Chemical Kinetics
Prelab

1. What is the purpose of this experiment?

2. What is the function of SCN⁻ in the experiment?

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

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

5. 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>
<td>0.075</td>
</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 \( k \).
Chemical Kinetics

Special mention goes to Ms. Rebecca Mack who single-handedly developed 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:

\[ \text{rate} = k[A]^x[B]^y[C]^z \]  \hspace{1cm} (1)

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:

\[ 2 \text{Fe}^{3+} + \text{Sn}^{2+} \rightarrow 2 \text{Fe}^{2+} + \text{Sn}^{4+} \]  \hspace{1cm} (2)

Because iron(III) precipitates out of solution unless in an acidic environment, all of the iron solutions are prepared in acidic solution. The tin(II) solutions are prepared the same way for the same reasons as iron. The concentration of acid also has an effect on the rate of this reaction, but will be held constant in this experiment. Iron(III) has a yellow color and iron(II) is colorless. In this experiment, you will add some thiocyanate (SCN\(^-\)) ion to form the intensely red colored FeSCN\(^{2+}\) ion from Fe\(^{3+}\). Fe\(^{2+}\) does not combine with SCN\(^-\), so the reaction mixture will go from red to colorless. The reaction, then is:

\[ 2 \text{FeSCN}^{2+} + \text{Sn}^{2+} \rightarrow 2 \text{Fe}^{2+} + \text{Sn}^{4+} + 2 \text{SCN}^- \]  \hspace{1cm} (3)

The intensity of the red allows you to follow the reaction over a longer period of time. You will monitor the reaction between iron(III) and tin(II) by observing the change in color of iron(III) as it becomes iron(II) using a Spectronic 20. As you know from last week's Beer’s law experiment, concentration and absorbance are directly related. The reaction rate is a measure of how fast the concentration of a reactant decreases or a product formed. In this experiment you will be observing a decrease in the concentration of iron(III) (as absorbance) over some specific time interval.
The rate law for our reaction is in the following form, where \( x \), and \( y \) are to be determined experimentally:

\[
\text{rate} = k[\text{Fe}^{3+}]^x[\text{Sn}^{2+}]^y
\]  \hspace{1cm} (4)

If the concentration of the tin(II) is in large excess compared to iron(III), then its concentration will not change appreciably over the course of the reaction and therefore, remain essentially constant throughout the reaction. The concentration of Sn\(^{2+}\) can be incorporated into a new constant, \( k' \). The rate law under these conditions can be written

\[
\text{rate} = k'[\text{Fe}^{3+}]^x
\]  \hspace{1cm} (5)

with

\[
k' = k[\text{Sn}^{2+}]^y
\]  \hspace{1cm} (6)

**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

\[
\ln[\text{Fe}^{3+}]_t = -k't + \ln[\text{Fe}^{3+}]_0
\]  \hspace{1cm} (7)

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 \( \ln[\text{Fe}^{3+}] \) 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

\[
\frac{1}{[\text{Fe}^{3+}]_t} = k't + \frac{1}{[\text{Fe}^{3+}]_0}
\]  \hspace{1cm} (8)

If a plot of \( 1/[\text{Fe}^{3+}] \) 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 iron(III) thiocyanate solution as it reacts with tin(II) 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. \( \ln(\text{absorbance}) \) vs. time and 3. \( 1/\text{absorbance} \) vs. time. The plot that gives the best straight line indicates the order of the reaction in iron(III). The slope of the best straight line gives the rate constant \( k' \).

Changing the concentrations of Sn\(^{2+}\) by known amounts while keeping the concentration of the Fe\(^{3+}\) constant will allow you to determine the order of Sn\(^{2+}\) in the reaction (equation 6). 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 FeSCN\(^{2+}\), 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 Iron(III)**

Set the Spectronic 20 to 460 nm. Blank with 0.32 M HCl solution.

Pipet 10.0 mL of \(2.5 \times 10^{-3}\) M Fe\(^{3+}\) into a small beaker. Add one drop of 4 M KSCN solution. Pipet 10.0 mL of \(1.4 \times 10^{-2}\) M Sn\(^{2+}\) 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 5 seconds for about 3 minutes (or until there is little to no change in the absorbance).

**Part II  Determining the Order of Tin(II)**

Follow the procedure in Part I, using:

- 10.0 mL of \(2.5 \times 10^{-3}\) M Fe\(^{3+}\) and 10.0 mL of \(2.1 \times 10^{-2}\) M Sn\(^{2+}\).
- 10.0 mL of \(2.5 \times 10^{-3}\) M Fe\(^{3+}\) and 10.0 mL of \(2.8 \times 10^{-2}\) M Sn\(^{2+}\).
- 10.0 mL of \(2.5 \times 10^{-3}\) M Fe\(^{3+}\) and 10.0 mL of \(3.5 \times 10^{-2}\) M Sn\(^{2+}\).

Blank with 0.32 M HCl solution.

**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(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 \(R^2\)), will indicate the order of the reaction in iron(III). The order of iron(III) 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 Fe\(^{3+}\). Determine the rate
constants $k'$, $k'$, and $k'$ 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 $[\text{Sn}^{2+}]$, plot $\log(k')$ versus $\log[\text{Sn}^{2+}]$ for $k'_{1-4}$ and the corresponding $[\text{Sn}^{2+}]$ (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 $\text{Fe}^{3+}$ and $\text{Sn}^{2+}$ are determined, write the rate law.

Determine the average value of $k$ calculated from $k'_{1}$, $k'_{2}$, $k'_{3}$ and $k'_{4}$ (equation 6 with the exponent (y) of your rate law (determined above) and $[\text{Sn}^{2+}]_{1-4}$ used in Parts I and II and compare with the value obtained from the y-intercept.

Conclusion

The rate law and the rate constant, $k$ (average from equation 6 and from the graph).