Introduction

The composition of our world is controlled by detailed chemical mechanisms and their rates. Extremely complex mechanisms determine the characteristics of everything from living cells to the atmosphere. For example, chemists are creating mechanisms for the reactions of organic compounds in the polluted urban atmosphere that include almost two million elementary reactions. The goal of chemical kinetics is to better understand the mechanisms and rates of chemical reactions. In this laboratory you will learn some methods that can be applied to understand the mechanisms of many kinds of reactions.

Hydrogen peroxide is an oxidant that is ubiquitous in the environment that is formed by atmospheric processes (Stockwell et al., 1997). Hydrogen peroxide is injurious to cells because it attacks unsaturated fatty acids (lipids) found in cell membranes and consequently cells produce a powerful catalyst, catalase, that decomposes H2O2 (Keusch). Catalase is a catalyst (rather than just another reactant) because it reacts both as an electron donor and as an electron acceptor. Catalase is an example of an enzyme, a biological catalyst.

There are many other compounds that decompose hydrogen peroxide such as iodide ion under acidic conditions. The decomposition is characterized by the stoichiometric reaction (\(\text{ref}(\text{EQ1})\)).

\[
[2 \ I^- + 2 \ H^+ + H_2O_2 \rightarrow I_2 + 2 \ H_2O \ \text{\textit{label(EQ1)}}]
\]

If the solution is relatively acidic (with a pH is less than about 3) the rate of reaction (\(\text{ref}(\text{EQ1})\)) is independent of the pH. Assume that the rate of the reaction under acidic conditions is given by Equation (\(\text{ref}(\text{EQ2})\)).

\[
\text{Rate} = k[ I^- ]^a [ H_2O_2 ]^b \ \text{\textit{label(EQ2)}}
\]

where \( k \) is the rate coefficient, \( [ I^- ] \) is the iodide concentration, \( [ H_2O_2 ] \) is the hydrogen peroxide concentration and \( a \) and \( b \) are the order of the reaction with respect to iodide and hydrogen peroxide, respectively. We will learn something about kinetics by experimentally determining \( a \) and \( b \) and by estimating \( k \) as a pseudo rate coefficient. This laboratory is based on a similar experiment (Hutton, 1968).

**Measuring the order of the reaction with respect to the iodide and hydrogen concentrations,**
“a” and “b”

We could mix many different concentrations of iodide and hydrogen peroxide and measure the rate but the data analysis would be very difficult and confusing. Suppose that we measured the rate using some baseline concentrations of iodide and hydrogen peroxide, \( \left[ I^{-} \right]_{o} \) and \( \left[ H_{2} O_{2} \right]_{o} \) respectively. The baseline rate will be called \( \left( \text{Rate}_{o} \right) \) as in equation (3).

\[
\text{Rate}_{o} = k\left[ I^{-} \right]_{o}^{a} \left[ H_{2} O_{2} \right]_{o}^{b} \tag{EQ3}
\]

constant at \( \left[ H_{2} O_{2} \right]_{o} \). The ratio between the new rate and the baseline rate is given by equation \( \ref{EQ4} \).

\[
\frac{\text{Rate}}{\text{Rate}_{o}} = \frac{k\left[ I^{-} \right]^{a} \left[ H_{2} O_{2} \right]_{o}^{b}}{k\left[ I^{-} \right]_{o}^{a} \left[ H_{2} O_{2} \right]_{o}^{b}} \tag{EQ4}
\]

Equation \( \ref{EQ4} \) simplifies to equation \( \ref{EQ5} \).

\[
\frac{\text{Rate}}{\text{Rate}_{o}} = \left( \frac{\left[ I^{-} \right]}{\left[ I^{-} \right]_{o}} \right)^{a} \tag{EQ5}
\]

A typical experimental “trick” is to find a way of linearizing the experiment so that its’ results can be fit by a straight line as given by equation (6).

\[
y = \text{slope} \cdot x + \text{constant} \tag{EQ6}
\]

where \( y \) is the dependent variable and \( x \) is the independent value. In this case linear regression can be used to determine an experimental value. We will do that here by taking the natural logarithms of both sides of equation (6).

\[
\ln \left( \frac{\text{Rate}}{\text{Rate}_{o}} \right) = a \ln \left( \frac{\left[ I^{-} \right]}{\left[ I^{-} \right]_{o}} \right)
\]

Therefore if we measure the reaction rate at some concentration of iodide and then make several more measurements at differing concentrations of iodide and plot \( \ln \left( \frac{\text{Rate}}{\text{Rate}_{o}} \right) \) as a function of \( \ln \left( \frac{\left[ I^{-} \right]}{\left[ I^{-} \right]_{o}} \right) \) the slope will be equal to \( a \), the order of the reaction with respect to the iodide concentration.

We can follow similar reasoning to measure \( b \), the order of the reaction with respect to the hydrogen peroxide concentration.

\[
\ln \left( \frac{\text{Rate}}{\text{Rate}_{o}} \right) = b \ln \left( \frac{\left[ H_{2} O_{2} \right]}{\left[ H_{2} O_{2} \right]_{o}} \right)
\]

Measuring the reaction rate

How can the reaction rate of reaction (1) be measured? Thiosulfate ion reacts with iodine to convert it back to iodide as shown in reaction (9) and it does not react to any significant extent with anything else in the solution.

\[
I_{2} + 2 S_{2}O_{3}^{2-} \rightarrow 2 I^{-} + S_{4}O_{6}^{2-}
\]
Iodine concentrations remain low as long as there is thiosulfate in the solution. After the thiosulfate is consumed iodine concentrations will increase and in the presence of starch a blue colored complex will form. We can measure the rate of reaction (1) by adding a known amount of a standard sodium thiosulfate solution and some starch to the reacting solution. The time required for the solution to turn blue is measured. The rate is given by equation (10).

\[
\text{Rate} = \frac{\text{Moles H}_2\text{O}_2 \text{ reacted}}{\text{Time (s)}} = \frac{\text{Moles thiosulfate reacted}}{\text{Time to turn blue}}
\]

The formula of sodium thiosulfate is Na$_2$S$_2$O$_3$. Sodium thiosulfate may absorb water or react with impurities in solution. Therefore to measure the rate coefficient accurately we should do several different titrations of the sodium thiosulfate solution to accurately establish its’ concentration. However we can make estimates by simply assuming the formula to calculate the thiosulfate concentration. This uncertainty does not affect the determination of reaction order at all but it does affect the determination of the rate coefficient.

**Estimating a pseudo rate coefficient**

We will estimate a pseudo rate coefficient with respect to iodide and another pseudo rate coefficient with respect to hydrogen peroxide.

To estimate a pseudo rate coefficient with respect to iodide, use the data were the iodide was varied and the hydrogen peroxide concentration was kept constant. Under these conditions we may define \( \{k\}' \), where \( \{k\}' = k \left [ \text{H}_2\text{O}_2 \right ]^{b} \) and the expression for the reaction rate becomes:

\[
\text{Rate} = \{k\}' \left [ \text{I}^{-} \right ]^{a}
\]

If the measured reaction rate, \( \langle \text{Rate} \rangle \), is plotted as a function of \( \langle \left [ \text{I}^{-} \right ]^{a} \rangle \) then \( \langle \{k\}' \rangle \) can be determined from the slope.

To estimate a pseudo rate coefficient with respect to hydrogen peroxide, use the data were the hydrogen peroxide was varied and the iodide concentration was kept constant. Define this pseudo rate coefficient, \( \{k\}'' \), as \( \{k\}'' = k \left [ \text{I}^{-} \right ]^{a} \) and the expression for the reaction rate becomes:

\[
\text{Rate} = \{k\}'' \left [ \text{H}_2\text{O}_2 \right ]^{b}
\]

If the measured reaction rate, \( \langle \text{Rate} \rangle \), is plotted as a function of \( \langle \left [ \text{H}_2\text{O}_2 \right ]^{b} \rangle \) then \( \langle \{k\}'' \rangle \) can be determined from the slope.

**Temperature Dependence of Rate Coefficients**

The temperature dependence of rate coefficients for many reactions is given by the Arrhenius equation:

\[
\text{k} = A \exp \left ( \frac{-E_{a}}{RT} \right )
\]

where \( \langle A \rangle \) is the preexponential factor, \( \langle E_{a} \rangle \) is the activation energy, \( \langle R \rangle \) is the ideal gas constant and \( \langle T \rangle \) is the temperature. In applying this equation be certain the units of \( \langle E_{a} \rangle \) and \( \langle R \rangle \) are consistent. Substituting the Arrhenius equation into the general rate equation for the reaction of hydrogen peroxide with iodide yields,
\[
\text{Rate} = A \exp \left( \frac{-E_a}{RT} \right) \times \left[ I^- \right]^a \left[ H_2O_2 \right]^b
\]

Take the natural logarithm of both sides.

\[
\ln \left( \text{Rate} \right) = \frac{-E_a}{RT} + \ln \left( A \left[ I^- \right]^a \left[ H_2O_2 \right]^b \right)
\]

Therefore if we measure the reaction rate at several temperatures at the same concentration of iodide and hydrogen peroxide and then plot \( \ln \left( \text{Rate} \right) \) as the dependent axis (y-axis) and \( \frac{1}{T} \) as the independent axis (x-axis) the slope will be equal to \( \frac{-E_a}{R} \).

**Procedure Part 1:**

Prepare a KI solution with a concentration that is about 0.3 M. Use an analytical balance to accurately weigh 25 g of KI. Use a volumetric flask to dilute to 500 ml. Calculate the concentration.

Prepare a H$_2$O$_2$ solution with a concentration that is about 0.1 M. Dissolve about 6 ml of 30% hydrogen peroxide in 500 ml distilled water. You do not need to calculate the concentration.

Prepare a sodium thiosulfate solution with a concentration that is about 0.02 M. S$_2$O$_3^{2-}$ Use an analytical balance to accurately weigh 1.5 g of Na$_2$S$_2$O$_3$. Use a volumetric flask to dilute to 500 ml. Calculate the approximate concentration.

Make a 500 ml buffer solution with 0.5 M of acetic acid and 0.5 M sodium acetate.

To see the colors of the reaction products do the following:

Record your observations as you do the following. Place about 5 ml of the KI solution in a test tube. Add a few drops of the hydrogen peroxide solution.

Divide the mixture of KI and hydrogen peroxide between three test tubes. Label as I, 2 and 3.
Test tube 1) Keep as a reference.
Test tube 2) Add a couple drops of starch solution.
Test tube 3) Add a couple drops of sodium thiosulfate solution and observe. Add a couple of drops of starch solution and observe again.

Keep these test tubes as a reference as you perform the kinetics measurements.

<table>
<thead>
<tr>
<th>Table 1. Experimental Solutions for Part 1.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Distilled Water (ml)</td>
</tr>
<tr>
<td>------------------------------------------</td>
</tr>
<tr>
<td>KI Variation</td>
</tr>
<tr>
<td>A</td>
</tr>
</tbody>
</table>
First note the temperature of the solutions and record in your notebook. Mix the solutions 1 – 6 together to make solution A but do not add the hydrogen peroxide. Measure the volumes of the KI and of sodium thiosulfate as accurately as possible. Pour the solution into a 500 ml beaker. Accurately measure the volume of the hydrogen peroxide solution. Mix solution A and the hydrogen peroxide solution and determine the time from mixing until the solution turns to a light blue. Record the time to the nearest second. Repeat for all solutions in Table 1. You do not need to repeat solution E, it is listed in Table 1 to indicate that it is part of both the hydrogen peroxide and potassium iodide variations.

**Data Summary Sheet**

<table>
<thead>
<tr>
<th></th>
<th>Time (Min)</th>
<th>Measured Temperature C°</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Part 2 Temperature Variation

Table 2 gives the composition of the reaction mixture.

Table 2. Experimental Solutions for Temperature Variation. Part 2.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Distilled Water (ml)</th>
<th>Buffer (ml)</th>
<th>KI Solution (ml)</th>
<th>Starch Solution (ml)</th>
<th>Na$_2$S$_2$O$_3$ Solution (ml)</th>
<th>More Distilled Water (ml)</th>
<th>H$_2$O$_2$ Solution (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1 25</td>
<td>300</td>
<td>25</td>
<td>25</td>
<td>2</td>
<td>25</td>
<td>To make 475</td>
<td>25</td>
</tr>
<tr>
<td>E2 30</td>
<td>300</td>
<td>25</td>
<td>25</td>
<td>2</td>
<td>25</td>
<td>To make 475</td>
<td>25</td>
</tr>
<tr>
<td>E3 35</td>
<td>300</td>
<td>25</td>
<td>25</td>
<td>2</td>
<td>25</td>
<td>To make 475</td>
<td>25</td>
</tr>
<tr>
<td>E4 40</td>
<td>300</td>
<td>25</td>
<td>25</td>
<td>2</td>
<td>25</td>
<td>To Make 475</td>
<td>25</td>
</tr>
<tr>
<td>E5 45</td>
<td>300</td>
<td>25</td>
<td>25</td>
<td>2</td>
<td>25</td>
<td>To Make 475</td>
<td>25</td>
</tr>
<tr>
<td>E6 50</td>
<td>300</td>
<td>25</td>
<td>25</td>
<td>2</td>
<td>25</td>
<td>To Make 475</td>
<td>25</td>
</tr>
</tbody>
</table>

First perform the experiment at room temperature. Repeat the experiment near 30, 35, 40, 45 and 50 °C. For all measurements mix solutions 1 – 6 together but do not add the hydrogen peroxide. Measure the volumes of the KI and of sodium thiosulfate as accurately as possible. Pour the solution into a 500 ml flask. Either perform at room temperature or place in a water bath to warm to the desired temperature. There will be three warm water baths available. Do not heat the hydrogen peroxide to avoid decomposition.

Accurately measure the volume of the hydrogen peroxide solution. Mix the solution and the hydrogen peroxide solution and determine the time from mixing until the solution turns to a light blue – brown color. Record the time to the nearest second. Record the temperature of the final solution and record in your notebook.
Each group will perform a measurement at room temperature and near 30, 35, 40, 45 and 50 °C (five total measurements per group).

Data Summary Sheet for Part 2.

<table>
<thead>
<tr>
<th>Time (Min)</th>
<th>Measured Temperature C°</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td></td>
</tr>
<tr>
<td>E2</td>
<td></td>
</tr>
<tr>
<td>E3</td>
<td></td>
</tr>
<tr>
<td>E4</td>
<td></td>
</tr>
<tr>
<td>E5</td>
<td></td>
</tr>
<tr>
<td>E6</td>
<td></td>
</tr>
</tbody>
</table>

Calculations and Graphs

In your report organize the results of your calculations in tables and show example calculations.

Iodide variation

Use solution E as the baseline solution. Note that the ratios, $[I^-]/[I^-]_0$, for solutions A – E are 1, 2, 3, 4 and 5, respectively. Calculate the ratio of the measured rates (measured times for the solutions to turn blue (Rate/Rate$_0$). Take the natural logs and plot ln($[I^-]/[I^-]_0$) as the independent variable (x-axis) and plot ln(Rate/Rate$_0$) as the dependent variable (y-axis). Perform a linear regression using Excel or similar program to determine the order of the reaction with respect to iodide from slope. Also determine the $r^2$ (shared variance) of the fit.

Hydrogen peroxide variation

Use solution E as the baseline solution. Note that the ratios, $[H_2O_2]/[H_2O_2]_0$, for solutions E – I are 1, 2, 3, 4 and 5, respectively. Calculate the ratio of the measured rates (measured times for the solutions to turn blue (Rate/Rate$_0$). Take the natural logs and plot ln($[H_2O_2]/[H_2O_2]_0$) as the independent variable (x-axis) and plot ln(Rate/Rate$_0$) as the dependent variable (y-axis). Perform a linear regression using Excel or similar program to determine the order of the reaction with respect to hydrogen peroxide from the slope. Also determine the $r^2$ (shared variance) of the fit.

Estimate the pseudo rate coefficients

For solutions A – E calculate the reaction rate (Rate) in terms of moles of hydrogen peroxide per second and calculate $[I^-]^a$. Plot $[I^-]^a$ as the independent variable (x-axis) and plot the Rate as the dependent variable (y-axis). Perform a linear regression using Excel or similar program to determine the pseudo rate coefficient from the slope. Also determine the $r^2$
For solutions E – I calculate the reaction rate (Rate) in terms of moles of hydrogen peroxide per second and calculate $[\text{H}_2\text{O}_2]^b$. Plot $[\text{H}_2\text{O}_2]^b$ as the independent variable (x-axis) and plot the Rate as the dependent variable (y-axis). Perform a linear regression using Excel or similar program to determine the pseudo rate coefficient from the slope. Also determine the $r^2$ (shared variance) of the fit.

Temperature Variation
For Part 2 plot the natural logarithm of the reaction time as a function of $1/T$ to determine the activation energy of the rate coefficient. Use Kelvin (K) as your temperature unit.

**Report**

Structure the report as discussed in class and include a discussion of the following questions in your conclusions section.

1. To determine the reaction order of KI or H$_2$O$_2$ why is it not necessary to know the either the initial or actual concentrations of KI or H$_2$O$_2$ during the experiment?
2. What are the major uncertainties in the results for the reaction orders? What are the major sources of error for the pseudo rate coefficient. What are the $r$ and shared variance ($r^2$)?
3. Suggest a reaction mechanism from the data. Can you distinguish between the following two elementary reaction mechanisms on the basis of your data?

<table>
<thead>
<tr>
<th>Scheme I</th>
<th>Scheme II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1:</td>
<td>$\text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{H}_3\text{O}_2^+$</td>
</tr>
<tr>
<td>Step 2:</td>
<td>$\text{H}_3\text{O}_2^+ + \text{I}^- \rightarrow \text{HOI} + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Step 3:</td>
<td>$\text{HOI} + \text{I}^- \rightarrow \text{I}_2 + \text{OH}^-$</td>
</tr>
<tr>
<td>Step 4:</td>
<td>$\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}$</td>
</tr>
</tbody>
</table>

4. Why is the ionic strength kept constant?
5. What are the lessons that can be transferred from this laboratory exercise to life sciences research?

References

Hutton, W., “General Chemistry Laboratory Text with Qualitative Analysis,” Experiment 14, Kinetics of the Reaction Between Hydrogen Peroxide and Iodide Ion, Charles E. Merrill Publishing Company Columbus, Ohio (1968).

Keusch, P. Enzyme Kinetics, Enzymatic Decomposition of Hydrogen Peroxide, http://www.uniregensburg.de/Fakultae...yl_kat-e.htm