A modified Oregonator model exhibiting complicated limit cycle behavior in a flow system

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(Received 13 February 1978)

A reversible Oregonator model has been used to simulate recent experimental measurements by Schmitz, Graziani, and Hudson of complicated oscillations by a Belousov–Zhabotinsky system in a stirred tank reactor. The experimental observations indicate chaotic behavior of the small amplitude oscillations occurring between major excursions, but our computer simulation with a small error parameter apparently generates a true limit cycle with six relative maxima before the pattern repeats. The differences between experiment and simulation suggest the chaotic behavior observed experimentally may result from fluctuations too small to measure in any other way. The computations also indicate that reversibility of the reaction of bromate with bromide is important in a continuously stirred tank reactor under conditions such that the (unstable) steady state has a very low concentration of bromide ion.

INTRODUCTION.

The Belousov–Zhabotinsky reaction is the best established example of a chemical system exhibiting temporal oscillations. Most of the initial studies were done in closed batch reactors, and concentrations of key intermediates oscillated through tens or even hundreds of cycles with only gradual change in period and amplitude. However, no closed system can sustain exactly repetitive oscillations indefinitely.

Truly sustained oscillations are possible in principle with a continuously stirred tank reactor (CSTR) to which reactants are added at a constant rate while an equal volume of effluent is removed from the stirred reactor. Such a system may exhibit behavior much more complex than limit cycle repetition of oscillations with a single amplitude and period. Probably the most complete experimental characterization of possibilities is due to Schmitz, Graziani, and Hudson. They showed that for the same composition of input solutions an increasing total flow rate could generate in succession (a) repetitive large amplitude oscillations, (b) alternating large and small amplitude oscillations, (c) large amplitude oscillations separated by chaotic collections of small amplitude oscillations, (d) regular small amplitude oscillations, and (e) non-oscillatory steady flow! Their experimental observations are illustrated in Fig. 1.

Much of the interest in this type of system has concerned the possibility of "chaos" such that there is no repetitive pattern of behavior no matter how long the period of observation. Both Schmitz et al. and Rössler and Wegmann recognize that any experimental system is subject to unavoidable external perturbations. Therefore, failure to observe exact repetition in a CSTR cannot prove the system would be truly chaotic in the complete absence of perturbation. To the extent the chemistry is understood, mathematical analysis and numerical computation on model systems may reveal more about the possibilities of chaos than will experimental measurements.

Theoretical efforts to model chaos are agreed that concentrations of at least three intermediate species...
must be used as independent parameters to describe the instantaneous state of the system. If the system is constrained to move on a surface folded in a phase space of three parameters, and if an unstable steady state exists on that surface, hysteresis transitions between folds of the surface can generate behavior that is chaotic. Such a situation is illustrated in Fig. 2 due to Schmitz et al.\textsuperscript{5} and based on a previous model by Rössler.\textsuperscript{5}

The detailed chemistry of the Belousov–Zhabotinsky reaction is quite complex\textsuperscript{6,7} and involves many intermediate species. Field and Noyes\textsuperscript{8} have extracted the most essential features with the "Oregonator" model involving five chemical steps and three intermediate species whose concentrations may vary periodically. In the original model,\textsuperscript{8} all five steps were treated as irreversible. Tyson\textsuperscript{9} has recently modified the kinetics of the autocatalytic third step to prevent indefinite buildup of species $Z$ and has shown this modification generates bistability in a flow system. He also shows this modified model could generate chaos but does not compute any trajectories.

We were unsuccessful in efforts to use the irreversible Oregonator model to compute trajectories resembling those observed by Schmitz et al.\textsuperscript{3} However, we were successful when we used a model developed by Field\textsuperscript{10} in which the first four steps of the Oregonator are made reversible with rate constant ratios determined by thermodynamics. In order to model the chemistry existing in a CSTR, we also found it necessary to replace the autocatalytic step with two steps which necessitate an additional variable.

**PROCEDURE**

The modified Oregonator\textsuperscript{8} mechanism used for these computations consists of six steps:

\begin{align*}
A + Y & = X + P \quad \text{(F1)} \\
X + Y & = 2P \quad \text{(F2)} \\
A + X & = 2W \quad \text{(F3)} \\
C + W & = X + Z' \quad \text{(F4)} \\
2X & = A + P \quad \text{(F5)} \\
Z' & = gY + C. \quad \text{(F6)}
\end{align*}

These equations involve seven species whose chemical identities are indicated by the following assignments: $A = BrO_2^-$, $C = M(n)$, $P = HOBr$, $W = BrO_2^+$, $X = HBrO_2$, $Y = Br^-$, $Z' = M(n+1)$. In these assignments, $M(n)$ is the reduced form of a metal ion catalyst, and $M(n+1)$ is that form oxidized by one equivalent. Note that the third step of the original Oregonator has been replaced by two steps that introduce the additional species $W$ and make the assignment for the new species $Z'$ differ from that for the original $Z$ by a stoichiometric factor of 2. The parameter $g$ is therefore half of the $f$ in the original Oregonator.\textsuperscript{8} The chemical significance of this model is discussed below.

The changes with time of the seven concentrations can be described by as many differential equations of forms indicated by (1) and (2), which apply to species which were or were not, respectively, present in the feed:

$$dY/dt = k_0(Y_0 - Y) - k_1 AY + k_{-1}XP-k_2XY+k_{-2}P^2+gk_6Z'$$

\hspace{1cm} (1)

$$dZ'/dt = -k_0Z' + k_4 CW - k_{-4}XZ' - k_6 Z'.$$

\hspace{1cm} (2)

In these equations, the species $A$, $C$, and $Y$ were assumed present in the feed and generated terms like $k_0 Y_0$ where $k_0$ is the reciprocal of the residence time in the reactor and $Y_0$ is the concentration this feed would have generated if no chemical reaction took place. All seven equations contained terms like $-k_0 Z'$ to describe slow diffusion from the reactor.

In the calculations described here, feed concentrations were $A_0 = 0.14 M$, $C_0 = 1.25 \times 10^{-4} M$. The parameters $k_0$, $k_1$, $k_2$, and $g$ were varied for different computations as indicated in the figures. Values of the other rate constants in $M^{-1} \text{sec}^{-1}$ were assigned as follows based on best present estimates\textsuperscript{11} for chemical behavior if $[\text{H}^+]^0 = 0.2 M$.

\begin{align*}
&k_1 = 0.084, \quad k_{-1} = 1 \times 10^4, \\
&k_2 = 4 \times 10^6, \quad k_{-2} = 5 \times 10^{-6}, \\
&k_3 = 2 \times 10^8, \quad k_{-3} = 2 \times 10^7, \\
&k_4 = 1.3 \times 10^8, \quad k_{-4} = 2.4 \times 10^4, \\
&k_5 = 4 \times 10^7, \quad k_6 = 4 \times 10^{-41}.
\end{align*}

The seven simultaneous equations were integrated numerically by the method of Gear,\textsuperscript{12} and the results
presented here apply to computations continued until they generated repetitive behavior that did not change further with time.

RESULTS

The plots in Fig. 3 illustrate the time dependence of \( Y \) for three situations identical except for changes in \( k_0 \). These computations, which were among our first, show a dependence on flow rate that reproduces the essential features of Figs. 1(a) and 1(b). As \( k_0 \) increased further, more small amplitude oscillations were observed between the large amplitude ones, and at \( k_0 = 8.466 \times 10^{-4} \text{ sec}^{-1} \) the system generated a stable steady state resembling Fig. 1(e). However, we could not find a \( k_0 \) value that generated solely small amplitude oscillations like those in Fig. 1(d).

We found we could obtain greater sensitivity if \( Y_0 \) was reduced by a factor of about 2.3 and if \( k_0 \) and \( g \) were also changed somewhat. Figure 4 shows the last computations we did; they reproduce the essential features of experimental Figs. 1(d) and 1(e).

A major objective of our computations was to determine whether the chaotic behavior observed experimentally in Fig. 1(c) is inherent in the differential equations describing the system or whether that behavior results from random uncontrolled perturbations acting on a very sensitive system. All the remaining figures involve computations with a single value of \( k_0 \) and with a different parameter set based on slightly smaller values of \( k_0 \) and \( g \) than were used in Fig. 4.

Figure 5(a) shows the resulting complicated behavior which somewhat resembles experimental Fig. 1(c) but
the latter scarcely responds to the small amplitude oscillations. Species \( W \) is so stiffly coupled to \( X \) it did not appear useful to display its behavior also.

The limit cycle trajectory in three-dimensional \( PYZ' \) phase space can be recovered from projections in two planes. Figure 7 shows the projection in the \( Y-Z' \) plane. Note that the small amplitude oscillations occur when \( Z' \) is near its maximum value. This region of the projection is shown in larger scale in Fig. 8, and this figure also indicates the projection of the (unstable) steady state obtained if rates of change of all seven concentrations are simultaneously zero. The composition of that steady state is shown in Table I.

**FIG. 4.** Logarithmic plots of \( Y \) computed for \( A_0=0.14M \), \( C_0=1.25\times10^{-7}M \), \( Y_0=1.51\times10^{-6}M \), \( k_4=0.68 \text{ sec}^{-1} \), \( g=0.588 \), and \( k_8 \) values in sec\(^{-1}\) of (a) \( 5.976\times10^{-3} \), (b) \( 7.97\times10^{-3} \). Compare with Figs. 1(d) and 1(e).

is much more regular. The behavior in Fig. 5(a) resembles an exact limit cycle in which \( Y \) passes through six relative maxima and minima before the pattern is repeated.

Figure 5(b) shows the detail our computations generate for the small amplitude oscillations. Note that the amplitudes are largest at the ends of this period and pass through a minimum in the middle. The significance of these observations for the Rössler–Schmitz model of chaos is discussed below.

Figure 6 shows the temporal behavior of four key species during one complete period. The behavior of \( Z' \) uses a linear rather than a logarithmic scale because

**FIG. 5.** Logarithmic plots of \( Y \) computed for \( A_0=0.14M \), \( C_0=1.25\times10^{-7}M \), \( Y_0=1.51\times10^{-6}M \), \( k_4=0.68 \text{ sec}^{-1} \), \( g=0.462 \), and \( k_8=7.97\times10^{-3} \text{ sec}^{-1} \). Full scale oscillations are shown in (a) while (b) amplifies a single set of small amplitude oscillations. Compare with Fig. 1(e).
Figure 9 shows the projection of the same limit cycle in the \( Y-P \) plane and also shows the projection of the steady state, which falls outside the projection of the limit cycle but is on the projected axis of the small amplitude oscillations. Note that the \( Y-Z' \) spiral in Fig. 8 moves roughly parallel to the \( P \) axis and goes through a minimum amplitude in the middle as though it were moving on the surface of an hourglass. Note also that...
FIG. 7. Projection in $Y-Z'$ phase plane of limit cycle trajectory derived from plots of Figs. 6 (a) and 6(b). Box shows region enlarged in Fig. 8.

FIG. 8. Projection in $Y-Z'$ phase plane of small amplitude oscillations during interval shown in Fig. 5(b). This plot is an enlargement of the box in Fig. 7.
TABLE I. Composition of steady state for system based on parameters of Figs. 5–8.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.1403 M</td>
</tr>
<tr>
<td>C</td>
<td>1.195 × 10^4 M</td>
</tr>
<tr>
<td>P</td>
<td>4.312 × 10^4 M</td>
</tr>
<tr>
<td>W</td>
<td>3.628 × 10^3 M</td>
</tr>
<tr>
<td>X</td>
<td>1.576 × 10^4 M</td>
</tr>
<tr>
<td>Y</td>
<td>2.704 × 10^4 M</td>
</tr>
<tr>
<td>Z'</td>
<td>5.440 × 10^4 M</td>
</tr>
</tbody>
</table>

Y and Z' change by several orders of magnitude during a complete cycle, while P ranges only about a factor of 2.

DISCUSSION

Semiquantitative explanation of results

The regularity in Fig. 5(a) suggests that the trajectory is completely deterministic and generates a true limit cycle. When that trajectory is projected in the Y–Z' plane (Figs. 7 and 8), some segments cross each other; such behavior is possible only if a description of the instantaneous state requires more than two parameters.

The model we use involves seven concentration parameters, but C + Z' = C0 at all times so these two are not mutually independent. The model does not develop any other stoichiometric constraints such as conservation of bromine atoms or of degree of oxidation. However, A8 is so much larger than the concentration of any other species that A (or at least A + P) can be regarded as invariant. The species X and W are always present in very small concentrations stiffly coupled to the other species in the system; the k0 terms do not contribute significantly to their dynamic equations.

We therefore conclude that to a fair approximation the instantaneous state of the system can be described in terms of the three phase-determining13 intermediates Y, Z', and P. It is important that P is present in the greatest concentration of the three and is most sluggish in its responses.

The trajectories shown in Fig. 6 exhibit two very different intervals. Interval α starts when Y has just passed its absolute maximum and is decreasing slowly. During this interval, Z' is initially large but decreases rapidly, P has just passed its maximum and is decreasing slowly, and X is very small and hardly changes during most of interval α. As the end of the interval approaches, Y is decreasing toward a critical value at which X rises dramatically by several orders of magnitude while Y decreases and Z' increases; the system switches to interval β.

Interval β starts when Y has just passed its absolute minimum, Z' has reached its absolute maximum, P is at its minimum, and X is very large. During this interval, Y increases very rapidly at first while X decreases and Z' and P change relatively little. A point is soon reached at which small amplitude oscillations occur in X, Y, and Z'. During these small oscillations, P increases monotonically, X and Z' undergo net decreases, and Y undergoes a net increase. When Y attains a critical value, X falls precipitously while Y increases to its maximum, and the system returns to interval α.

The behavior of the system can be described by approximations similar to those used previously.8,13 We shall continue to consider steps (F2), (F5), and (F6) as virtually irreversible but allow the possibility of reversibility for steps (F1), (F3), and (F4). When Y is large as during interval α, X can be described very well by the approximation $X_{\text{small}}$:

$$X_{\text{small}} = \frac{k_1 A Y}{k_0 + k_1 P + k_2 Y - k_3 A} .$$

In this equation, $k_1$ is a composite parameter which equals $k_2$ if steps F3 and F4 are irreversible; even for systems in which it differs from $k_2$, it probably does not vary much14 during the parts of a cycle for which it is important.

![Graph of projection in Y–P phase plane of limit cycle trajectory derived from plots of Figs. 6(a) and 6(c).](image)

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When \( Y \) is small as during interval \( \beta \), \( X \) can be described very well by the approximation \( X_{\text{approx}} \):

\[
X_{\text{approx}} = \frac{k_2 A - \frac{A}{b_0} - \frac{k_2}{b_0} P - \frac{k_2}{b_0} Y}{k_2}.
\]

The system makes almost discontinuous changes between \( X_{\text{small}} \) and \( X_{\text{approx}} \) whenever even very small changes in \( Y \) or in \( P \) cause \( Y \) to pass through \( Y_{\text{crit}} \):

\[
Y_{\text{crit}} = \frac{k_2 A - \frac{A}{b_0} - \frac{k_2}{b_0} P}{k_2}.
\]

There will be at least one steady state with positive concentrations of all species such that the seven rate equations like (1) and (2) are all simultaneously zero. If we designate this state by the subscript \( ss \), Eqs. (6)–(8) become very good approximations:

\[
Z'_{ss} = \frac{2k_2 A X_{ss}}{k_0 + k_2},
\]

\[
Y_{ss} = \frac{k_0 Y_{ss} + k_2 X_{ss} P_{ss} + g k_2 Z'_{ss}}{k_0 + k_1 A + k_2 X_{ss}},
\]

\[
P_{ss} = \frac{k_2 A Y_{ss} + 2k_2 X_{ss} Y_{ss} + k_2 X_{ss}^2}{k_0 + k_2 X_{ss}}.
\]

Of course \( X_{ss} \) will be between \( X_{\text{small}} \) and \( X_{\text{approx}} \). For the examples computed here, the \( k_2 \) terms in the denominators will be dominant in Eq. (8), negligible in (7), and comparable to \( k_2 \) in Eq. (6).

When flow rates are sufficiently small, the \( k_2 \) terms are all negligible, and the system resembles a batch Orogenator as shown in Fig. 3(a) in agreement with Fig. 1(a).

When flow rates are sufficiently large, \( Z'_{ss} \) is reduced, \( Y_{ss} \) increases above \( Y_{\text{crit}} \), \( X \) is held in the \( X_{\text{small}} \) approximation, and the system goes to a stable steady state as shown in Fig. 4(b) and as illustrated experimentally in Fig. 1(c).

The remarkable behavior in Figs. 5–9 occurs for a critical intermediate range of \( k_2 \) values. For such a system, the behavior during interval \( \alpha \) is qualitatively similar to that of an irreversible Orogenator in a batch reactor\(^{6,13}\) and need not be described here.

The initial stages of interval \( \beta \) also resemble a batch Orogenator. However, increasing \( Y \) brings the system to the small amplitude oscillations illustrated in Figs. 5(b) and 8.

These small amplitude oscillations require a very fine balance of opposing forces while \( P \) increases monotonically. As \( P \) increases, \( Y \) attains \( Y_{\text{crit}} \) before \( P \) attains \( P_{ss} \). Then \( X \) switches to the \( X_{\text{small}} \) approximation, \( P \) and \( Z' \) are removed by outflow more rapidly than they are produced chemically, and \( Y \) rises precipitously to the start of interval \( \alpha \). If a trajectory is constrained to move in two dimensions, a limit cycle passes around an unstable steady state. We see there is no such restriction for this three-dimensional limit cycle; the value of \( P \) always remains well below \( P_{ss} \).

Behavior like that in Figs. 5–9 is very dependent upon flow rate. Thus, for those figures \( Y_{ss} = 2.704 \times 10^6 \) and \( Y_{\text{crit}} = 2.733 \times 10^4 \) when all other species are at steady state values. Because the steady state is unstable, even a small oscillation carries \( Y \) through \( Y_{\text{crit}} \) and generates a large amplitude oscillation. If \( k_2 \) increases just a little bit, \( Y_{ss} \) will be sufficiently below \( Y_{\text{crit}} \) that large amplitude oscillations will not be initiated even by small amplitude ones, and the system will resemble Fig. 1(d). At still larger \( k_2 \), the steady state will become stable to infinitesimal perturbations.

This analysis is strongly supported by the calculations illustrated in Fig. 10. At each indicated value of \( P \), calculations were performed while maintaining both \( A \) and \( P \) constant at the values they had when this value of \( P \) was reached during a trajectory like that shown in Figs. 5–9. The calculations essentially maintained \( A + P = 0.14064 \) while \( P \) was varied.

If \( P \) was less than about 2,35 \times 10^4 M, a system at constant \( P \) went to a stable steady state having the indicated value of \( Y \). For larger values of \( P \), the steady state was unstable as indicated by the dashed line in Fig. 10. Below about 2.40 \times 10^4 M, the oscillations close to the steady state involved very small amplitudes; at larger \( P \) values, the amplitudes were very much larger. Large amplitude oscillations were only possible when \( P \) was greater than about 2.34 \times 10^4 M.

Figure 10 has important implications for the trajectory in Fig. 5(b). For the first two oscillations in that figure, \( P \) is small enough that the system is undergoing damped oscillations that would reach a steady state if \( P \) were maintained constant. However, \( P \) is simultaneously increasing and attains a value such that if it were then maintained constant the system would execute large amplitude oscillations; the amplitude in Fig. 5(b)
then increases for two or three periods until \( Y_{\text{crit}} \) is reached and the very large excursion is instigated.

**Chemical implications of the model**

Our model uses six steps given \( F \) designations. Those steps were chosen to reproduce the chemistry of the steps with \( C \) designations if \( \text{BrMA} \) is bromomalonic acid and \( \text{Fe(II)} \) is Fe(phen)

\[
\begin{align*}
\text{BrO}_3^- + \text{Br}^- + 2H^+ & \rightarrow \text{HBrO}_3^- + \text{HOBr}, \\
\text{HBrO}_3^- + \text{Br}^- + H^+ & \rightarrow 2\text{HBrO}_3^- \quad (C1) \\
\text{BrO}_3^- + \text{HBrO}_3^- + H^+ & \rightarrow 2\text{BrO}_3^- + H_2O, \\
\text{BrO}_3^- + \text{Fe(II)} + H^+ & \rightarrow \text{HBrO}_3^- + \text{Fe(III)}, \\
2\text{HBrO}_3^- & \rightarrow \text{BrO}_3^- + \text{HOBr} + H^+, \\
\text{Fe(III)} + \text{BrMA} - g \text{Br}^- + \text{Fe(II)} + \text{stable products} \quad (C6)
\end{align*}
\]

This model makes two major improvements on the Oregonator\(^8\) as originally formulated. First, it adds the species \( W \) (for \( \text{BrO}_3^- \)). This additon provides a stoichiometric constraint so that \( Z^c \) can not become larger than \( C^0 \). Such a constraint need not be important for modeling an irreversible step (3) in a batch reactor, but it is important for this system. It has the disadvantage that the number of intermediates is increased from three to four, but \( W \) can be treated as stably coupled to the other species. Tyson\(^8\) has also recognized the importance of a stoichiometric constraint when modeling a flow reactor, and he has satisfied it in an alternative way discussed below.

The second improvement is the introduction of reversibility. If all steps were irreversible, the value of \( P \) would have no effect on the dynamic behavior of the system. The previous section shows it is reversibility of step (F1) that permits the value of \( P \) to affect behavior in a flow system. The rate constants we employed retain virtual irreversibility for steps (F2) and (F5) which also produce \( P \).

In spite of these improvements, our model contains three simplifications that may have affected its ability to model the Schmitz\(^2\) experiments. The first simplification is that we treat \( P \) as \( \text{HOBr} \) and neglect the fact that at least half of this species must be consumed to form the \( \text{BrMA} \) reacting in step (C6). When we first learned that amplitudes of oscillations might follow a complex pattern in a flow system, one of us\(^18\) suggested the effects could be explained by treating \( \text{BrMA} \) as another intermediate affecting the rate of step (C6). We were unsuccessful when we tried to model the system in this way, but we were successful when we regarded \( P \) as \( \text{HOBr} \) and made step (F1) reversible. However, if \( \text{HOBr} \) is consumed in brominating malonic acid, we should not continue to make all of \( P \) available for the reverse of step (F1). We have undoubtedly introduced a small discrepancy, but an improvement would require separate designations for \( \text{HOBr} \) and for \( \text{BrMA} \); the model is already complicated enough.

The second simplification is that we used values of \( k_4 \) and \( k_4 \) based on the ratio if \( M(n+1) \) were cerium (IV) with a reduction potential of 1.44 V. We did so because we have used these same rate constants for model calculations\(^11\) on such a system. Schmitz \textit{et al.}\(^3\) used a different catalyst, and Fe(phen)\(^3\) has a reduction potential of only 1.06 V. The effect would appear in a difference between \( k_4 \) and \( k_3 \) as previously mentioned.\(^14\) Rate constants would probably not have to be changed much to adjust for such an effect, and Schmitz\(^9\) has reported other experiments with cerium catalyst in which he observed very similar behavior.

The third simplification is that we completely neglect the complicated chemistry of oxidation of organic compounds\(^17,18\) and the effects of such species on the rate of step (C6). The experiments dealt with a situation in which there was barely enough \( \text{BrMA} \) to produce the bromide ion necessary to drive the system out of the oxidized state of interval \( \beta \) corresponding to \( X_{\text{max}} \). The complications of these oxidation reactions could hardly have had negligible influence on the experimental results.

In spite of these admittedly incomplete features of our model, the computations do a remarkably effective job of reproducing the main features observed by Schmitz \textit{et al.}\(^3\). We used \( k_4 \) and \( g \) as somewhat disposable parameters and found conditions such that varying \( k_4 \) could reproduce most of the effects observed by experimental variation of the same quantity.

**Implications for "chaotic" behavior**

Part of the interest in this system arises because experimental measurements such as in Fig. 1(c) indicate random variations in the numbers and amplitudes of the small oscillations occurring between those of large amplitude. Schmitz \textit{et al.}\(^3\) very clearly recognize these effects might have been due to uncontrolled fluctuations in the experimental system.

The computed curve in Fig. 5(a) differs from the experimental one in Fig. 1(c) that a complex trajectory with six successive maxima and minima apparently repeats indefinitely. We made two types of calculations to obtain numerical evidence as to whether our model did indeed generate a true limit cycle.

One type of calculation was to vary the error parameter which determines the goodness of fit program will accept for joining solutions in adjacent time intervals. Figure 5(a) was calculated with an error parameter of \( 10^{-4} \), and the trajectory was not significantly affected if a smaller value was used. However, if the error parameter was increased to \( 4 \times 10^{-6} \), the behavior was less regular. The large amplitude oscillations were little affected by the reduced sensitivity, but the duration and number of small-amplitude oscillations varied from one period to the next. Therefore, the time between large-amplitude oscillations became irregular, although the variations were not as great as those observed experimentally in Fig. 1(c). We interpret these results to indicate that the behavior computed during the small-amplitude oscillations is very sensitive to numerical effects like round-off errors. Such a result suggests

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the experimental system might also be extremely sensitive to small perturbations during the same portion of the cycle.

The other type of calculation was to deliberately perturb the system to determine whether the computed trajectory seemed to be stable. We chose the time of perturbation to be near the midpoint of the small amplitude oscillations when the error parameter computations had indicated the greatest sensitivity of the system. In each of four runs, the value of $X$, $Y$, $Z^*$, or $P$ was reduced by a factor of 2 and the subsequent evolution of the system was followed. In two other runs, values of $Y$ and $P$ were increased by factors of 10. All six of these perturbed systems returned to the original behavior after a few atypical major periods, and the nature of the return trajectories supported the semiquantitative explanation developed above. Of course these perturbation effects do not constitute a formal mathematical proof that our trajectory is a true limit cycle. However, they provide strong numerical evidence that the computed trajectory is stable to perturbations in opposite directions just as a limit cycle should be.

If our interpretation of our computations is correct, and if we have properly modeled the reaction, the fluctuations observed in the experimental system would disappear in a completely isotropic medium subject to deterministic rate laws. Of course kinetic rate laws are ultimately stochastic, and step (F5) of the model is a bimolecular process between species present at about $10^{40}$ M or about $10^{42}$ molecules in a 25 militer reactor. However, even at this dilution we would not expect significant contribution from fluctuations due to the statistical nature of the second law of thermodynamics. We believe the apparently chaotic features observed by Schmitz et al. were due to more mechanical effects such as vibrations in the feed, inability to mix the feed instantaneously and uniformly throughout the reactor, etc.

Comparison with other models

Our conclusion that we are examining a true limit cycle is of interest because two theoretical models have been claimed to indicate chaotic behavior in this very system. One model by Tyson\textsuperscript{5} seems very similar to our own. He made all steps irreversible and eliminated the need for species $W$ by proposing a single step of stoichiometry $A + 2C + X - 2X + 2Z^*$ corresponding to (F3) + 2(F4). Tyson made the rate of this step first order in each of $A$, $C$, and $X$. He thereby imposed a stoichiometric ceiling on $Z^*$ that was missing from the original Oregonator\textsuperscript{4} but that was also generated by our present model. The Tyson kinetics do not exactly reproduce those generated by our model if $W$ becomes a transient intermediate stiffly coupled to $C$ and $X$, but the difference is not necessarily serious. Tyson also modified our step (6) to be $B + Z - k Y + Q$ where $Z = 2Z^*$ and $k = 2g$. In this equation, $B$ is claimed to be organic matter, some of it brominated, and $Q$ is unreacted oxidized organic matter.

The Tyson\textsuperscript{5} model is not obviously different from ours except perhaps in the irreversibility of all steps. The important point for the generation of chaos is that the Tyson model generates multiple steady states of potential experimental significance. We have searched for multiple steady states to our model by Newton's method\textsuperscript{41} and have been unable to identify more than one for which all concentrations are positive. We did discover other steady states with some negative concentrations, but they obviously have no physical significance. Of course our one steady state is unstable to perturbation, and the stable state of the system is the limit cycle represented by Figs. 7 and 9. We anticipate our model would generate physically significant multiple steady states for some parameter values, but we note we can reproduce the Schmitz observations with values that generate only one such steady state.

Figure 2 illustrates an alternative model for chaos that has been proposed by Rössler and amplified by Schmitz et al. The system is definable by three parameters and tends to move on a folded surface in three-dimensional phase space. Even though the system is constrained to move on that surface, it is repelled by one point and spirals away from it until it reaches a fold and undergoes a hysteresis transition to another portion of the surface. No system of elementary chemical processes is suggested that might generate such behavior, although Rössler claims his differential equations could arise from a chemical model.

We can not accommodate our trajectories to the Rössler-Schmitz model at least in the form of Fig. 2. In that figure, the system moving in a spiral on the upper surface must follow a trajectory such that its distance from the focus in any direction increases monotonically with number of turns. It appears inconceivable such a trajectory could generate the projection shown in Fig. 8. Our model does not generate chaos of the type proposed by Rössler.

Concluding remarks

We believe the computations described here have led to two major accomplishments. One is an improved understanding of the Belousov-Zhabotinsky chemistry in a type of situation not previously examined mechanically. All models related to the Oregonator generate $X_{\text{large}}$ and $X_{\text{small}}$ values that are interconverted by an extremely rapid transition whenever $Y$ passes through a critical value. The behavior is of most interest when the system has a steady state in which $Y_{\text{cr}}$ is near this $Y_{\text{crit}}$. The original Oregonator manuscript\textsuperscript{4} modeled a system with maximum instability to temporal oscillation by generating a steady state in which $X_{\text{ss}}$ was near the geometric mean of the $X_{\text{large}}$ and $X_{\text{small}}$ limits.

Field and Noyes\textsuperscript{19} subsequently applied the same equations to model a marginally stable but excitable steady state in which $X_{\text{ss}}$ was little more than the minimum possible for $X_{\text{small}}$. This treatment was good for modeling trigger waves, which are zones of oxidation passing through an excitable medium in a reduced situation.

The present computations generate a steady state in which $X_{\text{ss}}$ is little less than the maximum possible for $X_{\text{large}}$. This situation corresponds to a batch reactor at
the end of its induction period. Such a system could not be studied experimentally in a batch arrangement because the reactions would irreversibly pull the medium out of this oxidizing situation by creating more BrMA and hence more bromide ion. However, a CSTR can maintain the system in a steady state just at this limit.

An unanticipated discovery by these computations was the importance of reversibility of step (F1). That step goes from left to right when \( Y \) is large, and reverse reaction is dominant only when \( Y \) is less than \( Y_{crit} \), so that \( X \) is in the \( X_{true} \) approximation. Such a situation exists only very briefly during our previous computations in which \( X_{true} \) was very much less than the upper limit of \( X_{true} \). The situation is different in the Schmitz CSTR experiments, and the availability of HOBr to affect the reversibility of step (C1) becomes important to describe the system. Any final decision about this interpretation should include a fuller model. The BrMA source of bromide ion was constantly being depleted by flow during the Schmitz experiments, and our model does not recognize the importance of that fact. We are surprised at how well our model does reproduce the essential experimental features.

The other major accomplishment of these computations is to generate new evidence concerning the possibility of chaotic behavior in truly unperturbed systems. Our computations apparently generate strictly deterministic limit cycle behavior even when applied to a very complicated system that obeys differential equations applicable to chemical kinetics. We are not presently aware of any example of a chemical mechanism based on elementary processes whose kinetic equations generate behavior that is truly "chaotic." We have personal doubts it will be possible to develop such a model if the requirements of thermodynamic reversibility are applied to the rate constants for the various steps.

In spite of the failure to generate a model for truly chaotic behavior, these deterministic computations have important implications for both theory and experiment. The system is extremely sensitive to fluctuations, and we needed considerable care to insure our computations did indeed generate a limit cycle. A very sensitive experimental system like this might greatly amplify the effects of fluctuations too small to determine in any other way. Our computations also generated nonperiodic behavior at sufficiently large values of the error parameter, but we are not sure this effect really resembles the randomness observed experimentally. Probably a more valid comparison with experiment would be provided by the stochastic procedures recently developed by Gillespie.\(^{20}\) Computations at different levels of computational indeterminacy could be used to estimate the level of fluctuations at which experimental variability was duplicated. Such comparisons might permit estimates of the magnitudes of extremely small fluctuations in very sensitive experimental systems. As was indicated above, we doubt such studies could be extended until the fluctuations arose from the stochastic nature of the very equations of chemical kinetics, but such a possibility should not be excluded.

ACKNOWLEDGMENT

This work was supported in part by a grant from the National Science Foundation. The comments of an anonymous referee led us to perform the computations showing our trajectory was stable to perturbation.

\(^{9}\)J. J. Tyson (personal communication).
\(^{14}\)If a steady state approximation is applied to species \( W \), the effects of reversibility of steps (3) and (4) are given by

\[
\begin{align*}
&k_c = k_c \frac{1 - k_{-2} k_{4} Z' / k_{2} A c}{1 + 2h_{4} A W / k_{2} C} \\
&= k_c(1 - k_{-2} Z' / k_{2} C - k_{-2} A X / k_{2} c)
\end{align*}
\]

where the approximation is to first order in \( W/C \).