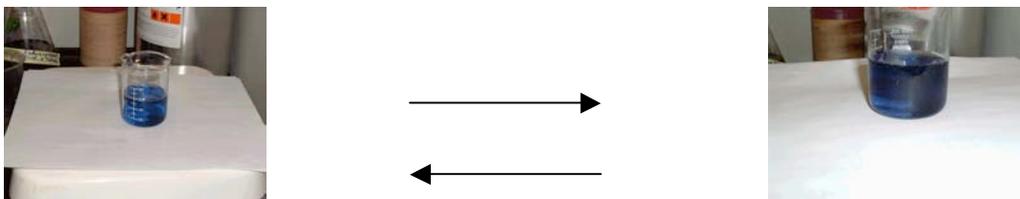


The vast majority of chemical reactions proceed to equilibrium through a monotonic mechanism. In recent years, however, nonlinear, oscillating chemical reactions have been widely studied, characterized, and modeled. Such chemical reactions share remarkable similarities with biological and neuronal processing that are capable of timing, switching, and signal propagation (Strizhak and Menzinger, 1996). Related reactions such as the Brusselator and the Belousov-Zhabotinskii reaction both display similar behavior and can be modeled with related differential equations. The oscillatory nature of these reactions can be described by a stable limit cycle.

The oscillatory behavior of these nonlinear systems was the topic of much debate in early years, as classical chemists argued that they violated the second law of thermodynamics (the Gibbs Free Energy of a system must decrease monotonically in a spontaneous process) (Pojman, Craven, and Leard, 1994). The spontaneous organization and the periodic changes in concentration of both reactants and products, however, can occur as long as the net entropy change in the universe is positive. Thus explaining why the concentrations of the intermediates can oscillate with time, while the free energy monotonically decreases. The oscillatory nature of these reactions was experimentally observed as shown below.



“The Brusselator” is an oscillating chemical reaction that was first described by Ilya Prigogine, a Belgian-American physical chemist. Generally, a reaction rate for a

given reaction is proportional to the concentration of the reactants. For the generic reaction



the reaction rate, which is the change in concentration of the reactants, can be written as a function of the rate constant, k , and the concentrations of the reactants, written as $[A]$ (Ault and Holmgreen, 2003).

$$r = k [A] [B] \quad (2)$$

With the addition of a second chemical reaction, the system becomes nonlinear and thus more complex.



Since the coefficients of the reagents are now greater than one, the reaction rate of A can now be described as a nonlinear system.

$$r = k_1[A][B] - 2k_3[A]^2 \quad (4)$$

The proposed mechanism for the Brusselator, which is the sum of these two reactions is described below.



The two reagents of interest are X and Y (intermediates) in these equations because they are the species involved in the autocatalytic steps. Autocatalytic steps are defined as a chemical that is involved in its own synthesis. The rate of the above set of reactions with respect to X is simply the sum of the individual rates and is thus given by:

$$r_x = [A] + [X]^2[Y] - [B][X] - [X] \quad (9)$$

A positive value denotes when X is being produced, while a negative value is used for the rate when X is being used. Similarly, the rate of the total reaction with respect to Y is given by:

$$r_y = [B][X] - [X]^2[Y] \quad (10)$$

The differential equations modeling this system are thus given by

$$dx/dt = A + (X^2)Y - BX - X \quad (11)$$

$$dy/dt = BX - (X^2)Y$$

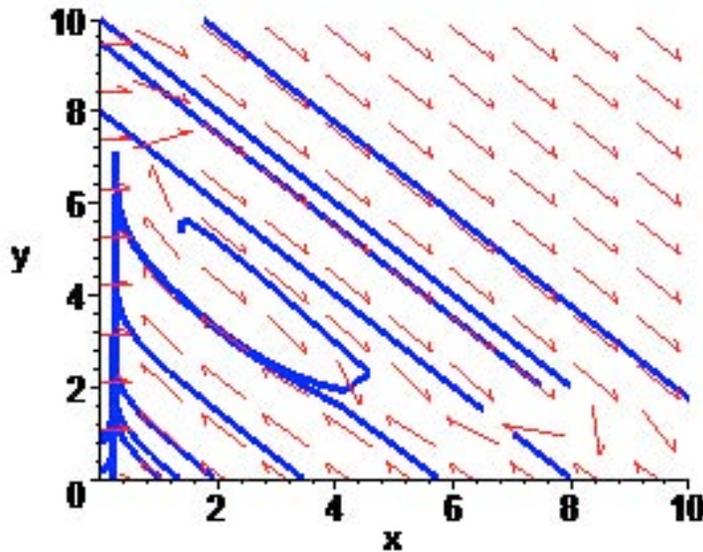
Such oscillating reactions, also known as “chemical clocks,” must satisfy two conditions. First, the reaction must be far from equilibrium by large excesses in both concentrations of reactants (Dissipative Systems 3). This guarantees that the concentration of the reactants A and B do not change with time (Ault and Holmgren, 2003). When this condition is imposed, it is not sufficient to guarantee chemical oscillations because all spontaneous reactions will proceed to equilibrium even when far from equilibrium. Hence, the necessity for the second condition, at least one autocatalytic step must be present in the mechanism of the reaction. A product of the chemical system that is involved in its own synthesis is defined as autocatalytic, and is thus what makes the equation nonlinear.

Equilibria points for the system of differential equations given in (11) can be calculated by solving the system of equations below.

$$a - bx - x + x^2y = 0 \quad (12)$$

$$bx - x^2y = 0$$

By adding the two equations, x is found to equal a , and by plugging that into (12), the equilibrium point is determined to be $(a, b/a)$. Therefore, this is the only equilibrium point of the system. Shown below is the phase diagram for the system of differential equations, clearly showing the single equilibrium point.



To begin to determine the stability of the system, the Jacobian matrix is calculated next.

$$Df(x,y) = \begin{bmatrix} -b-1+2xy & x^2 \\ b-2xy & -x^2 \end{bmatrix} \quad (13)$$

When evaluated at the equilibrium point, the Jacobian becomes:

$$Df(a, b/a) = \begin{bmatrix} b-1 & a^2 \\ -b & -a^2 \end{bmatrix} \quad (14)$$

The trace and determinant of (12) can also be computed.

$$\text{Trace}(Df(a, b/a)) = -a^2 + b - 1 \quad (15)$$

$$\text{Det}(Df(a, b/a)) = a^2 \quad (16)$$

Because the determinant is greater than zero (a is always positive), and a is greater than zero, the equilibrium point is locally never a saddle point (Ault and Holmgren, 2003). In order for the trace to be less than zero (stable), $b < a^2 + 1$. In this situation, the equilibrium point is an attractor or stable. When $b > a^2 + 1$, the equilibrium point is a repeller and thus the local phase portrait is an unstable spiral.

Thus the Brusselator has the possibility of Hopf bifurcation. A Hopf bifurcation is defined as “a bifurcation of a fixed point to a limit cycle” (Weisstein, 2004). Using the critical stable and unstable values of b above, one can determine that a Hopf bifurcation, and therefore a stable limit cycle, is a possible solution to this nonlinear differential equation. For example, when $a = 2$, and $b < a^2 + 1$ ($b < 5$) there is no limit cycle for the solution (Verhulst, 1980). This is, in fact, when the trace is less than zero and stable, and therefore would produce a phase portrait that is locally a stable spiral. While no proof will be given in this dissertation, this can be argued visually, as a stable spiral will always approach zero and never be bounded by a limit cycle, and thus never oscillate. However, for $b > 5$, the possibility of a limit cycle does exist because the local phase portrait would be an unstable spiral (spiraling away from zero) so the possibility of this spiral approaching a limit cycle does exist. This point, $b = a^2 + 1$, is therefore a subcritical Hopf bifurcation (Verhulst, 1980).

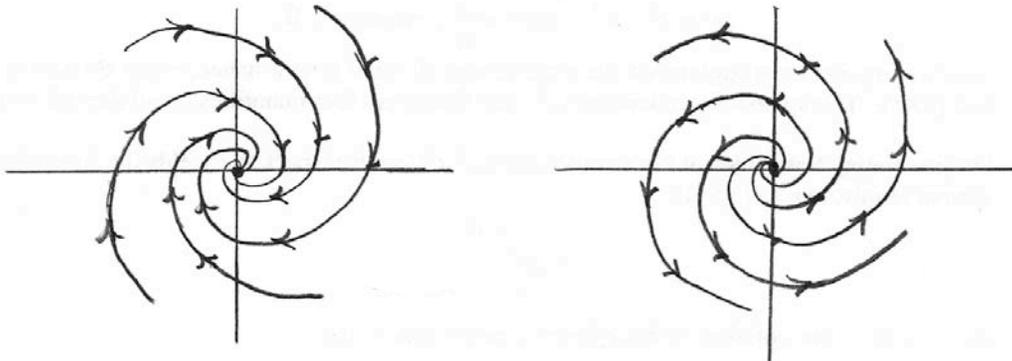


Figure 1. Phase diagrams of local phase portraits for an equilibrium point that is either a spiral sink (left) or a spiral source (right). (McKibben, 2004).

Locally, the equilibrium point $(a, b/a)$ would either be a spiral sink (when $b < a^2 + 1$) or a spiral source (when $b > a^2 + 1$). The latter case is thus the only time a limit cycle (oscillations) may exist, as the spiral source can approach a limit cycle, while a spiral sink only approaches the equilibrium point (and therefore can't oscillate).

Another oscillating chemical reaction, or chemical clock is the reaction described by Belousov-Zhabotinsky reaction, also known as the BZ reaction. Because the mechanism is extremely complicated, with over 80 elementary steps, they will not be included in this dissertation (Benini, Cervellati, and Fetto, 1996). Instead an experimentally based argument for the existence of a limit cycle solution will be discussed. The oscillation is due to the changing oxidation state of the metal ions present in the solution. Generally, an indicator is used to better visualize what is occurring on the microscopic level. When this experiment was conducted in the laboratory, periodic oscillations between the two species were visualized with an indicator, with the reaction changing at a predictable, periodic rate, when the starting concentrations were such to make the equilibrium point a repeller. Below this critical value for reactants A and B, the reaction went to completion in a non-oscillatory fashion, suggesting the existence of a bifurcation, more specifically, a Hopf bifurcation.

The BZ reaction has been studied extensively as an oscillating chemical system. According to one study, there are two types of Hopf bifurcations that can exist in this system. The Hopf bifurcation can be either supercritical or subcritical for the BZ reaction (Strizhak and Menzinger, 1996). Supercritical cases are characterized by the

monotonically growing amplitude of the oscillations with distance from the equilibrium point. These supercritical bifurcations are independent of the parameter, while subcritical bifurcations are dependent on time, and are characterized by oscillations that appear suddenly and have finite amplitudes at the given value. Either bifurcation is possible, depending on the parameter values.

The BZ reaction that was performed in the laboratory, matches with the observed data by another research group. The reaction first goes through an induction period, in which no oscillations occurred. This is due to the initial production of the substrate that will undergo oscillating oxidation/reduction steps. Once the critical concentration of this reactant is reached, oscillations begin with finite amplitude and are thus characterized as a subcritical Hopf bifurcation. Eventually, the limit cycles will die out, fading gradually until they cease to exist. This is an example of a supercritical Hopf bifurcation, as the amplitude fades gradually as it approaches the equilibrium point. After the critical values are crossed, the system continues towards its equilibrium state in a non-oscillatory manner (Strizhak and Mezinger, 1996).

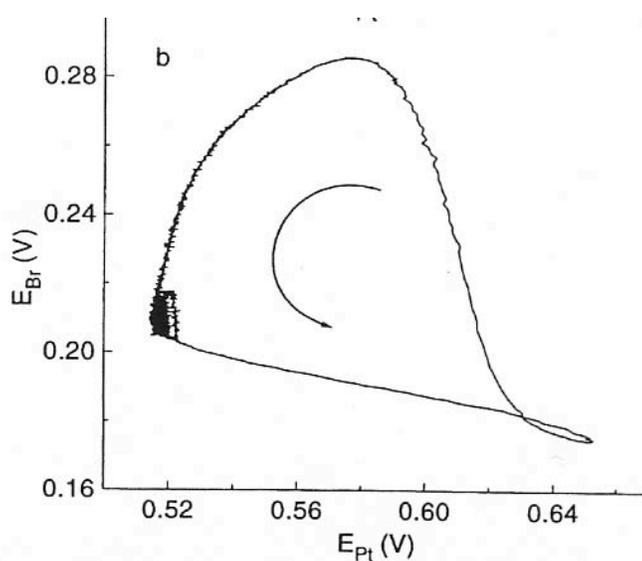


Figure 2. Illustration of the limit cycle that the BZ reaction undergoes between the subcritical Hopf bifurcation and the supercritical Hopf bifurcation value. (Strizham and Menzinger, 1996).

The Brusselator and BZ reactions are both examples of oscillating chemical systems. These “chemical clocks” can be described with nonlinear differential equations that yield one equilibrium point which is locally either a stable or an unstable spiral. With proper starting concentrations, an oscillating chemical system can be produced and can be described mathematically as a stable limit cycle.

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