

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⁺, which is shown in Figure 1a. CV⁺ 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.

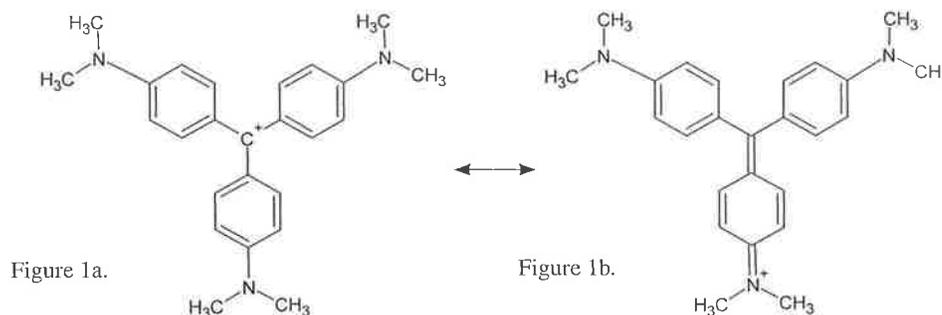


Figure 1.

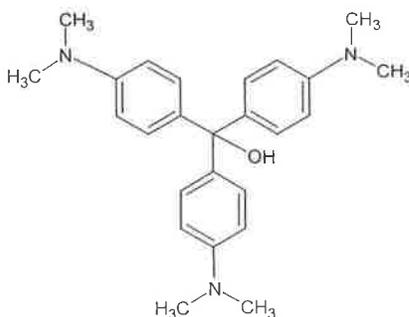


Figure 2.

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In strongly basic solutions, the purple CV⁺ cation slowly combines with hydroxide ions to form a neutral product, 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 CV⁺ with OH⁻ ion, the rate law has the general form

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

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

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

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

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 OH⁻ ions is much greater than the concentration of 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.

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

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 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^+ , is shown in Figure 3. The concentration of the dye was $12.5 \mu\text{M}$ ($12.5 \times 10^{-6} \text{ M}$).

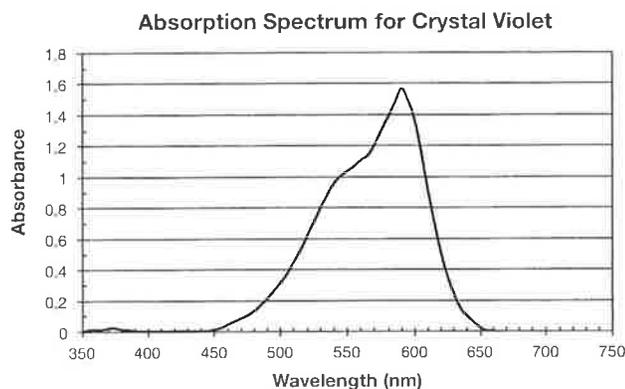


Figure 3.

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^+ with OH^- ? 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 $25 \mu\text{M}$ CV solution as the stock solution, complete the following table to show how you would prepare 2.5 , 5 , 7.5 , 10 and $12.5 \mu\text{M}$ solutions of CV^+ . 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)	$25 \mu\text{M}$	$2.5 \mu\text{M}$	$5.0 \mu\text{M}$	$7.5 \mu\text{M}$	$10.0 \mu\text{M}$	$12.5 \mu\text{M}$
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, $25 \mu\text{M}$ ($2.5 \times 10^{-5} \text{ M}$), 50 mL	Cuvets or test tubes
Sodium hydroxide solution, NaOH , 0.02 M , 30 mL	Pipet, serological, 10-mL
Water, distilled or deionized	Pipet bulb filler
Beaker, borosilicate, 50-mL	Stirring rod
Spectrophotometer or colorimeter	

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

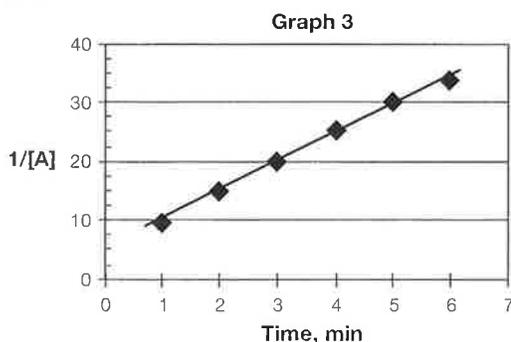
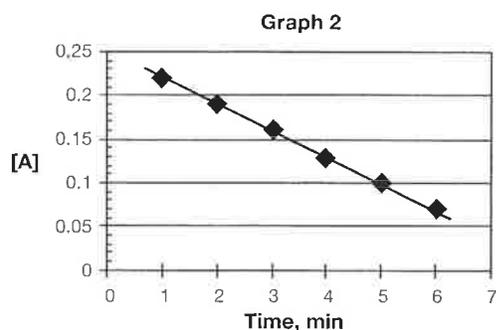
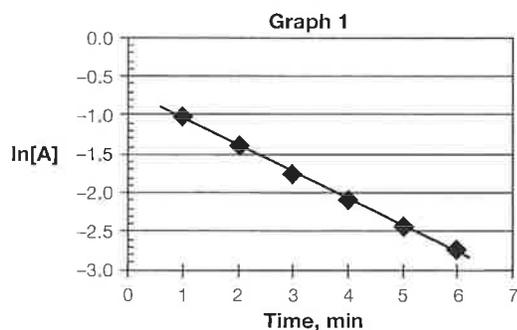
1. Turn on the spectrophotometer and allow it to warm up for 15–20 minutes before use. Adjust the wavelength setting to the optimum wavelength determined in the *Pre-Lab* section.
2. Read the entire procedure before beginning and construct an appropriate data table to record measurements. *Note:* As 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 CV^+ with OH^- ions (Equation 1) proceeds to completion, that is, the solution turns colorless. What percentage of 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 CV^+ and 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 $[A]$.



- 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.
- 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 CV^+ . Include all 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.
- Review additional variables that may affect the reproducibility or accuracy of the experiment and how these variables will be controlled.
- Carry out the experiment and record results in an appropriate data table.

Analyze the results: Use the calibration curve to determine the concentration of CV^+ over the course of the rate trial. Calculate the values of $\ln[\text{CV}^+]$ and $1/[\text{CV}^+]$ and perform the graphical analysis described in Question 3 to determine the order of reaction n and the value of the pseudo-rate constant k' .

B. Order of Reaction with Respect to Sodium Hydroxide

- 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 .

$$0.13 = k' = k[0.2]^m \quad \text{and} \quad 0.061 = k' = k[0.1]^m$$

- Propose or recommend the concentration of $[\text{CV}^+]$ that should be used in this part of the experiment when varying the hydroxide ion concentration. Explain.
- 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 $[\text{OH}^-]$ will give reactions that occur at convenient rates, that is, neither too fast nor too slow.
- Review additional variables that may influence the results and write a detailed step-by-step procedure for Part B.

Analyze the results: Combine the class data as needed. Graph the results as in Part A to determine the values of k' at the new hydroxide ion concentrations. Use the mathematical treatment derived in the answer to Question 1 to calculate the reaction order m with respect to hydroxide ions $[\text{OH}^-]$.

Opportunities for Inquiry

Dye-Fading Reactions of Phenolphthalein and Malachite Green

Phenolphthalein, which is one of the most common acid–base indicators in general chemistry, belongs to the same general class of compounds as crystal violet. It is a triphenylmethane derivative. Malachite green, a beautiful green dye, also has the same general structure (see Figures 4 and 5). Delocalization of the charge from the central carbon atom in these structures across the system of pi bonds in the attached benzene rings stabilizes the ions and gives rise to intense absorption bands in the visible spectrum. At high pH values, both phenolphthalein and malachite green undergo slow combination reactions with sodium hydroxide to form colorless products, similar to the reaction of crystal violet.

Stock solutions of phenolphthalein and malachite green are available from your instructor. Obtain the spectra of these dyes and design experiments to verify the kinetics of their decolorization reactions at an appropriate wavelength and pH value.

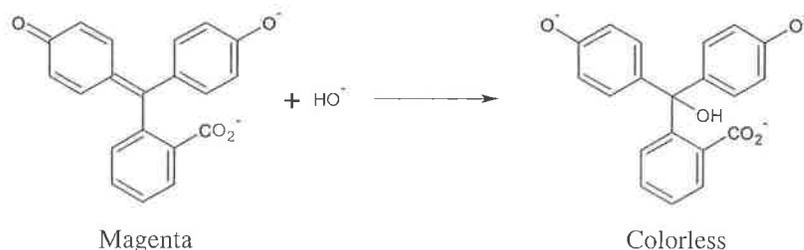


Figure 4. Phenolphthalein

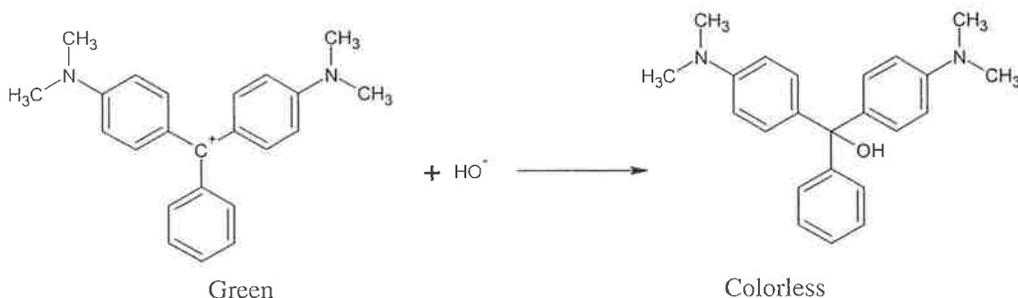


Figure 5. Malachite Green

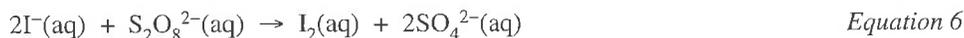
AP Chemistry Review Questions

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 a 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 a 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 ⁻]	[S ₂ O ₈ ²⁻]	Initial rate (mole/L·sec)
1	0.040 M	0.040 M	7.4 × 10 ⁻⁶
2	0.080 M	0.040 M	1.5 × 10 ⁻⁵
3	0.040 M	0.080 M	1.4 × 10 ⁻⁵

- 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.