

# **An Investigation of the Briggs-Rauscher Reaction**

## **Milestone 5**

**Math512  
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## **Abstract**

The purpose of this project is to study the Briggs-Rauscher (BR) reaction. The BR mechanism is an oscillating chemical system, with many different reactions taking place at the same time. The color and voltage potential cyclically change, corresponding with the varying chemical species in solution. Ideally, this project will further the understanding of mechanisms by which the various oscillations occur. The goal of this project is to build a mathematical model that aligns with the results found from our experimentation. We are basing our work on the experimentation that has been done before us, but hope to find a better mathematical representation of the reaction that corresponds with our data. This milestone will discuss our past and current findings, as well as a reflective summary of the project work this semester.

The study of the Briggs-Rauscher reaction has many important applications. Studies that relate to human health are always of the highest importance and the Briggs-Rauscher system is significant in this area of research. For instance, electromagnetic waves traveling through muscle tissue resemble the oscillations in the BR mechanism. These waves can help to understand complex phenomena such as the beating of the human heart and nerve tissues. Also, a greater understanding of this chemical oscillator can also help model spiral waves in mold aggregates, intact and cultured cardiac tissue and retinal and cortical neural preparations.

## **What is the Briggs-Rauscher Reaction?**

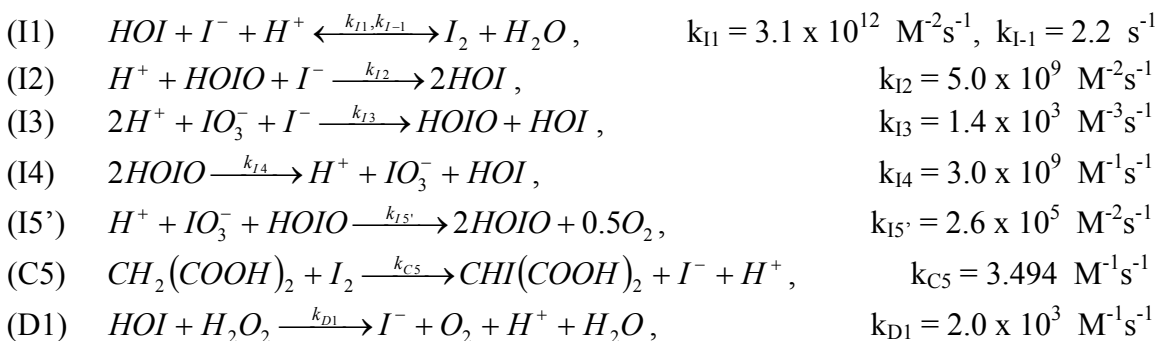
The Briggs-Rauscher reaction is a damped chemical oscillator. The reaction was discovered by two high school chemistry teachers, Thomas Briggs and Warren Rauscher, and has re-ignited an interest in chemical oscillators. It is probably the most visually-impressive oscillating chemical system known to science. During one cycle of oscillation, the color of the solution drastically changes from a deep purple to amber to clear.

There are three main characteristics of the BR reaction. The first is that it is an oscillating chemical system. When water, sodium iodate, malonic acid, sulfamic acid, manganese sulfate and hydrogen peroxide are mixed in solution, the result is a chemically unstable system that undergoes numerous reactions, all occurring simultaneously, until finally the system reaches a steady-state. The second critical component to the reaction is that there is quantitative evidence of the chemical reactions taking place, in the form of a varying voltage potential. As the reaction is taking place, the voltage potential measured across the mixture oscillates. This is important because when the experiment is conducted, we can plot the voltage potential versus time, which will be invaluable when testing the validity of our mathematical model. The third area of interest of the Briggs-Rauscher reaction is that there is a distinct, visual confirmation of the reaction. When the different chemicals are mixed in solution, the result is an impressive display of cyclic color changes from clear to yellow to dark blue. When conducting the experiment, a video camera will be used to record the timing of the color changes. These data can then be compared to the voltage potential data and to our mathematical model to give a better understanding of what is happening in the reaction.

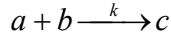
## The Chemistry

Since the Briggs-Rauscher reaction is a chemical process, it is necessary to have some understanding of the chemistry behind it, before attempting to model it mathematically. Specifically, the basic system of reactions and the corresponding reaction rates must be identified. Furthermore, the mathematical model for the BR reaction is constructed from laws from chemistry; and therefore, it must be understood, as well, before any modeling can be done.

The chemistry involved in the Briggs-Rauscher reaction is quite complicated. As a result, it is necessary to make simplifications, in order to create a system of reactions that is easier to study. There has been a significant amount of research done by various scientists, all of whom constructed different models of the reaction based on the simplifications that they made to the problem. For example, Vukojevic *et al.* (8) created a model for the BR reaction with 22 reaction steps and 13 variables. In contrast, Turanyi developed a mechanism consisting of only 8 steps. Our group has decided to follow the model set up by Kim, Lee and Shin (3). We decided to use this model because of its simplicity. We believe analyzing a model with the smallest number of steps and the fewest chemical species will provide a strong basis for the study of more complex models. This mechanism set up by Kim *et al.* is composed of 7 steps and 11 different variables:



The 11 variables are concentrations of HOI, I<sup>-</sup>, H<sup>+</sup>, I<sub>2</sub>, H<sub>2</sub>O, HOIO, IO<sub>3</sub><sup>-</sup>, O<sub>2</sub>, CH<sub>2</sub>(COOH)<sub>2</sub>, CHI(COOH)<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O. The k for each reaction is a rate constant. These constants have been defined in the Kim, Lee and Shin model, but it is important to note that they can vary based on the chemical model being used and have a drastic effect on the accuracy of the model. All 7 of these reactions are occurring simultaneously and the concentration of each chemical is dependent on time. Also, most of the chemicals are either products or reactants in several different reactions, which makes the complexity of this system obvious. It is necessary to have some way of modeling the concentration of the substances in time, and take into consideration that more than one reaction is occurring at any given moment. The Law of Mass Action is the method of choice. This law states that the rate of change of the amount of a single species in the reaction is directly proportional to the product of the concentration of the reactants in the reaction. This will give us the means to derive a system of differential equations that governs the time-dependent concentrations of the chemicals. For a simple chemical reaction of the form:



The Law of Mass Action gives:

$$\frac{da}{dt} = -kab$$

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In these equations, a and b represent the concentration of the respective reactants, c is the concentration of the product and k is the rate constant of the reaction. The units of a, b and c are concentration, which is moles per volume [mol / V], where the volume is the total volume of the solution. The units of k vary with each individual reaction; however, it is of the form, M<sup>n</sup> / t, where M is concentration, t is time and n is equal to one less than the sum of the number of moles of reactants. Therefore, the fundamental units of k are mol<sup>2</sup> / (V<sup>2</sup>\*t).

It is also important to realize that chemicals in the BR model above are not the same compounds that are being mixed in the actual experiment, with the exception of water and hydrogen peroxide. In the experiment, the components of the mixture are water (H<sub>2</sub>O), sodium iodate (NaHIO<sub>3</sub>), malonic acid (C<sub>3</sub>H<sub>4</sub>O<sub>4</sub>), sulfamic acid (H<sub>3</sub>NO<sub>3</sub>S), manganese sulfate (MnSO<sub>4</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and a starch indicator. It is relatively easy to spot the sources of some of the constituents from the BR model. For example, the only source of iodine in the system is from the sodium iodate. Also, the carbon in CH<sub>2</sub>(COOH)<sub>2</sub> and CHI(COOH)<sub>2</sub> is provided solely by the malonic acid. This causes some difficulty in determining the initial concentrations for our model, as the disassociation step is not included.

## The Math

With a basic understanding of the chemistry of the system, it is now possible to begin to model the reaction mathematically. The system of equations is derived using the Law of Mass Action. This was a relatively simple task. On the other hand, there is some difficulty in defining a set of initial conditions of the system. This arises from both an ambiguity in the model used by Kim, Lee and Shin and the uncertainty in converting the initial concentrations of the chemicals in the experiment to initial concentrations of the reactants in the chemical model. Matlab is used to solve the system of equations.

Once the system of reactions has been defined and the Law of Mass Action has been introduced, it is possible to construct a system of differential equations governing the reaction. Applying the Law of Mass Action to the Briggs-Rauscher reaction gives us a system of 11 differential equations. The bracket notation used below defines a particular species' concentration in mol/L.

$$(1) \quad (d/dt)[HOI] = -k_{11}[HOI][I^-][H^+] + k_{1-1}[I_2][H_2O] + k_{12}(2)[H^+][HOIO][I^-] + k_{13}[H^+]^2[IO_3^-][I^-] + k_{14}[HOIO]^2 - k_{D1}[HOI][H_2O_2]$$

$$(2) \quad (d/dt)[I^-] = -k_{11}[HOI][I^-][H^+] + k_{1-1}[I_2][H_2O] - k_{12}[H^+][HOIO][I^-] -$$

$$k_{13}[H^+]^2[IO_3^-][I^-] + k_{c5}[CH(COOH)_2][I_2] + k_{D1}[HOI][H_2O_2]$$

(3)  $(d/dt)[H^+] = -k_{11}[HOI][I^-][H^+] + k_{1-1}[I_2][H_2O] - k_{12}[H^+][HOIO][I^-] - k_{13}(2)[H^+]^2[IO_3^-][I^-] + k_{14}[HOIO]^2 - k_{15}[H^+][IO_3^-][HOIO] + k_{c5}[CH_2(COOH)_2][I_2] + k_{D1}[HOI][H_2O_2]$

(4)  $(d/dt)[I_2] = k_{11}[HOI][I^-][H^+] - k_{1-1}[I_2][H_2O] - k_{c5}[CH_2(COOH)_2][I_2]$

(5)  $(d/dt)[H_2O] = k_{11}[HOI][I^-][H^+] - k_{1-1}[I_2][H_2O] + k_{D1}[HOI][H_2O_2]$

(6)  $(d/dt)[HOIO] = -k_{12}[H^+][HOIO][I^-] + k_{13}[H^+]^2[IO_3^-][I^-] - k_{14}(2)[HOIO]^2 + k_{15}[H^+][IO_3^-][HOIO]$

(7)  $(d/dt)[IO_3^-] = -k_{13}[H^+]^2[IO_3^-][I^-] + k_{14}[HOIO]^2 - k_{15}[H^+][IO_3^-][HOIO]$

(8)  $(d/dt)[CH_2(COOH)_2] = -k_{c5}[CH_2(COOH)_2][I_2]$

(9)  $(d/dt)[CHI(COOH)_2] = k_{c5}[CH_2(COOH)_2][I_2]$

(10)  $(d/dt)[O_2] = k_{15}(1/2)[H^+][IO_3^-][HOIO] + k_{D1}[HOI][H_2O_2]$

(11)  $(d/dt)[H_2O_2] = -k_{D1}[HOI][H_2O_2]$

There is a differential equation for each variable that describes how the concentration varies with time. These equations are non-linear and very difficult to solve by hand; therefore, a computer solver is necessary to produce any solutions. Our group will be using MatLab to solve the system because of the programs simplicity.

Also, note that the non dimensional system of equations can be found in Appendix F. Each of the chemical concentrations was compared to its initial concentration, and the timescale was determined by the fastest reaction rate. This is likely not the best scaling, due to several low, and one zero, starting concentrations. The system is being analyzed to try to find a better scaling, possibly using the largest chemical concentration across the board. Once this is done, each non dimensional term can be evaluated and small terms can be ignored.

We attempted to find the steady state solution to the differential equations. Maple was used, and the code can be found in Appendix C. Using the rate constants from Kim (3), we obtained some interesting results. In the solution set, malonic acid, hydrogen peroxide, HOIO and  $IO_3^-$  all reach steady state at a concentration of zero. This means they are used up entirely by the time the reaction is completed. We also found a limiting ratio of  $I_2$ . This ratio was found to be

$$[I_2] = 1.409E^{12} * [HOI][I^-][H^+][H_2O]^{-1}$$

We can conclude that the reaction will reach completion or steady state when that particular concentration of iodine is reached. Linear stability analysis could not be completed because there are no critical points in the system.

The next step in solving this system is to define the initial conditions of the reaction. The initial conditions for the system are the initial concentrations of all of the variables in the Briggs-Rauscher reaction. This is a problem, however, since the initial concentrations are only known for the chemicals being used in the experiment. As mentioned above, the chemicals being used in the experiment are not the same as the variables that are used in the BR model. We are currently unsure in our method of converting the concentrations from the experiment to our mathematical model. This is because in other literature, the initial concentrations are much less than what we have calculated. Until we can better understand that conversion process, we will have to make reasonable assumptions as to what the initial conditions are. The initial concentrations for water and hydrogen peroxide are clearly defined since they are directly translated from the experiment to the model. Also, since  $[I^-]$ ,  $[H^+]$  and  $[IO_3^-]$  are ions, we can assume that they are created after the solution is mixed. Therefore, the initial concentration for those three variables is zero. It can be seen from equations (D1) and (C5) of the Briggs-Rauscher reaction that  $O_2$  and  $CHI(COOH)_2$  are only products; therefore, we will assume their initial concentrations are also zero.

### Linear Stability Analysis

Simplifying the chemical equations by grouping terms and renaming them gives the following chemical reactions. One such substitution is:  $R1=k_{11}[HOI][I^-][H^+]$ , and so on. Setting all the equations to zero gives a steady state approximation.

$$\begin{aligned}
 (d/dt)[HOI] &= -R1 + R-1 + 2R2 + R3 + R4 - R7 = 0 \\
 (d/dt)[I^-] &= -R1 + R-1 - R2 - R3 + R6 + R7 = 0 \\
 (d/dt)[H^+] &= -R1 + R-1 - R2 - 2R3 + R4 - R5 + R6 + R7 = 0 \\
 (d/dt)[I_2] &= R1 - R-1 - R6 = 0 \\
 (d/dt)[H_2O] &= R1 - R-1 + R7 = 0 \\
 (d/dt)[HOIO] &= -R2 + R3 - 2R4 + R5 = 0 \\
 (d/dt)[IO_3^-] &= -R3 + R4 - R5 = 0 \\
 (d/dt)[O_2] &= R5 = 0 \\
 (d/dt)[CH_2(COOH)_2] &= -R6 = 0 \\
 (d/dt)[CHI(COOH)_2] &= R6 = 0 \\
 (d/dt)[H_2O_2] &= -R7 = 0
 \end{aligned}$$

By observation, it can be seen that  $R5$ ,  $R6$  and  $R7$  equal zero. Substituting these terms back into the set of differential equations gives the following simplifications:  $R1=R-1$ ,  $R3=R4$ , and  $-R2=R3$ . These results show that the values of  $R-1$ ,  $R4$  and  $R2$  are determined by the arbitrary values  $R1$  and  $R3$ . It also shows that there are no critical points in the system, therefore a linear stability analysis cannot be completed. Although there may exist critical planes in an eight dimensional space, we chose not to investigate these due to time constraints.

## Model Solution

### Summary of Analyses

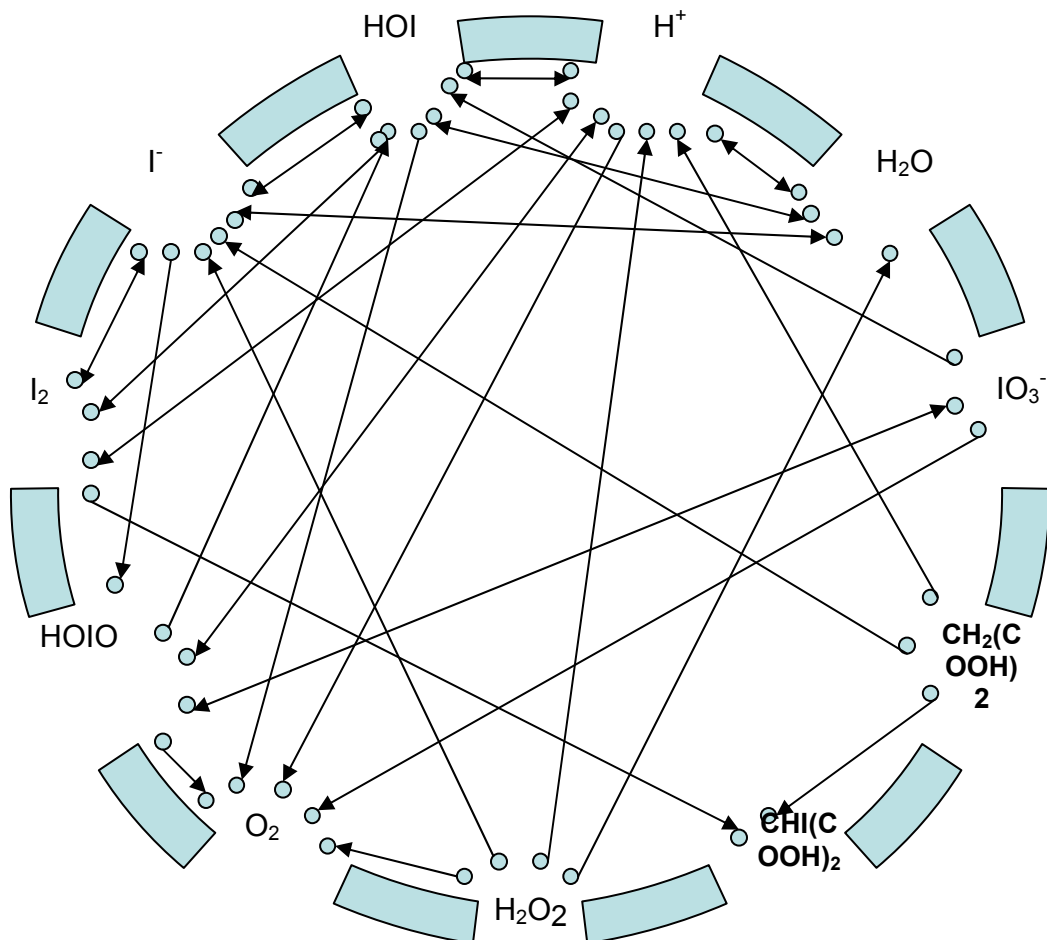
<b>Analysis Number</b>	<b>Matlab Solver</b>	<b>Initial Conditions</b>	<b>Error Tolerance</b>	<b>Max Step</b>	<b>Number of Equations</b>
1	ODE 23s	Experimental	Default	Default	11
2	ODE 15s	Literature	Default	Default	11
3	ODE 15s	Literature	Rel tol = 1E-20	Default	11
4	ODE 15s	Literature	Rel tol = 1E-20	0.001	6
Tunisia Model	ODE 15s	Given (Literature)	Rel tol = 1E-8	Default	10

### Description of Analyses

Now that a mathematical model has been constructed using the Law of Mass Action, an ODE solver from Matlab can be used to solve the system of equations. Solutions to the system will provide the behavior of the concentrations of the chemicals in the reaction. These concentrations can then be plotted versus time and compared to results obtained by other studies, notably Kim, Lee and Shin. In addition, the concentration behavior can be compared to the color and voltage oscillations from experimentation, in an effort to find consistencies between the theoretical and experimental results. The major concern of the model solution is the initial conditions. In the first analysis, the initial conditions were very roughly approximated from the input concentrations from the experiment. To further refine the initial concentrations, the second analysis refined them by drawing from data from figures in the Kim, Lee and Shin article. Although these would not be the exact concentrations used in the experiment, it would provide a basis on which our model could be compared to the one used by Kim, Lee and Shin. The third analysis used the same set of initial conditions from the second, but the relative tolerances of the Matlab solver were increased in an effort to obtain results that were more consistent with what was expected. The fourth and final analysis was our last attempt to produce oscillations within the model based on the work of Kim, Lee and Shin. To simplify the system and isolate the equations and reactions that were the most important, the model was reduced from 11 to 6 equations. This was done using assumptions from chemical kinetics and our observations of the behavior of the system. This, however, did not produce oscillations in the numerical results either. From this, our group decided to replicate the Mathematica code of the BR system from Binous' "Tunisia" model into Matlab and produce oscillations ( as we knew it would). Since it was known to work, at least, we would be able to compare the results of that model to the experimental data.

Before any mathematical modeling is done, the system can be visually modeled using a flow diagram. This is helpful to see how different chemicals move through the

system. The chart below illustrates the behavior of the different constituents throughout the system. Take  $I_2$  for example, from the direction of the arrows, it can be seen that  $I_2$  is a reactant in one reaction that produces  $CHI(COOH)_2$  and two other reversible reactions that produce  $I^-$  and  $H^+$ . On the other hand, it can be seen that  $HOI$ ,  $I^-$  and  $H^+$  all are used to produce  $I_2$  within the system.



By examining the above flow chart, there are several simple observations about the system that can be made. First,  $H_2O_2$  and  $CH_2(COOH)_2$  are never produced in any reaction; they are only consumed. Also,  $O_2$  and  $H_2O$  are only produced in the system. Therefore, we know that the concentrations of  $H_2O_2$  and  $CH_2(COOH)_2$  are zero at steady-state and serve as limiting factors in the system.

### First Analysis

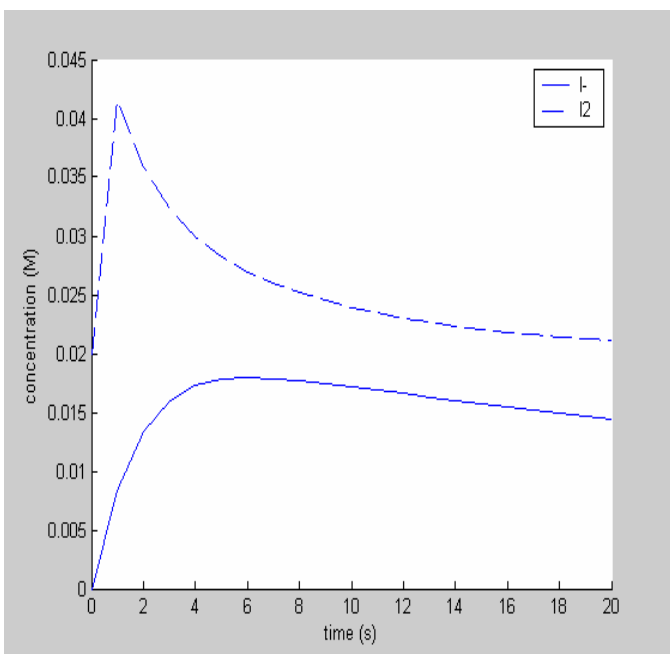
Once the initial conditions were identified, the initial concentrations of the other constituents were estimated to an approximate magnitude. These calculations were based on the amount of each of the substances being used in the experiment and converting



them into a form of mole per liter. A sample calculation is as follows for the malonic acid:

$$(0.65\text{g})\left(\frac{1\text{mol}}{104\text{g}}\right)\left(\frac{1}{0.1\text{L}}\right) = 0.0625\text{M}$$

This is an approximation of the magnitude of the reactants in the reaction. We used the stiff, ordinary differential solver from Matlab (ODE23s) to solve the system of differential equations with the defined initial conditions. Appendix A can be referenced to see the code for the Matlab program. Appendix B gives the solved code for the Matlab program, including the initial conditions. The rate constants used were found from Kim *et al.* (3), since we are using their chemical model. Shown below is a plot of the concentrations of iodide [I<sup>-</sup>] and iodine [I<sub>2</sub>] versus time. There is a close resemblance in the initial trend of the plot to that of the plot by Kim, Lee and Shin (3). However, lacking in our model is any oscillation after the first inflection. This may be due to a variety of factors. Most importantly, our initial conditions are only approximations and require a great deal of refinement.



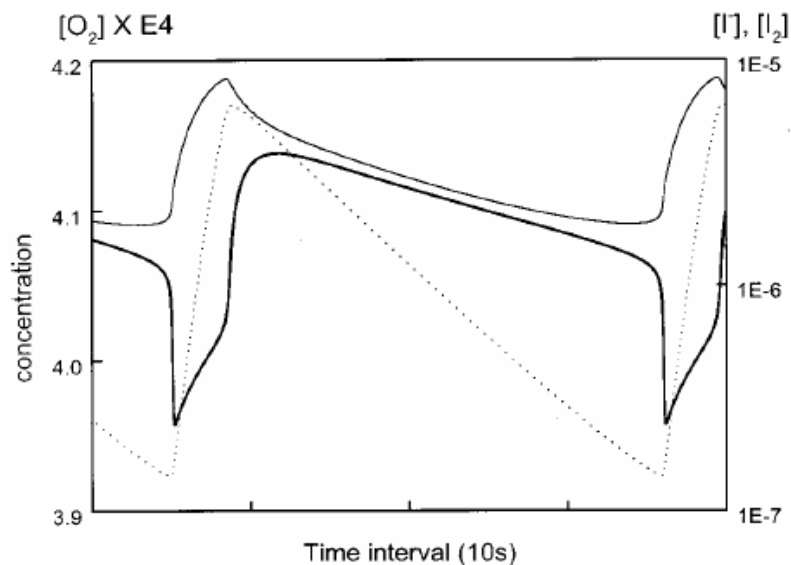


FIG. 2. Oscillations of  $[I_2]$  (solid line),  $[I^-]$  (heavy solid line), and  $[O_2]$  (dotted line) in the present model with  $k_{II} = 3.1 \times 10^{11} \text{ M}^{-2} \text{ s}^{-1}$  and  $k_{CS} = 20 \text{ M}^{-1} \text{ s}^{-1}$ . Other parameter values are the same as in Fig. 1.

## Second Analysis

There were two amendments made to the first analysis prior to modeling the system for a second time. First, a different ODE solver is being used for the Matlab modeling. The solver was changed from ode23s to ode15s because of the lower error tolerance in the ode15s solver. Second, a more refined set of initial conditions has been defined. They are not the initial conditions that were used in the experiment that we ran, but they are the input concentrations used in one of the model solutions in the article by Kim, *et al.* Initial conditions were given in the captions of figures and approximated from the figures themselves. Unfortunately, there was no information as to where these initial conditions came from. Assumptions were made for the initial concentration of water and malonic acid and were based on the approximations used in the first analysis. The set of input concentrations (M) initially used in the second analysis are as follow:

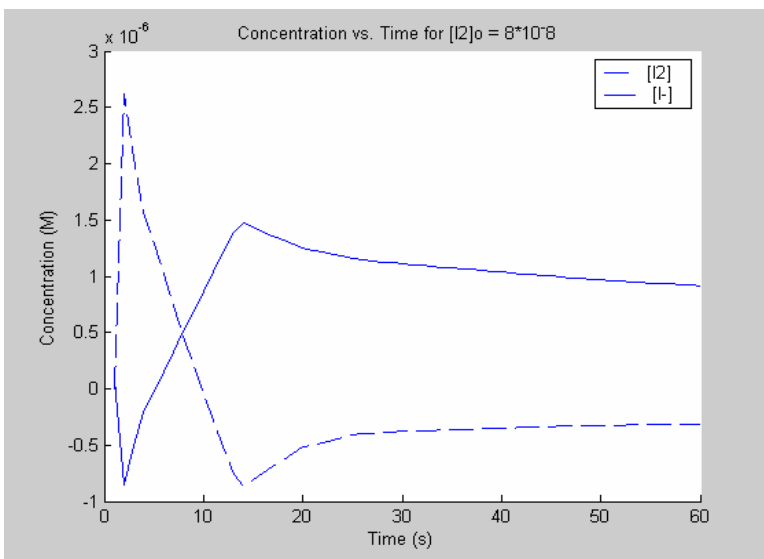
$[I^-]$	=	$10^{-10}$	$[IO_3^-]$	=	0.01
$[I_2]$	=	$8 \cdot 10^{-8}$	$[O_2]$	=	$2.5 \cdot 10^3$
$[HOI]$	=	$8 \cdot 10^{-11}$	$[CH_2(COOH)_2]$	=	0.0015
$[H^+]$	=	0.056	$[CHI(COOH)_2]$	=	0
$[H_2O]$	=	1.0	$[H_2O_2]$	=	0.33
$[HOIO]$	=	$9 \cdot 10^{-11}$			

All units in Molarity, (M)

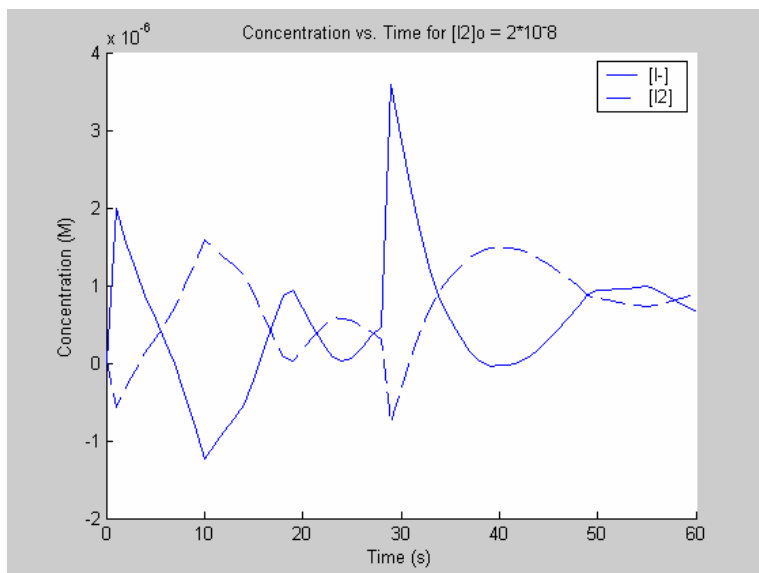
In addition to these two changes, during the second analysis we looked at the effects of varying two different parameters of the problem: initial conditions and time step. We found that variations in these factors have very large effects on the solution of

our model. The initial conditions were the first factors that were examined and the time step was assumed to be one second for the solutions.

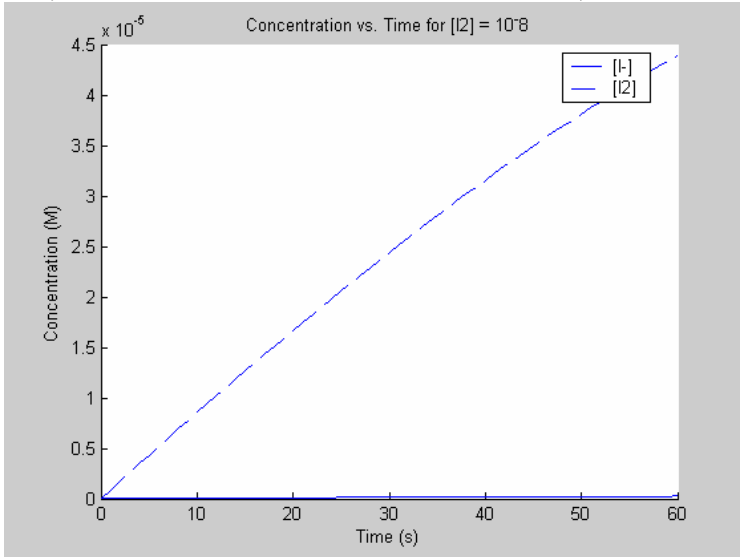
Using the initial conditions from above, a program similar to that of the first analysis was run in Matlab and the plot of  $[I^-]$  and  $[I_2]$  is shown below. It should be noted that the analyses are focused on  $[I^-]$  and  $[I_2]$  because their concentrations demonstrate the oscillations of the system and are also responsible for the oscillations in color. Therefore, if the model exhibits oscillations for these two constituents, it is an indication that the model is progressing in the right direction.



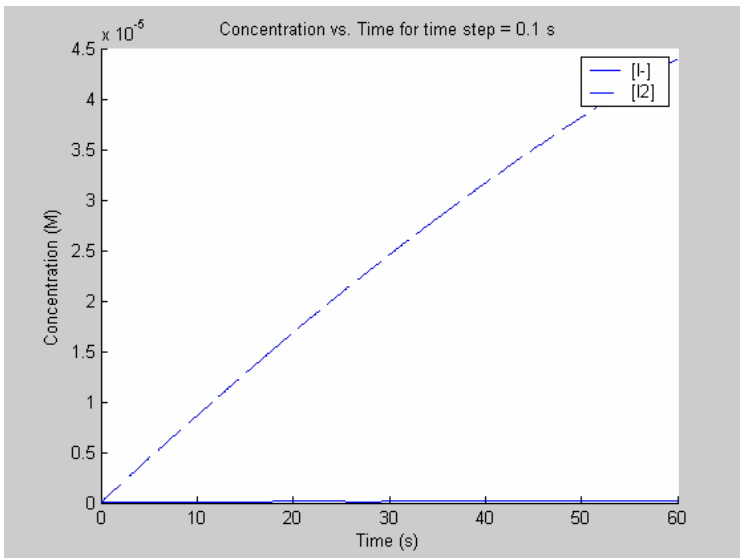
This plot is concurrent with the expectation that a maximum for iodine occurs when there is a minimum for iodide and vice versa. As an attempt to get a better understanding of the effect of initial conditions on the system, the input concentration of iodine was changed slightly from  $8 \times 10^{-8}$  M to  $2 \times 10^{-8}$  M. The plot of the concentrations versus time for the new initial conditions is below.



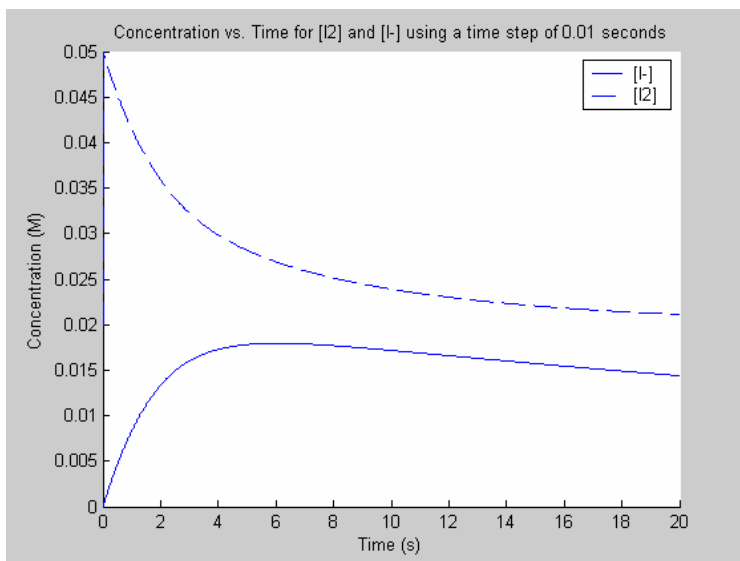
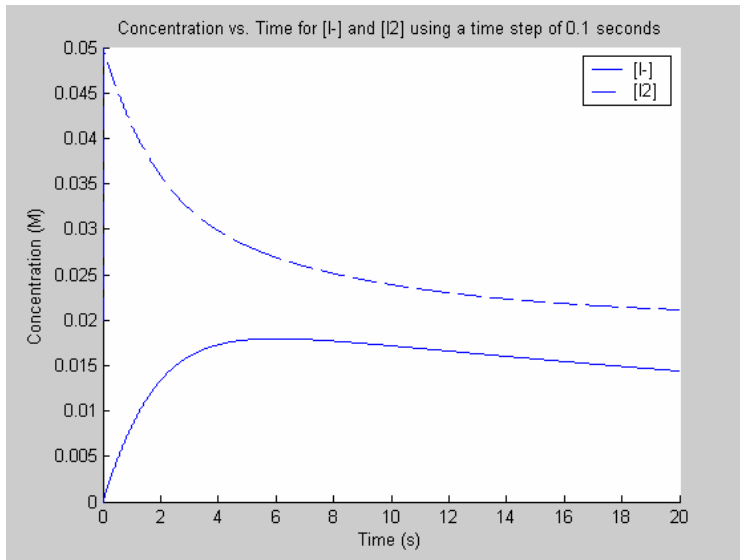
There is a large disparity between the two plots and the curves of the second plot seem sporadic and lack a clear pattern, in spite of evidence of oscillations. To try to explain this, other initial conditions were tried. Next, we tried setting  $[I_2]_0$  to  $10^{-8}$  M.



This plot demonstrates no correlation with the other two. This made it clear that we needed to reexamine our model and the assumptions that went into it. The first assumption to be reevaluated is the time step for the solver. A major indication that there may be a problem with the time step is that there are negative concentrations in the first two plots. This, of course, is physically impossible and may be the result of an overshoot or accuracy problem within the solver. With this in mind, it is very possible that the apparent oscillations in the previous solution were nothing more than error within the solver. So, to investigate this, the time step was varied within Matlab while keeping the input concentration of  $[I_2]$  as  $8 \times 10^{-8}$  M as a basis for comparison. The first time step to be tried was 0.1 seconds.



This is very strange because it looks exactly like the model using  $[I_2]_0$  as  $10^{-8}$ , yet for this solution,  $[I_2]_0$  was set as  $8 \cdot 10^{-8}$ . To further isolate the effects of time step on our model, a smaller time step was used with the initial conditions used in the first analysis. These results can be compared with what was found using a larger time step (1 second) during the first analysis. The plots of the concentrations of  $[I^-]$  and  $[I_2]$  using a time step of (0.1 and 0.01 seconds) and the input concentrations from the first analysis are found below.



As can be seen above, the plots are very consistent using different time steps in the solver. This is what is expected when time step is varied. Solutions using smaller time steps should resemble previous solutions, but are smoother and more refined.

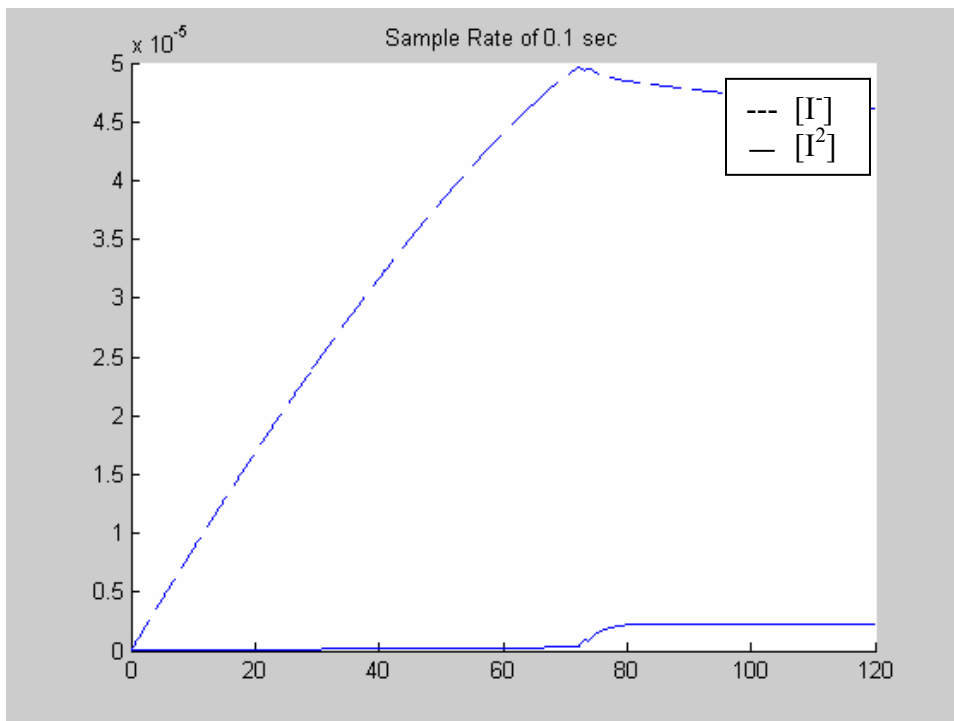
It is obvious that we have a long way to go in understanding the model, both mathematically and chemically, for the Briggs-Rauscher Reaction. Our results from the

second analysis leave many unanswered questions about our current model that we will be investigating in the near future. Other time steps were tried with the second initial conditions, but they did not lead to any helpful conclusions. We are approaching a refined set of initial conditions, but as can be seen from the erratic solutions, there is much to be learned about the initial conditions of our system and how the variation of these initial conditions affects the results of our model. Also, additional research and analysis is needed to determine what an acceptable time step will be for our system of equations.

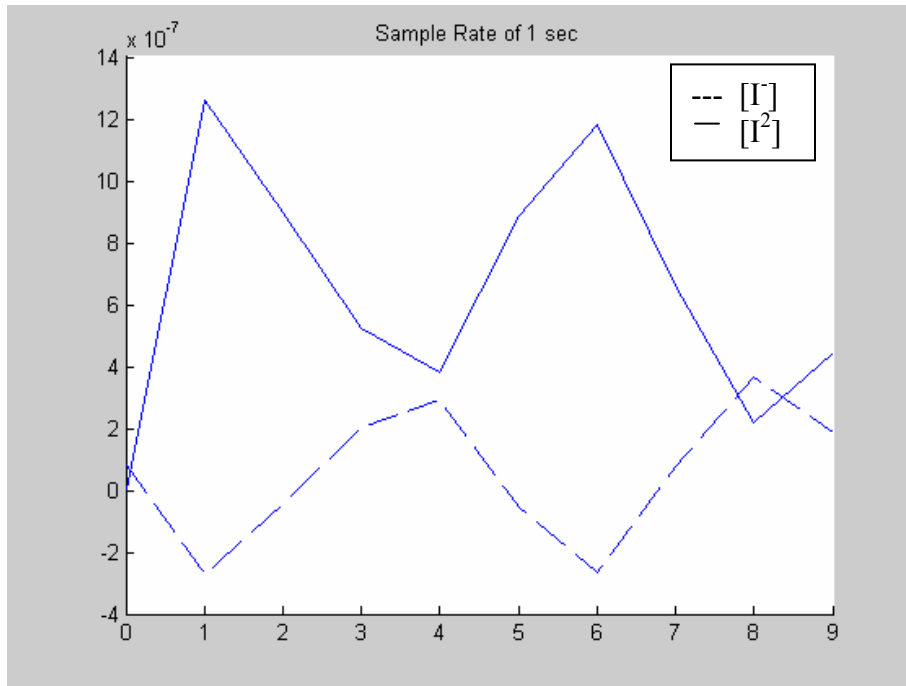
### Third Analysis

The second analysis gave results that were inconclusive and raised questions about the initial conditions and the Matlab model. The third analysis involved two modifications to the model used during the second analysis: the relative tolerance of the solver was decreased and alternate solvers were used. By decreasing the relative tolerance, the inconsistencies that were found by changing the sample rate were no longer evident. Also, the two other solvers that were tested in this analysis showed that the ode15s solver is solving the system accurately. Unfortunately, oscillations are still not present in the model. The reason for this is uncertain, but there may be a mistake in the equations of our model. This is currently being investigated.

The first change that was made to the second analysis for the third analysis was to decrease the relative tolerance of the Matlab solver. This would lower the permissible error of the solver while it was solving the system of equations and, hopefully, give clearer and more consistent results. Matlab uses a default tolerance of 1.0E-3. The first computation was made using a relative tolerance of 1.0E-4 and a sample rate of 0.1, the plot of concentrations of iodine and iodide was as follows:

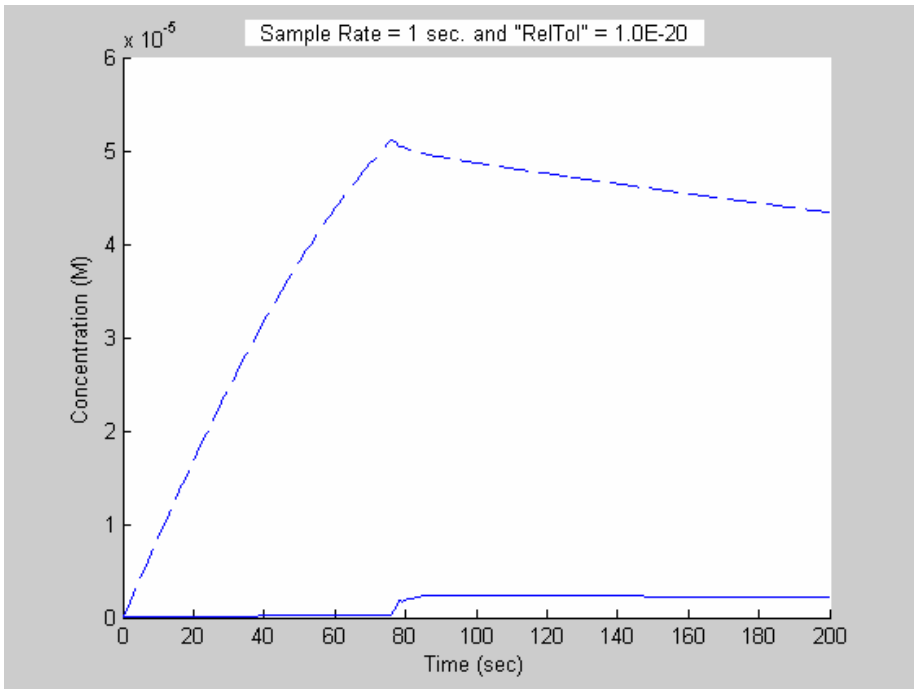
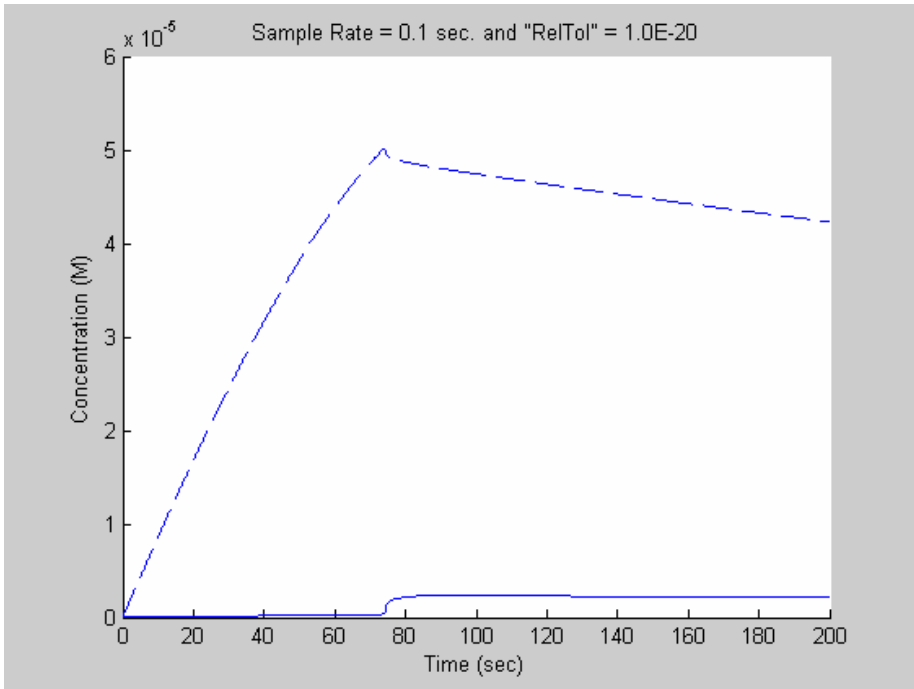


This plot resembles the concentration plot from the second analysis with the exception of the activity at 75 seconds that makes the iodide concentration begin to decrease and the iodine concentration sharply increases. Still, no oscillations were evident in the solution. It is not yet obvious as to whether or not the relative tolerance set on the solver can prevent changes in the sample rate from producing inconsistent solutions. So to test whether the relative tolerance has corrected the model, a sample rate of 1 second is used in the Matlab solver. The results produced the plot below:



As can be seen from the plot, the results obtained when using a sample rate of 1 second are bizarre. The solver does not solve the system past 9 seconds and once again negative concentrations are observed.

Since the magnitudes of the smallest input concentrations are on the magnitude of 1E-11, the relative tolerances of the solver should be at least that small. This may explain the poor results that were found above. So, the relative tolerance of Matlab was decreased to 1E-20. This change produced the following plots using a sample rate of 0.1 seconds and 1 second, respectively.

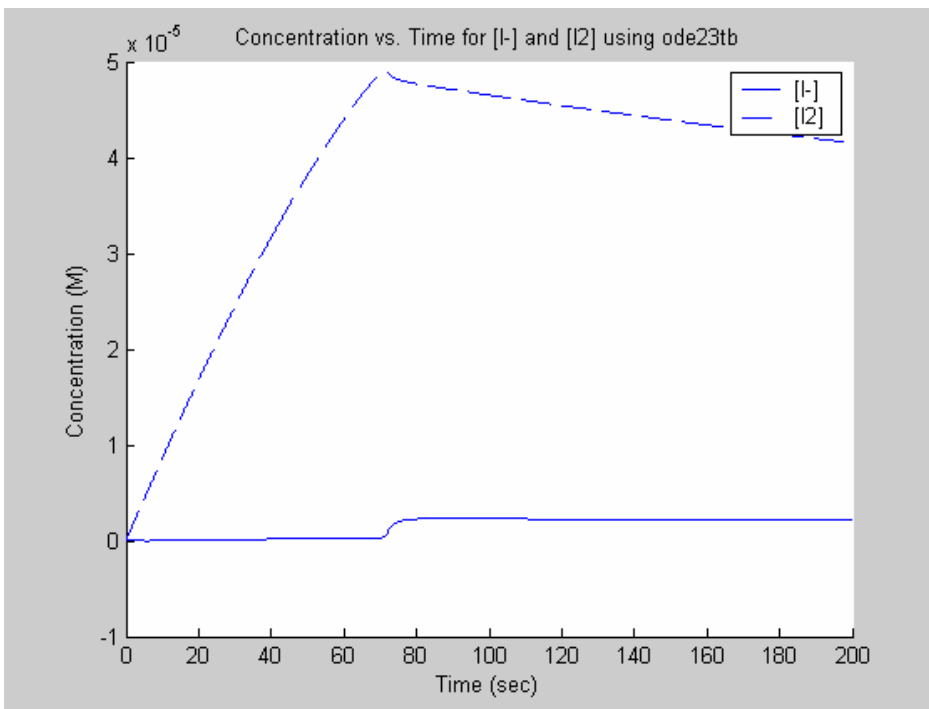
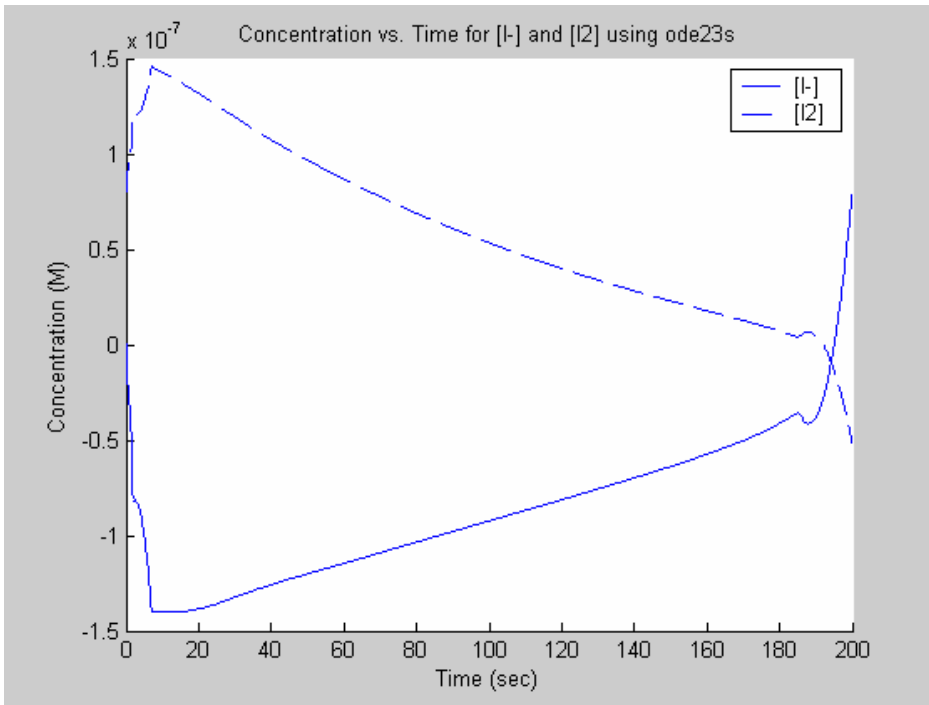


These two plots are very similar and demonstrate that the sample rate is not adversely affecting our results; rather it is the relative tolerances that the solver is using to solve the system of equations. It should also be noted that a relative tolerance of  $1E-15$  still produced inconsistent results with different time steps.

However, oscillations have yet to be seen in a solution. To verify that the ode15s solver is the strongest solver for our particular application, other solvers were used and the results were compared. This was done to test the ode15s solver and ensure that it was



solving the system correctly and accurately. The solvers that were used were ode23s and ode23tb. These are both stiff solvers; however, ode23tb is typically used for only moderately stiff problems.



The results from the ode23s solver are poor in that it shows negative concentrations. This is not physically possible and it can be concluded that the ode23s

solver is a poor choice for solving the system of equations for the Briggs-Rauscher reaction. The ode23tb solver gave results that were very consistent with the solution from the ode15s solver. This gives us confidence in using the ode15s solver for our modeling; however, for future analyses, the ode23tb solver will also be used to test for consistency of the results of the ode15s solver.

#### Fourth Analysis

In an effort to further simplify our current model and possibly produce oscillations in the numerical solution, the number of equations was reduced by using chemical kinetic theory and observations. Chemical kinetics suggests that the active intermediates in a system of reactions can be treated as constants and, therefore, their concentration does not change with time. Ions often act as active intermediates, so the rate of change of the concentrations of  $H^+$  and  $IO_3^-$  are assumed to be zero. Furthermore,  $CHI(COOH)_2$  does not have any affect on the behavior of the system because it is only a bi-product of the other reactions taking place (i.e. it is not used as a reactant in any equation).  $H_2O$  and  $H_2O_2$  were taken as constants based on assumptions made by Binous in the “Tunisia” model. The trials of Matlab were run using this new system. Unfortunately, none of them produced oscillations nor yielded any useful or insightful results.

#### Tunisia Model

Given the current state of the Kim, Lee, and Shin model, it was decided that another model should be analyzed for potential oscillations. The Tunisia model, based on the work of DeKepper and Epstein, was originally written in Mathematica; however, for this project, the code was converted into Matlab. The function code and solver can be found in Appendices G and H. It was reproduced exactly to yield oscillations in the concentrations of  $I^-$  and  $I_2$ , which is a great improvement over the Kim model. Unfortunately, the period of oscillation, while damped, starts at about 800 seconds. This is clearly a discrepancy with our experiments, which had a period of 1 to 2 seconds. Also, we believe that DeKepper and Epstein had the same issue, according to their article. The results from the “Tunisia” model are shown below.

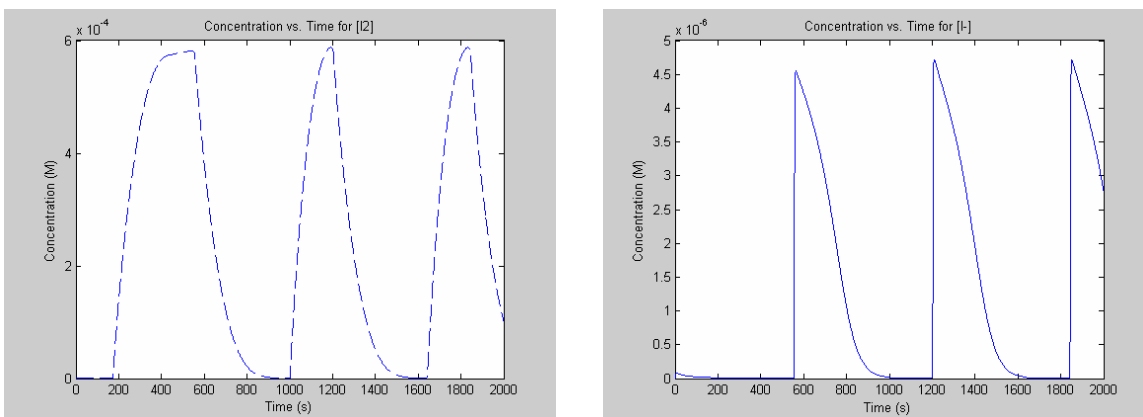


Figure: Above are the concentration versus time plots of  $[I^2]$  (left) and  $[I]$  (right) from the Tunisia model. Initial Conditions:  $[I^2]_0 = 6 \times 10^{-7} \text{ M}$ ;  $[I]_0 = 10^{-8} \text{ M}$ . Note the large period of oscillation and differing concentration axis multiple.

It appears that the model stagnates in the non-radical reaction sequence. DeKepper acknowledged this and was attempting to push the model through that slow stage. The period can be altered by slight changes to the rate constants, residence time, and initial concentrations. Given the complexity of the system, however, any drastic changes will send the reaction out of oscillation and into a region of mono- or bi-stability. While it would be interesting to pursue the adaptations DeKepper proposed, our background in chemical kinetics does not allow for us to make educated changes to the system at this time. To haphazardly alter values in a reactor with that many degrees of freedom is frivolous.

## Measurements and Experimentation

Summary of Experiments:

Experiment Number	Solution Used	Starch Used	Color Changes	Stir Rate
1	Pre-Mixed	Unknown	Amber-Clear	600 rpm
2	Mixed in Lab	Unknown	Amber-Clear	600 rpm
3	Mixed in Lab	Patrick's	Amber-Clear-Purple	600 rpm
4	Mixed in Lab	None	Amber-Clear	0 to 600 rpm
4-Redo	Mixed in Lab	None	Amber-Clear	600 rpm
5	Mixed in Lab	Patrick's	Amber-Clear-Purple	100 rpm

## Experiment Number 1

Two solutions were premixed for use in the laboratory. Solution A contained sodium iodate, sulfamic acid and water. Solution B contained hydrogen peroxide, malonic acid, manganese sulfate and a starch solution. It was noticed that the plastic jug containing solution B was bulged outward. We hypothesize the bulge was due to the breakdown of hydrogen peroxide into water and oxygen. 50 mL of each solution were mixed into a continuously stirred beaker, with a stirring rate at 600 rpm. The visual results were recorded with a video camera and the voltage potential was recorded at a rate of 10 samples per second through Data Studio.

Visually, there were only two noticeable color oscillations, amber to clear. The blue phase of the oscillation was missing. It was noted by Kim, *et al.* that oxygen also oscillated throughout the reaction. One possible explanation is that due to the lack of oxygen, the blue phase was absent. Throughout each oscillation the amber color got darker and darker, taking longer each oscillation to turn clear. After about 3 minutes, the color oscillations ceased and the resulting color in the beaker was brown. Voltage potential still oscillated, yet not in the scale we were expecting. A sample plot of Patrick Zulkowski's results of potential vs. time, a range between -0.12 to .02 volts was recorded. Our results obtained values between -.03 to .035 volts. We have not determined the sensitivity of the voltmeter to check the validity of our data. Zulkowski also describes the reaction as taking between 150 to 245 seconds to come to an end. Oscillations stopped for our reaction at approximately 100 seconds. That is about 1/3 shorter than expected. We speculate the smaller amplitude of voltage oscillation and shorter time span is due chemical breakdown which we also associate with the lack of blue color change. We plan on comparing the color oscillations to the voltage oscillations and expect there to be a strong correlation between color change and voltage potential. The graph of potential versus time can be seen in appendix D.

## Experiment Number 2

For the second experiment, solutions were mixed immediately before use. First we measured 50mL water, 1.2 g sodium iodate and 0.65 g sulfamic acid and placed these reactants into beaker A. We then stirred this mixture for 5 minutes at 600 rpm. While this was mixing, we measured out 50 mL of 3% hydrogen peroxide, 0.65 g malonic acid, 0.45g manganese sulfate and 4 drops of starch solution into beaker B. We removed beaker A and used the magnetic stirrer to mix beaker B. Beaker B was stirred at 600 rpm for 5 minutes. After Beaker B was stirred it was removed from the magnetic stirrer. We then placed the electrodes into Beaker A, hooked them up to DataStudio and recorded the data to make sure there was no potential between the electrodes. The mixer was turned on to 600 rpm and the contents of Beaker B was dumped into Beaker A. The resulting color changes were videotaped, and potential changes were recorded by data studio at a rate of 10 samples per second. As with our first experiment, we did not see any purple oscillations. We went back and reviewed the tape very slowly, and compared it to Patrick's experiments. From his data, there was a definite purple color change which was not observed in ours. We believe that because we are using a different starch solution, it

may be reacting differently with the iodine concentrations, somehow skipping the purple color change. For our next experiment, we plan to use the same starch solution as Patrick used in his experiments. Our voltage data was still dissimilar to Patrick's. The voltage potential we obtained appears more stable, yet oscillated over a shorter amount of time. Patrick's data has the same number of oscillations, and the damping is very significant. Our experiment lasted for approximately 4 minutes, and oscillations were recorded for approximately 100 seconds. From the graph, it can be seen that there were 9 distinct oscillations with a frequency of 1 Hz, and a maximum amplitude of 1.5 volts. The graph of our data can be seen in appendix E.

### Experiment 3

For our third experiment, the solutions were mixed immediately before use. The only change was that of the starch indicator. The starch indicator used in this experiment is the same as the one Patrick used to conduct his experiments. The stirring rate was kept at a constant 600 rpm. We observed a distinct purple color change. The purple phase lasted the longest, immediately after purple came the amber phase. The amber phase was by far the shortest of the three phases and briefly flashed in the beaker. The solution then cleared and returned to purple. Our voltage data was very good, and looks identical to Patrick's.

### Experiment 4

Experiment 4 consisted of the same setup as experiments 2 and 3, except no starch solution was to be used. The magnetic stirrer was turned on late, we still obtained oscillations, but they are very poor. The experiment still lasted approximately 3 minutes, consistent with the previous experiments. The color changes oscillated between amber and clear with the purple phase missing. This was expected due to the lack of starch solution.

### Experiment 4 – Redo

Experiment 4 was redone due to the failure of the previous experiment. The stirrer was started on time and we obtained the same color changes as the previous experiment. Again, the experiment time was approximately 3 minutes, but this time we obtained much better oscillations. Unfortunately, our data was overwritten, so this experiment will be conducted again.

### Experiment 5

For this experiment, we changed to stirring rate to 100 rpm. The oscillations occurred slowly; the purple phase appeared to be longer than in previous experiments. The experiment also lasted 3 minutes, which is the same as having a stirring rate of 600 rpm.

## Project Summary

The goal of this project was to gain a better understanding of the Briggs-Rauscher mechanism through attempting to model it mathematically. Experiments were conducted in the lab to collect voltage data and the period of color oscillations. The experimental and theoretical results could then be compared, mainly using the period and amplitude of oscillations, and the discrepancy between the two sets of results could be determined. Overall, the results from our numerical solutions were disappointing. We attempted several. Our research and background did not give us the knowledge and understanding to make educated and justifiable changes within our basic mathematical model that would bring it closer to the experimental and expected results. We simply did not have the understanding of the chemistry involved in the system to make accurate hypotheses as to how the system would behave.

In the long run, our group strongly felt that, although we did not get the results that we had hoped for, we made significant progress throughout our study. With each successive analysis, our model was refined to the best of our ability and understanding (at that time) and we learned from each step of the modeling process. Our refinements centered on smoothing out the problems and challenges that occurred throughout the duration of the project. The major hindrances were the initial conditions of the system, the accuracy and time step of the Matlab solvers and identifying the most important aspects of the Briggs-Rauscher mechanism. Our level of learning of the system is at a level of comprehension. We have not been capable of building and developing our own model. We have lacked the ability to formulate a model based on our own understanding, but rather, we have depended on the synthesis of prior studies.

In conclusion, we have learned a great deal through our investigation of the chemical oscillating system. We have learned how to approach the process of modeling complex systems and some of the tools that are at our disposal for handling such problems. Throughout our project, we have utilized linear stability analysis, non-dimensionalization, numerical ordinary differential equation solvers in Matlab and a host of other methods of gaining a deeper understanding of a problem. These are all certainly techniques that can be applied to any open-ended problem that we may face in the future.

## Annotated Bibliography

- (1) Thomas Briggs and Warren Rauscher, "An Oscillating Iodine Clock", *Journal of Chemical Education*, **50** (1973), 496.

This article is the original publication of Briggs and Rauscher's experiment. It was very informative and gave us a better understanding of the mechanisms that drive the reaction. Specifically, there are visible fluctuations in concentration of iodide ions. The blue starch complex is not visible until the iodide concentration approaches its peak value ( $10^{-4}$  M using their initial concentrations) during each cycle. Replacing manganese with cerium gives higher frequency oscillations. Invisible oscillations in iodide occur in the absence of a metal catalyst. If malonic acid is not present in demonstration mixture, manganese catalyzes a rapid initial formation of iodine. Malonic acid is a halogen consumer and a halide producer.

- (2) C. Vidal, A. Pacault, *Nonlinear Phenomena in Chemical Dynamics*, Springer: New York, 1981

This book is a compilation of the proceedings of an international conference in Bordeaux, France, September 7-11, 1981. New experimental examples and mathematical modeling are discussed in the context of bistability in a continually stirred tank reaction (CSTR). Outlined is a differential equation relating species concentration and reaction rates. It states:

$$\frac{dX}{dt} = F(X) + \frac{X_0 - X}{\tau}$$

Where  $X$  is the specific concentration,  $X_0$  is the input concentration,  $F$  is the chemical reaction rate, and  $\tau$  is the reciprocal of residence time. Steady state can be found by setting the right hand side to zero and solving the resulting algebraic equations. We plan to analyze this equation and possibly use it as our model. This text also talks about the Oregonator. The Oregonator is a simple mathematical model of the Belousov-Zhabotinskii reaction invented by R.J. Field and R.M. Noyes. This model consolidates the number of reaction steps into a system of rate equations governed by the Law of Mass Action. The resulting system of nonlinear ordinary differential equations can then be solved using a computer program. We also will investigate the usefulness of the Oregonator to the Briggs-Rauscher mechanism.

- (3) Kyoung-Ran Kim, Dong J. Lee and Kook Joe Shin, "A simplified model for the Briggs- Rauscher reaction mechanism" *Journal of Chemical physics*, Volume 117, **6** (2002), 2710-17.

Kim, *et al.* gives a solid background of the different studies carried out on the Briggs-Rauscher mechanism. They discuss the differences between the various models, and choose to model the system as laid out by De-Kepper and Epstein (the DE model). The DE model uses a skeleton mechanism of the B-R reaction consisting of two main processes, a radical process and a nonradical process. These two processes are then

further reduced to a system of 7 reactions. A list of these reactions is included in our report.

The mechanism by which color change occurs is also discussed in the article. When the solution turns yellow, the iodide concentration is low. As the iodide concentration increases along with the iodine concentration, it reaches a maximum and a blue starch-iodide complex forms. The iodine concentration begins to fall, though the iodide concentration increases and remains high. As the iodine continues to drop, the solution finally clears and the oscillations begin over again. The decrease in iodide and iodine are governed by the nonradical process. We also learned that oxygen oscillates throughout the reaction as well as iodine and iodide.

- (4) Casey R. Grey, "An Analysis of the Belousov-Zhabotinskii Reaction" The High School Summer Science Research Program, Department of Mathematics, Baylor University, Waco, Texas.

This report gave us many important things. First, we observed the layout of the paper and felt this would be a good way to lay out our report. It led us step by step through the solving of the B-Z reaction mathematically, which is very similar to the B-R reaction. The report was surprisingly readable and also contained helpful information about the steps taken to put a set of chemical reactions into differential equations by means of the Oregonator scheme, which was briefly discussed above. The paper also describes the steps taken in the dimensional analysis of the nonlinear ordinary differential equations and the change of variable used in the process. We plan to study this resource much more extensively in the next couple weeks.

- (5) Stanley D. Furrow, "Comparison of Several Substrates in the Briggs-Rauscher Oscillating System", *Journal of Physical Chemistry*, **99** (1995), 11131-40

In this article, Furrow describes the Briggs-Rauscher in terms of five unique chemical species. These are an acid, an iodate ion, hydrogen peroxide, a metal catalyst and an organic substrate to react with the iodine. The addition of starch causes sharper color changes. The oscillating mechanism is described in much depth, and Furrow goes on to list many substrates and their effect on the iodine consumption and its effect on the production rate for the oscillator. It is stated that with an increase in substrate concentration, iodine production increases as well. We hope this article will become more helpful as our knowledge of the mechanism increases.

- (6) Housam Binous, "Briggs-Rauscher Mechanism", Department of Chemical Engineering, National Institute of Applied Sciences and Technology, Tunis, Tunisia

This paper is merely a mathematical solution to the Briggs-Rauscher mechanism. It gives no detail of how the author came to this solution. Assuming the findings are correct, we plan to use the equations and graphs provided to compare our solution and hopefully we will see a strong correlation between the author's data and our own.

- (7) Joseph Noggle, *Physical Chemistry*, Harper Collins College Publishers, 3d edition



This textbook helped us to understand the mathematics in turning chemical reactions into differential equations. We were able to understand how chemical reaction velocity changes with respect to chemical concentration.

- (8) V. Vukojevic, P.G. Sorensen, F. Hynne, “Predictive Value of a Model of the Briggs-Rauscher Reaction Fitted to Quenching Experiments”, *Journal of Physical Chemistry*, **100** (1996), 17175

This article outlines a model of the Briggs-Rauscher reaction similar to Furrow-Noyes model and DeKepper-Epstein. The authors describe in detail how they came upon their model of 22 reaction steps, and also how they treat the concentration of their 13 chemical species as dynamic variables. Hopefully this article we help us to determine the input concentrations for our model.

## Appendix A – Matlab code for Kim model solution

function dy = F(t, y, flag)

k11 = 3.1\*10<sup>12</sup>; %Rate constants for the 7 basic chemical equations

k11r = 2.2; % in the Briggs-Rauscher Reaction

k12 = 5\*10<sup>9</sup>;

k13 = 1.4\*10<sup>3</sup>;

k14 = 3.0\*10<sup>9</sup>;

k15 = 2.6\*10<sup>5</sup>;

kc5 = 3.494;

kd1 = 2.0\*10<sup>3</sup>;

A = y(1); %Naming Convention: A = I-

B = y(2); % B = I2

C = y(3); % C = HOI

D = y(4); % D = H+

E = y(5); % E = H2O

F = y(6); % F = HOIO

G = y(7); % G = IO3-

H = y(8); % H = O2

I = y(9); % I = CH2(COOH)2

J = y(10); % J = CHI(COOH)2

K = y(11); % K = H2O2

%System of differential equations from the Law of Mass Action. Each row

% corresponds to a rate equation. Row 1 = dA/dt

% Row 2 = dB/dt

% ...

% Row 11 = dK/dt

dy=[-k11\*C\*A\*D + k11r\*B\*E - k12\*D\*F\*A - k13\*D^2\*G\*A + kc5\*I\*B + kd1\*C\*K;  
k11\*C\*A\*D - k11r\*B\*E - kc5\*I\*B;  
-k11\*C\*A\*D + k11r\*B\*E + 2\*k12\*D\*F\*A + k13\*D^2\*G\*A + k14\*F^2 - kd1\*C\*K;  
-k11\*C\*A\*D + k11r\*B\*E - k12\*D\*F\*A - 2\*k13\*D^2\*G\*A + k14\*F^2 - k15\*D\*G\*F  
+ kc5\*I\*B + kd1\*C\*K;  
k11\*C\*A\*D - k11r\*B\*E + kd1\*C\*K;  
-k12\*D\*F\*A + k13\*D^2\*G\*A - 2\*k14\*F^2 + k15\*D\*G\*F;  
-k13\*D^2\*G\*A + k14\*F^2 - k15\*D\*G\*F;  
1/2\*k15\*D\*G\*F + kd1\*C\*K;  
-kc5\*I\*B;  
kc5\*I\*B;  
-kd1\*C\*K];

## Appendix B

```
tspan=[0:1:20]; % Time step in seconds  
yo=[0; 0.02; 0.04; 0; 1; 0.04; 0; 0; 0.06; 0; 0.5]; %Initial concentrations for  
chemicals/ions A-K
```

```
[T,sol]=ODE23s('dfuncs',tspan,yo)
```

```
hold on  
plot(T,sol(:,1))  
plot(T,sol(:,2),'--')  
%plot(T,sol(:,3),'.')  
%plot(T,sol(:,4),'-.'  
%plot(T,sol(:,5),'d')  
%plot(T,sol(:,6),'x')  
%plot(T,sol(:,7),'o')  
%plot(T,sol(:,8),'s')  
%plot(T,sol(:,9),'*')  
%plot(T,sol(:,10),'t')  
%plot(T,sol(:,11),'<')
```

## Appendix C – Maple Code for Steady State

STEADY STATE SOLUTION TO BRIGGS-RAUSCHER

```

> restart;
> k11:=3.1*10^12:
> k11r:=2.2:
> k12:=5.0*10^9:
> k13:=1.4*10^3:
> k14:=3.0*10^9:
> k15:=2.6*10^5:
> kc5:=3.494:
> kd1:=2.0*10^3:
a = [I-]
b = [I2]
c = [HOI]
d = [H+]
e = [H2O]
f = [HOIO]
g = [IO3-]
h = [O2]
i = [CH2(COOH)2]
j = [CHI(COOH)2]
k = [H2O2]
> y1:=-k11*c*a*d + k11r*b*e - k12*d*f*a - k13*d^2*g*a + kc5*i*b +
kd1*c*k;
      y1 := -0.31000000001013 c a d + 2.2 b e - 0.50000000001010 d f a - 1400.0 d2 g a
      + 3.494 i b + 2000.0 c k

> y2:=k11*c*a*d - k11r*b*e - kc5*i*b;
      y2 := 0.31000000001013 c a d - 2.2 b e - 3.494 i b

> y3:=-k11*c*a*d + k11r*b*e + 2*k12*d*f*a + k13*d^2*g*a + k14*f^2 -
kd1*c*k;
      y3 := -0.31000000001013 c a d + 2.2 b e + 0.10000000001011 d f a + 1400.0 d2 g a
      + 0.30000000001010 f2 - 2000.0 c k

> y4:=-k11*c*a*d + k11r*b*e - k12*d*f*a - 2*k13*d^2*g*a + k14*f^2 -
k15*d*g*f + kc5*i*b + kd1*c*k;
      y4 := -0.31000000001013 c a d + 2.2 b e - 0.50000000001010 d f a - 2800.0 d2 g a
      + 0.30000000001010 f2 - 260000.0 d g f + 3.494 i b + 2000.0 c k

> y5:=k11*c*a*d - k11r*b*e + kd1*c*k;
      y5 := 0.31000000001013 c a d - 2.2 b e + 2000.0 c k

> y6:=-k12*d*f*a + k13*d^2*g*a - 2*k14*f^2 + k15*d*g*f;
      y6 := -0.50000000001010 d f a + 1400.0 d2 g a - 0.60000000001010 f2 + 260000.0 d g f

> y7:=-k13*d^2*g*a + k14*f^2 - k15*d*g*f;
      y7 := -1400.0 d2 g a + 0.30000000001010 f2 - 260000.0 d g f

> y8:=1/2*k15*d*g*f + kd1*c*k;
      y8 := 130000.0000 d g f + 2000.0 c k

```

```

> y9:=-kc5*i*b;
y9 := -3.494 i b

> y10:=kc5*i*b;
y10 := 3.494 i b

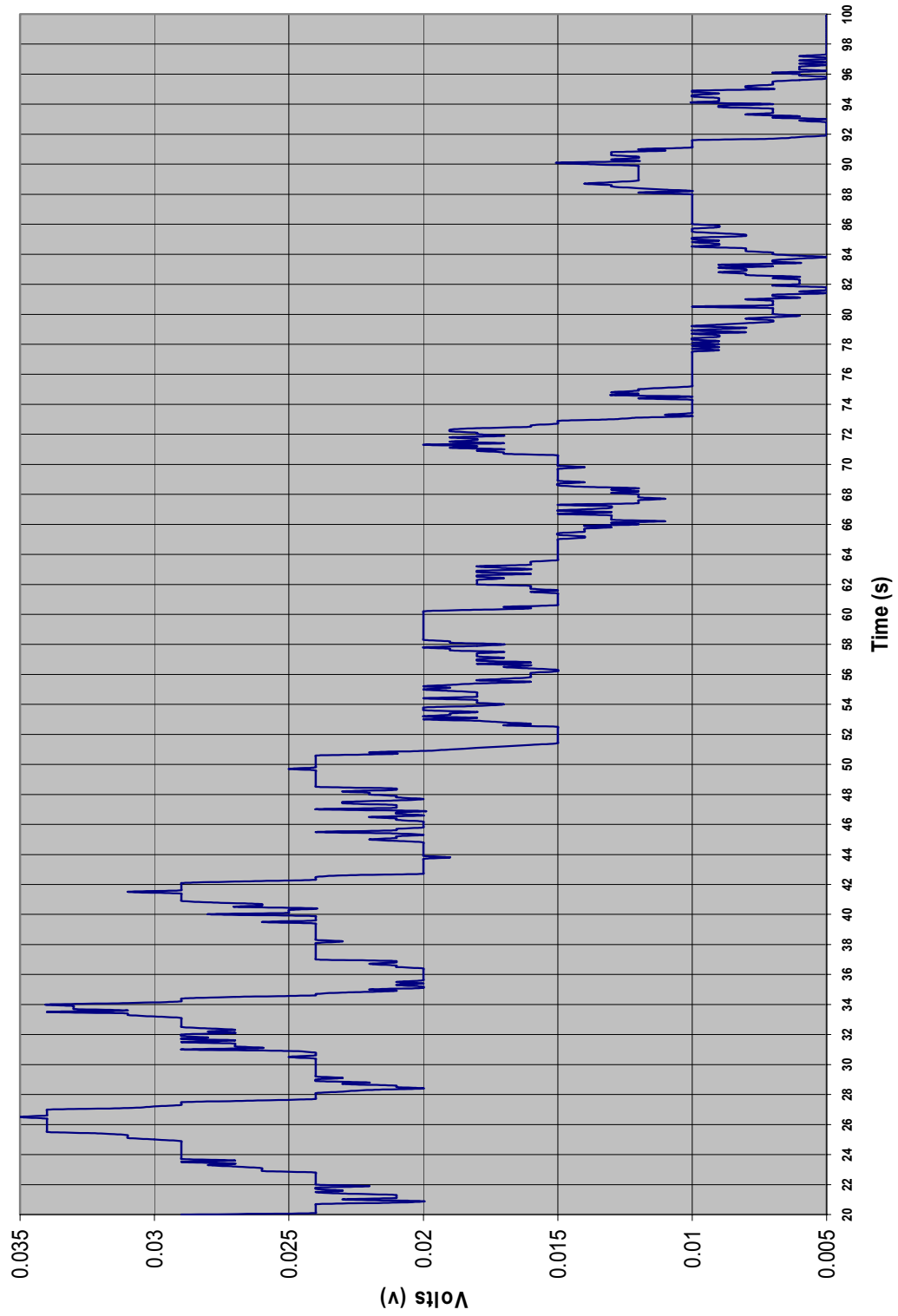
> y11:=-kd1*c*k;
y11 := -2000.0 c k

>
solve({y1=0,y2=0,y3=0,y4=0,y5=0,y6=0,y7=0,y8=0,y9=0,y10=0,y11=0},{a,b,c,
d,e,f,g,h,i,j,k});
{j=j,h=h,d=d,e=e,a=a,c=c,k=0.,i=0.,g=0.,f=0.,
b= $\frac{0.1409090910^{13} c a d}{e}$ },
{j=j,h=h,d=d,c=c,g=g,b=b,k=0.,i=0.,f=0.,e=0.,a=0.},
{j=j,h=h,a=a,c=c,g=g,b=b,k=0.,i=0.,f=0.,e=0.,d=0.},
{j=j,h=h,e=e,a=a,c=c,g=g,i=i,k=0.,f=0.,d=0.,b=0.},
{j=j,h=h,d=d,e=e,c=c,g=g,i=i,k=0.,f=0.,a=0.,b=0.},
{k=k,j=j,h=h,d=d,a=a,b=b,i=0.,g=0.,f=0.,e=0.,c=0.},
{k=k,j=j,h=h,d=d,g=g,b=b,i=0.,f=0.,e=0.,c=0.,a=0.},
{k=k,j=j,h=h,a=a,g=g,b=b,i=0.,f=0.,e=0.,c=0.,d=0.},
{k=k,j=j,h=h,d=d,e=e,a=a,i=i,g=0.,f=0.,c=0.,b=0.},
{k=k,j=j,h=h,d=d,e=e,g=g,i=i,f=0.,c=0.,a=0.,b=0.},
{k=k,j=j,h=h,e=e,a=a,g=g,i=i,f=0.,c=0.,d=0.,b=0.}

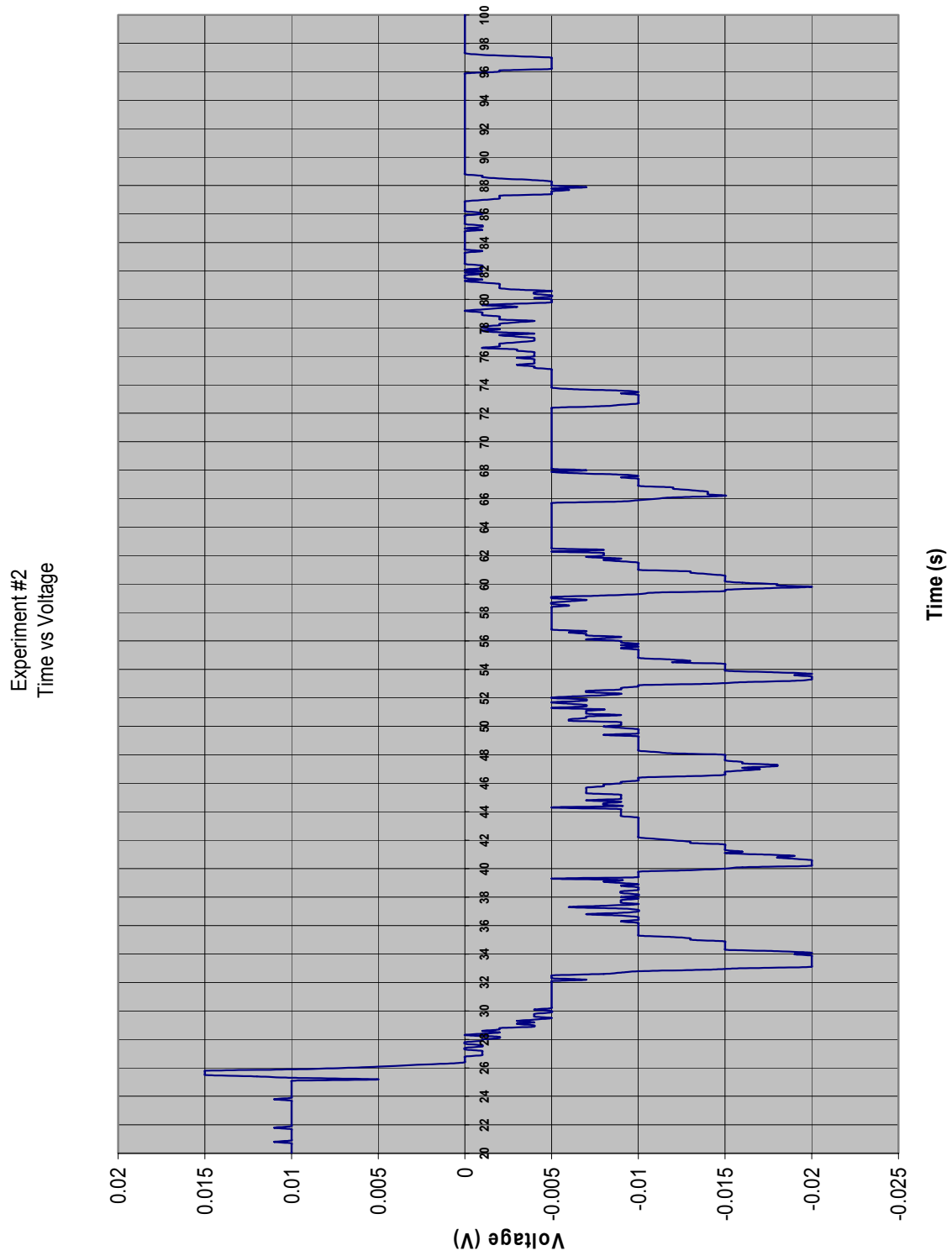
```

# Appendix D – Potential vs. Time for Experiment 1

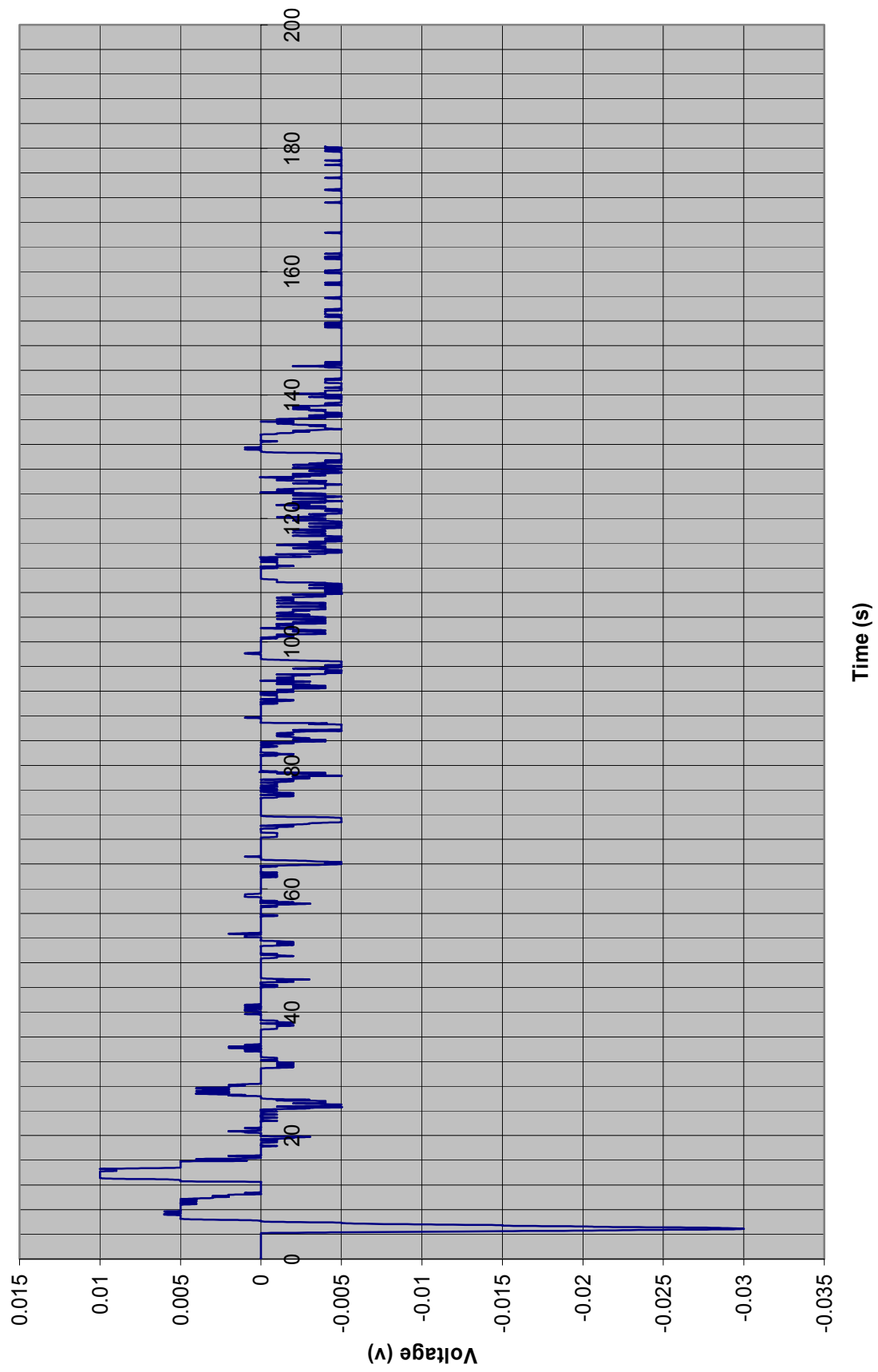
Experiment 1  
Time vs. Voltage



## Appendix E – Potential vs. Time for Experiment 2

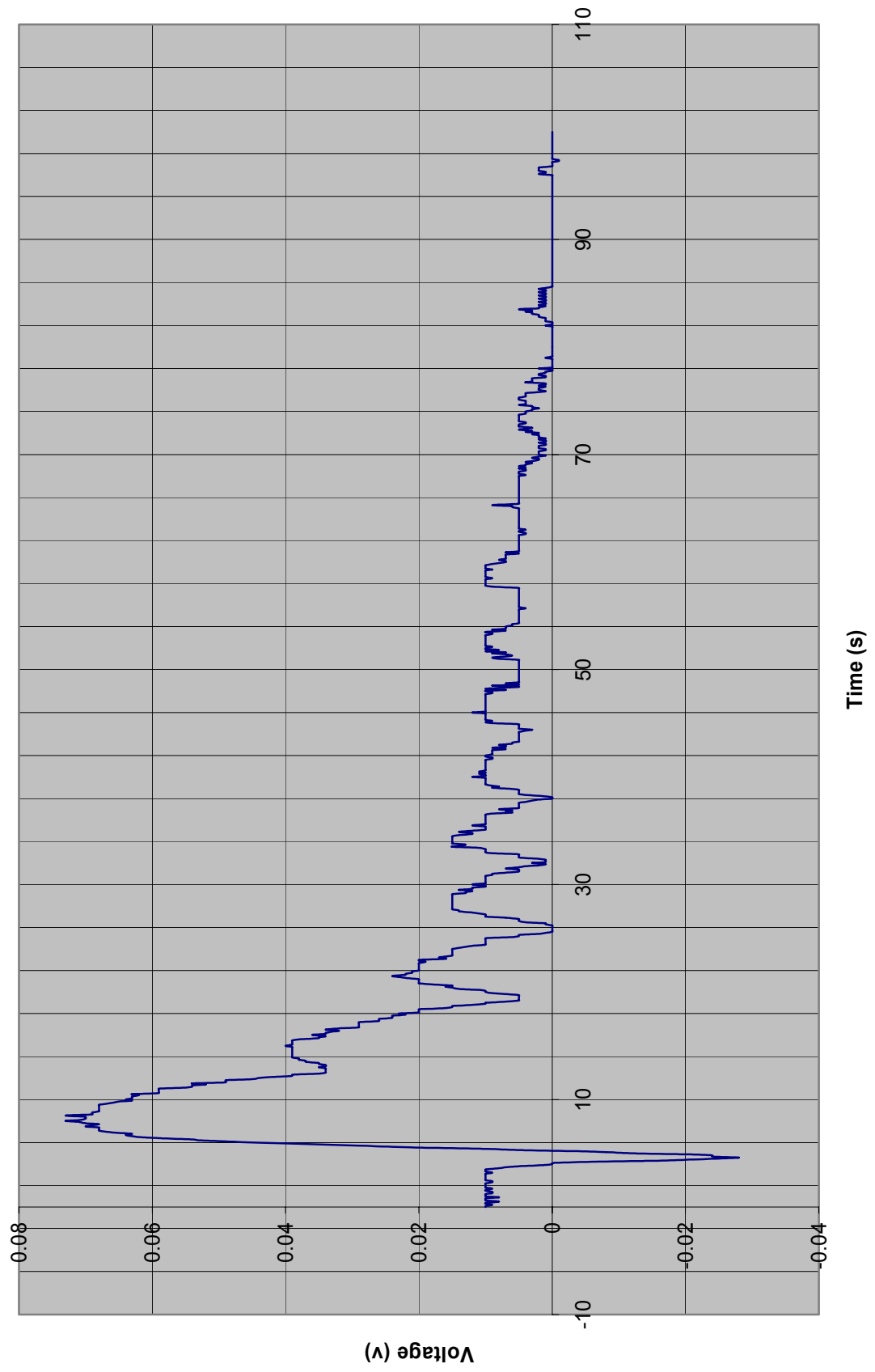


### Experiment 4a - Late Stir





Experiment 5 - Stir Rate = 100rpm



## Appendix F – Non Dimensional System of Equations

Here is the fully non dimensional system:

$$A = [A] / a_o \quad \% \text{The same naming convention is being used as in Appendix A}$$

$$B = [B] / b_o$$

$$C = [C] / c_o$$

$$D = [D] / d_o$$

$$E = [E] / e_o$$

$$F = [F] / f_o$$

$$G = [G] / g_o$$

$$H = [H] / h_o$$

$$I = [I] / i_o$$

$$J = [J] / j_o$$

$$K = [K] / k_o$$

$$\tau = t * a_o * k_{11r}$$

$$\begin{aligned} (dA/d\tau) = & - (k_{11}/k_{11r} * c_o d_o/a_o) * CAD + (b_o e_o/a_o^2) * BE - (k_{12}/k_{11r} * d_o f_o/a_o) * DFA \\ & - (k_{13}/k_{11r} * d_o^2 g_o/a_o) * D^2GA + (k_{c5}/k_{11r} * c_o b_o/a_o^2) * IB \\ & + (k_{d1}/k_{11r} * c_o k_o/a_o^2) * CK \end{aligned}$$

$$(dB/d\tau) = (k_{11}/k_{11r} * c_o d_o/b_o) * CAD - (e_o/b_o) * BE - (k_{c5}/k_{11r} * i_o/a_o) * IB$$

$$\begin{aligned} (dC/d\tau) = & - (k_{11}/k_{11r} * d_o) * CAD - (b_o e_o/a_o c_o) * BE + 2 * (k_{12}/k_{11r} * d_o f_o/c_o) * DFA \\ & + (k_{13}/k_{11r} * d_o^2 g_o/c_o) * D^2GA + (k_{14}/k_{11r} * f_o^2/a_o c_o) * F^2 \\ & - (k_{d1}/k_{11r} * k_o/a_o) * CK \end{aligned}$$

$$\begin{aligned} (dD/d\tau) = & - (k_{11}/k_{11r} * c_o) * CAD + (b_o e_o/a_o d_o) * BE - (k_{12}/k_{11r} * f_o) * DFA \\ & - 2 * (k_{13}/k_{11r} * d_o g_o) * D^2GA + (k_{14}/k_{11r} * f_o/a_o d_o) * F^2 \\ & - (k_{15}/k_{11r} * g_o f_o/a_o) * DGF + (k_{c5}/k_{11r} * i_o b_o/a_o d_o) * IB \\ & + (k_{d1}/k_{11r} * c_o k_o/a_o d_o) * CK \end{aligned}$$

$$(dE/d\tau) = (k_{11}/k_{11r} * c_o d_o/e_o) * CAD - (b_o/a_o) * BE + (k_{d1}/k_{11r} * d_o g_o/a_o) * CK$$

$$\begin{aligned} (dF/d\tau) = & - (k_{12}/k_{11r} * d_o) * DFA + (k_{13}/k_{11r} * d_o^2 g_o/f_o) * D^2GA \\ & - 2 * (k_{14}/k_{11r} * f_o/a_o) * F^2 + (k_{15}/k_{11r} * d_o g_o/a_o) * DGF \end{aligned}$$

$$(dG/d\tau) = (k_{13}/k_{11r} * d_o^2) * D^2GA + (k_{14}/k_{11r} * f_o^2/a_o g_o) * F^2 \\ - (k_{15}/k_{11r} * d_o f_o/a_o) * DGF$$

$$(dH/d\tau) = 1/2 * (k_{15}/k_{11r} * d_o g_o f_o/a_o h_o) * DGF + (k_{d1}/k_{11r} * c_o k_o/a_o h_o) * CK$$

$$(dI/d\tau) = - (k_{c5}/k_{11r} * b_o/a_o) * IB$$

$$(dJ/d\tau) = (k_{c5}/k_{11r} * i_o b_o/a_o j_o) * IB$$

$$(dK/d\tau) = - (k_{d1}/k_{11r} + c_o/a_o) * CK$$

## Appendix G – Tunisia Model, Matlab Code

```
function dy = F(t, y, flag)

A = y(1);    %A = I-
B = y(2);    %B = I2
C = y(3);    %C = IO3-
D = y(4);    %E = HIO2
E = y(5);    %D = HOI

F = y(6);    %F = IO2
G = y(7);    %G = MnOH2+
            %H Found below
I = y(8);    %I = H02
J = y(9);    %J = MA
K = y(10);   %K = H202

y1o = 0;
y2o = 10^-6;
y3o = 0.035;
y4o = 0;
y5o = 0;
y6o = 0;
y7o = 0;
y8o = 0;
y9o = 0.0015;
y10o = 0.33;

%Reaction Rates
R1 = 1.43 * 10^3;
R2 = 2*10^10;
R3 = 3.1*10^12;
R3r = 2.2 ;
R4 = 7.3*10^3;
R4r = 1.7*10^7;
R5 = 6*10^5;
R6 = 1*10^4;
R6r = 10^4;
R7 = 3.2*10^4;
R8 = 7.5*10^5;
R9 = 40;
R10 = 37;
```

%Extras for exact

H = 0.056;

k0 = 1/156;

C9 = 10^4;

MnC = 0.004;

```
dy = [  
- R1*H^2*A*C - R2*H*A*D - R3*E*H*A + R3r*B + R9*B*J/(1+C9*B) + R10*E*K +  
k0*(y1o-A);  
R3*E*H*A - R3r*B - R9*B*J/(1+C9*B) + k0*(y2o-B);  
- R1*H^2*A*C - R4*C*D*H + R4r*F^2 + R5*D^2 + k0*(y3o-C);  
R1*H^2*A*C - R2*H*A*D - R4*C*D*H + R4r*F^2 - 2*R5*D^2 + R6*F*(MnC - G) +  
k0*(y4o-D);  
R1*H^2*A*C + 2*R2*H*A*D - R3*E*H*A + R3r*B + R5*D^2 - R10*E*K + k0*(y5o-  
E);  
2*R4*C*D*H - 2*R4r*F^2 - R6*F*(MnC - G) + k0*(y6o-F);  
R6*F*(MnC - G) - R7*G*K + k0*(y7o-G);  
R7*G*K - 2*R8*I^2 + k0*(y8o-I);  
- R9*B*J/(1+C9*B) + k0*(y9o-J);  
- R7*G*K + R8*I^2 - R10*E*K + k0*(y10o-K);  
];
```

## Appendix H – Tunisia Model, Matlab Solver

```
tspan = [0:1:2000];  
yo = [10^-8, 6*10^-7, 10^-2, 10^-10, 10^-10, 10^-10, 10^-13, 0, 10^-3, 0];  
  
options = odeset('RelTol',1e-8,'AbsTol',1e-10);  
  
[T,sol] = ODE15s(@TunisiaExact, tspan, yo, options);  
  
plot(T, sol(:,1))  
plot(T, sol(:,2),'--')
```