

## GENERALIZATION OF THE THERMOKINETIC OREGONATOR MODEL

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**Abstract.** In this research work proposal, a way to generalize the thermokinetic Oregonator model in order to simulate the dynamics of oscillating chemical reactions. The simulations to be carried out use elementary numerical methods using the Runge Kutta method, which are a very good approximation of the mathematical solutions of the models of these complex systems of nonlinear chemistry. The implications of the results of the simulations lie in the reproduction of the nonlinear dynamics of thermokinetic oregonator model to temperatures different from room temperature. Additionally, the linear stability analysis is established to find the oscillation regions in the parameter space of the proposed model.

**Key words:** oregonator model, oscillating chemical reaction, nonlinear chemistry.

## INTRODUCTION

In the 1930's, the kinetics of oscillating chemical reactions was little understood and less studied. The pioneering work of Alfred Lotka in 1910, discovered and constructed a mathematical model of a chemical reaction whose irreversible autocatalytic process showed the behavior of color changes from dark to light (oscillations) [1,2]. In the 1920's other works developed by William C. Bray were published, who, by means of a reaction, whose product is the catalytic decomposition of hydrogen peroxide under the influence of iodite ions, also presented oscillations in terms of color change [3]. One more attempt to study the oscillating reactions, and perhaps the most important historically, was made by the Russian Boris P. Belousov, who was interested in investigating the process of glycolysis, succeeded in experimentally making an autocatalytic oxidation reaction that was equivalent to that process [4]. However, none of these works nor those elaborated in the following two decades succeeded in revealing the underlying mechanism of this type of chemical behavior. Even when Belousov tried to publish his results, he was refused, because his experiment could not exist since it violated the second law of thermodynamics. This confusion was resolved by Anatoly M. Zhabotinsky 25 years later, who proposed other chemical reagents such as malonic acid, cerium bromite and cerium bromate to find the mechanism of chemical oscillations: the existence of an autocatalytic oxidation-reduction reaction process [5]. Because of these historical events the latter chemical reaction is called the Belousov-Zhabotinsky reaction, or BZ reaction. Zhabotinsky himself proposed a variant of the experimental arrangement finding that the chemical oscillation process can be extended to spatio-temporal behaviors [6], as well as a further variant is the shape of the spatio-temporal patterns formed by the chemical reaction [7]. These experimental findings are studied with mathematical modeling. Taking as a starting point other similar oscillating reaction, mathematical models have been developed based on the dynamics of chemical kinetics such as the thermokinetic Oregonator [9], which can be extended and solved with computational simulation methods to reproduce the spatiotemporal patterns that present chaos [1].

## THE MODEL

**New Molarity model.** Based on the work of Marco and collaborators [1], we have the following:

Taking as references the equations presented in [1] [(see Eqs. (1) and (2))] applying the law of masses we have that the new nonlinear molarity model will be by:

Taking into consideration that,

$$x = \frac{2k_4[X]}{k_1[A]}; [X] = \frac{k_1[A]}{2k_4} x; y = \frac{k_5[Y]}{k_1[A]}; [Y] = \frac{k_1[A]}{k_5} y; \tau = \frac{k_8^2}{k_7} t \quad (1)$$

Using the fact that:

$$\frac{d}{dt} = \frac{d\tau}{dt} \frac{d}{d\tau} \Rightarrow \frac{d\tau}{dt} = \frac{k_8^2}{k_7} \quad (2)$$

Considering (1), for the law of mass action that,

$$\frac{d[X]}{dt} = h_0 [k_1[A][X] - k_5[X][Y] + k_7[A][Y] - 2k_4[X]^2] \quad (3)$$

Taking into account Eq. (2):

$$\frac{d[X]}{dt} = \frac{k_1[A]}{2k_4} \frac{d\tau}{dt} \frac{dx}{d\tau} = \frac{k_1[A]}{2k_4} \frac{k_8^2}{k_7} \frac{dx}{d\tau} = \frac{k_1[A]k_8^2}{2k_4k_7} \frac{dx}{d\tau} \Rightarrow \frac{dx}{d\tau} = \frac{2k_4k_7}{k_1[A]k_8^2} \frac{d[X]}{dt} \quad (4)$$

After some algebraic manipulation and substituting the above in (3), we obtain:

$$\frac{dx}{d\tau} = h_0 \frac{2k_4k_7}{k_1[A]k_8^2} \left\{ k_1[A] \left( \frac{k_1[A]}{2k_4} \right) x - k_5 \left( \frac{k_1[A]}{2k_4} \right) \left( \frac{k_1[A]}{k_5} \right) xy + k_7[A] \left( \frac{k_1[A]}{k_5} \right) y - 2k_4 \left( \frac{k_1[A]}{2k_4} \right)^2 x^2 \right\} \quad (5)$$

Simplifying we get,

$$\frac{dx}{d\tau} = h_0 \frac{2k_4 k_7 (k_1[A])^2}{2k_1[A]k_4 k_8^2} \{x - xy + \frac{2k_4 k_7}{k_1 k_5} y - x^2\} = h_0 \frac{k_7 k_1 [A]}{k_8^2} \{x - xy + \frac{2k_4 k_7}{k_1 k_5} y - x^2\} \quad (6)$$

Finally, we obtain that,

$$\frac{dx}{d\tau} = \frac{1}{\varepsilon} \{x - xy + qy - x^2\} \quad (7)$$

where,

$$\varepsilon(T) = \frac{1}{h_0 k_1(T) k_7(T) [A]}; q(T) = \frac{2k_4(T) k_7(T)}{k_1(T) k_5(T)} \quad (8)$$

These are dimensionless parameters.

By rewriting Eq. (7) as,

$$\frac{dx}{d\tau} = \frac{qy - xy + x - x^2}{\varepsilon} \quad (9)$$

Unlike the findings of Marco and his colleagues on the concentration of  $y$ , in which only the linear case was considered and non-linear terms were ignored, resulting in a linear equation (see reference [1]), our work expands on theirs by including second-order non-linear terms. This led us to obtain a non-linear ordinary differential equation for the concentration of  $y$ .

$$\frac{d[Y]}{dt} \approx f k_8 [B] [Z] (1 - \omega) - h_0 k_5 [X] [Y] - h_0 k_7 [A] [Y] + k_{12} [B] \quad (10a)$$

In which it was considered

$$\omega = h_0 \frac{k_{-8}}{k_9} ([C] - [Z]); [Z] = \frac{(k_1[A])^2}{k_4 k_7 [B]} z \Rightarrow \omega = h_0 \frac{k_{-8}}{k_9} \left( [C] - \frac{(k_1[A])^2}{k_4 k_7 [B]} z \right) \quad (10b)$$

additionally using,

$$y = \frac{k_5 [Y]}{k_1 [A]}; [Y] = \frac{k_1 [A]}{k_5} y; \tau = \frac{k_8^2}{k_7} t \quad (11)$$

we finally obtain,

$$\frac{dy}{d\tau} \approx 2 \frac{-h_0 p q y - \frac{1}{2} h_0 p x y + f z + p \alpha - h_0 f \beta z + h_0 f \beta \gamma z^2}{\delta} \quad (12)$$

where,

$$\alpha(T) = \frac{2k_4(T) k_{12}(T) [B]}{(k_1(T) [A])^2}; \beta(T) = \frac{k_{-8}(T) [C]}{k_9(T)}; \gamma(T) = \frac{(k_1(T) [A])^2}{k_4(T) k_7(T) [B] [C]} \quad (13)$$

$$\delta(T) = \frac{2k_4(T) k_8(T)}{k_1(T) k_5(T) [A]}; p(T) = \frac{k_7(T)}{k_8(T)}; q(T) = \frac{2k_4(T) k_7(T)}{k_1(T) k_5(T)} \quad (14)$$

Finally, we calculate the parameter for  $Z$ , taking into account

$$\frac{d[Z]}{dt} \approx 2h_0 k_7 [A] [X] - k_8 [B] [Z] (1 - \omega) \quad (15)$$

$$\omega = h_0 \frac{k_{-8}}{k_9} ([C] - [Z]); [Z] = \frac{(k_1[A])^2}{k_4 k_7 [B]} z \Rightarrow \omega = h_0 \frac{k_{-8}}{k_9} \left( [C] - \frac{(k_1[A])^2}{k_4 k_7 [B]} z \right); \tau = \frac{k_8^2}{k_7} t; [X] = \frac{k_1[A]}{2k_4} x \quad (16)$$

Thus, we finally obtain

$$\frac{dz}{d\tau} \approx h_0 p \left( r [B] p x - \frac{[B]}{h_0} z - \beta \gamma [B] z^2 + \beta [B] \right) \quad (17)$$

Whose parameters are dimensionless. In particular, if  $r$  and  $h_0 y [B]$  are equal to one and  $\beta = 0$ , the original model present in [1] is recovered. This implies  $k_9 \rightarrow \infty$  that while  $k_{-8} [C]$  remains approximately constant,  $k_7 \rightarrow k_1$  or vice versa and  $[B] \rightarrow h_0 \rightarrow 1$  (i.e. they tend to be maximums).

$$\alpha(T) = \frac{2k_4(T) k_{12}(T) [B]}{(k_1(T) [A])^2}; \beta(T) = \frac{k_{-8}(T) [C]}{k_9(T)}; \gamma(T) = \frac{(k_1(T) [A])^2}{k_4(T) k_7(T) [B] [C]} \quad (18)$$

$$\delta(T) = \frac{2k_4(T) k_8(T)}{k_1(T) k_5(T) [A]}; p(T) = \frac{k_7(T)}{k_8(T)}; q(T) = \frac{2k_4(T) k_7(T)}{k_1(T) k_5(T)}; r(T) = \frac{k_7(T)}{k_1(T)} \quad (19)$$

Therefore, the first-order generalized Zhabotinsky system in which the reaction-diffusion equations of the proposed model are as follows:

$$\begin{aligned} \frac{dx}{d\tau} &= \frac{qy - xy + x - x^2}{\varepsilon} = F(x, y, z), \\ \frac{dy}{d\tau} &\approx \frac{-p q y - p x y + (f - p \beta) z + f \beta \gamma z^2 + p \alpha}{\delta} = G(x, y, z), \\ \frac{dz}{d\tau} &\approx h_0 p [B] (r p x - z - \beta \gamma z^2 + \beta) = H(x, y, z). \end{aligned} \quad (20)$$

Considering that if  $h_0 = [H^+]$  (Hammett's acidity function) is equal to one, it means that the reaction takes place in an acidic medium.

LINEAR STABILITY ANALYSIS AND NUMERICAL SOLUTION

The stability analysis is the reflection of the work done from different references here. Here reference [1] is followed to study the stability of Eqs. (20) from the following process:

**a. Fixed points calculus.** For this analysis, the fixed points are calculated from the non-linear terms of the system in a temporally and spatially stationary state:

$$\begin{aligned} qy_0 - x_0y_0 + x_0 - x_0^2 &= 0, \\ -pqy_0 - px_0y_0 + (f - p\beta)z_0 + f\beta\gamma z_0^2 + p\alpha &= 0, \\ rpx_0 - z_0 - \beta\gamma z_0^2 + \beta &= 0. \end{aligned} \tag{21}$$

**1. Calculus of Jacobean and eigenvalues:** The Jacobian obtained from the non-linear terms of the dynamic system given by Eqs. (20) is presented.

$$J(k^2) = \begin{pmatrix} m_{11} & m_{12} & m_{13} \\ m_{21} & m_{22} & m_{23} \\ m_{31} & m_{32} & m_{33} \end{pmatrix} = \begin{pmatrix} \frac{1}{\varepsilon}[1 - y - 2x] & \frac{1}{\varepsilon}(q - x) & 0 \\ \frac{-1}{\delta}py & \frac{-1}{\delta}p(q + x) & \frac{1}{\delta}[f - p\beta + 2f\beta\gamma z] \\ p^2r[B] & 0 & -p[B](1 + 2\beta\gamma z) \end{pmatrix} \tag{22}$$

**2. Calculus of eigenvalues from the linearization of non-linear terms:**

$$\begin{aligned} &J(k^2) - \lambda I = 0 \Rightarrow \\ &\begin{vmatrix} \frac{1}{\varepsilon}[1 - y - 2x] - D_x k^2 - \lambda & \frac{1}{\varepsilon}(q - x) & 0 \\ \frac{-1}{\delta}py & \frac{-1}{\delta}p(q + x) - D_y k^2 - \lambda & \frac{1}{\delta}[f - p\beta + 2f\beta\gamma z] \\ p^2r[B] & 0 & -p[B](1 + 2\beta\gamma z) - D_z k^2 - \lambda \end{vmatrix} = 0, \end{aligned} \tag{23}$$

Obtaining the equation to solve:

$$\lambda^3 + a\lambda^2 + b\lambda + c = 0 \tag{24}$$

Where:

$$\begin{aligned} a &= -(m_{11} + m_{22} + m_{33}), b = m_{11}m_{33} + m_{22}m_{33} - m_{11}m_{22} - m_{12}m_{21}, \\ c &= m_{12}m_{21}m_{33} - m_{12}m_{31}m_{23} - m_{11}m_{22}m_{33} \end{aligned} \tag{25}$$

Being  $k$ , the wave number and replacing diffusion.

When at least 2 eigenvalues are pure imaginary, they are called **Hopf instability**, is the case considered in this work. An important case to mention is when we have: Complex eigenvalues, in this case, we consider: a). 2 complex conjugate eigenvalues and 1 positive real and b) 2 complex conjugate eigenvalues and 1 negative real. Therefore, in the most general case the eigenvalues are such that:

$$\lambda_{1,2} = \psi \pm i\omega, \lambda_3 = \phi \tag{26}$$

If equation (24) is solved using Cardano's equations, it can be shown that:

$$a = -(2\psi + \phi), b = \psi^2 + \phi^2 + 2\psi\phi, c = -(\psi^2 + \phi^2)\phi \tag{27}$$

n cases a) and b), we have:  $\psi = 0 \Rightarrow \lambda_{1,2} = \pm i\omega, a = -\phi, b = \phi^2, c = -\phi^3 \Rightarrow c - ab = 0$  [by equations (27)].

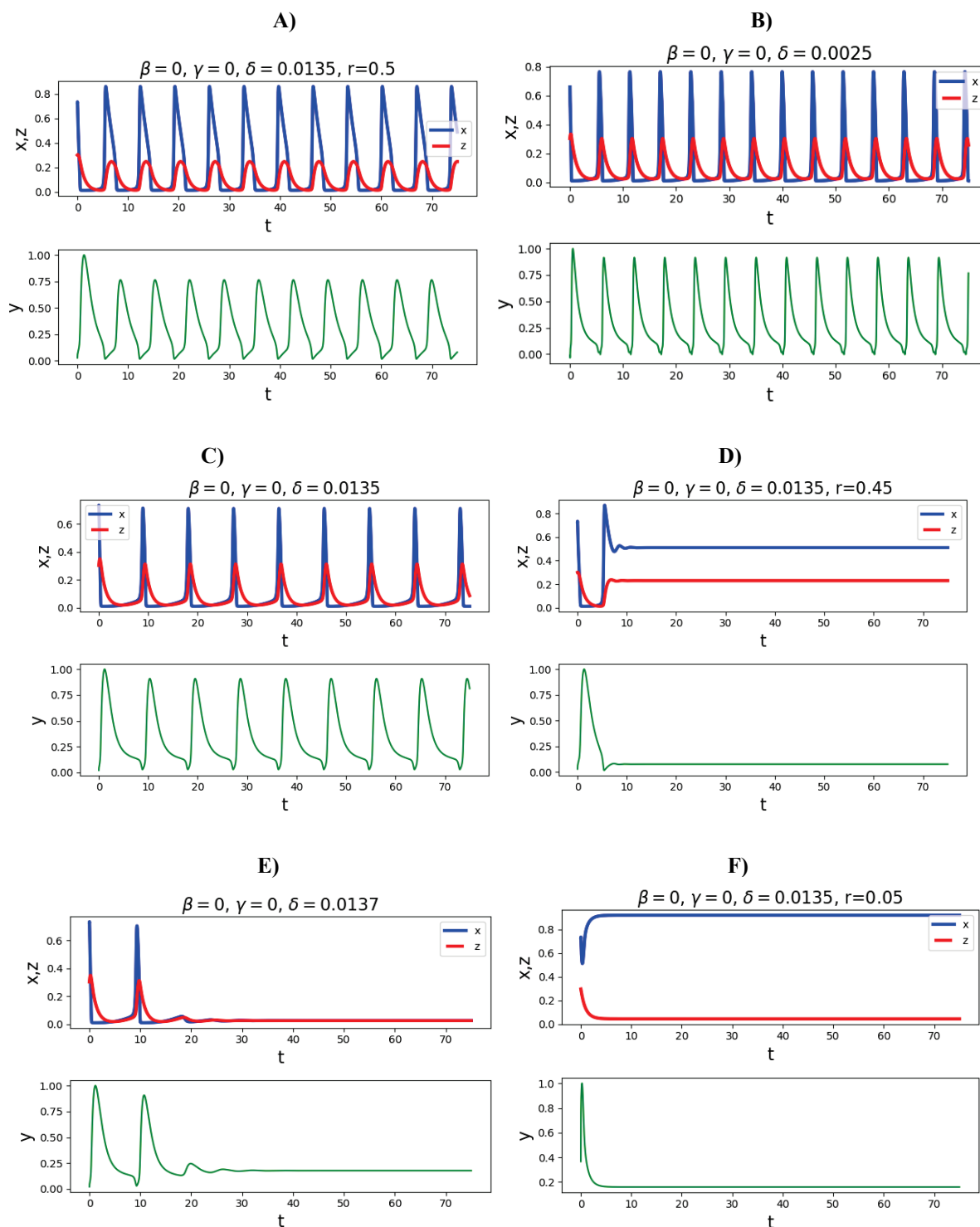
A condition that satisfies both cases is:  $c = 0$ .

So the Hopf instability is given by the condition:  $c - ab = 0$ , which by equation (24) is equivalent to,

$$m_{12}m_{21}m_{33} - m_{12}m_{23}m_{31} + m_{11}m_{22}m_{33} + (m_{11} + m_{22} + m_{33})(m_{11}m_{22} + m_{22}m_{33} + m_{33}m_{11} - m_{21}m_{21}) = 0 \tag{28}$$

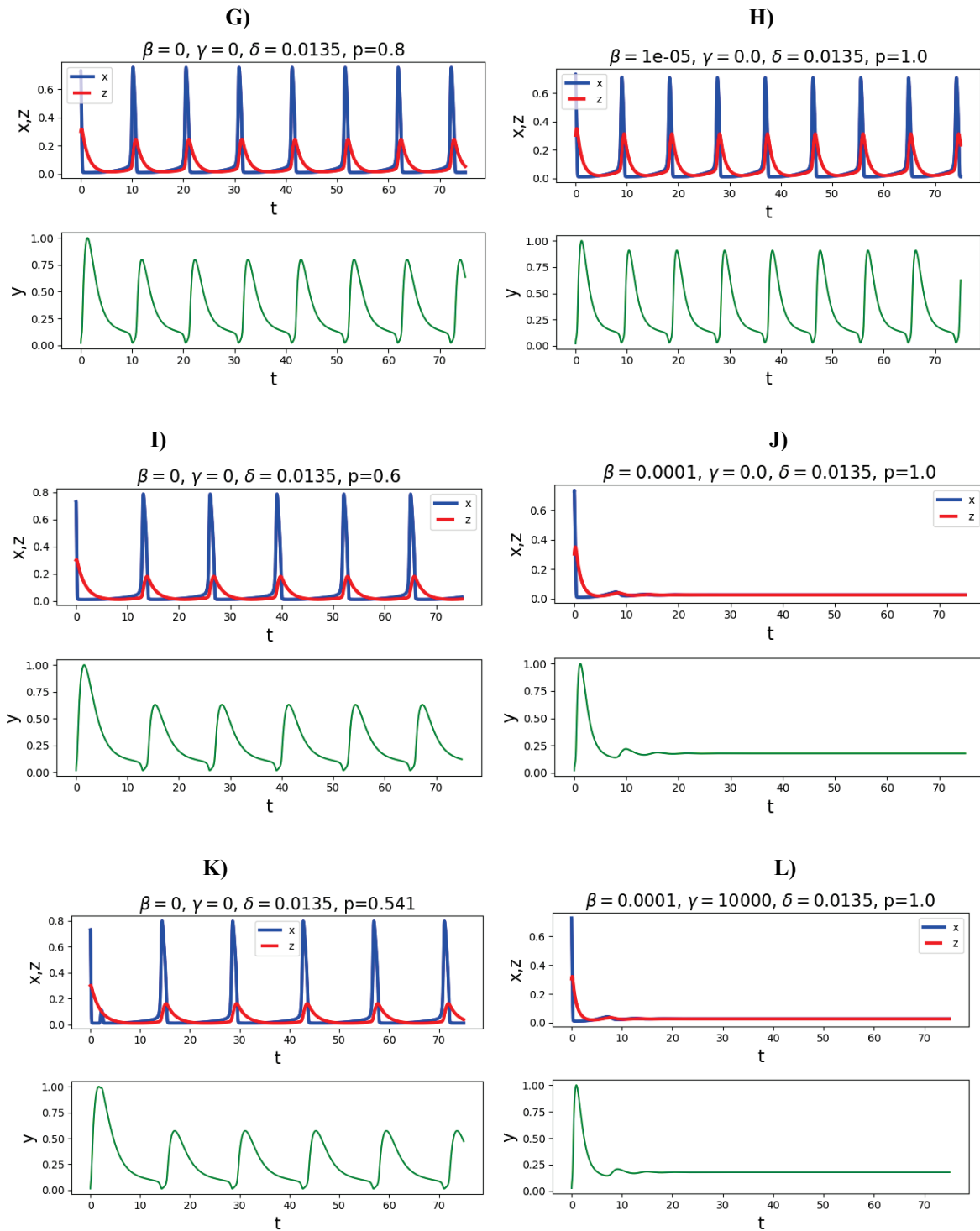
RESULTS OF SIMULATIONS

Next, we show the numerical results of the Hopf instability for certain values of the considered parameters. By numerically solving the Eq. (21) using the numerical method of Runge Kutta with step  $dt = 0.005$  time and fixed initial conditions  $x_0 = 0.3, y_0 = 0.7$ , are obtained the solutions shown in Figs. 1, 2.



**Figure 1.** The plots of the left column shows the elimination of the oscillations when the value of control parameter  $\delta$  is incremented for  $p = 1, B = 1$  and  $r = 1$ . The value change of the control parameter  $r$  alters the shape of the oscillations and when  $r \rightarrow 0$  for  $p = 1, B = 1$  the value of contractions  $x, y$  and  $z$  tend to their fixed point (see right panel)

In this work, we reproduce the general model already published (reference [1]) in which we consider  $\beta = 0, \gamma = 0$  and vary the value of  $\delta$  which in fact decreases from the value of  $\delta = 0,0025$  to  $\delta = 0,0137$  (see panels A-E of Figure 1) until it cancels out, i.e. a dither of the reaction is obtained and the oscillations disappear (panel E) by decreasing the oscillation frequencies and for intermediate values of  $\delta$  in the above given interval. It is found from these results that the parameter  $\delta$  modulates the oscillations until they decrease which turns out to be the only parameter that does so. An interesting result that can be observed from the graphs in the panels



**Figure 2.** The plots of the left column shows how changing the value of control parameter  $r$ , the oscillations number decremented for  $r = 1, B = 1$ . The difference between the control parameter  $p$  and  $r$  is that  $p$  does not eliminate oscillations, it simply extends the oscillation period. The control parameter  $B$  has a similar effect on the oscillations as that of  $r$  and  $p$ . The right column shows the effect of the  $\beta$  and  $\gamma$  control parameters on the oscillations, which are highly sensitive to the  $\beta$  parameter for  $r = 1$ , no matter how small its value is, in such a way that if its value is large enough, the oscillations are damped. While regardless of the value of the  $\gamma$  control parameter, the oscillations do not change in any way

on the left of Figure 1 is that the control parameter  $r$  determines when the oscillations end and at what concentration they stabilize. Unlike what might be considered, this parameter does not cancel out at the origin. On the other hand, when fixing the other parameters and varying  $p$ , as shown in panel G) of Figure 2, it can be seen that the value of beta  $\beta = 1 * 10^{-5}$ , although small, modulates the frequency and can make the oscillations advance faster or even destroy them. The beta parameter is the most sensitive of all, as small variations in it can significantly modify the oscillations, as can be seen in panels H, J, L of Figure 2. This is due to its association with the quadratic terms in the equations [see Ecs. (21)], resulting in the expansion in power series of the model already published in [1].

## CONCLUSIONS

The proposed thermo-kinetic Oregonator model is the generalization of models reported in Refs. [1-3, 5, 6], is easy to study numerically and analytically such that reproduces the models published in Refs. [7-9]. This property of our model allows extend this study to a thermodynamic and Physic-Chemical treatment [1, 8], but this point is a reason for future work. Furthermore, our model has a nonlinear chemical dynamic given by kinetic and physicochemical feedback mechanisms to reproduce the behavior of realistic chemical oscillations,

The proposed thermokinetic oregonator model is a second-order generalization of the model proposed in Ref. [1] [and its references therein] to study numerically and analytically what the model proposed in [1] reproduces. The properties of our model allow for an extension of the study towards a thermodynamic and physicochemical approach, making it a good basis for further studies on reaction-diffusion in nonlinear chemical systems, such as Turing instabilities, for example.

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**ОБОБЩЕНИЕ МОДЕЛИ ТЕРМОКИНЕТИЧЕСКОГО ОРЕГОНАТОРА**

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**Аннотация.** В работе предлагается способ обобщить термокинетическую модель орегонатора для моделирования динамики колебательных химических реакций. Для моделирования используются элементарные численные методы с использованием метода Рунге–Кутты, которые дают очень хорошую аппроксимацию математических решений моделей этих сложных систем нелинейной химии. Смысл результатов моделирования заключается в воспроизведении нелинейной динамики термокинетической модели орегонатора к температурам, отличным от комнатной. Кроме того, проводится анализ линейной устойчивости для поиска областей колебаний в пространстве параметров предлагаемой модели.

**Ключевые слова:** модель орегонатора, осциллирующая химическая реакция, нелинейная химия.