Modelling complex transient oscillations for the BZ reaction in a batch reactor

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The recent observations of transient complex oscillations in the Belousov–Zhabotinsky (BZ) reaction in a batch reactor are confirmed and an attempt is made to model this behavior using the Gyorgyi–Field mechanism (an extension of the classic Field–Körös–Noyes model). It is seen that the concentration of bromomalonic acid plays an important role, acting somewhat like a ”slowly-varying parameter,” causing the system to sweep through a region of oscillatory response even in the absence of reactant consumption. Complex behavior is not observed in the model if the usual ”pre-equilibrium” assumption in made for the intermediate species BrO_2 but does arise if a full steady-state approximation is applied to this radical. These results may bring into question some assumptions made in the usual treatment of the cerium-catalyzed BZ system in closed reactors.

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Chemical reactions in thermodynamically closed (batch) reactors, those with no exchange of chemical species with their surroundings, are known to possess a unique, stable state of chemical equilibrium. It is now well established, however, that such systems can exhibit oscillatory behavior: this is strictly a transient phenomenon but may be ”long lived.” The most widely studied chemical oscillator is the Belousov–Zhabotinsky (BZ) reaction. Recently, there have been observations of the transient development of complex oscillations in this system with evolution through ”chaotic” and ”mixed-mode” phases such that large and small amplitude excursions in species concentrations are interspersed before the system evolves back to simple oscillations and then to a quasi-steady approach to the final equilibrium state. Such behavior is likely to arise more widely than in this specific reaction and be of relevance in biology as well as chemistry. The BZ system has been shown to display genuine, transient-free chaotic responses in open (flow) reactors for which the behavior can be modelled at least semi-quantitatively on the basis of the Gyorgyi–Field mechanism (an extension of the classic Field–Körös–Noyes model). The mechanism driving the nonlinear chemistry is likely to be essentially the same in both batch and flow systems and this paper discusses the application of this mechanism to ”closed reactor chaos.” It is seen that some conventional assumptions made in the mechanism are brought into question by the experimental observations.

I. INTRODUCTION

The Belousov–Zhabotinsky (BZ) reaction is certainly the most widely known oscillatory chemical reaction. In a closed (batch) reactor, the reaction typically shows a preoscillatory induction period, followed by an oscillatory phase that may last for several hours. The oscillations occur in the concentrations of various intermediate species, including Br^-, HBrO_2, and the redox catalyst. For most of this stage of the reaction, the amplitude and period of individual oscillations varies only slightly from that of the previous event. However, the oscillatory behavior is strictly transient and the effects of reactant consumption cause an end to oscillation and a final monotonic approach to the chemical equilibrium state.

In a recent set of papers, two groups have reported observations of additional types of oscillatory response, with greater complexity revealed in the development of the oscillatory wave form. Wang et al. investigated the cerium-catalyzed system, monitoring the absorption at $\lambda = 344$ nm due to Ce(IV) and describe bifurcation sequences with transient ”period doubling” and ”tori.” Strizhak and Kawczynski have observed a ”mixed mode” sequence in the ferroin-catalyzed system, monitored with a bromide ion specific electrode, on increasing the catalyst concentration.

In this paper, we seek to model these complex, transient sequences on the basis of the Gyorgyi–Field (GF) mechanism. This development from the original Field–Körös–Noyes (FKN) mechanism arose in order to model the complex and chaotic sequences observed in the BZ system in open (flow) reactors, and provides a somewhat more realistic representation of the clock-resetting ”Process C,” involving the species bromomalonic acid (BrMA). It is to be expected that the GF mechanism should also be applicable to the same reaction under essentially similar concentration ranges in a batch system. A priori, we may anticipate that a model that ignores the consumption of the major reactant species BrO_2, malonic acid (MA), and H^+ would produce sustained simple or, perhaps, complex oscillations over a range of parameter values and that then including reactant consumption will provide a sweep through this parameter region. In fact, it is observed that a straightforward implementation of the GF mechanism predicts a transient oscillatory phases, even without reactant consumption. This can be readily understood from the computed concentration histories as arising from a steady increase in time of the BrMA concentration, with oscillations arising only over a range of
[BrMA]. The role of [BrMA] as a slowly varying parameter can be rationalized through a nondimensionalization of the governing rate equations which reveals that this species evolves on a slower characteristic time scale than the “significant” intermediate species HBrO2 and the oxidized form of the redox catalyst, Ce(IV) in this case. (The remaining species, Br−, is also seen to evolve on a much faster time scale so that it remains in pseudo-steady state with HBrO2 and Ce(IV), as is known from previous analyses.)

II. EXPERIMENT

Separate stock solutions, thermostated at 25 °C and degassed with N2, of malonic acid, potassium bromate, and cerium (III) nitrate, each in 1 M H2SO4 were freshly prepared each day with doubly distilled, deionized water. Appropriate volumes were then mixed, in this order, in a batch reactor to a total solution volume of 150 cm³, also thermostated at 25 °C and degassed following Wang et al. throughout the subsequent reaction. The evolution of the reaction is monitored with Pt and Br−-ion specific electrodes, both referenced to a double-junction calomel electrode, thus complementing the spectroscopic studies of Wang et al.5,6

Figures 1 and 2 present a typical set of results. Following a short, preoscillatory stage (lasting approximately 2 min), the system exhibits large amplitude oscillatory excursions as registered by Br− electrode. Each oscillation has essentially the same amplitude as its predecessor and the period between excursions remains fixed. This waveform is maintained for approximately 84 min, with ca. 100 excursions, but then there is a transition to a more complex response, as indicated in Fig. 1(a). This has the appearance of a supercritical period doubling, so that we observe one repeating unit consisting of two excursions—one of slightly smaller amplitude than the other. This waveform soon gives way to a more characteristic one–large–one-small or 11 “mixed mode” pattern. Later in the reaction, after approximately 124 min, there is a further “bifurcation” again with an initial period doubling character. [Fig. 1(b)], but this then evolves to a 12-type response. For the particular initial concentrations in Fig. 1, there is no further increase in the complexity and the 12 state eventually gives way to a return to a period-2 and then a simple period-1 evolution, now of smaller overall amplitude, after approximately 3 h [Fig. 1(c)]. Eventually, the oscillatory response gives way to quasi-steady-state evolution, via a supercritical Hopf bifurcation (the amplitude tends smoothly to zero as t increases).

A bifurcation diagram can be constructed by plotting the minimum potential from the bromide ion electrode time series against oscillation number, n, as shown in Fig. 2. For the initial, large amplitude period-1-type oscillations, the amplitude simply varies smoothly and slowly with oscillation number. At the first period doubling, there is a characteristic bifurcation as there is a small and a large minimum in each repeating unit. Between n = 128 and 170 approximately, there is an extended region of the 11-type, which is then followed by evidence of another “cascade” before the range of 12 from n = 200–250 approximately. The reverse cascade to small amplitude period-1 can also be seen in Fig. 2. Similar transient bifurcation diagrams have been observed in numerical studies of simple models with chemical feedback in which the sequence of events was clearly linked to the underlying bifurcations between sustained oscillatory states obtained when reactant consumption is neglected. In that
study, the transition between different mixed-mode states was also mediated by period-doubling cascades. In the next section, we seek to establish a similar understanding based on a realistic mechanism for the BZ chemistry.

Other types of complex response have been observed experimentally as the initial concentrations are varied between experiment. We have concentrated on varying the initial malonic acid concentration as earlier workers have investigated the effects of bromate and catalyst concentrations. Particularly striking is the apparent possibility that the oscillatory phase can be interrupted by a period in which the system returns to quasi-steady evolution for several minutes, before regaining its oscillatory character. This behavior is observed at relatively low initial malonic acid concentration ([MA]₀<0.27 M). If [MA]₀ is increased, the regime of complexity appears to decrease. The highest initial malonic acid concentration at which period doubling was observed in our study was [MA]₀=0.475 M, with the other initial reactant concentrations as in Eq. 1.

Individual experiments have limited reproducibility. For a constant set of initial concentrations, the development of complex oscillations at some stage is reproducible from one experiment to the next, but the exact time at which complex behavior first emerges and then ceases varies quite widely from run to run.

III. MECHANISTIC MODELING

A. The model

The Gyorgyi–Field (GF) model for the BZ reaction involves the following reaction steps:

1. \[ \text{BrO}_3^- + \text{Br}^- + 2\text{H}^+ \rightarrow \text{HBrO}_2 + \text{Br}^- \]
   \[ r_1 = k_1[\text{BrO}_3^-][\text{Br}^-][\text{H}^+] \]

2. \[ \text{HBrO}_2 + \text{Br}^- + \text{H}^+ \rightarrow 2\text{BrMA} \]
   \[ r_2 = k_2[\text{HBrO}_2][\text{Br}^-][\text{H}^+] \]

3. \[ \text{HBrO}_2 + \text{HBrO}_2 + \text{Br}^- + \text{MA} + \text{H}^+ \]
   \[ r_3 = k_3[\text{HBrO}_2]^2 \]

4. \[ \text{HBrO}_2 + \text{Br}^- + \text{H}^+ \rightarrow 2\text{BrO}_2 + \text{H}_2\text{O} \]
   \[ r_4 = k_4[\text{HBrO}_2][\text{Br}^-][\text{H}^+] \]

5. \[ 2\text{BrO}_2 + \text{H}_2\text{O} \rightarrow \text{HBrO}_2 + \text{BrO}_3^- + \text{H}^+ \]
   \[ r_5 = k_5[\text{BrO}_2]^2 \]

6. \[ \text{BrO}_2 + \text{Ce}^{III'} + \text{H}^+ \rightarrow \text{HBrO}_2 + \text{Ce}^{IV'} \]
   \[ r_6 = k_6[\text{BrO}_2][\text{Ce}^{III'}][\text{H}^+] \]

7. \[ \text{HBrO}_2 + \text{Ce}^{IV'} \rightarrow \text{BrO}_2 + \text{Ce}^{III'} + \text{H}^+ \]
   \[ r_7 = k_7[\text{HBrO}_2][\text{Ce}^{IV'}] \]

8. \[ \text{MA} + \text{Ce}^{IV'} \rightarrow \text{MA}^- + \text{Ce}^{III'} + \text{H}^+ \]
   \[ r_8 = k_8[\text{MA}][\text{Ce}^{IV'}] \]

9. \[ \text{BrMA} + \text{Ce}^{IV'} \rightarrow \text{Ce}^{III'} + \text{Br}^- + \cdots \]
   \[ r_9 = k_9[\text{BrMA}][\text{Ce}^{IV'}] \]

10. \[ \text{MA} + \text{BrMA} \rightarrow \text{MA} + \text{Br}^- + \cdots \]
    \[ r_{10} = k_{10}[\text{MA}][\text{BrMA}] \]

11. \[ \text{MA} + \text{MA} \rightarrow \text{MA} + \cdots \]
    \[ r_{11} = k_{11}[\text{MA}]^2 \]

The following values for the reaction rate constants are appropriate:

\[ k_1 = 2 \text{ M}^{-3} \text s^{-1}; \quad k_2 = 2 \times 10^6 \text M^{-2} \text s^{-1}; \]
\[ k_3 = 3 \times 10^3 \text M^{-1} \text s^{-1}; \quad k_4 = 33 \text M^{-2} \text s^{-1}; \quad k_5 = 4.24 \times 10^7 \text M^{-1} \text s^{-1}; \]
\[ k_6 = 6.2 \times 10^4 \text M^{-2} \text s^{-1}; \quad k_7 = 7 \times 10^3 \text M^{-1} \text s^{-1}; \quad k_8 = 0.3 \text M^{-1} \text s^{-1}; \]
\[ k_9 = 30 \text M^{-1} \text s^{-1}; \quad k_{10} = 2.4 \times 10^4 \text M^{-2} \text s^{-1}; \quad k_{11} = 3 \times 10^9 \text M^{-1} \text s^{-1}. \]

Their Model D is obtained by assuming that the concentrations of the major reactants BrO₃⁻, H⁺, and MA remain constant while the concentration of BrO₂ is obtained by assuming reactions (4) and (5) establish and maintain “pre-equilibrium.” The malonyl radical concentration [MA⁻] is obtained from a quasi-steady state involving reactions (8), (10), and (11). The concentration of the reduced form of the catalyst, Ce(III), at any time can be expressed explicitly as the difference between the constant total redox catalyst concentration Ceₜₒₜ and the instantaneous concentration of the oxidised form, Ce(IV).

Following established convention, we denote the constant concentrations as

\[ [\text{BrO}_3^-] = A; \quad [\text{MA}] = B \]
\[ [\text{H}^+] = 0.006 + 1.276[\text{H}_2\text{SO}_4] = H, \]

and the four variable concentrations as

\[ [\text{HBrO}_2] = X; \quad [\text{Br}^-] = Y, \]
\[ [\text{Ce}(IV)] = Z, \quad \text{and} \quad [\text{BrMA}] = W, \]

so that [Ce(III)]=Ceₜₒₜ−Z. We will also denote \( R = [\text{BrO}_2] \).

B. Governing rate equations

The rate equations then become

\( \frac{dX}{dt} = k_1AYH^2 - k_2HXY - 2k_3X^2 - k_4AHX + k_5R^2 \)
\( + k_6HR(Ce_{tot} - Z) - k_7ZX, \quad (1a) \)

\( \frac{dY}{dt} = -k_1AYH^2 - k_2HXY + k_9WZ + k_{10}[\text{MA}^-]W, \quad (1b) \)

\( \frac{dZ}{dt} = k_8RH(Ce_{tot} - Z) - k_7ZX - k_8BZ - k_9ZW, \quad (1c) \)
\[
\frac{dW}{dt} = k_1AYH^2 + 2k_2HXY + k_3X^2 - k_5WZ \\
- k_{10}[MA \cdot ]W,
\]

with the preequilibrium and steady-state conditions being

\[
R_{eq} = \frac{k_3AHX}{k_9}
\]

and

\[
2k_{11}[MA \cdot ]_s + k_{10}W[MA \cdot ]_s - k_8BZ = 0
\]

The quadratic equation yields only one positive root for \([MA]_s\).

C. Stoichiometric factor, \(f\)

The classic Oregonator representation of the clock resetting “Process C” is as a single overall step, written in the form

\[
(C) \quad 2Ce(IV) + BrMA + MA \rightarrow fBr^- + \cdots,
\]

where the parameter \(f\) is known as the stoichiometric factor, relating the relative rates of production of bromide ion to catalyst reduction in this part of the reaction. The clock resetting steps in the GF model are \((8)-(11)\), and we can calculate a dynamic value for \(f\) at any stage in the reaction in the following terms:

\[
f = 2 \left( \frac{d[Br^-]/dt}{d[Ce(IV)]/dt} \right)_{(8)-(11)} = 2 \left( \frac{r_4 + r_{10}}{r_8 + r_9} \right),
\]

where the subscript indicates that the “rates” are only evaluated from the “Process C” steps.

IV. TYPICAL RESULTS FOR MODEL D

Figure 3(a)–3(f) shows the variation of the intermediate species concentrations with time for a system with \([H_2SO_4] = 1.0 \text{ M}, [BrO}_2] = 0.09 \text{ M}, [MA] = 0.46 \text{ M} and \([Ce]_w = 1.6 \times 10^{-3} \text{ M}. The initial concentrations of Ce(IV), HBrO_2, and BrMA are taken to be zero with that for Br^- being 0.05% of the bromate concentration, based on the quoted maximum impurity concentration provided by the suppliers. Also shown is the variation of the stoichiometric factor \(f\) according to Eq. (2). There is a preoscillatory induction period of approximately 300 s during which \(X([HBrO_2])\) and \(Z([Ce(IV)])\) rise very rapidly to values of ca. \(5 \times 10^{-3} \text{ M}\) and \(2.4 \times 10^{-4} \text{ M}\), respectively, and then fall steadily, and in which \(Y([Br^-])\) and \(W([BrMA])\) rise slowly. The effective value of the stoichiometric factor \(f\) also increases during this period. After approximately 5 min, the system develops into a transient oscillatory response which lasts until \(t = 950 \text{ s}. The onset of oscillations is relatively abrupt, perhaps indicating a subcritical event, with the amplitude of successive peaks decreasing after the first couple of events. There are no maxima or minima in the \(W\) time series [Fig. 3(d)]. The increase in the concentration of BrMA does, however, exhibit a steplike evolution during this stage [see enlargement in Fig. 3(e)]. The evolution of the stoichiometric factor [Fig. 3(f)] suggests that this quantity shows small amplitude oscillations about \(f = 2\) during the oscillations. The extinction of the oscillations has a characteristic supercritical decay in the amplitude as the quasi-steady evolution is regained at long times. We may note that \(W\) increases throughout the oscillatory period, with \(W = 0.03 \text{ M}\) at \(t = 300 \text{ s}\) and \(W = 0.110 \text{ M}\) at \(t = 950 \text{ s}.

A somewhat surprising feature of this evolution, which is relatively insensitive to the exact choice of initial conditions, is that, even without reactant consumption, the oscillations are transient. It is clear that oscillatory behavior only occurs over a finite range of the \(BrMA\) concentration, with the preoscillatory period corresponding to the initial growth of \(W\) and the end of the oscillations arising as \(W\) grows beyond some upper “critical” value. If the initial value of \(W\) is increased, the induction period for the oscillatory phase is reduced. For \(W(t=0) > 0.03\), oscillations begin immediately. If \(W(t=0)\) is chosen to be larger than 0.11, no oscillations are observed in the system at all. These observations are consistent with the variable \(W\) playing the role of a “slowly varying parameter,” as we discuss in the next section.

Various other parameter combinations (representing the concentrations of the pool chemical species \(A\), \(B\) and \(H\) and of the total redox catalyst concentration) have been examined and similar qualitative behavior is observed over a wide range. In all cases, any transient oscillatory evolution is of an essentially “simple” character.

V. NONDIMENSIONALISATION

The reaction rate equations (1a)–(1e) can be nondimensionalized using the following scalings:

\[
x = \frac{2k_3X}{k_3A}; \quad y = \frac{k_2Y}{k_3A}; \quad z = \frac{Z}{Ce_{tot}}; \quad w = \frac{2k_3k_9W}{k_3k_7A}; \quad r = \frac{k_4R}{k_3A}; \quad m = \frac{k_7k_10[MA \cdot ]_s}{k_3k_9AH}.
\]

The dimensionless rate equations then become

\[
\frac{dx}{d\tau} = (q - x)y - x(1 + x) + sr_{eq}^2 + pmr_{eq}(1 - z) - Mxz,
\]

\[
\frac{dy}{d\tau} = -(q + x)y + Mwz + mw,
\]

\[
\frac{dz}{d\tau} = gr_{eq}(1 - z) - \frac{gz}{p} (w + x) - ez,
\]

\[
\frac{dw}{d\tau} = (q + 2x)y + \frac{1}{2} x^2 - mwz - Mwz.
\]
with preequilibrium condition \( r_{eq} = (x/s)^{1/2} \), and quasi-steady state condition \( m_{ss} = \frac{1}{2} \gamma w \left( -1 + \sqrt{1 + \frac{4 \epsilon \rho M_z}{\gamma g w^2}} \right) \).
These equations involve the following dimensionless parameters:

\[ e = \frac{k_8 B}{k_4 A H}, \quad e' = \frac{2k_3 k_8 B}{k_2 k_4 A H^2}, \quad \delta = \frac{k_7 k_8 B}{k_4 A H}, \]

\[ \gamma = \frac{k_{2} k_{10}}{4k_{4} k_{5} k_{11}}, \quad q = \frac{2k_1 k_3}{k_2 k_4}, \quad p = \frac{2k_3 k_4 H}{k_2 k_7}, \quad M = \frac{k_7 C_{tot}}{k_4 A H}, \]

\[ s = \frac{2k_3}{k_5}, \quad g = \frac{k_8 H}{k_{5}}. \] (5)

Using the typical values for the reactant concentrations given above, \( A = 0.09 \) M, \( B = 0.46 \) M, \( C_{tot} = 0.0016 \) M, and \( H^+ = 1.282 \) M, these groups have the following values:

\[ e = 3.9 \times 10^{-2}, \quad e' = 9.13 \times 10^{-5}, \quad \delta = 9.1, \]

\[ \gamma = 0.871, \quad q = 1.82 \times 10^{-4}, \]

\[ p = 1.61 \times 10^{-3}, \quad M = 2.75, \quad s = 1.41 \times 10^{-4}, \]

\[ g = 1.87 \times 10^{-3}. \] (6)

The dimensionless forms for \( x, y, q, e, \) and \( e' \) are consistent with the usual Tyson scalings, but the oxidized form of the catalyst is here scaled by the total catalyst concentration, so we have \( 0 \leq z \leq 1. \)

The slow variation in \( w \) seen in the calculations can be expected from the magnitude of the “time scale” parameter \( \delta \) multiplying the differential operator in Eq. (4d): \( \delta \) is several orders of magnitude greater than the other time scale parameters \( e \) and \( e' \) which govern the rates of change of \( x \) and \( z \) and of \( y \), respectively. The dimensionless bromide ion concentration, \( y \), in particular can be expected to be a “fast variable” maintaining a quasisteady state with respect to \( x \), \( y \), and \( w \). The relative magnitudes of \( e' \), \( e \), and \( \delta \) suggest, from the above argument, that the system will behave for most of the period as a system of essentially two dynamical variables \( (x \) and \( z) \) system being “swept” through a slow variation in a “parameter” \( w \). If the quasi-steady state for \( x \) and \( z \) becomes unstable to small perturbations over some range of \( w \), then a transition to oscillatory (limit cycle) evolution may arise, but we would expect only simple oscillations with a slowly varying amplitude, as observed in Fig. 3.

The effects of other parameters on the existence of oscillatory behavior in the time series can be investigated by additional computations. If \( \delta \) is reduced by a factor of 10, to 0.91, then the length of the transient oscillatory phase is greatly reduced as \( w \) increases more rapidly (as \( dw/d\tau \) is proportional to \( 1/\delta \)). Increasing the value of \( M \) (e.g., by increasing the total redox catalyst concentration) also decreases the length of the transient oscillatory phase, but more slowly. The induction period gets shorter as \( M \) increases and the period between successive excursions also shortens as \( M \) increases. The oscillatory response is not greatly affected by modest variations in the parameter \( \gamma \), with the length of the oscillatory phase decreasing slightly as \( \gamma \) is decreased by a factor of 10; the period between successive excursions decreases as \( \gamma \) is decreased, producing sharper peaks.

The parameters \( g \) and \( p \) play complimentary roles, as might be expected as they appear as the ratio \( g/p \) in two of their occurrences in governing equations. Increasing \( g \) (decreasing \( p \)) shortens the length of the oscillatory phase and lengthens the period between successive excursions. Decreasing \( g \) (increasing \( p \)) dramatically lengthens the transient oscillatory stage of the reaction and produces sharp peaks with a short period.

VI. MODIFICATION OF MODEL

The straightforward adoption here of the GF scheme produces transient oscillations (even though the consumption of the reactants is not included at this stage), but these have essentially simple waveforms. There is a variation of amplitude and period with the parameters, but no apparent bifurcation to more complex oscillatory structures. As argued in the previous section, this relates to the underlying two-variable nature of the model, with the concentration of BrMA acting as a slowly varying parameter. In the computations described above, \( W \) shows essentially a monotonic increase in time. In the CSTR calculations of Gyorgyi and Field, \( W \) plays more of the role of a genuine variable, decreasing in time at some stages of the evolution in response to variations in other species concentrations. Comparing the batch and open reactor equations, one obvious difference is the presence of an additional “loss” term in the equations relating to the outflow of the species. With these set equal to zero for the batch system, \( W \) appears to be able to grow in an unlimited fashion. Based on a similar comparison, Wang et al. invoked a simple additional step of the form

\[ 12 \text{ BrMA} \rightarrow \text{products rate} = k_{12} \text{[BrMA]}, \]

i.e., a step that removes BrMA without producing bromide ions. This seems a fairly noncontroversial modification of the model and allowed those authors to obtain complex oscillatory responses that were transient in a model with bromate and malonic acid consumption.

The model employed by Wang et al. is somewhat simpler than the GF scheme and, for instance, does not retain the known reversibility of step (4), i.e., it omits step (5). In this paper, we seek to retain the main features of the GF scheme and instead of adding step (12) choose to relax some of the assumptions involved in deriving Model D. In particular, we have examined the influence of the “preequilibrium” assumption for \( \text{BrO}_2 \) based on steps (4) and (5). This is thought to be reliable for cerium-catalyzed systems, but the transient complexity of the BZ system may suggest otherwise. Two alternative approaches arise. The first involves ignoring the “reverse step” (5) and making a quasi-steady-state approximation for \( [\text{BrO}_2] \) based on steps (4) and (6). This assumption is generally made for the ferroin-catalyzed system. The second approach adopts a full quasi-steady-state treatment for \( \text{BrO}_2 \) through steps (4)–(6). In this latter case, the appropriate form for \( R_{ss} \) is given by the quadratic equation

\[ 2k_3 R_{ss}^2 + k_8 H(C_{tot} - Z)R_{ss} - 2k_4 A H X = 0. \]

(7)
The evolution of the system with the same parameter values employed for Fig. 3, but now with the full quasi-steady-state approximation for $\text{BrO}_2$ radical, is shown in Fig. 4. Some significant quantitative and qualitative differences emerge. The preoscillatory period is shortened to approximately 150 s and the duration of the transient oscillatory phase is lengthened. The period between successive excursions is generally lengthened compared to that obtained with

FIG. 4. Concentration histories for GF Model D with full steady-state approximation for $\text{BrO}_2$ radical, showing transient oscillatory response and complex behaviour in (a) $X(\text{HBrO}_2)$, (b) $Y(\text{Br}^-)$, (c) $Z(\text{Ce}^{IV})$, (d) and (e) $W(\text{BrMA})$. Also shown, (f), is the evolution of the stoichiometric factor $f$ calculated from Eq. (2).
the preequilibrium approximation and the maximum amplitude in Br and HBrO₂ is reduced, although higher Ce(IV) concentrations are attained with the full steady-state treatment. Most significant, perhaps, is the qualitative change in behavior that develops at t = ca. 650 s. There is a departure from the simple, slow variation in the amplitude and the basic simple waveform to a (transient) complex oscillation. This complex stage lasts until t = ca. 800 s at which time the system returns to simple (small amplitude) oscillation. Larger oscillations are observed in the stoichiometric factor f, as defined by Eq. (2), with the oscillatory sequence beginning when f ≈ 1 [Fig. 4(f)]. The complex development of f is also a feature in this time series. There is additional, interesting structure in the evolution of BrMA. Instead of a simple stepwise increase during the oscillatory stage, each excursion causes a small spike in W, with then a small decrease in this concentration before the “tread” of the stair, as shown in the enlargement in the Fig. 4(e). Thus, the system has developed a nonmonotonic evolution of this “controlling” species which was absent with the imposition of the preequilibrium assumption. Comparing Eqs. (1e) and (7), we see that with the full steady-state treatment, W depends on the instantaneous value of Z, the oxidized form of the redox catalyst, as well as on the autocatalyst concentration X.

VII. DISCUSSION

The computations described above have shown that the four-variable model proposed by Gyorgyi and Field for the cerium-catalyzed BZ system is capable of predicting complex transient evolution in batch systems as well as in open reactors. In order for this feature to arise, it is necessary to retain a full quasi-steady-state treatment for the instantaneous concentration of the BrO₂ radical rather than making the more usual preequilibrium assumption. With this modification, the four-variable model performs in a very similar manner to the full six-variable model (i.e., that for which no steady-state assumption is made and BrO₂ and MA are treated as genuine variables). Once complex behavior has been observed in these models for which the consumption of the major reactants has been ignored, we can begin to search for transient complex sequences in the full scheme in which the consumption of bromate and malonic acid is incorporated. One surprising feature, however, of the present modeling is that, even without this reactant consumption, the computed oscillatory responses are only transient. As revealed above, this is related to the net build-up of the BrMA concentration during the reaction. Clearly, this concentration must be limited by the initial concentration of its precursor, malonic acid, and consumption of MA will both provide an upper limit on the final concentration of BrMA and reduce its rate of formation at any stage (hence, possibly, prolonging the oscillatory stage).

The time series computed above are not in particularly good quantitative agreement with experiment: the length of the oscillatory stage and of the complex development is significantly shorter than that observed in experiment. In a sense, such quantitative agreement is not the major aim of the present investigation, which seeks more to use the observation of transient complexity to test further the interpretation of the BZ mechanism based on the GF model, which appears to be the most satisfactory under open conditions. Certainly some effects not incorporated into the GF scheme have been demonstrated in the real situation. In particular, the influence of O₂ has been the subject of much work, both in general terms for the BZ system and Wang et al. have very recently shown the effect of O₂ on the development of the complex transients in this system. In their earlier modeling, Wang et al. also achieved rather better match with the observed time scales, although they used a truncated (Oregonator) model, through a somewhat arbitrary variation in some of the reaction rate constants. In particular, they treated the rate constant for steps (8)–(10), along with their additional step (12), as adjustable parameters, modified the Gyorgyi–Field values for steps (1) and (2), and they ignored the reversibility of step (4), i.e., the present step (5). If we adopt the “Wang” values, the length of the transient oscillatory stage increases as does the range of complexity observed within it, with the response being particularly sensitive to the variation of k₂.

We have also investigated the effect of including step (12) in our model without reactant consumption. This extra removal step prevents the concentration of BrMA increasing without limit. As k₁₂ increases, so its influence is greater. The smallest, nonzero values for k₁₂ ~ 10⁻¹² s⁻¹, remove the complex behaviour seen above. However, for larger values, e.g., with k₁₂ = 1×10⁻⁷, the small amplitude oscillatory stage is substantially extended, lasting up to t = ca. 3300 s. With k₁₂ in the range 2.5–7.5×10⁻⁴, these small amplitude oscillations develop into complex (aperiodic) oscillations which appear to be indefinitely sustained in the absence of reactant consumption.

The complex behavior computed here shows symptoms of “sensitivity to initial conditions.” The precise times both for the onset of simple oscillatory evolution and for the transition to the complex waveform depend on the initial conditions. The latter also depends on the number of species treated as variables in the computation. Even the apparently simple change of treating Ce(III) and Ce(IV) as separate variables instead of invoking the explicit mass conservation condition has some (small) effect on the timing of the transition to complex behavior. This feature, and the form of the experimental bifurcation diagram shown in Fig. 2, add fairly conclusive support to interpretation of this phenomenon as that of transient chaos.

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