Extending Vernier Chemistry Lab 30
The Rate Order of Crystal Violet Decoloring in Hydroxide

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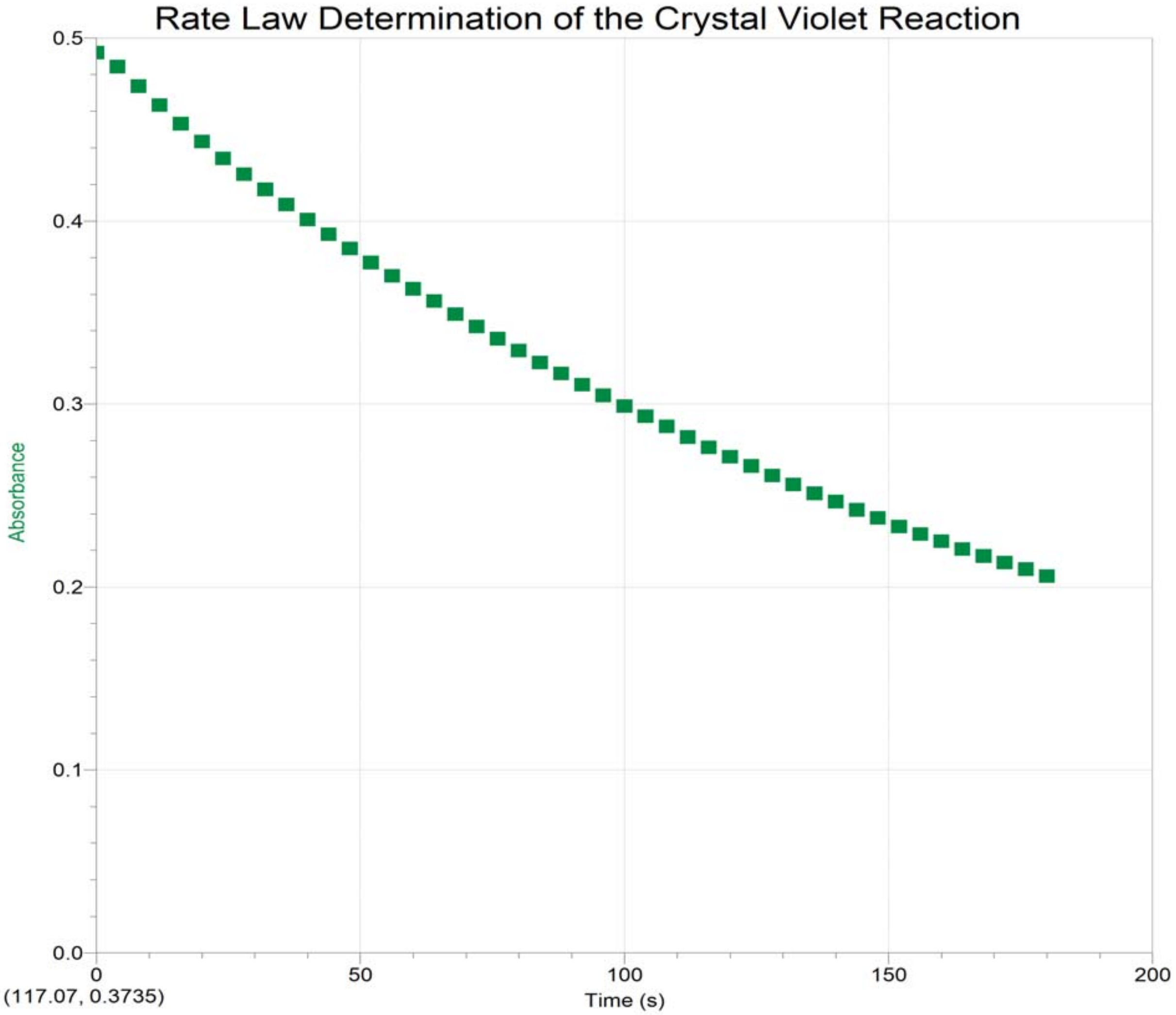
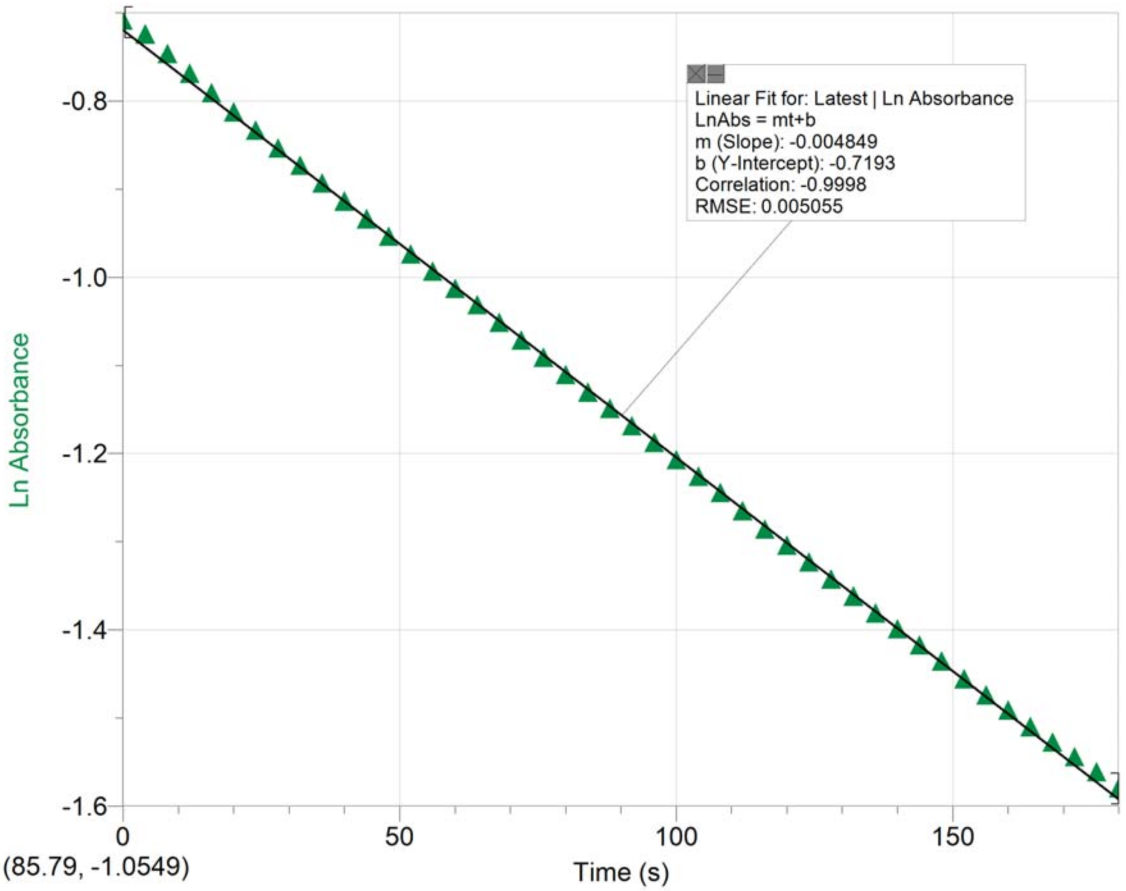
One of the more interesting rate law labs in the Vernier catalog is the decoloring of crystal violet in the presence of hydroxide (*Chemistry with Vernier* experiment 30). With a single run of the experiment, lasting 180 seconds, a plot of absorbance v time is generated (figure 1). With a simple manipulation of the data in software, a plot of ln absorbance v time is generated (figure 2), giving a straight line with negative slope. From this a pseudo rate constant can be calculated, and the rate order in crystal violet (1.0) derived.





2Natural log of absorbance of crystal violet v time, with linear regression showing first order rate law in CV concentration

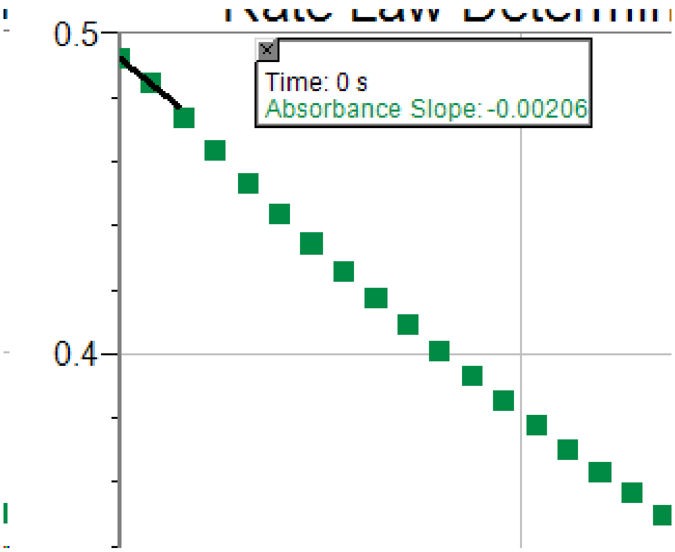
1 Absorbance v. time for decoloring of crystal violet

With appropriate pre-lab instructions and a second period for data analysis, the actual running of the lab can be accomplished in one fifty minute period. In my six lab sections during spring, 2013, almost all lab groups of three and four students generated useable data, even when exclusively comprised of students in chemistry 1, the “terminal” chem course at Johnson High School. In fact, data used above was gathered by one such chemistry 1 lab group, table 1 in period 3.

While very successful and quick because of the light-absorbing properties of crystal violet, the lab has two drawbacks: it generates incomplete data, since the rate order of the reaction in hydroxide ion is not studied, and it taxes the mathematical skills of the students by using the natural logarithm function. About half of the students in pre-AP classes are proficient with logs, while none of the chemistry 1 students are. They all understand what an exponent is, but the log function does not "connect" well with their math and science maturity.

In an attempt to extend the experiment for another period or two (the time was available because we had just finished high-stakes testing for the year), and to develop a completed rate law for the reaction, I devised a protocol for studying the concentration effect of the hydroxide ion on the rate. Students used a protocol modified to accommodate multiple runs with the same concentration of crystal violet and varying concentrations of hydroxide (Appendix I). Over the day of the experiment, indifferent student results convinced me to change the concentrations of the hydroxide solution, eliminating the lowest (approximately 0.01 *M*) and adding higher concentrations.

Because the hydroxide concentration cannot be followed with colorimetry, and a preparatory investigation showed that at levels about 100 times that of the crystal violet its pH does not change appreciably with the progress of the reaction, the protocol follows the crystal violet decoloring. It is possible to measure the rate of decoloring by finding the slope of the absorbance-time curve. The "tangent" feature of the Vernier Logger *Pro* software makes this quite easy (figure 3).



3 Sample "tangent" rate determination

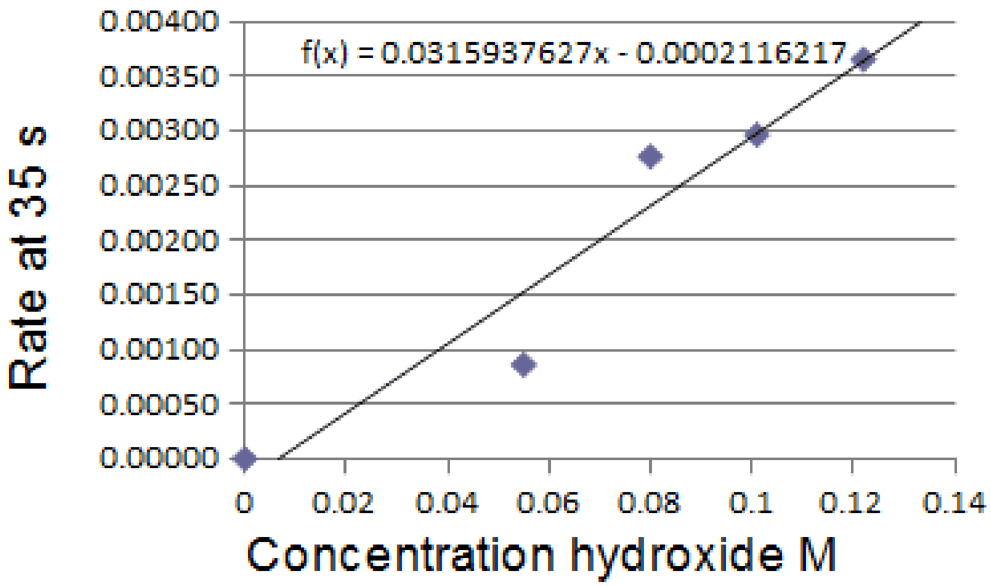
Now a proper study of rate v concentration of the hydroxide would use the initial rate of decoloring, but the mixing, rinsing of the colorimeter cuvette with the reaction mixture, addition of the mixture to the cuvette and placing in the colorimeter cuvette holder took, at a minimum, 30 seconds. So all students were instructed to time from the moment of mixing and start the data collection at 35 seconds. Hence, the rates measured were not the initial rate but the rate at 35 seconds, as given by Logger *Pro*.

The results of all student runs are given in table 1.

Concentration M	0.122	0.101	0.08	0.055	0
Rates |(□Abs/□t)|	0.00344	0.00273	0.00367	0.00079	
	0.00274	0.00314	0.00271	0.00080	
	0.00399	0.00303	0.00278	0.00069	
	0.00378	0.00311	0.00298	0.00069	
	0.00423	0.00303	0.00279	0.00065	
	0.00261	0.00304	0.00217	0.00167	
	0.00384	0.00303	0.00280	0.00024	
	0.00437	0.00262	0.00284	0.00136	
	0.00304	0.00302	0.00252		
	0.00339	0.00291	0.00307		
	0.00415		0.00257		
	0.00277		0.00232		
	0.00429				
	0.00424				
	0.00346				
	0.00417				

Table 1: Concentration v rates–student data

I averaged the data, and using 2x standard deviation tests, eliminated two outliers to create the graph of rate v hydroxide concentration (Figure 4).



The conclusion students drew from this investigation is that the rate of the chemical reaction is

4 Rate at 35 seconds v concentration of hydroxide

directly proportional to the concentration of the hydroxide, and that the rate law, hydroxide dependent, is

Rate = k$[OH^-]$

This makes the reaction first-order in hydroxide. The prior work showed that it is also first-order in crystal violet. Therefore the overall rate law is

Rate = k[CV] $[OH^-]$

And the reaction is second-order overall. This suggests that the rate-determining step for the reaction is a collision between the CV^+ ion and the OH^- ion.

Pedagogical Analysis:

The experiment, which students wrote up for extra credit, had a number of advantages for student understanding. First, it completed the work of finding the overall rate order and rate law for the decoloring reaction, leading students by their own experimental work to the conclusion above. Second, it obviated the need for a thorough understanding of logarithms, because all students, even those who have not studied logs, understood the concept of slope as rate, and could see that the rate v concentration graph for all the class data was a straight line.

Safety considerations:

The safety considerations for this extension are the same as for experiment 30. The only addition is that students could show some nervousness about being under a 35 second time constraint for the mixing, cuvette preparation, and data collection. In two cases out of thirty-eight, students made basic errors leading to a higher prep time and had to start over.

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Appendix I: Student Protocol, unredacted

Chemistry with Vernier Experiment 30b Extension

Finding the Reaction Order of OH^- in the decoloration of Crystal Violet

Background: In the lab in which the colorimeter is used to determine the reaction order of Crystal Violet in its decoloration, it was determined that ln(Absorbance) graphed as a straight line. We then conclude that the reaction is **first order** in Crystal Violet. The reaction may be represented as

$$R^+Cl^- + Na^+OH^- \longrightarrow ROH + Na^+Cl^-$$

"R" is used to represent the complicated formula of crystal violet.

We know from the work we did in experiment 30b that the CV molecule is involved in the rate determining step. It is first order in CV. Is the OH- ion also involved in the rate-determining step? We propose to study it in the same way as we studied the CV molecule. It will involve more work, but should give an answer. We will find the initial rate of the reaction for three concentrations of sodium hydroxide and graph the initial rate against the concentration. *If* the graph is a straight line, or close to a straight line, then we can be pretty sure the reaction is first order in the hydroxide ion, and the rate determining step involves a collision between the CV and the OH^-. If not, more work will be needed.

I. Follow the directions given in your Crystal Violet reaction protocol, but do the reaction three times and graph it three times on Logger *Pro*. Use 10.0 mL of three different concentrations of NaOH and record those concentrations in the lab notebook.

It is **very important**, since you can't catch the actual initial rate when you mix the chemicals, that you start the collection of data on each run exactly the same number of seconds after the mixing. So time the mixing with the most concentrated NaOH solution and duplicate that time delay with the other two.

It is not necessary to graph the ln(Absorbance) v time function. You already know it's a straight line and that the reaction is first-order in the CV.

II. For each run, graph the **rate** of the chemical reaction against time. You may use the formula

$$\text{Rate} = \frac{\Delta\text{Absorbance}}{\Delta t}$$

Alternately, you may find the first derivative of the Absorbance-time graph. Then project back your linear fit to find the vertical intercept, which should be the **initial rate**.

III. Your report should have an objective, data, the three graphs of Absorbance v time, a table of initial rate v. concentration, and a graph of initial rate v. concentration. Finish with an appropriate conclusion about the order of the reaction and a proposed rate law.