Kinetics of Crystal Violet Bleaching

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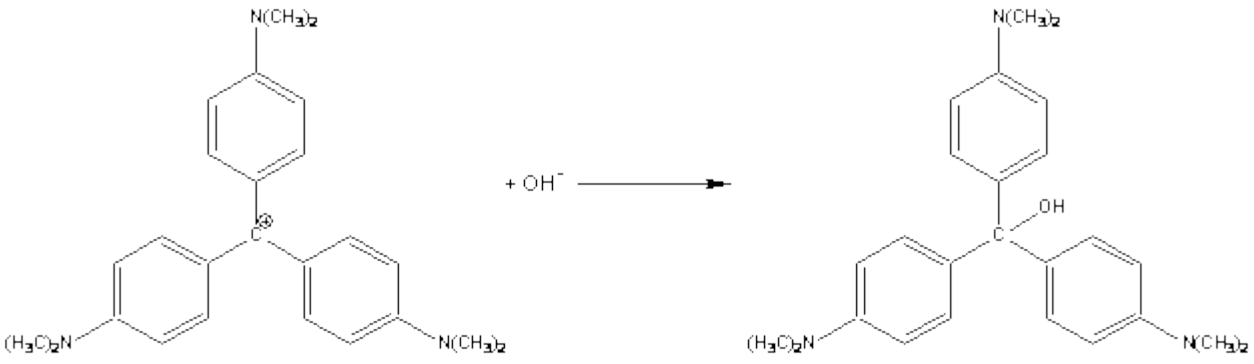
Introduction

Chemists are always interested in whether a chemical reaction can occur and exactly how it occurs. The first question is answered though thermodynamics, as you saw in a previous laboratory exercise, while the second is the domain of kinetics. In a kinetics experiment, a chemist attempts to understand the step-by-step transformation of reactants to products. Taken together, these *elementary steps* give us the *mechanism* by which the reaction proceeds. Note that a reaction's kinetics are very much tied to the pathway the reactants take to the products (i.e., the mechanism), which is very different from the reaction's thermodynamic properties (i.e., ΔH, ΔS, and ΔG) that do not depend on the path. While the thermodynamics and kinetics of a reaction may at times seem complementary, and at other times seem contradictory, it is always important to have a detailed understanding of both.

In this experiment you will determine the *rate law* for a chemical reaction. The rate law is a mathematical expression that relates the amount of time it takes a reaction to happen to the concentrations of the starting materials. The disappearance of reactant over time depends on the *rate constant* and the concentration of each reactant raised to some power. This power is known as the order with respect to that reactant. The sum of the individual orders is the *overall order of the reaction*. The order of reaction with respect to each reactant, as well as the rate law itself, cannot be determined from the balanced chemical equation; each must be found experimentally. The rate law is the basic equation of kinetics and it will be the standard against which we judge possible mechanisms.



Scheme 1. Reaction of crystal violet with OH^-.

In this experiment you will determine the rate law for the reaction of the dye crystal violet (CV) with OH^- in aqueous solution according to the balanced net ionic equation given in Scheme 1. We define the rate of reaction as the disappearance of the colored CV over time, which can be expressed in differential form as $-d[CV]/dt$. So, the rate law for this reaction can be written as shown in Eqn. 1 in terms of the concentrations of CV and OH^- and the rate constant for the reaction, k. In writing this equation we assume that both CV and OH^- are involved in the reaction (that is x and y are both not zero and are likely integers), but only the experiment will tell us whether these assumptions are valid.

$$rate = -\frac{d[CV]}{dt} = k[CV]^x[OH^-]^y \qquad (1)$$

The point of any kinetics experiment is to determine the order with respect to each reactant (i.e., find x and y) and to find the value of k. This is a problem if we have more than one reactant (as we do here), in which case the *isolation method* is often used. The isolation method entails making the concentration of all but one of the reactants very high (so their concentrations do not change appreciably over the course of the reaction). The order with respect to the isolated reactant is then determined. The process is then repeated, isolating each of the other reactants in turn, until all of the orders have been determined.

In this experiment we will make the $[OH^-]$ very large and, therefore, essentially constant. We can then simplify Eqn. 1 to Eqn. 2, where we have defined a new rate constant, k_{obs}, which is the observed rate constant at some specific $[OH^-]$. The relationship between k_{obs} and the intrinsic rate constant, k, for this reaction is given by Eqn. 3.

$$rate = k_{obs}[CV]^x \qquad (2)$$

$$k_{obs} = k[OH^-]^y \qquad (3)$$

Under conditions of high, constant $[OH^-]$, the order with respect to CV can be determined by graphically applying the integrated rate laws. Since the absorbance of a CV solution is directly proportional to the concentration of CV, according to Beers' Law, the actual [CV] can be replaced by A_{max}, the solution's maximum absorbance (somewhere around 600 nm). [Beers' Law states that for a sufficiently dilute solution, the amount of light absorbed at a particular wavelength by a chemical species present in the solution is given by A = ε•b•C, where A is the absorbance (how much light the sample absorbs compared to a solution that does not contain the absorbing species), ε is the molar absorptivity (also known as an extinction coefficient; ε depends on the compound and the wavelength of light), b is the pathlength (how much sample the light must pass through) and C is the concentration of the chemical species. According to Beer's Law the amount of color absorbed (and, therefore, the intensity of the color) is linearly dependent on the amount of material absorbing the light. Note that the absorbance has no units (although sometimes 'absorbance units' are used, abbreviated 'AU'). The concentration's unit is molar, M, and the pathlength's unit is usually cm. Therefore, the unit of the molar absorptivity is M^{-1} cm^{-1}. You might also look at http://teaching.shu.ac.uk/hwb/chemistry/tutorials/molspec/beers1.htm] A graph of A_{max} as a function of time will give a straight line if the reaction is zero-order in CV ($x = 0$). If the reaction is first-order in CV ($x = 1$), then a graph of $\ln(A_{max})$ as a function of time is linear. And finally, if a graph of $1/A_{max}$ as a function of time is linear, it indicates that the reaction is second-order with respect to

CV (x = 2). In each case, if a particular relationship is linear, then the slope of that graph can be used to determine k_{obs}. Note that only <u>one</u> of these three graphs should be linear!

In some instances it is not possible to isolate one of the reactants, because the concentration of that reactant must remain high for the system to behave predictably, as is the case here. However, the order of the reaction with respect to OH^-, and k, can still be found. First we need to change Eqn. 3 into an easily-graphed form by taking the logarithm of both sides to give Eqn. 4 (note that the natural logarithm would also work). To determine the order with respect to OH^- and k, we first perform the kinetics experiment at different, albeit still high, OH^- concentrations and then graph $\log(k_{obs})$ for these reactions as a function of $\log[OH^-]$. The slope of this graph is y, the order with respect to OH^-, and the intercept is $\log(k)$.

$$\log(k_{obs}) = y \log([OH^-]) + \log(k) \qquad (4)$$

In this experiment each you will work in a group with the other students at your laboratory table. Each group will measure the absorbance of CV as a function of time at a different assigned hydroxide concentration using a Vernier spectrometer. Each group will determine the order of reaction for CV at their $[OH^-]$. The class data (k_{obs} at different $[OH^-]$) will then be pooled and used to determine the order with respect to OH- and the intrinsic rate constant.

Experimental [1]

You will be assigned hydroxide concentrations (either 0.050 M, 0.040 M, 0.030 M, 0.025 M, 0.020 M, 0.010 M, or 0.0050 M). Before you come to the laboratory, work out the dilution you will need to do to prepare 50.0 mL of each of these solutions by dilution of a 0.050 M NaOH stock solution.

Prepare your assigned concentration in a beaker using graduated cylinders for measuring the stock solution and the required volume of water. **CAUTION!** The NaOH solution is caustic. Stir the solution and cover the beaker with a watch glass.

Find the bottle of CV stock solution at your table. **CAUTION!** Crystal violet will stain skin and clothing! Record the concentration of CV (it should be around 2 x 10^{-5} M).

To collect absorbance data, first connect the Vernier spectrometer to your computer with the USB cable and open LoggerPro. Your computer screen should display 

, or something similar, in the second line of icons at the top left of the screen, and the full screen should look similar to the following:

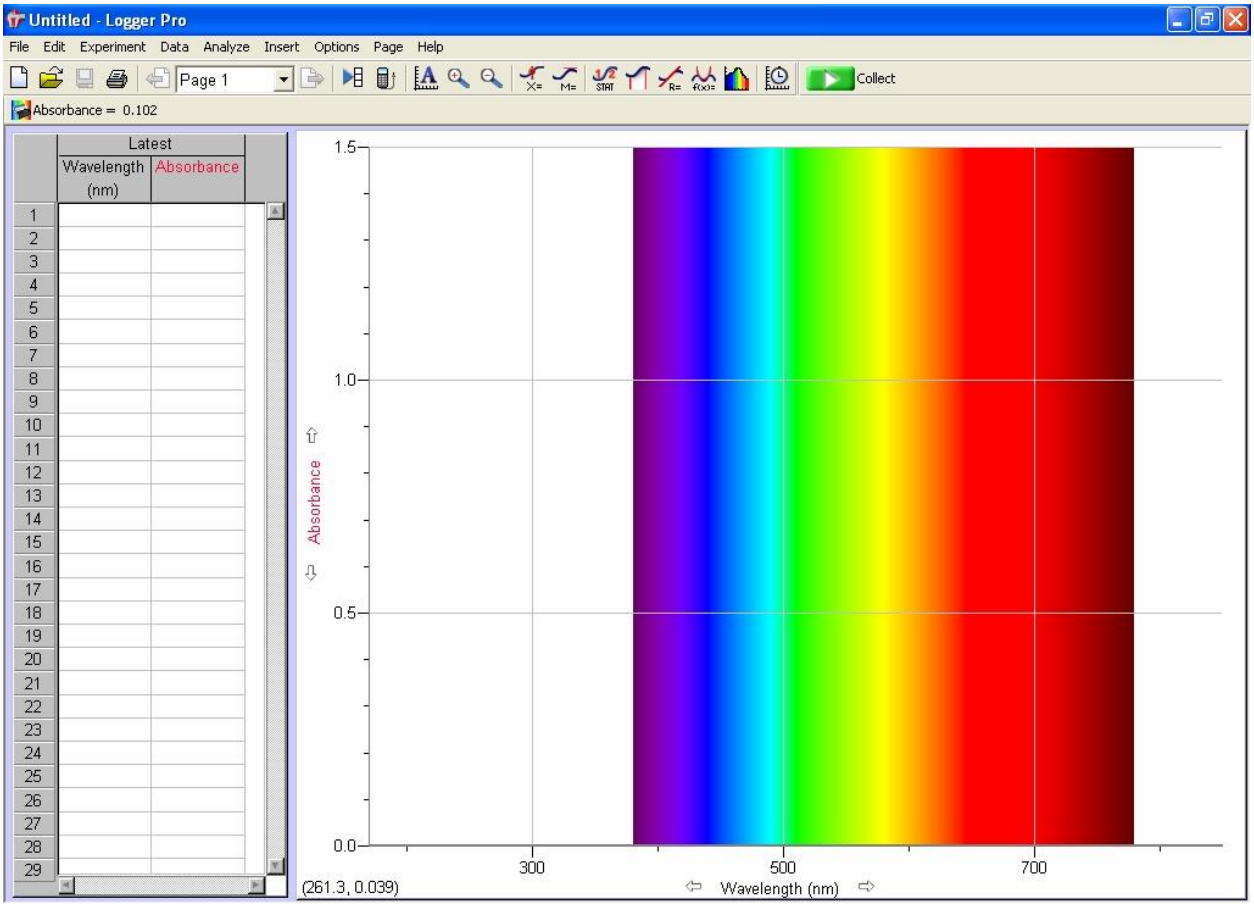


Figure 1. LoggerPro screen after the spectrometer has been found by the software.

Now prepare to collect data. Click on the spectrometer icon 

(or select from menu bar *Experiment, Set Up Sensors* and select *Spectrometer:1*). The Set Up Sensors pop-up shown in Fig. 2 will appear.

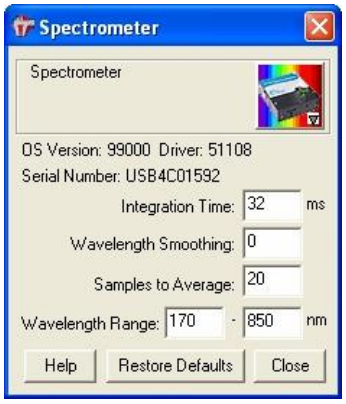


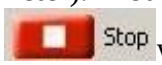
Figure 2. Set Up Sensors pop-up box for the spectrometer.

In the Set Up Sensors pop-up, click on the spectrometer icon  and a new pop-up will appear. Your options here are *Calibrate*, *Configure Collection* and *Current Units* (under *Current Units*, *Absorbance* should be selected; do not change). Select *Calibrate*.

While waiting for the spectrometer to warm up, prepare a cuvette containing your blank. [A blank is usually a solution that is identical in composition to the sample except that it does not contain the chemical species of interest. By running a blank first, we should remove the contribution of everything in the sample that absorbs or scatters light, except for what we are interested in.] Use distilled water as the blank in the same cuvette that you will use for the rest of your measurements. Rinse the cuvette several times with distilled water and then fill to about 8 mm from the top of the cuvette. Wipe the outside of the cuvette with a Kim-Wipe. Insert the cuvette into the spectrometer so that the triangle at the top of the cuvette is by the triangle on the spectrometer. Light must pass through the clear sides of the cuvette.

After warm-up is complete and the cuvette is inserted into the spectrometer, click *Finish Calibration* to complete the spectrometer calibration. After calibration is complete, close the pop-up. The *Collect button* 

should be active and you are ready to acquire absorbance data as a function of wavelength (the default for the spectrometer). You will click on the *Collect button* 

to acquire the spectrum and *Stop button* 

when you are done. Absorbance must be on the y-axis and wavelength must be on the x-axis.

Dilute about 5 mL of the CV solution with an equal volume of distilled water in a small beaker. Rinse a cuvette three times with small portions of this solution and then fill the cuvette approximately three-quarters full. Remove any bubbles by gently tapping the cuvette with your finger. **Under absolutely no circumstances are you to tap a cuvette on a table top.** Before placing the cuvette in the spectrometer, be sure to thoroughly wipe the cuvette's clear sides with a Kim-Wipe (do **not** use a paper towel). Obtain the solution's absorption spectrum. Use the cursor to determine the point of maximum absorbance, which should be near 600 nm. The maximum absorbance should be around 1. Record the wavelength for the maximum absorbance in your notebook. Select your data in LoggerPro's data window and copy and paste into an Excel workbook. Save the file and send it as an email attachment to your group members.

Now prepare for kinetics measurements. Open the Set Up Sensors pop-up box again, click on spectrometer icon  and select *Configure Collection* or click on the *Configure Spectrometer Data Collection*  icon on the tool bar. The window shown in Fig. 3 will open. Set the data collection mode to *Abs(orbance) vs Time* (for kinetics experiments), changing from *Abs(orbance) vs Wavelength* (used to obtain a spectrum). When *Absorbance vs Time* is selected, the check boxes under *Full Spectrum* are activated and you can choose which wavelength, or wavelengths, to follow as a function of time. When you check the *Absorbance vs Time* box, the program will automatically select a wavelength to monitor. If you used the *Examine Data* button

 , the software will default to the wavelength that the cursor was last set to; otherwise the software automatically selects the first point in the list and you must manually check a box for the desired wavelength. Click *OK* when finished to close this window.

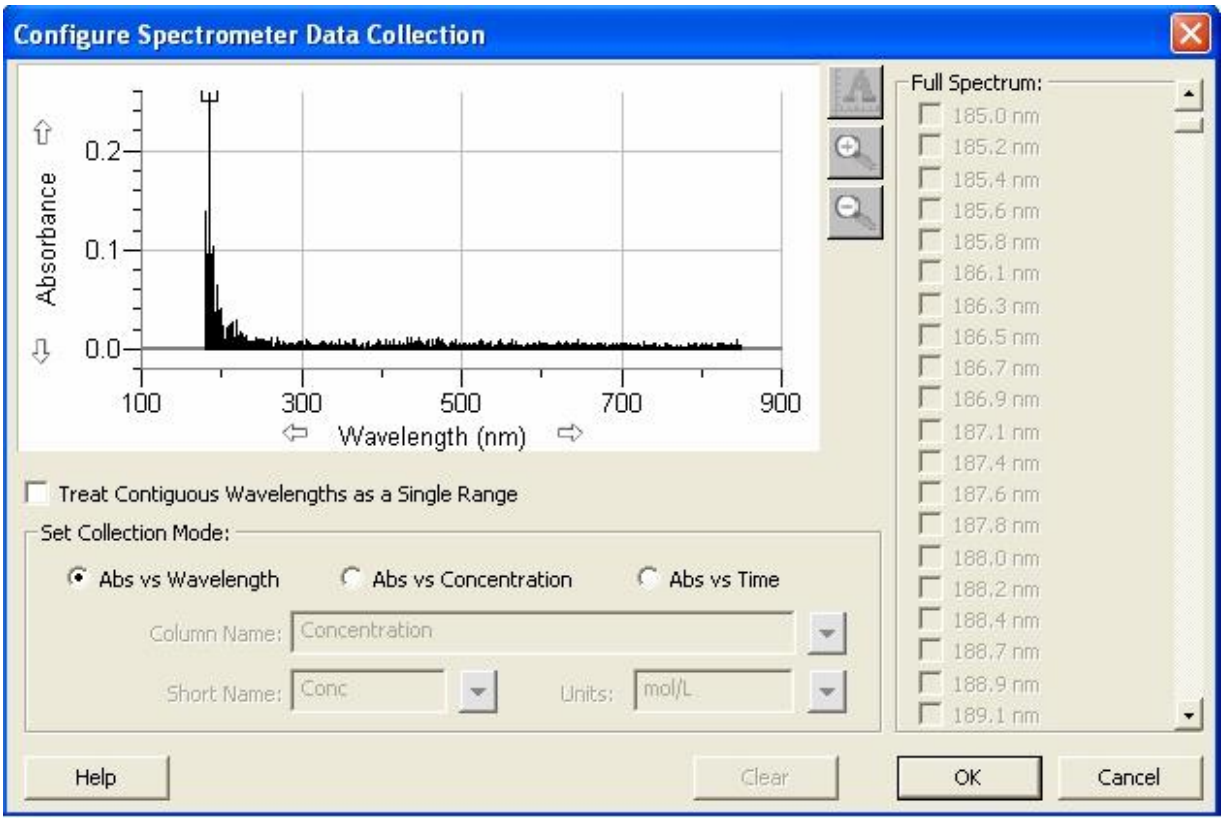


Figure 3. Configure Spectrometer Data Collection window.

Upon closing the Configure Spectrometer Data Collection window, the main LoggerPro page should now have absorbance on the y axis and time on the x axis, as shown in Fig. 4. The current absorbance at the wavelength(s) that you specified will be displayed in the lower left-hand portion of the screen.

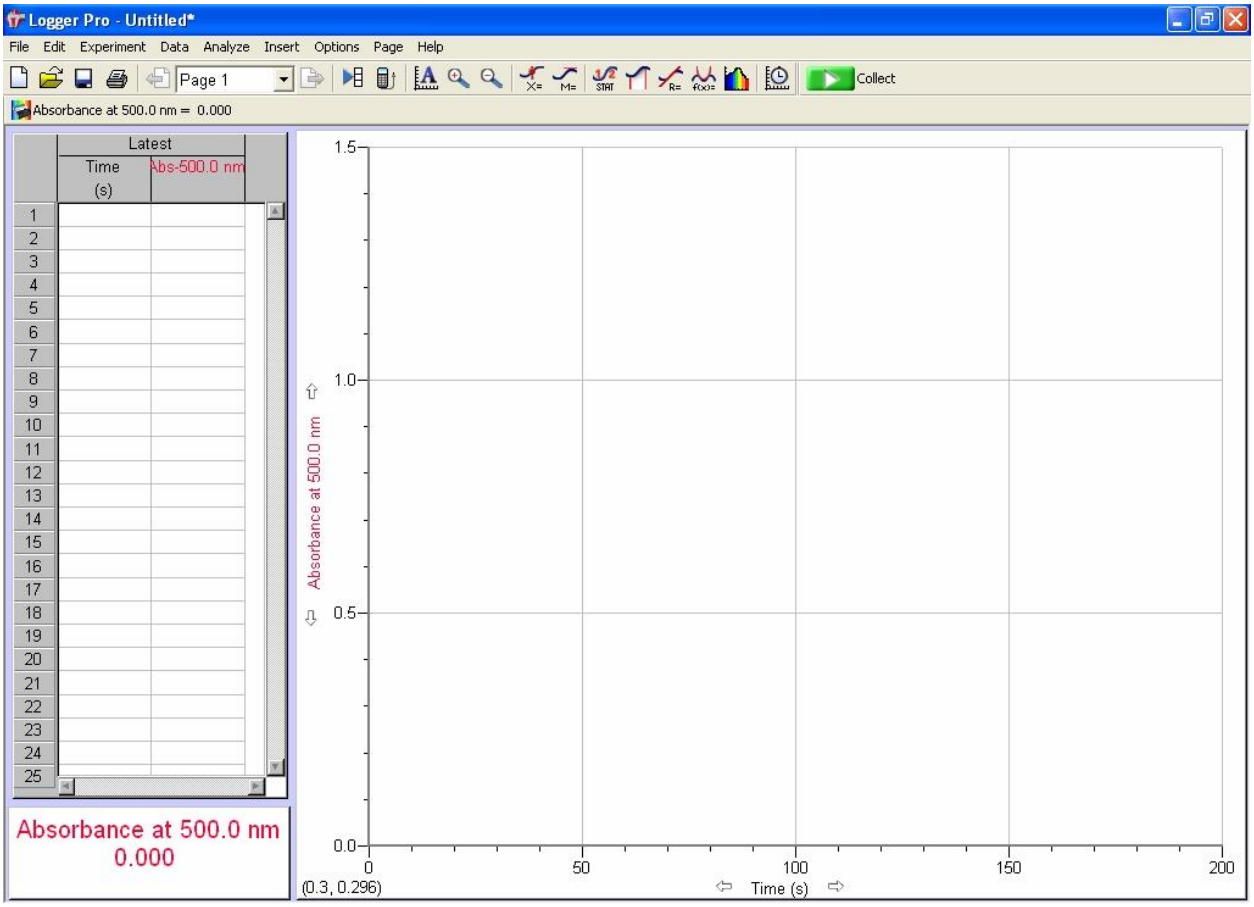


Figure 4. LoggerPro screen after data collection mode is set to absorbance as a function of time.

At the menu bar select *Experiment*, *Data Collection*. Switch the spectrometer to time-based measurement mode. Select the *Length* of the experiment (enter the number in the first box and the units in the second). Check the *Sample at Time Zero check box* if you want the computer to measure the absorbance immediately at the start of the experiment (a good idea in most cases). Select *Sampling Rate*. Some important things to know about the sampling rate: 1) the units on the sampling rate are the same as those you selected in the *Length* of the experiment, 2) when you type a value in one the sampling rate boxes, the computer automatically calculates the other and 3) if you select a sampling rate that is faster than the spectrometer can actually do, a message will be displayed giving the actual sampling rate, as shown in Fig. 5.

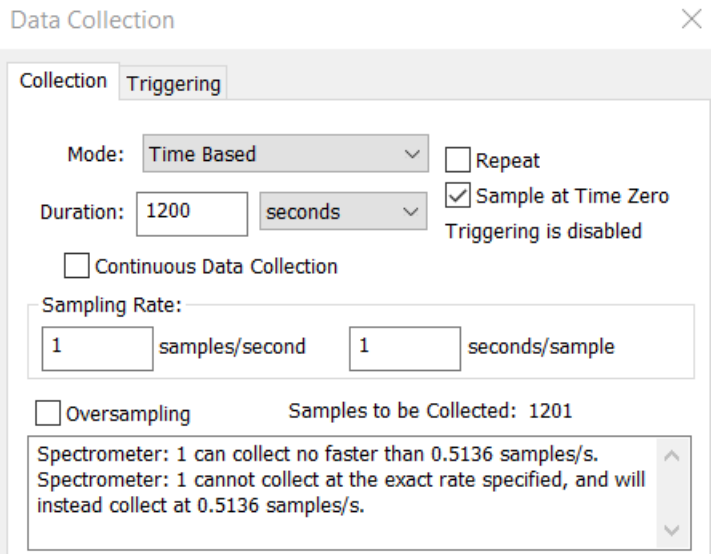


Figure 5. . Data Collection window for time-based measurements.

When you finish setting up the collection parameters for your experiment, click *Done*. You should be ready to make a run. To initiate the run, push the *Collect button* 

. To stop data acquisition simply click the *Stop button* 

.

Initially set the spectrometer to acquire data every 10 seconds for 1200 seconds. Set the time in seconds to facilitate sharing data. The instrument does not need to be set for a delay or for triggering, but do select the option *Sample at Time Zero* in the main *Data Collection* setup window once you have selected a time-based measurement.

Transfer 10 mL of your NaOH solution to a clean, dry beaker. Add 10 mL of the stock crystal violet solution and stir the resulting reaction mixture well. Rinse a cuvette three times with small portions of the reaction mixture and fill the cuvette three-quarters full with the reaction mixture. Wipe the outside of the cuvette with a KimWipe and place the cuvette in the spectrometer's cell holder. Push the *Collect button* 

to start the kinetics run. Work efficiently so as to not lose too much data while you are preparing the cuvette. The spectrometer will record the absorbance as a function of time. **CAUTION!** Do not adjust any of the spectrometer settings during a kinetics run; it will ruin your data. If the absorbance goes negative, stop your run and treat the run as done.

When the kinetics run is over, discard the reaction mixture and then clean and dry the beaker in which you ran the reaction. Select your data in LoggerPro's data window and copy and paste them into a different sheet of your Excel workbook. Save the file. Obtain two more kinetics data sets with your assigned [OH^-] (for a total of three). While you are performing these runs, you can be working up the previous data as described below. Note that one or two groups may

need to change the length of their kinetics run, if practical, depending on their [OH^-]. What groups are they and why must they change the length of their runs?

IMPORTANT! Do not throw away your hydroxide solution until you have prepared graphs for all three runs and they have been approved by your instructor.

Results and Analysis

Prepare three graphs for the first run: the first graph is A_{max} as a function of time, the second is $ln(A_{max})$ as a function of time, and the third is $1/A_{max}$ as a function of time. One of these graphs will give a straight line; from this graph determine order with respect to crystal violet at your [OH^-] and the rate constant, k_{obs}. Compare your results to other groups in the laboratory. Do you get results that are consistent (that is, do all groups have the same graph being linear, does the rate of reaction go up with increasing [OH^-], etc.)?

Prepare graphs for the other two runs, but you only need to prepare the graph that gave you a linear result for the first run (i.e., if the second-order integrated rate law graph was linear for the first run, then you only need to do a second-order integrated rate law graph for each of the other two runs). Average your three k_{obs}, determine the estimated standard deviation and the uncertainty at the 95% confidence level. Share your results with the rest of the class and then prepare Table 1 using the class data.

[OH^-] (M)	k_{obs} ( )

Table 1. Model table to summarize the class data; your table may have up six rows of data. Note that k_{obs}'s units have been omitted; determine them and place them in your table.

From the class data at different [OH^-], prepare a graph of $\log(k_{obs})$ as a function of $\log[OH^-]$ to determine the order of reaction with respect to OH^-. You do not need to determine the uncertainty in k.

Print out the absorbance spectrum of CV using Excel with absorbance (no units necessary) as a function of wavelength (units are nm). Set the x-axis so that only the absorbance in the range 450 to 900 nm is displayed. Set the y-axis so that the absorbance near 600 nm is clearly seen (choose the scale so that A_{max} is about three-quarters of the full y-axis). Include the spectrum in your lab notebook.

Conclusions

The conclusion should use the outline for a measurement exercise.
Report the order with respect to each reactant and the value of k with its units.

References

1. Holmquist, D. D. and Volz, D. L. *Chemistry with Computers: Using Logger ProTM*; Vernier Software: Portland, OR, 1997, p. 30-1 ff.