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A NOTE ON OSCILLATIONS IN A SIMPLE MODEL OF A CHEMICAL REACTION

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Abstract

We investigate oscillatory behaviour in the famous Belousov-Zhabotinskii chemical reaction, as described by the simple two-variable Oregonator model. It is shown that oscillations are possible only in certain parameter regions. Numerical results are presented, and the presence of fold bifurcations discussed.

1. Introduction

One usually thinks of a chemical reaction beginning with certain reactants and then proceeding in a uniform manner until the concentrations have reached their equilibrium values. This note is concerned with oscillatory solutions, which only relatively recently have been discovered and accepted in chemical reactions. Epstein *et al.* [1] review the history and extent of this now widely accepted phenomenon.

A particularly famous oscillating reaction is the Belousov-Zhabotinskii reaction. Perhaps the simplest model is given by Field and Noyes [2], which they named the Oregonator.

In dimensionless form, the governing equations, as suggested by Tyson [7], are

$$\epsilon_1 \frac{dx}{d\tau} = \frac{(q-x)fz}{(q+x)} + x(1-x),$$
$$\frac{dz}{d\tau} = x - z. \tag{1}$$

Here $x(\tau)$ and $z(\tau)$ represent the concentrations of $HBrO_2$ and $Ce(IV)$ respectively. The parameter ϵ_1 is a dimensionless combination of some of the rate constants, the quantity q is related to the concentration of a certain chemical reagent and f is a stoichiometric parameter in one of the reactions. Further details are given in Gray

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and Scott [4]. In this note, we present a theorem relating to the existence of periodic solutions of (1), and illustrate some of these numerically.

2. Qualitative results

This section begins with a trapping theorem for the functions $x(\tau)$ and $z(\tau)$.

LEMMA. *The two-variable Oregonator model (1) always possesses a finite attractor for* $q < 1$.

PROOF. When $x = q$, $\epsilon_1 dx/d\tau = q(1-q)$ which is positive provided $0 < q < 1$. Hence trajectories move right from $x = q$. When $x = 1$, then $\epsilon_1 dx/d\tau = (q-1)fz/(q+1)$ which is negative when $0 < q < 1$, and therefore trajectories move left from $x = 1$. When $z = 0$, $dz/d\tau = x$ and this is positive, making trajectories move up the z-axis. Finally, when $z = 1, dz/d\tau = x - 1$ which is negative since $0 < q < 1$, and trajectories move down from $z = 1$. Hence, the trajectories are *trapped* in the region $q < x < 1$ and $0 < z < 1$.

We are now in a position to state the major result.

THEOREM. *Oscillatory solutions are not possible in the 2-variable Oregonator when*

(1) $\epsilon_1 > 1$,

(2) $f > \dfrac{(1+q)^2}{2q}\left(\dfrac{1-\epsilon_1}{q} - 2\right)$.

PROOF. The proof that periodic solutions to the governing equations are not possible in certain parameter regions is established by using Dulac's theorem. This theorem is a generalization of Bendixson's negative criterion and may be found in Jordan and Smith [6, pages 84, 93]. Periodic solutions are not possible if there exists a function $B(x, z)$ such that the quantity

$$S = \frac{\partial}{\partial x}\left(\frac{B}{\epsilon_1}\left[\frac{(q-x)fz}{(q+x)} + x(1-x)\right]\right) + \frac{\partial}{\partial z}\left(B(x-z)\right) \tag{2}$$

is nonzero and does not change sign.

By choosing $B(x, z) = 1$, (2) simplifies to

$$S = \frac{-2qfx}{\epsilon_1(q+x)^2} + \left(\frac{1}{\epsilon_1} - 1\right) - \frac{2}{\epsilon_1}x.$$

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As before, q, f and x are all positive quantities; therefore in order to keep S of one sign (negative), it is necessary to choose $\epsilon_1 > 1$.

The proof of part (2) of the theorem is achieved in a similar manner. Its proof chooses a positive Dulac function $B(x, z)$ of the form

$$B(x,z) = B_0 x^{-(1-\epsilon_1)}(1-x)^{-(k+1+\epsilon_1)}\exp(kz/\epsilon_1) \tag{3}$$

which simplifies (2) to

$$S = Bz\left(\frac{f(q-x)(x(2+k)-(1-\epsilon_1))}{\epsilon_1(q+x)x(1-x)} - \frac{2qf}{\epsilon_1(q+x)^2} + \frac{k}{\epsilon_1}\right). \tag{4}$$

The impossibility of limit cycle behaviour is established by showing that certain choices of the constant k lead to an expression for S that is always of one sign. If one chooses k such that $q(2+k)-(1-\epsilon_1) > 0$, then

$$k > -2 + \frac{1-\epsilon_1}{q}$$

and the first term in (4) is negative, by the lemma. Now let

$$k = -2 + \frac{1-\epsilon_1}{q} + t, \qquad t \geq 0. \tag{5}$$

The function S in (4) can be guaranteed negative if the last two terms in the parentheses, written here as

$$H(x) = \frac{-2qf}{\epsilon_1(q+x)^2} + \frac{k}{\epsilon_1},$$

are made negative. By the lemma, x lies in the interval $q < x < 1$, and the function $H(x)$ can easily be shown to have no maxima within this interval, since $H'(x) > 0$. Therefore $H(x) < 0$ if $H(1) < 0$, where

$$H(1) = \frac{-2qf}{\epsilon_1(q+1)^2} + \frac{k}{\epsilon_1}.$$

To keep this quantity negative, choose

$$k < \frac{2qf}{(1+q)^2}.$$

Substituting k from (5) gives

$$\frac{2qf}{(1+q)^2} > -2 + \frac{1-\epsilon_1}{q} + t.$$

On setting $t = 0$, the result follows.

Part (1) of this theorem extends the observation of Gray and Scott [4] page 384, that oscillations born from Hopf points are not possible for $\epsilon_1 \gtrsim .88$, since this theorem now eliminates the possibility of oscillations from *any* source for $\epsilon_1 > 1$.

3. Relaxation oscillations ($\epsilon_1 = 0$)

In the case when $\epsilon_1 \to 0$, limit cycles possessing discontinuous jumps are possible, as indicated by Gray and Scott [4] for example. The system (1) becomes

$$0 = \frac{(q-x)}{(q+x)fz} + x(1-x) = g(x,z),$$
$$\frac{dz}{d\tau} = x - z = h(x,z). \tag{6}$$

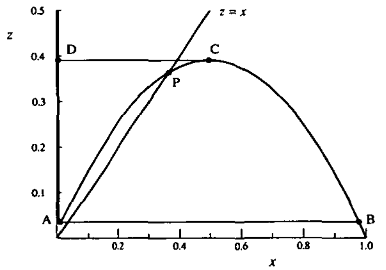

FIGURE 1. Illustration of the nullclines $g(x, z) = 0$ and $h(x, z) = 0$ for the parameter values of $\epsilon_1 = 0$, $f = .65$ and $q = .004$. The nullclines intersect at point P, and the stable relaxation oscillation is the cycle ABCDA.

The first equation in this system is now purely algebraic, and limit cycles consist of portions of this nullcline curve $g(x, z) = 0$, connected by discontinuous jumps. This condition $g(x, z) = 0$ describes the cubic curve

$$z = \frac{x(q+x)(x-1)}{f(q-x)} \tag{7}$$

shown in Figure 1, in which z decreases from infinity at $x = q$, through the point D, to a minimum at A and a local maximum at C, then continues through point B to cross the axis at $x = 1$.

The second equation in the system (6) reveals another nullcline when $dz/d\tau = 0$, giving the condition $h(x, z) = 0$, which is simply the straight line $z = x$ in the phase plane. This second nullcline, passing through the origin and point P, is shown in Figure 1. The resulting stable limit cycle is the curve ABCDA in the phase plane, and consists of the portions DA and BC of the nullcline $g(x, z) = 0$, connected by the discontinuous jumps AB and CD. Thus a large stable limit cycle of relaxation type exists for $\epsilon_1 = 0$, and this structure persists for small $\epsilon_1 > 0$, as the numerical results of the next section indicate. In addition, small unstable limit cycles are also possible when $\epsilon_1 > 0$.

4. Numerical examples

Periodic solutions have been obtained for a variety of parameters using a shooting algorithm, in the manner described by Forbes [3]. The results confirm the predictions of the theorem in Section 2. Here, limit cycles are illustrated for $\epsilon_1 = .004$, since this value is experimentally feasible, and allows several extra features of these oscillations to be highlighted.

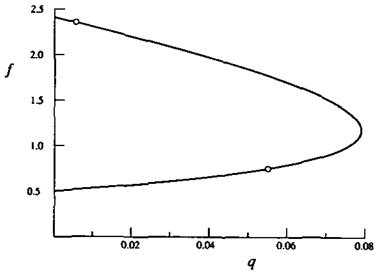

FIGURE 2. A periodic solution can be born from each point on this Hopf curve in the $f - q$ parameter plane. Oscillations will occur in the region enclosed by the curve. The circles represent the two points of degenerate Hopf bifurcation.

Figure 2 shows the location of Hopf points in the $f - q$ parameter plane, for the case $\epsilon_1 = .004$. Oscillatory behaviour is therefore to be expected within the region enclosed by this curve. The two circles on this curve indicate points of degenerate Hopf bifurcation where the limit cycle changes from supercritical to subcritical, and the possibility of multiple limit cycles arises. These points were computed using a simplified version of the algorithm of Hassard, Kazarinoff and Wan [5]. The numerics indicate that the upper degenerate Hopf bifurcation point on this curve is present for ϵ_1 in the approximate range $0 < \epsilon_1 \leq 0.187$, whereas the lower degenerate point is always present on the curve for $\epsilon_1 > 0$.

Multiple limit cycles are illustrated in Figure 3(a), for the case $f = .51391697$ and $q = .004$, with $\epsilon_1 = .004$ as in Figure 2. The outer limit cycle is stable, and the inner cycle, of smaller amplitude, is unstable. Within this region of parameters, relaxation oscillations occur. These are characterized by rapid changes in x and z over a very short time interval, followed by long intervals of only slight variation, similar to the behaviour with $\epsilon_1 = 0$ described in Section 3. This behaviour may be seen for the

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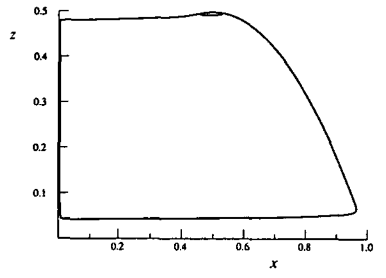

Figure 3(a). Two limit cycles can simultaneously exist at certain parameters. For $f = .51391697$ and $q = .004$, this behaviour occurs. The outer stable limit cycle surrounds the inner, unstable limit cycle.

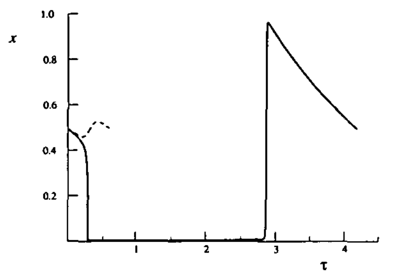

Figure 3(b). The concentration of x is shown as a function of τ for the two limit cycles which exist for the parameters $f = .51391697$ and $q = .004$. The dashed line represents the unstable limit cycle, while the solid line illustrates the stable limit cycle.

large amplitude solution in Figure 3(b), in which the concentration x is shown as a function of τ. The small amplitude solution, sketched with a dashed line, also occurs at the same parameter values, and is unstable.

The amplitude A_x of periodic solutions, that are born from the Hopf points, is shown in Figure 4 as it varies with the stoichiometric parameter f, for the case $q = .004$. Amplitude is defined here as the difference between the maximum and minimum value of x on the limit cycle shown in Figure 3(a). For small amplitudes, the numerically obtained periodic solutions have followed precisely the theoretical prediction given by Hassard *et al.* [5]. For the above parameters, Figure 2 indicates that both Hopf points give rise to oscillatory behaviour through subcritical bifurcations; this means that in some neighbourhood of each Hopf point, the curve in Figure 4 must undergo a fold, resulting in two simultaneous solutions, as in Figure 3(a). This behaviour has indeed been found numerically near the lower Hopf point. The extreme sensitivity of the numerically obtained limit cycles near the upper Hopf point has prevented us from completing this portion of the curve in Figure 4. Nevertheless, stable orbits have been

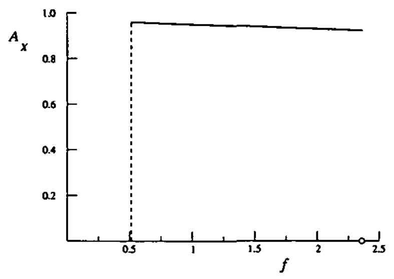

Figure 4. The amplitude A_x of periodic solutions, that are born from the Hopf points, is shown as it varies with the parameter f for $q = .004$. The circle shown on the f axis is the upper Hopf point.

computed for values of f above the upper Hopf point, confirming the predictions of the theory.

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