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Micropatterning of Chemical Oscillating Reactions

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A Senior Project submitted to
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by
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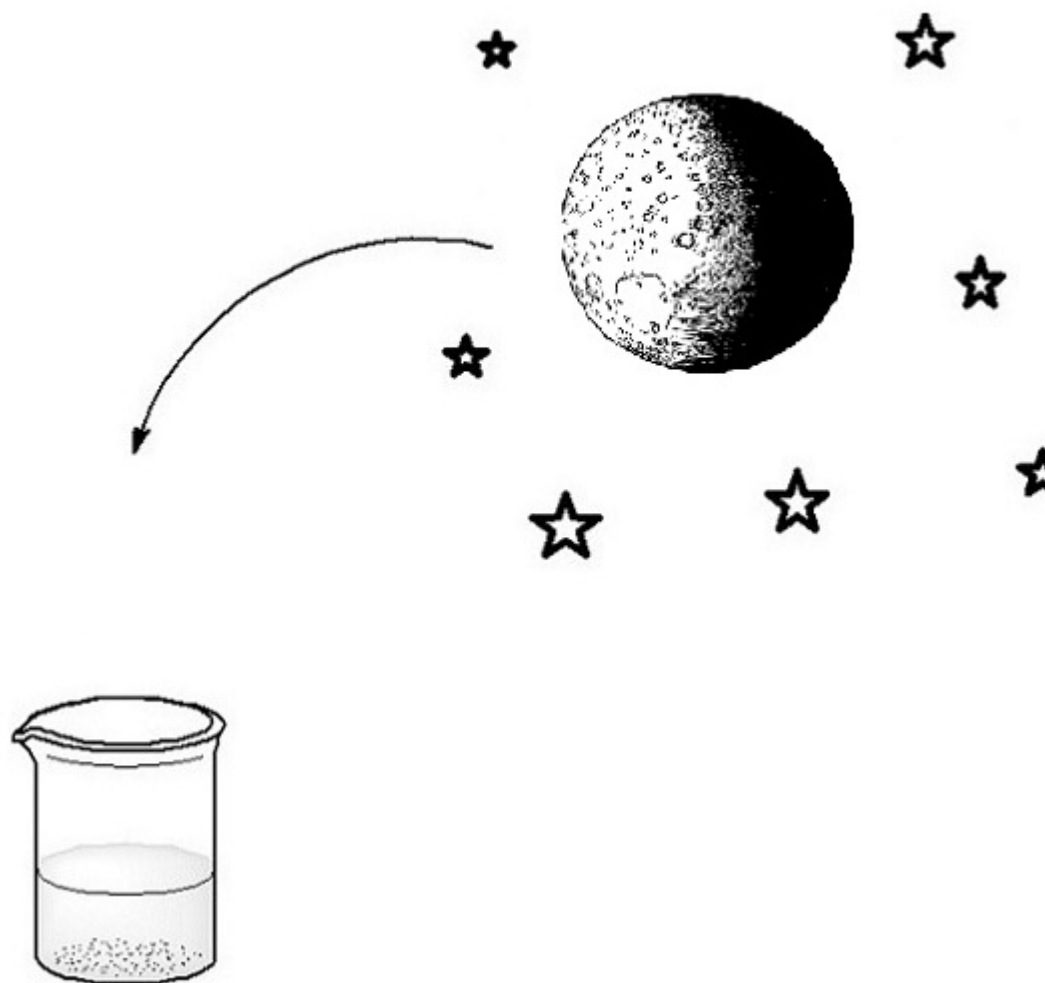
Abstract

Chemical oscillating reactions are of interest to researchers because they provide a unique way to create self-assembling patterns. The Briggs-Rauscher (BR) reaction is one such reaction that displays oscillating colors from amber to deep blue several times as the concentrations of iodine and iodide change. This oscillating reaction was modeled using ordinary differential equations. Experiments were also performed to generate novel patterns. To provide more control over the BR reaction, a Wet Stamping Technique (WETS) was used, where two gels were soaked with appropriate reagents and then pressed together to initiate the reaction. The oscillations depended on spatial as well as temporal variables. The reaction takes place on gels that are molded on microstructured polymer films, which were made using a laser. The patterned gels limit where the reaction can take place and result in reaction waves that interfere with one another creating complex patterns.

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Dedication

I would like to dedicate this work to my dear parents who have sacrificed more than what I can imagine for my education as well as my well-being. Without their never-ending love and support, I could not have made this far in my journey. With all my heart, I would like to present my first work of achievement to my parents. I love you, Mom and Dad.

아빠. 엄마. 고맙습니다. 그리고 사랑해요.

Acknowledgments

Our Father which art in heaven, hallowed be thy name, thy kingdom come, thy will be done on earth as it is in heaven. In everything that I do, may you find joy, for whatever I do is for the glory of God. It's you who gave me life and it's you who I live for everyday. I give all that I am to you.

You are my strength when I am weak, for it is your righteous right hand that upholds me and calls me out of darkness into your marvelous light. I thank you Lord, for you were, you are and you will forever be with me. Whom or what shall I fear when a king above all kings stands before me.

With all that I am, I will give my thanks to you, O Lord, among the Gentiles; I will sing praises to thy name. You have given me wisdom and might, and you have made known to me what I asked of you. In times of weariness, I casted my burdens upon you, my Lord and found rest in the arms of your mercy. Let us remember that all of our work is not to us, but to your name, may it be the glory.

I will praise you, O Lord my God, with all my heart; I will glorify your name forever.

Amen.

Last, but certainly not least, I would like to thank everyone in Team Chem, especially the Seniors of 2012: Nicole Camasso, Madison Fletcher, Nicole Kfoury, Eli Sidman, Izzy Taylor and Jing Yang. I will never forget the last four years that I spent with you guys. Studying four years of chemistry would not have been possible without the support that my friends provided me. The memories of working safely in Chem Labs, playing with dry ice during gen. chem labs, struggling together through a year of organic chemistry, displaying our stress to each other about how we didn't know how to synthesize a cyclobutane from a cyclopropane, complaining about how difficult physical chemistry was, enjoying our times presenting our posters at the ACS-URS poster sessions, participating in events created by Bard ACS chapter, comforting each other during the bad days of doing research, and finally spending sleepless nights working on our Synthesis proposals and writing our senior projects, will never be forgotten. I would like to thank all the Team Chem Seniors of 2012, and the rest of my friends for being there with me for my four years of Bard College.

My success and completion of this work would not have been possible without all my friends, advisors and professors of Bard College.

1
Introduction

Ever since its discovery, chemical oscillating reactions have attracted the attention of theoretical chemists. A chemical oscillating system describes a set of chemical reactions in which the concentrations of one or more of its intermediate species exhibit periodic changes [1]. Evidence suggests that these oscillating chemical reactions often occur in nature, resulting in structures and materials with unique properties. Some of these examples include stripes in zebras, tigers, and seashells, and formations in trees, agates, and rocks [14]. Even though these patterns have been observed for a long time, the mechanism behind how these patterns are formed still remains a mystery. It is believed that if these chemical oscillations were to be understood, then certain natural phenomena could be explained.

The Briggs-Rauscher (BR) reaction is an example of a chemical oscillating reaction that displays a periodic change of colors between amber and blue. Studies have been done to try and understand the mechanism of the BR reaction without much success. The BR reaction includes over thirty participating intermediates that react by both radical and non-radical mechanisms [4]. The presence of radical mechanisms, which are notorious for involving a high number of intermediate species and yielding undesired side products, complicate the

understanding of the BR reaction. Even after forty years of intense investigation, there are still more chemical reactions to be discovered. Many attempts have been made to formulate a mathematical model that can be used to analyze all of the reaction equations; however with this many variables, that method is simply inefficient. Decreasing the number of variables and simplifying the chemical equations have allowed some progress in the modeling of the oscillating behavior, but these simplified models remain quite complex.

The goal of this research is to improve our understanding of the BR reaction through experimentation and mathematical modeling. Several steps have been taken for this investigation. First, we replicated and recorded qualitative, as well as quantitative data of the BR oscillation. Many trials of the BR reaction ensured the precision of the reaction conditions. The data recorded from these trials were then utilized in formulating a mathematical model in *Mathematica*. For our model, we further reduced the number of variables, as well as the number of chemical equations to the minimum required to create the oscillatory events. Reaction conditions were imported from the laboratory data.

After a model had been developed for the BR reaction in a beaker, we applied the Wet Stamping technique (WETS) to it. WETS is a method to pattern chemical reactions in 2-D using two textured gels soaked with reagents, which are pressed together to initiate the reaction. WETS has been recently developed to allow control over spatial as well as temporal variables [13]. With these advantages, we have generated complex patterns that incorporate oscillatory behaviors (oscillations of colors between amber and blue) of the BR reaction. Patterns by WETS are typically on the order of one millimeter, so we also tested whether the same procedure would still occur when conducted in microscales (less than 100 μm).

2
Background

2.1   Chemical Oscillating Systems

A general form of oscillation can be described as a repetitive variation, typically in time, of a certain measure about a central value, often referred to as a point of equilibrium between two or more states. In chemical oscillating systems, the function of concentrations of different chemicals being formed and consumed throughout the chemical reaction, often referred to as the intermediate species, tend to fluctuate about the equilibrium condition, displaying neither a converging nor a diverging behavior for a certain period of time. The oscillating behaviors of chemical systems are different from the oscillating behaviors of ordinary mechanical systems, such as a pendulum or a mass on a spring, and it is important to note the distinguishing features between these systems. Chemical systems are not as *free* as the mechanical systems; they cycle about their point of equilibrium, also known as their resting positions for a pendulum or a mass on a spring, in a damped oscillatory manner. Isolated chemical systems attain their equilibrium composition, given enough time, through a monotonic approach. Once the equilibrium state has been reached, there are no more oscillations, whether they are damped or not, because a state of equilibrium describes

a dynamic state; the net rates at which each of the various participating intermediates being formed equals the rate they are being consumed, resulting in no net change of any of the species [1].

In closed systems, unaffected by any outside factors beyond the system of chemical reaction, the only concentrations which vary in an oscillatory way are those of the intermediates: generally there is a monotonic decrease in reactant concentrations, and a monotonic, not necessarily smooth nor linear, increase in concentration of the product. Often these intermediates throughout the course of the reaction tend to diffuse through the reaction medium and this diffusion, under some circumstances, lead to traveling waves of chemical activity in which their concentrations in a specific region are either far above or far below compared to the bulk of the reaction. In a sense, this converts the oscillating behavior from time to space. Because these propagating waves are proportionally big enough to be observed by naked eyes, these chemical oscillating systems are often utilized for visual demonstrations [1], [2].

The history of oscillations in chemical systems is long, with the first example of a gas-phase system being discovered in 1828. However, with limited knowledge at that time, this area of research was not studied in detail until recently. In 1951, a liquid-phase oscillation was observed in Belousov's laboratory in Russia during the cerium-ion-catalyzed oxidation, Ce(IV) to Ce(III), of citric acid by bromate ion. Zhabotinskii continued Belousov's work and generalized the class of chemical oscillations utilizing bromate ions and these reactions are now referred to as the Belousov-Zhabotinskii (BZ) reaction. The discovery of this BZ reaction has sparked the interest of many scientists to further investigate the area of chemical oscillating systems. To grasp a better understanding, scientists have tried to answer two questions; 1) how does this reaction occur? and 2) what is the driving force behind this reaction? [2]

The answer to the first question remains somewhat elusive, as there appear to be approximately 30 possible reactions that can occur simultaneously. It also seems difficult to experimentally isolate them. In attempts to model the systems, people have assumed many of the reactions to be insignificant, and focused their attention on a more manageable number of reactions, as we did in this work.

The basis for imposing the question of the driving force behind this reaction was built upon the fact that these oscillations do not occur during a chemical equilibrium, where the rates of forward reactions are equal to those of the reverse reactions. In fact, it is proposed that in the cases of long-lived oscillations, the behavior of chemicals is thought to have started far from the equilibrium. Then what are the factors that are responsible for the oscillating behaviors? It certainly cannot be the Gibbs free-energy ($\triangle$G) of the closed system. It has been calculated that the $\triangle$G of oscillatory systems decrease continuously during the course of the reaction: $\triangle$G does not oscillate. Then this is suggestive of the fact that the oscillating behavior is not due to an external factor, but due to an internal factor. Today it is believed that the fluctuation of the concentrations of the intermediate species is the cause of oscillations [1].

2.2 Briggs-Rauscher Reaction

One of many variations of the BZ reaction is called, the Briggs-Rauscher Reaction (BR reaction). The BR reaction was reported by two high school teachers in San Francisco (Briggs and Rauscher, 1973) within a year after the *Journal of Chemical Education* ran an issue covering recent advances in the understanding of chemical oscillators. The overall chemical equation of the BR reaction is as follows:

$$IO_3^- + 2H_2O_2 + CH_2(COOH)_2 + H^+ \rightarrow ICH(COOH)_2 + 2O_2 + 3H_2O \qquad (2.2.1)$$
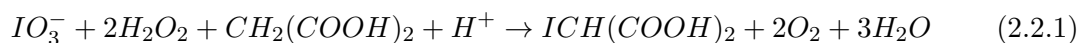
The BR reaction was astonishing because of its striking color changes as the oscillations took place. An initially colorless solution soon turned amber and then turned deep blue, back to amber and then blue. This cycle repeated with a frequency of several cycles per minute. The concentrations of the reactants that yielded the best color changes seem to have been the following:

0.067M potassium iodate,   1.2M hydrogen peroxide,

0.053M perchloric acid (an equivalent amount of sulfuric acid may replace it),

0.050M malonic acid,   0.0067M manganese(II) sulfate,   and 0.01% starch

At that time, Briggs and Rauscher seemed to have an understanding that the two intermediates that were responsible for the display of two colors were iodine (amber) and iodide (blue). Hence, they took the reasonable next step; to measure the concentrations of these two intermediates throughout the course of the reaction. They mention in their published article in *Journal of Chemical Education* that the concentration of iodide can be easily obtained by means of a silver-silver iodide electrode immersed in the oscillating mixture. The quantitative evidence of the chemical reaction can be obtained by measuring the various voltage potentials produced by the iodide ions and converting these voltages into concentration using techniques of electro-analytical chemistry. A graph of their obtained data, which was included in their published article, is illustrated below.
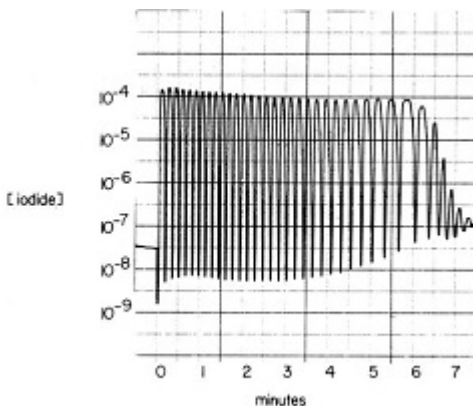
Figure 2.2.1. Oscillation of Iodide by Briggs and Rauscher

Briggs and Rauscher also noted that the role of starch in this reaction was to bind with iodine (I_2) to form iodide-starch complex, leaving iodide ion(I^-) as a side product, which was responsible for the display of deep blue color. This iodide-starch complex does not interfere with any other intermediates as they just precipitate out of the reaction, meaning that these complexes are solidified and sink to the bottom of the reaction without reacting any further. Additionally, they noted that in the absence of the manganese catalyst, invisible oscillations in iodide occurred in a narrow region of higher concentration, e.g., 0.092M potassium iodate, 0.069M malonic acid, 3.24M hydrogen peroxide, and 0.16M sulfuric acid. Therefore, for both striking color oscillating purposes and also for efficiency sake (use minimal amount of reactants), a catalytic amount of the manganese catalyst seems to be favorable [3].

2.3   Understanding BR Reaction Oscillation

The details of the oscillatory BR reaction remained a mystery until 1981, when Noyes and Furrow published an article showing major progress in the understanding of these reactions. Their focus was to identify the elementary processes occurring in this complex system. They have simplified the system a bit by assuming that the act of proton transfer to and from oxygen and iodine is so rapid that they can be considered equilibrated at all times. With this assumption, they were able to postulate 30 pseudo-elementary processes that might play a significant role in this system [4].

Further modification of this possible mechanism has been researched and the simplest and the most accurate mechanism that is being used by numerous scientists for their analysis of the BR reaction have been documented by Shakhashiri. Most importantly, this simplified mechanism was able to explain the origin of the oscillations in the concentrations of I_2 and I^- [5].

This simplified mechanism consists of two sets of processes that are significantly different in terms of their rates of producing an important intermediate for the BR reaction, HOI. HOI is important because as soon as HOI is created, it is quickly consumed to produce I_2, the chemical responsible for the amber color. At the same time, I_2 is being converted to produce I^-, which then can combine with starch to form the iodide-starch complex and produce the deep blue color. It is reasonable to assume that as soon as I^- is formed, it will react with starch, purely due to the fact that there is an abundance of starch molecules in the reaction mixture. So for simplicity, Shakhashiri assigned I^- to be responsible for producing the deep blue color [5].

It is strongly believed that the oscillation between amber and blue is purely dependent on the concentration of these two chemicals, displaying amber color when $[I_2]$, the concentration of I_2, is higher than $[I^-]$. On the contrary, if $[I^-] > [I_2]$, then it would display deep blue color. Therefore, the fact that there are oscillations of these two colors would now mean that there is an oscillation of the concentrations of the two chemicals throughout the reaction. The concentrations depend on the rate at which they are being produced and consumed and there are two different sets of processes, each with different rates that are responsible for the oscillation of concentrations. These two sets of processes are called, the radical process and the non-radical process [4].

The oscillation can be illustrated as follows: the radical process increases the concentration of HOI rapidly. When [HOI] increases, then this allows more of HOI to be consumed to produce more I_2 which then can be converted to I^-. Hence, the rapid radical process would be more influential than the non-radical process when the $[I^-]$ is low. The possible mechanism for this radical process is as follows [6]:

Radical Process (when $[I^-]$ is low):

$$IO_3^- + H_2O_2 + H^+ \rightarrow HIO_2 + O_2 + H_2O \qquad (2.3.1)$$

$$IO_3^- + HIO_2 + H^+ \rightarrow 2IO_2^{\bullet} + H_2O \qquad (2.3.2)$$

$$IO_2^{\bullet} + Mn^{2+} + H_2O \rightarrow HIO_2 + Mn(OH)^{2+} \qquad (2.3.3)$$

$$Mn(OH)^{2+} + H_2O_2 \rightarrow Mn^{2+} + H_2O + HOO^{\bullet} \qquad (2.3.4)$$

$$2HOO^{\bullet} \rightarrow H_2O_2 + O_2 \qquad (2.3.5)$$

$$2HIO_2 \rightarrow IO_3^- + \textbf{HOI} + H^+ \qquad (2.3.6)$$
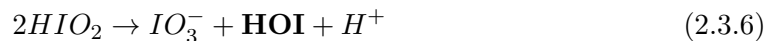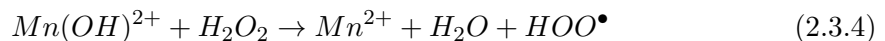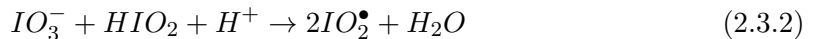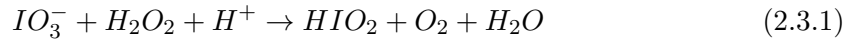
It is worth noting that HOI is a crucial intermediate that is responsible for the oscillation. Both radical (fast rate) and non-radical (slow rate) processes exist to produce HOI, just at different rates. HOI is crucial because it is the only chemical that can be consumed to produce I_2, which then can be consumed to produce I^-. Just like the radical process, the non-radical process also produces HOI, but the rate in which HOI is being produced is much slower when compared to the radical process. The possible mechanism for the non-radical process is as follows:

Non-radical Process (when $[I^-]$ is high):

$$IO_3^- + I^- + 2H^+ \rightarrow HIO_2 + HOI \qquad (2.3.7)$$

Furthermore, HIO_2 can be consumed to produce more HOI as well, as illustrated below.

$$HIO_2 + I^- + H^+ \rightarrow 2HOI \qquad (2.3.8)$$
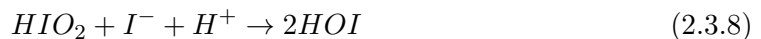
As previously stated, the radical process is fast and the non-radical process is slow, but both of those terms are relative. The rate of producing HOI via the radical process is faster than the rate of consumption of I_2 to produce I^- and the rate of producing HOI via the non-radical process is slower than the rate of consumption of I_2 to produce I^-. Using this important fact, I will try again to clarify why the oscillation takes place [5].

At the beginning stage of the reaction, when $[I^-]$ is low, or zero, the radical process will be dominant over the non-radical process because $[I^-]$ is low, so in order to get to the equilibrium state, producing I^- rapidly is favorable. The radical process will be dominating for a certain period of time and make lots of HOI. As HOI is produced, it can be consumed to produce I_2 by the following mechanism:

$$HOI + H_2O_2 \rightarrow I^- + O_2 + H^+ + H_2O \tag{2.3.9}$$

$$I^- + HOI + H^+ \leftrightarrow I_2 + H_2O \tag{2.3.10}$$
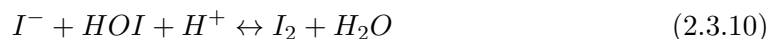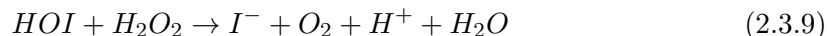
When $[I_2] > [I^-]$, the color of the overall chemical reaction is amber. This is the case at the beginning stage of the chemical reaction because I_2 is being rapidly produced, as there are high concentrations of HOI, but I^- is not being produced yet [5].

However, it is true that as soon as I_2 is produced, it will be consumed to produce I^- by the following mechanism:

$$I_2 + CH_2(COOH)_2 + H^+ \rightarrow ICH(COOH)_2 + I^- + H^+ \tag{2.3.11}$$
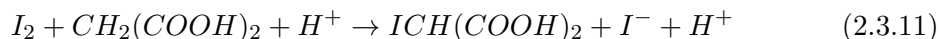
Nevertheless, at the beginning stage of the chemical reaction, HOI is being produced faster than the consumption of I_2, so for a while, $[I_2] > [I^-]$ and that is why the reaction appears as amber color. However, as $[I_2]$ increases over the course of the reaction, the rate in which I_2 is being consumed to produce I^- would increase as well, since the production rate of I^- is directly proportional to the concentration of I_2. Therefore, at a specific time, $[I^-] > [I_2]$, and color of the reaction would change from amber to blue. At the same time, the non-radical process will now be dominant over the radical process [5].

With non-radical process being dominant, now the production of HOI is slower than the consumption of I_2 to make I^-, so the concentration of HOI falls, causing a dramatic decrease in the concentration of I_2, which causes a dramatic decrease in the concentration of I^- as well. Once $[I^-] < [\text{HOI}]$ (which can be treated as equivalent to $[I_2]$), then the

color flips back to amber and the radical process once again dominates over the non-radical process. This oscillation proceeds and thus oscillation of colors continue until one of the starting reagents run out. Then HOI (and iodine as a direct consequence) can no longer be made and the $[I^-] > [I_2]$. As a result, the reaction would always end in deep blue color, and large amounts of iodide-starch complex precipitates would be found at the bottom of the reaction medium [5].

2.4   BR Reaction Kinetics

Recently, the investigators of the BR reaction have tried to make a quantitative comparison between the theory and the experiments that were carried out. The quantitative analysis of BR reaction began with Furrow and Noyes and their investigation regarding the mechanism of BR reaction in 1982. They discuss their measurements of different rate constants of the major intermediate species found throughout the reaction. Since their model at that time consisted of at least 30 chemical reactions and many more intermediate species than that, they reported only certain kinetic data of the reactions that they were able to measure. Some of these data are consistent with a more recent measured data [3].

   More recently, a group in South Korea (KLS group) developed a more simplified model for the BR reaction mechanism using just a total of seven steps that were proposed by the De Kepper and the Epstein groups (a more simplified version than the set of mechanistic steps proposed earlier, documented by Shakhashiri) to obtain more accurate chemical kinetic data [7]. The KLS group mentions the difficulties in determining the values of the rate constants by experiments due to the presence of unstable intermediates. For example, the kinetic data suggested by different groups on the same reaction may be inconsistent with each other. Nevertheless, they approached this difficulty by measuring the value of the kinetic data of $CH_2(COOH)_2$, the most stable of the participating intermediates, and from that data, worked on obtaining the values of other intermediates. The kinetic data

that they used for their research along with the seven chemical equations are listed below:

$$I^- + HOI + H^+ \leftrightarrow I_2 + H_2O \qquad\qquad k_{11} = 3.1 \cdot 10^{12} M^{-2} s^{-1}, k_{1-1} = 2.2 s^{-1} \quad (2.4.1)$$
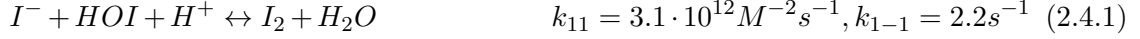
where k_{11} indicates the rate constant of forward reaction and k_{1-1} indicates the rate constant of the reverse reaction.

$$HIO_2 + I^- + H^+ \rightarrow 2HOI \qquad\qquad k_{12} = 5.0 \cdot 10^9 M^{-2} s^{-1} \quad (2.4.2)$$

$$IO_3^- + I^- + 2H^+ \rightarrow HIO_2 + HOI \qquad\qquad k_{13} = 1.4 \cdot 10^3 M^{-3} s^{-1} \quad (2.4.3)$$

$$2HIO_2 \rightarrow IO_3^- + HOI + H^+ \qquad\qquad k_{14} = 3.0 \cdot 10^9 M^{-1} s^{-1} \quad (2.4.4)$$

$$IO_3^- + HIO_2 + H^+ \rightarrow 2IO_2^\bullet + 0.5O_2 \qquad\qquad k_{15} = 2.6 \cdot 10^5 M^{-2} s^{-1} \quad (2.4.5)$$

$$I_2 + CH_2(COOH)_2 + H^+ \rightarrow ICH(COOH)_2 + I^- + H^+ \qquad k_{16} = 3.494 M^{-1} s^{-1} \quad (2.4.6)$$

$$HOI + H_2O_2 \rightarrow I^- + O_2 + H^+ + H_2O \qquad\qquad k_{17} = 2.0 \cdot 10^3 M^{-1} s^{-1} \quad (2.4.7)$$
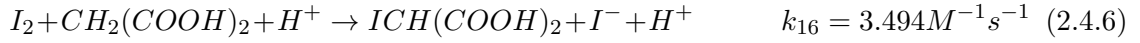
The 10 variables, which were called the intermediates of the chemical reactions, are the concentrations of HOI, I^-, H^+, I_2, HIO_2, IO_3^-, O_2, $CH_2(COOH)_2$, $ICH(COOH)_2$, and H_2O_2. As stated before, the k for each reaction is a rate constant. These constants can vary based on the chemical model being used, and thus can drastically affect the accuracy of the model. The constants given above follow the model suggested by the KLS group. They suggest that all seven of these reactions occur simultaneously and the concentration of each chemical is dependent on time. This system is complex because most of the intermediates are either products or reactants in several different reactions. Therefore, it is challenging to have a method of modeling the concentration of substances vs. time, and to take all these multiple reactions into consideration at once [8].

The Law of Mass Action can be used. 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 raised to the power of their coefficients. For example, take a simple chemical reaction of the form:

$$X + Y \rightarrow Z \qquad\qquad k_1 \qquad\qquad (2.4.8)$$

$$Z + 2Y \rightarrow X \qquad\qquad k_2 \qquad\qquad (2.4.9)$$

In order to convert these chemical equations with rate constants to a system of differential equations, the Law of Mass Action should be used. To calculate the $\dfrac{d[X]}{dt}$, one must take into account the concentrations of all the different chemicals that directly affect chemical X. Looking at the first chemical equation, it seems like that the concentrations of both chemicals, X and Y directly influence the rate of change of [X]. In fact, [X] and [Y] decrease the overall [X] because they react with each other to make another compound, consequently lowering [X] in the process. Therefore, the overall sign of the expression $k_1[X][Y]$ should be negative. However, chemical X appears in the second chemical equation as well. This time, Z and 2Y are used to produce X. Therefore, the overall sign of the expression should be positive. One thing to note is that since the coefficient in front of Y is a 2, the expression regarding [Y] is $[Y]^2$. Hence, putting all this information together, the rate law of X is:

$$\frac{d[X]}{dt} = -k_1[X][Y] + k_2[Y]^2[Z] \qquad\qquad (2.4.10)$$

Similar approach can be made for $\dfrac{d[Y]}{dt}$. Looking at the first chemical equation, the first expression regarding the first equation is exactly the same as it was for $\dfrac{d[X]}{dt}$, being $-k_1[X][Y]$. However, the second expression is a bit different as Y is found on the reactant side rather than the product side, so the sign is negative. Furthermore, two Y's are required for this reaction to occur, so the entire second expression should be multiplied by 2:

$$\frac{d[Y]}{dt} = -k_1[X][Y] - 2k_2[Y]^2[Z] \qquad\qquad (2.4.11)$$

Similar approach can be made for $\dfrac{d[Z]}{dt}$ as well:

$$\frac{d[Z]}{dt} = k_1[X][Y] - k_2[Y]^2[Z] \tag{2.4.12}$$

Therefore for the ten intermediates that were discussed regarding the BR reaction, the same Law of Mass Action can be used to derive a set of ten rate laws. It is worth noting that H_2O, one of the intermediates not included in the ten, participates in just one reaction that occurs in a reversible manner, and does not have its own set of kinetic law because water is found in abundant quantity as it is the solvent. Therefore, we assume that the concentration of water does not change throughout the reaction. Illustrated below are the ten rate laws [9]:

$$\frac{d[HOI]}{dt} = -k_{11}[HOI][I^-][H^+] + k_{1-1}[I_2] + 2k_{12}[H^+][HIO_2][I^-] +$$
$$k_{13}[H^+]^2[IO_3^-][I^-] + k_{14}[HIO_2]^2 - k_{17}[HOI][H_2O_2] \tag{2.4.13}$$

$$\frac{d[I^-]}{dt} = -k_{11}[HOI][I^-][H^+] + k_{1-1}[I_2] - k_{12}[H^+][HIO_2][I^-] -$$
$$k_{13}[H^+]^2[IO_3^-][I^-] + k_{16}[CH_2(COOH)_2][I_2] + k_{17}[HOI][H_2O_2] \tag{2.4.14}$$

$$\frac{d[H^+]}{dt} = -k_{11}[HOI][I^-][H^+] + k_{1-1}[I_2] - k_{12}[H^+][HIO_2][I^-] -$$
$$2k_{13}[H^+]^2[IO_3^-][I^-] + k_{14}[HIO_2]^2 - k_{15}[H^+][IO_3^-][HIO_2] + \tag{2.4.15}$$
$$k_{16}[CH_2(COOH)_2][I_2] + k_{17}[HOI][H_2O_2]$$

$$\frac{d[I_2]}{dt} = k_{11}[HOI][I^-][H^+] - k_{1-1}[I_2] - k_{16}[CH_2(COOH)_2][I_2] \tag{2.4.16}$$

$$\frac{d[HIO_2]}{dt} = -k_{12}[H^+][HIO_2][I^-] + k_{13}[H^+]^2[IO_3^-][I^-] - 2k_{14}[HIO_2]^2 +$$
$$k_{15}[H^+][IO_3^-][HIO_2] \tag{2.4.17}$$

$$\frac{d[IO_3^-]}{dt} = -k_{13}[H^+]^2[IO_3^-][I^-] + k_{14}[HIO_2]^2 - k_{15}[H^+][IO_3^-][HIO_2] \tag{2.4.18}$$

$$\frac{d[CH_2(COOH)_2]}{dt} = -k_{16}[CH_2(COOH)_2][I_2] \tag{2.4.19}$$

$$\frac{d[ICH_2(COOH)_2]}{dt} = k_{16}[CH_2(COOH)_2][I_2] \tag{2.4.20}$$

$$\frac{d[O_2]}{dt} = \frac{1}{2}k_{15}[H^+][IO_3^-][HIO_2] + k_{17}[HOI][H_2O_2] \tag{2.4.21}$$

$$\frac{d[H_2O_2]}{dt} = -k_{17}[HOI][H_2O_2] \tag{2.4.22}$$

These sets of reactions, even when simplified to just ten equations, are difficult to study. Hence, we used the mathematical software *Mathematica* to study these types of equations.

2.5   Wet Stamping Technique

The Briggs-Rauscher reaction shows an outstanding visual effects as the reaction is stirred inside a beaker. Simply observing the oscillation of colors without any input is not only uncommon, but also astounding. However as scientists are beings of curiosity, the BR reaction has been further studied in different mediums to enhance its visual effect. One of the studies of BR reaction was done in Grzybowski lab at Northwestern University and involves a recently developed technique called, the Wet Stamping Technique, or simply WETS.

Grzybowski lab developed WETS to serve a specific purpose; to overcome the limitations that hindered the scientific community for the last hundred years while attempting to study these oscillating chemical reactions, such as the BR reaction. Most of the research on oscillating chemical reactions thus far focused on macroscopic systems and simple geometries because the empirical laws that characterize the emerging patterns have already

been formulated. Some examples of these systems include quasi-1D gel columns, single droplets and infinite fronts [10].

At the same time, little is known about these oscillating chemical reactions on the microscopic scale and in complex geometries, mainly because of the lack of suitable experimental techniques that would allow the spatially controlled delivery of chemicals. Hence, the Grzybowski lab developed the WETS technique to study oscillating chemical reactions induced from arrays of microscopic features of arbitrary shapes stamped onto a surface of a thin film of a dry gel. WETS uses micropatterned hydrogel (usually agarose) stamps to deliver a solution of one or more reagents into films of dry gels doped with a chemical(s) that reacts with those delivered from the stamp. From this investigation, they have shown that both the periodicity, as well as the propagation of precipitates in the emerging oscillating chemical patterns depend on and can be precisely controlled by the dimensions and geometries of the features in the stamp and the thickness of the gel layer [11].

(A). Illustration of the WETS procedure
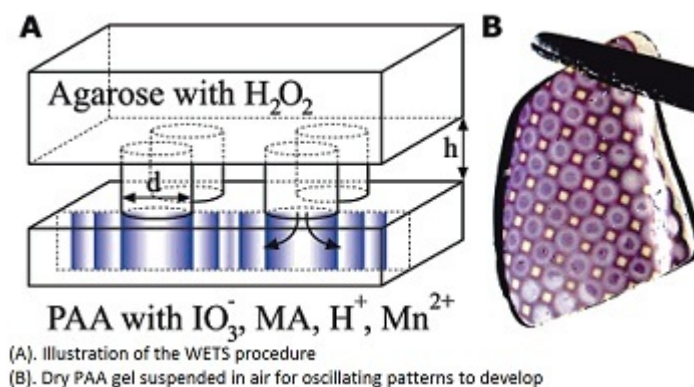(B). Dry PAA gel suspended in air for oscillating patterns to develop

Figure 2.5.1. WETS developed by Grzybowski Lab [13]

The procedure of an agarose gel fabrication is as follows: first step is to prepare a micropatterned master. Then the casting of the gel can be achieved as soon as the hot agarose mixture is poured into the master. Soaking the solidified gel in a desired reagent

and placing onto another dry gel substrate completes the WETS procedure. Upon contact, reagents flow from the stamp's micropatterns into the film and initiate a reaction-diffusion process therein. It is important to note that the difference in hydration of the stamp and the dry substrate ensures not only the direction but also purely diffusion-dependent transport of chemicals. This property of WETS eliminates the strong hydrodynamic/backflow effects caused by the migration of water to equalize the osmotic pressure difference that exists in this two-gel medium. Thereby, WETS can be performed on micro and even nanoscopic features of a stamp to generate oscillating chemical patterns [12].

The complex phenomena that are observed by applying WETS can be attributed to fact that oscillation frequency is dependent on the local concentrations of chemicals as well as the system's geometry. This statement applies to all oscillating systems that fulfill these two requirements: (1) the function of the oscillation period has to depend on the concentration of a chemical that triggers the oscillations and (2) the rate of oscillation has to depend on the rate of diffusion [13].

2.6   Experimental Investigation and Application

Competition between reaction and diffusion (RD) can lead to the emergence of intricate spatial and/or temporal patterns in both chemical and biological systems, as it does for the BR reaction applied to the WETS technique. Interestingly, nature often uses RD as a means of making structures and materials of unique properties or morphologies in macro- (e.g., stripes in zebras and seashells, and formation in trees) as well as microscopic (e.g., cellular growth, and biological waves) scales. Even with abundant examples found in nature, RD phenomena have not yet been applied in modern material science and micro-, as well as nanotechnology. In this context, RD systems exhibit promising behaviors for the micropattering of surfaces. Unlike previously applied micropattering techniques that modify the properties of the substrate only at the location to which a modifying agent-

be it a chemical or radiation- is delivered, RD can deliver appropriate chemicals onto a surface for the formation of intricate patterns without any modification of the surface. Furthermore, it has been documented that RD can also deliver chemicals into a surface that will evolve into structures of dimensions significantly smaller than that of the original pattern [14].

With these advantages of RD systems in mind, this project intends to first investigate the Briggs-Rauscher reaction in a *free-chemical* medium, meaning not in any spatially bounded gels. This eliminates the possibility of the reaction-diffusion taking place. In this pursuit, we hope to obtain a better understanding of the mechanism behind the BR reaction. The BR reaction will be monitored by the means of UV-Vis and this data that will display the oscillating behavior of I^- will then be compared to the mathematical model based on the kinetic data from the literature and our laboratory. With a better insight of how the oscillation occurs, the BR reagents will then be embedded into two gels and the WETS technique will be used to show the reaction-diffusion. From this investigation, we hope to develop a general protocol for applying WETS technique to the BR reaction for further research, such as an examination of lower size limit of the WET Stamping technique.

3
Experimental Procedures

3.1   Briggs-Rauscher Reaction Condition

In a 100 mL of deionized water, 2.15 g of KIO_3, 0.78 g of $CH_2(COOH)_2$, 0.018 g of manganese(II) catalyst, $Mn(OH)_2$, and 0.5 mL of concentrated H_2SO_4 were dissolved. To this system, 3.0 g of starch dissolved in 100 mL of deionized water was added. The BR reaction was initiated by adding 10 mL of 50% hydrogen peroxide to now a total of 200 mL solution [13].

3.2   Preparation of Polyacrylamide Gel

PAA gel was made using: 10% w/v acrylamide (OmniPur 40% w/v acrylamide/bis-acrylamide: 19: 1), 0.1% v/v TEMED (1,2-di-(dimethylamino)ethane), 0.07% w/v APS (ammonium persulfate), and 3% w/v thyodene [13]. The PAA gel is a polymerized gel that is made mostly out of monomeric acrylamide that are linked to each other via bis-acrylamide. This polymerization process is initiated by both APS and TEMED [13].
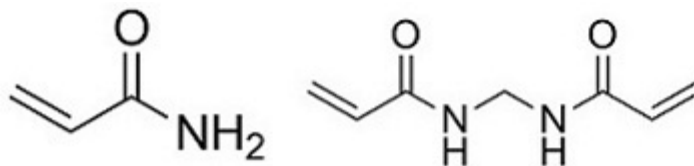
Figure 3.2.1. Acrylamide and Bisacrylamide

The 40% w/v acrylamide was prepared by adding 38.0 g of acrylamide and 2.0 g of bisacrylamide in a 400 mL beaker. Then a slurry was made with the addition of 25 mL of deionized water. This mixture was then covered with aluminum foil to prevent it from being exposed to light, which will trigger the polymerization process. This mixture was stirred for 2 hrs. This mixture was then transferred to a 100 mL of graduated cylinder and was filled with deionized water until the 100 mL mark. The final acrylamide solution was then vacuum filtered using Whatman filter paper.

The 0.07% w/v APS solution was made by dissolving 35 mg of ammonium persulfate in 500 μL of deionized water.

Using the 40% w/v acrylamide/bis-acrylamide solution, the desired 10% w/v acrylamide PAA gel was prepared by adding 350 μL of acrylamide/bis-acrylamide solution, 750 μL of 3% w/v thyodene solution, 14 μL of 1% TEMED and 14 μL of 0.07 % APS to yield a 1428 μL mixture. This was then casted for two to three hours between two glass walls, separated by a couple of 330 μM gel spacers to give the gels its appropriate thickness.

In order to ensure that all the reagents of the BR reaction were soaked into the gel, the PAA gel was first removed carefully and stored with plastic wrap. Then this plastic wrap with PAA gel was placed in a crystalline dish and the solution with BR ingredients were poured onto the gel. This setup was kept inside a 8°C refrigerator overnight.

3.3 Acrylate Master

Direct Laser Writing (DLW) of polymer templates has been known for years in the lithographic community. This is similar to conventional photolithography where patterning is accomplished by illuminating a photosensitive material with UV light. The key difference between DLW and photolithography is that the former is accomplished without the use of photomasks. DLW relies on the absorption of the material at the focused laser beam to initiate the polymerization reaction. By scanning the sample with respect to the laser, a chemical change (often polymerization) occurs at the focal point of the laser in the photosensitive material. This polymerization process can be controlled to create an arbitrary two-dimensional pattern [18].

In synthesizing our polymer master of the agarose stamp, we made use of DLW. This microfabrication technique was employed to polymerize a solvent that included 48.5% of SR-499 (Ethoxylated (6) trimethylolpropane triacrylate), 48.5% of SR-368 (Dipentaerythritol Pentaacrylate), and 3% of Lucirin TPO-L, which was the photoinitiator.
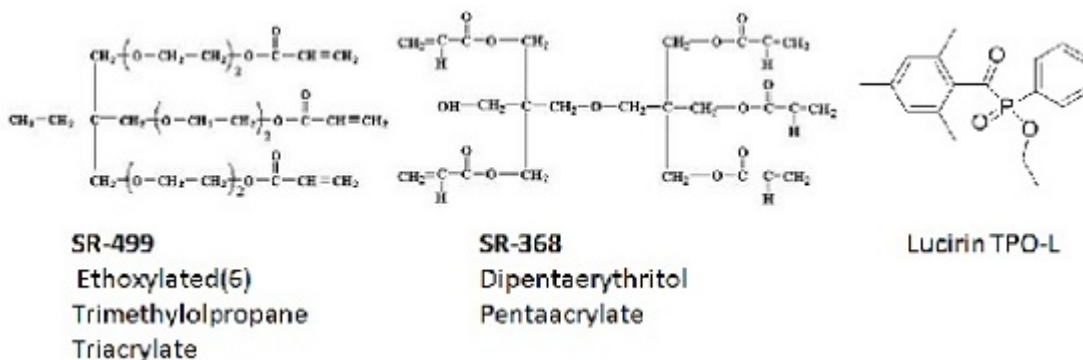
Figure 3.3.1. Acrylate Resin Composition

First step in making an acrylate master is modifying a cover slip. Cover slips are modified by first exposing it to an air plasma, followed by treating it with Heptadecafluoro-1,1,2,2-tetrahydrodecylo trichlorosilane. This treatment process involves placing the pre-modified

cover slip on one side of the desiccator and a drop of the silane on the other side. Afterwards, the vacuum was turned on for about 30 min.

Two drops of the resin was placed on the center of a glass slide that was taped on both sides with objects of appropriate height. In our case, we wanted to make post arrays of 0.5 mm in diameter and 1.0 mm in height. Since the thickness of a standard glass slide is approximately a millimeter, a piece of glass slides was placed on either side of the drops of resin. Then a previously modified cover slip was taped above the drop in order to trap this drop to a confined space of a millimeter in height. As a result, this drop of resin was flattened to form a circular region.

The patterns then were made in this region with the use of a laser. Any point where the laser passed through the resin became solidified by a radical polymerization process. A program was written to move the laser to appropriate spots and expose the beams for a desired amount of time. If the time of exposure of the laser is lengthened, the radius of posts increases.

After all the desired points were solidified by DLW, the undesired residue of resin was eliminated so that only the arrays of posts remain. Hence, the treatment of the *glass slides and cover slip complex* with ethanol always follows the direct laser writing process. Separating the cover slip from the glass slide is the tricky portion of this procedure, but if the cover slip has been modified previously to make its surface hydrophillic, then the posts should stick to the cover slip rather than the glass slide.
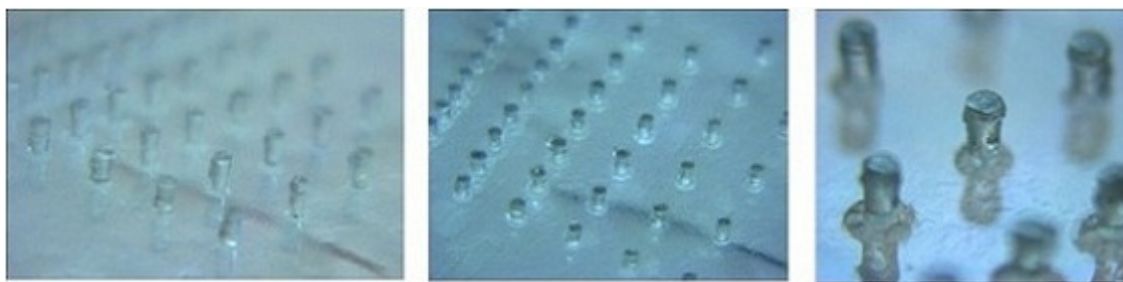
Figure 3.3.2. Acrylate Post Arrays

Successful synthesis of acrylate posts on the surface of a cover slip allows us to use them to cure a polydimethylsiloxane mold for our next step.

3.4   Polydimethylsiloxane Mold

Polydimethylsiloxane, commonly referred to as PDMS, describes a group of polymeric organosilicon compounds (silicones). PDMS is mostly widely used silicon-based organic polymer, especially in the field of microfluidic devices.

The first microfluidic device used silicon and glass, since the techniques for fabrication in these materials were well-developed. These techniques, however, were expensive, time-consuming, and only accessible to restricted groups. PDMS is much simpler to use so its popularity has grown considerably in the last decade.

Fabrication with polymers is relatively easy and their application as materials reduces the time, complexity, and cost of manufacturing. PDMS has been one of the most popular polymers, especially in the field of microfluidics. Two advantages of using PDMS for fabrication process are that the procedure is very simple, and that it can be used to incorporate other materials and structures through encapsulation or sealing (both reversible and irreversible).

The soft lithography with PDMS starts by molding a replica of a master structure, which in our case is the acrylate master. The PDMS used in this experiment was supplied in two components, a base and a curing agent. Silicon hydrides of the curing agent will react with the vinyl groups of the base and form a cross-linked, elastomeric solid. For the best result, the two parts were mixed together at 10:1 (v/v) base:curing agent. This pre-polymer liquid was poured over the acrylate master and then cured. The liquid PDMS pre-polymer conformed to the shape of the master and replicate the features of the master. It has been reported that the PDMS can accurately replicate features of the master with high (10's of nm) fidelity [16].
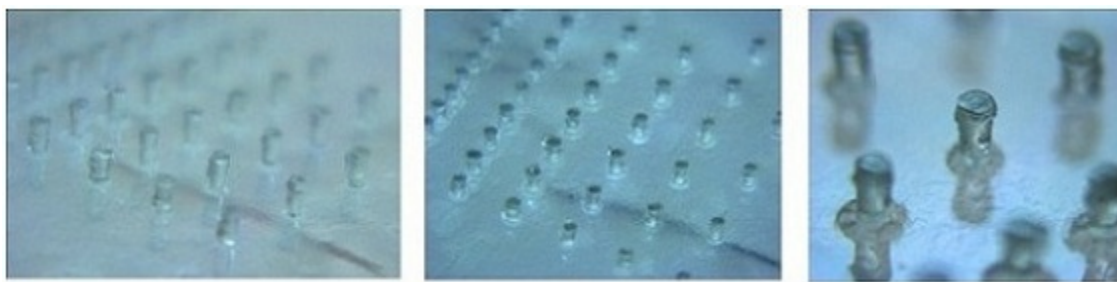
Acrylate post array (above), PDMS mold (below)

Figure 3.4.1. Acrylate Post Arrays and PDMS Mold

PDMS mold was released easily from the acrylate master without much damage to the master or itself.

3.5   Agarose Stamp

After polymerization and cross-linking, the solid PDMS mold has a hydrophobic surface. This surface chemistry of PDMS made it difficult for polar solvents such as water, which is the primary component of a hydrogel, to wet the PDMS surface. The Whiteside's group has presented a solution to this problem. The surface of the PDMS can be oxidized by exposure to an air plasma and this oxidizes the surface and enhances the hydrophillicity of the PDMS surface [16].
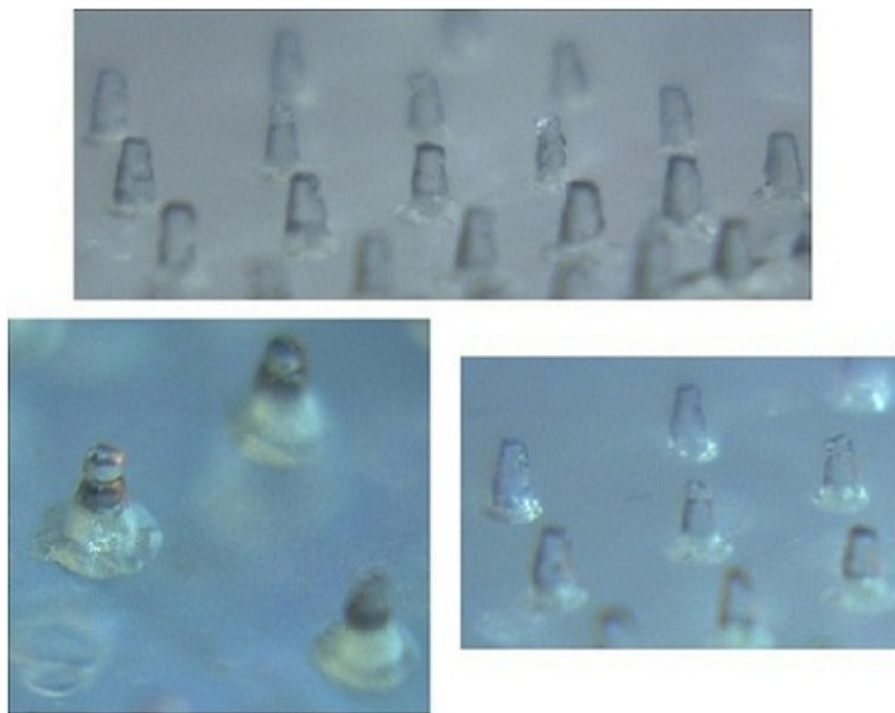
Figure 3.5.1. Agarose Post Arrays

Our hydrogel of choice was an agarose gel. Our procedure for making our agarose stamp was modified from the procedure used by the Grzybowski group. The stamps were made by pouring a hot 8% w/w solution of high strength agarose (OmniPur Agarose) in deionized water against an oxidized PDMS master having an array of posts embossed on its surface. This was then put through a centrifuge (3750 rpm, 60 sec) to give an agarose stamp with array of posts on its surface [17].

3.6 WETS Procedure

For the WETS procedure, both the PAA and the agarose gels were soaked into their appropriate reagents of the BR reaction. The sheet of PAA gel (with 3% thyodene already embedded in it) was soaked in a 50 mL solution containing 0.1075 g KIO_3, 0.38 g of malonic acid, 0.09 g of $Mn(OH)_2$ and 250 μL of H_2SO_4. Immediately prior to use, the

PAA sheet was cut into little squares with dimensions that match the dimensions of the patterns on the surface of the stamp, usually about 1 cm^2.

As for the agarose gel, after it has been cured it was cut into 1-2 cm x 1-2 cm blocks patterned with the negative of the array of features in the PDMS master. It was then soaked in 50% hydrogen peroxide for 60 minutes. Immediately prior to use, stamps were dried of excess water by placing them on filter paper for 10 min and dried further with air when necessary. We also note that soaking the agarose stamp for a prolonged period of time diminished its structural integrity of the posts [17].

Figure 3.6.1. WETS: PAA Sheet in contact with Agarose Gel

The stamp was held in contact with the PAA sheet for 20 seconds. The PAA gel was then suspended vertically as any patterns developed. This specific arrangement of exposing both faces of the gel to air eliminates the formation of a by-product of the BR reaction, oxygen bubbles [13]. If these bubbles are not eliminated, then they would interfere with the controlled wave propagation.

3.7 Smaller Scale WETS

A similar procedure was followed in performing WETS in smaller scales (50 μm). For example, the preparation and the soaking of the PAA gel were identical to the ones previously described. The agarose stamp, however, had a few things changed to accommodate the array of smaller posts.

The change in sizes of the posts started while we prepared the acrylate master. First, the power of the laser was decreased from 1.7 mW to 220 μW and this resulted in the decrease of the diameter of the posts to the desired 50 μm. The height of the posts were also reduced to 330 μm so that the posts can stand on their own. We also decided to make more arrays of posts (24 x 24 posts) because we were concerned that the impact of the PAA gel when placed above the posts would be strong enough to knock down the posts. We expected that increasing the number of the posts will allow them to withstand the weight of the PAA gel.

Figure 3.7.1. Small Acrylate Post Arrays

The procedure for molding the PDMS was also the same as before. However, we faced some trouble when we were peeling the PDMS off of the acrylate master. Since these posts were so fragile, some of them inevitably broke during the peeling process. The black cylinders in Figure 3.7.1 represent the holes that were supposed to be present in the PDMS mold by the posts of the acrylate master. The white cylinders represent the holes that

were supposed to be made by the acrylate posts, but these posts have been ripped from the master during the peeling process, and thus have been left in the holes.
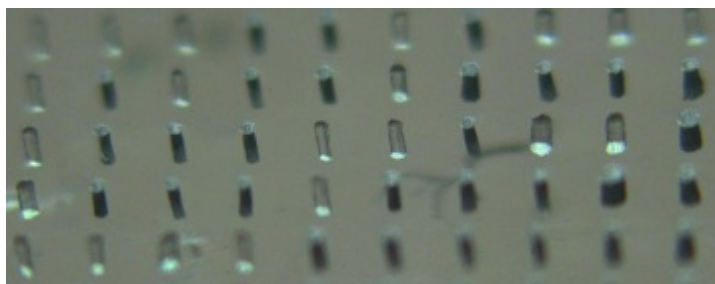
Figure 3.7.2. Small PDMS Mold

The concentration of the agarose stamp had to be increased from 8 to 12% w/w to strengthen the posts. When 8% w/w agarose gel with poles of diameter equal to 50 μm on its surface were casted, the poles fell, not being able to withstand their own weight (as shown on the right picture below). However when the 12% stamp has been casted instead, the posts were found standing upright. The time spent in the centrifuge was also increased from 60 to 120 seconds, but the speed was kept constant at 3750 rpm. These modifications yielded a patterned array of posts of 50 μm by 330 μm on the surface of the agarose gel.
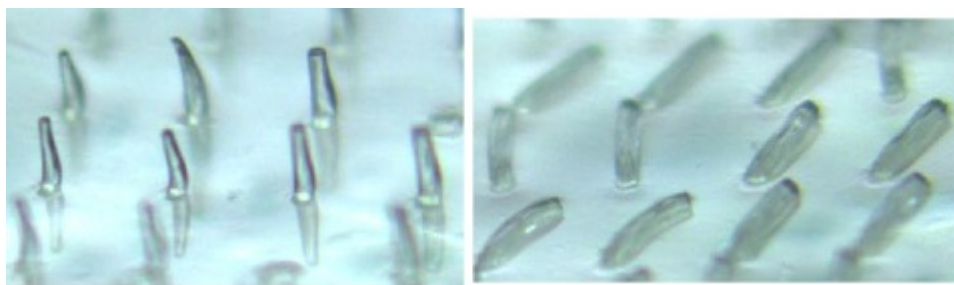
Figure 3.7.3. Small Agarose Posts

The time for the soaking of the micropatterened agarose gel was shortened. Soaking these fragile posts for longer than ten minutes followed by five minute of air drying resulted in

round bumps in place of erect posts. Instead, we added just enough peroxide to the bottom of the agarose stamp so the stamp can float on peroxide and the stamp was left untouched for ten minutes. Ten minutes was the right amount of time to both preserve the posts from falling down and allow enough peroxide to be soaked into the stamp.

4
Results and Discussion

4.1 Briggs-Rauscher Reaction in Free-Medium

The oscillating behavior exhibited in Briggs-Rauscher reaction is highly sensitive to the initial concentrations of the chemical reagents. This fact posed the greatest challenge in being able to demonstrate and replicate the BR reaction in the laboratory. At a first glance, the BR reaction deceptively looks straightfoward. There were several ingredients (KIO_3, malonic acid, $Mn(OH)_2$, concentrated H_2SO_4 and starch) that needed to be dissolved in water and to that system, an activator (H_2O_2) was to be added to start the reaction. However the first obstacle we faced was that most of the solid chemicals did not dissolve in water. Neither potassium iodate nor the manganese(II) catalyst dissolved and even starch, which was thought to be fairly soluble in water ended up presenting hardships. Increasing the dissolving time did not aid in dissolving much of the solids and after an extended period of time, the minute amount that was dissolved precipitated out again.

This problem of reagents not dissolving was conquered with the introduction of a sonicator. One of many ways that sonicators can be of assistance is in dissolving particles. Sonicators apply sound energy and small amount of heat energy can be added as well, and

the particles in a sample are agitated. The sonicator greatly aided in dissolving potassium iodate as well as the mangaese catalyst. Malonic acids are highly soluble in water, so sonication was unnecessary for dissolving malonic acids.

However, sonication did not help with dissolving starch in water. The problem can be traced back to the fact that starch solution was relatively concentrated (3 grams in 100 mL of DI water). We found that by heating the water to its boiling temperature prior to adding starch in small increments completely dissolved the necessary amount of starch.

At this point, all the necessary solids are dissolved in water, so what is left is adding the two liquids, concentrated sulfuric acid and hydrogen peroxide. Only problem is that both of those liquids are hard to handle. Concentrated H_2SO_4 presented its own impediment to this investigation because protons are catalytic species, so even in total, only a minute amount is needed (in the order of couple of microliters). Typically one would achieve the transfer of solvents in microliters using a micropipettor. However, suction of concentrated sulfuric acid would damage the pipette. Hence, Pasteur pipettes were used as a replacement and the required amount of sulfuric acid had to be estimated.

Hydrogen peroxide, the activator of the BR reaction, presented the greatest challenge for this project. Not only did different literature sources employ hydrogen peroxide of varying concentrations, but even in articles using the same concentration of hydrogen peroxide, their amount of hydrogen peroxide added varied somewhat significantly. We had to find the optimal amount of peroxide by trial and error. Changing the amount of hydrogen peroxide had a great impact on the oscillation behavior. If too much was added, only the initial ephemeral amber phase occurred and the rest of the reaction stayed in the blue phase without any oscillations. If too little peroxide was added, the color change from amber to blue did not occur. Even when the range was narrowed, a slight change in the amount of peroxide added changed the amount of oscillations occurring. When an appropriate amount of peroxide was added, as many as twenty oscillations were observed

in one reaction medium. This number of oscillations can be decreased to as little as seven oscillations when the amount of peroxide added was not optimal.

4.1.1 Analysis of BR reaction data from Laboratory

The BR reaction was conducted multiple times in our laboratory. Pictures and videos of the oscillations were taken for more in-depth investigation. Several pictures of the reaction are presented below, along with the observations that were made for these trials.
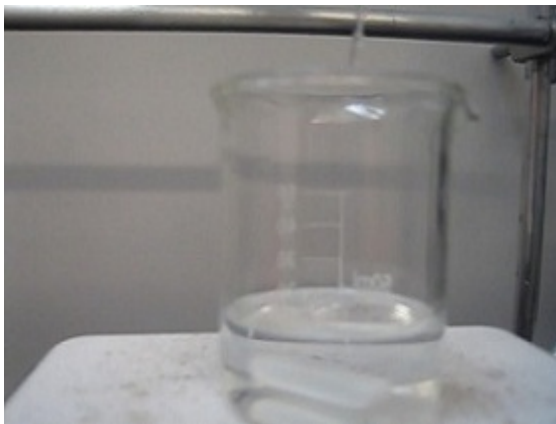
Figure 4.1.1. BR reaction at 0 sec

At time zero, hydrogen peroxide was not added yet, so the solution appears as clear white. All the other solids that were dissolved in the deionized water were white and did not contribute any color to the solution. The only exception would be $MnOH_2$ which was light pink in color, but this reagent was used in very small quantities so no color was exhibited in the solution. The starch is responsible for the white shade of the solution. It is thought that the starch dissolves as a colloid.

Figure 4.1.2. BR reaction at 25 sec

Then as soon as peroxide is added to the system, the solution turns amber due to the rapidly occurring radical mechanisms. The initial amber phase lasts for approximately 60 seconds and the amber phases becomes shorter as more oscillations occur over the course of the reaction.
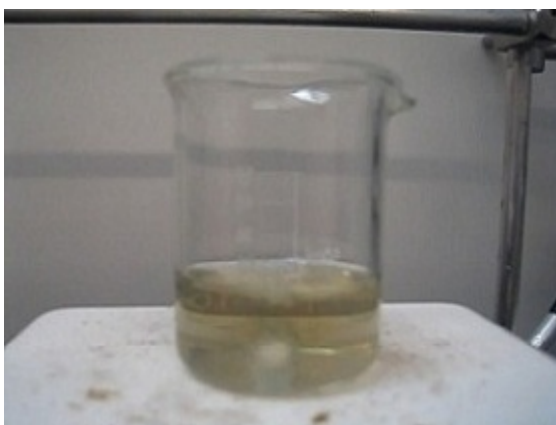
Figure 4.1.3. BR reaction at 60 sec

Right at the cusp between 60 and 61 seconds, the transition from amber to blue occurs. The picture below shows the presence of blue precipitates during this transition. This blue precipitate is thought to be the iodide-malonic acid complex, which is bound to the thyodene(starch) indicator. The role of thyodene indicator is that it displays a very deep

blue color when bound to iodide-malonic acid complex, it, thereby indicating whether iodide-malonic acid is present or not.
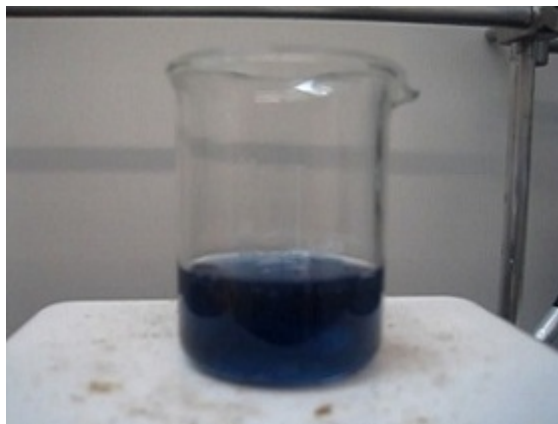
Figure 4.1.4. BR reaction at 61 sec

The transition between amber to blue occurs in less than one second and the solution appears as deep blue color by the 61 seconds mark. Although it is difficult to determine in the picture, we believe that the reason why this solution appears deep blue is because there are large quantities of the iodide-malonic acid-thyodene complex generated. To be more specific, the concentration of iodide-malonic acid-thyodene complex is greater than that of I_2. The suction of the deep blue solution with a Pasteur pipette demonstrates the ample amount of these precipitates freely floating within the reaction system. Furthermore on average, the phase in which the solution appears deep blue is longer than the amber phase, and in contrast to the amber phase becoming shorter as more oscillations occur, the deep blue phase becomes longer as the reaction evolves with respect to time.
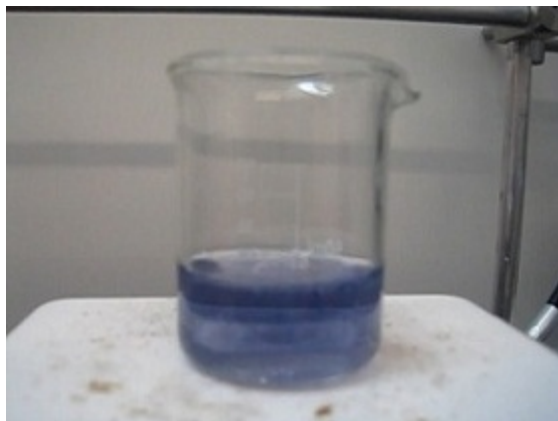
Figure 4.1.5. BR reaction at 76 sec

The instant this BR reaction has occurred for 76 seconds, the solution is on the verge of turning amber. The precipitates appear to be fading away, but since we know that chemicals cannot just disappear from the reaction medium, we can assume that the concentration of iodine has been increasing to the point that it is now greater than the concentration of the precipitates.
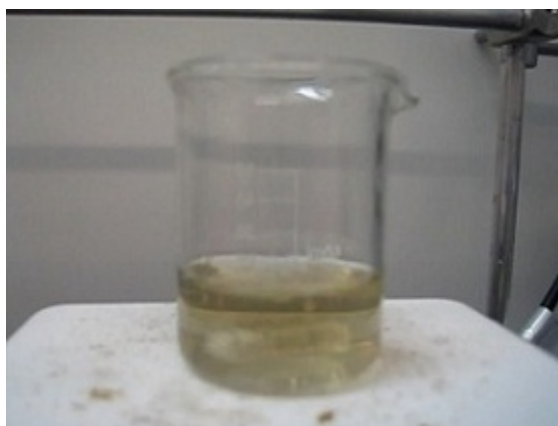
Figure 4.1.6. BR reaction at 97 sec

Immediately after 76 seconds, the solution of the reaction is now amber and the oscillating cycle repeats many more times. The next amber phase lasts for 22 seconds, which

is considerably shorter than the first amber phase. Also, it is worthy to note that during the amber phase, lots of bubbles are being formed. This can be seen with the picture of the BR reaction taken after 97 seconds have passed. This observation is consistent with the suggested reaction mechanism that the radical mechanism creates several intermediate species which interact with each other to eventually yield I_2.

The next blue phase occurs for 17 seconds until the next oscillation. This is an increase from the 15 seconds of the first blue phase. Then the next amber occurs for 18 seconds, followed by 19 seconds of blue phase. This pattern of the duration of the blue phase increasing and that of amber phase decreasing continues for the next thirty minutes. About twenty oscillations between amber and blue are produced until it eventually stays in the blue phase.

4.1.2 Ultraviolet-Visible Spectroscopy

We monitored the changing colors using UV-vis spectroscopy. When the solution is amber, it transmits orange light and when it is blue, it absorbs orange light. By following the absorbance of the orange light, we can track the color changes of the solution.
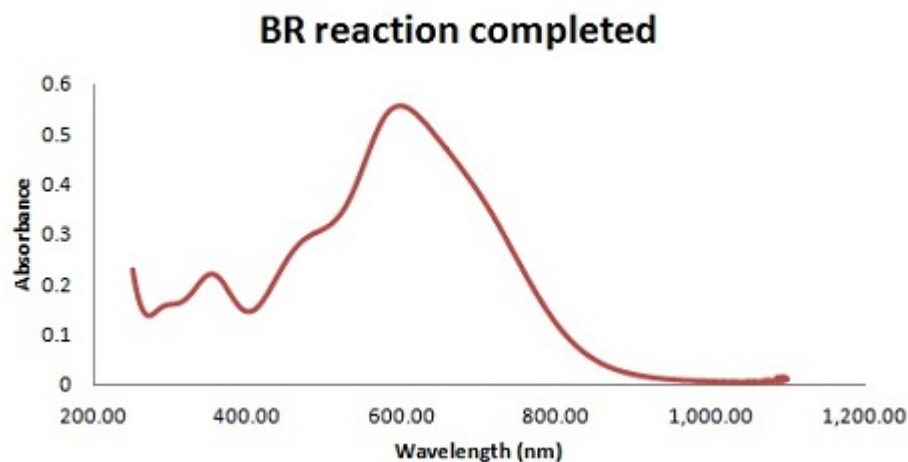
Figure 4.1.7. UV-Vis Spectroscopy of Blue Phase

It seems that the orange light is best absorbed at 589.6 nm, corresponding to the absorbance of 0.555. Therefore for this trial, we dissolved all the appropriate reagents in a beaker with only hydrogen peroxide left out. This solution was then poured into a cuvette with a magnetic stir bar and was set to absorb at 589.6 nm. Then the peroxide was added to start the BR reaction.
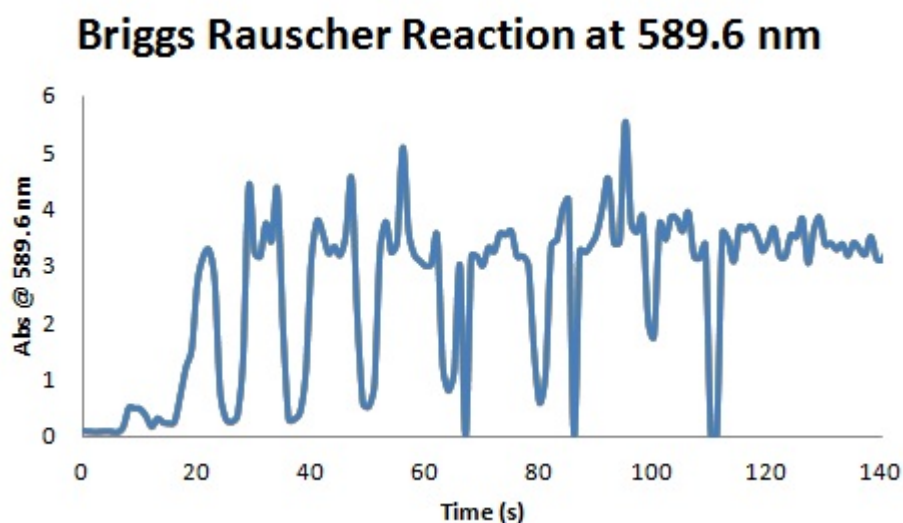
Figure 4.1.8. UV-Vis Spectroscopy of BR reaction

The UV-Vis absorbance data at 589.6 nm shows that this reaction indeed oscillates. Peaks of absorbance were observed when the blue color was displayed. For this trial, the BR reaction took place in a period of 140 seconds with seven oscillations.

4.2 Mathematical Modeling

In order to model the Briggs-Rauscher reaction, it was crucial that we simplify the systems of equations that participate in the reaction. As stated in the background chapter, the history of analyzing these BR reactions can be traced back to 1981 with Noyes and Furrow's first attempt to understand the mechanism for oscillations [4]. Their systems of equations included over 30 chemicals (including reagents and intermediate species) that served as variables, but this system was too complicated. Hence, no further significant advances were made with that exact model. In 2002, the KLS model was reported as a simplified model that used only ten variables [8]. For our analysis, we were only interested in understanding how the oscillation is displayed in this BR reaction, so we considered only the variables that were necessary to display the oscillating behavior.

4.2.1 Our Simplified BR Reaction Model

Our model only considers **five variables** that were crucial in producing the oscillating behavior between the two intermediates, I_2 and I^-. These five variables that play major roles in the chemical reaction, are I^-, I_2, IO_2, HIO_2, and HIO. To set up a system of ordinary differential equations (ODE's) that govern the oscillating behavior, we needed reaction parameters, such as initial conditions and rate constants of the reactions. Since

the KLS model already published their sets of reactions that exhibit oscillating behavior, we decided to import their reaction conditions for our model. Some modifications were made, as our set of ODE's only included five variables whereas theirs had ten. A sample copy of the *Mathematica* notebooks that include our simplified reactions as well as the parameters are illustrated below:

```
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;
k0 = 0;
C9 = 10^4;
H = 0.056
MnC = 0.004;

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

Figure 4.2.1. Mathematica Code: Rate Constants

```
solv =
  NDSolve[{i'[t] ==    -r1 H^2 i[t] IO3[t]    -r2 H i[t] HIO2[t]    -r3 HIO[t] H i[t]    +

      r3r I2[t]    + r9 I2[t] MA[t]        + r10 HIO[t] H2O2[t]    + k0 (y1o - i[t]),
                    ─────────────
                          2


    I2'[t] ==    r3 HIO[t] H i[t]    - r3r I2[t]    - r9 I2[t] MA[t]    + k0 (y2o - I2[t]),
                                                      ─────────────
                                                            2


    IO3'[t] == 0,

    HIO2'[t] ==
     r1 H^2 i[t] IO3[t]    - r2 H i[t] HIO2[t]    - r4 IO3[t] HIO2[t] H    + r4r IO2[t]^2    -
       2 r5 HIO2[t]^2    + r6 IO2[t] (MnC - MnOH2[t])    + k0 (y4o - HIO2[t]),

    HIO'[t] ==    r1 H^2 i[t] IO3[t]    + 2 r2 H i[t] HIO2[t]    - r3 HIO[t] H i[t]    +
       r3r I2[t]    + r5 HIO2[t]^2    - r10 HIO[t] H2O2[t]    + k0 (y5o - HIO[t]),

    IO2'[t] ==    2 r4 IO3[t] HIO2[t] H    -
       2 r4r IO2[t]^2    - r6 IO2[t] (MnC - MnOH2[t])    + k0 (y6o - IO2[t]),

    MnOH2'[t] == 0,

    HO2'[t] == 0,

    MA'[t] == 0,

    H2O2'[t] == 0,
```

Figure 4.2.2. Mathematica Code: Simplified Set of ODE's

```
i[0] == 10^-8, I2[0] == 6 × 10^-7, IO3[0] == 0.034, HIO2[0] == 10^-10, HIO[0] == 10^-10,
   IO2[0] == 10^-10, MnOH2[0] == 10^-13, HO2[0] == 10^-7, MA[0] == 10^-3,
   H2O2[0] == 0.324}, {i, I2, IO3, HIO2, HIO, IO2, MnOH2, HO2, MA, H2O2},
   {t, 0, 2000}, MaxStepSize → 0.1, MaxSteps → 100 000][[1]];
```

Figure 4.2.3. Mathematica Code: Initial Conditions and Logistics

The list of constants that are labeled r1 through r10 in Figure 4.2.1 are rate constants, and these values were adopted from the KLS model. The variables, k0, C9, MnC, as well as y1o to y10o were newly inserted variables that are not crucial in producing oscillating behaviors, but with the inclusion of these factors, the graphs produced by *Mathematica* were much clearer. The variable, H, represents the concentration of H^+ (in moles) that

participate in the BR reaction. We noticed that the concentration of protons remain relatively constant over the course of the reaction. Presumably this is due to the fact that H^+ fulfills its role as a catalyst in this reaction. Over the course of the BR reaction, we suspect that the proton catalyst is consumed and then regenerated in relatively equal quantities.

Figure 4.2.2 illustrates the set of differential equations that are necessary in producing chemical oscillations. Although there are ten differential equations, only five of them have interesting terms because the other five are set as zero. The other five differential equations that have their derivative set to zero are differential equations of variables: IO_3, $Mn(OH)_2$, HO_2, MA (an abbreviation for malonic acid), and H_2O_2. For the cases of IO_3, HO_2, MA, and H_2O_2, we assumed that the concentrations of these chemicals are much greater than that of the five intermediates that are responsible for the oscillating behavior. In perspective of the five intermediates, the changes in these four chemicals are negligible. Therefore, the derivatives of the equations, which explain the behavior of these four chemicals, are set to zero for simplification. Finally, $Mn(OH)_2'[t] = 0$, because the role of $Mn(OH)_2$ is similar to that of H^+. $Mn(OH)_2$i another catalyst that is consumed and regenerated in approximately equal quantities.

Finally, Figure 4.2.3 illustrates the initial conditions of these ten chemicals. Even though only five crucial intermediates are considered for the oscillation behavior, we still need to include the initial concentrations of other five chemicals because their presence facilitate the display of oscillation. It would be a mistake to believe that the concentrations of these chemicals do not change over the course of the reaction, so their derivatives should be set to zero. Their concentrations throughout the reaction actually do change, but this change is negligible compared to that of the intermediate species. Reported initial concentrations of reagents, such as IO_3, $Mn(OH)_2$, MA, and H_2O_2 are obtained from our experimental conditions that were used to observe the oscillating behavior. Initial concentrations of any

other chemicals should be zero, as other chemicals should be intermediates and are not found at the start of the reaction. However for the modeling conditions, their initial concentrations are not set to be zero, but an arbitrary value that is slightly greater than zero. A rationalization for the assignment of a non-zero initial concentration for the intermediate species is that our model mainly focuses on the time period in which oscillations are taking place. Therefore, we neglected the beginning as well as the end phase of the reaction. Noyes and Furrows [4],[6] suggests that the radical mechanism of this reaction takes place at the start of the reaction as hydrogen peroxide interacts with potassium iodate and produces iodide ions as well as iodine. Since we neglected this phase, we decided to assign a slightly positive value for the initial concentrations of these intermediate species.

4.2.2 Chemical Equations and Oscillations of the BR reaction

Before continuing with the investigation of oscillating behavior, it is important that these set of differential equations are translated to chemical equations. From the analysis of these mathematical models, we can correlate the behavior back to chemical interactions and verify that the results produced by the model coincide with the data obtained from the laboratory. Since there were thirteen rate constants, it is reasonable that we should have thirteen chemical equations, assigning one rate constant per chemical equation. However, once again we were mainly interested in just the oscillation behavior, so we decided to disregard certain equations that when eliminated, left the oscillation behavior still intact. The final set of chemical equations that we used to analyze the BR reaction included **eight** equations with eight reaction constants, but only five variables:

$$
\begin{aligned}
\text{reaction 1} \qquad &(r1): \qquad 2H^+ + I^- + IO_3 \rightarrow HIO_2 + HIO \\[4pt]
\text{reaction 2} \qquad &(r2): \qquad H^+ + I^- + HIO_2 \rightarrow 2HIO \\[4pt]
\text{reaction 3} \quad (r3),(r3r): \qquad &H^+ + I^- + HIO \rightleftharpoons I_2 \\[4pt]
\text{reaction 4} \qquad &(r4): \qquad H^+ + IO_3 + HIO_2 \rightarrow 2IO_2 \qquad\qquad (4.2.1) \\[4pt]
\text{reaction 6} \qquad &(r6): \qquad IO_2 \rightarrow HIO_2 \\[4pt]
\text{reaction 9} \qquad &(r9): \qquad I_2 + MA \rightarrow I^- + IMA \\[4pt]
\text{reaction 10} \qquad &(r10): \qquad H_2O_2 + HIO \rightarrow I^-
\end{aligned}
$$
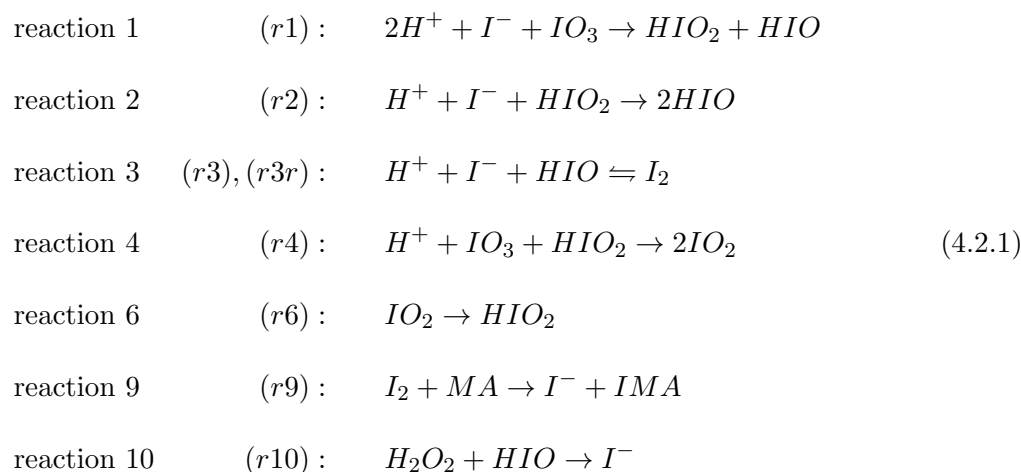
The first reaction of the set is labeled as *reaction 1* and this reaction has a rate constant of r1. The same interpretation can be applied to all eight chemical equations.

The oscillating behavior of BR reaction was extensively investigated using all the chemical equations, the corresponding ordinary different equations, as well as appropriate reaction parameters. According to the observations made in the laboratory and the data obtained by UV-Vis spectroscopy, the oscillations of color from amber to deep blue can be correlated to the oscillations of $[I_2]$ and $[I^-]$ respectively. Hence, to model the chemical oscillations of BR reaction, we created a graph of $i[t]$ vs $I2[t]$.
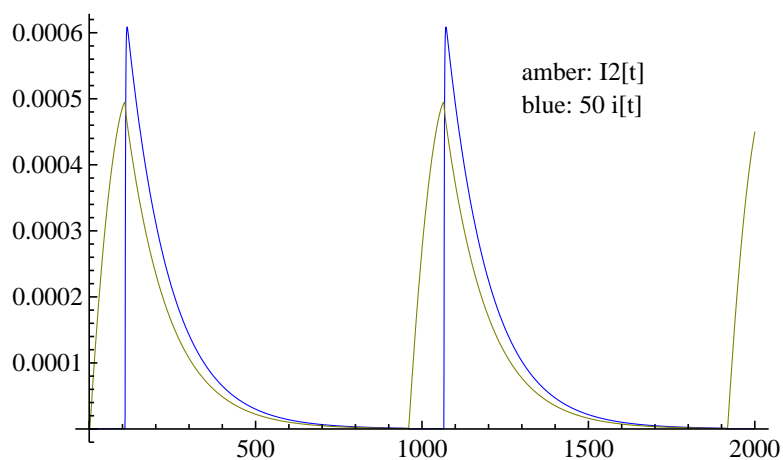

Figure 4.2.4. Concentrations of 50 i[t] and I2[t] VS. time (s)

Note that the model only illustrates the phases of oscillations, so the fact that the oscillation starts in $t = 0$ is not realistic. However, the oscillating phases are certainly present in the figure above. In the first portion of the graph, $[I_2]$, highlighted in amber color, is higher than $[I^-]$. Then there is a sudden rise of $[I^-]$ and so $[I^-]$ exceeds $[I_2]$. This phenomenon is consistent with the laboratory observation that the switch of colors from amber to blue was abrupt. The graph below which illustrates the ratio of I^- to I_2 exemplifies this statement.
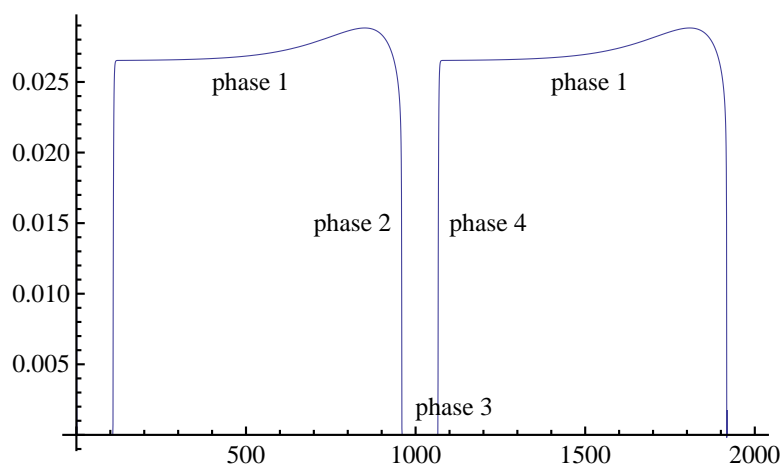
Figure 4.2.5. Ratio of Iodide to Iodine vs. Time (s)

Then both $[I_2]$ and $[I^-]$ decrease with $[I^-]$ still greater than $[I_2]$, indicating that the phase displaying blue color is longer than that of amber color. This is also consistent with the observations made from the laboratory. Then for a short period, $[I_2]$ rises again, which is indicative of a sudden color change from blue to amber. Figure 4.2.6 which illustrates the ratio of I_2 to I^- exemplifies this statement. However, this short phase is once again followed by sudden rise in $[I^-]$ and this changes the color display to blue.
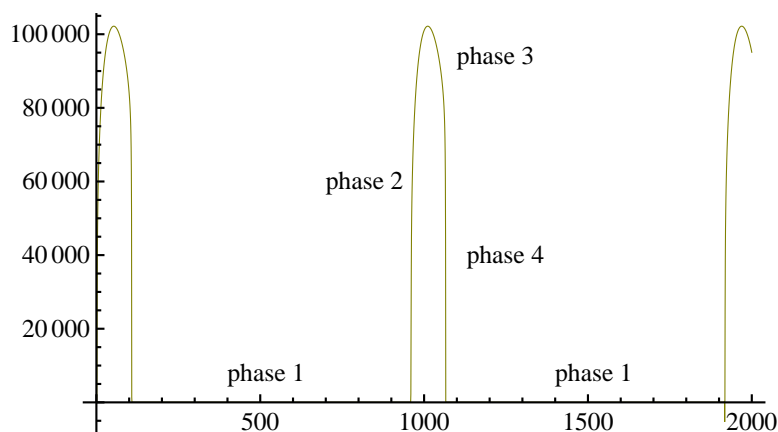
Figure 4.2.6. Ratio of Iodine to Iodide vs. Time (s)

Satisfied by the consistency of the behavior observed in the mathematical modeling and in laboratory experiment, the differential equations of other three variables were investigated.
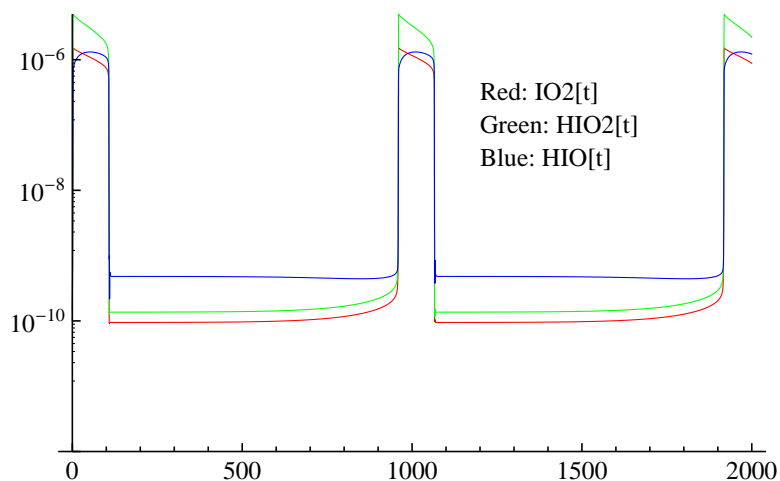
Figure 4.2.7. Log of Concentrations of IO2[t], HIO2[t] and HIO[t] VS. time (s)

There was a strong indication from the set of chemical equations that these three intermediate species (IO_2, HIO_2, and HIO) were highly related with chemical oscillations of iodide and iodine. Notice that for analyzing the changes in concentrations of these three intermediates, a log plot was used. An advantage of using a log plot is that first, the concentrations of these intermediates are very small and second, the changes in concentrations

of these variables cover a wide range over many orders of magnitude. A log plot is best to show the changes in these concentrations.

Matching the graph of iodine and iodide with the graph of three other intermediates, it can be seen that the dynamics of these five intermediates are congruent. The concentrations of all the intermediates either rise or fall in the same time interval and changes are all abrupt. For example, at around 980 seconds, a sudden rise of the three intermediates can be seen in the second graph. The same is true for I_2. This suggests that the three intermediates are responsible for the sudden rise of iodide and iodine, and vice versa.

4.2.3   Four Phases of Chemical Oscillation

When analyzing oscillating systems, the dynamics of different behaviors throughout the oscillations can be broken into separate phases and each phase can be analyzed separately. For example, when analyzing a horizontal oscillation of a mass on a spring, one can observe the four different phases of oscillating behavior from analyzing the momentum of the mass. Similarly, the oscillating behavior between iodine and iodide can be analyzed by subdividing into different phases. One oscillation cycle was divided into four phases for complete analysis.
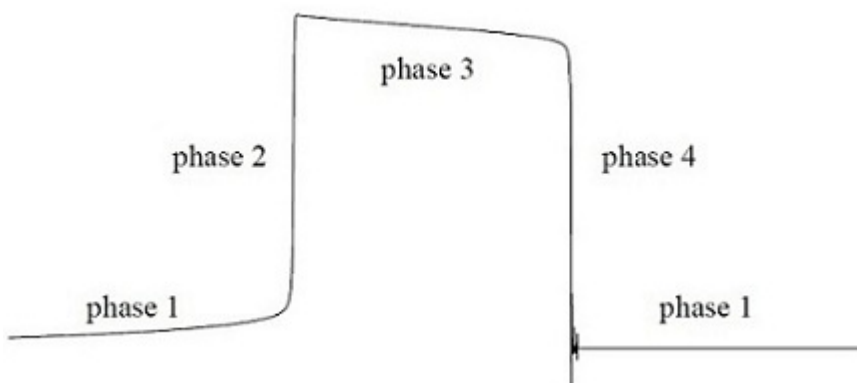
Figure 4.2.8. Four phases of an Oscillation

The base line of this graph is a zoom-in version of a graph of $IO_2[t]$, which is essentially equivalent to $HIO_2[t]$ and $HIO[t]$. This means that in phase 1, $[IO_2]$, $[HIO_2]$ and $[HIO]$ are all very low. In phase 2, they exponentially increase. In phase 3, the concentrations slightly decrease, but they are still very high. In phase 4, sudden drop in their concentrations restart the cycle.

The graph of $i'[t]$ (iodide, I^-) and the graph of $I2'[t]$ (iodine, I_2), are shown for one oscillation and likewise are subdivided into four phases. A log plot was used again while analyzing the changes in $[I^-]$ and $[I_2]$ over the course of an oscillation.
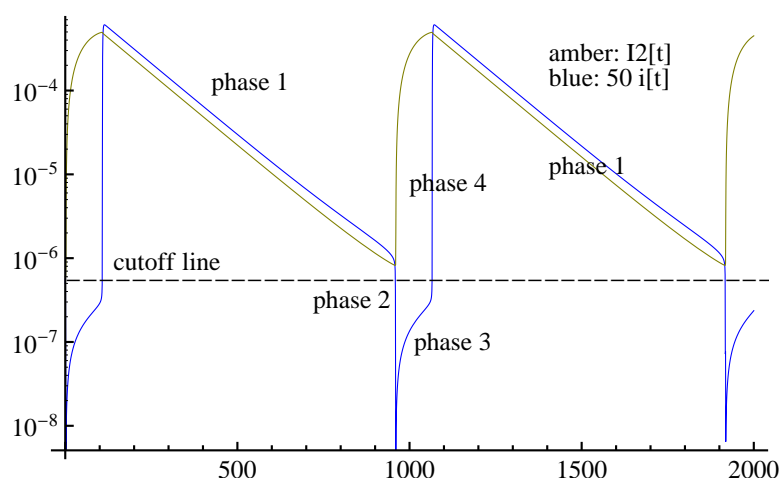
Figure 4.2.9. Log of Concentration of 50 i[t] and I2[t] Vs. time (s) in 4 Phases

In Phase 1, which takes place after the radical mechanisms, high concentrations of I^- and I_2 are found but the concentrations of IO_2, HIO_2, and HIO are low. This is because during the radical mechanism, iodate reacts with hydrogen peroxide to generate abundant IO_2, HIO_2, and HIO, as shown by reaction 1, 2, 4, and 6. However, these intermediates are quickly consumed to yield a lot of I^- and I_2, as shown by reaction 3 and 10. The rate of generating the three intermediates and the rate of consuming them to produce I^-

and I_2 quickly reach equilibrium and therefore in phase one, the graph is constant. In summary, very little of the three intermediates are found, but there are lots of I^- and I_2.

It is crucial to note that $I^{-\prime}(t)$ and $I_2'(t)$ are decreasing in phase 1. This is due to the *fallout reaction* with malonic acid. Reaction 9, $I_2 + MA \rightarrow I^- + IMA$ is what we call a fallout reaction. This reaction should only be taken into consideration when a high concentration of I_2 is found in the system. Only then, the abundant amount of iodide forces the reaction with malonic acid. The result of this interaction is that only one iodide ion is formed while the other iodine forms a bond with malonic acid and precipitates out of the reaction system. The reason why we call this a fallout reaction is because one of the iodine is *lost* to malonic acid each time this reaction occurs. Because I^- is needed to produce I_2 (reaction 3) as $[I_2]$ decreases, so does $[I^-]$. However since the fallout reaction converts I_2 to I^-, $[I^-]$ is still greater than $[I_2]$ in phase 1, and so the blue color is displayed.

Phase 2 begins when the decreasing $[I^-]$ in phase 1 reaches a threshold concentration. In phase 2, I^- is converted to I_2 with the consumption of HIO (reaction 3), perhaps because the $[I_2]$ is very close to its minimum concentration. This causes the $[I^-]$ to decrease and reach its lowest concentration (below its threshold). During phase 2, the color of the solution switches to amber. As for IO_2, HIO_2 and HIO, they are no longer being consumed so their concentrations increase exponentially in this phase. By the end of the transient phase 2, $[I^-]$ is at its lowest dip, but $[IO_2]$, $[HIO_2]$, and $[HIO]$ are at their maximum concentrations.

Phase 3 starts when $[I^-]$ reaches its lowest concentration. At the beginning of phase 3, the concentrations of the other three intermediates are at their maximum, whereas the concentrations of iodide and iodine are very low. Hence, the three intermediates are being consumed in this phase to increase $[I^-]$ and $[I_2]$. All three intermediates, IO_2, HIO_2, and HIO are consumed to produce I^- and a fair amount of I^- is converted to I_2 (reaction 3). Since $[I_2]$ was higher than $[I^-]$ at the beginning of phase 3 and also since those two

intermediates are being created in equal rates, the $[I_2]$ is still higher than $[I^-]$ throughout phase 3. Therefore, the color of the solution remains amber throughout this phase.

Phase 4 begins when the $[I^-]$ is raised enough so that it reaches the cutoff concentration once again. In phase 4, I_2 begins its conversion to I^- (reverse reaction 3) since $[I_2]$ was maximum at the end of phase 3 and beginning of phase 4. Furthermore since the concentration of the three intermediates are high, these intermediates are quickly consumed to rapidly raise the $[I^-]$ (reaction 6, 2, and 10). In this transient phase, the color of the solution switches to blue, as I_2 is being slowly consumed, but I^- is being produced swiftly. When the $[I^-]$ is at its maximum, then the $[I_2]$ is still relatively high, but the $[IO_2]$, $[HIO_2]$, and $[HIO]$ are very low. This is the signal for the phase 4 to terminate and for the phase 1 to start the cycle of oscillation over again.

Thus the summary of four phases can be included in one graph shown below.
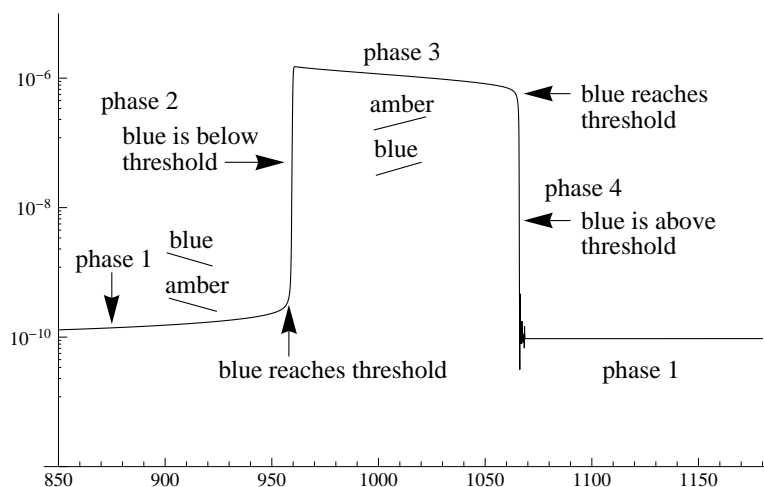

Figure 4.2.10. Oscillation Summary: Concentration vs. time (s)

4.2.4 Importance of all the Intermediates

From this analysis provided by the mathematical models, a better understanding of the five intermediates' absolute presence in initiating and maintaining the chemical oscillations can be achieved. Obviously, the concentrations of I^- and I_2 are crucial because the ratio

of these concentrations determine which color is displayed by the reaction at any point. However, $[IO_2]$, $[HIO_2]$, and $[HIO]$ are important as well because the concentrations of these intermediates are the ones that dictate the ratio of I^- to I_2. A big part of why the oscillation occurs is due to the fact that I^- and I_2 can convert to each other by reaction 3 and its reverse reaction. This crucial reaction is the only reaction that bridges $[I^-]$ and $[I_2]$. However in order for I^- to convert to I_2, HIO needs to be consumed in the process. Let us examine this reaction more carefully.

$$r3, r3r: \qquad H^+ + I^- + HIO \rightleftharpoons I_2 \tag{4.2.2}$$
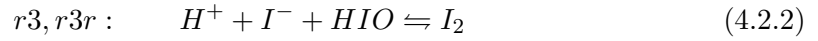
$$\frac{d[I_2]}{dt} = r3[I^-][HIO][H] - r3r[I_2] \tag{4.2.3}$$

$$\frac{d[I^-]}{dt} = r3r[I_2] - r3[I^-][HIO][H] \tag{4.2.4}$$

To determine what factor is involved in determining the ratio of I_2 to I^-, the steady state of those two variables can be studied by setting their derivatives equal to zero. So when $\dfrac{d[I_2]}{dt} = \dfrac{d[I^-]}{dt} = 0$,

$$r3[I^-][HIO][H] - r3r[I_2] = 0$$

$$r3[I^-][HIO][H] = r3r[I_2] \tag{4.2.5}$$

$$\frac{[I_2]}{[I^-]} = \frac{r3[H]}{r3r}[HIO]$$

Hence, the ratio of I_2 to I^- is determined by the concentration of HIO. Also note that reaction 3 and also reverse reaction 3 does not change the total concentration of $I_2 + I^-$. The reaction only converts I^- to I_2 and vice versa.

A mathematical proof for this statement is:

$$\frac{d[I_2]}{dt} + \frac{d[I^-]}{dt} = r3[I^-][HIO][H] - r3r[I_2] + r3r[I_2] - r3[I^-][HIO][H] = 0 \qquad (4.2.6)$$

This is why HIO is a crucial intermediate to this oscillating reaction. HIO_2 is important because it serves as a reactant for the synthesis of HIO (reaction 2). Finally, the purpose of IO_2 is to be consumed to make HIO_2 (reaction 6).

To summarize, IO_2 produces HIO_2 which makes HIO and HIO is one of the necessary ingredients for I^- to convert into I_2. This cascade of events explains why the reaction always ends in blue color. The reagents for the BR reaction, such as iodate and peroxide are consumed to yield the three intermediates, IO_2, HIO_2 and HIO. Hence if one of the starting ingredients are completely consumed, then ultimately, the $[HIO]$ would be very low and this will prevent the color change from blue to amber. Theoretically if one were to provide an endless supply of these reagents, then the oscillation will be maintained forever, but in reality, one or more of the reagents are expected to run out. Hence, it is no longer a surprise that the reaction will eventually cease to change from blue to amber, and maintain its blue phase.

Another intriguing relation between these five intermediates is that $[IO_2]$, $[HIO_2]$, and $[HIO]$ control the growth and decay rate of I^- and I_2. For example in phase 3, the concentrations of the three intermediates were very high. The abundance of the three intermediates in this phase caused the growth in I^- and I_2. Similarly in phase 1, the concentrations of the three intermediates were very low. The deficiency of the three intermediates in this phase caused the decay in I^- and I_2. Interestingly, $[I^-]$ directs the $[IO_2]$, $[HIO_2]$, and $[HIO]$. When $[I^-]$ is decreasing, such as in phase 2, $[IO_2]$, $[HIO_2]$, and $[HIO]$ all increased. Conversely in phase 4 when $[I^-]$ increased rapidly, $[IO_2]$, $[HIO_2]$,

and $[HIO]$ all decreased quickly. It is precisely these opposing behaviors that can instantaneously change the behavior of the chemical reaction. These abrupt changes in direction can be observed as $[I^-]$ reaches its cutoff value, resulting in oscillating behaviors.

However that is not the entire story to the oscillation. Although it is true that the rates of three intermediates and I^- are inversely proportional to each other and these rates also drive the oscillating behavior until the concentrations reach their respective cutoff values, without the presence of I_2, the same oscillation would be not be observed. For example let us assume that the same reaction is conducted with only the three intermediates and I^-. The set of radical reactions and phase 1 of the oscillation would occur as if nothing has changed. During phase 1, $[I^-]$ would be relatively high since it is being produced constantly by consuming the three intermediates. As a consequence, the concentrations of the three intermediates would be really low. At the end of phase 1, the I^- would hit the cutoff value and the concentrations of the three intermediates would increase exponentially. Increasing the concentrations of the three intermediates will increase the $[I^-]$. Thus if the graph of $I^{-\prime}[t]$ were to be analyzed, there would only be a little dip at the cutoff region and it would rise again and quickly return to the cutoff value. Furthermore as time progresses, I^- would find equilibrium with the three intermediates, thus leading to no oscillation. In conclusion, there would be no chemical oscillations if the entity of I_2 were absent in the reaction.

4.2.5   Mechanical Analogy

Perhaps an analogy to a real-world mechanical problem would aid in understanding how oscillations work. Imagine a watermill system consisting of two buckets instead of the wheel. There are two types of liquid in this system and each bucket only holds one of the liquid or the other. Bucket 1 only holds a blue 'weighted liquid' but has a little hole at the bottom so it is constantly leaking. Bucket 2 holds an amber 'weightless liquid' and the

amount of amber liquid does not change. This system of water buckets rotates underneath a faucet that often expels blue liquid if bucket 1 is right under it. So let's assume that for our initial condition that there is zero blue liquid in Bucket 1 and also that bucket 2 (without amber liquid) is heavier than bucket 1 (without blue liquid) so that bucket 1 can start at the top. With bucket 1 at the top, the faucet will quickly fill the bucket with blue liquid and bucket 1 will quickly fall to lower altitude. This causes bucket 2 to rise to a higher altitude. This system would be stable this way if it was not for that small hole in bucket 1. Blue liquid is continuously leaking and once just the right amount of blue liquid has exited the system, the two buckets will change places and the process will cycle again.

This somewhat realistic scenario closely resembles the oscillating behavior of the BR system with some details missing. The positioning of the buckets resembles the role of the three intermediates, IO_2, HIO_2, and HIO. This is similar to how these three intermediates control the ratio of blue to amber and decide which color will be displayed at certain instance of the reaction. Obviously the blue liquid resembles I^- and amber liquid resembles I_2. The reason why blue liquid is weighted as opposed to amber being weighted is due to the fact that $[I^-]$ is the factor that changes the directions of the three intermediates, as previously explained. Weight is the factor that changes the position of the buckets in a water system, so it is reasonable that the blue liquid ended up being a weighted liquid. The little hole in bucket 1 stands for the fallout reaction which ultimately decreases the amount of iodide in the system. In BR system, malonic acid binds with iodide and precipitates out of the reaction medium, so a little hole for the water to leak out of the system seemed appropriate. The major flaw of this water system is the fact that the transition state in which the buckets switch places is not abrupt enough as they are in BR system. Also, amber liquid staying constant throughout the process is inconsistent with the BR system. However, how realistic would the story be if the blue liquid can suddenly turn

into the amber liquid and vice versa?

It is undoubtedly true that mathematical modeling has assisted in establishing a deeper understanding how the color oscillation occurs between iodide and iodine. Not only that, but this model provides an acceptable explanation for certain observations such as color oscillation occurring abruptly and also why the oscillation always ends in blue. Furthermore, the initial data from the laboratory experiments were used to construct this model, so this model serves as a rather accurate model of the BR reaction that has been observed in lab. The only discrepancy that existed between the oscillation provided by the model and the oscillation that was observed in lab would be the time interval. Our model provided somewhere between 2 and 3 oscillations for 2000 seconds, whereas in lab, seven to twelve oscillations were often observed in less than a 1000 seconds. It is strongly believed that this difference in time factor can be corrected with changing either the rate constants or the initial conditions. Since the initial conditions were transferred from the lab to construct the model, it is believed that adjusting the rate constants can enhance this model to an even higher accuracy to the laboratory observation.

4.3   Briggs-Rauscher Reaction with WETS

WET Stamping technique is a process in which the thin PAA layer is in physical contact with a micropatterened agarose stamp and a complex pattern is formed in the PAA gel. We had to overcome several challenges in order to successfully utilize this technique.

The first challenge was in creating the agarose stamp. The agarose stamp is made by pouring a hot agarose solution into a PDMS mold that is composed of engraved holes that resembles the poles of acrylates. The greatest challenge imposed while preparing the agarose stamp was that this array of poles was thin so while removing the desired piece of the already cured PDMS, some of the poles broke. The issue was that while

trying to carefully remove the agarose stamp from the PDMS mold, small movements such as wiggling the stamp while it was not completely removed from the PDMS mold was enough to break the poles. Hence, the removal of the stamp had to be done in quick one step without any other movements except one straight motion of pulling the stamp away from the mold. The edges of the stamp were carefully separated from the mold with the end of a tweezers and the stamp was then rapidly removed in one motion.

The next challenge that was brought to our attention was curing of the agarose stamp. The problem was clear, the hot agarose solution was not filling in the holes of the PDMS mold, either because the surface is still not hydrophillic enough even after oxidation by plasma, and/or that the agarose medium is too viscous (8-12% w/w) and need additional motivation to fill in the holes. Increasing the process of oxidation to 120 seconds from 60 seconds and also putting the PDMs mold into a centrifuge (3750 rpm, 60 sec) after the hot agarose solution has been poured onto the mold, solved the problem. One more modification to this process would involve an employment of a heat trap. Since the agarose solution was in high concentration, the time of solidification was shorted to less than two minutes after expose to heat. Transfer of the hot agarose to a centrifuge would take too long and the agarose solution would already solidify before it was placed in to the centrifuge. In an attempt to slow down the solidification process, *heat trap* (which is basically pre-heated thermowell sand) was used to encapsulate the cooling agarose solution while it was transferred to a centrifuge.

Still, the greatest challenge with WET Stamping was handling of the two gels, hence the technique itself. The PAA gel was very thin (330 μm in thickness) so handling this gel was a great barrier. Several attempts were made to increase the thickness of the PAA gel. When the thicker PAA gel was put in physical contact with the agarose stamp, we knew that peroxide did diffuse from the stamp to PAA because purple precipitates were found in PAA. However instead of finding a nice pattern on the PAA gel, we only found the

precipitates embedded within the region of the PAA gel where stamps made contact with the gel. Hence, we realized that the thickness of the PAA gels was crucial in producing the propagating chemical waves of the BR reaction.

Even after the handling of the PAA gels was improved, the next hardship was to put this gel in contact with only the top of the poles of the agarose stamp. This would be best accomplished if a bit of tension was applied to the PAA gel, flattening the surface of the PAA gel, but as previously mentioned, the PAA gels were too thin so this suggestion was not an option. Unfortunately, this problem was not completely solved, and the best idea that was employed for our analysis was cutting the PAA gel to best match the dimensions of the array of posts so that the ends of the PAA gel would be held up by the posts. However, this is hard to accomplish and many of our trials had the edges of PAA gel touching the agarose outside of the post array. This caused the edges to turn blue/purple even before the post patterns developed. This problem resulted in limiting our field of view for analysis.
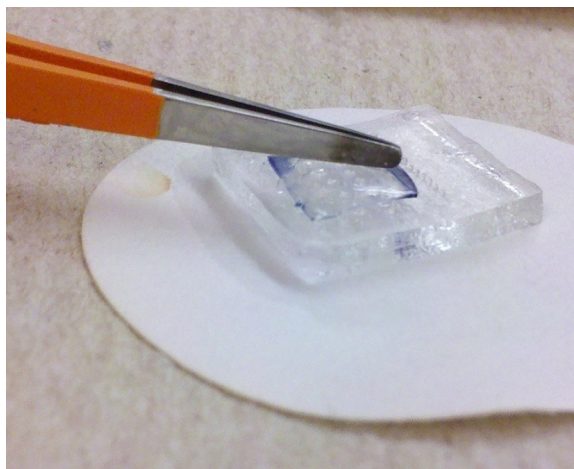

Figure 4.3.1. WETS: handling of the PAA gel

The mechanism behind how WET Stamping is quite clever. While the stamp is in contact with PAA, H_2O_2 diffuses from the top of the poles into the bulk of the PAA layer. The diffusion of H_2O_2 is further enhanced by the osmotic pressure due to the presence of ionic species embedded in PAA. As the peroxide enters the thin layer of PAA gel, it initiates chemical oscillations of the BR system and simultaneously diffuses outwards from the poles. This gives rise to the propagation of chemical waves. Consequently, oscillating colors of amber and blue chemical waves can be observed on the PAA layer [13].

The analysis was conducted while observing the PAA layer with a 4x lens of a microscope. Also for our analysis, a simple array of cylindrical posts was employed. The diameter of these posts was approximately half a millimeter long and the height was 1 millimeter. To observe the propagation of chemical waves forming intricate patterns, a video clip was taken for each trial and snapshots were taken from the video for analysis.
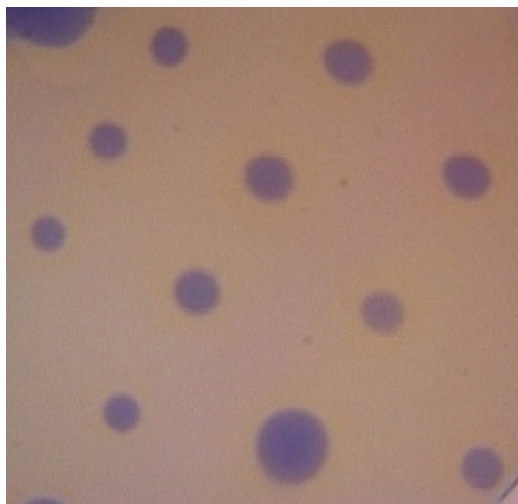

Figure 4.3.2. WET Stamping: after 60 seconds of contact

The PAA gel was held in physical contact with the post array of the agarose stamp for 20 - 25 seconds. Then the PAA gel was transferred to a setting where video can be taken. A stopwatch was started at contact so the time being reported in the movie includes

the twenty or so seconds of physical contact. For example in the picture above, the time

reported is 60 seconds after the contact. This means 20 seconds of contact and 40 seconds

of non-contact, allowing the patterns to develop on the surface of PAA gel. Immediately

after 20 seconds of contact and PAA gel was lifted from the patterned stamp, the arrays of

violet (it corresponds to the deep blue color of the BR reaction, but the brightness setting

of the camera changed the appearance of color) circles were present. By 60 s, the color

change of violet to amber has already occurred as can be seen by the faint appearance of

white circles (this corresponds to the amber color of the BR reaction, but once again the

camera setting has changed the appearance) around the violet center.

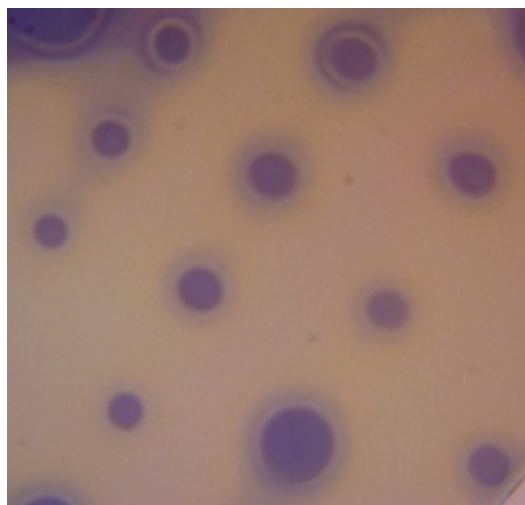Figure 4.3.3. WET Stamping: after 100 seconds of contact

By the 100 seconds mark, the presence of the white circle is less ambiguous due to the

formation of the third circle (color is violet) around the white circle. The formation of

the violet circle around the white circle verifies the oscillation occurring on the PAA gel,

confirming success in the application of the WET Stamping technique on the BR reaction.
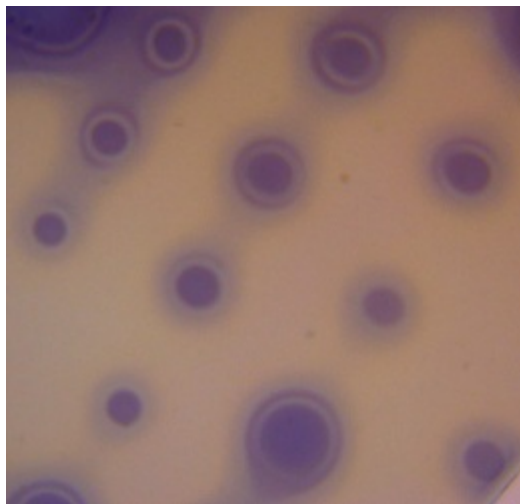
Figure 4.3.4. WET Stamping: after 120 seconds of contact

By the 120 seconds mark, the presence of the outer violet circle has been established. Furthermore, the top row, where the poles were closer to each other than the lower rows, we saw the outer circles interacting with adjacent ones, slowly covering the space in between them with violet color. The entire gel was covered in violet color by 200 seconds, and no further patterns were observed beyond what was observed at the 120 seconds.

4.4 WETS in Smaller Scale

Decreasing the size of the posts caused them to be more fragile. So even when 12% w/w agarose gel were cast, the poles fell after about fifteen minutes of air-drying. Submerging the entire stamp with patterns on its surface for longer than ten minutes was also not an option. After ten minutes, the stamp was found with no upright poles. Instead what we found were small hills where posts used to stand. We contributed this effect to the capillary forces of the water pulling the posts down as the stamp is being air-dried. When the posts were bigger and stronger, the posts were not disturbed by the weak capillary forces. However this force became an issue once the sizes of the poles were decreased by an order of magnitude.

Instead, we added just enough peroxide to the bottom the agarose gel so that there would be no direct contact of peroxide with the poles, but the peroxide would be taken up by the agarose via diffusion. The dry agarose stamp showed affinity for the peroxide as it was being slowly added, so adding a small amount of peroxide was easily controlled. After thirty minutes of agarose floating on peroxide, we found no posts on the surface of the gel. However when we decreased the amount of time to ten minutes, some poles were found upright. After these poles made direct contact with PAA gel for 90 seconds (as opposed to the 20 seconds with the larger posts), the edges of the PAA sheet was found to be purple, but not where the posts made contact with the PAA sheet.

Right after the PAA gel was released from direct contact with the stamp, the surface of the region where the posts made contact with the PAA was as clear and colorless as before the contact with the stamp. However over time, the saturation of the patterns increased. The first notable concentric circles of purple center and white circle around it was detected on the surface 150 seconds after the PAA gel made its contact with the stamp. This was longer than with the larger posts, which took 90 seconds of PAA gel making contact with the agarose stamp.
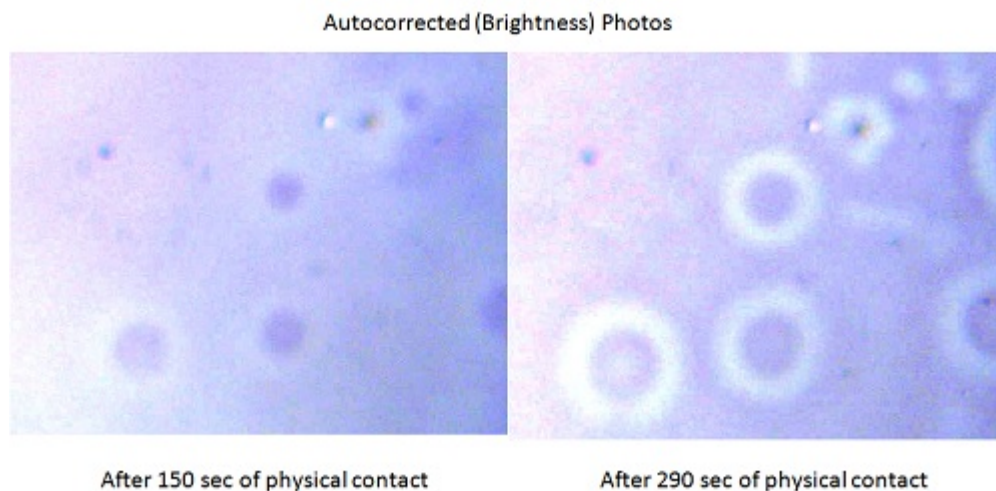

Figure 4.4.1. WETS: 50 μm Posts

As stated before, these circles became easier to detect with more saturated colors as the time progressed. Interestingly, we also observed the radius of both the inner purple and outer white circles enlarging as the waves propagated outwards from the point of contact. This feature was unique to the posts with diameter of 50 μm.

5
Conclusion

An oscillating chemical reaction, specifically the Briggs-Rauscher reaction, was theoretically and experimentally studied. It was observed to periodically change between two colors over an extended period of time. Once the activating reagent, hydrogen peroxide, was added, the reaction proceeded on its own without the need for additional reagents. However, reproducing the BR reaction proved to be a challenging task. It is highly sensitive to initial concentrations of the starting materials. This fact was confirmed by both experiment as well as math modeling. To observe any oscillation at all, many trials had to be conducted in order to master the input range of hydrogen peroxide to the reaction. Even after the oscillation had been observed, to receive the maximum number of oscillations (20 was our highest), dozens of trials had to be tested.

We verified through this investigation that the oscillations of the colors from amber to blue corresponded to the oscillating chemical concentrations of I_2 and I^-. These chemicals oscillated because of their involvement in approximately 30 coupled reactions, and the oscillation of intermediates in these reactions. This system was modeled using a simplified set of reations and their associated differential equations using *Mathematica*.

The results of our analysis can be divided it into four phases. In phases 2 and 3, the color of the solution is amber and in phases 1 and 4, the color of the solution is deep blue. the transition between the phases is dependent on the $[I^-]$. $[I^-]$ has a threshold value during the reaction and as the concentration changes due to the concentrations of the intermediates, it reaches its threshold concentration. Then, the phase change occurs and a dramatic change in the concentrations of all five crucial intermediates begins.

At the root of the oscillation are the three intermediates: IO_2, HIO_2 and HIO and the reaction 3. IO_2 is created to produce more HIO_2 by reaction 6. HIO_2 is used to produce more HIO by reaction 2. HIO is an important intermediate that is required for reaction 3 to take place because in order for one equivalent of I^- to convert to one equivalent of I_2, one equivalent of HIO is necessary. Reaction 3 is the crucial reaction in our model. It shows that I^- and I_2 can reversibly convert into each other so when the intermediates dictate that $[I^-]$ is to be decreased, then I^- simply converts to I_2 by reaction 3. Whereas, if the intermediate cause $[I^-]$ to be increased, then the stored I_2 can convert to I^- by reverse reaction 3.

After studying the BR reaction in a beaker and *in silico*, we attempted to generate complex patterns with the Wet Stamping technique (WETS). WETS requires two types of gels (PAA and agarose) to be soaked in the BR reagents so that when they are in contact with each other, the chemical waves of the BR reaction can propagate on the surface of the PAA gel. The preparation of the PAA gel proved to be easier than the agarose gel, which posed a number of challenges. The agarose gel required production of an acrylate master with direct laser writing which was used to make the PDMS mold, and this mold was used to cast the hot agarose solution. After successfully making both gels, we faced one of the most technically difficult problems of the project, which was the proper adherence of the PAA and agarose gels.

After improving our skills in the handling of the gels, WETS of the BR reaction was conducted and analyzed. Our patterned agarose stamps were simple arrays of posts. If the BR oscillations were to occur using WETS with the array of posts, we expected an array of alternating colors of concentric circles to be formed in the PAA. Indeed, this pattern was seen on the PAA gels, although we did not observe as many oscillations as expected. We speculate this was caused by our inefficiency to allow PAA gel to properly make contact with the patterned agarose stamp. While transferring PAA gel to the surface of the agarose stamp, the air-dried PAA gel becomes deformed, and thus is no longer a flat sheet to make proper contact with the micropatterned agarose stamp. Optimization of this process should result in more patterns appearing in the PAA gel.

Next, we extended WETS to significantly smaller features to test whether the behavior would remain constant. When the diameters of the posts were scaled down from 500 μm to 50 μm, we did observe virtually the same pattern. Using modeling and simplifying assumptions, complex reactions can be better comprehended. Understanding these complex reactions, while initially just a curiosity, may provide further explanations for these mysterious patterns in nature.

Bibliography

[1] Peter Gray and Stephen K. Scott, *Chemical Oscillations and Instabilities: Non-linear Chemical Kinetics*, Clarendon Press, Oxford, 1994.

[2] Richard J. Field and Maria Burger, *Oscillations and Traveling Waves in Chemical Systems*, A Wiley-Interscience publication, USA, 1985.

[3] Thomas S. Briggs and Warren C. Rauscher, *An Oscillating Iodine Clock*, J. Chem. Edu. **50** (1973), 496.

[4] Richard M. Noyes and Stanley D. Furrow, *The Oscillatory Briggs-Rauscher Reaction. 3. A Skeleton Mechanim for Oscillations*, J. Am. Chem. Soc. **104** (1982), 45-48.

[5] Bassam Z. Shakhashiri, *Chemical Demonstrations: A Handbook for Teachers of Chemistry, Volume 2*, The University of Wisconsin Press, USA, 1985.

[6] Richard M. Noyes and Stanley D. Furrow, *The Oscillatory Briggs-Rauscher Reaction. 1. Examination of Subsystems*, J. Am. Chem. Soc. **104** (1982), 38-42.

[7] Patrick De Kepper and Irving R. Epstein, *A Mechanisic Study of Oscillations and Bistability in the Briggs-Rauscher Reaction*, J. Am. Chem. Soc. **104** (1982), 49-55.

[8] Kyoung-Ran Kim, Dong J. Lee, and Kook Joe Shin, *A simplified model for the Briggs-Rauscher reaction mechanism*, J. Chem. Phys. **117** (2002), 2710-2717.

[9] Ryan Basch, Sean Castorani, and Seiders Matthew, *An Investigation of the Briggs-Rauscher Reaction*, `http://ece.utah.edu/~cfurse/NSF/All_files/filesfordemo/Oscillatingreaction/OscillatingReactionBriggsmath.pdf`.

[10] R. Matalon and A. Packter, J. Colloid. Sci. **10** (1955), 46.

[11] B. A. Grzybowski, I. T. Bensemann, and M. Fialkowski, *Wet Stamping of Microscale Periodic Precipitation Patterns*, J. Phys. Chem. B. **109** (2005), 2774-2778.

[12] K. J. M. Bishop, T. P. Gray, M. Fialkowski, and B. A. Grzybowski, *Microchameleons: Nonlinear Chemical Microsystems for Amplification and Sensing*, Chaos **16** (2006), 037102-1 - 037102-8.

[13] Kyle J. M. Bishop, Marcin Fialkowski, and Bartosz A. Grzybowski, *Micropatterning Chemical Oscillations: Waves, Autofocusing, and Symmetry Breaking*, J. Am. Chem. Soc. **127** (2005), 15943-15948.

[14] Christopher J. Campbell, Marcin Fialkowski, Rafal Klajn, Igor T. Bensemann, and Bartosz A. Grzybowski, *Color Micro- and Nanopatterning with Counter-Propagating Reaction-Diffusion Fronts*, Adv. Mater. **16** (2004), 1912-1917.

[15] M. Deubal, G. Freymann, M. Wegener, S. Pereira, K. Busch, and C. M. Soukoulis, *Direct Laser Writing of Three-dimensional Photonic-crystal Templates for Telecommunications*, Nature Materials **3** (2004), 444-447.

[16] George M. Whitesides and J. Cooper McDonald, *Polu(dimethylsiloxane) as a Material for Fabricating Microfluidic Devices*, Accounts of Chemical Research **35** (2002), 491-499.

[17] Christopher J. Campbell, Stoyan K. Smoukov, Kyle J. M. Bishop, and Bartosz A. Grzybowski, *Reactive Surface Micropatterning by Wet Stamping*, Langmuir **21** (2005), 2637-2640.

[18] Shoji Maruo and Koji Ikuta, *Submicron Stereolithography for the Production of Freely Movable Mechanisms by using Single-Photon Polymerization*, Sensors and Actuators A **100** (2002), 70-76.