**Challenge Question:** Can you use the color of a crystal violet and sodium hydroxide solution to determine the rate law of the reaction?

**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:** (You fill in based on what you have read)

**Background:** Crystal violet belongs to a class of intensely colored organic compounds called triphenylmethane dyes. The structure and color of crystal violet (CV) depend on pH, making it a valuable acid-base indicator as well as an excellent dye.

In strongly basic solutions the purple CV+ cation slowly combines with hydroxide ions to form a neutral product. CVOH, which is colorless. 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.

CV+ + OH- 🡪 CVOH *Equation 1*

purple colorless

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 CV+ with OH- ion, the rate law has the general form

rate = k[CV+]n[OH-]m  *Equation 2*

The values of *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

rate = k’[CV+]n *Equation 3*

where k’ = k[OH-]m  *Equation 4*

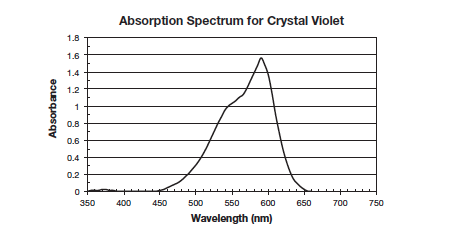
The constant k’ is a new “pseudo” rate constant incorporating both the “true” constant k and [OH-]m term. Equation 3 is referred to as a pseudo-rate law because it is a simplification of the actual rate law, Equation 2.

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 [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 equation.

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

A = ε*l*c *Equation 5*

**Pre-Lab Questions:**

The visible spectrum, for crystal violet, CV+, is shown in the Figure below. The concentration of the dye was 12.5 μM. 

1. What is the concentration of crystal violet in units of M?
2. 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 CV+ with OH-? Explain your answer. Recall that absorbance measurements are most accurate and sensitive in the range of 0.2-1.0.
3. 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 CV+. Assume that the final solution volume should be 10.0 mL in all cases.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | **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 |  |  |  |  |  |
| Stock Solution (mL) | 10.0 |  |  |  |  |  |

1. Using your optimum wavelength for the experiment, predict the estimated absorbance value for each solution the table above. Record these values.

**Safety (Summarize this):**

*Dilute sodium hydroxide solution is irritating to eyes and skin. Crystal violet (CV) 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.*

**Materials**

Crystal Violet Stock Solution, 30mL Kimwipes  
50mL Beaker x 2 10mL Volumetric Flask x2   
Cuvette with lids Disposable Pipets  
Wash bottle, distilled water Serological Pipet 10mL  
TI-nspire with Lab Cradle Colorimeter   
Scissors Parafilm   
0.02 M NaOH, 15mL 250mL Waste Beaker

**Procedure Part 1-Calibration Curve:**

1. Set the colorimeter to the wave λmax, ~565nm, for the reaction, allow it to warm up for approximately 15 minutes.
2. Rinse one of your cuvettes with some distilled water and empty it into the waste beaker. Then fill the cuvettes approximately ¾ of the way with distilled water and cap it. This will be the blank value of the colorimeter. Remember to handle the cuvettes only on the sides and wipe the clear faces with Kimwipes.
3. Insert a cuvette, filled with distilled water, for your blank cuvette. ***Important: Line up one of the clear sides of the cuvette with the arrow at the top of the cuvette slot.*** Close the Colorimeter lid. Press the CAL button to begin the calibration process. Release the CAL button when the red LED begins to flash. The absorbance should now be 0.000 or 0.001. Record the displayed value in the data table as the blank solution.
4. Using a serological pipet for accuracy, prepare the series of standard dilutions of the crystal violet stock solution. Use the table below to make the standards. To avoid contaminating the stock solution, first use the pipet to add the required amount of distilled water to volumetric flask. Rinse the pipet three times with a small amount of the stock solution, and then measure and add the required amount of stock solution to each flask.
5. Fill a cuvette ¾ (approximately 3mL) with the most concentrated solution and insert it into the colorimeter / spectrophotometer and record the absorbance.
6. Empty the cuvette and then fill it with the next concentrated and repeat until the absorbance for all the standards have been recorded.
7. This data will be used to construct a calibration curve of absorbance vs. concentration for crystal violet.

Sample Table Calibration Curve Data

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Concentration (μM) | Absorbance |  | Concentration (μM) | Absorbance |
| 25 μM |  |  | 7.5 μM |  |
| 12.5 μM |  |  | 5.0 μM |  |
| 10.0 μM |  |  | 2.5 μM |  |

**Procedure Part 2-Determining the Rate of Reaction of Crystal Violet with Sodium Hydroxide:**

1. Set the colorimeter 565 nm and zero the instrument using a blank of equal volumes, approximately ¾ full cuvettes, of distilled or deionized water and 0.02 M NaOH.
   1. After blanking the solution do the following:
      1. Make sure that the Mode is set to Time Based
      2. The interval should be set to 20seconds/sample
      3. The duration should be set to 900s, to make sure that there is enough time to collect all of the data.
2. Measure 10.0 mL of 25 μM crystal violet in a serological pipet and add it to a clean 50-mL beaker.
3. 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.
4. 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 cuvette and clean the out­side with a lint-free wipe. Place into the colorimeter and close the lid.
5. Once the experiment is done go to the table view and copy the absorbance and time data into your lab notebook.\*\*
6. Graph the data following the teachers’ instructions to determine the “order” of the reaction in terms of [CV]. (Be sure to include these graphs in your lab note book)

\*\*This data table is a sample and needs to have enough entries to go from time = 0s to time = 900s in 20s intervals (Approximately 46 data points)

Sample Table Absorbance and Time for CV and NaOH (0.02M

|  |  |
| --- | --- |
| Time (s) | Abs |
| 0 |  |
| 20 |  |
| 40 |  |

**Data/Calculations**

1. Write the equation for your line of best fit from the calibration curve in y = mx where:   
   y = Absorbance, and x = [CV+]
2. Show an example calculation for finding the concentration of the [CV+] based the absorbance value from time = 40s from your Part 2 data.

**Analysis Questions:**

1. Based on the 3 order graphs generated for this lab what is the “order” of this reaction in terms of crystal violet? Justify your answer.
2. Calculate the rate constant, *k’*, using the slope of the linear regression line for your linear curve

(k = |slope|). Be sure to include correct units for the (pseudo) rate constant.

1. Using collision theory, predict how increasing the temperature any amount should affect the rate of a chemical reaction. State the pre­diction in the form of a hypothesis and explain your reasoning.
2. Why did you blank the instrument with the sodium hydroxide as well as the distilled water?