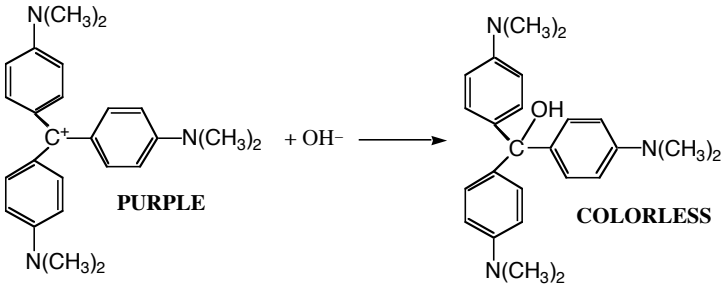
Experiment 1 – Chemical Kinetics[1]

Purpose: Determine the rate law for the reaction of the dye crystal violet with hydroxide.
Reading: Brown, *et. al., Chemistry The Central Science*, sections 14.1–14.4.

Introduction

The reaction of crystal violet with hydroxide is:



This reaction can be represented as follows:

$$CV^+ + OH^- \longrightarrow CVOH$$
purple colorless

The kinetics of this reaction can be monitored with a spectrophotometer by observing the decrease in absorbance of crystal violet, which can be used as a measure of the rate to determine the rate law through the following relationships:

$$\text{rate of disappearance of CV} = \text{rate of appearance of CVOH} = [CV]^x\,[OH^-]^y \quad (1)$$

Chemical Kinetics

Chemical reactions occur at varying speeds with a vast spectrum of rates, ranging from very slow to extremely fast. For example, the rusting of iron is fairly slow, whereas the decomposition of TNT proceeds explosively fast. Experiments have shown that the rate of a homogeneous reaction in solution depends upon the nature of the reactants, their concentrations, the temperature of the system, and the use of catalysts.

Consider the hypothetical reaction:

$$A + B \longrightarrow C + D$$

The rate of this reaction may be measured by observing the rate of disappearance of the reactants A or B, or the rate of appearance of the products C or D. Which species is observed is a matter of convenience. For example if A, B, and C are colorless and D is colored, the rate of appearance of D can be conveniently measured by observing an increase in the intensity of the color of the solution as a function of time. Mathematically, the rate of reaction may be expressed as follows:

$$\text{Rate of disappearance of A} = \frac{\text{Change in the concentration of A}}{\text{Change in time}} = \frac{-\Delta[A]}{\Delta t}$$

$$\text{Rate of appearance of D} = \frac{\text{Change in the concentration of D}}{\text{Change in time}} = \frac{\Delta[D]}{\Delta t}$$

In general, the rate of the reaction depends upon the concentration of one or more of the reactants. Thus, the rate of the hypothetical reaction above may be expressed as:

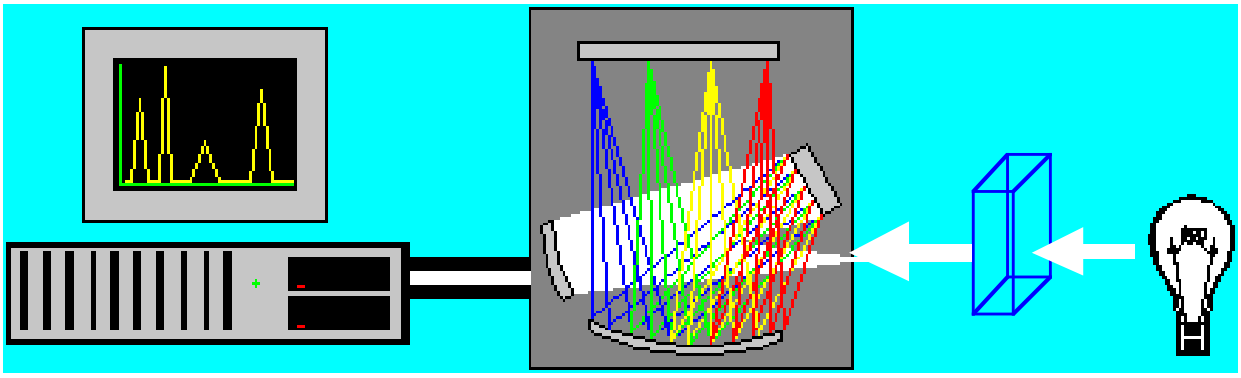
$$\text{Rate} = k[A]^x [B]^y$$

where [A] and [B] are the molar concentrations of A and B, x and y are the powers to which the respective concentrations must be raised to describe the rate, and k is the specific rate constant. The values of x and y must be determined experimentally. For example, if x = 2 and y = 1, then the rate law is:

$$\text{Rate} = k[A]^2[B]$$

This reaction is first order in B, meaning that doubling the concentration of B while keeping A constant causes the reaction rate to double. Simultaneously, this reaction is second order in A, meaning that doubling the concentration of A while keeping B constant causes the rate to increase by a factor of four since the rate of the reaction is proportional to the square of the concentration of A. The overall order of the reaction is the sum of the exponents: or third order in this case. It is possible to determine these orders experimentally by noting the effects of changing reagent concentrations on the rate of the reaction. The specific rate constant, k, has a definite value that is independent of the concentration. The rate constant is characteristic for a given reaction and varies only with temperature. Once the rate is known for a given set of concentrations, the value of k can be calculated.

For our reaction of interest, the rate law will be determined by spectrophotometrically measuring the amount of reactant disappearing as a function of time. The values of x and y as well as the rate constant k will be determined for the rate law: rate = $k[A]^x [B]^y$.



White light illuminates the sample and can be absorbed. The remaining light enters an optical fiber and is efficiently transmitted to the spectrophotometer and then analyzed by a computer. The amount of light absorbed by the sample can be determined by measuring the light signal with the sample in the optical path relative to a reagent blank. Beer's Law relates the measured absorbance, A, to concentration, C, of the chromophore as follows (see the Beer's Law Primer for a more complete explanation):

$$A = \varepsilon l C$$

where l is the path length, which is 1 cm in our case, and ε is the molar extinction coefficient

Therefore, determination of the *absorbance* allows calculation of the *concentration* if the molar extinction coefficient ε is known for the chromophore. Moreover, determination of absorbance, and thus concentration, over time allows an experimental determination of the rate of the reaction.

Crystal Violet Decolorization

The most convenient means of monitoring the rate of crystal violet decolorization is to monitor the loss of purple color over time. Equation (2) shows that the rate of the reaction is equal to the opposite of the change in concentration of crystal violet over time, where the change in CV concentration (Δ[CV]) is measured by the change in color of the solution and the change in time (Δt) is the time between measurements. This is an approximation because the rate changes over the course of the reaction and is not constant. However, since we are only studying the *initial rate* of this reaction, it is reasonable to assume a linear relationship between concentration and time. Initial rate experiments are performed so that the concentration of reactants remains within 1% of their starting values.

$$\text{rate} = \frac{-\Delta[CV]}{\Delta t} = k\,[CV]^x\,[OH^-]^y \qquad (2)$$

Beer's Law allows calculation of the concentration of crystal violet using the experimentally determined value of ε. That is,

$$[CV] = \text{Absorbance} / (\varepsilon)\,(1\text{ cm}) \qquad (3)$$

.

The first step in this analysis will be to determine the wavelength of maximal absorbance for crystal violet and the corresponding molar extinction coefficient at that wavelength. This wavelength will be used to monitor the disappearance of crystal violet throughout the course of the experiment. Once you have determined the value of ε, then you can use it in your subsequent spreadsheets of kinetic data, which will contain absorbance values versus time, to convert each absorbance value to its corresponding concentration of crystal violet.

A practical approach to find the order of the chemical reaction by the initial rate method is to vary the concentration of one reactant while leaving the concentration of the other reactant constant. Thus, two different sets of experiments will be performed: during Week 1 you will vary the concentration of crystal violet, allowing determination of x in equation (2), and during Week 2 you will vary the concentration of hydroxide, allowing determination of y in equation (2).

Because this reaction has two reactants and is likely to follow a complicated mechanistic pathway to products, it may not have simple whole number values for reaction orders. Therefore, we cannot determine the reaction order through the simple linear plots we have used to solve problems in the textbook to determine whether a reaction is zero, first, or second order. Initial rate studies work well with non-integer reaction orders. Taking the (log) of both sides of the rate equation,

$$\text{rate} = k\,[CV]^x\,[OH^-]^y, \text{ gives:}$$

$$\log(\text{rate}) = \log(k) + x \log[CV] + y \log[OH^-]$$

For Week 1, the term **y log [OH^-]** is constant because the [OH^-] is constant. The term **log (k)** is also constant since the rate constant, k, is characteristic of each reaction. Therefore, a plot of log (rate) vs. log [CV] should give a straight line with a slope of x, the rate order with respect to CV. Similarly, for Week 2 both the terms **x log [CV]** and **log (k)** are constant. Thus, the rate order with respect to OH^- can be determined through a plot of log (rate) vs. log [OH^-].

Example Analysis

Use the kinetic data provided below for the hypothetical reaction:

$$A + B \longrightarrow C + D$$

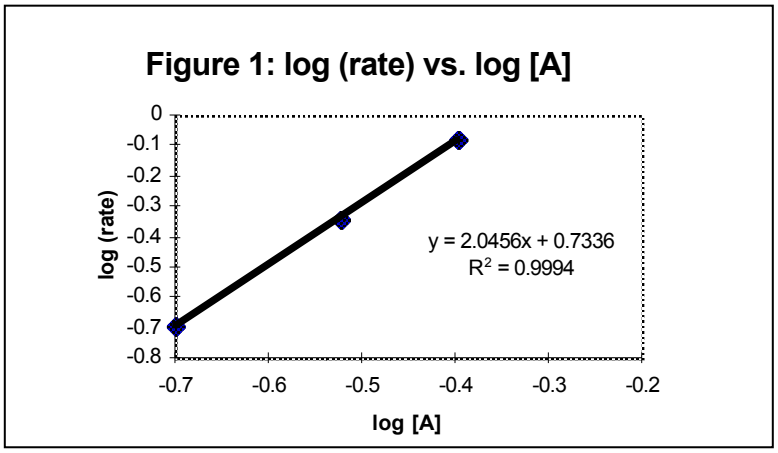
1. To determine the order of the reaction with respect to A.
2. To determine the order of the reaction with respect to B.
3. To write the rate expression for the reaction.
4. To calculate the rate constant of the reaction.

EXPERIMENT	[A] (M)	[B] (M)	RATE (M/SEC)
1	0.1	0.1	0.0101
2	0.1	0.2	0.0206
3	0.1	0.4	0.0403
4	0.2	0.5	0.203
5	0.3	0.5	0.452
6	0.4	0.5	0.841

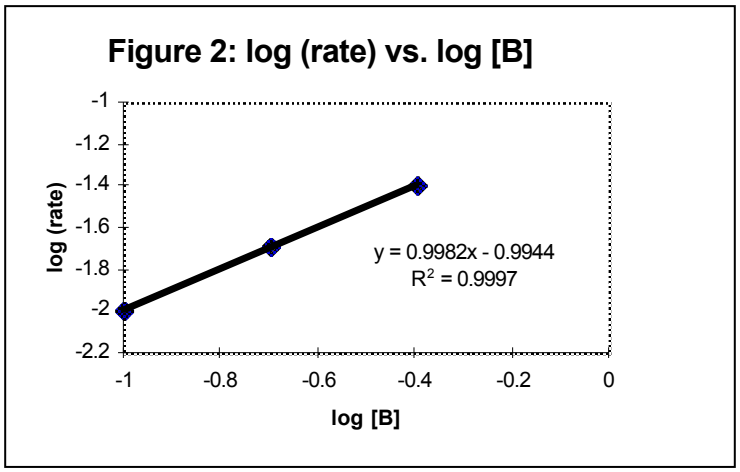
Solution

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

1. To determine "x", the data from experiments 4-6 are used because [A] varies while [B] remains constant in these experiments. A plot of log (rate) vs. log [A] for experiments 4-6 gives a slope of about 2 (Figure 1). Therefore $x \sim 2$.



2. The value of "y" can be determined by plotting log (rate) vs. log [B] for experiments 1-3. This yields a slope of about 1 (Figure 2). Therefore y ~ 1.



3. Rate = k $[A]^2$ [B].

4. The rate constant "k" can be determined from the data in any experiment. For example, using the data in experiment 3: 0.0403 M/sec= k $(0.1\ M)^2$ (0.4 M), or k = 10.1 $M^{-2}sec^{-1}$.

Experimental Procedure

You will use automatic micropipettors in this experiment for precise and accurate delivery of small volumes. There are multiple sizes of Finn pipettes®, but for this lab you should only need to use the 200-1000 µL (blue) pipettes with respective blue boxed tips and the 40-200µL (yellow) pipettes with respective yellow boxed tips. These numbers refer to the maximum volume in **microliters** (µL) that can be achieved. Never dial a pipettor past the maximum volume. Likewise do not dial below the minimum volume printed on the side of a given pipette. To draw up the sample into the pipette tip, first place a clean tip on your pipette. Pour some reagent into the provided beaker. Push the top pipette button downwards until you feel it catch on a notch, immerse the pipette tip in the sample, and slowly release the pressure you are exerting on the button. Check the tip to make sure you didn't capture any air bubbles. To

dispense the sample, push the button all the way down. You can keep a pipette tip in each beaker and use it over and over.

You will work in pairs for this experiment. The first step in your analysis will be to determine the wavelength of maximal absorbance of the chromophore (crystal violet in this case). You will use the absorbance of a solution of known concentration of crystal violet to calculate the value of the extinction coefficient at this wavelength. You will then perform two sets of kinetics experiments: one which holds the concentration of hydroxide constant while varying the crystal violet concentration (Week 1) and the other which holds the concentration of crystal violet constant while varying the hydroxide concentration (Week 2). These two sets of experiments will allow you to determine the average rate constant, reaction order for crystal violet and hydroxide, respectively, and thus the rate law.

Week 1: Determination of the Reaction Order for Crystal Violet

A. Preliminary Experiment to Determine λ_{max} and ε

1. Please consult the Vernier SpectroVis Plus Spectrophotometers User Guide, which will be available in the laboratory, for detailed instructions for how to first calibrate and then use the instrument.

   Keeping your total solution volume 3.00 mL in all cases, take the absorbance of a solution of crystal violet in water. A stock solution of 1.00×10^{-4} M will be available for you to use, and you should try to keep the maximum absorbance value at around 1.5. It may take you a few dilutions to obtain a good spectrum that is on-scale, but you can collaborate with another research team to zone in on an appropriate amount of crystal violet that will be on-scale. Be as accurate as possible when making up your solution as you will use this concentration to calculate the extinction coefficient. When ready to measure the absorbance of this solution refer back to your User Guide.

2. Once you find an appropriate dilution, make sure that you record both the λ_{max} and the absorbance at that wavelength <u>on your own spectrophotometer</u>. Wavelengths may differ from spectrophotometer to spectrophotometer.

3. Use Beer's Law to calculate the value of ε for crystal violet based on your measured absorbance value and your concentration (the path length is 1 cm).

B. Kinetics Experiments with Hydroxide Constant, Variable Crystal Violet

Note that in this set of experiments you will vary the volume of crystal violet added while keeping the volume of hydroxide constant. Follow the **Running a Kinetics Trial** directions provided in the User Guide.

1. The total volume of each trial should be 3.00 mL. Your first kinetics trial should contain a volume of crystal violet that will give an absorbance of about 1.5 (based on your findings from **Part A**). Plan to add the same volume of 0.100 M NaOH as you have of crystal violet, but don't add it yet! In your User Guide, go to **Running a Kinetics Trial**. Complete steps

one thru eight. You should see the absorbance signal drop as the crystal violet decolorizes in the presence of base for each trial conducted.

2. Set up a new 3.00 mL reaction, this time with less crystal violet than in the first trial (but make sure that you know this amount exactly). Again, add crystal violet, water (make sure that you increase the volume of water to make up for the decrease in the amount of crystal violet), and the same volume of 0.100 NaOH in the first trial (this amount will remain constant in this whole series of trials). To collect kinetics data again repeat steps four thru eight from **Running a Kinetics Trial**, again.

3. Repeat until you have five kinetics trials, each with a total volume of 3.00 mL, a constant volume of 0.100 M NaOH, and a known but varying amount of crystal violet. Ideally, the absorbance at the start of each kinetics trial will be 0.1 or higher.

C. Data Analysis

1. Record the slope of each graph created today along with corresponding amounts of CV, OH^- and H_2O used for each trial. Print just one of your 5 Logger Pro Conc. Vs Time graphs saved on the desktop to use for a future report. Print the given graph by going to **File** slide down to **Print Graph** and click. You will have an option to label the print out each time, which will help you keep track of which graph goes with which trial.

2. Open Excel and set up a spreadsheet that will enable you to plot log (rate) vs. log $[CV]_{initial}$. The slope of the best-fit line is the reaction order for crystal violet. This will be "x" in the rate law equation (2).

Before leaving lab today….

- Complete your spreadsheet of rates and concentrations. Make sure your Table is labeled.
- Complete your plot of log (rate) vs. log $[CV]_{initial}$. Make sure you have a caption.
- What is the order of the reaction with respect to crystal violet? Write your answer as part of the caption of your log-log plot.
- Show all of these things to your lab instructor

<u>What you should have in your laboratory notebook (Week 1):</u>

Title: Summarize the chemical concept being explored

Name and date: Your name and the name of your partner(s), and the date

Purpose: Briefly state the scientific purpose of the experiment

Procedure / Data / Observations:

- Describe the steps you follow during the experiment in concise terms
- Write down what you do – as you do it
- Record all data and observations (retain your graphs and spreadsheets so they can be attached to your report for Week 2)

- Include an example calculation of each formula used in any Excel spreadsheets
- Include the literature reference for your lab handout
- Include the manufacturer and model of any instrumentation used
- The slope of each graph created today along with corresponding amounts of CV, OH^- and H_2O used for each trial.

Week 2: Determination of the Reaction Order for Hydroxide

Make sure that you use the same spectrophotometer this week as you did last week; otherwise, you will have to repeat Part A to determine the wavelength of maximal absorbance and the extinction coefficient on that particular set-up. Note that in this set of experiments you will vary the volume of hydroxide added while keeping the volume of crystal violet constant. You will use the same computer instructions as last week, and **you will need to calibrate the spectrophotometer using a cuvette of water just as you did last week**.

A. Kinetics Experiments with Crystal Violet Constant, Variable Hydroxide

1. Again, the total volume of each trial should be 3.00 mL. Your first kinetics trial should contain the volume of crystal violet that gives an absorbance of about 1.2-1.5 (based on your findings from **last week**). Plan to add the same volume of 0.100 M NaOH as you have of crystal violet, but don't add it yet! Add the crystal violet to your cuvette, then the appropriate volume of water that will make your final volume 3.00 mL (be sure to account for the NaOH that you're about to add). Just like last week, by the time you reach step #6 of your **Running a Kinetics Trial** instructions, you will have a cuvette in the spectrophotometer and a magnet spinning inside the cuvette. Add the NaOH, and continue to follow the computer instructions. You should see the signal drop as the crystal violet decolorizes in the presence of base. When data collection is done save it using **File**, **Save As**, and put it on your Desktop.

2. Set up another 3.00 mL reaction that will contain less hydroxide than the first trial (but make sure that you know the amount exactly). To set up this reaction, again add the crystal violet (same volume as you just used in trial 1, today), water (make sure that you increase the volume of water to make up for the decrease in the amount of sodium hydroxide), and the new, reduced volume of 0.100 M NaOH. Collect kinetics data again and SAVE AS with a new name to your desktop.

3. Repeat until you have five kinetics trials, each with a total volume of 3.00 mL, a constant volume of crystal violet, and a known, varying amount of sodium hydroxide.

B. Data Analysis

1. Return to the data analysis section above, see step **C**, from last week to find the slope of the best fit line for each of your 5 kinetic trials today.

2. Open Excel and set up a spreadsheet that will enable you to plot log (rate) vs. log $[OH^-]_{initial}$. The slope of the best-fit line is the reaction order for hydroxide. This will be "y" in the rate law equation (2).

3. Now that you have determined the values of both "x" and "y", determine the value of the rate constant, k, for all ten of the reactions in Excel using the expression: rate = $k[CV]^x[OH^-]^y$. Show sample calculations in your lab notebook for each type of calculation made. Print your spreadsheet for your client report. Calculate the average, the standard deviation, and the % relative uncertainty (SDOM) of the 10 rate constants.

What you should have in your laboratory notebook (Week 2):

Continue your notebook entry from week 1, adding additional Procedure / Data / Observations:

- Describe the steps you follow during the experiment in concise terms
- Write down what you do – as you do it
- Record all data and observations (retain your graphs and spreadsheets so they can be attached to your report)
- Include an example calculation of each formula used in any Excel spreadsheets
- The slope of each graph created today along with corresponding amounts of CV, OH^- and H_2O used for each trial.

Literature Cited:

[1]Adapted from Chemistry The Central Science, Laboratory Experiments, 6th Edition, by J.H. Nelson and K.C. Kemp and Laboratory Inquiry in Chemistry, by R. C. Bauer, J. P. Birk, and D. J. Sawyer.

Laboratory Report: Use the Report Form for this experiment from the website. Your report is due in one week (at the beginning of your next lab period).