

A Kinetics Experiment  
The Rate of a Chemical Reaction: A Clock Reaction

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**Introduction:**

The rates of chemical reactions and the ability to control those rates are crucial aspects of life. Chemical kinetics is the study of the rates at which chemical reactions occur, the factors that affect the speed of reactions, and the mechanisms by which reactions proceed. The reaction rate depends on the reactants, the concentrations of the reactants, the temperature at which the reaction takes place, and any catalysts or inhibitors that affect the reaction. If a chemical reaction has a fast rate, a large portion of the molecules react to form products in a given time period. If a chemical reaction has a slow rate, a small portion of molecules react to form products in a given time period.

This experiment studied the kinetics of a reaction between an iodide ion ( $\text{I}^-$ ) and a peroxydisulfate ion ( $\text{S}_2\text{O}_8^{2-}$ ) in the first reaction:  $2\text{I}^- + \text{S}_2\text{O}_8^{2-} \rightarrow \text{I}_2 + 2\text{SO}_4^{2-}$ . This is a relatively slow reaction. The reaction rate is dependent on the concentrations of the reactants, following the rate law:  $\text{Rate} = k[\text{I}^-]^m[\text{S}_2\text{O}_8^{2-}]^n$ .

In order to study the kinetics of this reaction, or any reaction, there must be an experimental way to measure the concentration of at least one of the reactants or products as a function of time. This was done in this experiment using a second reaction,  $2\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^-$ , which occurred simultaneously with the reaction under investigation. Adding starch to the mixture allowed the  $\text{S}_2\text{O}_3^{2-}$  of the second reaction to act as a built in "clock;" the mixture turned blue when all of the  $\text{S}_2\text{O}_3^{2-}$  had been consumed. Thus, the concentration of the  $\text{S}_2\text{O}_3^{2-}$  could be measured over a period of time, using the initial concentration of  $\text{S}_2\text{O}_3^{2-}$  in the mixture, calculated to be 0.00126M, and the final concentration, 0M. These values could be used to calculate the rate according to the formula:  $\text{Rate} = -\frac{1}{2} \Delta[\text{S}_2\text{O}_3^{2-}] / \Delta t$ , where  $\Delta t$  was the time required for the color change to occur.

After solving for the reaction rate in the first 3 experiments, one could obtain the values for  $m$  and  $n$  in the rate law equation ( $\text{Rate} = k[\text{I}^-]^m[\text{S}_2\text{O}_8^{2-}]^n$ ). The values of  $m$  and  $n$  were determined by observing the change in the reaction rate that occurred as the result of a change in the concentration of  $\text{I}^-$  and  $\text{S}_2\text{O}_8^{2-}$ , respectively.

In this experiment, the reactions were done at four different temperatures in order to observe the effect of temperature on the rate of reaction. In studying the kinetics of a reaction, it is also important to consider the effects that potential catalysts or inhibitors can have on the reaction rate. These effects were observed by adding one drop of  $\text{Ag}^+$  or  $\text{Cu}^{+2}$  solution to some of the data runs and comparing the results to data runs with no additives.

The frequency factor and activation energy are two additional quantities that are important in understanding the kinetics of any reaction. In order to measure these factors, the Arrhenius equation,  $k = Ae^{-E_a/RT}$ , can be used. After taking the natural log of both sides of the equation, the

resulting new equation is  $\ln k = -E_a/RT + \ln A$ . This is a linear equation in the form of  $y = mx + b$ , where  $y = \ln k$ ,  $m = -E_a/R$ ,  $x = 1/T$ , and  $b = \ln A$ . The data from this experiment could be used to create a plot of  $\ln k$  vs.  $1/T$ , and the linear trendline of the plot could be used to determine activation energy and frequency factor.

### **Experimental Procedure:**

The class was split into groups in order to determine which group was responsible for each of the various data runs as listed in Table 1, which was taken from the laboratory manual.

**Table 1.**

Group(s)	Expt. #	Pot. cat.	T (°C)	FLASK "A"				FLASK "B"	
				starch 0.20%	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> 1.2x10 <sup>-2</sup> M	KI 0.2 M	KNO <sub>3</sub> 0.2 M	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> 0.2 M	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> 0.2 M
1,2,3,4	1	none	RT	1	2	4	4	4	4
1,2,3,4	2	none	RT	1	2	4	4	2	6
1,2,3,4	3	none	RT	1	2	2	6	4	4
1	4	none	10	1	2	4	4	2	6
1	5	Cu <sup>2+</sup>	10	1	2	4	4	2	6
1	6	Ag <sup>+</sup>	10	1	2	4	4	2	6
2	7	Cu <sup>2+</sup>	RT	1	2	4	4	2	6
2	8	Ag <sup>+</sup>	RT	1	2	4	4	2	6
3	9	none	30	1	2	4	4	2	6
3	10	Cu <sup>2+</sup>	30	1	2	4	4	2	6
3	11	Ag <sup>+</sup>	30	1	2	4	4	2	6
4	12	none	40	1	2	4	4	2	6
4	13	Cu <sup>2+</sup>	40	1	2	4	4	2	6
4	14	Ag <sup>+</sup>	40	1	2	4	4	2	6

All of the experiments were done using two clean and dry 50mL Erlenmeyer flasks, one labeled "A" and the other labeled "B". In order to ensure accuracy, each experiment was conducted twice and the average reaction time from the two runs was used. Prior to each experiment, the groups used a thermometer to determine the temperature at which the reaction would take place. For the experiments performed at approximately room temperature, students completed the reaction at the lab benches. For the experiments done at around 10°C, 30°C, and 40°C, water baths were used to achieve the desired temperature for the reaction.

The groups prepared the solutions as indicated by Table 1. The solution in Flask "A" was made with varying volumes of 0.20% starch, 1.2x10<sup>-2</sup>M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, 0.2M KI, and 0.2M KNO<sub>3</sub>. The solution in Flask "B" was made with varying volumes of 0.2M (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and 0.2M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.

After the solutions for the room temperature runs were prepared in the two flasks, the solutions were mixed to create the reaction. One person acted as the mixer and one person acted as the timer. The timer began timing as the mixer poured the solution from one flask into the other, then back and forth a few times. Then, the mixer gently swirled the contents in the flask that contained both solutions. The flask was swirled continuously until the color change was observed. As soon as the color change was observed, the timer stopped the stopwatch and

recorded the time. This procedure was followed for each experiment, and as mentioned above, each run was repeated a second time in order to ensure accuracy.

The procedure was only slightly different for the runs conducted in the water baths. After the solutions were prepared in Flasks “A” and “B”, a loosely-fitting cork was placed in each flask before they were immersed in the appropriate water bath for a 15 minute equilibration period. During the equilibration period, the group gently swirled the flasks every 3 minutes. At the end of the 15 minutes, the mixer uncorked the flasks and began mixing in the same manner described for the room temperature experiments. Again, the timer began timing as soon as the mixer poured the solution from one flask into the other. While mixing, the mixer kept the flasks immersed in the water bath as much as possible in order to maintain the desired temperature for the reaction. Each run was repeated a second time just as the runs were repeated for the room temperature experiments.

Finally the group cleaned up the equipment and solutions used in the experiment. The solutions that were contaminated with the metal solutions were disposed of in the waste containers under the hood. Then the glassware and thermometers were cleaned in the sinks.

### **Results:**

Table 2 is a summary of the data obtained by running the experiments indicated in Table 1. The initial concentrations were determined by using the equation  $M_1V_1=M_2V_2$ . The reaction time and the temperatures were recorded from the experiments. The reaction rates were calculated using the equation:  $\text{Rate} = -\frac{1}{2} \Delta[\text{S}_2\text{O}_3^{2-}] / \Delta t$ , where  $\Delta t$  was the time required for the color change to occur. Looking at the initial concentrations of the reactants and the effects they have on the reaction rate in the first 3 experiments, both reactants were determined to be first order. Thus, the general rate law equation,  $\text{Rate} = k[\text{I}^-]^m[\text{S}_2\text{O}_8^{2-}]^n$ , can be used to solve for  $k$  where Rate is the calculated reaction rate and  $m$  and  $n$  are both 1.

**Table 2.**

Experiment #	$[\text{I}^-]_0$ after mixing	$[\text{S}_2\text{O}_8^{2-}]_0$ after mixing	Time for color change, $t$ (sec)	Solution Temp, K	Reaction Rate ( $\text{M s}^{-1}$ )	Rate Constant, $k$ ( $\text{M}^{-1} \text{s}^{-1}$ )
1	0.0421	0.0421	75.6	294	8.33E-06	4.70E-03
2	0.0421	0.0211	159.5	294	3.95E-06	4.45E-03
3	0.0211	0.0421	153.9	294	4.09E-06	4.60E-03
4	0.0421	0.0211	459	283	1.37E-06	1.54E-03
5	0.0421	0.0211	47	283	1.34E-05	1.51E-02
6	0.0421	0.0211	404	283	1.56E-06	1.76E-03
7	0.0421	0.0211	20	294	3.15E-05	3.55E-02
8	0.0421	0.0211	174	294	3.62E-06	4.08E-03
9	0.0421	0.0211	107.8	303	5.84E-06	6.57E-03
10	0.0421	0.0211	30.4	303	2.07E-05	2.33E-02
11	0.0421	0.0211	99.4	303	6.34E-06	7.14E-03
12	0.0421	0.0211	52	313	1.21E-05	1.36E-02

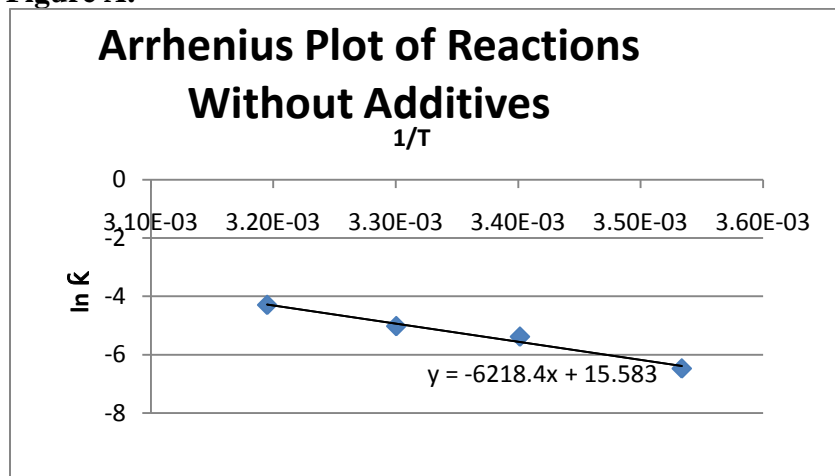
13	0.0421	0.0211	10.5	313	6.00E-05	6.75E-02
14	0.0421	0.0211	51.5	313	1.22E-05	1.37E-02
Avg of 1,2,3				294		4.58E-03

The natural log of the Arrhenius equation,  $\ln k = -E_a/RT + \ln A$ , can be applied to the Solution Temperature and Rate Constant data from Table 2 to create Arrhenius plots of  $\ln k$  vs.  $1/T$ . Table 3 contains the data that corresponds with Figure A, the Arrhenius plot of reactions without additives. Table 4 contains the data that corresponds with Figure B, the Arrhenius plot of reactions for which  $\text{Cu}^{+2}$  was added. Table 5 contains the data that corresponds with Figure C, the Arrhenius plot of reactions for which  $\text{Ag}^{+1}$  was added.

**Table 3.**

Experiment # (No Additives)	1/T (K)	lnk
Avg of 1,2,3	3.40E-03	-5.38533
4	3.53E-03	-6.47597
9	3.30E-03	-5.02524
12	3.19E-03	-4.29769

**Figure A.**



**Table 4.**

Experiment ( $\text{Cu}^{+2}$ added)	1/T (in K)	lnk
5	3.53E-03	-4.19306
7	3.40E-03	-3.33822
10	3.30E-03	-3.7593
13	3.19E-03	-2.69563

Figure B.

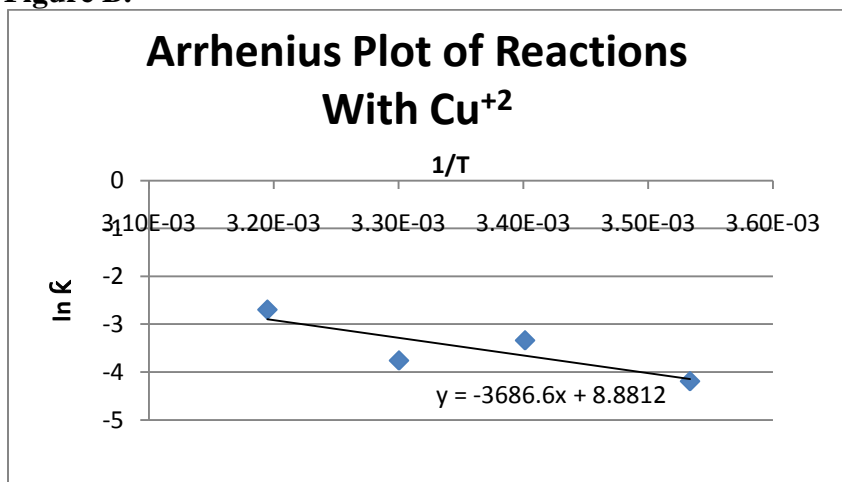
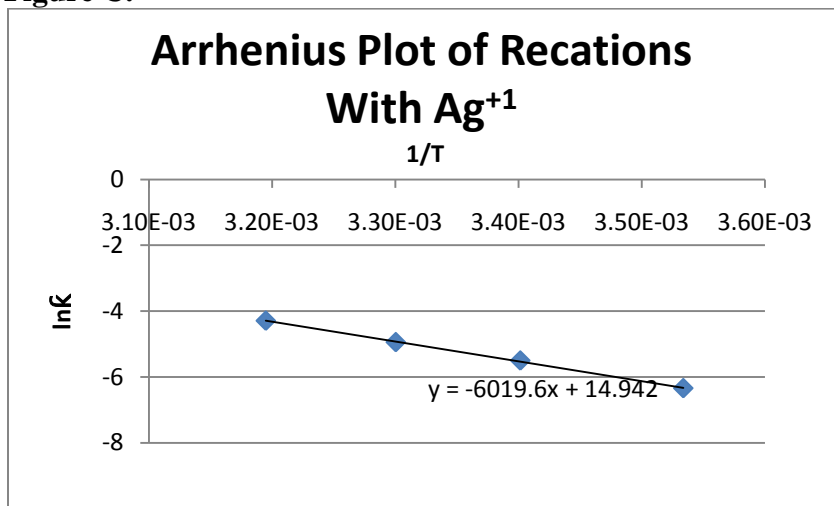


Table 5.

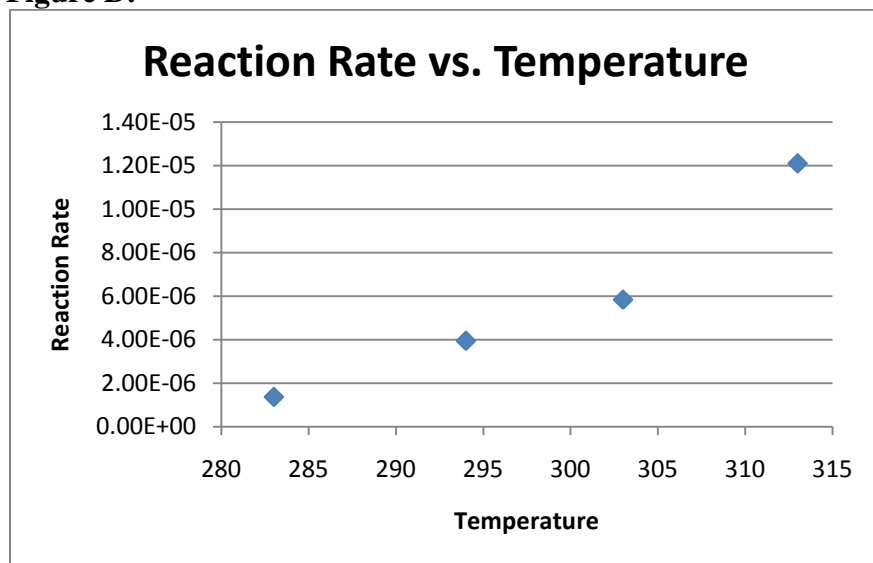
Experiment ( $\text{Ag}^{+1}$ Added)	$1/T$ (in K)	$\ln k$
6	$3.53 \times 10^{-3}$	-6.34244
8	$3.40 \times 10^{-3}$	-5.50166
11	$3.30 \times 10^{-3}$	-4.94204
14	$3.19 \times 10^{-3}$	-4.29036

Figure C.



Experiments 2, 4, 9, and 12, were very similar runs, only differing in the temperature at which the reaction was conducted. Thus, in order to observe the effects of temperature on the rate of reaction, a plot of reaction rate vs. temperature was constructed for those four experiments (Figure D).

Figure D.



### Discussion and Conclusions:

After examining the experimental data depicted in the tables and plots, several important conclusions can be made regarding the chemical kinetics of the equation under investigation ( $2\text{I}^{-1} + \text{S}_2\text{O}_8^{-2} \rightarrow \text{I}_2 + 2\text{SO}_4^{-2}$ ). The results demonstrate the general effects that reactant concentration, temperature, and catalysts have on reactions.

In experiments 1, 2, and 3, all factors are held constant with the exception of the concentration of the reactants. These conditions make it possible to observe how changing reactant concentration affects the reaction rate. The data demonstrate that if the concentration of one of the reactants is doubled while the other reactant concentration is held constant, the reaction rate doubles. This is true for both reactants. Thus, it was concluded that each of the reactants have a reaction order of 1.

In experiments 2, 4, 9, and 12, the reactant concentrations are constant and no potential catalysts or inhibitors are added. The only variation of the four runs is that they were conducted at different temperatures. Thus, a general trend can be observed regarding the effects of temperature on reaction rate. Figure D is a plot of the rates of the reaction at the four different temperatures of experiments 2, 4, 9, and 12. The data trend is consistent with the theory that as the temperature of the reaction increases, the reaction rate will increase.

On each of the three Arrhenius plots (Figures A, B, and C) in the *Results* section, there is a linear trendline equation in the form of  $y = mx + b$ . The equations of the trendlines in Figures A, B, and C can be used to solve for the activation energy of the reactions without additives, reactions with  $\text{Cu}^{+2}$ , and reactions with  $\text{Ag}^{+1}$ , respectively. As mentioned in the *Introduction* section, each linear trendline represents the natural log of the Arrhenius equation for the given set of data points. Accordingly,  $y = \ln k$ ,  $m = -E_a/R$ ,  $x = 1/T$ , and  $b = \ln A$ . Since the slope,  $m$ , is equal to  $-E_a/R$ , the equation  $E_a = mR$  can be used to solve for the activation energy. So, the activation energy of the reactions without additives was about 51.7kJ/mol, the activation energy of the

reactions where  $\text{Cu}^{+2}$  was added was about 30.7kJ/mol, and the activation energy of the reactions where  $\text{Ag}^{+1}$  was added was about 50.0kJ/mol. Catalysts work by altering the mechanism for the reaction, which speeds up the rate of the reaction and lowers the activation barrier. So, reactions with a catalyst present will have lower activation energy. Accordingly, one can conclude that  $\text{Cu}^{+2}$  is a catalyst to reaction under investigation. Furthermore, the  $\text{Ag}^{+1}$  was neither a catalyst nor an inhibitor to this reaction. Instead, the  $\text{Ag}^{+1}$  had no effect on the reaction because the reaction rates and activation energies were approximately the same for reactions with no additives and reactions where  $\text{Ag}^{+1}$  was added.