Mathematical Modeling of the Brusselator

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ABSTRACT

A mathematical approach to showing the consistency of chemical oscillations with the second law of thermodynamics is described. These chemical oscillations arise from non-equilibrium conditions in which one may characterize dissipative structures by the spontaneous appearance of symmetry-breaking and the formation of chaotic structures. This paper will examine the limit cycle, or a closed trajectory in phase space having the property that at least one other trajectory spirals into it either as time approaches infinity or as time approaches minus-infinity. If the trajectories approach the limit cycle as time approaches infinity it is called a stable or attractive limit cycle. If the trajectories approach the limit cycle as time approaches minus-infinity it is an unstable or non-attractive limit cycle. The so-called Brusselator system is used to develop a theoretical understanding of instability of non-equilibrium states, which will be described in detail. Although this method is viewed skeptically by a large portion of the scientific community, students must understand these basic principles in order to understand thermodynamics as a whole. Classical thermodynamics models a good representation of numerous concepts of thermodynamics, but does not take into consideration how the breaking of time-translation symmetry leads to oscillatory behavior.

1. INTRODUCTION

This report will describe the mathematical model of the Brusselator, which is a model predicting oscillations in chemical reactions, and then provide an argument as to why it is important to include modern thermodynamics as part of the curriculum for students. The goal of modern thermodynamics is to analyze a system that continuously interacts with its environment, which is operating far from thermodynamic equilibrium. This report can be divided into five main sections: Section 2 is a review of basic thermodynamics; Section 3 is a discussion of the mathematical modeling of the Brusselator; Section 4 documents the results of this paper; and Section 5 is a discussion on allowing modern thermodynamics into the academic curriculum.

2. REVIEW OF CLASSICAL THERMODYNAMICS

As we progress, various models have been used to represent natural phenomenon. In classical thermodynamics, we model phenomena through simple linear equations. However, in the recent past, it is common to represent nature by non-linear equations. There are four laws [2] that dominate traditional thermodynamics, which still hold true today:

Zeroth Law: If two thermodynamic systems are each in thermal equilibrium with a third, then they are in thermal equilibrium with each other.

First Law: When a system undergoes a transformation of state, the algebraic sum of the different energy changes, heat exchanged, work done, is independent of the manner of the transformation. It depends only on the initial and final states of the transformation.

Second Law: The total entropy of any isolated thermodynamic system tends to increase over time, approaching a maximum value.

Third Law: As temperature approaches absolute zero, the entropy of a system approaches a constant minimum.

With a basic grounding in these four laws, one can begin to delve deeper into thermodynamics. In reviewing classical thermodynamics, one must consider all problems in terms of large systems.[2] The reader is led through the basic 19th century progression of thermodynamics: fire leads to chemical reactions, an increase in volume, melting, and evaporation. One finds the relationship between heat and work, represented in the first law of thermodynamics[1]:

$$dU = dQ + dW. \tag{1}$$

In Equation (1) dQ is the heat added to the system, dU is the total change of energy, and

dW is the work done on the system. Both dQ and dW are dependent on the manner of the transformation, unlike dU. Carnot then realized that reversible cyclic engines must produce the maximum amount of work. Although Carnot could not find a way of calculating the maximum work that can be generated, he did provide an equation that calculates the efficiency of the heat engine (Carnot's Theorem):

$$\eta = 1 - \frac{Q_2}{Q_1}, \tag{2}$$
$$\eta = 1 - f(T_1, T_2). \tag{3}$$

In Equation (3) $f(T_1, T_2)$ is a function only of temperatures T_1 and T_2 of the hot and

cold reservoirs, respectively. This observation enables us to define an absolute scale of temperature that is independent of the material property used to measure it. Entropy, S, is

a function of a quantity of heat which shows the possibility of conversion of that heat into work. Entropy, in one sense, is synonomous with disorder. It is defined by the equation:

$$dS = \frac{dQ}{T}. \tag{4}$$

In Equation (4) dQ is the amount of heat absorbed in an isothermal (temperature remains

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[1]Note: Other texts may use a different sign convention for Equation (1): $dU = dQ - dW$.

constant) and reverisible process in which the system goes from one state to another, and T is the absolute temperature. As we go "forward" in time the entropy of an isolated system tends to increase or remain the same, but never decreases. For irreversible processes, most texts identify the Clausius inequality:

$$dS \geq \frac{dQ}{T}.$$

(5)

With this basic grounding in the second law of thermodynamics, one can move onto the third law of thermodynamics for a pure substance, or the Nernst Equation:

$$\lim_{T \to 0} S = 0.$$

(6)

In Equation (6) S is the entropy approaching zero and T is the temperature approaching zero Kelvin. This law enables us to give the absolute value for the entropy. One of the most interesting concepts of classical thermodynamics is Maxwell's Demon. This was a thought experiment proposed by Maxwell in 1867. [4] The purpose was to raise questions regarding the possibility of violating the second law of thermodynamics. Maxwell says, "...if we conceive of a being whose faculties are so sharpened that he can follow every molecule in its course, such a being, whose attributes are as essentially finite as our own, would be able to do what is impossible to us. For we have seen that molecules in a vessel full of air at uniform temperature are moving with velocities by no means uniform, though the mean velocity of any great number of them, arbitrarily selected, is almost exactly uniform. Now let us suppose that such a vessel is divided into two portions, A and B, by a division in which there is a small hole, and that a being, who can see the individual molecules, opens and closes this hole, so as to allow only the swifter molecules to pass from A to B, and only the slower molecules to pass from B to A. He will thus, without expenditure of work, raise the temperature of B and lower that of A, in contradiction to the second law of thermodynamics." The fundamentals of thermodynamics came about in very unique methods, trials, thought

experiments, and physical experiments. However, now there is another method to describe natural phenomenon, which will be described in the following section.

3. DISSCUSSION OF PRIGOGINE'S APPROACH

The Brusselator or trimolecular model is used because of its theoretical simplicity, while retaining the functional form of more complex reaction networks. The reaction scheme is as follows:

$$A \rightarrow X, \tag{7}$$

$$B + X \rightarrow Y + D, \tag{8}$$

$$2X + Y \rightarrow 3X, \tag{9}$$

$$X \rightarrow E. \tag{10}$$

In Equations (7-10) k_i is the reaction rate for each individual reaction, while A, B, D, E, X, and Y are species. Molar concentrations are denoted by $[\ ]$ with $[A]$, the molar concentration of A in units of $\frac{mole}{\ell}$. Also, $[A]$, $[B]$, $[D]$, and $[E]$ are constants. The concentrations $[X]$ and $[Y]$ come from an infinite supply in this reaction scheme. The variable k_i is represented in units of $\left(\frac{mole}{\ell\ s}\right)^{-1}$. The equations for the evolution of $[X]$ and $[Y]$ are as follows:

$$\frac{d[X]}{dt} = k_1[A] - k_2[B][X] + k_3[X]^2[Y] - k_4[X], \tag{11}$$

$$\frac{d[Y]}{dt} = k_2[B][X] - k_3[X]^2[Y], \tag{12}$$

$$[X](0) = 0, \tag{13}$$

$$[Y](0) = 0. \tag{14}$$

$$\tag{15}$$

Equations (11) and (12) are of the form:

$$\frac{d[X]}{dt} = Z_1\left([X],[Y]\right), \tag{16}$$

$$\frac{d[Y]}{dt} = Z_2\left([X],[Y]\right), \tag{17}$$

where

$$Z_1\left([X],[Y]\right) = k_1[A] - k_2[B][X] + k_3[X]^2[Y] - k_4[X], \tag{18}$$

$$Z_2\left([X],[Y]\right) = k_2[B][X] - k_3[X]^2[Y]. \tag{19}$$

In order to solve for the stationary solutions, one must Equations (18) and (19) equal to zero:

$$Z_1\left([X],[Y]\right) = k_1[A] - k_2[B][X] + k_3[X]^2[Y] - k_4[X] = 0, \tag{20}$$

$$Z_2\left([X],[Y]\right) = k_2[B][X] - k_3[X]^2[Y] = 0. \tag{21}$$

Then, one must solve for $[X]$ and $[Y]$ in the equations that result. Replacing the $[X]$ with $[X]_{eq}$ after solving for $[Y]_{eq}$ gives the following equations:

$$[X]_{eq} = \frac{k_1[A]}{k_4,} \tag{22}$$

$$[Y]_{eq} = \frac{k_4 k_2[B]}{k_3 k_1[A].} \tag{23}$$

To evaluate stability [2], we evaluate the Jacobian at the stationary state. The following equations must be used:

$$\mathbf{J} = \begin{pmatrix} \left.\frac{\partial Z_1}{\partial [X]}\right|_{eq} & \left.\frac{\partial Z_1}{\partial [Y]}\right|_{eq} \\ \left.\frac{\partial Z_2}{\partial [X]}\right|_{eq} & \left.\frac{\partial Z_2}{\partial [Y]}\right|_{eq} \end{pmatrix}, \tag{24}$$

$$\left.\frac{\partial Z_1}{\partial [X]}\right|_{eq} = -k_2[B][X]_{eq} - k_4, \tag{25}$$

$$\left.\frac{\partial Z_1}{\partial [Y]}\right|_{eq} = -k_3[X]_{eq}^2, \tag{26}$$

$$\left.\frac{\partial Z_2}{\partial [X]}\right|_{eq} = k_2[B], \tag{27}$$

$$\left.\frac{\partial Z_2}{\partial [Y]}\right|_{eq} = -k_3[X]_{eq}^2. \tag{28}$$

The eigenvalue equation or characteristic equation is applied, in order to evaluate the stationary state:

$$\det\left(\mathbf{J} - \lambda\mathbf{I}\right) = 0. \tag{29}$$

Arranging these values into matrix form gives:

$$\begin{pmatrix} k_2[B] - k_4 - \lambda & k_3[X]_{eq}^2 \\ -k_2[B] & -k_3[X]_{eq}^2 - \lambda \end{pmatrix} = 0, \tag{30}$$

$$\lambda^2 - \left(k_2[B] - k_4 - k_3[X]_{eq}^2\right)\lambda + (-k_4)\left(-k_3[X]_{eq}^2\right) = 0. \tag{31}$$

After solving for equation (31), one obtains $\pm\lambda = k_2[B] - k_4 - k_3[X]_{eq}^2$. If the real parts of $\pm\lambda$ are negative then $k_2[B] - k_4 - k_3[X]_{eq}^2 < 0$; if the values are positive then $k_2[B] - k_4 - k_3[X]_{eq}^2 > 0$. The stationary state becomes unstable when a complex conjugate pair of eigenvalues cross the imaginary axis. For this particular model, the Brusselator, this occurs when:

$$k_2[B] - k_4 - k_3[X]_{eq}^2 > 0. \tag{32}$$

The system makes a transition to an unstable oscillatory state when equation this equation is satisfied. This can be easily investigated by the Wolfram Mathematica code given in Appendix A.

4. RESULTS

Solving for the determinant of this matrix Equation (30), then using the quadratic formula to solve for λ gives the eigenvalues of the Jacobian matrix. Based on the initial conditions and parameters seen in Appendix A, one can vary a rate of reaction to obtain a series of eigenvalues that satisfy the equation. One can classify the critical points according to the real and imaginary parts of the eigenvalues. These limit cycles are described as follows:

Table 1: Description of eigenvalues in terms of limit cycles [3]

$Classification$	$Eigenvalues$
Hyperbolic	Non-zero real part
Saddle	Some real parts negative, others positive
Stable node or sink	All real parts negative
Ordinary sink	All real parts negative, imaginary parts zero
Spiral sink	All real parts negative, imaginary parts non-zero
Unstable node or source	All real parts positive
Ordinary Source	All real parts positive, imaginary parts zero
Spiral Source	All real parts positive, imaginary parts non-zero
Center	All purely imaginary and non-zero

We solve for the determinant of matrix (30) because according to Cramer's Rule, we must insist that the determinant of the denominator must be equal to an indeterminate form.

Figure 1 describes the brusselator under the following conditions:

Table 2: Corresponding Rates of Reaction, Eigenvalues, and Limit Cycles.

k_1	λ	$Source, Sink, or Saddle$
0.1	1.9849 and 0.0050381	Nodal Source at (0.1, 29.9995)
0.5	1.5931 and 0.15693	Nodal Source at (0.5, 6)
1.0	$0.5 \pm 0.86602i$	Spiral Source at (1,3)
2.0	$-1 \pm 1.7321i$	Spiral Sink at (2, 1.5)
5.0	-1.1438 and -21.8562	Nodal Sink at (5, 0.6)
10.0	-1.0313 and -96.9687	Nodal Sink at (10, 0.3)
30	-1.0033 and -896.9967	Saddle Point at (-6, -0.5)

$$k_1 = 1 \left(\frac{mole}{\ell \, s} \right)^{-1}, \tag{33}$$

$$k_2 = 1 \left(\frac{mole}{\ell \, s} \right)^{-1}, \tag{34}$$

$$k_3 = 1 \left(\frac{mole}{\ell \, s} \right)^{-1}. \tag{35}$$

$$k_4 = 1 \left(\frac{mole}{\ell \, s} \right)^{-1}, \tag{36}$$

$$[A] = 1 \, \frac{mole}{\ell}, \tag{37}$$

$$[B] = 3 \, \frac{mole}{\ell}. \tag{38}$$

Figure 2 is a graph of the Brusselator which directly shows its limit cycle. According to the assessment of equations (11) and (12), this figure has a spiral source at the point (1,3), and eigenvalues $0.5 \pm 0.86602i$.

5. Discussion

My opinion is that modern thermodynamics should have a prominent role in a student's education. Classical thermodynamics is a good model for the simple basics, but there is much that is left out. Oscillatory behavior in chemical equations has been shown to compliment
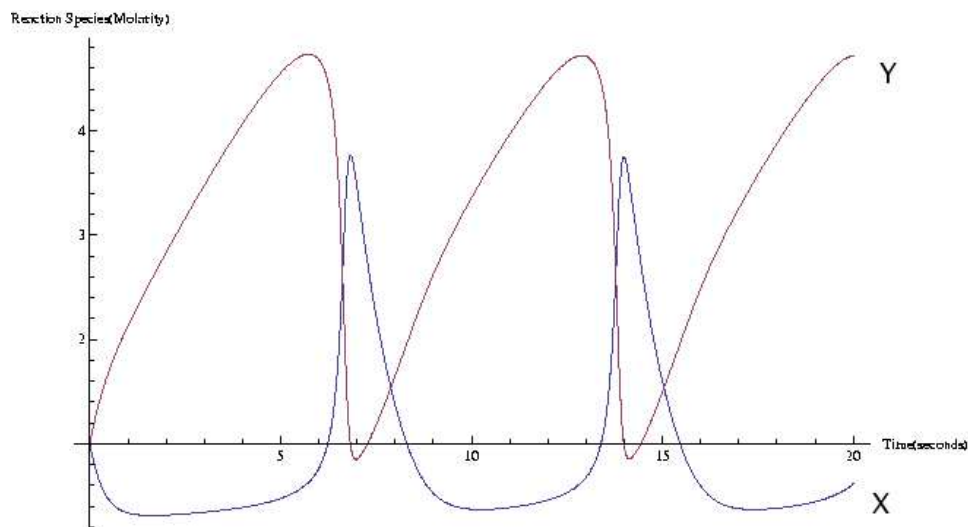
Figure 1: Oscillations of the Brusselator over time in $[X]$ and $[Y]$.

the second law of thermodynamics, not violate it. These specific behaviors are applicable to various patterns of nature and other mathematical models that describe the universe. Kondepudi and Prigogine [2] are correct in trying to let this material appeal to higher level undergraduates and graduate students. An opponent to this view may argue that classical thermodynamics is an accurate model that satisfies the basic needs of a college student. The vast majority of systems can be approximated by classical thermodynamics, therefore, there is no need to change the curriculum. Although this argument is viable, it masks the fact that situations which are impossible to realize at equilibrium become possible in far-from-equilibrium situations. A realistic example of this is the Belousov-Zhabotinsky Reaction [2], which is a catalytic oxidation of an organic compound such as malonic acid. The oscillatory behavior can be seen in the concentration of a particular ion, which changes in color from colorless to yellow. Another example is the glycolytic reaction, in which yeast may display oscillations of its metabolites while it is converting glucose [1]. The far-from-equilibrium problems that are present in this book are clearly comprehensible for a student of an intermediate level of knowledge of thermodynamics. A particular aspect that is common to all these non-equilibrium situations is the appearance of long range coherence. Equilibrium
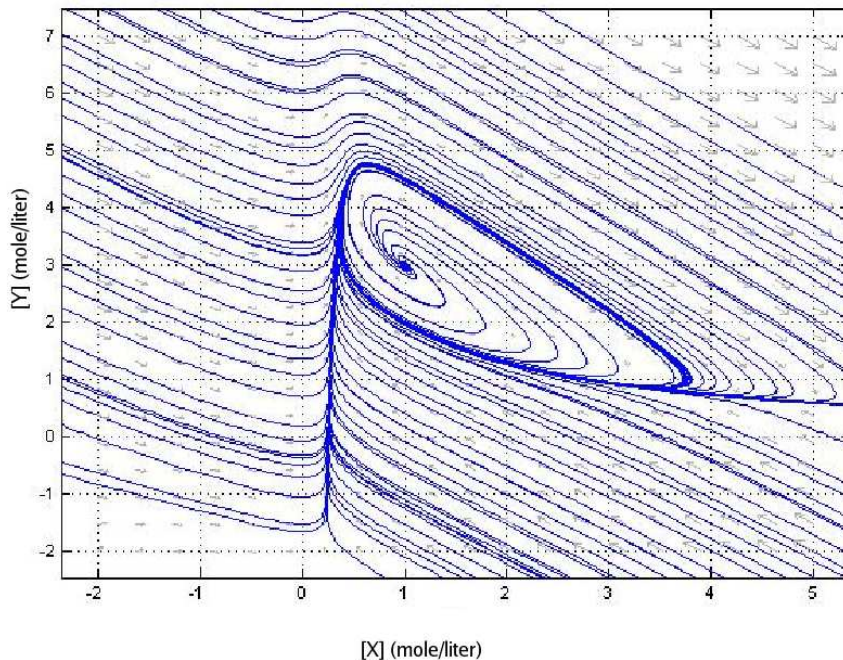
Figure 2: PPLANE7 analysis of $k_1 = 1$. Plotted are various solutions to equations (11) and (12) with an equilibrium point at (1,3). By varying the value of k_1, different equilibrium positions can be obtained which is shown in Table 2.

thermodynamics only covers a small number of our everyday experiences. As entropy is viewed as the arrow of time, the authors are clearly angered when skeptics attempt to deny the concept of entropy and blame it on ignorance. Clearly, as Kondepudi and Prigogine [2] tell us, "we are the children of evolution, not its progenitors." By simply taking basic thermodynamics as an undergraduate student, one neglects time-dependent thermodynamic systems. In contrast to most physical theories that rely on thermodynamic equilibrium, most systems found in nature are not in equilibrium. By studying the concepts of non-equilibrium thermodynamics and dissipative structures in addition to classical thermodynamics, the student can have a more realistic understanding of nature, as well as, numerous reversible processes that are governed by classical thermodynamics.

Appendix A

The Wolfram Mathematica program below plots the solutions to the differential equations (11) and (12), then using a parametric plot, shows the limit cycle of the unstable oscillatory state. This code was developed by Ilya Prigogine at the University of Texas at Austin. (* Chemical kinetics: the Brusselator *)

$k1 = 1.0;$

$k2 = 1.0;$

$k3 = 1.0;$

$k4 = 1.0;$

$A = 1.0;$

$B = 3.0;$

$Soln2 = NDSolve[X'[t] = k1 * A - k2 * B * X[t] + k3 * (X[t]^2) * Y[t] - k4 * X[t],$

$Y'[t] == k2 * B * X[t] - k3 * (X[t]^2) * Y[t],$

$X[0] == 1.0, Y[0] == 1.0, X, Y, t, 0, 200, MaxSteps \rightarrow 500]$

$xx = X[t]/.Soln2$

$yy = Y[t]/.Soln2$

$Plot[Evaluate[X[t]/.Soln2], t, 0, 20, PlotRange \rightarrow All]$

$Plot[Evaluate[Y[t]/.Soln2], t, 0, 20, PlotRange \rightarrow All]$

$Plot[Evaluate[X[t], Y[t]/.Soln2], t, 0, 20, PlotRange \rightarrow All]$

$ParametricPlot[xx, yy, t, 0, 20, PlotRange \rightarrow All, AspectRatio \rightarrow 1]$

Appendix B

The following is a Wolfram Mathematical code which was used to obtain a variety of eigenvalues by changing the parameter B. This code was developed by Dr. Joseph Powers of the University of Notre Dame.

$xp = k1 * A - k2 * B * x + k3 * x^2 * y - k4 * x$

$yp = k2 * B * x - k3 * x^2 * y$

$sol = Solve[xp == 0, yp == 0, x, y]$

$xeq = (x/.sol)$

$yeq = (y/.sol)$

$Expand[xp/.x- > xx + xeq, y- > yy + yeq]$

$Expand[yp/.x- > xx + xeq, y- > yy + yeq]$

$J = B * k2 - k4, A^2 k1^2 * k3/k4^2, -B * k2, -A^2 * k1^2 * k3/k4^2;$

$J//MatrixForm$

$JJ = J/.k1- > 1, k2- > 1, k3- > 1, k4- > 1, A- > 1$

$\lambda_1, \lambda_2 = Eigenvalues[JJ]$

$Plot[\lambda_1, \lambda_2, B, -10, 10, PlotRange- > 0, 10]$

References

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