Autocatalytic Modeling

Nathan Claasen and Shalise Radford
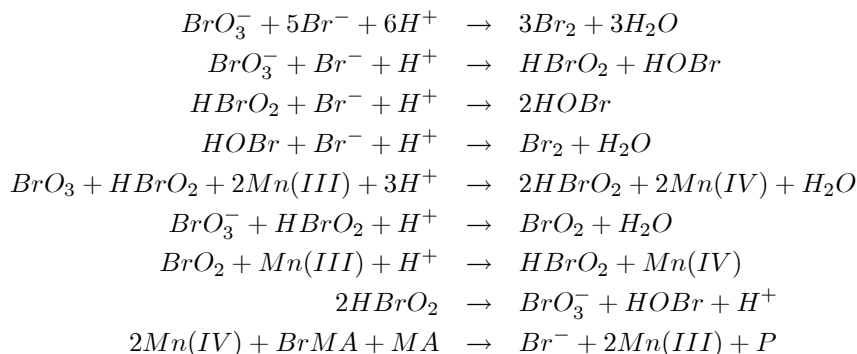Differential Equations

Spring 1997

Abstract

This paper is a study of a variation of the famous Belousov/Zhabotinskii reaction. We attempt to model the intermediate steps of the reaction, the actual oscillating portions. The model derived and discussed is somewhat simplified, but provides a good idea of how the chemicals interact.

1 Introduction

The road to scientific discovery is marked with many numbers of phenomenon initially rejected as spurious, yet later identified as fact. One such class of phenomenon is the oscillating reaction in chemistry. Although the probability of the oscillatory reaction was demonstrated as early as 1828 by Fechner, who produced an electrochemical cell which generated an oscillating current, the idea really has not received its due credit until the last fifteen years. One of the earliest pioneers who was able to see the depth of applications in biology and chemistry for ocsillating reactions was Alfred Lotka. In 1910, he showed that a set of consecutive reactions can give rise to damped oscillations on their way to equilibrium.. It was his work in this field that was adapted later for use by ecologists in their study of predator/prey systems. The first homogenous isothermal reaction to be described was the reaction of iodate, iodine, and hydrogen peroxide in 1921 by Berkley chemist William C. Bray. For more than fifty years the validity of this reaction was challenged on the basis that the oscillation was due to dust or bubbles, even though Bray explicitly addressed these issues. The dawn of modern chemical dynamics studies can be traced to Boris Belousov, who stumbled upon an oscillating reaction when trying to find an inorganic analog of the Krebs cycle. Editors of the journals in which he sought to publish his findings claimed that his "supposed discoveries" were impossible. His contemporary, Anatol Zhabotinskii, furthered his research by discovering that there are many variations of the oscillating reaction. All the while in the west chemists were working on papers explaining why oscillating reactions were impossible. Perhaps this is why there is such an explosion of interest of late in oscillating reactions. For chemists, the reactions are relatively new and little is known about the actual mechanisms, what is known has largely come

from the work of students at the University of Oregon in Eugene. Essential in the development of an accurate model is the understanding the determinants of the rate of a chemical reaction. Of primary importance are temperature, concentrations of reactants, surface area, and catalysts. In essence the rate of a reaction is based on the number of successful collisions per time interval. In this project we attempt to use a simplified three equation model to predict the concentrations of the reactants in a modified Belousov experiment. Our model was originally developed by the University of Oregon group.
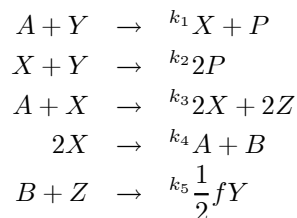
The Experiment Our experiment took place in a 300 ml. solution of 2 M H_2SO_4. On a heated stirring plate we added 5.02 g of Malonic acid and 3.48 g of $KBrO_3$. When the solution achieved $30°$ C, we added .66 g $MnSO_4$, instantly the solution colored orange. It began to oscillate after about 28 seconds with a period of 7.64 seconds initially. The net reaction is described in the following chemical equations.

$$
\begin{aligned}
BrO_3^- + 5Br^- + 6H^+ &\rightarrow 3Br_2 + 3H_2O \\
BrO_3^- + Br^- + H^+ &\rightarrow HBrO_2 + HOBr \\
HBrO_2 + Br^- + H^+ &\rightarrow 2HOBr \\
HOBr + Br^- + H^+ &\rightarrow Br_2 + H_2O \\
BrO_3 + HBrO_2 + 2Mn(III) + 3H^+ &\rightarrow 2HBrO_2 + 2Mn(IV) + H_2O \\
BrO_3^- + HBrO_2 + H^+ &\rightarrow BrO_2 + H_2O \\
BrO_2 + Mn(III) + H^+ &\rightarrow HBrO_2 + Mn(IV) \\
2HBrO_2 &\rightarrow BrO_3^- + HOBr + H^+ \\
2Mn(IV) + BrMA + MA &\rightarrow Br^- + 2Mn(III) + P
\end{aligned}
$$

Where MA is malonic acid and P stands for the organic products of the final reaction. This process can be grouped into three phases. The first phase, reactions 1-4 describe a period of slow Bromide consumption. The second phase, reactions 5-8, describes the rapid consumption of bromide due to the oxidation of the metal catalyst, Manganese. The final phase, reaction 9, slows the experiment by returning control to the first phase and reducing the Manganese back to its former state. It is due to this simple grouping that we can reduce the complicated mechanism to a simple model.

2   The Model

The chemical species in our simplified model are : $X = HBrO_2, Y = Br^-, Z = Mn^{4+}, A = BrO_3^-, P = HOBr, B = MalonicAcid.$ f is a chemical constant approximately equal to one, and therefore will be ignored. The model is simplified by the assumption that reactants A and B are in such large supply that their concentrations are effectively constant.

$$
\begin{aligned}
A + Y &\rightarrow \ ^{k_1} X + P \\
X + Y &\rightarrow \ ^{k_2} 2P \\
A + X &\rightarrow \ ^{k_3} 2X + 2Z \\
2X &\rightarrow \ ^{k_4} A + B \\
B + Z &\rightarrow \ ^{k_5} \frac{1}{2} fY
\end{aligned}
$$

In chemistry we learn that every reaction proceeds as a multiple of the product of the concentrations of the reactants. To derive rate equations we first assigned a constant (k_n) to each of the five reactions included in our model. Since A and B are assumed to be constant, we needed only three rate equations, one each for X, Y, and Z. The following equations simply sum the rates of production and disappearance of each of the species.

$$
\begin{aligned}
\frac{dX}{dt} &= k_3 AY - k_2 XY + k_5 AX - 2k_4 X^2 \\
\frac{dY}{dt} &= -k_3 AY - k_2 XY + 2k_1 BX \\
\frac{dZ}{dt} &= k_3 AX - k_2 BX
\end{aligned}
$$

At our lab book's suggestion we simplified our equations by making the following substitutions:

$$
\begin{aligned}
x &= \frac{2k_4 X}{k_5 A} \\
y &= \frac{k_2 Y}{k_5 A} \\
z &= \frac{k_4 k_1 BX}{k_5^2 A^2} \\
a_1 &= \frac{k_5 A}{k_1 B} \\
a_2 &= \frac{k_2 k_5 A}{2k_1 k_4 B} \\
a_3 &= \frac{2k_3 k_4}{k_2 k_5}
\end{aligned}
$$

Using these substitutions, we derived these final dimensionless rate equations:

$$\frac{dx}{dT} = a_1(a_3 y - xy + x(1-x))$$

$$\frac{dy}{dT} = a_2(-a_3 y - xy + fz)$$

$$\frac{dz}{dT} = x - z$$

The advantage of dimensionless systems is that the behavior of the functions can be shown to be inherent in the ODEs, and not just a product of a particular set of physical units. What we have arrived at is a system that we can tune to model our specific reaction. Of particular interest is the period of the oscillations, which, as pointed out earlier, was about 7.64 seconds. In fact, in order to be determined, the other constants of the experiment require more sophisticated apparatus that we have access to at this point.

3   Specific Solution

In order for us to accurately describe the system, we had first to determine both an initial condition, and the constant which affects the period of the oscillations. In our explorations, we were again guided by the lab book. It directed us that, for our experiment a_1 should be very close to 15, a_2 is 2500, and a_3 should be determined by the data. In order to find a_3 we used the period of the oscillations in the experiment, and sought to match it with our functions. Due to the fact that there are no analytic methods to solve our ODEs, we enlisted the help of the ODE23s solver in MATLAB. We found a_3 to be .0005. These constants produced the following graphs. Note: $y(t)$ is scaled by $\frac{1}{150}$ to provide a better image.

4   Limitations

In our explorations we became familiar with the basic aspects of both the chemistry and the mathematics involved in this complex system. However, our understanding is somewhat limited. The complicated chemical analysis involved and high knowledge requirement forced us to make several assumptions. In the first place the reaction actually contains nearly twenty steps. Our nine chemical equations simplify it to a degree, our five rate equations simplify it even more, and modeling it with three differential equations simplify it further. The second assumption was that the concentrations of Malonic acid and the Bromate ion remained constant. In reality, we observed a noticeable decay in the frequency of the oscillations after only four minutes. This could be due to the scarcity of the organic acid and the ion, and therefore our model may only apply to the short time at the start of the reaction. Also by nondimensionalizing our system, we lost the ability to give answers that are physically significant. In reality our

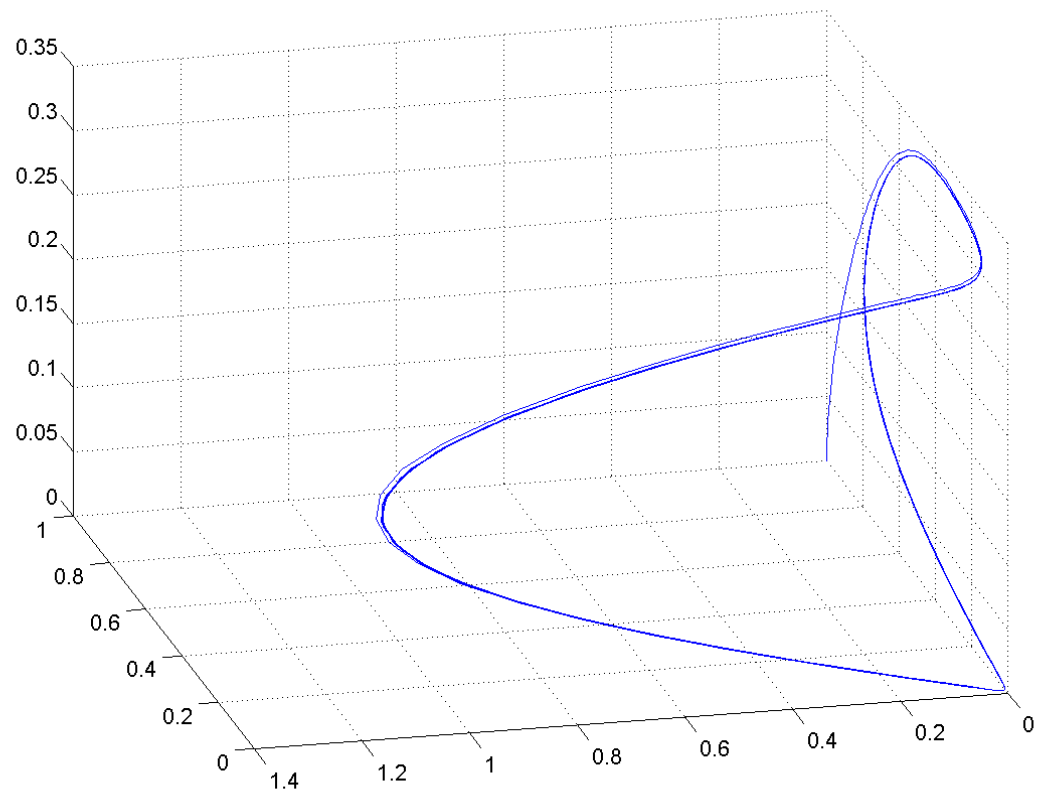Figure 1: Figure 1. The plots of x(t),y(t), and z(t).

Figure 2: Figure 2. The plot of x,y, and z.

model can only predict relative concentrations of the intermediate products in the reaction.

5   Conclusion

In conclusion, we have fit a simplified model to an observed phenomenon. In doing so we discovered that although chemical reactions are simple when only one step is considered, they become quite complex when they occur as a part of a larger system. This project has piqued our curiosity in the field of chemical kinetics. We are interested in learning more and understanding the actual mechanism involved in this and other oscillating chemical reactions. We thank Kevin Yokoyama for introducing us to this problem, Paul Farnham for his help in understanding the reaction, Claire Christian for her cooperation in procuring the necessary supplies, and Robert L Borrelli, Courtney Coleman, and William E. Boyce, authors of Differential Equations Laboratory Workbook. A note of appreciation also goes to David Arnold, our differential equations professor, who provided impetous for our exploration.