A Study of Kinetics
Prelab

1. What is the purpose of this experiment?

2. Why do you discard the last data points of the kinetic runs?

3. Why do the solutions have to be mixed quickly before measuring the absorbance data?

4. The following data were obtained in an unrelated kinetics experiment:

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Absorbance</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>
<td>0.388</td>
</tr>
<tr>
<td>35</td>
<td>0.324</td>
</tr>
<tr>
<td>40</td>
<td>0.271</td>
</tr>
<tr>
<td>45</td>
<td>0.227</td>
</tr>
<tr>
<td>50</td>
<td>0.190</td>
</tr>
<tr>
<td>55</td>
<td>0.162</td>
</tr>
<tr>
<td>60</td>
<td>0.138</td>
</tr>
<tr>
<td>65</td>
<td>0.117</td>
</tr>
<tr>
<td>70</td>
<td>0.100</td>
</tr>
<tr>
<td>75</td>
<td>0.086</td>
</tr>
<tr>
<td>80</td>
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</tr>
<tr>
<td>85</td>
<td>0.065</td>
</tr>
<tr>
<td>90</td>
<td>0.058</td>
</tr>
<tr>
<td>95</td>
<td>0.052</td>
</tr>
<tr>
<td>100</td>
<td>0.051</td>
</tr>
</tbody>
</table>

Plot the three functions (page 16) of $A$ (remember $A$ is proportional to concentration according to Beer’s Law) and determine the order of the reaction. You may discard data points for the reasons discussed in the introduction. 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 studying the concentration dependence on the rate of a reaction between methyl violet (also known as crystal violet) and sodium hydroxide.

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

When methyl violet reacts with sodium hydroxide, the solution goes from violet 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:

\[
\text{rate} = k[\text{MV}^+]^x[\text{OH}^-]^y
\]  

(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

\[
\text{rate} = k'[\text{MV}^+]^x
\]  

(4)

with

\[
k' = k[\text{OH}^-]^y
\]  

(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

\[
\ln[\text{MV}^+]_t = -k't + \ln[\text{MV}^+]_0
\]

\[
y = mx + b
\]  

(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 \( \ln[\text{MV}^+] \) 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

\[
\frac{1}{[\text{MV}^+]_t} = k't + \frac{1}{[\text{MV}^+]_0}
\]

\[
y = mx + b
\]  

(7)

If a plot of \( 1/[\text{MV}^+] \) 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 treat the data. The data points collected at the end of the reaction are not reliable for obtaining usable rate data and will actually adversely affect your calculations. There are a couple of reasons for this. 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 Spec 20 does not respond as accurately to slight fluctuations in the amount of transmitted light. The overall effect will be data points that give a flat noisy line. The last of your data points should therefore be discarded and noted in your notebook.

Procedure

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

Set the Spectronic 20 to 590 nm. Blank distilled water.

Pipet 10.0 mL of 1.0 x 10⁻⁵ M methyl violet into a small beaker. Pipet 10.0 mL of 2.5 x 10⁻² M sodium hydroxide into a different beaker. Mix quickly by pouring the contents of one beaker into the other and then quickly fill the cuvette. Record the first absorbance, then every 10 seconds until the absorbance is less than 0.050.

**Part II  Determining the Order of Hydroxide**

Follow the procedure in Part I, using:

1.0 x 10⁻⁵ M methyl violet and 10.0 mL of 5.0 x 10⁻² M OH⁻.

1.0 x 10⁻⁵ M methyl violet and 10.0 mL of 1.0 x 10⁻¹ M OH⁻.

1.0 x 10⁻⁵ M methyl violet and 10.0 mL of 1.5 x 10⁻¹ M OH⁻.

Blank with distilled water.

Data Treatment

Include the following. Show samples of all calculations.
For Part I, using just your **good** data (noting which points you are not using (see above)) construct a table with columns for time, absorbance, \(\ln(\text{absorbance})\) and \(1/\text{absorbance}\). Make plots of absorbance vs. time, \(\ln(\text{absorbance})\) vs. time and \(1/\text{absorbance}\) vs. time. The graph, which gives the best straight-line (according to \(R^2\)), 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 \(k_1\).

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 \(\log([\text{OH}^-])\) for \(k_1\text{-}4\) 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).