1. What is the purpose of this experiment?

2. Why is data collected only between absorbances of 1 to 0.1?

3. Why is the reaction mixture quickly transferred to the cuvette for data collecting?

4. The following data were obtained in a kinetics experiment of the reaction:

   \[ \text{A} + \text{B} \rightarrow \text{C} \]

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>A of B</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.174</td>
</tr>
<tr>
<td>5</td>
<td>0.979</td>
</tr>
<tr>
<td>10</td>
<td>0.813</td>
</tr>
<tr>
<td>15</td>
<td>0.676</td>
</tr>
<tr>
<td>20</td>
<td>0.561</td>
</tr>
<tr>
<td>25</td>
<td>0.467</td>
</tr>
<tr>
<td>30</td>
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</tr>
<tr>
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<tr>
<td>80</td>
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<tr>
<td>85</td>
<td>0.065</td>
</tr>
<tr>
<td>90</td>
<td>0.058</td>
</tr>
</tbody>
</table>

Plot the three functions (page 3) of absorbance (remember absorbance is proportional to concentration according to Beer’s Law) and determine the order of the reaction. Determine \( k \).
A Study of Kinetics

Special mention goes to Nevin Gundez, John Curtin, Kelly Ann Lyons, Thomas Pomorski, Grace Zimmerly and Chris Southard who helped develop this experiment so that you could have a better understanding of kinetics.

Introduction

Chemical kinetics is the area of chemistry concerned with the rates of chemical reactions. There are essentially three variables that affect rate. These variables are the concentration of the reactants, temperature, and the presence of a catalyst. Usually, the more concentrated the solutions of one or more of the reactants, the faster the reaction will proceed. As the temperature increases, the rate of the reaction usually increases. A catalyst increases the rate of a reaction without being consumed in the reaction itself. This experiment is concerned with concentration and rate.

The dependence of reaction rate on concentration is given by the rate law:

\[
\text{rate} = k[A]^x[B]^y[C]^z
\]

Where \( k \) is the reactions rate constant, \([\ ]\) is the concentration of each reactant (in moles/liter), and \( x, y \) and \( z \) are the orders of reactant \( A, B \) and \( C \), respectively. The rate law is always determined experimentally. It cannot be determined from the balanced chemical equation.

In this experiment, you will be determining the rate law of the reaction between methyl violet (also known as crystal violet) and sodium hydroxide (2).

Methyl violet (MV\(^+\)), is an acid-base indicator as well as an antibacterial agent. It has a very intense violet color.

\[
\begin{array}{c}
\text{N(CH}_3\text{)}_2 \\
\text{(H}_3\text{C)}_2\text{N} \\
\text{N(CH}_3\text{)}_2
\end{array}
\]

methyl violet

When methyl violet reacts with sodium hydroxide, the solution goes from blue to colorless. The hydroxide ion in the sodium hydroxide bonds to the central carbon of methyl violet. The hydroxide ion is in excess in the following chemical reaction:
The rate law for our reaction is in the following form, where $x$ and $y$ are to be determined experimentally:

$$\text{rate} = k[\text{MV}^+]^x[\text{OH}^-]^y \quad (3)$$

Since the concentration of the hydroxide ion is in large excess compared to methyl violet, its concentration will not change appreciably over the course of the reaction and therefore, remain essentially constant throughout the reaction. The concentration of hydroxide ion can be incorporated into a new constant, $k'$. The rate law under these conditions can be written

$$\text{rate} = k'[\text{MV}^+]^x \quad (4)$$

with

$$k' = k[\text{OH}^-]^y \quad (5)$$

Most reactants are either zero, first or second order. Integrating the rate law will give a way to determine the order of a reactant. If the order is 1, then the integrated form of the rate law is

$$\ln[\text{MV}^+]_t = -k't + \ln[\text{MV}^+]_0 \quad y = mx + b \quad (6)$$

This equation has the form of the general equation for a straight line. The slope is $m$ and $b$ is the $y$-intercept of the line. If a plot of $\ln[\text{MV}^+]_t$ versus time yields a straight line, this indicates that the reactant is first order ($x = 1$). The slope of the line is $-k'$.

If the order is 2, then the integrated form of the rate law is

$$\frac{1}{[\text{MV}^+]_t} = k't + \frac{1}{[\text{MV}^+]_0} \quad y = mx + b \quad (7)$$

If a plot of $1/[\text{MV}^+]_t$ versus time yields a straight line, this indicates that the reactant is second order ($x = 2$). The slope of the line is $k'$.

If a direct plot of absorbance vs. time is the best straight line, then the order of the reactant is zero ($x = 0$), with a slope of $-k'$. 
In this experiment, you will record the absorbance of the methyl violet solution as it reacts with the sodium hydroxide solution over a period of time. After you have treated your data properly, you will plot this data in three ways: 1. absorbance vs. time, 2. ln(absorbance) vs. time and 3. 1/absorbance vs. time. The plot that gives the best straight line indicates the order of the reaction in methyl violet. The slope of the best straight line gives the rate constant $k'$. Changing the concentrations of OH⁻ by known amounts while keeping the concentration of the methyl violet constant will allow you to determine the order of OH⁻ in the reaction (equation 5). You can also then calculate $k$ and write the rate law of the reaction.

One additional point to keep in mind as you collect the data. The data points collected at the beginning of the reaction are not reliable for obtaining usable rate data because a spectrometer does not accurately measure absorbances above 1. The data at low absorbance values are also unreliable for a couple of reasons. First, the reaction stops (reaches equilibrium) before it has gone to completion and so you are no longer measuring a reaction rate. Second, at low concentrations of methyl violet, the detector of the spectrometer does not respond accurately to the large amount of transmitted light. The data is only collected between absorbances of 1 and 0.1.

**Procedure**

**Part I Determining the Order of Methyl Violet**

1. Double click **LoggerPro**.
2. Make sure the program recognizes the spectrometer. Data Set section (on the left) should start with Abs vs $\lambda$.
3. Fill a cuvette at least ½ full with distilled water (blank). Dry the cuvette with a Kimwipe.
4. On the menu bar, select **Experiment, Calibrate, Spectrometer:1**. Wait for lamp to warm up (1.5 minutes).
5. Place blank in **SpectroVis**, with line on cuvette toward arrow on the **SpectroVis**. Click **Finish Calibration**. When it goes gray, click **OK**.
6. Fill cuvette at least ½ full of $\approx 2.0 \times 10^{-5}$ M methyl violet solution (record exact molarity).
7. Click **Collect** button on the far right. When spectrum appears, click **Stop**.
8. Click **Configure Spectrometer** to collect kinetics data.
9. Click **Absorbance vs. time** button. A wavelength of $\approx 590$ nm should already be checked. Do **not** save the spectrum.
10. Click **Experiment, Data Collection** (or click ![Experiment](image)). On the menu, on **Collection** tab, change **Length:** from 200 to 900 (units: seconds). Under **Sampling Rate:** change 1 to 0.1. Click **Done.** This sets the **SpectroVis** to collect 1 data point every 10 seconds for a maximum of 900 seconds (15 minutes).

11. **Rinse** and **dry** the cuvette.

12. Pipet 10.0 mL of 2.0 x 10⁻⁵ M methyl violet into a 50-mL beaker. Pipet 10.0 mL of 0.025 M sodium hydroxide into a different 50-mL beaker. Working **quickly,** pour the contents of one beaker into the other and back, then fill the cuvette ½ full. Place it into the spectrometer. When the absorbance is 1.1 or below, click ![Collect](image).

13. When the absorbance is about 0.1, click ![Stop](image).

14. On the menu bar, click **File,** then **Export As.** Choose CSV (Excel, InspireData, etc). Save on your flash drive as **MV025**.

15. Make sure the graph is selected by clicking on it. On the menu bar, click **Analyze**, then **Linear Fit** (or click ![Linear Fit](image)). Record the slope and the correlation value.

16. On the menu bar, click **Data, New Calculated Column.** On the menu, on **Column Definition** tab, **Labels and Units,** add the following:

   Name: lnA  
   Short Name: lnA  
   Functions > button, select “ln”  
   Variables (Columns) > button, select “Absorbance at xxx nm”. Click **Done.**

17. On the menu bar, click **Data, New Calculated Column.** On the menu, under the **Column Definition** tab and **Labels and Units,** add the following:

   Name: 1/A  
   Short Name: 1/A  
   In the **Equation:** box, type “1/” then click the **Variables (Columns) >** button, and select “Absorbance at xxx nm”. Click **Done.**

18. On the graph, click on the **y-axis label.** Choose lnA. Record the **slope** and the **correlation** value. Click on the **y-axis label.** Choose 1/A. Record the **slope** and the **correlation** value. The plot with an absolute correlation value closest to 1 determines the order of the methyl violet. This will be the only plot used in Part II.
Part II  Determining the Order of Hydroxide

On the menu bar, click **Data, Delete Column** and select either lnA or 1/A depending on which graph from Part I was most linear. Delete the column that was not linear. Then click **Data, Clear All Data**. Then follow the procedure of Part I, steps 12 – 14 and 18, using:

- 10.0 mL of $2.0 \times 10^{-5}$ M methyl violet and 10.0 mL of $0.050$ M OH$^-$. 
- 10.0 mL of $2.0 \times 10^{-5}$ M methyl violet and 10.0 mL of $0.10$ M OH$^-$. 
- 10.0 mL of $2.0 \times 10^{-5}$ M methyl violet and 10.0 mL of $0.20$ M OH$^-$. 

Record the slope and the correlation for the three experiments.

Clear the data each time (after exporting as MV050, MV10 and MV20).

Data Treatment and Discussion

Include the following. Show samples of all calculations.

For Part I, construct a table with columns for time, absorbance, ln(absorbance) and 1/absorbance. Make plots of absorbance vs. time, ln(absorbance) vs. time and 1/absorbance vs. time. The graph, which gives the best straight-line (according to $R^2$; should be similar to what you saw in the laboratory), will indicate the order of the reaction in methyl violet. The order of methyl violet is fixed for the rest of this experiment. Find the slope of the trendline to determine $k'$.

Plot the three sets of data from Part II using only the function that gave the best straight line in Part I. You are still following the change in the concentration of methyl violet. **Determine the rate constants $k'_{2}, k'_{3}$ and $k'_{4}$** from the slope of each graph of Part II. Be sure to include proper units and significant figures.

To determine the order of the reaction in [OH$^-$], plot log($k'$) versus log[OH$^-$] for $k'_{1-4}$ and the corresponding [OH$^-$] (experiments 1 – 4). The slope of the plot, to the closest integer, is the order. The y-intercept is log($k$).

Once the order in methyl violet and OH$^-$ are determined, write the rate law.

Determine the average value of $k$ calculated from $k'_{1}, k'_{2}, k'_{3}$ and $k'_{4}$ (equation 5 with the exponent (y) of your rate law (determined above) and [OH$^-$]$_{1-4}$ used in Parts I and II and compare with the value obtained from the y-intercept.

Conclusion

Write the rate law and the rate constant, $k$ (average from equation 5 and from the graph).