Belousov-Zhabotinsky Reaction

A Thesis

Presented in Partial Fulfillment of the Requirements for the Degree Master of Science in the Graduate School of The Ohio State University

By

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The Belousov-Zhabotinsky system exhibits oscillations. Some models have been proposed to explain the whole system mathematically. Field–Körös–Noyes (FKN) proposed the first mechanistic model for Belousov-Zhabotinsky (BZ) system. After this work, Oregonator was proposed as a 3-dimensional ode system by using some basic reduction techniques. In 1990, Györgi, Turányi and Field (GTF) introduced an 80-reaction, 26-molecule mechanistic model of oscillatory BZ system. We explain the methods they used to obtain reduced systems. These methods are due to Turányi. We derive two 3-dimensional systems from their full model. We compare two of these reduced ode systems and the Oregonator model with the full 80-reaction system and show which is the most accurate.
To my lovely daughter B. Rabia and my wife,
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CHAPTER 1

INTRODUCTION

1.1 Historical Review of the Belousov-Zhabotinsky System

What constitutes a real discovery in science? The Oxford dictionary defines a
discovery as something “that is new or unexpected, or existing but not yet known.”
A scientific discovery must become well-known and be accepted as a part of reliable
scientific knowledge. There are numerous examples where erroneous findings were
first termed discoveries. On the other hand, real discoveries have often been ignored,
even discarded, by the scientific community because they did not appeal to
conventional scientific wisdom, often because the discoverers were ahead of their time.
Consequently, it took some time before the ideas became well-understood. These
discoverers were often rewarded – posthumously.

Boris Pavlovich Belousov was one such discoverer. He discovered an important
chemical system which is still being studied by many researchers, and he was awarded
the Lenin Prize, posthumously, in 1980. Unfortunately, he was completely unknown
during his life time. Even today, it is difficult to find his biography in any scientific
bibliographic sources. Here, we shall provide a brief bibliography.
Figure 1.1: Boris Pavlovich Belousov (1893-1970)
B.P. Belousov was born in 1893, one of five children in an ordinary Russian family. After the Russian revolution of 1905, the Belousov family was forced to move out of the USSR. They moved to Zurich, Switzerland, where he got his initial chemical education. By the beginning of World War I, he and his family went back to Russia where he tried to enter to the Russian military. He was rejected because of health problems so he went to work in a military laboratory to be of help to his homeland. He was awarded the military rank Combring (which can be considered as a general in a modern army) because of his work. This award was very unusual for a chemist to get [1].

His discovery occurred around 1950 when he was the manager of a Biophysics Laboratory under the USSR Ministry of Health. One of his interests was biochemistry. While Belousov was working on the Krebs cycle\(^1\) he was surprised by an unfamiliar reaction in his test-tube. In technical terms, when malonic acid (Ma) is oxidized by BrO\(_3^-\) in sulfuric acid solution using the [Ce\(^{4+}\)] and [Ce\(^{3+}\)] couple as catalyst, Belousov noticed that there is a periodic oscillation in the ratio [Ce\(^{4+}\)]/[Ce\(^{3+}\)] which is visible as an oscillation in color between clear and yellow. The entire tank does not oscillate between yellow and clear. Instead, as shown in Figure 1.2, waves propagate outward in concentric circles through the tank. For this system, the typical scales are observed as a period of oscillation 1 min, a wavelength of 1mm, and a velocity of 1mm/min.

\(^1\)Mitochondria is the power source of the cells and it transforms the energy from food to a form that cells can use. Several hundred mitochondria, shaped like sausages, 2 to 10 microns long and 0.5 to 1.0 micron in diameter, may be contained in a cell. Several biochemical functions essential to the life of a cell occur in the mitochondria. A critically important function is aerobic respiration, in which food molecules are broken into carbon dioxide, water, and some other molecules, releasing biologically useful energy in the process. Hydrogen atoms are revealed from food molecules and some acetic acid residues are oxidized to carbon dioxide. This oxidation process is called a Krebs cycle.
Figure 1.2: In the Belousov-Zhabotinsky reaction, waves look like moving outwardly propagating circulars. (Approximate size of dish.) From *Clocks to Chaos. The Rhythms of life*, by L. Glass and M.C. Mackey, Princeton, 1988, (page15).

These waves persist for an hour. However, we need the pde to model this. Instead, we use the odes to model the temporal oscillations in a very small test tube [2, 1].

In 1951, he submitted a paper explaining his findings to a chemical journal. However, the referees rejected Belousov’s paper – the editor of the journal claimed his discovery was impossible. According to the conventional opinion, chemical reactions should go to thermodynamic equilibrium smoothly [1], so Belousov’s temporal oscillations must be in error. Belousov did not quit, but returned to his laboratory and continued his work. In 1957, he sent another paper to a different chemical journal, but it was again rejected. Unfortunately, Belousov left science and withdrew his claim after this second rejection, but preserved his original manuscript [2]. Thus, the scientific world lost a chance to observe an astounding discovery.
Professor S. E. Shnoll from the Institute of Theoretical and Experimental Biophysics in Puschino, Russia, heard about the Belousov’s claim and met him in Moscow. They agreed to publish his work in the Radiobiology Institutes 1957 annual essay [1]. At the end of 1961, A.M. Zhabotinsky, under the supervision by Prof. Shnoll, undertook an investigation of Belousov’s claim. Zhabotinsky followed Belousov’s recipe and got the same results in his laboratory at Moscow State University. Later, he obtained the same oscillations using a simpler chemical system [3].

The modern history of the study of oscillating chemical reactions was started by B.P. Belousov. Over the past three decades, much theoretical, numerical and experimental work has been done on what has became the known as “Belousov-Zhabotinsky reaction.” The first English translation of B.P. Belousov’s discovery was published by A.M. Zhabotinsky in 1964 [3]. More discussions about the Belousov-Zhabotinsky system can be found in Winfree, A.T. (1984) and Zhabotinsky A.M. (1985).

1.2 Thesis Outline

There are four chapters in this thesis. So far, we have discussed the historical development of Belousov-Zhabotinsky reaction.

In Chapter two, it is given chemical terminology and discussed enzyme, biological catalyst, kinetics. By using the perturbation theory, we also find a solution of the enzymatic mechanism proposed by Michaelis and Menten.
Chapter three discusses the methods of reduction of a chemical system. There is a summary of how the reduction can be done. For the application of the methods, the Chapman mechanism for the ozone is tested.

Finally, Chapter four discusses the models proposed for the Belousov–Zhabotinsky (BZ) reaction. Field–Körös–Noyes (FKN) postulated the first mechanism for the BZ reaction in 1972. In 1974, this mechanism was reduced to a smaller mechanism called Oregonator. After these works, the experimental and theoretical investigations of the BZ reaction got a new appearance. Moreover, a large number of variations of the classic BZ reaction has been defined after FKN. Györgi, Turányi and Field (GTF) is one of these variations (1990). So far, among the all models for the BZ reaction, GTF is acceptable as correct and complete in every aspects. At the end of this chapter, it is given some graphics of concentrations to compare with each other for different cases.
CHAPTER 2

CHEMICAL RULES

2.1 Knowledge of Chemistry

A chemical change in which new substances are formed is called a reaction. In a chemical reaction, the initial molecules are termed the reactants while the final materials are called the products. For example, when methane burns in air, the chemical reaction that occurs is described by the equation

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}. \]

Here, CH\(_4\) and O\(_2\) are the reactants and CO\(_2\) and H\(_2\)O are the products.

Consider the reaction

\[ A + B \stackrel{k_1}{\rightarrow} C \] (2.1)

where the symbol \(\rightarrow\) indicates that the reaction is irreversible, i.e., it can go only one way. In 2.1, C is formed by the reaction of A and B, and \(k_1\) is the constant parameter associated with the rate of reaction, which is defined below. For this reaction, we need to define ordinary differential equations for each species to describe the time evolution.

The speed of the reaction is called the reaction rate that tells us how the concentration of a reactant or product changes with time. The odes are obtained
by *The Law of Mass Action* postulated by Cato Maximilian Guldberg (1836-1902) and Peter Waage (1833-1900) in 1864. The law states that: The rate of a chemical reaction is proportional to the concentration of each of the reacting substances. For example, consider the following reaction

\[ n_1A_1 + n_2A_2 + \cdots + n_rA_r \rightarrow m_1B_1 + m_2B_2 + \cdots + m_sB_s \]

where the proportionality constant \( k \) is called the rate constant and \([A_i]\) denotes the concentration of the species \( A_i \). The reaction rate of this reaction is \( k[A_1]^{n_1}[A_2]^{n_2} \cdots [A_r]^{n_r} \). For the ode of \([A_i]\), there is ‘−’ since we lose \([A_i]\). For the ode of \([B_i]\), there is ‘+’ since we gain \([B_i]\).

\[
\frac{d[A_i]}{dt} = -k[A_1]^{n_1}[A_2]^{n_2} \cdots [A_r]^{n_r} \\
\frac{d[B_i]}{dt} = +k[A_1]^{n_1}[A_2]^{n_2} \cdots [A_r]^{n_r}
\]

By applying the law of mass action to 2.1, we have the following system of differential equations:

\[
\frac{da}{dt} = -k_1ab, \\
\frac{db}{dt} = -k_1ab \\
\frac{dc}{dt} = +k_1ab, \tag{2.2}
\]

where \( a = [A], b = [B] \) and \( c = [C] \) are the concentrations and the initial conditions are \( a(0) = a_0, \ b(0) = b_0, \) and \( c(0) = 0 \). The solution of eqs. 2.2 can be calculated easily by using the initial conditions:

\[
\frac{da}{dt} - \frac{db}{dt} = 0 \implies a(t) - b(t) = a_0 - b_0 = M_0
\]

or

\[
a(t) = b(t) + M_0. \tag{2.3}
\]
Using the latter result in the second equation of 2.2 gives, if $M_0 \neq 0$,

$$
\frac{1}{M_0} \left( \frac{db}{dt} - \frac{db}{b + M_0} \right) = -k_1 \frac{b}{t + M_0}
$$

so

$$
b(t) = M_0 \frac{e^{M_0(-k_1 t+C)}}{1 - e^{M_0(-k_1 t+C)}}
$$

(2.4)

where $C$ is a constant. Using the initial condition $b(0) = b_0$, the constant $C$ is

$$
C = \frac{1}{M_0} \ln \frac{b_0}{b_0 + M_0}.
$$

From 2.3,

$$
a(t) = \frac{M_0}{1 - e^{M_0(-k_1 t+C)}}
$$

(2.5)

Once we have $a(t)$ and $b(t)$, $c(t)$ can be calculated by

$$
c(t) = \int_0^t k_1 a(\tau) b(\tau) d\tau
$$

$$
= k_1 M_0^2 \int_0^t \frac{e^{M_0(-k_1 \tau+C)}}{(1 - e^{M_0(-k_1 \tau+C)})^2} d\tau
$$

$$
c(t) = -M_0 \left[ \frac{1}{1 - e^{M_0(-k_1 t+C)}} \right] + \frac{M_0}{1 - e^{M_0 C}}
$$

(2.6)

where $C$ is the constant defined above.

Finally, from the eqs. 2.4, 2.5 and 2.6, we conclude three results for each three cases:

1. if $a_0 > b_0$, then we observe that when $t \to \infty$, $b(t) \to 0$, i.e., $b(t)$ goes down from $b_0$ to 0, while $a(t)$ goes down from $a_0$ to $M_0$. The product $C$ goes to
\[-M_0 + \frac{M_0}{1 - e^{M_0 c}}, \text{ as } t \to \infty.\] More precisely, we can say that the molecule B is used up totally, while the molecule A is particularly consumed in a small amount.

2. if \(a_0 = b_0\), then \(M_0 = 0\) which gives \(a(t) = b(t) = \frac{1}{k_1 C},\) and \(c(t) = \frac{k_{1/2}}{c^2 C k_{1/2}}\) where \(C = -1/a_0\). In detail, while the concentrations \([A]\) and \([B]\) go to \(\frac{1}{k_1 C}\), the product \([C]\) goes to \(\frac{k_{1/2}}{c^2 C k_{1/2}}\).

3. If \(a_0 < b_0\), then \(M_0 < 0\). In this case, \(b(t) \to -M_0\) while \(a(t) \to 0\) as \(t \to \infty\).

Briefly, we get the same results as in the first case but with A and B reversed.

Now suppose the following reaction is given

\[A + B \xrightleftharpoons[k_{-1}]{k_1} C \quad (2.7)\]

where the symbol \(\xrightleftharpoons{}\) denotes the reversibility of the reaction, which means the reaction can go both ways. In detail, reaction 2.7 says A and B react to form C, which can also dissolve back to A and B. By applying the law of mass action to 2.7, we have the following differential equation system:

\[\begin{align*}
\frac{da}{dt} &= -k_1 ab + k_{-1} c, \\
\frac{db}{dt} &= -k_1 ab + k_{-1} c, \\
\frac{dc}{dt} &= +k_1 ab - k_{-1} c, \quad (2.8)
\end{align*}\]

with the initial conditions

\[a(0) = a_0, \quad b(0) = b_0, \quad \text{and} \quad c(0) = c_0.\]

The solution of eqs. 2.8 can be calculated easily by using the initial conditions

\[\frac{db}{dt} + \frac{dc}{dt} = 0 \quad \Rightarrow \quad b(t) + c(t) = b_0 + c_0 = C_0, \quad (2.9)\]

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\[
\frac{da}{dt} + \frac{dc}{dt} = 0 \quad \Rightarrow \quad a(t) + c(t) = a_0 + c_0 = C_1. \quad (2.10)
\]

From eqs. 2.9 and 2.10, we conclude that
\[
b(t) = -c(t) + C_0, \quad a(t) = -c(t) + C_1. \quad (2.11)
\]

Replacing the last two equalities into equation 2.8 gives
\[
\frac{dc}{dt} = k_1c^2 - [\{C_0 + C_1\}k_1 + k_{-1}]c + k_1C_1C_0
\]
\[
= k_1c^2 - K_0c + k_1C_1C_0
\]

or
\[
\frac{1}{k_1} \frac{dc}{dt} = c^2 - \frac{K_0}{k_1}c + C_0C_1 + \left(\frac{K_0}{2k_1}\right)^2 - \left(\frac{K_0}{2k_1}\right)^2
\]
\[
= \left(c - \frac{K_0}{2k_1}\right)^2 + C_0C_1 - \left(\frac{K_0}{2k_1}\right)^2
\]

Thus,
\[
\frac{dc}{\left(c - \frac{K_0}{2k_1}\right)^2 + \kappa^2} = k_1 dt \quad (2.12)
\]

where \(K_0 = (C_0 + C_1)k_1 + k_{-1}\), and \(\kappa^2 = C_0C_1 - \left(\frac{K_0}{2k_1}\right)^2\). Integrating 2.12 gives
\[
c(t) = \kappa \tan(\kappa k_1 t) + \frac{K_0}{2k_1} \quad (2.13)
\]

Substituting \(c(t)\) in eqn. 2.11 we get
\[
a(t) = -\kappa \tan(\kappa k_1 t) + \frac{K_0}{2k_1} + C_0
\]
\[
b(t) = -\kappa \tan(\kappa k_1 t) + \frac{K_0}{2k_1} + C_1.
\]

Beside the reaction types 2.1 and 2.7, there is another type. A sequence of steps that occurs in the course of a chemical reaction is called a mechanism. For example,
\[
A + B \frac{k_1}{k_{-1}} C
\]

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\[ C \xrightarrow{k_3} P + B \quad (2.14) \]

is a mechanism, where an enzyme B (a biological catalyst) reacts with a molecule A to form one molecule C which is converted to a product P and the enzyme. This mechanism is a very basic enzymatic reaction proposed by Michaelis and Menten (1913) about which we shall talk more in the coming paragraphs [4].

### 2.2 Enzyme Kinetics

There are some certain species, called catalysts, that can increase the rate of a reaction without being consumed by it. A catalyst neither increases nor decreases the yield of a product. However, by speeding up the reaction, it allows the reaction to occur more quickly.

In the body, many reactions that occur slowly under normal conditions take place in the presence of catalyst. All vital biological reactions in the body are assisted by enzymes (biological catalysts). Biochemical reactions in a cell involve proteins called enzymes which are remarkably efficient catalysts.

Nonlinear differential equations for the Michaelis-Menten mechanism of 2.14 cannot be solved analytically, unlike the system 2.8. To see this, let us look at the system of nonlinear reaction equations for the mechanism of 2.14

\[
\begin{align*}
\frac{da}{dt} &= -k_1 ab + k_{-1} c \\
\frac{db}{dt} &= -k_1 ab + (k_1 + k_2) c \\
\frac{dc}{dt} &= k_1 ab - (k_1 + k_2) c \\
\frac{dp}{dt} &= k_2 c. \\
\end{align*}
\quad (2.15)
\]
Here $a, b, c,$ and $s$ denote the concentrations of the reactants in the application of the law of mass action. For example, the first equation for $A$ gives us the rate of change of the concentration $[A]$ which is formed of a loss rate proportional to $[A][B]$ and a gain rate proportional to $[C]$.

Let us take the following initial conditions for Eqs 2.15:

$$a(0) = a_0 > 0, \quad b(0) = b_0 > 0, \quad c(0) = 0, \quad p(0) = 0$$  \hspace{1cm} (2.16)

In the ode system 2.15, we can calculate the product $p$ by using the last equation after $c(t)$ has been determined by

$$p(t) = k_2 \int_0^t c(\bar{t})d\bar{t}$$  \hspace{1cm} (2.17)

Since the enzyme B is a catalyst in the mechanism 2.14, by adding the 2nd and 3rd equations in 2.15, we obtain the conservation law for the enzyme as

$$\frac{db}{dt} + \frac{dc}{dt} = 0 \quad \Rightarrow \quad b(t) + c(t) = b_0$$  \hspace{1cm} (2.18)

where the initial conditions 2.16 has been used.

Next, the remaining equation system from 2.15 is given as:

$$\frac{da}{dt} = -k_1b_0a + (k_1a + k_{-1})c,$$

$$\frac{dc}{dt} = k_1b_0a - (k_1a + k_{-1} + k_2)c,$$  \hspace{1cm} (2.19)

with the initial conditions $a(0) = a_0, \quad c(0) = 0$. By setting,

$$\sigma = k_1b_0t, \quad u(\sigma) = \frac{a(t)}{a_0}, \quad v(\sigma) = \frac{c(t)}{b_0}$$

$$\lambda = \frac{k_2}{k_1a_0}, \quad M = \frac{k_{-1} + k_2}{k_1a_0}, \quad \epsilon = \frac{b_0}{a_0},$$

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we nondimensionalize the system 2.19. In these transformations, $\epsilon \ll 1$ since the enzyme, $b_0$, is so small while the concentration of molecule A is so big. Then the equations 2.19 and the initial conditions turn into

$$\frac{du}{d\sigma} = -u + (u + M - \lambda)v$$
$$\epsilon \frac{dv}{d\sigma} = u - (u + M)v \quad (2.20)$$

$$u(0) = 1, \quad v(0) = 0.$$ 

Here, we are interested in the time evaluation of the reaction so we have to solve the nonlinear system 2.20. The nonlinear system 2.20 cannot be solved analytically, but qualitatively we can determine what $u(\sigma)$ and $v(\sigma)$ look like. To find a numerical solution, we use the method which will be mentioned in the next paragraphs, then we will focus on the solution of 2.20.

**Perturbation and Solution Methods:**

When we cannot find an analytical solution of equations, we use approximate solutions of the system that depend on a small parameter. The solution is represented as an asymptotic expansion in terms of the small parameter, $\epsilon$. Accuracy of asymptotic solutions to the exact solutions is remarkable. We choose the $\epsilon$ small enough for the error to be small as we like. Consider the equation

$$y'' + \epsilon y' + y = 0 \quad (2.21)$$

This type of equations is called a *regular perturbation problem*. If we set $\epsilon = 0$, we get

$$y'' + y = 0 \quad (2.22)$$
called the reduced equation. When $\epsilon$ is small enough, the solutions of 2.21 and 2.22 only are slightly different. For an approximate solution, we assume that the solutions have expansions in the form

$$ y = y_0 + \epsilon y_1 + \epsilon^2 y_2 + \ldots $$

Now, consider the following simple boundary value problem

$$ \epsilon \frac{d^2 y}{dx^2} + \frac{dy}{dx} + y = 0 $$

or as a system

$$ x'_1 = x_2 $$

$$ \epsilon x'_2 = -(x_2 + x_1) $$

where $x_1 = y$ and $x_2 = y'$. The boundary conditions for this system are given by $y(0) = \alpha, y(1) = \beta$. Since 2.23 is a second order differential equation, it has two solutions. However, when $\epsilon = 0$, the equation 2.23 reduces to

$$ y' + y = 0 $$

which is a first order differential equation. From the latter equation, we get one solution even though our original differential equation was second order. Such perturbation problems are called *singular perturbation problems*.

The exact solution of the linear constant coefficient equation 2.23 is given by

$$ y = \frac{(\alpha e^{k_2} - \beta)e^{k_1 x} + (\beta - \alpha e^{k_1})e^{k_2 x}}{e^{k_2} - e^{k_1}} $$

where $k_1 = \frac{-1+\sqrt{1-4\epsilon}}{2 \epsilon}$, $k_2 = \frac{-1+\sqrt{1-4\epsilon}}{2 \epsilon}$. Even though we can solve the ode exactly, we show the technique used to solve a typical singular perturbation ode. The solution of
the reduced equation 2.24 is

$$y = Ce^{1-x}.$$  \hspace{1cm} (2.25)

Using the boundary conditions, we get

$$y = ae^{-x} \quad \text{from} \quad y(0) = a$$  \hspace{1cm} (2.26)

and

$$y = be^{1-x} \quad \text{from} \quad y(1) = b.$$  \hspace{1cm} (2.27)

Comparing 2.26 and 2.27, we conclude the boundary conditions require two different values for $C$, which are incompatible if $\alpha \neq \beta e$ coincidently. Hence we note that one of the boundary conditions is not satisfied or must be dropped. Since the coefficient of $y'$ is positive, we keep the right boundary condition $y(1) = \beta$. We seek a solution in the form

$$y = y_0(x) + \epsilon y_1(x) + \epsilon^2 y_2(x) + \cdots.$$

Substituting this into 2.23 with $y(1) = \beta$, we get

$$y = \beta e^{1-x} + \cdots.$$

The solution is called outer solution and is denoted by $y_0$. It can be seen that $y_0$ agrees with the exact solution for small $\epsilon$, except in a small interval near 0, called the boundary layer. In this interval the exact solution changes quickly in order to satisfy the boundary condition.

Now, we have to define a new expansion which is valid in the boundary layer, so we magnify this layer using the transformation

$$\gamma = \frac{x}{\epsilon}.$$  \hspace{1cm} (2.28)
With this transformation, the equation 2.23 turns into
\[
\frac{d^2 y}{d\gamma^2} + \frac{dy}{d\gamma} + \epsilon y = 0
\]  
(2.29)
with \(y(0) = \alpha\). As \(\epsilon \to 0\) and for fixed \(\gamma\), we have
\[
\frac{d^2 y}{d\gamma^2} + \frac{dy}{d\gamma} = 0.
\]  
(2.30)
The general solution of 2.30 is
\[
y = c_1 + c_2 e^{-\gamma}
\]  
(2.31)
where \(c_1, c_2\) are constants. Since the solution is valid in the boundary layer, it is valid at the origin; hence it must satisfy the boundary conditions. Then using the boundary condition \(y(0) = \alpha\), we get
\[
y = \alpha - c_1 + c_1 e^{-\gamma}
\]  
(2.32)
where \(c_1\) is an arbitrary constant. This solution is called inner solution and denoted by \(y_I\). For a fixed \(0 < x \ll 1, \gamma \to \infty\) as \(\epsilon \to 0\). Thus, we anticipate the outer solution as \(x \to 0\) to be equal to the inner solution as \(\gamma \to \infty\),
\[
\lim_{x \to 0} y_O(x; \epsilon) = \lim_{\gamma \to \infty} y_I(x; \epsilon).
\]  
(2.33)
This is the essence of matching in singular perturbation theory. To determine \(c_1\) in 2.32, we use the matching principle, which yields
\[
\alpha - c_1 = \beta \epsilon.
\]  
Hence \(c_1 = \alpha - \beta \epsilon\) and
\[
y_I = \alpha + (e^{-\gamma} - 1)(\alpha - \beta \epsilon)
\]  
(2.34)
Now, let us turn to our original problem. To get more accurate approximate solutions to \(2.20\) for \(0 < \epsilon \ll 1\), singular perturbation methods are very important and powerful methods. Assume \(u(\sigma)\) and \(v(\sigma)\) are analytic functions of \(\epsilon\) as \(\epsilon \to 0\). A regular Taylor expansion of solutions \(u\) and \(v\) in \(2.20\) is of the form

\[
\begin{align*}
u(\sigma; \epsilon) &= u_0(\sigma) + \epsilon u_1(\sigma) + \epsilon^2 u_2(\sigma) + \cdots \\
v(\sigma; \epsilon) &= v_0(\sigma) + \epsilon v_1(\sigma) + \epsilon^2 v_2(\sigma) + \cdots.
\end{align*}
\tag{2.35}
\]

On substituting these into \(2.20\), and equating the powers of \(\epsilon\), we get a sequence of differential equations for the \(u_n(\sigma)\) and \(v_n(\sigma)\).

From the coefficient of the \(\epsilon^0\), we obtain

\[
\frac{du_0}{d\sigma} = -u_0 + (u_0 + M - \lambda) v_0,
\]

\[
u_0 - (u_0 + M)v_0 = 0
\]

(2.36)

with the initial conditions \(u_0(0) = 1\), \(v_0(0) = 0\), as before. From the algebraic equation in the system 2.36, we conclude

\[
v_0 = \frac{u_0}{u_0 + M}
\]

(2.37)

and then the first equation becomes

\[
\frac{du_0}{d\sigma} = -u_0 + (u_0 + M - \lambda) \frac{u_0}{u_0 + M}
\]

\[= -\lambda \frac{u_0}{u_0 + M}
\]

(2.38)

with the initial condition \(u_0(0) = 1\).

Finally, we derive from 2.38

\[
u_0(\sigma) + M \ln u_0(\sigma) = C - \lambda \sigma
\]

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where $C$ is a constant. The initial condition $u_0(0) = 1$ determines the constant in the latter equation as 1. Thus, we have a solution of 2.36 given as:

$$u_0(\sigma) + M \ln u_0(\sigma) = 1 - \lambda \sigma,$$

$$v_0(\sigma) = \frac{u_0(\sigma)}{u_0(\sigma) + M}$$  \hfill (2.39)

From the above results, we observe that $u$ is decreasing near $\sigma = 0$ from $u_0 = 1$ since $\frac{du_0}{d\sigma} < 0$. Besides, $u_0$ satisfies

$$0 \leq e^{-\frac{\lambda \sigma}{M}} \leq u_0 \leq e^{-\frac{\lambda \sigma}{(1+M)}} \leq 1$$

since $-\frac{\lambda u_0}{M} \leq \frac{du_0}{d\sigma} \leq -\frac{\lambda u_0}{1+M}$. With this restriction, we are able to decide the behavior of $u_0$ throughout $\sigma \geq 0$. Since $v_0(0) = \frac{1}{1+M} \neq 0 = v(0)$, $v_0$ is not a good approximation to $v$ near $\sigma = 0$.

Therefore, we will use our knowledge from the previous section. Let us define a new transformation as in 2.28, i.e., let

$$\gamma = \frac{\sigma}{\epsilon},$$

$$u(\sigma; \epsilon) = \bar{u}(\gamma; \epsilon), \quad v(\sigma; \epsilon) = \bar{v}(\gamma; \epsilon)$$  \hfill (2.40)

With these transformations, equations 2.20 turn into

$$\frac{d\bar{u}}{d\gamma} = -\epsilon \bar{u} + \epsilon (\bar{u} + M - \lambda) \bar{v},$$

$$\frac{d\bar{v}}{d\gamma} = \bar{u} - (\bar{u} + M) \bar{v},$$

$$\bar{u}(0) = 1, \quad \bar{v}(0) = 0$$  \hfill (2.41)

Substituting a regular Taylor expansions of $\bar{u}(\gamma; \epsilon)$ and $\bar{v}(\gamma; \epsilon)$

$$\bar{u}(\gamma; \epsilon) = \bar{u}_0(\gamma) + \epsilon \bar{u}_1(\gamma) + \epsilon^2 \bar{u}_2(\gamma) + \cdots,$$

$$\bar{v}(\gamma; \epsilon) = \bar{v}_0(\gamma) + \epsilon \bar{v}_1(\gamma) + \epsilon^2 \bar{v}_2(\gamma) + \cdots$$

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into 2.41 and equating the first order $e^0$ equations gives

\[
\frac{d\bar{u}}{d\gamma} = 0, \quad \frac{d\bar{v}}{d\gamma} = \bar{u} - (\bar{u} + M)\bar{v} \tag{2.42}
\]

with the initial conditions $\bar{u}(0) = 1, \bar{v}(0) = 0$. The solution of 2.42 is

\[
\bar{u}(\gamma) = 1, \quad \bar{v}(\gamma) = \frac{1 - \exp(-[1 + M]\gamma)}{1 + M}. \tag{2.43}
\]

The solution 2.43 is the inner solution of 2.41 which is valid in $0 \leq \sigma \ll 1$ for $u$ and $v$. The solution 2.39 is the outer solution which is valid for all $\sigma$ except a small neighborhood of $\sigma = 0$. Using the matching in singular perturbation theory, we get

\[
\lim_{\gamma \to \infty} \bar{u}(\gamma) = \lim_{\sigma \to 0} u_0(\sigma), \quad \lim_{\gamma \to \infty} \bar{v}(\gamma) = \frac{1}{1 + M} = \lim_{\sigma \to 0} v_0(\sigma).
\]

We thus get the solution for the equations 2.20 putting inner and outer solutions together to leading order

\[
u(\sigma) = u(\sigma) + M \ln u(\sigma) = 1 - \lambda \sigma
\]

\[
\bar{v}(\sigma) = \frac{u(\sigma)}{M + u(\sigma)} (1 - \exp(-[1 + M]\sigma/\epsilon)).
\]
CHAPTER 3

REDUCTION
FOR THE COMPLEX CHEMICAL MECHANISMS

Full mechanisms are constructed in order to get certain requirements fulfilled such as, reproduction of some experimental concentrations or temperature points. In some cases, it is not easy to follow the competition between reaction steps, or species, for large chemical mechanisms. Therefore, it is evident that the reduction of large mechanisms is necessary to understand the results of the full mechanism. In doing so, we should get the same results from the smaller subset of reactions as the original one. We can do this reduction since some of the reactions of the mechanism may not affect the results in case of omitted.

Techniques for the study of complex chemical reactions by mathematical modeling have advanced rapidly in the last three decades [5, 6]. The solution of the mass-action differential equations derived from the chemical model and studying on the effect of parameters on the model upon its behavior are the main methods. A review of many of these methods and their applications have appeared [7]. One of the tools of mechanism reduction is “sensitivity analysis” which was proposed by H. Poicèrè [8] and has been developed for the analytic solutions [5]. Up to 1985, the classical approximation techniques of chemical kinetics was the rate-determining-step and quasi-steady-state
approximation (QSSA) [9]. In 1985, Vajda et. al proposed and used the principal component analysis with sensitivity analysis [10].

In this chapter, we shall show how the reduction of a full mechanism can be done. In doing so, we shall address the importance of the eigenvalues and eigenvectors of the matrix \( \mathbf{M}^T \mathbf{M} \), where \( \mathbf{M} \) defines the array of the normalized sensitivity coefficients [9]. After the analysis of eigenvalues, one can reach a decision for the significance of some parts of the mechanism; moreover, one can get some dependencies among the parameters. In this chapter, we will partially follow a review given by Turáyi [11].

### 3.1 Sensitivity Analysis

Sensitivity analysis is the combination of methods for the study of parametric information in mathematical modeling and provides the investigation of the outputs of the models as a function of parameters. Sensitivity analysis and components of the mechanism reduction techniques described below provide a good method of understanding the details and the behavior of the complex chemical kinetic processes. The purpose of these methods, of course, is to gain some ideas about the model. As a result of the mass action law, we have the following ordinary differential equations (odes) for a chemical mechanism:

\[
\frac{ds_i}{dt} = f_i(s, p), \quad s_i(0) = s_i^0, \quad i = 1, 2, ..., n
\]

where \( s_i \) denotes the concentration of species, \( p \) defines the rate coefficients, \( s_i^0 \) the initial conditions, and \( f_i \) is typically nonlinear in the chemical concentration vector \( s \). In eq. 3.1, if \( p_i \) changes and the solutions do not change, then the corresponding reaction to \( p_i \) is not important. Eq. 3.1 is referred to as autonomous system since
there is no time dependence on the right side of the equations. The solutions for the system 3.1 depend on the concentration-time variables.

Sensitivity methods can be divided into two sections:

- Local Concentration Sensitivity

- Rate Sensitivity

3.1.1 Local Concentration Sensitivity

A parameter change in the system affects the solution. This dependence can be explained mathematically by the Taylor expansion

\[ s_i(p + \Delta p, t) = s_i(p, t) + \sum_{j=1}^{m} \frac{\partial s_i}{\partial p_j} \Delta p_j + \frac{1}{2} \sum_{i=1}^{m} \sum_{j=1}^{m} \frac{\partial^2 s_i}{\partial p_i \partial p_j} \Delta p_i \Delta p_j + \cdots \]

where the partial derivatives \( \frac{\partial s_i}{\partial p_j} \) denote the first-order local concentration sensitivity coefficients, while the partial derivatives \( \frac{\partial^2 s_i}{\partial p_i \partial p_j} \) denote the second-order local concentration sensitivity coefficients. The local sensitivities can be calculated easily by perturbing each of the individual parameters, re-running the model, and getting some approximation to the sensitivities by differences. But this method is only useful if a better method is not available. The local sensitivities \( \frac{\partial s_i}{\partial p_j}, \frac{\partial^2 s_i}{\partial p_i \partial p_j}, \) and so on, can give some information about the solution of the vicinity of the desired time points.

Generally, the first-order sensitivity coefficients are most useful to study. With these coefficients, we can constitute the concentration sensitivity matrix \( \mathbf{M} \) which is the measure of a linear approximation for the solutions as the parameters change. \( \mathbf{M} = (M_1, M_2, \ldots, M_r)^T \) with respect to selected time points \( t_1, t_2, \ldots, t_r \) and each
\( M_i \) is defined by

\[
M_i = \begin{bmatrix}
\frac{\partial s_1}{\partial p_1} & \frac{\partial s_1}{\partial p_2} & \cdots & \frac{\partial s_1}{\partial p_m} \\
\frac{\partial s_2}{\partial p_1} & \frac{\partial s_2}{\partial p_2} & \cdots & \frac{\partial s_2}{\partial p_m} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial s_m}{\partial p_1} & \frac{\partial s_m}{\partial p_2} & \cdots & \frac{\partial s_m}{\partial p_m}
\end{bmatrix}_{t=t_i}.
\]

In the following, we mention some of the methods to calculate the local concentration sensitivity coefficients.

**Brute Force**

Brute force, also called an indirect method, is one of the simplest ways to calculate the local concentration sensitivity. In this technique, the finite difference approximation is the main tool. Suppose all parameters are fixed other than the \( i \)th parameter, which is changed by \( \Delta p_i \). The difference of the original and perturbed solution defines the matrix \( M \) by

\[
\frac{\partial s}{\partial p_i} \approx \frac{s(p_i + \Delta p_i) - s(p_i - \Delta p_i)}{2\Delta p_i} \quad i = 1, 2, \ldots, m
\]  

(3.2)

The equation 3.2 is called a *central-difference approximation*. From the equation 3.2, we observe that once \( 2m \)-solutions are derived from eqs 3.1 with their perturbed solutions, we can calculate the local sensitivity coefficients.

As it is understood from this technique, we do not need any other code other than the ode solver. However, it requires much computer time. There are some efficient algorithms, e.g., *decoupled direct method* (DDM) applied by Dunker [12].

**Direct Method**

We need to provide a more efficient and rapid means of calculating the local concentration sensitivity coefficients than is generally given by 3.2. If we differentiate
the original system of kinetic equation 3.1 with respect to \( p_j \), the following set of sensitivity differential equations is obtained by chain rule:

\[
\frac{d}{dt} \left( \frac{\partial s_i}{\partial p_j} \right) = \frac{\partial f_i}{\partial p_j} + \sum_k \frac{\partial f_i}{\partial s_k} \left( \frac{\partial s_k}{\partial p_j} \right)
\]

or

\[
\frac{d}{dt} \frac{\partial s}{\partial p_j} = \frac{\partial f}{\partial p_j} + J(t) \frac{\partial s}{\partial p_j} \tag{3.3}
\]

where \( J(t) = \frac{\partial r}{\partial s} \). The equation 3.3 provides the base for a number of methods to calculate the local concentration sensitivity coefficients. For this system, the following initial conditions are given: The initial condition for the sensitivity coefficient \( \frac{\partial s_i(0)}{\partial p_j} \) is zero if \( s_i \) is not initial concentration, otherwise it is equal to one.

If equations 3.1 and 3.3 are examined together, it appears \( \frac{\partial L}{\partial s} \) and \( \frac{\partial L}{\partial p} \) are the common matrices in two equations. The system, 3.1 and 3.3, can only be solved if the concentration values, calculated from Eqs. 3.1, are available at required time steps. Therefore, the association between these two equations can be built up in the following way. The pair of equations 3.1 and 3.3 are solved for \( j = 1, 2, \ldots, m \), which necessitates the solution of \( 2n \) odes \( m \) times. Although this way looks easy to code, it is not productive and may cause some numerical problem because of numerous steps.

### 3.1.2 Rate Sensitivity

In chemical kinetics, the investigation of the production rate of species is very crucial and their sensitivities are very informative. Rate sensitivity is given by

\[
\frac{\partial}{\partial t} \left( \frac{\partial s_i}{\partial p_j} \right) = \frac{\partial f_i}{\partial p_j}.
\]
The local concentration sensitivities can be used for the calculations of the values of rate sensitivity coefficients by using the sensitivity differential equation 3.3

\[ \dot{M} = JM + R. \]

Rate sensitivity coefficients, \( \frac{\partial \dot{f}_i}{\partial \mu_j} \), give more details about a reaction system which are not intrinsic in the concentration sensitivity coefficients. Therefore, the matrix \( R \) is a measure of sensitivities. Let \( p \) designate the vector of rate coefficients, then the normed rate sensitivity matrix is given by \( R = (R_1, R_2, \ldots, R_r)^T \) for the time points \( t_1, t_2, \ldots, t_r \) and each \( R_i \) is defined by

\[
R_i = \begin{bmatrix}
\frac{\partial \ln f_1}{\partial \ln p_1} & \frac{\partial \ln f_1}{\partial \ln p_2} & \cdots & \frac{\partial \ln f_1}{\partial \ln p_m} \\
\frac{\partial \ln f_2}{\partial \ln p_1} & \frac{\partial \ln f_2}{\partial \ln p_2} & \cdots & \frac{\partial \ln f_2}{\partial \ln p_m} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial \ln f_n}{\partial \ln p_1} & \frac{\partial \ln f_n}{\partial \ln p_2} & \cdots & \frac{\partial \ln f_n}{\partial \ln p_m}
\end{bmatrix}_{t=t_i}.
\]

Thus, the ratio of the rate of formation or consumption of species \( i \) in the reaction \( j \) and the amount of concentration change of species \( i \) are given by a component of the matrix \( R \). Concentration sensitivity analysis and rate-of-production analysis are connected by the matrix \( R \). The analysis and reduction of a complex chemical mechanism can be based on the study of the matrix \( R \).

### 3.2 Usage of Sensitivity Knowledge

If units of parameters are different then the sensitivity coefficients are incapable. Therefore, a comparison of sensitivity coefficients necessitates the equality of the physical dimensions or dimensionless of them. One can handle this problem by introducing the normalized concentration sensitivity matrix \( \mathcal{M} = (\mathcal{M}_1, \mathcal{M}_2, \ldots, \mathcal{M}_r)^T \)
with respect to selected time points \( t_1, t_2, \ldots, t_r \) and each \( \mathcal{M}_i \) is defined by

\[
\mathcal{M}_i = \begin{bmatrix}
\frac{\partial \ln s_1}{\partial \ln p_1} & \frac{\partial \ln s_1}{\partial \ln p_2} & \cdots & \frac{\partial \ln s_1}{\partial \ln p_m} \\
\frac{\partial \ln s_2}{\partial \ln p_1} & \frac{\partial \ln s_2}{\partial \ln p_2} & \cdots & \frac{\partial \ln s_2}{\partial \ln p_m} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial \ln s_n}{\partial \ln p_1} & \frac{\partial \ln s_n}{\partial \ln p_2} & \cdots & \frac{\partial \ln s_n}{\partial \ln p_m}
\end{bmatrix}_{t=t_i}
\]

where the components of \( \mathcal{M} \) are dimensionless. Here, the coefficients symbolize the effect of \( p_j \) on concentration \( s_i \) with percentage changes.

In many cases one is interested in the effect of a parameter change on the concentrations of several species out of all the species of the full system. To elucidate this information, the objective functions are the remedy, so that more mathematical methods can be inserted. Objective functions establish the difference between the perturbed solutions and the original solutions. Some of the objective functions can be written as

\[
O = \int_{t_1}^{t_2} \sum_{i=1}^{n} \left[ \frac{s_i^{(p)} - s_i}{s_i} \right]^2 dt \quad (3.4)
\]

\[
O_1 = \sum_{i=1}^{n} \left| \frac{s_i^{(p)} - s_i}{s_i} \right| \quad (3.5)
\]

\[
O_2 = \sum_{i=1}^{n} \left[ \frac{s_i^{(p)} - s_i}{s_i} \right]^2 \quad (3.6)
\]

From an objective function, one can get some ideas about the results of a particular change of the parameter values. By differentiating an objective function with respect to \( \ln p_j \), we get

\[
\frac{\partial O}{\partial \ln p_j} = \sum_{h=2}^{r} \sum_{i=1}^{n} \left[ \frac{\partial \ln s_i(t_h)}{\partial \ln p_j(t_1)} \right]^2 ,
\]

\[
\frac{\partial O_1}{\partial \ln p_j} = \sum_{i=1}^{n} \left[ \frac{\partial \ln s_i}{\partial \ln p_j} \right] ,
\]

\[
\frac{\partial O_2}{\partial \ln p_j} = \sum_{i=1}^{n} \left[ \frac{\partial \ln s_i}{\partial \ln p_j} \right]^2
\]

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where the effect of the change of parameter $p_j$ is given for $n$ species and the integral in equation 3.4 is replaced by the summation. This effect can be given as the sensitivity value which can be calculated by

$$B_j = \sum_i \left( \frac{\partial \ln s_i}{\partial \ln p_j} \right)^2$$

where $i$ runs over the indices of species of the investigated group. The overall sensitivity related with the objective function of least-squares method is defined by $B_j$.

So far, we have discussed the effect of parameters change on the time interval. On the contrary, we can obtain this information for a specific time point. This can be done by the study of the algebraic rate sensitivity $\mathfrak{R}$. The $i$th column of the matrix $\mathfrak{R}$ determines the reactions which are the major ones affecting on the rate of production of species $i$ at a considered time. When a reaction is proved to be important at a single time point, it must be considered as one of the important reactions in the mechanism. We are interested in the effect of a group of parameters on concentration, as well as, the individual parameters. Functional relations between sensitivity coefficients can be defined by the parameter groups which are identified by the elements of the normalized local concentration sensitivity matrix.

Finally, we can say that a reaction is negligible if the sensitivity of all species for the appropriate rate coefficients is small in the considered time interval. In the following, we describe how the identification of a parameter group can be done more conveniently. This method is developed by Turányi.
Principal Component Analysis

Principal component analysis (PCA) is one of the mathematical models. It gives us the condensation of the information about what we have got from the sensitivity matrix and reveals the relations between parameters. Let \( s_1(t, p), \ldots, s_n(t, p) \) be the concentration of interested species of sensitivities at chosen time steps \( t_1, t_2, \ldots, t_r \). Now, the normalized parameters are defined as

\[
\nu_j = \ln p_j, \quad j = 1, 2, \ldots, m. \tag{3.10}
\]

Then for the initial value \( p^0 \), we have \( \nu_j^0 = \ln p_j^0 \). The objective function \( O \) can be rewritten by using 3.10 as

\[
O(\nu) = \sum_{j=1}^{r} \sum_{i=1}^{n} \left( \frac{\Delta s_{i,j}}{s_{i,j}} \right)^2
\]

where \( \Delta s_{i,j} = s_i(t_j, p) - s_i(t_j, p^0) \). Expanding the objective function into its Taylor series gives us

\[
O(\nu) \approx O(\nu^0) + A^T (\nu^0) \Delta \nu + \frac{1}{2} (\Delta \nu)^T B(\nu^0) \Delta \nu \tag{3.11}
\]

where \( \Delta \nu = \nu - \nu^0 \), \( A = \left( \frac{\partial \mathcal{R}}{\partial \nu} \right) \) and \( B = \left( \frac{\partial^2 \mathcal{R}}{\partial \nu \partial \nu} \right)_{i,j=1,2,\ldots,m} \). Since \( \nu^0 \) is a minimum of \( \mathcal{R} \), \( A(\nu^0) = 0 \) and \( \mathcal{R}(\nu^0) = 0 \). Thus, Eqs. 3.11 turns into

\[
O(\nu) \approx \frac{1}{2} (\Delta (\nu))^T B(\nu^0) \Delta (\nu).
\]

Moreover, \( B \) can be rewritten as

\[
2 \mathbf{M}^T \mathbf{M} + Q.
\]

By using Gauss approximation and second derivatives of concentrations \( Q \), we have

\[
O(\nu) \approx \mathcal{Q}(\nu) = (\Delta \nu)^T (\mathbf{M}^T \mathbf{M})(\Delta \nu) \tag{3.12}
\]

as the approximate objective function for the study of the effects of parameter changes.
There is an advantage of using the PCA in terms of assessing the effect of simultaneously changing a number of parameters on a few outputs of a model, while the sensitivity matrix assesses the effect of individual parameter changes on the calculated concentrations [9]. As mentioned above, to be able to conclude some results from the full system, one works on the objective function. According to Eq. 3.12, the objective function is a quadratic function of $\Delta \nu_i, \quad i = 1, 2, \ldots, m$. For a fixed $\epsilon$ the inequality $Q(\nu) \leq \epsilon$ defines an ellipsoid in the parameter space with principal axes (see Fig. 3.1). Therefore, the changes of $Q$ are proportional to $M^T M$. As a matter of fact, if one diagonalizes the matrix $M^T M$, then it is more efficient to do some algebraic calculations with the matrix $M^T M$. So, let

$$V^T (M^T M) V = D$$
where $D$ is a diagonal matrix formed by setting the eigenvalues of $\mathbf{M}^T \mathbf{M}$ on the diagonal; then, $V$ given by

$$
V = \begin{bmatrix}
  v_{1,1} & v_{2,1} & \cdots & v_{m,1} \\
  v_{1,2} & v_{2,2} & \cdots & v_{m,2} \\
  \vdots & \vdots & \ddots & \vdots \\
  v_{1,m} & v_{2,m} & \cdots & v_{m,m}
\end{bmatrix}
$$

consists of the normalized eigenvectors $v_i$ of $\mathbf{M}^T \mathbf{M}$ for $i = 1, 2, \ldots, m$ such that, $v_i^T \cdot v_i = 1$ for all $i$. Now, let us introduce a new notation for the parameters, i.e.,

$$
\xi = V^T \nu
$$

called principal components [11]. Using the latter notation and some algebraic rules, Eq. 3.12 can be written as

$$
Q(\nu) = \sum_{i=1}^{m} \tilde{\lambda}_i \| \Delta \xi_i \|^2
$$

(3.13)

where $\tilde{\lambda}_1 > \tilde{\lambda}_2 > \ldots > \tilde{\lambda}_m$ are the eigenvalues of $\mathbf{M}^T \mathbf{M}$ and $\| \Delta \xi_i \|^2 = (\Delta \xi_i)^T (\Delta \xi_i)$. The eigenvalues $\tilde{\lambda}_1, \tilde{\lambda}_2, \ldots, \tilde{\lambda}_q$ can be considered as large if $\frac{\sum_{i=q+1}^{m} \tilde{\lambda}_i}{\sum_{i=1}^{m} \tilde{\lambda}_i} > 0.99$ [10]. If $v_1 = (v_{1,1}, v_{1,2}, \ldots, v_{1,m})^T$ defines the eigenvector corresponding to the largest eigenvalue $\tilde{\lambda}_i$, then $\xi_1 = (v_{1,1} \nu_1, v_{1,2} \nu_2, \ldots, v_{1,m} \nu_m)^T$. Setting $\Delta \nu_i = \ln \left( \frac{p_i}{p_i^0} \right) = v_{1,i} \quad i = 1, 2, \ldots, m$ gives $\| \Delta \xi_1 \| = 1$, i.e., it moves along the vector $v_1$ in $\nu$ space. Finally, by using the property of orthogonality, one gets $Q(\xi) = \tilde{\lambda}_1$. If some components $v_{1,k}$ of the eigenvector $v_1$ is less than or equal to 0.2, then the contribution of $\Delta \nu_k$ is less than 4% to this effect and, therefore, we can discard such reactions corresponding to components of $v_1$ from our consideration [9]. As a practical consideration, let us assume that we have the following eigenvector: $v_1 = (v_{1,1}, v_{1,2}, \ldots, v_{1,q}, 0, \ldots, 0)$ where the entries less than or equal to 0.2 are replaced by 0. Thus, a simultaneous change in the rate constants $p_1, p_2, \ldots, p_q$ gives the largest effect on concentrations.
From the corresponding elementary reactions, we get the kernel of the mechanism. If 
\( \dot{\lambda}_i < 10^{-4} n_r \), then the effect of the reactions corresponding to these eigenvalues on the concentrations is small averaging less than 1\%. On this way, we can also eliminate reactions corresponding to those eigenvalues [10].

Even though the principal component analysis was developed for the analysis of the local concentration sensitivity matrices, it can be used to study of the other sensitivity matrices.

3.3 Identification of Redundant Species and Reactions

3.3.1 Redundant Species

To find the redundant species is a primary stage on the way of determination of reduced mechanisms. Turányi classified the chemical species into three categories as important, necessary, and redundant species [6]. The objectives of the model determine which species are important. The purpose of the modeling process is the reproduction of the concentration profiles of important species which can be either products or initial reactants. Necessary species are those which have to be present in the model to get the accurate reproduction of concentration profiles of important species. And the remaining species in the full mechanism are redundant species.

There are two methods to decide which are the redundant species. When one species is neglected from the full system, i.e., if it has no significant effect on the solution of the full system with respect to the concentration of important species, then it is a redundant species. In this method one has to do this procedure for each species to decide the non-important species. Once a species is determined as a redundant species, then a reaction including the redundant species on the left hand
side can be excluded from the full mechanism without effecting on the output of the model. If redundant species are on the right hand side of a reaction, then the reaction may or may not be eliminated. Even if the reaction has to be kept, still the redundant species can be eliminated from the list of products of the reaction.

The second method is the investigation of Jacobian of the kinetic system of odes $J = \frac{\partial f}{\partial \mu}$. If change in concentration of a species does not affect on the rate of production of important species, then this species is redundant. The fractional change of the rate of production of species $i$ caused by the fractional change of the concentration of species $j$ is determined by an element of the normed Jacobian $\frac{\partial \ln f_i}{\partial \ln s_j}$. The rate of the production of M-membered group of important species is effected by the change of the concentration species $i$ as the sum of squares of normalized Jacobian elements,

$$B_i = \sum_{k=1}^{M} \left( \frac{\partial \ln f_k}{\partial \ln s_i} \right)^2.$$  

A species’ direct effect on important species gets higher with respect to the higher $B_i$ value of the species.

In the first method, the number of simulations is of the order of the number of species. It is necessary to simulate different reduced models for each eliminated species. But the second method requires one simulation of the original model where the Jacobian is calculated from the concentrations at several reaction times. Therefore it seems this method is more efficient than the first one.

### 3.3.2 Redundant Reactions

Once we have got the necessary species, then one has to decide what are the unimportant reactions on the way of reducing the full mechanism. A classical and
reliable method is to figure out the effect of reactions to the production rate of necessary species. In this way, we have to consider the reaction effects for several reaction times that must be considered for each necessary species. But this method necessitates analyzing big matrices. Conversely, there is an alternative way for reduction of mechanism which considers reaction rates based on the sensitivity of production rates to changes in rate parameters. Again using the least squares objective function to consider the effect of each parameter on several production rates, one uses the following formula

\[ B_j = \sum_k \left( \frac{\partial \ln f_k}{\partial \ln p_j} \right)^2. \]

for the overall sensitivity. One can study of PCA for the eigenvalue-eigenvector analysis of the matrix \( \mathbf{R}^T \mathbf{R} \) in a very similar way to the case of PCA of the concentration sensitivity matrix which concludes the importance of reaction groups for the set of important and necessary species.

### 3.4 Summary

So far, we have discussed the methods of reduction for a mechanism. We can summarize them under two titles:

To find a reduced mechanism by identifying reactions:

1. Determine the large eigenvalues. (An eigenvalue or eigenvector is looked upon as large, if it is greater than a threshold value which can be different for different systems. The threshold value for the eigenvalues was given as \( mq10^{-4} \) or could be \( 10^{-4} \), while 0.1 or 0.2 is recommended for the eigenvectors.)
2. Identify reactions belonging to large elements of eigenvectors which correspond to the eigenvalues determined in the first step.

After this process, the remaining reactions are considered as unimportant reactions in the mechanism.

**To identify redundant species:**

A species is redundant if its both direct and indirect effects on the group of important species are small. An overall sensitivity which was defined as the sum of squares of normalized Jacobian elements gives direct effects. In this procedure, first, calculate the overall sensitivities for the important species. Second, decide the highest overall sensitivities among the rest of the species which shall be considered as necessary species. Then, again calculate the overall sensitivities by taking into account the new species in the summation. In this way, we deduce a list for necessary species. Finally, the redundant species will be identified after deciding the necessary species.

### 3.5 Application

In the upper atmosphere, many different reactions occur, launched by radiation from the sun as well as by cosmic rays. One of the most important of these occurs in the stratosphere: the transformation of oxygen to its allotropic form *ozone*, (trioxygen) O₃.

Ozone has an individual significance in the chemistry of the Earth’s atmosphere, although there exists in a small amount. If the ozone were collected in a column under the pressure 1 atm, it would occupy a column about 3mm tall. Ozone filters the radiation in the 2100-2900-Å region of the sun’s spectrum. If this ultraviolet radiation were to reach the Earth’s surface, it would kill all living tissues. Instead
of being found in a constant fractional abundance, the ozone concentrations depend
sharply on altitude. Ozone layer, about 20 km at an altitude of about 25-30 km,
contains of the ozone. In this region, the ozone is made up in two steps: First, an O$_2$
molecule is detached,

$$O_2 \rightarrow 2O.$$ (3.14)

Next step is a collision between an oxygen and an O$_2$ molecule,

$$O_2 + O \rightarrow O_3.$$ (3.15)

This reaction gives ozone molecules. Decomposition of ozone can be occurred by
several mechanism. One of the most important is

$$O_3 + O \rightarrow 2O.$$ (3.16)

But this reaction takes place at a slow rate. It can be speeded up by using the catalyst
such as Cl, N;

**Mechanism**  
\[ Cl + O_3 \rightarrow ClO + O_2 \]

\[ ClO + O \rightarrow Cl + O_2 \]

**Overall**  
\[ O_3 + O \rightarrow 2O_2 \]

The reactions 3.14, 3.15 and 3.16 were proposed by Chapman, S., A. in 1930. This
was the first approach to a theoretical explanation of the ozone layer. The resulting
system of odes for the Chapman system is

\[
\frac{dx}{dt} = -[k_1y + k_2z]x + 2k_3y + k_4z
\]

\[
\frac{dy}{dt} = -[k_1x + k_3]y + [2k_2x + k_4]z
\]

\[
\frac{dz}{dt} = k_1yx - [k_2x + k_4]z
\]
\[
\begin{array}{|c|c|c|}
\hline
No. & Reactions & Rate Constants \\
\hline
1 & O + O_2 \rightarrow O_3 & k_1 = 1.630 \text{E}-16 \\
2 & O + O_3 \rightarrow 2O_2 & k_2 = 4.660 \text{E}-16 \\
3 & O_2 \rightarrow 2O & k_3 = 5.000 \text{E}-11 \\
4 & O_3 \rightarrow O + O_2 & k_4 = 2.500 \text{E}-04 \\
\hline
\end{array}
\]

Table 3.1: Reactions of Chapman System and Initial Conditions

where \( x = [O], y = [O_2] \) and \( z = [O_3] \) and the initial conditions are given by \( [O] = 1.00 \text{D} + 06, [O_2] = 3.70 \text{D} + 16, [O_3] = 1.00 \text{D} + 12 \).

In the following section, we will introduce a package written by Turányi for the reduction of chemical systems and will give the Chapman system as an example of this Fortran77 program.

### 3.5.1 Description of KINAL

KINAL is a program package for kinetic analysis of chemical reaction mechanisms. In this package, there are five programs, DIFF, SENS, PROC, ROPA, and YRED. DIFF solves stiff differential equations and SENS calculates the local concentration sensitivities. The rate sensitivity matrix or quasi-stationary sensitivity matrix is calculated by PROC. PROC lists the eigenvalues with the corresponding eigenvectors and the numbers belonging to eigenvector elements. It also provides a reduced mechanism. ROPA gives the contribution of reaction steps to the production rate of species. Finally, YRED provides hints for the elimination of species from reaction mechanism. All these programs use the methods given in the preceding sections.
Results from the KINAL for the Chapman System:
The eigenvalues and eigenvectors of the matrix $\mathbf{R}^T \mathbf{R}$ are listed in table 3.2. From this, we observe that all four reactions in the Chapman system must be kept for the mechanism; to get this fact, we used two rules given in the preceding section. The threshold values $10^{-4}$ and .1 are taken for the eigenvalues and eigenvectors, respectively. Then, the package proposed a reduced mechanism by determining the reactions belonging to large elements in eigenvector which corresponds to large eigenvalues.

In the program YRED, $O_3$ was given as an important species, then running program gives $O, O_2$ as necessary species. The time evaluation of concentrations $[O_3], [O], [O_2]$ are shown in figures 3.2 and 3.4. In table 3.2, the top line shows the reaction numbers.

<table>
<thead>
<tr>
<th>$\lambda_i$</th>
<th>Eigenvectors</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>5.30083E+00</td>
<td>0.704</td>
<td>$-0.696$</td>
</tr>
<tr>
<td>1.03515E+00</td>
<td>0.938</td>
<td>$-0.317$</td>
</tr>
<tr>
<td>5.33456E-05</td>
<td>0.598</td>
<td>$-0.553$</td>
</tr>
<tr>
<td>7.83773E-06</td>
<td>$-0.735$</td>
<td>$-0.447$</td>
</tr>
</tbody>
</table>

Table 3.2: Eigenvalues and Eigenvectors

As it appears in figures 3.2 and 3.3, the concentration of $O_2$ is constant during the run. Suppose $[O_2]$ is constant in the Chapman system, then we have the following
odes

\[ \begin{align*}
\dot{x}' &= -k_1 \dot{x} - k_2 \dot{y} + 2k_3 \dot{y} + k_4 \\
\dot{y}' &= k_1 \dot{x} - k_2 \dot{y} - k_4 
\end{align*} \]

where \( x = [O] \), \( y = [O_3] \), and \( o = [O_2] \). For the steady state, \( \dot{x}' = \dot{y}' = 0 \) (see Figure 3.5), we get

\[ \begin{align*}
x &= \frac{k_4 \dot{y}}{k_1 \dot{o} - k_2 \dot{y}} \\
y &= \frac{-\dot{o} k_2 k_3 + \sqrt{\dot{o}^2 k_2^2 k_3^2 + 4\dot{o}^2 k_1 k_2 k_3 k_4}}{2k_2 k_4}
\end{align*} \]

In figure 3.5, it is measured simultaneously how much \( O_3 \) and \( O \) change with altitude. For these calculations, we used the following reaction rates;

\[ k_1 = \frac{(0.6)^p k_0(t) n(M)}{1 + k_0(t) n(M)} \]

where \( p = 1/[1 + 2 \log(k_0(t) n(M))] \) and \( k_0(t) = 6 \times 10(-34) \left(\frac{300}{t}\right)^{-2.3} \). Here, \( t \) is temperature and \( n(M) \) is number density [13].

\[ k_2 = 8 \times 10^{-12} \exp(-2060/t) \]

where \( t \) is temperature [14]. The reaction rates \( k_3 \) and \( k_4 \) are constant.
Figure 3.2: Time evolution of $\text{O}_2$, $\text{O}_3$, for constant rates.
Figure 3.5: Concentrations of O and O₃ in Atmosphere at steady state.
CHAPTER 4

THE BELOUSOV-ZHABOTINSKY MECHANISM

The Belousov–Zhabotinsky (BZ) system is relatively widely known for its long sequences of oscillations. Even though there has been recent debates about some detailed aspects, the fundamental idea of the BZ mechanism looks to be well constituted. In 1990’s, A. Barr and co-workers [15] contributed something which was quite different from the former works of BZ system. According to their works malonic acid in the system does not affect on the bromide (Br\(^-\)) production. We do not know what future will bring to BZ but it seems that A. Barr and coworkers start to change its appearance from now.

In an open system, chemicals to set a mechanism are constantly being added to the dish and equivalent amount is removed. On the other hand, no chemicals are added or removed in a closed system. The BZ system demonstrates sustained oscillations in a closed system, bistability, birhythmicity and complex limit cycles in an open system.

In the classical Belousov system, there are bromate ions, malonic acid (CH\(_2\)(COOH)\(_2\)) and Ce\(^{3+}\) or Ce\(^{4+}\) as a catalyst in sulfuric acid. The reaction steps to get the cycles in Belousov system can be summarized:
Ce$^{3+}$ is oxidized to Ce$^{4+}$ by BrO$_3^-$

$$\text{Ce}^{3+} \xrightarrow{\text{HBrO}_2} \text{Ce}^{4+} \quad (4.1)$$

The autocatalytic species was HBrO$_2$ or some other free-radical intermediates.

Bromide is strong inhibitor in reaction 4.1. It is produced during the oxidation of bromomalonic acid by Ce$^{4+}$

$$\text{Ce}^{4+} + \text{CHBr(COOH)}_2 \rightarrow \text{Ce}^{3+} + \text{Br}^- + \text{other products} \quad (4.2)$$

An oscillatory cycle can be portrayed in the following way. If Ce$^{4+}$ is in the system, then Br$^-$ is produced in the reaction 4.2. This Br$^-$ may either remove the autocatalysis species or simply vanished from the system. When [Br$^-$] is high enough, the autocatalysis is totally inhibited in reaction 4.1. Ce$^{4+}$ is removed by 4.2, and [Br$^-$] falls rapidly when [Ce$^{4+}$] gets to a lower threshold. Reaction 4.1 then starts to take place rapidly and [Ce$^{4+}$] increases. When [Ce$^{4+}$] gets to an upper threshold, [Br$^-$] sharply increases and inhibits reaction 4.1, and the cycle manifests.

Zhabotinsky observed the same behavior as Belousov did when [Ce$^{4+}$]/[Ce$^{3+}$] was replaced by [Fe(III)]/[Fe(II)] or [Mn(III)]/[Mn(II)] and malonic acid was replaced by other organic acids (Fig. 4.1). Fig. 4.1 says there are four steps in the system:

1. There is an autocatalytic reaction including bromus acid and the amount of the bromus acid is increasing exponentially. Also the production of ferriin, oxidation of ferroin, is the other result of this step.

2. Once the amount of ferriin waxes, it commences to change to ferroin slowly because of the interactions between ferriin and organic components.

45
3. Since the bromide is a strong inhibitor in the autocatalytic process, the production of bromus acid is abandoned and its amount is decreased.

4. In the second step of the system, ferriin changes to ferroin slowly. With time, bromide ions are binded and the system turns back to the first step.

Field, Kőrös, and Noyes developed the first mechanism for the BZ system in 1972 to try to understand the oscillations mathematically. They used 11 reactions and 15 molecules; it is known as the FKN mechanism. Other mechanisms were developed later which used FKN as their starting point. Moreover, a large number of variations of the classic BZ system has been defined after FKN. Györgi, Turányi and Field (GTF) is one of these variations which was discovered in 1990 [16]. GTF tried to understand the experiment by using as complete and full mechanism as they could.
They used 80 reactions and 26 molecules. So far, among the all models for BZ system, GTF is accepted as the most complete mechanism at present but there is still some disagreements [17].

4.1 Simple Models of the BZ system

Field-Noyes reduced the 11 reactions and 15 molecules of FKN to 5 reactions and 9 molecules to understand the mechanism. They used simple rate reducing method. Finally, a number of final reactions were obtained which differed in some details but had the same qualitative behavior. GTF mechanism was also reduced by using some reduction methods mentioned in previous chapter which are, of course, much more complicated since GTF has 80 reactions and 26 molecules.

Here, we want to analyze oscillations in the BZ system. In the following sections we shall emphasize two points. First, we show arguments which explain why many (or most) of the reactions can be neglected. Second, we show the comparisons between a number of models with graphs.

4.1.1 The FKN Model

The analysis of temporal oscillations in the BZ system was done by the FKN in 1972. In table 4.1, we give the FKN mechanism and the estimated rate constants. There are two overall processes in FKN mechanism which are necessary to get oscillations in the BZ system.

Molecular bromine supplies the bromination of malonic acid. There are two ways to produce bromine ions. First, bromate ion (BrO−) is reduced to bromine (Br2) by transferring some oxygens (two electrons reduction). By adding (R3) + (R2) +
<table>
<thead>
<tr>
<th>Reaction Number</th>
<th>Reaction</th>
<th>Rate Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R1)</td>
<td>HOBr + Br⁻ + H⁺ ⇌ Br₂ + H₂O</td>
<td>( k_1 = 8 \times 10^6 M^{-2} s^{-1} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( k_{-1} = 10^2 s^{-1} )</td>
</tr>
<tr>
<td>(R2)</td>
<td>HBrO₂ + Br⁻ + H⁺ ⇌ 2HOBr</td>
<td>( k_2 = 2 \times 10^9 M^{-2} s^{-1} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( k_{-2} = 5 \times 10^{-5} M^{-1} s^{-1} )</td>
</tr>
<tr>
<td>(R3)</td>
<td>BrO₃⁻ + Br⁻ + 2H⁺ ⇌ HBrO₂ + HOBr</td>
<td>( k_3 = 2 M^{-3} s^{-1} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( k_{-3} = 10^4 M^{-1} s^{-1} )</td>
</tr>
<tr>
<td>(R4)</td>
<td>2HBrO₂ ⇌ BrO₃ + HOBr + H⁺</td>
<td>( k_4 = 4 \times 10^7 M^{-1} s^{-1} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( k_{-4} = 2 \times 10^{-10} M^{-2} s^{-1} )</td>
</tr>
<tr>
<td>(R5)</td>
<td>BrO₃⁻ + HBrO₂ + H⁺ ⇌ 2BrO₂⁺ + H₂O</td>
<td>( k_5 = 10^4 M^{-2} s^{-1} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( k_{-5} = 2 \times 10^7 M^{-1} s^{-1} )</td>
</tr>
<tr>
<td>(R6)</td>
<td>BrO₂⁺ + Ce³⁺ + H⁺ ⇌ HBrO₂ + Ce⁴⁺</td>
<td>( k_6 = 6 \times 10^5 M^{-2} s^{-1} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( k_{-6} = 5 \times 10^7 M^{-1} s^{-1} )</td>
</tr>
<tr>
<td>(R7)</td>
<td>BrO₂⁺ + Ce⁴⁺ + H₂O ⇌ BrO₃⁻ + Ce³⁺ + H⁺</td>
<td>( k_7 = 10 M^{-1} s^{-1} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( k_{-7} = 5 \times 10^{-5} M^{-3} s^{-1} )</td>
</tr>
<tr>
<td>(R8)</td>
<td>Br₂ + CH₂(COOH)₂ → BrCH(COOH)₂ + Br⁻ + H⁺</td>
<td>( v_8 = k_8 [H⁺][MA] )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( k_8 = 10^{-2} M^{-1} s^{-1} )</td>
</tr>
<tr>
<td>(R9)</td>
<td>6Ce⁴⁺ + CH₂(COOH)₂ + 2H₂O →</td>
<td>( v_9 = k_9 [MA][Ce³⁺] )</td>
</tr>
<tr>
<td></td>
<td>6Ce³⁺ + HCOOH + 2CO₂ + 6H⁺</td>
<td>( k_9 = 0.09 s^{-1}/(0.5 M + [MA]) )</td>
</tr>
<tr>
<td>(R10)</td>
<td>4Ce⁴⁺ + BrCH(COOH)₂ + 2H₂O →</td>
<td>( v_{10} = k_{10}[BrMA][Ce³⁺] )</td>
</tr>
<tr>
<td></td>
<td>4Ce³⁺ + HCOOH + Br⁻ + 2CO₂ + 5H⁺</td>
<td>( k_{10} = 0.015 s^{-1}/(0.2 M + [BrMA]) )</td>
</tr>
<tr>
<td>(R11)</td>
<td>Br₂ + HCOOH → 2Br⁻ + CO₂ + 2H⁺</td>
<td>( v_{11} = k_{11}[Br₂][HCOOH]/[H⁺] )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( k_{11} = 7.5 \times 10^{-3} s^{-1} )</td>
</tr>
</tbody>
</table>

Table 4.1: Reactions of Field–Korös–Noyes System and Rate Constants
3(R1), we have

\[ \text{BrO}_3^- + 5\text{Br}^- + 6\text{H}^+ \rightarrow 3\text{Br}_2 + 3\text{H}_2\text{O}. \]  \hfill (A)

Second, bromus acid is produced autocatalytically by involving metal ions to get bromine ions. Combining (R5) and 2(R6), we obtain

\[ \text{BrO}_3^- + \text{HBrO}_2 + 3\text{H}^+ + 2\text{Ce}^{3+} \rightarrow 2\text{HBrO}_2 + \text{H}_2\text{O} + 2\text{Ce}^{4+}. \]  \hfill (B)

The exponential growth of \([\text{HBrO}_2]\) is prevented by (R4) which establishes a steady state concentration of bromus acid. With \(5(B) + 3(R4) + (R1) - (R2)\), we have

\[ 2\text{BrO}_3^- + 12\text{H}^+ + 10\text{Ce}^{3+} \rightarrow \text{Br}_2 + 6\text{H}_2\text{O} + 10\text{Ce}^{4+}. \]  \hfill (C)

Since bromine does not accumulate in noticeable amounts in the BZ system, it must be consumed whenever it is produced. But bromine can be consumed with MA to get BrMA (R8) and by bromination of other organic elements. On the other hand, we can make bromine disappear completely, and use HOBr as brominating agent

\[ \text{HOBr} + \text{CH}_2(\text{COOH})_2 \rightarrow \text{BrCH( COOH)}_2 + \text{H}_2\text{O}. \]  \hfill (R8')

In this case, we have to modify (A) and (C) as

\[ \text{BrO}_3^- + 2\text{Br}^- + 3\text{H}^+ \rightarrow 3\text{HOBr}, \]  \hfill (A')

\[ \text{BrO}_3^- + 5\text{H}^+ + 4\text{Ce}^{3+} \rightarrow \text{HOBr} + 2\text{H}_2\text{O} + 4\text{Ce}^{4+}. \]  \hfill (C')

Finally, we have two methods to produce BrMA. Since the reaction of bromide with bromus acid (R2) is very rapid, these two methods are not compatible with each other. Because of this reason, bromus acid and bromide ions cannot exist in significant amounts. Bromate will react dominantly with bromide by reaction (R3)
if $[\text{Br}^-]$ is large and $[\text{HBrO}_2]$ is small, and $[\text{HBrO}_2]$ will remain small as long as $k_2[\text{Br}^-] \geq k_5[\text{BrO}_3^-]$. With these conditions, bromine ions are always produced by Process (A). Since Process (A) uses bromide ions, $[\text{Br}^-]$ will decrease and eventually reach

$$[\text{Br}^-]_{\text{crit}} = \frac{k_5}{k_2}[\text{BrO}_3^-].$$

If $[\text{Br}^-]$ goes below $[\text{Br}^-]_{\text{crit}}$, bromus acid begins to accumulate exponentially. This keeps $[\text{Br}^-]$ still lower (step R2) and causes to return to Process (C) during the oxidation of the transition metal ion. If the metal ion catalyst were not returned to the lower oxidation state Process (C) would stop soon. This happens by the oxidation of MA by Ce$^{4+}$ (reaction R9). Now to get oscillation, dominance must be returned from Process (C) to Process (A) which is accomplished by oxidation of BrMA by the transition metal ion (R10) to reproduce bromide ion. To do this, we add (R9), (R10), and 2(R11) and we obtain

$$10\text{Ce}^{4+} + \text{CH}_2(\text{COOH})_2 + \text{BrCH}(\text{COOH})_2 + 4\text{H}_2\text{O} + 2\text{Br}_2 \rightarrow 10\text{Ce}^{3+} + 5\text{Br}^- + 6\text{CO}_2 + 15\text{H}^+. \quad (J)$$

When Process (J) starts, the transition metal is returned to the lower oxidation state and $[\text{Br}^-]$ starts going up. Once $[\text{Br}^-]$ drops $[\text{Br}^-]_{\text{crit}}$ from below, the autocatalytic production of bromus acid can not be compatible with its reduction by bromide (Reaction (R2)). Thus reaction changes from Process (C) to Process (A) and the whole sequence of reactions repeats. From the above explanations oscillations in the BZ system is a sequence of reactions in which Processes (A), (C), and (J) are predominant.
4.1.2 Oregonator

From the FKN system, Field and Noyes (1974) [18] brought out a simpler model that keeps the most important features of the Field–Körös–Noyes mechanism. This system is called Oregonator since this work has been done in University of Oregon. According to Field and Noyes’ understanding of the FKN mechanism, they took most important five reactions which are
(R3) - The rate limiting step for process (A)
(R5) - The rate limiting step for process (C)
(R2) - The step controlling the switching between (A) and (C)
(R4) - The step limiting the autocatalytic production of HBrO₂
(i) - The process that generates Br⁻ and Ce³⁺.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>[HOBr]</td>
</tr>
<tr>
<td>T</td>
<td>Time</td>
</tr>
<tr>
<td>U</td>
<td>[BrO₃⁻]</td>
</tr>
<tr>
<td>V</td>
<td>[Organic intermediates]</td>
</tr>
<tr>
<td>X</td>
<td>[HBrO₂]</td>
</tr>
<tr>
<td>Y</td>
<td>[Br⁻]</td>
</tr>
<tr>
<td>Z</td>
<td>[Ce⁴⁺]</td>
</tr>
<tr>
<td>Z</td>
<td>[Ce³⁺]</td>
</tr>
<tr>
<td>H</td>
<td>[H⁺]</td>
</tr>
<tr>
<td>C</td>
<td>[Ce]_{total}</td>
</tr>
</tbody>
</table>

Table 4.2: Table of Notations
Field-Noyes model can be written by using the notation given in Table 4.1.2, as

\[
\frac{dX}{dT} = k_3 H^2 U Y - k_2 H X Y + k_5 H U X - 2k_4 X^2
\]

\[
\frac{dY}{dT} = -k_3 H^2 U Y - k_2 H X Y + l k_j V Z
\]

\[
\frac{dZ}{dT} = k_5 H U X - k_j V Z
\]

(4.3)

where \(k_i\)'s are the rate constant of the FKN mechanism, and \(l\) is the rate number of bromine ions set free per \(Ce^{4+}\) consumed during the oxidation of organic species. The estimated six parameters in the system 4.4 are

\[
k_2 H \approx 1.6 \times 10^9 M^{-1}s^{-1}
\]

\[
k_3 H^2 U \approx 0.08 s^{-1}
\]

\[
k_4 \approx 4 \times 10^7 M^{-1}s^{-1}
\]

\[
k_5 H U \approx 500 s^{-1}
\]

\[
k_j V \approx 1 s^{-1}
\]

\[
l \approx 0.5
\]

and \(H = 0.8\) M and \(U = 0.06\) M.

The system 4.4 can be handled more easily in dimensionless form introducing dimensionless variables \(\alpha, \beta, \gamma,\) and \(\tau\) and by employing the dimensionless constants \(q, s,\) and \(w.\)

Let

\[
\alpha = X/X_0, \quad X_0 = \frac{k_5 H U}{k_2} \approx 5 \times 10^{-11} M
\]

\[
\beta = Y/Y_0, \quad Y_0 = \frac{k_5 U}{k_2} \approx 3 \times 10^{-7} M
\]

\[
\gamma = Z/Z_0, \quad Z_0 = \frac{2k_5 k_6 H^2 U^2}{k_2 k_j V} \approx 5 \times 10^{-8} M
\]
\[ \tau = \frac{T}{T_0}, \quad T_0 = (k_3k_5H^3U^2)^{-1/2} \approx 0.16s \]

\[ s = \frac{k_3V}{k_3H} = 77.27 \]

\[ w = \frac{1}{\sqrt{k_3k_5H^3V}} = 0.1610 \]

\[ q = \frac{2k_3k_4U}{k_2k_5V} = 8.375 \times 10^{-6} \]

\[ f = 2l \approx 1 \]

with these terms, we have

\[
\frac{d\alpha}{d\tau} = s(\beta - \alpha\beta + \alpha - q\alpha^2) \\
\frac{d\beta}{d\tau} = s^{-1}(-\beta - \alpha\beta + f\gamma) \\
\frac{d\gamma}{d\tau} = w(\alpha - \gamma).
\] (4.4)

Since we were looking for the concentration-time relations, we now come up with the system 4.5 to realize our goal. In the following sections, we shall look at the numerical solutions.

### 4.1.3 GTF Model

Györgi, Turányi and Field (GTF) introduced a 80-reaction and 26-species mechanistic model (see Table 4.2) for BZ system [16]. By using the reduction methods mentioned in chapter 3, they reduced this system to 42-reaction and 22-species which agrees qualitatively with the original system. This reduced system was further simplified to skeletons including 3-variable which are HBrO₂, Br⁻ and Ce⁴⁺. We will also observe that these skeletons contrast with the Oregonator. Indeed, we get more accurate approximations to original system with skeleton models than Oregonator.
The interpretation of oscillations in simulations follows by recognizing the major feedback$^2$ loops in the GTF mechanism. The oxidation of Ce$^{3+}$ to Ce$^{4+}$ and the autocatalysis$^3$ of HBrO$_2$ occur in a sequence which is reactions 9–14. In this mechanism, HBrO$_2$ is the primary positive feedback. At the end of this sequence of reactions, we would have a high-[HBrO$_2$], high-[Ce$^{4+}$], and oxidized steady state given by low-[Br$^-$] because of reaction 3. The oxidized state cannot recover permanent dominance since the Ce$^{4+}$ made in reaction 13 generates an intermediate that wipes out HBrO$_2$, thus it inhibits the autocatalytic reaction which is called “delayed negative feedback.” Since the rate of reaction 3 is much larger than the rate of reaction 9, the autocatalysis is abandoned. After this result, [Br$^-$] becomes high, and the system turns to high-[Br$^-$], low-[HBrO$_2$], low-[Ce$^{4+}$], called “reduced state.” When the consumption of Br$^-$ is enough in reaction 5 to lessen its concentration to a step where the reaction 9 is faster than reaction 3, the reduced state ends. Finally, the autocatalytic process may commence again.

In the following paragraphs, we shall describe the reduction method of GTF mechanism. As we mentioned in chapter 3, by doing the reduction of mechanism, we identify the minimal set of reactions that still quantitatively reproduces the behavior of the original mechanism.

$^2$In a reaction mechanism, if the product of one step has an effect on other reaction steps, then this product is called feedback.

$^3$Autocatalysis is the process in which a chemical component is engaged to its own production. For example,

$$A + B \rightleftharpoons 2B$$

where a molecule B reacts on one of A to constitute two molecules of B.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) HOBr + Br− + H+ → Br2 + H2O</td>
<td>2.3E+9 M−2 s−1</td>
</tr>
<tr>
<td>(2) Br2 + H2O → HOBr + Br− + H+</td>
<td>2.6E−1 s−1</td>
</tr>
<tr>
<td>(3) Br− + HBrO2 + H+ → 2HBr</td>
<td>2.0E+4 M−1 s−1</td>
</tr>
<tr>
<td>(4) 2HBrO → Br− + HBrO2 + H+</td>
<td>2.0E−3 M−1 s−1</td>
</tr>
<tr>
<td>(5) Br− + BrO− + 2H+ → HOBr + HBrO2</td>
<td>3.0E−5 M−1 s−1</td>
</tr>
<tr>
<td>(6) HOBr + HBrO2 → Br− + BrO− + 2H+</td>
<td>3.3E−2 M−1 s−1</td>
</tr>
<tr>
<td>(7) HBrO2 → BrO− + HOBr + H+</td>
<td>3.0E+3 M−1 s−1</td>
</tr>
<tr>
<td>(8) BrO− + H2O → Br− + H2O</td>
<td>7.5E−5 s−1</td>
</tr>
<tr>
<td>(9) BrO− + H2 + Br2O3 + H2O</td>
<td>3.3E+1 M−1 s−1</td>
</tr>
<tr>
<td>(10) BrO− + H2O → Br2O5 + H2O + H+</td>
<td>2.2E−3 s−1</td>
</tr>
<tr>
<td>(11) Br2O5 → 2BrO3</td>
<td>7.4E−5 s−1</td>
</tr>
<tr>
<td>(12) 2BrO3− → Br2O4</td>
<td>1.4E+9 M−2 s−1</td>
</tr>
<tr>
<td>(13) Ce4+ + Ce3+ + H+ → HBrO2 + Ce5+</td>
<td>6.2E+4 M−1 s−1</td>
</tr>
<tr>
<td>(14) HBrO2 + Ce5+ → Ce6+ + BrO− + H+</td>
<td>7.0E−3 M−1 s−1</td>
</tr>
<tr>
<td>(15) MA = ENOL</td>
<td>3.0E−3 s−1</td>
</tr>
<tr>
<td>(16) ENOL = MA</td>
<td>2.0E+9 s−1</td>
</tr>
<tr>
<td>(17) ENOL + Br2 → BrMA + Br− + H+</td>
<td>1.9E+6 M−1 s−1</td>
</tr>
<tr>
<td>(18) MA + HOBr → BrMA + H2O</td>
<td>6.2E−3 s−1</td>
</tr>
<tr>
<td>(19) BrMA + HOBr → Br2MA + H2O</td>
<td>1.0E−1 M−1 s−1</td>
</tr>
<tr>
<td>(20) TTA + HOBr → BrTTA + H+</td>
<td>5.0E−5 M−1 s−1</td>
</tr>
<tr>
<td>(21) Br2MA + H2O → HBrO2 + TTA</td>
<td>1.0E−1 s−1</td>
</tr>
<tr>
<td>(22) Br2MA → HOb → H2O</td>
<td>1.0E−1 s−1</td>
</tr>
<tr>
<td>(23) Br2TTA → HBrO2 + MOA</td>
<td>1.0E−1 s−1</td>
</tr>
<tr>
<td>(24) BrTTA → Br− + MOA + H+</td>
<td>1.0E−1 s−1</td>
</tr>
<tr>
<td>(25) Ce4+ + BrMA → Ce5+ + BrMA + H+</td>
<td>9.0E−2 M−1 s−1</td>
</tr>
<tr>
<td>(26) Ce4+ + MA → Ce5+ + MA + H+</td>
<td>2.3E−3 M−1 s−1</td>
</tr>
<tr>
<td>(27) Ce4+ + TTA → Ce5+ + TTA + H+</td>
<td>6.0E−3 M−1 s−1</td>
</tr>
<tr>
<td>(28) HOBr + MOA + Br− + OA + *COOH</td>
<td>1.4E+2 M−1 s−1</td>
</tr>
<tr>
<td>(29) Ce4+ + MOA + H2O → Ce5+ + MOA + *COOH + H+</td>
<td>1.0E+1 M−1 s−1</td>
</tr>
<tr>
<td>(30) HOBr + OA → Br− + *COOH + CO2 + H2O</td>
<td>1.4E−2 M−1 s−1</td>
</tr>
<tr>
<td>(31) Ce5+ + OA → Ce4+ + *COOH + CO2 + H2O</td>
<td>1.0E+1 M−1 s−1</td>
</tr>
<tr>
<td>(32) Br− + MOA</td>
<td>1.6E−5 M−1 s−1</td>
</tr>
<tr>
<td>(33) Br2MA</td>
<td>1.6E+8 M−1 s−1</td>
</tr>
<tr>
<td>(34) Br2MA → Br2MA</td>
<td>1.6E+9 s−1</td>
</tr>
<tr>
<td>(35) Br2MA + H2O → Br2MA + BrTTA</td>
<td>1.6E+8 M−1 s−1</td>
</tr>
<tr>
<td>(36) Br2MA + *MA + H2O → MA + BrTTA</td>
<td>6.0E−9 M−1 s−1</td>
</tr>
<tr>
<td>(37) Br2MA − TTA + H2O → TTA</td>
<td>1.0E−9 s−1</td>
</tr>
<tr>
<td>(38) Br2MA + Ce4+ + H2O → Ce5+ + BrTTA + H+</td>
<td>6.0E−7 s−1</td>
</tr>
<tr>
<td>(39) Br2MA + BrO− + H2O → HBrO2 + BrTTA</td>
<td>5.0E−9 M−1 s−1</td>
</tr>
<tr>
<td>(40) Br2MA + *COOH → BrMA + CO2</td>
<td>5.0E−9 M−1 s−1</td>
</tr>
</tbody>
</table>

Figure 4.2: The GTF Mechanism.
Reduction of GTF Mechanism:

The first step in a reduction of a system is to determine the classification of the components of the system into three groups, important, necessary and redundant species. The important species in GTF are \( \text{Br}^- \), \( \text{Ce}^{4+} \), \( \text{BrO}_5^- \), MA, \( \text{Br}_2 \), \( \text{CO}_2 \), HBrO, BrMA, and MA*. To omit a reaction from the full system without any major effect, we perform a principal component analysis (PCA) on the full model, but only with the important and necessary species in the objective function.

Turányi et al. showed the consuming and producing reactions of redundant species of GTF mechanism can be removed from the full mechanism without affecting the behavior of the model. With this procedure, we get three species as redundant which are TTA, TTA*, and BrO2TTA. Since Br2MA is only a product species which was not assumed as an important species above, it can be eliminated from the mechanism. The important reactions are determined by observing large elements, greater than 0.2 in absolute value, with eigenvalues larger than 0.01, and are not consuming reactions of any non-important species. Turányi et al. gave also a table of summarizing the results from their simulations[17].

Skeleton Models:

In this step, the goal is the identification of the minimal set of reactions and species that still generates the limit cycles in concentrations \( \text{Br}^- \) and \( \text{Ce}^{4+} \). Since our aim is to get models that produce limit-cycle oscillations, Turányi et al. took pool-component approximation for a number of species, specifically for MA, \( \text{BrO}_3^- \), \( \text{H}^+ \). The concentration of these species was kept at the initial value during simulations. It has been shown that reactions 11 and 12 are in a fast equilibrium most of the time.
In the analysis of GTF model, if these are not fast then reactions 10 and 12 behave much slower than reactions 9 and 11. In the last case, the rate determining step is reaction 9. Then we can switch reactions 9–12 with equilibrium reaction

$$\text{BrO}_3^- + \text{HBrO}_2 + \text{H}^+ \rightleftharpoons 2\text{BrO}_2^* + \text{H}_2\text{O} \quad (82,83)$$

where $k_{82} = k_9 = 33.0 M^{-2}s^{-1}$, and $k_{83} = k_{10}(k_{11}/k_{12}) = 4.2 \times 10^7 M^{-1}s^{-1}$. The resulting mechanism contains the following reactions:

$$\begin{align*}
\text{HBrO}_2 + \text{Br}^- + \{\text{H}^+\} & \rightarrow /2\text{HOBr}/ \quad (3) \\
\text{Br}^- + \{\text{BrO}_3^-\} + \{2\text{H}^+\} & \rightarrow \text{HBrO}_2 + /\text{HOB}r/ \quad (5) \\
2\text{HBrO}_2 & \rightarrow \{\text{BrO}_3^-\} + /\text{HOBr} + \{\text{H}^+\} \quad (7) \\
\text{HBrO}_2 + \{\text{BrO}_3^-\} + \{\text{H}^+\} & \rightleftharpoons 2\text{BrO}_2^* + \{\text{H}_2\text{O}\} \quad (82,83) \\
\text{Ce}^{3+} + \text{BrO}_2^* + \{\text{H}^+\} & \rightleftharpoons \text{Ce}^{4+} + \text{HBrO}_2 \quad (13,14) \\
\text{Ce}^{4+} + \{\text{MA}\} & \rightarrow 2\text{Ce}^{3+} + \text{Br}^- + \{3\text{H}^+\} + \{\text{MA}\} \quad (81) \\
& \quad + /\text{MOA}/ - \text{Ce}^{4+} - \{\text{BrMA}\}
\end{align*}$$

where curly brackets indicate pool components (that is, concentrations remain constant) and slashes denote inactive products (that is, we are ignoring their time evolutions). This is called model A. From this model, we derive three skeleton models.

By elimination of two components, Ce$^{3+}$ ions and BrO$_2^*$, we get the models. The classic Oregonator does not consist of reactions 83 and 14, and BrO$_2^*$ is at quasi-steady-state since reaction 82 produces and reaction 13 consumes it.

But experimental studies showed that we cannot ignore the reactions 83 and 14. Ce$^{3+}$ ions were eliminated since Ce$^{3+}$ ions does not show up in the rate equations.
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>[HBrO₂]</td>
</tr>
<tr>
<td>Y</td>
<td>[Br⁻]</td>
</tr>
<tr>
<td>Z</td>
<td>[Ce⁴⁺]</td>
</tr>
<tr>
<td>A</td>
<td>[HOBr]</td>
</tr>
<tr>
<td>c</td>
<td>[Ce]_{total}</td>
</tr>
<tr>
<td>T</td>
<td>Time</td>
</tr>
<tr>
<td>U</td>
<td>[BrO₃⁻]</td>
</tr>
<tr>
<td>V</td>
<td>Malonic Acid</td>
</tr>
<tr>
<td>H</td>
<td>[H⁺]</td>
</tr>
</tbody>
</table>

Table 4.3: Table of Notations

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-1</td>
<td>(X + Y + H \rightarrow /2A/) (k_{3xyh})</td>
</tr>
<tr>
<td>O-2</td>
<td>(Y + U + 2H \rightarrow X + /A/) (k_{5yuH²})</td>
</tr>
<tr>
<td>O-3</td>
<td>(2X \rightarrow /A/ + U + H) (k_{7X²})</td>
</tr>
<tr>
<td>O-4</td>
<td>(X + U + H \rightarrow 2X + Z) (k_{9xuh})</td>
</tr>
<tr>
<td>O-5</td>
<td>(Z + V \rightarrow Y) (k_{26vz})</td>
</tr>
</tbody>
</table>

Table 4.4: The Oregonator Model

For the elimination of \(\text{BrO}_2^*\) radical, there are two ways. In the first approach, it is assumed reactions 82 and 83 are at equilibrium,

\[
[\text{BrO}_2^*]_{\text{EQ}} = \left( \frac{k_{82}}{k_{83}}[\text{BrO}_2^-][\text{H}^+] \right)^{1/2} \left( [\text{HBrO}_2] \right)^{1/2}.
\]

As a second approach, but more accurate, we use the quasi-steady-state assumption (QSSA). It takes all steps that affect the concentration of \(\text{BrO}_2^*\) and gets

\[
[\text{BrO}_2^*]_{\text{QSS}} = \frac{1}{2} \left[ - \frac{k_{13}}{2k_{83}}[\text{H}^+][\text{Ce}^{3+}] + Q \right]
\]
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC-1</td>
<td>$X + Y + H \rightarrow /2A/ k_3xuh$</td>
</tr>
<tr>
<td>BC-2</td>
<td>$Y + U + 2H \rightarrow X + /A/ k_3yu h^2$</td>
</tr>
<tr>
<td>BC-3</td>
<td>$2X \rightarrow /A/ + U + H k_7x^2$</td>
</tr>
<tr>
<td>BC-4</td>
<td>$0.5X + U + H \rightarrow X + Z k_{13}(c - z)u_{est}h$</td>
</tr>
<tr>
<td>BC-5</td>
<td>$X + Z \rightarrow 0.5X + U + H k_{14}xz$</td>
</tr>
<tr>
<td>BC-6</td>
<td>$Z + V \rightarrow Y - Z k_{26}vz$</td>
</tr>
</tbody>
</table>

Table 4.5: Model B and Model C

where

$$Q = \left( \left( \frac{k_{13}}{2k_{83}} [H^+] [\text{Ce}^{3+}] \right)^2 + 4 \frac{[\text{HBrO}_2]}{k_{83}} \left( k_{82} [\text{BrO}_3^-][H^+] + \frac{k_{14}}{2} [\text{Ce}^{4+}] \right) \right)^{1/2}.$$  

The $\text{Ce}^{3+}$ can be calculated from

$$[\text{Ce}]_{\text{total}} = [\text{Ce}^{3+}] + [\text{Ce}^{4+}].$$

Ultimately, we get two models B and C: In model B, we use equilibrium assumption to estimate $[\text{BrO}_2^2]$ while QSSA is used in model C. Here we will focus on the model C.

After these two models, we can still derive one more model that is as simple as the Oregonator and still approaches the behavior of GTF mechanism. To get this model, it is assumed that the reactions (82,83) followed by the reactions (13,14) are reversible, but the reactions 82 and 14 are the rate determining steps in the forward and backward directions, respectively. In the Oregonator, there is a similar assumption that eliminates $\text{Ce}^{3+}$ ion from the mechanism, and that accepts reaction 9 is the rate determining steps for $\text{HBrO}_2$. The reverse stoichiometry is represented by the sequence (14,83) which is the only difference. This model is called D.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-1 X + Y + H → /2A/</td>
<td>$k_3xyh$</td>
</tr>
<tr>
<td>D-2 Y + U + 2H → X + /A/</td>
<td>$k_3yuh^2$</td>
</tr>
<tr>
<td>D-3 2X → /A/ + U + H</td>
<td>$k_7x^2$</td>
</tr>
<tr>
<td>D-4 X + U + H → 2X + 2Z</td>
<td>$k_9xuh$</td>
</tr>
<tr>
<td>D-5 X + Z → 0.5X + U + H</td>
<td>$k_{14}xz$</td>
</tr>
<tr>
<td>D-6 Z + V → Y - Z</td>
<td>$k_{26}vz$</td>
</tr>
</tbody>
</table>

Table 4.6: Model D

We will observe the graphics for three cases:

**A.** $[\text{HBrO}_2] = 0.162 \times 10^{-04} M$, $[\text{Br}^-] = 0.598 \times 10^{-03} M$, $[\text{Ce}^{4+}] = 0.200 \times 10^{-02} M$, $[\text{BrO}_3^-] = 0.0866 M$, $[\text{H}^+] = 1.3 M$, $[\text{MA}] = 0.5739 M$, and $[\text{Ce}]_{\text{tot}} = 0.001 M$,

**B.** $[\text{HBrO}_2] = 3.420 \times 10^{-06} M$, $[\text{Br}^-] = 1.090 \times 10^{-04} M$, $[\text{Ce}^{4+}] = 4.580 \times 10^{-04} M$, $[\text{BrO}_3^-] = 0.0895 M$, $[\text{H}^+] = 1.3 M$, $[\text{MA}] = 0.3696 M$, and $[\text{Ce}]_{\text{tot}} = 0.02 M$,

**C.** $[\text{HBrO}_2] = 2.780 \times 10^{-08} M$, $[\text{Br}^-] = 1.640 \times 10^{-05} M$, $[\text{Ce}^{4+}] = 0.0001 M$, $[\text{BrO}_3^-] = 0.0986 M$, $[\text{H}^+] = 1.3 M$, $[\text{MA}] = 0.2174 M$, and $[\text{Ce}]_{\text{tot}} = 0.0005 M$.

In all figures, we see the comparison of the oscillations produced by model B, model C, GTF model and the Oregonator. To compare the period of the oscillations and behavior of concentrations for four different models, we drew the graphs for $[\text{Br}^-]$ (short-dashed line), $[\text{HBrO}_2]$ (long-dashed line), $[\text{Ce}^{4+}]$ (solid line) in figures 4.3–4.8. For the calculations of the concentrations in the GTF model, we used the initial concentrations given above and $10^{-10}$ for the remaining concentrations. In each case, we use two sets of comparisons. The first is for times 0–600 and the second blows up a small region from 400 to 600 which has periodic oscillations. We notice that GTF
takes some time to begin oscillating while the others do not (see Figure 4.3(d)). If we look at the figures 4.5(d), 4.6(d), we notice that the full GTF mechanism goes to steady-state – as does real experiment – unlike the other 3 models.

In case A, the periods of the Oregonator model are 3 times bigger than the periods of the model D and 2 times bigger than the periods of model C and the full GTF model, and the peak of $[\text{Ce}^{4+}]$ in model D is 3 times higher than the full GTF mechanism while this is 10 times bigger than GTF mechanism for the others. In case B, the periods of the Oregonator model are 3 times bigger than the periods of the other models. In case C, the periods of the Oregonator model are 4 times bigger than the periods of the other models. The peak values of the other two concentrations are almost same as the full GTF mechanism. Finally, we can say the models C and D give better results than the Oregonator model.

Figures 4.9–4.11 show the $\log[\text{Br}^-] - \log[\text{Ce}^{4+}]$ phase plane in order to observe the limit cycle behavior of the skeletons for 0–600 seconds. In these figures, we observe the model C is better than the others.
Figure 4.3: Plots of concentrations vs time produced by case A.
Figure 4.4: Blow up of Figure 4.3.

(a) The Oregonator Model

(b) Model D

(c) Model C

(d) The GTF model
Figure 4.5: Plots of concentrations vs time produced by case B.
Figure 4.5: Blow up of Figure 4.5.
Figure 4.7: Plots of concentrations vs time produced by case C.
Figure 4.8: Blow up of Figure 4.7.
Figure 4.9: Limit cycles in the $\log[\text{Br}^-]$ – $\log[\text{Ce}^{4+}]$ phase plane produced by model GTF (solid line), model D (short-dashed line), model C (dotted line) and the Oregonator model (long-dashed line) for 0–600 seconds.
Figure 4.10: Limit cycles in the log[Br⁻] – log[Ce⁴⁺] phase plane produced by model GTF (solid line), model D (short-dashed line), model C (dotted line) and the Oregonator model (long-dashed line) for 0–600 seconds.
Figure 4.11: Limit cycles in the log[Br−] − log[Ce4+] phase plane produced by model GTF (solid line), model D (short-dashed line), model C (dotted line) and the Oregonator model (long-dashed line) for 0–600 seconds.
BIBLIOGRAPHY


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