Uncatalyzed Room Temperature Runs - The reaction under study in this experiment is:

\[ 2 \text{H}_2 \text{O}_2 (\text{aq}) + 2 \text{I}^- (\text{aq}) \rightarrow \text{I}_2 (\text{aq}) + 2 \text{H}_2 \text{O} (\text{l}) \]

In the first part of this experiment, you will verify the order of reaction with respect to both iodide ion and peroxide. The reaction was studied by using a starch indicator to demonstrate that iodine is formed.

\[ \text{fast} \quad \text{I}_2 + \text{I}^- \rightarrow \text{I}_3^- \]

\[ \text{fast} \quad \text{I}_2(\text{aq}) + \text{starch} \rightarrow \text{blue-black starch complex} \]

We “clocked” the reaction by adding a fixed amount of thiosulfate (S\(_2\)O\(_3^{2-}\)) to every reaction mixture. Thus, the starch color does not appear until all the thiosulfate is gone. Therefore, it is critical to know the concentration of thiosulfate present in all of the reaction trials (these are all equal!). Show a calculation of this concentration here:

Since we know the reaction between iodine and thiosulfate is known to be

\[ \text{very fast} \quad \text{I}_2 + 2 \text{S}_2\text{O}_3^{2-} \rightarrow \text{S}_4\text{O}_6^{2-} + 2 \text{I}^- \]

we can express the observed rate of reaction as:

\[
\text{rate of reaction} = \frac{1}{2} \left( \frac{\text{moles S}_2\text{O}_3^{2-}}{\text{L \ \text{seconds}}} \right)
\]

Since we held [S\(_2\)O\(_3^{2-}\)] the numerator of this expression is constant. To calculate the rate of reaction, merely divide [S\(_2\)O\(_3^{2-}\)] by 2 and then divide that number by the time for each trial.

Also calculate the concentration of iodide and peroxide in each of the reaction mixtures. It is important to recognize that the concentration of iodide in the reaction is NOT 0.060 M and the concentration of peroxide is NOT 0.040 M. You must do the dilution calculations to determine the concentration present in each of the 100 mL reaction mixtures.

In the table at the top of the next page, fill in the columns for [I\(^-\)], [H\(_2\)O\(_2\)], and reaction rate.
Table A. Uncatalyzed room temperature results.

<table>
<thead>
<tr>
<th>Trial</th>
<th>[I⁻], M</th>
<th>[H₂O₂], M</th>
<th>Reaction time, sec</th>
<th>Rate, M/sec</th>
<th>log Rate</th>
<th>log[I⁻]</th>
<th>log[H₂O₂]</th>
<th>Value of k_{obs}</th>
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When the concentration of hydrogen ion is held constant (as it was in the trials above), the rate law can be written as

\[ rate_{obs} = k_{obs}[H₂O₂]^m[I⁻]^n \]

We can determine the exponents in this rate law in several ways. However, one of the better methods is a graphical approach. If the equation above is expressed in log form we find:

\[ \log rate_{obs} = \log k_{obs} + m \log[H₂O₂] + n \log[I⁻] \]

In trials 1-3 the concentration of iodide was a constant and this equation simplifies to:

\[ \log rate_{obs} = \text{constant} + m \log[H₂O₂] \]

Likewise, in trials 3 - 5 the concentration of peroxide was a constant and the equation simplifies to:

\[ \log rate_{obs} = \text{constant} + n \log[I⁻] \]

Both of these are straight-line equations. The slope of each is equal to the reaction order for the reactant whose concentration was varied.

Calculate log Rate, log [I⁻], and log [H₂O₂] and record the results in the Table A. above.

**Prepare two graphs:** on one graph plot log Rate (y-axis) vs. log[H₂O₂] (x-axis) for trials 1 - 3 (the slope of this line is m) and on the second graph plot log Rate (y-axis) vs. log[I⁻] (x-axis) for trials 3 - 5 (the slope of this line is n). **Attach the graphs to your report.**

**Report your slopes with three significant figures in the following spaces.**
What is the order of this reaction with respect to H₂O₂ (m in the rate law)? __________
What is the order of this reaction with respect to I⁻ (n in the rate law)? __________
Calculation of \( k \) at room temperature *(include the units for \( k \))*:

Round the values of \( m \) and \( n \) to whole numbers and use the rates and concentrations listed in Table A to calculate \( k_{\text{obs}} \) from the following equation. List the results in Table A.

\[
k_{\text{obs}} = \frac{\text{rate}_{\text{obs}}}{[H_2O_2]^m[I^-]^n}
\]

Report the average value of \( k_{\text{obs}} \) here: ____________________

Note any trials that were excluded from the average here: ____________________

Unraveling the “Catalyzed” and Non-catalyzed Reaction Pathways

In trials 6 - 13 the concentration of iodide and peroxide was held constant. The concentration of iodide in the reaction is NOT 0.060 M nor is the concentration of peroxide 0.040 M. Do the dilution calculations to determine the concentrations present.

\[
[I^-] = \text{________}, \text{ M} \quad \quad [H_2O_2] = \text{________}, \text{ M}
\]

The variation in reaction rate in trials 6 - 13 was due to varying the [H\(^+\)]. Calculate the concentration of nitric acid in each reaction mixture. The concentration of nitric acid is NOT 0.50 M in each trial (remember to account for dilution)! Report these concentrations in Table B.

Now calculate the reaction rate and the value of \( k_{\text{obs}} \) using the same method employed for the trials in Table A. above (Note: use the same values for \( m \) and \( n \)). Report these values in Table B.

**Table B. Summary of results from Trials 6 - 13.**

<table>
<thead>
<tr>
<th>Trial</th>
<th>([H^+]), M</th>
<th>Reaction time, sec</th>
<th>Reaction Rate, M/sec</th>
<th>Value of ( k_{\text{obs}} )</th>
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Reaction temperature for trials 6 - 9: _____ °C

<table>
<thead>
<tr>
<th>Trial</th>
<th>([H^+]), M</th>
<th>Reaction time, sec</th>
<th>Reaction Rate, M/sec</th>
<th>Value of ( k_{\text{obs}} )</th>
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Reaction temperature for trials 10 - 13: ___~1°C
Earlier you determined a rate law for the reaction that has the form

\[ \text{rate}_{\text{obs}} = k_{\text{obs}}[H_2O_2][I^-] \]

Also, in the introductory information for this experiment it was stated that the total observed rate of reaction can be represented as the sum of the rates of the two predicted reaction pathways:

\[ \text{rate}_{\text{obs}} = k_{\text{non}}[H_2O_2][I^-] + k_{\text{cat}}[H_2O_2][I^-][H^+] \]

If you set these two equations equal to one another and divide by the common term \([H_2O_2][I^-]\), you find the following equation:

\[ k_{\text{obs}} = k_{\text{non}} + k_{\text{cat}}[H^+] \]

This equation has the form of a straight line. The y-intercept is equal to the rate constant for the non-catalytic pathway (\(k_{\text{non}}\)) and the slope is equal to the rate constant for the catalytic pathway (\(k_{\text{cat}}\)).

**Prepare two graphs:** on one graph plot \(k_{\text{obs}}\) (y-axis) vs. \([H^+]\) (x-axis) for trials 6 - 9 (the room temperature data) and on the second graph plot \(k_{\text{obs}}\) (y-axis) vs. \([H^+]\) (x-axis) for trials 10 - 13 (the low temperature data). **Attach the graphs to your report.**

Now we are almost done! Earlier in the discussion it was pointed out that the second step is rate-determining in the “catalyzed” mechanism and that \(k_{\text{cat}}\) is actually equal to the product of the equilibrium constant of the fast equilibria (\(K_1\)) and the rate constant of the second step (\(k_H\)). In other words:

\[ k_{\text{cat}} = K_1k_H \]

Acceptable literature values for \(K_1\) are \(2.0 \times 10^{-5}\) at 25°C and \(1.0 \times 10^{-5}\) at 1°C. Use these values and the slopes and intercepts from the appropriate graph (room or low T) to complete the following table. If your instructor indicates that it is desirable, you should use the van’t Hoff equation to calculate a value of \(K_1\) for your temperatures (using \(\Delta H = +17.6\) kJ) if they differed from 25°C and 1°C.

**Table C.** Variable Temperature values of k.

<table>
<thead>
<tr>
<th>Temp., Kelvin</th>
<th>y-intercept, (k_{\text{non}})</th>
<th>Slope, (k_{\text{cat}})</th>
<th>(K_1)</th>
<th>(k_H)</th>
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4
Show the calculation of activation energy, $E_a$, from the values of $k_{non}$ and $k_H$ using the appropriate Kelvin temperatures. Express the answers in kJ.

$E_a$ (non-catalytic): ________________  $E_a$ (catalytic): ________________

Answer the following (see the back of this sheet too!).

1. Give two examples in which the rate of a chemical reaction is important in daily life.

2. Why are mechanisms important?

3. Examine the numerical values for $k_{obs}$ (in the “non-catalyzed” trials), $k_{non}$, and $k_{cat}$ (all at room temperature). Discuss the meaning of the term “rate-determining” step as it pertains to the reaction studied. Be sure to include in your discussion the significance of the numerical values of $k$! (continue your answer on the back of this page)
4. Write the reactions for the non-catalyzed reaction mechanism and for the “catalyzed” reaction mechanism. **Discuss** the conditions under which the each of these mechanisms would be expected to account for forming most of the iodine produced by the reaction.

Support your assertions with calculations using the following OVERALL rate equation with appropriate values for $k_{\text{non}}$, and $k_{\text{cat}}$ at room temperature.

$$rate_{\text{obs}} = k_{\text{non}}[H_2O_2][I^-] + k_{\text{cat}}[H_2O_2][I^-][H^+]$$

Hint: first use concentrations from a non-catalyzed trial to calculate $rate_{\text{obs}}$ and then repeat the calculation of $rate_{\text{obs}}$ using concentrations from a catalyzed trial.

What percentage of $rate_{\text{obs}}$ is accounted for by each of the two reaction pathways in each case?