An Analysis of the Belousov-Zhabotinskii Reaction

Casey R. Gray*

Calhoun High School

Port Lavaca, TX 77979

and

The High School Summer Science Research Program

Department of Mathematics

Baylor University

Waco, TX 76798

graycrjj@tisd.net

Abstract

We begin with a brief history of the celebrated Belousov-Zhabotinskii (BZ) reaction. In particular, we consider the BZ reaction in a continuously stirred, closed vessel in the presence of a ferroin indicator. We examine the underlying chemical kinetics of the most significant reactions involved. This leads to the Oregonator model and an associated 3×3 system of nonlinear ordinary differential equations. We nondimensionalize this system and further reduce it to a 2×2 stiff system. Relaxation oscillations are expected and an analysis of the phase plane confirms this. Finally, we solve the system numerically for a certain set of system parameters and compare our computations with experimental results.

1   Background

The Belousov-Zhabotinskii (BZ) reaction is an intriguing experiment that displays unexpected behavior. When certain reactants are combined, an "induction" period of inactivity is followed by sudden oscillations in color from red to blue. In spatially nonhomogeneous systems (such as a simple petri dish), the red and blue oscillations propogate as spiral wave fronts. The oscillations last about one minute and are repeated over a long period of time. Eventually, the reaction stops oscillating and approaches an equilibrium state. We now know

---

*Faculty Advisor: John M. Davis, Department of Mathematics, Baylor University, Waco, TX 76798. Email: John_M_Davis@baylor.edu

that the color changes are caused by alternating oxidation-reductions in which cerium changes its oxidation state from Ce(III) (producing a magenta solution) to Ce(IV) (producing a blue solution) or vice versa. Because of this, we call the BZ reaction an "oscillating reaction"; this simply means a reaction in which there is a regular, periodic change in the concentration of one or more reactants. Because this reaction is well understood, it is considered the prototype oscillator. An excellent, accessible reference for this material is [15].

Although the BZ reaction is a chemical rather than biological oscillator, understanding its mechanics will also help us understand biological oscillations such as the beating of the heart. The chemical traveling waves observed in the BZ reaction are very similar to the electromagnetic traveling waves in muscle tissue. Also, the system of differential equations derived for the BZ reaction (the Oreganator model [4]) is similar to the system of differential equations modeling electromagnetic waves in heart tissue (the Beeler-Reuter model [1]). Parallel investigations have been made studying such diverse phenomena as nerve tissues (the Hodgkin-Huxley model [8] and the Fitzhugh-Nagumo equations [6, 13]) and slime mold aggregation (the Martiel-Goldbeter equations [11]). The trademark spiral waves of the BZ reaction have also been observed in other types of media such as intact and cultured cardiac tissue, retinal and cortical neural preparations, and mold aggregates. The existence of spiral patterns is a characteristic of excitable media. As a result, the mechanisms of onset and stability of spiral waves is the subject of extensive ongoing investigation. The very recent article [18] is an example of current work in the area of pattern formation.
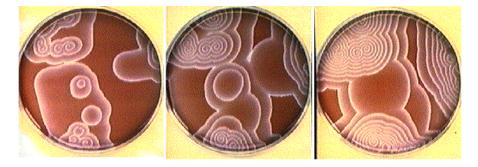

Figure 1: Spatiotemporal patterns in the BZ reaction [23].

2 History

Boris Pavlovich Belousov was born in Russia during the 19th century and was one of five children. His older brother first interested Belousov in science while constructing an explosive to assasinate the Czar. (It should be noted that they were unsuccessful in this attempt.) After moving to Switzerland, Belousov devoted himself to science and studied chemistry in Zurich. When World War
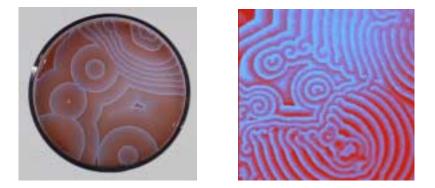
Figure 2: A closer look at spiral target patterns [24, 25].

I began, he returned to Russia to fight, but he was not admitted to the army because of a health problem. He worked in a military laboratory and eventually studied under the famous chemistry professor, Ipatiev. Belousov was quickly recognized for his research and was awarded the very high rank of *Combrig*. Later in his career, he became head of the Laboratory of Biophysics associated with the USSR Ministry of Health. During his research on the Krebs cycle, he discovered that a solution of citric acid in water (with acidified bromate as oxidant and yellow ceric ions as catalyst) turned colorless and then back to yellow for an hour while effervescing carbon dioxide. The study of oscillating reactions was born.

In 1951, Belousov wrote a paper describing this reaction, but his article was rejected. During that time, chemists believed that oscillations in closed homogeneous systems were impossible because that would imply that the reaction did not go to thermodynamic equilibrium smoothly. The journal editor commented that the paper could be published only if Belousov explained the flaw in the existing theory. Undeterred, he returned to his lab to work on a comprehensive analysis of his findings. Six years later, Belousov submitted an exhaustive manuscript with detailed evidence of his conclusions to a different journal. Again, his results were met with skepticism. The journal would only offer to publish his work as a short claim without including his new analysis. Infuriated, the 64-year-old Belousov vowed never to publish again.

In 1961, a young graduate student at Moscow State University named A.M. Zhabotinskii (working under S.E. Schnoll) rediscovered the oscillating reaction. Since Schnoll knew of Belousov's earlier results, he had Zhabotinskii send Belousov a copy of his report. For several years, Zhabotinskii tried to engage Belousov and arrange a personal meeting, but he never succeeded. It was not until a 1968 Symposium on Biological and Biochemical Oscillators in Prague that the West was exposed to this seminal research on oscillating reactions. Unfortunately, Belousov died in 1970 before he and Zhabotinskii were awarded the prestigious Lenin Prize in 1980. For more on the history of Belousov and

Zhabotinskii, see [20] and the excellent article by Winfree [19].

Figure 3: B.P. Belousov (left) and A.M. Zhabotinskii (right).

3   Chemical Kinetics

Oscillators are not uncommon when studying complex dynamical systems. Lotka proposed the predator-prey model as early as 1920. In the early 1970s, Field, Körös, and Noyes while at the University of Oregon proposed the *Oregon*ator model for the BZ reaction. In the early 1980s, Smith and Noyes used the *Bubbel*ator to model a gas-evolution oscillator where a reaction that produces gas will cause the system to foam up and then calm down repeatedly. We will discuss the Oregonator in Section 4 of this article; we refer the reader to [14] for details on the other two.

Table 1: A recipe for the BZ reaction.

Species	Concentration
Malonic acid	0.2 M
Sodium bromate	0.3 M
Sulfuric acid	0.3 M
Ferroin	0.005 M

There are many recipes and variations of the BZ reaction. An excellent collection can be found at [21]. In our lab experiments, we used the recipe in Table 1 in a closed system without stirring. We added 10 mL of the solution to a petri dish. After an induction period of 20 minutes, spiral target patterns began which alternated between blue and red as shown in Figure 2.

However, the chemical and mathematical analysis in this article will focus on the BZ reaction in a closed reactor with continuous stirring. An excellent video demonstration of this can be found at [22]. Although we used a slightly different recipe than the one shown on the video, this demonstration allows the reader to see how the BZ reaction is conducted in a continuously-stirred, closed reactor. By eliminating spatial nonhomogeneities through continuous stirring, we only have to deal with changes of the concentrations with respect to time (i.e., a model involving ordinary differential equations) as opposed to including spatial variations and diffusion which would require partial differential equations. Therefore, we will analyze a slightly different recipe than in Table 1 (but still using a ferroin indicator to highlight the sudden oscillations between red and blue) which can be found in [7, 12, 17, 21].

Table 2: Abbreviated FKN mechanism governing the BZ reaction.

	Reaction	Rate constant
(R1)	$Br^- + HOBr + H^+ \rightarrow Br_2 + H_2O$	$k_{R1} = 8 \times 10^9 \, M^{-2} \, s^{-1}$
(R2)	$HBrO_2 + Br^- + H^+ \rightarrow 2HOBr$	$k_{R2} = 10^6 \, M^{-2} \, s^{-1}$
(R3)	$BrO_3^- + Br^- + 2H^+ \rightarrow HBrO_2 + HOBr$	$k_{R3} = 2 \, M^{-3} \, s^{-1}$
(R4)	$2HBrO_2 \rightarrow BrO_3^-$	$k_{R4} = 2 \times 10^3 \, M^{-1} \, s^{-1}$
(R5)	$BrO_3^- + HBrO_2 + H^+ \rightarrow 2BrO_2 \cdot + H_2O$	$k_{R5} = 10 \, M^{-2} \, s^{-1}$
(R6)	$BrO_2 \cdot + Ce(III) + H^+ \rightarrow HBrO_2 + Ce(IV)$	$k_{R6} = 6 \times 10^5 \, M^{-2} \, s^{-1}$
(C1)	$CH_2(COOH)_2 \rightleftharpoons (HO)_2C = CHCOOH$	see [7]
(C2)	$(HO)_2C = CHCOOH + Br_2$	
	$\rightarrow BrCH(COOH)_2 + H^+ + Br^-$	see [7]
(C3)	$2Ce(IV) + CH_2(COOH)_2 + BrCH(COOH)_2$	
	$\rightarrow fBr^- + \text{other products}$	see [7]

The mechanism of the BZ reaction is very complicated: a recent improved model for the Ce(IV)/Ce(III)-catalyzed reaction contains 80 elementary steps and 26 variable species concentrations [2]. However, in a sequence of landmark papers, Field, Körös, and Noyes [4] formulated a model for the most important parts of the kinetic mechanism that gives rise to oscillations in the BZ reaction. This is often referred to as the FKN mechanism and is summarized in Table 2. The FKN mechanism for the BZ reaction can be described as three concurrent (and at times competing) processes.

- Process A: The three step reduction of bromate to bromine.

- Process B: The introduction of hypobromous acid to compete as a reducing

agent for bromate.

- Process C: The reduction of the catalyst formed from Processes A and B.

In Process A, we have the reduction of bromate (BrO_3^-) to bromine (Br) by the reducing agent bromide (Br^-). This three-step process makes up (R1)–(R3). As a result, the bromate is reduced, bromomalonic acid (BrMA) is produced, and the concentration of bromide eventually falls below some critical level $[Br^-]_{cr}$. It is at this point that Process B begins to dominate Process A: the hypobromous acid $(HBrO_2)$ begins to compete with the bromide to reduce the bromate. Reactions (R5) and (R6) constitute a two-step autocatalytic sequence. As a result, the amount of hypobromous acid increases at an accelerating rate and Ce(IV) is produced. This causes the solution to change suddenly from red to blue (in the presence of a ferroin indicator).

Process B: (R4)–(R6)
$HBrO_2$ competes with Br^- as a reducing agent for BrO_3^-.
Ce(IV) is produced from the autocatalytic sequence.
Color change: red→blue.

Process A: (R1)–(R3)
Reduction of BrO_3^- to Br via the reducing agent Br^-.
BrMA is produced as a result.

$[Br^-]$

$[Br^-]_{cr}$

Process C: (C1)–(C3)
The BrMA and Ce(IV) react causing the concurrent oxidation of the organic species.
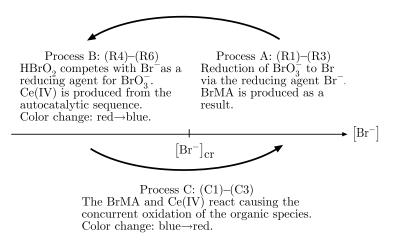Color change: blue→red.

Figure 4: Three subreactions which comprise the BZ reaction.

As Processes A and B cycle back and forth depending on whether $[Br^-]$ is above or below $[Br^-]_{cr}$, the products of these processes, BrMA and Ce(IV), react. The concurrent oxidation of the organic species in (C3) reduces the cerium catalyst Ce(IV) to Ce(III) causing a color change from blue to red (in the presence of a ferroin indicator). This change is gradual since there is no autocatalysis here. We are then back to Process A and the whole cycle repeats itself as outlined in Figure 4.

4 Mathematical Analysis

Following the conventional notation used in [4, 7, 17], let

$$
\begin{aligned}
X &= [\mathrm{HBrO_2}] && \text{(hypobromous acid)}, \\
Y &= [\mathrm{Br^-}] && \text{(bromide)} \\
Z &= [\mathrm{Ce(IV)}] && \text{(cerium-4)} \\
A &= [\mathrm{BrO_3^-}] && \text{(bromate)} \\
B &= [\mathrm{Org}] && \text{(organic species)} \\
P &= [\mathrm{HOBr}].
\end{aligned}
$$

The Oregonator scheme is outlined in Table 3. Note the correspondence between the Oregonator scheme and the FKN mechanism in Table 3: (O1) is equivalent to reaction (R3); (O2) is equivalent to reaction (R2); (O4) is equivalent to reaction (R4); (O5) represents the organic species in Process C. The autocatalytic sequence is given by $(R5) + 2(R6)$ and can be consolidated into the single reaction (O3).

Table 3: The Oregonator Scheme.

	Reaction	Rate
(O1)	$A + Y \rightarrow X + P$	$k_3 = k_{R3}[\mathrm{H^+}]^2 AY$
(O2)	$X + Y \rightarrow 2P$	$k_2 = k_{R2}[\mathrm{H^+}]XY$
(O3)	$A + X \rightarrow 2X + 2Z$	$k_5 = k_{R5}[\mathrm{H^+}]AX$
(O4)	$2X \rightarrow A + P$	$k_4 = k_{R4}X^2$
(O5)	$B + Z \rightarrow \frac{1}{2}fY$	$k_0 BZ$

Our goal is to consolidate (O1)–(O5) into a corresponding system of rate equations. The Law of Mass Action is the tool we need here. It states that the rate of a reaction is proportional to the product of the reactant concentrations. Since a reaction may very well involve m molecules of one of the reactants, in this case the concentration of that reactant is raised to the mth power in the corresponding rate equation. See [9] for several examples of how to write the rate equations for various systems.

The Law of Mass Action yields the following rate equations for (O1)–(O5) as a 3×3 system of nonlinear ordinary differential equations:

$$\frac{dX}{dt} = k_3 AY - k_2 XY + k_5 AX - 2k_4 X^2, \tag{1}$$

$$\frac{dY}{dt} = -k_3 AY - k_2 XY + \frac{1}{2}fk_0 BZ, \tag{2}$$

$$\frac{dZ}{dt} = 2k_5 AX - k_0 BZ. \tag{3}$$

Putting the system (1)–(3) in dimensionless form will make our analysis more clear. Tyson [17] used the change of variables

$$x = \frac{X}{X_0}, \quad y = \frac{Y}{Y_0}, \quad z = \frac{Z}{Z_0}, \quad \tau = \frac{t}{T_0}, \tag{4}$$

where

$$X_0 = \frac{k_5 A}{2k_4}, \quad Y_0 = \frac{k_5 A}{k_2}, \quad Z_0 = \frac{(k_5 A)^2}{k_4 k_0 B}, \quad T_0 = \frac{1}{k_0 B}.$$

There is notational as well as mathematical convenience here: x, y, z now represent the *dimensionless* concentrations of $HBrO_2$, Br^-, and $Ce(IV)$, respectively. This renders the bracket notation (such as $[HBrO_2]$) unnecessary. The dimensionless system then has the form

$$\varepsilon \frac{dx}{d\tau} = qy - xy + x(1 - x), \tag{5}$$

$$\delta \frac{dy}{d\tau} = -qy - xy + fz, \tag{6}$$

$$\frac{dz}{d\tau} = x - z, \tag{7}$$

where the system parameters ε, δ, and q are given by

$$\varepsilon = \frac{k_0 B}{k_5 A}, \quad \delta = \frac{2k_0 k_4 B}{k_2 k_5 A}, \quad q = \frac{2k_3 k_4}{k_2 k_5}.$$

In particular, a solution with $[H^+] = 0.8$ M (pH $= 0.097$) yields the rate constants

$$k_2 = 8 \times 10^5 \ M^{-1} s^{-1},$$
$$k_3 = 1.28 \ M^{-1} s^{-1},$$
$$k_4 = 2 \times 10^3 \ M^{-1} s^{-1},$$
$$k_5 = 8.0 \ M^{-1} s^{-1}.$$

Furthermore, we assume the reasonable initial concentrations $A_0 = [BrO_3^-]_0 = 0.06$ M and $B_0 = [Org]_0 = 0.02$ M, taking $k_0 = 1 \ M^{-1} s^{-1}$. Together, these yield the system parameters

$$\varepsilon = 4 \times 10^{-2}, \quad \delta = 4 \times 10^{-4}, \quad q = 8 \times 10^{-4}.$$

Although (5)–(7) is much simpler than (1)–(3), we can reduce this model even further. Since δ is particularly small relative to ε, we may regard the left-hand side of (6) as approximately zero. This forces

$$y \approx \frac{fz}{q + x}.$$

8

With this explicit formula for y in terms of x and z, we can recast the dimensionless 3×3 system (5)–(7) as a very tractable 2×2 system in the variables x and z:

$$\varepsilon \frac{dx}{d\tau} = x(1-x) + \frac{f(q-x)}{q+x}z \equiv g(x,z), \tag{8}$$

$$\frac{dz}{d\tau} = x - z \equiv h(x,z). \tag{9}$$

Due to the small parameter ε in (8), this is a stiff system of ordinary differential equations. We expect *relaxation oscillator* behavior for the orbits in the phase plane. A careful analysis of the phase plane will reveal this.
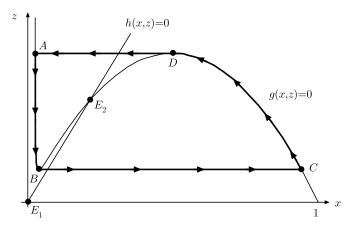

Figure 5: The x-z phase plane with nullclines $g(x,z) = 0$ and $h(x,z) = 0$.

Because ε is a very small parameter in (8), we expect x to maintain a value (with respect to z) such that the right-hand side of (8) is close to zero; when this cannot be achieved, there will be rapid jumps in x. This behavior is typical of relaxation oscillators. The first step in our analysis is to calculate the nullclines of the system. They are

$$g(x,z) = 0 \iff z = x(1-x)\frac{x+q}{(x-q)f}, \tag{10}$$

$$h(x,z) = 0 \iff z = x. \tag{11}$$

Hence, there are four regions in the x-z phase plane which dictate the behavior of the orbits by the sign pattern of the time derivatives of x and z. Above the curve $h(x,z) = 0$, we have $z > x$. Then (9) implies $\frac{dz}{d\tau} < 0$. Below the curve $h(x,z) = 0$, we have $\frac{dz}{d\tau} > 0$. Similarly, above the curve $g(x,z) = 0$, we see $\frac{dx}{d\tau} < 0$; below it, we have $\frac{dx}{d\tau} > 0$. See Figure 5.

We have some freedom in selecting the stoichiometric factor f. For reasons discussed by Murray [12] and Gray and Scott [7], we will take $f = 2/3$. However, this is in line with empirical evidence that f is generally between $1/2$ and 1.
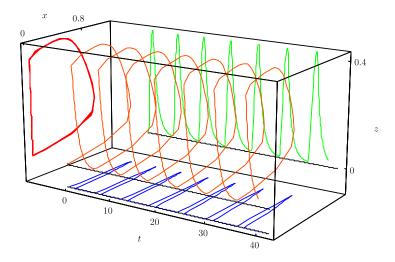
9

Figure 6: The parametric time-state plot for (8)–(9) done in *Mathematica*. Here, $f = 2/3$, $\varepsilon = 4 \times 10^{-2}$, and $q = 8 \times 10^{-4}$.

The coordinates of the points A, B, C, D in Figure 5 can now be found analytically. Using *Mathematica*, we computed the power series expansions about $q = 0$ for each of the following:

$$B : \quad x_B = (1 + \sqrt{2})q, \quad z_B = \frac{(1 + \sqrt{2})^2 q}{f}, \quad y_B = 1 + \frac{1}{\sqrt{2}},$$

$$D : \quad x_D = \frac{1}{2} - q, \quad z_D = \frac{1 + 4q}{4f}, \quad y_D = \frac{1}{2} + 2q,$$

$$A : \quad x_A = (1 + 8q)q, \quad z_A = \frac{1 + 4q}{4f}, \quad y_A = \frac{1}{8q},$$

$$C : \quad x_C = 1 - 6q, \quad z_C = \frac{(1 + \sqrt{2})^2 q}{f}, \quad y_C = (1 + \sqrt{2})^2 q.$$

We are now in a position to determine conditions on the parameter f under which the system will oscillate. Let (x^*, z^*) denote the positive equilibrium point. Then x^* will be unstable if

$$(1 + \sqrt{2})q = x_B < x^* < x_D = \frac{1}{2} - q. \tag{12}$$

From (11), $x^* = z^*$; hence (10) implies

$$(1 - x^*)(q + x^*) + f(q - x^*) = 0. \tag{13}$$

This quadratic has a positive root for any positive q and f. Therefore, we are guaranteed the existence of a positive equilibrium point (x^*, z^*).
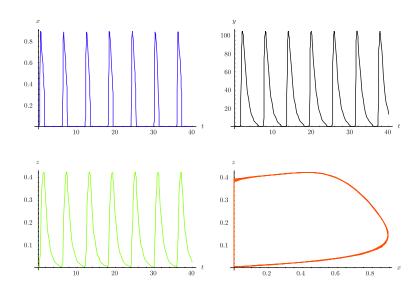
10

Figure 7: The dimensionless time-state spaces and the phase space.

We can use (12) together with the coordinates x_B and x_D to determine the values of f which will induce oscillations. When $x^* = x_B$, (12) yields $f = 1 + \sqrt{2} - (3 + 2\sqrt{2})q$. When $x^* = x_D$, we see $f = \frac{1+2q}{2-8q}$. Therefore, oscillations occur for

$$\frac{1 + 2q}{2 - 8q} < f < 1 + \sqrt{2} - (3 + 2\sqrt{2})q. \tag{14}$$

With the typical initial concentrations discussed earlier, we had $q = 8 \times 10^{-4}$ and hence $0.5024 < f < 2.41$. Again, this is in line with experimental data showing the stoichiometric factor is generally between $1/2$ and 1.

A natural question to ask here is the following: how does the oscillatory range depend on the initial concentrations $[A]_0$ and $[Org]_0$? Assuming q is fixed, we can provide an answer in terms of ε and f by finding the locus of *Hopf bifurcation points*. In general, a *bifurcation* refers to a qualitative change in the behavior of a system as a parameter is varied. In our case, we are interested in a particular type of change in behavior: the change from steady state to oscillatory reaction as f changes. This is called a *Hopf bifurcation*. See [15] as well as [10] for more on Hopf bifurcations.

The equilibrium point (x^*, z^*) will exhibit a Hopf bifurcation provided the trace of the Jacobian matrix for the system (8)–(9) evaluated at (x^*, z^*) is zero, i.e. $\mathrm{tr}\mathcal{J}(x^*, z^*) = 0$. First, this positive equilibrium point is easily found: x^* is the positive root of (13) given by

$$x^* = \frac{1}{2}\left(1 - f - q + \sqrt{f^2 + (1 + q)^2 + f(6q - 2)}\right), \tag{15}$$

11

and $z^* = x^*$. On the other hand, the trace condition requires

$$\text{tr}(\mathcal{J}) = \frac{\partial}{\partial x}\left(\frac{dx}{d\tau}\right) + \frac{\partial}{\partial z}\left(\frac{dz}{d\tau}\right) = 0,$$

that is,
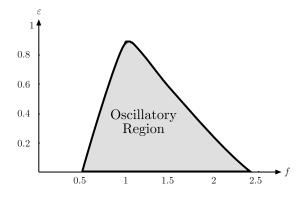
$$\varepsilon = 1 - 2x^* - \frac{2fqx^*}{(q + x^*)^2}. \tag{16}$$

Figure 8: The locus of Hopf bifurcation points.

For a given q, we use (15) to determine ε as a function of f in (16). This locus of Hopf bifurcation points is shown in Figure 8. Notice that as $\varepsilon \to 0$, the region of oscillation is precisely that found in (14). Most importantly, this analysis shows that in fact there is a nonempty range of parameter values corresponding to feasible experimental conditions which lead to oscillations.

Table 4: Comparison of computed versus experimental *dimensionalized* results.

	Calculated	Experimental
Period	210 s	110 s
$[\text{Br}^-]_B = [\text{Br}^-]_{\text{cr}}$	$(1.71 \times 10^{-5})[\text{BrO}_3^-]$	$(2 \times 10^{-5})[\text{BrO}_3^-]$
$[\text{Br}^-]_A = [\text{Br}^-]_{\text{max}}$	$(1.6 \times 10^{-3})[\text{BrO}_3^-]$	$(6 \times 10^{-5})[\text{BrO}_3^-]$

Another test of the model is its ability to predict accurately certain qualitative features of the reaction. One feature is the critical bromide ion concentration, $[\text{Br}^-]_{\text{cr}}$, at which Process A or Process B will trade dominance. Other features are the period of the oscillations and the amplitudes, especially for the bromide concentration. These are easily calculated using the coordinates of A, B, C, and D found earlier, the assumed initial concentrations, and the empirical rate constants. We summarize the computed versus experimental results

12

possible with our analysis in the Table 4 above. Please note that the numbers in Table 4 are *dimensionalized* results; numerical agreement with Figures 6–7 is not expected. We refer the reader to Murray [12] for details of period calculation.

It is interesting that we get somewhat mixed results from this model. We do have good order of magnitude agreement for the period of the oscillations. Furthermore, this model predicts $[Br^-]_{cr}$ extremely well. However, the maximum bromide concentration (which of course is linked to the the amplitude of Y) is not predicted very well. In retrospect, this was the least important aspect of our model. The particular change of variables (4) we used played a significant role in determining which parts of the model would be most accurate. In fact, Tyson uses different changes of variables to exploit different facets of the Oregonator model in [17].

5   Conclusion

It is interesting to note that before 1980, all chemical (not biological) oscillators were either discovered accidentally or were minor variants of the two accidentally discovered oscillators. Since that time, nearly three dozen new oscillating chemical reactions have been discovered. Most of these were found using a particular schematic described in [3]. These discoveries generally involve halogen chemistry and are driven by the large oxidation potentials of species such as BrO_3^-, IO_3^-, ClO_2^-, O_2, or H_2O_2. The wide range ($+5$ to -1) of oxidation states for halogens as well as their ability to participate in radical and nonradical reactions seem critical to the appearance of oscillations. The Bray-Liebhafsky (BL) reaction (dating back to 1921) and the Briggs-Rauscher (BR) reaction are some examples of this. We refer the reader to [5] and [16] for more on this topic.

The study of oscillating reactions by chemists and mathematicians has led to new applications of the theory of differential equations. "Bifurcation" and "nonlinear dynamics" are words no longer restricted to a mathematician's vocabulary. New mathematical questions are being asked based on findings in the laboratory. The 30-year-old approach analyzing the BZ reaction taken in this paper is but one, simple method of tackling these types of problems. Most modern research focuses on wave propagation and pattern formation in spatially nonhomogeneous systems such as those shown in Figures 1 and 2. These problems lead to very complex systems of partial differential equations.

6   Aknowledgments

in this paper for which we are very grateful. (Of course, any errors remaining are ours.)

Finally, I especially want to thank Dr. John Davis for directing me through this project in Summer 2001. He played a pivotal role in the creation of this paper. Without his dedication to Baylor, support of its research program, and faith in me, this paper may never have come into being. He spent valuable time mentoring me which I will never forget.

7　Appendix

See http://www.rose–hulman.edu/mathjournal/ and go to the download area for this paper for QuickTime movies showing the evolution of limit cycles in the phase space (limit_cycle.mov) and the 3D parametric plot (parametric.mov). There is also an animation of the propagation of spiral waves in the BZ reaction (spirals.mov). QuickTime 5 is most likely needed to view these files.

If anyone is interested in obtaining a *Mathematica* notebook for the calculations in this paper, please contact Dr. John Davis at the address on the cover page.

References

[1] G.W. Beeler and H. Reuter, Reconstruction of the action potential of ventricular myocardial fibers, *Journal of Physiology* **268** (1977), 177–210.

[2] O. Benini, R. Cervellati, and P. Fetto, The BZ reaction: experimental and model studies in the physical chemistry laboratory, *Journal of Chemical Education* **73** (1996), 865–868.

[3] I.R. Epstein, The role of flow systems in far-from-equilibrium dynamics, *Journal of Chemical Education* **66** (1989), 191–195.

[4] R.J. Field, E. Körös, and R.M. Noyes, Oscillations in chemical systems, Part 2. Thorough analysis of temporal oscialltions in the bromate-cerium-malonic acid system, *Journal of the American Chemical Society* **94** (1972), 8649–8664.

[5] R.J. Field and F.W. Schneider, Oscillating chemical reactions and nonlinear dynamics, *Journal of Chemical Education* **66** (1989), 195–204.

[6] R. Fitzhugh, Impulses and physiological states in theoretical models of nerve membrane, *Biophysical Journal* **1** (1961), 445–466.

[7] P. Gray and S.K. Scott, *Chemical Oscillations and Instabilities: Nonlinear Chemical Kinetics*, Oxford Science Publications, Oxford, 1990.

[8] A.L. Hodgkin and A.F. Huxley, A quantitative description of membrane current and its application to conduction and excitation in nerve, *Journal of Physiology* **117** (1952), 500–544.

[9] S. Hollis, *Differential Equations with Boundary Value Problems*, Prentice Hall, Upper Saddle River, 2001.

[10] J.E. Marsden and M. McCracken, *The Hopf Bifurcation and Its Applications*, Springer-Verlag, New York, 1976.

[11] J.-L. Martiel and A. Golbeter, A model based on receptor desensitization for cyclic AMP signaling in *Dictyostelium* cells, *Biophysical Journal* **52** (1987), 807–828.

[12] J.D. Murray, *Mathematical Biology*, Springer-Verlag, New York, 1993.

[13] J.S. Nagumo, S. Arimoto, and S. Yoshizawa, An active pulse transmission line simulating nerve axon, *Proceedings of IRE* **50** (1962), 2061–2071.

[14] R.M. Noyes, Some models of chemical oscillators, *Journal of Chemical Education* **66** (1989), 190–191.

[15] S.K. Scott, *Oscillations, Waves, and Chaos in Chemical Kinetics*, Oxford Science Publications, Oxford, 1994.

[16] M.M. Slin'ko and N.I. Jaeger, *Oscillating Heterogeneous Catalytic Systems*, Elsevier, Amsterdam, 1994.

[17] J.J. Tyson, *The Belousov-Zhabotinskii Reaction*, Springer-Verlag, New York, 1976.

[18] V.K. Vanag and I.R. Epstein, Inwardly rotating spiral waves in a reaction-diffusion system, *Chemical and Engineering News* **79** (2001), 835–837.

[19] A.T. Winfree, The prehistory of the Belousov-Zhabotinsky Oscillator, *Journal of Chemical Education* **61** (1984), 661–663.

[20] ⟨http://www.musc.edu/∼alievr/rubin.html⟩

[21] ⟨http://www.clubtre.sky.net.ua/denis/recipes.html⟩

[22] ⟨http://neon.chem.ox.ac.uk/vrchemistry/FilmStudio/oscillating/HTML/page03.htm⟩

[23] ⟨http://www.chem.leeds.ac.uk/People/SKS/sks_research/sks_group_page.htm⟩

[24] ⟨http://genchem.chem.wisc.edu/demonstrations/Gen_Chem_Pages/12kineticpage/⟩

[25] ⟨http://hopf.chem.brandeis.edu/anatol.htm⟩