

# Kinetics of Crystal Violet Fading

## AP\* Chemistry Big Idea 4, Investigation 11

### An Advanced Inquiry Lab

#### Introduction

Crystal violet is a common, beautiful purple dye. In strongly basic solutions, the bright color of the dye slowly fades and the solution becomes colorless. The kinetics of this "fading" reaction can be analyzed by measuring the color intensity or absorbance of the solution versus time to determine the rate law.

#### Concepts

- Kinetics
- Reaction rate
- Rate law
- Order of reaction
- Spectroscopy
- Beer's law

#### Background

Crystal violet belongs to a class of intensely colored organic compounds called triphenylmethane dyes. The structure and color of crystal violet depend on pH, making it a valuable acid–base indicator as well as an excellent dye. The major structural form of crystal violet is the monovalent cation, abbreviated CV<sup>+</sup>, which is shown in Figure 1a. CV<sup>+</sup> is the predominant form of crystal violet in the solid state and in aqueous solution across a broad range of pH values from pH 1 to 13. The positive charge shown on the central carbon atom in Figure 1a is delocalized via resonance to the three nitrogen atoms. See Figure 1b for one of the three additional resonance forms with the positive charge on a nitrogen atom. Delocalization of the charge across the system of double bonds in the benzene rings stabilizes the carbocation and is responsible for the vibrant purple color of the dye.

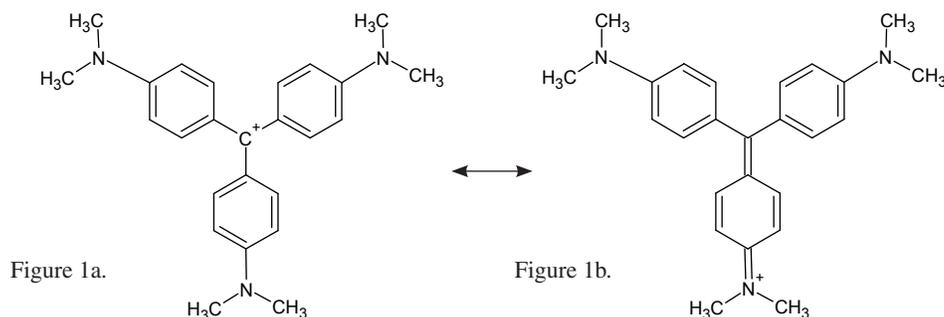


Figure 1.

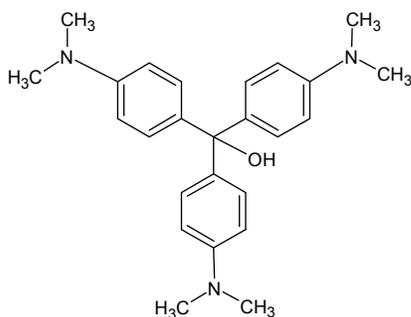


Figure 2.

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In strongly basic solutions the purple  $\text{CV}^+$  cation slowly combines with hydroxide ions to form a neutral product,  $\text{CVOH}$ , which is colorless (see Figure 2). The rate of this reaction (Equation 1) is slower than typical acid–base proton transfer reactions and depends on the initial concentration of both crystal violet and hydroxide ions.



Exactly how much the rate changes as the reactant concentration is varied depends on the rate law for the reaction. In the case of the reaction of  $\text{CV}^+$  with  $\text{OH}^-$  ion, the rate law has the general form

$$\text{Rate} = k [\text{CV}^+]^n [\text{OH}^-]^m \qquad \text{Equation 2}$$

The exponents  $n$  and  $m$  are defined as the order of reaction for each reactant and  $k$  is the rate constant for the reaction at a particular temperature. The values of the exponents  $n$  and  $m$  must be determined by experiment. If the reaction is carried out under certain conditions then Equation 2 will reduce to the form

$$\text{Rate} = k' [\text{CV}^+]^n \qquad \text{Equation 3}$$

where

$$k' = k [\text{OH}^-]^m \qquad \text{Equation 4}$$

The constant  $k'$  is a new “pseudo” rate constant incorporating both the “true” rate constant  $k$  and the  $[\text{OH}^-]^m$  term. Equation 3 is referred to as a pseudo-rate law because it is a simplification of the actual rate law, Equation 2.

The pseudo-rate law is valid when the concentration of  $\text{OH}^-$  ions is much greater than the concentration of  $\text{CV}^+$  ions. Under these conditions the  $[\text{OH}^-]^m$  term in Equation 2 will not change much over the course of the reaction and may be treated as a constant in the rate equation.

Recall that the absorbance for a specific concentration of a solution with a fixed path length varies directly with the absorptivity coefficient of the solution. This relationship is known as Beer’s law.

$$A = abc \qquad \text{Equation 5}$$

where  $A$  is absorbance,  $a$  is the molar absorptivity coefficient,  $b$  is the path length in cm, corresponding to the distance light travels through the solution, and  $c$  is the concentration of the solution. Beer’s law provides the basis of using spectroscopy in quantitative analysis. Using this relationship, concentration and absorbance may be calculated if one variable is known while keeping  $a$  and  $b$  constant. This relationship is also extremely valuable in kinetics experiments, making it possible to follow the rate of disappearance of a colored substance by measuring its absorbance as a function of time.

## Experiment Overview

The purpose of this advanced inquiry lab activity is to use spectroscopy and graphical analysis to determine the rate law for the color-fading reaction of crystal violet with sodium hydroxide. The lab begins with an introductory activity (laboratory technique) for constructing a calibration curve of absorbance versus concentration for the dye crystal violet. A series of known or standard solutions is prepared from a stock solution of crystal violet and the absorbance of each solution is measured at an optimum wavelength. A Beer’s law plot of absorbance as a function of concentration may be used to calculate the concentration of any “unknown” solution of the dye in a rate law experiment. The procedure provides a model for guided-inquiry design of experiments to determine the order of reaction with respect to both crystal violet and sodium hydroxide. Additional triphenylmethane dyes, malachite green and phenolphthalein, are also available for optional extension or cooperative class studies.

## Pre-Lab Questions

The visible absorption spectrum for crystal violet, CV<sup>+</sup>, is shown in Figure 3. The concentration of the dye was 12.5 μM (12.5 × 10<sup>-6</sup> M).

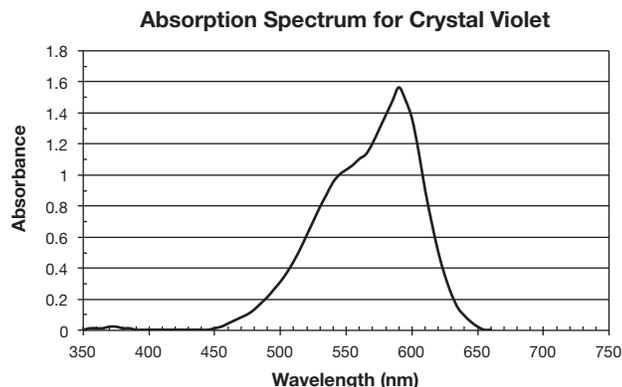


Figure 3.

1. What would be the optimum wavelength for generating a Beer's law calibration curve for crystal violet and measuring absorbance versus time for the reaction of CV<sup>+</sup> with OH<sup>-</sup>? Explain your answer. Recall that absorbance measurements are most accurate and sensitive in the range 0.2–1.0.
2. A calibration curve requires the use of several concentrations of the test solution. Using 25 μM CV solution as the stock solution, complete the following table to show how you would prepare 2.5, 5, 7.5, 10, and 12.5 μM solutions of CV<sup>+</sup>. Assume that the final solution volume should be 10.0 mL in all cases.

Table 1

	CV Stock Solution	A	B	C	D	E
Concentration (micromolar, μM)	25 μM	2.5 μM	5.0 μM	7.5 μM	10.0 μM	12.5 μM
Water (mL)	0					5.0 mL
Stock Solution (mL)	10.0					5.0 mL

3. Using your optimum wavelength for the experiment, predict the estimated absorbance value for each solution in Table 1. Record these values in the table. *Hint:* Keep in mind Beer's law from Equation 5 and the fact that the path length (b) and wavelength are constant.

## Materials

Crystal violet solution, 25 μM (2.5 × 10<sup>-5</sup> M), 50 mL

Sodium hydroxide solution, NaOH, 0.02 M, 30 mL

Water, distilled or deionized

Beaker, borosilicate, 50-mL

Spectrophotometer or colorimeter

Cuvets or test tubes

Pipet, serological, 10-mL

Pipet bulb filler

Stirring rod

## Safety Precautions

*Dilute sodium hydroxide solution is irritating to eyes and skin. Crystal violet is a strong dye and will stain clothes and skin. Clean up all spills immediately. Wear chemical splash goggles, chemical-resistant gloves, and a chemical-resistant apron. Avoid contact of all chemicals with eyes and skin and wash hands thoroughly with soap and water before leaving the laboratory. Please follow all laboratory safety guidelines.*

## Laboratory Technique

### Constructing a Calibration Curve for Crystal Violet

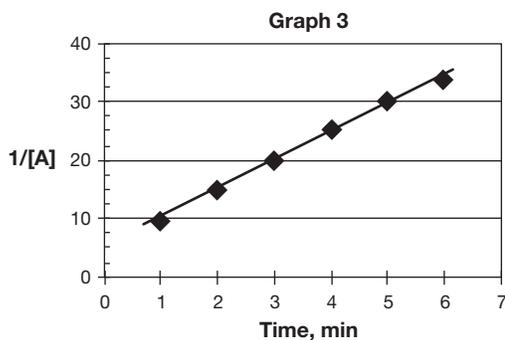
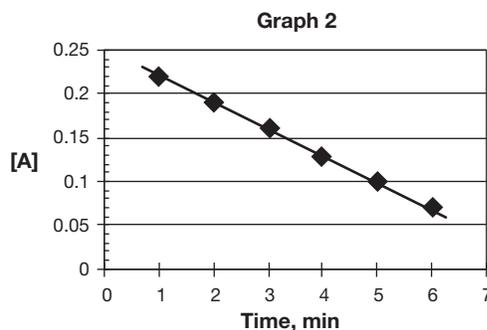
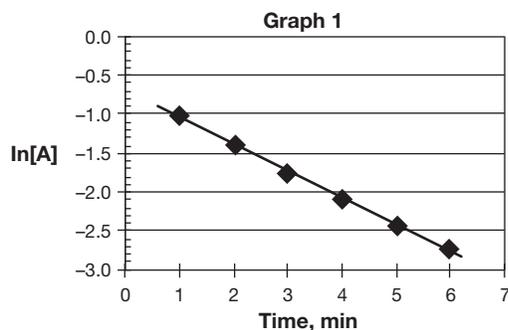
1. Turn on the spectrophotometer and allow it to warm up for 15–20 minutes before use. Adjust the wavelength setting to the optimum wavelength determined in the *Pre-Lab* section.
2. Read the entire procedure before beginning and construct an appropriate data table to record measurements. *Note:* As part of a cooperative laboratory activity, your instructor may assign different groups to prepare different solutions. Each group will need to transcribe and analyze data for all of the solutions and resulting measurements in order to complete the guided-inquiry activity.
3. Using a serological pipet for accuracy, prepare the series of standard dilutions of the crystal violet stock solution. Use the amounts calculated in the *Pre-Lab* assignment. *Lab Hint:* To avoid contaminating the stock solution, first use the pipet to add the required amount of distilled water to each test tube. Rinse the pipet three times with the stock solution, and then measure and add the required amount of stock solution to each test tube. Mix as needed.
4. Measure and record the absorbance ( $A$ ) of the stock solution and each standard solution (dilution) at the selected wavelength.
5. Prepare a Beer's law calibration curve of absorbance versus concentration for crystal violet.

## Guided-Inquiry Design and Procedure

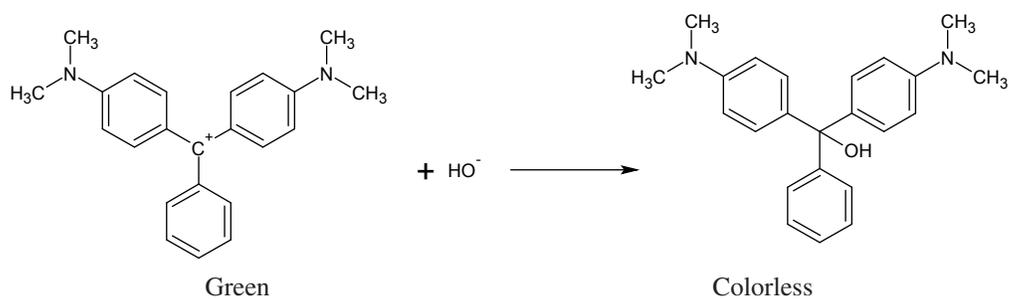
### A. Rate of Reaction of Crystal Violet with Sodium Hydroxide

Form a working group with other students and discuss the following questions.

1. Assume that the reaction of  $\text{CV}^+$  with  $\text{OH}^-$  ions (*Equation 1*) proceeds to completion, that is, the solution turns colorless. What percentage of  $\text{OH}^-$  ions will remain at the end of reaction if the initial crystal violet to sodium hydroxide mole ratio is 1:1? What if the initial ratio is 1:1000?
2. Review the conditions for a pseudo-rate law in the *Background* section. Which mole ratio described above should be used to ensure that the reaction between  $\text{CV}^+$  and  $\text{OH}^-$  ions can be treated using a pseudo-rate law to determine the reaction order  $n$  with respect to  $[\text{CV}^+]$ ?
3. Consult your textbook or other resources for mathematical treatment and graphical analysis of experimental data of concentration versus time for disappearance of a reactant  $[A]$  in a reaction. Match each linear graph shown below with that expected if the reaction is (a) zero order, (b) first order, and (c) second order with respect to  $[A]$ .







**Figure 5.** Malachite Green

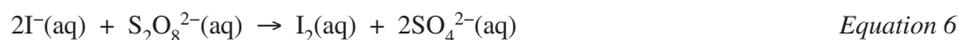
## AP Chemistry Review Questions

### *Integrating Content, Inquiry and Reasoning*

Collision theory offers a simple explanation for how reactions occur—reacting molecules must first collide. In order for colliding molecules to be converted into products, they must collide with enough energy and with a suitable orientation to break existing bonds in the reactants and form new bonds in the products. Any factor that changes either the total number of collisions or the average energy of the colliding molecules should affect the reaction rate.

- Using collision theory, predict how increasing the temperature should affect the rate of a chemical reaction. State the prediction in the form of an hypothesis and explain your reasoning.
- Using collision theory, predict how increasing the concentration of a reactant should affect the rate of a chemical reaction. State the prediction in the form of an hypothesis and explain your reasoning.

Two general methods may be used to determine the rate law for a reaction. The graphical method used in this lab is an integrated rate law experiment—it shows how the concentration of a reactant or product depends on time. An alternative method for determining the rate law relies on measuring the initial rate of a reaction for different initial concentrations of reactants. This alternative method may be called a differential rate law experiment. Consider a classic iodine clock reaction between iodide ions and persulfate ions (Equation 6).



The following rate data was collected for different initial concentrations of iodide and persulfate ions.

Trial	[I <sup>-</sup> ]	[S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> ]	Initial rate (mole/L·sec)
1	0.040 M	0.040 M	7.4 × 10 <sup>-6</sup>
2	0.080 M	0.040 M	1.5 × 10 <sup>-5</sup>
3	0.040 M	0.080 M	1.4 × 10 <sup>-5</sup>

- Compare trials 1 and 2: How did the concentration of iodide ions change in these two trials, and how did the rate change accordingly? What is the reaction order for iodide ions?
- Which two trials should be compared to determine the order of reaction with respect to persulfate ions? What is the reaction order for persulfate?
- Write the combined rate law for this version of an iodine clock reaction. Could the rate law have been predicted using the coefficients in the balanced chemical equation? Explain.

# Teacher's Notes

## Kinetics of Crystal Violet Fading

### Materials Included in Kit (for 24 students working in pairs, or 12 pairs)

Crystal violet, 1% alcoholic, 25 mL

Malachite green, 1% aqueous, 25 mL

Phenolphthalein, 1% alcoholic, 35 mL

Sodium hydroxide solution, NaOH, 0.02 M, 500 mL

Pipets, serological, 10-mL, 12

### Additional Materials Needed (for each lab group)

Water, distilled or deionized

Beaker, 50-mL

Computer interface system\*

Computer or calculator for data collection\*

Cuvets or test tubes

Data collection software (LoggerPro)

*\*For use with colorimeter option.*

Pipet bulb filler

Spectrophotometer or colorimeter\*

Stirring rod

Stopwatch (if not using data collection software)

Tissue or lens paper, lint-free

### Additional Materials Needed (for Pre-Lab Preparation)

Water, distilled or deionized

Flask, borosilicate, volumetric, 1000-mL

Pipet, serological, 1-mL

Pipet bulb filler

### Pre-Lab Preparation

#### Crystal Violet solution, $2.5 \times 10^{-5}$ M, 1000 mL

To prepare 1000 mL of  $2.5 \times 10^{-5}$  M crystal violet solution:

1. Fill the volumetric flask about one-half full with distilled or deionized water.
2. Withdraw 1 mL of 1% crystal violet solution using a 1-mL serological pipet. Add this to the 1-liter volumetric flask.
3. Dilute the crystal violet solution to the 1-liter mark. Mix well before dispensing.

#### Malachite Green solution, $2.7 \times 10^{-5}$ M, 1000 mL (optional)

To prepare 1000 mL of  $2.7 \times 10^{-5}$  M malachite green solution:

1. Fill the volumetric flask about one-half full with distilled or deionized water.
2. Withdraw 1 mL of 1% malachite green solution using a 1-mL serological pipet. Add this to the 1-liter volumetric flask.
3. Dilute the malachite green solution to the 1-liter mark. Mix well before dispensing.

#### Phenolphthalein solution, $3.1 \times 10^{-5}$ M, 1000 mL (optional)

To prepare 1000 mL of  $3.1 \times 10^{-5}$  M phenolphthalein solution:

1. Fill the volumetric flask about one-half full with distilled or deionized water.
2. Withdraw 1 mL of 1% phenolphthalein solution using a 1-mL serological pipet. Add this to the 1-liter volumetric flask.
3. Dilute the phenolphthalein solution to the 1-liter mark. Mix well before dispensing.

## Teacher's Notes *continued*

### **Safety Precautions**

*Dilute sodium hydroxide solution is irritating to eyes and skin. The crystal violet stock solution is flammable. Crystal violet is a strong dye and will stain clothes and skin. Clean up all spills immediately. Wear chemical splash goggles, chemical-resistant gloves, and a chemical-resistant apron. Avoid contact of all chemicals with eyes and skin and wash hands thoroughly with soap and water before leaving the laboratory. Please follow all laboratory safety guidelines. Please review current Material Safety Data Sheets for additional safety, handling, and disposal information.*

### **Disposal**

Please consult your current *Flinn Scientific Catalog/Reference Manual* for general guidelines and specific procedures, and review all federal, state and local regulations that may apply, before proceeding. The crystal violet and sodium hydroxide reaction mixture should be collected and may be neutralized with acid and rinsed down the drain with plenty of water according to Flinn Suggested Disposal Method #10. The leftover sodium hydroxide may be stored for future use or neutralized with acid prior to disposal according to Flinn Suggested Disposal Method #10. The excess crystal violet solution may be stored for future use or rinsed down the drain with plenty of excess water according to Flinn Suggested Disposal Method #26b.

### **Alignment to AP\* Chemistry Curriculum Framework**

#### **Enduring Understanding and Essential Knowledge**

Atoms are so small that they are difficult to study directly; atomic models are constructed to explain experimental data on collections of atoms.

1D3: The interaction of electromagnetic waves or light with matter is a powerful means to probe the structure of atoms and molecules, and to measure their concentration.

Chemical changes are represented by a balanced chemical equation that identifies the ratios with which reactants react and products form.

3A2: Quantitative information can be derived from stoichiometric calculations that utilize the mole ratios from the balanced chemical equations. The role of stoichiometry in real-world applications is important to note, so that it does not seem to be simply an exercise done only by chemists.

Reaction rates that depend on temperature and other environmental factors are determined by measuring changes in concentrations of reactants or products over time.

4A2: The rate law shows how the rate depends on reactant concentrations.

#### **Learning Objectives**

4.2 The student is able to analyze concentration versus time data to determine the rate law for a zeroth-, first-, or second-order reaction.

4.1 The student is able to design and/or interpret the results of an experiment regarding the factors (i.e., temperature, concentration, surface area) that may influence the rate of a reaction.

#### **Science Practices**

1.4 The student can use representations and models to analyze situations or solve problems qualitatively and quantitatively.

2.1 The student can justify the selection of mathematical routine to solve problems.

2.2 The student can apply mathematical routines to quantities that describe natural phenomena.

4.2 The student can design a plan for collecting data to answer a particular scientific question.

5.1 The student can analyze data to identify patterns or relationships.

6.4 The student can make claims and predictions about natural phenomena based on scientific theories and models.

## Teacher's Notes *continued*

### Lab Hints

- Enough materials are provided in this kit for 24 students working in pairs, or for 12 groups of students. For best results, schedule two 50-minute class periods for this guided-inquiry lab. An additional lab period would be needed for students to complete an optional inquiry investigation (see *Opportunities for Inquiry*). The pre-laboratory assignment may be completed before coming to lab, and the results and analysis may be completed the day after the lab or as homework.
- Remind students to only touch the cuvetts on the ribbed sides. If using test tubes, students should only touch the very top. Fingerprints will give false absorbance measurements. Smudges can be cleaned off using a lint-free wipe, like Kimwipes<sup>®</sup>, before placing the cuvet or test tube in the colorimeter or spectrophotometer.
- Data collection for a duration of 15 minutes provides enough of a range of data to give accurate results. Measurements may be taken every 20 seconds.
- Remind students to begin timing *immediately* after mixing the crystal violet and sodium hydroxide. One partner may start the clock while the other mixes the solution, transfers it a cuvet, wipes it clean, and places it in the instrument. This process should be done within 20 seconds to give an accurate measurement of the initial concentration of crystal violet.
- Mohr or serological-type pipets are recommended for preparation of the Beer's law dilution solutions and the reaction solutions. Using graduated cylinders to measure and transfer the liquids does not give the precision needed to achieve constant values of the rate of reaction. Serological pipets are considered "throw-away" pipets by the medical community and are very affordable. They can be reused several times before the graduations come off. Used as disposable pipets, however, they eliminate the need for dishwashing and save valuable time.
- During the preparation of the Beer's law concentrations in the *Laboratory Technique* section, students should rinse the serological pipet with distilled or deionized water between measuring the crystal violet and DI water. One option is to measure the required volumes of either solution first, then measure the required volumes of the other solution.
- The use of computer- or calculator-based technology for data collection and analysis is suggested for this experiment.
- Students may benefit from a review of the principles of light absorption and transmission. The crystal violet solution in this experiment has a purple color. That means that when ordinary "white" light is passed through the solution, only the violet color (wavelength) is transmitted. All of the other colors (wavelengths of light) are absorbed. The colorimeter or spectrophotometer sends a beam of monochromatic (one color or wavelength) light through the solution. The wavelength of light used in the sample data is 565 nm, corresponding to green light. This is the complementary color of the violet color of the solution and is almost totally absorbed. The beam of light is passed through the sample, and the intensity of the green light transmitted is measured electronically. The rest of the green light is absorbed by the solution. The greater the concentration of crystal violet in solution, the more green light the solution absorbs.
- The absorption spectrum in Figure 3 was generated using 12.5  $\mu\text{M}$  crystal violet. The reason for doing this is to ensure that when data is gathered from the reaction of equal volumes of crystal violet and sodium hydroxide the maximum absorbance will not exceed the absorbance found in the Beer's law curve. When students transform their absorption data into concentration, the slope of the Beer's law curve will more closely match the actual concentration.
- The experiment may also be performed using a conventional spectrophotometer rather than colorimeter to measure absorbance as a function of time. Below is the list of indicators and their corresponding maximum absorbance wavelengths to set for a conventional spectrophotometer.

Crystal Violet	590 nm
Malachite Green	615 nm
Phenolphthalein	555 nm

- See pages 11–18 for representative sample data, analysis, and answers to all discussion questions for all parts of this Advanced Inquiry Lab.

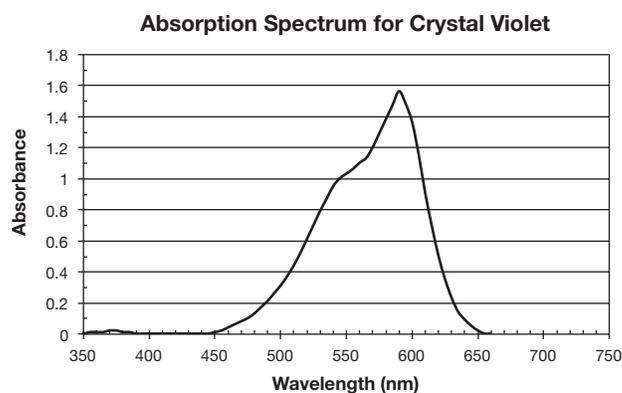
## Teacher's Notes *continued*

### Teaching Tips

- Crystal violet is purple in aqueous solution across a broad range of pH values from pH 1 to 13. In highly acidic solutions (pH < 1), crystal violet does behave as an acid–base indicator. As shown in Figure 1b on page 1, there are two very weakly basic nitrogen atoms in the structure of CV<sup>+</sup>. In solutions of concentrated strong acids, pH < 0, both of the nitrogen atoms can be protonated to give a diacid, CVH<sub>2</sub><sup>3+</sup>, which is yellow. As the pH slowly increases, CVH<sub>2</sub><sup>3+</sup> undergoes stepwise deprotonation to form first CVH<sup>2+</sup>, which is greenish blue (pH 1), and then CV<sup>+</sup> (purple) at pH 1.8.
- This experiment may be used to explore the effects of chemical buildup in the environment. The environmental impact of chemicals is a widely studied subject. The build-up of slow-decomposing molecules poses health risks to plant and animal life. Experiments to determine the decomposition rate provide scientists with key insight into the short- and long-term effects of certain chemicals.

### Answers to Pre-Lab Questions *(Student answers will vary.)*

The visible absorption spectrum for crystal violet, CV<sup>+</sup>, is shown in Figure 3. The concentration of the dye was 12.5 μM (12.5 × 10<sup>-6</sup> M).



**Figure 3.**

1. What would be the optimum wavelength for generating a Beer's law calibration curve for crystal violet and measuring absorbance versus time for the reaction of CV<sup>+</sup> with OH<sup>-</sup>? Explain your answer. Recall that absorbance measurements are most accurate and sensitive in the range 0.2–1.0.

*There is a maximum absorbance value of about 1.56 at 590 nm. This wavelength would not be optimal because the absorbance is too high and will yield inaccurate results. An absorbance value of 1.0 is near 540 nm and 610 nm. Either wavelength would be an option because the absorbance is high enough for the stock solution and that more dilute solutions would not have very low absorbance values.*

2. A calibration curve requires the use of several concentrations of the test solution. Using 25 μM CV solution as the stock solution, complete the following table to show how you would prepare 2.5, 5, 7.5, 10, and 12.5 μM solutions of CV<sup>+</sup>. Assume that the final solution volume should be 10.0 mL in all cases.

**Table 1**

	CV Stock Solution	A	B	C	D	E
Concentration (micromolar, μM)	25 μM	2.5 μM	5.0 μM	7.5 μM	10.0 μM	12.5 μM
Water (mL)	0	9.0	8.0	7.0	6.0	5.0 mL
Stock Solution (mL)	10.0	1.0	2.0	3.0	4.0	5.0 mL

*Measure the required volume of distilled water using a serological pipet. Add this to a clean 50-mL beaker or test tube. Rinse the pipet with the dye solution and then measure the required amount of dye in a serological pipet and add to the beaker. Mix each solution and then transfer to a cuvet for measuring. Rinse the serological pipet **thoroughly** before each use.*

## Teacher's Notes *continued*

3. Using your optimum wavelength for the experiment, predict the estimated absorbance value for each solution in Table 1. Record these values in the table. *Hint:* Keep in mind Beer's law from Equation 6 and the fact that the path length ( $b$ ) and wavelength are constant.

Concentration ( $\mu\text{M}$ )	Predicted Absorbance*
12.5	0.95
10	0.76
7.5	0.57
5	0.38
2.5	0.19

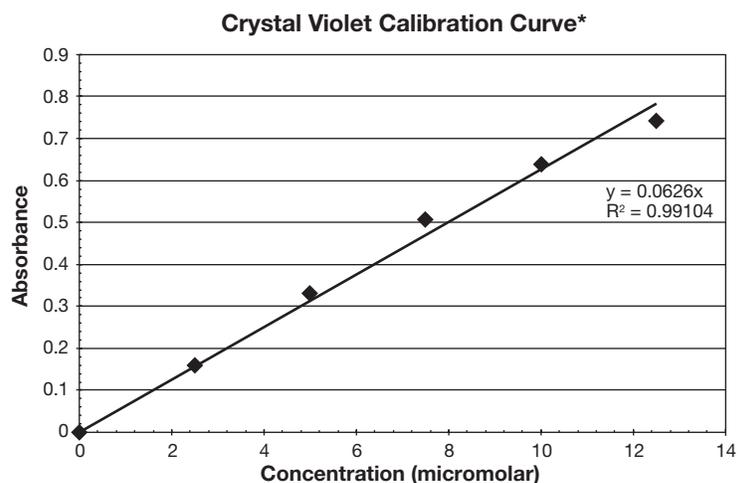
\* Wavelength chosen was 540 nm.

## Sample Data, Results, and Analysis

### Calibration Curve for Crystal Violet

Concentration ( $\mu\text{M}$ )	Absorbance*
12.5	0.742
10	0.639
7.5	0.508
5	0.332
2.5	0.159

\* Measurement wavelength was 565 nm.



\* Measurement wavelength was 565 nm.

## Teacher's Notes *continued*

### Part A. Rate of Reaction of Crystal Violet with Sodium Hydroxide

#### Discussion Questions

1. Assume that the reaction of  $\text{CV}^+$  with  $\text{OH}^-$  ions (*Equation 1*) proceeds to completion, that is, the solution turns colorless. What percentage of  $\text{OH}^-$  ions will remain at the end of reaction if the initial crystal violet to sodium hydroxide mole ratio is 1:1? What if the initial ratio is 1:1000?

**Reaction 1**  
 $\text{CV}^+ + \text{OH}^- \rightarrow \text{CVOH}$

<i>I</i>	<i>1</i>	<i>1</i>	<i>0</i>
<i>C</i>	<i>-1</i>	<i>-1</i>	<i>+1</i>
<i>E</i>	<i>0</i>	<i>0</i>	<i>1</i>

$$\% \text{CV}^+ = 0/1 \times 100 = 0\%$$

$$\% \text{OH}^- = 0/1 \times 100 = 0\%$$

**Reaction 2**  
 $\text{CV}^+ + \text{OH}^- \rightarrow \text{CVOH}$

<i>I</i>	<i>1</i>	<i>1000</i>	<i>0</i>
<i>C</i>	<i>-1</i>	<i>-1</i>	<i>+1</i>
<i>E</i>	<i>0</i>	<i>999</i>	<i>1</i>

$$\% \text{CV}^+ = 0/1 \times 100 = 0\%$$

$$\% \text{OH}^- = 999/1000 \times 100 = 99.9\%$$

2. Review the conditions for a pseudo-rate law in the *Background* section. Which mole ratio described above should be used to ensure that the reaction between  $\text{CV}^+$  and  $\text{OH}^-$  ions can be treated using a pseudo-rate law to determine the reaction order  $n$  with respect to  $[\text{CV}^+]$ ?

*In reaction 1, there will be 0% of both reactants remaining. The mole ratio of  $\text{CV}^+:\text{OH}^-$  is 1:1, therefore, all of the reactants would be consumed in the reaction. In reaction 2, there will be 0% of  $\text{CV}^+$  remaining and 99.9%  $\text{OH}^-$  remaining. The mole ratio remains the same but with the large excess of  $\text{OH}^-$  in reaction 2, the amount changes very little. Reaction 2 fits the criterion to be used to find the pseudo-rate law because the concentration of hydroxide ions is effectively constant in the reaction.*

3. Consult your textbook or other resources for mathematical treatment and graphical analysis of experimental data of concentration versus time for disappearance of a reactant [A] in a reaction. Match each linear graph shown below with that expected if the reaction is (a) zero order, (b) first order, and (c) second order with respect to [A].

*Graph 1 is a first order reaction. Graph 2 is a zero order reaction. Graph 3 is a second order reaction.*

4. Explain how the value of the pseudo-rate constant  $k'$  can be calculated from the appropriate linear graph shown above for a first-order reaction.

*The pseudo-rate constant  $k'$  can be calculated from Graph 1 by adding a line of best-fit to the data points and taking the negative of the slope.*

5. Write a detailed step-by-step procedure for a kinetics experiment between crystal violet and sodium hydroxide to determine the order of reaction with respect to  $\text{CV}^+$ . Include the materials, glassware and equipment that will be needed, safety precautions that must be followed, the concentrations of reactants, total volume of solution, order of mixing, timing, accuracy, etc.

*Set the colorimeter or spectrophotometer to 565 nm and zero the instrument using a "blank" of equal volumes of DI water and 0.02 M NaOH. Measure 10.0 mL of 25  $\mu\text{M}$  crystal violet in a serological pipet and add it to a clean 50-mL beaker. Rinse the pipet with distilled water several times and also with the sodium hydroxide solution. Measure 10.0 mL of 0.02 M sodium hydroxide in a serological pipet. Add the sodium hydroxide into the 50-mL beaker with crystal violet. Mix and immediately press "Collect" to begin timing. Transfer the reacting solutions to a cuvet and clean the outside with a lint-free wipe. Place into the colorimeter and close the lid. Record absorbance measurements every 20 seconds for 15 minutes.*

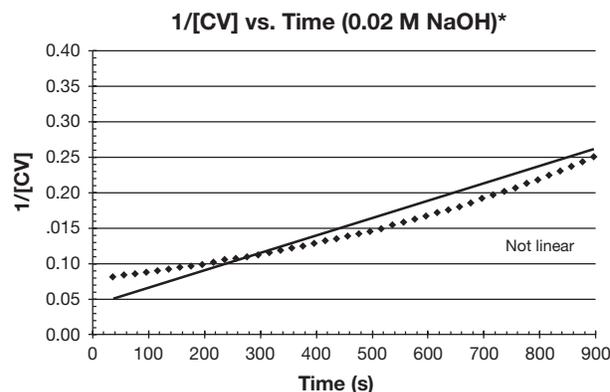
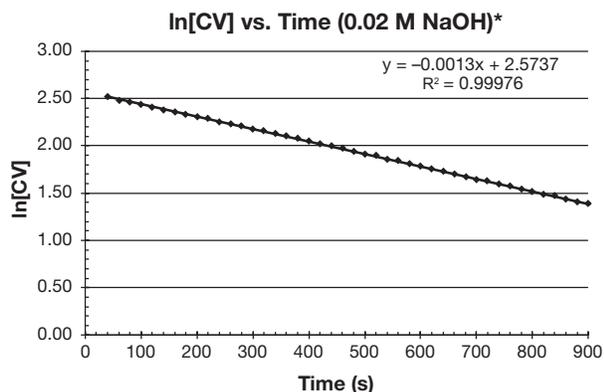
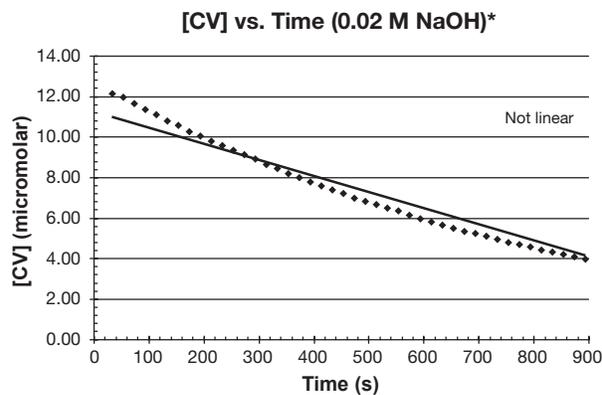
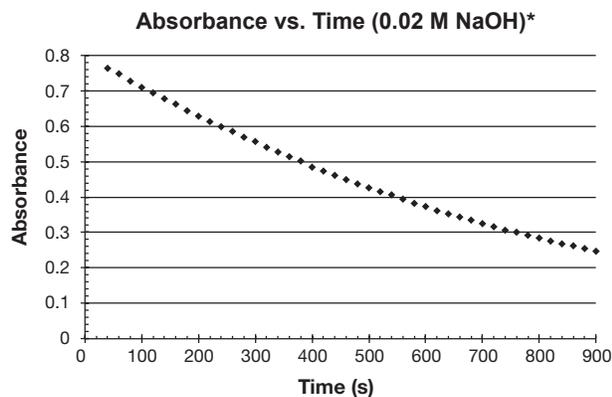
## Teacher's Notes *continued*

### Part A. Reaction Order with Respect to Crystal Violet

Time (s)	Abs	[CV] (micromolar)	ln[CV]	1/[CV]
0*	—	—	—	—
20*	—	—	—	—
40	0.761	12.164	2.499	0.082
60	0.746	11.917	2.478	0.084
80	0.727	11.615	2.452	0.086
100	0.710	11.350	2.429	0.088
120	0.695	11.094	2.406	0.090
140	0.676	10.801	2.380	0.093
160	0.661	10.565	2.358	0.095
180	0.644	10.283	2.330	0.097
200	0.630	10.063	2.309	0.099
220	0.614	9.811	2.283	0.102
240	0.598	9.557	2.257	0.105
260	0.587	9.377	2.238	0.107
280	0.572	9.130	2.212	0.110
300	0.557	8.900	2.186	0.112
320	0.543	8.669	2.160	0.115
340	0.529	8.445	2.134	0.118
360	0.515	8.220	2.107	0.122
380	0.500	7.995	2.079	0.125
400	0.487	7.784	2.052	0.128
420	0.475	7.587	2.026	0.132
440	0.463	7.402	2.002	0.135
460	0.451	7.201	1.974	0.139
480	0.439	7.007	1.947	0.143
500	0.428	6.830	1.921	0.146
520	0.417	6.664	1.897	0.150
540	0.406	6.489	1.870	0.154
560	0.396	6.319	1.844	0.158
580	0.384	6.141	1.815	0.163
600	0.375	5.985	1.789	0.167
620	0.364	5.821	1.762	0.172
640	0.355	5.667	1.735	0.176
660	0.345	5.515	1.708	0.181
680	0.336	5.362	1.679	0.186
700	0.327	5.217	1.652	0.192
720	0.318	5.085	1.626	0.197
740	0.310	4.946	1.599	0.202
760	0.301	4.814	1.572	0.208
780	0.294	4.694	1.546	0.213
800	0.286	4.567	1.519	0.219
820	0.278	4.447	1.492	0.225
840	0.271	4.329	1.465	0.231
860	0.263	4.208	1.437	0.238
880	0.257	4.098	1.411	0.244
900	0.250	3.986	1.383	0.251

\*The absorbance values for time = 0 and 20 seconds are omitted because the cuvet was not in place during those times and no measurements were taken. Wavelength = 565 nm.

## Teacher's Notes *continued*



\*This is the initial concentration of the sodium hydroxide.

Based on the shapes of the graphs and lines of best-fit, the order of reaction with respect to crystal violet is first-order. The graph of  $\ln[\text{CV}]$  vs. Time provided a straight line which indicates a first-order reaction. Therefore, the value of  $k'$  = -slope of the graph:  $k' = 0.0013$ .

### Part B. Order of Reaction with Respect to Sodium Hydroxide

#### Discussion Questions

- The experiment can be extended to determine the order of reaction  $m$  with respect to  $[\text{OH}^-]$  by varying the concentration of hydroxide ions  $[\text{OH}^-]$ . Assume that the value of the pseudo-rate constant  $k'$  was measured for two different concentrations of  $[\text{OH}^-]$ . The value of  $k'$  was found to be 0.13 at  $[\text{OH}^-] = 0.2 \text{ M}$ , and 0.061 when  $[\text{OH}^-] = 0.1 \text{ M}$ . Show how you can rearrange and combine the following two equations (see Equation 4) to solve for  $m$ .

$$\begin{array}{ll}
 \text{At } [\text{OH}^-] = 0.02 \text{ M} & \text{At } [\text{OH}^-] = 0.01 \text{ M} \\
 0.13 = k' = k[0.2]^m & 0.061 = k' = k[0.1]^m \\
 k' = k[\text{OH}^-]^m & k' = k[\text{OH}^-]^m \\
 0.13 = k[0.02]^m & 0.061 = k[0.01]^m
 \end{array}$$

A ratio of the pseudo-rate constants of Trial 1: Trial 2:

$$\begin{aligned}
 \frac{0.13}{0.061} &= \frac{k[0.02]^m}{k[0.01]^m} \\
 2.13 &= 2^m \\
 m &= \text{approx. } 1 \text{ (1.09)}
 \end{aligned}$$

When the concentration of sodium hydroxide was reduced by half, the value of the pseudo-rate constant decreased by half; therefore the order of reaction with respect to sodium hydroxide is first-order.

## Teacher's Notes *continued*

- Propose or recommend the concentration of  $[CV^+]$  that should be used in this part of the experiment when varying the hydroxide ion concentration. Explain.

*The concentration of  $CV^+$  should be the same in both sets of experiments, Parts A and B. Only one variable should be changed at a time in order to determine the effect each has on the reaction rate. If the concentrations of both  $CV^+$  and  $OH^-$  are changed, it would be impossible to determine which reactant caused a change in the rate.*

- Working cooperatively with other student groups, identify appropriate concentrations of sodium hydroxide for two additional rate trials of the color-fading reaction between crystal violet and hydroxide ions. If needed, carry out some rough trial-and-error experiments to make sure the new concentrations of  $[OH^-]$  will give reactions that occur at convenient rates, that is, neither too fast nor too slow.

*Two possible concentrations of sodium hydroxide that can be used are 0.01 M and 0.005 M. These concentrations give convenient concentration ratios to determine the change in the value of  $k'$ .*

- Review any additional variables that may influence the results and write a detailed step-by-step procedure for Part B.

*In order to determine the order of reaction with respect to NaOH, the concentration of NaOH needs to be changed and the effect on the  $k'$  calculated. The concentration of crystal violet needs to remain unchanged.*

*First the colorimeter will be zeroed using a "blank" of equal volumes of DI water and 0.01 M NaOH.*

*To make 10 mL of 0.01 M NaOH, measure 5.0 mL of 0.02 M sodium hydroxide in a serological pipet and add it to a clean 50-mL beaker. Rinse the pipet several times with DI water. Measure 5.0 mL of DI water with the pipet and add to the beaker. Mix. This will give 0.01 M NaOH (half of the initial reaction).*

*Clean the pipet with small portions of the crystal violet solution. Measure 10.0 mL of 25  $\mu$ M crystal violet solution in the pipet. Transfer this to the 50-mL beaker containing 0.01 M NaOH, mix, and immediately press "Collect" to begin timing. Transfer the mixture from the beaker to a cuvet and clean the outside with a lint-free wipe. Place the cuvet into the colorimeter and close the lid. Record absorbance values every 20 seconds for 15 minutes.*

*After the absorbance values have been recorded, the values need to be converted to concentration of crystal violet by using the Beer's law curve. The concentration versus time data will be manipulated and graphed to determine the value of  $k'$ .*

## Teacher's Notes *continued*

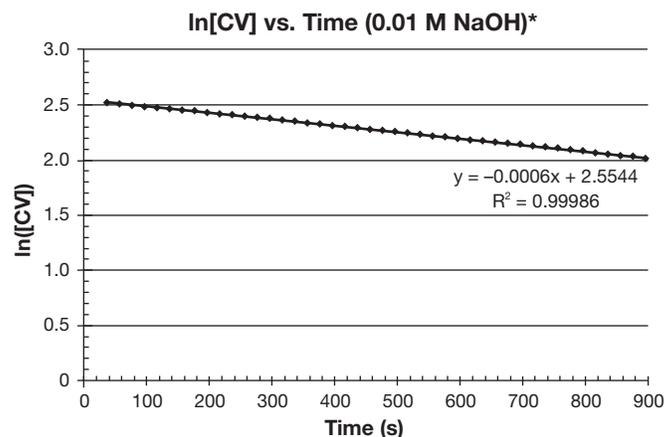
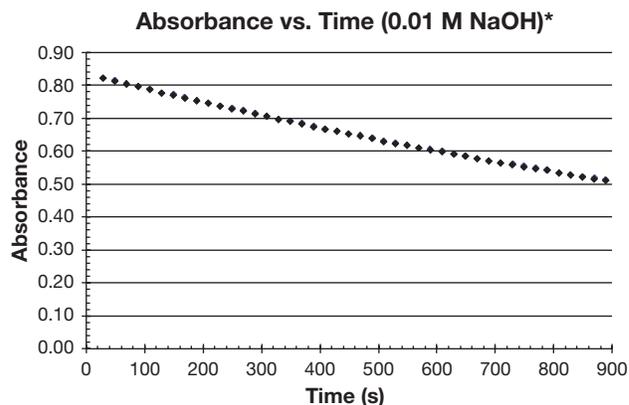
### Part B. Reaction Order with Respect to Sodium Hydroxide

Time (s)	Abs	[CV] (micromolar)	ln[CV]	1/[CV]
0*	—	—	—	—
20*	—	—	—	—
40	0.783	12.507	2.526	0.080
60	0.776	12.391	2.517	0.081
80	0.767	12.248	2.505	0.082
100	0.759	12.123	2.495	0.082
120	0.750	11.985	2.484	0.083
140	0.739	11.810	2.469	0.085
160	0.733	11.706	2.460	0.085
180	0.724	11.563	2.448	0.086
200	0.716	11.437	2.437	0.087
220	0.707	11.300	2.425	0.088
240	0.700	11.190	2.415	0.089
260	0.692	11.058	2.403	0.090
280	0.684	10.929	2.391	0.092
300	0.677	10.813	2.381	0.092
320	0.670	10.699	2.370	0.093
340	0.661	10.565	2.358	0.095
360	0.653	10.434	2.345	0.096
380	0.646	10.315	2.334	0.097
400	0.637	10.177	2.320	0.098
420	0.630	10.063	2.309	0.099
440	0.623	9.951	2.298	0.100
460	0.616	9.841	2.287	0.102
480	0.609	9.732	2.275	0.103
500	0.602	9.615	2.263	0.104
520	0.594	9.481	2.249	0.105
540	0.588	9.387	2.239	0.107
560	0.581	9.276	2.227	0.108
580	0.574	9.166	2.216	0.109
600	0.566	9.049	2.203	0.111
620	0.560	8.952	2.192	0.112
640	0.553	8.839	2.179	0.113
660	0.547	8.737	2.168	0.114
680	0.539	8.610	2.153	0.116
700	0.534	8.535	2.144	0.117
720	0.528	8.437	2.133	0.119
740	0.522	8.339	2.121	0.120
760	0.517	8.252	2.110	0.121
780	0.510	8.149	2.098	0.123
800	0.504	8.049	2.086	0.124
820	0.497	7.942	2.072	0.126
840	0.491	7.844	2.060	0.127
860	0.485	7.747	2.047	0.129
880	0.479	7.659	2.036	0.131
900	0.474	7.572	2.025	0.132

\*The absorbance values for time = 0 and 20 seconds are omitted because the cuvet was not in place during those times and no measurements were taken. Wavelength = 565 nm.

## Teacher's Notes *continued*

Because the order of reaction is first-order with respect to crystal violet and the concentration of sodium hydroxide will still remain relatively unchanged, only a graph for  $\ln[\text{CV}]$  vs. time is needed.

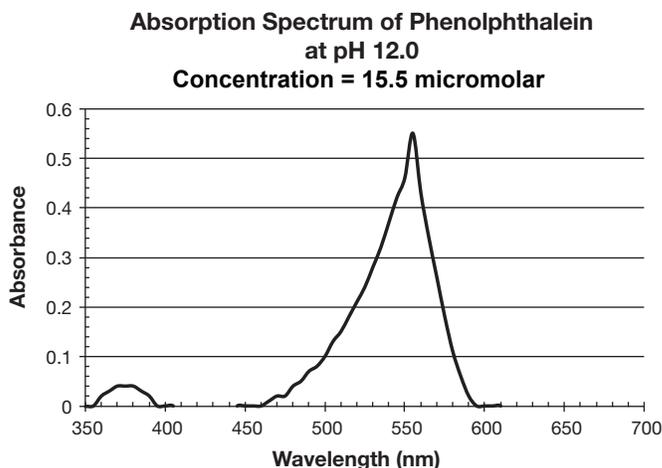
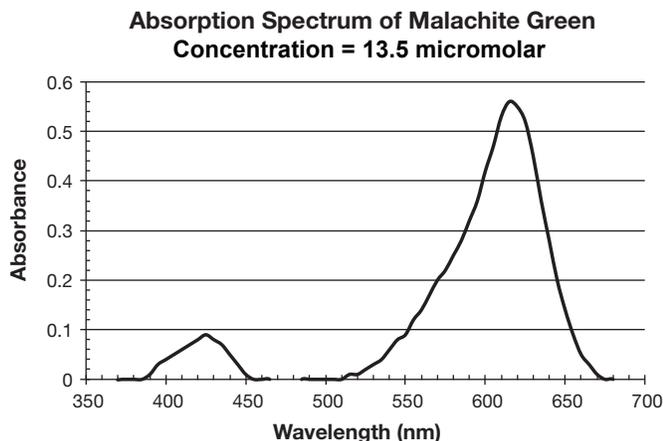


\*This is the initial concentration of the sodium hydroxide.

## Opportunities for Inquiry

### Dye-Fading Reactions of Phenolphthalein and Malachite Green

The absorption spectra below are for reference if students will be required to complete this section of the experiment.



## Answers to AP Chemistry Review Questions

Collision theory offers a simple explanation for how reactions occur—reacting molecules must first collide. In order for colliding molecules to be converted into products, they must collide with enough energy and with a suitable orientation to break existing bonds in the reactants and form new bonds in the products. Any factor that changes either the total number of collisions or the average energy of the colliding molecules should affect the reaction rate.

1. Using collision theory, predict how increasing the temperature should affect the rate of a chemical reaction. State the prediction in the form of an hypothesis and explain your reasoning.

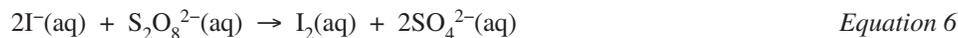
*If the temperature of a reaction increases, then the rate of the reaction should also increase. This hypothesis is based on the idea that increasing the temperature increases the average speed of the molecules, which should in turn, increase both the number of collisions and, more importantly, the average energy of the collisions.*

2. Using collision theory, predict how increasing the concentration of a reactant should affect the rate of a chemical reaction. State the prediction in the form of an hypothesis and explain your reasoning.

*If the concentration of reactants increases, then the rate of the reaction should also increase. This hypothesis is based on the idea that increasing the number of molecules present in solution should increase the rate of collisions between molecules.*

## Teacher's Notes *continued*

Two general methods may be used to determine the rate law for a reaction. The graphical method used in this lab is an integrated rate law experiment—it shows how the concentration of a reactant or product depends on time. An alternative method for determining the rate law relies on measuring the initial rate of a reaction for different initial concentrations of reactants. This alternative method may be called a differential rate law experiment. Consider a classic iodine clock reaction between iodide ions and persulfate ions (Equation 6).



The following rate data was collected for different initial concentrations of iodide and persulfate ions.

Trial	[I <sup>-</sup> ]	[S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> ]	Initial rate (mole/L·sec)
1	0.040 M	0.040 M	$7.4 \times 10^{-6}$
2	0.080 M	0.040 M	$1.5 \times 10^{-5}$
3	0.040 M	0.080 M	$1.4 \times 10^{-5}$

3. Compare trials 1 and 2: How did the concentration of iodide ions change in these two trials, and how did the rate change accordingly? What is the reaction order for iodide ions?

*In trials 1 and 2, the concentration of persulfate ions was held constant, while the concentration of iodide ions was doubled. The rate increased by a factor of two when [I<sup>-</sup>] was doubled. Therefore, the reaction is first order with respect to iodide.*

4. Which two trials should be compared to determine the order of reaction with respect to persulfate ions? What is the reaction order for persulfate?

*Comparing the rates of trials 1 and 3 will show how the rate of the reaction depends on the concentration of persulfate ions. In trials 1 and 3, the concentration of iodide ions was held constant while the concentration of persulfate ions was doubled. The rate increased by a factor of two when [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] was doubled. Therefore, the reaction is first order with respect to persulfate.*

5. Write the combined rate law for this version of an iodine clock reaction. Could the rate law have been predicted using the coefficients in the balanced chemical equation? Explain.

$$\text{Rate} = k[\text{I}^{-}][\text{S}_2\text{O}_8^{2-}]$$

*The rate law cannot be predicted simply by looking at the balanced chemical equation. The exponents are not the same as the coefficients in the balanced equation.*

## Reference

AP\* Chemistry Guided-Inquiry Experiments, published by the College Board (2013).

**Kinetics of Crystal Violet Fading and supporting supplies are available from Flinn Scientific, Inc.**

Catalog No.	Description
AP7644	Kinetics of Crystal Violet Fading
AP1887	Pipet Filler
AP1141	Kimwipes, 4½" × 8½"
GP7056	Serological Pipet, 1-mL
AP1082	Test Tubes, 13 mm × 100 mm, Box/12
AP9149	Cuvets, ½", Square Disposable, Pkg./100

Consult your *Flinn Scientific Catalog/Reference Manual* for current prices.