EXPERIMENT 1

## REACTION RATE, RATE LAW, AND ACTIVATION ENERGY THE IODINE "CLOCK" REACTION

## PURPOSE:

To determine the Rate Law and the Activation Energy for a reaction from experimental data.

## PRINCIPLES:

The "Rate Law" is a mathematical expression that predicts the rate of a reaction from the concentration of reactants. This "Rate Law" is the product of the rate constant (k) and each reactant concentration taken to some power (almost always $0,1,2,-1$, or 0.5 ).
The values for the rate constant and the concentration powers have to be determined experimentally.
An example of a rate law and its rate constant is shown below:
Consider the hypothetical reaction:

$$
\mathbf{X}+\mathbf{2 Y} \longrightarrow \mathbf{Z}
$$

Rate is the change of a reactant or product concentration per unit time during reaction (in $\mathrm{M} / \mathrm{s}$ )
Mathematically: Rate $=-\underbrace{\frac{\Delta[\mathrm{X}]}{\Delta \mathrm{t}}}_{\begin{array}{c}\text { Rate of disappearance } \\ \text { of reactants }\end{array}}=-\frac{\Delta[\mathrm{Y}]}{2 \Delta \mathrm{t}} \underbrace{\underbrace{}_{\Delta \mathrm{t}}}_{\begin{array}{c}\text { Rate of formation } \\ \text { of product }\end{array}}$
General form for Rate Law:

$$
\text { Rate }=k[\mathrm{X}]^{\mathrm{m}}[\mathrm{Y}]^{\mathrm{n}}
$$

$\mathbf{m}$ and $\mathbf{n} \quad$ - are frequently, but not always integers (almost always $0,1,2,-1$, or 0.5 ).

- must be determined experimentally
k - Rate Constant: - its units depend upon the form of Rate Law
- is temperature dependent

Suppose the rate law was the following: $\quad$ Rate $=\mathbf{k}[\mathbf{X}][\mathbf{Y}]^{2}$
The rate is "first order" with respect to $[\mathrm{X}]$ which means: Rate is proportional to $[\mathrm{X}]^{1}$

- When [X] is doubled, the rate is doubled. [2] $]^{1}=2$
- When [X] is tripled, the rate is tripled $\quad[3]^{1}=3$

The rate is "second order" with respect to [Y] which means: Rate is proportional to [Y] ${ }^{\mathbf{2}}$

- When [Y] is doubled, the rate is quadrupled. $\quad[2]^{2}=4$
- When [Y] is tripled, the rate is increased by $9 \quad[3]^{2}=9$

NOTE:The Reaction Orders are not necessarily equal to the coefficients in the overall equation. They could be (as it is the case in this example), but that will not always be so.
The Reaction Orders must be determined experimentally

The rate constant (k) is calculated from one of the experiments after we determined the powers of [ X ] and $[\mathrm{Y}]$
To calculate k: - choose any experiment,

- plug in the concentrations [ X ] and $[\mathrm{Y}]$ and then the corresponding rate into the rate law,
- algebraically solve for k

Changing the temperature can also change the Rate of Reaction. During a reaction, there is often a particular step in the overall process that slows the entire reaction down. This is often a difficult step where the molecules involved must collide with a minimum amount of energy for the reaction to occur. This minimum energy requirement is called the "Activation Energy, Ea". Knowing the "Activation Energy, Ea" helps us predict the reaction rate at other temperature. The "Activation Energy, Ea" manifests itself through the "Rate Constant, k".

## PROCEDURE:

In this experiment we will observe how the rate of reaction given below is changed by variations in reactant concentrations, catalyst concentrations and temperature:
$\underset{\text { iodide ion }}{\mathbf{2} \mathbf{I}^{-}+} \underset{\text { persulfate ion }}{\mathbf{S}_{\mathbf{2}} \mathbf{O}_{8}{ }^{2-} \longrightarrow \underset{\text { iodine }}{\mathbf{I}_{2}}+\underset{\text { sulfate ion }}{\mathbf{2 ~ S O}}{ }^{2-} \quad \text { (Reaction 1) }}$ Based on the experimental data, we will determine the The Rate Law (PART I) and The Effect of Temperature on Reaction Rate (PART II)

An overview of the Procedure is outlined below:

## Part I: THE RATE LAW

## A. Effect of Concentration on Reaction Rate

1. Reactant Concentrations and Corresponding Reaction Rates
2. Reaction Orders with respect to Reactants:
(a) Reaction Order with respect to [I'] ("m")
(b) Reaction Order with respect to $\left[\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}\right]$ (" n ")
B. The Determination of the Rate Constant " $k$ "
C. The Effect of the Catalyst on Reaction Rate

Reaction Order with respect to Catalyst ("p")

Part II: EFFECT OF TEMPERATURE ON REACTION RATE
Determination of the Activation Energy, $\mathrm{E}_{\mathrm{a}}$
The table on next page summarizes the volumes of reactants and the reaction conditions under which experimental data will be obtained.

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Summary of Volumes of Reactants, Volume of Catalyst and Reaction Conditions for all Reaction Runs

| $\begin{aligned} & \text { Run } \\ & \text { No. } \end{aligned}$ | Temp | 250 mL Reaction Flask |  |  |  | 50 mL Flask |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $\begin{array}{\|c\|} \hline \text { KI } \\ (0.200 \mathrm{M}) \\ \hline \end{array}$ | $\begin{array}{\|c\|} \hline \mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3} \\ (\mathbf{0 . 0 0 5 0 0} \mathrm{M}) \\ \hline \end{array}$ | $\begin{gathered} \hline \mathrm{KCl} \\ (0.200 \mathrm{M}) \\ \hline \end{gathered}$ | Soluble Starch | $\begin{gathered} \left(\mathrm{NH}_{4}\right)_{2} \mathrm{~S}_{2} \mathrm{O}_{8} \\ (0.100 \mathrm{M}) \end{gathered}$ | $\begin{gathered} \left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4} \\ (\mathbf{0 . 1 0 0 \mathrm { M } )} \end{gathered}$ | $\begin{gathered} \mathrm{CuSO}_{4} \\ (0.100 \mathrm{M}) \\ \hline \end{gathered}$ |
| 1 | Room <br> Temp | 20.0 mL | 10.0 mL | 0.0 mL | 3-4 drops | 20.0 mL | 0.0 mL | 0.0 mL |
| 2 | Room <br> Temp | 10.0 mL | 10.0 mL | 10.0 mL | 3-4 drops | 20.0 mL | 0.0 mL | 0.0 mL |
| 3 | Room Temp | 20.0 mL | 10.0 mL | 0.0 mL | 3-4 drops | 10.0 mL | 10.0 mL | 0.0 mL |
| 4 | Room Temp | 20.0 mL | 10.0 mL | 0.0 mL | 3-4 drops | 5.0 mL | 15.0 mL | 0.0 mL |
| 5 | Room <br> Temp | 8.0 mL | 10.0 mL | 12.0 mL | 3-4 drops | 20.0 mL | 0.0 mL | 0.0 mL |
| 6 | Room <br> Temp | 15.0 mL | 10.0 mL | 5.0 mL | 3-4 drops | 15.0 mL | 5.0 mL | 0.0 mL |
| 7 | Room Temp | 20.0 mL | 10.0 mL | 0.0 mL | 3-4 drops | 20.0 mL | 0.0 mL | 4 drops |
| 8 | Room <br> Temp | 20.0 mL | 10.0 mL | 0.0 mL | 3-4 drops | 20.0 mL | 0.0 mL | 2 drops |
| 9 | $\begin{aligned} & \text { about } \\ & 40^{\circ} \mathrm{C} \end{aligned}$ | 20.0 mL | 10.0 mL | 0.0 mL | 3-4 drops | 20.0 mL | 0.0 mL | 0.0 mL |
| 10 | about $10^{\circ} \mathrm{C}$ | 20.0 mL | 10.0 mL | 0.0 mL | 3-4 drops | 20.0 mL | 0.0 mL | 0.0 mL |
| 11 | about $0^{0} \mathrm{C}$ | 20.0 mL | 10.0 mL | 0.0 mL | 3-4 drops | 20.0 mL | 0.0 mL | 0.0 mL |

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## PART I: DETERMINATION OF THE RATE LAW

## A. The Effect of Concentration on Reaction Rate

The Reaction Rate for Reaction 1 can be measured through the formation of elemental iodine, $\mathrm{I}_{2}$, since the presence of even small amounts of iodine can be detected by virtue of the intensely blue colored complex formed between iodine and starch:

| $2 \text { I }^{-}+$ <br> iodide ion |  | te ion | $\mathbf{I}_{\mathbf{2}}$ <br> iodine | $2 \mathrm{SO}_{4}{ }^{2-}$ <br> sulfate ion | (Reaction 1) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Iodine | + | Starch |  | Starch-Iodi <br> (deep | Complex <br> e) |

One creative way of measuring the rate of formation of Iodine is to couple the reaction in which the Iodine is formed (Reaction 1 ) with a much faster reaction that consumes all of the Iodine (Reaction 2)

$$
\mathbf{I}_{2}+\underset{\text { thiosulfate ion }}{2 \mathbf{S}_{2} \mathbf{O}_{3}{ }^{2-} \longrightarrow 2 \mathbf{I}^{-} \quad+\quad \mathbf{S}_{4} \mathbf{O}_{6}{ }^{2-} \quad \text { (Reaction 2) }}
$$

Reaction 2 immediately consumes the $\mathrm{I}_{2}$ generated in the first reaction until all of the $\mathbf{S}_{2} \mathbf{O}_{3}{ }^{2-}$ (thiosulfate ion) is used up. When the $\mathbf{S}_{2} \mathbf{O}_{3}{ }^{2-}$ is consumed, $\mathbf{I}_{2}$ builds up and reacts with starch to form the deep blue Starch-Iodine Complex, according to Reaction 1 given above:


The appearance of the deep-blue complex tells us that at this point in time ( $\mathbf{t}_{\text {color }}$, sufficient $\mathrm{I}_{2}$ has been produced by Reaction 1 to use up all of the $\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}$ (thiosulfate) ion originally added. From this observation we can easily calculate the concentration of Iodine produced by Reaction 1, by observing that according to the stoichiometry of Reaction 2, 1 mole of $\mathrm{I}_{2}$ reacts with 2 moles of $\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}$ (thiosulfate), or $1 / 2$ mole $\mathrm{I}_{2}$ reacts with $\mathbf{1}$ mole of $\mathrm{S}_{2} \mathbf{O}_{3}{ }^{2-}$ (thiosulfate).

It follows, that at the time the deep blue color ( $\mathrm{t}_{\text {color }}$ ) appears:

$$
\left[\mathrm{I}_{2}\right]_{\text {produced }}=\frac{\left[\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}\right]_{\text {originally added and used up }}}{2}
$$

Knowing the molar concentration of $\mathrm{I}_{2}$ at a specific, exactly measured time gives us the Rate of formation of $\mathrm{I}_{2}$ which in turn permits us to calculate the Rate of Reaction 1 for any combination of reaction conditions, as long as the amount of the $\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}$ is kept constant.
$\underset{\text { iodide ion }}{\mathbf{2} \mathbf{I}^{-}}+\underset{\text { persulfate ion }}{\mathbf{S}_{2} \mathbf{O}_{8}{ }^{2-}} \longrightarrow \underset{\text { iodine }}{\mathbf{I}_{\mathbf{2}}}+\underset{\text { sulfate ion }}{\mathbf{2} \mathbf{S O}_{4}{ }^{2-}} \quad$ (Reaction 1)

The difference between the initial and the final concentrations of $\mathbf{I}_{2}$ divided by the amount of time needed for this change to occur is the Rate of the Reaction.

Rate $1=+\frac{\Delta\left[I_{2}\right]}{\Delta t}$
If we know the starting concentration of $\mathbf{S}_{\mathbf{2}} \mathbf{O}_{3}{ }^{2-}$ (thiosulfate) and remember that it is all used up when the color of the reaction changes, then we also know that half that amount of $\mathbf{I}_{2}$ was also consumed in the reaction.
This means that the change in the $\mathbf{I}_{2}$ concentration is equal to half the starting (initial) concentration of $\mathbf{S}_{2} \mathbf{O}_{3}{ }^{2-}$ (thiosulfate) :
$\Delta\left[I_{2}\right]=\frac{\left[\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}\right]_{\text {initial }}}{2}$
The time of the color change $\left(\mathbf{t}_{\text {color }}\right)$ is also the time that passed during the reaction ( $\Delta \mathbf{t}$ ) It follows that the rate of the First Reaction can be calculated as:


1. Reactant Concentrations and corresponding Reaction Rates

The table below summarizes the volumes of reactants to be used in making up six different mixtures:

| Table 1: Kinetic Runs at Varying Concentrations |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Rxn <br> Run <br> No. | $\mathbf{2 5 0} \mathbf{- \mathbf { m L } \text { Reaction Flask }}$ |  |  |  |  |  |
|  | KI <br> $(0.200 ~ M)$ | $\mathbf{N a}_{2} \mathbf{S}_{\mathbf{2}} \mathbf{O}_{\mathbf{3}}$ <br> $(0.00500 \mathrm{M})$ | KCl <br> $(0.200 \mathrm{M})$ | Soluble <br> Starch | $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{~S}_{2} \mathrm{O}_{8}$ <br> $(0.100 \mathrm{M})$ | $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ <br> $(0.100 \mathrm{M})$ |
| 1 | 20.0 mL | 10.0 mL | 0.0 mL | $3-4$ drops | 20.0 mL | 0.0 mL |
| 2 | 10.0 mL | 10.0 mL | 10.0 mL | $3-4$ drops | 20.0 mL | 0.0 mL |
| 3 | 20.0 mL | 10.0 mL | 0.0 mL | $3-4$ drops | 10.0 mL | 10.0 mL |
| 4 | 20.0 mL | 10.0 mL | 0.0 mL | $3-4$ drops | 5.0 mL | 15.0 mL |
| 5 | 8.0 mL | 10.0 mL | 12.0 mL | $3-4$ drops | 20.0 mL | 0.0 mL |
| 6 | 15.0 mL | 10.0 mL | 5.0 mL | $3-4$ drops | 15.0 mL | 5.0 mL |

The actual procedure for carrying out each reaction will be much the same and it will be described in detail for Reaction Run 1:
(a). Filling the $\mathbf{2 5 0}$ - mL Erlenmeyer Flask (Reaction Flask)
$\Rightarrow$ Use a buret to add exactly $\mathbf{2 0 . 0} \mathbf{~ m L}$ of $\mathbf{0 . 2 0 0} \mathbf{~ M ~ K I}$ into the $250-\mathrm{mL}$ Erlenmeyer which we will call the Reaction Flask and which will serve as the container for the reaction.
$\Rightarrow$ Use a buret to add exactly 10.0 mL of $\mathbf{0 . 0 0 5 0} \mathbf{M ~ N a}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ into this flask.
$\Rightarrow$ Add 3 or 4 drops of starch solution to the flask
(b). Filling the $50-\mathrm{mL}$ Erlenmeyer Flask
$\Rightarrow$ Use a buret to add exactly $\mathbf{2 0 . 0} \mathbf{~ m L}$ of $\mathbf{0 . 1 0 0} \mathbf{M}\left(\mathbf{N H}_{4}\right)_{2} \mathrm{~S}_{\mathbf{2}} \mathrm{O}_{\mathbf{8}}$ into this flask
(c). $\Rightarrow$ Temperature Reading

Read the temperature of the solution in the 250 - mL reaction flask with a rinsed, dried thermometer.
$\Rightarrow$ Remove the thermometer, rinse and dry it, and measure the temperature of the solution in the $50-\mathrm{mL}$ flask. The solutions in both flasks should be at the same temperature $\pm 0.2^{\circ} \mathrm{C}$. If necessary, adjust the temperature by external warming or cooling to some convenient point in the range of $20^{\circ} \mathrm{C}-25^{\circ} \mathrm{C}$, best place being room temperature.
Record this temperature to the nearest $0.1^{\circ} \mathrm{C}$.
$\Rightarrow$ Remove the thermometer from the flask, rinse and dry it.
(d).Mixing and Timing (have a stopwatch available)
$\Rightarrow$ Pour the solution from the $50-\mathrm{mL}$ flask into the reaction flask (you can leave the 50 ml flask over the mouth of the reaction flask). Note the time at which the solutions were mixed.
$\Rightarrow$ Swirl the solutions to mix them thoroughly.
Continue swirling the solution until the blue color appears.
Note and record the time at which at the instant the blue color appears (it should take less than a minute). Record all times to the nearest second (no fractions of seconds should be recorded).
Note that the time elapsed for the blue color to appear ( $\mathbf{t}$ color) is the time interval required to consume all of the $\mathbf{S}_{2} \mathbf{O}_{3}{ }^{2-}$ (thiosulfate) ion.
$\Rightarrow$ Check the temperature again. If the temperature has changed by more than $\pm 0.5$, or if the timing was faulty, repeat the entire run.
(e). Repeat the experiment with the other mixtures in the table
$\Rightarrow$ The flasks used should be rinsed with distilled water between experiments and drained before being used again.
$\Rightarrow$ Burets should be used in measuring the volumes of all the five solutions:
KI, $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}, \mathrm{KCl},\left(\mathrm{NH}_{4}\right)_{2} \mathrm{~S}_{2} \mathrm{O}_{8}$, and $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$
NOTE: Although $\mathbf{K C l}$ and $\left(\mathbf{N H}_{4}\right)_{2} \mathbf{S O}_{\mathbf{4}}$ ], do not enter the reaction directly, these reagents serve to maintain the effective concentrations of all ions ("ionic strength") at a constant level. Holding the ionic strength constant removes the dependence of the reaction rate on variations in the solvent.

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## 2. Reaction Orders with respect to Reactants

Once, experimental data is available for several concentrations and corresponding Reaction Rates, the Reaction Orders with respect to Reactants can be determined by calculations:

$$
2 \mathrm{I}^{-}+\quad \mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-} \quad \longrightarrow \quad \mathbf{I}_{2} \quad+\quad 2 \mathbf{S O}_{4}{ }^{2-}
$$

Rate $=k\left[I^{-}\right]^{\mathrm{m}}\left[\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}\right]^{\mathrm{n}}$
where: " $\mathbf{m}$ " and " $\mathbf{n}$ " are the respective Reaction Orders,
" $k$ " is the Rate constant
To obtain " $\mathbf{m}$ " and " $\mathbf{n}$ " two different reaction runs in which the concentration of one reactant is the same will be divided by each other. This will permit cancellation of several identical terms and will yield an equation in which the reaction order (" $\mathbf{m}$ " or " $\mathbf{n}$ ") is the only unknown. Solving the equation will yield " $\mathbf{m}$ ", respectively " $\mathbf{n}$ ".

## B. The Determination of the Rate Constant " $k$ "

The Rate Constant " $\mathbf{k}$ " is characteristic for this reaction and is independent of the concentration of the reactants. However, " $k$ " is temperature dependent.
As such, " $\mathbf{k}$ " can be calculated from any of the six experiments, since the temperature has been maintained essentially constant (Room temperature)
To calculate " $\mathbf{k}$ " plug in the Concentrations of [ $\left.\mathbf{I}^{-}\right]$and $\left[\mathbf{S}_{2} \mathbf{O}_{8}{ }^{2-}\right.$ ] and the corresponding Rate into the Rate Law and then solve algebraically for " $\mathbf{k}$ ".
The closeness of the six values that you will obtain for " $k$ " is indicative of the precision of your experimental data.

## C. The Effect of the Catalyst on the Reaction Rate

Another way of controlling the rate of a reaction is by the addition of a catalyst. Catalysts change the individual steps involved in the overall reaction and avoid the slow steps.
As a result, catalysts are often incorporated in the rate law and accelerate the reaction.
Metallic cations (such as $\mathrm{Cu}^{2+}$ ) have a pronounced catalytic effect on the rate of this reaction. Perform Reaction Runs 7 and 8 as Reaction Run 1, including the same temperature (room temperature), except add small volumes of $0.1 \mathrm{M} \mathrm{CuSO}_{4}$ solution to the $\mathbf{5 0} \mathbf{~ m L}$ flask, just before pouring the contents into the reaction flask.
Record the temperatures and the reaction times.
Reaction Mixtures with varying amounts of Catalyst

| Reaction <br> Run \# | Reaction Mixture | Temperature | $\mathbf{C u}^{2+}$ <br> $\mathbf{( \mathbf { 0 . 1 ~ M ) }}$ |
| :---: | :---: | :---: | :---: |
| 7 | same as in Rxn. Run \# 1 | Room temperature | 4 drops |
| 8 | same as in Rxn. Run \# 1 | Room temperature | 2 drops |

Determine the order of the reaction with respect to catalyst concentration " $\mathbf{p}$ "
Note: To find " $\mathbf{p}$ ", you do not need to calculate the actual concentration of the catalyst in the Reaction Flask for Reaction Runs 7 and 8.
Noting that one concentration is twice as large as the other one, will allow you to cancel out the concentration of $\left[\mathrm{Cu}^{2+}\right]$

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## PART II: THE EFFECT OF TEMPERATURE ON REACTION RATE

Changing the temperature can also change the Rate of Reaction. During a reaction, there is often a particular step in the overall process that slows the entire reaction down. This is often a difficult step where the molecules involved must collide with a minimum amount of energy for the reaction to occur. This minimum energy requirement is called the "Activation Energy, Ea". Knowing the "Activation Energy, Ea" helps us predict the reaction rate at other temperature. The "Activation Energy, Ea" manifests itself through the "Rate Constant, k".

## Arrhenius Equation

| $\mathbf{k}=\mathbf{A} \mathbf{e}$ |
| :---: |$\quad$| $\mathbf{k}=$ the rate constant in the rate law |
| :--- |
| $\mathrm{A}=$ a constant for the reaction at all temperatures and concentrations |
| Ea = the Activation Energy |
| $\mathrm{R}=$ the universal gas constant $=8.315 \mathrm{~J} / \mathrm{K} \mathrm{x} \mathrm{mol}$ |
| $\mathbf{T}=$ absolute temperature |
| $\mathrm{e}=2.718$ |

To determine Ea experimentally we need to focus on the effect of Ea on the Rate Constant , k. This is done by:

- holding the reactant concentrations constant, so that all the rate changes are due to changes in the Rate Constant, k , and
- measuring how the Reaction Rate responds to temperature changes

The calculations can be greatly simplified by substituting the value of $\mathbf{k}$ from the Arrhenius Equation into the expression of the Rate Law, and then taking the natural logarithm of both side of the equation: Reaction Rate:

constants
grouped together

Recall that the logarithm of a product is equal to the sum of the individual logarithms:

$$
\ln (\mathrm{X} \mathrm{Y}) \quad=\quad \ln \mathrm{X}+\ln \mathrm{Y}
$$




The resulting Equation is similar to the equation of a straight line $(\mathbf{y}=\mathbf{b}+\mathbf{m x})$ :


From a plot of $\mathbf{l n}$ Rate as a function of $\mathbf{1 / T}$, the slope of the graph can be easily determined.
From the slope, the Activation Energy, Ea is calculated by algebra.
Once Ea has been determined, it is possible to predict reaction rates at any temperatures and any set of concentrations.
To obtain experimental data reflecting the dependence of the Reaction Rate on Temperature, the reaction will be carried out at several different temperatures, but with the same concentration of all reactants.

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The table below indicates the reaction conditions:

## Reaction Mixtures at Different Temperatures

| Reaction Run \# | Temperature | Reaction Mixture |
| :---: | :---: | :---: |
| 1 | Room temperature | same as in Rxn. Run \# 1 |
| 9 | about $40^{\circ} \mathrm{C}$ | same as in Rxn. Run \# 1 |
| 10 | about $10^{\circ} \mathrm{C}$ | same as in Rxn. Run \# 1 |
| 11 | about $0^{\circ} \mathrm{C}$ | same as in Rxn. Run \# 1 |

## Reaction Run \# 1: Data for the Reaction Rate is already available (Part I)

Reaction Run \# 9: The reaction is carried out by adding the same volumes of the same solutions as in Reaction Run \# 1.
Slowly swirl the 250 mL and the 50 mL flasks separately for approximately 3 minutes in a large beaker of water at a temperature of about $40^{\circ} \mathrm{C}$. Record the exact temperature (nearest $0.1^{\circ} \mathrm{C}$ ) of the solution in the 250 mL reaction flask.
When the temperatures in both flasks are about $40^{\circ} \mathrm{C}$ and nearly the same, mix the solutions together by pouring the contents of the 50 mL flsk in the reaction flask as in previous runs. Note the time of mixing. Keep the reaction flask immersed in the beaker for the entire reaction interval in order to maintain as constant a temperature as possible.
Record the time at which the color change occurs and the temperature of the mixture at that point.

Reaction Run \# 10: Repeat the experiment at about $10^{\circ} \mathrm{C}$, cooling all reactants in a large beaker to that temperature before starting the reaction.
Record the time required for the reaction and the final temperature of the reaction mixture.

Reaction Run \# 11: Repeat once again at about $0^{\circ} \mathrm{C}$, this time using an ice-water bath to cool the reactant solutions.

Calculate the Activation Energy ( $\mathbf{E}_{\mathbf{a}}$ ) from the experimental data.

NAME: $\qquad$
PARTNER: $\qquad$

## REPORT FORM

## PART I: DETERMINATION OF THE RATE LAW

## A. The Effect of Concentration on Reaction Rate

1. Reactant Concentrations and corresponding Reaction Rates

For each kinetic run, calculate the initial concentrations for the two reactants which react: $\left[\mathrm{I}^{-}\right]$and $\left[\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}\right.$.
Since the reaction whose rate is being measured takes place in a total volume of 50.0 mL , this volume must be taken into account in calculating the initial concentrations of the two reactants
For example in Run1, since the 20.0 mL of 0.200 M KI added reacts in a total volume of 50.0 mL , the initial concentration of [ $\mathrm{I}^{-}$] can be calculated to be:
20.0 mL solution
$\left[\mathrm{I}^{-}\right]_{1}=0.200 \mathrm{M} \mathrm{KI} \frac{}{50.0 \mathrm{~mL} \text { solution }}=0.0800 \mathrm{M} \mathrm{KI}$
Similarly, in Run 1, the initial concentration of $\left[\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}\right]$ is:
20.0 mL solution

$$
\left[\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}\right]_{1}=0.100 \mathrm{M}\left(\mathrm{NH}_{4}\right)_{2} \mathrm{~S}_{2} \mathrm{O}_{8} \frac{}{50.0 \mathrm{~mL} \text { solution }}=0.0400 \mathrm{M}\left(\mathrm{NH}_{4}\right)_{2} \mathrm{~S}_{2} \mathrm{O}_{8}
$$

Carry out similar calculations for all other initial values of [ $\left.\mathrm{I}^{-}\right],\left[\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}\right.$ ] and $\left[\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}\right.$ ] and complete the appropriate columns in the Data Table.

$$
\left[\mathbf{S}_{2} \mathrm{O}_{3}{ }^{2-}\right], \mathrm{M}
$$

$\square$

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|  | [ $\mathrm{I}^{-}$] | $\left[\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}\right]$ |
| :---: | :---: | :---: |
| Run 1 | $\text { 0.200 M KI } \frac{20.0 \mathrm{~mL}}{50.0 \mathrm{~mL}}=\mathbf{0 . 0 8 0 0} \mathbf{~ M}$ | $0.100 \mathrm{M}\left(\mathrm{NH}_{4}\right)_{2} \mathrm{~S}_{2} \mathrm{O}_{8} \frac{20.0 \mathrm{~mL}}{50.0 \mathrm{~mL}}=\mathbf{0 . 0 4 0 0} \mathbf{~ M}$ |
| Run 2 |  | same as in Run 1 |
| Run 3 | same as in Run 1 |  |
| Run 4 | same as in Run 1 |  |
| Run 5 |  | same as in Run 1 |
| Run 6 |  |  |

Table 1: Reactant Concentrations and corresponding Reaction Rates

| Run <br> No. | Temp $\left({ }^{0} \mathrm{C}\right)$ | KI |  |  | $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{~S}_{2} \mathrm{O}_{8}$ |  |  | Time (t color) <br> (s) | $\begin{gathered} \text { RATE }^{*} \\ \frac{\left.\mathrm{~S}_{2} \mathrm{O}_{3}{ }^{2-}\right]_{0}}{2 \mathrm{t}_{\text {color }}} \\ \hline \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $\begin{gathered} \mathrm{mL} \\ \text { added } \end{gathered}$ | M | $\left[\mathrm{I}^{-}\right]_{0}, \mathrm{M}$ | mL <br> added | M | $\left[\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}\right]_{0}, \mathrm{M}$ |  |  |
| 1 |  | 20.0 | 0.200 | 0.0800 | 20.0 | 0.100 | 0.0400 |  |  |
| 2 |  | 10.0 | 0.200 |  | 20.0 | 0.100 |  |  |  |
| 3 |  | 20.0 | 0.200 |  | 10.0 | 0.100 |  |  |  |
| 4 |  | 20.0 | 0.200 |  | 5.0 | 0.100 |  |  |  |
| 5 |  | 8.0 | 0.200 |  | 20.0 | 0.100 |  |  |  |
| 6 |  | 15.0 | 0.200 |  | 15.0 | 0.100 |  |  |  |

Rate $^{*} \leadsto$ Express Rate as $\left(\mathrm{A} \times 10^{-6}\right)$ and in 3 significant figures
2. Reaction Orders with respect to reactants

Summarize the relevant data from Table1 into Table 2.
Table 2: Reactant Concentrations and corresponding Reaction Rates

| Run <br> No. | $\begin{aligned} & {\left[\mathrm{I}^{-}\right]_{0}} \\ & \text { (M) } \end{aligned}$ | $\left[\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}\right]_{0}$ <br> (M) | [ $\left.\mathbf{I}_{2}\right]_{\text {produced }}$ (at $\mathrm{t}_{\text {color }}$ ) <br> (M) | $\begin{aligned} & \text { Time, } \\ & \text { (seconds) } \end{aligned}$ | Rate $^{*}$ ${\left.\text { [ } I_{2}\right]}^{\mathbf{t}_{\text {color }}}(\mathrm{M} / \mathrm{s})$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 |  |  |  |  |  |
| 2 |  |  |  |  |  |
| 3 |  |  |  |  |  |
| 4 |  |  |  |  |  |
| 5 |  |  |  |  |  |
| 6 |  |  |  |  |  |

(a) Calculating the Reaction Orders with respect to [ $\mathrm{I}^{-}$]

## From Run 1 and Run 2:

The general formulas for the Rate Law for Runs 1 and 2 are:
Rate $_{1}=k\left[I^{-}\right]^{\mathrm{m}}\left[\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}\right]^{\mathrm{n}}$
Rate $_{2}=\mathbf{k}\left[\mathbf{I}^{-}\right]^{\mathrm{m}}\left[\mathrm{S}_{2} \mathbf{O}_{8}{ }^{2-}\right]^{\mathrm{n}}$
Substitute the known concentrations of [ $\mathrm{I}^{-}$] and $\left[\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}\right.$ ] ions and the known Reaction Rates for these runs. Include reaction orders, " $\mathbf{m}$ " and " $\mathbf{n}$ "

Divide the first equation by the second and cancel out identical terms.

Note that you have obtained and equation involving only " $\mathbf{m}$ " as an unknown: To solve for " $\mathbf{m}$ ", take the log of both sides of the equation and then solve for " $\mathbf{m}$ "


## From Run 1 and Run 5

Do the same calculation you did for Runs 1 and 2, but use instead the values for Runs 1 and 5 to obtain " $m$ "
Then substitute the known concentrations of $\left[\mathrm{I}^{-}\right]$and $\left[\mathrm{S}_{2} \mathrm{O}_{8}{ }^{2-}\right.$ ] ions and the known Reaction Rates. Include reaction orders, " $\mathbf{m}$ " and " $\mathbf{n}$ ". Show all calculations.


## From Run 2 and Run 5

Do the same calculation you did for Runs 1 and 2, but use instead the values for Runs 2 and 5 to obtain "m". Show all calculations


Calculate the average value for " m ":

$\mathrm{m}_{\text {average }}: \quad$ (as calculated)

(rounded off to an integer)
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(b) Calculating the Reaction Orders with respect to $\left[\mathrm{S}_{2} \underline{O}_{8}{ }^{2-}\right]$

Applying the same approach you used for the calculation of " $\mathbf{m}$ " find the value of " $\mathbf{n}$ " From Runs 1 and 3:


## From Runs 1 and 4:



From Runs 3 and 4:


Calculate the average value for " n "

$\mathbf{n}_{\text {average }}$ : $\qquad$ (as calculated)
$\mathbf{n}_{\text {average }}=$
(rounded off to an integer)
B. Determination of the Rate Constant " $k$ "

Having found " $\mathbf{m}$ " and " $\mathbf{n}$ ", the specific rate constant " $\mathbf{k}$ " can be calculated by substitution of " $\mathbf{m}$ " and " $\mathbf{n}$ " and the known rates and reactant concentrations into the Rate Law. Write the equation for the Rate Law, by substituting the values for " $\mathbf{m}$ " and " $\mathbf{n}$ " :

$$
\text { Rate }=\square \quad \text { Recall: " } \mathbf{m} \text { " and " } \mathbf{n} \text { " are integers }
$$

Evaluate " $k$ " for Reactions 1 through 6. Include units in your calculations

| $\left[\mathrm{I}^{-}\right]_{1}=$$\text { Rate }_{1}=$ | $\frac{\text { Run } 1}{\left[\mathrm{~S}_{2} \mathrm{O}_{8}{ }^{2-}\right]_{1}=}$$\mathbf{k}_{1}=$ | $\begin{aligned} & {\left[\mathbf{I}^{-}\right]_{2}=} \\ & \text { Rate }_{2}= \end{aligned}$ | $\frac{\operatorname{Run} 2}{\left[\mathrm{~S}_{2} \mathrm{O}_{8}{ }^{2-}\right]_{2}=}$ |
| :---: | :---: | :---: | :---: |
|  |  |  | $\mathrm{k}_{2}=$ |
| $\left[\begin{array}{l} {\left[\mathrm{I}^{-}\right]_{3}=} \\ \text { Rate }_{3}= \end{array}\right.$ | $\left.\frac{\text { Run 3 }}{\left[\mathbf{S}_{2} \mathbf{O}_{8}\right.}{ }^{2-}\right]_{3}=$ | $\begin{aligned} & {\left[\mathbf{I}^{-}\right]_{4}=} \\ & \text { Rate }_{4}= \end{aligned}$ | $\left.\frac{\text { Run } 4}{\left[\mathrm{~S}_{2} \mathrm{O}_{8}\right.}{ }^{2-}\right]_{4}=$ |
|  | $\mathbf{k}_{3}=$ |  | $\mathbf{k}_{4}=$ |
| $\begin{aligned} & {\left[\mathbf{I}^{-}\right]_{5}=} \\ & \text { Rate }_{5}= \end{aligned}$ | $\frac{\operatorname{Run} 5}{\left[\mathrm{~S}_{2} \mathrm{O}_{8}{ }^{2-}\right]_{5}=}$ | $\begin{aligned} & {\left[\mathrm{I}^{-}\right]_{6}=} \\ & \text { Rate }_{6}= \end{aligned}$ | $\left.\frac{\operatorname{Run} 6}{\left[\mathrm{~S}_{2} \mathrm{O}_{8}\right.}{ }^{2-}\right]_{6}=$ |
|  | $\mathbf{k}_{5}=$ |  | $\mathrm{k}_{6}=$ |

Summary of Rate Constants ' $k$ " for Runs at Room Temperature

| Run No. | 1 | 2 | 3 | 4 | 5 | 6 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| k |  |  |  |  |  |  |
| ( ) |  |  |  |  |  |  |
| $\begin{aligned} & \mathbf{k} \text { (Average) } \\ & (\quad) \end{aligned}$ |  |  |  |  |  |  |

Write the Rate Law for the reaction studied, by substituting the values for "m", "n" and "k":

Include units!

## REACTION RATE, RATE LAW, AND ACTIVATION ENERGY THE IODINE "CLOCK" REACTION

## C. The Effect of the Catalyst on the Reaction Rate

$\mathrm{Cu}^{2+}$ is a catalyst in the reaction studied. As such, the Rate Law of the catalyzed reaction could be written as:

## Rate $=\mathbf{k}\left[\mathbf{I}^{-}\right]^{\mathrm{m}}\left[\mathrm{S}_{\mathbf{2}} \mathrm{O}_{\mathbf{8}}{ }^{2-}\right]^{\mathrm{n}}\left[\mathrm{Cu}^{2+}\right]^{\mathrm{p}}$

where the reaction orders " $\mathbf{m}$ " and " $\mathbf{n}$ " are the same as in the uncatalyzed reaction.
To determine if there is a quantitative relationship between reaction rate and catalyst (that is " $\mathbf{p}$ ", the reaction order with respect to the catalyst), summarize your data for Reaction Runs with the same concentrations, at the same temperature, but with varying amounts of catalyst added.
In this manner, the effect of the concentration of catalyst on the Reaction Rates may be evaluated independent of other factors.

Reaction Mixtures with varying amounts of Catalyst

| Run <br> No. | Temp. $\left({ }^{0} \mathrm{C}\right)$ | $\begin{gathered} \hline \text { Drops of } \\ \mathrm{CuSO}_{4} \\ \mathbf{( 0 . 1 ~ M )} \end{gathered}$ | $\begin{gathered} \text { Time } \\ \left(\mathrm{t}_{\text {color }}\right) \\ \text { (s) } \end{gathered}$ | $\begin{gathered} {\left[\mathbf{S}_{2} \mathbf{O}_{3}{ }^{2-}\right]} \\ \mathbf{M} \end{gathered}$ | RATE <br> $\left[\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}\right]_{0}$ <br> $2 \mathrm{t}_{\text {color }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 7 |  |  |  |  |  |
| 8 |  |  |  |  |  |

From the data in this table, calculate " $\mathbf{p}$ ", the reaction order with respect to $\left[\mathrm{Cu}^{2-}\right]$ (nearest whole number or zero).
The calculations are similar to those done for the reaction order with respect
to [ $\left.\mathbf{I}^{-}\right]$("m") and [ $\mathbf{S}_{2} \mathbf{O}_{8}{ }^{2-}$ ] ("n")
Show calculations below:


Write the complete form of the Rate Law (include both reactants and the catalyst with their respective orders of reaction) and substitute "k" with the experimentally determined value.

Include units! $\quad$ Rate $=$

EXPERIMENT 1
REACTION RATE, RATE LAW, AND ACTIVATION ENERGY
THE IODINE "CLOCK" REACTION

PART II: THE EFFECT OF TEMPERATURE ON REACTION RATE
To determine the quantitative relationship between reaction rate and temperature, summarize your data for Reaction Runs with the same concentrations of all reactants but run at different temperatures. In this manner, the corresponding reaction rates for these runs will be affected by temperature changes only.

| Run <br> No. | Temp. <br> $\left({ }^{0} \mathrm{C}\right)$ | Temp. <br> $(\mathrm{K})$ | $\frac{\mathbf{1}}{\mathbf{T}}$ <br> $\left(\mathrm{K}^{-1}\right)$ | Time <br> $\left(\mathbf{t}_{\text {color }}\right)$ <br> $(\mathbf{s})$ | $\left[\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2}\right]$ <br> M | RATE <br> $\left[\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}\right]$ | ln <br> (RATE) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{1}$ |  |  |  |  |  |  |  |
| $\mathbf{9}$ |  |  |  |  |  |  |  |
| $\mathbf{1 0}$ |  |  |  |  |  |  |  |
| $\mathbf{1 1}$ |  |  |  |  |  |  |  |

To evaluate the Activation Energy $\left(\mathbf{E}_{\mathrm{a}}\right)$, make a graph of $\ln ($ Rate $)$ vs. $\mathbf{1 / T}\left(\mathbf{X} \mathbf{x} \mathbf{1 0}^{-\mathbf{3}}\right.$ ) on graph paper provided. In the upper-right hand side of the graph provide a table that includes that data being plotted. Recall that every graph must have a title.
Find the slope of the line obtained by drawing the best straight line through the 4 experimental points. Show calculations for slope on the graph


From the slope, calculate the Activation Energy ( $\mathbf{E}_{\mathbf{a}}$ ). Recall that R $=8.315 \mathrm{~J} / \mathrm{K} \mathrm{x} \mathrm{mol}$ Show calculations below. Please include units in your calculations.


