

# Pedagogical Approach to the Modeling and Simulation of Oscillating Chemical Systems with Modern Software: The Brusselator Model

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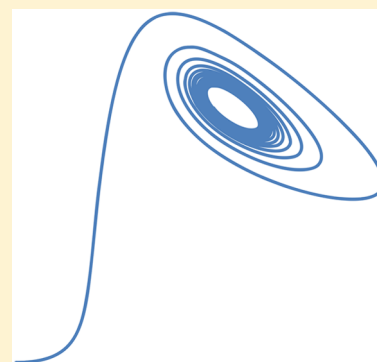
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## S Supporting Information

**ABSTRACT:** A classical nonlinear system, the “Brusselator”, was used to illustrate the modeling and simulation of oscillating chemical systems using stability analysis techniques with modern software tools such as Comsol Multiphysics, Matlab, and Excel. A systematic approach is proposed in order to establish a regime of parametric conditions that lead to oscillations in chemical systems. A Matlab script that symbolically finds the equilibrium points of the system, and the Jacobian of the assembly matrix at equilibrium was written. The Matlab script also calculates the trace, determinant and discriminant of the Jacobian and finds the critical points for which the trace and determinant are zero. An emphasis on finding the bifurcation points is made in the simulations and on the conditions for the onset of limit cycles, which are of most interest in biological systems.

**KEYWORDS:** Upper-Division Undergraduate, Graduate Education/Research, Computer-Based Learning, Computational Chemistry, Kinetics, Mechanisms of Reaction, Mathematics/Symbolic Mathematics, Professional Development, Rate Law, Reactions



## ■ INTRODUCTION

Nonlinear systems play an important role in many areas of science and engineering. They are present in the oscillatory behavior of electrical circuits,<sup>1</sup> nonlinear control systems,<sup>2,3</sup> nonlinear dynamics and chaos,<sup>4</sup> chemical systems,<sup>5</sup> etc. Nonlinear models are fundamental to understanding cyclic biological phenomena like circadian rhythms,<sup>6</sup> photosynthesis, glycolysis, nerve signal transmission,<sup>7</sup> and so forth. Nonlinear equations can display a great variety of spatial and temporal patterns which can emerge spontaneously from a structureless set of initial conditions.<sup>8</sup>

The study of oscillating chemical reactions dates back to the 19th century, but for a long time these types of reactions were mostly ignored since they were nonreproducible and it was believed that they violate the second law of thermodynamics.<sup>9</sup> It was not until 1958 with the experiments of B. P. Belousov and later of those of A. Zhabotinsky (BZ reaction) that the field of oscillating reaction chemistry received renewed attention, rekindled by the interest in systems governed by nonlinear dynamic laws.<sup>10</sup> There are many types of oscillating chemical reactions, but the BZ reaction is perhaps the most studied one both experimentally and numerically. In an article published in this *Journal*,<sup>11</sup> a review of the literature about different aspects of oscillating chemical reactions is presented. A simple search on Google Scholar or in the online archives of this *Journal* reveals a vast body of knowledge concerning oscillating reactions; however, there are few publications on the pedagogy of nonlinear methods employed to solve the differential equations that result from applying the mass action law to a

set of oscillating chemical reactions using modern software packages. In this paper, we focus on the conditions that lead to oscillations in dynamical systems as a way to introduce undergraduate students to the study of oscillating chemical systems using software tools such as Matlab, Comsol Multiphysics (reaction engineering module), and Microsoft Excel.

Traditionally, the way to study dynamical systems has been through coding of the governing equations in a given programming language; however, many science and engineering students do not take advanced courses in programming, so usually, when faced with these problems, they tend to focus more on numerical methods and coding issues rather than on the physics of the dynamical systems *per se*. On the other hand, those software packages are straightforward to use, and there are many tutorials on Web sites such as Youtube where the student can learn at his own pace. There are many nonlinear systems that could be used as test cases; however, we have chosen the so-called “Brusselator” system<sup>12</sup> (initially proposed by the chemist Nobel Laureate Ilya Prigogine), which, despite being an ideal system, is nevertheless a good example of the kind of autocatalytic oscillating chemical systems that can be studied by means of analytical modeling and computer simulation. This paper is organized systematically, showing the calculations in detail and presenting an analysis of different

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cases where the system is at a given dynamical state. Of special interest is the study of the onset of limit cycles,<sup>13</sup> which are of crucial importance in the dynamics of biological systems.<sup>14</sup>

Many examples of Matlab and Comsol for nonlinear systems can be found on their respective Web sites. For instance, Comsol's Web site contains a tutorial on oscillating reactions; however, the tutorial does not thoroughly explain the physics behind the model since its purpose is merely to show how such a problem can be set up. In this article, we will set up test cases and explain the interrelation of the different variables involved. We also attach the working files (see [Supporting Information](#)) so the student can adjust the model by changing different dynamic parameters. In this way, the student will be able to explore the whole range of parameters in the model, for example, the parameters that establish the conditions that lead to the onset of limit cycles.

We emphasize the need to first conduct an analytical study of the stability of the system which can serve as a guide to find the set of parameters that produce a given chemical oscillatory regime. For this, a symbolic script in Matlab was written.

## GOVERNING EQUATIONS

The Brusselator model can be expressed as a simple reaction scheme, as follows:



Here,  $A$ ,  $B$ ,  $X$ ,  $Y$ ,  $D$ , and  $E$  are the concentrations [mol/m<sup>3</sup>] of chemical species in the reaction scheme,  $k_i$ ,  $i = 1, 2, 3, 4$  are the reaction rate coefficients which can either be found in the literature, calculated or measured experimentally.  $k_1$  has units of [s<sup>-1</sup>],  $k_2$  units of [m<sup>3</sup>/mol s],  $k_3$  units of [m<sup>6</sup>/mol<sup>2</sup> s], and  $k_4$  units of [s<sup>-1</sup>].

Considering a mass action law for the reaction scheme (eqs 1–4), which states that the reaction rates are proportional to the product of the reactant concentrations, we can convert it into a set of differential equations that can be solved numerically.

The mass action law for species  $X$  and  $Y$  produces the rate equations

$$\frac{dX}{dt} = \dot{X} = k_1A - k_2BX + k_3X^2Y - k_4X + D_x \nabla^2 X \quad (5)$$

$$\frac{dY}{dt} = \dot{Y} = k_2BX - k_3X^2Y + D_y \nabla^2 Y \quad (6)$$

where the dot notation is used to denote time derivatives (i.e.,  $\dot{X} = dX/dt$ ) and the  $D_i$  values,  $i = x, y$ , are the diffusivities of  $X$  and  $Y$ . Concentrations of species  $A$  and  $B$  are positive ( $A, B > 0$ ) and kept constant in space and time, which is equivalent to saying that these species are continuously fed to the reactor. Since this chemical system is an open system, its oscillatory nature does not violate the second law of thermodynamics.  $X$  and  $Y$  are autocatalytic to each other since the amount of  $X$  produced by  $A$  (reaction 1) is converted into  $Y$  through reaction 2; in turn,  $Y$  is converted back into  $X$  (reaction 3). Species  $D$  and  $E$  are considered “neutralized” in the sense of

being removed from the reactor volume or being chemically inert, and thus are not considered in the numerical simulations.

Since the Brusselator is an ideal system, reactions 1–4 can be assumed to be exothermal, and their respective reverse reactions can be assumed to be negligible. Nevertheless, the conditions for oscillation can be met even in the presence of reverse reactions. As noticed by Schnittker,<sup>15</sup> irreversibility is not a necessary condition for oscillation.

In the following analysis, it is assumed that all species are homogeneously distributed in the reactor volume; hence, neither their diffusivities nor any other spatial transport phenomena are considered. These are the conditions typical of a batch reactor. Such a model is known as a 0D model since there are no spatial dependencies.

With all these approximations, the Brusselator can be expressed as

$$\dot{X} = k_1A - k_2BX + k_3X^2Y - k_4X \quad (7)$$

$$\dot{Y} = k_2BX - k_3X^2Y \quad (8)$$

## NONDIMENSIONAL FORM OF THE BRUSSELTOR

It is convenient to express the Brusselator (eqs 7–8) in nondimensional form, with some scaling factors that simplify the equations.

The scaling of concentrations and time would be

$$X^* = \frac{X}{X_0} \quad Y^* = \frac{Y}{Y_0} \quad t^* = \frac{t}{t_0} \quad (9)$$

where  $X_0$ ,  $Y_0$ , and  $t_0$  are the scaling factors for  $X$ ,  $Y$ , and  $t$ , respectively. With these scalings, eqs 7 and 8 can be expressed as

$$\dot{X}^* = \frac{k_1 t_0}{X_0} A - k_2 t_0 B X^* + k_3 t_0 X_0 Y_0 X^{*2} Y^* - k_4 t_0 X^* \quad (10)$$

$$\dot{Y}^* = \frac{k_2 t_0 X_0}{Y_0} B X^* - k_3 t_0 X_0^2 X^{*2} Y^* \quad (11)$$

where the \* symbol denotes the scaled variables. Now, there are several possibilities for nondimensionalization depending on which terms we are interested in linearizing. Let us choose the fourth term on the right-hand side (RHS) of eq 10 to scale time as  $t_0 = k_4^{-1}$ .

Then, eqs 10 and 11 become

$$\dot{X}^* = \frac{k_1}{k_4 X_0} A - \frac{k_2}{k_4} B X^* + \frac{k_3 X_0 Y_0}{k_4} X^{*2} Y^* - X^* \quad (12)$$

$$\dot{Y}^* = \frac{k_2 X_0}{k_4 Y_0} B X^* - \frac{k_3 X_0^2}{k_4} X^{*2} Y^* \quad (13)$$

Making the term involving  $X^{*2} Y^*$  in eqs 12 and 13 of order 1, we get

$$\frac{k_3 X_0^2}{k_4} = 1 \Rightarrow X_0 = \sqrt{\frac{k_4}{k_3}} \quad (14)$$

and

$$\frac{k_3 X_0 Y_0}{k_4} = 1 \quad (15)$$

Replacing eq 14 into 15 we get

$$\frac{k_3}{k_4} \sqrt{\frac{k_4}{k_3}} Y_0 = 1 \Rightarrow Y_0 = \sqrt{\frac{k_4}{k_3}} \quad (16)$$

Notice that  $X_0$  and  $Y_0$  have the same scaling, which can also be seen by comparing the coefficients of the terms containing  $BX^*$ . Now, scaling terms that contain  $A$  and  $B$  we get

$$\frac{k_1 A}{k_4 X_0} = Q \Rightarrow Q = \sqrt{\frac{k_1^2 k_3}{k_4^3}} A \quad (17)$$

$$P = \frac{k_2 B}{k_4} \quad (18)$$

$P$  and  $Q$  must be positive numbers since the  $k$ 's,  $A$ , and  $B$  are positive numbers.

Table 1 shows the scaling factors for the variables in the model.

Table 1. Scaling Factors

Variable	Scaling
$X$	$X^* = \frac{X}{X_0} \quad X_0 = \sqrt{\frac{k_4}{k_3}}$
$Y$	$Y^* = \frac{Y}{Y_0} \quad Y_0 = \sqrt{\frac{k_4}{k_3}}$
$t$	$t^* = \frac{t}{t_0} \quad t_0 = k_4^{-1}$
$Q$	$\sqrt{\frac{k_1^2 k_3}{k_4^3}} A$
$A$	$\sqrt{\frac{k_4^3}{k_1^2 k_3}}$
$P$	$\frac{k_2 B}{k_4}$
$B$	$\frac{k_4}{k_2}$
$\frac{P}{Q}$	$\frac{k_2}{k_1} \sqrt{\frac{k_4}{k_3}} \frac{B}{A}$

Then, with these scalings the nondimensional Brusselator becomes

$$\dot{X}^* = Q - PX^* + X^{*2}Y^* - X^* \quad (19)$$

$$\dot{Y}^* = PX^* - X^{*2}Y^* \quad (20)$$

rearranging terms and dropping the  $*$  symbol we get

$$\dot{X} = Q - (P + 1)X + X^2Y \quad (21)$$

$$\dot{Y} = PX - X^2Y \quad (22)$$

Equations 21 and 22 are the dimensionless form of the Brusselator. These equations are of the form

$$\dot{X} = U(X, Y) = Q - (P + 1)X + X^2Y \quad (23)$$

$$\dot{Y} = V(X, Y) = PX - X^2Y \quad (24)$$

## SOLUTION AT EQUILIBRIUM

In steady state, species concentrations  $X$  and  $Y$  are space and time independent; hence, all time derivatives vanish. Then, the Brusselator (eqs 21 and 22) becomes

$$U(X, Y) = 0 \Rightarrow Q - (P + 1)X_s + X_s^2Y_s = 0 \quad (25)$$

$$V(X, Y) = 0 \Rightarrow PX_s - X_s^2Y_s = 0 \quad (26)$$

Equations 25 and 26 form a set of ordinary algebraic equations for which an equilibrium point  $E_0$  can be found. From eq 26 it can be seen that there is a solution at  $X_s = 0$  which produces  $Q = 0$  when replacing  $X_s = 0$  into eq 25. This solution is not real since  $Q$  cannot be zero. Instead, if we add eqs 25 and 26, we get

$$Q - (P + 1)X_s + PX_s = 0 \quad (27)$$

where  $X_s = Q$

Replacing eqn 27 into eqn 26 we get

$$PQ - Q^2Y_s = 0 \Rightarrow Y_s = \frac{P}{Q} = \frac{k_2}{k_1} \sqrt{\frac{k_4}{k_3}} \frac{B}{A} \quad (28)$$

Equations 27 and 28 form the fixed point  $E_0 = (X_s = Q, Y_s = P/Q)$  which is the only equilibrium point in the system.

## STABILITY ANALYSIS

The stability of the Brusselator can be evaluated through the Jacobian of eqs 23 and 24

$$J = \begin{bmatrix} \frac{\partial U}{\partial X} & \frac{\partial U}{\partial Y} \\ \frac{\partial V}{\partial X} & \frac{\partial V}{\partial Y} \end{bmatrix} = \begin{bmatrix} -(P + 1) + 2XY & X^2 \\ P - 2XY & -X^2 \end{bmatrix} \quad (29)$$

Evaluating the Jacobian at the equilibrium point  $(X_s, Y_s) = (Q, P/Q)$  we get

$$J_s = \begin{bmatrix} P - 1 & Q^2 \\ -P & -Q^2 \end{bmatrix} \quad (30)$$

In order to evaluate the stability of the stationary state  $E_0$  ( $Q, P/Q$ ), the eigenvalue equation of the Jacobian matrix is expressed as

$$\det(J_s - \lambda I) = 0 \quad (31)$$

where the  $\lambda$ 's are the eigenvalues and  $I$  is the identity matrix. Arranging the coefficients into a matrix form gives

$$\det \begin{bmatrix} P - 1 - \lambda & Q^2 \\ -P & -Q^2 - \lambda \end{bmatrix} = 0 \quad (32)$$

which has the characteristic equation

$$\lambda^2 + (Q^2 + 1 - P)\lambda + Q^2 = 0 \quad (33)$$

Equation 33 has the form

$$\lambda^2 - \tau(J_s)\lambda + \det(J_s) = 0 \quad (34)$$

where

$$\tau(J_s) = P - 1 - Q^2 \quad (35)$$

is the trace of the Jacobian matrix at equilibrium, and

$$\det(J_s) = Q^2 \quad (36)$$

is the determinant of the Jacobian matrix at equilibrium. The eigenvalues of eq 33 have the form

$$\lambda_{1,2} = \frac{1}{2}(\tau(J_s) \pm \sqrt{\Delta}) \quad (37)$$

where

$$\Delta = \tau(\mathbf{J}_s)^2 - 4 \det(\mathbf{J}_s) = (P - 1 - Q^2)^2 - 4Q^2 \quad (38)$$

is the discriminant of the Jacobian at equilibrium. Thus, the two eigenvalues are

$$\lambda_{1,2} = \frac{1}{2}(P - 1 - Q^2) \pm \frac{1}{2}\sqrt{(P - 1 - Q^2)^2 - 4Q^2} \quad (39)$$

The dynamical behavior of the Brusselator can be ascertained depending on the values of its trace and discriminant.

### ■ CASE 1: $\Delta > 0$ , $(P - 1 - Q^2)^2 - 4Q^2 > 0$

There are two eigenvalues and eigenvectors that are real. In the vicinity of the fixed point, the derivatives of the orbit in the  $(x, y)$  plane tend asymptotically to a definite limit. The largest eigenvalue defines the direction in which orbits asymptotically converge to the fixed point. In this case, there are two subcases:

- (a)  $\tau(\mathbf{J}_s) < 0$ ,  $\det(\mathbf{J}_s) > 0$ . In this case, both eigenvalues are negative real numbers (say,  $0 > \lambda_1 > \lambda_2$ ). The equilibrium point is called a *stable node* or *sink* (Routh–Hurwitz stability criterion<sup>16</sup>), the term “node” referring to the characteristic shape of the ensemble of orbits around the equilibrium point. Any perturbation to this steady state will monotonically decrease and disappear. Then the equilibrium point is an *attractor*.

$$(P - 1 - Q^2) < 0 \Rightarrow P < 1 + Q^2 \quad (40)$$

- (b)  $\tau(\mathbf{J}_s) > 0$ ,  $\det(\mathbf{J}_s) > 0$ . In this case, both eigenvalues are positive real numbers (say,  $\lambda_1 > \lambda_2 > 0$ ) so the steady state is unstable. Any perturbation will grow exponentially away from the steady state. Then the equilibrium point is called an *unstable node* or a *repeller*.

$$(P - 1 - Q^2) > 0 \Rightarrow P > 1 + Q^2 \quad (41)$$

### ■ CASE 2: $\Delta < 0$ , $(P - 1 - Q^2)^2 - 4Q^2 < 0$

In this case, the eigenvalues are complex conjugate pairs, and the motion is oscillatory. Depending on the sign of  $\tau(\mathbf{J}_{eq})$ , three cases can be distinguished:

- (a)  $\tau(\mathbf{J}_s) < 0$ ,  $\det(\mathbf{J}_s) > 0$ . In this case, any perturbation will oscillate as it decays back to the steady state. The equilibrium point is known as a *vortex* or as *stable focus*.
- (b)  $\tau(\mathbf{J}_s) > 0$ ,  $\det(\mathbf{J}_s) > 0$ . In this case, the strength of the oscillations (amplitude) gets larger and larger as time evolves, and the system diverges from the equilibrium point. This is an *unstable focus*.
- (c)  $\tau(\mathbf{J}_s) = 0$ . In this case, the eigenvalues are purely imaginary. This state is known as a *critical point*. At this point, a Hopf bifurcation occurs, which is a point where the system switches from a stable critical point to a limit cycle. A limit cycle is a periodic oscillation surrounding the steady state that is stable to perturbations. Orbits around the vortex neither converge nor diverge, but oscillate around it with constant amplitude, which depends on the set of initial conditions. The frequency is given by  $\sqrt{\det(\mathbf{J}_s)}/2\pi$ . When the limit cycle is orbital-stable, the bifurcation is termed as *supercritical*.

Otherwise, it is unstable, and the bifurcation is termed as *subcritical*.

If  $\text{Re}(\lambda) \neq 0$ , no strict periodicity can be defined; instead, a conditional period equal to  $T = 2\pi/\text{Im}(\lambda)$  can be defined as the length of time between two successive peaks of a variable. The frequency  $f = 1/T$  can be determined by counting the number of oscillations per unit time. The strength (amplitude) of the oscillations depends on the initial conditions.

### ■ CASE 3: $\Delta = 0$ , $(P - 1 - Q^2)^2 - 4Q^2 = 0$

The eigenvalues are both real and equal, ( $\lambda_1 = \lambda_2 = \lambda$ ). If  $\mathbf{J}_s \neq \lambda \mathbf{I}$ , only one eigenvector can be determined. The equilibrium node is called a *Jordan node*.<sup>17</sup> It is a straight line, along which the system asymptotically converges to equilibrium when the eigenvalue is negative, or diverges from equilibrium when the eigenvalue is positive. If  $\mathbf{J}_{eq} = \lambda \mathbf{I}$ , the equilibrium node is called a *bicritical node*. Medio and Lines<sup>18</sup> present a more detailed discussion about the mathematical conditions of stability in nonlinear systems.

## ■ SIMULATION OF THE BRUSSELTATOR

A simple symbolic Matlab script (see [Supporting Information](#)) was written to determine the values of the input parameters used in the Comsol Multiphysics simulations. This script takes the values for  $k_1, k_2, k_3, k_4$ , and  $A$  as input parameters, calculates the Jacobian of the assembly matrix (the matrix formed by the governing equations of the Brusselator), and evaluates the Jacobian at the equilibrium point. It also calculates the trace, the determinant, and the discriminant of the Jacobian at equilibrium. With these parameters, the different stability regimes of the Brusselator can be assessed. The Matlab script provides a guide for the simulations in terms of finding the set of working parameters that produce a given dynamical state.

Figure 1 shows several regimes for the  $B$ -parameter. For  $B = 2$  there is a critical point at which  $\tau = 0$ . This is a bifurcation

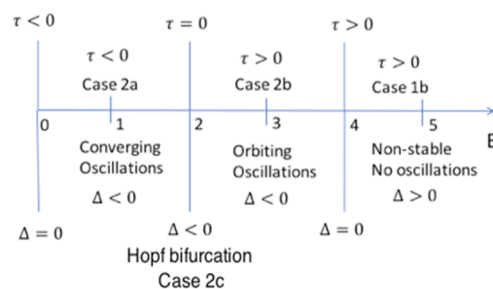
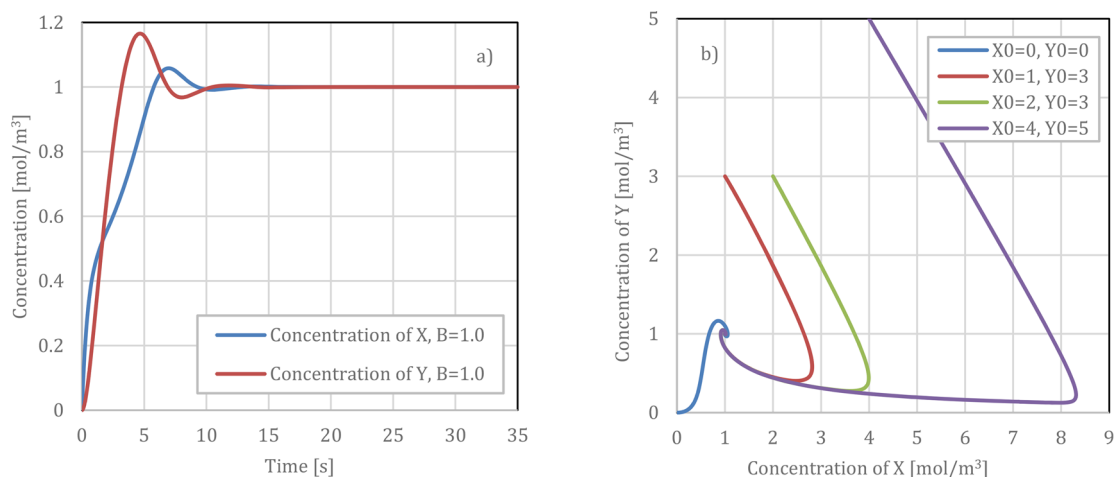


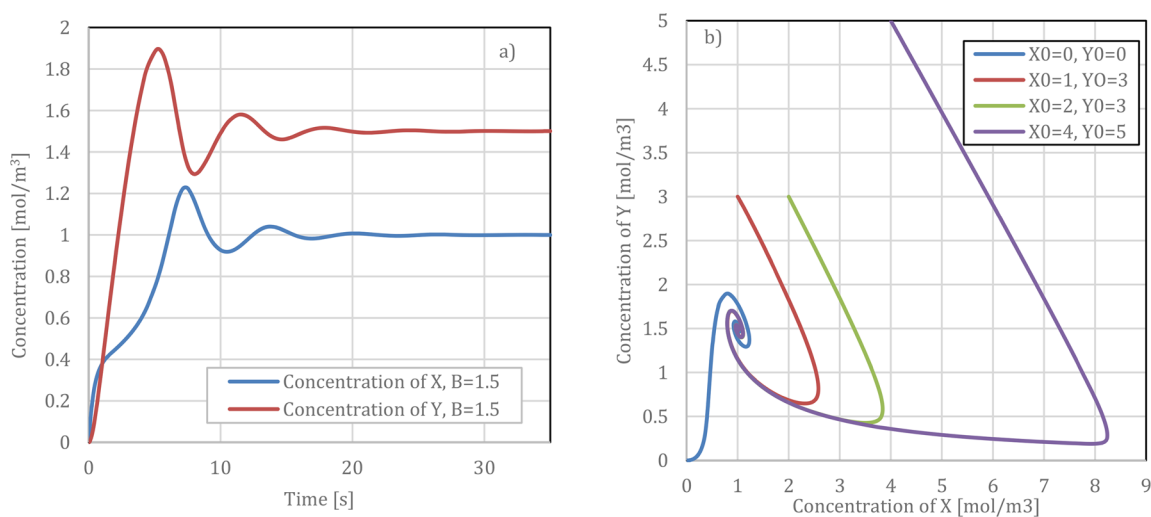
Figure 1.  $B$ -parameter distribution

point at which the eigenvalues are pure imaginary numbers and cross the imaginary axis from left to right.

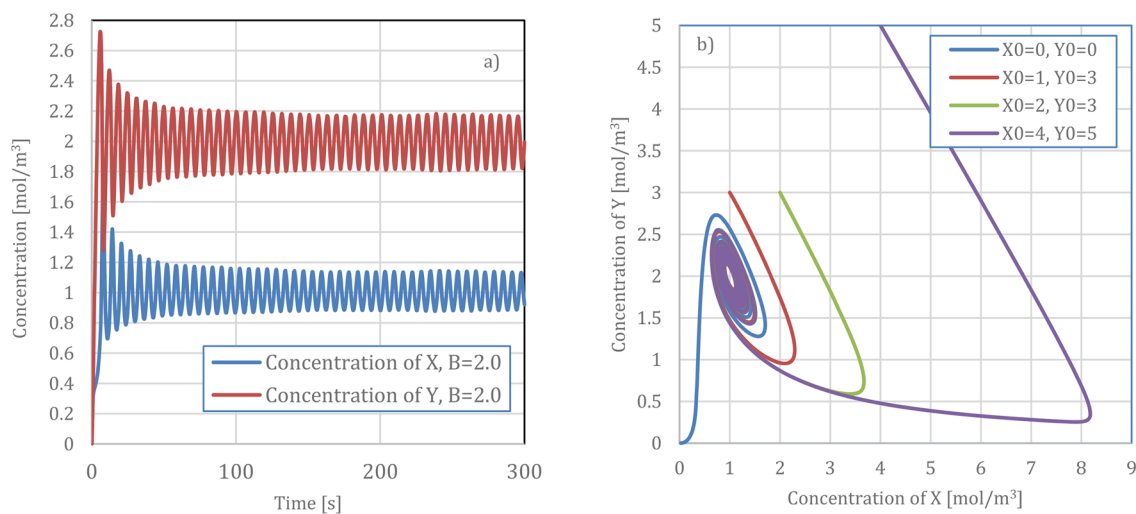
The Brusselator kinetic model was simulated using the Reaction Engineering Module (RE) from Comsol Multiphysics 5.2. Comsol uses the finite element method (FEM) to numerically approximate solutions. It is very easy to set up a simulation run in the RE module; the user only needs to enter the reaction formulas, kinetic data, and a set of initial conditions for the species concentrations, and the RE module does all the bookkeeping. All of this is done without writing a single line of code. This is not to say that coding is not important, but rather that a lack of programming skills is not an impediment to the study of dynamical systems. The RE module implements three direct solvers for these kinds of problems: MUMPS, PARDISO,



**Figure 2.** (a) Time evolution of species X and Y. (b) Phase diagram for  $B = 1.0$  and several initial conditions.



**Figure 3.** (a) Evolution of species X and Y. (b) Phase diagram for  $B = 1.5$  and several initial conditions.



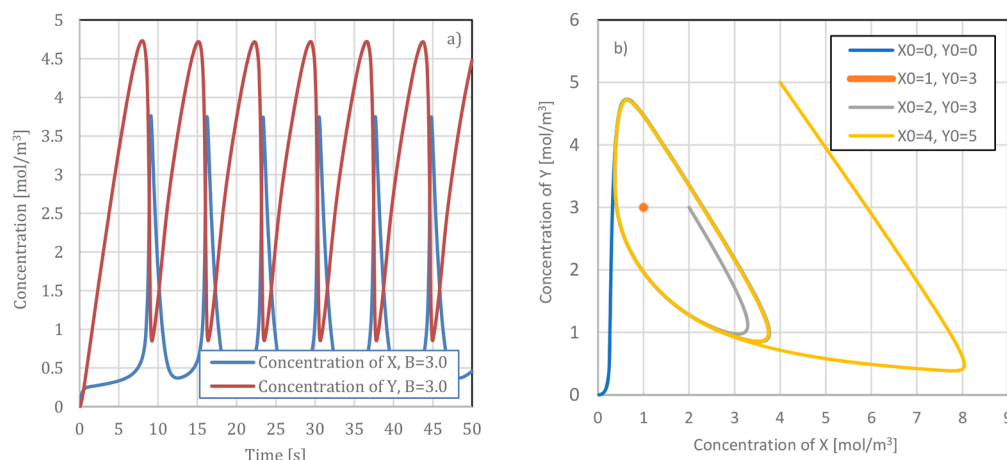
**Figure 4.** (a) Evolution of species X and Y at  $B = 2.0$ . (b) Phase diagram for  $B = 2.0$  and several initial conditions.

and SPOOLES solvers. All of these solvers were tested under some given parameters and produced very similar results.

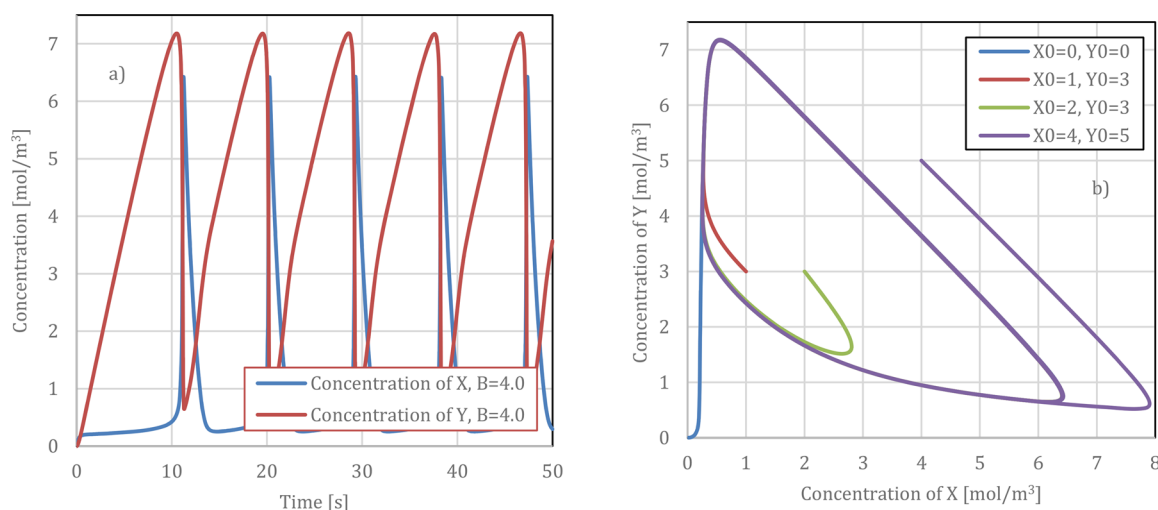
The working parameters, calculated with the Matlab script, were fed to the Comsol setup in sets corresponding to the cases

above. In the simulations, the concentrations of species D and E were locked, which in Comsol terms means that their concentrations are fixed and therefore a material balance for these species is not performed.





**Figure 5.** (a) Evolution of species  $X$  and  $Y$  for  $B = 3.0$ . (b) Phase diagram for several initial conditions. Notice the point at  $E_0 = (1, 3)$  which corresponds to an initial condition that coincides with the equilibrium point.



**Figure 6.** (a) Time evolution of concentrations  $X$  and  $Y$  for  $B = 4.0$ . (b) Phase diagram for  $B = 4.0$  and several initial conditions.

For simplicity, all the  $k$ 's are constant, and species  $A$  is fixed but arbitrary;  $B$  is allowed to vary parametrically, so with its variation, the different cases mentioned above can be studied.

Additionally, the Brusselator model was also solved in a Microsoft Excel spreadsheet, which is a very popular and powerful software tool. An Excel spreadsheet is also very easy to implement and has the advantage that it provides direct control over the numerical method to be implemented and that the results can be plotted along with the data in the same spreadsheet. The variations in the dynamical state of the Brusselator which result from the variation in the operating parameters ( $k$ 's,  $A$ ,  $B$ ) can be presented in “real time” with the inclusion of sliders. As the slider is moved, the values of the parameters change, and so the plots of concentration versus time dynamically change accordingly. Furthermore, the Excel analysis provides a means to validate the results from the analysis in Comsol.

## ANALYSIS AND DISCUSSIONS

All the reaction rate coefficients ( $k_1$ – $k_4$ ) were given a value of unity. This is done for two reasons: first, to make the setup of the calculations easier and, second, to prevent the system from becoming stiff (stiffness happens when the elements of the assembly matrix are very different in magnitude from each

other). While this is a nonessential and artificial constraint, nevertheless it is numerically convenient and does not lack generality, since with those values we can still conduct the same type of analysis that could be done with values other than unity. Moreover, the focus in this paper is on the analysis of dynamical systems through the study of an easy to set up model such as the Brusselator. The concentration of species  $A$  will be equal to 1.0 unless stated otherwise.

Figures 2–6 show plots of the evolution of concentrations of species  $X$  and  $Y$  as concentration  $B$  is parametrically varied. This set of parameters is representative of the cases stated above.

For  $B = 1.0$  and zero-initial conditions for  $X$  and  $Y$  (Figure 2a), the Matlab script (see Supporting Information) calculates the trace, determinant, and discriminant of the Jacobian matrix. According to the Routh–Hurwitz stability criterion, the motion is stable and oscillatory since both the trace and the discriminant are negative (case 2a); the system makes an incipient oscillation but rapidly converges to a steady state (stable focus) given by eqs 27 and 28. Figure 2b shows a phase plot for several initial conditions for  $X$  and  $Y$  (including the zero-initial condition). It can be seen that the system converges to the equilibrium point  $E_0 (1, 1)$  independently of the initial conditions.

For  $B = 1.5$  (Figure 3a, case 2a), the trace and the discriminant are still negative (see Figure 1); the concentrations oscillate for longer and at higher amplitudes, but their motion is damped down toward the equilibrium point  $E_0$  (1, 1.5). The phase diagram in Figure 3b also shows that for different initial conditions the systems is stable and converges to the equilibrium point.

The picture changes conceptually at  $B = 2.0$ . At this point, the discriminant is still negative (case 2c), but the Jacobian's trace becomes zero, which implies that the eigenvalues are purely imaginary. The system switches from a point-converging regime to a limit cycle according to the Poincaré–Bendixson theorem. This critical point is a bifurcation point known as Hopf bifurcation; an orbiting pattern emerges around the equilibrium point  $E_0$  (1, 2) as can be seen in Figure 4a. The phase diagram in Figure 4b shows the limit cycle onset under several initial conditions; i.e., the amplitude settles asymptotically into a stable orbit some distance  $\varepsilon$  from the equilibrium point.

Figure 5a,b shows the concentration of species X and Y, and the phase diagram for  $B = 3.0$ . Here, it can be seen that the amplitude of oscillations grows as the concentration of B grows (comparing the amplitudes in Figures 2a, 3a, 4a, and 5a). The oscillation period can be inferred by taking the times of successive oscillation peaks, which for Figure 5a corresponds to approximately 7.17 s. This value was determined by exporting the simulation data from Comsol to plotting software and capturing the time coordinates of two successive peaks. Calculating this period from the expression  $T = 2\pi/\text{Im}(\lambda)$  where  $\text{Im}(\lambda) = 1/2\sqrt{\Delta}$  and the discriminant  $\Delta$  given by eq 38 gives a period of 7.25 s. The two values agree within about 1%. The phase diagram in Figure 5b shows that, for different initial conditions for X and Y, the system settles asymptotically into a stable orbit (limit cycle), as predicted by the Poincaré–Bendixson theorem. Notice the dot at  $E_0 = (1, 3)$  in Figure 5b which corresponds to an initial condition that exactly coincides with the equilibrium point. Since the system at this initial condition is at equilibrium, there is no motion.

Figure 6a,b shows the time evolution of species X and Y and the phase diagram for  $B = 4.0$ . The amplitude and the time period of the oscillations grow as the concentration of species B grows, in a similar fashion to previous cases. In fact, if the value of B grows continuously, the amplitude of the oscillations will grow dramatically and the time period will also increase up to a point in which there are no more oscillations in the time span of the simulations.

Figure 7 shows phase diagrams for different values of B. It can also be seen from this graph that the period of oscillation grows as B increases; the system orbits in increasing limit cycles, which is equivalent to saying that it takes longer for the system to complete an orbit. Notice the transition from a stable attractive solution at  $B = 1.5$  to the onset of a limit cycle for  $B = 2.0$ .

Comparing the time evolution of concentrations X and Y for all the values of B analyzed, one notices that the concentration of Y is always higher than that of X. It has to do with the initial values of A. If the values of A were increased, the concentration of X would be the most abundant one. This can be discerned from the Brusselator's reaction scheme (eqs 1–4): high values of A compared to B would produce X in abundance.

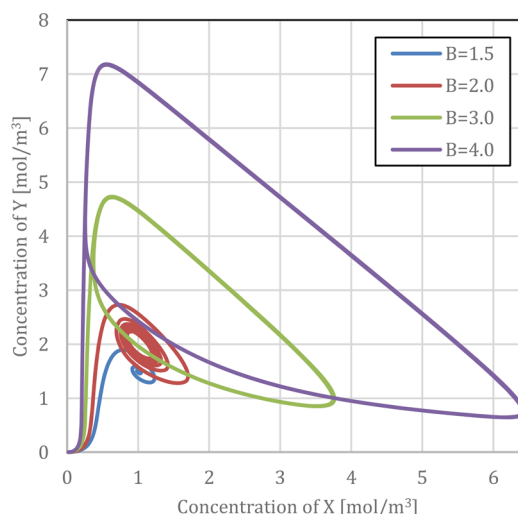


Figure 7. Phase diagram for several values of B.

## ■ SOLVING THE BRUSSELTATOR IN EXCEL

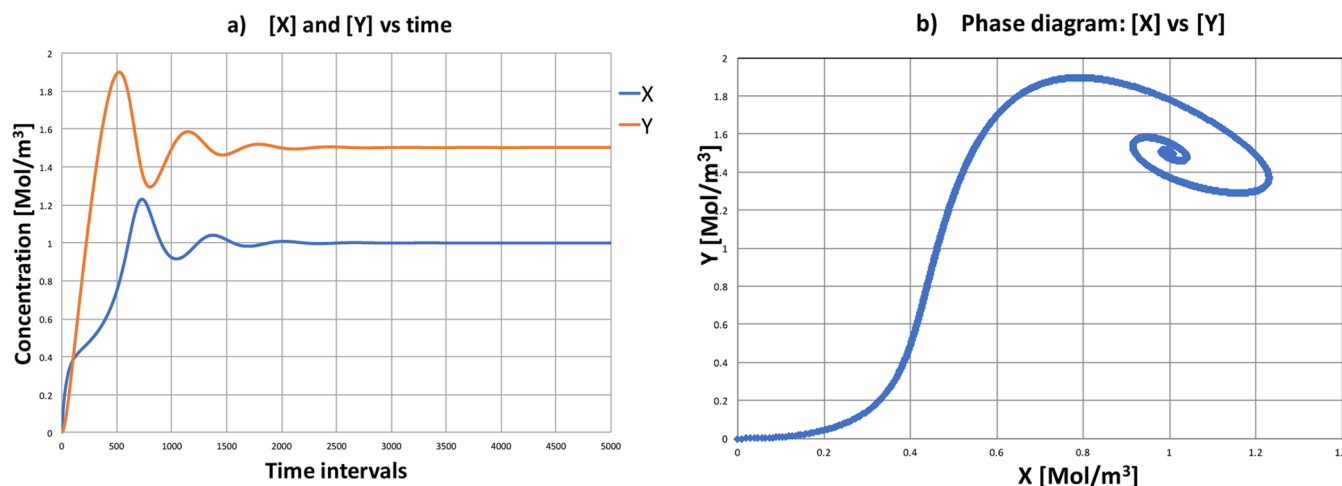
As previously mentioned, the Brusselator model can also be solved in Microsoft Excel (see Excel file in the Supporting Information). The explicit Euler's method was used to discretize eqs 7 and 8. This method is one of the earliest methods used to solve differential equations; it is not very accurate for large time steps since its truncation error is proportional to  $O(h^2)$ . However, for small time steps it produces results that agree well with those from Comsol. As a comparison, Figure 8a,b shows the time evolution of concentrations of X and Y and the phase diagram, respectively, for the same conditions as in Figure 3a,b. It can be seen that the Excel solution agrees very well with the solution in Comsol. Notice that the time intervals in Figure 8a are related to  $\Delta t$  in the Excel file (see Supporting Information); thus, 5000 time intervals correspond to a time of 50 s for  $\Delta t = 0.01$ . In a similar fashion, other values of the parameter B were tried, and the results also agree very well with those from Comsol.

## ■ CONCLUSIONS

With the use of modern software tools, such as Comsol, Matlab, and Microsoft Excel, it is possible to conduct a thorough analysis of nonlinear oscillating chemical systems in an easy and quick way, since it does not require in-depth knowledge of any programming language. Thus, students without a strong background in coding can draw meaningful conclusions from the simulation of such systems. In this case, the Brusselator chemical system was chosen because of its simplicity and because it is a well-known example of an autocatalytic set of reactions that leads to stable oscillations, as could be corroborated in the simulations under different concentrations of the species B and different initial concentrations of X and Y.

Although the nondimensionalization of the Brusselator model was included in order to simplify the governing equations, by giving all the  $k$ 's the value of unity, it turns out that the dimensional and the nondimensional forms are equivalent.

From the stability analysis, the existence of limit cycles is evident, which produce oscillations over stable orbits. This, in fact, is very important to determine since many biochemical processes can be described by this kind of stable oscillation.



**Figure 8.** (a) Time evolution of concentrations  $X$  and  $Y$ . (b) Phase diagram. The conditions are the same as in Figures 3a and 3b.

The ease with which a given reaction scheme can be set in Comsol's reaction module (RE) opens up the possibility not only to study other oscillating systems but also to try to find chemical equivalents for oscillating systems that are not chemical in nature, with a method similar to the implementation of electric circuits to find solutions of differential equations in analogue computers in the times when digital computers were not readily available. An example of this could be the Van der Pol oscillator, which was originally proposed to study the dynamical behavior of nonlinear circuits.

An Excel spreadsheet was implemented as an alternative form of solution of the Brusselator model. The results in Excel agree very well with those from Comsol for all the cases analyzed. The explicit Euler's method was used to numerically solve the Brusselator equations; nonetheless, many other numerical methods can be implemented in Excel. The reader can use both solutions in Comsol and Excel to compare the results of the simulations and the appropriateness of the numerical methods in the solution of dynamical systems.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.7b00703.

Matlab script (PDF, DOCX)

Comsol files (ZIP)

Spreadsheet for Euler method and Brusselator model (XLSX)

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Chua, L. O.; Desoer, C. A.; Kuh, E. S. *Linear and Nonlinear Circuits*; McGraw-Hill Book Company: New York, 1987.
- (2) Ding, Z. *Nonlinear and Adaptive Control Systems*; The Institution of Engineering and Technology: London, U.K., 2013.
- (3) Azar, A. T.; Vaidyanathan, S. *Chaos Modeling and Control Systems Design*; Springer, 2015.
- (4) Strogatz, S. H. *Nonlinear Dynamics and Chaos with Applications to Physics, Biology, Chemistry and Engineering*; Perseus Books: Reading, MA, 1994.
- (5) Epstein, I. R.; Pojman, J. K. *An Introduction to Nonlinear Chemical Dynamics, Oscillations, Waves, Patterns, and Chaos*; Oxford University Press: New York, 1998.
- (6) Bell-Pedersen, D.; Cassone, V. M.; Earnest, D. J.; Golden, S. S.; Hardin, P. E.; Thomas, T. L.; Zoran, M. J. Circadian Rhythms from Multiple Oscillators: Lessons from Diverse Organisms. *Nat. Rev. Genet.* **2005**, 6, 544–556.
- (7) Ma, J.; Tang, J. A review for Dynamics of Collective Behaviors of Network of Neurons. *Sci. China: Technol. Sci.* **2015**, 58 (12), 2038–2045.
- (8) Punckt, C.; Bodega, P. S.; Kaira, P.; Rotermund, H. H. Wildfires in the Lab: Simple Experiment and Models for the Exploration of Excitable Dynamics. *J. Chem. Educ.* **2015**, 92, 1330–1337.
- (9) Chang, R.; Thoman, J. W. *Physical Chemistry for the Chemical Sciences*; University Science Books: Canada, 2014.
- (10) Field, R. J.; Schneider, F. W. Oscillating Chemical Reactions and Nonlinear Dynamics. *J. Chem. Educ.* **1989**, 66 (3), 195–204.
- (11) Pellitero, M. A.; Alvarez Lamsfus, C.; Borge, J. The Belousov-Zhabotinsky Reaction: Improving the Oregonator Model with the Arrhenius Equation. *J. Chem. Educ.* **2013**, 90 (1), 82–89.
- (12) Siraj-ul-Islam; Ali, A.; Haq, S. A. Computational Modeling of the Behavior of the Two-Dimensional Reaction–Diffusion Brusselator System. *Applied Mathematical Modelling* **2010**, 34, 3896–3909.
- (13) Sarmah, H. K.; Das, M. C.; Baishya, T. K. Hopf Bifurcation in a Chemical Model. *IJIRST—International Journal for Innovative Research in Science & Technology* **2015**, 1 (9), 22–23.
- (14) Grasman, J.; Jansen, M. J. W. Mutually Synchronized Relaxation Oscillators as Prototypes of Oscillating Systems in Biology. *J. Math. Biology* **1979**, 7, 171–197.
- (15) Schnittker, P. Conditions for Oscillations in Chemical Reactions. *J. Non-Equilib. Thermodyn.* **1978**, 3, 93–102.



- (16) Dorf, R. C.; Bishop, R. H. *Modern Control Systems*, 12th ed.; Prentice Hall: NJ, 2011.
- (17) Anosov, D. V.; Aronson, S. Kh.; Arnold, V. I.; Bronshtein, I. U.; Grines, V. Z.; Ilyashenko, Y. S. *Ordinary Differential Equations and Smooth Dynamical Systems*; Springer-Verlag: Berlin, 1997.
- (18) Medio, A.; Lines, M. *Nonlinear Dynamics: A Primer*; Cambridge University Press: New York, 2015.