Experiment 2 Decomposition of Hydrogen Peroxide

The decomposition of hydrogen peroxide in aqueous solution proceeds very slowly. A bottle of 3% hydrogen peroxide sitting on a grocery store shelf is stable for a long period of time. The decomposition takes place according to the reaction below.

\[ 2 \text{H}_2\text{O}_2(\text{aq}) \rightarrow 2 \text{H}_2\text{O} + \text{O}_2(\text{g}) \]

A number of catalysts can be used to speed up this reaction, including potassium iodide, manganese (IV) oxide, and the enzyme catalase. If you conduct the catalyzed decomposition of hydrogen peroxide in a closed vessel, you will be able to determine the reaction rate as a function of the pressure increase in the vessel that is caused by the production of oxygen gas. If you vary the initial molar concentration of the H\textsubscript{2}O\textsubscript{2} solution, the rate law for the reaction can also be determined. Finally, by conducting the reaction at different temperatures, the activation energy, \(E_a\), can be calculated.

**OBJECTIVES**

In this experiment, you will

- Conduct the catalyzed decomposition of hydrogen peroxide under various conditions.
- Calculate the average rate constant for the reaction at room temperature.
- Determine the rate law expression for the reaction.
- Calculate the activation energy for the reaction.

The rate law for this reaction can be determined using the observed rates of reactions from a series of different experiments. The concentration of one reactant is held constant between two different experiments, acting as the control, while the concentration of the second reactant is different between the two experiments. The rate of reaction is measured in each experiment so the impact of changing the concentration of the second reactant can be determined. The order of the reaction with respect to each reactant is determined in this fashion and once the order of each reactant is know the rate law can then be written.

(A) Sample Exercise for Determining Reaction Order

Consider the following reaction: \((\text{CH}_3)_3\text{CBr}(aq) + \text{OH}^-(aq) \rightarrow (\text{CH}_3)_3\text{COH}(aq) + \text{Br}^-(aq)\)

A series of experiments is carried out with the following results:

<table>
<thead>
<tr>
<th></th>
<th>Exp 1</th>
<th>Exp 2</th>
<th>Exp 3</th>
<th>Exp 4</th>
<th>Exp 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(CH\textsubscript{3})\textsubscript{3}CBr]</td>
<td>0.50</td>
<td>1.0</td>
<td>1.5</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>[OH\textsuperscript{-}]</td>
<td>0.050</td>
<td>0.050</td>
<td>0.050</td>
<td>0.10</td>
<td>0.20</td>
</tr>
<tr>
<td>Rate (M/s)</td>
<td>0.0050</td>
<td>0.010</td>
<td>0.015</td>
<td>0.010</td>
<td>0.040</td>
</tr>
</tbody>
</table>

Find the order of the reaction with respect to both (CH\textsubscript{3})\textsubscript{3}CBr and OH\textsuperscript{-}.
To find the order of the reaction with respect to (CH\textsubscript{3})\textsubscript{3}CBr, choose two experiments, 1 and 3 for example, where [OH\textsuperscript{-}] is constant. A similar approach can be used to find the order of the reaction with respect to OH\textsuperscript{-}, comparing experiments 2 and 5, where [(CH\textsubscript{3})\textsubscript{3}CBr]

(1) Order with Respect to (CH\textsubscript{3})\textsubscript{3}CBr:

\[
\text{Rate exp 3} = k[(\text{(CH}_3)_3\text{CBr})_{\text{exp 3}}]^m(\text{[OH}^-)_{\text{exp 3}})^n
\]
\[
\text{Rate exp 1} = k[(\text{(CH}_3)_3\text{CBr})_{\text{exp 1}}]^m(\text{[OH}^-)_{\text{exp 1}})^n
\]

0.015 M/s = \( k[(1.5 \text{ M})]^m (0.050 \text{ M})^n \)

0.0050 M/s = \( k[(0.50 \text{ M})]^m (0.050 \text{ M})^n \)

simplifies to: 3.0 = (3.0)^m

Using the natural log applied to both sides and solving for “m”

\[
\text{Ln 3.0} = (\text{Ln 3.0}) \cdot (m) \quad (\text{Ln 3.0}) / (\text{Ln 3.0}) = 1.10 / 1.10 = 1 = m
\]

Since “m” = 1 the reaction is first order with respect to (CH\textsubscript{3})\textsubscript{3}CBr.

(2) Order with Respect to [OH\textsuperscript{-}]:

\[
\text{Rate exp 5} = k[(\text{(CH}_3)_3\text{CBr})_{\text{exp 5}}]^m(\text{[OH}^-)_{\text{exp 5}})^n
\]
\[
\text{Rate exp 4} = k[(\text{(CH}_3)_3\text{CBr})_{\text{exp 2}}]^m(\text{[OH}^-)_{\text{exp 2}})^n
\]

0.040 M/s = \( k[(1.0 \text{ M})]^m (0.20 \text{ M})^n \)

0.010 M/s = \( k[(1.0 \text{ M})]^m (0.10 \text{ M})^n \)

simplifies to: 4.0 = (2.0)^n

Using the natural log applied to both sides and solving for “m”

\[
\text{Ln 4.0} = (\text{Ln 2.0}) \cdot (m) \quad (\text{Ln 4.0}) / (\text{Ln 2.0}) = 1.39 / 0.69 = 2.01 = n
\]

Since “n” = 2 the reaction is second order with respect to (CH\textsubscript{3})\textsubscript{3}CBr.

Now that the order of the reaction for each reactant has been determined the rate law can be written for this equation:

\[
\text{Rate} = k \quad [(\text{(CH}_3)_3\text{CBr}) \quad [\text{OH}^-]^2
\]

(B) Sample Exercise for Determining Molarity of a Diluted Solution

When two solutions are mixed in an experiment the total volume of the solutions is increased and the concentration of each solution is diluted. Recall:

\[
\text{Moles solute before dilution} = \text{moles solute after dilution}
\]

\[
\text{(Molarity)}_{\text{conc}} \times (\text{Volume})_{\text{conc}} = \text{(Molarity)}_{\text{dil}} \times (\text{Volume})_{\text{dil}}
\]

\[
\text{Advanced Chemistry with Vernier}
\]

3
What is the concentration of each compound when 6.0 mL of a 0.60 M solution of \( \text{H}_2\text{O}_2 \) is mixed with 2.0 mL of a 0.25 M potassium iodide solution?

1. First consider the total volume of the solution after mixing:
   
   \[ 6.0 \text{ mL H}_2\text{O}_2 + 2.0 \text{ mL KI} = 8.0 \text{ mL total volume of diluted solution} \]

2. Determine the concentration of \( \text{H}_2\text{O}_2 \) after mixing:
   
   \[
   [0.75 \text{ M}]_{\text{conc}} \times (6.0 \text{ mL})_{\text{conc}} = [\text{H}_2\text{O}_2]_{\text{dil}} \times (8.0 \text{ mL})_{\text{dil}}
   
   (0.60 \text{ M})(6.0 \text{ mL}) / (8.0 \text{ mL}) = 0.45 \text{ M} = [\text{H}_2\text{O}_2]_{\text{dil}}
   
3. Determine the concentration of KI after mixing:
   
   \[
   [0.25 \text{ M}]_{\text{conc}} \times (2.0 \text{ mL})_{\text{conc}} = [\text{H}_2\text{O}_2]_{\text{dil}} \times (8.0 \text{ mL})_{\text{dil}}
   
   (0.40 \text{ M})(2.0 \text{ mL}) / (8.0 \text{ mL}) = 0.10 \text{ M} = [\text{KI}]_{\text{dil}}
   
   The concentration of the \( \text{H}_2\text{O}_2 \) decreased from 0.60 M to 0.45 M and the concentration of KI decreased from 0.25 M to 0.10 M after the two solutions are mixed. The solutions will be diluted as the reactions begin so be sure to use the diluted concentrations of each reactant when determining the reaction orders or rate constants.

(C) Sample Exercise for Converting Pressure Rate Data to Molarity Units

The data rate recorded in this experiment is in kilopascals per second (kPa/s). Since pressure is a unit of concentration in the gas phase it can be used to determine rate when the change of pressure is measured over the change in time. However, in this experiment the reactants are in the aqueous phase and the concentration unit for the solutions is in molarity (M). kPa/s can be converted to M/s by using a derivation from the ideal gas law:

\[ \text{Molarity} = \frac{P}{RT} \]

In which \( P = \text{kPa/s} \), \( R = 8.314 \text{ L} \times \text{kPa} / \text{K} \times \text{mol} \) (one of ideal gas constants), and \( T = \text{temperature on Kelvin} \).

In one experiment the rate of \( \text{O}_2 \) production was 0.22 kPa/s when the temperature of the water bath was 19.0 °C. What is this rate in M/s?

\[
\text{Molarity} = \frac{(0.22 \text{ kPa/s}) / (8.314 \text{ L} \times \text{kPa/K} \times \text{mol})(292.0 \text{ K})}{(0.22 \text{ kPa} / 2.43 \times 10^3 \text{ L} \times \text{kPa} / \text{mol})} = (0.22 \text{ kPa} / 2.43 \times 10^3 \text{ L} \times \text{kPa} / \text{mol})
\]

Molarity = \[ 9.05 \times 10^{-5} \text{ M/s} \]

The units kPa and Kelvin cancel leaving mol/L*s or M/s.

(D) Sample Exercise for Converting Percent Solutions (mass/volume) to Molarity Units

Assumed 100 mL of total volume of solution in a percent (mass/volume) solution and the percent value will represent the grams of solute dissolved in water to make a total volume of 100 mL. For example a 10% NaCl solution will have 10 g of NaCl dissolved in 100 mL of solution.

What is the molarity of this 10% NaCl solution?
Molarity = moles of solute / liters of solution

If you assume 10 g NaCl and 100 mL of solution and the molar mass of NaCl is 58.5 g / mol then:

(1) Moles NaCl = (10 g NaCl)(1 mole NaCl / 58.5 g NaCl) = 0.17 moles NaCl

(2) Liters solution = (100 mL solution)(1 L solution / 100 mL solution) = 0.100 L solution

(3) Molarity = (0.17 moles NaCl / 0.100 L solution) = 1.7 M

Diagram of the equipment set for this experiment:

**MATERIALS**

<table>
<thead>
<tr>
<th>Material</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vernier computer interface</td>
<td>3% hydrogen peroxide, H₂O₂, solution</td>
</tr>
<tr>
<td>distilled water</td>
<td>0.5 M potassium iodide, KI, solution</td>
</tr>
<tr>
<td>Vernier Gas Pressure Sensor</td>
<td>18 × 150 mm test tube</td>
</tr>
<tr>
<td>thermometer or Temperature Probe</td>
<td>two 10 mL graduated cylinders</td>
</tr>
<tr>
<td>one-hole rubber stopper with stem</td>
<td>graduated plastic Beral pipet</td>
</tr>
<tr>
<td>tubing with two Luer-lock connectors</td>
<td>1 liter beaker</td>
</tr>
<tr>
<td>solid rubber stopper (#1)</td>
<td>~800 mL room temperature water</td>
</tr>
</tbody>
</table>

**Procedure**

Part I  Decompose 3% H₂O₂ solution with 0.5 M KI solution at ~20°C.
1. Obtain and wear goggles.

2. Prepare the reagents for temperature equilibration.
   a. Obtain room temperature water to set up a water bath to completely immerse the test tube. Use a thermometer or a Temperature Probe to measure the temperature of the bath. Record this temperature in your data table for Parts I-III; presume that the water bath temperature remains constant throughout.
   b. Measure out 4 mL of 3% H₂O₂ solution into the test tube. Seal the test tube with the solid rubber stopper and place the test tube in the water bath.
   c. Measure out 2 mL of 0.5 M KI solution in a graduated cylinder. Draw about 1 mL of the KI solution into a graduated Beral pipet. Invert the pipet and immerse the reservoir end of the pipet in the water bath.

3. Connect a Gas Pressure Sensor to Channel 1 of the Vernier computer interface. Connect the interface to the computer using the proper cable.

4. Use the plastic tubing to connect the one-hole rubber stopper to the Gas Pressure Sensor, as shown in Figure 1. About one-half turn of the fittings will secure the tubing tightly.

5. Start the Logger Pro program on your computer. Open the file “12 Peroxide” from the Advanced Chemistry with Vernier folder.

6. Prepare to run the reaction and collect pressure data.
   d. Remove the test tube from the water bath and remove the solid stopper.
   e. Remove the plastic Beral pipet from the water bath and quickly transfer 1 mL of KI solution into the test tube. Tap or lightly shake the test tube to mix the reagents.
   f. Seal the test tube with the one-hole stopper connected to the Gas Pressure Sensor.
   g. Place the test tube back in the water bath.

7. Click to begin data collection. Data will be gathered for three minutes. If necessary, gently hold the test tube so that it stays completely immersed in the water bath.

8. When the data collection is complete, carefully remove the stopper from the test tube to relieve the pressure. Dispose of the contents of the test tube as directed.

9. Examine the graph of Part I. Select a linear region just beyond the initial flat portion of the graph that covers one minute of the reaction. Click the Linear Regression button, to calculate the best-fit line equation. Record the slope as the initial rate of the reaction in your data table. Store the results from the first trial by choosing Store Latest Run from the Experiment menu.

10. Rinse and clean the test tube for the second trial.

Part II Decompose 3% H₂O₂ solution with 0.25 M KI solution at ~20°C

11. Measure out 4 mL of 3% H₂O₂ solution into the test tube. Seal the test tube with the solid rubber stopper and place the test tube in the water bath.

12. Add 1 mL of distilled water to the remaining 1 mL of KI solution in the graduated cylinder. Swirl the mixture gently to mix the solution.

13. Draw 1 mL of the KI solution into a plastic Beral pipet. Invert the pipet and immerse the reservoir end of the pipet in the water bath. Allow both the test tube and the Beral pipet to remain in the water bath for at least two minutes before proceeding.

14. Repeat Steps 6–10 to complete Part II. Remember to store the data.
The Decomposition of Hydrogen Peroxide

Part III  Decompose 1.5% H₂O₂ solution with 0.5 M KI solution at ~20°C

15. Prepare a 1.5% H₂O₂ solution by mixing 2 mL of distilled water with 2 mL of 3% H₂O₂ solution. Transfer the resulting 4 mL of the 1.5% H₂O₂ solution to the test tube, seal the test tube with the solid stopper, and place the test tube in the water bath.

16. Rinse and clean the graduated cylinder that you have used for the KI solution. Add a fresh 2 mL of 0.5 M KI solution to the graduated cylinder.

17. Draw 1 mL of the KI solution into a plastic Beral pipet. Invert the pipet and immerse the reservoir end of the pipet in the water bath. Allow both the test tube and the Beral pipet to remain in the water bath for at least two minutes before proceeding.

18. Repeat Steps 6–10 to complete Part III, and store the data.

Part IV  Decompose 3% H₂O₂ solution with 0.5 M KI solution at ~30°C

19. Conduct Part IV identically to the procedure in Part I, with one exception: set the water bath at 30°C.

Part V  Decompose 3% H₂O₂ solution with 0.5 M KI solution at 5-10°C

20. Conduct Part V identically to the procedure in Part I, with one exception: use ice to cool the water bath to the 5-10 °C range – record the temperature of the bath using a thermometer.

PRE-LAB EXERCISE – to be completed before coming to class

The hydrogen peroxide solution that you are using in this experiment is labeled as a 3% solution, mass/volume. However, in order to complete the calculations, the concentration must be in molarity. Calculate the molarity of a 3% mass/volume H₂O₂ solution (Part I, II, and IV) and a 1.5% mass/volume H₂O₂ solution (Part III) and record these values in the table below. This table should be completed in your lab notebook as part of the pre-lab assignment for this experiment.

<table>
<thead>
<tr>
<th>Part</th>
<th>Volume H₂O₂ (mL)</th>
<th>[H₂O₂] before mixing</th>
<th>Volume KI (mL)</th>
<th>[KI] before mixing</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>4</td>
<td>.88M</td>
<td>1</td>
<td>0.50 M</td>
</tr>
<tr>
<td>II</td>
<td>4</td>
<td>.88M</td>
<td>1</td>
<td>0.25 M</td>
</tr>
<tr>
<td>III</td>
<td>4</td>
<td>.44M</td>
<td>1</td>
<td>0.50 M</td>
</tr>
<tr>
<td>IV</td>
<td>4</td>
<td>.88M</td>
<td>1</td>
<td>0.50 M</td>
</tr>
<tr>
<td>V</td>
<td>4</td>
<td>.88M</td>
<td>1</td>
<td>0.50 M</td>
</tr>
</tbody>
</table>

Show the calculations used in determining the [H₂O₂] in the carbonless notebook as part of your pre-lab assignment.
**DATA TABLE**

Type up the following two tables and include them in your formal lab report.

<table>
<thead>
<tr>
<th>Part</th>
<th>Reactants</th>
<th>Temperature (°C)</th>
<th>Initial rate (kPa/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>4 mL 3.0% H₂O₂ + 1 mL 0.5 M KI</td>
<td>21.9</td>
<td>.20775</td>
</tr>
<tr>
<td>II</td>
<td>4 mL 3.0% H₂O₂ + 1 mL 0.25 M KI</td>
<td>21.9</td>
<td>.09819</td>
</tr>
<tr>
<td>III</td>
<td>4 mL 1.5% H₂O₂ + 1 mL 0.5 M KI</td>
<td>21.9</td>
<td>.1007</td>
</tr>
<tr>
<td>IV</td>
<td>4 mL 3.0% H₂O₂ + 1 mL 0.5 M KI</td>
<td>30.4</td>
<td>.4012</td>
</tr>
<tr>
<td>V</td>
<td>4 mL 3.0% H₂O₂ + 1 mL 0.5 M KI</td>
<td>10.0</td>
<td>.08099</td>
</tr>
</tbody>
</table>

**DATA ANALYSIS**

<table>
<thead>
<tr>
<th>Part</th>
<th>Initial rate (mol/L-s)</th>
<th>[H₂O₂] after mixing</th>
<th>[I⁻] after mixing</th>
<th>Rate constant $k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>III</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>IV</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Show the calculations used to answer questions 1 – 4 below after the data section of your formal lab report and explain the chemical principles behind each calculation in your discussion section. You should also explain the chemistry behind your answer to question 5 and define the two different roles described in 5(a) and 5(b).

1. What is the reaction order with respect to hydrogen peroxide?

2. What is the reaction order with respect to potassium iodide?
3. Write the rate law expression for the catalyzed decomposition of hydrogen peroxide and explain how you determined the order of the reaction in H$_2$O$_2$ and KI.

2. Calculate the rate constant, $k$, for each part of this experiment. Calculate an average rate constant at ~room temperature. Do any of the parts of the experiment have rate constants that are equal or almost equal?

3. Compare the rate of the reaction in part 1 at room temperature with the rate of the reaction in part 4 at approximately 10°C above room temperature. Approximately how much does rate increase with a 10°C increase in temperature? Use your values to explain your answer to this question.

4. Use the Arrhenius equation to determine the activation energy, $E_a$, for this reaction. Temperature needs to be expressed in Kelvin when using the Arrhenius equation. This determination requires analysis of an Arrhenius plot (ln $k$ vs 1/T) as discussed in class and detailed in your textbook. Use a graphing program to complete the graph and have the program determine the best straight-line fit to the data (it is not acceptable to do this graph by hand). From the equation of the line, you can calculate $E_a$. Show all calculations. Print your graph and attach it to your lab report when you turn it in…no lab is complete without this plot.

5. The following mechanism has been proposed for this reaction:

$$H_2O_2(aq) + I^-(aq) \rightarrow IO^-(aq) + H_2O(aq)$$
$$H_2O_2(aq) + IO^-(aq) \rightarrow I^-(aq) + H_2O(l) + O_2(g)$$

If this mechanism is correct, which step must be the rate-determining step? Please explain your choice.

(a) What is IO$^-$ (aq) called in this reaction? (What type of role the ion is playing in the reaction not its actual ionic name, hypiodite.)

(b) What is I$^-$ (aq) called in this reaction? (What type of role the ion is playing in the reaction not its actual ionic name, iodide.)

Note: $E_a$ should be in J/mol or KJ/mol
convert 'C to 'Kelvin
Discussion Section

The discussion section should relate the results of this experiment to the impacts of concentration and temperature to the rate of a chemical reaction. For example your discussion should include an explanation of why or how changing the concentration of a reactant impacts the rate of a reaction. You should also include why or how changing the temperature of the solutions impacts the rate of the chemical reactions observed. Cite your data/results as evidence when you discuss the impact of concentration (and temperature) changes on the rate of the reaction.

Since any experiment done in lab involves procedures and measurements the discussion section should also include analysis of errors associated with these. You should include a paragraph or two describing the errors you may have made in this experiment (any procedural errors) and the errors inherent to any measurements (measurement errors) made in the experiment. Explain how each type of error may have influenced the result of the experiment. Since graphical decisions were crucial in this experiment (and can also contribute significantly to the error) be sure to explain how you determined the rate of each reaction (why you chose a certain region of the graph), why it is important to be consistent in this process, and the role this decision plays in the confidence you have in your results. You are welcome to include a small drawing to aid in your discussion if it helps to make an idea more clear.

Conclusion

Write a paragraph with a brief conclusion summarizing the results of your experiment and describing what you learned in the process of doing this experiment. Be sure to include the results for the quantities you determined (average rate constant at room temperature, the rate law, and the activation energy) and indicate the largest source of error in your experiment.