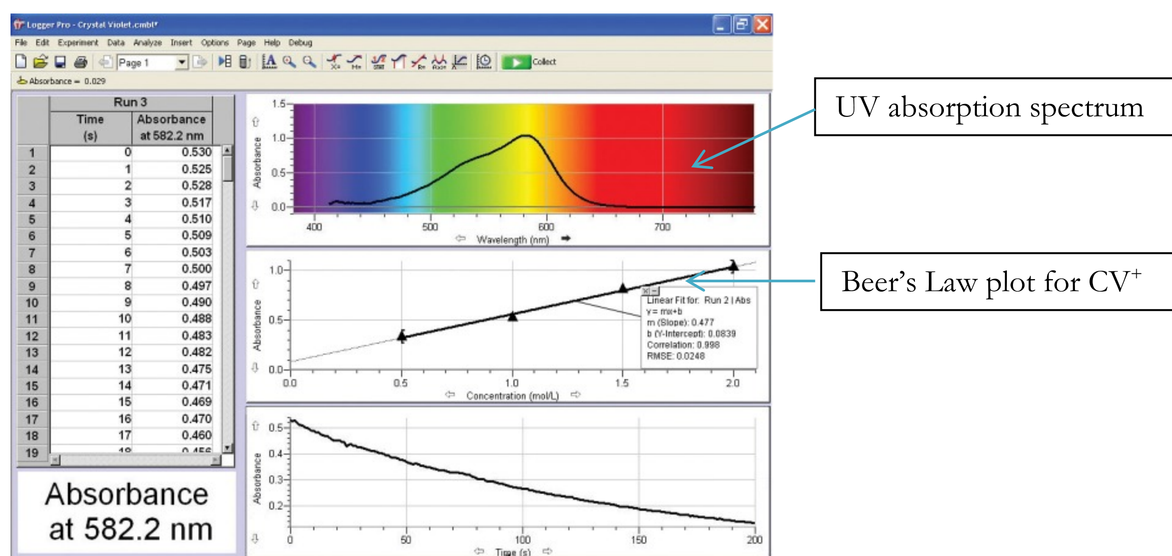
SUGGESTED DATA TABLE FOR BEER'S LAW PLOT

Trial	**[CV^+]**	**% T**	**Absorbance**
1			
2			
3			
4			
5			

APPENDIX I

UV ABSORPTION SPECTRUM FOR CV^+ AND BEER'S LAW PLOT

One of the most convenient, accurate and sensitive methods for measuring the concentrations of dilute solutions is by colorimetry or absorption spectrophotometry. The technique is based upon the measurement of the amount of light energy a solution absorbs from a beam of light of a certain wavelength. The wavelength chosen is usually that one at which the absorbance, of the species to be analyzed, is at a maximum.

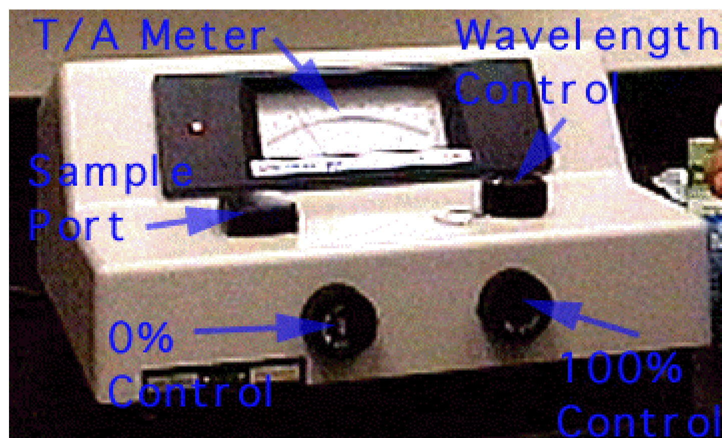


Relationship between Absorbance, Transmittance and Light Intensity

$$A = -\log_{10} T = -\log_{10}\left(\frac{I}{I_0}\right)$$

APPENDIX II

SPECTRONIC 20



Calibrating the Spectronic 20

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1. Plug in and turn on the Spec 20. It must warm up for 30 minutes before use.
2. Set the instrument to the proper wavelength by turning the *knob* located on the right hand surface of the spectrophotometer. The wavelength setting can be seen through the window next to the knob. For crystal violet solution, adjust wavelength control know to 580 nm. Adjust filter lever (bottom, front left side of instrument) to proper position.
3. Obtain a properly cleaned cuvette and fill it about 3/4 full of the reference solution (usually water).
4. With no cuvette in the *sample holder*, close the cover and rotate the *zero light control knob* (left front knob) to display a reading of 0.0% transmittance. Provided that the instrument is not turned off and this knob is not moved, no other adjustments to this control are needed.
5. Place the reference solution cuvette in the sample holder, close the cover, and rotate the *light control knob* (front right knob) to display a reading of 100.0% transmittance. This procedure must be repeated every time measurements are taken at a new wavelength or if several measurements are made at the same wavelength.

POSSIBLE PROBLEMS

A. Make sure the cuvettes are clean.

B. Fill cuvettes two-thirds full or to the top of the triangular mark.

C. Always use the same cuvette for the blank solution and the other one for the sample.

D. Make certain that the index mark on the cuvette is lined up with the index mark on the sample compartment before taking a reading. Doing so insures that the cuvette is in the same position for each measurement.

E. If the wavelength control is moved in the slightest it is necessary to reset zero and 100 %T.

F. If you suspect that your cuvettes are showing differences greater than 3% T, you should search for a pair which has closer agreement. To find such a pair, fill two clean cuvettes with distilled water. Calibrate the instrument using one as a blank. The read %T on the other. If your reading is less than 97%T or greater than 103%T, fill a third with distilled water and take a new reading. Any pair showing differences greater than 3%T may adversely affect your readings on an experiment which uses the Spectronic 20.