## Experiment B3: Chemical Kinetics

## Learning Outcomes

Upon completion of this lab, the student will be able to:

1) Measure the rate of a chemical reaction and determine the rate law.
2) Evaluate the effect of temperature on the rate of a chemical reaction and determine the activation energy.
3) Assess the role of a catalyst on the rate of a chemical reaction.

## Introduction

Chemical kinetics is the study of speed of chemical reactions. The rate law is a mathematical expression that indicates the relationship between the concentrations of the reactants and the rate of the reaction. The rate of a reaction may be expressed in two forms: 1) the change in concentration of products over time or 2) the change in concentration of reactants over time. Consider the following chemical reaction:

$$
\mathrm{aA}_{(\mathrm{aq})}+\mathrm{bB}_{(\mathrm{aq})} \rightarrow \mathrm{cC}_{(\mathrm{aq})}+\mathrm{dD}_{(\mathrm{aq})}
$$

Equation 1
In the above equation, $\mathrm{a}, \mathrm{b}, \mathrm{c}$, and d are stoichiometric coefficients of the reactants and products. The rate of the reaction can be expressed as follows:

$$
\text { Reaction Rate }=-\frac{1}{a} \frac{\Delta[A]}{\Delta t}=-\frac{1}{b} \frac{\Delta[B]}{\Delta t}=+\frac{1}{c} \frac{\Delta[C]}{\Delta t}=+\frac{1}{d} \frac{\Delta[D]}{\Delta t} \quad \text { Equation } 2
$$

In the expression for Reaction Rate, $\Delta t$ is a unit of time during which the changes in concentrations of the reactants or products are measured. The unit for Reaction Rate is therefore molarity per time and is $\mathrm{Ms}^{-1}$ or $\mathrm{Mmin}^{-1}$.

The rate law for this reaction is written as:

$$
\text { Rate Law: Reaction Rate }=k \times[A]^{x} \times[B]^{y}
$$

In the Rate Law expression, " $k$ " is referred to as the rate constant, a proportionality constant. " $x$ " is referred to as the "order" of the reaction with respect to the reactant A and " $y$ " is referred to as the "order" of the reaction with respect to the reactant B.

The overall order of the reaction is given by $x+y$.
Most chemical reactions are zero order, first order, or second order. The order of a chemical reaction and the order with respect to each individual reactant, can only be determined experimentally and is unrelated to the stoichiometric coefficients of the balanced chemical equation.

Therefore, for the reaction in Equation 1, "x" and " $y$ " are unrelated to " $a$ " and " $b$ " and " $x$ " and " $y$ " can only be determined experimentally. If the values of " $x$ " and/or " $y$ " happen to be the same as " $a$ " and/or " $b$ ", it is purely a coincidence.

The order of a reaction is always an integer or half-integer. Values of reaction order larger than three are almost impossible due to the extremely low probability collisions that would be necessary to result in such an order.

If the experimental value of " $x$ " in Equation 3 is 0 , then it implies that the rate of the reaction is independent of the concentration of $A$. If the experimental value of " $x$ " in Equation 3 is 1 , then it implies that the rate of the reaction is proportional to the first power of the concentration of $A$.

An important piece of information obtained from the Rate Law is the unit of the rate constant " $k$ ". The unit of the rate constant depends on the order of the reaction. For instance, suppose for a particular reaction $x=1$ and $y=2$, the unit of " $k$ " may be derived by dimensional analysis as follows:

$$
\begin{aligned}
& \text { Reaction Rate }=k \times[A]^{1} \times[\mathrm{B}]^{2} \\
& k=\frac{\text { Reaction Rate }}{[A]^{1} \times[B]^{2}} \\
& \text { Unit of } \mathrm{k}=\frac{M s^{-1}}{M^{1} M^{2}}=M^{-2} s^{-1}
\end{aligned}
$$

## Experimental Determination of Order of a Reaction

In order to determine the order of a reaction with respect to each reagent, the reaction rate must be determined using various concentrations of the reactants, A and $B$. The experiment must be designed such that the rate of the reaction is measured by varying the concentration of A while keeping the concentration B a constant, and vice versa.

Consider the following data:

| Experiment | $[\mathrm{A}], \mathrm{M}$ | $[\mathrm{B}], \mathrm{M}$ | Rate, $\mathrm{Ms}^{-1}$ |
| :--- | :--- | :--- | :--- |
| 1 | 0.1 | 0.1 | 0.1 |
| 2 | 0.2 | 0.1 | 0.2 |
| 3 | 0.1 | 0.2 | 0.4 |

Equation 3 gives the rate law expression: Reaction Rate $=k \times[A]^{x} \times[B]^{y}$.
Substituting the experimental data into the expression for the rate law results in the following three equations:

$$
0.1 \mathrm{Ms}^{-1}=\mathrm{k}[0.1]^{\mathrm{x}}[0.1]^{\mathrm{y}}
$$

Equation 4
Equation 5
Equation 6

To solve for " $x$ ", divide Equation 5 by Equation 4:

$$
\begin{aligned}
\frac{0.2 M s^{-1}}{0.1 M s^{-1}} & =\frac{k[0.2]^{x}[0.1]^{y}}{k[0.1]^{x}[0.1]^{y}} \\
2 & =2^{x} \\
x & =1
\end{aligned}
$$

To solve for " $y$ " divide Equation 6 by Equation 4:

$$
\begin{aligned}
\frac{0.4 M s^{-1}}{0.1 M s^{-1}} & =\frac{k[0.1]^{x}[0.2]^{y}}{k[0.1]^{x}[0.1]^{y}} \\
4 & =2^{y} \\
y & =2
\end{aligned}
$$

Therefore, based on the experimental data, the order of the reaction with respect to $A$ is one and the order of the reaction with respect to $B$ is two.

NOTE 1: Using the data provided above, the values of " $x$ " and " $y$ " determined were exact integers. However, when using laboratory experimental data this will likely not be the case. Since reaction orders are necessarily integer or half-integer values, the values of " $x$ " and " $y$ " must be rounded appropriately before proceeding further with the calculations.

NOTE 2: The above data set was obtained from the minimum number of experiments need to solve the rate law expression mathematically. However, in the laboratory more number of experiments must be conducted to account for experimental errors.

## Determination of Rate Constant and Rate Law

In order to determine the Rate Law, the exact value of the rate constant is also required.

Since the order of the reaction is known, the rate constant can be determined by substituting the values of " $x$ " and " $y$ " in Equations 4, 5, and 6 and solving for " $k$ " from each equation and then obtaining the average value of " $k$ ".

Equation 4 is rewritten as: $0.1 \mathrm{Ms}^{-1}=\mathrm{k}[0.1]^{1}[0.1]^{2} \quad$ Therefore $\mathrm{k}=100 \mathrm{M}^{-2} \mathrm{~s}^{-1}$
Equation 5 is rewritten as: $0.2 \mathrm{Ms}^{-1}=\mathrm{k}[0.2]^{1}[0.1]^{2} \quad$ Therefore $\mathrm{k}=100 \mathrm{M}^{-2} \mathrm{~s}^{-1}$
Equation 6 is rewritten as: $0.4 \mathrm{Ms}^{-1}=\mathrm{k}[0.1]^{1}[0.2]^{2} \quad$ Therefore $\mathrm{k}=100 \mathrm{M}^{-2} \mathrm{~s}^{-1}$
The average value of the rate constant $k=100 \mathrm{M}^{-2} \mathrm{~s}^{-1}$
Therefore the Rate Law is: Reaction Rate $=100 \mathrm{M}^{-2} \mathrm{~s}^{-1}[\mathrm{~A}]^{1}[\mathrm{~B}]^{2}$

## Effect of Temperature on the Rate of a Reaction

When reactions are conducted at elevated temperatures, the number of collisions of the reacting molecules increases due to the fact that the kinetic energy of the reacting molecules has increased. As a result, the rate of the reaction increases when the temperature is increased.

The effect of temperature on the rate of a reaction is given by the Arrhenius equation.

$$
\begin{equation*}
k=A e^{-\frac{E_{a}}{R T}} \tag{Equation 7}
\end{equation*}
$$

In Equation 7:
k is the rate constant
A is the Arrhenius constant
$\mathrm{E}_{\mathrm{a}}$ is the activation energy of the reaction
$R$ is the universal gas constant ( $8.314 \mathrm{~J} / \mathrm{molK}$ )
T is the absolute temperature
The activation energy, $\mathrm{E}_{\mathrm{a}}$, can be determined graphically by measuring the rate constant, k , and different temperatures. The mathematical manipulation of Equation 7 leading to the determination of the activation energy is shown below.

$$
\begin{aligned}
k & =A e^{-\frac{E_{a}}{R T}} \\
\ln k & =\ln A-\frac{E_{a}}{R T} \\
\ln k & =\left(-\frac{E_{a}}{R}\right) \frac{1}{T}+\ln A
\end{aligned}
$$

Therefore, a plot of the natural logarithm of the rate constant (ln k on the y-axis) vs. reciprocal of the absolute temperature (1/T) should yield a straight line whose
slope will be $-\frac{E_{a}}{R}$. Since, R is the universal gas constant whose value is known ( $8.314 \mathrm{~J} / \mathrm{mol} . \mathrm{K}$ ), the activation energy $\mathrm{E}_{\mathrm{a}}$ can be calculated.

## Effect of Catalyst on the Rate of a Reaction

Catalysts are chemical substances that increase the rate of a chemical reaction. A catalyst is not chemically modified as a result of the reaction and is recovered completely at the end of the reaction. Only a small amount of the catalyst is required for the rate enhancement. Metals and concentrated acids are examples of some common catalysts.

The rate of a reaction depends on the activation energy of the reaction. The activation energy may be thought of as an energy barrier that reactants must cross prior to being transformed into products. Consider the exothermic transformation of reactant A to product B, in a single mechanistic step, whose energy diagram is shown in Figure 1.


Reaction Progress

Figure 1
As shown in Figure 1, the transformation of $A$ to $B$ is a one-step mechanism that passes through a single transition state with an activation energy of $\mathrm{E}_{\mathrm{a}}$.

The catalyst alters the reaction mechanism. The mechanism of the reaction in the presence of a catalyst, say X, will have more than a single step, but with lower activation energy. A possible reaction mechanism is shown below.

$$
\begin{aligned}
A+C & \Leftrightarrow A C \\
A C & \rightarrow B+C
\end{aligned}
$$

In the reaction mechanism shown above, the reactant A, first combines with the catalyst C, to form a complex AC. The complex AC in the second step forms the product $B$, and regenerates the catalyst in its original form. In this scheme, $A C$ is known as a Reaction Intermediate.

NOTE: The above scheme is just one possible mechanistic scheme in the presence of a catalyst. Different catalysts will work differently and result in a variety of possible mechanisms. The only constant feature of all these possibilities is that there will be more number of mechanistic steps compared to when no catalyst is present.

The energy diagram for the transformation of A to B in the presence of the catalyst under the scheme discussed above is shown in Figure 2 (dashed lines). The plot for the transformation of A to B in the absence of the catalyst is also included in Figure 2 for comparison.


Reaction Progress

Figure 2
Due to the fact that the catalyst has altered the reaction mechanism such that there are now two steps in the mechanism, there are now two transition states as well (Transition State 1 and Transition State 2). The energy difference between Transition State 1 and the reactant A is the activation energy, $\mathrm{Eac}_{\mathrm{a}}$, in the presence of the catalyst.

By providing an alternate path for the reaction, the catalyst, like high temperature, also increases the number of collisions of the reacting molecules. As a result the rate constant $k$, for the reaction is also altered in the presence of the catalyst. The effect of the catalyst on the rate constant of a reaction will be explored in this experiment.

## Experimental Design

The kinetics of the reaction between iodide ( $\mathrm{I}^{-}$) and peroxydisulfate ( $\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}$ ) will be explored in this experiment. The reaction is also referred to as the "Iodine Clock Reaction". The chemical reaction between these two substances is shown in Equation 8 below.

$$
3 \mathrm{I}^{-}(\mathrm{aq})+\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}(\mathrm{aq}) \Leftrightarrow \mathrm{I}_{3}^{-}\left(\mathrm{aq)}+2 \mathrm{SO}_{4}{ }^{2-}(\mathrm{aq})\right.
$$

Equation 8
Both the reactants in Equation 8 are colorless aqueous solutions. In order to measure the rate of the reaction, further manipulations are necessary.

A fixed amount of thiosulfate, $\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}$ and starch are added to the reaction mixture. The thiosulfate, reacts with the triiodide ( $\mathrm{I}_{3}{ }^{-}$) produced in Equation 8 according to the following chemical reaction.

$$
\begin{equation*}
\mathrm{I}_{3}^{-}{ }_{(\mathrm{aq})}+2 \mathrm{~S}_{2} \mathrm{O}_{3}{ }^{2-}{ }_{(\mathrm{aq})} \rightarrow 3 \mathrm{I}^{-}(\mathrm{aq})+\mathrm{S}_{4} \mathrm{O}_{6}{ }^{2-}(\mathrm{aq}) \tag{Equation 9}
\end{equation*}
$$

Once all the thiosulfate, $\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}$, is consumed, the chemical reaction shown in Equation 9 will stop. At this point, the triiodide, $\mathrm{I}_{3}{ }^{-}$will combine with the starch and form a complex that is dark blue/purple in color.

$$
\begin{equation*}
\mathrm{I}_{3}{ }^{-}(\mathrm{aq})+\text { starch } \rightarrow \mathrm{I}_{3}-\text {-starch } \tag{Equation 10}
\end{equation*}
$$

The rate of a reaction may be measured by two different methods:

1. The amount of time it takes for a certain amount of reactant to be consumed.
2. The amount of time it takes for a certain amount of product to be formed.

In this experiment, the amount of time taken for a fixed amount of one of the products, $\mathrm{I}_{3}{ }^{-}$, to form is measured indirectly. Due to the fact that a constant amount of thiosulfate, $\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}$, is added to all the reactions, each reaction is then carried out until a constant amount of $\mathrm{I}_{3}{ }^{-}$is formed. As soon as this amount of $\mathrm{I}_{3}{ }^{-}$is formed, all the thiosulfate, $\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}$, is consumed (as per Equation 9), and the $\mathrm{I}_{3}{ }^{-}$formed thereafter forms a complex with the starch (as per Equation 10) and gives the reaction mixture the dark blue/purple color.

Therefore, by measuring the time it takes for the appearance of the dark blue/purple color, the time it takes for a fixed amount of $\mathrm{I}_{3}-$ to form is being measured.

The molarity of the thiosulfate and the volume of thiosulfate used in this experiment are respectively, 0.012 M and 0.20 mL . The total volume of the reaction mixture is 1.9 mL . According to Equation 9,1 mole of $\mathrm{I}_{3}^{-}$reacts with 2 moles of $\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}$.

Therefore the molarity of $\mathrm{I}_{3}-$ that will be formed to determine the reaction rate is given by:

1. Moles of thiosulfate $=$ Molarity of $\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-} \times$ Volume of $\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}$

$$
\begin{aligned}
& =0.012 \mathrm{M} \times 0.20 \times 10^{-3} \mathrm{~L} \\
& =0.0000024
\end{aligned}
$$

2. Moles of $\mathrm{I}_{3}{ }^{-} \quad=0.0000024{\text { moles } \mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-} \times \frac{1 \mathrm{~mole}_{3}{ }^{-}}{2 \mathrm{moles}_{2} \mathrm{O}_{3}{ }^{2-}}}^{2}$
$=0.0000012$ moles $\mathrm{I}_{3}{ }^{-}$
3. Molarity of $\mathrm{I}_{3}{ }^{-}=\frac{0.0000012 \mathrm{moles}}{0.0019 \mathrm{~L}}=0.00063 \frac{\mathrm{moles}}{\mathrm{L}}$

The rate of the reaction can then be calculated as: $\frac{\Delta\left[I_{3}^{-}\right]}{\Delta t}$ where $\Delta \mathrm{t}$ is the time it takes for the appearance of the dark blue/purple color.

Part 1: Determination of order of the reaction with respect to $I^{-}$: The concentration of $I^{-}$in the reaction mixture will be varied while keeping all other reagents at a constant amount. The rate of the reaction will be measured according to methods described above.

Part 2: Determination of order of the reaction with respect to $\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}$ : The concentration of $\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}$ in the reaction mixture will be varied while keeping all other reagents at a constant amount. The rate of the reaction will be measured according to methods described above.

Part 3: Determination of activation energy of the reaction: The reaction will be conducted at four different temperatures. The rate of the reaction will be measured according to methods described above at each temperature. The activation energy will be determined graphically.

Part 4: Study the effect of a catalyst on the rate of the reaction: The reaction will be carried out in the presence and absence of a catalyst. The rate of the reaction will be measured according to methods described under each condition. The catalyst to be used for this reaction is copper (II) nitrate.

## Reagents and Supplies

$0.2 \%$ starch, $0.012 \mathrm{M} \mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}, 0.20 \mathrm{M} \mathrm{KI}, 0.20 \mathrm{M} \mathrm{KNO}_{3}, 0.20 \mathrm{M}\left(\mathrm{NH}_{4}\right)_{2} \mathrm{~S}_{2} \mathrm{O}_{8}, 0.20 \mathrm{M}$ $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}, 0.0020 \mathrm{M} \mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2}$

Hot plate, thermometer, stopwatch
(See posted Material Safety Data Sheets)
NOTE: Even though the reaction mixture only consists of $0.2 \%$ starch, 0.012 M $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}, 0.20 \mathrm{M} \mathrm{KI}$, and $0.20 \mathrm{M}\left(\mathrm{NH}_{4}\right)_{2} \mathrm{~S}_{2} \mathrm{O}_{8}$, the following two reagents- 0.20 M $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ and $0.20 \mathrm{M} \mathrm{KNO}_{3}$ are also needed in order to maintain a constant ionic strength in all the reaction mixtures.

## Procedure

## Part 1: DETERMINATION OF ORDER OF THE REACTION WITH RESPECT TO I-

1. Obtain four test tubes and label them as $1 \mathrm{~A}, 2 \mathrm{~A}, 3 \mathrm{~A}$, and 4 A .
2. Obtain four test tubes and label them as $1 \mathrm{~B}, 2 \mathrm{~B}, 3 \mathrm{~B}$, and 4 B .
3. Add the following volumes of the indicated reagents to test tubes labeled $1 \mathrm{~A}, 2 \mathrm{~A}$, 3 A , and 4 A (All volumes are in mL ).

| Reaction | Test <br> Tube | $\mathbf{0 . 2}$ \% <br> Starch | $\mathbf{0 . 0 1 2} \mathbf{~ M}$ <br> $\mathbf{N a}_{2} \mathbf{S}_{\mathbf{2}} \mathbf{O}_{\mathbf{3}}$ | $\mathbf{0 . 2 0} \mathbf{M}$ <br> KI | $\mathbf{0 . 2 0} \mathbf{M}$ <br> $\mathbf{K N O}_{\mathbf{3}}$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathbf{1}$ | 1 A | 0.10 | 0.20 | 0.80 | 0.00 |
| $\mathbf{2}$ | 2 A | 0.10 | 0.20 | 0.40 | 0.40 |
| $\mathbf{3}$ | 3 A | 0.10 | 0.20 | 0.20 | 0.60 |
| $\mathbf{4}$ | 4 A | 0.10 | 0.20 | 0.10 | 0.70 |

4. Add the following volumes of the indicated reagents to test tubes labeled 1B, 2B, 3 B , and 4B (All volumes are in mL ).

| Reaction | Test <br> Tube | $\mathbf{0 . 2 0} \mathbf{M}$ <br> $(\mathbf{N H})_{2} \mathbf{S}_{\mathbf{2}} \mathbf{O}_{\mathbf{8}}$ | $\mathbf{0 . 2 0 \mathrm { M }}$ <br> $\left(\mathbf{N H}_{\mathbf{4}} \mathbf{)}_{\mathbf{2}} \mathbf{S O}_{\mathbf{4}}\right.$ |
| :--- | :--- | :--- | :--- |
| $\mathbf{1}$ | 1 B | 0.40 | 0.40 |
| $\mathbf{2}$ | 2 B | 0.40 | 0.40 |
| $\mathbf{3}$ | 3 B | 0.40 | 0.40 |
| $\mathbf{4}$ | 4 B | 0.40 | 0.40 |

5. Prepare to start the stopwatch to record the time of the reaction. Press "start" as soon as the reagents have been combined as described below.
6. Combine contents of test tube 1 A and 1 B . Start the stopwatch. Thoroughly mix the contents of the combined solution by transferring it back and forth between the two test tubes.
7. When the dark blue/purple color forms, press the "stop" button on the stopwatch and the record the time in seconds in the data table.
8. Repeat steps 6 and 7 with each of the other pairs of test tubes (combine 2 A with $2 \mathrm{~B}, 3 \mathrm{~A}$ with 3 B , and 4 A with 4 B ).
9. Empty the reaction mixtures into a large beaker labeled as "waste". Empty the contents of the waste into a waste disposal container provided by the instructor.
10. Perform a second trial of each reaction ensuring that the times are within $10 \%$ of each other.

## PART 2: DETERMINATION OF ORDER OF THE REACTION WITH RESPECT TO $\underline{S}_{2} \underline{O}_{\underline{8}} \underline{\underline{2}}$

1. Obtain four test tubes and label them as $5 \mathrm{~A}, 6 \mathrm{~A}, 7 \mathrm{~A}$, and 8 A .
2. Obtain four test tubes and label them as 5B, 6B, 7B, and 8B.
3. Add the following volumes of the indicated reagents to test tubes labeled $5 \mathrm{~A}, 6 \mathrm{~A}$, 7 A , and 8 A (All volumes are in mL ).

| Reaction | Test <br> Tube | $\mathbf{0 . 2}$ \% <br> Starch | $\mathbf{0 . 0 1 2} \mathbf{~ M}$ <br> $\mathbf{N a}_{2} \mathbf{S}_{\mathbf{2}} \mathbf{O}_{\mathbf{3}}$ | $\mathbf{0 . 2 0} \mathbf{~ M}$ <br> KI | $\mathbf{0 . 2 0} \mathbf{~ M}$ <br> $\mathbf{K N O}_{\mathbf{3}}$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathbf{5}$ | 5 A | 0.10 | 0.20 | 0.40 | 0.40 |
| $\mathbf{6}$ | 6 A | 0.10 | 0.20 | 0.40 | 0.40 |
| $\mathbf{7}$ | 7 A | 0.10 | 0.20 | 0.40 | 0.40 |
| $\mathbf{8}$ | 8 A | 0.10 | 0.20 | 0.40 | 0.40 |

4. Add the following volumes of the indicated reagents to test tubes labeled $5 B, 6 B$, 7B, and 8B (All volumes are in mL ).

| Reaction | Test <br> Tube | $\mathbf{0 . 2 0} \mathbf{M}$ <br> $(\mathbf{N H})_{2} \mathbf{S}_{\mathbf{2}} \mathbf{O}_{\mathbf{8}}$ | $\mathbf{0 . 2 0 \mathbf { M }}$ <br> $\left(\mathbf{N H}_{\mathbf{4}}\right)_{2} \mathbf{S O}_{\mathbf{4}}$ |
| :--- | :--- | :--- | :--- |
| $\mathbf{5}$ | 5 B | 0.80 | 0.00 |
| $\mathbf{6}$ | 6 B | 0.40 | 0.40 |
| 7 | 7 B | 0.20 | 0.60 |
| $\mathbf{8}$ | 8 B | 0.10 | 0.70 |

5. Prepare to start the stopwatch to record the time of the reaction. Press "start" as soon as the reagents have been combined as described below.
6. Combine contents of test tube 5A and 5B. Start the stopwatch. Thoroughly mix the contents of the combined solution by transferring it back and forth between the two test tubes.
7. When the dark blue/purple color forms, press the "stop" button on the stopwatch and the record the time in seconds in the data table.
8. Repeat steps 6 and 7 with each of the other pairs of test tubes (combine 6 A with $6 \mathrm{~B}, 7 \mathrm{~A}$ with 7 B , and 8 A with 8 B ).
9. Empty the reaction mixtures into a large beaker labeled as "waste". Empty the contents of the waste into a waste disposal container provided by the instructor.
10. Perform a second trial of each reaction ensuring that the times are within $10 \%$ of each other.

## PART 3: DETERMINATION OF ACTIVATION ENERGY OF THE REACTION

1. Obtain four test tubes and label them as $9 \mathrm{~A}, 10 \mathrm{~A}, 11 \mathrm{~A}$, and 12A.
2. Obtain four test tubes and label them as $9 \mathrm{~B}, 10 \mathrm{~B}, 11 \mathrm{~B}$, and 12 B .
3. Add the following volumes of the indicated reagents to test tubes labeled 9A, $10 \mathrm{~A}, 11 \mathrm{~A}$, and 12 A (All volumes are in mL ).

| Reaction | Test Tube | $\mathbf{0 . 2} \%$ <br> Starch | $\mathbf{0 . 0 1 2} \mathbf{~ M}$ <br> $\mathbf{N a}_{2} \mathbf{S}_{\mathbf{2}} \mathbf{O}_{\mathbf{3}}$ | $\mathbf{0 . 2 0} \mathbf{M}$ <br> KI | $\mathbf{0 . 2 0 ~ M}$ <br> $\mathbf{K N O}_{\mathbf{3}}$ | Approximate <br> temperature |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 9 | 9 A | 0.10 | 0.20 | 0.40 | 0.40 | $10^{\circ} \mathrm{C}$ |
| 10 | 10 A | 0.10 | 0.20 | 0.40 | 0.40 | $20^{\circ} \mathrm{C}$ |
| 11 | 11 A | 0.10 | 0.20 | 0.40 | 0.40 | $30^{\circ} \mathrm{C}$ |
| 12 | 12 A | 0.10 | 0.20 | 0.40 | 0.40 | $40^{\circ} \mathrm{C}$ |

4. Add the following volumes of the indicated reagents to test tubes labeled 9B, 10B, 11B, and 12B (All volumes are in mL ).

| Reaction | Test Tube | $\mathbf{0 . 2 0} \mathbf{M}$ <br> $(\mathbf{N H})_{\mathbf{2}} \mathbf{S}_{\mathbf{2}} \mathbf{O}_{\mathbf{8}}$ | $\mathbf{0 . 2 0 ~ M}$ <br> $\left(\mathbf{N H}_{4}\right)_{\mathbf{2}} \mathbf{S O}_{\mathbf{4}}$ | Approximate <br> temperature |
| :--- | :--- | :--- | :--- | :--- |
| 9 | 9 B | 0.20 | 0.60 | $10^{\circ} \mathrm{C}$ |
| 10 | 10 B | 0.20 | 0.60 | $20^{\circ} \mathrm{C}$ |
| 11 | 11 B | 0.20 | 0.60 | $30^{\circ} \mathrm{C}$ |
| 12 | 12 B | 0.20 | 0.60 | $40^{\circ} \mathrm{C}$ |

5. Prepare an ice bath to a temperature of around $10^{\circ} \mathrm{C}$.
6. Prepare to start the stopwatch to record the time of the reaction. Press "start" as soon as the reagents have been combined as described below.
7. Combine contents of test tube 9A and 9B. Start the stopwatch. Insert the reaction mixture into the ice bath and constantly mix the contents.
8. When the dark blue/purple color forms, press the "stop" button on the stopwatch and the record the time in seconds in the data table. Record the temperature of the reaction mixture.
9. Combine test tubes 10 A and 10 B at room temperature and record the time for the reaction and the temperature of the reaction mixture.
10. Prepare a hot water bath to a temperature of around $30^{\circ} \mathrm{C}$.
11. Combine contents of test tube 11A and 11B. Start the stopwatch. Insert the reaction mixture into the hot water bath and constantly mix the contents.
12. When the dark blue/purple color forms, press the "stop" button on the stopwatch and the record the time in seconds in the data table. Record the temperature of the reaction mixture.
13. Prepare a hot water bath to a temperature of around $40^{\circ} \mathrm{C}$.
14. Combine contents of test tube 12A and 12B. Start the stopwatch. Insert the reaction mixture into the hot water bath and constantly mix the contents.
15. When the dark blue/purple color forms, press the "stop" button on the stopwatch and the record the time in seconds in the data table. Record the temperature of the reaction mixture.
16. Empty the reaction mixtures into a large beaker labeled as "waste". Empty the contents of the waste into a waste disposal container provided by the instructor.
17. Perform a second trial of each reaction ensuring that the times are within $10 \%$ of each other and the temperatures are the same.

## PART 4: STUDY THE EFFECT OF A CATALYST ON THE RATE OF THE REACTION

1. Obtain four test tubes and label them as $13 \mathrm{~A}, 14 \mathrm{~A}, 15 \mathrm{~A}$, and 16 A .
2. Obtain four test tubes and label them as 13B, 14B, 15B, and 16B.
3. Add the following volumes of the indicated reagents to test tubes labeled $1 \mathrm{~A}, 2 \mathrm{~A}$, 3 A , and 4 A (All volumes are in mL ).

| Reaction | Test <br> Tube | $\mathbf{0 . 2}$ \% <br> Starch | $\mathbf{0 . 0 1 2} \mathbf{~ M}$ <br> $\mathbf{N a}_{2} \mathbf{S}_{\mathbf{2}} \mathbf{O}_{\mathbf{3}}$ | $\mathbf{0 . 2 0} \mathbf{M}$ <br> KI | $\mathbf{0 . 2 0} \mathbf{~ M}$ <br> KNO $_{3}$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathbf{1 3}$ | 13 A | 0.10 | 0.20 | 0.40 | 0.40 |
| $\mathbf{1 4}$ | 14 A | 0.10 | 0.20 | 0.40 | 0.40 |
| $\mathbf{1 5}$ | 15 A | 0.10 | 0.20 | 0.40 | 0.40 |
| $\mathbf{1 6}$ | 16 A | 0.10 | 0.20 | 0.40 | 0.40 |

4. Add the following volumes of the indicated reagents to test tubes labeled $1 \mathrm{~B}, 2 \mathrm{~B}$, 3B, and 4B (All volumes are in mL ).

| Reaction | Test <br> Tube | $\mathbf{0 . 2 0 ~ M}$ <br> $(\mathbf{N H})_{2} \mathbf{S}_{\mathbf{2}} \mathbf{O}_{\mathbf{8}}$ | $\mathbf{0 . 2 0 ~ M}$ <br> $\left(\mathbf{N H}_{4}\right)_{2} \mathbf{S O}_{\mathbf{4}}$ | $\mathbf{0 . 0 0 2 0} \mathbf{M}$ <br> $\mathbf{C u}\left(\mathbf{N O}_{3}\right)_{2}$ |
| :--- | :--- | :--- | :--- | :--- |
| $\mathbf{1 3}$ | 13 B | 0.80 | 0.00 | 1 drop |
| $\mathbf{1 4}$ | 14 B | 0.40 | 0.40 | 1 drop |
| $\mathbf{1 5}$ | 15 B | 0.20 | 0.60 | 1 drop |
| $\mathbf{1 6}$ | 16 B | 0.10 | 0.70 | 1 drop |

5. Prepare to start the stopwatch to record the time of the reaction. Press "start" as soon as the reagents have been combined as described below.
6. Combine contents of test tube 13A and 13B. Start the stopwatch. Thoroughly mix the contents of the combined solution by transferring it back and forth between the two test tubes.
7. When the dark blue/purple color forms, press the "stop" button on the stopwatch and the record the time in seconds in the data table.
8. Repeat steps 6 and 7 with each of the other pairs of test tubes (combine 14A with 14B, 15A with 15B, and 16A with 16B).
9. Empty the reaction mixtures into a large beaker labeled as "waste". Empty the contents of the waste into a waste disposal container provided by the instructor.
10. Perform a second trial of each reaction ensuring that the times are within $10 \%$ of each other.

## Data Table

PART 1: DETERMINATION OF ORDER OF THE REACTION WITH RESPECT TO I-

| Reaction | Time in seconds (Trial 1) | Time in seconds (Trial 2) |
| :---: | :--- | :--- |
| 1 |  |  |
| 2 |  |  |
| 3 |  |  |
| 4 |  |  |

PART 2: DETERMINATION OF ORDER OF THE REACTION WITH RESPECT TO $\mathrm{S}_{2} \underline{\mathrm{O}}_{8} \mathbf{8}^{2-}$

| Reaction | Time in seconds (Trial 1) | Time in seconds (Trial 2) |
| :---: | :--- | :--- |
| 5 |  |  |
| 6 |  |  |
| 7 |  |  |
| 8 |  |  |

PART 3: DETERMINATION OF ACTIVATION ENERGY OF THE REACTION

| Reaction | Time in seconds <br> (Trial 1) | Temperature, ${ }^{\circ} \mathrm{C}$ <br> (Trial 1) | Time in seconds <br> (Trial 2) | Temperature, ${ }^{\circ} \mathrm{C}$ <br> (Trial 2) |
| :---: | :--- | :--- | :--- | :--- |
| 9 |  |  |  |  |
| 10 |  |  |  |  |
| 11 |  |  |  |  |
| 12 |  |  |  |  |

## PART 4: STUDY THE EFFECT OF A CATALYST ON THE RATE OF THE REACTION

| Reaction | Time in seconds (Trial 1) | Time in seconds (Trial 2) |
| :---: | :--- | :--- |
| 13 |  |  |
| 14 |  |  |
| 15 |  |  |
| 16 |  |  |

## Data Analysis

## PART 1: DETERMINATION OF ORDER OF THE REACTION WITH RESPECT TO I-

1. Calculate the molarity of the $\mathrm{I}^{-}$in the reaction mixture for each reaction.

Example:
Reaction 1- $\mathrm{M}_{1}=0.20 \mathrm{M} \quad \mathrm{V}_{1}=0.80 \mathrm{~mL} \quad \mathrm{M}_{2}=? \quad \mathrm{~V}_{2}=1.9 \mathrm{~mL}$

$$
\begin{aligned}
& M_{1} V_{1}=M_{2} V_{2} \\
& M_{2}=\frac{0.20 \mathrm{M} \times 0.80 \mathrm{~mL}}{1.9 \mathrm{~mL}}=0.084 \mathrm{M}
\end{aligned}
$$

## Reaction 2-

## Reaction 3-

Reaction 4-
2. Calculate the molarity of the $\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}$ in the reaction mixture for each reaction.

Reactions 1-4
3. Calculate the average reaction time in seconds for each of the reactions.
4. Calculate the average rate of reaction for each of the reactions.

Reaction Rate $=\frac{\Delta\left[I_{3}^{-}\right]}{\Delta t}=\frac{0.00063 \mathrm{M}}{\Delta t}$
5. Enter the information from steps 1 through 4 in the following table.

| Reaction | $\left[\mathbf{I}^{-}\right], \mathbf{M}$ | $\left[\mathbf{S}_{\mathbf{2}} \mathbf{O}_{8}{ }^{2-}\right], \mathbf{M}$ | Average time (s) | Reaction Rate $\mathbf{M s}^{\mathbf{- 1}}$ |
| :---: | :--- | :--- | :--- | :--- |
| 1 | 0.084 |  |  |  |
| 2 |  |  |  |  |
| 3 |  |  |  |  |
| 4 |  |  |  |  |

6. Rate Law: Reaction Rate $=\mathrm{k} \times\left[\mathrm{I}^{-}\right]^{\mathrm{x}} \times\left[\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}\right]^{\mathrm{y}}$. Substitute the information for Reactions 1-4 from above table into the rate law expression and solve for " $x$ ".

Reaction 1

Reaction 2

Reaction 3

Reaction 4

## PART 2: DETERMINATION OF ORDER OF THE REACTION WITH RESPECT TO $\underline{S}_{2} \underline{O}_{\underline{8}} \underline{\underline{2}}$

1. Calculate the molarity of the $\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}$ in the reaction mixture for each reaction. Example:

Reaction 5- $\mathrm{M}_{1}=0.20 \mathrm{M} \quad \mathrm{V}_{1}=0.80 \mathrm{~mL} \quad \mathrm{M}_{2}=? \quad \mathrm{~V}_{2}=1.9 \mathrm{~mL}$

$$
\begin{aligned}
& M_{1} V_{1}=M_{2} V_{2} \\
& M_{2}=\frac{0.20 \mathrm{M} \times 0.80 \mathrm{~mL}}{1.9 \mathrm{~mL}}=0.084 \mathrm{M}
\end{aligned}
$$

Reaction 6-

Reaction 7-

Reaction 8-
2. Calculate the molarity of the $\mathrm{I}^{-}$in the reaction mixture for each reaction.

Reactions 5-8
3. Calculate the average reaction time in seconds for each of the reactions.
4. Calculate the average rate of reaction for each of the reactions.

Reaction Rate $=\frac{\Delta\left[I_{3}^{-}\right]}{\Delta t}=\frac{0.00063 M}{\Delta t}$
5. Enter the information from steps 1 through 4 in the following table.

| Reaction | $\left[\mathbf{I}^{-}\right], \mathbf{M}$ | $\left[\mathbf{S}_{\mathbf{2}} \mathbf{O}_{\mathbf{8}}{ }^{2}\right], \mathbf{M}$ | Average time (s) | Reaction Rate Ms ${ }^{\mathbf{1}}$ |
| :---: | :--- | :--- | :--- | :--- |
| 5 |  | 0.084 |  |  |
| 6 |  |  |  |  |
| 7 |  |  |  |  |
| 8 |  |  |  |  |

6. Rate Law: Reaction Rate $=\mathrm{k} \times\left[\mathrm{I}^{-}\right]^{\mathrm{x}} \times\left[\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}\right]^{\mathrm{y}}$. Substitute the information for Reactions 5-8 from above table into the rate law expression and solve for " $y$ ".

Reaction 5

Reaction 6

Reaction 7

Reaction 8

The order of the reaction with respect to $\mathrm{S}_{2} \mathrm{O}_{8^{2-}}{ }^{2-}$

## Determining the Rate Law

1. Rate Law: Reaction Rate $=\mathrm{k} \times\left[\mathrm{I}^{-}\right]^{\mathrm{x}} \times\left[\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}\right]^{\mathrm{y}}$. Substitute the values of Reaction Rate, "x", "y", [ $\left.I^{-}\right]$, and $\left[\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}\right]$ for reactions 1-8 and solve for the rate constant.

$$
k=\frac{\text { Reaction Rate }}{\left[I^{-}\right]^{x}\left[S_{2} O_{8}{ }^{2-}\right]^{Y \prime}}
$$

Equation 11

| Reaction | $\left[\mathbf{I}^{-}\right], \mathbf{M}$ | $\left[\mathbf{S}_{\mathbf{2}} \mathbf{O}_{\mathbf{8}}{ }^{\mathbf{-}}\right], \mathbf{M}$ | Reaction Rate $\mathbf{M s}^{\mathbf{- 1}}$ | Rate constant "k" |
| :---: | :--- | :--- | :--- | :--- |
| 1 | 0.084 |  |  |  |
| 2 |  |  |  |  |
| 3 |  |  |  |  |
| 4 |  | 0.084 |  |  |
| 5 |  |  |  |  |
| 6 |  |  |  |  |
| 7 |  |  |  |  |
| 8 |  |  |  |  |
|  |  |  |  |  |

2. Find the average value of the rate constant and give the correct unit.
3. Give the Rate Law

The Rate Law =

## PART 3: DETERMINATION OF ACTIVATION ENERGY OF THE REACTION

$$
\begin{aligned}
k & =A e^{-\frac{E_{a}}{R T}} \\
\ln k & =\ln A-\frac{E_{a}}{R T} \\
\ln k & =\left(-\frac{E_{a}}{R}\right) \frac{1}{T}+\ln A
\end{aligned}
$$

A comparison of the above equation with the equation of a straight line, $y=m x+b$, indicates the following:

$$
\begin{aligned}
& \ln \mathrm{k} \text { is analogous to } \mathrm{y} \\
& \frac{1}{T} \text { is analogous to } \mathrm{x} \\
& -\frac{E_{a}}{R} \text { is analogous to } \mathrm{m} \\
& \ln \mathrm{~A} \text { is analogous to } \mathrm{b}
\end{aligned}
$$

Therefore a linear regression of a plot of $\ln \mathrm{k}$ vs. $\frac{1}{T}$ should result in a straight line whose slope will be $-\frac{E_{a}}{R}$ and whose y-intercept will be $\ln$ A. Since R is the universal gas constant, the value of $\mathrm{E}_{\mathrm{a}}$ can be determined from the slope of the best fit line.

1. Calculate " $k$ " for reactions $9-12$ using Equation 11. Use the average value of the time and temperature of the two trials for each calculation.

$$
\begin{gathered}
\text { Reaction Rate }=\frac{\Delta\left[I_{3}^{-}\right]}{\Delta t}=\frac{0.00063 M}{\Delta t} \\
k=\frac{\text { Reaction Rate }}{\left[I^{-}\right]^{x}\left[S_{2} O_{8}^{2-}\right]^{y}}
\end{gathered}
$$

| Reaction | Average time <br> (seconds) | Reaction Rate, <br> $\mathbf{M s}^{-1}$ | Rate Constant, k |
| :---: | :--- | :--- | :--- |
| 9 |  |  |  |
| 10 |  |  |  |
| 11 |  |  |  |
| 12 |  |  |  |

2. Complete the following table (NOTE: You can use a spreadsheet such as Microsoft Excel to do this, See Below).

|  | $\mathbf{A}$ | $\mathbf{B}$ | $\mathbf{C}$ | $\mathbf{D}$ | $\mathbf{E}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{1}$ | Temperature, $\mathbf{T}$ <br> ${ }^{\circ} \mathbf{C}$ | $\mathbf{k}$ | T, Kelvin | $\mathbf{1 / T}$ | $\mathbf{l n}(\mathbf{k})$ |
| $\mathbf{2}$ | 10 |  | $=\mathrm{A} 2+273.15$ | $=1 / \mathrm{C} 2$ | $=\mathrm{LN}(\mathrm{B} 2)$ |
| $\mathbf{3}$ | 20 |  |  |  |  |
| $\mathbf{4}$ | 30 |  |  |  |  |
| $\mathbf{5}$ | 40 |  |  |  |  |

3. Enter the data (temperature in ${ }^{\circ} \mathrm{C}$ and k) in columns A and B. Use Row 1 for column headings.
4. Enter formulas in Row 2 for each calculation, as shown in the table above.
5. In each column, point the cursor to the bottom right corner of a cell (say C2) and drag down (till Row 5) the plus sign to copy the formula to the other cells. Repeat this for all the columns D through E.
6. To draw a graph, select the x and y data, which would be data in fields $\mathrm{D}: 2-5$ and E:2-5.
7. Click "Insert" and then "Chart". Choose "XY" scatter and select "Marked Scatter"
8. When the graph is displayed, click on any data point on the chart and from the toolbar, select "Chart" and then "Insert Trendline".
9. From the pop-up box, select the "Options" tab and check the boxes: 1) Display equation and 2) Display R-squared value and click OK.
10. From the equation of the straight line, obtain the slope and set that equal to $-\frac{E_{a}}{R}$. Using the fact that $\mathrm{R}=8.314 \mathrm{~J} / \mathrm{molK}$, calculate the value of $\mathrm{E}_{\mathrm{a}}$.

## PART 4: STUDY THE EFFECT OF A CATALYST ON THE RATE OF THE REACTION

1. Using the average time for the two trials, calculate the Reaction Rate and the Rate Constant " k " according to equation 11 for the reactions 13-16.

$$
\begin{gathered}
\text { Reaction Rate }=\frac{\Delta\left[I_{3}^{-}\right]}{\Delta t}=\frac{0.00063 \mathrm{M}}{\Delta t} \\
\qquad k=\frac{\text { Reaction Rate }}{\left[I^{-}\right]^{x}\left[S_{2} O_{8}^{2-}\right]^{y}}
\end{gathered}
$$

| Reaction | Average time <br> (seconds) | Reaction Rate, <br> Ms $^{-1}$ | Rate Constant, k |
| :---: | :--- | :--- | :--- |
| 13 |  |  |  |
| 14 |  |  |  |
| 15 |  |  |  |
| 16 |  |  |  |

2. Calculate the average rate constant of the catalyzed reactions (13-16).

## Average rate constant of the catalyzed reactions =

3. Compare the average rate constant for the uncatalyzed reactions (1-8) with the average rate constant of the catalyzed reactions (13-16) to determine the rate enhancement due to the catalyst.

Average " $k$ " for the uncatalyzed reactions (1-8) $=k$ (uncatalyzed) $=$

Average " $k$ " for the catalyzed reactions (13-16) $=k$ (catalyzed) $=$

Rate enhancement $=\frac{\mathrm{k}(\text { catalyzed })}{\mathrm{k}(\text { uncatalyzed })}=$

