Illinois Central College  
CHEMISTRY 132  
Name:___________________________

Reaction of Crystal Violet with Sodium Hydroxide: A Kinetic Study  
Part I.

Equipment

1-50 mL beaker  
1-10 mL beaker  
calibrated plastic dropper (1 ml)  
50 mL dispensing burette (for Crystal Violet)

Objectives.

The objectives of this experiment are to:

- study the rate of reaction of crystal violet with NaOH using the LabWorks interface colorimeter.

- determine the order of reaction with respect to Crystal Violet.

- calculate the rate constant for the reaction at room temperature.

Background

Chemical kinetics is the study of reaction rates. In this experiment, the kinetics of the reaction of crystal violet with NaOH will be studied using the LabWorks interface colorimeter to monitor concentrations as a function of time. The stoichiometry of the reaction is shown in Figure 1. below.

All of the reactants and products in Figure 1. are colorless except for crystal violet which has a maximum absorption wavelength of 590 nm and is an intense purple color. Thus, during the course of the reaction, the color of the reaction mixture becomes less and less intense, ultimately becoming colorless when all of the crystal violet has been consumed.
The color of crystal violet is due to the extensive system of alternating single and double bonds which extends over all three benzene rings and the central carbon atom. This alternation of double and single bonding is termed "conjugation", and molecules which have extensive conjugation are usually highly colored. Trace the conjugation in the structure of crystal violet and note that in the reaction product, the three rings are no longer in conjugation with one another, and hence, the material is colorless.

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**Kinetic Rate Laws**

**Dependence of Concentration on Reaction Rate**

In general, the "Rate Law" for a reaction is of the form:

\[ \text{Rate} = k \ [\text{Molarity of Reactants}]^m \]

For example, the rate law for the reaction

\[ 2 \text{NO}_2(g) + \text{F}_2(g) \rightarrow 2 \text{NO}_2\text{F}_2(g) \]

is

\[ \text{Rate} = k \ [\text{NO}_2]^1 [\text{F}_2]^1 \]

Note that both reactants are 1st order...see next section.

In this example, doubling the concentration of either reactant will double the rate of the reaction. Note that doubling the concentration of both reactants will cause the reaction to go four times as fast.

**Reaction Order**

Sometimes a particular reactant will have a greater effect on the reaction rate. For example, the following reaction

\[ 2 \text{NO}(g) + 2 \text{H}_2(g) \rightarrow \text{N}_2(g) + 2 \text{H}_2\text{O}(g) \]

Follows the rate law

\[ \text{Rate} = k \ [\text{NO}]^2 [\text{H}_2]^1 \]

Note that doubling the concentration of \(\text{H}_2\) will only double the rate (since its concentration is only taken to the 1st power), however, doubling the concentration of NO will cause a fourfold increase in the rate (since its concentration in the rate law is squared). Consequently, this reaction is said to have a "second-order dependence" with respect to NO...but only a "first order dependence" with respect to \(\text{H}_2\).

The overall order of the reaction is the sum of the orders of all reactants. In this case, the overall order is 3.

So the power to which a reactant appears in its rate law determines its "order".

**Fractional, zero, and negative orders** are also possible.

The practical advantage of knowing the rate law for a given reaction would allow the chemist to predict which reactant to increase in concentration in order to have the greatest effect on its rate.
Rate Law for the Reaction of Crystal Violet and NaOH

The rate of the reaction of crystal violet with NaOH is given by the generalized rate expression:

\[
\text{Rate} = k[\text{OH}^{-1}][\text{CV}]^x
\]  

Equation (1)

In Equation (1), \(k\) is the rate constant for the reaction, \(\text{CV}\) is an abbreviation for crystal violet, \(\text{C}_{25}\text{H}_{30}\text{N}^{+1}\), \(x\) is the order of reaction with respect to \(\text{OH}^{-1}\), and \(y\) is the order of reaction with respect to \(\text{CV}\). The values of \(x\) and \(y\) will be determined experimentally. Possible values are 0, 1, or 2 (zeroth order, first order or second order).

In the experiment you will perform, the \([\text{OH}^{-1}]\) will always be much greater than \([\text{CV}]\). Thus the change in \([\text{OH}^{-1}]\) has a negligible effect on the initial \([\text{OH}^{-1}]\). For this reason, \([\text{OH}^{-1}]\) can be treated as a constant and Equation 1 can be rewritten:

\[
\text{Rate} = k'[\text{CV}]^y
\]  

Equation (1b)

where \(k' = k[\text{OH}^{-1}]\). \(k'\) is termed a pseudo rate constant.

In order to experimentally determine the order of a reactant, we must follow the concentrations of reactant participants over time since reaction rates change as reactants are consumed. In this case, the concentration of the crystal violet will be followed colorimetrically.

With a little calculus, we can integrate the theoretical rate laws reflecting possible zeroth, first and second order dependence of the crystal violet with time. The integrated form of the rate law depends on the order of reaction with respect to the concentrations of \(\text{CV}\). This provides us with the following time vs concentration equations, below.

(zeroth order) \([\text{CV}]_t = -k't + [\text{CV}]_0\)  

(first order) \(\ln[\text{CV}]_t = -k't + \ln[\text{CV}]_0\)  

(second order) \(\frac{1}{[\text{CV}]_t} = k't + \frac{1}{[\text{CV}]_0}\)

In Equations (3) - (5), \([\text{CV}]_0\) is the concentration of crystal violet in the reaction mixture at time zero before any reaction occurs; \([\text{CV}]_t\) is the concentration at any time during the course of the reaction. A careful examination of Equations (3) - (5), reveals that each one is an equation of a straight line of the general form \("y = mx + b"\), where the slope of the line is either \(-k'\) or \(+k'\).

If we change the sign of Equations (3) and (4), we can give each relationship the same positive slope. Examine the equations below to convince yourself that the proportionality has remained unchanged.

(zeroth order) \(-[\text{CV}]_t = k't - [\text{CV}]_0\)  

(first order) \(-\ln[\text{CV}]_t = k't - \ln[\text{CV}]_0\)

(second order) \(\frac{1}{[\text{CV}]_t} = k't + \frac{1}{[\text{CV}]_0}\) (unchanged)
If a plot of $-[CV]_t$ versus time is linear, then the reaction is zeroth order with respect to CV and the exponent, $y$, in equation (1b) is zero.

Similarly, a linear plot of $-\ln[CV]_t$ versus time indicates a first order reaction in CV, and a linear plot of $1/[CV]_t$ versus time indicates second order dependence.

In every case, the slope of the resulting straight line would be the pseudo rate constant, $k'$. All three of these plots will be made to determine which is linear and thus, the order of the reaction with respect to crystal violet, that is, the actual value of the exponent, $y$, in Equation (1b). The slope of the linear relationship will then provide the value of $k'$.

In order to do the graphing just described, we will need to have data showing how the concentration of crystal violet changes with time.

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**Beer's Law**

In 1852, Beer discovered that the transmittance of light decreases exponentially in proportion to the concentration of the species absorbing the light. The fundamental law regarding the amount of incoming light absorbed by a sample is known as Beer's Law.

In a more mathematical sense, Beer's Law can be stated

$$Abs = ebc$$

where $Abs$ is the "absorbance" of a sample, $e$ is the molar absorbtivity characteristic to the substance being measured, $b$ is the path length the light must travel through the solution, and $c$ is the concentration of the absorbing species. Since $e$ and $b$ are both constants for a given experiment, then the **Absorbance of the solution is directly proportional to its concentration.**

In order to monitor the concentration of the crystal violet, we will measure the absorbance of light using the **Vernier Colorimeter** green LED light source with a wavelength of 565 nm.

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**Colorimeter**

A colorimeter measures the amount of light passing through a sample; this intensity of light is known as the transmittance.

You will use a Colorimeter (a side view is shown in Figure 2) to measure the concentration of each solution. In this experiment, red light from the LED light source will pass through the solution and strike a photocell. A higher concentration of the colored solution absorbs more light (and transmits less) than a solution of lower concentration.
The light sources in the colorimeter are light emitting diodes (LEDs). The LEDs emit a range of wavelengths with a peak, or most intense, wavelength near the center. The peak wavelengths for the colorimeter LEDs are 430 nm, 470 nm, 565 nm, 635 nm for the violet, blue, green and red colored LEDs, respectively. Due to the nature of LEDs, it is incorrect to assume that the light emitted by two LEDs will generate a third color. Therefore, any practical use of the colorimeter will involve only one LED at a given time.

Since the photocell detector simply changes resistance in proportion to the intensity of the light that strikes it, we can use the current that passes through the cell to determine the %Transmittance of the sample where

\[
%T = \frac{\text{sample current (microamps)}}{\text{blank current (microamps)}} \times 100
\]

The light from the LED will pass through the solution containing CV and NaOH and then fall on the system photocell. The photocell circuit will then produce in microamps (I) which is proportional to the light intensity striking the photocell surface.

Unfortunately, %T is not linearly proportional to Concentration. As stated before, it is an exponential relationship. However, Absorbance of light by the sample is linear with concentration. If the current reading (in microamperes) for the photocell without an absorbing specimen in the path is \(I_o\) and the current reading with an absorbing sample in the path is \(I\), (Figure 3.) then the absorbance of the sample is defined as:

\[
Abs = \log\left(\frac{I_o}{I}\right) \quad (6)
\]

or

\[
Abs = \log\left(\frac{100}{\%T}\right) = \varepsilon b [CV]_t \quad (6b)
\]

Equation (6b) combines equation (6) with Beer's Law, where, \(Abs\) is the reaction solution absorbance at any time \(t\); \(I_o\) is the photocell current observed for pure water; \(I\) is the current observed for the CV reaction mixture at time \(t\); \(\varepsilon\) is the molar absorbivity of crystal violet; \(b\) is the cell path length; and \([CV]_t\) is the molar concentration of crystal violet at time \(t\).

Since the absorbance, \(Abs\), is directly proportional to the concentration of crystal violet at any time during the reaction, it can be used in place of \([CV]_t\) in preparing the graphs described above. So, \(Abs \equiv [CV]_t\) that is, Absorbance is an equivalent representative of concentration for proportional relationships.
Connecting the Colorimeter

Locate the Logger Pro icon and double-click on it, or use the Start menu.

Connect the Vernier Colorimeter to the GoLink USB interface and connect the GoLink to the USB input on your computer.

From the Menu Bar select File/Open and click on the folder Chemistry with Computers. Open the file Xtalviol.cmbl. You should now see the window displayed here.

Use the arrow buttons on the colorimeter to select the 565 nm LED.

Select a single cuvette to use for both your blank and your samples for this experiment.

Safety Precautions

Crystal violet solutions may cause skin and eye irritation. Sodium hydroxide solutions are caustic and will cause skin burns if not immediately washed with copious amounts of water. Safety goggles must be worn at all times. As usual, wash hands with soap and water before leaving the lab.

PROCEDURE - PART 1

1. Fill the cuvette with distilled water to serve as a "blank". The blank contains all the constituents used in the analysis except the substance to be measured. We can assume then that the difference in the color between the blank and the sample is due only to the substance to be measured. Distilled water is the reference blank for this experiment.

2. Insert the cuvette containing the distilled water into the opening of the colorimeter. Note that the cuvette is "ribbed" on two sides. IMPORTANT: Be certain that the light path is passing through the CLEAR sides of the cuvette facing the arrow at the top of the cuvette slot. Close the lid of the colorimeter (to keep out stray light) and press the "CAL" button on the colorimeter to calibrate it. Release the CAL button when the red LED begins to flash. When the LED stops flashing, the calibration is complete and your unit is ready to collect data.

3. Empty the solution cell and dry it thoroughly inside and out.

4. Using the burette provided, dispense 9.00 mL of .000015 M crystal violet solution into a clean, dry 50 mL beaker.
5. Using the calibrated plastic dropper provided, add 1.0 mL of 0.05 M NaOH to the CV solution as rapidly as possible without splashing. **At the same instant, click the Collect button on the Toolbar to start the timer.** (you should see the statement "waiting for data" displayed on your graph). **Hustle**, because you only have 60 seconds before the first data point is collected.

6. **Thoroughly mix the CV/NaOH solution with a stirring rod** and then fill the cuvette 3/4 full. Position the cuvette in the colorimeter in exactly the same manner as was used for pure water. Shut the lid, and wait. At the 1 minute mark, the colorimeter should take its first reading. If so, you have 30 minutes to kill.

7. The program will take absorbance readings at one minute intervals for a period of 30 minutes and then automatically stop. If there is a need to stop data collection prior to the end of 30 minutes, **click the Stop button on the Toolbar** and the program will terminate.

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Data Analysis - Part 1

1. Select **Data** from the **Menu Bar** and click on **New Calculated Column**. In the New Calculated Column dialogue box enter `-Absorbance` for the name (-abs for the short name) and leave the units blank. This will represent the data for a **Zero Order** possibility.

   For the equation in our dialogue box, simply type `-"Absorbance"`. Click "Done".

2. Repeat step 1 for our First Order possibility. Select **Data** from the **Menu Bar** and click on **New Calculated Column**. In the New Calculated Column dialogue box enter `-ln(Absorbance)` for the name (-ln(abs) for the short name) and leave the units blank.

   For the equation in our dialogue box, simply type `-ln("Absorbance")`. Click "Done".

3. One more time for our Second Order possibility. Select **Data** from the **Menu Bar** and click on **New Calculated Column**. In the New Calculated Column dialogue box enter `1/Absorbance` for the name (1/abs for the short name) and leave the units blank.

   For the equation in our dialogue box, simply type `1/"Absorbance"`. Click "Done".

4. A plot of Absorbance versus time should currently be displayed. Simply click on the "Absorbance" label on the y-axis of your graph. A box containing column choices should appear. Choose "-Absorbance" to be plotted. **Click <Ctrl>J** to autoscale your graph.

   **If the reaction between crystal violet and NaOH is zeroth order in crystal violet, this plot will be linear.**

   **If and only if the plot is linear**, select **Analyze** from the **Menu Bar**, and choose **Linear Fit**. (Or click on the Linear Fit icon found on the Toolbar.) If the plot is **not** linear, skip to step 5.
5. Repeat step (4) plotting $-\ln(\text{Absorbance})$ on the y-axis. A linear line graph in this instance would indicate first order dependence on the concentration of crystal violet.

6. Finally, plot $1/\text{Absorbance}$ versus time to determine if the reaction is second order in crystal violet. A linear line graph in this instance would indicate second order dependence on the concentration of crystal violet.

7. Prepare and print a carefully labeled linear regression graph for the plot which exhibited a linear relationship. Do this by selecting Analyze from the Menu Bar, and choose Linear Fit. (Or click on the Linear Fit icon found on the Toolbar.) With this plot you have identified the value of $y$, i.e., the order of the reaction with respect to CV. Record the value of $y$ on your Report Sheet. The slope of the straight line displayed in the Linear Fit dialogue box is the best value of $k'$. Record this value with proper units and to correct number of significant figures on the Report Sheet.

8. Select File/Print Graph to obtain a print out of your regression plot. Also select File/Print Data Table to obtain the printout of your data. Attach your graph and data and to your Report Sheet.
REPORT SHEET
Reaction of Crystal Violet with Sodium Hydroxide: A Kinetic Study

1. What is plotted on the y-axis for the graph which is linear?

2. What is the value of $k'$ for the most linear plot? Include units and use appropriate significant figures.

3. Attach a printout of your labeled graph and data points to this report sheet.